SYNTHETIC, KINETIC, SPECTROSCOPIC AND STRUCTURAL
STUDIES ON HEAVIER TRANSITION METAL COMPLEXES

by

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ABSTRACT

In Part A, section 1), a chronological account of studies on various ruthenium(III) and (II) compounds containing group 5B donor ligands and/or cyclic dienes is presented. For example, a variety of products from reaction of \([\text{RuCl}_3(\text{MeOH})(\text{EPH}_3)_2](\text{E} = \text{P}, \text{As})\) with Lewis bases, including the Ru(III) anions \(\text{trans-}[\text{RuCl}_4(\text{EPH}_3)_2]^\text{−}\) have been fully characterised. Reaction of \([\{\text{Ru(CO)}\text{Cl}_2(\text{C}_7\text{H}_8)\}_{2,7,8,2}^\text{2}\) with MC1/HCl gave the first anionic Ru(II) diene complex \(\text{M}[\text{Ru(CO)}\text{Cl}_3(\text{C}_7\text{H}_8)]\) together with some \(\text{M}_2[\text{Ru(CO)}\text{Cl}_5]\) and diene displacement reactions on the former have been studied. Synthesis of the related \([\{\text{RuCl}_2(\text{CS})(\text{PR}_3)_2\}_{2,2}\) from \([\text{RuCl}_2(\text{PR}_3)_3]\) and CS also gave the triple chloride bridged complex \([\text{Ru}_2\text{Cl}_4\text{CS}(\text{PR}_3)_4]\) \([\text{PR}_3 = \text{PPh}_3, \text{P}(\text{p-tolyl})_3]\). The isomorphous \([\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PR}_3)_4]\) were prepared by intermolecular coupling of \([\text{RuCl}_2(\text{PR}_3)_3]\) with \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})(\text{PR}_3)_2]\). Cyclic voltammetric studies showed that these dimers undergo reversible one electron oxidation steps.

Self dimerisation of \([\text{RuYCl}_2(\text{dmf})(\text{PR}_3)_2]\) \((\text{Y} = \text{CO,CS})\) gave both \([\text{Ru}_2\text{YCl}_4(\text{PR}_3)_3]\) and \([\text{Ru}_2\text{YCl}_3(\text{PR}_3)_4]\). Similar compounds \([\text{Ru}_2\text{Cl}_4\text{L}_5]\) and \([\text{Ru}_2\text{Cl}_3\text{L}_6]\)-Cl \((\text{L} = \text{tertiary phosphine})\) have been synthesised by various methods and detailed mechanisms to rationalise the formation of these compounds suggested. Attempts to synthesise analogous neutral dimers by pyrolysis of \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)}\text{Ph}_2)_6]\)Cl and \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph}_2)_9]\)Cl gave the unusual dimers \([\text{P(OR)}\text{Ph}_2)_2\text{P(OH)}\text{Ph}_2\text{RuCl}_3\text{Ru(P(OH)}\text{Ph}_2)_2\text{PPh}_2]\).

In section 2), various reactions of the compounds \([\{\text{Ru(\text{arene})Cl}_2\}_{2}\] are described including the preparation of the triple bridged cations \([\text{areneRuX}_3\text{Ru(CF}_3)_3]\]^+ \((\text{X} = \text{Cl}^-, \text{OH}^-, \text{OR}^-)\) and the novel \([\{\text{Ru}\text{[(C_6 H_6)}\text{OH}^\text{4+}\text{C}_6\text{H}_6}\}_{4}\]) cation, shown by X-ray analysis to have a cubane-like structure. Some stable substituted \(\text{η}^5\)-cyclohexadienyl compounds \([\text{Ru(\text{η}^5\text{C}_6\text{H}_6)}\text{Y}(\text{PMe}_2\text{Ph})(\text{N-N})]\text{PF}_6\) \((\text{Y} = \text{H}^-, \text{OH}^-, \text{CN}^-; \text{N-N} = 2,2'\text{bipy}, 1, 10 \text{phen})\) have been synthesised by reaction of \([\text{Ru}(\text{η}^6\text{C}_6\text{H}_6)}\text{PMe}_2\text{Ph}(\text{N-N})]\text{PF}_6\text{2}) with various nucleophiles.
In Part B, a systematic study of some transition metal dioxo-, monothio- and dithio-acid complexes is presented. In particular, extensive studies on platinum and palladium sulphur compounds have shown that various facile molecular rearrangements occur and these have been monitored by infrared, $^1\text{H}$ and $^{31}\text{P} - \{^1\text{H}\}$ nmr spectroscopy. Related studies on sulphur compounds of ruthenium, rhodium and osmium are also described.
This thesis is most conveniently divided into two sections entitled:

A. "Ruthenium and rhodium complexes containing group 5B donor ligands, cyclic dienes and/or arenes" (35 publications).

B. "Transition metal complexes containing dioxo-, monothio- or dithio-acid ligands" (33 publications)

However, there is some overlap between the two sections, especially as regards the monothio- and dithio-acid ruthenium studies, since some of the compounds described in the first section have been reacted with sulphur-containing ligands as detailed in the second section.

The 35 publications in section A consist of one paper [1] and one synthetic procedure [2], which resulted from my Ph.D. studies under the supervision of Professor (now Sir) Geoffrey Wilkinson F.R.S. at Imperial College, London, and in which I carried out all the experimental work; thirteen papers [4,7,12,13,14,16,18,19,21,31,32,33,34] and two notes [26,35] with myself as sole senior author; five papers [22,23,27,28,29] with my co-senior author, Dr. R.O. Gould of Edinburgh University, who supervised the crystallographic studies described in these publications; one publication [30] with my co-senior author Dr. G.A. Heath of Stirling University; two reviews [9,17] and ten preliminary communications [3,5,6,8,10,11,15,20,24,25].

Section B consists of four papers [36,38,39,40] resulting from my Ph.D. studies, in which I carried out most of the experimental work; sixteen papers [42, 44,46,48,49,50,51,53,58,59,60,61,62,65,67,68] and two notes [41,47] of which I am the sole senior author; one paper [66] with co-senior author Dr. R.O. Gould; one paper [57] in which I supervised the preparation of the compound and helped to write the discussion section; and nine preliminary communications [37,43,45,52,54,55,56,63,64].

With the exception of the work arising from my Ph.D. studies, none
of these publications have been submitted for any other degree or diploma.

The publications are listed on pages 5 to 10 and reference will be made to them in the thesis by arabic numerals in parentheses. Other references are cited by the use of arabic numerals as superscripts and appear in a separate list on pages 42 and 43.
LIST OF PUBLICATIONS
Section A


"Cationic and neutral complexes of ruthenium-(II) and -(III) containing tertiary phosphines or arsines and nitrogen-donor ligands", L. Ruiz-Ramírez and T.A. Stephenson, J.C.S. Dalton, 1975, 2244-2249.


Section B


[64.] "Reactions of [RuCl₂L₄] (L = P(OMe)₅Ph₂, P(OEt)₅Ph) and RuCl₂L₄ (L = P(OMe)₅Ph, PMe₅Ph, PMe₃Ph) with various dithiocac ligands", W.J. Sime and T.A. Stephenson, Inorg. Nuclear Chem. Letters, 1977, 13 311-314.


[67.] "Metal complexes of sulphur ligands. Part 17 Reaction of palladium(II) and platinum(II) monothiobenzoates with various Lewis bases and further studies on the related dioxo- and dithiocac complexes", J.A. Goodfellow, T.A. Stephenson and (in part) M.C. Cornock, J.C.S. Dalton, 1978 000

[68.] "Metal complexes of sulphur ligands. Part 18 Reaction of [RuCl₂L₄] (L = PR₃, P(OR)₅Ph, P(OR)₅Ph) with various dithiocac ligands", W.J. Sime and T.A.₂ Stephenson, J.C.S. Dalton, 1978 000
SYNTETIC, KINETIC, SPECTROSCOPIC AND STRUCTURAL STUDIES ON HEAVIER TRANSITION METAL COMPLEXES.

A Ruthenium and rhodium complexes containing group 5B donor ligands, cyclic dienes and/or arenes.

(1) Group 5B Donor Ligand and Cyclic Diene Complexes

Work in this area was started in 1965 during the last year of my Ph.D. studies at Imperial College, London. At that time, although much information was available on the preparation and properties of tertiary phosphine and -arsine complexes of transition metals in general, relatively little was known about such complexes with ruthenium.

The reaction of "RuCl₃.xH₂O" with triphenylphosphine was found to give different products, depending on the ratio of reactants and the temperature employed for reaction. Thus, with excess PPh₃, shaking in methanol gave [RuCl₂(PPh₃)₄]⁺, whereas, under reflux, red-brown crystals of [RuCl₂(PPh₃)₃] were produced [1,2]. An X-ray structural analysis on crystals, prepared independently by Vaska, showed that the latter possesses a five coordinate square pyramidal structure.¹ This was the first compound with a d⁶ configuration to be shown unequivocally to have a five coordinate structure, although a number of such compounds are now known. Usually, metal ions with d⁶ configuration form six coordinate, octahedral compounds and this great desire for six coordination is the rationale behind much of the chemistry discussed in this section of the thesis (see later).

In contrast, shaking PPh₃ and "RuCl₃.xH₂O" (2:1 mol ratio) in methanol for several days was found to produce a small yield of the green paramagnetic complex [RuCl₃(MeOH)(PPh₃)₂]. The corresponding [RuCl₃MeOH(AsPh₃)₂] could be obtained in high yield, by refluxing methanolic solutions of "RuCl₃.xH₂O" with excess AsPh₃ [1]. These ruthenium(III) methanolates proved to be excellent precursors for synthesising a wide range of
ruthenium(III) compounds containing tertiary phosphines (or arsines) and other ligands. These types of compounds have always been difficult to synthesise because of the tendency to form Ru(II) complexes via reductive processes on reaction of various ruthenium species with ER₃ (E = P, As).

A comprehensive study of the reactions of these solvates with a wide range of Lewis bases showed the following types of behaviour [1, 8,12,19].

a) Displacement of methanol only to give [RuX₃L₂(EPh₃)] (X = Cl, Br; E = P, As; L = RCN, Me₂SO, CS₂, CS, Me₂CO).

b) Displacement of methanol and one EPh₃ group giving [RuX₃L₂(EPh₃)] (L = Me₂S, 2,2'-bipyridyl(bipy), 1,10-phenanthroline(phen), C₅H₅N).

c) Complete displacement of methanol, EPh₃ and X⁻ without reduction e.g. [Ru(S₂PPh₂)₃].

d) Reduction to neutral ruthenium(II) complexes with or without complete displacement of EPh₃ groups e.g. [RuX₂L₂(EPh₃)] (L = CO, C₇H₈, RCN) and [RuX₄L₄] (L = C₅H₅N, Me₂SO).

e) Reduction to cationic ruthenium(II) compounds when carried out in polar solvents e.g. [RuCl(PPh₃)(N-N)]Cl [(N-N) = bipy, phen]

It should be noted, however, that reactions (a)-(e) were not confined to one particular type of donor atom but depended critically on a combination of such diverse factors as the nature of the ligand, the reaction time, the solvent media and on the other ligands already present in the ruthenium ion coordination sphere. Full characterisation of products was obtained in most instances, using such physico-chemical techniques as magnetic susceptibility measurements, esr, electronic and infrared spectroscopy and, for ruthenium(II) compounds, ¹H and ³¹P nmr spectroscopy.

In addition, in non-coordinating solvents, the coordinated methanol group is readily lost, giving a rare example of a five coordinate Ru(III)
complex, eg. \([\text{RuCl}_3(\text{AsPh}_3)_2]\). On the basis of esr studies, a trigonal bipyramidal structure with axial AsPh\(_3\) groups was proposed \([12]\) and this has been verified by other workers. \(^2\) Interestingly, in refluxing benzene, dimerisation of \([\text{RuCl}_3(\text{AsPh}_3)_2\text{MeOH}]\) accompanied by loss of a AsPh\(_3\) group produced \([\text{Ru}_2\text{Cl}_6(\text{AsPh}_3)_3]^3\), which achieves six coordination by means of a triple chloride bridge. This dimerisation step, involving loss of AsPh\(_3\) (as opposed to formation of the double chloride bridged complex \([\text{Ru}_2\text{Cl}_6(\text{AsPh}_3)_4]\)), is consistent with the results of related studies on Ru(II) (and Rh(III)) complexes (see later).

The synthesis of Ru(II) cations, by reaction of \([\text{RuCl}_3\text{MeOH}(\text{EPH}_3)_2]\) with various bidentate nitrogen donor ligands in polar media, was later extended to an investigation with \(\text{mer-}[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]\). For unsubstituted 2,2-bipyridyl and 1,10 phenanthroline (N-N), this produced the compounds \([\text{RuCl}(\text{PMe}_2\text{Ph})_3(\text{N-N})]\text{Cl}\) and \([\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{N-N})(\text{Solv})]\text{Cl}\) (Solv = CH\(_2\text{Cl}_2\), Me\(_2\text{CO}\)) which were fully characterised by spectroscopic studies. Increasing methyl substitution of the 1,10-phenanthroline ligand led to steric constraints and the formation of different compounds, eg with 2,9-dimethyl-1,10-phenanthroline (Me\(_2\text{phen}\)), \([\text{Ru}_2\text{Cl}_2(\text{Me}_2\text{phen})_4]\text{Cl}_2\) and \([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}\) were obtained \([10,19]\). Preliminary studies on the monomeric solvates \([\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{N-N})(\text{Solv})]\text{Cl}\) suggest that they are useful precursors for generating a range of binuclear cations, such as \([\text{PM}_{2}\text{Ph}_2](\text{N-N})\text{ClRu(L)RuCl(N-N)(PMe}_2\text{Ph}_2)^{2+}\) (L = pyrazine, 4,4'-bipyridyl), and a detailed study of their redox behaviour is planned (cf. electrochemical studies on the related \([\text{(bipy)}_2\text{ClRu(L)RuCl(bipy)}_2]^{2+}\text{ etc}^4\)).

Reaction of \([\text{RuCl}_3\text{MeOH}(\text{EPH}_3)_2]\) with MCl/HCl (M = Ph\(_4\)As\(^+\), Me\(_4\)N\(^+\)) in acetone led to methanol displacement by halide ion to form M[\text{RuCl}_4(\text{EPH}_3)_2] (E = P,As) which was shown to have a trans ion by esr and far infrared studies. The compound (E = P) proved to be isomorphous with the corresponding trans-\([\text{RhCl}_4(\text{PPh}_3)_2]^{-}\) anion (trans isomer established
by X-ray analysis\(^5\) which was synthesised by reaction of either
\([\text{RhCl}(\text{PPh}_3)_3]\) or \(\text{trans-}[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]\) with \(\text{Ph}_4\text{AsClHCl}\) \([3,4]\). The
latter appeared to be the first reported reaction involving carbonyl
displacement by halide ion in a monocarbonyl complex. The related ruthenium(III)
anions \([\text{RuCl}_4(\text{PR}_3)_2]^-(\text{PR}_3=\text{PET}_3, \text{PETPh}_2)\) had been obtained earlier by
reaction of the "carbonyl-containing" red solution with an excess of
phosphine \([1]\) but a higher yield method was found to be direct exchange,
starting from the \([\text{RuCl}_4(\text{PPh}_3)_2]^-(3,4)\). By this method, \([\text{RuCl}_4-\text{(P\{OPh}(\text{PPh})_3\}_2)]^-(4)\) and \([\text{RuCl}_4(\text{P(OMe)}_2\text{Ph})]^3\) , the only examples to date of
ruthenium(III) tertiary phosphite and phosphonite complexes, can also be
prepared.

Rather surprisingly, reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\) with \(\text{Ph}_4\text{AsClHCl}\) also
gave the Ru(III) anion \([\text{RuCl}_4(\text{PPh}_3)_2]^3-\) rather than the expected \([\text{RuCl}_4-\text{(PPh}_3)_2]^2-\) ion \([3,4]\). Further studies revealed that in the absence of
acid, no reaction occurs. A possible explanation is that oxidative
addition of HCl occurs to give a Ru(IV) hydrido intermediate, which
readily eliminates H\(^+\) to generate the Ru(III) anion. Recent evidence
to support this conclusion is the observation of oxidative addition of
H\(_2\) to \([\text{RuH}(\text{PPh}_2\text{P(CH}_3\text{)}_3\text{PPh}_2)_2\text{MeOH}]\) PF\(_6\) to give the relatively stable Ru(IV)
trihydrido complex. \([\text{RuH}_3(\text{PPh}_2\text{P(CH}_3\text{)}_3\text{PPh}_2)_2]\) PF\(_6\), which reacts with Et\(_3\)N
to generate \([\text{RuH}_2(\text{PPh}_2\text{P(CH}_3\text{)}_3\text{PPh}_2)_2]\) \(^6\).

The well-known compound \(\text{trans-}[\text{Rh}(\text{PPh}_3)_2]\) ClCO, used to synthesise
the \([\text{RhCl}_4(\text{PPh}_3)_2]^3-\) ion, was prepared by reaction of \([\text{Rh}(\text{CO})_2\text{Cl}]_2\) with
excess of PPh\(_3\). It was reported in 1969 that reaction of \([\text{Rh}(\text{CO})_2\text{Cl}]_2\) with
PPh\(_3\) (1:2 molar ratio) gave \(\text{trans-}[\text{Rh}(\text{CO})_2\text{ClPPh}_3]\) \(^7\). However, in making the
mixed ligand complexes \([\text{Rh}(\text{CO})\text{ClPPh}_3L] (L = \text{PMePh}_2, \text{P(C}_6\text{H}_{11})_3, \text{AsPh}_3,\)
\text{etc}) via this compound, we discovered that it should be reformulated as
the dimeric \([\text{Rh}(\text{CO})\text{ClPPh}_3]\)_2 complex \([6,7]\). Oxidative addition of Cl\(_2\) and
MeI to this dimer was also observed to generate Rh(III) dimeric species.
The reaction with MeI produced an equilibrium mixture of dimers containing methyl and acetyl groups respectively and the mechanism of interconversion is closely related to that for the catalytic conversion of methanol to acetic acid using \( \text{[Rh(CO)\textsubscript{2}Cl\textsubscript{2}]_2} \) as catalyst.\(^8\) A review of this work, in which a number of parallel studies were made in different countries has since been published.\(^9\)

By analogy with earlier studies in rhodium(I) and platinum(II) chemistry, another approach to the syntheses of the elusive Ru(II) anions was investigated; namely cleavage by halide ions of dimeric halide-bridged ruthenium compounds containing tertiary phosphines and/or other ligands.

Thus, reaction of \( \text{[\{Ru(CO)Cl\textsubscript{2}(C\textsubscript{7}H\textsubscript{8})\}_2]} \) (\( C\textsubscript{7}H\textsubscript{8} = \text{norbornadiene} \)) with Ph\(_3\)(PhCH\(_2\))PCl/HCl in acetone gave the first anionic Ru(II) diene complex, Ph\(_3\)(PhCH\(_2\))P[Ru(CO)Cl\(_3\)(C\(_7\)H\(_8\))] \( [5,13] \), whose structure was established by X-ray analysis \( [29] \), \( ^1\)H \( [5,13] \) and \( ^{13}\)C \( [16] \) nmr studies. A second product was also isolated from the reaction mixture and shown by X-ray analysis to be the Ru(III) anion \( \text{[Ru(CO)Cl\textsubscript{5}]^{2-}} \). In contrast, refluxing \( \text{[\{Ru(CO)Cl\textsubscript{2}(C\textsubscript{7}H\textsubscript{8})\}_2]} \) with Ph\(_4\)AsCl/HCl in ethanol gave the Ru(II) dicarbonyl anion cis- \( \text{[Ru(CO)\textsubscript{2}Cl\textsubscript{4}]^{2-}} \). Rationalisation of these observations is now possible by reference to the established reaction of "RuCl\(_3\)XH\(_2\)O" with HCO\(_2\)H/HCl mixtures, which gives first \( \text{[Ru(CO)Cl\textsubscript{5}]^{2-}} \), later \( \text{[Ru(H\textsubscript{2}O)COCl\textsubscript{4}]^{2-}} \), then \( \text{[Ru(CO)\textsubscript{2}Cl\textsubscript{4}]^{2-}} \) and finally the \( \text{[Ru(CO)\textsubscript{3}Cl\textsubscript{3}]^{-}} \) anion.\(^10\) Presumably, a similar stepwise formation of \( \text{[Ru(CO)\textsubscript{2}Cl\textsubscript{4}]^{2-}} \) from \( \text{[Ru(CO)Cl\textsubscript{5}]^{2-}} \) occurs in the above reaction, with the extra CO group arising from ethanol. Decarbonylation of alcohols by platinum metal complexes is a well established reaction.\(^11\)

The \( \text{[Ru(CO)Cl\textsubscript{3}(C\textsubscript{7}H\textsubscript{8})]^{-}} \) ion proved to be a useful starting material for the syntheses of several new ruthenium(II) anions of formulae \( \text{[Ru(CO)\textsubscript{3}L\textsubscript{2}]^{-}} \)
(L = Me₂S, Me₂SO, CH₂ = CHCN etc). With larger bases such as AsPh₃, SbPh₃ and C₅H₅N, the neutral monomeric compounds [Ru(CO)Cl₂(C₅H₈)L] were also formed and, on this basis, a mechanism of reaction was postulated which involved an intermediate ᵇ-C₅H₈ complex. Evidence for the latter was obtained from hydrogenation studies, using [RhCl(PPh₃)₃] as catalyst [10,16]. Later it was found that reaction of [Ru(CO)Cl₂(C₅H₈)₂] (C₅H₁₂ = cyclo-octa-1,5-diene) with MeCN also gave the compound [Ru(CO)Cl₂(C₅H₁₂)MeCN] and X-ray analysis revealed a trans-OC-Ru-MeCN arrangement [22]. Detailed ¹H nmr studies had shown earlier that this could not be the isomer formed from the [Ru(CO)Cl₃(C₅H₈)]⁻ anion [10,16] and an explanation based on the different stereochemistries of the anion and [Ru(CO)Cl₂(C₅H₁₂)]₂ was therefore proposed [22].

Attempts to synthesise the anionic tertiary phosphine complexes [Ru(CO)Cl₃(Pr₃)₂]⁻ from [Ru(CO)Cl₃(C₅H₈)]⁻ were however unsuccessful. Thus with PMe₂Ph (1:2 molar ratio), the only product obtained was [RuCl₂(PMe₂Ph)₂(C₅H₈)], whereas PMe₃Ph gave an inseparable mixture of [RuCl₂(PMe₃Ph)₂C₅H₈] and [Ru(CO)Cl₂(PMe₃Ph)₂] (¹H and ³¹P nmr evidence). With PPh₃ (1:2 molar ratio), a mixture of products initially formulated as isomers of [{Ru(CO)Cl₂(PPh₃)₂}] was obtained [10,16] but, later, [21], detailed ³¹P nmr studies led to the reformation of these products as a mixture of [Ru(CO)Cl₂(PPh₃)₂] (67%) and [(PPh₃)Cl(OC)RuCl₃Ru(CO)PPh₃] (33%) isomers. More recently the [Ru(CO)Cl₃(PPh₃)]⁻ anion has been successfully synthesised by reaction of the methanolate [Ru(CO)Cl₂MeOH(PPh₃)] with AsPh₄ClHCl [21].

Another interesting related study was the reaction of MC1/HCl (M = Ph₄As⁺, Ph₃(SCH₂)⁺, Et₄N⁺) with the major product from the reaction of [RuCl₂(PPh₃)₃] with CS₂. This had been reported earlier¹₂ as [{RuCl₂(CS)(PPh₃)₂}₂] and, in keeping with this formulation, some of it reacted to give M[RuCl₃(CS)(PPh₃)₂]₂, an example of the first and, until very
recently, only anionic thiocarbonyl complex \([5,14]\). However, the remainder of the \("[{\text{RuCl}}_2(\text{CS})(\text{PPh}_3)_2]_2\)" complex reacted very slowly with the MCl/HCl mixture (later it was shown that the presence of MCl was not necessary) to give a sparingly soluble orange-brown solid. This was characterised by analytical, infrared and magnetic susceptibility measurements \((\mu_{\text{eff}} = 2.0/\text{dimer at 292K})\) as the mixed oxidation state, triple chloride bridged dimer \([{(\text{PPh}_3)_2\text{ClRuCl}_3\text{Ru}(\text{CS})(\text{PPh}_3)_2]}_2\).MeCO \((\text{I})\) [14].

Careful separation of the \("[{\text{RuCl}}_2(\text{CS})(\text{PPh}_3)_2]_2\)" product by extraction with acetone revealed the presence of two thiocarbonyl complexes: namely the acetone soluble double-chloride bridged dimer \([{(\text{RuCl}}_2(\text{CS})(\text{PPh}_3)_2]_2\) (II) (16%) and the acetone insoluble triple chloride bridged dimer \([{(\text{PPh}_3)_2\text{ClRuCl}_3\text{Ru}(\text{CS})(\text{PPh}_3)_2]}_2\) (III) (40%) [14], whose structure was verified by X-ray analysis. Thus, the formation of the mixed Ru(II)/Ru(III) dimer \((\text{I})\) by reaction of \((\text{III})\) with HCl is attributed to removal of a PPh\(_3\) group as \([\text{Ph}_3\text{PH}]\text{Cl}\) and its replacement with chloride ion.

Possible mechanisms to account for the formation of compound(III) were then considered. By a process of elimination, an intermolecular pathway involving coupling of the five coordinate intermediate \("[{\text{RuCl}}_2(\text{CS})(\text{PPh}_3)_2]\) and \([\text{RuCl}_2(\text{PPh}_3)_3]\) was believed to be the most feasible. The desire of compounds with \(d^6\) configurations to attain stable octahedral structures was presumably the driving force for this process (see earlier). Direct proof of this mechanism was impossible because of our inability to trap out \("[{\text{RuCl}}_2(\text{CS})(\text{PPh}_3)_2]\)" [14], but fortunately, the closely related solvated monocarbonyl complex \([\text{Ru(CO)}_2\text{Cl}_2\text{dmf}(\text{PPh}_3)_2]\) (\text{dmf} = \text{NN-dimethylformamide}) had just been synthesised by carbonylation of \([\text{RuCl}_2(\text{PPh}_3)_3]\) in \text{dmf} solution. \(^{15}\)

When this \text{dmf} solvate was heated under reflux in acetone \(^{15}\) In less basic solvents such as acetone, it had been well established that carbonylation of \([\text{RuCl}_2(\text{PPh}_3)_3]\) gave the dicarbonyl complex \([\text{Ru(CO)}_2\text{Cl}_2(\text{PPh}_3)_2]\), the isomer formed depending on the reaction conditions [1].
with [RuCl₂(PPh₃)₃] (1:1 molar ratio), deep red crystals of [(PPh₃)₂ClRuCl₃Ru(CO)(PPh₃)₂]₂ Me₂CO, isomorphous with compound (III), were isolated in high yield [15,21]. The success of this reaction confirmed the feasibility of the intermolecular coupling process for the formation of compound (III). Later, [RuCl₂(CS)dmf(PPh₃)₂] was synthesised by reaction of [{RuCl₂(CS)(PPh₃)}₂] with N,N-dimethylformamide and direct proof of the coupling mechanism obtained since its reaction with [RuCl₂(PPh₃)₃] in acetone (1:1 molar ratio) gave a high yield of (III) [21]. Extension of this type of coupling reaction to synthesise the mixed triple chloro/bromo bridged compounds [Ru₂(CO)Br₂Cl₂(PPh₃)₄] was successfully accomplished, although an inseparable mixture of geometrical isomers was generated [15,21].

The corresponding [Ru₂(CO)Cl₄{P(p-tol)_₃}₄] could also be synthesised by reaction of [Ru(CO)Cl₂{P(p-tol)_3)}₂] with [RuCl₂{P(p-tol)_3)₃] (1:1 mol ratio) and reaction of [RuCl₂{P(p-tol)_3)₃] with CS₂ gave both [{RuCl₂(CS){P(p-tol)_3}₂}₂] and [Ru₂Cl₄(CS){P(p-tol)_3)₄]. Furthermore, reaction of [Ru(CO)Cl₂{P(PPh₃)₂} and [RuCl₂{P(p-tol)_3)₃] gave a high yield of the mixed phosphine dimer [(PPh₃)₂CORuCl₃RuCl{P(p-tol)_3)₂]. The reverse coupling reaction, however, between [Ru(CO)Cl₂{P(p-tol)_3)₂] and [RuCl₂(PPh₃)₃] gave a complicated mixture of products (³¹P nmr evidence), probably because of facile phosphine exchange [32]. Nixon and Head have recently synthesised some mixed metal triple chloride bridged complexes [(PR₃)₂ClRuCl₃RhCl(PF₃)(PR₃)] by a related coupling reaction.

However, attempted coupling of [RuCl₂(PEtPh₂)₃] (see later) and [Ru(CO)Cl₂{P(PPh₃)₂}] (1:1 mol ratio) produced the following mixture of compounds: [Ru₂Cl₄(CO)(PEtPh₂)₄], [Ru₂Cl₄(CO)₂(PEtPh₂)₃], [RuCl₂CO(PEtPh₂)₃] and [Ru₂Cl₄(PEtPh₂)₅] (³¹P nmr evidence) i.e. both monomers undergo self-dimerisation as well as some cross-coupling [32].
An additional complication in these coupling reactions is this tendency of some of the solvated monomers \([\text{RuYCl}_2\text{S(PR}_3\text{)}_2]\) \((Y = \text{CO, CS; PR}_3 = \text{PPh}_3, \text{P(p-tol)}_3; \text{S} = \text{MeOH, dmf})\) to undergo self-dimerisation in low polarity solvents (with displacement of a \(\text{PR}_3\) group), giving the triple chloride bridged compounds \([\text{PR}_3\text{Cl}(Y)\text{RuCl}_3\text{Ru}(Y)(\text{PR}_3\text{)}_2]\) (IV). Three geometrical isomers are possible for (IV) and detailed \(^{31}\text{P} nmr\) studies indicated that all three were formed \([21,32]\) As mentioned earlier \([21]\), this isomer mixture was also formed, along with some \([\{\text{Ru(CO)}\text{Cl}_2\text{(PPh}_3\text{)}_2\text{)}_2\}\), when the \([\text{RuCOCl}_3\text{(C}_7\text{H}_8\text{)}\text{]}^-\) anion was treated with \(\text{PPh}_3\) (1:2 mol ratio). A similar behaviour has been observed for reactions of \([\text{RuCl}_2\text{(PPh}_3\text{)}_3]\) with \(\text{PF}_3\), a 1:1 molar ratio giving \([\text{Ru}_2\text{Cl}_4\text{(PF}_3\text{)}_2\text{(PPh}_3\text{)}_3]\) and a 2:1 molar ratio \([\text{Ru}_2\text{Cl}_4\text{(PF}_3\text{)}_2\text{(PPh}_3\text{)}_4]\)\(^{17}\) and analogous mechanisms of formation can be postulated \([21]\).

Preliminary cyclic voltammetric and A.C. polarographic studies on \([\text{Ru}_2\text{YCl}_4\text{(PR}_3\text{)}_4]\) \((Y = \text{CO, CS; PR}_3 = \text{PPh}_3, \text{P(p-tol)}_3)\) have shown that all these compounds undergo a reversible, one electron oxidation step, presumably to give the mixed Ru(II)/Ru(III) cations \([\text{PR}_3\text{)}_2\text{YRuCl}_3\text{RuCl(PR}_3\text{)}_2]^+\). Further oxidation and reduction steps showed irreversible behaviour indicative of rapid decomposition of these products \([30]\).

Furthermore, if the \([\text{Ru}_2\text{YCl}_4\text{(PPh}_3\text{)}_3]\) isomer mixtures were treated with \(\text{PPh}_3\) and \(\text{NaBPh}_4\) in either acetone, dichloromethane or ethanol for prolonged periods, displacement of the terminal chloride group by \(\text{PPh}_3\) occurred giving the cationic dimer \([\text{PPh}_3\text{)}_2\text{YRuCl}_3\text{RuY(PPh}_3\text{)}_2\text{BPh}_4]^-\). A small amount of this cation was also produced when \([\text{RuYCl}_2\text{(MeOH)(PPh}_3\text{)}_2]\) was heated in ethanol \([21]\).

Earlier \([1]\) it had been reported that treatment of the "carbonyl-containing" red solution with a mixture of \(\text{SnCl}_2\) and \(\text{PPh}_3\) in acetone gave a small yield of lemon yellow crystals, which analysed for \([\text{Ru}_2\text{(CO)}_2\text{Cl}_3\text{(SnCl}_3\text{)}\text{(PPh}_3\text{)}_3\text{(Me}_2\text{CO)}_2]\). In the light of the above studies it was
considered that this might be either a triple or double chloride bridged dimer, containing a terminal SnCl$_3$ ligand. A more recent $^{31}$P-$\text{H}$ nmr spectrum of the material was, however, inconsistent with either formulation since it revealed only one PPh$_3$ resonance [27]. X-ray structural analysis then showed the compound to be a monomeric solvate [RuCO(Me$_2$CO)Cl(SnCl$_3$)-(PPh$_3$)$_2$]Me$_2$CO(V) with trans PPh$_3$ groups. If (V) was gently warmed in benzene, however, self-dimerisation accompanied by PPh$_3$ and SnCl$_2$ loss occurred and some [(PPh$_3$)$_5$SnCl$_3$(CO)RuCl$_3$Ru(CO)(PPh$_3$)$_2$] was isolated. Unfortunately, this compound was not very stable in solution, readily eliminating another molecule of SnCl$_2$ to give some [Ru$_2$(CO)$_2$Cl$_4$(PPh$_3$)$_3$] ($^{31}$P nmr evidence) [27].

On the basis of the relative percentages of the various dimerisation products found in the RuCl$_2$(PPh$_3$)$_3$/CS$_2$, Ph$_3$(PhCH$_2$)P[RuCl$_3$CO(C$_7$H$_8$)]/2PPh$_3$ and thermolysis reactions of [RuYCl$_2$(PPh$_3$)$_2$] and [Ru(CO)Me$_2$CO(SnCl$_3$)-(PPh$_3$)$_2$]Me$_2$CO it was concluded that self-dimerisation with phosphine loss to give [Ru$_2$(Y)$_2$Cl$_4$(PPh$_3$)$_3$] occurred in low polarity solvents when the phosphine groups were trans to each other in the monomeric precursor. When the phosphine ligands were cis, however, dimerisation without phosphine loss occurred giving the double chloride bridged species [{RuYCl$_2$(PPh$_3$)$_2$}$_2$] [21]. This difference is attributed to the high trans influence of PPh$_3$ and the consequent electronic instability of trans-Ru(PPh$_3$)$_2$ compared to cis-Ru(PPh$_3$)$_2$ arrangements.

Further support for these conclusions comes from the formation of [(AsPh$_3$)$_2$ClRuCl$_3$RuCl$_2$(AsPh$_3$)$_2$] by heating [RuCl$_3$MeOH(AsPh$_3$)$_2$] (which contains trans AsPh$_3$) in benzene and the reported isolation of the double chloride bridged dimer [{Ru(CO)Cl$_2$(PMe$_2$Ph)$_2$}$_2$] from a solution which contains the monomer [RuOC1$_2$(PMe$_2$Ph)$_2$] with cis PMe$_2$Ph groups. Preliminary work on self-dimerisation reactions of [RhCl$_3$(solv)(PR$_3$)$_2$] species to give either [Rh$_2$Cl$_6$(PR$_3$)$_3$] and/or [Rh$_2$Cl$_6$(PR$_3$)$_4$] can probably also be correlated with the isomeric form of the solvated monomer.
In contrast, in more polar solvents, chloride ion displacement is facilitated leading to formation of the triple chloride bridged cations \([\text{Ru}_2(\text{Y})_2\text{Cl}_3(\text{PPh}_3)_4]\)Cl. Well known analogues of these cations, namely \([(\text{PR}_3)_3\text{RuCl}_3\text{Ru(PR}_3)_3]\)Cl, had previously been prepared by reaction of "RuCl_3\times H_2O" with various trialkyl, dialkylaryl- or alkyldiaryl-phosphines in either aqueous ethanol\(^{19}\) or 2-methoxyethanol.\(^{20}\) Rather surprisingly, however, these cations do not react with an excess of tertiary phosphine to give the monomeric \([\text{RuCl}_2(\text{PR}_3)_4]\) complexes. In fact, a detailed literature survey (in late 1973) revealed that, although the monomeric compounds \([\text{RuCl}_2L_3\text{ or }_4](L = \text{PHR}_2, \text{AsR}_3, \text{SbPh}_3, \text{C}_5\text{H}_5\text{N etc})\) were well characterised, only two compounds of this type containing tertiary phosphines (namely \(\text{PPh}_3[1,2] \text{ and } \text{R(p-tolyl)}_3\)) had been synthesised.

Earlier, it had been shown that, when \([\text{RuX}_2(\text{PPh}_3)_4]\) (\(X = \text{Cl, Br}\)) was heated under reflux with excess of triarylphosphites in dichloromethane, ethanol or hexane, the corresponding \([\text{RuX}_2(\text{P(OR)}_3)_4]\) compounds were produced.\(^{22}\) Extension of this exchange reaction to various tertiary phosphines revealed that the product isolated depended on both the nature of the solvent and the phosphine used \([11,18]\). Thus, in ethanol or dichloromethane, the ionic dimers \([\text{Ru}_2X_3(\text{PR}_3)_6]\)X were obtained; whereas in hexane (or light petroleum bp 60-80°C) neutral tertiary phosphine complexes were isolated. For \(\text{PMe}_2\text{Ph}, \text{PMePh}_2; \text{PET}_2\text{Ph; PET}_2\text{Ph and PClPh}_2,\) \([\text{RuX}_2(\text{PR}_3)_4], [\text{RuX}_2(\text{PR}_3)_3]\) and \([(\text{PR}_3)_2X\text{RuX}_3\text{Ru(PR}_3)_3]\) respectively were formed \([18,32]\).

Furthermore, these mononuclear species underwent facile rearrangement reactions in solution, which could be analysed by \(^{31}\text{P}\) nmr spectroscopy. From these studies, it was concluded that \([\text{Ru}_2X_3(\text{PR}_3)_6]\)X were always rapidly produced when the monomers were dissolovd in polar solvents and this accounted for the difficulties in synthesising \([\text{RuX}_2(\text{PR}_3)_3\text{ or }_4]\)
compounds. Only when bulky tertiary phosphines such as PPh₃ and P(p-tolyl)₃ were used are monomeric compounds isolated from "RuCl₃.xH₂O", since here steric constraints inhibited the associative rearrangement reactions. For these compounds variable temperature ³¹P nmr studies revealed the fluxional nature of the trisphosphine complexes [18,32] and showed that [RuCl₂(PPh₃)₄] was best formulated as [RuCl₂(PPh₃)₃.PPh₃] with one PPh₃ group trapped in the lattice [18]. In non-polar solvents, dimerisation of the [RuX₂(PR₃)₃ or 4] compounds (PR₃ = PMePh₂, PEtPh₂) readily occurred to produce the neutral triple halide bridged dimers [(PR₃)₂XRu₂Ru(PR₃)₃].

Initially [18] it was believed that these rearrangement reactions involved formation of an unstable double halide bridged complex [(RuX₂(PR₃)₃)₂] which then underwent further intramolecular rearrangement to generate either [Ru₂X₄(PR₃)₅] with PR₃ loss or [Ru₂X₃(PR₃)₆]X with halide ion displacement (Scheme 1).

Scheme 1
Later, however, the species thought to be \([\text{RuCl}_2(\text{PETPh}_2)_3]_2\) was reformulated as the cationic complex \([\text{RuCl(ETPh}_2)_3(\text{EtOH})_2]\)\(\text{Cl}\) [21] and the mechanism of formation of \([\text{Ru}_2X_3(\text{PR}_3)_6]X\) is now believed to involve direct intermolecular coupling of \([\text{RuX(}\text{PR}_3)_3\text{Solv}_2]X\) and \([\text{RuX}_2(\text{PR}_3)_3]\); for formation of \([\text{Ru}_2X_4(\text{PR}_3)_5]\), self-dimerisation of \([\text{RuX}_2(\text{PR}_3)_3]\) with loss of a \(\text{PR}_3\) group is the most feasible process [21,31] (cf the rearrangement of \([\text{RuYCl}_2\text{Solv}(\text{PPh}_3)_2]\) to \([\text{Ru}_2\text{YCl}_4(\text{PPh}_3)_3]\) discussed earlier). As before, the driving force for these rearrangements is the high stability of six coordinate ruthenium(II) complexes containing triple halide bridging units.

More recently, in an attempt to test the generality of this mechanism, the exchange reactions have been extended to tertiary phosphites, phosphonites and phosphinates [24,31]. With \(\text{P(OMe)}_3\) and \(\text{P(OMe)}_2\text{Ph}\), reaction with \([\text{RuCl}_2(\text{PPh}_3)_3]\) in hexane readily gave \([\text{RuCl}_2\text{L}_4]\), whereas, with \(\text{P(OR)}\text{Ph}_2\) (\(\text{R = Me, Et}\)), monomeric \([\text{RuCl}_2\text{L}_3]\) were produced. In polar solvents, the \(\text{P(OMe)}_2\text{Ph}\) and \(\text{P(OMe)}\text{Ph}_2\) complexes rearranged to the yellow ionic dimers \([\text{Ru}_2\text{Cl}_3\text{L}_6]\)\(\text{Cl}\) but the \(\text{P(OEt)}\text{Ph}_2\) complex produced the yellow ionic trimer \([\text{Ru}_3\text{Cl}_5\text{L}_9]\)\(\text{Cl}\). Exchange of \(\text{P(OR)}\text{Ph}_2\) with \([\text{RuCl}_2(\text{PPh}_3)_3]\) in polar solvents produced the same ionic species, via deep red solutions, from which the red cations \([\text{RuCl(OMe)}(\text{Ph}_2)_4]^+\) and \([\text{Ru}_2\text{Cl}_2(\text{POEt)}\text{Ph}_2)_8]^{2+}\) could be isolated by addition of \(\text{NaBPh}_4\).

A possible rationalisation of these results is obtained by postulating the formation of a double chloride bridged cationic intermediate by coupling of \([\text{RuCl}(\text{L})_3(\text{Solv})]^+\) with \([\text{RuCl}_2\text{L}_3]\) (Scheme 2). This could then either rearrange in intramolecular fashion to give \([\text{Ru}_2\text{Cl}_3\text{L}_6]\)\(\text{Cl}\) or combine with another molecule of \([\text{RuCl}_2\text{L}_3]\) to give \([\text{Ru}_3\text{Cl}_5\text{L}_9]\)\(\text{Cl}\).
A similar double bridged cation \([ L_3(OH)Ru(OH)_2RuL_3]^{+}\) which rearranges to \([ L_3Ru(OH)_3RuL_3]^{+}\) has recently been postulated by Ashworth et al.\(^{23}\) and such species are probably key intermediates in the mechanism of formation of all the triple bridged complexes discussed in this thesis. Further work is now in progress with a wider range of \(P(OR)\) ligands to try and establish the factors which determine the preferred pathway in Scheme 2.

Interestingly, no evidence has been found here for the formation of the neutral dimers \([ Ru_2Cl_4L_5] (L = P(OMe)_3, P(OMe)_2Ph, P(OR)Ph_2)\), which can presumably be attributed to the stronger Ru-P bonds found in alkoxy substituted phosphine complexes. In an attempt to obtain such compounds, \([Ru_2Cl_3(P(Ome)Ph_2)_6]\)Cl was pyrolysed at 120\(^\circ\)C for 12 hours since a similar reaction with \([Ru_2Cl_3(PEt_2Ph)_6]\)Cl had given
[Ru₂Cl₄(PEt₂Ph)₅]⁺ X-ray analysis showed, however, that the unusual neutral dimer [(P(OMe)Ph₂)₂(P(OH)Ph₂)RuCl₃Ru(P(OH)Ph₂)₂(Ph₂PO)] (VI) was formed [23]. The same compound was produced on pyrolysis of [Ru₂Cl₃[P(OMe)Ph₂]₆]X (X = SCN⁻, CN⁻ etc) suggesting that nucleophilic attack of X⁻ on a coordinated alkoxy group to give a Ph₂PO⁻ group and MeX, followed by stepwise hydrolysis of some of the P(OMe)Ph₂ groups probably occurred.

![Diagram](VI)

On the basis of analytical and infrared spectral data (the compounds were too insoluble for molecular weight and nmr studies), similar products were obtained by pyrolysis of [Ru₃Cl₅[P(OEt)Ph₂]₉]X (X = Cl, SCN⁻, CN⁻ etc) [23,31].

In an attempt to synthesise neutral dimeric complexes containing P(OR)Ph₂ or P(OR)₂Ph ligands, [Ru₂YCl₄(PPh₃)₄] (Y = CO,CS) were reacted with an excess of L in benzene. However, in every instance, PPh₃ displacement was accompanied by facile bridge cleavage to give a mixture of monomeric compounds [RuCl₂L₃or₄] and [Ru(Y)Cl₂L₃] [33]. The latter could also be synthesised by direct carboxylation of [RuCl₂L₃or₄] [33]. In polar solvents these compounds (L = P(OR)Ph₂) readily lost chloride ion and addition of BPh₄⁻ ion precipitated the cationic complexes [Ru(Y)Cl-(P(OMe)Ph₂)₃]BPh₄ and [Ru₂₂Cl₂(P(OEt)Ph₂)₆] (BPh₄)₂. In contrast, no cationic complexes were generated when [RuCl₂Y(P(OMe)₂Ph)₃] was dissolved in methanol and this is attributed to the smaller steric require-
ments of the P(OH)₂·Ph groups. Similar changes have been observed for
\[ MX_2\left(\text{Ph}_2P\left(\text{CH}_2\right)_n\text{PPh}_2\right)_2 \] (M = Ru, Os; X = Cl, Br), which lose a halide ion in boiling alcohol to give \[ MX\left(\text{Ph}_2P\left(\text{CH}_2\right)_3\text{PPh}_2\right)_2^+ \] (for n = 3) but not when n = 1 or 2.²⁵

Finally, reaction of \([\text{RuCl}_2(\text{PETPh}_2)_3]\) with \(\text{CS}_2\) gave "[Ru(\text{η}^2\text{-CS}_2)-
Cl(\text{PETPh}_2)_3]\text{Cl}^\text{--}", reformulated on the basis of \(\text{³¹P nmr and conductivity}
studies as \([\text{RuCl}_2(S_2\text{CPEtPh}_2)(\text{PETPh}_2)_2]\) (VII) containing the Ph₂EtP⁺-CS⁻
zwitterion ligand. In methanol, (VII) rearranged to the cationic
\[ [\text{RuCl}(\text{MeOH})\left(\text{S}_2\text{CPEtPh}_2\right)(\text{PETPh}_2)_2]^+ \] (VIII) isolated as its \(\text{BPh}_4^-\) salt.²²²

Further studies on reactions of \(\text{CS}_2\) with other \([\text{RuCl}_2\text{L}_3\text{or}_4]\) compounds are
now in progress.

²²²

(2) Arene complexes of Ruthenium

Interest in this area was first stimulated by the writing of two
reviews entitled "Metal complexes containing six and seven electron
organic ligands" [⁹,¹⁷] and research on the chemistry of \([\{\text{Ru(arene)Cl}_2\}_2]\)
complexes was started in 1974. The compound \([\{\text{Ru(\text{η}^6-\text{C}_6\text{H}_6})\text{Cl}_2\}_2]\) had
been synthesised by dehydrogenation of 1,3 or 1,4 cyclohexadienes with
"RuCl₃·H₂O"²⁶ and later²⁷ this was extended to substituted 1,4 cyclo-
hexadienes. The compounds underwent typical bridge cleavage reactions
with a variety of Lewis bases, giving \([\text{Ru(arene)Cl}_2\text{L}]\) (L = PR₃, AsR₃,
Me₂SO etc), although under more forcing conditions, arene ring displace-
ment also occurred.²⁶,²⁷
It was found that reaction of $\left[\text{Ru}(\eta^6-C_{6}H_{6})Cl_2\right]_2$ with CsCl/HCl in ethanol gave Cs$[\text{Ru}(\eta^6-C_{6}H_{6})Cl_3]$ and this represented the first example of an anionic $\pi$-arene transition metal complex [20,34]. Unfortunately, attempts to prepare the unknown $\text{fac-}[\text{RuCl}_3\text{L}_3]$ anions by reaction of Cs$[\text{Ru}(\eta^6-C_{6}H_{6})Cl_3]$ with excess L, gave either $[\text{Ru}(\eta^6C_{6}H_{6})Cl_2\text{L}] (L = C_5\text{H}_5$-$N, \text{Me}_2\text{SO, SbPPh}_3 \text{ etc})$ or, under more forcing conditions, $[\text{RuCl}_2\text{L}_4]$ ($L = C_5\text{H}_5\text{N, PMe}_2\text{Ph etc})[34]$. Clearly the lability of the coordinated arene group is much less than that of the diene in $[\text{Ru}(\eta^6C_{7}H_{8})Cl_3]$ and, thus, displacement of chloride ion occurs much more readily than loss of the benzene ring.

Reaction of $[\text{Ru}(\eta^6-C_{6}H_{6})Cl_2]_2$ with hot water had been reported to give an orange solution from which $\text{NH}_4\text{PF}_6$ slowly precipitated an orange solid, identified as $[\text{(}\eta^6-C_{6}H_{6})\text{RuCl}_3\text{Ru}(\eta^6-C_{6}H_{6})\text{]} \text{PF}_6 \text{(IX) (40% yield)}$ [27]. In one of our attempts to repeat this preparation, an additional compound containing 7% nitrogen was obtained. This was shown by X-ray analysis to be the monomeric cation $[\text{Ru}(\eta^6\text{C}_{7}H_{8})\text{Cl(NH}_{3})_2\text{]}_3\text{(PF}_6\text{)}_3 \text{NH}_4\text{PF}_6$ [28].

Shaking $[(\eta^6-C_{6}H_{6})\text{Cl}_2]_2$ with excess of $\text{NH}_4\text{PF}_6$ in methanol produced a higher yield of (IX) (>90%). Unfortunately, attempts to synthesise a range of new triple halide bridged complexes $[L_3\text{RuCl}_3\text{RuL}_3] \text{PF}_6 \text{(L = C}_5\text{H}_5\text{N, Me}_2\text{SO, Et}_2\text{S etc})$ by arene displacement from (IX) were unsuccessful, since bridge cleavage was a more facile process. However, this did give a convenient synthetic route to new $\eta^6$-arene cationic complexes of the type $[\text{Ru}(\eta^6\text{C}_{7}H_{8})\text{ClL}_2] \text{PF}_6 \text{(L = PR}_3\text{, C}_5\text{H}_5\text{N, AsPPh}_3 \text{ etc})$ [20,34].

By analogy with the related studies on triple halide bridged ruthenium(II) complexes containing group 5B donor ligands (see section 1A), the most likely mechanism of formation of (IX) is by intermolecular coupling of the solvated monomers $[\text{Ru}(\eta^6\text{C}_{6}H_{6})\text{Cl}_2(\text{MeOH})]_2$ and $[\text{Ru}(\eta^6\text{C}_{6}H_{6})\text{Cl}(\text{MeOH})]_2^+$. These could either form (IX) directly or via a cationic dimeric double bridged intermediate $[\text{(}\eta^6\text{C}_{6}H_{6})\text{ClRuCl}_2\text{Ru(MeOH)(}\eta^6\text{C}_{6}H_{6})]_2^+$,
which then rapidly rearranges to give (IX) (Scheme 3) (cf formation of \([\text{Ru}_3\text{Cl}_5(\text{P}^\text{OEt}_2\text{Ph}_2)_9]\text{Cl} - \text{section 1A}) [34].

Reaction of aqueous solutions of \([\{\text{Ru(arene}\text{Cl}_2\}_2}\] (arene = benzene, mesitylene) with an excess of either \(\text{NaOH}\) or \(\text{Na}_2\text{CO}_3\) resulted in the isolation of the yellow triple hydroxo-bridged compounds \([\text{areneRu(OH)}_3\text{Ru(arene)}]\text{Cl}_{13}\text{H}_{20}\) (X). Treatment of aqueous solutions of (X) with \(\text{NaBPh}_4\) readily gave the \(\text{BPh}_4^-\) salt but addition of \(\text{NH}_4\text{PF}_6\) led to the isolation of \([\text{Ru}(\eta^6\text{C}_6\text{H}_6)(\text{NH}_3)_3\] \(- \text{PF}_6)_2\) [20,25,35]. Unlike compound (IX), the triple hydroxo species (X) exhibited a surprising stability towards Lewis Bases. For example, they were recovered unchanged even after refluxing with various tertiary phosphines for prolonged periods. (cf. related studies with \([\text{Pt}_2(\text{OH})_2(\text{PR}_3)_4](\text{BF}_4)_2\) and \(\text{PR}_3^1\).28 In contrast, reaction of (X) with alcohols readily gave the triple alkoxo bridged complexes \([\text{areneRu(OR)}_3\text{Ru(arene)}] - \text{BPh}_4\) (\(R = \text{Me, Et}\)), which could also be synthesised by reaction of \([\{\text{Ru(arene}\text{Cl}_2\}_2}\] with \(\text{NaOH}\) [35]. A detailed study of the reactions of all these compounds is now in progress.29
If \( \{ \text{Ru}^{2+} \} \text{C}_6 \text{H}_6 \text{Cl}_2 \text{H}_2 \text{O}_2 \) in water was treated with less sodium carbonate \( \text{CO}_3^{2-} \) \( \text{Ca} \) 1:1 molar ratio and the resulting solution treated with excess of sodium sulphate, an orange solid was precipitated. This was shown by X-ray analysis to be the novel tetranuclear complex \( \{ \text{Ru}(\eta^6 \text{C}_6 \text{H}_6) \text{OH} \}_{4} \text{(SO}_4 \}_{2} \text{H}_2 \text{O} \text{(XI)} \) containing both \( \eta^6 \text{C}_6 \text{H}_6 \) rings and hydroxo bridges \( [25] \). This represents both the first ruthenium compound and the first transition metal arene complex with a cubane-like stereochemistry. Reaction of (XI) with more hydroxide ion gave \( \text{Ru}_2(\eta^6 \text{C}_6 \text{H}_6)_2(\text{OH})_{2}^{+} \) and, with LiBr, \( \text{Ru}_2(\eta^6 \text{C}_6 \text{H}_6)_2(\text{OH})_{2}^{+} \text{Br} \) was isolated as its PF$_6$- salt. With nitrogen donor ligands such as pyridine, the dicationic dimer \( \{ (\eta^6 \text{C}_6 \text{H}_6)(\text{C}_5 \text{H}_5 \text{N}) \text{-Ru(OH)}_{2} \text{Ru}(\text{C}_5 \text{H}_5 \text{N})(\text{C}_6 \text{H}_6) \} \text{(PF}_6 \}_{2} \) was isolated, although with 1,10-phenanthroline, only \( \text{Ru}(\text{phen})_3 \text{(PF}_6 \}_{2} \) was formed \( [25] \).

A possible mechanism of formation of (XI) could involve formation of the \( \{ \text{Ru}(\eta^6 \text{C}_6 \text{H}_6)(\text{OH})(\text{H}_2 \text{O})_2 \}^{+} \) cation via deprotonation of a coordinated water molecule in \( \{ \text{Ru}(\eta^6 \text{C}_6 \text{H}_6)(\text{H}_2 \text{O})_3 \}^{2+} \) followed by direct tetrarmerisation to \( \{ \text{Ru}(\eta^6 \text{C}_6 \text{H}_6)(\text{OH})_4 \}^{4+} \) and subsequent removal of this cation from solution by addition of sulphate ion.

Formation of \( \{ \text{Ru}_2(\text{arene})_{2}(\text{OH})_3 \}^{+} \) can, like \( \{ \text{Ru}_2(\text{arene})_2\text{Cl}_3 \}^{+} \), be ascribed to intermolecular coupling between \( \{ \text{Ru}(\text{arene})(\text{OH})(\text{H}_2 \text{O})_2 \}^{+} \) and the neutral \( \{ \text{Ru}(\text{arene})(\text{H}_2 \text{O})_2 \} \), probably via a cationic double hydroxop bridged intermediate \( \{ (\text{arene})\text{OHRu(OH)}_2 \text{Ru(H}_2 \text{O})(\text{arene}) \}^{+} \) \( \text{(XII)} \). Alternatively, (XII) could be formed by direct dimerisation of \( \{ \text{Ru}(\text{arene})(\text{OH})(\text{H}_2 \text{O})_2 \}^{+} \) to \( \{ (\text{arene})(\text{H}_2 \text{O})\text{Ru(OH)}_2 \text{Ru(H}_2 \text{O})(\text{arene}) \}^{2+} \) followed by deprotonation in more basic media. \( \text{(cf} \{ \text{L}_3 \text{(H}_2 \text{O})\text{Ru(OH)}_2 \text{RuL}_3 \}^{2+} \text{to} \{ \text{L}_3 \text{(OH)}\text{Ru(OH)}_2 \text{RuL}_3 \}^{+} \) \( \text{postulated in ref. 23} \).

Unlike the related \( \{ \text{Ru}_2 \text{YCl}_4(\text{PR}_3)_4 \} \) complexes which undergo reversible one-electron oxidation processes to generate \( \{ \text{Ru}_2 \text{YCl}_4(\text{PR}_3)_4 \}^{+} \) cations, none of the arene triple bridged cations exhibit reversible oxidation or reduction behaviour \( [30] \).
Finally, a study has been made of the reaction of various arene-ruthenium(II) cations with nucleophiles. Most published work in this area has indicated that, although substituted cyclohexadienyl complexes are generated, they are usually impossible to isolate, because of rapid decomposition. However, although this is true with the cations \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}(\text{N-N})]\)PF\(_6\) \((\text{N-N} = 2,2^1\)-bipyridyl, 1,10-phenanthroline), reaction of various nucleophiles with \([\text{Ru}(\text{N}-\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{N-N})]\)PF\(_6\) leads to the isolation of air-stable \(\eta^5\)-cyclohexadienyl complexes \([\text{Ru}(\text{N}-\text{C}_6\text{H}_6\text{Y})(\text{PMe}_2\text{Ph})(\text{N-N})]\)PF\(_6\) \((\text{Y} = \text{H}^-, \text{OH}^-, \text{CN}^-)\)\(^{26}\). Attempts to make various disubstituted cyclohexadiene complexes \([\text{Ru}(\eta^4\text{C}_6\text{H}_6\text{YZ})-(\text{PMe}_2\text{Ph})(\text{N-N})]\) \((\text{Y} = \text{H}^-; \text{Z} = \text{OH}^-\text{etc.})\) from these are now in progress.\(^{30}\) There is also some \(^1\text{H}\) nmr evidence that two hydride ions might add to one of the benzene rings in the \([\text{Ru}_2(\eta^1\text{C}_6\text{H}_3)(\text{OH})_3]^+\) cation to give a 1,3 cyclohexadiene complex \(^{26}\).

B Transition metal complexes containing dioxo-, monothio- or dithio-acid ligands.

The general theme of this collection of papers is the synthesis, characterisation and reactions of transition metal complexes containing ligands with O, O; S, O or S, S donor atoms. Important aims of this work were to observe the differences (if any) in structure and behaviour of these complexes on their reaction with a variety of Lewis bases and to study any molecular rearrangements of these products in solution, using infrared and nmr spectroscopic methods.

The earlier work (in conjunction with Professor (now Sir) Geoffrey Wilkinson FRS) from 1962-65 was concerned entirely with the chemistry of some second and third row transition metal carboxylates. In particular, earlier suggestions by Nakamoto,\(^{31}\) on the use of ir spectroscopy to determine the mode of carboxylate bonding, were utilised
extensively to infer the structures of a number of these carboxylate compounds.

For example, the important oxidation catalysts \([\{\text{Pd(OCOR)}_2\}_3]\) (R = Me, Et, Ph) were synthesised and their reactions with Lewis bases studied \([37,38,40]\). These studies clearly showed that reaction occurred with an excess of a wide range of bases (L) (P, As, Sb, N, O, S donors) to give the products \([\text{Pd(OCOR)}_2L_2]\). With stoichiometric amounts of EPh\(_3\) (E = P, As), the dimeric compounds \([\{\text{Pd(OCOME)}_2(\text{EPh}_3)\}_2]\) were also isolated. On the basis of molecular weight and detailed IR studies, these were formulated as square planar compounds with unidentate and unidentate/bridging \(\text{RCO}_2^-\) groups respectively. Much later, \(^1\text{H}\) NMR studies on \([\text{Pd(OCOME)}_2(\text{PR}_3)_2]\) (PR\(_3\) = PMe\(_2\)Ph, PMe\(_2\)Ph) showed them to have a cis configuration and variable temperature \(^1\text{H}\) NMR studies on \([\{\text{Pd(OCOME)}_2\}-\text{AsPH}_3\}_2]\) indicated that this compound exhibited a facile scrambling of terminal and bridging acetate groups via a solvent-assisted ring opening mechanism \([67]\). (cf. related studies on \([\{\text{Pd(OCOR)}_2(\text{PMe}_2\text{Ph})\}_2]\) made from \([\{\text{PdCl}_2(\text{PMe}_2\text{Ph})\}_2]\) and Ag[RCO\(_2\)]. \(^{32}\)

In contrast \([\{\text{Pt(OCOME)}_2\}_n]\) (formulated as a trimer from molecular weight measurements) did not undergo cleavage reactions but, instead, gave high molecular weight adducts of uncertain composition \([38]\). These observations are consistent with recent crystallographic studies on platinum(II) acetate (made by a different route), which showed it to be a tetramer with strong metal-metal interactions. \(^{33}\) Palladium(II) acetate on the other hand is a cyclic trimer with no metal-metal interactions. \(^{34}\)

Another important group of compounds are \([\text{Mo}_2(\text{OCOR})_4]\) (R = Me, Et, \(^n\text{Bu}, i\text{Bu}, \text{Ph} \text{etc}\)), made by direct reaction of Mo(CO)\(_6\) and RCO\(_2\)H \([36]\) and shown by subsequent X-ray analysis (for R = Me) \(^{35}\) to have the \([\text{Cu}_2(\text{OCOME})_4-2\text{H}_2\text{O}]\) structure (except for the absence of terminal groups). Reaction with
pyridine did, however, give very air-sensitive bisadducts \([\text{Mo}_2(\text{OCOR})_4(\text{C}_5\text{H}_5\text{N})_2]\) \([36]\). Interestingly, reaction with dry hydrogen chloride gave a new form of \(\text{MoCl}_2^+\) and this was later substantiated by other workers. \(^{36}\) These replacement reactions have been extended mainly by Cotton and coworkers, \(^3\) who synthesised a range of binuclear low valent molybdenum halides, such as \(\text{Mo}_2\text{Cl}_8^{4-}\) etc., from \([\text{Mo}_2(\text{OCOMe})_4]\).

The acetate groups in \([\text{Mo}_2(\text{OCOMe})_4]\) were later replaced by various dithioacetic ligands giving \([\text{Mo}_2(\text{S-S})_4]\) (S-S = \(\text{S}_2\text{COEt}, ~\text{S}_2\text{CN}^1\text{Pr}_2, ~\text{S}_2\text{CNET}_2, ~\text{S}_2\text{PPh}_3\)) and by monothiobenzoate ion to give \([\text{Mo}_2(\text{PhCOS})_4]\). For S-S = \(\text{S}_2\text{COEt}, \) stable adducts \([\text{Mo}_2(\text{S}_2\text{COEt})_4\text{L}_2]\) (\(\text{L} = \text{C}_5\text{H}_5\text{N}, \text{AsEt}_3\) etc) were readily formed but with \([\text{Mo}_2(\text{S}_2\text{CNR})_2]_2\) rapid rearrangement to the \(\"\text{carbene}\"\) complex(XIII) occurred, followed by oxidation to \([\text{Mo}_2\text{O}_3(\text{S}_2\text{CNR})_4]\) \([47]\). The structure of (XIII) was established independently by Weiss et al. \(^{38}\) using X-ray crystallography.

\[
\text{R}_2
\]

![Diagram](XIII)

Rather surprisingly, reaction of \(\text{W(CO)}_6\) and \(\text{MeCO}_2\text{H}\) did not give \([\text{W}_2(\text{OCOMe})_4]\) but, instead, a trinuclear species of composition \([\text{W}_3\text{O}(\text{OCOMe})_8(\text{OH})\text{H}_2\text{O}]\) was obtained\([41]\). Cotton and Jeremic independently reported very similar results. \(^{39}\)

Reaction between hydrated rhodium oxide and various carboxylic acids did give the rhodium(II) carboxylates \([\text{Rh}_2(\text{OCOR})_4(\text{H}_2\text{O})_2]\) and, here, ready replacement of terminal water molecules, by ligands such as pyridine, \(\text{PPh}_3\) etc, was possible \([38]\). Reaction of \("\text{RuCl}_3\text{xH}_2\text{O}\"\) with carboxylic
acid/acid anhydride mixtures, however, produced red-brown crystalline compounds and emerald green solutions. The former were shown to be \([\text{Ru}_2(\text{OCOR})_4\text{Cl}]\) and exhibited magnetic moments of 4.0–4.6 per dimer, indicative of 3 unpaired electrons \([39]\). An X-ray structural analysis on the \(n\)-butyrate confirmed this formulation and showed that the carboxylate bridged dimeric units were held together by single chloride bridges. The unusual magnetic properties were satisfactorily explained on the basis of molecular orbital theory \([40]\), and these compounds are the only "high spin" ruthenium complexes ever to have been prepared. The emerald green solutions gave very soluble species, formulated initially as dimers \([39]\) but shown later, by Spencer and Wilkinson \([41]\), to contain the trinuclear oxo centred cations \([\text{Ru}_3\text{O}(\text{OCOR})_6(\text{H}_2\text{O})_3]\) \text{OCOR}\.

In 1967, after a two year postdoctoral fellowship in America, working on a study of the kinetics of fast reactions using nmr spectroscopy, I started an examination, at Newcastle University of the reactions of \([\text{Pd}(\text{S}_2\text{PPh}_2)_2]\) with various Lewis bases. On the basis of infrared spectral arguments, analogous to those used earlier for the carboxylate compounds, the products \([\text{Pd}(\text{S}_2\text{PPh}_2)_2\text{PR}_3]\) and \([\text{Pd}(\text{S}_2\text{PPh}_2)_2(\text{PR})_3]\) were formulated as rare examples of five and six coordinate palladium(II) respectively and interconversion reactions between these species were monitored by ir spectroscopy \([42]\).

Later, however, at Edinburgh University, an extension of these studies to platinum revealed that the 1:2 adducts could be stabilised in polar solvents and were ionic in nature. Hence, the compounds were reformulated as four coordinate square planar complexes with uni-/bidentate and bidentate/ionic modes of bonding respectively \([43]\) and this was subsequently verified by X-ray structural studies on \([\text{Pd}(\text{S}_2\text{PPh}_2)_2\text{PPh}_3]\) and \([\text{Pd}(\text{S}_2\text{PPh}_2)^{-} (\text{PET}_3)_2]\) \text{S}_2\text{PPh}_2 \([44]\). Further studies on other dithioacid complexes of
palladium and platinum(II) of type \([M(S\text{-}S)_2]\) \((S\text{-}S^\text{-}=S_2\text{CNR}_2, S_2\text{PR}_2, S_2\text{P(OR)}_2, S_2\text{COR})\) showed that this stepwise cleavage of \(M\text{-}S\) bonds by strong Lewis bases, to give the monomeric 1:1 and 1:2 adducts (XIV) and (XV) respectively, was a general phenomenon\(^{[46,48]}\). Again, an X-ray analysis of \([\text{Pt}(S_2\text{CNET})_2(P\text{MePh}_2)]\) confirmed this conclusion and structure (XIV) has now been firmly established for various \(S\text{-}S\) ligands (see \(^{[67]}\) for references). Characteristic IR bands for \(S_2\text{PPh}_2\) \(^{[44]}\) and \(S_2\text{PMe}_2\) \(^{[48]}\) compounds were also used to determine the mode of bonding.

\[
\begin{align*}
\text{(XIV)} & \quad \text{S} \quad \text{L} \quad \text{M} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{M} \\
\text{S} & \quad \text{L}
\end{align*}
\]

In contrast, palladium(II) carboxylates formed 1:1 and 1:2 adducts of different structure (see earlier) and with a wider range of Lewis bases. Recently, studies on \([\{M(\text{PhCOS})\}_2]_n\) \((M = \text{Pd,Pt})\) with Lewis bases have shown that they behave like carboxylates giving neutral \([M(\text{PhCOS})_2L_2]\) with S-bonded unidentate groups. No evidence, however, has been found here for either 1:1 adducts (monomer or dimer) or cationic 1:2 complexes\(^{[67]}\).

The compounds \([M(S\text{-}S)_2L]\) and \([M(S\text{-}S)L_2]\) \((S\text{-}S)\) were shown by \(^1\text{H}\) nmr (and later \(^{31}\text{P}\) nmr) spectroscopy to undergo a number of interesting reversible rearrangement reactions in solution \(^{[44,46,48]}\). These were:-

a) Rapid unidentate/bidentate scrambling in \([M(S\text{-}S)_2L]\) compounds. Kinetic line shape analysis studies suggested a concerted mechanism, in which both bond breaking and bond making were important (equation 1).
b) Rapid bidentate/ionic exchange in \([M(S-S)L_2]_{(S-S)}\) compounds.
c) Slower intermolecular exchange of free and bound \(PR_3\) in \([M(S-S)_2PR_3]\).
d) Interconversion between the 1:1 and 1:2 adducts in solution (equation 2)

Equilibrium constants were measured for this process by nmr spectroscopy
and showed that the ionic compounds are stabilised at low temperatures.

\[
[M(S-S)(PR_3)_2]_{(S-S)} \rightleftharpoons [M(S-S)_2PR_3] + PR_3 \quad (2)
\]

Some irreversible rearrangement reactions also occurred. For
example, reaction of \([M(S_2CO)_2]\) and \([M(S_2{\text{P(OEt)}})_2]\) with excess of \(PR_3\)
gave the unusual products \([M(S_2CO)(PR_3)_2]\) and \([M(S_2{\text{P(O(OEt)}})(PR_3)_2]\) and
conductivity studies showed that these were formed by nucleophilic attacks
on the alkoxy group of the coordinated dithioacid group (equation 3).

These provided the first examples of compounds containing the unstable
\(S_2CO^{2-}\) and \(S_2{\text{P(O(OEt)}})^{2-}\) anions.

\[
\text{ROC} \quad \overset{\text{excess PR}_3}{\rightleftharpoons} \quad \begin{align*}
\text{M} & \quad \text{COR} \\
\text{S} & \quad \text{S} \\
\text{S} & \quad \text{COR}
\end{align*}
\]

Another irreversible rearrangement occurred with the \(-S_2CNR_2\) compounds
in chlorinated solvents such as \(CH_2Cl_2\), giving the complexes \([M(S_2CNR_2)^-]\)
(PR₃)₂][Cl.H₂O and CH₂(S₂CNR₂)₂. Interestingly, no such rearrangement occurred with other dithioacid anions.

For [Pd(S₂PR₂)(PPh₃)₂]BPh₄ (R = Me,Ph) dissolution in CH₂Cl₂-EtOH or CHX₂EtOH (X = Cl,Br) produced rapid rearrangement, to give [PdX(PPh₃)₂(S₂PR₂)], and this process was believed to involve a labile π- or σ-bonded phenyl group[48]. Unfortunately, this particular rearrangement was confined to compounds containing a combination of Pd, PPh₃, S₂PR₂ and BPh₄⁻ and thus did not provide a general method of synthesising the series [MX(PR₃)₂(S-S)]. It was found later, however, that these compounds could readily be synthesised by reaction of [MX₂(PR₃)₂] with alkali metal dithioacid salts (1:2 mol ratio). In contrast, reactions of carboxylate ions with these halide bridged dimers gave either [MX(OCOR)₂(PR₃)₂] (1:2 mol ratio)⁴² or [M(OCOR)₂(PR₃)₂] (1:4 mol ratio).³² These compounds were useful starting materials for the synthesis of the mixed dithioacid complexes [Pt(PR₃)₂(S₂CNET₂)(S₂PR₂)] (shown to be stereochemically rigid up to 330K by ¹H nmr spectroscopy) and the mixed ligand cations [PdL(PMe₂Ph)(S₂CNET₂)BPh₄ (L = PPh₃, C₅H₅N etc) [56,60]. With tetracyanoethylene, however, the unusual triphenylcyanoborolate complex [Pd(S₂CNET₂)(PMe₂Ph)(NCBP₃)] was isolated [63,65].

A wider range of compounds of type [PdX(L)(S-S)] (L = AsPh₃, SbPh₃, C₅H₅N etc) were made by cleavage of the halide bridged dimers [PdX(S-S)₂] (XVI) (S-S⁻ = S₂CNET₂, S₂PMe₂, S₂COEt). These were synthesised by reaction of [Pd(C₈H₁₂)Cl₂] with S-S⁻ (1:1 mol ratio), in contrast to previous reactions of this diene compound with nucleophiles, which gave substituted alkenyl compounds [54,61].

The corresponding [Pt(C₈H₁₂)Cl₂] with S₂CNET₂ behaved differently, giving the insoluble diene bridged complex ([PtCl(S₂CNET₂)]C₈H₁₂) (XVII), which was ascribed to stronger Pt-C bonds. Both (XVI) (S₂CNET₂) and (XVII)
however, reacted with $\text{Na}_2\text{PMe}_2\text{H}_2\text{O}$ to give the mixed dithioacid

$$\text{Cl} \quad \text{Cl}$$

$$\text{S} \quad \text{S}$$

$$\text{C} \quad \text{N}$$

$$\text{E} \quad \text{t}_2$$

(XVII)

$$\text{S} \quad \text{S} \quad \text{CNET}_2$$

(XVI)

compounds $[\text{M(S}_2\text{CNET}_2)(\text{S}_2\text{PMe}_2)]$, although the palladium species readily underwent partial disproportionation in solution. Reaction of these with $\text{PPh}_3$ then gave the stereochemically rigid $[\text{M(PPh}_3)(\text{S}_2\text{CNET}_2)(\text{S}_2\text{PMe}_2)]$ [61].

Another unusual reaction of $[\text{M(S-S)}]_2$ compounds was the reaction of $\text{[Pt(S}_2\text{COR)}_2]$ with $\text{K[S}_2\text{COR]}$ to give the $[\text{Pt(S}_2\text{COR)}_3]$ anions ($\text{R = Et, } \text{iPr}$). Unlike the $[\text{Ni(S}_2\text{COEt)}_3]$ anion, which is six coordinate, X-ray analysis showed the $[\text{Pt(S}_2\text{COEt)}_3]$ to be square planar with two unidentate $\text{S}_2\text{COEt}$ groups and $^1\text{H}$ nmr studies indicated rapid intramolecular exchange of xanthato ligands at ambient temperature. Furthermore, slow irreversible rearrangement occurred in solution to give the $[\text{Pt(S}_2\text{CO)(S}_2\text{COR)}]$ anions, which reacted with various Lewis bases to give $[\text{Pt(S}_2\text{CO)L)}_2]$ ($\text{L = PPh}_3$, $\text{PMe}_2\text{Ph}, \text{Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2$) [52,59].

Finally, these versatile $[\text{M(S-S)}]_2$ compounds reacted with excess of tertiary phosphinites (P(OR)Ph$_2$) to give $[\text{M(S-S)(PPh}_2\text{O)(PPh}_2\text{OH)}]$ complexes (XVIII) shown by X-ray analysis to contain the symmetrically hydrogen-bonded Ph$_2$POHOPPh$_2$ ligand.

(XVIII)
A careful study of this reaction has enabled intermediates such as \([\text{Pt}(S_2\text{CNET}_2)(\text{PPh}_2\text{OMe})_2]\text{BPh}_4\) and \([\text{Pt}(S_2\text{CNET}_2)(\text{PPh}_2\text{O})(\text{PPh}_2\text{OMe})]\) to be isolated and a detailed mechanism of formation of (XVIII) has been proposed. With \([\text{M}(S_2\text{CO})^\text{Pr}_2]\), however, only the compounds \([\text{M}(S_2\text{CO})(\text{PPh}_2^\text{OEt})_2]\) were formed [62].

In parallel with these studies on palladium and platinum, a thorough investigation on dithioacid complexes of ruthenium, rhodium, and osmium has been carried out. A series of ruthenium(II) complexes \([\text{Ru}(S-S)_2\text{L}_2]\) were prepared by prolonged reaction of dithioacid anions with some of the ruthenium(II) or (III) tertiary phosphine and phosphite compounds discussed in section A [45,49]. A cis-configuration was established by X-ray analysis for \([\text{Ru}(S_2\text{PET}_2)_2(\text{PMe}_2\text{Ph})_2]\). More recently it has been shown that under milder conditions of reaction, intermediates such as \([\text{RuCl}(S-S)_3]\), \([\text{Ru}(S-S)_2\text{L}_3]^+\) and \([\text{Ru}(S-S)_2\text{L}_3]\) can be trapped out and characterised by chemical and spectroscopic methods [64,68].

The complexes \([\text{Ru}(S_2\text{PR}_2)_2\text{L}_2]\) reacted with CO under very mild conditions to form the monocarbonyl species \([\text{Ru}(S_2\text{PR}_2)_2\text{LCO}]\) and underwent ligand exchange reactions with other phosphorus ligands (L') of greater basicity to give either \([\text{Ru}(S-S)_2\text{L'}/]\) and/or \([\text{Ru}(S-S)_2\text{L'}/]\) [45,49].

Most of these compounds exhibited temperature variable \(^1\text{H}\) nmr spectra attributed to facile interconversion of optical enantiomers (for \(S_2\text{PR}_2\) complexes) and restricted rotation about the \(-\text{CN}\) bond (for the \(S_2\text{CNR}_2\) compounds).

The mechanism proposed for the former involved five steps [50,53] viz:

a) attack of solvent to form a seven coordinate intermediate

b) rupture of the metal-sulphur bond trans to L

c) exchange of bidentate and unidentate ligands

d) reattack of the free sulphur atom in such a position that when the
solvent is expelled the attacking sulphur atom becomes trans to $L$.

Very recently a similar interconversion process has been observed for the monothiobenzoate complex cis-$[\text{Ru}(\text{PhCOS})_2(\text{PMe}_2\text{Ph})_2]$, made by reaction of mer-$[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]$ with Na[PhCOS]. Reaction with NH$_4$[PhCOS] in acetone, however, gave a nitrogen containing product, shown by X-ray analysis to be $[\text{Ru}(\text{PhCOS})_2(\text{PMe}_2\text{Ph})_2(\text{HN(C)}(\text{Me})\text{CH}_2\text{CMe}_2\text{NH}_2)]$ (XIX) and a mechanism of formation involving condensation of $[\text{Ru}(\text{PhCOS})_2(\text{PMe}_2\text{Ph})_2]^-$

$$\begin{array}{c}
\text{PhC} \\
\text{O} \equiv \text{S} \\
\text{Ru} \\
\text{PMe}_2\text{Ph} \\
\text{Me} \\
\text{H}_2\text{N} \\
\text{S} \equiv \text{O} \\
\text{CPh} \\
\text{Me} \\
\text{C} \equiv \text{C} \\
\text{H}_2 \\
\text{Me}
\end{array}
$$

(XIX)

$(\text{NH}_3)_2^-$ with mesityl oxide was suggested [66].

The tris(chelate) complexes $[\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{diene}]$ were synthesised by reaction of $[\text{RuCl}_2(\text{diene})]_n$ with Na$[\text{S}_2\text{PMe}_2\text{H}_2\text{O}]$ and the labile diene group readily replaced by various bidentate ligands such as $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1,2$) and $\text{C}_6\text{H}_4(\text{AsMe}_2)_2$ [53]. In contrast, reaction of $[\text{Ru}(\text{arene})\text{Cl}_2]_2$ with $\text{S}_2\text{PR}_2$ gave the compounds $[\text{Ru}(\text{arene})(\text{S}_2\text{PR}_2)_2]$ which contain both uni- and bi-dentate $\text{S}_2\text{PR}_2$ ligands. Similar compounds $[\text{Rh}(\text{C}_5\text{Me}_3)(\text{S-S})_2]$ were made with a wider range of dithiocarb ligands and kinetic line shape analysis studies indicated a dissociatively controlled uni-/bi-dentate exchange process for the latter compounds. Other compounds prepared included $[\text{Rh}(\text{C}_5\text{Me}_5)\text{Cl}(\text{S-S})]$, $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{PMe}_2)]$ and $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{S}_2\text{CNMe}_2)L]\text{BPh}_4$ ($L = \text{PPh}_3$, CO, AsPh$_3$, C$_5$H$_5$N etc) [55,65]. Reaction of $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{S-S})\text{MeOH}]\text{BPh}_4$ with $\text{C}_2(\text{CN})_4$, however, gave the triphenylcyanoborate complexes $[\text{Rh}(\eta\text{C}_5\text{Me}_5)(\text{S-S})(\text{NCBPh}_3)]$ as verified by X-ray analysis for $\text{S-S} = \text{S}_2\text{PMe}_2$ [63,65].
Earlier, a variety of rhodium(III) dithioacid complexes had been synthesised starting from \( \text{mer-[RhCl}_3(\text{PMe}_2\text{Ph})_3 \). These included species such as \( \text{[RhCl}_2(\text{S-S})(\text{PMe}_2\text{Ph})_3 \), \( \text{[RhCl}_2(\text{S-S})(\text{PMe}_2\text{Ph})_2 \), \( \text{[RhCl}(\text{S-S})(\text{PMe}_2\text{Ph})_3 \text{BPh}_4 \) and \( \text{[Rh}(\text{S-S})(\text{PMe}_2\text{Ph})_2 \text{BPh}_4 \). All these compounds were characterised by extensive spectroscopic studies and a detailed mechanism for the overall reaction postulated[51]. Similar studies on \( \text{mer-[OsCl}_3(\text{PMe}_2\text{Ph})_3 \) produced an even wider range of new dithioacid compounds of osmium(III) and (II) and, again, a mechanism for the overall reaction was proposed[58].

Finally, in an attempt to prepare \( \text{Et}_2\text{NC(Se)SeSeC(Se)NET}_2 \) by the oxidation of \( \text{NaSe}_2\text{CNET}_2 \), the two disproportionation products \( \text{Et}_2\text{NC-(Se)SeSeC(Se)NET}_2 \) (XX) and \( \text{Et}_2\text{N.C(Se)SeC(Se)NET}_2 \) were obtained. An X-ray structural analysis of (XX) showed it to be a bis(diethyl-diselenocarbamato)selenium(II) compound with two types of Se-Se bond [57] and this was correlated with earlier work on sulphur, selenium and tellerium(II) complexes of bidentate dithio and diseleno ligands. 

\[
\begin{align*}
\text{Et}_2\text{NC} & \quad \text{Se}^{2.7} \quad \text{Se}^{2.76} \quad \text{Se} \\
& \quad \text{Se}^{2.32} \quad \text{Se}^{2.32} \quad \text{CNET}_2
\end{align*}
\]

(XX)
I gratefully acknowledge the contributions of the following people to the work presented in this thesis. My former supervisor, Professor Sir Geoffrey Wilkinson FRS who taught me, above all, that enthusiasm is a prime asset in a research scientist; co-senior authors Drs. R.O. Gould and G.A. Heath; postdoctoral fellows J.D. Owen, C.L. Jones and W.J. Savage; postgraduate students Drs. J.M.C. Alison, E.S. Switkes, D.F. Steele, D.J. Cole-Hamilton, L. Ruiz-Ramírez, P.W. Armit, M.C. Cornock, W.J. Sime, D.R. Robertson, Miss M.A. Thomson and Messrs J.A. Goodfellow, T. Arthur and I. Robertson; 4th year undergraduates Dr. J. Sinclair and Miss L. Scott; Dr. A.S.F. Boyd and Mr. J.R.A. Millar who ran many of the $^{31}$P and $^1$H nmr spectra and Mr. J. Grunbaum for the determination of elemental analyses.

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30. I. Robertson and T.A. Stephenson - unpublished work.


NEW COMPLEXES OF RUTHENIUM (II) AND (III) WITH
TRIPHENYLPHOSPHINE, TRIPHENYLARSONE,
TRICHLOROSTANNATE, PYRIDINE AND
OTHER LIGANDS

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Abstract—The interaction of triphenylphosphine, -arsine and -stibine with hydrated ruthenium trichloride in methanol leads to a variety of complexes such as [RuCl₃(PPh₃)₂], [RuCl₃(P₂H₅)₃], [RuCl₃(P₂H₅)₂CH₂OH], [RuCl₃(AsPh₃)₂CH₂OH] and [RuCl₃(SbPh₃)₂]. The corresponding bromo complexes are also described. New mono and dicarbonyl complexes of ruthenium (II) and (III) have also been prepared by the interaction of Ph₃P, Ph₃As, Ph₃Sb, pyridine etc., with a carbonyl-containing solution. Complexes of type cis and trans-[RuCl₃(CO)₂L₂], [RuCl₃(CO)L₂] and [pyH][RuCl₃COPy] are described.

Although much information is available on the preparation and properties of tertiary phosphine and -arsine complexes of transition metals,¹ relatively little exists for those of ruthenium. The insoluble hydrido-carbonyl species, [RuHCl(CO)(MPh₃)₃], (M = P, As), have been prepared by refluxing hydrated ruthenium trichloride with an excess of ligand in 2-methoxyethanol.² A preliminary note by VASKA³ lists the products of triphenylphosphine, -arsine and -stibine with osmium and ruthenium halides in alcoholic media (ranging in b.p. from 25 to 270°) including the complexes [RuBr₃(CO)(PPh₃)₂], [RuBr₃(AsPh₃)₂CH₂OH] and [RuCl₃(P²H₅)₂CH₂OH] but detailed preparations are not available. The binuclear complexes [Ru₂Cl₆(PR₃)₆]Cl were obtained by the prolonged interaction of the phosphine with hydrated trichloride in boiling methanol (R = Et₂Ph, Et₂As etc.);⁴ although these complexes do not react with an excess of tertiary phosphine to give mononuclear complexes, [Ru₂Cl₆(PR₃)₄], analogous preparative methods using dimethylphenylarsine gave cis and trans-[RuCl₂(AsMe₂Ph)₄] (but not [Ru₂Cl₆(AsMe₂Ph)₆]Cl).⁵ The preparation of the mixed alkyl/aryl tertiary phosphine and arsine complexes [RuCl₃(P₃As)₂Et₂Ph]₃, [RuCl₂(CO)(PEt₂Ph)₃], [RuHX(CO)(PEt₂Ph)₃] (X = Cl, Br, I), cis-[RuX₂(CO)₂(P₃As)R₃] (R = Et₂Ph, X = Cl (and for P only), Br, I; R = Et₃ (for P only), X = Cl) and trans-[RuCl₂(CO)₂(PR₃)₂] (R = Et₂Ph, Et₃) by a variety of methods has been described.⁶ Complexes such as [RuCl₃(PEt₂Ph)₂L₂] (L₂ = bipy, o-phen,⁷ C₈H₁₂)⁸

⁶ B. L. SHAW. Personal communication (1965).
were prepared via \([\text{Ru}_2\text{Cl}_3(\text{PET}_3\text{Ph})_6]\)Cl and finally, the cis-dicarbonyl complexes \([\text{RuI}_2(\text{CO})_2\text{L}_2]\) (\(L = \text{PPPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{py}, \text{CH}_3\text{CN} \text{ etc.}\)) were prepared by action of the appropriate ligand on ruthenium carbonyl iodide.\(^{(7)}\)

In the present paper we report (1) the results of a further study of the interaction of \(\text{Ph}_3\text{P}, \text{Ph}_3\text{As} \text{ and Ph}_3\text{Sb} \) with hydrated ruthenium trichloride, (2) the utilization of the reaction, briefly reported by Chatt et al.\(^{(6a)}\) in order to prepare new mono- and dicarbonyl complexes of ruthenium (II) and (III) with various ligands.

![Diagram of complexes](image)

**Triphenylarsine, -arsine and -stibine complexes**

On passing carbon monoxide into a boiling solution of ethanolic commercial \(\text{RuCl}_3\text{3H}_2\text{O}\) for several hours, a deep red solution was formed;\(^{(5a)}\) addition of triethylphosphine (2 mole) then gave trans-\([\text{RuCl}_2(\text{CO})_2(\text{PET}_3\text{Ph})_2]\). The composition of the red solution itself has only been briefly examined. Removal of the solvent gave an intractable oil. The solution has a high conductivity indicating the presence of an electrolyte. Addition of tetramethylammonium chloride to the solution gave an immediate orange precipitate, which had three strong carbonyl bands in the infra-red spectrum but whose analysis clearly showed it to be a mixture; attempts to separate this mixture by crystallisation and by chromatographic methods were unsuccessful. However, we have now prepared the complexes cis-\([\text{RuCl}_2(\text{CO})_2(\text{MPh}_3)_2]\) (\(M = \text{P}, \text{As}, \text{Sb}\)) and \([\text{RuCl}_2(\text{CO})(\text{MPh}_3)_3]\) (\(M = \text{As}, \text{Sb}\)) via this red solution; the products formed depend upon the amount of ligand used. The similarity of the position of the carbonyl stretching frequencies (Table I) to those of mixed alkyl/aryl phosphine and arsine complexes\(^{(5a)}\) (for which dipole-moments were measured) suggest they possess a similar configuration (I). However, this configuration for the white compounds of formula \([\text{RuCl}_2(\text{CO})_2(\text{PR}_3)_2]\) now appears\(^{(5b)}\) to be different from that given earlier;\(^{(5a)}\) this result comes from NMR studies on the dimethylphenylphosphine ruthenium complex using the technique described for complexes of other metals.\(^{(5c)}\) It is in agreement with our observed infra-red spectra (Table I).

With mole ratios of 3:1, crystalline complexes whose infra-red spectra contained three carbonyl bands were initially deposited. On recrystallization from acetone or a dichloromethane/methanol mixture, the lowest frequency band disappeared, giving

TABLE 1.—COLOURS AND CARBONYL-STRETCHING FREQUENCIES OF SOME RUTHENIUM COMPLEXES

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>ν(CO)(cm⁻¹)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[RuCl₂(CO)₄(PPh₃)₂]</td>
<td>White</td>
<td>2064, 2001</td>
</tr>
<tr>
<td>cis-[RuBr₂(CO)₄(PPh₃)₂]</td>
<td>White</td>
<td>2061, 1980</td>
</tr>
<tr>
<td>trans-[RuCl₂(CO)₄(PPh₃)₂]</td>
<td>Pale yellow</td>
<td>2005</td>
</tr>
<tr>
<td>trans-[RuBr₂(CO)₄(PPh₃)₂]</td>
<td>Fawn</td>
<td>2004</td>
</tr>
<tr>
<td>cis-[RuCl₂(CO)₄(AsPh₃)₂]</td>
<td>White</td>
<td>2063, 2002</td>
</tr>
<tr>
<td>cis-[RuBr₂(CO)₄(AsPh₃)₂]</td>
<td>White</td>
<td>2060, 1988</td>
</tr>
<tr>
<td>cis-[RuCl₂(CO)₄(SbPh₃)₂]</td>
<td>White</td>
<td>2056, 1992</td>
</tr>
<tr>
<td>cis-[RuCl₂(CO)₄(py)₂]</td>
<td>Orange-yellow</td>
<td>2059, 1988</td>
</tr>
<tr>
<td>cis-[RuCl₂(CO)₄(β-pic)₂]</td>
<td>Pale yellow-green</td>
<td>2061, 2007, 1980</td>
</tr>
<tr>
<td>trans-[RuCl₂(CO)₄(quin)₂]</td>
<td>Orange-brown</td>
<td>1942</td>
</tr>
<tr>
<td>[RuCl₄CO(AsPh₃)₂]</td>
<td>Fawn</td>
<td>2010 ν, 1961</td>
</tr>
<tr>
<td>[RuCl₆(CO)(SbPh₃)₄]</td>
<td>Orange-brown</td>
<td>2010 ν, 1961</td>
</tr>
<tr>
<td>[pyH][RuCl₄(CO)py]</td>
<td>Orange</td>
<td>2052, 2046</td>
</tr>
<tr>
<td>[AsPh₃][RuCl₄(CO)py]</td>
<td>Orange-brown</td>
<td>2042, 2040</td>
</tr>
<tr>
<td>[Ru₂Cl₆(SnCl₄)(CO)₄(PPh₃)₄(Me₄CO)₂]</td>
<td>Lemon-yellow</td>
<td>1957</td>
</tr>
<tr>
<td>[Ru₂Cl₆(SnCl₄)(CO)₄(PPh₃)₄]</td>
<td>Pale yellow</td>
<td>1969</td>
</tr>
<tr>
<td>[Me₄N]₁[RuCl₄(CO)₂(SnCl₄)₂]</td>
<td>Yellow</td>
<td>2058, 2000</td>
</tr>
</tbody>
</table>

* In Nujol mulls. Bands strong unless otherwise noted.

pure cis-[RuCl₂(CO)₄(MPh₃)₂] (M = P, As). In the reaction with Ph₃P, further precipitation (deeper yellow) gave a material which also analysed for [RuCl₂(CO)₂(PPh₃)₂]. The greater intensity of the lowest carbonyl band (1920 cm⁻¹) suggested that it contained a trans isomer but attempts to separate this isomer resulted in conversion to the more stable cis-form. A purer sample of the cis-form could initially be obtained by refluxing the red solution with a fourfold excess of Ph₃P or Ph₃As.

If a sixfold excess of Ph₃As was added to the cold freshly-prepared red solution, the complex [RuCl₂(CO)(AsPh₃)₃] (II) was slowly deposited. The corresponding Ph₃P complex could not be isolated in a pure form. However, the corresponding Ph₃Sb complex, [RuCl₂(CO)(SbPh₃)₃], was obtained as insoluble orange–brown crystals by adding a two to threefold excess of ligand to the red solution. cis-[RuCl₂(CO)₄(SbPh₃)₂] could, however, be obtained indirectly via a stannous chloride–containing intermediate. Thus, when the red solution was refluxed for 30 min with a fourfold excess of anhydrous stannous chloride, a pale yellow solution containing anionic trichlorostannate complexes is formed. The addition of NMe₄Cl to this solution gave a yellow precipitate but this was invariably contaminated with [Me₄N]SnCl₃. On refluxing the yellow solution with excess Ph₃P or Ph₃As, the complex cis-[RuCl₂(CO)₂(MPh₃)₂] was obtained. By preparing the initial solution in the presence of excess lithium bromide (a green solution is now formed), the corresponding bromides, cis-[RuBr₂(CO)₂(MPh₃)₂] could be obtained analogously.

Attempts to prepare the monocarbonyl complexes of PPh₂Et and PE₃ directly from the red solution in a similar way by using a large excess of ligand gave instead green crystals of empirical formula [RuCl₄(PR₃)₃] which showed no carbonyl bands in the infra-red. Since these compounds in nitromethane give conductivities corresponding almost to those for 1:1 electrolytes, (e.g., for R = Et₂Ph; λ₀⁻₀₀ M⁻¹ cm⁻¹ = 60 Ω⁻¹ cm² mole⁻¹), contain P—H stretching frequencies at ca. 2400 cm⁻¹, and have magnetic moments of ca. 1·8 BM, indicative of ruthenium (III) spin-paired complexes, they are best formulated as the salts [R₃PH][RuCl₃(PR₃)₂]. The salts were insoluble in and decomposed by water.
Attempts were also made to prepare the $\text{Ph}_3\text{P}$ and $\text{Ph}_3\text{As}$ complexes of ruthenium (III) of formula $[\text{RuCl}_2(\text{MPh}_3)_2]$ by the method used$^{(5)}$ by CHATT to obtain $[\text{RuCl}_2(\text{PET}_3\text{P})_2]$. However, only the mono and dicarbonyl species could be isolated. Further, completely substituted species could not be obtained either from the deep red chloride solution or by interaction of the carbonyl complexes with excess ligand. However, when an excess of $\text{Ph}_3\text{P}$ and hydrated ruthenium trichloride (6:1 mole ratio) was shaken in methanol at room temperature, dark-brown diamagnetic crystals of $[\text{RuCl}_2(\text{PPh}_3)_2]$ were deposited. These gave non-conducting yellow-brown solutions in acetone, benzene, chloroform which rapidly turned green on exposure to air. The oxidized solutions contained triphenylphosphine oxide. Molecular weight measurements carried out in acetone under nitrogen gave values about a third of those expected for a monomer suggesting dissociation in solution:

$$[\text{RuCl}_2(\text{PPh}_3)_2] + \text{solvent} \rightleftharpoons [\text{RuCl}_2(\text{PPh}_3)_2(\text{solvent})_2] + 2\text{PPh}_3.$$ 

This dissociation is similar to that found for $(\text{Ph}_3\text{P})_3\text{RhCl}$;$^{(8)}$ the solvated ruthenium complex also acts as a homogeneous hydrogenation catalyst for olefins, but is less efficient than the rhodium complex. This facile dissociation was confirmed by the rapid interaction of the solutions with carbon monoxide at room temperature and pressure and also with$^{(9)}$ norbornadiene to give respectively trans-$[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{RuCl}_2(\text{C}_7\text{H}_8)(\text{PPh}_3)_2]$. Recrystallization of the trans-carbonyl complex $[\nu(\text{CO}), 2005 \text{ cm}^{-1}]$ from a dichloromethane/methanol mixture gave the cis-isomer $[\nu(\text{CO}), 2064, 2001 \text{ cm}^{-1}]$. This trans-complex is apparently different from that obtained (but not isolated in a pure state) from the red solution $[\nu(\text{CO}), 1920 \text{ cm}^{-1}]$; the similarity in the position of its carbonyl band to that in $[\text{RuCl}_2(\text{CO})_2(\text{PET}_3)_2]$ (1988 cm$^{-1}$) suggests the same configuration (III). HAYTER$^{(10)}$ has recently prepared similar complexes $[\text{RuCl}_2(\text{PHR}_2)_2]$ $(\text{R} = \text{Et, Ph})$ by refluxing the trichloride and excess ligand in ethanol for two hours.

When the methanolic solution of $\text{Ph}_3\text{P}$ and ruthenium trichloride was refluxed under nitrogen instead of being shaken, red-brown crystals of empirical formula $[\text{RuCl}_2(\text{PPh}_3)_2]$ were deposited. This compound has evidently been made independently by VASKA in view of a recent X-ray diffraction study$^{(11)}$ on crystals obtained from him but no preparative details are available. The structure is five co-ordinate with the vacant octahedral site about the square-pyramidal configuration being effectively blocked by a phenyl ring. Acetone and benzene solutions of the complex were non-conducting, but the solutions again turned green on exposure to air. Molecular weights in benzene (under nitrogen) were about half the value expected for a monomer, and trans-$[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{RuCl}_2(\text{C}_7\text{H}_8)(\text{PPh}_3)_2]$ were also obtained by interaction with CO and C$_7$H$_8$ under very mild conditions. These facts suggest that in solution the solvated species $[\text{RuCl}_2(\text{PPh}_3)_2(\text{solv})_2]$ is again present. In nitromethane, conversion to an ionized complex, which is possibly $[\text{Ru}_2\text{Cl}_6(\text{PPh}_3)_6]\text{Cl}$ or $[\text{RuCl}(\text{PPh}_3)_2\text{MeNO}_3]\text{Cl}$, may occur, since the complex gives an air-stable pale yellow solution which has a conductivity corresponding to that of a 1:1 electrolyte ($\Lambda_{0.001M} = 68 \Omega^{-1}\text{ cm}^2 \text{ mole}^{-1}$). $[\text{RuCl}_2(\text{PPh}_3)_2]$ also gave a pale yellow conducting solution in nitromethane. We have been unable to isolate pure salts from these solutions.


On shaking $\text{Ph}_3\text{P}$ and ruthenium trichloride (2:1 mole ratio) in excess methanol for several days, green crystals of the complex $[\text{RuCl}_3(\text{PPh}_3)_2\text{CH}_3\text{OH}]$, briefly reported by VASKA\(^{(3)}\) were deposited. The infra-red spectrum contained bands at ca. 1000 cm\(^{-1}\) assigned to co-ordinated methanol plus weak hydroxy bands at 3509 and 3448 cm\(^{-1}\). The magnetic moment of 1.9 BM confirmed that the complex was one of ruthenium (III). Using ethanol as solvent, $[\text{RuCl}_3(\text{PPh}_3)_2\text{C}_2\text{H}_5\text{OH}]$ was also prepared. Dissolution of these alcohol complexes in benzene, chloroform etc. gave deep brown solutions. However, from the solution in cold acetone, brown crystals of $[\text{RuCl}_3(\text{PPh}_3)_2(\text{Me}_2\text{CO})]$ were quickly deposited, demonstrating the lability of the alcohol ligand. The position of the carbonyl stretching frequency (1656 cm\(^{-1}\) in the acetone complex is similar to those of similar adducts, e.g. $\text{F}_8\text{B.OCMe}_3$, $\nu_{\text{CO}} = 1640$ cm\(^{-1}\);\(^{(12)}\) the other acetone bands are readily assigned.

The corresponding reactions with $\text{Ph}_3\text{As}$ and $\text{Ph}_3\text{Sb}$ do not give the same range of complexes. Thus, on refluxing ruthenium trichloride with excess $\text{Ph}_3\text{As}(6:1$ mole ratio), paramagnetic (1.79 BM) green crystals of $[\text{RuCl}_3(\text{AsPh}_3)_2\text{CH}_3\text{OH}]$ were formed; these showed methanol bands in the 1000 cm\(^{-1}\) region. On treatment with acetone, brown crystals of the acetone complex $[\text{RuCl}_3(\text{AsPh}_3)_2(\text{Me}_2\text{CO})]$ ($\nu_{\text{CO}}$ 1656 cm\(^{-1}\)) are obtained. With pyridine under very mild reaction conditions, the complex gives $[\text{RuCl}_3(\text{AsPh}_3)(\text{py})_2]$ suggesting that one of the $\text{Ph}_3\text{As}$ groups is comparatively labile, especially in the presence of ligands having a lower trans-effect. It would also suggest that the $\text{Ph}_3\text{As}$ groups are trans to each other.

The interaction of ruthenium trichloride and excess $\text{Ph}_3\text{Sb}$ (6:1 mole ratio), shaken or refluxed in methanol or refluxed in 2-methoxyethanol, rapidly produces diamagnetic, red microcrystals which analyse for the empirical formula $[\text{RuCl}_4(\text{SbPh}_3)_2]$. The complex is sparingly soluble in solvents such as acetone, ethanol, benzene etc., although on warming with pyridine or quinoline, green and red solutions respectively are formed. It may well be quasi-octahedral like $[\text{RuCl}_6(\text{PPh}_3)_3]$. In contrast to the reactions with $\text{Ph}_3\text{P}$ and $\text{Ph}_3\text{As}$, no evidence was found for the formation of a hydrido-carbonyl complex containing $\text{Ph}_3\text{Sb}$ on refluxing in 2-methoxyethanol.

By shaking the hydrated trichloride for several hours with excess lithium bromide and then treating the solution with $\text{Ph}_3\text{P}$ and $\text{Ph}_3\text{As}$ as discussed above, we have also prepared the corresponding bromides $[\text{RuBr}_4(\text{PPh}_3)_4]$, $[\text{RuBr}_2(\text{PPh}_3)_3]$, $[\text{RuBr}_3(\text{PPh}_3)_2\text{CH}_3\text{OH}]$ (red–brown) and $[\text{RuBr}_3(\text{AsPh}_3)_2\text{CH}_3\text{OH}]$ (dark brown). Although the first two form fairly air-stable reddish-brown solutions in acetone, benzene etc. (slowly turning dark brown), reactions with carbon monoxide and norbornadiene give $\text{trans-}[\text{RuBr}_2(\text{CO})_3(\text{PPh}_3)_2]$ and $[\text{RuBr}_3(\text{C}_7\text{H}_8)(\text{PPh}_3)_2]$. Furthermore, a molecular weight determination on the tetrakis complex indicates some dissociation in solution.

**Nitrogen-containing complexes**

The reaction of excess pyridine with a freshly-prepared red solution led to the isolation of cis-$[\text{RuCl}_2(\text{CO})_2\text{py}_2]$. No evidence was found for the direct formation of $[\text{RuCl}_2(\text{CO})\text{py}_3]$ and it was also not formed on refluxing the dicarbonyl complex with excess pyridine. However, reaction of excess norbornadiene or cyclo-octa-1,5 diene with the red solution gave\(^{(9)}\) complexes of empirical formula $[\text{RuCl}_2(\text{CO})(\text{diene})]$; on warming these with excess pyridine, crystals of $[\text{RuCl}_2(\text{CO})\text{py}_3]$ are readily obtained.

If the red solution was left to "age" for 24 hr, refluxing with excess pyridine followed by addition of diethylether then gave an orange precipitate of empirical formula [RuCl₄(CO)₂py₂]. Since (1) the infra-red spectrum contained pyridinium bands; (2) a solution of the complex in nitromethane has the conductivity of a 1:1 electrolyte (Λ_0.001M = 87 Ω⁻¹ cm² mole⁻¹) and (3) it has a magnetic moment of 1.8 BM, the complex is best formulated as [pyH][RuCl₄(CO)py]. Some cis-[RuCl₂(CO)₂py₂] was also obtained from the reaction. Addition of a concentrated, slightly acid solution of tetrphenylarsonium chloride to an aqueous solution of the complex deposited [AsPh₄][RuCl₄(CO)py], which showed only a single band in the 1600 cm⁻¹ region (assigned to a pyridine ring vibrational mode) as expected. It is interesting to note that with a freshly-prepared red solution, addition of pyridine followed by ether gave only an oil. The "aging" process is possibly an oxidative one but since excess diethylphenylphosphine and triethylphosphine give ruthenium (III) species with a freshly-prepared solution, the changes involved are doubtless not simple. Attempts to prepare substituted pyridine and quinoline derivatives of ruthenium (III) by similar methods were unsuccessful. With freshly-prepared red solutions, β-picoline(3-methylpyridine) gave the cis-dicarbonyl complex. However, quinoline gave orange-brown crystals of trans-[RuCl₂(CO)₂(quin)₂] (single carbonyl band) which were unaffected by, and insoluble in, most organic solvents.

**Trichlorostannate complexes**

If the red solution is allowed to stand with a mixture of anhydrous stannous chloride and Ph₃P in the presence of acetone, lemon-yellow crystals which analysed for [Ru₂Cl₃(SnCl₃)(CO)₄(PPh₃)₃(Me₂CO)₂] were quickly deposited. The infra-red spectrum contained bands at 1701 and 1661 cm⁻¹ assigned to free and co-ordinated acetone groups respectively (plus other acetone bands) and a single carbonyl stretch at 1957 cm⁻¹. The complex is incompletely ionized in warm nitromethane (Λ_0.001M = 30 Ω⁻¹ cm² mole⁻¹) and appears not to be a salt containing the SnCl₃⁻ ion. On standing for longer periods, other products were precipitated from the solution, and these have carbonyl bands at 2067, 2015, 2000 and 1919 cm⁻¹; the rate of production of these products is accelerated by using more triphenylphosphine. Therefore, to obtain the pure acetone complex, a deficiency of triphenylphosphine (only a twofold excess) and excess acetone must be employed and the crystals removed within 25 min of formation. Warming the acetone complex in benzene gave a pale yellow solution from which an acetone-soluble product containing no acetone and a single carbonyl band at 1969 cm⁻¹ was isolated. The same product can also be obtained by refluxing a mixture of red solution, stannous chloride and Ph₃P in the presence of acetone; it analyses for [Ru₂Cl₃(SnCl₃)(CO)₄(PPh₃)₃]. If however, analogous reactions are carried out with acetone replaced by diethylether, no single product could be isolated. Attempts to separate the mixture of trichlorostannate complexes by recrystallization resulted in the loss of stannous chloride with the formation of cis-[RuCl₂(CO)₂(PPh₃)₂].

An anionic carbonyl complex of ruthenium with co-ordinated trichlorostannate can be obtained by interaction of polymeric Ru(CO)₂Cl₂ with stannous chloride solutions. No carbon monoxide is displaced and bridge cleavage occurs to give the discrete octahedral anion [RuCl₂(CO)₂(SnCl₃)₂]⁻.
EXPERIMENTAL

Microanalyses and molecular weight measurements (Mechrolab osmometer at 37°) were by the Microanalytical Laboratory, Imperial College. Mp’s were determined with a Kofler hot-stage microscope and are uncorrected. Infra-red spectra were taken on a Grubb-Parsons “Spectrometer” grating instrument using Nujol and hexachlorobutadiene mulls. Magnetic measurements were made by the standard Gouy method. The commercial ruthenium trichloride hydrate (Johnson-Matthey Ltd.) used in this work is a mixture of hydrated trichloride, tetrachloride and various polynuclear species. However, the complexes described below were obtained even when the salt was evaporated to dryness several times with concentrated hydrochloric acid in order to convert it to ruthenium (III) chloro complexes.

Analyses of the new ruthenium compounds are given in Table 2.

Ruthenium (II) complexes

 Dichlorotetraakis(triphenylphosphine)ruthenium (II). Ruthenium trichloride trihydrate (0.2 g) was dissolved in methanol (50 ml) and a sixfold excess (1.2 g) of triphenylphosphine added. After vigorous shaking, the solution was filtered and the deep brown solution shaken at room temperature under nitrogen for ca. 24 hr. The dark brown crystals of the complex were washed with methanol and diethylether and dried in vacuo (60°) for several hours (yield 70 per cent).

The compound gives yellow-brown solutions under nitrogen in warm chloroform, acetone, benzene and ethyl acetate which quickly turn green on exposure to air. It is insoluble in water, ether and only sparingly soluble in alcohols.

 Dibromotetraakis(triphenylphosphine)ruthenium (II). As for the chloro complex except that a methanolic solution of the trichloride was first shaken with a large excess (6:1 mole ratio) of lithium bromide for 24 hr. Addition of excess triphenylphosphine to the resulting purple solution followed by filtration and shaking for a few hours gave reddish brown crystals of the complex (yield 65 per cent).

 Diclorotris(triphenylphosphine)ruthenium (II). As for the tetrakis complex, except the solution was refluxed under nitrogen for several hours. The resulting reddish-brown crystals of the complex were well washed with methanol and ether and dried in vacuo (60°) (yield 75 per cent).

The compound has properties very similar to the tetrakis complex, but is somewhat more soluble in cold organic solvents.

 Dibromotris(triphenylphosphine)ruthenium (II). As for the chloro complex except that the trichloride was first shaken with a large excess of lithium bromide. Addition of excess triphenylphosphine followed by filtration and refluxing gave dark-brown crystals of the complex (60 per cent).

 Diclorotris(triphenylstibine)ruthenium (II). Ruthenium trichloride trihydrate (0.2 g) was dissolved in methanol (50 ml) and a six-fold excess of triphenylstibine (1.7 g) was added. Filtrating and shaking gave within 10 min, deep red microcrystals of the complex, which were purified as above (70 per cent). The same compound can be obtained by refluxing a mixture of trichloride and excess triphenylstibine either in methanol or 2-methoxyethanol:- in methanol (Found: C, 52.6; H, 3.7; Cl, 56.5%); in 2-methoxyethanol (Found: C, 53.2; H, 4.3%).

 cis-Dicarbonyl complexes of ruthenium (II): cis-dichloro(dicarbonyl)bis(triphenylphosphine)-ruthenium (II). Carbon monoxide was bubbled through a boiling solution of hydrated trichloride (1 g) in ethanol (30 ml) for 5 hr, giving a deep red solution.

(a) To 5 ml of freshly-prepared red solution, a fourfold excess of triphenylphosphine (0.7 g) in ether (10 ml) was added, and the whole diluted to 35 ml with ethanol. On refluxing gently under nitrogen, very pale yellow crystals were quickly deposited (ca. 10 min). Recrystallization from a dichloromethane/methanol mixture gave pure white crystals of the complex, which were washed with methanol and ether and dried in vacuo (60°) (45 per cent).

(b) Dichlorotetraakis(triphenylphosphine)ruthenium (II) (0.1 g) was dissolved under nitrogen in warm acetone (35 ml) and then, carbon monoxide bubbled into the solution. It immediately became pale yellow but no crystals separated. However, on concentrating the solution on a steam bath, white crystals of the complex were deposited (same infra-red spectrum and m.p.). They are also obtained by recrystallization of the trans complex (dichloromethane/methanol) or by interaction of [RuCl₂(PPh₃)₃] with carbon monoxide under the same conditions.

The compound is soluble in dichloromethane, acetone, benzene, nitromethane; insoluble in alcohols, ethers etc.
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* Prepared by VASKA$^{(2)}$

† Sn: found, 7-9; required, 8-0

‡ Sn: found, 29-1; required, 28-0
cis-Dibromo(dicarbonyl)bis(triphenylphosphine) ruthenium (II). As for the chloro complex except the initial solution was made by passing carbon monoxide through a boiling solution of hydrated trichloride and excess lithium bromide (6:1 mole ratio) in ethanol for 5 hr, giving a green solution. Addition of excess triphenylphosphine to this followed by refluxing deposited pale yellow crystals, recrystallized from a dichloromethane/methanol mixture to give pure white crystals of the complex (45 per cent).

cis-Dichloro(dicarbonyl)bis(triphenylarsine) ruthenium (II). As for the triphenylphosphine complex but using a fourfold excess of triphenylarsine (0.9 g). Pale yellow crystals were deposited after refluxing ca. 30 min and had to be filtered while still hot to avoid contamination from the monocarbonyl complex (impure) which separates out from the cooled solution. Recrystallization from a dichloromethane/methanol mixture gave white crystals of the complex, purified in the usual way (50 per cent).

The compound is similar in properties to the phosphine complex.

cis-Dibromo(dicarbonyl)bis(triphenylarsine) ruthenium (II). As for the phosphine bromo complex except using excess triphenylarsine, giving white crystals (recrystallized dichloromethane/methanol) (50 per cent).

cis-Dichloro(dicarbonyl)bis(triphenylstibine) ruthenium (II). The red solution (5 ml) was refluxed with an excess of anhydrous stannous chloride (0.8 g) (diluted with ethanol) under nitrogen for ca. 30 min to give a pale yellow solution. To this, a sixfold excess of triphenylstibine (1.4 g) in ether (10 ml) was added and the mixture gently refluxed under nitrogen. Within 10 min, very pale yellow crystals were deposited. Recrystallization from a dichloromethane/methanol mixture gave pure white crystals of the complex (40 per cent). The test for tin (II) (cacoethel test) was negative.

cis-Dichloro(dicarbonyl)bis(pyridine) ruthenium (II). To 10 ml of freshly-prepared red solution, excess pyridine (7 ml) was added and the whole diluted to 35 ml with ethanol. After refluxing under nitrogen for ca. 3 hr, the solution was allowed to cool in air. After a short period, orange-yellow crystals separated out which were recrystallized from ethanol to give the pure complex (60 per cent). The compound is soluble in acetone, benzene, dichloromethane; insoluble in water and ethers.

cis-Dichloro(dicarbonyl)bis(phenol) ruthenium (II). As for pyridine, depositing pale yellow-green crystals of the complex, which were washed with ether and dried in vacuo (60°) (60 per cent).

trans-Dichlorobis(1-phenylphosphine)(1) ruthenium (II).- trans-Dichloro(dicarbonyl)bis(quinoline) ruthenium (II). To 5 ml of freshly-prepared red solution, excess quinoline (3 ml) was added and the solution diluted to 35 ml with ethanol. On refluxing under nitrogen, the solution became dark brown and quickly deposited orange-brown crystals of the complex. These were washed with ethanol and ether and dried in vacuo (60°) (65 per cent). The compound is completely insoluble in dichloromethane, benzene, acetone, ether, ethanol etc.

trans-Dichloro(dicarbonyl)bis(triphenylphosphine) ruthenium (II). Dichlorotetakis(triphenylphosphine)ruthenium (II) (0.1 g) was dissolved under nitrogen in warm acetone (15 ml) and then, carbon monoxide was bubbled into the solution. It immediately became pale yellow and deposited yellow crystals. These were washed with ether and dried in vacuo (60°) (since recrystallization gives the white cis-isomer). The same compound can be obtained from [RuCl₂(PPh₃)₃] and carbon monoxide (concentrated solution). The compound is converted to the cis-isomer at ca. 200° without melting.

trans-Dibromo(dicarbonyl)bis(triphenylphosphite) ruthenium (II). As for the chloro complex, using very concentrated solutions of the tetrakis or trisphosphine bromo complex, a fawn powder being deposited. Recrystallization from a dichloromethane/methanol mixture gives the cis-isomer.

Monocarbonyl complexes of ruthenium (II). Dichloro(carbonyl)tris(triphenylarsine) ruthenium (II). To 5 ml of freshly prepared red solution (cold), a sixfold excess of triphenylarsine (1.4 g) in ether (10 ml) was added and the solution allowed to stand under nitrogen. Within 1 hr, a fawn powder was slowly deposited which was washed with ethanol and ether and dried in vacuo (40°). The compound is very soluble in dichloromethane, nitromethane (non-electrolyte) and warm acetone.

Dichloro(carbonyl)tris(triphenylstibine) ruthenium (II). To 5 ml of freshly-prepared red solution (cold), a two to threefold excess of triphenylstibine (0.6—0.9 g) in acetone (6 ml) was added. Within 10 min, orange-brown crystals of the complex began to appear and were slowly deposited over a period of several hours. These were washed with acetone and ether and dried in vacuo (40°) (50 per cent).

The compound is insoluble in methanol, acetone, benzene, ethyl acetate, nitromethane, water and sparingly soluble in warm dichloromethane.
Trichlorostannate complexes of ruthenium (II) and (III) with triphenylphosphine

[Ru₂Cl₄(SnCl₃)(CO)₆(PPh₃)₃(Me₂CO)₂]. To 5 ml of freshly-prepared red solution, a fourfold excess of anhydrous stannous chloride (0.5 g) in ethanol (5 ml) was added, followed immediately by triphenylphosphine (0.35 g) in acetone (7 ml). On standing for a short period under nitrogen (ca. 15–20 min), lemon-yellow crystals of the complex were deposited. These were removed immediately (to avoid contamination from other products which separate out at a later stage of the reaction), washed with acetone, ether and air-dried.

The compound is insoluble in acetone, ethanol, ether but dissolves in warm benzene, nitromethane and ethyl acetate giving an acetone-soluble complex containing no acetone (1969). The same compound is deposited if the red solution, stannous chloride and phosphine (same quantities) are refluxed instead of shaken. It analyses for [Ru₂Cl₄(SnCl₃)(CO)₆(PPh₃)₃]. The tin (II) (cacoetheline) test was positive.

Bis(tetramethylammonium)dicarbonyldichlorobis(trichlorostannato)ruthenate (II). (a) Dicarbonyldichlororuthenium (II) (0.3 g) was refluxed in 3 M-hydrochloric acid (25 ml) with SnCl₂2H₂O (1.2 g) for 1 hr. Addition of NMe₄Cl (0.5 g) in water (5 ml) to the yellow solution precipitated the yellow complex (0.7 g, 75 per cent); after recrystallization from 3 M-hydrochloric acid–ethanol. The salt is soluble in acetone, nitromethane and dimethylformamide. In dimethylformamide, a conductivity measurement showed the salt to be a 2:1 electrolyte ($\Lambda_{\text{aq}} = 97 \Omega^{-1} \text{cm}^2 \text{mole}^{-1}$).

(b) (Me₄N)₂[RuCl₄(SnCl₃)] (14) (0.5 g) was suspended in acetone (15 ml) and treated with carbon monoxide at 85 atm and 120° for 3 days. Most of the salt remained undissolved and unreacted, but evaporation of the acetone solution yielded a very small amount of solid showing carbonyl bands in the infra-red spectrum; it was not investigated further.

Ruthenium (III) complexes

Trichlorobis(triphenylphosphine)(methanol)ruthenium (III). Ruthenium trichloride trihydrate (0.2 g) was dissolved in methanol (50 ml) and a twofold excess of triphenylphosphine (0.4 g) was added. Filtering and then shaking for several days at room temperature gave green crystals of the complex, which were carefully washed with petroleum (40–40°) and air-dried (40 per cent).

Tribromobis(triphenylphosphine)(methanol)ruthenium (III). As for the chloro complex except that a methanolic solution of the trichloride was first shaken with a large excess of lithium bromide for 24 hr, further shaking with a two-fold excess of triphenylphosphine then giving reddish-brown crystals of the complex (50 per cent).

Trichlorobis(triphenylphosphine)(ethanol)ruthenium (III). Exactly as for the methanolic derivative using ethanol as solvent. Green crystals were deposited.

Trichlorobis(triphenylphosphine)(acetone)ruthenium (III). [RuCl₄(PPh₃)_2]CH₃OH] was shaken with excess acetone. Immediately, brown crystals of the complex were deposited, which were carefully washed with acetone and ether and air-dried.

Trichlorobis(triphenylarsine)(methanol)ruthenium (III). The hydrated chloride (0.2 g) and a six-fold excess of triphenylarsine (1.5 g) were refluxed together in methanol (after filtration). Within two hours, green crystals of the complex were deposited, washed with ether and air-dried (70 per cent).

Tribromobis(triphenylarsine)(methanol)ruthenium (III). As for the phosphine bromo complex except for refluxing or shaking with an excess of triphenylarsine, dark-brown crystals being deposited (70 per cent). The complex has a magnetic moment of 1.74 BM.

Trichlorobis(triphenylarsine)(acetone)ruthenium (III). As for the phosphine complex giving yellow-brown crystals.

Trichloro(triphenylarsine)bis(pyridine)ruthenium (III). [RuCl₃(AsPh₃)₂CH₂OH] was gently warmed with dry pyridine to give a bright yellow solution. Addition of excess petroleum (100–120°) precipitated an orange-yellow powder, recrystallized from an acetone/diethyl ether mixture as orange-brown crystals (65 per cent).

Pyridinium tetrachlorocarbonylpyridine ruthenate (III). The red solution was allowed to stand in contact with air for 24 hr. Then, 10 ml of it were refluxed with excess pyridine (7 ml) (diluted with 20 ml of ethanol), for ca. 3 hr. Addition of excess diethyl ether or petroleum (100–120°) gave the complex in the form of an orange powder. This was thoroughly washed with ether and dried in vacuo.

* We thank Dr. J. F. Young who first made this complex in these laboratories for this information.

(60°) (40 per cent). The compound is soluble in acetone, water, ethanol and nitromethane; insoluble in ethers and benzene.

_Tetraphenylarsonium tetrachloro(carbonyl)pyridine ruthenate_ (III). The pyridinium complex was dissolved in warm distilled water and filtered into a concentrated acidified (HCl) solution of tetraphenylarsonium chloride. The resulting colloidal orange-brown precipitate (coagulated by addition of sodium chloride) was centrifuged, well-washed with water and diethylether and dried _in vacuo_ (30°) for several hours.

_Diethylphenylphosphonium tetrachlorobis(diethylphenylphosphine) ruthenate_ (III). Excess diethylphenylphosphine (1 ml) was added to 5 ml of freshly-prepared red solution under nitrogen. The solution immediately turned bright-green and deposited green crystals of the complex which were washed with petroleum (30–40°) and air-dried (60 per cent). The compound is soluble in warm nitromethane, methanol and cold dichloromethane giving red solutions; insoluble in ethers and water (decomposes).

_Triethylphosphonium tetrachlorobis(triethylphosphine)ruthenate_ (III). Exactly as the diethylphenylphosphine complex giving green crystals (60 per cent).

_Acknowledgements.—_We thank E. I. du Pont de Nemours and Co. for financial assistance (T.A.S.) and Johnson-Matthey Ltd. for loan of ruthenium salts.
The interaction of triphenylphosphine with methanolic solutions of commercial hydrated ruthenium trichloride leads to mononuclear complexes [RuCl₂[P(C₆H₅)₃]₄] and [RuCl₂[P(C₆H₅)₃]₃], the product depending upon the reaction conditions. However, similar reactions, involving mixed alkyl aryl tertiary phosphines, yield binuclear complexes of the type [Ru₂Cl₃(PR₃)₄]Cl [R = (C₂H₅)₂(C₆H₅), (C₂H₅)(C₆H₅)₂, etc.].

† Johnson Matthey Ltd., London, supply "ruthenium trichloride trihydrate" with ca. 44.6% Ru; other suppliers' products are similar. These materials are mainly ruthenium(IV) complexes. On repeated evaporation almost to dryness with concentrated hydrochloric acid, a solution containing the ruthenium(III) complex ion RuCl₄⁻ is obtained. For the present purpose, the commercial material may be used; identical complexes are obtained by using the Ru(III) solutions, however.
A. TETRAKIS(TRIPHENYLPHOSPHINE)-DICHLORORUTHENIUM(II)

\[ \text{RuCl}_3\cdot3\text{H}_2\text{O} + n(C_6\text{H}_5)_3\text{P} \xrightarrow{25^\circ\text{C.}} \text{N}_2 \text{ atm.} \quad [\text{RuCl}_2\{\text{P}(C_6\text{H}_5)_3\}_4] + \text{other products} \]

24 hours in methanol solution

Checked by RICHARD SINGLER* and ROBERT D. FELTHAM*

Procedure

Ruthenium trichloride trihydrate (0.6 g., 2.2 mmoles) is dissolved in methanol (150 ml.), filtered, and then refluxed for 5 minutes under nitrogen. The solution is allowed to cool in this inert atmosphere, and a sixfold excess (3.6 g., 13.7 mmoles) of triphenylphosphine is added. The solution, which becomes deep brown, is shaken at ca. 25°C. under nitrogen for 24 hours. The dark brown crystals which separate out are collected under nitrogen, washed with degassed methanol and diethyl ether, and dried under vacuum. The yield is approximately 1.85 g. (70% based on ruthenium); m.p. 130–132°C. Anal. Calcd. for C\text{\textsubscript{72}}H\text{\textsubscript{60}}Cl\text{\textsubscript{4}}P\text{\textsubscript{4}}Ru: C, 70.8%; H, 5.0%; Cl, 5.8%; P, 10.1%. Found: C, 70.0%; H, 5.2%; Cl, 6.2%; P, 10.5%.

B. TRIS(TRIPHENYLPHOSPHINE)-DICHLORORUTHENIUM(II)

\[ \text{RuCl}_3\cdot3\text{H}_2\text{O} + n(C_6\text{H}_5)_3\text{P} \xrightarrow{65^\circ\text{C.}, 3 \text{ hours N}_2 \text{ atm.}} \quad [\text{RuCl}_2\{\text{P}(C_6\text{H}_5)_3\}_3] + \text{other products} \]

Checked by RICHARD HOLM†

Procedure

Ruthenium trichloride trihydrate (1.0 g., 3.8 mmoles) is dissolved in methanol (250 ml.) and the solution refluxed under

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nitrogen for 5 minutes. After cooling, triphenylphosphine (6.0 g., 22.9 mmoles) is added in the ratio of 6 moles of \((\text{C}_6\text{H}_5)_3\text{P}\) per mole of \(\text{RuCl}_3 \cdot 3\text{H}_2\text{O}\), and the solution is again refluxed under nitrogen for 3 hours. The complex precipitates from the hot solution as shiny black crystals; on cooling, they are filtered under nitrogen, washed several times with degassed ether, and dried under vacuum. The yield is ca. 2.7 g. (74\% based on ruthenium); m.p. 132–134°C. Anal. Calcd. for \(\text{C}_{56}\text{H}_{48}\text{Cl}_2\text{P}_3\text{Ru}\): C, 67.6\%; H, 4.7\%; Cl, 7.4\%; P, 10.3\%; Ru, 10.6\%. Found: C, 67.9\%; H, 4.9\%; Cl, 7.1\%; P, 10.4\%; Ru, 9.9\%.

Properties

The tetrakis- and tris(triphenylphosphine) ruthenium(II) complexes are moderately soluble in warm chloroform, acetone, benzene, and ethyl acetate to give yellow-brown solutions. These solutions are air-sensitive, becoming green. Molecular-weight determinations\(^1\) give low values indicating dissociation. The x-ray crystal structure of \([\text{RuCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]^3\) indicates a distorted octahedral structure with a vacant site which is occupied by an \(\alpha\)-hydrogen atom of one of the phenyl rings of a phosphine ligand.

Solutions of the complexes behave similarly. Thus they react with carbon monoxide\(^2\) at room temperature and pressure, and with norbornadiene\(^3\) to give, respectively, trans-[\(\text{RuCl}_2\)\((\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3\)] and [\(\text{RuCl}_2\)\((\text{C}_7\text{H}_8)\{\text{P}(\text{C}_6\text{H}_5)_3\}_3\)]. The tris complex in ethanol–benzene has been shown\(^5\) to be a homogeneous hydrogenation catalyst for reduction of 1-alkenes; however, the active catalytic species is chlorohydridotris(triphenylphosphine) ruthenium(III), formed by hydrogenolysis.\(^5\).\(^6\)

References

ANIONIC RUTHENIUM(III) COMPLEXES OF TERTIARY
PHOSPHINES AND ARSINES

T. A. Stephenson

Department of Inorganic Chemistry, The University, Newcastle upon Tyne, U.K.

(Received 27 August 1968)

Although quite a wide variety of ruthenium(II) tertiary phosphine and
arsine complexes have been synthesized in recent years (1), relatively few
complexes of ruthenium(III) containing these ligands have been reported. We
now wish to report some convenient methods of preparing the ruthenium(III)
anionic complexes M[RuX₄(AsPh₃)₂] (M=AsPh₄⁺, (CH₃)₄N⁺; X=Cl, Br) and
M[RuCl₄(PR₃)₂] (M=AsPh₄⁺, (CH₃)₄N⁺; PR₃=PPh₃, PET₃, PMe₂Ph). The
preparation of R₃PH[RuCl₄(PR₃)₂] (PR₃=PET₃, PET₂Ph) via an ethanolic carbonyl-
containing ruthenium solution has been briefly mentioned (2).

Reaction of [RuCl₃(LPh₃)₂CH₃OH] (L=P, As) (2) with a large excess
of MCl in acetone slowly forms red crystals of M[RuCl₄(LPh₃)₂] (75-80% yield);
with [RuBr₃(AsPh₃)₂CH₃OH] (2) and MBr, purple acetone-soluble crystals of
the bromo anion are readily isolated. The PPh₃ anion can also be obtained
from the reaction of [RuCl₂(PPh₃)₃] or [4] (2) and MCl. As for PET₃ and PET₂Ph,
the phosphonium salt of the PMe₂Ph anion can be isolated as a dark brown
crystalline material by treating an ethanolic carbonyl-containing
ruthenium solution with PMe₂Ph (35-40% yield); other products from this
reaction are $[\text{RuCl}_2\text{CO(PMe}_2\text{Ph}_2)_3]$ and trans-$[\text{RuCl}_2(\text{CO})_2\text{PMe}_2\text{Ph}_2]$ (3). Reaction of these phosphonium salts with MCl in concentrated ethanol or acetone solution readily gives $\text{M[RuCl}_4\text{(PR}_3)_2]$. However, a more convenient method of preparing these anions in much higher yield is by treatment of $\text{M[RuCl}_4\text{(PPh}_3)_2]$ with the appropriate phosphine when quantitative conversion to $\text{M[RuCl}_4\text{(PR}_3)_2]$ occurs over a period of several days.

Evidence for the correct formulation of these anions is based on elemental analyses, (e.g. for $\text{(CH}_3)_4\text{N[RuCl}_4\text{(PPh}_3)_2]$ prepared from $\text{RuCl}_2\text{(PPh}_3)_4$; Found: C, 57.0; H, 5.04; Cl, 16.9; N, 1.70; P, 7.26%. $\text{C}_{40}\text{H}_{42}\text{Cl}_4\text{NP}_2\text{Ru}$ requires C, 57.0; H, 5.0; Cl, 16.9; N, 1.66; P, 7.4%). Magnetic moments at room temperature corresponding to ruthenium(III) spin-paired complexes and conductivity measurements in nitromethane which are in close agreement with the value expected for an uni-univalent electrolyte in this solvent (4). The latter measurements were always made on freshly prepared solutions because of the ready conversion to green $[\text{RuCl}_3\text{(LPh}_3)_2\text{CH}_3\text{NO}_2]$ ($\text{L=As, As}$); these complexes were also synthesized by direct interaction of $[\text{RuCl}_3\text{(LPh}_3)_2\text{CH}_3\text{OH}]$ and $\text{CH}_3\text{NO}_2$. Representative magnetic and conductance data are given in Table 1.

A direct attempt to establish the configuration of the $[\text{RuCl}_4\text{(PMe}_2\text{Ph}_2)_2]^-\text{ion}$ using the NMR technique developed by Shaw et al (5) was unsuccessful because of the broadness of the methyl resonance ($\text{cf. mer-}[\text{RuCl}_3\text{(PMe}_2\text{Ph}_3)_3]$ (6)). However, the close similarity between the infrared spectra ($4000-200 \text{ cm}^{-1}$) of this paramagnetic ion and the diamagnetic $[\text{M}^{1}\text{Cl}_4\text{(PMe}_2\text{Ph})_2]^-\text{ions (M}^{1}\text{=Rh, Ir)}$, shown by NMR (5, 7) to
#### TABLE 1

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<th>T(^{\circ})K</th>
<th>(\omega)(_{\text{eff}}) (B.M.)</th>
<th>(\Lambda) (0.001M)cm(^2)ohm(^{-1})mole(^{-1})(^a)</th>
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<td>1.84</td>
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</table>

\(^a\) Measured at 295\(^{\circ}\)K
\(^b\) Prepared from RuCl\(_2\)(PPh\(_3\))\(_4\)

have a trans structure suggests the same configuration for this ruthenium ion. The absence of any strong bands below 300 cm\(^{-1}\) in the other ruthenium anions, (indicative of no chloride trans to a tertiary phosphine or arsine (1)) coupled with the exchange of PMe\(_2\)Ph for PPh\(_3\) under very mild reaction conditions suggests a similar configuration for them.

Similar high yield syntheses of the corresponding rhodium(III) and iridium(III) anions are now being developed.

**Acknowledgement** We thank Johnson-Matthey Ltd. for a loan of ruthenium trichloride.

**References**


Some Anionic Ruthenium(III) and Rhodium(III) Complexes of Tertiary Monophosphines and Arsines

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Some Anionic Ruthenium(II) and Rhodium(III) Complexes of Tertiary Monophosphines and Arsines

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Various methods of preparing ruthenium(III) anions of formula $M[RuCl_3(PR_3)_2]$ ($M = Me_2N^+$, Ph$_2$As$^+$; $PR_3 = PPh_3$, PMe$_2$Ph, PEt$_3$, P(OPh)$_2$, and $M[RuX_2(AsPh_3)_2]$ ($M = Me_2N^+$, Et$_2$N$^+$, Ph$_2$As$^+$; $X = Cl$, Br) are described including one involving 'oxidation' of $RuCl_3(PPh_3)_3$ by concentrated hydrochloric acid. Methods of synthesising the isomorphos complexes $Ph_2As[RhCl_4(PR_3)_2]$ ($PR_3 = PPh_3$, PMe$_2$Ph) via RhCl($PPh_3)_3$ and trans-$[RhClCO(PPh_3)_3]$ are also described. A comparison of the stability of these anions towards solvolysis and various exchange reactions is made. From n.m.r. and i.r. spectral studies, the probable structures of the complexes are shown to be trans.

Although a wide variety of the complexes of ruthenium(II) with tertiary phosphines and arsines have been synthesised, there have been few reported preparations of the analogous compounds of ruthenium(III). Those described in the literature are as follows.

(a) A brief note on the preparation of $RuBr_3CO(PPh_3)_2$ (ref. 3). The only other ruthenium(III) carbonyl complexes are $Me_2[CoCl_3]$ ($M = NH_4^+$ (ref. 4)), Cs$^+$ (ref. 5), $[Ru(CO)_3(PhCH_2)NC(S)=CICl]$ (ref. 6), and $M[RuCl_4]$ (P$_2$As$^+$) ($M = HY^+$, Ph$_2$As$^+$). The synthesis of $[RuCl_3(LPeHMeOH)]$ ($L = P$, As) obtained by treatment of $RuCl_3$ in $H_2O$ with a stoichiometric amount of triphenylphosphine in methanol and by heating $RuCl_3$ in $H_2O$ under reflux with an excess of triphenylarsine. The bromo-compounds can also be obtained; reaction with acetonitrile gives $[RuCl_3(PhH_2MeCN)]$ and with pyridine $[RuCl_3(AsPh_3)$_2$]$. (b) Various methods for the preparation of the complexes $mer-[RuX_3(PR_3)_3]$ ($X = Cl$, $Br$; $L = As$, $P$; $R = alkyl and/or aryl) have been reported, culminating in a recent paper by Chatt et al. (c) Various methods for the preparation of the complexes postulated to contain a triple chloride bridge with two chloride ions replacing two phosphine groups to give a neutral complex with formal mixed oxidation states of (II) and (III). (d) A brief report of the preparations of $R_3PH[RuCl_4]$ (PR$_3$)$_2$ ($PR_3 = PEt$_3$ and PEt$_2$P$^-$) is available, obtained by treatment of ethanolic carboxyl-containing ruthenium solutions with excess tertiary phosphate.

Here we describe more convenient methods of preparing the ruthenium(III) anions of tertiary phosphines and arsines, particularly those of triphenyl-phosphine and -arsine which cannot be prepared by method (e), the only products being $[RuCl_3CO(LPeH)$ and $[RuCl_3]$ ($L = P$, As). The preparation of the isomorphous rhodium(III)-tertiary phosphine anions are also described. Various reactions of these anions will be discussed in later publications.

Ruthenium(III) Anions of Triphenyl-phosphine and -arsine.—The ready reaction of $[RuCl_3(LPeHMeOH)]$ ($L = P$, As) with solvents and Lewis bases prompted an attempt to displace the solvent group with halide ion to form anionic ruthenium complexes. Although an attempt with potassium chloride produced no obvious reaction, when $[RuCl_3(LPeHMeOH)]$ was suspended in acetonitrile and thoroughly shaken for several hours with a large excess of tetramethlammonium chloride, an 80% conversion of the initially formed $[RuCl_3(LPeHMeCN)]$ into the red crystalline $Me_3N[RuCl_3(PhH_2MeCN)$_2$]$. Similar crystalline complexes were obtained upon treatment $[RuCl_3(LPeHMeOH)]$ with an excess of $Ph_2AsCl$, HCl and Et$_2NCl$, $H_2O$.

Similarly, treatment of $[RuBr_3(AsPh_3)$_2$]MeOH$ in acetone with hydrobromic acid followed by addition of a large excess of $Ph_2AsBr$ or $Me_2NB$ and removal of the solvent gave the purple crystalline $M[RuBr_3(AsPh_3)_2]$ ($M = Ph_2As^+$, $Me_2N^+$).

In all cases, the complexes were characterised by elemental analyses, by magnetic moments at room temperature (ranging from 1.80 to 2.20 B.M. indicative of ruthenium(III) spin-paired complexes) and by conductance measurements on $10^{-3}$-solutions in nitromethane at 25° (Table 1). These gave values almost in

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3 L. Vaska, Chem. and Ind., 1961, 1402.
the range expected for 1:1 electrolytes in this solvent.14 A molecular-weight measurement in acetone on \(\text{Me}_2\text{N-}[\text{RuBr}_4(\text{AsPh}_3)_2]\) gave a value of half that expected for a monomeric complex (since a 1:1 electrolyte in acetone).

The attempt to obtain the corresponding bromophosphine anion via \([\text{RuBr}_3(\text{PPPh}_3)_2\text{MeOH}]\) and \(\text{MBR}\) was unsuccessful; the red-brown solids isolated contained no large cations (i.e., evidence) and were non-electrolytes in acetone and nitromethane solution. Treatment of a suspension of \(\text{Me}_2\text{N}[\text{RuCl}_4(\text{PPPh}_3)_2]\) in acetone with an excess of lithium bromide immediately gave a purple solution but after complete removal of the solvent or addition of excess water, the paramagnetic product contained no \(\text{Me}_2\text{N}^+\) (characterised by a strong band in the i.r. region at ca. 950 cm\(^{-1}\)) and had an analysis very close to that for \([\text{RuBr}_3(\text{PPPh}_3)_2\text{H}_2\text{O}]\). This formulation was supported by the very low conductance (Table I) in acetone and nitromethane solutions and by the presence of weak bands at 3300 and 1600 cm\(^{-1}\) in the i.r. spectrum of the complex which were assigned to hydroxy stretching and bending vibrations respectively.

It is interesting to note that a similar reaction between the \([\text{RuCl}_4(\text{AsPh}_3)_2]^-\) anion and lithium bromide produced the bromo-anion, provided that the solvent was removed within minutes of the reactants; when they were not, solvation occurred to give \([\text{RuBr}_3(\text{AsPh}_3)_2\text{H}_2\text{O}]\). The anion could, however, be washed with hot water without any apparent effect. Results presented later for the chloro-anions, both with reference to the rate of solvolysis and exchange reactions with other tertiary phosphines, clearly indicated the increased lability of the \(\text{Ph}_3\text{P}\) anion compared to the \(\text{Ph}_3\text{As}\) anion. It is concluded, therefore, that the inability to prepare the bromophosphine anion stems from its kinetic instability with respect to the solvated bromo-complex.

Because of this ready solvolysis, few attempts have been made to generate a series of ruthenium(III) anions \([\text{RuX}_2(\text{LPh}_3)_2]^-\) (X = SCN\(^-\), I\(^-\), etc.) by metathetical reactions. In contrast, similar reactions with \([\text{RhCl}_4(\text{PPPh}_3)_2]^-\) readily produced \([\text{RhX}_4(\text{PPPh}_3)_2]^-\) (X = Br\(^-\), SCN\(^-\)) which did not undergo solvolysis.

A feature of the tetraphenylarsonium salts of the ruthenium(III) triphenyl-phosphate- and arsine anions was that they crystallised with two molecular equivalents of acetone. This was shown by direct oxygen analyses and by the i.r. spectra of the complexes which contained bands characteristic of acetone at ca. 1700 (\(v\text{co}\)) and 1220 cm\(^{-1}\) (\(\text{wco}\)).15 The position of \(\text{wco}\) indicated that the acetone was probably present as molecules of solvation and not co-ordinated, [cf. \(v\text{co} 1655 \text{ cm}^{-1}\) in \([\text{RuCl}_4(\text{AsPh}_3)_2\text{MeCO}]7\); 1604 cm\(^{-1}\) in \(\text{F}_2\text{BOCMe}_2\)].15


However, the quaternary ammonium salts crystallised out with no associated solvent. This suggests that either the solvent molecules are associated only with the tetraphenylarsenium ion or that the crystal packing is such that acetone is incorporated in the lattice cavities as in a clathrate complex.

In view of the success in preparing these ruthenium-(III) anions, an attempt was made to synthesise the unknown ruthenium(II) anion \([\text{RuCl}_4(\text{PPPh}_3)_2]^-\) via \(\text{RuCl}_3\)-\(\text{PPPh}_3\) or \(\text{PPPh}_3\). There is only one example in the literature of a ruthenium(II) anionic complex containing a tertiary phosphine group: the rather strange \([\text{RuCl}_4(\text{PET}_{2}\text{Ph})_2]\) \([\text{RuCl}_4(\text{PET}_{2}\text{Ph})_2]\) prepared by heating \([\text{RuCl}_4(\text{PET}_{2}\text{Ph})_2]\) \(\text{Cl}\) at 60° in methyl acetate.16,17 At 120° in this solvent, \([\text{RuCl}_4(\text{PET}_{2}\text{Ph})_2]\) is formed.16,18 However, the corresponding halogenoarylonyl anions \(\text{Cs}[\text{RuX}_2(\text{CO})_2]\) \((X = \text{Cl}, \text{Br})\)6 as well as \(\text{M}[\text{RuX}_2(\text{CO})_2]\) \((M = \text{Cs}\) (refs. 5 and 19), \(\text{NH}_4^+\) (ref. 4); \(X = \text{Cl}, \text{Br}, \text{I}\) and \(\text{M}[\text{RuCl}_4(\text{CO})_2(\text{H}_2\text{O})]\) \((M = \text{Cs}\) (ref. 5); \(\text{NH}_4^+\) (ref. 20)) are well known.

However, reaction of \(\text{RuCl}_4(\text{PPPh}_3)_2\) with an excess of \(\text{Ph}_3\text{AsCl}\cdots\text{HCl}\) in acetone produced orange crystals of \(\text{Ph}_3\text{As}[\text{RuCl}_4(\text{PPPh}_3)_2]\) \((\text{MeCO})_2\) identical to the product obtained from \([\text{RuCl}_4(\text{PPPh}_3)_2\text{MeOH}]\). With \(\text{MeNCl}\), there was no apparent reaction except on pre-treatment of the acetone solution with concentrated hydrochloric acid when the air-sensitive yellow-brown solution was converted into an air-stable reddish-brown solution. Addition of an excess of \(\text{MeNCl}\) to a portion of this then rapidly deposited orange \(\text{Me}_2\text{N}[\text{RCl}_4(\text{PPPh}_3)_2]\). Removal of the solvent from the remainder of the acidified solution gave an air-stable, paramagnetic, yellow-brown powder which was partially ionised in nitromethane and acetone (Table I) and had an analysis close to that for \(\text{H}_2\text{O}[\text{RuCl}_4(\text{PPPh}_3)_2]\). However, an i.r. spectrum of the carefully dried compound contained no evidence for either hydroxonium ion or aquo-groups and a better formulation may be \(\text{H}[\text{RuCl}_4(\text{PPPh}_3)_2]\) (cf. \(\text{H}[\text{RuCl}_4(\text{o-phen})]\) obtained by reduction of \([\text{RuCl}_4(\text{o-phen})]\) with alcohol in the presence of hydrochloric acid).21 The structure of these complexes may be similar to that postulated for \(\text{H}_2\text{N}[\text{Ru(CN)}_6]\)22 with hydrogen bonding between the hydrogen and chloride groups.

Ruthenium(III) Anions of Other Tertiary Monophosphines.—Although the \(\text{Ph}_3\text{P}\) anion can be readily obtained from \([\text{RuCl}_4(\text{PPPh}_3)_2\text{MeOH}]\), similar routes for the preparation of other ruthenium(III)-tertiary phosphine anions are unavailable because the corresponding starting materials containing a labile alcoholic group are unknown. Instead, refluxing methanolic23 or 2-methoxy-ethanolic2 solutions of \(\text{R}_3\text{P}\) and \(\text{RuCl}_4\cdots\text{H}_2\text{O}\) gives \([\text{RuCl}_4(\text{Pr}_3\text{P})]\) \(\text{Cl}\); in an acidic ethanolic solution
mer-RuCl₃(PR₃)₂ is formed⁸ and attempts to obtain anionic complexes by reactions of these compounds with MCl-hydrochloric acid mixtures have been unsuccessful.

An attempted preparation of the unknown complex RuCl₅(PF₆)₂ by treatment of monomeric RuCl₅(PPh₃)₃ with an excess of neat triethylphosphine gave a deep emerald-green solution. In view of the recent paper by Leigh et al.,²⁴ in which it is suggested that in solution [RuX₂(PMe₂Ph)₃(EBT)]⁻ (X = Cl or Br) readily decomposes to give green [RuX₂(PMe₂Ph)₃], the method is probably successful; only a very soluble oil could, however, be isolated. When the solution was set aside for several hours, the green colour was discharged and very pale yellow crystals were deposited; these had an

crystals of R₂PH[RuCl₄(PR₃)₂]. This reaction has now been extended to the preparation of the phosphonium salt of Me₂Ph₃P⁺ by reaction of an excess of Me₂Ph₃P with a cold freshly prepared 'red solution' produced a mixture of Me₂Ph₃P[RuCl₄(PPh₃)₃] (ca. yield 40%), RuCl₅CO-(Me₂Ph₃)₃, and RuCl₅(CO)₃(PMe₂Ph)₃. The carbonyl complexes have been well characterised by previous workers.³⁰ Treatment of the phosphonium salts with MCl in a minimum volume of solvent then gave M[RuCl₄(PR₃)₂] (M = Ph₃As⁺ or Me₄N⁺).

A more direct method of obtaining these salts is by treatment of M[RuCl₅(LPh₃)₂] with an excess of neat tertiary phosphine for several days under nitrogen, when almost quantitative conversion into the corresponding

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<th>Complex</th>
<th>A₀-0.01 (cm⁻¹ mol⁻¹)</th>
<th>Solvent</th>
<th>μₑq (μM)</th>
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<td>64, 62</td>
<td>MeNO₂</td>
<td>1.90</td>
<td>294</td>
</tr>
<tr>
<td>Ph₄As<a href="Me%E2%82%82CO">RhCl₅(PPh₃)₃</a>₂</td>
<td>49, 53</td>
<td>Diamagnetic</td>
<td>296</td>
<td></td>
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<tr>
<td>Me₄N[RuCl₅(PPh₃)₃]</td>
<td>80</td>
<td>MeNO₂</td>
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<td>293</td>
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<tr>
<td>Ph₄As<a href="Me%E2%82%82CO">RhBr₅(PPh₃)₂</a></td>
<td>54</td>
<td>MeNO₂</td>
<td>2.00</td>
<td>293</td>
</tr>
<tr>
<td>Ph₄As[RhCl₅(PPh₃)₂]</td>
<td>98</td>
<td>MeNO₂</td>
<td>2.00</td>
<td>293</td>
</tr>
</tbody>
</table>

* Prepared from RuCl₅(PPh₃), * Prepared from RuCl₅(PPh₃)₃, MeOH, Ph₃As⁺ salt. * Prepared from RuCl₅(PPh₃)₃, MeOH, Ph₃As⁺ salt. * Prepared from RuCl₅(PPh₃)₃, MeOH, Ph₃As⁺ salt.

analysis which was consistent with the empirical formula [RuCl₅(PPh₃)₃]. The far-i.r. spectrum [νυ(RuCl) > 270 cm⁻¹], conductivity in nitromethane (A₀-0.01 = 49 ohm⁻¹ mole⁻¹ cm⁻³), and melting point were identical with those of a sample of [RuCl₅(PPh₃)₃]Cl, prepared from RuCl₅H₂O, E₅TP, and 2-methoxyethanol.² A similar result was obtained when RuH₂(PMe₂Ph)₄ was treated with hydrochloric acid when [RuCl₅(PMe₂Ph)₃]Cl, and not the expected [RuCl₅(PMe₂Ph)₃] was isolated.²⁵ It is concluded, therefore, that although mononuclear halide complexes of ruthenium(II) with R₂P do exist, they are unstable with respect to the halogeno-bridged binuclear complex. The only exceptions are RuCl₅-

(PPh₃)₃ or 4.

As briefly reported earlier,⁷ treatment of a ruthenium carbonyl-containing solution with a large excess of E₅TP or E₅TPH gives immediate precipitation of green

Solvolyis of Ruthenium(III) Anions.—When the red anionic complexes $M[RuCl_4(LPh_3)_2]$ were dissolved in nitromethane, the initial yellow solutions rapidly turned green and if concentrated solutions were used, green crystals could be isolated. This colour change was accelerated by heat and the rate of conversion was qualitatively the same as that found for the exchange with tertiary phosphines. Similarly, when the green triethylphosphonium compound (and its $Ph_3As^+$ salt) was dissolved in dichloromethane, the initial green solution rapidly turned yellow-brown; dissolution of the brown dimethylphenylphosphonium salt in acetone followed by addition of water rapidly gave a green solution.

Similar colour changes have been reported in relation systems. For example, persistent treatment of red $H[RuCl_4]_2$ in $H_2O$ with alcohol gives a green solid and Griffith has suggested that these may be cis- and trans-isomers of the $[RuCl_4(H_2O)_2]$- anion. A recent X-ray analysis of red $Ph_3As[RuCl_4(Ph_2O)_2]$ in $H_2O$ has shown it to contain cis-aquo-groups. The brown complexes phenH$[RuCl_4(phcn)]$ and bipyH$[RuCl_4(bipy)]$ are also known and for steric reasons must have a cis-configuration. In contrast, e.s.r. and far-i.r. evidence for green $Et_2Ph[ClRuCl_4(PEt_3)_2]$ suggest that this anion has a trans-configuration.

Therefore, on the basis of this evidence, the most likely explanation for the colour changes observed in this work was the existence of both cis- and trans-isomers: a red cis- and a green trans-form. However, in every case, the colour change could be suppressed by addition of an excess of MCl to the solution, and, further, the addition of MCl to the green solids (from the $[RuCl_4(LPh_3)_2]$- anions) in acetone rapidly gave the original red complexes. The green complexes were found to be non-conducting in nitromethane and to contain no large cation (i.r. evidence); in fact, they had melting points and analyses identical to $[RuCl_4(LPh_3)_2]$ in $MeNO_2$, which was obtained by treating $[RuCl_4(LPh_3)_2]$ with nitromethane. A similar behaviour was observed in acetonitrile solutions. Thus the red-green colour change can be ascribed to the equilibrium:

$$[RuCl_4(LPh_3)_2]^+ + S \rightleftharpoons [RuCl_4(LPh_3)_2]S + Cl^- (S = MeNO_2, MeCN)$$

A similar behaviour has been found for the complexes $M[IrX_4(SbPPh_3)_2]$ ($M = Na, K$; $X = Cl, Br$) which on dissolution in methanol slowly give $[IrX_4(SbPPh_3)_2]$ in $CH_2OH$. Rather surprisingly, the i.r. spectra of the ruthenium complexes showed no evidence for solvent co-ordination, although the nitrogen analyses clearly indicated their presence. The reason for the absence of characteristic solvent absorptions is unknown. Investigation of the colour change in dichloromethane of the $Et_2P$ anion led to isolation of a red-brown solid, non-conducting in dichloromethane and nitrromethane and containing no large cation (i.r. evidence).

Therefore, it is concluded that the colour changes observed arise from solvolysis of the anions and not a cis-trans isomerisation. It also suggests that the colour change observed when $[RuCl_4(H_2O)_2]$ is treated with ethanol is probably due to the formation of green $[RuCl_4(H_2O)_2]$ in $EtOH$.

Rhodium(III) Anions of Tertiary Monophosphines.—Although a substantial literature exists for a variety of rhodium(III) complexes of tertiary phosphines, there is only one reported example of a rhodium(III) anion containing a tertiary phosphine group, namely $[RhCl_4(PMe_2Ph)_3]$, isolated as its phosphonium salt (2-3% yield) in the reaction of $RhCl_3$ with $PMe_2PhP$ to give mer- and fac-$[RhCl_4(PMe_2Ph)_3]$. Reaction of the phosphonium salt with $Ph_3AsCl$ then gave $[Ph_3As][RhCl_4(PMe_2Ph)_3]$. Attempts to prepare this anion in larger yields by treatment of $[RhCl_2(PMe_2Ph)_4]$ with an excess of $PMe_2NCI$ have proved unsuccessful since only slow isomerisation to the fac-complex occurred (cf. the recent report by Shaw et al. on photochemical isomerisation of platinum-metal phosphine complexes).

However, when a suspension of $RhCl(PPh_3)_3$ in acetone was treated with a large excess of $Ph_3AsCl$, HCl, conversion into orange crystalline $Ph_3As[RhCl_4(PPh_3)_2]$ occurred during several hours. As for the ruthenium anion, the complex crystallises out with two molecular equivalents of solvent acetone. With $PMe_2NCI$, the same anion was isolated (with no solvent acetone) provided that the suspension was pretreated with concentrated hydrochloric acid. Attempts to obtain the unknown rhodium(III) anion, analogous to the well-known $[RhCl_4(CO)_2]$ with a stoichiometric quantity of $Ph_3AsCl$, HCl were unsuccessful; only the rhodium(III) anion and unchanged $RhCl(PPh_3)_3$ were isolated from the reaction mixture.

The rhodium(III) anion was also obtained as a side-product (ca. 20% yield) by prolonged treatment of $[RhCl_4(PPh_3)_3]$, with a large excess of $Ph_3AsCl$, HCl in an acetone-chloroform mixture. The main product was $trans-[RhCl_4(CO)(PPh_3)_2]$, previously obtained by direct interaction of chlorine with $trans-[RhCl_4(CO)(PPh_3)_2]$. Although carbonyl groups have been replaced in metal carbonyls by halide ion to give halogeno-carbonyl anions, this appears to be the first reported reaction involving carbonyl displacement by halide ion in a monocarbonyl complex.

As for the ruthenium anions, treatment of this triphenylphosphine anion with neat Me₂PPh gave Ph₃As-[RuCl₄(Ph₃PMe₂P)]⁺; however with Et₃P and (PhO)₂PF, only the unchanged arylphosphine anion could be isolated. The decreased lability of the rhodium anions, compared with ruthenium, was also illustrated by the relative stability of these complexes in solution; whereas the ruthenium ions underwent rapid solvolysis, the rhodium ions appeared quite stable in nitromethane, acetonitrile, etc. Furthermore, treatment of the rhodium triphenylphosphine chloride-anion with various lithium salts gave [RhX₄(PPh₃)]⁻ ions (X = Br⁻ and SCN⁻) which were quite stable in solution. Unlike reactions of mer-[RhCl₃(PMe₂P)₆] with lithium salts, which require 'triplet' indicative of trans-Me₂PPh groups. The complex Ph₃As[RhCl₄(PMe₂P)]⁺ reported in this paper has an identical m.p. and n.m.r. and far-i.r. spectral properties (except for the absence of the characteristic doublet of the Ph₃As⁺ ion at 351 and 339 cm⁻¹ in ref. 31) to that reported by Shaw et al.31 Similar i.r. evidence suggests a trans-structure for the [RuCl₄(PPh₃)]⁺ ion and this has been recently substantiated by e.s.r. measurements on Et₃P[RuCl₄(PPh₃)]⁺.

For the chloro-P₃P and -P₃As anions, no strong bands below 300 cm⁻¹ are found in their far-i.r. spectra. Superposition of the far-i.r. spectra of the chloro- and bromo-ions enables ν(MX) to be assigned and the ratio of ν(MCl) : ν(MBr) (1.25 — 1.30) is in the range found by several hours at reflux temperature for complete exchange,31 these exchange reactions occurred quite rapidly at room temperature.

Conductance data on these diamagnetic rhodium(III) anions are given in Table 1.

### Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequency of other bands (cm⁻¹)</th>
<th>ν(M-X) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃As[RuCl₄(AsPh₃)]⁺(Me₂CO)⁺</td>
<td>358, 338, 328, 319, 296, 253, 245, 225, 215</td>
<td>311 vs, 296 m *</td>
</tr>
<tr>
<td>Ph₃As[RuBr₄(AsPh₃)]⁺(Me₂CO)⁺</td>
<td>352, 347, 328, 322, 306, 224, 220</td>
<td>246 s</td>
</tr>
<tr>
<td>Ph₃As[RuCl₄(PPh₃)]⁺(Me₂CO)⁺</td>
<td>358, 344, 328, 226</td>
<td>317 vs, 307 vs</td>
</tr>
<tr>
<td>Ph₃As[RuCl₄(PPh₃)]⁺(Me₂CO)⁺</td>
<td>356, 342, 306, 290, 236, 230</td>
<td>334 vs, 329 s *</td>
</tr>
<tr>
<td>Ph₃As[RuBr₄(PPh₃)]⁺(Me₂CO)⁺</td>
<td>357, 347, 329, 226</td>
<td>263 s</td>
</tr>
<tr>
<td>Ph₃As[RuCl₄(PMe₂P)]⁺+</td>
<td>354, 341, 322, 240, 217, 213</td>
<td>311 vs, 290 s</td>
</tr>
<tr>
<td>Ph₃As[RuCl₄(PPEt₃)]⁺</td>
<td>346, 315, 318, 264, 244, 224</td>
<td>316 vs, 305 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(AsPh₃)]⁺</td>
<td>340, 318, 309, 257, 226</td>
<td>312 vs, 303 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(PPh₃)]⁺</td>
<td>325, 326, 326, 326, 226</td>
<td>312 vs, 307 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>340, 318, 309, 257, 226</td>
<td>315 vs, 308 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>325, 326, 326, 326, 226</td>
<td>308 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>340, 318, 309, 257, 226</td>
<td>312 vs, 303 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>325, 326, 326, 326, 226</td>
<td>308 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>340, 318, 309, 257, 226</td>
<td>315 vs, 308 s</td>
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<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>325, 326, 326, 326, 226</td>
<td>308 s</td>
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<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>340, 318, 309, 257, 226</td>
<td>312 vs, 303 s</td>
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<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>325, 326, 326, 326, 226</td>
<td>308 s</td>
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<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>340, 318, 309, 257, 226</td>
<td>315 vs, 308 s</td>
</tr>
<tr>
<td>Me₅N[RuCl₄(PPEt₃)]⁺</td>
<td>325, 326, 326, 326, 226</td>
<td>308 s</td>
</tr>
</tbody>
</table>

* From RuCl₄(PPh₃)⁺. * From trans-[RhCl₄(PPh₃)]⁺. * From Ph₃P anion. * From RuCl₄(PPh₃)⁺. * From RuCl₄(AsPh₃)⁺-CH₂OH. * From Ph₃As⁺ salt. * Prepared as in ref. 8.

other workers38 and supports these assignments. However, unlike mer-[MCl₄(PR₃)₂][M = Ru,10 Rh,10,31 Os,10 Ir,10,36 and Re10]: R² = R³ alkyl or R² = alkyl, R¹ = aryl) strong bands, assignable to ν(RuCl) below 300 cm⁻¹ are also absent in the far-i.r. spectra. Thus, it appears that the criteria established by Shaw and his coworkers for distinguishing between chloride trans to chloride or trans to tertiary phosphate may be invalid for triphenylphosphine (and arsine) complexes. The reason for this presumably arises from the fact that Ph₃P is a weaker σ-donor than Et₃P or Me₂PPh and that in octahedral complexes of the platinum metals, the trans-bond weakening effect of a ligand seems to depend on its σ bond properties.39

Although far-i.r. evidence is, therefore, by no means conclusive, the ready exchange of Me₂PPh, etc., for Ph₃L

under very mild reaction conditions to give trans-isomers strongly suggests that the starting materials are also trans. However, in view of the different isomers obtained during oxidative addition reactions of trans-[IRX(CO)L]2 (X = halogen, L = tertiary phosphate, arsine, or olefin) and recent observations on the influence of solvent on the isomer formed in some of these reactions, this evidence is also not conclusive.

In Ph₃As[Rh(SCN)₄(PPh₃)₃], the unsplit ν(CN) absorption (2105 cm⁻¹) is consistent with a trans-configuration. Comparison with the i.r. spectrum of the chloro-anion results from 400—200 cm⁻¹. Conductivity measurements were made on a Mullard conductivity bridge: magnetic susceptibilities were determined by the Faraday method. X.m.r. spectra were obtained on a Bruker Spectrospin HFX3 at 90 MHz and X-ray powder photographs in Lindemann glass tubes were taken with a Debye–Scherrer Powder Camera, 15-75-cm. radius with cobalt radiation; ca. 10 hr. exposure.

Analytical data for the ruthenium(III) and rhodium(III) anions are given in Table 3.

Materials.—These were obtained from the following sources. Commercial ruthenium trichloride and rhodium

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (%)</th>
<th>Required (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₄As[RuCl₃(AsPh₃)₂]</td>
<td>58-9 4-4 17-7 11-0 2-7</td>
<td>58-5 4-6 16-6 10-5 1-5</td>
</tr>
<tr>
<td>Me₄N[RuCl₃(AsPh₃)₂]</td>
<td>61-6 4-5 18-4 15-0 1-9</td>
<td>51-7 4-5 16-1 15-5 1-5</td>
</tr>
<tr>
<td>Et₄N[RuCl₃(AsPh₃)₂]</td>
<td>53-9 5-5 14-5</td>
<td>53-6 5-1 14-4</td>
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<tr>
<td>Ph₃As[RuCl₃(PH₃)₂]</td>
<td>62-6 4-5 16-0</td>
<td>60-6 4-8 16-8</td>
</tr>
<tr>
<td>Me₄N[RuCl₃(PH₃)₂]</td>
<td>62-3 4-5 16-0</td>
<td>57-1 5-0 16-9 1-7 7-4</td>
</tr>
<tr>
<td>Ph₃As[RuBr₃(AsPh₃)₂]</td>
<td>61-6 4-5 15-8 21-9 2-7</td>
<td>51-7 4-1 14-8 20-9 2-1</td>
</tr>
<tr>
<td>Me₄N[RuBr₃(AsPh₃)₂]</td>
<td>63-2 4-0 28-1</td>
<td>43-4 3-5 28-0</td>
</tr>
<tr>
<td>Me₄N[Ph₃P=Cl(PMe₃)₂]</td>
<td>44-0 5-5 20-9</td>
<td>43-8 5-2 21-0</td>
</tr>
<tr>
<td>Me₄N[RuCl₃(PMe₃)₂]</td>
<td>53-7 4-7</td>
<td>53-2 4-7 15-7</td>
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<tr>
<td>Ph₄As[RuCl₃(PEt₃)₂]</td>
<td>53-8 4-9</td>
<td>16-1</td>
</tr>
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<td>34-7 7-8</td>
</tr>
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<td>41-0 4-8</td>
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<tr>
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<td>51-2 4-5</td>
</tr>
<tr>
<td>Ph₄As[RuCl₃(PPh₃)₂]</td>
<td>62-7 4-5 6-4 11-8</td>
<td>62-4 4-9 5-9 11-2 2-5 4-9</td>
</tr>
<tr>
<td>Me₄N[RuCl₃(PPh₃)₂]</td>
<td>61-9 4-5 5-8 11-8</td>
<td>56-9 5-0 16-8 1-7</td>
</tr>
<tr>
<td>Ph₄As[RuBr₃(PPh₃)₂]</td>
<td>53-4 4-1 24-3</td>
<td>54-4 4-0 23-1</td>
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<tr>
<td>Ph₄As[RhCl₃(PPh₃)₂]</td>
<td>61-3 4-2</td>
<td>61-4 4-0</td>
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<tr>
<td>Ph₄As[RhCl₃(PMe₃)₂]</td>
<td>53-2 4-9</td>
<td>53-2 4-7</td>
</tr>
</tbody>
</table>

Show there is no additional band in the M—NCS range (780—860 cm⁻¹) but that a weak extra band occurs at 638 cm⁻¹, close to the range expected for the (predominantly) C=S stretching mode of vibration of an S-bonded thiocyanate ligand (690—720 cm⁻¹).41 The region 690—720 cm⁻¹ is obscured by bands due to the triphenylphosphine ligands.

Finally, X-ray powder photographs of Ph₄As[MC₅(PH₃)₃] (M = Ru and Rh) are identical indicating that the compounds are isomorphous; this also provides support, although by no means proves, that the compounds have the same isomeric form.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College or A. Bernhardt, West Germany. Molecular weights were determined on a Perkin-Elmer Hitachi osmometer (model 115) at 35°. I.r. spectra were recorded in the region 4000—400 cm⁻¹ on a Perkin-Elmer model 125 spectrometer and in the region 400—200 cm⁻¹ by means of a Grubb-Parsons DM4 mark II spectrometer; an R.L.C. Fourier spectrometer F.S. 520 with a Meline beam divider and an effective resolution of 5 cm⁻¹ was also used to obtain trichloride, Johnson Matthey Ltd.; triphenylphosphine, triphenylarsine, tetramethyl- and tetraethyl-ammonium chloride, dimethylphenylphosphine, B.D.H. Laboratories; triethylphosphine, B. Newton Mian Ltd.; tetraphenylarsinum chloride and HCl, Koch–Light Ltd.

Ruthenium Complexes

Tetraphenylarsonium Tetrachlorobis(triphenylarsine)ruthenium(III).—Diacetone.—Trichlorobis(triphenylarsine)methanol(ruthenium(III) (0-15 g.) was suspended in solvent acetone (35 ml.) and thoroughly shaken with tetraphenylarsonium chloride and hydrochloric acid (0-80 g.) for several hours to produce complete conversion of the initially formed brown trichlorobis(triphenylarsine)-acetone(ruthenium(III) to deep red crystals of the complex; these were washed with cold acetone (20 ml.), water (15 ml.), methanol, and diethyl ether and were then dried in vacuo at 40° for several hours (0-27 g., 70%), m.p. 195° (decomp.) (pcO 1709 cm⁻¹; pcO 1219 cm⁻¹). The complex is reasonably stable in dichloromethane but decomposes in hot acetone.

Tetramethylammonium Tetrachlorobis(triphenylarsine)ruthenate(II).—This was prepared as for the Ph₄As⁺ salt with [RuCl₃(AsPh₃)₂]MeOH (0.25 g) and Me₄NCl (1.20 g) in an acetone (25 ml)–methanol (6 ml) mixture. Orange-red crystals of the complex were deposited and purified as above (0–23 g, 83%), m.p. 262–263° (decomp.). The complex is insoluble in dichloromethane.

Tetraethylammonium Tetrachlorobis(triphenylarsine)ruthenate(II).—This was prepared as for the other salts from [RuCl₃(AsPh₃)₂]MeOH (0.25 g) and Et₄NCl, H₂O (1.00 g) in acetone (30 ml); it was obtained as orange-brown crystals (0.24 g, 82%), m.p. 218° (decomp.). This compound is more soluble than the Me₄N⁺ salt.

Tetraphenylarsonium Tetrachlorobis(triphenylphosphine)ruthenate(II).—Diacetone. Method (A). This was prepared as for the corresponding triphenylarsine salt from [RuCl₃(PPh₃)₂]MeOH (0.15 g) and Ph₃AsCl, HCl (0.80 g) in acetone (30 ml); it was obtained as orange crystals (0.20 g, 79%), m.p. 207° [ν₀ 1708 cm⁻¹; ν₀ 1216 cm⁻¹].

Method (B). Dichlorotetrakis(triphenylphosphine)ruthenium(II) (0.15 g) dissolved under nitrogen in warm acetone (25 ml) gave a yellow-brown solution to which Ph₃AsCl, HCl (0.60 g) in acetone (5 ml) was added. An air-stable, red-brown solution was produced which on prolonged shaking deposited orange crystals of the complex which were purified as above (0–11 g, 70%), m.p. 208° [ν₀ 1708 cm⁻¹; ν₀ 1216 cm⁻¹]. The same product is formed if RuCl₃(PPh₃)₂ is used.

Tetramethylammonium Tetrachlorobis(triphenylphosphine)ruthenate(II).—This was prepared as for the Ph₄As⁺ salt with [RuCl₃(PPh₃)₂]MeOH (0.15 g) and Me₄NCl (0.60 g) and gave orange crystals (0.12 g, 86%), m.p. 220° (decomp.). This compound is insoluble in dichloromethane.

Reaction of Dichlorotris(triphenylphosphine)ruthenium(II) with Hydrochloric Acid. —RuCl₃(PPh₃)₂ (0.15 g) dissolved under nitrogen in warm acetone gave a yellow-brown solution which upon addition of concentrated hydrochloric acid (2 ml) immediately gave an air-stable red-brown solution. Removal of the solvent from this under reduced pressure gave a yellow-brown solid which was washed with light petroleum (b.p. 60–80°) and diethyl ether and dried in vacuo at 40° for several hours (0–10 g, 86%), m.p. 122–125° (decomp.). [Found: C, 54.7; H, 5.0; Cl, 18.1%; H[RuCl₃(PPh₃)₂] requires C, 56.3; H, 4.2; Cl, 18.5%]. A closer formulation is H₂O[RuCl₃(PPh₃)₂] (Requires C, 55.6; H, 4.2; Cl, 18.0; O, 20%) but the i.r. spectrum shows no evidence for aquo or hydroxion groups; in view of the i.r. spectrum of [RuCl₃(L₃)₂MeNO₂] (no evidence for MeNO₂) this may be inconclusive. An oxygen analyses was, in fact, obtained (5.5%) but the delay was considerable and some hydrolysis may have occurred.

When a methanol (3 ml) solution of Me₄NCl (0.60 g) was added to the red-brown solution, orange crystals of tetramethylammonium tetrachlorobis(triphenylphosphine)ruthenate(II) were slowly deposited (0.09 g, 68%), m.p. 220–222° (decomp.). The same compound can be obtained from RuCl₃(PPh₃)₂.

Tetraphenylarsonium Tetraethylarsonium(ruthenium(III).—Diacetone. [RuBr₃(AsPh₃)₂]MeOH (0.30 g) was suspended in acetone (35 ml) and treated with concentrated hydrobromic acid (3 ml) to give a deep red-brown solution. Ph₃AsBr (0.80 g) was added to this solution and the mixture was thoroughly shaken for several hours. Concentration of the solution under reduced pressure gave dark purple crystals of the complex, which were washed with small portions of cold acetone, hot water, ethano, and diethyl ether and then dried in vacuo at 40° for several hours (0–30 g, 65%), m.p. 180° (decomp.) [ν₀ 1701 cm⁻¹; ν₀ 1211 cm⁻¹]. The compound can also be made by treating the corresponding chloro-ruthenium with an excess of lithium bromide in acetone; removal of the solvent under reduced pressure (within 5 min.) gave the purple solid, purified as above (m.p. 182° [ν₀ 1700 cm⁻¹]). The compound is soluble in dichloromethane and nitromethane to give purple solutions; the latter rapidly turns red-brown.

Tetraethylammonium Tetraethylruthenium(III) with Lithium Bromide. —Me₄N⁺[RuCl₃(AsPh₃)₂] (0.30 g) was shaken with lithium bromide (1–50 g) in acetone (30 ml) to give a purple solution. After 3–4 min., a portion (10 ml) of this was decanted off and an excess of water was added to it; the purple precipitate was filtered off and washed with water, methanol, and diethyl ether (0.11 g, 87%), m.p. 220° (decomp.); its i.r. spectrum was identical with that of Me₄N[RuBr₃(AsPh₃)₂].

The remaining solution was left for a further 2 hr. Removal of the solvent from this under reduced pressure gave a dark brown residue which was washed with water and diethyl ether and dried in vacuo at 40° for several hours (0–15 g, 80%), m.p. 154–156° (decomp.). [Found: C, 43.8; H, 3.6%; [RuBr₃(AsPh₃)₂]H₂O requires C, 43.5; H, 3.5%]. The i.r. spectrum shows weak bands at 3400 and 1600 cm⁻¹; no band at 950 cm⁻¹ corresponding to Me₄N⁺.

Reaction of Tetramethylammonium Tetrachlorobis(triphenylphosphine)ruthenate(II) with Lithium Bromide. —This was prepared as for the triphenylarsine complex from Me₄N[RuCl₃(PPh₃)₂] (0.30 g) and lithium bromide (1–50 g) in acetone (20 ml). The purple solution was filtered after 2–3 min., and an excess of distilled water was added to it. The resulting red-brown precipitate was washed with water and diethyl ether (0.28 g, 87%), m.p. 148–150° (decomp.). [Found: C, 48.0; H, 3.5; Br, 26.5% [RuBr₃(PPh₃)₂]H₂O]-H₂O requires C, 48.0; H, 3.8; Br, 26.6%]. The same product is obtained if the solvent is removed under reduced pressure or if RuCl₃(PPh₃)₂ MeOH is treated with a mixture of Me₄NBr and HBr.

Trichlorobis(triphenylarsine)(nitromethane)ruthenium(II).—Ph₄As[RuCl₃(AsPh₃)₂] (0.20 g) was gently warmed with nitromethane (5 ml) and the solution was cooled. The initial yellow solution slowly turned green and after ca. 30 min., green crystals of the complex were deposited; these were washed with water, methanol, and diethyl ether and dried in vacuo at 40° for several hours (0–10 g, 76%), m.p. 198–199° (decomp.). [Found: C, 51.5; H, 3.9; N, 1.8%; C₃H₅AsCl₂NO₂Ru requires C, 50.4; H, 3.8; Cl, 12.2; N, 1.6%].

Similarly, a solution of RuCl₃(AsPh₃)₂MeOH (0.20 g) in nitromethane (5 ml) when warmed gently, rapidly (2 min.)
deposited lime-green crystals of the complex (0.16 g., 78%), m.p. 200° (decomp.) (Found: C, 50.0; H, 4.0; Cl, 12.7; N, 1.3%).

With Me₄N[RuCl₃(AsPh₃)₂], a mixture of unchanged solid and green complex is obtained when the reaction mixture is set aside for several hours. Treatment of the green complex in acetonitrile with an excess of Me₂NCl regenerated red Me₄N[RuCl₃(AsPh₃)₂] (2 hr.).

Trichlorobis(triphenylphosphate)(nitromethane) ruthenium(II).—This was prepared as for the Ph₃As complex from Ph₃As[RuCl₃(PPh₃)₂] (0.20 g.) and nitromethane (5 ml.); the reaction mixture almost immediately gave green crystals of the complex (0.10 g., 80%), m.p. 185° (decomp.) (Found: Cl, 13.6; N, 2.0%. C₁₇H₁₂Cl₃NₙO₃P₂Ru requires C, 13.5; N, 1.8%). Similarly, Me₄N[RuCl₃(PPh₃)₂] and MeNO₃ (10 min.) gave the complex.

Dimethylphenylphosphonium Tetrachlorobis(dimethylphenylphosphine) ruthenium(II).—Carbon monoxide was bubbled through a boiling solution of commercial ruthenium tetrachloride hydrate (1-10 g.) in ethanol (75 ml.) for 5 hr. to give a deep red solution. An excess of dimethylphenylphosphine (2-50 g.) was added to the solution; the mixture was then stirred at 60° for 1 hr. yellow crystals of [RuCl₂CO(Me₂PPh₂)] [VCO 1961, configuration (I)] and [RuCl₂(CO)₂(Me₂PPh₂)] [VCO 1966, configuration (V)]. Partly removal of the solvent under reduced pressure from the filtered solution gave more carbonyl complexes mixed with dark brown crystals of the complex; these were washed with benzene (to remove the carbonyl complexes) and diethyl ether and dried in vacuo at 40° (1.05 g., 4%), m.p. 157° (decomp.) [vOH 2450 cm⁻¹]. The compound is soluble in dichloromethane, acetonitrile, nitromethane, and chloroform but is insoluble in ethanol and water.

Tetracyanobenzene Ruthenium(III) Complexes

Tetracyanobenzene Ruthenium(III) Complexes

shaken for 1 hr. with Me$_2$NCl (2·7 g.). The solution was filtered and set aside 24 hr. when orange-yellow crystals of the complex were deposited; these were purified as above (0·40 g., 73%), m.p. 230—234° (decomp.).

Tetraphenyl arsonium Tetraammonium bromide(triphenylphosphine)-
rhodate(III).—A suspension of Ph$_3$As[RhCl$_4$(PPh$_3$)$_2$] (0·10 g.) was shaken with lithium bromide (3·0 g.) in acetone (35 ml.) for 24 hr. The yellow-brown solution was filtered, two-thirds of the solvent were removed under reduced pressure, and the unchanged lithium bromide and chloride were filtered off; removal of the remainder of the solvent gave a yellow-brown powder, which was washed with water and diethyl ether and dried in vacuo at 40° (0·10 g., 88%), m.p. 170° (decomp.) (v$_{oo}$ 1705 cm.$^{-1}$; v$_{so}$ 1220 cm.$^{-1}$). The compound is very soluble in acetone and methanol.

Tetraphenyl arsonium Tetraammonium thiocyanotris(triphenylphosphine)-
rhodate(III).—This was prepared as for the bromo-
complex, with lithium thiocyanate (2·0 g.); removal of the solvent from the yellow solution gave the lemon-yellow powder which was purified as above (0·09 g., 91%), m.p. 96—98° (v$_{so}$ 2105 cm.$^{-1}$). The compound contained no acetone (i.r.) and is very soluble in acetone and methanol.

Tetraphenyl arsonium Tetraammonium dimethyl(triphenylphosphine)-
rhodate(III).—This was prepared as for the correlative ruthenium complex from the Ph$_3$P anion (0·15 g.) which was treated with neat Me$_2$PhP (1·5 ml.) for 10 days under nitrogen; the red-brown complex was purified as before (0·09 g., 92%), m.p. 224—226° (decomp.); the n.m.r. in CH$_2$Cl$_2$ showed methyl resonance (1:2:1 triplet) at 8 8·07 apparent coupling constant J(P—H) 4·0 c./sec.

Similar attempts to prepare the rhodium(III) anions of Et$_3$P and (PhO)$_3$P gave only the unchanged Ph$_3$P anion.

Reaction of mer-Trichlorotris(dimethylphenylphosphine)-
rhodium(III) with Tetramethylammonium Chloride.—mer-
[RhCl$_3$(PMe$_2$Ph)$_3$] (0·20 g.) was dissolved in chloroform (10 ml.) and Me$_2$NCl (2·0 g.) in methanol (10 ml.) was added to it. After several days, a crystalline pale yellow solid was deposited, m.p. 217—221° (decomp.), which had an i.r. spectrum identical with that of fac-[RhCl$_4$(PMe$_3$Ph)$_3$].

More of this complex was obtained when the reaction mixture was set aside but no anionic complex was isolated from the residue.

We thank Johnson Matthey Ltd., for generous loans of ruthenium and rhodium trichlorides.

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SYNTHESIS OF SOME RUTHENIUM(II) ANIONIC COMPLEXES

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In spite of a wealth of information on coordination complexes of ruthenium (II), particularly with ligands such as PR₃, CO, and various organic molecules, few anionic ruthenium (II) complexes have been characterised other than those for nitrosyl derivatives (1). In fact, the only anionic tertiary phosphine complex of ruthenium (II) is the rather strange [Ru₂Cl₃(P₆Ph₂)₆][RuCl₃(P₆Et₂Ph)₆] (2).

In this preliminary communication, we wish to report the synthesis and characterisation of the ruthenium (II) carbonyl (bicyclo-[2.2.1]-2,5 heptadiene) anion, M[RuCl₃(CO)C₇H₆]⁻ (M = Cs⁺, Ph₃BzP⁺) and the ruthenium (II) thiocarbonyl triphenylphosphine anion M[RuCl₃(CS)(PPh₃)₃]⁻ (M = Ph₄As⁺, Ph₃BzP⁺, Et₄N⁺).

(Ph₃BzP)[RuCl₃(CO)C₇H₆] was prepared by shaking [RuCl₂(CO)C₇H₆]₂ with a large excess of Ph₃BzPCl and a few drops of concentrated hydrochloric acid in acetone for several days. The resulting orange solid was recrystallized from dichloromethane/heptane in 62% yield, (mp. 177-180°C).

[Found: C, 57.8; H, 4.4; Cl, 15.8; O, 2.5; P, 4.7%]

C₃₃Cl₃H₈₀OFRu requires: C, 58.2; H, 4.5; Cl, 15.6; O, 2.4; P, 4.6%.

The compound is diamagnetic, a 1:1 electrolyte in dichloromethane and the infrared spectrum shows a single carbonyl band at 2009cm⁻¹ (nujol). The 'H nmr spectrum (Table) suggests configuration I (Figure I) for the anion.
TABLE

\(^1H\) nmr Spectrum of \((\text{Ph}_3\text{BzF})[\text{RuCl}_3(\text{CO})\text{C}_7\text{H}_8]^a\)

<table>
<thead>
<tr>
<th>(\tau)</th>
<th>Ratio</th>
<th>Assignment (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.38</td>
<td>20</td>
<td>phenyl</td>
</tr>
<tr>
<td>2.90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.80</td>
<td>2</td>
<td>doublet</td>
</tr>
<tr>
<td>4.78</td>
<td>2</td>
<td>triplet</td>
</tr>
<tr>
<td>5.48</td>
<td>2</td>
<td>triplet</td>
</tr>
<tr>
<td>5.80</td>
<td>1</td>
<td>broad singlet</td>
</tr>
<tr>
<td>6.34</td>
<td>1</td>
<td>broad singlet</td>
</tr>
<tr>
<td>8.71</td>
<td>2</td>
<td>triplet</td>
</tr>
</tbody>
</table>

\(J_{H_7,8-H_1} = 1.25\text{Hz}, J_{H_7,8-H_4} = 1.50\text{Hz}, J_{H_2-H_6} = J_{H_6-H_6} = 4.5\text{Hz},
\(J_{H_1-H_6} = J_{H_1-H_2} = 3.0\text{Hz}, J_{H_3-H_4} = J_{H_4-H_6} = 3.0\text{Hz}\)

\(^a\) Measured in CDCl\(_3\) \(^b\) See Figure I

This assignment was confirmed by decoupling experiments and the coupling constants shown in the Table were obtained. Note that it is the effect of the ligands cis to the diene which produce the nonequivalence of the norbornadiene protons along a plane through the olefin bonds and the bridgehead carbon. In the more common case, such as in [RhCl(C\(_7\)H\(_8\))]\(^–\)(Ph\(_3\)F) \((4\ a, \ b)\), it is dissimilar trans groups which produce nonequivalence.
of olefin protons along a plane through the bridgehead carbon and protons $H_A$ and $H_B$ (see Figure II).

![Figure II](image)

For the anion $[\text{RuCl}_3(\text{CO})C_7H_8]^-$, only one isomer has been found. Furthermore, addition of free diene (to the Ph$_3$BzP$^+$ salt) or excess CsCl (to a D$_2$O solution of the caesium salt) does not affect the nmr spectrum.

Rather surprisingly, attempts to prepare the Ph$_4$As$^+$ salt have resulted in the formation of the cis-$[\text{RuCl}_4(\text{CO})_2]^-$ anion (with $\nu_{\text{CO}}$ 1940, 2030 cm$^{-1}$, nujol) compared to Cs$_2[\text{RuCl}_4(\text{CO})_2]$ (5) with $\nu_{\text{CO}}$ 1935 and 2036 cm$^{-1}$). An intermediate in this reaction appears to be the previously unknown trans-$[\text{RuCl}_4(\text{CO})_2]^-$-anion ($\nu_{\text{CO}}$ 2010cm$^{-1}$) which rapidly isomerises to the cis form.

Although it was expected that $[\text{RuCl}_3(\text{CO})C_7H_8]^-$ might prove an excellent precursor for a general synthesis of the series $[\text{RuCl}_3\text{CO}(\text{PR}_3)_3]^-$, preliminary experiments with various tertiary phosphines indicate that a chloride ion as well as the diene group is readily displaced to give the neutral complexes $[\text{RuCl}_3\text{CO}(\text{PR}_3)_3]$. However, the products formed are very sensitive to the particular reaction conditions employed and detailed studies with a wider range of ligands are now in progress.

A tertiary phosphine ruthenium (II) anion has however been synthesised by the reaction of $[\text{RuCl}_2(\text{CS})(\text{Ph}_3\text{P})_2]_2$ (6) with MCl/HCl ($M = \text{Ph}_4\text{As}^+$, Ph$_3$BzP$^+$, Et$_4$N$^+$) to give $M[\text{RuCl}_3(\text{CS})(\text{Ph}_3\text{P})_2]$. The red crystalline complexes
were characterised by elemental analyses (e.g. for Ph₄As[RuCl₃(CS)(Ph₃P)]
2.2(CH₃)₂CO; Found: C, 62.8; H, 4.7; % S, 2.6. C₈H₁₅AsCl₃P₃SRu requires:
C, 63.1; H, 4.9; S, 2.5%). The diamagnetic complexes are 1:1 electrolytes
(dichloromethane) and infrared spectra show the characteristic cation bands,
triphenylphosphine and a thiocarbonyl band at 1272cm⁻¹ (murol).

In other attempts to synthesise ruthenium (II) anions, reaction of
[RuCl₂(P₃Ph₂) acetone] (7) with MCl/HCl or MCl alone gave only the
ruthenium (III) complexes M[RuCl₄(P₃Ph₂)] (M = Ph₄As⁺, Et₄N⁺) previously
obtained by the reaction of [RuCl₂(P₃Ph₂)₃ or 4] or [RuCl₂(P₃Ph₂)CH₃OH] with
MCl/HCl (8). With [RuCl₂(Me₂P₃Ph₂)₂EtOH] (9) and MCl/HCl, instead of the
expected [RuCl₃(Me₂P₃Ph₂)]⁻ anion, the well known (10) mer-[RuCl₃(Me₂P₃Ph₂)] was
obtained. Finally, with [RuCl₂C₇H₈]ₙ(11) and MCl/HCl, the polymeric diene
complex was recovered unchanged.

Acknowledgment

We thank Johnson-Matthey Ltd. for a loan of ruthenium trichloride and
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SYNTHESIS OF MIXED LIGAND CARBONYL COMPLEXES
OF RHODIUM(I) AND RHODIUM(III)

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Recently, the reaction of \([\text{RhCl}(\text{CO})_2]_2\) with triphenylphosphine (1:2 molar ratio) to give the complex \(\text{trans-}[\text{RhCl}(\text{CO})_2(\text{PPh}_3)](\text{Ia})\) has been reported (1). Further papers have discussed oxidative addition reactions of \(\text{Ia}\) (2,3), reaction with electronegative olefins (1,4) and with various bidentate ligands (1,4). However, in a very recent communication (5), this compound has been reformulated as the bimolecular monocarbonyl complex \([\text{RhCl}(\text{CO})(\text{PPh}_3)]_2\) (Ib). In this note, further evidence supporting the dimeric structure is presented and the synthesis and reactions of the mixed ligand complexes \(\text{trans-}[\text{RhCl}(\text{CO})(\text{PPh}_3)L'] (\text{II})\) (L' = AsPh_3, SbPh_3, C_8H_8N, N_2S etc) are briefly discussed.

\[
\begin{align*}
\text{OC} & \quad \text{PPh}_3 \\
\text{Cl} & \quad \text{CO} \\
(\text{Ia}) \\
\end{align*}
\]

\[
\begin{align*}
\text{OC} & \quad \text{PPh}_3 \\
\text{Cl} & \quad \text{CO} \\
(\text{Ib}) \\
\end{align*}
\]

Treatment of benzene or dichloromethane solutions of I with an excess of L', followed by concentration and precipitation with pentane gave good yields of the mixed ligand complexes II. These complexes have been characterised by elemental analyses (e.g. for \([\text{PhCl}(\text{CO})(\text{PPh}_3)(\text{AsPh}_3)]\); Found: C, 60.4; H, 4.1; As, 9.7; 0, 2.2% \text{C}_8\text{H}_{10}\text{AsClO}FRh requires C, 60.5; H, 4.1, As, 10.2; 0, 2.2%) and infrared spectra which confirms the presence of both PPh_3 and L'. Thin
layer chromatography on II (L' = AsPh₃) reveals that this is not an equimolar mixture of [RhCl(CO)(PPh₃)₂] and [RhCl(CO)(AsPh₃)₂]. In fact, this compound can be recrystallised from an acetone/dichloromethane solution (unlike the SbPh₃ and C₆H₅N compounds, which readily decompose) and an osmometric molecular weight determination (in CHCl₃) confirms its monomeric formulation (found 737; required 734). The trans configuration of II is assigned on the basis of the similarity of the positions of both ν₀(CO) (ca 1962cm⁻¹) and ν₀RhCl (ca 310cm⁻¹) to those found for trans-[RhCl(CO)(PPh₃)₂] (6,7).

As expected, the chemistry of the mixed complexes is analogous to that established for trans-[RhCl(CO)(PPh₃)₂]. Thus II (L' = AsPh₃) readily undergoes oxidative addition reactions to give the rhodium(III) compounds [RhClXY(CO)(PPh₃)(AsPh₃)] (XY = Cl₂, I₂, CH₃COCl, CH₃I etc.). With CH₃I, the infrared spectrum shows the acetyl complex [RhCl(CH₃CO)(PPh₃)(AsPh₃)] (ν₀ 1718 cm⁻¹) is also formed.

Further evidence for the revised formulation of "trans-[RhCl(CO)₂PPh₃]" is as follows:-

a) I is a dimer measured osmometrically in chloroform (found 865; calc 857). A similar result is found in benzene (5).
b) Reaction of I with AsPh₃ or PPh₃ gives negligible amounts of carbon monoxide (mass spectral evidence) and this supports structure Ib.
c) Reaction of I with carbon monoxide in either benzene or dichloromethane gives a complex with two ν₀(CO) at 2010cm⁻¹ and 2090cm⁻¹. Removing the solvent or simply bubbling nitrogen through the solution regenerates I (ν₀(CO) 1980cm⁻¹). This behaviour is identical to that observed in toluene (5) and attributed to the equilibrium:-

$$2 \text{cis-[RhCl(CO)₂PPh₃]} \rightleftharpoons \frac{2\text{CO}}{2\text{CO}} \text{[RhCl(CO)(PPh₃)]}_2$$
d) Belluco et al (1) support their formulation of the compound as a on the observed position of ν₀RhCl (295cm⁻¹), which is in agreement with a chloride trans to a tertiary aryolphosphine in a rhodium(I) complex (7). However, since ν₀RhCl is assigned at 284, 274cm⁻¹ and 303cm⁻¹ in the bridged chloro
compounds [RhCl(CO)₂]₂ and [RhCl(PPh₃)₂]₂ respectively (7), it is reasonable to expect that νRhCl will occur for the mixed dimer [RhCl(CO)(PPh₃)]₂ in the region 285-295cm⁻¹.

e) Finally, the product from the reaction of I with Cl₂ (previously formulated as the dicarbonyl monomer [RhCl₃(CO)₄(PPh₃)] (ν₀CO 2111cm⁻¹) (2)), reacts with AsPh₃ without evolution of carbon monoxide, to give [RhCl₃(CO)(PPh₃)(AsPh₃)] (ν₀CO 2102cm⁻¹). Therefore, it is suggested that the rhodium(III) dicarbonyl compounds, reported in reference 2 should be reformulated as the binuclear rhodium(III) monocarbonyl complexes [RhClₓY(CO)(PPh₃)]₂.

Acknowledgment

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References

Mixed Ligand Carbonyl Complexes of Rhodium(II) and Rhodium(III)¹

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1972
Mixed Ligand Carbonyl Complexes of Rhodium(II) and Rhodium(III)

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Evidence is presented which suggests that the compounds trans-[Rh(CO)₅PPh₃] (Ia) (X = Cl, Br, I), made from [RhCl(CO)₅] and triphenylphosphine (1:2 molar ratio), should be reformulated as the dimeric complexes trans-[Rh(CO)₅Cl₂PPh₃] (Ib). Reactor compounds with X = SCN, COOMe are also described. Detailed i.r. solution studies of the preparative reaction for X = Cl are presented in terms of the initial formation of a labile intermediate cis-[RhCl(CO)₅PPh₃] (II), followed by isomerization and isolation of (Ib) and a small amount of cis-[RhCl(CO)₅PPh₃] (Ic). The compounds (Ib) undergo bridge cleavage reactions with various Lewis bases, giving [Rh.NO(CO)(PPh₃)] (L = PPh₃, PMe₃, P(η⁵-C₅H₅), AsPh₃, SbPh₃, C₅H₅N, Me₃S, etc.). With SbPh₃ the five-co-ordinate complex [RhCl(CO)(PPh₃)](SbPh₃)₂ is also formed. The same i.m.m.r. m. of [RhCl(CO)(PPh₃)](PMe₃) shows a single singlet for the methyl resonance, indicative of easy phosphine exchange in a strongly coupled PE complex. As expected, [RhCl(CO)(PPh₃)](AsPh₃) readily undergoes oxidative addition reactions, giving [RhCl₂(CO)(PPh₃)(AsPh₃)] (YZ = Cl₂, I₂, CH₃I). The latter product is in equilibrium with its acetyl isomer [RhCl₂(CO)(CH₃)(PPh₃)(AsPh₃)](OCH₃). However, pure [RhCl₂(CO)(CH₃)(PPh₃)(AsPh₃)] can be synthesized by reaction of the acetyl-ethyl mixture [RhCl₂(CO)(CH₃)(PPh₃)] (IV) and [RhCl₂(CO)(CH₃)(PPh₃)] (V) (previously formulated as the single compound [RhCl₂(CO)(CH₃)(PPh₃)] with AsPh₃). Similarly, [RhCl₂(CO)(CH₃)](PPh₃)(L) (L = PPh₃ or SbPh₃) can be obtained. The compounds readily undergo isomerisation to the more stable acetyl isomer. Finally, [RhCl₂(CO)(PPh₃)(AsPh₃)] can also be prepared by reaction of trans-[RhCl₂(CO)](PPh₃) (originally formulated as trans-[RhCl₂(CO)₂PPh₃]) with AsPh₃.

Recently the reaction of [RhCl(CO)₅] with triphenylphosphine (1:2 molar ratio) was reported to give the complex trans-[RhCl(CO)₅PPh₃] (Ia; X = Cl). Further papers by the same authors discussed oxidative addition reactions of complex (Ia), reaction of electron-negative olefins and with various bidentate ligands. Our initial interest in this novel starting material was based on the observation that reaction of (Ia; X = Cl) with more PPh₃ gave the well-known 6 trans-[RhCl(CO)(Pϕ₃)] (Pϕ₃)₂. Thus, by reacting other ligands L (L = AsPh₃, SbPh₃, PMe₃, C₅H₅N, etc.) with (Ia), we hoped to synthesise the mixed ligand complexes [RhCl(NO)(Pϕ₃)] (II), which may be useful catalytic precursors for olefin hydrosulphuration, etc. (cf. trans-[RhCl(NO)(Pϕ₃)] ).

Although some mixed ligand complexes containing thiophosphine have been recently reported, e.g. [HRh(NO)(Pϕ₃)](AsPh₃) (0-5C₅H₅) and [RhCl(NO)(Pϕ₃)]₃(PO₃Me₃), the only reported complex of type II is [RhCl(NO)(Pϕ₃)](1-5C₅H₅), made by reacting trans-[RhCl(NO)(Pϕ₃)] with 1-5C₅H₅ (ten-fold excess) in toluene at 25°C for 24 h. In this instance, 100% conversion to the mixed ligand complex is observed. However, in other systems investigated by this method, the result has been either mixtures of [RhCl(NO)(Pϕ₃)] and [RhCl(NO)(Pϕ₃)] or completely exchanged products (i.e. evidence).

RESULTS AND DISCUSSION

(a) Reaction of I with Arsenic-, Nitrogen-, and Sulphur-containing Ligands.-Reaction of trans-[RhCl(CO)₅Pϕ₃] with excess of L (L = AsPh₃, C₅H₅N, p-

CH₃C₆H₄NH₂, Me₂S) in benzene solution at room temperature, followed by concentration in vacuo and precipitation with pentane or ether, gives good yields of the mixed ligand complexes [RhCl(NO)(Pϕ₃)] (II). These compounds have been fully characterised by elemental analyses, molecular weights (Table), and detailed i.r. spectra (4000—200 cm⁻¹), which confirm the presence of Pϕ₃, L, and NO. The compounds are non-electrolytes and diamagnetic. T.l.c. of (II; L = AsPh₃) clearly shows that the observed single spot has an Rₚ value intermediate between that of the bis-phosphine and -arsine compounds, proving that the compound is not an equimolar mixture of trans-[RhCl(NO)(Pϕ₃)] and trans-[RhCl(NO)(AsPh₃)]. In fact this compound can be recrystallised from dichloromethane-acetone and appears indefinitely stable both in solid and solution state. In contrast, (II; L = C₅H₅N) decomposes slowly in solution and (II; L = Me₂S) gradually loses Me₂S on prolonged air-exposure of the solid. A trans-configuration for (II) (i.e., L = Pϕ₃ to Pϕ₃) is assigned on the basis of the similarity of the positions of both ν(CO) (ca. 1900 cm⁻¹) and νRhCl (ca. 310 cm⁻¹) to those found for [RhCl(NO)(Pϕ₃)] (II).12

As expected, [RhCl(NO)(Pϕ₃)](AsPh₃) readily undergoes oxidative addition reactions, giving [RhCl(NO)(Pϕ₃)](AsPh₃) (YZ = Cl₂, I₂, CH₃I, etc.). For YZ = Cl₂, I₂, analytical and mass spectral data indicate the presence of some Cl₂, solvate (ca. 0-25 mol/rhodium). Refluxing for short periods (ca. 30 min) with methyl iodide gives a brown solid with i.r. bands 2060s, 1980w, 1712m cm⁻¹ and, in addition, the absorptions expected


for PPh₃ and AsPh₃. After 4 h under reflux, a deeper brown solid is isolated with very weak bands at 2060, 1980 cm⁻¹ and a strong broad band at 1712 cm⁻¹. This brown solid analyses closely for [RhCl(CO)₂PPh₃] (Table). The presence of methyl iodide solvate is confirmed by mass spectrometry. These results are consistent with those reported in detail by Douek and Wilkinson for the reaction of trans-[RhX(CO)(PR₃)₂] with CH₃I, viz. rapid oxidative addition of CH₃I giving initially [RhX(CH₃)(CO)(PR₃)₂], followed by a slower isomerisation to the acetyl complex [RhX(COCH₃)(PR₃)₂]. Neither in this work nor in that reported by Wilkinson et al. has it been possible to separate the two isomers when prepared by this method (but see section f).

(b) Reformulation of ‘trans-[RhCl(CO)₂PPh₃]’—Rather surprisingly, the reactions of ‘trans-[RhCl(CO)₂PPh₃]’ with L show very little evidence of carbon monoxide evolution (visual and subsequently mass spectral evidence), an observation which casts grave doubt on the ‘dicarbonyl’ formulation. An osmometric molecular weight determination on complex (Ia) in chloroform indicates a dimeric structure and, together with a direct oxygen analysis, suggests that ‘trans-[RhCl(CO)₂PPh₃]’ should be reformulated as the binuclear complex trans-[RhCl(CO)₂PPh₃]₂ (Ib, X = Cl). Uguagliati et al. support their formulation of the compound as (Ia) on the observed position of ν(RhCl) (295 cm⁻¹), which is in agreement with that expected for a chloride atom trans to a tertiary arylphosphine in a rhodium(i) complex. However, since ν(RhCl) is assigned at 284, 274, and 303 cm⁻¹ in the bridged chloro-compounds, [RhCl(CO)₂] and [RhCl(PPPh₂)₂] respectively, it is reasonable to expect that ν(RhCl) will occur

for the mixed dimer [RhCl(CO)₂PPh₃]₂ in the region 285–295 cm⁻¹. In fact, reaction of equimolar amounts of [RhCl(CO)₂] and [RhCl(PPh₃)₂] in benzene does give a small amount of complex (Ib). The extreme insolubility of the phosphine dimer is probably the reason

![Diagram](https://example.com/diagram.png)
investigation, Poilblanc and Gallay\textsuperscript{15} reached the same conclusions as those given in this work on the basis of gas evolution and molecular weight measurements. In addition, they synthesised the complex \(\text{trans-}[\text{RhCl(CO)}_2(\text{PMe}_3)_2]\), where the analytical and molecular weight data unequivocally support the dimeric formulation. (Ib) \((X = \text{Cl})\) has also been recently prepared by reaction of \([\text{C}_3\text{H}_5\text{Rh}(\text{CO})\text{PPh}_3])\) with \(\text{HCl}\).\textsuperscript{16}

The complexes \(\text{trans-}[\text{RhX(CO)}_2\text{PPh}_3]\) made by metathetical reactions on (Ia)\textsuperscript{3} can also be reformulated as the dimers (Ib) \((X = \text{Br, I})\), \(\text{SCN, OCOMe}\) (see Table). Examination of the i.r. spectrum of the thioyanato-complex shows \(\nu_{\text{CN}} \approx 2135\ \text{cm}^{-1}\), close to that expected for a bridging SCN group [cf. 2153–2162 cm\(^{-1}\) in similar palladium(ii) compounds].\textsuperscript{17} The acetate complexes have i.r. bands at 1572 and 1439 cm\(^{-1}\), attributed to asymmetric \(\langle \nu_{\alpha} \rangle\) and symmetric \(\langle \nu_{\beta} \rangle\) carboxylate stretching frequencies respectively [cf. \(\text{[Rh(CO)}_2\text{OCOME})_4\text{I}_2\approx 1560\) and 1439 cm\(^{-1}\)].\textsuperscript{18} The separation \((\Delta)\) of 133 cm\(^{-1}\) between these frequencies is indicative of symmetrical co-ordination of the acetate ligand.\textsuperscript{19} These complexes also readily undergo bridge cleavage with \(\text{AsPh}_3\), etc., giving monomeric mixed ligand complexes \(\text{[RhXCO(PPh}_3\text{)](I)}\) (Table). Examination of the i.r. spectrum of \([\text{Rh(NCS)}(\text{CO})(\text{PPh}_3)(\text{AsPh}_3)](\text{AsPh}_3)\) \((\nu_{\alpha} 2064, \nu_{\beta} 840\ \text{cm}^{-1})\) indicates that the thioyanato ligand is bound through the nitrogen atom. This is a feature common to all known rhodium(i) compounds containing a terminal SCN group.\textsuperscript{17, 20} The acetato-complex \(\text{[Rh(OCOMe)}_2\text{CO}(\text{PPh}_3)(\text{AsPh}_3)](\text{AsPh}_3)\) has \(\nu_{\alpha} 1606, \nu_{\beta} 1325, \Delta 283\ \text{cm}^{-1}\), indicative of unidentate co-ordination \textsuperscript{19} (cf. \([\text{Rh(OCOMe)}_2\text{CO}(\text{PPh}_3)]\) made from \([\text{Rh(Cl(OCOMe)}_2(\text{OCOME})_2] \) and excess \(\text{PPh}_3\) with \(\nu_{\alpha} 1610, \nu_{\beta} 1325, \Delta 285\ \text{cm}^{-1}\)).

The compounds \(\text{[RhXCO(PPh}_3\text{)](AsPh}_3\text{)}\) can also be synthesised directly from \([\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{AsPh}_3)]\) and \(\text{LiX}\). Pure products are obtained with \(\text{LiBr}\) and \(\text{LiScN}\) provided that short reaction times (5–20 min) are employed. Longer reaction times lead to contamination by rhodium(iii) species \((\nu_{\text{CO}} > 2000\ \text{cm}^{-1})\).\textsuperscript{11} With \(\text{LiI}\), even short reaction times give a small amount of rhodium(iii).

The i.r. spectrum of the orange-yellow product (Ib, \(X = \text{Cl}\)), isolated by the method given in ref. 2, shows two very weak bands at 2091 and 2023 cm\(^{-1}\) (Nujol); 2090 and 2023 cm\(^{-1}\) (benzene) in addition to the strong, broad absorption at 1980 cm\(^{-1}\). The compound giving rise to these weak absorptions can be removed by refluxing compound (Ib) in benzene for ca. 30 min, after which pure \(\text{trans-}[\text{RhCl(CO)}_2(\text{PPh}_3)](\nu_{\alpha} 1980\ \text{cm}^{-1})\) is recovered (Uguagliati et al.\textsuperscript{2} note that their product \(\text{Ia}^+\) readily disproportionates to \(\text{[RhCl(CO)}_2(\text{PPh}_3)]\) \((\nu_{\alpha} 1960\ \text{cm}^{-1}\) in warm benzene solution)). Carbonylation of (Ib) with or without the extra i.r. bands in benzene, toluene, or chloroform gives a lemon-yellow solution, whose i.r. spectrum contains two sharp, intense bands at 2090 and 2008 cm\(^{-1}\) (benzene); 2094 and 2013 cm\(^{-1}\) (chloroform); 2090 and 2007 cm\(^{-1}\) (toluene). If nitrogen is bubbled through the yellow benzene solution, it rapidly turns orange and the i.r. spectrum shows several interesting changes: the band at 2090 cm\(^{-1}\) decreases considerably in intensity, the 2008 cm\(^{-1}\) band disappears and is replaced by a weaker one at 2023 cm\(^{-1}\), and a very strong band appears at 1980 cm\(^{-1}\). Removal of solvent regenerates (Ib), together with the complex with weak i.r. bands at 2090 and 2023 cm\(^{-1}\). Deganello et al.\textsuperscript{3} have reported the isolation of a red labile intermediate with very similar i.r. absorptions \((2082\) and 2019 cm\(^{-1}\) (Nujol)). This readily converts to \(\text{Ia}^+\) at room temperature and has been assigned the structure \(\text{cis-}[\text{RhCl(CO)}_2(\text{PPh}_3)]\) (IIIa).\textsuperscript{3} Poilblanc and Gallay\textsuperscript{15} observed similar behaviour, on carbonylation of (Ib) in toluene, to that reported here \((i.e.\) two \(\nu_{\alpha} 2088\) and 2002 cm\(^{-1}\)) and showed that the CO uptake was one CO per rhodium. Furthermore, they observed that a compound with the same i.r. spectrum was formed in solution when \([\text{RhCl(CO)}_2(\text{PPh}_3)](1:2)\) mixture was mixed. Attempts to isolate this species resulted in CO evolution \((1:\text{CO/Rh})\) and formation of \(\text{trans-}[\text{RhCl(CO)}_2(\text{PPh}_3)](1:2)\). We have also followed the i.r. changes of this reaction in benzene and confirm that the first step is the loss of \([\text{RhCl(CO)}_2]_2\) carbonyl bands and the growth of two strong bands at 2090 and 2008 cm\(^{-1}\). Then, concentrations of the solution results (as just described) in the appearance of two weak absorptions at 2090 and 2023 cm\(^{-1}\) and the strong band at 1980 cm\(^{-1}\).

Poilblanc et al.\textsuperscript{15} interpreted their observations in terms of equation (I) with the same postulated intermediate as Deganello et al.\textsuperscript{3} \(\text{cis-}[\text{RhCl(CO)}_2(\text{PPh}_3)]\) (IIIa).

\[
\text{[Rh}_2\text{Cl}_2(\text{CO})_4] + 2\text{PPh}_3 \rightarrow 2\text{cis-}[\text{RhCl(CO)}_2(\text{PPh}_3)]
\]

\(\text{trans-}[\text{RhCl(CO)}(\text{PPh}_3)]_2 + 2\text{CO} \rightarrow (I)
\]

However, this implies that \(\text{PPh}_3\) initially reacts with \([\text{RhCl(CO)}_2(\text{PPh}_3)](\text{IIIa})\) with halide bridge cleavage and formation of complex (IIIa). On attempted isolation, one CO group is lost from each molecule of (IIIa) and the coordinatively unsaturated fragments recombine to give the halide bridged species (Ib). Finally, with more \(\text{PPh}_3\), (Ib) is cleaved giving \(\text{trans-}[\text{RhCl(CO)}(\text{PPh}_3)]_2\). We suggest that a more plausible interpretation is that the yellow labile intermediate \((\nu_{\text{CO}} 2090\) and 2008 cm\(^{-1}\) (benzene)) is the dimeric \(\text{cis-}[\text{RhCl(CO)}_2(\text{PPh}_3)](\text{IIb})\), probably with \(\text{trans-addition of PPh}_3\) to minimise steric

\textsuperscript{13} For detailed references, see M. A. Jennings and A. Wojciech, \textit{Inorg. Chem.}, 1967, 6, 1854.


repulsions. This intermediate readily loses CO to give mainly (Ib). In this way, bridge cleavage and subsequent recombination need not be invoked to explain the observations. Because of the low stability of this compound it has proved impossible to directly verify whether the compound is of formula (IIIA) or (IIIB). However, carbonylation of trans-[Rh(OCOMe)CO(PPh₃)]₂ gives an orange solution with νₒₗ 2094 and 2009; νₛₗ 1570, νₗ 1435, Δ 135 cm⁻¹, indicative of symmetrical acetate co-ordination, as expected for (IIIB) and not unidentate co-ordination as expected for (IIIA).

![Diagram of reaction mechanism](image)

**Scheme** Proposed mechanism for reaction of [RhCl(CO)]₃ with PPh₃

A similar intermediate [RhCl(CO)(PPh₃)L]₂ could be postulated for the reaction of (Ib) with L [PPh₃, AsPh₃, etc.] followed by halide bridge cleavage and formation of [RhCl(CO)]PPh₃L. However, an i.r. study of the reaction of (Ib, X = Cl) with AsPh₃ shows that the immediate yellow solution has νₒₗ 1980, ν(RhCl) 310 cm⁻¹ identical with that found for [RhCl(CO)]-

(PPh₃)[AsPh₃] in benzene solution. This could indicate either that νₒₗ and ν(RhCl) are the same for [RhCl(CO)]-

(PPh₃)[AsPh₃]ₙ (n = 1 and 2), that the dimeric intermediate is very labile or that it never forms!

We suggest that the other compound isolated with (Ib) is cis-[RhCl(CO)]PPh₃L₂ [IC; νₒₗ 2093 and 2023 cm⁻¹], formed simultaneously with (Ib) by CO displacement from (IIIB) and readily isomerised to (Ib) by warming in benzene. Although the i.r. spectrum is also consistent with the other cis-dicarbonyl isomer (Ic) [and would possibly be more compatible with the observed ν(CO) values than (Ic)] * the observation that recarbonylation of a mixture of (Ib) and another dicarbonyl compound gives only the single product (IIIB) we can discount the formulation (Ic). Reaction of [RhCl(CO)]₃ and PPh₃ at a lower temperature gave the same products but an attempted chromatographic separation was unsuccessful. Only a single ‘streaky’ band was obtained (t.l.c.) suggesting similar Rₖ values for the isomers. For clarity, our suggestions are summarised in the Scheme shown opposite.

(c) Reaction with Triphenylstibine.—Reaction of [RhCl(CO)]PPh₃L₂ with triphenylstibine (1:2 molar ratio) in benzene gives an orange solution which, on concentration and pentane addition, gives yellow solid [RhCl(CO)](PPh₃)(SbPh₃)]. In addition, the filtrate contains another rhodium complex; the red-brown five-co-ordinate [RhCl(CO)]PPh₃(SbPh₃)]. A better method of making this compound is to react benzene solutions of [RhCl(CO)]PPh₃L₂, [RhCl(CO)](PPh₃)(AsPh₃)], or [RhCl(CO)](PPh₃)(C₆H₅N)] with a four-fold excess of SbPh₃. However, if the reaction of (Ib) (X = Cl) and excess SbPh₃ is carried out in CH₂Cl₂, concentration of the deep red solution gives a yellow precipitate of trans-

[RhCl(CO)](PPh₃)₂ and the filtrate contains [RhCl(CO)]-

(SbPh₃)₂ and some free PPh₃. Furthermore, in the absence of excess SbPh₃, [RhCl(CO)]PPh₃(SbPh₃)] in benzene readily dissociates to [RhCl(CO)]PPh₃(SbPh₃)] and SbPh₃ (cf. the behaviour of [RhCl(CO)](SbPh₃)].¹¹ This suggests that in solution the following complexes are present in equilibria (equation (2)):

\[
3[RhCl(CO)](PPh₃)(SbPh₃)] \leftrightarrow 3SbPh₃ + 3[RhCl(CO)]PPh₃L₂
\]

\[
[RhCl(CO)](SbPh₃)₃C₆H₆ can be prepared directly from [RhCl(CO)]₃ and excess SbPh₃. The most interesting features of this compound are the low position of ν(RhCl) (270 cm⁻¹) (confirmed by preparing the corresponding bromo-compound) and the presence of a

* We thank a referee for this suggestion.


strongly clathrated benzene molecule.\textsuperscript{21} The latter might provide an explanation for the stability of [RhCl(CO)-PPh\textsubscript{3}] in benzene compared to dichloromethane, although a more likely explanation is the low solubility of [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] in CH\textsubscript{2}Cl\textsubscript{2} (as compared to C\textsubscript{6}H\textsubscript{6}) which results in a shift of the equilibrium to the right hand side of equation (2)

Reaction of [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}]\textsubscript{1} with excess AsPh\textsubscript{3} regenerates [RhCl(CO)(AsPh\textsubscript{3})\textsubscript{2}], similarly, [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] gives [RhCl(CO)(PPh\textsubscript{3})(AsPh\textsubscript{3})]. Thus, [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] and [RhCl(CO)(PPh\textsubscript{3})(SbPh\textsubscript{3})\textsubscript{2}] are two members of a series containing five-co-ordinate rhodium(\textit{i}) and triphenylstibine. A third is the cation [Rh(CO)\textsubscript{4}(SbPh\textsubscript{3})\textsuperscript{3+}] recently prepared by Hieber et al.\textsuperscript{22} Reaction of trans-[RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] and excess triphenylstibine gives an orange-yellow solution, probably containing the unknown [RhCl(CO)(SbPh\textsubscript{3})\textsubscript{2}] complex but removal of solvent gives only trans-[RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}]. This and earlier work\textsuperscript{22} clearly indicates that, as SbPh\textsubscript{3} groups are replaced by PPh\textsubscript{3} (and AsPh\textsubscript{3}), the stability of the five-co-ordinate rhodium(\textit{i}) complexes decrease. Similarly, Westland\textsuperscript{23} concluded that for palladium(\textit{n}) and platinum(\textit{n}), the tendency of ligand donor atoms to force upon the metal atom the ability to engage in five-co-ordination increases in the sequence N < P < As < Sb.\textsuperscript{24} The reasons why antimony donor ligands promote five-co-ordination in low-spin states is not present obvious although, doubtless, both steric and electronic factors play an important role, e.g., the longer ligand–antimony bond distances allow more SbPh\textsubscript{3} molecules to be packed around the rhodium atom.

All these results suggest that the only remaining six-co-ordinate rhodium(\textit{i}) compound containing triphenylstibine [Rh(C\textsubscript{5}H\textsubscript{4}O\textsubscript{2})(SbPh\textsubscript{3})] \textsubscript{25} is probably the five-co-ordinate [Rh(C\textsubscript{5}H\textsubscript{4}O\textsubscript{2})(SbPh\textsubscript{3})\textsubscript{3}]. The quoted analytical figures C, 54-5; H, 4-2; O, 3-7% are intermediate between those required for [Rh(C\textsubscript{5}H\textsubscript{4}O\textsubscript{2})(SbPh\textsubscript{3})\textsubscript{3}] (C, 55-9; H, 4-0; O, 3-2, Sb 28-4%) and [Rh(C\textsubscript{5}H\textsubscript{4}O\textsubscript{2})(SbPh\textsubscript{3})\textsubscript{2}] (C, 53-8; H, 4-0; O, 5-1, Sb 26-0%). An antimony analysis is required to distinguish between these possibilities and the rarity of six-co-ordinate rhodium(\textit{i}) complexes and the close similarity of the compound to [RhCl(CO)-PPh\textsubscript{3}] and [RhCl(CO)(PPh\textsubscript{3})(SbPh\textsubscript{3})\textsubscript{2}] strongly favours the five-co-ordinate bis-stibine formulation.

\textbf{(d) Reaction of Complex (Ib) with Tertiary Phosphines.}

- Treatment of [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] with methylidiphosphine or tricyclohexylphosphine (1: 2 molar ratio) in acetone, followed by solvent removal and addition of ether give the products [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}], characterised by analysis, m.p. (Table), and i.r. spectra. The i spectrum of methyl group of [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] in deuterochloroform shows only a single resonance (\textit{T} 7-86). Similarly, examination of the n.m.r. spectrum of an equimol mixture of trans-[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}] and trans-[RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] (in CDCl\textsubscript{3}) shows a single methyl peak (\textit{T} 7-82). In contrast, trans-[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}] in CDCl\textsubscript{3} shows the expected doublet of triplets \textsuperscript{25} (\textit{J}_{\text{RhP}} 1-0 Hz) centred at \textit{T} 7-84. Addition of trans-[RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] to this solution gives a single resonance (\textit{T} 7-82) at a minimum ratio (PMe\textsubscript{3} to PPh\textsubscript{3}) of ca. 10:1. The same effect is observed when the n.m.r. spectrum of trans-[RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] is run in CS\textsubscript{2}.

The only explanation which appears applicable in this instance to explain the loss of P–H coupling is that given by Fackler et al.\textsuperscript{26} to explain the H n.m.r. spectra of compounds such as cis-[PdCl\textsubscript{2}(PMe\textsubscript{3})\textsubscript{2}] and trans-[RhCl(CO)(PMe\textsubscript{2}P\textsubscript{3})\textsubscript{2}].\textsuperscript{27} Namely that P–H decoupling occurs in strongly coupled PP systems because of easy phosphine exchange. The singlet observed in this mixed ligand complex corresponds to the calculated n.m.r. spectra given in Figure 2, ref. 26 (i.e. that expected at intermediate exchange rates). Cooling a CDCl\textsubscript{3} solution of [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] to \textit{T} 60\textsuperscript{°} produces the line broadening expected for a slower exchange rate but not the triplet predicted in the slow exchange limit. Similarly, heating in chlorobenzene to \textit{T} 80\textsuperscript{°} does not give the doublet expected in the fast exchange limit. Presumably, the small amount of free phosphine required to cause P–H decoupling in trans-[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}] comes from either partial dissociation of the added [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] and/or some displacement of PMe\textsubscript{3} by PPh\textsubscript{3} and consequent scrambling of phosphine groups in these labile, square-planar \textit{d}\textsuperscript{5} compounds. The singlet found for trans-[RhCl(CO)(PMe\textsubscript{3})\textsubscript{2}] in CS\textsubscript{2} could be the result of enhanced dissociation in this solvent compared to CDCl\textsubscript{3} due to the ready formation of 1:1 adducts between tertiary phosphines and CS\textsubscript{2}.\textsuperscript{28} For [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] in solution, the existence of an equilibrium of the type given by equation 3 would account for easy phosphine exchange processes and consequent P–H decoupling. There is more convincing evidence for the existence of this equilibrium for compounds [RhCl(CO)-PPh\textsubscript{3}]\textsubscript{L}. Reaction of [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] with tertiary phosphines (L = PMe\textsubscript{3} or PPh\textsubscript{3}) gives oils on solvent removal which on trituration with ethers or pentane gives a precipitate of trans-[RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] and evidence in solution for [RhCl(CO)L\textsubscript{2}]. Similar results are found when using excess AsEt\textsubscript{3} and Me\textsubscript{3}SO. However, we suggest that for all the [RhCl(CO)(PPh\textsubscript{3})\textsubscript{2}] compounds reported (and attempted) in this paper, the equilibrium in solution lies predominantly to the left-hand side of equation (3). Thus, precipitation from solution with

pentane, etc., gives pure samples of [RhCl(CO)PPh₂L] (L = AsPh₃ (t.i.c.), PMe₅Ph₂ (t.i.c.), SbPh₃, etc.) since these compounds are expected to be of similar low solubility in these solvents to that of trans-[RhCl(CO)₂(PPh₃)₂]ₙ postulated to be present in low concentration. However, when L is a more alkylated phosphine, arsine, or an alkyl sulphoxide, the mixed compounds (and [RhCl(CO)L₂]) will be of higher solubility in pentane, etc., than trans-[RhCl(CO)(PPh₃)₂]. Thus, preferential precipitation of the latter will occur and the equilibrium will be pushed to the right-hand side of equation 3.

An excellent confirmation of this hypothesis is provided by the low pressure carbonylation of [RhCl(CO)₆PPh₂] in various solvents. As discussed in detail earlier, benzene, toluene and chloroform (in which [RhCl(CO)(PPh₃)₂] is soluble) contain a complex with two νₘ₀ > 2000 cm⁻¹, believed to be cis-[RhCl(CO)₂PPh₃]₂ (III) (with n probably 2). However, carboxylation of a methanol suspension (or concentrated dichloromethane solution) of (Ib) gives a precipitate of trans-[RhCl(CO)(PPh₃)₂] and [RhCl(CO)₆PPh₃] can be isolated from the solution, i.e., trans-[RhCl(CO)(PPh₃)₂] is of much lower solubility in these solvents than cis-[RhCl(CO)₂PPh₃]. Note that equation (3) predicts that the other product should be [RhCl(CO)₆] but it is not conceivable that this compound (at present unknown) might readily lose carbon monoxide and then dimerise (cf. 2RhCl[PPh₃]₃ = [RhCl(PPh₃)₂] + 2PPh₃).²⁹

(c) Oxidative Addition Reactions of Complex (Ib).—

The reformation of trans-[RhX(CO)₆PPh₃] as trans-[RhX(CO)₆PPh₃] also implies that the reported oxidative addition products [RhXY(CO)₆PPh₃] (YZ = Cl₂, PhI, ClCO₂Et, etc.) are incorrect. This is readily verified by an oxygen analysis on trans-[RhCl(CO)₆PPh₃] (required 6:1; found 3:3%) which suggests that the compound should be formed as trans-[RhXY(CO)₆PPh₃] (IV, X = Cl, YZ = Cl₂; required 0:3; found 3:3%). The position of ν(RhX) 354 and 340 cm⁻¹ suggests the substitution of the halogen. This compound is too insoluble for a molecular weight determination but it reacts with excess triphenylarsine (without CO evolution) giving [RhCl(CO)(PPh₃)₃(AsPh₃)]; with SbPh₃ a product close in analysis to [RhCl(CO)(PPh₃)₃(SbPh₃)] is formed but partial reduction to [RhCl(CO)(PPh₃)₃(SbPh₃)] also occurs. Triphenylarsine gives mainly trans-[RhCl(CO)(PPh₃)₃] as the dimeric compound (IV) (or isomers of this compound).

(f) Reaction of Complex (Ib) with Methyl Iodide.—

Deganello et al.⁴ report that the reaction of methyl iodide with [RhCl(CO)₆PPh₃] gives [RhCl(CO)(COMe)(PPh₃)]₂, probably via a labile intermediate [RhCl(CH₃)(CO)(PPh₃)₂]. The final product has an i.r. spectrum exhibiting both terminal metal carbonyl (2065 cm⁻¹) and acyl carbonyl (1710 cm⁻¹) stretching frequencies. We have undertaken a detailed re-examination of this reaction and find that on prolonged reaction between methyl iodide and complex (Ib, X = Cl) (followed by i.r. spectroscopy) the terminal carbonyl band decreases and the acyl carbonyl band increases in intensity as the reaction proceeds. Unfortunately, the compound is not sufficiently stable in solution for molecular weight measurements and a mass spectrum shows only the fragmentation pattern of triphenylarsine. However, by analogy with the other oxidative addition reactions of complex (Ib) and earlier work by Wilkinson et al.,²⁹ we suggest that the terminal carbonyl stretch arises from compound (IV) (Y = CH₃, X = Cl), which is in equilibrium with an acetylrhodium(III) dimer (V) and that, on extended reaction, most of the product is present as the acetyl dimer. This explanation is consistent with the results of a kinetic study carried out by Uguagliati et al.,⁶ where rapid formation of an intermediate followed by a slower rate determining step was observed.

The reaction of this mixture of isomers with an excess of L (L = AsPh₃, PPh₃, SbPh₃) in chloroform or dichloromethane gives, on immediate precipitation with pentane or ether, orange-yellow crystalline compounds, which analyse for [RhCl(CH₃)(CO)(PPh₃)₂] (Table).

The i.r. spectra of these compounds shows a strong terminal rhodium(III) carbonyl band, a very weak rhodium(I) carbonyl band but no acyl band (e.g., L = AsPh₃, 2065 s, 2056 m, and 1980 cm⁻¹ [Nujol]; 2070 s and 1990 cm⁻¹ [CHCl₃]). These compounds also precipitate out when the reaction is carried out in concentrated dichloromethane or methyl iodide solution.

There are few reports of the isolation of pure rhodium(III) methyl carbonyl compounds because of the ready isomerisation to the acyl form. Heck²² reports the preparation of [RhCl(CH₃)(CO)(PBU₃)₂] which absorbs CO at 1 atm and 25°C to give the acyl compound [RhCl(CO)(COMe)(PBU₃)₂] and Wilkinson et al.³³ by reaction of acetyl chloride with RhCl(PPh₃)₃ at 0°C, have isolated the compound [RhCl₂(CH₃)(CO)(PPh₃)₂]. In solution, this rapidly isomerises to [RhCl₂(CO)(PPh₃)₃] (PPh₃)₂. Graham et al.³⁴ also report the preparation of [RhCl₂(CH₃)(CO)(PMe₅Ph)(PPh₃)] by treatment of the acyl complex ([C₃H₅(Ph)]Br(Et)(PMe₅Ph)] with NaPPh₃. The thorioiodo-compounds reported here are reasonably

stable if stored under nitrogen in the absence of light. However, on light exposure, they slowly turn darker brown and the i.r. spectrum shows the growth of an acyl band (1712 cm\(^{-1}\)) but the analytical figures (carbon and hydrogen) remain virtually unchanged (Table). Similarly, if the compounds are dissolved in CHCl\(_3\)-CH\(_2\)I, the solution rapidly darkens in colour and is accompanied by the growth of an acyl carbonyl band and a decrease in the terminal carbonyl band intensity. In CHCl\(_3\) alone, the acyl band also increases in intensity but this is followed by the rapid growth of a band at 1980 cm\(^{-1}\), i.e., reductive elimination of methyl iodide is probably occurring (cf. refs. 13 and 33) giving [RhClCO-(PPh\(_3\))(AsPPh\(_3\)]

Thus, it appears that cleavage of the mixture of dimers (IV) and (V) by Lewis bases provides a convenient preparation of pure rhodium methyl carboxyl compounds. The reason for the formation of the pure alkyl form from a solution predominantly containing the acetyl complex (V) lies probably in the greater lability of the alkyl dimer (IV) [compared to (V)] towards bridge cleavage by Lewis bases and also to the low solubility of the resultant monomeric alkyl compound in various solvents. Hence, the equilibrium in solution is shifted towards the formation of more alkyl dimer. A well established precedent is the isolation of the more insoluble cis-[PdCl\(_2\)(SbPh\(_3\))]\(_2\)] from solutions containing predominantly the trans-isomer.\(^{35}\)

CONCLUSION

The reaction of [RhCl(CO)\(_2\)] with PPh\(_3\), originally reported by Vallarino,\(^4\) to give trans-[RhCl(CO)(PPh\(_3\))]\(_2\) reveals, on closer examination, a number of isolatable intermediates which exhibit some interesting chemical properties. It is likely that similar detailed studies on other rhodium(I) dimers will be equally valuable both in providing an insight into the reaction pathways of these complicated reactions and synthesising new rhodium(I) and (III) compounds.

EXPERIMENTAL

Microanalyses were by the N.P.L., Teddington, A. Bernhardt, West Germany and the University of Edinburgh, Chemistry Department. Analytical data for many of the new compounds are given in the Table. Molecular weights were determined on a Mechrolab Osmometer at 37\(^\circ\) in ethanol-free chloroform. I.r. spectra were recorded in the region 4000--200 cm\(^{-1}\) on a Perkin-Elmer 225 grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Useful i.r. data is given below for each compound (measured as null unless otherwise stated). \(^1\)H N.m.r. spectra were obtained on a Perkin-Elmer model RS10 60 MHz spectrometer and a Varian Associates HA-100 spectrometer. Mass spectra were measured on an A.E.I. MS 9 mass spectrometer and conductivity measurements on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.


Materials.—Rhodium trichloride trihydrate (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine, iodomethane, dimethylsulphide (B.D.H.); triphenylarsine (Ralph Emanuel); triphenylstibine (Koch-Light); and carbon monoxide (Air Products Ltd.). The other tertiary phosphines were prepared by standard literature methods.

Rhodium(I) Compounds

trans-Di-\(\mu\)-chloro-dicarbonylbis(triphenylphosphine)dirhodium(I).—Triphenylphosphine (0.52 g, 2.0 mmol) in benzene (20 ml) was added, dropwise with stirring to a solution of \(\mu\)-chlorotetraacarbonyldirhodium(I) (11) (0.39 g, 1.0 mmol) in dry benzene (20 ml). The mixture was stirred for 15 min, the solution concentrated in vacuo, and pentane added to precipitate the product as a golden yellow powder (0.8 g, 95\%) \(\text{v}_{\text{max}}\) 2011, 2023 cm\(^{-1}\); \(\nu(\text{RhCl}) 295 \text{ cm}^{-1}\). Recrystallisation from hot benzene gives the pure trans-isomer \(\text{v}_{\text{max}}\) 1980 cm\(^{-1}\).
	rans-Di-\(\mu\)-bromo-dicarbonylbis(triphenylphosphine)dirhodium(I).—[RhCl(CO)PPh\(_3\)]\(_2\) (0.43 g, 0.50 mmol) was suspended in acetone (25 ml) and an excess of lithium bromide (ca. 3.0 g) was added. The suspension dissolved and, after shaking for 10 min, acetone was removed in vacuo and the product precipitated with distilled water. The orange-brown powder was filtered, washed well with methanol, ether and dried in \(\text{vacuo}\) at 40\(^\circ\) (0.43 g, 91\%) \(\text{v}_{\text{max}}\) 2030 cm\(^{-1}\); \(\nu(\text{RhBr}) 230 \text{ cm}^{-1}\). trans-Di-\(\mu\)-iodo-dicarbonylbis(triphenylphosphine)dirhodium(I) \(\text{v}_{\text{max}}\) 1980 cm\(^{-1}\) and trans-\(\mu\)-thiocyanato-dicarbonylbis(triphenylphosphine)dirhodium(I) \(\text{v}_{\text{max}}\) 2001; \(\text{v}_{\text{max}}\) 2135; \(\text{v}_{\text{max}}\) 781 cm\(^{-1}\) were prepared by analogous metathetical reactions with the appropriate lithium salts.
	rans-Di-\(\mu\)-acetato-dicarbonylbis(triphenylphosphine)dirhodium(I).—[RhCl(CO)PPh\(_3\)]\(_2\) was treated with an excess of silver acetate in dry benzene for 1 h giving a dark orange-red solution. After filtering off the excess of silver acetate and precipitated silver chloride, the solution was concentrated in vacuo and the orange crystalline product was precipitated with dry pentane and dried in the usual way \(\text{v}_{\text{max}}\) 1974; \(\text{v}_{\text{max}}\) 1572; \(\text{v}_{\text{max}}\) 1439 [CHCl\(_3\)]; \(\Delta 133 \text{ cm}^{-1}\).

Chlorocarbonylbis(triphenylarsine)(triphenylarsine)rhodium(I).—[RhCl(CO)PPh\(_3\)]\(_2\) (0.39 g, 0.45 mmol) was suspended in benzene (25 ml) and triphenylarsine (0.61 g, 2.0 mmol) in benzene (10 ml) was added. The suspension immediately dissolved giving a pale yellow solution. Removal of solvent and addition of pentane gave the product, recrystallised from dichloromethane-acetone as pale yellow needles (0.61 g, 91\%) \(\text{v}_{\text{BCF}}\) 311 cm\(^{-1}\). Bromocarbonyl(triphenylphosphine)(triphenylarsine)rhodium(I) \(\text{v}_{\text{max}}\) 1959 cm\(^{-1}\), iso-thiocyanato-bromocarbonyl(triphenylphosphine)(triphenylarsine)rhodium(I) \(\text{v}_{\text{max}}\) 1981; \(\text{v}_{\text{BCF}}\) 840 cm\(^{-1}\) and acetoxy-carbonyl(triphenylphosphine)(triphenylarsine)rhodium(I) \(\text{v}_{\text{max}}\) 1969; \(\text{v}_{\text{BCF}}\) 1606; \(\text{v}_{\text{BCF}}\) 1323; \(\Delta 283 \text{ cm}^{-1}\) were also synthesised from the respective dimers and excess AsPPh\(_3\). The bromo- and thiocyanato-compounds can also be prepared by reaction of [RhCl(CO)PPh\(_3\)AsPPh\(_3\)] with the appropriate lithium salts (short reaction times). For LiCl, even short reaction times gave a mixture of [RhCl(CO)PPh\(_3\)AsPPh\(_3\)] \(\text{v}_{\text{max}}\) 1982 cm\(^{-1}\) and [RhCl(CO)PPh\(_3\)AsPPh\(_3\)] \(\text{v}_{\text{max}}\) 2080 cm\(^{-1}\) \(\text{v}_{\text{BCF}}\) analytical figures in the Table.

Chlorocarbonylbis(triphenylphosphine)(pyridine)rhodium(I).—[RhCl(CO)PPh\(_3\)] \(0.20 \text{ g}, 0.23 \text{ mmol} \) was suspended in benzene (20 ml) and dry distilled pyridine (1.6 ml, 2.0 mmol) was added slowly with stirring. The suspension
dissolved giving a pale yellow solution. Removal of solvent in vacuo gave a red-brown oil which on trituration with light petroleum (b.p. 60—80°) gave the buff-yellow powder (0.20 g, 85%) (v CH 3 162; ν RCl 304 cm⁻¹). Attempts to recrystallise or prolong standing in chloroform led to extensive decomposition. Bromocarbonyl(bis(triphenylphosphine)(pyridine)rhodium(I) (ν CH 3 1866 cm⁻¹) was similarly prepared from the bromo-dimer. Chlorocarbonyl(bis(triphenylphosphine)(p-toluidine)rhodium(I) (ν CH 3 1760; ν RCl 310 cm⁻¹) and chlorocarbonyl(bis(triphenylphosphine)(dimethyl sulfoxide)rhodium(I) (ν CH 3 1635; ν RCl 310 cm⁻¹) were prepared in analogous manner to [Rh(CO)(PPh₃)₂(C₆H₅-N)] using [RhCl(CO)PPh₃] and excess p-toluidine or dimethyl sulfoxide respectively. The latter compound slowly loses dimethyl sulfoxide on exposure to air.

Chlorocarbonyl(bis(triphenylphosphine)triphénylstibine)rhodium(I)—[RhCl(CO)PPh₃]₂ (0.30 g, 0.35 mmol) was dissolved in benzene (20 ml) and treated dropwise with a benzene (10 ml) solution of triphenylstibine (0.25 g, 0.70 mmol). The orange solution rapidly gave a pale orange-yellow solution. Removal of some solvent in vacuo and addition of pentane precipitated the yellow product which was washed with ether and dried in vacuo (80-80%) (v CH 3 1659; ν RCl 311 cm⁻¹). The orange-yellow filtrate on evaporation of solvent gave the reddish-brown crystalline solid chlorocarbonyl(bis(triphenylphosphine)triphénylstibine)rhodium(I) (v CH 3 1690; ν RCl 317 cm⁻¹).

The same compound can be made in high yield by reaction of benzene solutions of [RhCl(CO)PPh₃]₂ and [RhCl(CO)PPh₃AsPh₃] or [RhCl(CO)PPh₃(C₆H₅-N)] with a four-fold excess of SbPh₃. Removal of solvent and addition of ether gave the same red-brown crystalline product. However, in dichloromethane, the initial dark red solution from [RhCl(CO)PPh₃]₂ and an excess of SbPh₃ gave, on concentration, the pale yellow solid trans-[RhCl(CO)(PPh₃)₂] (characterised by i.r. spectrum and m.p.). The remaining orange-red solution on solvent removal and addition of diethyl ether—pentane gave a dark red precipitate of chlorocarbonyltriphénylstibine)rhodium(I) (v CH 3 270 cm⁻¹). The ethereal filtrate contained triphenylphosphine. An authentic sample of [RhCl(CO)(SbPh₃)₂]C₆H₆ was prepared by the method of Ugo et al. [RhCl(CO)(PPh₃)₂] and an excess of SbPh₃. The same compound can also be prepared from the reaction of trans-[RhCl(CO)(AsPh₃)₂] and excess SbPh₃ in benzene (Found: C, 54.8; H, 3.7; Cl, 2.2; O, 1.1; Sb, 31.2. Calc. for C₆H₅ClO₃Sb₂Rh: C, 56.2; H, 3.8; Cl, 2.7; O, 1.1; Sb, 28.2%).

Chlorocarbonyl(bis(triphenylphosphine)methylidithiophosphinophosphate)rhodium(I)—[RhCl(CO)PPh₃]₂ (0.10 g, 0.11 mmol) was suspended in dry acetone (15 ml) and methylidithiophosphate (0.04 g, 0.22 mmol) in acetone (5 ml) was added slowly with stirring. The suspension dissolved giving a pale yellow solution. Removal of solvent and addition of ether to the resultant oily solid gave the product as a lemon-yellow powder (v CH 3 1863; ν RCl 308 cm⁻¹). T.l.c. showed a single spot with a Rₚ value slightly larger than trans-[RhCl(CO)(PPh₃)₂]. Similarly, chlorocarbonyl(triphenylphosphine)tricyclohexylyphosphinophosphate)rhodium(I) (v CH 3 1850; ν RCl 310 cm⁻¹) was made in chloroform solution, precipitating the product with light petroleum (b.p. 40-60%).

Attempts to prepare [RhCl(CO)PPh₃]L (L = PMe₃Ph, PEB₃Ph) by the same method gave only a precipitate of trans-[RhCl(CO)(PPh₃)₂] and yellow ethereal solutions containing [RhCl(CO)L] (confirmed by comparison with authentic samples made by literature methods). Similarly, only trans-[RhCl(CO)(PPh₃)]L was isolated from the reaction of [RhCl(CO)PPh₃] with excess AsEt₃ or Me₂SO.

Carbonylation of [RhCl(CO)(PPh₃)]L—(a) In benzene, toluene, or chloroform. Reaction of the orange benzene solution with CO at room temperature gives an immediate lemon-yellow solution (v CH 3 2090 and 2080 cm⁻¹) which on removal of solvent in vacuo or purging with nitrogen reverts to [RhCl(CO)PPh₃]L (v CH 3 19050, 2090 cm⁻¹, 2033 cm⁻¹). (b) In methanol suspension. [RhCl(CO)(PPh₃)]L was suspended in methanol and CO passed for 1 h giving a pale yellow precipitate and an orange solution. The yellow precipitate was trans-[RhCl(CO)(PPh₃)]L (i.r. spectrum and analysis) (Found: C, 64.7; H, 4.4. Calc. for C₆H₅ClO₃P₃: Rh: C, 64.3; H, 4.3%). Removal of solvent from the methanolic orange solution gave a black solid. Extraction with light petroleum (b.p. 60-80°) and concentration of the resultant orange solution gave orange-red needles of [RhCl(CO)Cl]L. The same behaviour was observed in concentrated dichloromethane solution.

Rhodium(III) Compounds

trans-Di-μ-chloro-tetrachlorodicarbonyl(triphenylphosphine)dichloro(rhodium(III)).—Dry chloride was bubbled through a suspension of trans-[RhCl(CO)(PPh₃)]L in dichloromethane for ca. 5 min. The solid dissolved completely giving an orange-yellow solution which on concentration in vacuo and addition of pentane gave the product as an orange-yellow powder (v CH 3 2100 cm⁻¹). Di-μ-chloro-di-tetradecylcarbonyl(bis(triphenylphosphine) rhodium(III)) and di-μ-chloro-di-tetradecylcarbonyl(bis(triphenylphosphine)rhodium(III) mixture.—[RhCl(CO)(PPh₃)]L was treated with methyl iodide for 3 h giving a red-brown solution. Removal of solvent and addition of pentane gave the product as a dark brown powder (v CH 3 1710 cm⁻¹). If the reaction was carried out for 18 h the same products were formed but the amount of methyl isomer had substantially decreased and that of acyl increased (i.r. evidence).

Trichlorocarbonyl(bis(triphenylphosphine)(triphenylarsine)- rhodium(III).—[RhCl₃(CO)(PPh₃)]L was shaken in chloroform with excess AsPh₃ for ca. 30 min. Removal of solvent and addition of pentane gave the product as a deep yellow crystalline powder (v CH 3 2102 cm⁻¹). A small amount of [RhCl(CO)(PPh₃)]L (AsPh₃)] was also formed. Similarly, trichlorocarbonyl(triphenylphosphine)(triphénylstibine)rhodium(III) (v CH 3 2008, ν RCl 345 cm⁻¹) was prepared from [RhCl₃(CO)(PPh₃)]L and excess SbPh₃. Again some [RhCl₃(CO)(PPh₃)]L was also formed. With [RhCl₃(CO)(PPh₃)]L and PPh₃ (1:2 molar ratio) the main product was trans-[RhCl₃(CO)(PPh₃)]L. [RhCl₃(CO)(PPh₃)]L was also prepared by chlorination of [RhCl₃(CO)(PPh₃)]L in CCl₄ (the compound contained ca. 0.25 mol CCl₄ solution per rhodium). Similarly, treatment of [RhCl₃(CO)(PPh₃)]L with iodine in CCl₄ gave chlorodi-tetradecylcarbonyl(triphenylphosphine)(triphenylarsine)rhodium(III) 0.25 carbon tetrachloride (v CH 3 2080 cm⁻¹).

Reaction of [RhCl₃(CO)(PPh₃)]L with methyl iodide heated under reflux for 30 min followed by concentration and addition of pentane gave a dark brown powder which is a mixture of predominantly chlorodi-tetradecylcarbonyl(triphenylphosphine)(triphenylarsine)rhodium(III) 0.50 methyl iodide (v CO₃ 1712 cm⁻¹) and chlorodi-tetradecylcarbonyl(triphenylphosphine)-triphenylarsine rhodium(III) (ν CH 3 2060 cm⁻¹). After 4 h heating under reflux, almost all the product was in the
acetyl form. A small amount of rhodium(i) complex ($\nu_{CO}$ 1980 cm$^{-1}$) is also present.

Reaction of the isomeric mixture $[\text{RhCl(CO)}(\text{CH}_3)]_2$ and $[\text{RhCl}([\text{COCH}_3])\text{PPh}_3]_2$ with excess AsPh$_3$ in chloroform or dichloromethane followed by immediate precipitation with pentane gave the pure orange-yellow product $[\text{RhCl}([\text{CO}])\text{PPh}_3](\text{AsPh}_3)_2$ ($\nu_{CO}$ 2065 cm$^{-1}$). Similarly, reaction with L ($L = \text{PPh}_3$ or SbPh$_3$) gave $[\text{RhCl}([\text{CO}])\text{PPh}_3L]$. In solution, these rapidly isomerise to the corresponding acyl isomer.

Trichlorotris(pyridine)rhodium(III).— $[\text{RhCl}_3(\text{CO})\text{PPh}_3]_2$ was treated with an excess of pyridine in benzene for 24 h, giving a yellow solution. Removal of solvent and addition of light petroleum (b.p. 60—80$^\circ$) gave an oil which after prolonged treatment with ether (24 h) gave a yellow powder, washed with methanol and dried in vacuo (Found: C, 40.2; H, 3.3; N, 8.6. Calc. for $C_{15}H_{13}Cl_2N_3$: C, 40.3; H, 3.4; N, 9.4%). Comparison with the i.r. spectra of authentic samples of 1,2,3- and 1,2,6-$[\text{RhCl}_3(C_2H_2N)]_2$ indicates the latter has been formed.

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NEW RUTHENIUM (III) AND (II) COMPLEXES CONTAINING
TRIPHENYL-ARSINE, -PHOSPHINE AND OTHER LIGANDS

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There is an extensive chemistry of ruthenium (II) compounds with ligands
such as tertiary phosphines. In particular, the complexes RuX₂(PPh₃)_₃ or 4
(X = Cl, Br) (1) are good starting materials for the synthesis of a range of
ruthenium (II) compounds still containing triphenylphosphine (2). In addition,
such complexes as [Ru₂Cl₃(PR₃)_6]Cl (3) and methanolic solutions of
Ru₅Cl₁₂⁻ (4) are excellent precursors for synthesising a wide range of
ruthenium (II) compounds.

In contrast, relatively few ruthenium (III) compounds containing tertiary
monophosphines or arsines have been reported. Such compounds include the
series mer-RuX₃L₃ (L = various tertiary phosphines and arsines) (5)
RuX₃(MPh₃)₂S (M = P, As; S = CH₃OH (1, 6), CH₃NO₂ (7) ), the anions
trans-[RuX₄L₃]⁻ (X = Cl, Br; L = PPh₃, AsPh₃, PMe₂Ph, PEt₃ (7) ) and
the binuclear complexes [RuCl₃(PR₃)₂]₂ and [Ru₂Cl₅(PR₃)₄] (R = Prⁿ, Buⁿ) (8).
In order that such a deficiency might be remedied, we wish in this preliminary
communication to report the results of a systematic study of the reactions of
RuX₃(MPh₃)₂S(A) with some ligands containing carbon, nitrogen, sulphur and
oxygen donor groups. Five different types of behaviour towards various ligands
have been exhibited by A:-
1) The labile solvent ligand is readily displaced giving the six co-ordinated ruthenium (III) compounds \( \text{RuX}_3(\text{MPh}_3)_2\text{L} \) \((\text{L} = \text{RCN}, \ (\text{R} = \text{Me}, \text{Ph}, \text{PhCH}_2, \text{CH}_2 = \text{CH}), \text{acetone (1), T.H.F, Me}_2\text{SO, CS}_2)\). The infrared spectra (i.r.) of all the nitrile compounds contain a very weak \( \nu\text{CN} \) at ca. 2300 cm\(^{-1}\), 50 cm\(^{-1}\) higher than in the free ligands which suggest that bonding occurs through the nitrogen (9). The dimethylsulphoxide complexes have strong absorptions in the i.r. spectra between 900-1000 cm\(^{-1}\) suggestive of an O-bonded sulfoxide group (cf. \( \text{RuCl}_3(\text{Me}_2\text{SO})_3 \) (4)). The i.r. of the \( \text{CS}_2 \) complexes contain a broad band at ca. 1510 cm\(^{-1}\) indicating the presence of a linearly bonded \( \text{CS}_2 \) group. No bands due to thiocarbonyl (ca. 1280-1330 cm\(^{-1}\)) or to \( \pi\text{-CS}_2 \) (ca. 1020 cm\(^{-1}\) or 1120 cm\(^{-1}\)) linkages are present (10) and attempted recrystallisation of these complexes from benzene results in loss of \( \text{CS}_2 \) and formation of \( \text{RuX}_3(\text{MPh}_3)_2 \).

Examination of the far i.r. spectra of these compounds (400-200 cm\(^{-1}\)) indicates a similar configuration to that of the starting materials A and configuration I with trans halide (\( \nu\text{RuCl} \) 347-299 cm\(^{-1}\)) (11) and trans \( \text{MPh}_3 \) groups is suggested.
2) The solvent ligand and one MPh₃ group are displaced giving the six co-ordinate ruthenium (III) compounds: RuX₃(MPh₃)L₂ [L = Me₂S, pyridine (1); L₂ = bipy, o-phen] The latter are the first reported examples of ruthenium (III) compounds containing both MPh₃ and 2,2'-bipyridyl (or 1,10-phenanthroline) groups. Examination of the far i.r. spectrum of these compounds indicates νRuCl ca 330 cm⁻¹ and 285 cm⁻¹, suggesting configuration II with a trans-ClRuCl grouping. The similarity of the far i.r. spectrum of RuCl₃(MPh₃)(Me₂S)₂ to that of RuCl₃(MPh₃)₂S also suggests configuration II although, in this instance, III cannot be eliminated on the evidence at present available.

All the compounds* in 1) and 2) have magnetic moments characteristic of ruthenium (III) spin-paired complexes (Faraday and n.m.r. solution methods). The 'H n.m.r. spectra are too broadened to be observed except for RuCl₃(AsPh₃)(Me₂S)₂, which shows resonances (T1.33{para}, T2.62{ortho}, T3.34{meta}, T4.6O methyl) shifted and broadened by the presence of the paramagnetic ion.

The colours of the compounds vary widely, eg. RuCl₃(MPh₃)₂PhCH₂CN (green), RuCl₃(MPh₃)(Me₂S)₂ (red), RuBr₃(MPh₃)₂CH₂CN (purple) and a detailed examination of their electronic spectra (50,000 - 10,000 cm⁻¹) suggests that the lower energy absorptions (15,000 - 30,000 cm⁻¹) arise from X→Ru charge transfer transitions. Similar results are found in compounds containing the [RuX₂(bipy)₂]⁺ ion (12).

* The compounds have been fully characterised by elemental analyses and molecular weight measurements.
In some instances, substitution is accompanied by reduction. Thus, with norbornadiene, the complexes RuX₂(MPh₃)₂C₇H₈ are readily obtained. For M = P, the same compounds can be synthesised from RuX₂(PPh₃)₃ or 4 and C₇H₈ (13). With carbon monoxide, reaction with RuCl₃(AsPh₃)₂CH₃OH at room temperature gives trans-RuCl₂(CO)₂(AsPh₃)₂ (ν₃CO: 1993 cm⁻¹[CH₂Cl₂]). Comparison with earlier triphenylphosphine work (1, 14) suggests configuration IV.

Recrystallisation from hot benzene gives the cis isomer (ν2O61 and 1999 cm⁻¹) (1) (configuration V). Recrystallisation from cold CH₂Cl₂/methanol causes several bands to develop. A band at 1943 cm⁻¹ appears, which may be due to the other trans isomer VI.
In addition the growth of bands at 2036 cm\(^{-1}\) and 1978 cm\(^{-1}\) may be assigned to the other cis isomer VII (\(\nu_{CO} = 2038, 1983, 1967\)sh cm\(^{-1}\) for the phosphine analogue (14)). There is no evidence for RuCl\(_3\)(AsPh\(_3\))\(_2\)CO although earlier workers have briefly reported the synthesis of RuBr\(_3\)(PPh\(_3\))\(_2\)CO\(_2\). With benzyl cyanide and M = P, reaction under mild conditions gives RuX\(_3\)(PPh\(_3\))\(_2\)PhCH\(_2\)CN. However, under more rigorous conditions, reduction to RuX\(_2\)(PPh\(_3\))\(_2\)(PhCH\(_2\)CN)\(_2\) readily occurs. These compounds can also be made from RuX\(_2\)(PPh\(_3\))\(_3\) and benzyl cyanide (2).

4) In some instances, MPh\(_3\) is completely displaced with or without reduction. Thus, reaction of RuCl\(_3\)(AsPh\(_3\))\(_2\)L\(_2\) (L = CH\(_3\)OH, PhCH\(_2\)CN) with excess NaS\(_2\)PPh\(_2\) gives Ru(S\(_2\)PPh\(_2\))\(_3\) and prolonged reaction of RuX\(_3\)(AsPh\(_3\))\(_2\)CH\(_3\)OH with pyridine gives RuX\(_2\)(C\(_5\)H\(_5\)N)\(_4\).

5) Finally, the choice of solvent is an important consideration. Reaction of RuX\(_3\)(AsPh\(_3\))\(_2\)CH\(_3\)OH with excess 2,2'-bipyridyl in dichloromethane gives RuX\(_3\)(AsPh\(_3\))bipy. However, in methanol, preliminary results indicate that products containing the [RuX\(_2\)(bipy)]\(^+\) cation are preferentially formed, whereas if the reaction is carried out in the presence of NaBPh\(_4\), [RuX\(_2\)bipy(AsPh\(_3\))\(_2\)]BPh\(_4\) can be isolated.

Further studies of these versatile complexes will be presented in future publications.

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Metal Compounds Containing Six-Electron and Seven-Electron Organic Ligands
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10.1 INTRODUCTION

In order that the similarities and differences between the various types of complexes can be illustrated as fully as possible, this review has been divided into the six sections. Sections 2–5 will be discussed triad by triad from left to right across the periodic table: Sections 6 and 7 will only cover the few metals which are at present known to bind to each specific organic ligand in these groups.

Over the last 15 years a number of books and reviews containing references to the chemistry of six- and seven-electron donor complexes have been published. However, the earlier (pre-1965) information found in these sources will not generally be reproduced here, in any detail, unless work published in the last 5 years extends, modifies or even contradicts these earlier results. Such books and reviews include ‘Benzenoid-Metal Complexes’ by Zeiss, Wheatley and Winkler1, ‘Metal π-Complexes’ Volume 1 by Fischer and Werner2, ‘Olefin Complexes of the Transition Metals’ by Quinn and Tsai3, ‘Organometallic Compounds’ Volume 2 by M. L. H. Green4 and articles by D. A. White entitled ‘Electrophilic and Nucleophilic attack on Organo-transition Metal Compounds’5 and by Wheatley called ‘π-Complexes of Transition Metals with Aromatic Systems’6.

10.2 ARENE–METAL CARBONYL COMPLEXES

This section will cover all compounds which contain one or more delocalised, six-membered rings, bound to a transition metal in addition to one or more carbonyl groups.
10.2.1 Titanium, zirconium and hafnium

Since the only known carbonyl compound is the air-sensitive \((C_5H_5)_2\) \(\text{Ti(CO)}_2\)^\(^7\), it is hardly surprising that no compounds of this type have been prepared.

10.2.2 Vanadium, niobium and tantalum

As yet, compounds of this type are known only for vanadium. Until very recently, the only compounds synthesised for vanadium were the \([\text{arene} \text{V(CO)}_4]^+\) cations \(^1\) (arene = benzene, toluene, methyl-substituted benzenes etc.), obtained by direct reaction between the arene and \(\text{V(CO)}_6\)^\(^8\) and isolated as the hexacarbonyl vanadate salt \([\text{arene}\text{V(CO)}_4]\)[\(\text{V(CO)}_6\])

\[
\begin{align*}
\text{[1]} & \quad \text{[2]}
\end{align*}
\]

Attempts to obtain the still unknown \((C_6\text{H}_6)^2\) \(\text{V(CO)}_3\) complex by reduction of this cation with \(\text{NaBH}_4\), gave, instead the \(\pi\)-cyclohexadienyl derivative \([C_6\text{H}_7\text{V(CO)}_4]^+\) \(^2\) \(\text{(2)}\). Similar methyl-substituted \(\pi\)-cyclohexadienyl derivatives were obtained by reduction of the methyl-substituted arene—vanadium compounds \([\text{Me}_n\text{C}_6\text{H}_6-n\text{V(CO)}_4]^+\). It is interesting to note that, in this reaction, no evidence was obtained for complexes containing metal–hydrogen or metal–B–H bonds (cf. reduction of \([\text{arene–Mn(CO)}_3]^+\) with \(\text{NaBH}_4\); Section 10.2.4). However, the author \(^9\) suggests that the most likely mechanism of formation involves a preliminary nucleophilic attack of hydride ion on the vanadium cation, followed by a concerted electron transfer to the metal and formation of the \(>\text{CH}_2\) group, rather than direct attack on a carbon atom of the benzene ring. The former mechanism will lead to addition of hydrogen preferentially in the endo position (with respect to the metal) whereas the latter implies hydrogen can be introduced in either endo or exo positions. However, recent x-ray studies on compounds such as \([\text{C}_6\text{Me}_8\text{HRe(CO)}_3]^+\) \(^10\), Section 10.2.4); \([\text{C}_7\text{H}_7\text{PhCr(CO)}_3]^+\) \(^11\), (Section 10.3.3); and \([\text{C}_5\text{H}_5\text{PhCoC}_5\text{H}_5]^+\) \(^12\) show that the entering nucleophile occupies an exo-position, which suggests that attack occurs on the side of the ligand remote from the metal (see Sections 10.3.3 and 10.5.5 for further discussion).

In a very recent paper, Davison and Reger \(^13\) have discussed the synthesis of \([\text{Me}_3\text{C}_5\text{H}_3\text{V(CO)}_3\text{I}]\) by treatment of \([\text{Me}_3\text{C}_6\text{H}_3\text{V(CO)}_4]^+\) with \(\text{NaI}\) in THF. Reduction of this with \(\text{NaBH}_4\) gave \([\text{Me}_3\text{C}_6\text{H}_3\text{V(CO)}_3\text{H}]\) (with \(\tau_{\text{V–H}} = 15.8\)). This is the first characterised carbonyl-hydride of vanadium. Heating solutions of this hydride led to decomposition rather than conversion
into the expected arene–vanadium tricarbonyl. However, reaction of the hydride with aqueous NaOH gave the $[\text{Me}_3\text{C}_6\text{H}_3\text{V(CO)}_3]^{-}$ anion isolated as its tetrabutylammonium salt.

### 10.2.3 Chromium, molybdenum and tungsten

The complexes of type $[(\text{arene})\text{Cr(CO)}_3]$ (where arene = benzene, substituted benzenes, condensed aromatic ring systems) constitute by far the greatest number of arene–metal carbonyls (see detailed list in reference 1 up to January 1965). In contrast, the corresponding $[(\text{arene})\text{Mo(CO)}_3] \text{ } (\text{M} = \text{Mo, W})$ are limited to benzene and methyl-substituted benzene complexes.

**a) Preparations of $(\text{arene})\text{M(CO)}_3$** — The standard preparative method is by direct reaction of arene with Group VIA hexacarboxyls, although reaction between $[(\text{CH}_3\text{CN})_3\text{W(CO)}_3]$ and arene$^{14}$ or $[(\text{C}_5\text{H}_5\text{N})_3\text{Cr(CO)}_3]$, arene and BF$_3$$^{15}$ has enabled milder conditions to be employed with, consequently, less decomposition. Several more interesting chromium compounds prepared by this general method in recent years are as follows:

(i) Tricarbonylchromium complexes of $\alpha, \beta, \gamma, \delta$-tetraphenylporphyrin zinc $[\text{Zn(tpp)}]^{16}$, formulated by n.m.r. as $\text{Zn(tpp)Cr(CO)}_3 \text{ (3)}$ and $\text{Zn(tpp)2Cr(CO)}_3$. Preliminary results indicated that similar complexes are formed with other $\text{M(tpp)}$ complexes ($\text{M} = 1$st row transition metal).

(ii) Mixed iron–chromium complexes formed from phenyl-substituted ferrocene derivatives and Cr(CO)$_6$, e.g.

$[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{C}_6\text{H}_5\text{Cr(CO)}_3]^\text{17, 18}(4)$

Other iron–chromium complexes were synthesised in 1961$^{19, 20}$ by reaction of diphenylbutadienechromiumtricarbonyl (5) with Fe(CO)$_5$ (or Fe$_3$(CO)$_{12}$) to give $[\text{Ph}_2\text{C}_4\text{H}_4\text{Cr(CO)}_3\text{Fe(CO)}_3] \text{ (6)}$. 

![Diagram](https://via.placeholder.com/150)
It is probable that many more mixed metal complexes (containing no direct metal–metal bonds) will be synthesised by reactions of this type in the near future.

(iii) Earlier, Fischer and Öfele reported that pyrolysis of N-methylpyridinium iodopenaerobonylchromate(0) gave a π-C-methylpyridinechromiumtricarbonyl complex (7). However, on the basis of n.m.r. evidence, the same authors have reformulated the product as (1-methyl-1,2-dihydropyridine) chromiumtricarbonyl(0) (8). This can also be prepared by direct reaction of 1-methyl-1,2-dihydropyridine and Cr(CO)₅, and is the first of a new series of metal–carbonyl complexes of dihydropyridines.

(b) Reactions involving displacement of arene or carbonyl groups—A large amount of work on arene exchange reactions of [areneCr(CO)₅] complexes has been published by Strohmeier et al. in the period 1960–1964 but this work is excellently discussed elsewhere. A very recent paper on the kinetics of the displacement reaction (10.1) showed the reaction to be first order in each reactant and a simple S_n 2 mechanism was suggested.

\[
[\text{arene W(CO)₅}] + 3(\text{MeO})₃P \rightarrow \text{fac } [\text{W(CO)₅ (MeO)}₃ P ] \]  

A similar rate expression was observed earlier for the displacement of arene by (MeO)₃P and other ligands from [arene Mo(CO)₅] and the displacement of cycloheptatriene from [C₇H₈M(CO)₅] (M = Cr, Mo, W). It is suggested that in the activated complex the arene (and triene) ligand changes its function from a six- to a four-electron donor complex (9). A preferred mechanism

\[
\begin{align*}
\text{(MeO)}₃ P \\
\text{M(CO)}₅
\end{align*}
\]  

(though little evidence is available) for the rapid steps following the formation of the transition state involves addition of a second molecule of phosphite followed by complete displacement of arene by a third molecule. The
lower activation energy for C$_2$H$_8$ compared to arene displacement is attributed to weaker binding in the former and its more ready ability to function as a four-electron donor (see iron–triene chemistry; Section 10.3.5); thus stabilising the transition state.

In some instances, particularly in photolytic processes, the entering nucleophile displaces one carbonyl group rather than the arene. Work prior to 1965 is reviewed elsewhere$^{15}$ but recent examples include synthesis of various [areneCr(CO)$_2$(OSR)$_2$]$^{27}$ complexes and a study of the kinetics of the reaction$^{26}$ (10.2):

$$[C_6Me_6Cr(CO)_2(PhC≡CPh)] + L \rightarrow [C_6Me_6Cr(CO)_2L] + Ph_2C_2$$

with rate law $= k[C_6Me_6Cr(CO)_2(PhC≡CPh)]$, suggesting an $S_N1$ mechanism. Complete displacement occurs in the photolysis of dry methanolic solutions of [areneCr(CO)$_3$] giving [Cr(OMe)$_3$]$^{29}$.

(c) Electrophilic attack at the arene group — [Arene M(CO)$_3$] complexes are much less prone to electrophilic attack than the free arene. The reasons advanced are the susceptibility of the compounds towards decomposition under conditions necessary for electrophilic substitution (e.g. nitration, sulphonation) and the tendency for some electron transfer from arene ring to metal to occur, resulting in electron deactivation of the ring.

Recent evidence for the latter is as follows:

(i) $^1$H n.m.r. studies of [arene M(CO)$_3$] complexes by various workers between 1964 and 1969$^{30}$ have shown that the most obvious characteristic is the upfield shift of ring proton resonances upon complexation. A recent investigation$^{30}$ has correlated these shifts with three effects, namely: withdrawal of $\pi$-electron density from the ring; the magnetic anisotropy of the $-Cr(CO)_3$ moiety; and the quenching of the ring current. The decrease of coupling constants between ring protons on complex formation is also discussed in terms of reduced $\pi$-electron density on the complexed arene ring. These interpretations are consistent with earlier work$^{14}$ on the observed direction of the metal-ring dipole moments in [(substituted arene)Cr(CO)$_3$] complexes.

(ii) Infrared studies$^{14,40,31}$ on the variation of $\nu$CO with substituents on the arene ring, clearly show that electronic effects are transmitted from the ring to the carbonyls. This is reflected in a reduction of the CO bond order (and hence stretching frequency) as more $\pi$-electron density is transmitted to the carbonyl groups. Recent studies$^{32}$ on the effect of solvents on $\nu$CO shifts indicate that $\pi$-bonding between the metal and carbonyl groups increases in the sequence Cr < Mo < W. Attempts to correlate the shifts of the CO bending modes and ring-metal stretching frequencies with electronic factors was unsuccessful$^{33}$, presumably due to extensive coupling of these vibrations and large mass effects.

[AreneM(CO)$_3$] complexes also show differences in product distribution as compared to that found in free arenes. For example, the isomer distribution obtained by acetylation of [(toluene)Cr(CO)$_3$]$^{34}$ ($p; \sigma; m = 46; 39; 15$) is substantially different from that obtained by acetylation of free toluene ($p; \sigma; m = 92; 8; 0$). A more recent example is found in the acetylation of some alkylbenzenecromiumtricarbonyls$^{35}$, in which the percentage of
meta isomer increases as the alkyl group becomes more bulky. The authors suggest that this high proportion of meta isomer may be associated with steric hindrance to the departing proton by the superimposed carboxyl groups in the o- and p-positions of conformer (10). An earlier communication by these and other authors \(^3\) gave temperature dependent n.m.r. evidence for severe restriction of rotation of the arene group in \([\text{(t-butylbenzene)Cr(CO)}_3]\) and partial restriction in \([\text{(isopropylbenzene)Cr(CO)}_3]\). However, more recent work \(^3\) has suggested that these changes are probably due to viscosity effects and, furthermore, that the complexity of aromatic proton resonances in arene complexes with bulky substituents is probably the result of differences in magnetic environment, which are also present in the free arene. In a recent paper \(^3\) these viscosity effects have been refuted by Jackson et al. who now ascribe the temperature variation of their n.m.r. spectra to an equilibrium between two conformations, one preferred for electronic reasons (11) and one for steric reasons (12).

In agreement with this, a substantial number of crystal structures \(^3\) on mono-substituted benzenechromium tricarboxyls have established that the eclipsed orientation of the \(-\text{Cr(CO)}_3\) group, with respect to the arene ring, is controlled by mesomeric electron repulsion or withdrawal by the substituent, such that when substituent X is a \(+\) M group, conformer (11) is more stable: when X is a \(-\) M group, conformer (10) is stabilised. For more bulky substituents, the staggered orientation (12) is favoured in order to minimise steric effects. Emanuel and Randall \(^3\) have suggested that, in the eclipsed conformers, the effect of the magnetic anisotropy of the \(-\text{CrCO}_3\) group will produce different chemical shifts at the starred and unstarred ring protons. Thus, if either conformer is preferred in solution, there will be a differential shift of the two sets of ring protons.

![Diagram](image)

On consideration of their n.m.r. data, these authors conclude that (11) is the preferred conformer for \([\text{toluene Cr(CO)}_3]\). Similar observations by Price and Sorensen \(^4\) are explained by invoking partial three point bonding of the \(-\text{M(CO)}_3\) moiety to the arene ring. However, the x-ray structures of \([\text{C}_6\text{H}_6\text{Cr(CO)}_3]\) \(^4\) and others cited earlier \(^3\) show no evidence for bond alternation in the arene ring. Therefore, on present evidence, this reviewer tentatively agrees with the interpretation of Emanuel and Randall and Jackson et al. that preferred conformers are retained in solution and that the n.m.r. variations are due to differential magnetic anisotropy effects present in the conformers. It is also very probable that the differences in isomer distribution in electrophilic reactions of free and complexed arenes are due to the electronic and steric consequences of these preferred conformations. However, caution
must be exercised in the interpretation of rate and isomer distribution data in studies of electrophilic substitution on metal complexes as exemplified by a recent kinetic study\textsuperscript{43} of Friedel–Crafts acetylation of $[\text{C}_6\text{H}_6\text{Cr(CO)}_3]$ in which a parallel reaction of AlCl$_3$ at the chromium atom was observed.

It should be noted that in symmetrically substituted $[\text{areneCr(CO)}_3]$ complexes ($\text{arene} = \text{C}_6\text{H}_6\text{, C}_6\text{Me}_6\text{, C}_6\text{Me}_6\text{,}$) the staggered orientation (12) is adopted. A similar orientation is found in the $-\text{Cr(CO)}_3$ derivatives of the $o$- and $m$-toluate anions\textsuperscript{45} and this is attributed to the enhanced ($-I$) and diminished ($-M$) effects of the $-\text{CO}_2^-$ group by the powerful withdrawing effect of the $-\text{Cr(CO)}_3$ group. A recent X-ray determination of $[\text{anthracene (Cr(CO)}_3]^{46}$ shows a staggered conformation with the $-\text{Cr(CO)}_3$ group bound to a side ring of the anthracene molecule, which confirms an earlier prediction\textsuperscript{47} based on n.m.r. evidence. A similar geometric arrangement has been found in both the orthorhombic\textsuperscript{48} and monoclinic\textsuperscript{49} forms of $[\text{phenanthrene Cr(CO)}_3]$.

In contrast to other electrophilic reagents, reaction with strong acids gave yellow protonated species $[\text{arene Cr(CO)}_3\text{H}]^{+\text{50}}$ (characterised by $r\text{M}_{-\text{H}} \sim 14$).

Reaction of $[\text{C}_6\text{Me}_6\text{M(CO)}_3] \quad (M = \text{Cr, Mo, W})$ with SbCl$_5$ in CH$_2$Cl$_2$\textsuperscript{51} gave $[\text{C}_6\text{Me}_6\text{M(CO)}_3\text{Cl}][\text{SbCl}_6$ the first characterised oxidation product of $[\text{areneM(CO)}_3]$ complexes (cf. $\text{arene}_2\text{M}^{n+}$ systems; Section 10.4). These in turn readily gave $[\text{M(CO)}_3\text{L}_2\text{Cl}_2] \quad (L = \text{PPPh}_3, \text{AsPh}_3$) and $[\text{M(CO)}_2\text{D}_2\text{Cl}_2][\text{BPh}_4$ ($D = \text{bipy; o-phen; diarsine}$) with mono- and bidentate ligands respectively. A related arene cation $[\text{C}_5\text{H}_4\text{M(CO)}_2\text{C}_6\text{H}_6]^{+}$ was reported earlier\textsuperscript{52}. Reaction of $[(\text{Me}_3\text{C}_6\text{H}_3)]\text{M(CO)}_3]$ ($M = \text{Cr, Mo}$) with mercuric halides in diethyl ether gave both 1:1 and 1:2 adducts\textsuperscript{53}. These are best formulated as (13) and (14) respectively and may thus be regarded as Lewis acid–base adducts with donation from the metal to the mercuric halide.

\begin{align*}
\text{(d) Nucleophilic substitution of arene metal carbonyls} & - \text{Although nucleophilic attacks on benzenoid molecules are relatively rare reactions, it was demonstrated some years ago}^{54} \text{(by the facile reaction of } [\text{ClC}_6\text{H}_5\text{Cr(CO)}_3] \text{ with NaOCH}_3 \text{ to give } [\text{CH}_3\text{OC}_6\text{H}_5\text{Cr(CO)}_3], \text{ that coordinated arenes have an enhanced reactivity towards nucleophiles. More recent kinetic studies of methoxide attack on } [\text{halogenobenzeneCr(CO)}_3]^{55} \text{ indicate a typical } S_{N2} \text{ displacement mechanism and confirm the enhanced reactivity. However, most nucleophilic substitutions in } [\text{areneM(CO)}_3] \text{ complexes have involved reactions in the aromatic side-chain. For example, although benzoic acid and } \text{Cr(CO)}_6 \text{ do not give } [\text{C}_6\text{H}_5\text{CO}_2\text{HCr(CO)}_3], \text{ this compound can be synthesised}^{54} \text{ by alkaline hydrolysis, followed by acidification of } [\text{C}_6\text{H}_5\text{CO}_2\text{MeCr(CO)}_3]. \text{ The rate of solvolysis of } [\text{C}_6\text{H}_5\text{CH}_2\text{ClCr(CO)}_3] \text{ is surprisingly high:}\n\end{align*}
is a factor of \( c. 10^5 \) greater than that of free arene and it is suggested\(^{56} \) that the mechanism involves the carbonium ion (15) which is stabilised by direct interaction with the chromium atom. Similar results are obtained in the alkaline hydrolysis of chromiumtricarboxyl complexes of benzoic acid esters\(^{57} \).

\[
\begin{align*}
\text{OC} & \quad \text{CO} \\
\text{Cr} & \quad \text{CH}_2^+ \\
\end{align*}
\]

(15)

Finally, there are a number of recent papers on nucleophilic substitution reactions by French workers\(^{58} - {63} \), in which resolution of the products into their optically-active forms was achieved.

10.2.4 Manganese, technetium and rhenium

Very little recent work has been published on the arene carbonyls of this triad. In earlier work on the reduction of \([C_6H_6Mn(CO)_3]^+\) with LiAlH\(_4\) in THF, Winkhaus, Pratt and Wilkinson\(^{64} \) reported the formation of the \(\pi\)-cyclohexadienyl complex \([C_6H_7Mn(CO)_3]\) (16) and, later, Winkhaus\(^{65} \) also isolated a small amount of the cyclohexadienemanganese carbonyl hydride \([C_6H_8Mn(CO)_3H]\) (17). Although the evidence for this formulation is rather tenuous (see reference 1e for discussion), it is possible that a similar diene vanadium carbonyl hydride may be a minor product in the reduction of the \([\text{arene V(CO)}_4]^+\) cations (Section 10.2.2). With other nucleophiles\(^{66} \),

\[
\begin{align*}
\text{OC} & \quad \text{CO} \\
\text{Mn} & \quad \text{H} \\
\end{align*}
\]

(16)

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\text{Mn} & \quad \text{C} \\
\text{CO} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

(17)

the substituted cyclohexadienyl complexes \([C_6H_6YMn(CO)_3]\) (\(Y = \text{Me, Ph}\)) were obtained. A recent x-ray analysis of\([[(C_6\text{Me}_6H)\text{Re(CO)}_3]](18)\)\(^{10} \), obtained by reduction of \([C_6\text{Me}_6\text{Re(CO)}_3]^+\) with LiAlH\(_4\)\(^{67} \), confirms that the entering hydride ion occupies an exo position. Thus, the anomalously low \(v\text{CH} (2700-2800 \text{ cm}^{-1})\) found here and in many cyclopentadiene complexes, arises from the exo hydrogen atom, although the factors responsible for this low value are not clear (see reference 4b and Section 10.5.5 for discussion).
No arene-carbonyl compounds of technetium are yet known.

\[
\begin{align*}
\text{(18)}
\end{align*}
\]

10.2.5 Iron, ruthenium and osmium

The only reported six-electron arene carbonyl complex of iron is that formed by reaction of hexamethyl-Dewar-benzene and Fe(CO)\(_5\)\(^{68}\) and formulated as \([\text{C}_6\text{Me}_6\text{Fe(CO)}\text{]_2}\)\(^{19}\). However, the similarity of this postulated structure with \text{trans-[C}_5\text{H}_5\text{Fe(CO)}\text{]_2}\)\(^{69}\) and also the recent report by Kang and Maitlis\(^{70}\) (Section 10.4.6), that reaction of hexamethyl-Dewar-benzene with RhCl\(_3\)3H\(_2\)O leads to ring contraction and the formation of penta-methylcyclopentadienylrhodium(III) chloride, suggests that (19) may be \([\text{C}_5\text{Me}_5\text{Fe(CO)}\text{]_2}\)\(^{20}\). However, the reported parent ion peak \((m/e = 548)\)

\[
\begin{align*}
\text{(19)}
\end{align*}
\]

and analytical data are consistent with formulation (19). Furthermore, in another communication\(^{71}\), Maitlis \textit{et al.} note that the reaction of the rearranged ring contraction product of hexamethyl-Dewar-benzene (3) with Fe(CO)\(_5\) gives hexamethylbenzene and ferrous chloride. With Fe\(_2\)(CO)\(_9\) and hexamethyl-Dewar-benzene, a compound of empirical
formula $[\text{Fe}_2\text{C}_{19}\text{H}_{16}\text{O}_2]$ has been obtained\textsuperscript{72}, formulated on the basis of n.m.r. and i.r. evidence as (21). Earlier attempts\textsuperscript{17} to obtain $\pi$-bonded arene compounds have proved unsuccessful. A recent paper\textsuperscript{73} reports the synthesis of compounds $[(\text{aromatic ligand})\text{Fe(CO)}_3]$ (aromatic ring $=$ acridine, phenazine etc.) but detailed n.m.r. studies suggest that the side rings are bound ‘diene-fashion’.

In contrast, reaction of $\text{Ru}_3(\text{CO})_{12}$ with various arenes\textsuperscript{74} ($\text{Me}_3\text{C}_6\text{H}_3$, $\text{m-Me}_2\text{C}_6\text{H}_4$, $\text{MeC}_6\text{H}_4$) gives the unusual ‘carbide’ complexes $[\text{Ru}_6\text{C(CO)}_{17}]$ and $[\text{Ru}_6\text{C(CO)}_{14}($arene$)]$. N.M.R. studies\textsuperscript{74} and a preliminary x-ray structure determination\textsuperscript{74} on the mesitylene derivative (22) have confirmed that the arene acts as a 6-electron donor.

No arene carbonyl complexes of osmium have been reported.

10.2.6 Cobalt, rhodium and iridium

No arene carbonyl complexes of rhodium and iridium have been synthesised. Reaction of $\text{Hg}[\text{Co(CO)}_4]_2$\textsuperscript{76} or $\text{Co}_2(\text{CO})_8$\textsuperscript{77} with $\text{AlCl}_3$ and benzene
gives a salt, formulated as \([\text{Co(CO)}_4]^{-}\) (23). In a very recent note, reaction of norbornadiene with \([\text{RC} \equiv \text{CH}]\text{Co}_2(\text{CO})_6\) (\(\text{R} = \text{H, Ph}\)) complexes in aromatic hydrocarbon solvents is reported as giving, as major products, compounds formulated as \([(\text{arene})\text{Co}_4(\text{CO})_9]^{70}\) (24) (arene = benzene, xylene, anisole etc.). The same products are obtained by warming \(\text{Co}_4(\text{CO})_{12}\) (or \(\text{Co}_2(\text{CO})_8\)) with the appropriate arene.

\[\text{(23)}\]

\[\text{(24)}\]

10.2.7 Nickel, palladium and platinum

No arene carbonyls of these metals are known.

10.3 CYCLOHEPTATRIENE AND CYCLOHEPTATRIENYL COMPLEXES

This section covers all complexes of these ligands except those of mixed sandwich compounds.

10.3.1 Titanium, zirconium and hafnium

The only cycloheptatrienyl complexes reported in this group are the brownish-black crystals of \([\text{MC}_2(\text{C}_7\text{H}_7)_2]^{-}\) (\(\text{M} = \text{Ti, Zr}\)), obtained by direct interaction of \(\text{MC}_4\) and \(\text{C}_7\text{H}_8^{79}\). According to the authors, these compounds contain an anionic \(\text{C}_7\text{H}_7\) group but, until substantially more physical and chemical evidence is available (only i.r. spectra are quoted), this reviewer refuses to speculate further on the nature of the bonding between the metal and ring.

10.3.2 Vanadium, niobium and tantalum

Several years ago, the preparation of \([\text{C}_7\text{H}_7\text{V(CO)}_3]^{80,81}\) and \([\text{C}_7\text{H}_7\text{VC}_2\text{H}_8]\) \([\text{V(CO)}_6]^{81}\) (see Section 10.5.2) by reaction of \(\text{V(CO)}_6\) and \(\text{C}_7\text{H}_8\) was reported. No definite information is yet available concerning the mechanism of this reaction, although it is suggested that both products
may be formed from a common intermediate. The formulation of (25) as a
cycloheptatrienyl complex has been confirmed by x-ray studies.\(^2\)

\[
\begin{align*}
\text{OC} & \quad \text{V} \quad \text{CO} \\
\text{CO} & \quad \text{CO}
\end{align*}
\]

(25)

The \(^1\text{H}\) n.m.r. of this compound is, however, rather strange, in that the
single n.m.r. peak, observed in toluene at \(-50\, ^\circ\text{C}\), becomes more complex
as the temperature increases. Fritz and Kreiter\(^3\) have suggested as a possible
explanation, that the symmetrical structure established by x-ray work was
in temperature-dependent equilibrium in solution and that one or more
species were present in which the C\(_7\) ring symmetry was not preserved. In a
more recent paper, Whitesides and Mitchell\(^4\) have elegantly demonstrated
that the signal obtained at ambient temperature is due to \(\text{V}^{51}\)-\(^1\text{H}\) spin-spin
coupling and that the temperature dependence of the line shape reflects
variations in the rate of \(\text{V}^{51}\) spin-lattice relaxation. The temperature-depen-
dent behaviour of the high field resonance in \([\text{Me}_3\text{C}_6\text{H}_3\text{V(CO)}_3\text{H}]\)\(^\text{13}\)
[very broad (\(\sim 51\) Hz) at \(-20\, ^\circ\text{C}\); narrower (\(\sim 19\) Hz) at \(-52\, ^\circ\text{C}\)] is also
probably due to \(\text{V}^{51}\)-\(^1\text{H}\) spin-spin coupling. However, the increase in
complexity of the i.r. spectrum of \([\text{C}\(_7\)\text{H}_7\text{V(CO)}_3\)] when dissolved in solu-
tion\(^5\), is not explicable in terms of coupling constants and may, in fact,
reflect preferential solvation effects or a change in structure.

The compound \([\text{TaCl}_3(\text{C}\(_7\)\text{H}_7)_2]\)\(^\text{6}\) has recently been reported (see
Section 10.3.1 for comments).

10.3.3 Chromium, molybdenum and tungsten

As for the arene–metal carbonyls (Section 10.2.3), most of the studies of C\(_7\)H\(_7\)
and C\(_7\)H\(_8\) complexes are connected with the Group VIA metal carbonyls.
An unusual molecule, containing a cycloheptatriene ring can be obtained
from the reaction of diphenylketen and ethoxyacetylene. The molecular
structure of this compound was deduced chemically by Barton et al.\(^8\) in
1962 and this was later confirmed by the x-ray analysis\(^9\) of its tricarboxyl-
chromium derivative (26).

\[
\begin{align*}
\text{OC} & \quad \text{Cr} \quad \text{CO} \\
\text{CO} & \quad \text{OEt}
\end{align*}
\]

(26)
However, the standard method of preparation of \([C_7H_8M(CO)_3]\) is by direct reaction of \(C_7H_8\) with \(M(CO)_6\) \(^{88}\) (\(M = \text{Cr, Mo}\)); with \([\text{CH}_3\text{CN}]_3\text{W(CO)}_3\) \(^{14}\), or with \([[(\text{C}_5\text{H}_5\text{N})_3\text{Cr}]\text{(CO)}_3]\) and BF\(_3\) in ether\(^{89}\). These reactions have been extended to the synthesis of many 7-substituted cycloheptatriene metal carbonyl complexes and n.m.r. studies\(^{89,90}\) have recently shown that the 7-endo-\(C_7H_7YCr(CO)_3\) complex (27) is exclusively formed in most instances. In contrast, reaction of the cycloheptatrienyl cation \([C_7H_7\text{Cr(CO)}_3]^+\) (28), (prepared by hydride abstraction from \([C_7H_8\text{Cr(CO)}_3]\) using \(\text{Ph}_3\text{CBF}_4\) \(^{91}\) or \(\text{Et}_3\text{OBF}_4\) \(^{92}\)) with the majority of nucleophilic reagents (\(Y\)) \(^{90}\) leads to the formation of 7-exo-\(C_7H_7YCr(CO)_3\) complexes (29).

These can readily be distinguished from the endo-isomer on the basis of n.m.r. \(^{93,96}\) and mass spectroscopy\(^{93}\) and the validity of this interpretation has been confirmed by an x-ray analysis\(^{91}\) of (29) (\(Y = \text{Ph}\)). It is therefore suggested that the stereospecific addition observed here and in related reactions (see reference \(90\) and Section 10.2.1) is strong proof that intermediate bonding of anions to the metal plays no part in these reactions.

A more convenient synthesis of a range of 7-exo-\(C_7H_7Y\)-complexes is by methoxide displacement from 7-exo-\(C_7H_7\text{OCH}_3\text{Cr(CO)}_3\) \(^{90}\). Use of \([[(\text{CH}_3\text{CN})_3\text{Cr(CO)}_3]\) and \(C_7H_7Y\) ligands provide a facile route to 7-endo-\(C_7H_7Y\) complexes\(^{94}\). By this means, compounds of \(C_7H_7\text{CO}_2\text{Me}\) (7-endo, 1 and 3 isomers)\(^{95}\), 7-endo-\(C_7H_7\text{OR}\) (\(R = \text{Me, Et}\) etc.)\(^{94}\) have been synthesised for the first time. Reaction of these compounds (and the 7-endo-\(C_7H_7\text{Me}\) complex) with \(\text{Ph}_3\text{CBF}_4\) leads to the stereospecific removal of the 7-exo-hydrogen atom and formation of the 7-Y-tropylium cations \([C_7H_8\text{YCr(CO)}_3]^+\) \(^{94,95}\) (30). In contrast, \(\text{Ph}_3\text{CBF}_4\) does not react with the 7-exo-\(C_7H_7\text{Me}\) complex and Pauson et al.\(^{90}\) therefore conclude that the hydride abstraction reaction is also stereospecific, involving removal of hydride from the exo position.
Earlier studies\(^9\) have shown that, on reaction of \([\text{C}_7\text{H}_7\text{M(CO)}_3]^+\) (M = Cr, Mo) with the nucleophiles \(\text{NaC}_5\text{H}_5\) and \(\text{NaCH(CO}_2\text{Et)}_2\), a ring contraction occurs to give \([\text{C}_6\text{H}_6\text{M(CO)}_3]\). The simultaneous isolation of 7-\(\text{C}_7\text{H}_7\text{CH(CO}_2\text{Et)}_2\text{Cr(CO)}_3\) (later shown to be exo) suggests that the 'normal' nucleophilic addition is a prerequisite step in these rearrangements. By substitution with tritium and methyl, it can be shown that the benzene ring is derived entirely from the \(\text{C}_7\) ring by extrusion of a carbon atom. Later studies\(^9\) have demonstrated that 7-endo-\(\text{C}_7\text{H}_7\text{CH(CO}_2\text{Et)}_2\text{Cr(CO)}_3\) also readily rearranges in the presence of base to form \([\text{C}_6\text{H}_6\text{Cr(CO)}_3]\) and the following mechanism (iv) for this rearrangement has, therefore, been proposed.

![Diagram](image)

The salt \([\text{C}_7\text{H}_6\text{CO}_2\text{MeCr(CO)}_3]^+\) \([30]; \ Y = \text{CO}_2\text{Me}\) also reacts with nucleophiles to give \([\text{RC}_7\text{H}_6\text{CO}_2\text{MeCr(CO)}_3]\) \([31]; \ R = \text{OMe}\)\(^9\). However, when chromatography was attempted on alumina some ring contraction to \([\text{C}_6\text{H}_6\text{CO}_2\text{MeCr(CO)}_3]\) occurred\(^9\). This constitutes the mildest conditions yet found for the ring contraction rearrangement.

Initial results on a study of directive effects in nucleophilic addition to the substituted tropylum cations \([30]; \ Y = \text{OMe}; \ \text{CO}_2\text{Me}\) have recently been presented\(^9\). Considerable selectivity is found, depending on both the directive effect of \(Y\) and the nature of the entering group, i.e. with \(Y = \text{OMe}, \ \text{MeO}^-\) attacks at position 1 but \(\text{H}^-\) attacks chiefly at position 3; in contrast, \(-\text{CO}_2\text{Me}\) directs \(\text{MeO}^-, \ \text{CN}^-\) and \(\text{H}^-\) into position 2. Therefore, the authors conclude that \(Y\) groups with a +M effect favour nucleophilic additions at the 1- and 3- positions (the former being almost exclusively attacked by weaker nucleophiles, whereas stronger nucleophiles favour attack at the 3-position), and those with a −M effect direct more uniformly to position 2.

In contrast, the \([\text{C}_7\text{H}_7\text{Mo(CO)}_3]^+\) cation\(^9\) forms few 7-exo-\(\text{C}_7\text{H}_7\text{YMo(CO)}_3\) complexes. This may be partially attributed to the instability of the \([\text{C}_7\text{H}_7\text{Mo(CO)}_3]^+\) cation under the conditions required for nucleophilic addition\(^9\),\(^9\) but another factor may be the preferred tendency of the nucleophile for attack at the metal, rather than at the ring. Thus, reaction of \([\text{C}_7\text{H}_7\text{M}^+\)
(CO)₃]⁺ (M = Mo⁹⁹, W¹⁴) with NaX (X = Cl, Br, I) in acetone gives the neutral [C₇H₇M(CO)₂X]. This would suggest that the positive charge resides largely on the metal atom for molybdenum and tungsten and on the ring for chromium. A recent x-ray study of [C₇H₇Mo(CO)₃]BF₄ shows an average MO—C(carbonyl) distance of 2.035 Å, which is appreciably longer than in other olefin—Mo(CO)₃ complexes. Similar x-ray studies of the chromium and tungsten compounds should help to determine the reason for this anomalous increase.

In an attempt to obtain [C₇H₇MC₅H₅] (see Section 10.5.3), [C₇H₇M(CO)₂I] (M = Mo⁹⁹, W¹⁴) was reacted with NaC₅H₅. The product was the unexpected, orange [C₇H₇M(CO)₂C₅H₅], postulated to have structure (32) with an h⁺-C₇H₇ moiety, despite the fact that its room temperature H n.m.r. spectrum shows only a single resonance arising from the C₇H₇ ring. Further detailed n.m.r. studies by several groups of workers¹⁰¹⁻¹⁰³ indeed show that the molecule is fluxional. However, the close similarity of the low temperature n.m.r. spectrum with that expected for an h⁺-C₇H₇ attachment (33)¹⁰²⁻¹⁰³ still leaves some doubt as to the actual formulation and this can probably only be resolved by x-ray analysis. In addition, the fact that there are four νCO bands in the room temperature solution i.r.¹⁰¹⁻¹⁰³ suggests the presence of conformers A and B (32) [or h⁻-C₇H₇ conformers?]. The low temperature n.m.r. spectrum only indicates the presence of one conformer and, in agreement with this¹⁰³, two of the νCO bands almost disappear at −60 °C.

Photochemical reaction of [C₇H₇Mo(CO)₂C₅H₅] with Fe(CO)₅ (or Fe₂(CO)₉) gives [C₅H₅(CO)₂MoC₇H₇Fe(CO)₃]¹⁰⁴, which appears to have structure (34), where the C₅H₅(CO)₂Mo group lies over one face of the C₇H₇
ring and interacts with three carbon atoms, while the Fe(CO)\textsubscript{3} lies over the other face and interacts with a butadiene-like sequence of carbon atoms. In addition the molecule is fluxional and gives a n.m.r. spectrum consistent with this structure only below $-50$ °C. At room temperature, the C\textsubscript{7}H\textsubscript{7} ring exhibits a single resonance. A detailed analysis suggests a rearrangement pathway of either 1, 2 shifts or a mixture of 1, 2 and 1, 3 shifts.

In contrast, reaction of [C\textsubscript{7}H\textsubscript{7}Mo(CO)\textsubscript{2}I] and C\textsubscript{6}F\textsubscript{5}MgBr gives [C\textsubscript{7}H\textsubscript{7}Mo(CO)\textsubscript{2}C\textsubscript{6}F\textsubscript{5}]\textsuperscript{105} (35) with a $\sigma$-bonded pentafluorophenyl group

![Chemical structure](image)

and a symmetrically bound C\textsubscript{7}H\textsubscript{7} ring.

Kinetic studies on the displacement of C\textsubscript{7}H\textsubscript{8} by monodentate Lewis bases from [C\textsubscript{7}H\textsubscript{8}M(CO)\textsubscript{3}] complexes are discussed elsewhere (Section 10.2.3). Recent displacement reactions with bidentate ligands D (D = bipy; $\sigma$-phen) in polar solvents (S) have given complexes [M(CO)\textsubscript{3}D(S)], whereas in non-polar solvents, the carbonyl bridged binuclear complexes [M(CO)\textsubscript{3}D]\textsubscript{2} are obtained\textsuperscript{106}. If the reaction is carried out in the presence of X$^-$ (X = Cl, Br, I etc.), the anionic compounds [M(CO)\textsubscript{3}DX]$^-$ are obtained\textsuperscript{107}.

Finally, reaction of MOCl\textsubscript{3} (M = Mo, W) and C\textsubscript{7}H\textsubscript{8} gives [MOCl\textsubscript{2}(C\textsubscript{7}H\textsubscript{7})\textsubscript{2}]\textsuperscript{79}.

10.3.4 Manganese, technetium and rhenium

Rather surprisingly, the only cycloheptatrienyl compound formed in this triad appears to be the mixed sandwich cation [C\textsubscript{7}H\textsubscript{6}RMnC\textsubscript{5}H\textsubscript{5}]$^+$, which is discussed in Section 10.5.4.

10.3.5 Iron, ruthenium and osmium

Very little recent work concerning C\textsubscript{7}H\textsubscript{8} and C\textsubscript{7}H\textsubscript{7} complexes of this triad has appeared in the literature. Earlier work\textsuperscript{26,108} has shown that reaction of Fe(CO)\textsubscript{3} and C\textsubscript{7}H\textsubscript{8} gives [C\textsubscript{7}H\textsubscript{8}Fe(CO)\textsubscript{3}] in which the triene is bound through only two double bonds (36). The free double bond could readily be hydrogenated, giving [C\textsubscript{7}H\textsubscript{10}Fe(CO)\textsubscript{3}] (37). Reaction of the former with HBF\textsubscript{4} or the latter with Ph\textsubscript{3}CBF\textsubscript{4} gives the cycloheptadienyl cation [C\textsubscript{7}H\textsubscript{9}Fe(CO)\textsubscript{3}]$^+$BF\textsubscript{4} (38).
However, a cycloheptatrienyl iron complex has been prepared by treating 7-C₇H₇OCH₃Fe(CO)₃ with HBF₄ to give CH₃OH and [C₇H₇Fe(CO)₃]BF₄. Although the room temperature ¹H n.m.r. shows a single resonance, the νCH region of the i.r. is more complex than the corresponding Group VIA [C₇H₇M(CO)₃]⁺ compounds and the fluxional structure (39) was postulated. Likewise if [C₇H₇Fe(CO)₂]⁺ is treated with KI, the compound [C₇H₇Fe(CO)₂I] is formed. Rather surprisingly, no variable temperature n.m.r. studies appear to have been reported on these compounds.

Very recently, reaction of [h⁵-C₅H₅Fe(CO)_2]⁻ and C₇H₇BF₄ has been reported to give [h⁵-C₅H₅Fe(CO)_2h¹-C₇H₇]⁺. However, this has recently been reformulated as [h⁵-C₅H₅Fe(CO)h³-C₇H₇] (40), because of the close similarity of its variable temperature n.m.r. spectrum with those of [C₇H₇Mo(CO)_2C₅H₅] and [C₇H₇Co(CO)_3] (41). (Section 10.3.6.)

Recently, the compound 1,2-benzocycloheptatriene iron tricarbonyl has been synthesised (42) and shown to undergo a hydride abstraction reaction to give the benzotropyliumirontricarbonyl cation (43).
Reaction of $\text{RuCl}_3$ and $\text{C}_7\text{H}_8$ gives a polymeric compound $[\text{C}_7\text{H}_8\text{RuCl}_2]_n$, which has been assigned the structure (44) in which the olefin molecule assumes the boat configuration, with coordination at the 1,5 double bonds.

There are also a number of bi- and tri-nuclear iron (and ruthenium) complexes containing a cycloheptatriene, cyclo-octatriene or cyclo-octa-tetraene ring but these are not considered further in this review, since in no instance is the ring bound to each metal atom with more than four carbon atoms.

10.3.6 Cobalt, rhodium and iridium

The only cycloheptatrienyl complex of cobalt is the air-sensitive $[\text{C}_7\text{H}_7\text{Co(CO)}_3]$, prepared by photochemical reaction of $\text{Co}_2(\text{CO})_8$ and $\text{C}_7\text{H}_8$. Variable temperature n.m.r. studies have recently confirmed the trihapto coordination of the $\text{C}_7\text{H}_7$ ring (41) and the fluxional character of the complex.

There are no -triene or -triynyl complexes of rhodium and iridium. An earlier report stating that reaction of $[\text{Rh(CO)}_2(\text{acac})]$ and cycloheptatriene gives the norbornadiene complex $[\text{C}_7\text{H}_8\text{Rh(acac)}]$ due to isomerisation
of the triene is incorrect: the diene complex is formed because the triene contains 3% norbornadiene\textsuperscript{116}.

10.3.7 Nickel, palladium and platinum

The only work published in this triad is some early work on platinum compounds\textsuperscript{117}. Reaction of \( \text{H}_2\text{PtX}_6 \) (\( \text{X} = \text{Cl}, \text{Br} \)) with \( \text{C}_7\text{H}_8 \) gives a mixture of \( (\text{C}_7\text{H}_7)_2[\text{PtX}_6] \) and \( \text{C}_7\text{H}_8\text{PtX}_2 \). The triene ligand is readily displaced from the latter with pyridine, giving cis-[PtX\(_2\)(C\(_5\)H\(_5\)N)\(_2\)]\(_\text{e}^{-}\), which would suggest h\(^4\)-C\(_7\)H\(_8\) coordination. However, unlike h\(^4\)-C\(_7\)H\(_8\)Fe(CO)\(_3\), the platinum compound does not undergo protonation (or hydride abstraction) reactions.

10.4 METAL–ARENE COMPLEXES

This section covers all complexes containing arene as a ligand with the exception of carbonyl and mixed sandwich compounds.

10.4.1 Titanium, zirconium and hafnium

There is little recent work on arene compounds of this triad. Various investigators\textsuperscript{118} have suggested that the \( \sigma \)-phenyl aluminium compound TiCl\(_3\)·AlCl\(_3\)·AlCl\(_2\)C\(_6\)H\(_5\)\textsuperscript{119} should be reformulated as the \( \pi \)-arene complex [(C\(_6\)H\(_6\))TiCl\(_2\)(AlCl\(_3\))]\(_2\) and Russian workers\textsuperscript{120} have shown that, on warming [(C\(_6\)H\(_5\))\(_2\)Ti], black pyrophoric [(C\(_6\)H\(_5\))\(_2\)Ti] and biphenyl are the decomposition products.

Reaction of C\(_6\)Me\(_6\), Al and AlCl\(_3\) with MCl\(_4\) (M = Ti, Zr) is reported to give the trinuclear cationic complexes [(C\(_6\)Me\(_6\))\(_3\)M\(_3\)Cl\(_6\)]Cl (45)\textsuperscript{121} [see Section 10.4.2].

10.4.2 Vanadium, niobium and tantalum

There are no normal bis-arene complexes of niobium and tantalum. Reaction of their pentachlorides with C\(_6\)Me\(_6\), Al and AlCl\(_3\) gives instead the trinuclear cationic compounds (45) and in addition the binuclear [(C\(_6\)Me\(_6\)) NbCl\(_2\)]\(_2\)\textsuperscript{121} (46).

In contrast, a similar reaction with VCl\(_4\) gives V(C\(_6\)H\(_6\))\(_2\) which is readily air-oxidised to V(C\(_6\)H\(_6\))\(_2\)\textsuperscript{122}. E.S.R. studies on the paramagnetic V(arene)\(_2\) and the isoelectronic Cr(arene)\(_2\)\(_\text{e}^{-}\) compounds (arene = benzene, toluene, mesitylene) indicate that all the ring hydrogens are magnetically equivalent and that the methyl groups produce no hyperfine splitting of the signal\textsuperscript{123}. Very recently, bisnaphthalene complexes of V(0) and Cr(I) have been detected in solution by a comparison of their \( g \) values and hyperfine coupling constants with those of known bis-arene species\textsuperscript{124}. An examination of the number and intensity distribution of the hydrogen hyperfine lines indicate that only one ring of each C\(_{10}\)H\(_8\) molecule interacts with the metal. At higher lithium
naphthalide/chromium concentrations, further signals appear, which are tentatively attributed to the formation of Cr(−I) and Cr(−II) C_{10}H_{8} complexes. At higher lithium naphthalide/vanadium concentrations, reduction leads to disappearance of the e.s.r. signal^{124,125}.

10.4.3 Chromium, molybdenum and tungsten

Earlier work on the synthesis of σ-organochromium compounds and their conversion to π-arene complexes is adequately documented^{19,126}. More recent work has been concerned with the unravelling of the mechanism for this conversion (see Reference 4c for a detailed discussion).

However, bis-arene complexes of chromium, molybdenum and tungsten are best prepared by the reducing Friedel–Crafts reaction. This gives the M(arene)$_2^+$ cations which are readily reduced to the M(arene)$_2$ compounds$^{127}$. E.S.R. evidence for Cr(−I) and Cr(−II) bis-arene complexes is also available$^{124}$.

(a) Structure and bonding in bis-arene complexes—The structure of dibenzenechromium has been the subject of some controversy, since it was reported by Jellinek in 1960$^{128}$ that the benzene rings possess alternat-
ing carbon–carbon bond lengths (1.36 Å and 1.45 Å), indicating that little or no delocalisation of bonding electrons takes place within the ligands of Cr(C₆H₆)₂. This threefold symmetry of the benzene rings was supported by earlier i.r. studies. However, more recent i.r., Raman and diffraction studies (x-ray and electron), including one at 100 K by Jellinek, find no evidence for significant differences in C–C bond lengths and the expected sixfold symmetry of the molecule has been confirmed. It is suggested that the discrepancies in the earlier data may be due to the presence of small amounts of π-mesitylene compounds producing disordered crystals (since mesitylene is often used as a catalyst in the preparation of Cr(C₆H₆)₂). This wealth of experimental data also casts doubts on the qualitative theoretical treatments which have tried to explain the ‘distortion’ of complexed benzene in Cr(C₆H₆)₂ by invoking metal-ring orbital interactions.

Recently, semi-empirical extended Hückel MO calculations on metal diarene and bisbicyclooctadienyl compounds have been published which extend the basis set to include the σ-molecular orbitals (comprising carbon 2s, 2pₓ, 2pᵧ and hydrogen 1s atomic orbitals) in addition to the π-molecular orbitals (carbon 2pₓ atomic orbitals) of the benzene ligands. These calculations suggest that an interaction between the metal orbitals and the ligand σ-orbitals does occur and that this interaction is comparable in strength to that between the metal orbitals and the ligand π orbitals. Experimental evidence for these conclusions has subsequently been presented by Anderson and Drago from a careful examination of the n.m.r. contact shifts observed for a large number of paramagnetic bisbenzene and methyl substituted bisbenzene complexes of first row transition metals [V⁰, Cr⁰, Fe¹, Fe¹, Co¹, Co¹ and Ni¹]. The observed delocalisation of spin density has been rationalised on the basis of competing direct σ and indirect π delocalisation mechanisms, the π mechanism becoming more dominant on going from left to right across the periodic table. Similar results have been obtained by Prins from an analysis of the isotropic proton hyperfine coupling constants of metalloocene and arene compounds and by Rettig and Drago from n.m.r. work on metalloocene compounds. Furthermore, it was shown that the highest energy electrons reside in molecular orbitals of largely metal character, whose energy ordering is precisely that predicted by ligand field theory namely dₓz-y₂, dₓy<dₓz<dₓᵧ, dᵧz. This is contrary to earlier proposals which placed these electrons in ring antibonding orbitals (see reference 137 for a detailed discussion).

Recent mass spectroscopic studies on various diarene chromium compounds show that fragment formation proceeds almost exclusively by successive elimination of the ring ligands and that the metal–ligand bond strengths increase in the order:

C₆H₆<Me₃C₆H₃<Me₃C₆H₅—C₆H₅<Me₆C₆

(b) Reactions of bis-arene compounds — The organic chemistry of bis-arene compounds has received relatively little attention, the few studies to date being confined to Cr(C₆H₆)₂. Compared with benzene and [C₆H₆Cr(CO)₃], the aromatic chemistry of Cr(C₆H₆)₂ is very limited. This is partly due to the nature of the reaction products which generally do not exhibit significant chemical substitutions. However, it is possible to prepare a number of similar compounds by a process of substitution.
due to the instability of the compound under the conditions required for reaction but is also the result of the ready oxidation to \([\text{Cr}(\text{C}_6\text{H}_6)_2]^+\) on attempted electrophilic substitution of the benzene rings [cf. [arene M(CO)_3] oxidations; Section 10.2.3]. In fact, the only substitution reaction known until quite recently has been the transmetallation of \(\text{Cr}(\text{C}_6\text{H}_6)_2\) using n-amylsodium\(^{141}\). This reaction is not facile, the products are mixed and the yields are generally low, but, nevertheless, reaction of the metallated species with organic carboxyls \(\text{RCOR}'(R = R' \text{ is } \text{H}, \text{Me}, \text{Ph etc.})\), for example, gives the alcohols \([\text{C}_6\text{H}_6\text{CrC}_6\text{H}_5\text{CRR'}(\text{OH})]\) (47), which in turn are readily oxidised with aluminium isopropoxide to give the ketones \([\text{C}_6\text{H}_6\text{CrC}_6\text{H}_5\text{COR}]\) (48)\(^{141}\). This, therefore, provides a means of obtaining a limited range of substituted bisbenzene complexes, which are inaccessible by the reducing Friedel-Crafts reaction because of side reactions with the AlCl_3 catalyst.

\[\text{R} \quad \begin{array}{c}
\text{Cr} \\
\text{C} - \text{R'} \\
\text{OH}
\end{array}\]

\[\begin{array}{c}
\text{R} \\
\text{C} = \text{O}
\end{array}\]

(47) (48)

More recently, it has been shown that, whilst n-BuLi alone does not metallate \(\text{Cr}(\text{C}_6\text{H}_6)_2\)\(^{142}\), metallation does occur in the presence of \(\text{NNN'}\text{N'-}
\text{tetramethylenediamine}\)\(^{143}\). By reaction of the resulting bis(lithiobenzene)-
chromium with Me_3SiCl\(^{144}\), \([\text{Cr}(\text{C}_6\text{H}_5\text{SiMe}_3)_2]\) (49) was synthesised. Evi-

\[\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{SiMe}_3
\end{array}\]

\[\text{Cr} \\
\begin{array}{c}
\text{Me}_3\text{Si} \\
\text{SiMe}_3
\end{array}\]

(49)

dence has also been presented\(^{143}\) to show that \(\pi\)-bonded benzene is metallated preferentially to free benzene and this rate enhancement is rationalised in terms of the stabilisation of a \(\text{Cr}(\text{C}_6\text{H}_6)_2\) carbanion related to a benzene carbanion transition state, probably by means of d-orbital participation [cf. carboxonium ion stabilisation in the solvolysis of \([\text{C}_6\text{H}_5\text{CH}_2\text{ClCr(CO)_3}]\)\(^{56}\).
Section 10.2.3. It is to be expected that a range of substituted bisbenzene complexes will be synthesised via these lithiated species in the near future. Reactions leading to displacement of both benzene ligands in \( \text{Cr(C}_6\text{H}_6)_2 \) with ligands such as PF\(_3\) have also been reported\(^{145}\).

### 10.4.4 Manganese, technetium and rhenium

It was reported in 1961\(^{146}\) that the reaction of MnCl\(_2\), PhMgBr and 2-butyne leads to cyclic condensation of the latter and the isolation of \([\text{Mn(C}_6\text{Me}_6)_2]^+\) in 11% yield as its tetrphenylborate salt. However, Fischer and Schmidt\(^{147}\) have been unable to reproduce this result and have obtained instead a 2% yield of \([\text{C}_6\text{H}_6\text{MnC}_6\text{Me}_6]^+\) isolated as its hexafluorophosphate salt. Reaction of this with LiAlH\(_4\) leads to stereospecific attack on the unsubstituted benzene ring with formation of \([\text{C}_6\text{H}_7\text{MnC}_6\text{Me}_6]^+\)\(^{147}\).

In contrast, \([\text{Re(arene)}_2]^+\) (arene = \(\text{C}_6\text{H}_6\)\(^{148}\), \(\text{C}_6\text{Me}_6\)\(^{149}\)) can be synthesised by the reducing Friedel–Crafts reaction. A recent report\(^{149}\) on reduction of the latter demonstrates the importance of the reducing reagent in determining the nature of the product. With sodium in liquid ammonia, the complex \([\text{C}_6\text{Me}_6\text{HReC}_6\text{Me}_6]\) (50) containing a \(\pi\)-cyclohexadienyl ring is obtained; it is very probable that, as in \([\text{C}_6\text{Me}_6\text{HRe(CO)}_3]\)\(^{10}\) (Section 10.2.4), the hydrido ion occupies an exo position. However, with liquid lithium in the absence of solvent (or any other source of protons), a diamagnetic orange dimer \([\text{Re(C}_6\text{Me}_6)_2]_2\) of apparent structure (51) is obtained. If this dimer is immediately sublimed onto a cold finger at \(-196\) °C, appreciable amounts of monomeric, paramagnetic \(\text{Re(C}_6\text{Me}_6)_2\) characterised by its e.s.r. spectrum is obtained. On warming this monomer dimerises irreversibly back to (51) with disappearance of the e.s.r. signal [cf. the behaviour of \(\text{Rh(C}_5\text{H}_5)_2\)]\(^{150}\).

The behaviour of the \([\text{Tc(C}_6\text{Me}_6)_2]^+\) cation with reducing agents is analogous, except that only a trace of the dimer is obtained\(^{151}\).
10.4.5 Iron, ruthenium and osmium

By the standard reducing Friedel–Crafts reaction followed by hydrolysis in the presence of NH₄PF₆, the [M(arene)](PF₆)₂ complexes (M = Ru¹⁵²,¹⁵³, Os¹⁵²) can be synthesised: in contrast, the [Fe(arene)]²⁺ cations are obtained directly from the ferrous ion and arenes¹⁵⁴. These compounds show an increased stability to hydrolysis, both with increasing atomic number of the metal and with increasing methyl substitution on the ring. The latter observation may be attributed to the increasing strength of the metal—ring bond on substitution [cf. mass spectroscopic studies on Cr(arene)₂ compounds¹⁴⁰; Section 10.4.3] although the influence of steric factors on the rate of hydrolysis cannot be discounted. Hence, although [Fe(C₆H₆)₂]²⁺ is too unstable hydrolytically to be isolated, the hexamethylbenzene cation is sufficiently stable to undergo stepwise reduction with dithionite ion to the monopositive [Fe(C₆Me₆)₂]⁺ and the neutral Fe(C₆Me₆)₂. Very recently, reduction of the corresponding [Ru(C₆Me₆)₂]²⁺ cation to Ru(C₆Me₆)₂, using sodium in liquid ammonia, has been reported¹⁵². The n.m.r. spectrum of the latter is of interest in that the single peak at 70 °C becomes a multiplet at 5 °C and the authors suggest that this ‘fluxional’ behaviour arises from a structure (52), in which one of the benzene rings is bonded ‘diene-fashion’. In view of the work discussed earlier (Section 10.2.3) it may also be possible to interpret these n.m.r. data on the basis of an equilibrium involving different conformers of the Ru(C₆Me₆)₂ complex.

![Diagram](image)

(52)

E.S.R. evidence¹⁵⁶ also suggests that [Fe(C₆Me₆)₂]⁺ has lost the axial symmetry characteristic of its 18-electron homologues and that it contains the two aromatic ring ligands oblique to each other. These authors¹⁵⁶ suggest this asymmetry to have arisen from a Jahn–Teller distortion, produced by the removal of degeneracy in the singly-occupied non-bonding ligand orbital e₂u. This assignment has been questioned by Anderson and Drago¹⁵⁷ who, on the basis of n.m.r. contact shift studies, suggest that the unpaired electron resides in the e₁g molecular orbital (which is mainly associated with the metal). This would give rise to a ²E₁g ground state and a small dynamic distortion, whereas for a ²E₂u ground state, a large static distortion accompanied by large contact shifts (which are not found) would be expected.
The $[\text{Ru(C}_6\text{H}_6\text{)}_2]^{2+}$ cation can also be obtained by treatment of the 1,3-cyclohexadiene-benzene complex $[\text{C}_6\text{H}_8\text{RuC}_6\text{H}_6]$ (Section 10.5.5) with $\text{Ph}_3\text{CBF}_4$; attempts to remove only one hydrogen atom from the $\text{C}_6\text{H}_8$ ring were unsuccessful. A similar double hydride abstraction reaction occurs with $\text{C}_5\text{H}_5\text{CoC}_6\text{H}_8$ to give $[\text{C}_5\text{H}_5\text{CoC}_6\text{H}_6]^{2+}$ (Section 10.5.6). Direct reaction of $'\text{RuCl}_3\text{XH}_2\text{O}'$ and $\text{OsCl}_3$ with 1,3 cyclohexadiene gives the polymeric compounds $[\text{C}_6\text{H}_6\text{MCl}_2]_n$, in which the presence of diene coordination is suggested [cf. $[\text{C}_7\text{H}_8\text{RuCl}_2]_n$ (44); Section 10.3.5]. These react with tertiary phosphines to give the dimeric $[\text{C}_6\text{H}_6\text{MCl}_2(\text{PR}_3)]_2$ compounds.

Finally, by means of the reducing Friedel–Crafts method, the first bis-arene complex of naphthalene $[\text{Ru(C}_{10}\text{H}_8\text{)}_2](\text{PF}_6)_2$ was synthesised. The only other naphthalene complex of ruthenium is the one obtained by reduction of $\text{RuCl}_2(\text{DMPE})_2$ [$\text{DMPE} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMMe}_2$] with sodium naphthalide. The reduction product displays chemical properties corresponding to the π-arene formulation but its spectroscopic properties and structure are consistent with the hydride structure. A growing number of these labile tautomeric equilibria between a low-valent structure and a higher-valent hydridic structure have been recently discovered and the subject has been reviewed.

\[(\text{DMPE})_2\text{Ru} \leftrightarrow (\text{DMPE})_2\text{Rh} \quad \text{(53)}\]

\[(\text{DMPE})_2\text{Ru} \quad \text{(54)}\]

### 10.4.6 Cobalt, rhodium and iridium

There is very little recent work on the bisarene complexes of this triad. Compounds of type $[\text{M}($arene$)_2]^{n+}$ ($\text{M} = \text{Co, Rh, Ir}$; $n = 2, 1, 0$) have been characterised and in addition evidence found for $[\text{Co(C}_6\text{Me}_6)_2]^{3+}$ although this could not be isolated. The non-zero dipole moment for $\text{Co(C}_6\text{Me}_6)_2$ and magnetic moment corresponding to one rather than the expected three unpaired electrons have been the subject of some discussion. As suggested for $\text{Ru(C}_6\text{Me}_6)_2$, it is possible that one of the benzene rings acts as a four- rather than a six-electron donor.

As mentioned earlier (Section 10.2.5) reaction of hexamethyl-Dewarbenzene and $\text{RhCl}_3\text{H}_2\text{O}$ leads to ring contraction and the formation of a pentamethylcyclopentadienylrhodium(III)chloride dimer (55) rather than a π-hexamethylbenzenerhodium(III)chloride cation (56).

\[(\text{55})\]
Very recently, the first example of a complex in which the BPh₄ group is directly bonded to a transition metal atom has been reported. Addition of NaBPh₄ to \([C₈H₁₂RhCl]₂\) and an excess of P(OMe)₃ in methanol gave the 5-coordinate ionic compound \([\text{Rh}\{\text{P(OMe)}₃\}₃\text{BPh}_₄]\). This decomposes in air to give the neutral complex \([\text{Rh}\{\text{P(OMe)}₃\}_₂\text{BPh}_₄]\), shown by x-ray analysis to have structure (57) in which the BPh₄ group is \(\pi\)-bonded to the rhodium through an arene ring\(^{165}\). A wider range of \([\text{RhL}_₂\text{BPh}_₄]\) \((L_₂ = C₅H₆, C₇H₈, C₈H₁₂, C₈H₈ etc.)\) and the analogous \([\text{IrL}_₂\text{BPh}_₄]\) \((L_₂ = C₈H₁₂, 1,5-hexadiene)\) compounds have since been characterised\(^{166}\).

\[
\begin{align*}
\text{Ph} & \quad \text{P} & \quad \text{Ph} \\
\text{P} & \quad \text{Rh} & \quad \text{P} \\
\text{Ph} & \quad \text{MeO)}₂ & \quad \text{P(OMe)}₃
\end{align*}
\]

(57)

### 10.4.7 Nickel, palladium and platinum

A preliminary report on the synthesis of \([\text{Ni(C₆Me₆)}₂]^{n⁺}\) \((n = 1, 2)\) has been given\(^{167}\), the former obtained by a direct and the latter by a reducing Friedel-Crafts reaction.

The only other well characterised arene compound in this triad is obtained by a reducing Friedel-Crafts reaction with \(\text{PdCl}_₂\). A palladium–aluminium complex \([\text{PdAl}_₂\text{Cl}_₇(C₆H₆)]₂\) is produced, shown by preliminary x-ray work to have structure (58)\(^{168}\). It is suggested that, in order to conform with the 18-electron rule, each benzene ring behaves as a \(\pi\)-enyl system towards each palladium atom but no further evidence has been presented to support this speculative conclusion.

\[
\begin{align*}
\text{Cl} & \quad \text{Al} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Al} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Pd} & \quad \text{Cl} & \quad \text{Al} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

(58)
A recent paper\textsuperscript{169} reports that nickel (and Cu, Cr, Mn and Co) halides react with AlCl$_3$ in the presence of hydrocarbons to give compounds containing metal, AlCl$_3$ and hydrocarbon. However, empirical formulae such as \([\text{C}_6\text{H}_6\text{Ni(AlCl}_3\text{)}_4\text{.3}],[\text{C}_6\text{H}_6\text{Co(AlCl}_3\text{)}_3\text{.5}]\) etc. are rather inconclusive and more work is required to characterise these potentially interesting cluster compounds.

10.5 MIXED SANDWICH COMPLEXES

This section covers all mixed sandwich complexes involving six- and/or seven-electron organic ligands.

10.5.1 Titanium, zirconium and hafnium

The only mixed sandwich compound known for this triad is the recently characterised \([\text{C}_5\text{H}_5\text{TiC}_7\text{H}_7]\)\textsuperscript{170}. The compound is thermally stable, moisture-sensitive, diamagnetic and has an n.m.r. spectrum indicative of a sandwich structure. The similarity of its visible, i.r. and mass spectrum to that of \([\text{C}_5\text{H}_5\text{VC}_7\text{H}_7]\) (Section 10.5.2) suggests structure (59) \([M = \text{Ti}]\).

10.5.2 Vanadium, niobium, tantalum

At present, mixed sandwich compounds are known only for vanadium. Reaction of \(\text{C}_5\text{H}_5\text{V(CO)}_4\) with \(\text{C}_7\text{H}_8\) gives \([\text{C}_5\text{H}_5\text{VC}_7\text{H}_7]\)\textsuperscript{171}, shown by x-ray analysis\textsuperscript{172} to have structure (59) \([M = \text{V}]\). Electrochemical studies\textsuperscript{173}

\[\text{M}
\]

\[\text{M}
\]

\[\text{(59)}\]

of this compound indicated the formation of \([\text{C}_5\text{H}_5\text{VC}_7\text{H}_7]^+\) and recently, by means of iodine oxidation, this has been isolated as its stable tri-iodide\textsuperscript{174}. Rather surprisingly, \([\text{C}_5\text{H}_5\text{VC}_7\text{H}_7]\)\textsubscript{13} has a magnetic susceptibility \((\chi_M)\) of only \(200 \times 10^{-6}\) c.g.s.u.\textsuperscript{174}, rather than the expected moment corresponding to \(c.\) two unpaired electrons [cf. the isoelectronic \([\text{V(Me}_3\text{C}_6\text{H}_3)]\)\textsubscript{I} with \(\chi_M = 3456 \times 10^{-6}\) c.g.s.u.; \(\mu_{\text{eff}}(295 \text{ K}) = 2.87 \text{ BM}\)]. A possible explanation of this low moment may be the loss of axial symmetry on oxidation due to
Jahn-Teller distortion etc? [cf. $[\text{Fe}(\text{C}_6\text{Me}_6)_2]^+$; Section 10.4.5] but as yet the evidence is too scanty to draw any definite conclusions.

The compound $[\text{C}_7\text{H}_7\text{VC}_7\text{H}_8][\text{V(CO)}_6]$ has also been reported. This is formed together with $\text{C}_7\text{H}_7\text{V(CO)}_3$ (Section 10.3.2) by reaction of $\text{V(CO)}_6$ and $\text{C}_7\text{H}_8$. Its formulation as a compound containing both cycloheptatriene and -triynyl groups (60) is based solely on spectroscopic evidence.

![Diagram](image)

(60)

No mixed sandwich compounds of vanadium containing arene groups are known.

### 10.5.3 Chromium, molybdenum and tungsten

Mixed sandwich compounds of this triad can be divided into two groups; cyclopentadienyl arene complexes and cyclopentadienylcycloheptatrienyl (and triene) complexes.

The mixed sandwich compound $[\text{C}_5\text{H}_5\text{CrC}_6\text{H}_6]$ (61) $[\text{M} = \text{Cr}]$ has recently been isolated in 20% yield by reaction of $\text{CrCl}_3$ with a mixture of $\text{NaC}_5\text{H}_5$ and $\text{PhMgBr}$, followed by hydrolysis. The corresponding molybdenum compound can be prepared either by reaction of $\text{MoCl}_5$, $\text{i-C}_3\text{H}_7\text{MgBr}$, $\text{C}_3\text{H}_5\text{MgBr}$ and 1,3-cyclohexadiene in ether or by lithium aluminium hydride reduction of $[\text{C}_5\text{H}_5\text{Mo(CO)}\text{C}_6\text{H}_6]\text{PF}_6$ (see Section 10.2.3) in THF. In contrast, reduction of $[\text{C}_5\text{H}_5\text{W(CO)}\text{C}_6\text{H}_6]\text{PF}_6$ with $\text{NaBH}_4$...
in a water/methanol mixture gives the 1,3 cyclohexadiene tungsten carbonyl hydride complex \([C_5H_5WH(CO)C_6H_8]\) \((62)\). Thus, reaction of the molybdenum cation with hydrido ion leads to formal reduction and the loss of a carbonyl group, whereas the tungsten cation apparently undergoes nucleophilic attack at both arene ring and metal to give a diene hydride with retention of CO. The reason for this markedly different behaviour is unknown but such factors as the relative labilities (and stabilities) of molybdenum and tungsten, carbonyl and hydride bonds, as well as the different reducing agents and solvent media employed, may all play an important role.

Similarly, reaction of WCl₆, i-C₃H₇MgBr, C₅H₅MgBr and 1,3-C₆H₈ in ether gives the diamagnetic hydrido compound \([C_5H_5WH(C_6H_6)]\) \((62)\). This compound is isoelectronic with \([C_5H_5ReH(C_6H_6)]^+\) (Section 11.5.4) and both probably have the structure (63) with non-parallel rings \([C_5H_5)_2MoH_2]\) \((62)\).

\[
\begin{align*}
&\text{(63)} & \text{M} - H \quad \text{Cr} - R \\
&\text{R} = \text{Me, Ph} & \text{R} = \text{Me, Ph}
\end{align*}
\]

Unexpectedly, attempted Friedel–Crafts acylation of \([C_5H_5CrC_6H_6]\) and the corresponding manganese complex; Section 10.5.4) led to ring expansion and the formation of the substituted cycloheptatrienyl complex cations \([C_5H_5MC_7H_6R]^+\) \((64)\) \([R = \text{Me, Ph}]\). The same compounds can be prepared by an exchange reaction between \([C_5H_5CrC_6H_6]\) and \([C_5H_6R]^+\). The chromium compounds are readily reduced with alkaline dithionite solution to give \([C_5H_5CrC_7H_6R]\). The mechanism of this ring expansion reaction is unknown but it is suggested that the first step is probably attack of the acyl cation on the metal, followed by insertion into the C₆ ring. A similar reaction with the molybdenum complex would be of interest in view of recent studies with \([C_5H_5ReC_6H_6]\), in which only competitive acetylation if the C₆ and C₅ rings is observed (Section 10.5.4).

More conventional methods of synthesising \([C_5H_5MC_7H_7]^+\) \((64)\) \([R = \text{H}]\) \((n = 0, 1; M = \text{Cr, Mo}^\text{180}, W^\text{177})\) are also available (see References 2b and 182 for a summary of the chromium syntheses). Reaction of \([C_5H_5CrC_7H_7]I\) with excess phenyl lithium \((65)\) \([Y = \text{Ph}]\) (presumably an exo substituted triene complex) and \([C_5H_5CrC_7H_7]I\). It is likely that a systematic study of these compounds with a variety of nucleophiles will prove to be of interest [cf. reactions of nucleophiles with \([C_7H_7Cr(CO)_3]\) (Section 10.3.3) and \([C_5H_5FeC_6H_6]^+\) (Section 10.5.5)]. The unsubstituted triene complex \([C_5H_5CrC_7H_8]\) \((65)\) \([Y = \text{H}]\) is also known; from this, \([C_5H_5CrC_6H_7]\)
is obtained by catalytic dehydrogenation and \([C_5H_5CrC_7H_7]^+\) by atmospheric oxidation\(^{183}\).

Finally, on reacting anhydrous \(\text{CrCl}_3\), \(\text{EtMgBr}\) and \(C_7H_8\) in an attempt to prepare \(\text{Cr}(C_7H_8)_2\), the novel cycloheptatrienyl/1,3-cycloheptadiene complex \([C_7H_7\text{CrC}_7\text{H}_{10}]\) (66) was synthesised\(^{184}\).

![Diagram of compounds (65) and (66)]

The sandwich compounds \([C_7H_7\text{M(CO)}_2C_5H_5]\) (\(M = \text{Mo, W}\)) are fully discussed in Section 10.3.3.

10.5.4 Manganese, technetium and rhenium

As discussed in the last section, \([C_5H_5\text{MnC}_6\text{H}_6]\) (61) (\(M = \text{Mn}\)) undergoes ring expansion to \([C_5H_5\text{MC}_7\text{H}_6\text{R}]^+\) (64) on attempted Friedel–Crafts acylation\(^{176}\). In contrast, acetylation of the corresponding \([C_5H_5\text{ReC}_6\text{H}_6]\) complex gives \([C_5H_5\text{ReC}_6\text{H}_2\text{COCH}_3]\) (16%) and \([C_5H_4\text{COCH}_3\text{ReC}_6\text{H}_6]\) (18%)\(^{181}\). The cyclopentadienyllarene compound can be protonated in aqueous HCl to give the hydrido cation \([C_5H_5\text{Re}\cdot\text{H}(C_6\text{H}_6)]\text{Cl}\) (63) \(\text{cf.} [C_5H_5\text{W}\cdot\text{H}(C_6\text{H}_6)];\) Section 10.5.3\(^{181}\).

The mass spectra of various mixed sandwich compounds namely \([C_5H_5\text{MC}_6\text{H}_6]\) (\(M = \text{Cr, Mn}\)), \([C_5H_5\text{MC}_7\text{H}_7]\) (\(M = \text{V, Cr}\)) have recently been reported. The fragment formation proceeds predominantly by successive elimination of the ring ligands, the first step being the elimination of the six- and seven-membered ring respectively\(^{185}\).

10.5.5 Iron, ruthenium and osmium

The mixed sandwich complexes of this triad can be divided into two sections: arenecyclopentadienylliron cations and their reactions with various nucleophiles and compounds containing only arene/diene or triene/diene ligands.

A series of recent papers by Khand, Pauson and Watts\(^{186}\) have examined in detail the factors controlling the addition of nucleophiles (\(Y\) \(Y = H^-\), \(\text{Me}^-\), \(\text{Ph}^-\)) to the substituted arenecyclopentadienylliron cations \([C_5H_5\text{FeC}_6\text{H}_n\text{R}_{6-n}]^+\) (67) \((R = \text{Me, Cl, Br, MeO}; n = 0–6)\). In principle,
addition of nucleophiles (Y) to the cations (67) can give products in which addition occurs either at the unsubstituted positions of the C₆ ring (68), the substituted positions of the C₆ ring (69) or at the C₅ ring (70). [N.B. as established earlier for nucleophilic additions to [C₆Me₆Re(CO)₃]⁺ (Section 10.2.4) and [C₇H₇Cr(CO)₃]⁺ (Section 10.3.3), only exo-addition is found.] Irrespective of the nature of R and the number of substituents, hydride attack occurs exclusively at the arene ring and, usually at the unsubstituted positions, unless the number of such position is small. In addition, it has been shown that methyl directs equally to o, m and p positions, whereas halogeno-substitution favours ortho and methoxide meta substitution. With methanide addition, the same results as for hydride are obtained, except for addition to [C₅H₅FeC₆Me₆]⁺. Whereas hydride attack occurs exclusively at the arene, giving (69), methanide attacks the C₅ ring, to give the neutral compound (70). This anomaly is attributed to steric overcrowding in the transition state for nucleophilic addition to the arene ring. Furthermore, the cyclopentadiene complex (70) can be converted into the cation (71) by the use of Ph₃CBF₄; this appears to be the first example of endo hydride abstraction by this reagent. In contrast, N-bromosuccinimide in methanol is less selective, removing both exo and endo hydrogens from compounds of type (68). However, N-bromosuccinimide will preferentially remove exo hydrogen atoms when both exo and endo hydrogens are present.
In the final paper, these authors cited the results of some preliminary MO calculations by Professor Perkins of Strathclyde University, which indicate the occurrence of appreciable overlap between the C-H\textsubscript{exo} \( \sigma \)-bond orbitals and the adjacent ligand \( \pi \) orbitals (which are directly involved in metal–carbon bonding). They conclude that such an interaction could account for the anomalously low \( \nu \text{CH} \) found experimentally and that the alternative explanation, involving direct interaction between the metal and the methylene carbon\textsuperscript{46}, is improbable.

The arene/diene complexes \([C_6\text{H}_6\text{Ml},3\text{-}C_6\text{H}_8](M = \text{Fe, Ru})\) have been prepared, the former by photolysis of a mixture of \( \text{FeCl}_3 \), \( i\text{-}C_3\text{H}_7\text{MgBr} \) and 1,3-cyclohexadiene\textsuperscript{167} and the latter either by reaction of \([\text{Ru}(C_6\text{H}_6)_2](\text{ClO}_4)_2\) with \( \text{NaBH}_4 \)\textsuperscript{56} or by irradiation of a mixture of \([\text{diene RuCl}_2]_n\) (diene = 1,5-cyclo-octadiene or norbornadiene), 1,3-\( C_6\text{H}_8 \) and \( i\text{-}C_3\text{H}_7\text{MgBr}\textsuperscript{168} \).

Reaction of \([(\text{diene})\text{RuCl}_2]_n\) with cycloheptatriene and \( i\text{-}C_3\text{H}_7\text{MgBr} \) gives the mixed compounds \([(\text{diene})\text{RuC}_7\text{H}_8]\).\textsuperscript{168} Photolysis of a mixture of \( \text{MCl}_3(M = \text{Fe,Ru}) \), 1,3,5-cyclo-octatriene and \( i\text{-}C_3\text{H}_7\text{MgBr} \) gives the compounds \([C_8\text{H}_{10}\text{MC}_8\text{H}_{10}]\), shown by n.m.r. to have structure (72) in which isomerisation of the triene to bicyclo[4,2,0] octa-2,4-diene has occurred\textsuperscript{168} (see Section 10.6.1 for further examples). Finally, in an earlier paper, the compounds \([C_8\text{H}_{12}\text{MC}_8\text{H}_{10}]\)\textsuperscript{169} (73) \([M = \text{Fe,Ru}]\) have been synthesised by reaction of \( \text{MCl}_3 \), 1,3,5-\( C_8\text{H}_{10} \), 1,5-\( C_8\text{H}_{12} \) and \( i\text{-}C_3\text{H}_7\text{MgBr} \).

10.5.6 Cobalt, rhodium and iridium

The only recent work on mixed sandwich compounds in this triad is the synthesis of \([\text{Ph}_4\text{C}_4\text{Co}(C_7\text{H}_8)]^+ \) (74) and \([\text{Ph}_4\text{C}_4\text{Co}(\text{arene})]^+ \) (75) cations\textsuperscript{190}. Nucleophilic attack occurs readily with the former and with difficulty with the latter, giving the \([\text{Ph}_4\text{C}_4\text{Co}(\text{cycloheptadienyl})]\) and \([\text{Ph}_4\text{C}_4\text{Co}(\text{cyclohexadienyl})]\) complexes respectively. Reaction with \( N\text{-bromosuccinimide} \) in methanol leads to endo hydride ion abstraction from these \( \text{exo} \) substituted compounds, whereas \( \text{Ph}_3\text{CBF}_4 \) has no effect (see Section 10.5.5). On the
basis of these and other studies, Efraty and Maitlis\textsuperscript{190} suggest that the order of reactivity of \(\pi\)-complexed ligands towards nucleophiles is:

\[
C_7H_8 > C_6H_6 > Ph_4C_4 > C_5H_5
\]

Finally, the arenecyclopentadienylocarbalt cation \([C_5H_5CoC_6H_6]^2+\)\textsuperscript{157} has been isolated as its PF\(_6\) salt by double hydride abstraction from \([C_5H_5Co 1,3-C_6H_8]\)\textsuperscript{191} with Ph\(_3\)CBF\(_4\).

### 10.5.7 Nickel, palladium and platinum

There are no mixed sandwich compounds known for this triad.

### 10.6 COMPLEXES OF LARGER RING TRIENES

This section discusses recent work on metal complexes of cyclo-octatrienes, bicyclononatrienes, and cyclododecatrienes.

#### 10.6.1 Cyclo-octatriene complexes

There is little recent work (post 1965) on cyclo-octatriene complexes and the earlier studies are well documented in Reference 2c. One paper of interest is a recent note by Aumann and Winstein\textsuperscript{192} in which a hydride abstraction reaction on the triene complex \([C_8H_{10}M(CO)\_3]\)\textsuperscript{(76)} (\(M = \text{Cr, Mo, W}\)) gives \([C_8H_9M(CO)\_3]^+\), assigned, on the basis of n.m.r. as the homotropylium structure (77)\textsuperscript{(77)} [see Section 10.7.1 for alternative synthesis]. Earlier attempts to abstract two hydride ions from \([C_8H_{10}Mo(CO)\_3]\) in the hope of forming a metal complex of the hypothetical \(C_8H_8^{2+}\) cation were unsuccessful\textsuperscript{2c}.

A complication in reactions with either 1,3,5- or 1,3,6-cyclo-octatrienes is the ease with which they undergo isomerisation to the bicyclo[4,2,0]octa-2,4-diene[cf.\(C_8H_{10}MC_8H_{10}\) (72); Section 10.5.5]. Thus, one of the
products in the reaction of $\text{Fe}_3(\text{CO})_{12}$ and $1,3,5-\text{C}_8\text{H}_{10}$ is $[\text{C}_8\text{H}_{10}\text{Fe}(\text{CO})_3]$, in which the triene has isomerised to give the diene complex (78).}

Finally, recent papers have reported the reaction of tetrafluorobenzo-bicyclo [2,2,2]octatriene (tetrafluorobenzobarrelene) with $\text{Fe}_3(\text{CO})_{12}$, to give compounds of type $\text{LFe}(\text{CO})_3$. Spectroscopic evidence (n.m.r. and Mössbauer) suggest structure (79) and this has recently been confirmed by x-ray analysis.

### 10.6.2 Bicyclononatriene complexes

Here again, the only work not covered by an earlier review is that of Grimme who, by reaction of bicyclo[6,1,0]nona-2,4,6-triene and $[(\text{THF})_3\text{Mo}(\text{CO})_3]$ has synthesised $[\text{C}_9\text{H}_{10}\text{Mo}(\text{CO})_3]$ (80). On heating at $125^\circ\text{C}$, this isomerises to give the bicyclo[4,2,1]nona-2,4,7-triene complex (81).
The corresponding bicyclononatriene is obtained when either compound is heated with diethylenetriamine.

Earlier work on complexes of other C₈H₁₀ olefins, such as 5-6-dimethylenebicyclo[2,2,1]hept-2-ene and 1-vinylcyclohepta-2,4,6-triene is discussed in Reference 2d.

10.6.3 Cyclododecatriene complexes

Earlier work on the cyclododeca-1,5,9-triene nickel complex C₁₂H₁₈Ni is discussed elsewhere²⁵. More recent studies have investigated the reaction of cyclododeca-1,5,9-trienes with rhodium¹⁹⁶, platinum¹⁹⁷, iron²⁵ and ruthenium¹⁹⁸ but, unlike the nickel complex, none of them appear to involve coordination of all three double bonds; instead diene or allylic bonding is favoured. In view of this, further discussion of these compounds is left to the reviewer of three- and four-electron donor complexes.

10.7 MISCELLANEOUS COMPLEXES

This final short section will include any other complexes which contain organic groups acting as six- or seven-electron donors.

10.7.1 Cyclo-octatetraene complexes

Recent x-ray analyses of \([\text{C}_8\text{H}_8\text{Mo(CO)}_3]\)¹⁹⁹ and \([1,3,5,7-\text{Me}_4\text{C}_8\text{H}_4\text{Cr(CO)}_3]\)²⁰⁰ indicate that the \(-\text{M(CO)}_3\) moiety interacts with six of the carbon atoms [cf. \text{C}_7\text{H}_8\text{M(CO)}_3; Section 10.3.3], as shown in (82). Earlier variable temperature \(^1\text{H} \text{n.m.r. studies}¹⁹¹-²⁰² have indicated that these compounds are fluxional, showing a single resonance at room temperature and a complex spectrum below \(-30 \degree\ C\). The limiting low temperature spectra can be interpreted in terms of the instantaneous structures shown in (82), although in the case of the substituted cyclo-octatetraene complex, the n.m.r. changes

\[
\text{R} = \text{H, Me}
\]

(82)
observed are very complex and apparently involve at least two distinct phases of intramolecular rearrangement\textsuperscript{203}. Protonation of the $[\text{C}_8\text{H}_8\text{Mo(CO)}_3]$ complex\textsuperscript{201} gives the homotropylium cation $[\text{C}_8\text{H}_9\text{Mo(CO)}_3]^+$ (77) (see Section 10.6.1 for alternative synthesis), whereas carbonylation\textsuperscript{204} gives the $[\text{C}_8\text{H}_8\text{Mo(CO)}_4]$ complex where the $\text{C}_8\text{H}_8$ ring is coordinated `diene-fashion' (83). Protonation of this results in CO evolution and the formation of (77).

\[
\begin{array}{c}
\text{OC} & \text{Mo} & \text{OC} \\
\text{OC} & & \text{CO}
\end{array}
\]

(83)

The compound $\text{Fe(C}_8\text{H}_8)_2$ has also been synthesised\textsuperscript{205} and shown by x-ray analysis\textsuperscript{206} to have structure (84) i.e. $($h$^6$.C$_8$H$_8$)Fe(h$^4$.C$_8$H$_8$).

\[
\begin{array}{c}
\text{Fe}
\end{array}
\]

(84)

At room temperature the $^1\text{H}$ n.m.r. spectrum\textsuperscript{207} shows only a single peak and at $-84$ °C a four line spectrum corresponding to a `frozen' h$^6$-ring [by comparison with the spectra of C$_8$H$_8$M(CO)$_3$] and a time-averaged h$^4$-ring. The equivalence of all protons of the h$^4$-ring between the coalescence temperature (c. $-40$ °C) and $-84$ °C is explained by postulating an intranuclear double-bond rearrangement. Unfortunately, it was not possible to carry out n.m.r. measurements at lower temperatures when it is expected that this time-averaged signal would also split. Finally, the observance of a single resonance down to $-35$ °C suggests the presence of an internuclear rearrangement process transforming the h$^4$-ring to a h$^6$-ring (and vice versa) with consequent interconversion of the conformation of the two rings and interchange of all bonds.

10.7.2 1,6-Methanocyclocapentaenechromiumtricarbonyl

The reaction of 1,6-methanocyclocapentaene with Cr(CO)$_6$ leads to the formation of the complex $\text{C}_{11}\text{H}_{10}\text{Cr(CO)}_3$\textsuperscript{208}. N.M.R. studies\textsuperscript{209} suggest that the delocalised 10 π-electron system of the free ligand is retained on coordination and this has been confirmed by a recent x-ray structure determination (85)$^{210}$. 

10.7.3 Azulenium cation complexes

For completion, readers are referred to the recent review by Churchill\(^{21}\) (literature coverage up to December 1968) in which references (all pre-1965) to complexes containing the azulenium ion \(\text{C}_{10}\text{H}_7^+\) are cited.

References

1. Zeiss, H., Wheatley, P. J. and Winkler, H. J. S. (1966). Benzenoid-Metal Complexes, (a) 51, (b) 57, (c) 73, (d) 79, (e) 68, (f) 49, (g) 17, (h) 27 (New York: The Ronald Press Company).
Preliminary communication

New anionic, neutral and cationic complexes of ruthenium(II)

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(Received December 14th, 1972)

Recently we reported the synthesis and characterization of a ruthenium(II) carbonyl diene anion M[RuCl₃CO(C₇H₈)] (M = Ph₃BzP⁺, Cs⁺)¹ [1]. We now report the reactions of this anion with a range of Lewis bases (L) to generate a series of new anionic, neutral and cationic ruthenium(II) species*. Different types of behaviour are observed depending on both the nature and amount of added L.

For L = Me₂S, Me₂SO, CH₂=CHCN (A/L 1/2 mole ratio), displacement of diene occurs giving the new anionic compounds Ph₃BzP[RuCl₃COL₂]. Similar compounds are obtained for L = AsPh₃, SbPh₃, C₆H₆N together with neutral species of composition [RuCl₂CO(C₇H₈)L], shown by detailed ¹H NMR studies to have structure I. With an excess of SbPh₃, the well-known tris-stibine compound [RuCl₂CO(SbPh₃)₃]² is obtained. Reaction with PPh₃ (1/2 mole ratio) gives the dimeric carbonyl phosphine [RuCl₂CO(PPh₃)₂]; with an excess of PPh₃ bridge cleavage occurs to give [RuCl₂CO(PPh₃)₃]. In contrast, reaction with PMe₂Ph (1/2 or excess) gives only [RuCl₂(PMe₂Ph)₂C₇H₈] shown by ¹H NMR and far IR studies to have structure II. Reaction of A with 2,2'-bipyridyl or 1,10-phenanthroline (N-N) (1/1 mole ratio) gives both Ph₃BzP[RuCl₃CO(N-N)] and [RuCl₂CO(N-N)]₂ with an excess of (N-N), small amounts of the new cationic species [RuCl(CO(N-N)₂)Cl are also obtained.

The analogous tertiary phosphine cations [RuCl(PPh₃)(N-N)₂]Cl can be prepared by treatment of either [RuCl₂(PPh₃)₃]² or [RuCl₃(PPh₃)(N-N)]³ with an excess of (N-N) in methanol. Small amounts of the dimeric chloro-bridged cations [Ru₂Cl₂(PPh₃)₄(N-N)₂]Cl₂ are also obtained. Similarly, with mer-[RuCl₃(PMe₂Ph)₃]⁴ and excess (N-N), the orange crystalline cationic compounds [RuCl(PMe₂Ph)₃(N-N)]Cl·H₂O are readily isolated (structure III) together with small amounts of the other geometrical isomer (IV).

*All these compounds have been fully characterized by elemental analyses, molecular weights, conductivity measurements, ¹H NMR, and IR studies.
ACKNOWLEDGEMENT

We thank Johnson-Matthey Ltd for loans of ruthenium trichloride and the National A. University of Mexico (LR) and the National Institutes of Health (ES) for fellowships.

REFERENCES

Preliminary communication

Syntheses of ruthenium tertiary phosphine complexes of type \([\text{RuX}_2(\text{PR}_3)_3\text{ or } 4]\)

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(Received July 19th, 1973)

Since the preparation of \([\text{RuX}_2(\text{PPh}_3)_n]\) (\(X = \text{Cl, Br; } n = 3, 4\)) in 1966\(^1\), numerous papers have been published on the reactions of these compounds with carbon, sulphur, nitrogen and oxygen donor ligands\(^2\) and on their usefulness as catalytic precursors in various olefin hydrogenation\(^3\) and oxidation\(^4\) reactions. A number of similar compounds of type \([\text{RuX}_2\text{L}_4]\) containing phosphorus donor ligands (\(L = \text{secondary phosphine}^5\), tertiary phosphite\(^6\); \(L_2 = \text{ditertiary phosphine}^7\)) have also been prepared, either by reaction between \(\text{RuX}_3\) and \(L\) or by direct replacement of \(\text{PPh}_3\) in \([\text{RuX}_2(\text{PPh}_3)_4]\). However, reaction of other tertiary phosphines with \(\text{RuX}_3\) in either aqueous/ethanol\(^7\) or 2-methoxyethanol\(^8\) gives only the lemon-yellow dimeric tripal halide-bridged cations \([\text{Ru}_2\text{X}_3(\text{PR}_3)_6]^+\times^-\) (\(\text{PR}_3 = \text{PMe}_2\text{Ph, PMePh}_2, \text{PET}_2\text{Ph, PPh}_2\), \(\text{PPr}_2\text{Ph, PBu}_2\text{Ph, PEt}_3\)) which are not very useful starting materials in comparison with \([\text{RuX}_2(\text{PPh}_3)_3\text{ or } 4]\).

In this note, we wish to report a convenient general synthetic method for the preparation of ruthenium tertiary phosphine complexes of type \([\text{RuX}_2(\text{PR}_3)_3]\) and \([\text{RuX}_2(\text{PR}_3)_4]\) which, on the indications of preliminary work, are excellent starting materials for the facile synthesis of a wide range of ruthenium(II) phosphine compounds. These complexes can be prepared by refluxing \([\text{RuX}_2(\text{PPh}_3)_4]\) in hexane or light petroleum (b.p. 60–80\(^\circ\)) with an excess of tertiary phosphine, \textit{e.g.}, \(\text{PMe}_2\text{Ph, PMePh}_2, \text{PET}_2\text{Ph, PPh}_2\), \(\text{PPr}_2\text{Ph, PBu}_2\text{Ph, PEt}_3\). The ethylphosphine complexes are exclusively of type \([\text{RuX}_2(\text{PR}_3)_3]\) (orange or green) whereas the methylphosphine complexes are of type \([\text{RuX}_2(\text{PR}_3)_4]\) (yellow); chlorodiphenylphosphine forms the tris complex (\(X = \text{Cl}\)) and the tetrakis complex (\(X = \text{Br}\)). Examination of the low temperature \(^1\text{H}\) NMR of \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) indicates a cis-configuration \textit{(cf. cis-}[\text{RuH}_2(\text{PMe}_2\text{Ph})_4])^9\).

The compounds are soluble in most common organic solvents and are initially non-conducting. However, on standing, the conductivity slowly increases. This is particularly true for \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) where removal of dichloromethane solvent after ca. 5 h gives \([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\) Cl. For the other \([\text{RuX}_2(\text{PR}_3)_3\text{ or } 4]\) compounds, refluxing gently in ethanol (with a small amount of free phosphine in the case of the tris compounds) readily gives the ionic species. If the reactions between \([\text{RuX}_2(\text{PPh}_3)_3]\) and
excess \( \text{PR}_3 \) are carried out in \( \text{CH}_2\text{Cl}_2 \) or ethanol, the main product is the ionic dimer. Thus, these various reactions which are summarised in Scheme 1 effectively demonstrate the relative stabilities of these monomeric and dimeric ruthenium tertiary phosphine complexes and the importance of the solvent media in synthetic inorganic chemistry.

ACKNOWLEDGEMENT

We thank Johnson-Matthey Ltd for loans of ruthenium trichloride and the S.R.C. for a research studentship (to PWA).

REFERENCES

New Ruthenium(III) and Ruthenium(II) Complexes containing Triphenylarsine and -phosphine and Other Ligands

By Lena Ruiz-Ramirez, T. Anthony Stephenson,* and Ellen S. Switkes, Department of Chemistry of Edinburgh, Edinburgh EH9 3JJ

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1973
New Ruthenium(III) and Ruthenium(II) Complexes containing Triphenylarsine and -phosphone and Other Ligands

By Lena Ruiz-Ramírez, T. Anthony Stephenson,* and Ellen S. Switkes, Department of Chemistry of Edinburgh, Edinburgh EH9 3JJ

A detailed investigation of the reactions of [RuX₃(EP₄₃)₃MeOH] (A) (X = Cl or Br; E = P or As) with ligands containing nitrogen (alkyl and aryl cyanides, pyridine, 2,2'-bipyridyl, 1,10-phenanthroline), sulphur (dimethyl sulfoxide, dialkyl sulphides, carbon disulphide, sodium diphosphopyridinodithioate), oxygen (tetrahydrofurane, acetone, nitrilotetraethane) and carbon (norbornadiene, 1,5-cyclo-octadiene, carbon monoxide) donor atoms is presented. Five different types of behaviour towards those ligands are exhibited by (A): (1) displacement of methanol giving the ruthenium(III) compounds [RuX₃(EP₄₃)₃]⁺, e.g. L = RCN, Me₃SO, CS₂, CS; (2) displacement of methanol and one EP₄₃ group giving [RuX₃(EP₄₃)₂]⁺, e.g. L = Me₃S, bipy, C₅H₅N; (3) complete displacement of methanol, EP₄₃ and X without reduction, e.g. [Ru(S₄P₄H₄)₂]⁺; (4) reduction to ruthenium(II) with or without complete displacement of EP₄₃ groups, e.g. [RuX₃L₂(EP₄₃)]⁺ (L = CO, C₅H₅, RCN) and [RuX₃L]⁺ (L = C₅H₅N, Me₃SO); (5) reduction to cationic ruthenium(II) compounds in methanol, e.g. [RuCl₂(PPh₃)₃][N(NMe₃)]₄Cl [(N = bipy or phen). Several of these compounds can also be synthesised from [RuX₃(PPh₃)₃]. The compounds are characterised by elemental analyses, molecular weights, e.s.r. and magnetic measurements, and configurations tentatively suggested on the basis of detailed far-i.r. [ruthenium(III)] and H.H.n.m.r. [ruthenium(II)] studies. Finally, electronic spectra (50 000–12 000 cm⁻¹) are presented and discussed.

There is now an extensive chemistry of ruthenium(II) compounds with ligands such as tertiary phosphines. In particular, the complexes [RuX₃(PPh₃)₃][L] (X = Cl or Br)² are excellent starting materials for the synthesis of a wide range of ruthenium(II) compounds still containing triphenylphosphine.³ Such compounds as [RuCl₃(PPh₃)₃]Cl⁴ and the blue methanolic solutions of 'RuCl₃(PPh₃)₃'⁵ are also excellent precursors for synthesising ruthenium(II) complexes with a range of other ligands.

In contrast, relatively few ruthenium(III) compounds containing tertiary monophosphines or arsines have been reported. Such compounds include the series mer-[RuX₃L₃]⁺ (L = PMe₃Ph, PET₃Ph, PBu₃PPh₂PPh₃)⁶ [RuX₃(EP₄₃)S]⁻ (E = P or As; S = MeOH)⁷ MeNO₂.⁸

data on convenient syntheses of ruthenium(III) tertiary phosphine and arsine compounds containing other ligands, we have undertaken a detailed study of the reactions of [RuX₃(EPh₃)₂(MeOH)] (A) with ligands containing nitrogen, sulphur, oxygen, and carbon donor atoms. A preliminary account of this work has appeared.¹

RESULTS AND DISCUSSION

Five different types of behaviour towards these ligands are exhibited by the complexes (A). These are (1) displacement of methanol giving the six-co-ordinate ruthenium(III) compounds [RuX₃(EPh₃)₂]; (2) displacement of solvent ligand and one EPh₃ group giving the six-co-ordinate ruthenium(III) compounds [RuX₃(EPh₃)L₂]; (3) displacement of all ligands with retention of the ruthenium(III) oxidation state; (4) reduction to ruthenium(II) with or without complete displacement of EPh₃ groups giving [RuX₃L₄] or [RuX₃(EPh₃)L₃]; (5) reduction to cationic ruthenium(II) compounds when the reaction is carried out in more polar solvents.

However, most of these ligands exhibit several of the different types of behaviour and in addition, the product obtained depends critically on a combination of such diverse factors as the nature of the ligand, the reaction time, the solvent media, and on the other ligands already present in the ruthenium ion co-ordination sphere. Therefore, in order best to illustrate the sensitivity of the product composition to changes in these various factors, the results are presented and discussed below under ligand headings.

Nitrogen Ligands

(a) Alkyl and Aryl Cyanides.—Several syntheses of ruthenium(II) alkyl and aryl cyanide compounds have recently been published. From [RuCl₃(PPh₃)₃] and CN⁻, the compounds [RuCl₂(RCN)₄(PPh₃)₃] are readily obtained.² From the blue solution of ruthenium(II) in methanol, the phenyl cyanide dimer [RuCl₃(PPh₃)Cl₂] can be isolated and halide bridge cleavage with Lewis bases gives [RuCl₃(PPh₃)L₂] (L = PR₃, MeCN, H₂N₂, CO, etc).³ In contrast, reaction of the blue solution with succino- and glutarocyanides (L') gives brown insoluble compounds of approximate stoichiometry RuCl₃L₅.⁴ Preparation of the blue solution in methyl cyanide gives [RuCl₃(MeCN)₂] which reacts further to produce [RuCl₃(MeCN)L₂] (L = PhNH₂, CO);⁵ [RuCl₃(MeCN)₂] is also obtained from [RuCl₃(CO)₂], and MeCN.⁶ Cleavage of the halogenocarbonyl dimer [RuX₃(CO)₃] with nitriles gives cis-[RuX₃(RCN)₃] (R = Et, Ph, CH₃-CH₂)⁷ and [RuCl₃NO(MeCN)] is obtained from the reaction of RuCl₃NO and MeCN.⁸

In recent years, a number of cationic ruthenium(II) compounds containing RCN ligands have also been reported. These include [RuH₂(PhCN)(Et₃P)]₁₈, [RuH₂(PhCN)(Ph₃P)]₁₉, [RuH₂(PhCN)(Ph₅P)]₂₀ and the series [Ru(NH₃)₃(RCN)] and [Ru(NH₃)₂(CN)]²¹. Several of the latter can be readily oxidised to the corresponding ruthenium(III) species [Ru(NH₃)₄(RCN)]²². The only other ruthenium(III) nitrate compounds known (to us) are the recently reported [RuCl₃(PhSP₃)₃] and [RuCl₃(MeCN)]-MeCN.²³

We now report that reaction of excess of RCN with (A) in dichloromethane gives the crystalline compounds [RuX₃(EPh₃)L₂]RCN (E = P or As; X = Cl or Br; R = Me, Ph, PhCH₂, CH₃-CH₂). These compounds (which are non-electrolytes in CH₂Cl₂) have been characterised by elemental analyses and molecular weights, magnetic moments at room temperature (solid and solution state) (Table I), and e.s.r. studies at 77 K. The values of μₑₑₑ (300 K), ranging from 1.80 to 2.20 B.M. are indicative of monomeric, spin-paired ruthenium(II) compounds and all the compounds exhibit intense e.s.r. spectra with a three g value pattern very similar to those reported by Hudson and Kennedy for various [RuX₃L₄] compounds (L = PMe₃, SMePh, etc). E.s.r. spectra of all the new ruthenium(III) compounds reported in this paper will be discussed more fully in a separate publication. The i.r. spectra of all these compounds contain a very weak band ν(CN) at ca. 2300 cm⁻¹, 50–100 cm⁻¹ higher than in the free ligands, which suggests that bonding occurs through the nitrogen (cf. [RuCl₃(PrSP₃)₃] ν(CN) 2310 cm⁻¹). As expected, the ¹H n.m.r. spectra of these compounds are either too broadened by the paramagnetic ion to be observed or consist of broad contact-shifted resonances, from which little structural information can be derived. Although the electronic spectra (50 000–12 000 cm⁻¹) of all these compounds have been recorded and the spectral bands satisfactorily assigned to intraligand and charge-transfer transitions (see Table 2 and later discussion), these measurements are of little use in determining the

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⁶ J. R. Leith, et al., to be published.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M.p. (°C)</th>
<th>Found (%)</th>
<th>Required (%)</th>
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<tr>
<td>[RuCl₄(AsPh₅)]₂MeCN</td>
<td>Dark green</td>
<td>194</td>
<td>52.6</td>
<td>3.7</td>
<td>1.6</td>
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<td>3.7</td>
<td>1.6</td>
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<tr>
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<td>4.0</td>
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<tr>
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<td>1.4</td>
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<td>3.6</td>
<td>4.5</td>
</tr>
<tr>
<td>[RuBr₄(AsPh₅)(bipy)]</td>
<td>Brown</td>
<td>216</td>
<td>42.1</td>
<td>2.1</td>
<td>2.5</td>
</tr>
<tr>
<td>[RuCl₄(AsPh₅)(phen)]</td>
<td>Brown</td>
<td>264</td>
<td>52.6</td>
<td>3.4</td>
<td>3.6</td>
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<tr>
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<td>Pale</td>
<td>280</td>
<td>56.8</td>
<td>3.7</td>
<td>4.3</td>
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<tr>
<td>[RuCl₄(AsPh₅)(phen)]</td>
<td>Brown</td>
<td>225</td>
<td>47.7</td>
<td>3.1</td>
<td>4.0</td>
</tr>
<tr>
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<td>3.8</td>
<td>4.1</td>
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<tr>
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<td>195</td>
<td>42.1</td>
<td>3.1</td>
<td>3.5</td>
</tr>
<tr>
<td>[RuCl₄(AsPh₅)(py)]</td>
<td>Orange</td>
<td>204</td>
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<td>4.9</td>
</tr>
<tr>
<td>[RuBr₄(PhPh₃)(py)]</td>
<td>Purple</td>
<td>205</td>
<td>45.0</td>
<td>3.3</td>
<td>3.7</td>
</tr>
<tr>
<td>[RuCl₄(AsPh₅)₄(dmso)]</td>
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<td>51.1</td>
<td>4.1</td>
<td>50.8</td>
</tr>
<tr>
<td>[RuCl₄(AsPh₅)₄(dmso)]</td>
<td>Tan</td>
<td>206</td>
<td>47.8</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>[RuBr₄(AsPh₅)₄(dmso)]</td>
<td>Dark</td>
<td>167</td>
<td>44.0</td>
<td>3.4</td>
<td>4.4</td>
</tr>
<tr>
<td>[RuCl₄(PhPh₃)₄(dmso)]</td>
<td>Tan</td>
<td>168</td>
<td>55.9</td>
<td>4.0</td>
<td>56.4</td>
</tr>
<tr>
<td>[RuBr₄(PhPh₃)₄(dmso)]</td>
<td>Dark</td>
<td>169</td>
<td>47.9</td>
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<td>48.4</td>
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<tr>
<td>[RuCl₄(AsPh₅)(Me₂S)]</td>
<td>Red</td>
<td>176</td>
<td>43.2</td>
<td>4.2</td>
<td>Cl, 16-2</td>
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<tr>
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<tr>
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<td>44.5</td>
</tr>
<tr>
<td>[RuBr₄(PhPh₃)(Me₂S)]</td>
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<tr>
<td>[RuCl₄(AsPh₅)(Et₂S)]</td>
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</tr>
<tr>
<td>[RuBr₄(AsPh₅)(Et₂S)]</td>
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<td>46.0</td>
</tr>
<tr>
<td>[RuCl₄(AsPh₅)₄]</td>
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<td>260</td>
<td>49.1</td>
<td>3.3</td>
<td>Cl, 12-5</td>
</tr>
<tr>
<td>[RuBr₄(AsPh₅)₄]</td>
<td>Dark</td>
<td>176</td>
<td>55.0</td>
<td>3.7</td>
<td>55.0</td>
</tr>
<tr>
<td>[RuCl₄(AsPh₅)₄]</td>
<td>Brown</td>
<td>178</td>
<td>46.6</td>
<td>3.3</td>
<td>48.8</td>
</tr>
<tr>
<td>[RuBr₄(AsPh₅)₄]</td>
<td>Dark</td>
<td>185</td>
<td>42.3</td>
<td>3.0</td>
<td>44.5</td>
</tr>
<tr>
<td>[RuCl₄(AsPh₅)₄]</td>
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<td>51.8</td>
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<td>928</td>
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<td>161</td>
<td>45.5</td>
<td>3.7</td>
<td>46.5</td>
</tr>
<tr>
<td>[RuCl₄(PhPh₃)₄]</td>
<td>Dark green</td>
<td>175</td>
<td>57.6</td>
<td>3.5</td>
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<tr>
<td>[RuBr₄(PhPh₃)₄]</td>
<td>Red-brown</td>
<td>180</td>
<td>48.7</td>
<td>3.6</td>
<td>51.2</td>
</tr>
<tr>
<td>[RuCl₄(PhPh₃)₄]</td>
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<td>&gt; 399</td>
<td>52.7</td>
<td>3.6</td>
<td>62.7</td>
</tr>
<tr>
<td>[RuBr₄(PhPh₃)₄]</td>
<td>Brown</td>
<td>&gt; 300</td>
<td>43.4</td>
<td>3.2</td>
<td>45.3</td>
</tr>
</tbody>
</table>

* Osmometrically at 27°(C₆H₆).  \(^{1}\) Magnetic moment, measured by Faraday method (solid) at 294 K; in parentheses, as measured by Evans' method (solution) at 301 K.  \(^{2}\) Measured in CHCl₃.  \(^{3}\) Measured in CH₂Cl₂.  \(^{4}\) H + D%.
detailed isomeric form(s) of the compounds. However, the fact that the compounds are sharp melting, give single spots on t.l.c. plates and exhibit very similar electronic and e.s.r. spectral patterns strongly suggests that only one of the three possible geometric isomers (Figure 1) is produced in each case.

In Table 3, the far i.r. spectra (400—200 cm⁻¹) of these compounds are listed. By careful examination of these bands, particularly for the triphenylphosphine compounds where masking by ligand absorptions is minimised, at least one of the \( \nu \text{(RuX)} \) vibrations can be assigned and the ratio of \( \nu \text{(RuCl)} : \nu \text{(RuBr)} \) (ca. 1:30), which is in the range found by other workers, supports these assignments. It is well established that the influence of the group \( \text{trans} \) to the halide may be substantial. Thus, terminal \( \nu \text{(RuCl)} \) are generally found reaction of (A) with RCN. However, prolonged reaction of \( \text{[RuX}_{3} \text{(EPPh)}_{3}] \text{MeOH} \) with RCN results in the formation of some \( \text{[RuX}_{3} \text{(RCN)}_{3}] \text{EPPh}_{3} \). A careful examination of the product for \( X = \text{Cl}, \text{R} = \text{PhCH}_{2} \) confirms that it is identical to \( \text{[RuCl}_{3} \text{(EPPh)}_{3}] \text{MeCN} \) obtained directly from \( \text{[RuCl}_{3}(\text{EPPh})_{3}] \). The ease of reduction depends on \( \text{X} \) and a qualitative order is found to be \( \text{MeCN} > \text{PhCH}_{2} > \text{PhCH}_{3} \text{CN} > \text{CH}_{2} \text{CHCN} \). Under the same conditions no reduction products are found for \( \text{X} = \text{As} \).

(b) Pyridine.—In contrast to the reaction with nitriles the products of reaction between (A) and pyridine are very dependent on the reaction conditions. Re-examining for 5—10 min with an excess of pyridine in dichloromethane gives the crystalline compounds \( \text{[RuX}_{3} \text{(EPPh)}_{3}] \text{py}_{3} \) (mentioned earlier for \( X = \text{Cl}, \text{E} = \text{As} \)). These have been characterised by elemental analyses, molecular weight determinations, e.s.r., and magnetic measurements (Table 1). Electronic spectra are given in Table 2 and discussed later. The presence of EPPh and \( \text{C}_{6} \text{H}_{5} \text{N} \) is confirmed by i.r. spectroscopy and the strong \( \nu \text{(RuCl)} \) band at ca. 340 cm⁻¹ (Table 3) is indicative.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu \text{(RuCl)} ) cm⁻¹</th>
<th>( \nu \text{(RuBr)} ) cm⁻¹</th>
<th>( \nu \text{(RCN)} ) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{[RuCl}<em>{3}(\text{EPPh})</em>{3}] \text{MeCN} )</td>
<td>328</td>
<td>250</td>
<td>222</td>
</tr>
<tr>
<td>( \text{[RuBr}<em>{3}(\text{EPPh})</em>{3}] \text{MeCN} )</td>
<td>321</td>
<td>262</td>
<td>220</td>
</tr>
</tbody>
</table>

According to the data in Table 2, the electronic spectra (50 000—12 000 cm⁻¹) of some ruthenium(III) compounds (shoulders in italics) have been calculated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu \text{(RuCl)} ) cm⁻¹</th>
<th>( \nu \text{(RuBr)} ) cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{[RuCl}<em>{3}(\text{EPPh})</em>{3}] \text{MeCN} )</td>
<td>328</td>
<td>250</td>
</tr>
<tr>
<td>( \text{[RuBr}<em>{3}(\text{EPPh})</em>{3}] \text{MeCN} )</td>
<td>321</td>
<td>262</td>
</tr>
</tbody>
</table>

\( * \) Band energy (cm⁻¹). \( ^{1} \) Maximum molar extinction coefficient (mol⁻¹ cm⁻¹). \( ^{2} \) Oscillator strength \( \beta_{0} \) if \( f = 4 \times 10^{4} \times \nu_{\text{max}} \times \nu_{\text{int}} \), \( \nu_{\text{int}} = \frac{1}{2} \times \nu_{\text{max}} \times \nu_{\text{int}} \).
### Table 3 (Continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(RuX)</th>
<th>Other bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru₂Br₂(PPh₃)₄(bipy)]Br₂</td>
<td>&lt;200</td>
<td>300w, 275s, 264w, 261m, 248s, 220s</td>
</tr>
<tr>
<td>[Ru₂Cl₂(PPh₃)₂(phen)]Cl₂</td>
<td>233s</td>
<td>335w, 309w, 245v, 215m</td>
</tr>
</tbody>
</table>

* Nujol mulls.
* Partially masked by strong AsPh₃ vibrations.

of a trans-RuCl₃ arrangement. Although differentiation between isomers (IV) and (V) is not possible on this evidence alone (Figure 2), the close similarity of the e.s.r. and electronic spectra of these compounds with [RuX₃(EPh₃)[bipy]] (see section c) suggests configuration (IV). This is also the configuration expected on the basis of the higher trans effect of EPh₃ compared to C₃H₅N.³¹

![Figure 2](image)

These appear to be the first well characterised ruthenium(III) compounds containing both pyridine and tertiary phosphine (or arsine) ligands although a number of ruthenium(III) pyridine complexes are known. These include mer-²³,²² [RuCl₃(py)₃], [RuCl₃(py)Cl]Cl,³³ pyH[RuCl₃(py)₃],³² pyH[RuCl₃(phen)]² and a number of 2,2'-bipyridyl (1,10-phenanthroline) compounds such as [RuCl₃(py)[bipy]] and [RuCl₃(py)₃(bipy)]Cl.³⁴

If [RuX₃(AsPh₃)₃(MeOH)] is refluxed with neat pyridine for ca. 20 minutes, [RuX₃(py)₃] is obtained. This well known compound has been synthesised by several methods in the trans-form and more recently the cis-isomer has been prepared.³⁵ A comparison of the i.r. and ¹H n.m.r. spectra of our products with those given in ref. 35 confirms the trans-configuration. In contrast, reaction of [RuX₃(PPh₃)₃(MeOH)] with neat pyridine gives a mixture of products which we could not separate satisfactorily. However, the ¹H n.m.r. spectra shows that one of the components is trans-[RuX₃(py)₃] and that the other(s) are probably ruthenium(II) species (since sharp n.m.r. signals) containing both pyridine and triphenylphosphine. By reaction of [RuBr₃(PPh₃)₃]² with neat pyridine for short reaction times, it is possible to isolate a pure sample of the latter species, subsequently shown by elemental analyses to be [RuBr₃(PPh₃)₂py]. Longer reaction times result in the formation of a solid mixture which can be rationalised according to reaction of the tris-complex with pyridine.

times lead to precipitation of trans-[RuBr₃(py)₄]. Unfortunately, various attempts to obtain the corresponding chloro-compound from [RuCl₃(PPh₃)₂] and pyridine gave either [RuCl₃(PPh₃)(py)]₂, together with a small amount of [RuCl₃(py)₄] (H n.m.r., i.r., and analytical evidence) or, on longer reaction times, pure trans-[RuCl₃(py)₂]. Although [RuCl₃(PPh₃)(py)]₂ could not be satisfactorily separated from [RuCl₃(py)₄], a careful examination of the far i.r. of the mixture, in conjunction with that of [RuBr₃(PPh₃)(py)]₂ indicates ν(RuCl) 340 cm⁻¹, supporting the expected trans-configuration (VI). Rather surprisingly, in view of the normal reaction of [RuX₃(PPh₃)₁] with Lewis bases,⁵ no evidence has been found for the unknown [RuX₃(PPh₃)₁] (PPh₃)₂, although the carbonyl analogues [RuX₃(CO)₅(PPh₃)₁] (X = Cl, Br, I), cis-[RuX₃(CO)₅(PPh₃)₁] (X = Cl, Br, I), and [RuCl₃(CO)₅(PPh₃)₁] are a well established series of compounds. Although trans-[RuX₃(PPh₃)₁] and trans-[RuX₃(PPh₃)₂(PPh₃)] appear quite air-stable in the solid state, dissolution in dichloromethane, benzene, or acetone results in a rapid (24 h) conversion of the initial yellow-brown solutions to deep green solutions (cf. ref. 35). This change is accompanied by the broadening of the n.m.r. spectral lines and the appearance of e.s.r. signals, confirming that the process is oxidative in nature. Similar oxidised species are formed when [RuBr₃(PPh₃)(py)]₂ is melted. However, analytical data indicate that only partial oxidation to ruthenium(III) has probably occurred and therefore, these studies were not further pursued.

(c) 2,2'-Bipyridyl and 1,10-Phenanthroline.—Reaction of (A) with either excess 2,2'-bipyridyl or 1,10-phenanthroline (N-N) in dichloromethane (shaken or refluxed) gives [RuX₃(EPh₃)(N-N)] Cl₂. These were characterised as previously (Tables 1–3) and represent the first examples of ruthenium complexes containing bipy (or phen) and tertiary arsines and of ruthenium(III) compounds containing bipy (or phen) and tertiary phosphines. The far i.r. spectra are complicated due to the many absorptions of the chelate ligands and it is therefore difficult to assign ν(RuX) vibrations with certainty. Nevertheless, careful examination of all these compounds (Table 3) suggests for (N-N) = bipy, ν(RuCl) 335, 295 (PPh₃); 311, 285 cm⁻¹ (AsPh₃) which is consistent with configuration (VII).

* Note added in proof: Samples of [RuCl₃(PPh₃)(py)₂] and [RuCl₃(PPh₃)(py)₄(PPh₃)] have been obtained by reaction of [RuCl₃(PPh₃)] with pyridine (R. K. Poddar and U. Agarwala, J. Inorg. Nuclear Chem., 1973, 35, 567).

For E = P, X = Br, a small amount of a ruthenium(III) compound of empirical formula [RuBr₃(AsPh₃)₂(bipy)] is also formed. The same compound is obtained in higher yield by reaction of [RuBr₃(PPh₃)₂] and 2,2'-bipyridyl in dichloromethane; similarly, [RuCl₃(PPh₃)₂(bipy)] can be synthesised from [RuCl₃(PPh₃)₂] and 2,2'-bipyridyl. The chloro-compound has been previously prepared by the reaction of [RuCl₃(CS)(PPh₃)]₂ and 2,2'-bipyridyl in methanol or benzene solution, the compounds are conducting in methanol and exhibit a ν(RuCl) band at 234 cm⁻¹ consistent with the dimeric halide-bridged catonic structure (VIII) suggested earlier. ⁴° N.B. comparison of the far i.r. of the chloro- and bromo-compounds (Table 3) shows the bands assigned earlier to ν(RuCl) are probably ligand vibrations. The compound [RuCl₃(PPh₃)(phen)₂Cl] [ν(RuCl) 235 cm⁻¹] is also obtained from dichloromethane solutions of [RuCl₃(PPh₃)₂] and 1,10-phenanthroline.

However, reaction of [RuCl₃(PPh₃)₂] with excess of (N-N) in methanol gives red solutions from which the monomeric cations [RuCl₃(PPh₃)(N-N)] Cl are isolated, together with small amounts of the rather insoluble [Ru₄Cl₆(PPh₃)₄(N-N)] Cl₂. The monomer formulation is confirmed by the ready synthesis of the hexafluorophosphate and tetraphenylboron salts. The monomeric cations are also prepared by reaction of [RuCl₃(PPh₃)(N-N)] and an excess of (N-N) in methanol. In contrast, the reaction of [RuCl₃(AsPh₃)(bipy)] with an excess of bipyridyl in methanol gives a mixture of products, neither of which contain triphenylarsine. One of these is the well known orange [Ru(bipy)_₃Cl₂(H₂O)] which we have also characterised by synthesis of the BPh₄ salt. In addition, small amounts of [RuCl₃(H₂O)(bipy)_₂Cl,H₂O previously synthesised in higher yields by several methods, ¹⁴,¹⁵ can be isolated, However, if a mixture of [RuCl₃(AsPh₃)(bipy)], bipyridyl, and sodium tetraphenylboron are refluxed in methanol, the only product is [Ru(AsPh₃)(bipy)]BPh₄.

The detailed chemistry of these and other ionic ruthenium(III) compounds will be discussed more fully in a later publication.

**Sulphur Ligands**

(a) Dimethyl Sulphoxide.—As for pyridine, the products of reaction between A and dimethyl sulphoxide are dependent on the reaction conditions. If A and a DMSO-water mixture (1:1 by volume) are shaken for 24 h, the only products are [RuX₂(EPh₃)₂(dmsso)].

The i.r. spectra show several absorptions in the region 1000—900 cm⁻¹, indicative of O-bonded dmsso but no band >1100 cm⁻¹, which could be attributed to an S-bonded sulphoxide group.⁴² Synthesis of the corresponding [H₄S]dmsso compound (for X = Cl, E = As) confirms the formation of only an O-bonded isomer (ν(SO) 935 cm⁻¹). The presence of a strong ν(RuCl) band at ca. 330 cm⁻¹, together with the close similarity of e.s.r. and electronic spectral patterns to other [RuX₂(EPh₃)₂L] complexes is consistent with configuration (I).

The same compounds are rapidly formed when the reaction is carried out in neat DMSO. However, on further shaking (for E = As), the orange-brown suspensions slowly dissolve giving a lemon-yellow solution (X = Cl), whereas for the bromide, a substantial amount of pale yellow crystalline precipitate is formed. The latter contains no triphenylarsine and analyses for [RuBr₂(dmsso)]⁴². The i.r. spectrum of this compound shows a strong band at 1080 cm⁻¹ assigned to S-bonded dmsso (cf. [Ru(NH₃)₆](dmsso))²⁺ ν(SO) 1042 cm⁻¹) but no bands which can be definitely attributed to O-bonded dmsso. The absence of O-bonded dmsso groups are confirmed by synthesis of [RuBr₂(H₄S)-dmsso] (see Experimental section). The ¹H n.m.r. spectrum of [RuBr₂(dmsso)] in (CDCl₃) is rather complex. At 301 K, it consists of five singlets at 9 6-09, 6-52, 6-56, 6-61, and 7-39. By analogy with recent studies on palladium and platinum(ii) dialkyl sulphoxide compounds,⁴³ the four resonances at 9 6-09—6-61 correspond to S-bonded dmsso and the peak at 9 7-39 to free DMSO. In agreement with the i.r. evidence, there is no evidence for any O-bonded dmsso (ca. 9 7-6).⁴⁴ The relative intensity of the S-bonded resonances to free DMSO is ca. 3:1. However, cooling the solution to 241 K changes the relative intensities to ca. 4:1 and an examination of the relative intensities of the S-bonded resonances indicates that the one at 9 6-56 decreases with respect to the rest. Addition of free DMSO at 301 K also produces a substantial decrease in the intensity of the 6-56 resonance. Thus, these observations are consistent with dissociation of [RuBr₂(dmsso)] in solution, probably to [RuBr₂(dmso)₂(solvent)] (9 5-66)

*Note added in proof: Samples of [RuCl₂(dmsso)] and [RuCl₁₂(H₄S)](dmsso) have been isolated from very concentrated DMSO and [H₄S]/DMSO solutions respectively. The ¹H n.m.r. spectrum of the former is very similar to that recently reported for [RuCl₃(dmso)] prepared from RuCl₃Cl₂O and DMSO (Wilkinson et al., J.C.S. Dalton, 1973, 2041, i.e. singlets at 9 6-48, 6-51, 6-57, 6-62, 6-66, 7-27, 7-31, and 7-39. However, our i.r. studies reveal only a very weak O-bonded dmsso band (9(SO) 980 cm⁻¹ in the [H₄S]dmsso complex) and this is consistent with the very low intensity of the resonances at 9 7-27 and 7-31 compared to the S-bonded resonances.*


and DMSO (9 7-39) (cf. the facile dissociation of [RuX₄(EP₃)₄]³⁻). Unfortunately, [RuBr₂(dmsso)] appears too insoluble for direct molecular weight measurements.

The three singlets at 9 6-09, 6-52, and 6-61 do not decrease in intensity on addition of DMSO, indicating they do not arise from dissociation products of [RuBr₂(dmsso)]. The best explanation for these we can offer, at present, is to assign the 9 6-09 resonance to the eight equivalent methyl groups in trans-[RuBr₂(dmsso)] (assuming free rotation of methyl groups even at 241 K (cf. ref. 44) and the 6-52 and 6-61 resonances to the two different dmso sets in cis-[RuBr₂(dmsso)]⁻, the higher resonance corresponding to the dmsso ligands trans to the bromo-groups. Raising the temperature increases the intensity of the resonance at 9 6-09 with respect to those at 9 6-52 and 6-61. This is consistent with a report by James et al.⁴⁵ who have recently synthesised [RuX₂(dmsso)] (X = Cl or Br) by reaction of RuX₄ and DMSO mixtures with hydrogen at 80° for 20 h. The far-i.r. spectrum shows ν(RuCl) 345 cm⁻¹, indicative of a trans-structure.

However, they also suggest that their chloro-compound may contain both S- and O-bonded dmso groups although the i.r. spectrum of the deuteriated compound is required for confirmation. Unfortunately, our attempts to isolate [RuCl₂(dmsso)] from the reaction of [RuCl₄(EP₃)₄]MeOH and DMSO have proved so far to be unsuccessful. This can be attributed to the high solubility of [RuCl₂(dmso)] in DMSO and the consequent difficulty of removing the high boiling solvent without decomposition of the product.*

However, heating [RuBr₂(dmso)] to 335 K in an n.m.r. tube and then cooling the solution to low temperature reveals an extra resonance at 9 7-09 (241 K). On raising the temperature, this moves to higher field. Similarly, recrystallisation of [RuBr₂(dmso)] from hot CHCl₃-acetone solution gives a darker coloured material with additional i.r. bands at 1120, 930, and 890 cm⁻¹ (cf. ref. 45). In addition, the ¹H n.m.r. (301 K) shows an extra weak peak at 9 7-30 indicative of some O-bonded dmso. However, the analysis of the recrystallised product is ca. 3% too low in carbon for [RuBr₂(dmso)] and the resonance at 9 6-09 has broadened considerably, suggesting that some oxidation of the product may have occurred. In fact, if solutions of [RuBr₂(dmso)] are left exposed to air for prolonged periods, dark green solutions are formed which exhibit very broad n.m.r. signals, indicating that substantial oxidation has occurred.

Clearly, the method of preparation of [RuX₄(dmso)] is very critical in determining the isomeric composition of the product and further studies are in progress to unravel this interesting problem.

(b) Dialkyl Sulphides.—Reaction of (A) with Me₂S in
CH₂Cl₂ gives [RuX₃(EPh₃)(Me₂S₂)]. The ¹H n.m.r. spectrum of [RuCl₃(AsPh₃)(Me₂S₂)] shows resonances τ 1-33 (para), 2-62 (ortho), 3-34 (meta), and 4-60 (methyl) which have been shifted and broadened by the paramagnetic ruthenium(III) ion. This is unusual since in the majority of ruthenium(III) compounds made from (A), the n.m.r. resonances are too broadened to be observed. However, similar contact-shifted spectra are observed for mer-[RuCl₃(PMe₂Ph₂)] and [Ru(S₂PPh₃)] (see section 4) whereas [RuBr₃AsPh₃(Me₂S₂)] gives very broad n.m.r. signals. The differences are probably due to substantial variations in the electron spin–lattice relaxation time in these compounds although the factors responsible for these variations are not at present clear.

Examination of the far-i.r. spectra of [RuX₃(EPh₃)(Me₂S₂)] reveals a strong ν[RuCl] band at ca. 335 cm⁻¹ consistent with configuration (IV). For X = Cl, E = P, an additional product was isolated from the reaction mixture. Unfortunately, analyses (and m.p.) indicate a mixture of [RuCl₃(PPh₃)₂(Me₂S₂)] and [RuCl₃(PPh₃)(Me₂S₂)], which have been unable to separate by either chromatography or recrystallisation. However, a pure sample of the latter was readily obtained by reaction of [RuCl₃(PPh₃)₂] and Me₂S₂.

In contrast, reaction of [RuX₃(AsPh₃)(Me₂S₂)] with an excess of Et₂S gives [RuX₃(AsPh₃)₂Et₂S] [ν[RuCl] 334 cm⁻¹ consistent with configuration (II)]. Extended reaction leads to products possibly containing the bis-sulphides but these could not be separated satisfactorily from the mono-sulphides. For [RuX₃(PPh₃)₂MeOH] even short reaction times give a complicated mixture of products which could not be separated, even by dry column chromatography.

Reaction of PPh₃ with [RuCl₃(AsPh₃)] gives a brown solid which i.r. spectroscopy and analyses confirm contains no PPh₃ but is [RuCl₃(AsPh₃)]. These results suggest that the donor ability of organic sulphides in these compounds is Me₂S > Et₂S > PPh₃ but this does not necessarily reflect the intrinsic bonding ability of the sulphur atom towards ruthenium(III) since steric repulsions of PPh₃ groups will probably play an important role.

Although a number of ruthenium mono-, di-, and tri-sulphide compounds have been recently reported, these complexes represent the first examples of dialkyl sulphides and tertiary phosphines (or arsines) bonded to ruthenium(II) and (III).

\[ \text{(c) Carbon Disulphide.} \]

Reaction of [RuCl₃(EPh₃)₂MeOH] with CS₂ under reflux conditions gives microcrystalline brown precipitates whose i.r. spectra (4000-400 cm⁻¹) are similar to the starting materials, except for the presence of a broad band at 1510 cm⁻¹ which indicates a linearly bonded CS₃ group. No bands due to thioacetyl (ca. 1280-1330 cm⁻¹) or π-CS₂ (ca. 1120 or 1020 cm⁻¹) linkages are present. The compounds for [RuCl₃(EPh₃)₂CS₂] a formulation supported by magnetic measurements. The far-i.r. spectra are rather complex but the probable assignment of ν[RuCl] (E = P) at 335 cm⁻¹ supports configuration (I). As in other complexes containing linearly bonded CS₂, the CS₂ in [RuCl₃(AsPh₃)(CS₂)] is easily lost. Attempts to recrystallise the compound from CH₂Cl₂ or C₆H₆ give only [RuCl₃(AsPh₃)]. However, the CS₂ group is not lost from the solid even after prolonged drying in vacuo at 80°C and the solid does not smell of CS₂. In contrast, several rhodium and iridium complexes with linear CS₂ ligands readily lose CS₂ from the solid by pumping in vacuo or even washing with ether.

However, reaction of [RuBr₃(EPh₃)₂MeOH] with CS₂ under reflux for 30 min gives products whose i.r. spectra exhibit thioacetyl bands at ca. 1300 but no bands at 1500 cm⁻¹. These compounds analysed for [RuBr₃(EPh₃)₂CS₂]. Shorter reaction times give a mixture of this compound and [RuBr₃(EPh₃)](CS₂) (i.r. and analytical evidence). The reason for the non-formation of the thioacetyl complex for X = Cl is not understood. These represent the first carbon disulphide and thioacetyl compounds of ruthenium(III) although ruthenium(II) compounds such as [RuCl₃−(π-CS₂)PP₃]Cl₃ have been synthesised.

\[ \text{(d) Sodium Diphenylphosphinodithioate.} \]

Reaction of [RuCl₃(AsPh₃)](L = MeOH or PhCH₂CN) with Na₂S₂PPh₃ in acetonitrile produces the violet, crystalline compound [Ru(S₂PPh₃)]. The same compound is also prepared from Me₂N[Br₄(AsPh₃)]₂(μ-Cl₃CO) (or [Ru₃(μ-xH₂O)] and Na₂S₂PPh₃. This compound is of interest in that its ¹H n.m.r. spectrum exhibits contact shifted ortho-, meta-, and para-protons at ν 4-35, 2-64, and 2-94 respectively and also because it is a rare example, in this series, of the displacement of all ligands with retention of the ruthenium(III) oxidation state. The corresponding [Ru(S₂P₂Et₃)] is mentioned briefly, elsewhere, but no preparative details have been given.

In contrast, reaction of [RuCl₃(AsPh₃)](MeOH) with Na₂S₂PR₃ (R = Me or Et) gives the ruthenium(II) compounds trans-[Ru(S₂P₂R₃)₂(AsPh₃)]. The chemistry of these and related dithioacid compounds of ruthenium(II) are discussed in detail elsewhere.

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\[ \text{References:} \]

53. T. A. Stephenson and E. S. Switkes, to be published.
Oxygen Ligands

If (A) is shaken in tetrahydrofuran (THF), displacement of methanol occurs and the compounds [RuX₃(EPh₃)₂(MeOH)] can be isolated from the reaction mixture. These compounds are not very stable, readily losing THF on recrystallisation and slowly on air-exposure of the solid.

[RuX₃(AsPh₃)MeOH] also loses the methanol group in CHCl₃, CHCl₃ or C₆H₆ solution giving yellow-brown solutions. Addition of heptane gives brown solids, analysed closely for [RuX₃(AsPh₃)₂] irrespective of the solvent used. The i.r. spectra (4000–400 cm⁻¹) are identical to the starting materials except for the absence of methanol bands at 3480 and 1010 cm⁻¹ and the far-i.r. spectrum reveals strong ν(RuCl) vibrations at 330 and 311 cm⁻¹ but no evidence for bridging chloro-groups. Although the compounds are not sufficiently soluble for molecular weight measurements, an e.s.r. spectrum of [RuCl₃(AsPh₃)MeOH] in CHCl₃ shows a 2 g value spectrum, (g₁ 2.52; g₂ 2.03 in CHCl₃ at 77 K), which indicates the presence of an axially symmetric complex such as (IX). The intensity of the e.s.r. signals, coupled with the normal magnetic moments found for the [RuX₃(EPh₃)₂MeOH] compounds in both solid and solution state also support their formulation as monomeric, magnetically-dilute ruthenium(III) compounds. Several five-co-ordinate ruthenium(III) compounds of this type are known, e.g. [RuCl₃(EPh₃)₂] (E = P₅⁷ or As₅⁸) and the compounds [RuX₃(EPh₃)₂] (E = P or As) were mentioned by Vaska and Sloane₅⁹ but no preparative or other details about them are available.

In contrast, dissolution of [RuX₃(EPh₃)₂MeOH] in acetone or nitromethane gives solvates which are surprisingly stable and which can be recrystallised without loss of solvent. The nitromethane compound [RuCl₃(PPh₃)MeNO₃] is an excellent precursor for the synthesis of most of the chloro-phosphine compounds reported in this paper. Its main advantage over [RuCl₃(PPh₃)MeOH] is the ease of preparation via AsPh₃[RuCl₃(PPh₃)₂] (which is prepared from [RuCl₃(PPh₃)₂]₆⁸. The methanol solvate can only be prepared in low yield (40%) and on a small scale from 'RuCl₃.xH₂O' (0.2 g) and stoichiometric amounts of PPh₃. Attempts to 'scale-up' this reaction (to 1.0 g of 'RuCl₃.xH₂O') gave only the reduced product 'RuCl₂'.


Carbon Donors

(a) Bicyclo[2.2.1]hepta-2,5-diene (Norbornadiene).—A number of ruthenium(II) diolefin compounds, such as [RuX₃C₆H₄(C₆H₅)], [RuX₃CO(C₆H₅)]₆³⁸ and [RuX₃CO=C₆H₄]⁻₅⁴ have been synthesised in recent years but no diene compounds of ruthenium(III) are known. An attempt to prepare a ruthenium(III) diene compound by reaction of (A) with excess of C₆H₄ in refluxing CHCl₃ produced no reaction. However, in refluxing benzene, crystalline, diamagnetic precipitates are obtained which analyse quite closely for [RuX₃(EPh₃)₂C₆H₄]. For E = P, the same compounds can be synthesised from [RuX₃(PPh₃)₆] and C₆H₄.₆⁸ Although the compounds are too insoluble for H n.m.r. studies, a careful examination of their far-i.r. spectra (Table 3) suggests that two ν(RuCl) vibrations occur at 278 and 253 cm⁻¹ (E = P). Thus, configuration (X) with trans-chlorides is unlikely because of the low ν(RuCl) values. The other possibilities, i.e. where both chloride groups are trans to the diene (XI) or where one chloride is trans to the diene and the other is trans to a phosphine (or arsine) (XII), cannot be distinguished on i.r. evidence alone, especially since earlier work₂⁹ indicates that olefins, tertiary phosphines, and arsines all have a similar trans effect on ν(MCl) vibrations.

However, we have also prepared the corresponding [RuCl₃(PMe₃)₂C₆H₄] ν(RuCl) 277 and 253 cm⁻¹ from P₃Bz[P[RuCl₃(CO)C₆H₄]₆₄ and PMe₃ and the H n.m.r. spectrum unequivocally shows trans-PMe₃.

and attempts to prepare ethylene and diphenylacetylene complexes gave only [RuCl₃(AsPh₃)]:

(b) Carbon Monoxide.—The reaction of [RuCl₃(AsPh₃)₂MeOH] with carbon monoxide in dichloromethane results in the formation of a pale yellow, diamagnetic, monomeric solid which analyses for trans-[RuCl₃(CO)₃(AsPh₃)]: ν(CO) 1993 cm⁻¹ (CH₂Cl₂). A similar product is obtained from [RuCl₃(PPh₃)₂] (S = MeOH or MeNO₂). This isomer (for E = P) has been prepared earlier [from RuCl₃(PPh₃)₂] and assigned configuration VII [ν(RuCl) 334 cm⁻¹]. Recrystallisation of (XIII) from hot benzene gives the cis-isomer [ν(CO) 2061 and 1999 cm⁻¹] whose far-i.r. spectrum (E = P) shows ν(RuCl) bands at 300 and 275 cm⁻¹ which is consistent with configuration XIV but not (XV). However, recrystallisation of (XIII) (E = As) from cold CH₂Cl₂-methanol solutions causes several carbonyl bands to appear; and then the growth of further bands at 2036 and 1978 cm⁻¹ occurs although the mixture still analyses for [RuCl₃(CO)₃(AsPh₃)₂]. By analogy with the earlier PPh₃ studies, the 1943 cm⁻¹ band is assigned to the other trans-isomer (XVI) and the 2036, 1978 cm⁻¹ bands to the cis-isomer (XVII). Similar results were found for [RuBr₃(CO)₃(AsPh₃)₂].

However, no evidence has been found for the formation of ruthenium(III) compounds such as the unknown [RuCl₃(AsPh₃)₂CO]. The compound [RuBr₃(PPh₃)₂CO] has been briefly reported but no further details are available.

The electronic spectra (50 000—12 000 cm⁻¹) of a number of these ruthenium(III) compounds are given in Table 2. A close examination of these results reveals that the absorptions between 30 000 and 12 000 cm⁻¹ are virtually independent of whether E = P or As, or of the nature of L. However, the position of the absorption bands depends markedly on the nature of X, shifting to lower energy when X changes from chloride to bromide. Similar results have been found in the electronic spectra of [RuX₆]³⁻ and various halogenobipyridylruthenium(III) compounds. Hence, these can be assigned principally to X → Ru charge transfer transitions.

The more intense absorptions >30 000 cm⁻¹ can be assigned to intra-ligand transitions superimposed on ligand metal charge-transfer transitions which arise from the tertiary phosphine, arsine, and the other ligand groups (cf. [Ru(NH₃)₃RCN]³⁺ with an absorption band at 31 500 cm⁻¹ assigned to RCN → Ru charge transfer transitions). However, the complexity of this region makes assignment of the bands to specific energy processes an impossible task.

**EXPERIMENTAL**

Microanalyses were by the N.P.L., Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Perkin-Elmer–Hitachi osmometer (model 115) at 25 °C. I.r. spectra were recorded in the region 4000—200 cm⁻¹ on a Perkin-Elmer 228 grating spectrometer, using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer using unmatched silica cells. ¹H N.m.r. spectra and solution magnetic moments (Evans' method) were obtained on a Varian HA 100 spectrometer. Magnetic susceptibility (solid) were measured on the Faraday balance at Newcastle University. E.s.r. measurements were performed on a Hilger & Watts 'Microspin' spectrometer operated at 9.3 GHz and employing 100 MHz magnetic field modulation and phase-sensitive detection. The magnetic field was measured by means of a proton resonance meter and g factors were calculated by using a dilute polycrystalline sample of 1,1-diphenyl-2-picrylhydrazyl (g = 2.0036) as reference. Conductivity measurements were made on a Portland Electronics conductivity bridge (model 310) and m.p.s were determined with a Rofrhot hot-stage microscope and are uncorrected.

**Nitrogen Ligands**

(a) Nitriles.—Trichlorobis(triphenylarsine)(methyl cyanide)ruthenium(III). Trichlorobis(triphenylarsine)(methylthio)ruthenium(III) (10-10 g) was added to methyl cyanide (5 ml) and the green suspension shaken for 1 h. The resulting dark green crystals were collected and recrystallised from CH₂Cl₂-pentane (Yield 75% [ν(CN) 2306 cm⁻¹]). Similarly, [RuBr₃(AsPh₃)₂MeCN] [ν(CN) 2310 cm⁻¹] was prepared and recrystallised (78%). The reaction of [RuCl₃(PPh₃)₂MeOH] with MeCN gave [RuCl₃(PPh₃)₂MeCN] [ν(CN) 2306 cm⁻¹] (75%) and the bromophosphine compound was similarly prepared [ν(CN) 2310 cm⁻¹] (74%).

Trichlorobis(triphenylarsine)(benzyl cyanide)ruthenium(III). [RuCl₃(AsPh₃)₂MeOH] (0.3 g) was stirred for 24 h in dichloromethane (40 ml) with an excess of benzyl cyanide (0-1 ml) under nitrogen. The resulting green solution was reduced in volume and the addition of diethyl ether gave a green precipitate. Recrystallisation from CH₂Cl₂-heptane gave the bright green powder (71%) [ν(CN) 2300 cm⁻¹].


Purple [RuBr₃(AsPh₃)₂(PbH₂CN)] was prepared by the same method (71%) \([\text{v(CN)}] 2300 \text{ cm}^{-1}\).

**Tricarbollorubrene(biphenylphosphine)[benzyl cyanyde]rubrenium** (ii). As for \([\text{RuCl₃}(\text{AsPh₃})₂(\text{PhB₃CN})]\) except the reaction time was only 5 h. Recryestallisation from CH₂Cl₂-pentane gave bright green microcrystals of the product (60%) \([\text{v(CN)}] 2310 \text{ cm}^{-1}\). However, prolonged treatment gave ciss-dichlorobis(triphénylphosphine)bis(benzyl cyanyde)rubrenium (ii) as a crystalline pale green solid (yellow when powdered), m.p. 158° (Found: C, 65; H, 4; N, 3). Calc. For C₅₄H₃₄Cl₂N₂P₀₂Ru C, 67; H, 4; N, 30%). This product is the same as that prepared from \([\text{RuCl₃}(\text{PPh₃})₃]\) and benzyl cyanyde. \([\text{v(CN)}] 2260, 2243 \text{ cm}^{-1}\). **Tricarbollorubrene(biphenylphosphine)[benzyl cyanyde]rubrenium** (iii) was prepared as for the chlorophosphine compound (60%) \([\text{v(CN)}] 2300 \text{ cm}^{-1}\), prolonged reaction giving some reduced species.

**Tricarbollorubrene(biphenylphosphine)quinoline rubrenium** (iii). \([\text{RuCl₃}(\text{AsPh₃})₂(\text{MeOH})]\) (0-20 g) was dissolved in CH₂Cl₂ (20 ml), an excess of phenyl cyanyde added (0-5 ml) and the solution refluxed for 1 h under nitrogen. The resulting green solution was reduced in volume and the green residue recrystallised from CH₂Cl₂-heptane (71%) \([\text{v(CN)}] 2280 \text{ cm}^{-1}\). The same product is obtained by stirring for 24 h \([\text{RuBr₃}(\text{AsPh₃})₂(\text{PhCN})]\) (70%) \([\text{v(CN)}] 2278 \text{ cm}^{-1}\) and \([\text{RuCl₃}(\text{PPh₃})₂(\text{PhCN})]\) (70%) \([\text{v(CN)}] 2280 \text{ cm}^{-1}\) were prepared by the same method. The corresponding \([\text{RuX₃}(\text{PPh₃})₂(\text{CH₂CN})]\) were also prepared by this method \([\text{E as } 75; \text{v(CN)}] 2305 \text{ cm}^{-1}\). P, 60%).

**Pyridine.** **Tricarbollorubrenebis(pyridine)rubrenium** (iii). \([\text{RuCl₃}(\text{AsPh₃})₂(\text{MeOH})]\) (0-20 g) and an excess of pyridine (0-4 ml) in CH₂Cl₂ (10 ml) were gently refluxed for 5 min. Addition of light petroleum (p.p. 100-120°) gave an orange precipitate recrystallised from CH₂Cl₂ heptane (88%). \([\text{RuBr₃}(\text{AsPh₃})₂(\text{py})]\) and \([\text{RuX₃}(\text{PPh₃})₂(\text{py})]\) were prepared in the same way (90%).

**trans-Dichlorotetrakis(p-dimethylaminobenzyl)rubrenium** (ii). \([\text{RuCl₃}(\text{AsPh₃})₂(\text{MeOH})]\) (0-20 g) and an excess of pyridine (0-4 ml) were heated for ca. 20 min and the resulting orange-red precipitate recrystallised from acetone-light petroleum (p.p. 100-120°) CH₂Cl₂-pentane, m.p. 270° (decomp. 9%). \([\text{Found: C, 49; H, 4; N, 11.6; } \text{calc. for } \text{C₅₄H₅₄Cl₂N₂P₀₂Ru } \text{C, 49; H, 4; N, 11.6}]\). Calc. For C₅₄H₅₄Cl₂N₂R₂Ru C, 40-2; H, 4-1; N, 11.5%). The same compound was prepared from \([\text{RuCl₃}(\text{PPh₃})₃]\) an \([\text{X(CN)}] 2300 \text{ cm}^{-1}\) under the same conditions.

\[13 \text{H N.m.r. (CDCl₃)} \tau=1-44(t), 2-40(t), 2-90(t) \text{ (see ref. 35). v(CN)} 340 \text{ cm}^{-1}\] Similarly, **trans-dibromotetrakis(p-dimethylaminobenzyl)rubrenium** (ii) was prepared starting from \([\text{RuBr₃}(\text{AsPh₃})₂(\text{MeOH})]\) or \([\text{RuBr₃}(\text{PPh₃})₃]\) m.p. > 280° (decomp. 90%). \([\text{Found: C, 43-1; H, 3-6; N, 10.0.}\] Calc. For C₅₄H₅₄Br₂N₂R₂Ru C, 41-7; H, 3-5; N, 9-7%).

**trans-Dibromotetraphosphine(triphenylphosphine)tris(p-dimethylaminobenzyl)rubrenium** (ii). \([\text{RuBr₃}(\text{PPh₃})₃] \text{(0-20 g)} \text{ was dissolved in an excess of pyridine (0-3 ml) and gently heated for 10-15 min. Addition of pentane gave a yellow powder recrystallised from CH₂Cl₂-pentane, m.p. 198° (71%) \([\text{Found: C, 53-1; H, 4-0; N, 5-7; } \text{M(C₄H₅)} 740. \text{C₅₄H₅₄Br₂N₂P₀₂Ru requires C, 52-1; H, 4-0; N, 5-5; M 671}\]. \[13 \text{H N.m.r. (CDCl₃)} \tau=1-00(t), 2-40(t), 3-26(t) \text{ [C₄H₅N], and 2-6-2-9 (multiplet [PPh₃]²)}\]. **trans-Dichlorotetraphosphine(triphenylphosphine)tris(p-dimethylaminobenzyl)rubrenium** (ii) was prepared from \([\text{RuCl₃}(\text{PPh₃})₃]\) by the same method but could not be satisfactorily separated from a small amount of \([\text{RuCl₃}(\text{py})]\) which is also formed.

\[13 \text{H N.m.r. (CDCl₃)} \text{of mixture: [RuCl₃(PPh₃)₃]}\]
was removed and the residue washed with water leaving a purple material (20%) and an orange solution. The solution was concentrated almost dryness to and on addition of an acetone-light petroleum (b.p. 100–120°) mixture (80:20 by volume), the orange tris(bipyridyl) ruthenium(II) chloride hexahydrate was obtained m.p. > 300° (60%) (Found: C, 47.8; H, 4.2; N, 11.1. Calc. for C₄₉H₄₄N₄O₂Ru: C, 48.1; H, 4.8; N, 11.2% [A (1 x 10⁻⁶) in MeOH = 170 S cm² mol⁻¹]. The corresponding BPh₃ salt was also prepared [Ru(bipy)₃(BPh₃)₂H₂O, m.p. 270° (Found: C, 76.7; H, 5.9; N, 6.1. Calc.: C, 75.7; H, 6.1; N, 7.3%]

If the residue was washed with CH₂Cl₂ (leaving the orange tris(bipyridyl) complex) and pentane added to the purple washings, purple microcrystals of chloro(aquo)bis(2,2'-bipyridyl)ruthenium(II) chloride dihydrate were obtained m.p. > 300° (Found: C, 45.7; H, 3.4; N, 10.2. Calc. for C₄₉H₄₄N₄O₂Ru₂·2H₂O: C, 40.1; H, 3.8; N, 10.7% [A (9 x 10⁻⁶) in CH₂Cl₂ = 7.0 S cm² mol⁻¹].

(d) 1,10-Phenanthroline.—[RuX₄(EPh₃)(phen)] (E = P or As; X = Cl or Br) were prepared by the same methods as the corresponding 2,2'-bipyridyl compounds.

Chloro(triphenylphosphine)bis(1,10-phenanthroline)ruthenium(II) chloride. [RuCl₂(PPh₃)(phen)] (0-10 g) was refluxed under nitrogen in methanol (100 ml) for 24 h with an excess of 1,10-phenanthroline (0-04 g). Concentration of the resulting orange solution and recrystallisation from CH₂Cl₂-pentane gave orange microcrystals m.p. 290° (decomp.) (78%) (Found: C, 60.9; H, 3.7; N, 6.9% [A (1 x 10⁻⁶) in CH₂Cl₂ = 28.6 S cm² mol⁻¹]. The same product was obtained from the reaction of [RuCl₂(PPh₃)₂MeNO] and an excess of 1,10-phenanthroline in methanol (50%) together with some [RuCl₂(PPh₃)₂(phen)] (30%). When [RuCl₂(PPh₃)₂] and 1,10-phenanthroline were refluxed in methanol, [RuCl₂(PPh₃)₂(phen)]Cl (58%) and the yellow-brown powder [RuCl₂PPh₃(phen)]Cl were obtained, m.p. > 300° (20%) (Found: C, 64.8; H, 4.2; N, 3.1. [C₄₉H₄₄N₄O₂RuCl₂ requires C, 65.7; H, 4.3; N, 3.1% [A (7 x 10⁻⁶) in MeOH = 11.5 S cm² mol⁻¹]. The latter compound was obtained in high yield (80%) by reaction of [RuCl₂(PPh₃)₂] and 1,10-phenanthroline in CH₂Cl₂.

Chloro(triphenylphosphine)bis(1,10-phenanthroline)ruthenium(II) hexafluorophosphate. A methanolic solution of [RuCl₂(PPh₃)(phen)]Cl was treated with an excess of NH₄PF₆. The resulting orange solution was concentrated to dryness, washed with water, and the red-orange product air-dried m.p. 215° (decomp.) (Found: C, 52.6; H, 3.4; N, 5.8%. [C₄₉H₄₄N₄O₂RuCl₂ requires C, 52.6; H, 3.4; N, 5.8%].

**Sulphur Ligands**

(a) Dimethyl Sulphoxide. — Trichlorobis(triphenylarsine)-(dimethyl sulphoxide)ruthenium(II) [RuCl₂(AsPh₃)₂MeOH] (0-20 g) was added to an aqueous solution of dimethyl sulphoxide (1: 1 by volume) and the suspension stirred for 24 h to give a tan precipitate. This was well washed with water and air-dried (80%). I.r. spectrum (1350—800 cm⁻¹): [1190s, 1160v, 1080s, 1005m, 955m, 850v, 825m cm⁻¹]. [RuBr₂(AsPh₃)₂(dms)] and [RuX₂(FPh₃)²(dms)] were readily prepared from aqueous DMSO solutions by the method given above (ca. 70% yields).

Dibromotetrakis(dimethyl sulphoxide)ruthenium(II). [RuBr₂(AsPh₃)₂MeOH] (0-20 g) was suspended in an excess of dimethyl sulphoxide (10 ml) and stirred under nitrogen for 24 h. The resulting pale yellow crystalline precipitate was filtered, washed with water, and air-dried, m.p. 219—220° (78%) (Found: C, 17.6; H, 4.2; Br, 28.6; S, 22.8. Calc. for C₄₉H₂₀Br₂O₃Ru₂: C, 16.7; H, 4.2; Br, 28.0; S, 22.3%). I.r. spectrum (1350—750 cm⁻¹) 1304m, 1208s, 1080s [v(νso)] 1025v, 978s, 942s cm⁻¹.

Dibromotetrakis([H₃(CH₃)₂SiO₂]Br)dimethyl sulphoxide)ruthenium(II) was prepared by the same method, m.p. 240° (decomp.) (80%) (Found: C, 17.0; D, 8.1; Br, 28.4. [C₄₉H₂₀Br₂MeOSi₂Ru₂ requires C, 18.0; D, 8.0; Br, 27.0%). I.r. spectrum (1350—750 cm⁻¹) 1080s, [v(νso)] 1025v, 900m, 900s, 780m, 770s cm⁻¹.

(b) Dialkyl Sulphides. — Trichlorobis(triphenylarsine)bis(dimethyl sulphide)ruthenium(II). [RuCl₂(AsPh₃)₂Me₂S] (0-21 g) in CH₂Cl₂ (40 ml) was treated with an excess of dimethyl sulphide (0-8 ml) under nitrogen. After 1 h, the red solution was concentrated to give a red solid recrystallised from CH₂Cl₂-heptane (78%). [RuBr₂(EPh₃)₂(Me₂S)] (E = P or As) were obtained by the same method except longer reaction times (ca. 2 h) were needed for complete conversion (75%).

Trichlorobis(triphenylphosphine)bis(dimethyl sulphide)ruthenium(II) was prepared as for the chloro-arsine compound, partial removal of solvent giving a dark green solid (52%). Concentration of the remaining red solution gave orange solids whose analyses and m.p.s were variable, suggesting a mixture of [RuCl₂(PPh₃)(Me₂S)₂] and [RuCl₂(FPh₃)(Me₂S)₂]. However, reaction of [RuCl₂(PPh₃)₂] and an excess of Me₂S in dichloromethane (ca. 5 min) under nitrogen gave an orange-red solution. Addition of heptane and recrystallisation of the orange-brown precipitate from CH₂Cl₂-heptane gave dichlorobis(triphenylphosphine)bis(dimethyl sulphide)ruthenium(II) (Found: C, 57.8; H, 4.6; Cl, 10.5, M. 986 (C₄₉H₄₄Cl₂P₂Ru₂S₂ requires C, 58.5; H, 5.1; Cl, 8.7%, M, 820). H n.m.r.: phenyl multiplet (δ 2.4—3.3); methyl singlet (δ 8.8).

Trichlorobis(triphenylarsine)bis(dimethyl sulphide)ruthenium(II). [RuCl₂(AsPh₃)₂Me₂S] (0-20 g) was dissolved in CH₂Cl₂ (40 ml) and stirred under nitrogen with an excess of Et₂S (0-1 ml) for 2 h. The resulting red solution was concentrated to dryness and a mixture of heptane-CH₂Cl₂ (6:1 ratio) added giving a red solid, recrystallised from CH₂Cl₂-heptane (82%). Longer reaction times gave mixtures containing [RuCl₂(AsPh₃)₂Et₂S₂] [RuBr₂(AsPh₃)₂Et₂S] was similarly prepared (85%).

(c) Carbon Disulphide. — Trichlorobis(triphenylarsine)-carbon disulphide)ruthenium(II). [RuCl₂(AsPh₃)₂Me₂S] (0-33 g) was refluxed in CS₂ (30 ml) under nitrogen for ca. 30 min and the resulting brown microcrystalline precipitate washed several times with carbon disulphide and air-dried (71%). The same product was formed if the reaction was continued for 6 h, even in the presence of an excess of triphenylarsine (added in an attempt to remove sulphur from the bound Cs₂ group). [RuCl₂(PPh₃)₂CS₂] was similarly prepared (70%).

Trichlorobis(triphenylarsine)bis(tricarbonyl) ruthenium(II). [RuBr₂(AsPh₃)₂CS₂] (0-20 g) was refluxed in CS₂ (20 ml)
under nitrogen for ca. 30 min. Concentration of the solution, followed by pentane addition gave the brown crystalline product, washed with CS₂ and air-dried (75%) [v(νCS₂) 2995 cm⁻¹].

Shorter reaction times gave products with i.r. bands at 1295 and 1520 cm⁻¹ [v(νCS₂)], i.e. a mixture of [RuBr₃(AsPh₃)₃(CS₂)] and [RuBr₂(AsPh₃)₂(CS₂)]. The corresponding [RuBr₂(PPh₃)₃(CS₂)] was prepared in an analogous way (68%).

* Dicarbollidophenylphosphinodithioate(ruthenium(lll)).

(RuCl₃(AsPh₃)₂MeOH) and a four-fold excess of sodium dicyclopentadienophosphinodithioate were shaken in acetone for two days. The violet crystals were then filtered, washed with water and diethyl ether, and dried in vacuo at 40°, m.p. 219-220° (Found: C, 50-5; H, 3-3. C₅₀H₃₀P₃Br₂RuS requires C, 50-9; H, 3-5%). The same compound is also prepared from [RuCl₃(AsPh₃)₃]PF₆CH₂CN, Me₂N[RuBr₄(AsPh₃)₂](acetone) or 'RuCl₃+xH₂O' and Na₃P₂Ph₃.

Oxygen Ligands

(a) Tetrahydrofuran.—Trichlorobis(triphenylarsine)(tetrahydrofuran) ruthenium(lll). [RuCl₃(AsPh₃)₃MeOH] (0-20 g) was suspended in an excess of tetrahydrofuran, THF (10 ml) and shaken for ca. 12 h. Addition of pentane to the red solution gave a yellow-orange precipitate which was washed with THF and air-dried (75%). The corresponding [RuBr₃(AsPh₃)₂(thf)] and [RuX₂(PPh₃)₂(thf)] were similarly prepared (35% yield).

(b) Acetone, nitromethane. The compounds [RuX₃(EPPh₃)S] (S = acetone, MeONO₂) were prepared as for the THF adducts (see ref. 2 and 8) and for S = MeONO₂, from Ph₃As[RuX₃(EPPh₃)₂]acetone (ref. 6).

Trichlorobis(triphenylarsine)ruthenium(lll). [RuCl₃(AsPh₃)₃MeOH] was dissolved in benzene (or dichloromethane) giving a yellow-brown solution. Addition of heptane gave the dark brown product. Similarly, [RuBr₃(AsPh₃)₂] was prepared.

Carbon Donors

(a) Bicyclo[2.2.1]2.5-heptadiene (Norbornadiene).—Dicarbollidobis(triphenylarsine)(norbornadiene)ruthenium(lll).

[RuCl₃(AsPh₃)₂MeOH] (0-40 g) and an excess of C₅H₄ (2-0 ml) in benzene were refluxed under nitrogen for 24 h. The resulting orange-red crystals were collected, washed with benzene and dried in vacuo, m.p. 256-260° (Found: C, 57-8; H, 4-2; As, 16-4; Cl, 7-8. C₅₀H₃₀As₂Cl₄Ru requires C, 58-9; H, 4-4. As, 17-1; Cl, 8-1%). Similarly, [RuBr₃(AsPh₃)₂C₂H₄] was prepared (Found: C, 55-2; H, 4-0; As, 10-6; Br, 16-8. C₅₀H₃₀As₂Br₂Ru requires C, 53-5; H, 4-0; As, 10-5; Br, 16-6%). These compounds are very insoluble in all common solvents. [RuCl₃(PPh₃)₂C₂H₄] was similarly prepared as for the chloro-arsine compound from [RuCl₃(PPh₃)₂S] (S = MeOH or MeNO₂) and C₅H₄ m.p. 220° (60%) (Found: C, 65-6; H, 4-9. Calc. for C₅₀H₃₀Cl₄P₃Ru: C, 65-5; H, 4-8%) (see ref. 38). [RuBr₂(PPh₃)₂C₂H₄]

We thank Dr. D. J. Cole-Hamilton and Mr. P. W. Armit for the preparation of this compound.

C₅H₄ was similarly prepared (Found: C, 60-8; H, 4-9. C₅₀H₃₀Br₂P₃Ru requires C, 58-8; H, 4-4%). These compounds are also very insoluble in all common solvents.

Dichlorobis(dimethylphenylphosphinophenyl) (norbornadiene)ruthenium(ii).—Ph₃PBr₃[RuCl₂CO(C₅H₄)] (0-20 g) was refluxed in CH₂Cl₂ (100 ml) under nitrogen with PMe₂Ph (0-1 ml) for ca. 24 h. Concentration of the yellow solution followed by diethyl ether addition gave a yellow solid. This was washed with methanol to remove free Ph₃PBrPCI and recrystallised from CH₂Cl₂-pentane, m.p. 247°.

[Found: C, 51-0; H, 5-8; M(C₅H₄) 600. C₅₀H₃₀Cl₂P₃Ru requires C, 51-0; H, 5-5%. M, 520. IH NMR: δ = 6-70(2), 7-20(4), 8-20(2) [diene]; 7-0-2-6(10) phenyl multiplet; 7-74(12) 1:2:1 'triplet' [PMe₂Ph].

Refluxing [RuCl₃(AsPh₃)MeOH] (0-20 g) with an excess of cyclo-octa-1,5-diene (1-2 ml) in benzene (40 ml) for 24 h gave the dark orange precipitate [RuCl₃(C₂H₄)₂] (Found: C, 36-1; H, 4-3. Calc. for C₅₀H₃₂Cl₂Ru; C, 34-4; H, 4-3%) (see ref. 60).

(b) Carbon Monoxide.—trans-Dichlorocarbonyl(bis(triphénylarsine)ruthenium(ii) (configuration XIII). Carbon monoxide was bubbled through an oxygen-free solution of [RuCl₃(AsPh₃)₂MeOH] (0-40 g) in CH₂Cl₂ (40 ml) for ca. 24 h. The solution was concentrated to dryness and the residue washed with acetone leaving a pale yellow solid, m.p. 220° (decomp.) (36%) (Found: C, 52-4; H, 3-6. Cl, 7-8. M(C₅H₄) 857. C₅₀H₃₀As₂Cl₂O₃Ru requires C, 54-2; H, 3-6; Cl, 8-4%. M, 841. v(co) 2081w, 2038w, 1938w, 1938s (Nujol); 1993 cm⁻¹ (CH₂Cl₂). Recrystallisation from hot benzene gave cis-[RuCl₃(CO)₂(AsPh₃)] (configuration XIV) (Found: C, 53-7; H, 3-7%. v(co) 2061s, 1989s cm⁻¹). Recrystallisation from CH₂Cl₂—methanol gave a mixture of isomers with v(co) 2026, 1978 cm⁻¹ (Nujol) (assigned to configuration XV and v(co) 1943 cm⁻¹ (Nujol) (assigned to confin. XVI). Similarly trans-[RuBr₃(CO)₂(AsPh₃)] (configuration XIII) was prepared from [RuBr₃(AsPh₃)₂MeOH] m.p. 285° (decomp.) (60%) (Found: C, 48-8; H, 3-3. C₅₀H₃₂BR₂Ru requires C, 49-1; H, 3-2%. v(co) 1995 cm⁻¹ (CH₂Cl₂). Recrystallisation from CH₂Cl₂—methanol gave a pinkish-brown product (Found: C, 49-0; H, 3-4%) with a number of carbononyl bands in the i.r. spectrum. v(co) 2090m, 1898 cm⁻¹ (configuration XVII); 1940w (configuration XVI).

trans-[RuCl₃(CO)₂(PPh₃)₂] (configuration XIII) was also prepared from [RuCl₃(PPh₃)₂S] (S = MeOH or MeNO₂) by the same method, m.p. 190° (35%) (Found: C, 60-3; H, 4-0. Calc. for C₅₀H₃₂Cl₂O₃P₃Ru: C, 60-6; H, 4-0%. v(co) 2050 cm⁻¹; see refs. 2 and 63).

We thank Johnson-Matthey Ltd. for generous loans of ruthenium trichloride, the National A. University of Mexico (L. R. R.) and the National Institutes of Health (E. S. S.) for fellowships, the Department of Inorganic Chemistry, University of Newcastle, for use of the Faraday Balance, Dr. I. R. Leith and Mr. A. Anderson for e.s.r. measurements, and Mr. J. Sinclair for experimental assistance.

[2/2774 Received, 11th December, 1972]
(Bicyclo[2.2.1]hepta-2,5-diene)carbonyltrihalogenoruthenate(II) Complexes

By T. Anthony Stephenson,* Ellen S. Switkes, and (in part) Lena Ruiz-Ramirez, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ
rhodium(t) diene complex [RhCl(C_7H_8)(PPh_3)] (III) illustrates the effect of trans-asymmetry on the norbornadiene proton resonances. Four magnetically inequivalent sets of protons are found (A—D) with the two sets of olefin protons A and B assigned at \( \tau \) 4.66 and 7.00 respectively, well separated because of the large

trans-effect difference between triphenylphosphine and chloride.\(^{11}\) Similar spectra would be expected if the ruthenium complexes had configuration (I). However, the \(^1\)H n.m.r. spectra of all the complexes show five diene resonances (Table 1), which is consistent with configuration (II) since H(1) and H(4) will be magnetically inequivalent. Furthermore, the smaller separation between the H(2), H(6) and H(3), H(5) olefin protons is consistent with cis-asymmetry. The detailed assignments have been confirmed by homonuclear decoupling experiments (Table 2) and the coupling constants obtained from these measurements are also shown in Table 2.

In support of the i.r. observations, no change in the \(^1\)H n.m.r. spectrum was observed on heating a deuteriochloroform solution of the Ph_3(PPhCH_2)P\(^+\) salt to ca. 323 K and, unlike the rhodium complexes, addition of an excess of diene or chloride ion produced no change in the diene resonance positions, even after setting aside for 3 days. Thus, it appears that these diene anions are formed stereospecifically and are of high kinetic stability.

<table>
<thead>
<tr>
<th>Irradiated at</th>
<th>Resonance observed</th>
<th>Assignment</th>
<th>Fine structure observed on irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-34 H(4)</td>
<td>( \tau ) 4-78</td>
<td>H(2), H(6)</td>
<td>Doublet</td>
</tr>
<tr>
<td></td>
<td>( \tau ) 5-39</td>
<td>H(3), H(5)</td>
<td>Doublet</td>
</tr>
<tr>
<td>5-80 H(1)</td>
<td>( \tau ) 5-80</td>
<td>H(1)</td>
<td>No change</td>
</tr>
<tr>
<td>5-80 H(1)</td>
<td>( \tau ) 6-34</td>
<td>H(3), H(5)</td>
<td>Doublet</td>
</tr>
<tr>
<td>5-80 H(1)</td>
<td>( \tau ) 6-34</td>
<td>H(4)</td>
<td>No change</td>
</tr>
<tr>
<td>5-80 H(1)</td>
<td>( \tau ) 6-34</td>
<td>H(5)</td>
<td>No change</td>
</tr>
<tr>
<td>4-78 H(2)</td>
<td>( \tau ) 5-80</td>
<td>H(3), H(5)</td>
<td>Doublet</td>
</tr>
<tr>
<td>4-78 H(2)</td>
<td>( \tau ) 5-80</td>
<td>H(1)</td>
<td>No change</td>
</tr>
<tr>
<td></td>
<td>( \tau ) 6-34</td>
<td>H(4)</td>
<td>No change</td>
</tr>
</tbody>
</table>

\( J(\text{H}(1)\text{H}(2)\text{H}(3)) = 1.25 \text{ Hz}; J(\text{H}(1)\text{H}(2)\text{H}(4)) = 1.50 \text{ Hz}; J(\text{H}(2)\text{H}(3)) = 5.05 \text{ Hz}; J(\text{H}(2)\text{H}(4)) = 4.5 \text{ Hz}; J(\text{H}(3)\text{H}(4)) = 3.0 \text{ Hz}; J(\text{H}(1)\text{H}(2)) = 3.5 \text{ Hz}.\)

undergoing neither ligand exchange, isomerisation, nor oxidisation under the conditions studied. However, the nature of the product is sensitive to the reaction conditions and, in particular, to which large cation is used. With Ph_3(PPhCH_2)PPhCl and CsCl, the only product isolated was the acetone-insoluble M[RuCl_2(CO)(C_7H_8)]. However, with Ph_3AsCl, HCl, reaction with [RuCl_2(CO)(C_7H_8)]_n in acetone at room temperature gave a mixture of acetone-soluble products which unfortunately proved impossible to separate satisfactorily. In addition, the reaction was irreproducible, leading to different product mixtures (i.e. and analytical evidence) under, ostensibly, the same reaction conditions.\(^*\)

If, however, Ph_3AsCl, HCl and [RuCl_2(CO)(C_7H_8)]_n were gently heated under reflux in acetone for ca. 1 h, a single product was obtained which analysis closely for cis-[Ph_3AsH]_2[RuCl_2(CO)]_4. In support of this formulation, the complex has a conductivity in dichloromethane characteristic of a 2:1 electrolyte \([0-001x] 48 \Omega \text{ cm}^2 \text{ mol}^{-1}\) and its i.r. spectrum shows two v(CO) bands at 2030 cm\(^{-1}\) and 1940 cm\(^{-1}\) (Nujol), very close to those reported earlier for cis-C_8H_8[RuCl_2(CO)]_4 [v(CO) 2036 and 1935 cm\(^{-1}\)].\(^{12}\) No evidence for norbornadiene was found in the i.r. or n.m.r. spectra. The mechanism by which a dicarbonyl monomer is obtained from a complex containing only one carbonyl ligand per ruthenium atom


**Table 1**

<table>
<thead>
<tr>
<th>M</th>
<th>X</th>
<th>( \tau )</th>
<th>( \delta )</th>
<th>( \gamma )</th>
<th>Relative</th>
<th>Finestructure</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph_3(PPhCH_2)P^+</td>
<td>Cl</td>
<td>2-38</td>
<td>2-52</td>
<td></td>
<td></td>
<td>Multiplet Phenyl</td>
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<tr>
<td>Ph_3(PPhCH_2)P^+</td>
<td>Br</td>
<td>2-90</td>
<td>2-90</td>
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<td></td>
<td></td>
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<tr>
<td>Ph_3(PPhCH_2)P^+</td>
<td>Cl</td>
<td>4-80</td>
<td>4-80</td>
<td>4-35</td>
<td></td>
<td>Doublet Methylene</td>
<td></td>
</tr>
<tr>
<td>Ph_3(PPhCH_2)P^+</td>
<td>Cl</td>
<td>5-80</td>
<td>5-40</td>
<td>5-40</td>
<td></td>
<td>Doublet Methylene</td>
<td></td>
</tr>
<tr>
<td>Ph_3(PPhCH_2)P^+</td>
<td>Cl</td>
<td>5-80</td>
<td>5-80</td>
<td>5-80</td>
<td></td>
<td>Doublet Methylene</td>
<td></td>
</tr>
<tr>
<td>Ph_3(PPhCH_2)P^+</td>
<td>Cl</td>
<td>6-34</td>
<td>6-36</td>
<td>5-87</td>
<td></td>
<td>Broad multiplet</td>
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</tr>
<tr>
<td>Ph_3(PPhCH_2)P^+</td>
<td>Cl</td>
<td>8-71</td>
<td>8-78</td>
<td>8-20</td>
<td>2</td>
<td>Multiplet</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) See configuration (II). \(^\dagger\) Measured in D_2O. \(^\ddagger\) Measured in D_2O. \(^\ast\) From double-resonance experiments to be overlapping doublet of doublets.

**Table 2**

<table>
<thead>
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<tr>
<td>5-80 H(1)</td>
<td>( \tau ) 5-80</td>
<td>H(1)</td>
<td>No change</td>
</tr>
<tr>
<td>5-80 H(1)</td>
<td>( \tau ) 6-34</td>
<td>H(2), H(6)</td>
<td>Doublet</td>
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</tr>
<tr>
<td>5-80 H(1)</td>
<td>( \tau ) 6-34</td>
<td>H(5)</td>
<td>No change</td>
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<tr>
<td>4-78 H(2)</td>
<td>( \tau ) 5-80</td>
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<tr>
<td>4-78 H(2)</td>
<td>( \tau ) 5-80</td>
<td>H(1)</td>
<td>No change</td>
</tr>
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<td></td>
<td>( \tau ) 6-34</td>
<td>H(4)</td>
<td>No change</td>
</tr>
</tbody>
</table>

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is not understood at present. The extra carbonyl group may arise from the solvent (cf. the synthesis of [Ru(H)Cl(CO)(PPh₃)₃]¹²) or from some intramolecular rearrangement process. It is of interest that Robinson and Wilkinson⁸ also isolated a dicarboxyl complex trans-[RuCl₂(CO)₂(quinoline)]₇ by reaction of [RuCl₂CO(C₇H₈)]₈ with an excess of quinoline in ethanol.

EXPERIMENTAL

Microanalyses were undertaken by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4000–200 cm⁻¹ on a Perkin-Elmer grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. ¹H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable temperature probe. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Benzyl(triphenyl)phosphonium (Bicyclo[2.2.1]hepta-2,5-diene)carbonylirichlororuthenate(tl).—A suspension of the complex [RuCl₂CO(C₇H₈)]₈ (ref. 6) (0.40 g) was shaken in degassed acetone (50 cm³) for 5 days with an excess of benzyl(triphenyl)phosphonium chloride (1.0 g) and concentrated hydrochloric acid (0.50 cm³). The resulting orange solid was filtered, washed free of acid and excess of benzyl(triphenyl)phosphonium chloride with warm water, then with acetone, and recrystallized from dichloromethane-heptane (62%). m.p. 178–180 °C (Found: C, 57.8; H, 4.4; Cl, 15.8; O, 2.5; P, 4.7). Calc. for C₅₄H₉₁ClO₄Ru: C, 58.2; H, 4.5; Cl, 15.5; O, 2.4; P, 4.6%. Δ(0-001m) 16-5 Ω cm² mol⁻¹ in CH₂Cl₂. Far i.r. spectrum (400–200 cm⁻¹): 3850; 3502; 3300; 3142; 3032; 2832; 2682; 2502; 2242, and 2024 cm⁻¹.

Benzyl(triphenyl)phosphonium (Bicyclo[2.2.1]hepta-2,5-diene)tribromoacarbonylruthenate(tl).—The salt Ph₃P[Br₂Ru₂CO(C₇H₈)]₁₂ (0.20 g) was suspended in degassed acetone (100 cm³) and shaken for ca. 6 h with an excess of lithium bromide (1.20 g). The resulting brown solution was concentrated to dryness, the residual solid leached with dichloromethane, and the unreacted lithium bromide filtered off. The brown solution, now free of lithium bromide, was concentrated to dryness and acetonitrile–diethyl ether addition then gave a brown microcrystalline solid (85%). m.p. 162 °C (Found: C, 48.4; H, 3.6; Br, 29.7. Calc. for C₃₃H₂₆Br₂OPRu: C, 48.7; H, 3.6; Br, 29.5%). Δ(0-001m) 25-4 Ω cm² mol⁻¹ in CH₂Cl₂. Far i.r. spectrum (400–200 cm⁻¹): 3850; 3502; 3300; 3182; 3032; 2812; 2692; 2552; 2492; 2252, and 2034 cm⁻¹.

Caesium (Bicyclo[2.2.1]hepta-2,5-diene)carbonylirichlororuthenate(tl).—A suspension of the complex [RuCl₂CO(C₇H₈)]₈ (0.50 g) was shaken with an excess of caesium chloride (1.0 g) and concentrated hydrochloric acid (0.50 cm³) in degassed acetone (50 cm³) for 6 days. The resulting yellow powder was decanted from the unreacted caesium chloride, filtered, washed with acetone, and recrystallised from hot methanol to give a yellow powder (80%). m.p. ca. 270 °C (decomp.) (Found: C, 21.2; H, 1.8; Cl, 22.8; O, 3.4. Calc. for Cs₂H₂₆Cl₂OPRu: C, 20.9; H, 1.8; Cl, 23.1; O, 3.5%). Δ(0-001m) 87-2 Ω cm² mol⁻¹ in methanol. Far i.r. spectrum (400–200 cm⁻¹): 3262; 2802; and 2602 cm⁻¹.

Bis(tetraphenylarsonium) cis-Dicarboxyltetrachlororuthenate(tl).—The complex [RuCl₂CO(C₇H₈)]₈ (0.23 g) was heated under reflux gently, under an atmosphere of nitrogen, in degassed acetone (50 cm³) with an excess of Ph₃AsCl·HCl (0.97 g) for ca. 1 h. The solution was filtered and then concentrated to dryness. The residue was washed with water to remove unreacted Ph₃AsCl and the yellow solid recrystallised from dichloromethane–light petroleum (b.p. 60–80 °C) (Found: C, 54.2; H, 3.7; Cl, 14.1. Calc. for C₄₅H₃₃ClO₄Ru·Ph₃As: C, 56.3; H, 3.7; Cl, 13.9%).

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New Thiocarbonyl Complexes of Ruthenium

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New Thiocarbonyl Complexes of Ruthenium

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Reaction of the complex [RuCl₂(CS)(PPPh₃)]₂⁺ (I), with MCl-HCl in acetone leads to chloride-bridge cleavage with formation of M[RuCl₂(CS)(PPPh₂)] (M = Ph₅As⁺, Ph₅P(CH₃)₃⁺, or Et₅N⁺) (II). A reinvestigation of the reaction between the complex [RuCl₂(PPPh₃)] and CS₂ reveals that, in addition to the previously reported [RuCl₂(μ-CS₄)] (PPPh₃)⁺ and (I), another thiocarbonyl complex (III), with very similar physicochemical properties to (I) is also formed. A full analytical data and 'H n.m.r. studies, together with an X-ray crystallographic study, show that complex (III) is the tri-µ-chloro-species (PPPh₃)₂Cl[RuCl₂(CS)(PPPh₃)] (IV). Although no evidence has been found for conversion of complex (I) into (III), prolonged shaking of an acetone solution of (I) gives a small amount of ([PPPh₃(CS)]Cl[RuCl₂(CS)(PPPh₃)]₂ Me₂CO, (IV). Reaction of complex (III) with concentrated hydrochloric acid gives paramagnetic ([PPPh₃]Cl[RuCl₂(CS)(PPPh₃)]₂ Me₂CO (V), which contains ruthenium in formal oxidation states of (II) and (II).

There are a large number of publications discussing syntheses and characterisation of neutral complexes of ruthenium(n), particularly those with ligands such as tertiary phosphines, carbonyl, and various organic molecules. Recent years have also produced an increasing amount of work on cationic ruthenium(n) complexes containing these types of ligands. However, relatively few anionic ruthenium(n) complexes of this type have been prepared other than those containing nitrosyl and, more recently, carbonyl groups, e.g. [RuX₄(CO)₆]⁻, [RuX₄(μ-C≡C)₃]⁻ and [RuX₄(μ-C≡N)]⁻ (X = Cl, Br, or I). In particular, only three papers on anionic tertiary phosphine (or phosphite) complexes of ruthenium(n) appear to have been published, none of which involve 'conventional' methods of preparation; e.g. the well known complex [RuCl₂(CS)]Cl and on heating in methyl acetate at 60 °C, gives [RuCl₂(CS)]Cl₂ [RuCl₂L₂] (L = P(OMe)₂Ph). Similar diamagnetic complexes have been reported for the ligands L = P(OEt)₂Ph, P(O(OMe)₂Ph, and P(O(OMe)₂Ph, obtained by direct reaction of RuCl₃ with L (although the authors inadvertently formulated them as [RuCl₂L₂]⁻, which would be paramagnetic). A recent note gives the results of a reinvestigation of the reaction between the complex [Ru(CO)₄(PPPh₃)] and methyl iodide which, instead of the previously reported [Ru(CO)₄(PPPh₃)I(μ-Me)], gives PPPh₃-Me[Ru(CO)₄(PPPh₃)]. This same anionic complex can be made from [Ru(CO)₄(PPPh₃)] and methyl iodide.

Several years ago, one of us reported that a convenient synthesis of the ruthenium(III) anions [RuCl₂L₂]⁻ (X = Cl or Br; L = PPPh₃, AsPh₃, etc.) was through methanol displacement by halide ion from the complex [RuCl₂L₂MeOH].Similar ruthenium(III) anions with L = pyridine (py), or aniline or L₄ = ethylenediamine (en), 2,2'-bipyridyl (bipy), and o-phenylenebis(dimethylamine) are also known. Unfortunately, our attempts to prepare the corresponding [RuX₄(PPPh₃)]⁺ ions by reaction of [RuX₄(PPPh₃)] or with Ph₅AsX-HX also gave [RuX₄(PPPh₃)]⁻. The detailed mechanism of this apparent oxidation on addition of hydrogen halides is not known at present although a ruthenium(tetra)hydrido-bridge or complex is by cleavage of halide-bridged dimeric species with halide ion, e.g. as in equation (I). We have recently reported the use of this type of reaction to synthesise the first anionic ruthenium diene complexes [RuX₄(CO)(C₅H₅)]⁻ (X = Cl or Br; C₅H₅ = bicyclo[2.2.2]dicarboxylic-2,5-diene) via [RuX₄(CO)(C₅H₅)]⁺. These complexes are very useful precursors for the preparation of a range of new anionic complexes of type [RuX₄CO₃]⁻ (L = AsPh₃, SbPh₃, py, Me₂S, CH₂CCHN, etc.), although, to date, attempts to prepare tertiary phosphine anions by this method have been unsuccessful; instead complexes such

as [RuCl₂CO(PPh₃)₂] and [RuCl₂(PMe₃Ph)₃(C₆H₄)] are preferentially formed.\(^\text{19}\) However, another halide-bridged dimer already containing triphenylphosphine groups is [RuCl₂(CS)(PPh₃)₂]₂ (I), prepared by Gilbert \textit{et al.} from [RuCl₂(PPh₃)_₃] and CS₂.\(^\text{20}\) In the present paper, reactions of complex (I) with halide ion are described, together with results of a careful reinvestigation of the [RuCl₂(PPh₃)_₃]-CS₂ reaction. A preliminary account of the first part of this work has been presented elsewhere.\(^\text{21}\)

**RESULTS AND DISCUSSION**

In accordance with the method of Gilbert \textit{et al.}\(^\text{20}\) the complex [RuCl₂(PPh₃)_₃] \(^\text{22}\) in carbon disulphide was heated under reflux an atmosphere of nitrogen for 5 min to give a deep red solution. After cooling the solution, filtration gave a small amount of a dark red, crystalline, solid readily identified as [RuCl₂(CS)(PPh₃)₂]. The red filtrate was concentrated in vacuo and then treated with excess of diethyl ether, giving a purple-red precipitate and red ethereal solution. The precipitate was well washed with diethyl ether and dried in vacuo (ca. 16% yield). This precipitate is almost certainly a sample of the complex [RuCl₂(CS)(PPh₃)_₂], (I), as established by full elemental analyses (C, H, P, Cl, and S) and osmometric molecular-weight measurement in benzene (see Experimental section). Furthermore, in agreement with the data in ref. 20, it is diamagnetic, non-conducting (in CH₂Cl₂), completely soluble in benzene, dichloromethane, and chloroform, and acetone, and, although quite air stable in the former, rapidly turns greenish brown in acetone solution. Its i.r. spectrum ν(CS) at 1290 cm⁻¹ and m.p. (165—166 °C (decomp.)) were very similar to those reported earlier.

When complex (I) was dissolved in degassed acetone and shaken under an atmosphere of nitrogen with excess of Ph₃AsCl.HCl for several days, slow conversion to a red crystalline precipitate of Ph₃As[RuCl₂CS(PPh₃)₂].2Me₂CO (II), occurred. The same anion was obtained by using either benzyltriphenylphosphonium chloride or tetraethylammonium chloride together with concentrated hydrochloric acid. In the absence of acid, no reaction occurred. These diamagnetic complexes are 1:1 electrolytes (CH₂Cl₂) and i.r. spectra show characteristic cation bands, triphenylphosphine, and a thioacetylonyl band at 1272 cm⁻¹ (Nujol). Although they are not sufficiently

\* In ref. 20 the word ether is used which we have taken to mean diethyl ether, not light petroleum.


[Diagram]

At this juncture, the only discrepancy with the work of Gilbert \textit{et al.} was our consistently low yield of complex (I) (16 as against 70% in ref. 20). Therefore, in order to remedy this, we removed most of the solvent from the red ethereal solution and added excess of light petroleum (b.p. 60—80 °C), which gave a pinkish red precipitate, (III) (ca. 40% yield). The same material was obtained in a more crystalline form (maroon red) when the ethereal solution was set aside for ca. 15 min. Both samples were then insoluble in diethyl ether. At first sight complex (III) appeared identical to the initial precipitate (I). Thus, the complex is diamagnetic, non-conducting (CH₂Cl₂), completely soluble in benzene, dichloromethane, and chloroform, analyses closely for [RuCl₂(CS)(PPh₃)_₂] (C, H, P, and Cl), and is dimeric in benzene. The complex melts at 167—168 °C and its i.r. spectrum is virtually identical to (I) except that ν(CS) occurs at 1284 cm⁻¹ and there are slight differences below 400 cm⁻¹ (see Experimental section).

However, closer examination revealed that (I) and (III) were not the same complex. Thus, benzene or chloroform solutions of complex (III) rapidly darkened when exposed to air. Furthermore, complex (III), although transiently soluble in acetone, rapidly precipitated from this solution as an acetone solvate ν(CO) 1705, ν(CC) 1221 cm⁻¹. Sulphur analyses on complex (III) consistently gave values 50% lower than found for (I); \(^{31}\)P n.m.r. studies revealed that (I) and (III) had quite different spectra and, finally, reaction of (III) and Ph₃AsCl.HCl did not give Ph₃As[RuCl₂CS(PPh₃)₂]. It is interesting to note that when light petroleum (b.p. 60—80 °C) was used instead of diethyl ether as precipitating solvent, both complexes (I) and (III) were immediately precipitated \(^{31}\)P n.m.r. evidence and were readily separated by a few minutes shaking in degassed acetone.

By means of the liquid-diffusion method\(^\text{24}\) using a dichloromethane-acetone solvent, crystals of complex (III) were obtained suitable for X-ray analysis. This structure determination, which is reported in full in the following paper\(^\text{25}\) has unequivocally established that


complex (III) has the molecular composition \([\text{PPh}_3\)ClRuCl_2Ru(CS)][\text{PPh}_3\)Cl], i.e. a tri-\(\mu\)-chloro-complex with one CS group. This formulation is consistent with the analytical data and \(^{31}\text{P}\) n.m.r. spectrum. The spectrum shown in the Figure can be readily interpreted as two AB quartets centred at 48.3 and 36.1 p.p.m. In contrast, the \(^{31}\text{P}\) n.m.r. spectrum of complex (I) in \(\text{C}_8\text{H}_8\cdot\text{C}_6\text{D}_5\) consisted of a strong singlet at 24.4 p.p.m. and a weak singlet at 31.3 p.p.m. which disappeared when the solution was set aside for several days. In CDCl_3, the singlet at 31.3 p.p.m. was more intense. A possible explanation of these observations is formation of two isomers (Ia) and (Ib) with the \textit{trans}-form favoured in benzene and the \textit{cis} form in chloroform. Irrespective of the detailed interpretation of these observations, the similarity in position of the higher-field quartet in complex (III) with the strong singlet of (I) in CDCl_3 suggests that this quartet arises from the PPh_3 groups numbered (3) and (4) which are \textit{cis} to the thiocarbonyl group.

Complex (III) represents another example of the increasing number of ruthenium complexes which contain a RuCl_2Ru bridging unit. Earlier examples are \([\text{L}_2\text{RuCl}_2\text{RuL}_2]\)Cl (L = \text{PET}_{2}\text{Ph}, etc.) \(^7\) (although this structure has not been verified by X-ray analysis), \([\text{RuCl}_2\text{L}_2][\text{RuCl}_2\text{L}_2]\) (L = \text{PET}_{2}\text{Ph}), \(^8\) \([\text{PET}_{2}\text{Ph})\text{ClRuCl}_2\text{Ru(PET}_{2}\text{Ph})\) made by heating \([\text{RuCl}_2\text{(PET}_{2}\text{Ph})\)Cl in methyl acetate at 120 °C, \(^9\) and the paramagnetic \([\text{FBu}_{3}^\text{a}[\text{ClRuCl}_2\text{RuCl(PBu}_{3}^\text{a})]\) made from RuCl_3 and PBu_3. \(^3,27\) A very recent example is the complex \([\text{PP}_{3}\)ClRuCl_2Ru(\text{N}_{3})(\text{PP}_{3})\) made from \([\text{RuCl}_2\text{PP}_{3})\) \(^22\) and molecular nitrogen by the novel technique of reverse osmosis. \(^28\) and closely related examples are \([\text{PP}_{3}\)ClRuCl_2Ru(\text{N}_{3}\text{PET}_{2}\text{HSM}_{3})\text{PP}_{3})\) \(^29\) and \([\text{CO}_{2}\text{SnCl}_{4}\text{ClRuCl}_2\text{Ru(CO}_{2}])\) made from Ru_3(\text{CO})_12 and SnCl_4. \(^30\) Details of the structural relations of (III) to these complexes are presented in the following paper. \(^35\)

It is tempting to speculate that complex (III) is formed via (I) perhaps by intramolecular rearrangement involving displacement of a thiocarbonyl group by chloride ion \([\text{equation (2)}]\). A related rearrangement reaction has been reported by Kang and Maitlis \([\text{equation (3)}]\). \(^31\) A study of the relative yields of complexes (I) and (III) as a function of reaction time would appear at first sight to support this hypothesis. Thus, increasing the time of reaction from 2 to 60 min increased the yield of complex (III) and decreased that of (I). However, further experiments showed that on heating complex (I) under reflux in Cs_2 for up to 10 h, none of the triply bridged species was produced. Similarly, there was no evidence for conversion of complex (I) into (III) in acetone, benzene, or chloroform solutions.

However, when complex (I) was shaken in degassed acetone for several days, a very small amount of golden-

yellow crystals were deposited. The i.r. spectrum of this material showed evidence of solvent acetonitrile, thiocarbonyl (ν(CS) 1300 cm⁻¹), and triphenylphosphine. The far-i.r. spectrum had bands at 326, 288, and 259 cm⁻¹, which may indicate both terminal and bridging chloride ligands, and the complex is diamagnetic (Evans' method). A possible formulation consistent with this evidence and the analytical data is [(PPH₃)₂(Ph₃P)₂(CS)ClRuCl₃Ru(CS)(PPH₃)₂], Me₂CO, (IV) [cf. (PET₃P)₂ClRuCl₃Ru(PET₃P)₂]. The ³¹P n.m.r. spectrum of complex (IV) in CDCl₃ consisted of two strong peaks at 48-1 and 37-7 p.p.m. of relative intensity 1:2.* The positions of these resonances were close to those found for complex (III), thus supporting the proposed formulation. The resonance arising from the two PPH₃ groups was only slightly split in this instance, indicating only a small chemical difference between these two phosphorus atoms, and therefore we tentatively attribute these signals to isomer (IVa). In addition, two other much weaker peaks at 50-2 and 33-5 p.p.m. of relative intensity 1:2 also occurred in some samples. We tentatively attribute these to isomer (IVb) since, in this instance, the more intense resonance appears to exhibit a greater splitting of the central peak compared to that observed for the resonance at 37-7 p.p.m. This suggests a bigger chemical-shift difference between the two phosphorus atoms, which might arise if these atoms were cis to a PPH₃ and Cl (or CS) group respectively (as in complexes (III) and (IVb)) rather than to a Cl and a CS group (as in complex (IVa)). The mechanism of formation of complex (IV) from (I) could involve intramolecular displacement of a PPH₃ group by chloride ion [equation (4)].

At this juncture, it must therefore be concluded that complexes (I) and (III) are probably formed by competing reactions from [RuCl₃(PPH₃)₂] or [RuCl₃(CS)₂].

* Note added in proof: These assignments are supported by the ³¹P n.m.r. spectrum in CDCl₃ at 298 K of the isomorphous [(PPH₃)₂ClRuCl₃Ru(CO)(PPH₃)₂], Me₂CO complex which has two AB quartets centred at 48-0 and 40-3 p.p.m.

It is hoped that current work on the reaction of other [RuX₃(PR₃)₂] (X = Cl or Br; PR₃ = PET₃P, PET₃P, etc.) complexes with CS₂ will help to clarify further the various rearrangement reactions exhibited by this interesting class of compounds.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4000–250 cm⁻¹ on a Perkin-Elmer 225 grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer and ³¹P n.m.r. spectra on a Varian Associates XL100 spectrometer with a 12 in wide gap magnet operating in the pulse and Fourier transform mode at 40-5 MHz. Magnetic susceptibilities

† Note added in proof: This mechanism is supported by the high yield synthesis of [(PPH₃)₂ClRuCl₃Ru(CO)(PPH₃)₂], Me₂CO from reaction of [RuCl₃(CO)(PPH₃)₂] (dmf) and [RuCl₃(PPH₃)₂] (1:1 mole ratio) in acetonitrile dmf = N⁵⁺dimethylformamide).
were measured by Faraday (solid) and Evans' n.m.r. methods (solution).\textsuperscript{23} Conductivity measurements were obtained on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Kölfer hot-stage microscope and are uncorrected.

Ruthenium(II) trichloride trihydrate (Johnson, Matthey Ltd), carbon disulphide (Fisons), tetraphenylarsonium chloride–hydrochloride (Koch-Light), tetraethylammonium chloride (B.D.H.), and benzytritylphosphinophosphine chloride (Alfa Inorganics) were obtained as indicated. The complex [RuCl$_4$(PPh$_3$)$_3$] was prepared as described earlier.\textsuperscript{22}

Reaction of Dichlororotris(triphenylphosphine)rhodium(II) with Carbon Disulphide.—The complex [RuCl$_4$(PPh$_3$)$_3$] (0.19 g) was heated under reflux for 5 min in degassed CS$_2$ (30 cm$^3$) under an atmosphere of nitrogen. The solution was then cooled in ice in a stream of nitrogen. Filtration of the deep red solution gave a red crystalline residue (0.016 g, 8%), m.p. 175–176 °C. This material initially contained some CS$_2$ of solvation [ν(CS$_2$) at 1515 cm$^{-1}$] but this was removed by gentle suction. The product was then identified (i.e. spectrum and analysis) to that reported earlier,\textsuperscript{2} i.e. [RuCl$_4$(PPh$_3$)$_2$(PPh)$_3$]Cl [Found: C, 64.0; H, 4.2. Calc. for C$_{44}$H$_{34}$Cl$_4$P$_4$RuS$_2$: C, 63.8; H, 4.4%].

The remaining red solution was concentrated on a rotary evaporator to ca. 5 cm$^3$ and then treated with excess of diethyl ether to give a microcrystalline purple-red solid and a red solution. The solid was shaken with degassed acetonitrile for ca. 10 min (virtually all soluble), filtered, and the solvent removed. The residue was redissolved in degassed benzene leaving a small undissolved amount of the complex [RuCl$_4$(PPh$_3$)$_3$]Cl (i.e. evidence). Removal of benzene, followed by washing with diethyl ether, then gave di-μ-chloro-bis[chlorotricarbonyl(tetraphenylphosphine)rhodium(II)]-triphenylphosphine)rhodium(II)]-triphenylphosphine)rhodium(II)]-acetone (1, IV). Complex (I) was shaken in degassed acetonitrile for several days to give a very small amount of golden-yellow crystals, m.p. 204 °C (CS$_2$) at 1 300, ν(CO) at 1 700 cm$^{-1}$ [Found: C, 33.5; H, 3.7%].

I.r. spectrum (CDCl$_3$): ν(phenyl) 7.9 (acetone).

Preparations.— Tri-μ-chloro-[chlorotricarbonyl(triphenylphosphine)rhodium(II)]-triphenylphosphine)rhodium(II)]-acetone (1, IV). Complex (I) was shaken in degassed acetonitrile for several days to give a very small amount of golden-yellow crystals, m.p. 204 °C (CS$_2$) at 1 300, ν(CO) at 1 700 cm$^{-1}$ [Found: C, 33.5; H, 3.7%].

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Tri-μ-chloro-[chlorotetraphenylphosphine)rhodium(II)]-triphenylphosphine)rhodium(II)]-acetone (1, IV). Complex (I) was shaken in degassed acetonitrile for several days to give a very small amount of golden-yellow crystals, m.p. 204 °C (CS$_2$) at 1 300, ν(CO) at 1 700 cm$^{-1}$ [Found: C, 33.5; H, 3.7%].

I.r. spectrum (CDCl$_3$): ν(phenyl) 7.9 (acetone).

Finally, the relative percentages of the complexes [RuCl$_4$(PPh$_3$)$_2$(PPh)$_3$]Cl (I) and (III) were dependent on the time of reaction. Thus, after only 2 min, percentage yields were 5, 24, and 50, after 5 min, 8, 16, and 39, and after 60 min, 11, 9, and 47 respectively. This clearly indicates that the yields of C$\equiv$S$_2$ and mono(CS)$_2$ complexes increase with time, whereas that of the bis(CS)$_2$ complex decreases with time.

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I.r. spectrum (CDCl$_3$): ν(phenyl) 7.9 (acetone).
nitrogen. The red precipitate was then collected and washed with small amounts of acidified acetone to remove Ph$_2$PhCH$_2$PCl, then with acetone and pentane, m.p. 190–195 °C, n(CS) at 1 272 cm$^{-1}$ (Found: C, 66-4; H, 4-7. Calc. for C$_{43}$H$_{55}$Cl$_3$P$_3$RuS: C, 65-9; H, 4-7%) [A(10$^{-3}$M) in CH$_2$Cl$_2$ = 20-1 g$^{-1}$ cm$^{-2}$ mol$^{-1}$].

Tetraethylammonium trichlorothiocarboxylbis(triphenylphosphine) ruthenate(II). This complex was prepared as above using excess of Et$_4$NCl and a small amount of conc. HCl (Found: C, 58-1; H, 5-1; N, 1-9. Calc. for C$_{43}$H$_{55}$Cl$_3$NP$_3$RuS: C, 59-6; H, 5-6; N, 1-6%).

We thank Johnson, Matthey Ltd., for generous loans of ruthenium(II1) trichloride, the National Institutes of Health (E. S. S.) and the S.R.C. (P. W. A.), for fellowships, Dr. A. S. F. Boyd, for obtaining $^{31}$P n.m.r. spectra, and the Universities of Newcastle and Dundee, for use of their Faraday balances.

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Preliminary communication

SYNTHESSES OF DI- AND TRI-μ-HALIDE COMPLEXES OF RUTHENIUM(II)-CONTAINING CARBONYL AND TERTIARY PHOSPHINE LIGANDS

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We have recently shown that the reaction of [RuCl₂(PPh₃)₃] and carbon disulphide gives, in addition to the previously reported [1] di-μ-chloro complex [RuCl₂(CS)(PPh₃)₂]₂ (I) and the μ-CS₂ cation [RuCl₂(μ-CS₂)(PPh₃)₂]Cl (II), the tri-μ-chloro complex [(PPh₃)₂ClRuCl₃Ru(CS)(PPh₃)₂] (III) which has been characterised by X-ray analysis [2] and ³¹P NMR studies. Initially, it was thought that (III) was probably formed from (I) by an intramolecular transfer of chloride ion accompanied by displacement of a thiocarbonyl group (eqn. 1), but attempts to carry out this conversion under the conditions of the original reaction were unsuccessful.

\[
\begin{align*}
\text{[RuCl}_2\text{(CS)(PPh}_3\text{)}_2\text{]} & \xrightarrow{\Delta} \text{[RuCl}_2\text{Cl}_2\text{RuCl}_3\text{Ru(CS)(PPh}_3\text{)}_2\text{]} + \text{CS} \\
\text{(I)}
\end{align*}
\]

Therefore, a speculative mechanism was suggested which involved formation of [RuCl₂(CS)(PPh₃)₂] (probably via abstraction of Ph₃PS from (II)) and then, either dimerisation of this five coordinate intermediate to give (I) or combination with some unreacted [RuCl₂(PPh₃)₃]⁺ to give (III) (eqn. 2).

Although this latter mechanism is difficult to verify for the thiocarbonyl compounds, we have now obtained good evidence for the feasibility of such a mechanism by synthesis of the corresponding carbonyl complexes by this method.

Thus, if the recently reported [RuCl₂CO(PPh₃)₂] (ν(CO) 1911 cm⁻¹; dmf = N,N'-dimethylformamide) [4] is gently refluxed in dichloromethane,

*Recent ³¹P NMR studies of this compound in this and other laboratories (S. Cenini, private communication) show that in the complete absence of oxygen, this compound is not dissociated in solution but when traces of oxygen are present, free triphenylphosphine oxide is rapidly produced.
dimerisation occurs to give the pale orange [RuCl\(_2\)(CO)(PPh\(_3\))\(_2\)]\(_2\) (I, Y = CO) (\(\nu\)(CO) 1960 (br) cm\(^{-1}\)) whereas if the dmf complex is refluxed with [RuCl\(_2\)-(PPh\(_3\))\(_3\)] in acetone (1/1 molar ratio), red crystals of the tri-\(\mu\)-chloro complex [(PPh\(_3\))\(_2\)ClRuCl\(_3\)Ru(CO)(PPh\(_3\))\(_2\)] (III, Y = CO) (\(\nu\)(CO) 1951 cm\(^{-1}\)) are formed. This latter compound is isomorphous with the corresponding thiocarbonyl complex and the \(^{31}\)P proton decoupled NMR spectra in CDCl\(_3\) which consists of two AB quartets centred at 48.0* and 40.3 ppm. (Y = CO) and 48.3 and 36.1 ppm (Y = CS) respectively confirm that the same structure is retained in solution.

The tri-\(\mu\)-bromo complex can be similarly prepared from [RuBr\(_2\)(PPh\(_3\))\(_3\)] and [RuBr\(_2\)CO(PPh\(_3\))\(_2\)dmf] and by reaction of 1/1 molar mixtures of [RuCl\(_2\)CO-(PPh\(_3\))\(_2\)dmf]/[RuBr\(_2\)(PPh\(_3\))\(_3\)] and [RuBr\(_2\)CO(PPh\(_3\))\(_2\)dmf]/[RuCl\(_2\)(PPh\(_3\))\(_3\)] respectively, the mixed tri-\(\mu\)-halide complexes [(PPh\(_3\))\(_2\)BrRuBrCl\(_2\)Ru(CO)(PPh\(_3\))\(_2\)] and [(PPh\(_3\))\(_2\)ClRuClBr\(_2\)Ru(CO)(PPh\(_3\))\(_2\)] are readily isolated. Preliminary work indicates that such coupling reactions can also be used to synthesise mixed tertiary phosphine complexes e.g. [(PPh\(_3\))\(_2\)ClRuCl\(_3\)Ru(CO)(PET\(_2\)Ph\(_2\))] from [RuCl\(_2\)(PPh\(_3\))\(_3\)] and [RuCl\(_2\)CO(PET\(_2\)Ph\(_2\))dmf].

Therefore, this work provides both an independent verification of the proposed mechanism of formation of the thiocarbonyl compounds described in ref. 3 and also a general route to the preparation of a wide range of binuclear metal compounds with different bridging and terminal ligands and probably even different metal ions.

Acknowledgement

We thank Johnson—Matthey Ltd, for loans of ruthenium trichloride, the S.R.C. for a research studentship (to P.W.A.) and Dr. A.S.F. Boyd for measuring the \(^{31}\)P NMR spectra.

*Chemical shifts are reported in ppm to high frequency of 85% H\(_3\)PO\(_4\).*
References

Reaction of Benzyltriphenylphosphonium Bicyclo[2.2.1]hepta-2,5-diene-carbonyltrichlororuthenate(II) with Lewis Bases ¹

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Reaction of Benzyltriphenylphosphonium Bicyclo[2.2.1]hepta-2,5-diencarbonyltrichlororuthenate(II) with Lewis Bases

By Lena Ruiz-Ramírez and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

A detailed investigation of the reactions of the salt \([\text{Ph}_3\text{P}(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(\text{C}_7\text{H}_8)]\) (I; \(\text{C}_7\text{H}_8 = \text{bicyclo}[2.2.1]-\text{hepta}-2,5\)-diene) with ligands \(L\) containing Group Vb or Vla donor atoms is presented. Several different types of behaviour are found, depending on both the nature and amount of added \(L\). For \(L = \text{Me}_2\text{S}, \text{Me}_2\text{SO}, \text{and CH}_2\text{=CH-CN}, \) the salts \([\text{Ph}_3\text{P}(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})L_4]\) (II), have been isolated in high yield, whereas for \(L = \text{AsPh}_3, \text{SbPh}_3, \) and \(\text{C}_5\text{H}_5\text{N}, \) a mixture of (II) and \([\text{RuCl}_3(\text{CO})L(\text{C}_7\text{H}_8)]\) (III), have been obtained \((I): L = 1\text{:}2\) molar ratio. Reaction of complex (I) with excess of \(\text{SbPh}_3\) gives (II), (III), and \([\text{RuCl}_3(\text{CO})(\text{SbPh}_3)_2]\) (IV). In contrast, reaction of complex (I) with \(\text{PPh}_3\) (1:2 molar ratio) gives \([\text{RuCl}_3(\text{CO})(\text{PPh}_3)_2]_2\) (V), whereas with \(\text{PMe}_3\text{Ph}, \) only \([\text{RuCl}_3(\text{PMe}_3\text{Ph})_2(\text{C}_7\text{H}_8)]\) (VI), is isolated. A similar complex of type (VI) is formed with \(\text{PMe}_3\text{Ph}, \) together with some \([\text{RuCl}_3(\text{CO})(\text{PMe}_3\text{Ph})_2]_2\) (IV), whilst with 2,2'-bipyridyl or 1,10-phenanthroline (\(L'\)), the complexes \([\text{RuCl}_3(\text{CO})(L')]_2\) (VII), and \([\text{Ph}_3\text{P}(\text{PhCH}_2)\text{P}][\text{RuCl}_3(\text{CO})(L')]\) (II), are obtained. Reaction mechanisms consistent with this observed variation in product composition are tentatively proposed.

Recently we reported the synthesis and characterisation of the first anionic diene complexes of ruthenium(II), \(\text{M[RuX}_3(\text{CO})(\text{C}_7\text{H}_8)]\) \((\text{M} = \text{Ph}_3\text{P(PhCH}_2)\text{P}^+ \text{or Cs}^+; \text{X} = \text{Cl or Br}; \text{C}_7\text{H}_8 = \eta_7\text{-bicyclo}[2.2.1]\text{hepta}-2,5\)-diene (norbornadiene)). \(^3\) Earlier workers, particularly in rhodium chemistry, have shown that olefin compounds are often

\(^{1}\) Preliminary communication. L. Ruiz-Ramírez, T. A. Stephenson, and E. S. Svitkis, *J. Organometallic Chem.* 1973, 49, C77.

very useful precursors for the synthesis of a range of complexes by substitution of the olefin groups. In view of the small amount of published work on convenient methods of synthesising anionic ruthenium(ii) complexes with ligands containing Group Vb and VIb donor atoms, we have undertaken a detailed study of the reactions of \( \text{Ph}_{2} \text{P} \text{HPhCH}_{2} \text{P} \text{[RuCl}_{6} \text{(CO)} \text{(C}_{2} \text{H}_{4}) \text{]} \) (I), with such ligands (L), in an attempt to obtain these complexes. However, several different types of behaviour are found experimentally, depending on the nature and amount of ligand used in these attempted exchange reactions. The different types of product are first described and then reaction mechanisms consistent with this observed variation are tentatively proposed.

RESULTS

When the complex \( \text{Ph}_{2} \text{P} \text{HPhCH}_{2} \text{P} \text{[RuCl}_{6} \text{(CO)} \text{(C}_{2} \text{H}_{4}) \text{]} \) (I), was dissolved in dichloromethane and heated under reflux under a nitrogen atmosphere with either \( \text{Me}_{3} \text{S} \), \( \text{Me}_{2} \text{SO} \), or \( \text{CH}_{2} \text{═CH-CN} \) \( \text{(I): L = 1:2 molar ratio} \) for ca. 12 h, complete displacement of the diene group occurred and yellow or orange crystalline complexes \( \text{Ph}_{2} \text{P} \text{HPhCH}_{2} \text{P} \text{[RuCl}_{6} \text{(CO)} \text{(L)} \text{]} \) (II), were isolated from the reaction mixture.

\[
\begin{align*}
\text{(IIa)} & \quad \text{L = Me}_{2} \text{S}, \text{Me}_{2} \text{SO}, \text{CH}_{2} \text{═CH-CN} \quad \text{AsPh}_{3}, \text{SbPh}_{3} \quad \text{or} \quad \text{C}_{5} \text{H}_{5} \text{N} \\
\text{(IIb)} & \quad \text{L = Me}_{2} \text{S}, \text{Me}_{2} \text{SO}, \text{CH}_{2} \text{═CH-CN} \quad \text{AsPh}_{3}, \text{SbPh}_{3} \quad \text{or} \quad \text{C}_{5} \text{H}_{5} \text{N} \\
\text{(IIc)} & \quad \text{L = Me}_{2} \text{S}, \text{Me}_{2} \text{SO}, \text{CH}_{2} \text{═CH-CN} \quad \text{AsPh}_{3}, \text{SbPh}_{3} \quad \text{or} \quad \text{C}_{5} \text{H}_{5} \text{N}
\end{align*}
\]

in 75—80% yield on addition of diethyl ether. For \( \text{L = Me}_{2} \text{S} \), the \( \text{H} \) n.m.r. spectrum (methyl region) consisted of a strong singlet at \( \tau = 7.37 \) together with very weak doublets \( \text{(ca. 5 Hz separation) centred at} \ = 6.58 \text{ and 7.37}. \text{There are three geometrical isomers possible for} \) (II) and the strong signal at \( \tau = 7.37 \) could be assigned to isomer (IIa) or (IIb) and the weaker ones to the presence of a small amount of isomer (IIc) (assuming restricted rotation of the methyl groups at 300 K). For \( \text{L = Me}_{2} \text{SO} \), the \( \text{H} \) n.m.r. spectrum revealed a strong singlet at \( \tau = 6.72 \) [attributed to isomer (IIa) or (IIb)] and weak signals at \( \tau = 6.80 \text{ and 7.36}. \text{The highest-field signal corresponds to free Me}_{2} \text{SO and the others to S-bonded Me}_{2} \text{SO} \) (cf. *).

* This assignment is based on the assumption that the cis-influence of CO produces a lower-field shift of the carbon atoms (1), (2), and (6) than that of chloride ion on (3), (4), and (5). This assumption is also made in ref. 2 for the \( \text{H} \) n.m.r. spectrum.

\[ 4 \]


\[ \text{RuX}_{2} \text{[Me}_{2} \text{SO}_{2}] \] (refs. 5 and 6). The i.r. spectrum of this complex showed a strong band at 1113 cm\(^{-1}\) assigned to \( \text{S}-\text{bonded Me}_{2} \text{SO} \), but no bands which can be attributed definitely to \( \text{O}-\text{bonded Me}_{2} \text{SO} \). The absence of the latter was confirmed by synthesis of the complex \( \text{Ph}_{2} \text{P} \text{HPhCH}_{2} \text{P} \text{[RuCl}_{6} \text{(CO)} \text{(L)} \text{]} \) \( \text{(II): L = 2,2'-bipyridyl or 1,10-phenanthroline (see later)} \) suggests that (IIa) is the most probable structure. This isomeric form is also consistent with that established for complex (I) by \( \text{H} \) (ref. 2) and \( \text{C}^{13} \) c.m.r. studies. The latter shows diene resonances at \( 77-10, 64-84, 60-92, 50-90, \) and 48-22 p.p.m., assignable to carbon atoms (2) and (6), (3) and (5), (7), (1), and (4) respectively. * In attempts to extend the range of complexes (II), ligands such as \( \text{Et}_{2} \text{S}, \text{Ph}_{2} \text{S}, \text{CS}_{2}, \text{MeCN}, \text{PhCH}_{2} \text{CN}, \) and PhCN were reacted under the same conditions with (I), but in all cases (I) was recovered unchanged. However, with \( \text{L = AsPh}_{3}, \text{SbPh}_{3}, \text{or} \text{C}_{5} \text{H}_{5} \text{N} \) \( \text{(I): L = 1:2 molar ratio, reaction in CH}_{2} \text{Cl}_{2} \) for 12 h, followed by addition of diethyl ether, also gave the complexes \( \text{Ph}_{2} \text{P} \text{HPhCH}_{2} \text{P} \text{[RuCl}_{6} \text{(CO)} \text{(L)} \text{]} \) (II), but with yields of only 18—25%. In this instance, treatment of the ether filtrate with pentane gave further yellow precipitates (60% yield). These were non-electrolytes containing CO, L, and \( \text{C}_{5} \text{H}_{5} \text{N} \) \( \text{groups (I) and results of i.r. and c.m.r. analyses and molecular-weight determinations indicated the composition} \text{[RuCl}_{6} \text{(CO)} \text{(L)} \text{]} \text{(III). There are three geometrical isomers possible for (III). The H n.m.r. spectra of all these complexes [Figure 1 (L = AsPh}_{3} \text{and Table I) consisted of seven diene resonances at relative intensities 1:1:1:1:1:1:2. This clearly eliminates isomer (IIIa), only one diene resonance should be observed. Homonuclear-decoupling experiments for L = AsPh}_{3} \text{indicated that only the resonance at} \text{r = 6.34} \text{is coupled to the resonances at} \text{r = 6.50} \text{and 6.82 and that at r = 7.92 is coupled to the peak at} \text{r = 4.25} \text{. The signals at r = 5.92 and 5.70 are too close for decoupling studies. This information, plus the assumption that the cis- and trans-influences of L and CO respectively (or} \text{vice versa}) \text{produce lower-field shifts than those of chloride ion, leads to the tentative assignments given in Table I. Unfortunately, it is not possible to distinguish between isomer (IIIa) and (IIIb) on this evidence, even by careful comparison of} \text{H} \text{n.m.r. spectra of complexes with different L groups, because of the lack of information concerning the relative magnitudes of such variables as cis-influence, trans-influence, ring-current effects,} \text{etc., of the other ligands on the chemical shifts of the diene protons. However, the similarity in position of the diene resonances for all these complexes, together with the similar position of} \text{w}_{\text{CO}} \text{in each case (ca. 2000 cm}^{-1}\text{), suggests that the same isomer is always produced. On leaving the} \]
complex [RuCl₂(CO)(AsPh₃)(C₆H₆)] in CDCl₃ for 48 h. Additional resonances appeared at \( \tau \) 3.25, 6.43, and 8.04 corresponding to free norbornadiene. This indicates that dissociation of the diene group in complexes (III) occurs slowly in solution and that intermolecular exchange between free and bound diene is negligible at ambient temperatures.

When complex (I) was refluxed with excess of SbPh₃ in CH₂Cl₂, the orange-red complex [RuCl₂(CO)(SbPh₃)], (IV) (\( \nu_{90} \) at 1948 cm⁻¹), was isolated, together with small amounts of (II) and (III). An orange-brown isomer of (IV) has been reported earlier (\( \nu_{90} \) at 1941 cm⁻¹) and was obtained by direct reaction of SbPh₃ with an ethanolic 'carbonyl-containing' ruthenium solution.⁷ Comparison of far-i.r. spectra indicates \( \nu_{90} \) at 320 cm⁻¹ for the orange-brown isomer and <300 cm⁻¹ for the orange-red isomer. This evidence, together with the similarity of the \( \nu_{90} \) positions to those of the two isomers established by \(^1\text{H} \) n.m.r. methods for the complex [RuCl₂(CO)(PMe₂Ph₃)].⁸ suggests that the orange-red isomer has configuration (IVa) and the other has configuration (IVb).

For \( L = \text{PPh}_3 \), reaction with complex (I) in CH₂Cl₂ [(I) : \( L = 1 : 2 \) molar ratio] gave a non-conducting, dimeric, orange complex analysing closely for [RuCl₂(CO)(PPh₃)₄].

*Added in proof:* However, this complex has now been synthesised by reaction of [RuCl₂(CO)(PPh₃)₄(dmf)] and [RuCl₂(PPh₃)₆] (1:1 molar ratio) in acetone (dma = NN-dimethylformamide).

(IV) A similar complex ([RuCl₂(CO)(PPh₃)]₄) has been obtained by reaction of [RuCl₂(PMe₂Ph₃)] with butyraldehyde.⁹ The i.r. spectrum of complex (V) showed several carbonyl bands (2029, 1934, 1969, 1905 cm⁻¹) indicative of a mixture of isomers. The \(^{31}\text{P} \) n.m.r. spectrum of this material, which contained a number of peaks, is consistent with this interpretation. Recrystallisation from dichloromethane–pentane gave a product still analysing for

<table>
<thead>
<tr>
<th>L = AsPh₃, SbPh₃ or C₆H₆N</th>
<th>L = SbPh₃</th>
<th>L = C₆H₆N</th>
<th>Rel. intensity</th>
<th>Fine structure</th>
<th>Assignment</th>
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<tr>
<td>4.25</td>
<td>4.29</td>
<td>4.35</td>
<td>1</td>
<td>Triplet⁺</td>
<td>( H_4 )</td>
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<tr>
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<td>4.46</td>
<td>4.53</td>
<td>1</td>
<td>Triplet⁺</td>
<td>( H_3 )</td>
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<tr>
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<td>5.05</td>
<td>5.10</td>
<td>1</td>
<td>Triplet⁺</td>
<td>( H_3 )</td>
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<tr>
<td>5.50</td>
<td>5.52</td>
<td>5.57</td>
<td>1</td>
<td>Triplet⁺</td>
<td>( H_3 )</td>
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<tr>
<td>5.92</td>
<td>5.85</td>
<td>5.97</td>
<td>1</td>
<td>Multiplet</td>
<td>( H_4 )</td>
</tr>
<tr>
<td>6.34</td>
<td>6.45</td>
<td>6.65</td>
<td>1</td>
<td>Multiplet</td>
<td>( H_4 )</td>
</tr>
<tr>
<td>8.57</td>
<td>8.50</td>
<td>8.60</td>
<td>2</td>
<td>Singlet⁺</td>
<td>( H_4 )</td>
</tr>
</tbody>
</table>

Also \( \tau \) 2.30–2.70 (15), *phenyl.* Also \( \tau \) 2.00–2.70 (15), *phenyl.* Also \( \tau \) 1.70, 2.30, and 2.72 (5) *pyridine.* Configuration (IIa) or (IIb). Shown by double-resonance experiments on \( L = \text{AsPh}_3 \) to be an overlapping doublet of doublets. *Broad.

* Numbers in parentheses indicate normalised integrated intensities.

[(RuCl₂(CO)(PPh₃)]₄] but with the carbonyl band at 1960 cm⁻¹ increased in intensity with respect to higher-frequency bands. There is no evidence here for formation of the triple-chloride-bridged dimer [(PPh₃)₂ClRuCl₂RuCl₃(CO)₆(PPh₃)]₂ but in addition to the double-chloride-bridged dimer

[(RuCl₂(CO)(PPh₃)₂)]₂. (V). This is in contrast to the reaction between the complex [(RuCl₂(PPh₃)₄] and CS₂, which produces both [(RuCl₂(CS)(PPh₃)₂] and [(PPh₃)₂ClRuCl₂Ru(CS)(PPh₃)₂].

When complex (V) was reacted with excess of P₃H₅ or when (I) was reacted directly with excess of P₃H₅, an orange solid was obtained which analysed for [RuCl₂(CO)(PPh₃)₂], (IV), and whose i.r. spectrum contained carbonyl bands at 2025m, 1982m, and 1945s cm⁻¹. One isomer of this complex has been previously reported with ν₀ at 1 950 cm⁻¹.¹⁰ By analogy with related work on PMe₂Ph complexes, the band at 1 945 cm⁻¹ is probably due to isomer (IVa) and that at 1 982 cm⁻¹ to isomer (IVb). The band at 2 025 cm⁻¹ may be due to isomer (IVc), which has not been previously observed in complexes of this type. Unfortunately, attempts to separate these products by either fractional recrystallisation or chromatography proved unsuccessful. It is of interest to note that no products of type (II) or (III) were isolated (or observed) with L = PPh₃.

In contrast, reaction of complex (I) with dimethylphenylphosphine in CH₂Cl₂ (1:2 molar ratio or excess) gave a single product, which contained no carbonyl group. This complex is monomeric, non-conducting, and analysed [P₃H₅(PPh₃)₂][RuBr₂(CO)(C₇H₅)] and PMe₂Ph gave [RuBr₂(PMMe₂Ph)₂(C₇H₅)], which had a very similar ²H n.m.r. spectrum. The same complexes were also obtained by reaction of [RuX₂(PMMe₂Ph)] with excess of C₇H₅N in methanol. Related complexes [RuX₂(L)₂(C₇H₅)] (L = PPh₃, AsPh₃, X = Cl or Br), [RuH(X)L₂(diene)] (L = PPh₃, P(OR)₃, etc.¹⁴ and [Ru(OH)₂(CO)₂(C₇H₅)] have been reported elsewhere.

Rather surprisingly, reaction of complex (VI) (X = Cl) with excess of pyridine, 2,2'-bipyridyl, or triphenylarsine led to recovery of the starting materials. We have no explanation of the kinetic inertness of complexes (VI) towards these nucleophiles, although, of course, chloride ion is known to be a low trans-effect ligand. If this is the correct explanation, then we must ascribe the higher reactivity of complex (I) (where the diene group is also trans to chloride ions) to its formal negative charge.

When complex (I) was heated under reflux with methylphenylphosphine in CH₂Cl₂ (1:2 molar ratio), a pale yellow solid was isolated and shown by ²H n.m.r. studies (Figure 2) to be a mixture of [RuCl₂(PMMe₂Ph)₂(C₇H₅)] and [RuCl₂(CO)(PMMe₂Ph)₂]. (IV). Although attempts to separate this mixture of complexes by either t.i.c. or fractional recrystallisation were unsuccessful, the formulation of the mixture as 53% [RuCl₂(PMMe₂Ph)₂(C₇H₅)] and 47% (IV) (from ²H n.m.r. integration) is consistent with the analytical data. The ²H n.m.r. spectrum of the diene complex was that expected for configuration (VI). For the complex [RuCl₂(CO)(PMMe₂Ph)₂], the doublet and triplet pattern of resonances are indicative of either isomer (IVA) or (IVb). The position of ν₀ (1 938s cm⁻¹) is consistent with isomer (IVA). The ³¹P n.m.r. spectrum consisted of three singlets at 7.53 (IVA), 8.17, and 14.54 p.p.m. (IVA). When excess of PMe₂Ph₂ is used, the same work-up procedure gave a yellow solid with a very similar i.r. spectrum for [RuCl₂(PMMe₂Ph)₂(C₇H₅)]. The ²H n.m.r. spectrum unequivocally showed trans-PMe₂Ph groups (virtually coupled 'triplet '1¹ and the three diene resonances expected for configuration (VI). The ³¹P n.m.r. spectrum, which consists of a singlet at 6.91 p.p.m., also supports this formulation. Similarly, reaction of the complex

![Figure 2](image_url)

**Figure 2** ²H N.m.r. spectrum in CDCl₃ (r = 6-0—9-0) of the product mixture from the reaction of complex (I) with PMe₂Ph₂(1); PMe₂Ph₂ = 1 : 2 molar ratio

to the mixture above but its ²H n.m.r. spectrum contained an extra peak at r = 8.50. Dissolution of the mixture in CH₂Cl₂ and reprecipitation with diethyl ether gave a yellow powder and a small amount of orange crystals which could be separated manually. The former consists of complexes (IVA) and (VI) and the orange solid is identical to the product isolated from complex (I).

(I.r. and \(^1\)H n.m.r. spectra) to [RuCl\(_6\)(PMePh\(_3\))]\(_6\), which we recently prepared in high yield by reaction of [RuCl\(_{12}\)-(PPPh\(_3\))]\(_3\) with PMePh\(_3\) in hexane. Presumably, the small amount of tetrakisphosphine complex arises from slow reaction of [RuCl\(_6\)(PMePh\(_3\))]\(_3\)(C\(_6\)H\(_6\)) with excess of PMePh\(_3\). Reaction for 12 h of complex (I) with 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (phen) \((L')\) \(\{L':L' = 1:1\) molar ratio\) in CH\(_2\)Cl\(_2\) gave yellow precipitates which analysed closely for \([\text{RuCl}_5\text{(CO)}}(\text{L'})_6\] \(_6\). These precipitates are too insoluble for either molecular-weight or \(^1\)H n.m.r. measurements, but the observation of only one carbonyl band in their i.r. spectrum \(\text{e.g. for } L' = \text{bipy}, \nu_{\text{CO}} \text{ is at } 1940 \text{ cm}^{-1}\) is consistent with a structure such as (VIIa) or (VIIb)

![Structure VIIa, VIIb, and VIIc](image)

[cf. \([\text{RuCl}_5\text{(CO)}}(\text{C}_6\text{H}_6)_6\] \(_6\), \(\nu_{\text{CO}} \text{ at } 2045 \text{ cm}^{-1}\). Work-up of the orange filtrates gave, in addition to \([\text{Ph}_3\text{(PhCH}_2\text{Cl}_2})\text{P}]\text{Cl}\), small amounts of orange solids which were reasonably close in analysis to \([\text{Ph}_3\text{(PhCH}_2\text{Cl}_2})\text{P}]\text{[RuCl}_5\text{(CO)}}(\text{L'})\]. In this instance, configuration (IIb) is impossible and therefore, on the basis of earlier results with \(L = \text{Me}_2\text{S}, \text{Me}_2\text{SO}, \text{etc. [which indicated either configuration (IIa) or (IIb) but not (IIc)]}, \) we tentatively suggest that (IIa) is the most probable structure.

Reaction of complex (I) with excess of bipy gave an orange precipitate which also analysed for \([\text{RuCl}_5\text{(CO)}}(\text{bipy})_6\] \(_6\) but contained two carbonyl bands in its i.r. spectrum at \(1952 \text{ and } 1918 \text{ cm}^{-1}\). Again, the material is too insoluble for further study but it could be formulated either as an isomer such as (VIIc), with cis-carbonyl groups, or a mixture of two isomers with trans-carbonyl groups. The filtrate from this experiment contained the anionic complex (II) together with a very small amount of a purple complex. Although insufficient of the latter was produced for examination, this might be a sample of \([\text{RuCl}_5\text{(CO)}}(\text{bipy})_4\]\(_2\)Cl \((\text{cf. purple } \[\text{RuCl}_5\text{(H}_2\text{O)}}(\text{bipy})_4\text{Cl}]\text{H}_2\text{O}\). 

**DISCUSSION**

It remains to devise an overall mechanism of reaction between complex (I) and the various ligands (L) which will explain the rather surprising differences in behaviour as a function of electronic and steric properties of the ligands. In Scheme 1, a mechanism for reaction of complex (I) with all the ligands \((1:2\) molar ratio\) except Pr\(_3\), bipy, and phen is presented. Thus, we postulate that in all these reactions, the initial step is cleavage of a ruthenium–olefin bond by L, to give an anionic intermediate (VIII) containing the \(\text{C}_6\text{H}_6\) group bound through only one olefinic bond. Further reaction can then occur by one of four competing paths: (i) reversion to complex (I) by displacement of L from (VIII) by the free double bond \((\text{this is very unlikely especially in the presence of free } L \text{ and is not considered further})\); (ii) cleavage of the second ruthenium–olefin bond by L to give (IIa); (iii) displacement of the chloride ion trans to CO by the free double bond with formation of (IIIB); and (iv) displacement of the chloride ion trans to L by the free double bond with formation of (IIIA). If this mechanism is valid, then the percentage yields of complexes (IIIA), (IIIA), and (IIIB) will depend on the relative magnitudes of the rates of these competing reactions. This assumes, of course, that none of these products undergo further reaction. For example, one

![Scheme 1](image)


other possible way to form either complex (IIIA) or (IIIB) is by reaction of (IIa) with free diene. However, this path has been eliminated by showing that there is no reaction between the complex [Ph3PPhCH2P]2[RuCl2(CO)(AsPh3)] and C6H6 when these are heated under reflux in CH2Cl2 for 12 h.

It is now reasonable to ask what properties of ligand L will enhance the rate of sub-step (ii) compared to that of (iii) or (iv). Clearly, if L is a fairly strong, small, nucleophile, this should favour step (ii). Conversely, the bulkier the nucleophile, the slower reaction (ii) should become and the more facile the ring-closure reaction [steps (iii) and (iv)] will become in order to relieve steric repulsions between the bulky L and the bicyclic diene groups. Experimentally, this is exactly what is found since for L = Me2S, Me2SO, and CH2=CH-CN (small bases) only complex (Ia) is formed [i.e., (ii) ñ (iii) or (iv)], whereas for L = AsPh3, SbPh3, and C6H6N (larger bases), a mixture of (IIa) and (III)

enhanced in the less-polar solvent. For L = Me2S in benzene, only complex (Ia) is isolated.

This proposed mechanism hinges on facile formation of a long-lived intermediate, (VIII), containing an unco-ordinated double bond. Although we were unable to isolate such an intermediate in a pure state, hydrogenalysis (after 30 min of reaction) of a dichloromethane solution containing (I), AsPh3 (1:2 molar ratio), and [RhCl(PPh3)3] (a good hydrogenation catalyst) gave a mixture of compounds whose 1H n.m.r. spectrum contained additional signals at 8 7.60, 8.74, and 8.90. These resonances are close to those found in this region for norbornene (8 8.48, 8.68, 8.93, and 9.06) Under the same conditions, no hydrogenation occurred using a mixture of either [RhCl(PPh3)3] and C6H6 or [RhCl(PPh3)3, C6H6, and AsPh3. Therefore, this evidence supports formation of an intermediate with one free double bond.

Finally, it is not easy to decide whether isomer (IIIA)

(a or b) is produced [i.e., (ii) ñ (iii) or (iv)]. The failure to observe reactions of complex (I) with bases such as Et3S and PhCN can presumably be attributed to the inability of these weaker nucleophiles to cleave the ruthenium-oxygen bonds. Furthermore, if the mechanism shown in Scheme 1 is valid, increasing solvent polarity should favour reaction (ii) rather than (iii) or (iv). In agreement with this, for L = AsPh3, changing the solvent medium from CH2Cl2 to MeOH increases the yield of complex (IIa) compared to that of (III), whereas in C6H6 the reverse is true. However, for L = Me2S, changing the solvent from CH2Cl2 to C6H6 gives a lower yield of complex (Ia) (62%) together with some [RuCl2(CO)(Me2S)] (20%) [v190 at 1 943 cm−1, configuration (IVA)]. The failure to isolate any diene complex here would suggest that even in benzene (ii) ñ (iii) or (iv), but that the tendency of the resulting anion to undergo further reaction with Me2S is considerably

| Scheme 2 |


from (VIII) of a chloride ion \textit{trans} to the PMe$_3$Ph group to give (IX) in preference to formation of (IIa) or (III). Ring closure of the free olefin group in complex (IX) with expulsion of carbon monoxide to give \([\text{RuCl}_2(\text{PMe}_3\text{Ph})_2(\text{C}_7\text{H}_8)]\), (VI), then appears to be a reasonable final step. The alternative site of attack (\textit{i.e.} the chloride ion \textit{trans} to CO) would give the complex \([\text{RuCl(CO)(PMe}_3\text{Ph})_2(\text{C}_7\text{H}_8)]\) which might be favoured in more polar solvents. In fact, reaction of complex (I) and PMe$_3$Ph in methanol gives a conducting green solution, but only an unstable green oil could be isolated from the reaction mixture. An alternative mechanism is shown in Scheme 2(b). Again, the affinity of PMe$_3$Ph for ruthenium(ii) and the high trans-effect of CO combine to give the complex \([\text{RuCl}_2(\text{CO})(\text{PMe}_3\text{Ph})(\text{C}_7\text{H}_8)]\), and this is followed by expulsion of CO by PMe$_3$Ph to give (VI). Both these mechanisms are consistent with results of earlier studies of ruthenium- phosphine chemistry \(^{22}\) which indicate that \textit{trans}-R$_2$P–Ru–PR$_3$ arrangements are not formed via isomerisation of cis-Ru(PP$_3$)$_2$ arrangements. A possible way of distinguishing between mechanisms 2(a) or 2(b) is by means of hydrogenation experiments. Reaction of complex (I) and PMe$_3$Ph solutions with [RhCl$_2$(PPh$_3$)$_2$] and hydrogen gave solutions with additional strong $^1$H n.m.r. signals at $\tau$ 8.29, 8.42, and 8.14. These resonances did not appear on reaction of hydrogen with dichloromethane solutions of [RhCl$_2$(PPh$_3$)$_2$], C$_7$H$_8$, and PMe$_3$Ph. Thus, the mechanism depicted in Scheme 2(a) involving an intermediate with a free olefin group is preferred.

For PMe$_3$Ph$_3$, a similar mechanistic path can be invoked to explain formation of the complex \([\text{RuCl}_2(\text{PMe}_3\text{Ph})_2(\text{C}_7\text{H}_8)]\). However, in this instance, the lower affinity of PMe$_3$Ph$_3$ for ruthenium(ii) might enable competing reaction steps to be more dominant as compared to the PMe$_3$Ph reaction, thus leading to formation of \([\text{RuCl}_2(\text{CO})(\text{PMe}_3\text{Ph})_3]\), (IVa).

For $L = \text{PPh}_3$, a mechanism to explain formation of an isomeric mixture of \([\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]\) is presented in Scheme 3. It seems reasonable to postulate that the same intermediate (VIII) is formed and then, since PPh$_3$ is a stronger nucleophile than EPPh (E = As or Sb), that reaction (ii) will be facilitated more than (iii) or (iv). After formation of complex (IIa), we suggest that the higher trans-influence of PPh$_3$ compared to the other ligands studied, together with the unfavourable cis-arrangement of these bulky groups in (IIa) (since PPh$_3$ has a larger ligand cone angle than EPPh on coordination to a metal) \(^{23}\) could readily lead to expulsion of a chloride ion, in order to relieve steric crowding, with formation of \([\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]\). This five-co-ordinate species might then be expected to undergo facile intramolecular rearrangement reactions in order to minimise further steric strains, e.g. by formation of isomers with axial-equatorial or axial-axial PPh$_3$ groups respectively. Similar rearrangements have been elegantly demonstrated for related complexes \([\text{IrH}(\text{CO})_2(\text{PPh}_3)_2]\) \((R = \text{Ph})^{24,25}\) or $\text{P}-\text{MeC}_6\text{H}_4$ \(^{26}\).

Finally, it seems reasonable to propose that the various five-co-ordinate isomers might then recombine to produce dimeric species containing energetically favourable six-co-ordinate ruthenium(ii) ions. Similar processes readily occur for \([\text{RuX}_2(\text{PPh}_3)_2]\) \((X = \text{Cl} \text{or Br}; R = \text{EtPh or EtPPh})\) to give the bimolecular complexes \([\text{RuX}_2(\text{PPh}_3)_2\text{X}]^{16}\). Reaction of more PPh$_3$ with this isomeric mixture of \([\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]\) complexes would then be expected to give an isomeric mixture of \([\text{RuCl}_2(\text{CO})(\text{PPh}_3)_3]\) complexes. However, a very recent paper \(^{27}\) reported the preparation of the yellow complex \([\text{RuCl}_2(\text{CO})(\text{PPh}_3)_3]\) (m.p. 259–263 °C) by recrystallis-

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ation of [RuCl₅(CO)(PPh₃)L] (L = NN-dimethyl-formamide or NN-dimethylacetamide) from CH₂Cl₂-MeOH. This monomeric complex [v̅₀ at 1 921 and 1 931 (Nujol), 1 940 cm⁻¹ (CH₂Cl₂)] is reported to isomerise in CH₂Cl₂ with the original 1 940 cm⁻¹ carbonyl band being gradually replaced by a rather broad band at 1 970 cm⁻¹; however, only the original isomer precipitates from solution on addition of methanol.

In view of the disagreement between the results of this work and that required to support our proposed mechanism, namely facile dimersation of a monomeric intermediate such as [RuCl₅(CO)(PPh₃)₂], we re-examined this ‘isomerisation’ reaction.(405,704),(979,705)

M.p.s were determined with a Koffler hot-stage microscope and are uncorrected. Analysstic data for the new ruthenium(ii) complexes are given in Table 2.

Preparations.—Benzyltriphenylphosphonium carbonyltetrachloro- chlorobis(dimethyl sulphide) ruthenate(ii), (1). The complex [Ph₃P(PhCH₂)P][RuCl₅(CO)(C₆H₄)], (1) (0.20 g), and dimethyl sulphide (0.04 cm³; 1:2 molar ratio) were dissolved in dichloromethane (100 cm³) and the solution gently heated under reflux for 12 h under an atmosphere of nitrogen. The resulting pale orange solution was then reduced in volume and a pale orange solid was precipitated on addition of excess of diethyl ether. This product was washed with warm distilled water and then recrystallised from dichloromethane-diethyl ether (70% yield) (v̅₀ at 1 959 cm⁻¹); i.r. (400—250 cm⁻¹) 325, 309, 2050, 295, 271, and 240 cm⁻¹. When the reaction was carried out in benzene under the same conditions, a yellow solution was obtained. After filtering off some [Ph₃P(PhCH₂)P]Cl, addition of excess of diethyl ether gave a pale orange solid (52%) identified as [Ph₃P(PhCH₂)P][RuCl₅(CO)(MeS)₂], (2). Concentration of the filtrate followed by pentane addition gave a yellow solid which was identified as benzyltriphenylphosphonium carbonyltetrachloro-[dimethyl sulphide]- ruthenate(ii), (IV) (20%) (v̅₀ at 1 943 cm⁻¹). H N.m.r. spectrum (CDCl₃): δ 7.48 (singlet) (1) * and 7.65 (singlet) (1) *. I.r. spectrum (400—250 cm⁻¹): 330w; 319w; and 275cm⁻¹.

Benzyltriphenylphosphonium carbonyltetrachlorobis(dimethyl sulphide) ruthenate(ii), (1). This complex was prepared from (1) and Me₂SO (1:2 molar ratio) heated under reflux in CH₂Cl₂ (12 h). The resulting yellow solution gave a crystalline yellow solid on addition of diethyl ether. The product was recrystallised from CH₂Cl₂-Et₂O (78%) (v̅₀ at 1 960 cm⁻¹) (A (0-015) 18-8 Ω⁻¹ cm⁻² mol⁻¹ in CH₂Cl₂). I.r. spectrum (400—250 cm⁻¹): 319s; 308; 295w; 283w; and 283 cm⁻¹. When benzene was used as solvent, the same product was formed (70%). Benzyltriphenylphosphonium carbonyltetrachlorobis(dimethyl sulphide) ruthenate(ii), (II), was prepared as above using [H₂NMe₂SO and the yellow product was recrystallised from dichloromethane-pentane (70%) (v̅₀ at 1 977 cm⁻¹). I.r. spectrum (400—250 cm⁻¹): 319s; 308; 295w; 283w; and 283 cm⁻¹. The complex [Ph₃P(PhCH₂)P][RuBr₅(CO)(MeS)₂] was prepared as for the chloro-complex from [Ph₃P(PhCH₂)P][RuBr₅(CO)(C₆H₄)] and Me₂SO to give a yellow crystalline solid (80%) (v̅₀ at 1 975; v̅₀ at 1 080 cm⁻¹). I.r. spectrum (400—250 cm⁻¹): 323w; 300s; and 280 cm⁻¹.

Benzyltriphenylphosphonium bis(acrylonitrile) carbonyltetrachlororuthenate(ii) monohydrate, (II). This was prepared as for the other anionic complexes as a yellow solid and was recrystallised from dichloromethane-pentane (80%) (v̅₀ at 1 960, v̅₀ at 2 245 cm⁻¹). The same product was formed when an excess of acrylonitrile rather than 1:2 molar ratios were used [A(0-001) 16-5 Ω⁻¹ cm⁻² mol⁻¹ in CH₂Cl₂]. I.r. spectrum (400—250 cm⁻¹): 316m; 307m; 281w; and 271 cm⁻¹.

Benzyltriphenylphosphonium carbonyltetrachlorobis(triphenyl- larane)ruthenate(ii), (II). Complex (1) (0-20 g) and triphenylarsine (0-20 g) were heated under...
reflux in CH₂Cl₂ (100 cm³) under a nitrogen atmosphere for 12 h. The resulting yellow solution (shown to be a mixture by t.l.c.) gave an orange precipitate on addition of diethyl ether. This was washed with light petroleum (b.p. 40—
60°C), then water, and recrystallised from dichloromethane-
pentane (20%) (v/v) at 1 828 cm⁻¹. I.r. spectrum (400—
250 cm⁻¹): 348; 332s; and 320 cm⁻¹. The remaining solution was concentrated and then treated with pentane to

TABLE 2

Analytical data for some new ruthenium(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Found (%)</th>
<th>Calc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂(Me₂S)₂</td>
<td>Orange</td>
<td>206 (decomp.)</td>
<td>C: 50.5; H: 4.2; Cl: 17.8</td>
<td>C: 50.5; H: 4.8; Cl: 14.9</td>
</tr>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂(Me₂SO₂)₂</td>
<td>Yellow</td>
<td>189—189 (decomp.)</td>
<td>C: 45.2; H: 4.5</td>
<td>C: 48.4; H: 4.6</td>
</tr>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂[Me₂(NH₂)₂]</td>
<td>Yellow</td>
<td>197—198 (decomp.)</td>
<td>C: 43.5; H: 4.3</td>
<td>C: 41.2; H: 3.9</td>
</tr>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂(H₂O)</td>
<td>Yellow</td>
<td>195—196 (decomp.)</td>
<td>C: 48.1; H: 3.8; Cl: 14.8</td>
<td>C: 53.9; H: 3.9; Cl: 14.9</td>
</tr>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂(AsPh₃)₂</td>
<td>Orange</td>
<td>215—217 (decomp.)</td>
<td>C: 50.0; H: 3.8; Cl: 8.6</td>
<td>C: 57.5; H: 4.0; Cl: 8.2</td>
</tr>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂(Ph₃P)₂</td>
<td>Orange</td>
<td>129—130 (decomp.)</td>
<td>C: 53.0; H: 3.5; Cl: 8.6</td>
<td>C: 57.9; H: 4.3; Cl: 3.7</td>
</tr>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂(C₆H₅N₂)₂</td>
<td>Yellow</td>
<td>173—175 (decomp.)</td>
<td>C: 45.9; H: 3.7; Cl: 4.0</td>
<td>C: 58.1; H: 4.0; Cl: 3.8</td>
</tr>
<tr>
<td>[Ph₃(PPh₂)₂]RuCl₂(bipy)</td>
<td>Orange</td>
<td>195—196 (decomp.)</td>
<td>C: 53.0; H: 3.5; Cl: 4.6</td>
<td>C: 59.3; H: 3.9; Cl: 3.7</td>
</tr>
<tr>
<td>[RuCl₂(C₆H₅N)₂(C₃H₄)₂]</td>
<td>yellow-brown</td>
<td>215—217 (decomp.)</td>
<td>C: 40.1; H: 3.8; Cl: 12.4</td>
<td>C: 52.2; H: 3.8; Cl: 11.9</td>
</tr>
<tr>
<td>[RuCl₂(Ph₃P)₂]</td>
<td>Yellow</td>
<td>231—232 (decomp.)</td>
<td>C: 48.4; H: 3.6</td>
<td>C: 48.4; H: 3.6</td>
</tr>
<tr>
<td>[RuCl₂(C₆H₅N)₂(C₃H₄)₂]</td>
<td>Yellow</td>
<td>171—174 (decomp.)</td>
<td>C: 43.2; H: 3.5; Cl: 3.7</td>
<td>C: 42.1; H: 3.5; Cl: 3.8</td>
</tr>
<tr>
<td>[RuCl₂(bipy)]</td>
<td>Yellow</td>
<td>&gt; 200 (decomp.)</td>
<td>C: 36.6; H: 2.1; Cl: 7.7; 20.5</td>
<td>C: 37.1; H: 2.2; Cl: 7.9; 20.6</td>
</tr>
<tr>
<td>[RuCl₂(phen)]</td>
<td>Yellow</td>
<td>&gt; 200 (decomp.)</td>
<td>C: 37.9; H: 2.3; Cl: 6.7</td>
<td>C: 38.2; H: 2.7; Cl: 6.9</td>
</tr>
<tr>
<td>[RuCl₂(PPPh₃)]</td>
<td>Orange</td>
<td>108—172 (decomp.)</td>
<td>C: 41.4; H: 4.2</td>
<td>C: 41.4; H: 4.2</td>
</tr>
<tr>
<td>[RuCl₂(Me₂PPh₂)(C₃H₄)₂]</td>
<td>Yellow</td>
<td>247 (decomp.)</td>
<td>C: 41.4; H: 4.2</td>
<td>C: 39.6; H: 4.2</td>
</tr>
<tr>
<td>[RuBr₃(PPPh₃)]</td>
<td>Yellow</td>
<td>214—215 (decomp.)</td>
<td>C: 44.0; H: 4.8</td>
<td>C: 44.0; H: 4.8</td>
</tr>
<tr>
<td>[RuCl₂(C₆H₅N)₂]</td>
<td>Yellow</td>
<td>290—292 (decomp.)</td>
<td>C: 21.8; H: 4.6</td>
<td>C: 21.8; H: 4.6</td>
</tr>
</tbody>
</table>


give a yellow solid which, on recrystallisation from dichloromethane-pentane, gave microcrystals of [bicyclo[2.2.1]hexa-2,5-diene]carbonyl dichloro(triphenylarsine)ruthenium(ii) (II), (III) (60%) (w/w) at 2 008 cm⁻¹. I.r. spectrum (400—
250 cm⁻¹): 354; 328; 235: 308w; 280m; and 250s cm⁻¹. When the reaction was carried out in the presence of excess of concentrated hydrochloric acid, the same relative amounts of products were found. However, if methanol was used instead of dichloromethane as solvent, under the same conditions, an increase of 35% in the yield of the complex (II) accompanied by a 42% decrease in the yield of (III) was observed.

Benzyltriphenylphosphonium dichloro(triphenylarsine)ruthenate(ii), (II). This complex was prepared as for the triphenylarsine derivative, isolated as a pink powder (18%), and recrystallised from CH₂Cl₂—Et₂O (v/v) at 2 002 cm⁻¹ [λ (0-001Ms⁻¹) 18.5 fM cm⁻¹] in CH₂Cl₂.

I.r. spectrum (400—250 cm⁻¹): 355w; 330w; 320w; 270s; and 250m cm⁻¹. Treating the residual solution with pentane gave a yellow precipitate of [bicyclo[2.2.1]hexa-2,5-diene]carbonyl dichloro(triphenylarsine)ruthenium(ii) (II) (60%) which was recrystallised from dichloromethane-
pentane. This complex is more insoluble than the corre-
sponding Ph₃As derivative in common organic solvents.

Reaction of complex (I) (0.20 g) with excess of SbPh₃

Dichloro-bis[carbonyl dichloro(triphenylphosphine)-
ruthenium(ii)] (V). Complex (I) (0.24 g) and triphenyl-
phosphine (0.20 g; 1:2 molar ratio) were dissolved in CH₂Cl₂ (100 cm³) and the solution heated under reflux...
under a nitrogen atmosphere for 12 h. The resulting pale orange solution was reduced in volume and diethyl ether added to give a white precipitate of \([\text{Ph}_2(\text{PhCH}_2)_2]\text{Cl}\). The remaining solution was treated with pentane to give the pale orange solid (70%) (\(\chi_\text{cyc} = 2.029 \text{m}, 1.938 \text{s}, 1.960 \text{cm}^{-1}\)). The N.m.r. spectrum (CDCl_3) showed \(2-3 \text{ singlet} \) (s), \(2.5-5 \text{ singlet} \) (s), \(3.5-3 \text{ multiplet} \) (w), \(4.2-3 \text{ multiplet} \) (w), and \(5.2-6 \text{ p.p.m.} \) (multiplet) (w). Recrystallisation from hot dichloromethane–pentane gave a deeper orange product (with the carbonyl band at 1.960 cm\(^{-1}\) increased in intensity with respect to higher-frequency bands) but still analysing for (V) \(\text{[RuCl}_3(\text{CO})(\text{PPh}_3)_2]\) requires C, 61.3%; H, 4.2%. When complex (I) (0-24 g) and excess of triphenylphosphine (0-40 g) were heated under reflux in CH\(_2\)Cl\(_2\) (100 cm\(^3\)) under a nitrogen atmosphere for 12 h and the resulting orange solution treated exactly as above, orange crystals of \(\text{[carbonyl dichloro(triphenylphosphine) ruthenium (IV)]} \text{(IV)}\) were isolated, m.p. 150°C (lit., \(\chi_\text{cyc} = 70-72\)°C) (Found: C, 60.3%; H, 4.6%). Calc. for \(\text{C}_9\text{H}_7\text{Cl}_4\text{Ru} \times \text{P}_3\text{H}_10\): C, 60.9%; H, 4.8% (\(\chi_\text{cyc} = 0.95\text{m}, 1.982\text{cm}^{-1}, 1.945\text{cm}^{-1}\)). The same mixture of isomers was obtained by reaction of \(\text{[RuCl}_3(\text{CO})(\text{PPh}_3)_2]\) with \(\text{PPh}_3\) under the same conditions.

\begin{align*}
\text{(Bicyclo[2.2.1]hepta-2,5-diene)dichlorobis(dimethyl} & \text{phosphine})\text{ruthenium (II)}, \text{(VI). Complex (I) (0-20 g) was} \text{ heated under reflux in \text{CH}_2\text{Cl}_2 (100 cm}^3\text{) under a nitrogen atmosphere} \text{ with \text{PMe}_3\text{H (0-10 cm}^3\text{) for ca. 12 h. Reduction in volume of the yellow solution followed by diethyl ether} \text{ addition gave a white precipitate of}\ \text{[Ph}_2(\text{PhCH}_2)_2]\text{Cl}. \text{The remaining solution was then treated with pentane to give the yellow solid which was washed with methanol and recrystallised from dichloromethane–pentane (80%)). The same complex was obtained when an excess of \text{PMe}_3\text{H was used.} \text{H N.m.r. spectrum in CDCl}_3 \text{ showed}\ \tau \text{ 7-6 (protons 1, 4): 7-7 (2, 3, 5, 6): 8-6 (a, b): 2-00–2-60 (phenyl multiplet): and 7-56 (1:2:1 triplet, PMe}_3\text{H).}
\end{align*}

Reactions.—Complex (I) and \text{PMe}_3\text{H. Complex (I) (0-20 g) and \text{PMe}_3\text{H (0-10 cm}^3\text{) \text{were heated under reflux in \text{CH}_2\text{Cl}_2 (100 cm}^3\text{) under a nitrogen atmosphere for ca. 12 h. Concentration of the solution followed by diethyl ether addition gave a white precipitate of} \text{[Ph}_2(\text{PhCH}_2)_2]\text{Cl. Pentane addition to the residual yellow solution gave a pale yellow solid, shown by H N.m.r. studies to be a mixture of complexes \text{[RuCl}_3(\text{PMe}_3\text{H})_2]\text{[Ph}_2(\text{PhCH}_2)_2]\text{Cl}.} \text{(VI), and \text{[RuCl}_3(\text{CO})(\text{PMe}_3\text{H})_2]} \text{ (IV) (\(\chi_\text{cyc} = 1.938 \text{cm}^{-1}\)) (53 and 47% respectively as established by integration). This mixture, which could not be separated by t.l.c. or fractional recrystallisation, analysed closely for the relative percentages of complexes indicated by the H N.m.r. studies (\text{[Cyclohexane]}: C, 59.3%; H, 4.4%. \text{[RuCl}_3(\text{PMe}_3\text{H})_2]\text{[Ph}_2(\text{PhCH}_2)_2]\text{Cl} \text{(I)): C, 58.7%; H, 4.9%).} \text{H N.m.r. spectrum in CDCl}_3 \text{ showed extra peaks at } \tau \text{ 8-90, 8-74, and 8-90 (cf. norborne: } \tau \text{ 8-43, 8-68, 8-93, and 9-06). The remainder of the solution was hydrogenated for a further hour. The orange complex (II) and the yellow solid were isolated by the same method as above and analysis of the latter product was consistent with a mixture of \text{[RuCl}_3(\text{CO})(\text{AsPh}_3)_2]\text{[Ph}_2(\text{PhCH}_2)_2]\text{Cl} \text{ and \text{[Ph}_2(\text{PhCH}_2)_2]\text{Cl} \text{[RuCl}_3(\text{CO})(\text{AsPh}_3)_2]} \text{(VII) (Found: C, 56.3%; H, 4.3%). Similarly, when the reaction was repeated but the \text{CH}_2\text{Cl}_2 solution was simply}
\end{align*}

*We thank Dr. E. S. Switkes for the preparation of this complex.
reduced in volume and a $^1$H n.m.r. spectrum obtained, additional resonances occurred at $\tau$ 8·29, 8·76, and 9·14 which shows that these peaks do not arise because of the work-up procedure. Under the same conditions, no such evidence for hydrogenation was found using a mixture of either $[\text{RhCl(PPh}_3\text{)}_2]$ and C$_7$H$_8$ or $[\text{RhCl(PPh}_3\text{)}_2]$, C$_7$H$_8$, and AsPh$_3$. Similarly, hydrogenation of dichloromethane solutions of complex (I), PMe$_2$Ph, and $[\text{RhCl(PPh}_3\text{)}_2]$ for 4 h gave a solution with additional $^1$H n.m.r. signals at $\tau$ 8·29, 8·42, and 9·14. No additional resonances were found when solutions of $[\text{RhCl(PPh}_3\text{)}_2]$, C$_7$H$_8$, and PMe$_2$Ph were treated with hydrogen under the same conditions.

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8 Metal Compounds containing Six-electron and Seven-electron Organic Ligands

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8.1 INTRODUCTION

The chemistry of these ligands is discussed under the same headings as in MTP International Review of Science, Series One. However, because of the restrictions of space, the chemistry is not sub-divided into triads, and diagrams are restricted to a minimum.

8.2 ARENE–METAL CARBONYL COMPLEXES

As in the earlier review, most of the recent work published in this area has dealt with the arene–Cr(CO)₃ compounds. Chromium π complexes of both
pyrrole and some of its \( N \)-substituted derivatives have been prepared for the first time; with 1-phenylpyrrole, the \( \text{Cr(CO)}_3 \) group coordinates either with the pyrrole or the benzene ring\(^2\), whereas with 2-phenylpyrrole, \( \text{Cr(CO)}_6 \) and \( \text{Mn}_2(\text{CO})_{10} \), complex (1) is formed\(^3\). Migration of a \( \text{Cr(CO)}_3 \) group from a six- to a five-membered ring has been proposed to account for the \(^{1}H\) n.m.r. spectral changes produced by addition of base to fluorenium-tricarbonyl\(^4\). Reaction of \( \text{Cr(CO)}_6 \) and \( \text{Ph}_2\text{AsCH}_2\text{AsPh}_2 \) in decane gives (2)\(^5\), whereas with tri(o-tolyl)phosphine and \( \text{M(CO)}_6 \) (\( M = \text{Cr, Mo, W} \)) complex (3) is produced\(^6\). Complexes of \( \alpha,\beta,\gamma,\delta \)-tetraphenyl-porphin and its metal chelates with \( \text{Cr(CO)}_3 \) have also been synthesised\(^7\).

![Chemical Structures]

Binuclear species \( [(\text{arene})_2\text{Cr}_2(\text{CO})_n]^+ \) (\( n = 0, 1, 2, 3 \)) have been detected in the mass spectra of \( \text{arene-Cr(CO)}_3 \) complexes\(^8\) and ionisation and appearance potential measurements reported\(^9\). Separation of an isomeric mixture of (2,3-dimethylnaphthalene)chromium tricarbonyl has been achieved by means of high-speed column liquid chromatography\(^10\). A normal-coordinate analysis of \( \text{C}_6\text{H}_6\text{Cr(CO)}_3 \) has been presented, incorporating a sixfold symmetry for the benzene ring\(^11\). However, more recent low-temperature, x-ray and neutron-diffraction studies on \( \text{C}_6\text{H}_6\text{Cr(CO)}_3 \) indicate some distortion of the molecule, consistent with a threefold symmetry of the benzene ring\(^12\).

More examples of carbonyl replacement in \( \text{arene-Cr(CO)}_3 \) complexes giving \( \text{arene-Cr(CO)}_2X \) [\( X = \text{SiHCl}_3 \)]\(^13\), \( \text{C(OMe)}_6\text{H}_5 \)]\(^14\), \( \text{P(C}_5\text{H}_4\text{FeC}_5\text{H}_2)_3 \)]\(^15\) have been reported. The factors influencing the ease of protonation in \( \text{arene-Cr(CO)}_3 \) and \( \text{arene-Cr(CO)}_2\text{PPh}_3 \) complexes have been discussed\(^16\), and a \(^{1}H\) n.m.r. spectroscopic method of distinguishing between metal or ring attack by hydride ion on these compounds has also been outlined\(^17\). Several investigators have examined the effect of complexation of a \( \text{Cr(CO)}_3 \) group\(^18\) on \( \text{arene ring substituent reactivity} \). \( \text{Arene-M(CO)}_3 \) compounds (\( M = \text{Cr, Mo, W} \)) are also effective homogeneous catalysts in promoting Friedel-Crafts-type reactions\(^19\) and the affinity of these compounds for halide ion is demonstrated by the ready formation of such compounds as \( \text{(R}_4\text{N)_3[CO}_3\text{MX}_3\text{M(CO)}_3] and (R}_4\text{N}_2[\text{CO}_3\text{MX}_2\text{M(CO)}_3]} \) (\( X = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{etc.})\(^20\).

A wide range of nucleophilic addition reactions to \( [(\text{arene})\text{Mn(CO)}_3]^+ \) cations giving substituted cyclohexadienyl compounds has been reported\(^21\). In contrast, reaction with primary alkylamines gives \( \text{arene-Mn(CO)}_2\text{CONHR} \) complexes\(^22\). With \( \text{(C}_6\text{H}_5)_n\text{Me}_n\text{CN})\text{Mn(CO)}_3 \), oxidation with ceric ion liberates the cyano-arenes, \( \text{C}_6\text{H}_{5-n}\text{Me}_n\text{CN} \), whereas thermal decomposition in polar solvents generates \( \text{arene-Mn(CO)}_2\text{CN} \). The latter undergo facile electrophilic attack on the coordinate cyano group, giving, for example, with \( \text{Ph}_3\text{CBF}_4 \), the \( [(\text{arene})\text{Mn(CO)}_2\text{CNCPh}_3]^+ \) cation\(^24\).
Reaction of YCCO$_3$(CO)$_6$ (Y = F, Me, Ph) and arenes gives YCCO$_3$(CO)$_6$- (arene)$_{25}$ and full preparative and spectroscopic details for the compounds (arene)Co$_4$(CO)$_6$ are now available$^{26}$.

8.3 CYCLOHEPTATRIENE AND CYCLOHEPTATRIENYL COMPLEXES

The preparation of C$_7$H$_8$Cr(CO)$_2$L [L = PPh$_3$, P(OPh)$_3$] by photochemical reactions of C$_7$H$_8$Cr(CO)$_3$ and L has been reported$^{27}$. In contrast, thermal reactions of C$_7$H$_8$Cr(CO)$_3$ with nitriles$^{28}$ or isocyanides$^{29}$ give fac-[X$_3$Cr(CO)$_3$]. Reaction of (h$^7$-C$_7$H$_7$)M(CO)$_2$I (M = Mo, W) with various tertiary phosphines and phosphites gives (h$^7$-C$_7$H$_7$M(CO)LI which, in some cases, appears to exist in two different isomeric forms$^{30}$. $^{13}$C n.m.r. studies on L'M(CO)$_3$ (M = Cr, Mo, W; L' = arene or triene) indicate stronger metal-arene bonds$^{31}$, e.g. YCCO$_3$(CO)$_6$(triene) is readily synthesised from YCCO$_3$(CO)$_6$(arene) and triene$^{25}$. An x-ray structure of (triphenyl)chromium tricarbonyl reveals a non-planar ring and $h^6$ coordination$^{32}$. In contrast, structural$^{33}$ and spectroscopic studies$^{34}$ on [H$_2$B(3,5-Me$_2$P$_2$)C$_7$H$_7$- (CO)$_2$Mo and related compounds indicate h$^3$-C$_7$H$_7$ bonding and sterically non-rigidity.

Reaction of [(h$^6$-C$_7$H$_8$)Mn(CO)$_3$]BF$_4$ made by hydride abstraction from (h$^5$-C$_7$H$_9$)Mn(CO)$_3$ with X$^-$ (X = H, OMe, OEt, etc.) gives the 6-exo-substituted cycloheptadienyl compounds, (h$^5$-C$_7$H$_8$X)Mn(CO)$_3$.$^{35}$ The compound (h$^5$-C$_7$H$_9$)Mn(CO)$_3$ has been synthesised by low-temperature photochemical decarbonylation of C$_7$H$_7$COMn(CO)$_5$, and its fluxional properties compared with those of the isoelectronic [(h$^5$-C$_7$H$_7$)Fe(CO)$_3)]^+$ ion$^{36}$. Other papers published in this period on iron-triene chemistry are mainly concerned with various aspects of the organic chemistry of (h$^4$-C$_7$H$_8$)Fe(CO)$_3$. These include electrophilic substitution and addition studies$^{37}$, reaction with tetracyanoethylene$^{38}$ and reaction with base$^{39}$. In the latter paper, evidence for [C$_7$H$_7$Fe(CO)$_3$] is presented. Organic reactions of cycloheptatrienone$^{40}$, cycloheptadienone$^{40}$ and heptafulvene-iron tricarbonyls$^{41}$ are also discussed and the chemistry of the latter compound is compared with that exhibited by (heptafulvene)chromium tricarbonyl$^{42}$ where $h^6$ coordination is present. Finally, the structure of C$_7$H$_8$Fe$_2$(CO)$_6$ has been published$^{43}$.

8.4 METAL–ARENE COMPLEXES

Oxidation of [(Me$_6$C$_6$)$_3$M$_3$X$_6$]$^+$ (M = Nb, Ta; X = Cl, Br) (see Ref. 1) gives compounds of empirical formula [(Me$_6$C$_6$)$_3$M$_3$X$_6$]$^{2+}$. These are formulated as the hexanuclear cations [(Me$_6$C$_6$)$_6$M$_6$X$_{12}$]$^{4+}$ on the basis of their diamagnetism and close similarity with the well-known [(M$_6$X$_{12}$)Y$_6$]$^-$ ($n = 2, 3, 4$) complexes$^{44}$.

Normal-coordinate analysis of molecular vibrations has been performed for Cr(C$_6$H$_8$)$_2$ assuming $D_{6h}$ symmetry$^{45}$ and the calculated mean amplitudes show excellent agreement with electron-diffraction data$^{46}$. Convenient methods of synthesising pure Cr(arene)$_2$ (arene = cumene, $m$-di-isopropylbenzene),
Cr(arene)(PF₃)₃ (arene = C₆H₆, C₆F₆, etc.) and Fe(C₆H₆)(PF₃)₂ by co-condensation reactions have been reported recently by Timms et al.⁴⁷; a new improved synthesis of [Fe(C₆H₆)₂](PF₆)₂ (79% yield) via FeCl₃, AlCl₃ and benzene has been described also⁴⁸. Isotopic hydrogen exchange in [Cr(arene)₂]⁺⁺ (n = 0, 1) has been demonstrated by Russian workers⁴⁹ and the rate constants for these reactions given.

A series of excellent papers by Green and co-workers on the reactions of (bis(arene))molybdenum(0) complexes has appeared. Treatment with tertiary phosphines or phosphites (L) gives C₆H₆MoL₃⁵⁰ which, for L = PMePh₂ and PMe₂Ph, are readily protonated to give both [C₆H₆MoL₃H]⁺ and [C₆H₆MoL₃H₂]²⁺ cations⁵⁰,⁵¹. Reaction with allyl chloride gives [(arene)Mo(h³-C₃H₅)Cl]₂ (4) which undergoes bridge cleavage with PR₃ giving (arene)Mo(h³-C₃H₅)(PR₃)Cl⁵²,⁵³. Reduction of this compound with NaBH₄ in the presence of excess PR₃ gives C₆H₆Mo(PO(Pr₃)₃), except for R = Ph when (arene)Mo(PO(Ph₃)₂H₂ is formed⁵²,⁵３. This dihydride reacts with nitrogen to form either (5) or (6) from which dinitrogen can be displaced by carbon monoxide to give (arene)Mo(PO(Pr₃)₂CO⁵². Further reactions of (4) with butadiene, allylmagnesium chloride, 2,2'-bipyridyl, etc. have also been outlined⁵¹ and (4) is shown to act as a homogeneous catalyst for the polymerisation of dienes and related reactions⁵⁴.

The compounds [(h⁶-arene)RuX₂]₂ (arene = C₆H₆; X = Cl, Br, I, SCN⁵⁵; arene = C₆H₅Me, p-MeC₆H₄CHMe₂, etc.; X = Cl⁵⁶) have also been fully characterised. Reaction with PR₃ gives (arene)RuX₂PR₃⁵⁵,⁵⁶ and x-ray analyses⁵⁶ of (arene)RuCl₂(PMePh₂) (arene = C₆H₆, p-MeC₆H₄CHMe₂) reveal that the ruthenium–carbon distances occur as one set of four equivalent short bonds and one set of two equivalent long bonds, an asymmetry attributed to the larger trans-bond weakening property of the tertiary phosphine.

The arene dimers also react with R₂Hg (R = Me, Ph) and then PPh₃, giving (h⁶-C₆H₆)Ru(R)Cl(PPh₃) and with tetra-allyltin to form (h⁶-C₆H₆)RuCl-(h³-C₃H₅)⁵⁷; reaction with cyanide and hydride ion forms cyanocyclohexadienyl and 1,3-cyclohexadiene complexes respectively (¹H n.m.r. spectral evidence)⁵⁵.

Full details of the structures of MH(C₁₀H₇)(Me₂P(CH₂)₂PMe₂) [M = Ru, Os] have now been reported⁵⁸ and the structure proposed earlier for
Ru(C₆Me₆)₂, namely (h⁶-C₆Me₆)Ru(h⁴-C₆Me₆), has been verified by x-ray analysis⁵⁹.

### 8.5 MIXED SANDWICH COMPLEXES

The first compound containing both a cycloheptatrienyl and a cycloheptadienyl ring, (h⁷-C₇H₇)Ti(h⁵-C₇H₉), has been reported⁶⁰. Reaction of VCl₄, i-C₃H₇MgBr and cycloheptatriene gives V(h⁶-C₇H₈)₂, which undergoes stepwise hydride abstraction with Ph₃CBF₄ to give (h⁷-C₇H₇)V(h⁶-C₇H₈)BF₄ and then V(h⁷-C₇H₇)₂(BF₄)₂⁶¹. An alternative synthesis of the previously-reported (h⁷-C₇H₇)Cr(h⁴-C₇H₁₀)⁶² has also been published⁶¹. A range of substituted cycloheptatrienyl complexes (h⁷-C₇H₆X)V(h⁵-C₅H₈) and (h⁷-C₇H₆X)V(CO)₃ (X = Me, Ph, etc.) has been reported and their mass spectra thoroughly discussed⁶³. E.S.R. and ¹H n.m.r. spectra for the compounds (h⁵-C₅H₅)Cr(h⁶-C₆H₆) and (h⁵-C₅H₅)Cr(h⁷-C₇H₇), have been recorded and the magnetic parameters related to ring size and the total charge of the complexes⁶⁴. The compound (h⁵-C₅H₅)Ru(h⁶-C₆H₆)Cl has been synthesised via [(h⁵-C₆H₆)-RuCl₂]₂ and TiC₅H₅⁵⁷ and the related (h⁵-C₅H₅)Ru(h⁶-PhBPh₃) has been obtained by reaction of (h⁵-C₅H₅)Ru(PPh₃)₂Cl and NaBPh₄⁶⁵. Reaction of [(h⁵-C₅H₅)Fe(h⁶-C₆H₆)]⁺ cations (arene = biphenyl, diphenylmethane, etc.) with ferrocene in the presence of a Lewis acid gives novel dications of type (7)⁶⁶ whereas reaction of bis(indenyl)iron with BF₃Et₂O induces intramolecular ligand exchange giving the cationic arene compound (8)⁶⁷. The monomeric dications [(h⁵-C₅Me₅)M(h⁶-arene)]²⁺ and monocations [(h⁵-C₅H₅)M-(π-pyrrole)]⁺ (M = Rh, Ir) have been synthesised from (h⁵-C₅Me₅)M-(OCCF₃)₂H₂O. The former, but not the latter, reacts with nucleophiles, giving exo-substituted cyclohexadienyl monocations⁶⁸. Finally, displacement of diene from [Rh(diene)₂]BF₄ with arenes⁶⁹,⁷₀ or cycloheptatriene⁶⁹ gives [(diene)Rh(arene)]BF₄ and [(diene)Rh(C₇H₈)]BF₄ (diene = C₇H₈, C₈H₁₂) respectively; the mono-ene complex [(C₂H₄)₂Rh(arene)]BF₄ may be prepared from Rh(C₂H₄)₂(acac), Ph₃CBF₄ and arene⁶⁹.

![Diagram](7)

![Diagram](8)

### 8.6 COMPLEXES OF LARGER RING TRIENES

The three dimensional x ray structure of all trans (cyclododeca 1,5,9 triene) nickel has been determined⁷¹ and evidence presented for the analogous Cu¹
complex\textsuperscript{72}. Proton addition to (bicyclo[6,1,0]nonatriene)molybdenum tricarbonyl (9) produces a $\pi \rightarrow \sigma$ rearrangement giving (10)\textsuperscript{73}. The x-ray structure of (bicyclo[4,4,1]undeca-1,3,5-triene)chromium tricarbonyl reveals the presence of a six $\pi$-electron homoaromatic ring\textsuperscript{74}.

\begin{center}
\includegraphics[width=0.5\textwidth]{complexes.png}
\end{center}

Other compounds of higher ring trienes published in this period do not involve $h^6$ or $h^7$ coordination. However, interested readers should consult the following papers: cobalt, rhodium and iridium cyclo-octa-trienes\textsuperscript{75} and -triennyls\textsuperscript{76}; reaction of Ru$_3$(CO)$_4$ with cyclododeca-1,5,9-triene\textsuperscript{77}; reactions of Fe$_2$(CO)$_9$ with cis-(bicyclo[6,2,0]deca-2,4,6-triene)\textsuperscript{78}, semi-\textsuperscript{79} and aza-bullvalene\textsuperscript{80} and iron, chromium and molybdenum compounds of anti-7,8-benzotricyclo[4,2,0,0]deca-3,7,9-triene\textsuperscript{81}.

8.7 MISCELLANEOUS COMPLEXES

Although none of the compounds exhibit $h^6$ or $h^7$ coordination, work on titanium\textsuperscript{82, 83}, vanadium\textsuperscript{83}, zirconium\textsuperscript{84}, iron\textsuperscript{85}, ruthenium\textsuperscript{86} and osmium\textsuperscript{86} cyclo-octatetraenes may be included for completion.

References

Synthesis and Rearrangement Reactions of Dihalogenotris- and Dihalogenotetrakis-(tertiary phosphine)ruthenium(II) Compounds

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The reaction of 'RuCl₂·3OH₂' with triphenylphosphine is a function of reaction time and solvent. Thus, in methanol, ethanol, or isopropyl alcohol at reflux for several hours [RuCl₂(PPh₃)₃] is formed, whereas shaking the reaction mixture at room temperature yields [RuCl₂(PPh₃)₂]. Prolonged reaction at room temperature using a 1:2 ratio of ruthenium to PPh₃ gives [RuCl₂(PPh₃)₂(HOME)] whereas the reactants in isobutyl alcohol or cyclohexanol yield [RuCl₂(PPh₃)₂] (which can also be heated [RuCl₂(PPh₃)₂] under reflux in methyl ethyl ketone). Solvents such as 2-methoxy- and 2-ethoxy-ethanol take part in the reaction itself, producing [RuH₃Cl⁴][CO](PPh₃)₃ and [RuCl₂(CO)(PPh₃)₂] respectively.

In contrast, trialkyl-, dialkylaryl-, and alkyldiaryl-phosphines react with 'RuCl₂·3OH₂' in aqueous ethanol or 2-methoxyethanol to give the tetra-coordinated compounds [RuCl₄L₄]²⁻ (L = phosphine) which do not react with an excess of phosphine to give [RuCl₂L₄]. Under acid conditions, however, [RuCl₂L₄] have been isolated. Bulky phosphines such as PBU₃ or PP₃ react in ethanol during 72 h to give [RuCl₂L₂] and [LaCl₂RuCl₂RuCl₂] with no evidence for mononuclear compounds. In contrast, related ligands give mononuclear Ru(II) compounds [RuCl₂(L₂)₂] (L = PPh₃, AsR₃, or SbP₃) and there is no evidence for compounds with tri-μ-halogeno-bridges.

Thus, although some monomeric tertiary-phosphine halide complexes of Ru(II) are known, no general synthesis is available and this we set out to find.

**RESULTS AND DISCUSSION**

It has been shown that when [RuX₂(PPh₃)₄] (X = Cl or Br) are heated under reflux with excess of triaryl phosphines in dichloromethane, ethanol, or hexane the corresponding [RuX₂L₄] compounds [L = P(OPh₃)₃, etc.] are produced. Our studies now show that the corresponding ligand-exchange reactions involving tertiary phosphines are much more sensitive both to the nature of the solvent and to the phosphine used. Thus, when [RuX₂(PPh₃)₄] were heated under reflux for prolonged periods with a six-fold excess of tertiary phosphine in either ethanol or dichloromethane the sole products were [RuX₂L₄]X, whereas when the same reaction was carried out in hexane (or light petroleum, b.p. 60—80 °C) neutral tertiary phosphine complexes of ruthenium(II) could be isolated. For L = P(OPh₃)₃, P(OMe)₃, and P(OEt)₃ and in CH₂Cl₂, [RuX₂L₄], [Ru₂X₄], and [La₂Cl₂RuX₄] were formed, respectively. The mononuclear species undergo facile rearrangement in solution in a complex fashion which we have analysed mainly by ¹³P n.m.r. and far-i.r. spectroscopy. These results are discussed separately for each phosphine, together with a proposed overall mechanism for the rearrangement reaction in solution of all tertiary phosphine compounds of type [RuX₂L₃ or L₄].
(a) L = PPh₃.—Although the compounds [RuX₂(PPh₃)₄] (X = Cl or Br; x = 3 or 4) were first reported in 1966,⁵ few studies have been made to ascertain the nature of the species present in solution (cf. the numerous studies on the related [RhCl(PPh₃)₅]).⁶ In the original paper reporting the preparation of these compounds, osmometric molecular-weight determinations in acetone on [RuCl₂(PPh₃)₅] and [RuCl₂(PPh₃)₄] gave values of about a third and a half respectively of those required for a monomer and it was therefore suggested that extensive dissociation of both compounds occurs in solution [equations (1) and (2)]; L = PPh₃.² Recent, spectrophotometric studies in deoxygenated benzene supported these conclusions showing that [RuCl₂(PPh₃)₄] was completely dissociated in solution and that a 10⁻⁴ M solution of [RuCl₂(PPh₃)₅] was ca. 80% dissociated at 298 K (K for equation (2) was calculated to be (2.7 ± 0.5) × 10⁻³ mol⁻¹ L⁻¹).* We have now examined the variable-temperature proton-noise-decoupled ³¹P n.m.r. spectra of more concentrated solutions of these compounds (ca. 0.01—0.1 M) in an attempt to identify more directly the species present in solution.†

Thus, the spectrum of [RuCl₂(PPh₃)₅] in deoxygenated CDCl₃, at ca. 200 K (ca. 0.1 M), consisted of two strong signals at 25.0 and 75.8 p.p.m. of relative intensity 2:1 [Figure 1(a)]. At 173 K in CH₃Cl₂-(CD₃)₂CO these signals were resolved into a doublet and triplet pattern respectively [J(PP) 30.3 Hz] which is consistent with the square-pyramidal structure (I) established for the compound by X-ray analysis.²² In addition [Figure 1(c)] there were some weak peaks centred at 56.0 p.p.m. which comprise an AB pattern [J(PP) 42 Hz, δ(³¹P) 320 Hz] and a small singlet at −7.3 p.p.m. (free PPh₃) also of relative intensity 2:1. On raising the temperature the intense signals first broadened and then coalesced (ca. 250 K) and finally gave a sharp singlet (>290 K) at 41.1 p.p.m.; the smaller peaks broadened and coalesced at slightly higher temperatures (ca. 290 K), but the free PPh₃ signal remained sharp to ambient temperature although it shifted slightly to lower field [see Figure 1(b) and (c)]. On lowering the temperature, the spectrum shown in Figure 1(a) was produced. In C₄D₄-toluene (ca. 0.01 M) at ca. 220 K the same spectrum as in Figure 1(a) was observed except that the AB pattern at 57.6 p.p.m. and the free PPh₃ peak were much more intense in comparison to the [RuCl₂(PPh₃)₅] signals [Figure 1(d)]. On addition of free PPh₃ the AB pattern disappeared, indicating the resonances arise from a dissociation product of [RuCl₂(PPh₃)₄].

* 1 mol dm⁻³.
† Although some of our results are very similar to those briefly reported by Caulton ¹¹ whilst this work was in progress, we propose to give them in detail here because they are of use in interpreting the more complicated behaviour observed with the other [RuX₂(PPh₃)₄] compounds in solution.

These observations are indicative of only slight dissociation (ca. 5%) of [RuCl₂(PPh₃)₅] at 0.1 M concentration, considerable dissociation at 0.01 M (ca. 30%).

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Figure 1. ³¹P N.m.r. spectra of [RuCl₂(PPh₃)₅] (ca. 0.1 M) in CDCl₃ at (a) 200, (b) 250, and (c) 308 K, and (d) in C₄D₄-toluene (ca. 0.01 M) at 229 K.

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shapes of (I) appear concentration independent, and slow intermolecular exchange between free and bound PPh₃ groups of either of the ruthenium complexes present in solution. The AB resonance pattern is attributed to

\[
\begin{align*}
\text{RuCl₂(PPh₃)₂} & \quad \text{RuCl₂(PPh₃)₂} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

(1)

the dissociation compound \([\text{RuCl₂(PPh₃)₂}]₆\) and, like Caulton, we conclude that such a pattern is incompatible with a monomeric \([\text{RuCl₂(PPh₃)₂}]\) species (only a \(31\text{P}\) n.m.r. singlet is expected for tetrahedral or square-planar configurations and stabilisation of a cis-octahedral compound \([\text{RuCl₄(PPh₃)₂(solvent)]₆}\) is very unlikely in solvents such as CDC₁₈ or toluene), but it is consistent with a dimeric structure of type (II).

Thus we suggest that equilibrium (2) should be reformulated as (3). This equilibrium is analogous to

\[2[\text{RuCl₂(L₂)}] \leftrightarrow [\text{RuCl₂L₂}] + 2L\] (3)

that now established for the behaviour of \([\text{RhCl₂}]\) \(L = \text{PPH₃}\) or \(\text{P(C₆H₄Me-ϕ)}\) in solution \(^{20}\) [equation (4)], although earlier spectrophotometric studies \(^{34}\) (for \(L = \text{PPH₃}\)) were erroneously interpreted in terms of equilibrium (5). Therefore, with the modification that there

\[2[\text{RhCl₂}] \leftrightarrow [\text{RhCl₂}] + 2L\] (4)

\[\text{[RhCl₂]} \leftrightarrow [\text{RhCl₂}] + L\] (5)

is a monomer-dimer, (3), and not a monomer-monomer equilibrium, (2), for \([\text{RuCl₂(PPh₃)₂}]\) in low polarity solvents, these \(31\text{P}\) n.m.r. results are in excellent agreement with those of the recent spectrophotometric studies \(^{21}\).

For \([\text{RuCl₂(PPh₃)₂}]\) (ca. 0.1m), \(31\text{P}\) n.m.r. measurements show even at 153 K in CH₂Cl₂-(CD₃)₂CO (Figure 2) complete dissociation into \([\text{RuCl₂(PPh₃)₂}]\) and PPh₃. On raising the temperature coalescence of the two signals from \([\text{RuCl₂(PPh₃)₂}]\) occurred but there is no evidence of the weak peaks at 56.0 p.p.m. This is further confirmation that these signals are due to a dissociated species since they are suppressed in the presence of excess of PPH₃. This behaviour of \([\text{RuCl₂(PPh₃)₂}]_₄\) is reminiscent of that reported for ML₄ compounds \((M = \text{Ni, Pd, or Pt; L = PPh₃, etc.})\) \(^{26}\) which are substantially dissociated into ML₃ and L at ambient temperature. A suggestion made by Tolman et al. \(^{28}\) could also be valid here, namely that the tetrakis complex might be best represented as \([\text{RuCl₂(PPh₃)₂PPh₃}]\) with one PPh₃ group trapped in the lattice. This suggestion is supported by the similar colours of \([\text{RuCl₂(PPh₃)₂}]\) \(^{29}\) and \([\text{Ni(PPh₃)₄}]\) \(^{29}\) and \([\text{Ni(PPh₃)₃}]\) \(^{29}\).

As noted earlier, solutions of \([\text{RuCl₂(PPh₃)₂}]\) are extremely sensitive to oxygen, rapidly changing from yellow-brown to green with the formation of Ph₃PO.

\[\text{[RuCl₂(PPh₃)₂]} + 1.5\text{O}_₂ \rightarrow 3\text{PPh₃PO} + \text{RuCl₂}\] (6)

Cenini et al. \(^{30}\) postulated the formation of an intermediate oxygen complex \([\text{RuCl₂(O₃)(PPH₃)₃}]\) during this process although no direct evidence has been found.

\[2\text{[RuCl₂(PPh₃)₂]} \leftrightarrow [\text{RuCl₂}(\text{PPh₃})_₄] \quad \text{(ca. 0.1m)} \quad \text{in CH₂Cl₂-(CD₃)₂CO at 153 K}

Therefore, we examined the \(31\text{P}\) n.m.r. spectra of \([\text{RuCl₂(PPh₃)₃}]\) and \([\text{RuCl₂(PPh₃)₄}]\) in the presence of small amounts of air. When the sealed tube was open to air for short periods, the CDC₁₈ solution (at 308 K) turned greenish brown and the \(31\text{P}\) n.m.r. spectrum showed an extra strong sharp resonance at 29.4 p.p.m. corresponding closely to that of free Ph₃PO. Addition of some Ph₃PO to this solution produced virtually no shift indicating that it does not arise from a Ru(OPPh₃)₄ compound in rapid exchange with free Ph₃PO. The formation of Ph₃PO was accompanied by a substantial decrease in the intensity of the resonance at 41.2 p.p.m. (and an increase in the intensity of the AB resonance pattern at 66.0


p.p.m.), but when excess of PPh₃ was present (or alternatively when solutions of [RuCl₄(PPh₃)₂] were exposed to air) much less Ph₃PO was generated. Presumably the presence of excess of PPh₃ inhibits the formation of Ph₃PO by shifting equilibrium (3) even further to the left. This is consistent with the observation that the tris(phosphine) complex is virtually inactive as a catalyst for this oxygenation reaction.²¹

Small extra singlet peaks were found in the ³¹P n.m.r. spectrum of [RuCl₄(PPh₃)₂] after air exposure. In CDC₅H₁₁ a peak at 48.1 p.p.m., whereas in CH₂Cl₂·(CD₃)₂CO extra peaks at 48.1 and 38.8 p.p.m., were observed. For [RuCl₄(PPh₃)₂] these extra peaks were absent, suggesting they arise by dissociative mechanisms. It is very difficult to unequivocally determine the species giving rise to these weak singlets. Possibilities for the signal at 48.1 p.p.m. are small amounts of [RuCl₄(PPh₃)₂], [RuCl₄(O₃P)(PPh₃)], a Ru(OPPh₃) complex, dimers such as (III) or (IV) with equivalent PPh₃ groups, or even a cationic Ru¹¹ compound (see below). Since the signal at 38.8 p.p.m. is only observed in acetone between ca. 230 and 270 K, it might arise from a solvate such as [(RuCl₄(PPh₃)₂(OCH₂CH₃))₄], although an ionic formulation cannot be discounted. Clearly, exposure of these solutions to air generates additional complications which are very difficult to analyse in detail.

An alternative dissociation path is available for [RuCl₄(PPh₃)₂] which would be facilitated in more polar solvents; namely loss of Cl⁻ to produce Ru¹¹ cations [equations (7) and (8)]. Spectrophotometric and conductometric studies on NN-dimethyformamide (dmf) solutions of [RuCl₄(PPh₃)₂] indicated that these types of equilibria were important in polar solvents but no cationic compounds were isolated.²² Also, [RuCl₂·(PPh₃)₂] gave a pale yellow air-stable solution in nitromethane which had a conductivity corresponding to that of a 1:1 electrolyte but attempts to isolate solid compounds by solvent removal were unsuccessful.²² However, ³¹P n.m.r. studies on [RuCl₄(PPh₃)₂] in MeNO₂ revealed an AB pattern centered at 46.1 p.p.m. and a strong singlet at 27.0 p.p.m. (Ph₃PO). A possible formulation of the compound in solution based on this evidence is [RuCl(PPh₃)₂(O₂NMe₂)₂]Cl, (V), which is consistent with the spectrophotometric results²¹ and with the recent synthesis of compounds such as [RuCl₂(C₅H₁₂)(NCMe)₃]·[PF₆]⁻ (L = PPh₃, etc.) via [RuCl(C₅H₁₂)(NCMe)₃][PF₆].²⁷

![Diagram](image)

Finally, it should be noted that no evidence has been found for any dimeric complexes containing more than two PPh₃ ligands per ruthenium atom.

(b) L = PEtPh₃. — When [RuCl₂(PPh₃)₂] was heated under reflux with excess of PEtPh₃ in degassed hexane under nitrogen for ca. 18 h green crystals were deposited which analysed closely for the empirical formula [RuCl₂(PPh₃)₂]. Likewise, reaction with [RuBr₂·(PPh₃)₂] gave green [RuBr₂(PPh₃)₂], whereas in ²³ T. V. Ashworth and E. Singleton, J. Organometallic Chem., 1974, 77, C31.

Far-i.r. spectra (400—150 cm⁻¹) of some ruthenium(II) phosphine complexes (shoulders in italics)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(RuX)</th>
<th>Other bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RuCl₄(PPh₃)₂]</td>
<td>315w</td>
<td>298w, 284w, 275w, 266w, 257w, 235w, 250, 197m, 183m, 175w, 155w</td>
</tr>
<tr>
<td>[RuBr₂(PPh₃)₂]</td>
<td>240w</td>
<td>307w, 277w, 266w, 257w, 235w, 196m, 184w, 154w</td>
</tr>
<tr>
<td>[(RuCl₄(PPh₃)₂(OCH₂CH₃))₄]</td>
<td>323vs, 250m</td>
<td>329, 290m, 280w, 267m, 260w, 239w, 224s, 216m, 196w, 192w, 182s, 154w</td>
</tr>
<tr>
<td>[RuCl₄(PPh₃)₂]</td>
<td>327s</td>
<td>298w, 272m(br), 246w, 173m(br)</td>
</tr>
<tr>
<td>[RuBr₂(PPh₃)₂]</td>
<td>225w</td>
<td>322w, 317w, 290w, 265m(br), 190w</td>
</tr>
<tr>
<td>[RuCl₂(PPh₃)₂]Cl</td>
<td>250m</td>
<td>296w, 299w, 298w, 180m</td>
</tr>
<tr>
<td>[RuCl₂(PEtPh₃)₂]Cl</td>
<td>312w, 260m(br)</td>
<td>300w, 206w</td>
</tr>
<tr>
<td>[RuCl₂(PEtPh₃)₂]Br</td>
<td>311s, 249m</td>
<td>319w, 299m, 217w</td>
</tr>
<tr>
<td>[RuCl₂(PEtPh₃)₂]Cl</td>
<td>220w</td>
<td>284w, 270m, 250w, 238w, 203w, 180m</td>
</tr>
<tr>
<td>[RuCl₂(C₅H₁₁)(NCMe)₃]</td>
<td>316w, 260m(br)</td>
<td>308</td>
</tr>
<tr>
<td>[RuCl₂(PMe₃Ph)₂]Cl</td>
<td>268w, 220w, 217w, 173m</td>
<td></td>
</tr>
<tr>
<td>[RuCl₂(PMe₃Ph)₂]Cl</td>
<td>241s</td>
<td>288w, 263w, 177m</td>
</tr>
</tbody>
</table>

ethanol or dichloromethane prolonged reflux of [RuCl$_5$-(PPh$_3$)$_4$] with PEtPh$_3$ gave lemon-yellow [Ru$_2$Cl$_3$-(PEtPh$_3$)$_6$]Cl, (VI). Comparison of the far-i.r. spectra of these compounds showed that the green compound contained no traces of (VI) (see Table) and that the position of ν(RuCl) was similar to that found for [RuCl$_5$-(PPh$_3$)$_3$], consistent with a structure of type (I). Although the $^1$H n.m.r. spectrum of this compound was of 30.4 and 73.3 p.p.m. (relative intensity 2:1) which in CH$_2$Cl$_2$-(CD$_2$)$_2$CO at 195 K were resolved into a doublet and triplet pattern respectively [J(PP) 30.0 Hz]. In addition, there was a very weak broad resonance at ca.
47 p.p.m., together with a very weak sharp peak at ca. 13 p.p.m. assigned to free P(\text{Et})Ph$_3$. Thus, by analogy with the PPh$_3$ studies, this indicates that the green compound has the same structure in solution as [RuCl$_4$(PPh$_3$)$_3$] and that there is very little dissociation of the type shown in either equation (2) or (3) at this temperature and concentration (ca. 0.1 M).

However, when [RuCl$_4$(P(\text{Et})Ph$_3$)$_3$] was first dissolved at room temperature and then cooled for examination, the observed $^{31}$P n.m.r. spectra were more complicated. Thus, at 195 K in CH$_2$Cl$_2$-(CD)$_3$CO, in addition to the peaks at 29.4 and 73.7 p.p.m. ([RuCl$_4$(P(\text{Et})Ph$_3$)$_3$]), the spectrum consisted of a broad resonance at 48.1 p.p.m., a strong sharp resonance at -14.7 p.p.m. (free P(\text{Et})Ph$_3$), and a broad asymmetric resonance between 31 and 34 p.p.m. (Figure 3(a)). On raising the temperature various changes occurred. The triplet and doublet resonances (29.4 and 73.7 p.p.m.) lost their fine structures, broadened, and also became progressively weaker with respect to the other peaks so that by ca. 250 K, there was very little [RuCl$_4$(P(\text{Et})Ph$_3$)$_3$] left in solution. At the same time the peak at 48.1 p.p.m. became sharper and more intense, and it can then be seen that there is a very weak resonance on the high-field side of this sharp singlet (at ca. 47 p.p.m.) (Figure 3(b)–3(d)). The free phosphine resonance also increased in intensity and shifted slightly to lower field and the broad resonance between 34 and 31 p.p.m. grew in intensity and became much sharper so that by ca. 250 K it exhibited an unmistakable AB$_2$ pattern [Figure 3(d)] [A 33.7, B 31.5 p.p.m.; 8(AB) 91.0, J(AB) 27.3 Hz]. Above 250 K a broad peak appeared at ca. 43 p.p.m. which corresponds to the averaged position of the [RuCl$_4$(P(\text{Et})Ph$_3$)$_3$] resonances [cf. [RuCl$_4$(PPh$_3$)$_3$]], all the other resonances being slightly decreased in intensity, and the AB$_2$ resonance pattern began to broaden [Figure 3(e)]. At 293 K the resonance at 43.0 p.p.m. had sharpened considerably and the AB$_2$ set collapsed to a broadened singlet at 32.0 p.p.m. with a strong shoulder at 33.0 p.p.m., whereas at 308 K there was a strong singlet at 32.6 p.p.m. and a weak shoulder at 32.1 p.p.m. The other peaks were much the same except that the P(\text{Et})Ph$_3$ resonance (now at -12.3 p.p.m.) was broader and weaker than at lower temperatures [Figure 3(f) and (g)].

Finally, when this solution was left for 3 h at 308 K and then recooled to ca. 213 K [Figure 3(b)] the spectrum was similar to that observed earlier at this temperature [Figure 3(b)] except for the following differences: (i) the resonances due to [RuCl$_4$(P(\text{Et})Ph$_3$)$_3$] and free P(\text{Et})Ph$_3$ were much weaker on recoupling; and (ii) the various signals between 31 and 34 p.p.m. were comparable in position and intensity with those shown in Figure 3(b) except that the peak at 32.8 p.p.m. [which was a weak shoulder in Figure 3(b)] was the strongest resonance.

The same variations in $^{31}$P n.m.r. spectra with temperature were observed for [RuCl$_4$(P(\text{Et})Ph$_3$)$_3$] in C$_6$D$_6$-C$_6$H$_6$ except that all the resonances were shifted ca. 2 p.p.m. to low field and that at 308 K there was only one broadened peak at 34.3 p.p.m. This indicates that, with the exception of the compound which forms irreversibly in CH$_2$Cl$_2$-(CD)$_3$CO and which is absent in benzene, all the other resonances arise from non-ionic species.

The $^{31}$P n.m.r. spectrum of [Ru$_2$Cl$_3$(P(\text{Et})Ph)$_6$]Cl$_2$ (VI), (made by refluxing 'Ru$_2$Cl$_3$8OH$_2$' and excess of P(\text{Et})Ph$_3$ in aqueous ethanol) in CDCl$_3$ at 308 K consisted of a sharp singlet at 32.7 p.p.m. This compound does not undergo further reaction under the experimental conditions present in this study (but see later). Next, when [RuCl$_4$(P(\text{Et})Ph)$_3$] was dissolved in CH$_2$Cl$_2$ at room temperature, the solvent removed from the green solution in vacuo, and light petroleum (b.p. 60–80 °C) added to the sticky residue, most of the material dissolved giving an orange-brown solution and a green residue. ([RuCl$_4$-(P(\text{Et})Ph)$_3$] is initially completely insoluble in light petroleum (b.p. 60–80 °C).) Removal of solvent then gave an orange-brown solid whose $^{31}$P n.m.r. spectrum at 290 K in C$_6$D$_6$–hexane consisted of a sharp singlet at 50.4 p.p.m. and an AB$_2$ pattern of resonances between 33 and 36 p.p.m. (relative intensity 2:3). This AB$_2$ pattern has identical parameters to that shown in Figure 3(d) (except for the low-field shift of ca. 2 p.p.m.). The orange-brown solid analysed for [Ru$_2$Cl$_3$(P(\text{Et})Ph)$_6$] (VII), and further support for this formulation comes from molecular-weight measurements in C$_6$H$_6$, far-i.r. studies which show both terminal and bridging ν(RuCl) vibrations [cf. (Ph$_3$P)$_2$YRuCl$_3$RuCl(PPh$_3$)$_3$] (Y = CO).
or CS), Table), and the similarity of this data to those for [RuCl₄(PPh₃)₃] (see later).

Furthermore, when [RuCl₄(PPh₃)₃] was heated under reflux with excess of PEtPh₂ in ethanol for 3 h a yellow conducting solution was formed which gave a yellow solid on solvent removal. The ³¹P n.m.r. spectrum of this material [which analysed closely for \( \text{RuCl}_4(\text{PETPh}_2)_2 \) ] in CDCl₃ at 220 K consisted of an \( \text{AB}_2 \) pattern on which was superimposed a sharp strong singlet at 33.1 p.p.m. \( \{\text{RuCl}_4(\text{PETPh}_2)_2\}_2\text{Cl} \) (Figure 4). However, the \( \text{AB}_2 \) pattern had a different set of parameters from \( \text{RuCl}_4(\text{PETPh}_2)_2 \), namely \( \delta(\text{AB}) 126.8, J(\text{AB}) 63.4 \text{ Hz} \). Similarly, reaction of \( \text{RuCl}_4(\text{PPh}_3)_2 \) with excess of PETPh₂ in refluxing ethanol for short periods gave a yellow solid with the same \( \text{³¹P} \) n.m.r. spectrum in CDCl₃ at 210 K as that shown in Figure 4. However, on raising the temperature to 308 K, the spectrum showed a very strong peak at 32.7 p.p.m. \( \{\text{RuCl}_4(\text{PETPh}_2)_2\}_2\text{Cl} \), a weak peak at 43.1 p.p.m. \( \{\text{RuCl}_4(\text{PETPh}_2)_2\}_2 \), weak peaks at 48.5 and 32.1 p.p.m. \( \{\text{RuCl}_4(\text{PETPh}_2)_2\}_2 \), —11.0 p.p.m. (free PETPh₂), and a very weak \( \text{AB}_2 \) pattern compared to that observed at 210 K. Thus the species (VIII) giving rise to this \( \text{AB}_2 \) pattern is only stabilised at low temperature or in the presence of excess of PETPh₂. On raising the temperature in the absence of free PETPh₂ it rearranges to form \( \text{RuCl}_4(\text{PETPh}_2)_2 \), [RuCl₄(PPh₃)₃], [RuCl₄(PPh₃)₃]-Cl, and free PETPh₂.

A complete rationalisation of all these experimental observations is provided by the rearrangement mechanism.

* Structure (VIII) with the three L groups cis is preferred to the isomer with two L groups mutually \( \text{trans} \) because the former is more likely to give a \( \text{³¹P} \) \( \text{AB}_2 \) resonance pattern and also because it readily leads to structures (VII) and (VI) by simple intramolecular rearrangement. Furthermore, the absence of any association process for \( \text{RuCl}_4(\text{PPh}_3)_2 \) is best explained by the steric constraints involved in arranging three PPh₃ groups cis to each other as in structures (VI), (VII), and (VIII).

Figure 3(c) shows extra signals (marked with asterisks) in addition to those from (VII) and (I) which can be attributed to \( \{\text{RuCl}_4(\text{PETPh}_2)_2\}_2\text{Cl} \) (cf. Figure 4). Precedents for intramolecular rearrangements of this type are provided by the rearrangement of the related \( \{\text{RuCl}_4(\text{CS})_2(\text{PPh}_3)_2\}_2 \) to \( \{\text{RuCl}_4(\text{CS})_2(\text{PPh}_3)_2\}_2 \) and of \( \{[(\tau-\text{C}_5\text{Me}_5)_2\text{RhCl}_2]_2 \) to \( \{[(\tau-\text{C}_5\text{Me}_5)_2\text{RhCl}_2]_2 \) [BPh₄]⁻. Thus step (iv) is favoured in polar solvents particularly in the presence of free PETPh₂. In non-polar solvents step (iii) is dominant and no ionic dimer is formed. However, in more polar solvents, after formation of (VII) and (VI).

† Recent studies show that this rearrangement process is much more facile for \( \text{Y} = \text{CO} \) and that it is difficult to isolate \( \{\text{RuCl}_4(\text{CO})(\text{PPh}_3)_2\}_2 \) without contamination from \( \{\text{RuCl}_4(\text{CO})(\text{PPh}_3)_2\}_2 \).

free PETPh₂, slow displacement of the terminal halide group by PETPh₂ occurs to give (VI) [step (vi)].

The observation of a broad resonance between 34 and 31 p.p.m. below 215 K which sharpened to an AB₃ pattern at higher temperatures and then coalesced to a singlet at ambient temperatures (Figure 3) appears rather baffling at first sight. However, the high-temperature broadening is ascribed to intermolecular exchange of the bound phosphine groups in (VII) with free PETPh₂ and this is readily demonstrated by addition of excess of PETPh₂. The low-temperature broadening which is also reversible is attributed to viscosity effects.

(c) L = PET₃Ph.—When [RuCl₃(Ph₃P)₃] was heated under reflux with excess of PET₃Ph in light petroleum (b.p. 60—80 °C) under nitrogen for 24 h, a dark green solution was formed. Removal of solvent gave a green oil which on treatment with light petroleum (b.p. 60—

80 °C) deposited an orange solid. The same orange solid separated out on allowing the reaction to proceed for 36 h. Although elemental analyses on this material were slightly variable (see Experimental section) and it was also impossible to distinguish on this evidence alone between [RuCl₃(PET₃Ph)₃] and [RuCl₃(PET₃Ph)(solvent)], the far-i.r. spectrum was very similar to that found for [RuCl₃(PET₃Ph)] and [RuCl₃(Y)(Ph₃P)] (Y = CO or CS) (Table), the compound was dimeric in benzene, and the ³¹P n.m.r. spectra in either CH₂Cl₂—(CD₂)₂CO or CDCl₃ from 210 to 310 K consisted of a sharp singlet at 49.3 p.p.m. and an AB₃ pattern of signals at higher field [A 39.1, B 35.4 p.p.m.; 8(AB) 84.2, J(AB) 29.0 Hz] (relative intensity 2:1:3) (Figure 5). However, conclusive proof that this compound was a sample of [(Ph₃P)₅RuCl₃PET₃Ph]Cl came from comparing its ³¹P n.m.r. and far-i.r. spectra with a genuine sample prepared by pyrolysis of [Ru₂Cl₃(PET₃Ph)₃]Cl in n-propyl propionate at 120 °C.¹¹

Attempts to isolate a green solid from this reaction were unsuccessful. Also, when [RuCl₃(PET₃Ph)] was heated under reflux in benzene with excess of PET₃Ph a yellowish green solution was obtained, but removal of solvent only gave the orange starting material. However, a ³¹P n.m.r. spectrum of this solution at 280 K revealed a weak broad resonance at ca. 43 p.p.m. (in addition to the [RuCl₃(PET₃Ph)] and free PET₃Ph signals) which can be attributed to the presence of some [RuCl₃(PET₃Ph)]₃ (I). When [RuCl₃(PET₃Ph)] was heated under reflux in ethanol with excess of PET₃Ph yellow [RuCl₃(PET₃Ph)]₃Cl (VI) (the ³¹P n.m.r. spectrum in CDCl₃ was a singlet at 35.4 p.p.m.), was formed.

The product from reaction of [RuBr₃(Ph₃P)₃] with excess of PET₃Ph was only briefly examined. Again, the analytical data did not unequivocally distinguish between the formulations [RuBr₃(PET₃Ph)₃] and [RuBr₃(PET₃Ph)(solvent)] but the ³¹P n.m.r. spectrum in CDCl₃ at 220 K, which consisted of a sharp singlet at 44.2 p.p.m. and a broadened resonance at 35.6 p.p.m. (relative intensity 2:3), indicates the latter.


Thus these reaction products are consistent with the Scheme.

(d) L = PCI₃Ph.—Reaction of [RuCl₃(Ph₃P)₃] with excess of PCI₃Ph in refluxing hexane for 3 h gave a non-conducting yellow precipitate. The ³¹P n.m.r. spectrum of this in CDCl₃ was temperature invariant from 210 to 290 K and consisted of a singlet at 165.4 p.p.m. and an AB₃ pattern at higher field [A 134.5, B 126.1 p.p.m.; 8(AB) 341.0, J(AB) 34 Hz] confirming the formulation

![Figure 5 ³¹P N.m.r. spectrum of [RuCl₃(PET₃Ph)] in CDCl₃ at 290 K](image-url)

[RuCl₃(PCI₃Ph)]₃. Attempts to carry out similar reactions in ethanol were unsuccessful due to extensive ethanalysis of the P-Cl bonds with the formation of an intractable mixture of compounds.

(e) L = PMe₃Ph.—Reaction of [RuCl₃(Ph₃P)₃] with excess of PMe₃Ph in refluxing light petroleum (b.p. 60—80 °C) for 3 h gave a crystalline yellow precipitate which analysed closely for [RuCl₃(PMe₃Ph)]₃. This compound can also be prepared by reaction of [RuCl₃(PMe₃Ph)]₃ with excess of PMe₃Ph in hexane. Although this compound is quite stable in the solid state, it rapidly rearranges in solvents such as CH₂Cl₂ to give [RuCl₃(PMe₃Ph)]₃Cl. This process can be monitored by the steady increase in conductivity of a CH₂Cl₂ solution with time. After ca. 5 h at 300 K removal of CH₂Cl₂ gave a quantitative yield of [RuCl₃(PMe₃Ph)]₃Cl. However, the compound is quite stable if it is dissolved in less polar solvents such as CDCl₃ and kept at temperatures below 270 K. Thus the ³¹P n.m.r. spectrum in
CDC$_3$ from 210 to 270 K showed two 1:2:1 triplets at 15.8 and -6.5 p.p.m. $[J(PP) 30.0$ Hz] [Figure 6(a)] consistent with the cis configuration (IX) (cf. cis-[RuH$_2$(PMe$_3$Ph)$_4$]). Above this temperature rapid conversion to the ionic dimer occurred as observed by the appearance of a sharp singlet at 22.0 p.p.m. and a decrease in the intensity of the two triplets [Figure 6(b)]. Rather surprisingly, there is no evidence for any intermediates such as [RuCl$_3$(PMe$_3$Ph)$_2$], [(RuCl$_4$(PMe$_3$Ph)$_2$)$_2$], [Ru$_2$Cl$_4$(PMe$_3$Ph)$_4$], or even free PMe$_3$Ph. However, the absence of the latter is due to fast intermolecular exchange at temperatures above 270 K between PMe$_3$Ph and the ionic dimer as was readily shown by adding free PMe$_3$Ph to [Ru$_2$Cl$_4$(PMe$_3$Ph)$_4$]Cl in CDC$_3$ solution. The failure to observe any of the other intermediates

* A ‘pseudo-triplet’ pattern consists of a sharp doublet with a broad hump situated between the doublet and signifies a relatively large $J(PP)$ compared to $[J(PP) + J(PH)]$ value (cf. cis-[Ru(S$_2$PMe$_3$Ph)$_4$(PMe$_3$Ph)]$^{39}$).


proposed in the Scheme does not necessarily invalidate the occurrence of this general rearrangement mechanism in this instance. The known high affinity of PMe$_3$Ph for Ru$^{	ext{II}}$ (ref. 33) is probably responsible for the short-lived nature of species such as (I) and (VIII).

The $^1$H n.m.r. spectrum of (IX) in CDC$_3$ at 250 K showed two triplets at $\tau$ 8.40 and 8.52 corresponding to the methyl protons of the mutually trans- and cis-phosphines respectively. This pattern is very similar to that observed for [RuH$_2$(PMe$_3$Ph)$_4$]. Except that in (IX) the cis-phosphorus nuclei are much more strongly coupled giving rise to a ‘pseudo-triplet’. On raising the temperature the $^1$H n.m.r. spectrum became a single ‘pseudo-triplet’ at $\tau$ 8.33 characteristic of [RuCl$_3$(PMe$_3$Ph)$_4$]Cl. At 250 K the $^{13}$C proton-noise-decoupled n.m.r. spectrum of (IX) in CDC$_3$ showed a pattern similar to the $^1$H n.m.r. spectrum, namely two triplets for the methyl carbons at 15.8 and 21.4 p.p.m. $[J(PC)$ 15 Hz], two triplets for the quaternary carbon atoms of the phenyl rings [140 p.p.m., $J(PC)$ 17 Hz], and a complex series of doublets for the remaining phenyl carbons between 126 and 139 p.p.m.

Conclusion.—These studies clearly show that earlier attempts to generate monomeric ruthenium(II) halide tertiary-phosphine compounds by direct reaction of RuCl$_3$~3OH$_2^{-}$ and PPh$_3$ have generally been unsuccessful because of the facile rearrangement processes to form dimeric compounds. The driving force for these rearrangements is presumably the high stability of six-coordinate Ru$^{	ext{II}}$ (4d$^9$) compounds containing a triple halide bridge. Only when bulky tertiary phosphines such as PPh$_3$ or P(C$_9$H$_7$Me-p)$_3$ are used are monomeric compounds isolated from the trichloride since steric constraints inhibit associative rearrangement reactions.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany and the University of Edinburgh, Chemistry Department. Molecular weights were determined on a Perkin-Elmer-Hitachi 115 osmometer in benzene at 37 $^\circ$C. I.r. spectra were recorded in the region 4 000–250 cm$^{-1}$ on Perkin-Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the region 400–150 cm$^{-1}$ on a Beckman RIC IR 720 far-i.r. spectrometer using pressed Polythene discs. $^1$H N.M.R.

spectra were obtained on a Varian Associates HA 100 spectrometer equipped with variable-temperature attachment and $^{13}$C and $^{31}$P n.m.r. spectra on a Varian Associates XL 100 spectrometer operating in the pulse and Fourier-transform mode at 25.2 and 40.5 MHz respectively. Chemical shifts are reported in p.p.m. to high frequency of tetramethylsilane and 85% H$_3$PO$_4$, respectively. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. M.ps were determined with a Kofler hot-stage microscope and are uncorrected.

The compounds [RuX$_2$(PPh$_3$)$_4$] (X = Cl or Br) were prepared as described earlier and their $^{31}$P n.m.r. spectra (X = Cl) were obtained on solutions which had been thoroughly deoxygenated by 'freeze-thaw' techniques and then sealed into 5 mm n.m.r. tubes. For the other tertiary phosphine compounds which are much less air sensitive, purging the solvents by heating under reflux in a stream of nitrogen was sufficient to eliminate formation of phoshine oxides and other oxidation products for the duration of the spectroscopic studies. Pure samples of the ionic dimers [Ru$_2$Cl$_4$]Cl (L = PPh$_3$, P$_2$Ph$_4$, or PMe$_2$Ph) were obtained by literature methods.$^{6,7}$

**Dicorrolitristsethylidiphosphorylphosphine**

The compound [RuCl$_2$(PPh$_3$)$_3$] (1.0 g) was heated under reflux in degassed hexane (30 cm$^3$) with ethyldiphosphinyolphosphine (0.40 cm$^3$) under nitrogen for 18 h. The resulting green crystalline precipitate was filtered off, washed thoroughly with light petroleum (b.p. 40–60 °C) to remove any free phosphine, and dried in vacuum at 40 °C (0.50 g, 88%). m. 142 °C (decomp.) (Found: C, 62.0; H, 5.7; Cl, 0.0. Calc. for C$_4$H$_2$Cl$_2$P$_2$Ru: C, 61.9; H, 5.5; Cl, 8.7%).

**Dibromotris(ethyldiphosphorylphosphine)**

The compound also was prepared using [RuBr$_2$(PPh$_3$)$_3$] (0.40 g) and P$_2$Ph$_4$ (0.40 cm$^3$) (0.92 g, 80%). m. 156–158 °C (Found: C, 55.4; H, 5.1. Calc. for C$_4$H$_2$Br$_2$P$_2$Ru: C, 55.8; H, 5.0%).

def-Tri-µ-chloro-µ-chloro-bcgph-pectakis(ethyldiphosphorylphosphine)dicorrolithenium(iii)

The compound [RuCl$_2$-(PPh$_3$)$_3$] (0.14 g), was heated under reflux in degassed ethanol (50 cm$^3$) with ethyldiphosphinyolphosphine (0.10 cm$^3$) under nitrogen for 3 h. The solution was filtered hot to remove excess of green starting material and then solvent removed in vacuum to leave a sticky residue. Addition of light petroleum (b.p. 60–80 °C) then gave an orange-brown solution and a green residue. Partial removal of solvent precipitated the orange-brown product, m. 118–122 °C (decomp.) (Found: C, 50.1; 59.2; H, 5.4; 5.6%; M (in C$_4$H$_2$) 1122. Calc. for C$_7$H$_2$Cl$_3$P$_2$Ru: C, 59.4; H, 5.3%; M 1414).

**Reaction of [RuCl$_2$(PPh$_3$)$_3$] with PPh$_3$ in Ethanol**

The compound [RuCl$_2$(PPh$_3$)$_4$] (I) (0.14 g) was heated under reflux in degassed ethanol (50 cm$^3$) with ethyldiphosphinyolphosphine (0.10 cm$^3$) under nitrogen for 3 h. The solution was filtered hot to remove excess of green starting material and then solvent removed in vacuum. Addition of light petroleum (b.p. 60–80 °C) to the resulting oil gave a yellow solid which analysed closely for [RuCl$_2$(PPh$_3$)$_3$] (Found: C, 60.6; H, 5.7. Calc. for [RuCl$_2$(PPh$_3$)$_3$]: C, 61.9; H, 5.5%). $^{31}$P n.m.r. studies indicated this material to be a mixture of [RuCl$_2$(PPh$_3$)$_3$]Cl (VI), and [RuCl$_2$(PPh$_3$)$_3$] (VIII).

def-Tri-µ-chloro-µ-chloro-bcgph-pectakis(ethyldiphosphorylphosphine)dicorrolithenium(iii)

The compound [RuCl$_2$(PPh$_3$)$_3$] (0.40 g) in degassed light petroleum (b.p. 60–80 °C) (50 cm$^3$) was heated under reflux with diethylidiphosphinyolphosphine (0.35 cm$^3$) for 24 h under nitrogen. The resulting dark green solution was filtered and evaporated to a green oil from which the orange product separated on addition of light petroleum (b.p. 60–80 °C). The product was filtered off and washed with light petroleum (b.p. 40–60 °C) to remove any free PPh$_3$ (0.11 g, 58%). m. 125–127 °C (Found: C, 53.5; 52.4; 61.9; H, 6.7; 6.8; 6.6; Cl, 10.6%; M (in C$_4$H$_2$) 112. Calc. for C$_7$H$_2$Cl$_3$P$_2$Ru: C, 51.1; H, 6.4; Cl, 12.1%; M 174). The variable analytical figures are ascribed to differing amounts of solvent of crystallisation (cf. the preparation of [RuCl$_2$(PPh$_3$)$_3$] from [RuCl$_2$(PPh$_3$)$_3$]Cl and n-propyl propionate).$^{31}$

(b) The same compound was made directly by heating [RuCl$_2$(PPh$_3$)$_3$] (0.40 g) under reflux in light petroleum (b.p. 60–80 °C) with PPh$_3$ (0.35 cm$^3$) for 30 h when orange crystals were precipitated.

def-Tri-µ-bromo-µ-bromo-bcgph-pectakis(diethylidiphosphorylphosphine)dicorrolithenium(iii)

This was prepared as for the chloro-compound using [RuBr$_2$(PPh$_3$)$_3$] (0.2 g) and P$_2$Ph$_4$ (0.16 cm$^3$). Orange-red crystals separated from the hot reaction mixture and were purified as above (0.05 g, 48%), m. 168–169 °C (Found: C, 47.2; H, 6.0%; M (in C$_4$H$_2$) 1348. Calc. for C$_7$H$_2$Br$_2$P$_2$Ru: C, 44.4; H, 5.5%; M 132). Again the high analyses figures are ascribed to the presence of solvent of crystallisation since the $^{31}$P n.m.r. spectrum (see text) indicated the dimeric formulation.

def-Tri-µ-chloro-µ-chloro-bcgph-pectakis(chlorodiphosphorylphosphine)dicorrolithenium(iii)

The compound [RuCl$_2$(PPh$_3$)$_3$] (0.40 g) in degassed hexane (50 cm$^3$) was treated with chlorodiphosphinyolphosphine (0.40 cm$^3$) and the mixture heated under reflux for 3 h under nitrogen. The complex was filtered off as a bright yellow powder and washed thoroughly with light petroleum (b.p. 40–60 °C) (0.14 g, 60%), m. 191–193 °C (Found: C, 51.2; H, 3.7; Cl, 21.2. Calc. for C$_7$H$_2$Cl$_3$P$_2$Ru: C, 49.8; H, 3.5; Cl, 22.0%).

**Dichlorotetraakis(dimethylidiphosphorylphosphine)dicorrolithenium(ii)**

The compound [RuCl$_2$(PPh$_3$)$_3$] (0.40 g) in degassed light petroleum (b.p. 60–80 °C) (70 cm$^3$) was heated under reflux with PMe$_2$Ph (0.30 cm$^3$) for 3 h under nitrogen. Yellow crystals of the product were filtered from the hot solution and washed thoroughly with light petroleum (b.p. 40–60 °C) to remove excess of phosphine (0.16 g, 65%), m. 165–170 °C (decomp.) (Found: C, 53.1; H, 5.6; Cl, 9.7. Calc. for C$_7$H$_2$Cl$_3$P$_2$Ru: C, 53.0; H, 6.1; Cl, 9.8%).

(b) The compound was heated under reflux in hexane (50 cm$^3$) with excess of PMe$_2$Ph (0.04 cm$^3$) for 12 h under nitrogen. The yellow solid formed was filtered off, washed with light petroleum (b.p. 100–120 °C), and dried (88%). The same reaction in methanol gave only [RuCl$_2$(PMe$_2$Ph)$_3$]Cl.*

**Dibromotetraakis(dimethylidiphosphorylphosphine)dicorrolithenium(ii)**

The compound [RuCl$_2$(PPh$_3$)$_3$] (0.40 g) in degassed light petroleum (b.p. 60–80 °C) (70 cm$^3$) was heated under reflux with P$_2$Ph$_4$ (0.13 cm$^3$) as a yellow solid (0.055 g, 41%), m. 144–160 °C (decomp.) (Found: C, 47.6; H, 5.6. Calc. for C$_7$H$_2$Br$_2$P$_2$Ru: C, 47.2; H, 5.4%).

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Cationic and Neutral Complexes of Ruthenium-(II) and -(III) containing Tertiary Phosphines or Arsines and Nitrogen-donor Ligands

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In contrast to the reaction of \([\text{RuX}_3(\text{EPPh})_2(\text{HOMe})]\) (X = Cl or Br; E = P or As) with N–N (N–N = 2,2′-bipyridyl or 1,10-phenanthroline) in CH₂Cl₂ which gives \([\text{RuX}_3(\text{EPPh})(\text{N–N})]\), the reaction in methanol gives \([\text{RuX}_3(\text{EPPh})(\text{N–N})_2\text{X}](X = \text{Cl or Br}; E = \text{P})\). For E = As these cations are only formed if \([\text{RuCl}_3(\text{AsPh})_2(\text{N–N})]\) and N–N in methanol are reacted in the presence of Na[BPh₄]. However, reaction of \([\text{RuCl}_3(\text{PPh}_3)_2(\text{O}_2\text{NMe})]\), bipy, and Na[BPh₄] in methanol gives both \([\text{RuCl}_3(\text{PPh}_3)_2(\text{bipy})][\text{BPh}_4]\) and \([\text{RuCl}_3(\text{PPh}_3)(\text{bipy})_2][\text{BPh}_4]\) whereas \([\text{RuCl}_4(\text{PPh}_3)(\text{bipy})]\) and PhCN give \([\text{RuCl}_4(\text{PPh}_3)(\text{NCPh})(\text{bipy})][\text{Cl} \cdot \text{H}_2\text{O}]\). Reaction of mer-[\text{RuCl}_3(\text{PMe}_2\text{Ph})_2(\text{PMe}_2\text{Ph}_{2}^\text{+})] and excess of bipy in methanol followed by recrystallisation from acetone–light petroleum gives \([\text{RuCl}(\text{PMe}_2\text{Ph})_3(\text{bipy})][\text{Cl} \cdot \text{H}_2\text{O}]\) and \([\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{bipy})][\text{OCMe}_3]\) Cl, whereas in CH₂Cl₂ \([\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{bipy})]\) and a small amount of [Hbipy][\text{RuCl}_3(\text{PMe}_2\text{Ph})(\text{bipy})] is formed. With phan the product from CH₂Cl₂–hexane is \([\text{RuCl}_3(\text{PMe}_2\text{Ph})_2(\text{phan})]\), but from methanol, followed by recrystallisation from CH₂Cl₂–light petroleum, the main product is \([\text{RuCl}(\text{PMe}_2\text{Ph})_3(\text{phan})(\text{CH}_2\text{Cl}_2)]\) Cl together with small amounts of [Hphan][\text{RuCl}_3(\text{PMe}_2\text{Ph})(\text{phan})] Cl₂·H₂O. With 3,4,7,8-tetramethyl-1,10-phenanthroline (Me₂phen), reaction with \([\text{RuCl}_3(\text{PMe}_2\text{Ph})_2]\) in methanol gives \([\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{Me}_2\text{phen})][\text{Cl}]\) which on recrystallisation from CH₂Cl₂–pentane gives \([\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{Me}_2\text{phen})][\text{Cl} \cdot \text{H}_2\text{O}]\). In contrast, reaction with 2,9-dimethyl-1,10-phenanthroline (Me₂phen) gives \([\text{Ru}_2\text{Cl}_4(\text{Me}_2\text{phen})_2][\text{Cl}_2]\) and \([\text{Ru}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_2][\text{Cl} \cdot \text{H}_2\text{O}]\). All the complexes have been characterised by elemental analysis, \(^1\)H and \(^31\)P n.m.r. spectra, and heteronuclear-decoupling studies and attempts have been made to rationalise the observed differences in product composition.

Several successful methods of preparation of neutral Ru(III) complexes containing tertiary phosphines and

arsines have been reported elsewhere.\(^2\) However, as reported briefly earlier,\(^3\) when some of these reactions are carried out in more polar solvents such as methanol,


rather than dichloromethane, reduction to cationic RuIII complexes occurs. Although a wide range of neutral RuII complexes has been reported, few cationic RuIII complexes containing phosphine (or arsine) ligands are known. Therefore we considered it of some importance to attempt to synthesise and characterise more complexes of this type, especially in view of the antibacterial activity recently demonstrated for rhodium(III) cations containing various nitrogen-donor ligands.

RESULTS AND DISCUSSION

(a) Triphenyl-phosphine and -arsine Complexes containing Nitrogen-donor Ligands.—A range of neutral RuII complexes containing tertiary phosphines or arsines and bidentate nitrogen-donor ligands was prepared by reaction of [RuX₂(EPh₃)₃(HOMe)] (X = Cl or Br; E = P or As) with either 2,2'-bipyridyl or 1,10-phenanthroline (N–N). When the reactions were carried out in CH₂Cl₂, the only products obtained were the neutral paramagnetic RuIII complexes [RuX₃(EPh₃)(N–N)] (except in the case where E = P, X = Br, and N–N = bipy, when a small amount of a yellow-brown solid identified as the halide-bridged complex [Ru₂Br₄(PPh₃)₄(bipy)]Br₂ was also isolated). The complex [Ru₂Br₄(PPh₃)₄(bipy)]Br₂ was obtained in higher yield by reaction of [RuBr₄(PPh₃)₃] and bipy in CH₂Cl₂; similarly [Ru₂Cl₄(PPh₃)₄(bipy)]Cl₂ was synthesised from [RuCl₄(PPh₃)₃] and bipy (see ref. 2).

However, when the reactions of [RuCl₄(PPh₃)₃(HOMe)] and excess of N–N were carried out in methanol [RuCl₄(PPh₃)(N–N)₂]Cl₂·H₂O, (I), were obtained together with very low yields of [RuCl₃(PPh₃)(N–N)]⁻. The monomeric cations can also be prepared by reactions of [RuCl₄(PPh₃)(N–N)] and excess of N–N in methanol. Similarly, reactions of [RuCl₃(PPh₃)₃] with excess of N–N in methanol gave the same cations together with small amounts of [Ru₂Cl₄(PPh₃)(N–N)₂]Cl₂·H₂O. The monomeric cations are confirmed by the ready synthesis of the [PF₆]⁻ and [BPh₄]⁻ salts (see ref. 2). In contrast, the reaction of [RuCl₃(AsPh₃)₃(HOMe)] or [RuCl₃(AsPh₃)(bipy)] with excess of bipy in methanol gave [Ru(bipy)₃Cl₂·H₂O]⁻ (II), and small amounts of purple [RuCl(OH₂)(bipy)]Cl₂·H₂O, (III). However, when a mixture of [RuCl₃(AsPh₃)(bipy)], bipy, and Na[BPh₄] was heated under reflux in methanol the only product was [RuCl₃(AsPh₃)(N–N)₂]BPh₄, (I) (see ref. 2).

In the Scheme possible modes of formation of complexes (I)–(III) are presented. The structures of [RuCl₃(EPh₃)₃(HOMe)] (A) and [RuCl₃(EPh₃)(N–N)] (B) have been previously established. Thus, in step (i) N–N displaces first the labile MeOH ligand and subsequently a EPh₃ group to form the RuIII complex (B).

Although no direct experimental evidence is available, we suggest that all complexes (I) have a cis configuration by analogy with earlier studies on [MC₁₂(N–N)₂]Cl (M = Co, Cr, or Rh) which only exhibit cis-octahedral geometry.


In CH₂Cl₂, further dissociation of halide groups is not encouraged and therefore (B) is the only product. However, step (ii) is facilitated when methanol is used as solvent. Here the more polar solvent encourages dissociation of the halide groups, probably initially of X₁ (trans to N–N) and then X₂ (or X₃) is subsequently displaced to give (I).* The displacement of halide groups is also accompanied by reduction of the metal to the bivalent state. For E = As further reaction occurs in methanol, namely displacement of the AsPh₃ group and the remaining halide ligand by N–N to give [Ru(N–N)₂X₃]⁻ (II) [step (iv)]. In addition, small amounts of [RuCl(OH₂)(N–N)₂]Cl₂·H₂O, (III), are produced, presumably by displacement from (I) of the AsPh₃ group by water [step (v)]. Reactions (iv) and (v) do not occur under these conditions when E = P, presumably because PPh₃ is a stronger nucleophile than AsPh₃. However, the synthesis of [RuCl₃(AsPh₃)(bipy)]⁻-[BPh₄]⁻ by reaction of [RuCl₃(AsPh₃)(bipy)], bipy, and


Na[BPh₄] in methanol confirms that (I) is initially formed even for E = As [step (iii)].

When [RuCl₃(PPh₃)₂(O₂NMe)₃]⁺ excess of bipy, and Na[BPh₄] were heated under reflux in methanol two orange products formed. The less soluble species, which is obtained in higher yield (60%), analysed for the Ru³⁺ cation [RuCl₃(PPh₃)₂(bipy)]⁺[BPh₄]⁻ (IV), and the other product is [RuCl₂(PPh₃)₂(bipy)]₂[BPh₄]⁻ (I). Therefore, in methanol, preferential replacement of halide ion rather than PPh₃ occurs and the resulting Ru³⁺ cation (IV) can be precipitated by [BPh₄]⁻ ion before substantial reduction to the Ru¹⁺ cation (I) occurs. Hence, in polar solvents, steps (vi) and (vii) (see Scheme) also constitute an important alternative path for formation of (I).

In an attempt to synthesise mixed nitrogen-donor ligand cationic complexes, [RuCl₃(PPh₃)(bipy)] was treated in methanol with excess of phenyl cyanide. A yellow solid was isolated which analysed for the Ru⁺⁺⁺ cation [RuCl₃(PPh₃)(NCPh)(bipy)]⁺[Cl]·H₂O [v(CCN) 178 B.M. by Evans' method]. The i.r. spectrum contained a weak band at 2.222 cm⁻¹ suggesting that bonding occurs through the nitrogen. Examination of the far-i.r. spectrum revealed two bands at 320 and 300 cm⁻¹ consistent with configuration (Va). However, recrystallisation from CH₂Cl₂-pentane gave a single product band at 331 cm⁻¹ and no changes in the rest of the spectrum. A possible explanation is facile isomerisation of (Va) to give (Vb). In this instance, the absence of Ru⁺⁺⁺ species (cf. the reaction of [RuCl₃(PPh₃)(bipy)] with bipy) can be attributed to the lower nucleophilicity of PhCN compared to bipy.

(b) Dimethylphenylphosphine Complexes containing Bis-dentate Nitrogen-donor Ligands.—Reaction of mer-
[RuCl₃(PMe₂Ph)₃] (A') with excess of bipy in refluxing methanol followed by solvent removal and recrystallisation from acetone-light petroleum gave an orange precipitate and a red filtrate. The former, whose i.r. spectrum showed the presence of PMe₂Ph, bipy, and water ligands, analysed for [RuCl₃(PMe₂Ph)₂(bipy)(OH₂)] Cl₂H₂O and is conducting in CH₂Cl₂. Its ¹H n.m.r. spectrum in CDCl₃ (Figure 1) signifies two mutually trans PMe₂Ph groups with no plane of symmetry passing through the phosphorus atoms and a third PMe₂Ph group cis to these ligands. The proton-noise decoupled ³¹P n.m.r. spectrum, which consisted of a triplet and doublet pattern (relative intensity 1 : 2), is in agreement with this proposed stereochemistry. In addition, there was a singlet in the ¹H n.m.r. spectrum at δ 7.73 (301 K) whose position was temperature and concentration dependent, indicating the presence of hydrogen-bonded water molecules (cf. [PtCl(S₂CNH)]([PR₃]₂)[Cl·H₂O] ).

There are three structures which fit these n.m.r. data namely (VIa)—(Vic). Structure (Vib) can be discounted because the conductivity data indicate a 1:1 electrolyte and this is verified by synthesis of [RuCl₃(PMe₂Ph)₂(bipy)][BPh₄]⁻·2H₂O; (Vic) seems even more unlikely but cannot be completely ruled out on the present evidence (cf. [PtCl(phen)(P(Et)₃)][BF₄] shown to have structure (VII) ). Nevertheless, (VIa) appears to be the most likely structure.

Concentration of the red filtrate gave a dark red conducting solid whose ¹H n.m.r. spectrum in CDCl₃ (methyl region) consisted of four doublets of equal intensity. This clearly indicates that the complex contains two mutually cis PMe₂Ph groups and the other ligands are so arranged that the phosphorus atoms do not lie on a plane of symmetry of the molecule: ²

* In ref. 2, it was shown that [RuCl₃(PPh₃)₂(O₂NMe)₃] undergoes the same reactions as [RuCl₃(PPh₃)(HOMe)₃] providing the entering ligand is a stronger nucleophile than MeNO₂.

† 1 B.M. ≈ 9.27 × 10⁻⁴ A m⁻¹ 1m⁻¹ = 1 mol dm⁻³⁻¹.

‡ On the basis of C, H, and N analyses alone this complex was initially considered to be a geometrical isomer of (VIa).³

Figure 1 ¹H n.m.r. spectrum of [RuCl₃(PMe₂Ph)₂(bipy)]Cl₂H₂O in CDCl₃ (methyl region) at 301 K.

VIa)

(Vic)

(Vib)

(VII)

VIa)

(Vic)

(Vib)

(VII)

other ligands are so arranged that the phosphorus atoms do not lie on a plane of symmetry of the molecule.²


† R. A. Walton, Quart. Rev., 1965, 19, 126.


The $^{31}$P n.m.r. spectrum (two doublets of equal intensity) and heteronuclear decoupling studies support this conclusion (see Experimental section). In addition, there was a singlet at $\tau$ 7.86 whose position was temperature invariant. This resonance is therefore assigned to co-ordinated acetone and this conclusion is supported by the weak i.r. band at 1 620 cm$^{-1}$ [v(CO)] \{cf. [RuCl$_2$-(AsPh)$_2$(OAc)$_2$] \}

$\text{S = Me}_2\text{CO or CH}_2\text{Cl}_2$

\[\begin{align*}
\text{VIIa} \\
\text{VIIIb}
\end{align*}\]

$\text{[Ru(bipy)(S)Cl]Cl (S = Me}_2\text{CO, MeCN, etc.) have been recently reported and proved useful intermediates for synthesising a range of complexes by solvent displacement, e.g. [Ru(bipy)Cl(py)]$^{+}$, [Ru(bipy)Cl(NO$_2$)], etc. (py = pyridine).}^{11}$

Likewise, preliminary investigations indicate that (VIII) is a useful starting material for reactions of this type. For example, reaction of (VIII) with PMe$_2$Ph readily gave the orange complex (VIa). Also, the conductivity of (VIII) in CH$_2$Cl$_2$ decreased with time such that after 4–5 h the $^1$H n.m.r. spectrum of the solution was identical with that of [RuCl$_2$(PMe$_2$Ph)$_2$(bipy)] (see below). Finally, red solutions of (VIII)\[\text{[RuCl(PMe$_2$Ph)$_2$(bipy)(Me$_2$CO)]Cl} \rightarrow \quad \text{[RuCl$_2$(PMe$_2$Ph)$_2$(bipy)] + Me$_2$CO (I)}\]

$\text{S = CH}_2\text{Cl}_2$ and PMe$_2$Ph were produced when CH$_2$Cl$_2$ solutions of (VIa) were left to stand for several weeks. This suggests that (VIIa) is the most likely structure of the solvated complex, which is consistent with the higher trans effect of PMe$_2$Ph compared to bipy. Complex (VIIa) was also slowly formed when [RuCl$_2$-(PMe$_2$Ph)$_2$(bipy)] was left in strongly solvating solvents for several days.

Reaction of A' with excess of bipy in CH$_2$Cl$_2$ gave the dark red non-conducting [RuCl$_2$(PMe$_2$Ph)$_2$(bipy)]. Its $^1$H n.m.r. spectrum in CDCl$_3$ at 233 K (methyl region) consisted of four doublets, suggesting structure (IX). Again, $^3$P n.m.r. and heteronuclear decoupling studies confirm this suggestion (see Experimental section). A minor product of this reaction was an orange-red solid which analysed for [Hbipy][RuCl$_2$(PMe$_2$Ph)$_2$(bipy)]. In support of this formulation, the i.r. spectrum showed extra bands in the region 1 500–1 600 cm$^{-1}$, assignable to the [Hbipy]$^+$ ion.\(^{12}\) In hexane–CH$_2$Cl$_2$ (10:1 ratio by volume) only [RuCl$_2$(PMe$_2$Ph)$_2$(bipy)] was isolated.

From earlier studies,\(^5\) it was expected that reactions of phen would follow the same pattern as those of bipy. However, although reaction of A' with excess of phen in methanol did give orange and red products, the orange product was not the expected [RuCl(PMe$_2$Ph)$_2$(phen)]Cl but analysed as [Hphen][RuCl$_2$(PMe$_2$Ph)(phen)]·H$_2$O. This complex is conducting in methanol and showed extra i.r. bands in the region 1 500–1 600 cm$^{-1}$ characteristic of [Hphen]$^+$ ion.\(^{12}\) The main product, which was separated from the orange solid by recrystallisation from CH$_2$Cl$_2$–light petroleum, was the expected dark red [RuCl(PMe$_2$Ph)$_2$(phen)]·(CH$_2$Cl$_2$)Cl, (VIIa) \(\text{pH and }$^3$P n.m.r. evidence). Although no evidence was found in this reaction for formation of [RuCl(PMe$_2$Ph)$_2$(phen)]Cl, addition of a large excess of PMe$_2$Ph to a red CDCl$_3$ solution of (VIIa) \(\text{N–N = phen, } S = \text{CH}_2\text{Cl}_2\) rapidly gave an orange solution with a $^1$H n.m.r. pattern very similar to that observed for the [RuCl(PMe$_2$Ph)$_2$(bipy)]$^+$ cation. The main reason for the instability of the (PMe$_2$Ph)$_2$ complex here is probably steric. In hexane–CH$_2$Cl$_2$ (10:1 v/v) reaction of A' with excess of phen gave neutral [RuCl$_2$(PMe$_2$Ph)$_2$(phen)], (IX).

In view of these differences in behaviour of bipy and phen, the reaction with A' was extended to some methyl-substituted 1,10-phenanthroline. Reaction between 3,4,7,8-tetramethyl-1,10-phenanthroline (Me$_4$phen) and A' in methanol gave a red solution which after concentration and addition of CH$_2$Cl$_2$–pentane gave orange-red [RuCl(PMe$_2$Ph)$_2$(Me$_4$phen)]Cl. This was confirmed by its proton-noise decoupled $^3$P n.m.r. spectrum which showed the expected triplet and doublet pattern (relative intensity 1:2). However, recrystallisation from CH$_2$Cl$_2$–pentane gave a dark red conducting solid whose $^3$P n.m.r. spectrum consisted of two doublets of equal intensity. Its $^1$H n.m.r. spectrum in CDCl$_3$ (Figure 2) consisted of two overlapping doublets centred at $\tau$ 7.47 and 7.51 (Me of Me$_4$phen), two doublets at $\tau$ 7.74 and 8.00, a 'triplet' at $\tau$ 8.64 (Me of PMe$_2$Ph), and a singlet at $\tau$ 4.76 (CH$_2$Cl$_2$). However, decoupling experiments revealed that the 'triplet' is in fact two overlapping doublets and thus the complex is formulated as [RuCl(PMe$_2$Ph)$_2$(Me$_4$phen)]·(CH$_2$Cl$_2$)Cl, (VIIa).

In contrast, the reaction of A' with excess of 2,9-dimethyl-1,10-phenanthroline (Me$_2$phen) in methanol gave a dark yellow solution which after concentration and addition of CH$_2$Cl$_2$–pentane gave a white crystalline


precipitate and a yellow filtrate from which a golden-yellow solid was isolated. The white solid was too insoluble for n.m.r. measurements but the i.r. spectrum revealed that it contained no PMe₃Ph ligands. The complex analysed for [RuCl₃(Me₂phen)₃] but is strongly suggesting the formulation [RuCl₃(Me₂phen)₂]Cl₂, (X) [cf. [RuCl₃(N-N)₂(PPh₃)]Cl₂]. The yellow complex was identical in analysis, i.r., and ¹H n.m.r. to the well known [RuCl₃(PMe₃Ph)₂]Cl₂.¹³

These studies clearly indicate that both solvent media and steric constraints on the ligands play an important role in these reactions. Thus, whereas bipy readily forms the (PMe₃Ph)₃ complex (VIa), phen and Me₂phen only give this complex with difficulty and the sterically encumbered Me₂phen gives no complexes containing itself and PMe₃Ph groups.

**EXPERIMENTAL**

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4000–250 cm⁻¹ on a Perkin-Elmer 225 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Solution spectra were obtained in potassium bromide plates. ¹H N.m.r. spectra and solution magnetic moments (Evans' method) were determined on a Varian Associates HA 100 spectrometer with variable-temperature attachment and ³¹P n.m.r. spectra on a Varian XL 100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz (³¹P chemical shifts quoted in p.p.m. to high frequency of 85% H₂PO₄). Heteronuclear-decoupling experiments were carried out on the HA 100 spectrometer using a second radio-frequency field provided by the Schlumberger FS30 frequency synthesiser. Conductivity measurements were made on a model 310 Portland Electronics bridge. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

![Figure 2](image-url)

The complexes [RuCl₂(PPh₃)(bipy)][Cl₄], RuCl₂[PPh₃(bipy)]₃Y (Y = PF₆ or BF₄), [RuCl₂(PPh₃)(phen)]₂Y (Y = Cl or PF₆), [RuCl₂(AsPh₃)(bipy)]₂[ZnCl₂], [RuCl₂(AsPh₃)(bipy)]₂[BF₄], [Ru₂(N₃)₃Cl₄]₂ (X = Cl or Br; N = bipy or phen), [Ru(bipy)₃]Cl₂·6H₂O, and [RuCl₂(OH₂)(bipy)]Cl₂·2H₂O were prepared as described in ref. 2.

(2,2'-Bipyridyl)dichlorobis(triphenylphosphine)ruthenium(II) Tetraphenylborate.—The complex [RuCl₂(PPh₃)(O₂NMe)] (0.10 g) was heated under reflux under nitrogen in methanol (120 cm³) with an excess of sodium tetraphenylborate (0.10 g) and 2,2'-bipyridyl (0.04 g) for 5 h. The initial green suspension became yellow and after ca. 2 h of reflux an orange solid started to precipitate and finally the solution became red. The solid was collected and washed with methanol (yield 60%), m.p. 195–196 °C (decomp.) (Found: C, 71.9; H, 5.3; N, 3.4. Calc. for C₇₀H₇₀Br₂Cl₂N₄P₆Ru: C, 71.9; H, 5.1; N, 2.2%). A (1.0 × 10⁻³m) in CH₂Cl₂ = 18.3 S cm² mol⁻¹. The red filtrate was concentrated and the orange complex bis(2,2'-bipyridyl)-chloro(triphenylphosphine)ruthenium(II) tetraphenylborate which precipitated was washed with light petroleum (b.p. 100–120 °C) and methanol (20%), m.p. 230 °C (Found: C, 73.9; H, 5.1; N, 5.5. Calc. for C₇₂H₇₂Br₂Cl₂N₄P₆Ru: C, 72.3; H, 4.9; N, 5.4%).

(2,2'-Bipyridyl)dichloro(phenyl cyanide)triphenylphosphine ruthenium(II) Chloride Monohydrate.—The complex [RuCl₂(PPh₃)(bipy)] (0.10 g) was heated under reflux under nitrogen in methanol (100 cm³) with excess phenyl cyanide (0.08 cm³) for ca. 12 h. The resulting orange solution was concentrated to dryness, the residue dissolved in dichloromethane followed by pentane addition, and a crystalline yellow solid was precipitated (72%), m.p. 165–167 °C (decomp.) (Found: C, 56.2; H, 4.0; N, 5.9. Calc. for C₇₀H₇₀Cl₄N₄O₂P₂Ru: C, 66.5; H, 4.0; N, 5.7%). A (6.0 × 10⁻³m) in CH₂Cl₂ = 8.2 S cm² mol⁻¹; ν(RuCl) at 320 and 300 cm⁻¹. Recrystallisation from CH₂Cl₂-pentane gave an orange isomer, m.p. 188 °C (α(RuCl) at 334 cm⁻¹).

(2,2'-Bipyridyl)dichlororuthenium(II) Chloride Dihydrate.—The complex [RuCl₂(PPh₃)]₂ (0.30 g)¹¹ was heated under reflux in methanol (200 cm³) under nitrogen with an excess of bipy for ca. 12 h. The resulting red solution containing a mixture of two components (t.i.c. evidence) was concentrated to dryness and acetone–light petroleum (b.p. 100–120 °C) was added to the residue giving the orange solid (60%), m.p. 123 °C (decomp.) (Found: C, 51.7; H, 5.4; Cl, 9.4; N, 3.7. Calc. for C₄₄H₃₄Cl₄N₄O₂P₂Ru: C, 62.4; H, 5.8; Cl, 9.1; N, 3.6%). A (1 × 10⁻³m) in CH₂Cl₂ = 16.5 S cm² mol⁻¹; τ in CDCl₃ (301 K) (Figure 1) 8.97 (s) and 8.81 (s) [J(PP) + J(PH) = 6.5]. 8.15 (d) [J(PH) = 75 Hz] (PM₃Ph₂), 7.75 (s) (H₂O); and 0–4 (PMe₃Ph and bipy); ³¹P n.m.r. 8 (in CDCl₃) 6.88 (s) and 0.38 p.p.m. (d) [relative intensity 1:2: J(PP) = 32.8 Hz].

Concentration of the red filtrate gave a red solid, (acetone) (2,2'-bipyridyl)dichlororuthenium(II) chloride (chloride) (50%), m.p. 115 °C (decomp.) (Found: C, 51.6; H, 5.5; Cl, 8.1; N, 4.0. Calc. for C₄₄H₃₄Cl₄N₄O₂Ru: C, 52.6; H, 5.4; Cl, 10.7; N, 4.2%). A (1 × 10⁻³m) in CH₂Cl₂ = 20.0 S cm² mol⁻¹; τ in CDCl₃ (301 K) 8.71, 8.56, 8.01, 7.82 (doubles) [J(PP) = 8.5 Hz] (PM₃Ph₂), 7.86 (s (acetone)), and 0–4 (PMe₃Ph and bipy); ³¹P n.m.r. 8 (in CDCl₃) 301 K 27.20 and 15.14 p.p.m. (doubles) (relative intensity 1:1).
1975

H-(31P) studies: irradiation at 40 481 715 Hz collapsed $\tau$ 8.71 and 8.56, whereas irradiation at 4

19 Hz collapsed $\tau$ 8.01 and 7.82 (doubles).

(2,2'-Bipyridine)chlororuthenium(dimethylphenylphosphine)

ruthenium(ii) Tetraphenylborate Dihydrate. — The complex $\text{[RuCl}_2\text{PMe}_2\text{Ph}_2\text{]}\text{[bipy]}\text{Cl}_2\text{H}_2\text{O}$ (0.10 g) was dissolved in methanol (10 cm$^3$) and a three-fold excess of Na[BPF$_4$] (0.12 g) added. After shaking for 4 hr the orange crystalline precipitate was filtered off, washed several times with methanol, and dried in vacuo at 40 °C (71%), m.p. 159—

160 °C (Found: C, 56.8; H, 5.9; N, 2.7. Calc. for $\text{C}_8\text{H}_6\text{BCl}_2\text{O}_2\text{P}_2\text{Ru}: \text{C}, 56.6; \text{H}, 6.1; \text{N}, 2.7% ; \Lambda (4 \times 10^8 \text{cm})$ in CH$_2$Cl$_2 = 40.0 \text{ S cm}^2 \text{ mol}^{-1} ; \tau (in \text{CDCl}_3) (301 \text{ K})$, 9.03 and 8.84 (triplets) $\Lambda (J(\text{PH}) + J(\text{PH})' 6.5, 8.25 (d)$ $\Lambda (J(\text{PH}) 7.5 Hz) \text{[PMe}_2\text{Ph}, 7.70 (s) \text{[H}_2\text{O}, and 0—5 (PMe}_2\text{Ph, BPF}_4])$.

(2,2'-Bipyridine)dichlororuthenium(dimethylphenylphosphine)
ruthenium(ii). — The complex $\text{[RuCl}_2\text{PMe}_2\text{Ph}_2\text{]}\text{[bipy]}\text{Cl}_2\text{H}_2\text{O}$ (0.20 g) was heated under reflux in hexane—dichloromethane (100 : 10 cm$^3$) under nitrogen with an excess of phen for ca. 12 hr. The resulting dark red solid was collected and washed with light petroleum (b.p. 100—120 °C) (70%), m.p. 190 °C (decomp.) (Found: C, 53.6; H, 4.6; N, 4.7. Calc. for $\text{C}_{8}\text{H}_{6}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}: \text{C}, 53.8; \text{H}, 4.8; \text{N}, 4.5%.)

Chlororuthenin(dimethylphenylphosphine)(3,4,7,8-tetramethyl-

1,10-phenanthroline)ruthenium(ii) Chloride. — The complex $\text{[RuCl}_2\text{PMe}_2\text{Ph}_2\text{]}\text{[bipy]}\text{Cl}_2\text{H}_2\text{O}$ (0.20 g) was heated under reflux in methanol (150 cm$^3$) under nitrogen with an excess of Me$_2$phen (0.08 g) for ca. 10 hr. The resulting red solution containing a mixture of two compounds (t.l.c. evidence) was concentrated to dryness and CH$_2$Cl$_2$—pentane was added to the residue to give an orange-red precipitate which was washed with light petroleum (b.p. 100—120 °C) and dried (8%), m.p. 190—200 °C (decomp.) (Found: C, 57.2; H, 5.8; N, 3.2. Calc. for $\text{C}_{8}\text{H}_{6}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}: \text{C}, 58.2; \text{H}, 5.9; \text{N}, 3.4% ; \Lambda (1 \times 10^8\text{cm})$ in CH$_2$Cl$_2 = 18.0 \text{ S cm}^2 \text{ mol}^{-1} ; \tau (in \text{CDCl}_3) (301 \text{ K})$ 9.01 (1) and 1.09 p.p.m. (d) (relative intensity 1 : 2, J(PP) 22.5 Hz). Recrystallisation of this complex from CH$_2$Cl$_2$—pentane gave red crystals of chloro-

(dichloromethane)bis(dimethylphenylphosphine)(3,4,7,8-tetra-

methyl-1,10-phenanthroline)ruthenium(ii) chloride, m.p. 200—

205 °C (decomp.) (Found: C, 51.6; H, 5.2; N, 3.6. Calc. for $\text{C}_{8}\text{H}_{6}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}: \text{C}, 51.5; \text{H}, 5.2; \text{N}, 3.6%; \Lambda (1 \times 10^8\text{cm})$ in CH$_2$Cl$_2 = 16.5 \text{ S cm}^2 \text{ mol}^{-1} ; \tau (in \text{CDCl}_3) (301 \text{ K})$ (Figure 2) 8.64 (t'), 8.00, 7.74 (doublets) $\Lambda (J(\text{PH}) 8.5 \text{ Hz}) \text{[PMe}_2\text{Ph}, 7.47, 7.61 (doublets) (Me of Me$_2$phen), and 4.76 (s) \text{[CH}_2\text{Cl}_2]).

μ-Dichlorobis(2,9-dimethyl-1,10-phenanthroline-

ruthenium(ii) Dichloride. — The complex $\text{[RuCl}_2\text{PMe}_2\text{Ph}_2\text{]}\text{Cl}_2\text{H}_2\text{O}$ (0.20 g) was heated under reflux in methanol (120 cm$^3$) under nitrogen with an excess of phen for ca. 12 hr. The resulting dark yellow solution was concentrated to dryness and CH$_2$Cl$_2$—pentane added to the residue to give a white crystalline precipitate, m.p. 205—206 °C (decomp.) (Found: C, 58.7; H, 5.1; Cl, 12.4; N, 9.9. Calc. for $\text{C}_{8}\text{H}_{6}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}: \text{C}, 56.5; \text{H}, 4.1; \text{Cl}, 12.1; \text{N}, 9.4% ; \Lambda (1 \times 10^8\text{cm})$ in MeOH = 150 S cm$^2$ mol$^{-1}$. Concentration of the filtrate gave yellow crystals of μ-ti-

chlororuthenin(dimethylphenylphosphine)ruthenium(ii) chloride, m.p. 120 °C (Found: C, 46.1; H, 5.5; Cl, 12.1. Calc. for $\text{C}_{8}\text{H}_{6}\text{Cl}_2\text{P}_2\text{Ru}: \text{C}, 49.4; \text{H}, 5.6; \text{Cl}, 12.2%)

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[\eta^6-C_6H_6Ru(OH)_3Ru(\eta^6-C_6H_6)]Cl 3H_2O (III), is deposited as a crystalline yellow solid. Likewise, with [\eta^6-C_6Me_3H_3RuCl_2]_2 and NaOH, [\eta^6-C_6Me_3H_3Ru(OH)_3Ru(\eta^6-C_6Me_3H_3)]Cl 3H_2O can be isolated*.

In contrast, reaction of I with an excess of caesium chloride and concentrated HCl in ethanol gives an orange powder analysing closely for Cs[\eta^6-C_6H_6RuCl_3] (IV), although it is always difficult to obtain this complex free of CsCl. This product, which is the first reported anionic ruthenium arenare complex, is closely related to M[RuCl_3COC_7H_8] (V) (M = Cs, Ph_3(PhCH_2)P; C_7H_8 = bicyclo[2.2.1]hepta-2,5-diene(norbormadiene)) formed by reaction of [RuCl_2CO(C_7H_8)]_2 with MCl/HCl [4]. However, although V is a good precursor for synthesis of a range of anionic complexes of type Ph_3(PhCH_2)P[RuCl_2COL_2] (L = AsPh_3, C_5H_5N, Me_2SO etc.) [5], attempts to synthesise the unknown fac-[RuCl_3L_3] by reaction of IV with an excess of L gave only the neutral [\eta^6-C_6H_6RuCl_2L] compounds.

\[ \text{IV} \quad \text{V} \]

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References


*All these compounds have been characterised satisfactorily by elemental analysis, conductivity measurements, IR and ^1H NMR spectra.
Ruthenium Complexes containing Group 5B Donor Ligands. Part 3.1,2 Rearrangement Reactions of Some Ruthenium(II) Carbonyl and Thiocarbonyl Triphenylphosphine Complexes

By Peter W. Armit, Wilma J. Sime, and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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Ruthenium Complexes containing Group 5B Donor Ligands. Part 3.1,2
Rearrangement Reactions of Some Ruthenium(II) Carbonyl and Thiocarboxylic Triphenylophosphine Complexes

By Peter W. Armit, Wilma J. Sime, and T. Anthony Stephenson, * Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of [RuCl₃(PPh₃)₃] with [Ru(CO)Cl₂(dmft)PPh₃] in acetone (1:1 molar ratio) (dmft = NN-dimethylformamide) gives a high yield of ([PPh₃]BrRuBrCl₂Ru(CO)(PPh₃)]₂Me₂CO, supporting the mechanism proposed earlier for formation of the analogous thio carbonyl complex. Extensions of this type of coupling reaction to form ([PPh₃]BrRuBrCl₂Ru(CO)(PPh₃)]₂Me₂CO and ([PPh₃]BrRuCl₂Br₂Ru(CO)(PPh₃)]₂Me₂CO are also described. Recrystallisation of [Ru(CO)Cl₂(dmft)PPh₃] from MeOH·CH₂Cl₂ gives [Ru(CO)Cl₂(HMe)₂](PPh₃)]₂ (4) and, prolonged refluxing of the latter in dichloromethane–light petroleum (b.p. 60–80 °C) produces displacement of a PPh₃ group with formation of an isomeric mixture of ([PPh₃]BrCl₂OC)aRuCl₂Ru(CO)PPh₃] (5). The same isomeric mixture, together with ([Ru(CO)Cl₂(PPh₃)]₃)₃, is also formed by reaction of PPh₃ with [PPh₃][CH₃P[N₃]] 2-

Ru(C₅H₄)(CO)(Cl)₂]PPh₃, and the closely related [RuX₃(PPh₃)]₃-[RuX₃(PPh₃)]X (X = Cl or Br, n = 3 or 4) systems.

In an earlier paper 1 we examined the reaction of [RuCl₃(PPh₃)₃] with carbon disulphide and showed that the three products [RuCl₃(PPh₃)₃]Cl (1), [Ru₃S₃(C₂S₃)Cl(PPh₃)₃]Cl (2), and [PPh₃]ClRuCl₃Ru(CS)(PPh₃) (3) are obtained. The structure of (3) was confirmed by X-ray structural analysis. ² In ref. 1 we indulged in some speculation as to the mechanism of formation of (3), and a scheme was proposed which involved coupling of an intermediate ' [Ru(CS)Cl₃(PPh₃)] ' possibly formed by elimination of PPh₃S from (2) with [RuCl₃(PPh₃)]Cl. A competing reaction was dimerisation of [Ru(CS)Cl₃(PPh₃)]Cl ' to give (1).

Because of our inability to isolate the ' [Ru(CS)(CS)Cl₃(PPh₃)] ' intermediate (but see later), it was impossible to prove this mechanism definitively. However, related reactions involving carbonyl(triphenylophosphine)ruthenium(II) complexes have now been studied in some detail ² and these are reported in this paper, together with further studies on thiocarbonyl complexes of Ru².

RESULTS

Carbonyl Complexes.—It is well established that reaction of [RuCl₃(PPh₃)₃] with CO in acetone or benzene gives [Ru(CO)Cl₂(PPh₃)₃], the isomer formed depending on the reaction conditions. ³ However, James et al. ⁴ have shown that if this carbonylation reaction is performed in more basic solvents such as NN-dimethylformamide (dmft) the complex [Ru(CO)Cl₂(dmft)PPh₃] can be isolated. When this was heated under reflux in acetone with [RuCl₃(PPh₃)₃]

¹ A related reaction is the formation of [P(F₃)ClRuCl₂Ru(PPh₃)₃(PF₃)] from [RuCl₃(PPh₃)₃] and PF₃ (2:1 molar ratio) ⁸ which, presumably, involves initial formation of an intermediate such as [RuCl₃(PPh₃)]PF₃ followed by coupling with unchanged [RuCl₃(PPh₃)]. Similarly, coupling of species such as [RuCl₃(N₂)PPh₃] and [RuCl₃(PPh₃)] could be invoked to explain the formation of [P(F₃)ClRuCl₂Ru(N₂)PPh₃] from [RuCl₃(PPh₃)] and N₂ in a reverse-osmosis cell. ⁷

35—42 p.p.m. Complete analysis of these spectra has, to
date, proved impossible but a close examination of both
the low- and high-frequency sets of resonances indicates that
they consist of a series of overlapping AB quartets suggest-
ing a mixture of geometrical isomers which we have been
able to separate by chromatography.

The behaviour of [Ru(CO)Cl₄(dmf)₂(PPh₃)₂] in solution in
the absence of [RuCl₃(PPh₃)₃] is also of some interest.
Thus, recrystallisation of this product from MeOH-CH₂Cl₂
under mild conditions was claimed to give the five-coor-
dinate [Ru(CO)Cl₄(PPh₃)₂] but our recent reinvestigation
of this product indicates that it should be re-
formulated as the six-co-ordinate [Ru(CO)Cl₄(HOME)-
(PPh₃)₂] [ν(CO) at 1940 cm⁻¹ (CH₂Cl₂)]. On the evidence of
far-i.r. spectra [ν(RuCl) at ca. 330 cm⁻¹] and ³¹P n.m.r.
spectra at 303 K in CDCl₃ (singlet at ca. 34 p.p.m.), both
these solvates are considered to have configuration (4) with
trans-chlorides and trans-phosphines.

\[
\text{[Ph₃P]Y = CO or CS} \quad \text{S = dmf or MeOH}
\]

When, however, [Ru(CO)Cl₄(HOME)(PPh₃)₂] was gently
heated under reflux in dichloromethane-light petroleum
(b.p. 60—80 °C) for several hours, removal of the CH₂Cl₂
of three singlets between 53 and 55 p.p.m. and a complex
series of peaks between 36 and 42 p.p.m. The latter are
readily interpreted as three overlapping AB quartets
(Table 1) and the product is formulated as the triple-
chloride-bridged [(Ph₃P)₂Cl(O)(RuCl₂RuCl₂)(PPh₃)₃] (5),
for which it analyses quite closely. As shown in Figure 1,
a small amount of unchanged [Ru(CO)Cl₄(HOME)(PPh₃)₂]
irreversibly contaminates the sample.

Three geometrical isomers are possible for (5) and the
³¹P n.m.r. spectrum indicates that all three are formed.
A tentative assignment of isomers to AB resonances is
possible, based on the values of δAB. Thus, two of the δAB
values are very similar (ca. 160 Hz), suggesting these
resonances arise from isomers in which one phosphorus
atom is eclipsed by a phosphorus atom and the other by
a CO or a Cl⁻ group [isomers (5b) and (5c)]. A further
distinction cannot be made on this evidence. The other
AB quartet has a much smaller δAB value (64.0 Hz),
indicating that the two phosphorus atoms are probably
eclipsed by CO and Cl⁻ groups respectively [isomer (5a)]
(see Table 1).† The unique phosphorus atom in isomers
(5b) and (5c) will be eclipsed by another phosphorus atom,
and, hence, the chemical shifts should be very similar
(53.2 and 53.6 p.p.m.), whereas in (5a) it will be eclipsed
by a CO group (54.7 p.p.m.). The relative intensities of
the three AB quartets and the three singlets support these
assignments. It should also be noted that all the ³¹F(PP)
values (ca. 25 Hz) are consistent with cis-phosphines bound
to Ru¹. Support for this interpretation comes from the

**Table 1**

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Assignment of isomeric forms of [(Ph₃P)₂Cl(O)(RuCl₂RuCl₂)(PPh₃)₃] to ³¹P n.m.r. resonances</th>
<th>³¹P n.m.r. (CDCl₃ at 213 K), δ/ppm.</th>
<th>Singlet position</th>
<th>AB Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5a)</td>
<td></td>
<td></td>
<td>54.7</td>
<td>40.8 (δAB 64.0 Hz)</td>
</tr>
<tr>
<td>(5b)</td>
<td></td>
<td></td>
<td>53.6</td>
<td>38.6 (δAB 160.9 Hz)</td>
</tr>
<tr>
<td>(5c)</td>
<td></td>
<td></td>
<td>53.2</td>
<td>38.6 (δAB 155.7 Hz)</td>
</tr>
</tbody>
</table>

produced a pale orange solid, whose i.r. spectrum contained
a broad peak at 1960 cm⁻¹ [ν(CO), in Nujol]. Earlier,¹⁰ we
suggested that this complex was a mixture of [(Ru(CO)Cl₄-
(PPh₃)₂)] isomers, formed by dimerisation of (4; S =
MeOH). However, examination of the ³¹P n.m.r. spectrum
of this material clearly shows that this double-chloride-
bridged dimer is not formed to any significant extent. At
213 K in CDCl₃ (Figure 1) the ³¹P n.m.r. spectrum
† Very recently, McCleverty et al.¹¹ briefly mentioned
the formation of (5) from reaction of [Ru(CO)Cl₂(PPh₃)₃] and
hydrogen chloride. We have repeated this preparation and
shown by ³¹P n.m.r. spectroscopy that the same isomeric mixture
as above is formed. Also, Head and Nixon⁸ reported the syn-
thesis of (5) from [Ru(CO)Cl₂(PPh₃)₃] and hydrogen chloride but
no spectral details were given.

very recent synthesis by similar methods of the related
[(Et₂P)(Ph₃P)₂Cl(RuCl₂RuCl₂)(PPh₃)₃], where a combination
of ³¹P and ¹³C n.m.r. spectroscopy provides unequivocal
evidence for this formulation and shows that, in this
instance, an isomer of type (5b) is the predominant one.⁸

A reinterpretation of the nature of the products from the
reaction of [PPh₃(CH₂Ph)][Ru(C₂H₄)(CO)Cl₄] and PPh₃
(1:2 molar ratio) in CH₂Cl₂ is also appropriate at this
juncture. Earlier,¹⁰ we formulated the product as a mixture
of [(Ru(CO)Cl₄(PPh₃)₂)] isomers (which could not

be separated by chromatography) but a re-examination of the $^{31}$P n.m.r. spectrum of this product (Figure 2) clearly shows that in addition to the doubly-bridged isomers (strong singlets at 17.2 and 25.5 p.p.m. cf. $[(Ru\text{C}=\text{S})\text{Cl}_2]\text{[PPH}_3\text{]}_2$) $^{1}$, there is a substantial amount of the $[(\text{PH}_3\text{P})\text{Cl}(OC)\text{RuCl}_2\text{Ru}(CO)(\text{PPH}_3)_2]_{\text{isomer mixture present.}}$ In fact, an estimate based on relative n.m.r. peak areas suggests 87% double bridging and 33% triple bridging and this is consistent with the analytical data quoted in ref. 10 (see Experimental section).

When $[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPPh}_3)_2]$ was shaken for several hours in more polar solvents, such as Me$_2$CO or EtOH, with an equimolar amount of PPh$_3$, a pale yellow solid was precipitated, whose i.r. spectrum (Nujol) contained two ν(CO) bands at 1978 br and 1928 cm$^{-1}$. The $^{31}$P n.m.r. spectra at 243 K in CDCl$_3$ reveal the products to be mixtures containing both $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPPh}_3)_2]$ [S = MeOH or Me$_2$CO or EtOH] and $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPPh}_3)_2]$ (5) isomers. However, in addition, another AB quartet was observed at 40.6 p.p.m. $^{1}J(PP) 26.5, \delta_{AB} 115$ Hz and also weak broad resonances at ca. 26 and 18 p.p.m., corresponding to isomers of $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPPh}_3)_2]$. The additional AB quartet was more intense than the signals from the $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPPh}_3)_2]$ (5) isomers, especially in the spectrum of the product from EtOH compared to that from Me$_2$CO. The same mixture of products was obtained when the reaction was repeated without free PPh$_3$ present, except that the bulk of the material now consists of uncharged $[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPPh}_3)_2]$ and the intensity of the additional AB quartet in the $^{31}$P n.m.r. spectrum was smaller than those signals arising from the $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPPh}_3)_2]$ isomers.

When (5) was mixed with PPh$_3$ and Na[BPPh$_4$] and shaken in either CH$_2$Cl$_2$, Me$_2$CO, or EtOH for 50 h, a pale yellow solid was isolated which analyses quite closely for $[(\text{PH}_3\text{P})\text{Cl}(OC)\text{RuCl}_2\text{Ru}(CO)(\text{PPPh}_3)_2][\text{BPPh}_4]$ (6) ν(CO) at 1976 cm$^{-1}$ (Nujol). Support for this formulation is obtained from the $^{31}$P n.m.r. spectrum in CDCl$_3$ at 213 K which consisted of an AB quartet centred at 40.8 p.p.m. $^{1}J(PP) 27.1, \delta_{AB} 113.3$ Hz (cf. for $[(\text{PH}_3\text{P})\text{Cl}R\text{uCl}_2\text{Ru}(CO)(\text{PPPh}_3)_2]$, the two phosphate groups cis to CO appear at 40.3 p.p.m. with $^{1}J(PP) 24.6$ Hz). Complex (6) is also a 1:1 electrolyte in CH$_2$Cl$_2$ and its far-i.r. spectrum showed no band indicative of terminal ν(RuCl). Thus, this evidence clearly indicates that the cationic dimer (6) is formed both directly from rearrangement of $[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPPh}_3)_2]$ in polar solvents and by reaction of $[\text{Ru}(\text{CO})\text{Cl}_2(\text{PPPh}_3)_2]$ with Na[BPPh$_4$] in the presence of PPh$_3$.

![Figure 1 Phosphorus-31 n.m.r. spectrum in CDCl$_3$ at 213 K of the product from reaction of $[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPPh}_3)_2]$ and dichloromethane-light petroleum (b.p. 60--80 °C)]

$^{1}J(PP)$ 25.6; $\delta_{AB}$ 115 Hz

![Figure 2 Phosphorus-31 n.m.r. spectrum in CDCl$_3$ at 303 K of the product from reaction of $[\text{PPPh}_3(\text{CH}_2\text{Ph})][\text{Ru}(\text{CH}_2\text{Ph})\text{Cl}(\text{CO})\text{Cl}_2]$ and 2 PPh$_3$]

$^{1}Y = \text{CO or CS}$

+ The slight discrepancy between the positions of the resonances from (5) in Figures 1 and 2 is due to the difference in the temperatures at which the spectra were recorded. As the temperature increased, the singlets moved slightly to lower frequency and the quartets to higher frequency, making spectral analysis more difficult.

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* In ref. 1, a $^{31}$P n.m.r. singlet at 24.4 p.p.m. (in C$_4$H$_8$-C$_6$D$_4$) was assigned to an isomer of (1) but subsequent studies have shown this to arise from PPh$_3$O.
Finally, when [Ru(CO)Cl₄(HOMe)(PP₃)₃] (4) was treated with [AsPH₃]Cl·HCl in Me₂CO the anionic [AsPH₃][Ru(CO)Cl₄(PP₃)₃]·Me₂CO (7) [ν(CO) at 1918 cm⁻¹ (Nujol)] can be isolated. Like the corresponding M[Ru(CS)Cl₄(PP₃)₃] (M = AsPH₃⁺, PP₃(CH₂Cl)₃⁺, or NEt₄⁺) formed by cleavage of [M[Ru(CS)Cl₄(PP₃)₃]] with MCICl[HCl]¹ (7) is too insoluble for ³¹P n.m.r. studies. However, the far-i.r. spectrum of (7) contained a strong peak at 3200 cm⁻¹ indicative of a trans-RuCl₄ group (cf. 3200 cm⁻¹ for the CS anion)¹, which is consistent with either structure (7a) or (7b). Structure (7a) with trans-phosphines is most likely in view of the established stereochemistry of (4) and the postulated instability of (7b) (see ref. 10 and following discussion).

**Thiocarbonyl Complexes.**—The success of coupling [Ru(CO)Cl₄(dmf)(PP₃)₃] and [RuCl₄(PP₃)₃] to give a high yield of [Ru₂(CO)Cl₄(PP₃)₃] strongly supports the proposed mechanism suggested in ref. 1 for the formation of the analogous CS complex. Although the existence of the intermediate ‘[Ru(CS)Cl₄(PP₃)₃]’ could not be verified directly in the [RuCl₄(PP₃)₃]–CS₂ reaction, we found that reaction of [Ru(CS)Cl₄(PP₃)₃] with refluxing dmf gave [Ru(CS)Cl₄(dmf)(PP₃)₃] [ν(CS) at 1275 cm⁻¹ (Nujol)], whose ³¹P n.m.r. spectrum at 303 K in CDC₁₄ (singlet at 30.2 p.p.m.) and far-i.r. spectrum [ν(RuCl) at 325 cm⁻¹] indicates that configuration (4) is the most likely. Reac- tion of [Ru(CS)Cl₄(dmf)(PP₃)₃] and [RuCl₄(PP₃)₃] in refluxing Me₂CO (1:1 molar ratio) then gave [Ru₂(CS)Cl₄(PP₃)₃] (3) [ν(CS) at 1284 cm⁻¹ (Nujol)] as the only product, which directly verifies the mechanism suggested earlier.

For completion, the behaviour of [Ru(CS)Cl₄(dmf)(PP₃)₃] in solution in the absence of [RuCl₄(PP₃)₃] was also briefly investigated. Recrystallisation from hot CH₂Cl₂–MeOH gave [Ru₂(CS)Cl₄(HOMe)(PP₃)₃], whose far-i.r. and ³¹P n.m.r. spectra indicate configuration (4) as the most likely. This complex, on treatment with hot dichloromethane–light petroleum (b.p. 60–80 °C), gave a yellow crystalline solid which analyses closely for [PP₃(Ph)Cl(CO)]Cl₂RuCl₂Ru(CS)Cl₄(PP₃)₃·0.5CH₂Cl₂. A small amount of this complex (Me₂CO solvate) has been prepared previously¹ by shaking ([Ru(CS)Cl₄(PP₃)₃]) in degassed Me₂CO for several days. Unlike the analogous CO complex, the ³¹P n.m.r. spectrum at 303 K is not very helpful, consisting of two strong broad peaks at 48.1 and 37.7 p.p.m. (relative intensity 1:2) and weaker peaks, also of relative intensity 1:2, at 50.3 and 35.6 p.p.m. (cf. ref. 1). However, at 213 K, the ³¹P n.m.r. spectrum was better resolved and a tentative assignment of the isotors to the various resonances is given in the Experimental section.

A good indication, however, that an isomeric mixture of [Ru₂(CS)Cl₄(PP₃)₃] complexes has been produced was obtained by its reaction with Na₂[BPh₄] and PPh₃ in CH₂Cl₂ which gave a high yield of [PP₃(Ph)]₄(SC)RuCl₂Ru(CS)₂[PPh₃] [BPh₄] (6). The ³¹P n.m.r. spectrum in CDC₁₄ at 213 K consisted of a sharp quartet centred at 37.5 p.p.m. [J(PP₃) 27.0, J(PP₃) 86.8 Hz]. A small amount of this cation, together with the [Ru₂(CS)Cl₄(PP₃)₃] isomeric mixture, was also formed when [Ru(CS)Cl₄(HOMe)(PP₃)₃] was shaken in ETOH with an equimolar amount of PPh₃ for several hours.

**DISCUSSION**

A summary of the preparative methods for the various dimeric complexes of Ru(II) reported in this paper is given in Table 2 and it is of some interest to conclude this paper with a discussion of these various reactions and the different amounts of dimeric complexes they produce.

We suggest that the mode of dimerisation is very dependent on the stereochemistry of either the starting material or the reactive intermediate. For [RuYCl₄(HOMe)(PP₃)₃], ³¹P n.m.r. and far-i.r. studies unequivocally show structure (4) with trans-phosphines and trans-chlorides, and here the dimerisation product in solvents of low polarity is almost entirely the [Ru₂Y₂Cl₄(PP₃)₃] isomeric mixture, accompanied by concomitant loss of one PPh₃ group. In more polar solvents this dimerisation step is accompanied by concomitant Cl⁻ displacement giving some [Ru₂Y₂Cl₄(PP₃)₃][Cl].

However, in the [RuCl₄(PP₃)₃]–CS₂ reaction, where very little [Ru₂(CS)Cl₄(PP₃)₃] is formed, it seems very reasonable to infer that the ‘[Ru₂(CS)Cl₄(PP₃)₃]’ intermediate will initially have cis-PPh₃ groups. Support for this statement comes from the X-ray structure
of [RuCl₃(PPh₃)₃]^{12} which shows that the apical Ru–P bond is considerably shorter than the basal Ru–P bonds, together with the structure of its dissociation product ([RuCl₄(PPh₃)₂]Cl, shown by ³¹P n.m.r. studies,²⁷ to contain cis-PPh₃ groups. Therefore, a likely structure for the five-co-ordinate intermediate in the [RuCl₃(PPh₃)₂]–CS₂ reaction is (8), formed by elimination of PPh₃S from either [Ru(η⁵-CS₂)Cl(PPh₃)₃]Cl and/or [RuCl₄(PPh₃)₃(SCS)] (see Scheme 1*).

It is then proposed that (8) will undergo three competing reactions, namely: (i) coupling with unchanged [RuCl₄(PPh₃)₃] {or [RuCl₄(PPh₃)₃(SCS)]} to give [Ru₄–(CS)Cl₄(PPh₃)₃] (3); (ii) self-dimerisation without phosphine loss to generate the six-co-ordinate [[Ru₄(CS)]₄(PPh₃)₆] (I); and (iii) isomerisation to form a complex such as (4) (probably solvated) with the sterically more stable trans-Ru(PPh₃)₆ arrangement. Isomer (4) can then dimerise with concomitant phosphine loss to give some [Ru₄(CS)Cl₄(PPh₃)₃] (5) [step (iv)] or dimerise with concomitant chloride-ion displacement to give [Ru₄(CS)₄Cl₄(PPh₃)₆]Cl [step (v)]. Formation of (6) from (4) is favoured in more polar solvents, particularly in the presence of free PPh₃ which both inhibits formation of (5) and also slowly reacts with (5) to produce some of the ionic dimer [step (vi)].

* Isomers (8), (10), and (11) are written with essentially square-pyramidal rather than trigonal-bipyramidal structures to conform to both the theoretical predictions of Pearson,³³ Burdett,⁴ and Roesi and Hoffmann³⁵ for d⁸ complexes and the available X-ray data³ for various five-co-ordinate d⁸ complexes.

A similar mechanism (Scheme 2) can be proposed to explain the products from the [PPh₃(CH₃Ph)][Ru(CH₃)₆–(CO)Cl₄]–2PPh₃ reaction. As discussed fully in ref. 10, it is reasonable to postulate that an intermediate containing an η⁵-C₅H₅ group is first formed and this then reacts further with PPh₃ to give [Ru(CO)Cl₄(PPh₃)₆] of structure (9). Analogous complexes [PPh₃(CH₃Ph)][Ru(CO)Cl₄] of this stereochemistry have been characterised for L = AsPh₃, SMe₂, 2,2’-bipyridyl, etc.¹⁰ However, for (9) the combination of the high trans influence of PPh₃, together with the sterically unfavourable cis arrangement of these bulky groups (large Tolman ligand cone angles¹⁶), leads to ready expulsion of a chloride ion to relieve steric crowding and initial formation of a five-co-ordinate complex [Ru(CO)Cl₄(PPh₃)₃] (10) containing cis-PPh₃ groups. As for the analogous CS intermediate, this can either dimerise without phosphine loss to form [[Ru(CO)Cl₄(PPh₃)₃]₂ or isomerise to a species (11) with trans-phosphines which, in turn, dimerises with concomitant PPh₃ loss to form [Ru₄(CO)₆Cl₄(PPh₃)₃]. In this instance the proportion of the latter is considerably higher (33%) than in the [RuCl₃(PPh₃)₃]–CS₂ reaction, because there is no [RuCl₄(PPh₃)₃] present to remove

either of the [Ru(CO)Cl₂(PPh₅)₂] isomers by generating [Ru₄(CO)Cl₄(PPh₅)₄].

The reason why five-co-ordinate complexes (or six-co-ordinate solvates) with trans-PPh₅ groups dimerise to form triple-chloride-bridged complexes with concomitant PPh₅ loss whereas those with cis-PPh₅ groups form double-chloride-bridged dimers without PPh₅ loss is attributed to the high trans influence of PPh₅ and the consequent electronic instability of trans-Ru(PPh₅)₃ compared to cis-Ru(PPh₅)₃ arrangements.* The driving force for all these rearrangements is presumably the

of Ru–L and Ru–X bonds and on the polarity of the solvent medium.

This revised mechanism is then consistent with the observations in this paper and also the earlier inability to obtain evidence for the proposed [RuCl₂L₂] intermediate (except for L = P(η⁵-C₅H₅)₃). In fact, further studies reveal that the product giving rise to the ³¹P n.m.r. AB₂ pattern (Figure 4, ref. 2) is not neutral [RuCl₂(PEtPh₂)₂] but a cationic complex of probable formula [RuCl(HOEt)₂(PEtPh₂)₂]Cl or [RuCl(HOEt)₃(PEtPh₂)₂Cl₂]. The disappearance of this ³¹P n.m.r.

high stability of six-co-ordinate ruthenium(II) (4d⁸) complexes.

Finally, the observations presented in this paper strongly suggest that the detailed mechanism proposed by us in ref. 2 for the related rearrangement reactions of [RuX₃L₃] (L = PR₃; X = Cl or Br; n = 3 or 4) complexes is incorrect. Thus, instead of dimerisation to a double-halide-bridged complex [[RuX₃L₃]₂] followed by intramolecular displacement by halide ion of either L to give [Ru₂X₃L₃] or X⁻ to give [Ru₂X₄L₃]X (see Scheme, ref. 2), it is now suggested (Scheme 3) that direct dimerisation of [RuX₃L₃] to form either [Ru₂X₃L₃] or [Ru₂X₄L₃]X occurs accompanied by concomitant loss of either L or X⁻ groups respectively. The amount of each product formed depends on the relative strengths

pattern above 220 K in CDCl₃ with formation of [RuCl₂(PEtPh₂)₂], [Ru₃Cl₄(PEtPh₂)₃], [Ru₃Cl₅(PEtPh₂)₄]Cl, and PEtPh₂Cl₂ is then readily rationalised by postulating nucleophilic displacement of solvent by chloride ion to form [RuCl₂(PEtPh₂)₃], which then undergoes the facile rearrangement steps shown in Scheme 3. This mechanism, in retrospect, is more reasonable than the previously postulated intramolecular rearrangements of a six-co-ordinate dimer, since six complexes of this co-ordination number are invariably kinetically inert.

* Note added in proof. Additional experimental evidence for this suggestion is the isolation of [Ru(CO)Cl₂(PMe₅Ph)₄] from a solution thought to contain [Ru(CO)Cl₂(PMe₅Ph)₄] with cis-PMe₅Ph groups (C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, J.C.S. Dalton, 1976, 953).
EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the 250-4000 cm⁻¹ region on Perkin-Elmer 457 and 235 grating spectrometers using Nujol and halochlorobutadiene mulls on caesium iodide plates and in the 150-400 cm⁻¹ region on a Beckman R1C IR 720 far-i.r. spectrometer using pressed Polyethylene discs. Phosphorus-31 n.m.r. spectra were obtained on a Varian Associates XL100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H₂PO₄. Conductivity measurements were made on a Portland Electronics model 310 conductivity bridge. Melting points were determined with a Koffler hot-stage microscope and are uncorrected.

Ruthenium(III) trichloro trihydrate (Johnson, Matthey Ltd.), carbon monoxide (Air products), triphenylphosphine (B.D.H.), sodium tetraphenylborate (B.D.H.), and carbon disulphide (Fisons) were obtained as indicated. The complexes [Ru₃X₃(PPh₃)₃]⁺ [Ru₃X₁(CO)_{dmf}(PPh₃)₂] X = Cl or Br, [PPh₃(CH₂Ph)]Ru(C₆H₅CO)[Cl]_{18} and [Ru(µ-ClPPh₃)₂] were prepared as described elsewhere.

(a) Carbonyl Complexes. Tri-µ-chloro-dia carbonyl-g-chloro
tetraakis(triphenylphosphine)diruthenium(II)-acetone (1/2).

The complexes [RuCl₂(PPh₃)₂], [RuCl₄(CO)(PPh₃)] (0.10 g) were heated under reflux for 2.5 h in degassed Me₂CO (30 cm³) under an atmosphere of nitrogen. The solution was then cooled and the deep red precipitate were filtered off and washed with diethyl ether. Further crystals of the complex were obtained by evaporation of the filtrate to ca. 10 cm³ (93.8 g), m.p. 170-171°C (decomp. [v(CO) at 1951 cm⁻¹, v(CO) (acetone) at 1710 cm⁻¹] [Nujol]) (Found: C, 61.7; H, 4.7; Cl, 9.4%.)

Calc. for C₄₇H₃₆Cl₂O₄P₂Ru₂: C, 61.6; H, 4.8; Cl, 9.3%.

(b) Tri-µ-ClPPh₃. Tri-µ-ClPPh₃ is one of the isomers obtained by heating [RuBr₃(PPh₃)₃] (0.20 g) and [RuCl₃(CO)(dmf)(PPh₃)] (0.08 g) were heated together under reflux for 3 h in degassed Me₂CO (30 cm³) under an atmosphere of nitrogen. The solution was then cooled and the deep red precipitate were filtered off and washed with diethyl ether (0.10 g, 56%), m.p. 159-160°C (decomp. [v(CO) at 1903 cm⁻¹, v(CO) (acetone) at 1710 cm⁻¹] [Nujol]) (Found: C, 59.0; H, 4.4; Br, 10.0; Cl, 4.6%.)

Calc. for C₄₇H₃₆Cl₂O₄P₂Ru₂: C, 58.2; H, 4.2; Br, 10.2; Cl, 4.5%.

Di-µ-bromo-dia carbonyl-g-chloro-tetrais(triphenylphosphine)
diruthenium(II)-acetone (1/1) was prepared as above using [RuCl₃(PPh₃)₂] (0.11 g) and [RuBr₃(CO)(dmf)(PPh₃)] (0.10 g) to give deep red crystals of the product (0.02 g, 51%), m.p. 160-162°C (decomp. [v(CO) at 1953 cm⁻¹, v(CO) (acetone) at 1710 cm⁻¹] [Nujol]) (Found: C, 58.5; H, 4.3; Br, 10.0; Cl, 4.6%.)

Calc. for C₄₇H₃₆Cl₂O₄P₂Ru₂: C, 58.2; H, 4.2; Br, 10.2; Cl, 4.5%.

Product: far-i.r. spectrum 317vs, 304w, 280s, 270vs, 260m, 250w, 244w, 236m, 228m, and 180bmr cm⁻¹.

Carbonyldichloro(methanol)bis(triphenylphosphine) ruthenium(II). The complex [RuCl₂(CO)(dmf)(PPh₃)] [P²] was recrystallised from hot CH₂Cl₂-MeOH to give the yellow product which was washed with diethyl ether (Found: C, 60.3; H, 4.3; Cl, 9.1. Calc. for C₆₅H₃₄Cl₂O₂P₂Ru: C, 60.5; H, 4.5; Cl, 9.4%.)

1P n.m.r. (CDCl₃ at 303 K) 33.9 (s) p.p.m., [v(CO) at 330 cm⁻¹]

Calc. for C₆₅H₃₄Cl₂O₂P₂Ru: C, 60.7; H, 4.3; Cl, 9.8%.

Product: far-i.r. spectrum were found at 35.9and 37.0 p.p.m. for dmf and MeOH solvents respectively.

Tri-µ-chloro-ag(dicarbonyl-b-chloro-iris(triphenylphosphine)
diruthenium) (1).

The complex [Ru(CO)₂Cl₂(HOMe)(PPh₃)] was dissolved in CH₂Cl₂ and light petroleum (b.p. 60-80°C) was added. The yellow solution was warmed gently on a water-bath for several hours to allow the CH₂Cl₂ to evaporate slowly. The resulting orange solid was redissolved in CH₂Cl₂, light petroleum (b.p. 60-80°C) was added, and the process repeated to give pale orange crystals of the product which were filtered off and washed with EtOH and diethyl ether, m.p. 247°C [v(CO) at 1960brr cm⁻¹] (Nujol) (Found: C, 58.7; H, 4.1%.)

Calc. for C₆₅H₃₄Cl₂O₂P₂Ru: C, 60.7; H, 4.3; Cl, 9.8%.

1P n.m.r. (CDCl₃ at 213 K) (Figure 1) given in Table 1. The slightly high carbon and hydrogen analyses are due to the presence of some unchanged [Ru(CO)₂(HOMe)(PPh₃)] (See Figure 1).

Reactivity of PPh₃(CH₂Ph)[Ru(C₆H₅CO)(PPh₃)]Cl and PPh₃. The complexes (0.24 g) and PPh₃ (0.20 g, 1:1 molar ratio) were dissolved in CH₂Cl₂ (100 cm³) and the solution was heated under reflux under a nitrogen atmosphere for 12 h. The resulting pale orange solution was reduced in volume and diethyl ether was added to give a white precipitate of [P₂Cl₂(PPh₃)]Cl. The remaining solution was treated with pentane to give a pale orange solid [v(CO) at 2 092m, 1 998s, and 1 960v cm⁻¹] (Nujol), 1P n.m.r. (CDCl₃ at 303 K) as shown in Figure 2 (Found: C, 59.8; H, 4.2%.)

Calc. for mixture of [RuCl₂(CO)(PPh₃)] + [P₂Cl₂(PPh₃)]Cl (OC)RuCl₂Ru(CO)(PPh₃) (67:33) [C, 59.8; H, 4.0%].

Tri-µ-chloro-bis(dicarbonyl(bis(triphenylphosphine) ruthenium)
(II) tetraphenylborate. The [P₂Cl₂(PPh₃)]Cl (0.12 g), Na[P₃P₂] (0.064 g), and PPh₃ (0.026 g) were shaken together in degassed CH₂Cl₂ (25 cm³) under nitrogen for 50 h. The solution was evaporated to dryness, triturated with MeOH, and the resulting solid was filtered off and washed with water, MeOH, and diethyl ether (0.14 g, 80%), m.p. 124-126°C [v(CO) at 1 976 cm⁻¹ (Nujol)] (Found: C, 66.7; H, 4.9. Calc. for C₆₅H₃₄Cl₂O₂P₂Ru: C, 67.9; H, 4.6%.)

1P n.m.r. in CDCl₃ at 213 K, 40.8 (s) p.p.m., [J(P₂F₃) 27.1, 8(P₃P₂)] 113.3 Hz [1(A × 10⁻³ mol dm⁻³) in CH₂Cl₂ = 30 S cm² mol⁻¹].

The complex [RuCl₂(CO)(PPh₃)]Cl was also formed by shaking [Ru(CO)₂(P₃P₂)]Cl with MeOH with or without free PPh₃ present. In these reactions, the [RuCl₂(CO)(P₃P₂)]Cl isomeric mixture and trace amounts of [RuCl₂(CO)(P₃P₂)]Cl were also found.

Tetraphenylarsionium carbonyl(bis(dicarbonyl phosphine)
rasenitum(II)-acetone (1/1). The complex [Ru(CO)Cl₂(HOMe)(P₃P₂)] (0.10 g) was suspended in degassed Me₂CO (2 cm³) and treated with a two-fold excess of [As(P₃P₂)Cl(HCl)] with P₃P₂ (ca. 0.01 M). The mixture was shaken for 4 h when orange yellow crystals of the product precipitated. These were filtered off, washed with water, MeOH, and diethyl ether, and dried in vacuo at 40°C (0.13 g, 70%), m.p. 155-158°C [v(CO) at 1 918 cm⁻¹, v(CO) (acetone) at 1 710 cm⁻¹] (Nujol) (Found: C, 64.1; H, 4.7; Cl, 9.0. Calc. for C₆₅H₃₄Cl₂O₂P₂Ru: C, 64.0; H, 4.7; Cl, 8.9%)

[A(1 × 10⁻³ mol dm⁻³) in CH₂Cl₂ = 45 S cm² mol⁻¹].
(b) Thiocarbonyl Complexes.—Dichloro(NN-dimethylformamide)-thiocarbonylbis(triphenylphosphine)ruthenium(II). The complex \([\text{RuCl}_2(\text{PPh}_3)_2]\) (0.20 g) was heated under reflux in degassed NN-dimethylformamide (15 cm\(^3\)) under nitrogen for 3 h. The resulting yellow solution was reduced in volume and diethyl ether was added to precipitate the pale yellow solid, m.p. 168—170 °C \([\nu(\text{CS}) \text{ at } 1 275 \text{ cm}^{-1}, \nu(\text{CO}) \text{ (dmf) at } 1 640 \text{ cm}^{-1}, \nu(\text{RuCl}) \text{ at } 325 \text{ cm}^{-1} \text{ (Nujol)} \text{ (Found: C, 57.5; H, 4.5; N, 1.7. Calc. for C\(_{29}\)H\(_33\)Cl\(_2\)NOP\(_2\)RuS: C, 59.0; H, 4.6; N, 1.7%) \}}\]\(^{\text{31P}}\) n.m.r. (CDCl\(_3\) at 303 K) 30.2 (s) p.p.m.

Tri-\(\mu\)-chboro-\(\mu\)-chloro-g-thiocarbonyl-tetraakis(triphenylphosphate)diruthenium(II). The complexes \([\text{RuCl}_4(\text{PPh}_3)_2]\) (0.19 g) and \([\text{Ru(CS)}_2(\text{PPh}_3)_2]\) (0.16 g) were heated under reflux for 4 h in degassed Me\(_2\)CO (30 cm\(^3\)) under an atmosphere of nitrogen. On cooling the solution, the red solid was deposited together with some unchanged \([\text{Ru(CS)}_2\text{(dmf)}(\text{PPh}_3)_2]\). Proof of the formation of (3) was obtained from the \(\text{31P}\) n.m.r. spectrum of the products in CDCl\(_3\) at 298 K (see ref. 2).

Dichloro(methano)thiocarbonylbis(triphenylphosphine)-ruthenium(II). The complex \([\text{Ru(Cl)}_2(\text{PPh}_3)_2]\) was recrystallised from hot CH\(_2\)Cl\(_2\)-MeOH to give yellow crystals which were washed with MeOH, m.p. 182—184 °C \(\text{(Found: C, 57.8; H, 4.5. Calc. for C\(_{29}\)H\(_{33}\)Cl\(_2\)OP\(_2\)RuS: C, 57.3; H, 4.4%) \}}\] i.r. spectrum (Nujol) 3 460 and 1 030 cm\(^{-1}\) (co-ordinated MeOH), \(\nu(\text{CS})\) at 1 280 cm\(^{-1}\), \(\nu(\text{RuCl})\) at 332 cm\(^{-1}\); \(\text{31P}\) n.m.r. (CDCl\(_3\) at 303 K) 30.7 (s) p.p.m.

Tri-\(\mu\)-chloro-\(\mu\)-dichloro-carbonyl-tris(triphenylphosphine)diruthenium(II)—dichloromethane (2/1). The complex \([\text{Ru(CS)}_2\text{Cl}(\text{HOMe})(\text{PPh}_3)_2]\) was dissolved in CH\(_2\)Cl\(_2\) and light petroleum (b.p. 60—80 °C) was added. The yellow solution was placed on a water-bath and the CH\(_2\)Cl\(_2\) was allowed to evaporate off slowly over a period of 2 h to give yellow crystals which were filtered off and washed with diethyl ether, m.p. 264 °C \(\text{[\nu(\text{CS}) at 1 300br cm}^{-1}\text{ (Nujol)} \text{ (Found: C, 52.7; H, 3.7. Calc. for C\(_{46}\)H\(_{82}\)Cl\(_2\)OP\(_2\)RuS: C, 53.8; H, 3.6%). \}}\]\(^{\text{31P}}\) n.m.r. in CDCl\(_3\) at 213 K: isomer (5a) 49.7 (s) and 37.0 (q) p.p.m. (J\(_{AB}\) 26.0; \(\delta_{AB}\) 15.0 Hz); isomers (5b) and (5c) 51.8 (s) and 35.8 (q) p.p.m. (J\(_{AB}\) 26.0; \(\delta_{AB}\) 7.4 Hz) and a very weak singlet at 50.9 p.p.m. and weak resonances between 38 and 38 p.p.m.

Tri-\(\mu\)-chloro-bis[thiocarbonylbis(triphenylphosphine)ruthenium(II)] tetrachlorophosphate. The \([\text{Ru}_2(\text{CS})_4(\text{PPh}_3)_4]\) isomeric mixture (0.08 g), Na[BPh\(_4\)] (0.022 g), and PPh\(_3\) (0.018 g) were shaken in degassed CH\(_2\)Cl\(_2\) (20 cm\(^3\)) under nitrogen for 48 h. The orange-yellow solution was evaporated to dryness and triturated with MeOH to give an orange-yellow solid which was filtered off and washed with water, MeOH, and diethyl ether, m.p. 118—120 °C \(\text{[\nu(\text{CS}) at 1 290 cm}^{-1}\text{ (Nujol)} \text{ (Found: C, 66.5; H, 4.6. Calc. for C\(_{54}\)H\(_{42}\)Cl\(_4\)OP\(_2\)RuS: C, 66.7; H, 4.5%). \}}\]\(^{\text{31P}}\) n.m.r. (CDCl\(_3\) at 213 K) 37.5 (q) p.p.m. (J(P\(_A\)P\(_B\)) 27.0; \(\delta(P\(_A\)P\(_B\)) 86.8 Hz \[\Lambda(1 \times 10^{-3} \text{ mol dm}^{-3}) \text{ in CHCl}_3 = 32 S \text{ cm}^2 \text{ mol}^{-1}\text{ s}^{-1}\].

We thank Johnson, Matthey Ltd for generous loans of ruthenium(III) trichloride, the S.R.C. for the award of research studentship (to P. W. A. and W. J. S.), and Dr. A. S. F. Boyd for obtaining the \(\text{31P}\) n.m.r. spectra.

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Synthesis, Crystal and Molecular Structure of Acetonitrilecarbonyldichloro(cyclo-octa-1,5-diene)ruthenium(II)

By Robert O. Gould, C. Lynn Jones, Donald R. Robertson, and T. Anthony Stephenson * Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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1977
Synthesis, Crystal and Molecular Structure of Acetonitrilecarbonyldichloro(cyclo-octa-1,5-diene)ruthenium(II)

By Robert O. Gould, C. Lynn Jones, Donald R. Robertson, and T. Anthony Stephenson

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Reaction of [RuCl₂(C₅H₅)]₄ with acetonitrile gives [RuCl₂(C₅H₅)NC₅H₅] (Ia), shown by X-ray diffraction analysis to have octahedral stereochemistry with a trans-OC-Ru-MeCN arrangement. Crystals are monoclinic, space group P2₁/c, with a = 12.933(2), b = 7.641(8), c = 13.435(3) Å, β = 104.36(2)°, and contain one molecule per asymmetric unit. The structure was solved by use of 1 086 film data, and refined to R 0.09. The related complexes [RuCl₂(C₅H₅)Cl] (L = acrylonitrile and cyclopentyl cyanide) have also been synthesised.

Although the carbonyl diene complexes [RuX₂(C₅H₅)Cl)(diene)] (X = Cl or Br, diene = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) or cyclo-octa-1,5-diene) were first reported in 1966, surprisingly little work on the reactions of these compounds has been published. Thus, Robinson and Wilkinson showed that with pyridine, bridge splitting and diene displacement occur giving [RuCl₂(C₅H₅)₂], whereas with quinoline (quin) trans-[RuCl₂(C₅H₅)₂](quin) is formed. More recently, cleavage of the halide bridge with halide ion to give the [RuX₂(C₅H₅)]⁻ anion has been achieved and there has been a detailed study of the reactions of [Ph₂(PhCH₂)]²[RuCl₂(C₅H₅)] with various Lewis bases.

In contrast, the chemistry of the related [RuX₂(diene)]₄ compounds has been extensively investigated. Very recently, Ashworth and Singleton reported that the cationic [RuCl₂(C₅H₅)]₃(MeCN)₂(PF₆) complexes can be readily synthesised by heating under reflux [RuCl₂(C₅H₅)]₄ with acetonitrile, followed by precipitation with [NH₄]PF₆. In an attempt to prepare the analogous cation [RuCl₂(C₅H₅)]₃(MeCN)₄, we have examined the reaction of [RuCl₂(C₅H₅)]₄ with excess of acetonitrile. However, the main product from this reaction was a crystalline orange compound with analysis corresponding closely to [RuCl₄(MeCN)₂(C₅H₅)] (I). Unfortunately, although the i.r. spectrum of this material showed the presence of carbonyl, acetonitrile, and cyclo-octadiene groups, it was too insoluble and involatile for n.m.r., mass spectroscopy, or molecular-weight studies. Therefore, an X-ray structural determination of (I) was undertaken both to verify the formulation and to ascertain the detailed geometry.

RESULTS

Crystal Data. — C₅H₅ClNORu, M = 349.2, Monoclinic, a = 12.993(2), b = 7.641(8), c = 13.435(3) Å, β = 104.36(2)°, U = 1 292 Å³, Dₘ = 1.77, Z = 4, D₀ = 1.795 g cm⁻³. Cu-Ka radiation, λ = 1.5418 Å; μ(Cu-Kα) = 138.1 cm⁻¹. Space group P2₁/c.

Intensity data were derived from multiple-packs of Weissenberg films by use of an SAAAD Mark II automatic film scanner. Layers 00 — 4l and 0 2l were measured for a small plate-like crystal of diameter 0.2 mm and thickness 0.1 mm. No absorption corrections were made. Cell dimensions were derived from the films by an adaptation of the method of Main and Woolfson.

From the Patterson function, the ruthenium atom could be placed near 4,0,0, where it contributes significantly only to reflections h = 2n, k = 2n, l = 2n. The rest of the structure was found by the DIRDIF procedure, by use of phased difference structure factors for those reflections with a ruthenium contribution, two origin-fixing reflections, and a permutation of signs for two other reflections, giving a fourfold solution. The correct solution could easily be distinguished, and all non-hydrogen atoms were located in a second difference-Fourier synthesis. No attempt was made to locate hydrogen atoms.

Refinement to a final R 0.092 based on 1 086 data was carried out by full-matrix least squares with the weighting scheme W = XᵲYᵲ, where X = sinθ/0.54 for sinθ < 0.54 (otherwise X = 1) and Y = 37/|F₀| for |F₀| > 37 (otherwise Y = 1.0). Lattice, anisotropic thermal parameters were used for the ruthenium and chlorine atoms only. On the final cycle of refinement, no parameter shifted by > 0.1σ. Final atomic parameters are given in Table 1, and structure factor tables are deposited as Supplementary Publication No. SUP 21643 (4 pp., 1 microfiche).*

DISCUSSION

Bond lengths and angles for (I) are given in Table 2, and a view of the molecule in the Figure. They show unequivocally that the product is (Ia). The co-ordination of the ruthenium is essentially octahedral, with the CO and MeCN ligands trans. The greatest deviation

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is shown by the N(1)–Ru–C(1) angle (167°). The cyclo-
octadiene ligand is in the normal tub conformation, and the
 carbonyl is approximately and the acetonitrile
 ligand is accurately collinear with the ruthenium atom.

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Positional and thermal parameters for (I)</td>
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<td>Atom</td>
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<tr>
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<td>C(9)</td>
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<tr>
<td>C(10)</td>
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<td>C(11)</td>
</tr>
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</table>

* Anisotropic parameters \((\AA^2 \times 10^4)\). The temperature factor is of form \(\exp(-2\pi^2\sum h_i^2a_i^2U_{ij})\).

The deviation of the N–Ru–C(1) angle from 180° may be associated with the inclination of theacenitrite group away from the cyclo-octadiene, shown by the normal N–Ru–Cl and N–Ru–X angles (90.5 and 86.3°). Even so, the contact distances N···C(10) and N···C(11) are 3.01 and 3.07 Å. The distortion is somewhat less marked for the more closely bound carbonyl group where the mean C(1)–Ru–Cl and C(1)–Ru–X angles are 85.8 and 93.0°, and the C(1)···C(6) and C(1)···C(7) contacts 2.99 and 3.02 Å. Here, however, the Ru–
C(1)–O angle is directed away from the cyclo-octadiene,
as shown by an angle of 105° between the lines O–C(1) and
Ru···X(3) where X(3) is the midpoint of the cyclo-octadiene
ring.

At first sight, the results are rather surprising, since earlier work on reactions of [Ph₄PhCH₂]P[RuCl₄CO-
(C₇H₈)] with various Lewis bases also gave [RuCl₄CO-

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
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</table>
| Bond lengths (Å) and bond angles (°) in (I). X(1) and
X(2) represent midpoints of the C(4)–C(5) and
C(8)–C(9) bonds respectively |
| (a) Distances |
| Ru–Cl(1) | 2.400(6) | N–C(2) | 1.073(3) |
| Ru–Cl(2) | 2.389(6) | Cl(2)–C(3) | 1.453(3) |
| Ru–C(1) | 1.797(29) | Cl(4)–C(5) | 1.463(4) |
| Ru–N | 2.166(18) | Cl(6)–C(7) | 1.54(4) |
| Ru–C(4) | 2.360(20) | Cl(7)–C(8) | 1.46(6) |
| Ru–C(5) | 2.276(29) | Cl(7)–C(8) | 1.52(4) |
| Ru–C(6) | 2.263(22) | Cl(9)–C(10) | 1.57(3) |
| Ru–C(9) | 2.232(22) | Cl(9)–C(10) | 1.51(4) |
| Ru–X(1) | 2.059(20) | Cl(10)–C(11) | 1.56(6) |
| Ru–X(2) | 2.166(25) | Cl(11)–C(14) | 1.43(4) |
| Cl(1)–O | 1.23(3) |

(b) Angles |
| Cl(1)–Ru–Cl(2) | 92.6(2) | N–Ru–X(2) | 95.7(8) |
| Cl(1)–Ru–C(1) | 93.9(9) | X(1)–Ru–X(2) | 84.4(8) |
| Cl(1)–Ru–N | 84.6(5) | Ru(1)–O | 173(2) |
| Cl(1)–Ru–X(1) | 176.6(6) | Ru(–N–C(2) | 179(2) |
| Cl(1)–Ru–X(2) | 92.0(6) | N–C(2)–C(3) | 176(3) |
| Cl(2)–Ru–C(1) | 87.7(9) | C(4)–C(5)–C(6) | 118(3) |
| Cl(2)–Ru–N | 86.0(5) | C(6)–C(7)–C(8) | 119(2) |
| Cl(2)–Ru–X(1) | 90.9(6) | C(7)–C(8)–C(9) | 124(2) |
| Cl(2)–Ru–X(2) | 175.2(6) | C(9)–C(10)–C(11) | 118(3) |
| Cl(3)–Ru–N | 166.6(9) | C(10)–C(11)–C(14) | 119(3) |
| Cl(3)–Ru–X(1) | 94.5(10) | N–Ru–X(1) | 97.4(8) |
| Cl(3)–Ru–X(2) | 91.5(11) | N–Ru–X(1) | 97.4(8) |
| C(11)–C(8)–C(5) | 126(2) |

[(L(C₇H₈))][L = AsPh₄, SbPh₃, or C₆H₅N] and detailed
¹H n.m.r. studies revealed that these compounds had
either structure (Ib) or (Ic) but not (Ia) or (Id)³ (see
Scheme 1).

However, this discrepancy is resolved if the possible
structures of the two starting materials are examined.
Detailed spectroscopic studies on [Ph₄PhCH₂]P[RuCl₄–
CO₇H₈] show unequivocally that only isomer (II) is
present in solution ² and thus, with the knowledge that

\[ \text{(Ia)} \Rightarrow \text{(Ic)} \]

\[ \text{(Ib)} \Rightarrow \text{(Ic)} \]

\[ \text{(Ic)} \Rightarrow \text{(Ic)} \]

\[ \text{(Id)} \Rightarrow \text{(Ic)} \]

\[ \text{(Ic)} \Rightarrow \text{(Ic)} \]

\[ \text{Scheme 1} \]

Bridge cleavage reactions of the various possible
isomers of [RuCl₄CO(C₇H₈)]
the reaction almost certainly involves initial cleavage of one of the Ru–C bonds (see Scheme 1 of ref. 3), it is impossible to form isomer (Ia).

For [RuCl₂CO(C₅H₁₂)]ₙ (assuming n = 2, as in ref. I) the three chloride-bridged structures (III; a—c) are possible.* Bridge cleavage of isomer (IIIa) with acetonitrile will then give isomer (Ia) if the bond *trans* to CO is broken or (Ic) if that *trans* to the diene group is broken. However, isomer (IIIb) can only give (Ic) and isomer (IIIc) can give either (Ib) or (Id) (see Scheme 1). Therefore, although it is not possible to determine directly the structure of [RuCl₂CO(C₅H₁₂)]ₙ (an insoluble powder), an X-ray structural analysis of its reaction product with acetonitrile strongly suggests that the starting material

then in the presence of excess of acetonitrile, either complete diene displacement or at least the formation of a complex containing two MeCN groups per ruthenium would be expected. The instability *n* of MeCN to displace the diene group in [P₉(PhCH₂)]₉[RuCl₂CO(C₅H₁₂)] also supports this conclusion.

Finally, reaction of [RuCl₂CO(C₅H₁₂)]ₙ with acrylonitrile and cyclopentyl nitrile (L) gives the related [RuCl₂(CO)L(C₅H₁₂)] complexes. The close similarity of the i.r. spectra of these compounds to the acetonitrile analogue suggests they also have configuration (Ia).

**EXPERIMENTAL**

I.r. spectra were recorded in the region 4 000—250 cm⁻¹ on Perkin Elmer 225 and 157 grating spectrometers for Nujol and hexachlorobutadiene mulls on caesium iodide plates. M.p.s. were determined with a Kofler hot-stage microscope. Standard crystallographic calculations used the X-Ray ’72 program system.

Acetonitrilecarbonyldichloro(cyclo-octa-1,5-diene) ruthenium(II).—[RuCl₂CO(C₅H₁₂)]ₙ was heated under reflux under nitrogen in acetonitrile for ca. 4 h. The resulting yellow solution was then filtered and concentrated to produce yellow-orange crystals (90%), m.p. 180 °C (decomp.) (Found: C, 37.8; H, 4.4; Cl, 20.3; N, 4.6. C₁₇H₁₈Cl₂NORu requires C, 37.8; H, 4.3; Cl, 20.3; N, 4.0%). I.r. spectrum: v(CN) 2 305, v(CO) 1 988, and v(C–C) 1 335 cm⁻¹; combination of symmetric CH₂ deformation and C–C stretching vibrations at 2 340 cm⁻¹.

Acrylonitrilecarbonyldichloro(cyclo-octa-1,5-diene) ruthenium(II).—This was prepared similarly as a yellow crystalline solid, m.p. 150 °C (decomp.) (Found: C, 39.2; H, 4.3; N, 4.4. C₁₇H₁₈Cl₂NORu requires C, 39.9; H, 4.2; N, 3.9%). I.r. spectrum: v(CN) 2 153, v(CO) 2 015, and v(C–C) 1 333 cm⁻¹.

Carbonyldichloro(cyclo-octa-1,5-diene)(cyclopentyl nitrile) ruthenium(II). This was prepared similarly as an orange solid, m.p. 100 °C (decomp.) (Found: C, 41.4; H, 4.5; N, 3.8. C₁₇H₁₈Cl₂NORu requires C, 41.6; H, 4.5; N, 3.7%). I.r. spectrum: v(CN) 2 388, v(CO) 2 018, and v(C–C) 1 335 cm⁻¹.

We thank Johnson Matthey Ltd. for loans of ruthenium trichloride and the S.R.C. for financial support (to C. L. J. and D. R. K.).
Ruthenium Complexes containing Group 5B Donor Ligands. Part 4.¹ Synthesis, Crystal and Molecular Structure of def-Tri-µ-chloro-h-diphenylphosphinito-bgi-tris(diphenylphosphinous acid)-ac-bis(methyl diphenylphosphinite)diruthenium(II)


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Ruthenium Complexes containing Group 5B Donor Ligands. Part 4.  
Synthesis, Crystal and Molecular Structure of \( \text{def-Tri-\(\mu\)-chloro-\(\mu\)-diphenylphosphino-bgi-tris(diphenylphosphinonic acid)} \)-ac-bis(methylphenylphosphinite)diruthenium(II) 


Pyrolysis of solutions containing \([\text{P(OMe)}_2\text{Ph}_2\text{RuCl}_2\text{Ru[OMe]}_2\text{Cl}]\) for 12 h at 120 °C gives yellow crystals (1) shown by X-ray diffraction analysis to be \([\text{P(OMe)}_2\text{Ph}_2\text{RuCl}_2\text{Ru[OMe]}_2\text{Cl}]\). The crystals are monoclinic, space group \(P2_1/c\) with \(a = 13.19, b = 21.98, c = 24.98 \text{ Å}, \beta = 109.40^\circ\), and contain one molecule per asymmetric unit. The structure was solved using 1,534 diffraction data and refined to \(R = 0.11\).

Related pyrolysis reactions give the compounds \([\text{P(OMe)}_2\text{Ph}_2\text{RuCl}_2\text{Ru[OMe]}_2\text{Cl}]\) (2) and \([\text{P(OMe)}_2\text{Ph}_2\text{RuCl}_2\text{Ru[OMe]}_2\text{Cl}]\) (3).

In recent years, a number of ruthenium(II) complexes containing tertiary phosphines \(\text{P(OR)}_3\) and phosphonites \(\text{P(OR)}_3\) have been synthesised. These include compounds such as \([\text{RuH}_2(\text{P(OEt)}_2\text{Ph})_4]_2\), \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]_2\), \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_2\text{Cl}]_2\) \((R = \text{Me, Et})\), \([\text{RuH}(\text{P(OMe)}_2\text{Ph})_2\text{X}]_2\) \((R = \text{Me, Et} \text{; } X = [\text{PF}_6]^-, \text{Cl} \text{; } X = [\text{BF}_4]^-, \text{Cl} \text{; } X = [\text{BF}_4]^-, \text{Cl} \text{; } X = [\text{BF}_4]^-, \text{Cl} \text{; } X = \text{Br})\).

However, unlike the related tertiary phosphines, no neutral dimeric or anionic complexes of type \([\text{L}_2\text{RuCl}_2\text{RuX}_2\text{L}_2]_2\) or \([\text{L}_2\text{RuCl}_2\text{RuX}_2\text{L}_2][\text{L}_2\text{RuCl}_2\text{RuX}_2\text{L}_2]\) \((L = \text{P(OR)}_3\text{Ph})_2\) or \([\text{P(OR)}_3\text{R}]_2\) are known \(\dagger\) and therefore, the aim of this present work was an attempt to synthesise such compounds.

RESULTS

Several years ago, Prince and Raspin \(\dagger\) demonstrated that the pyrolysis products of \([\text{PET}_{3}\text{Ph}_2\text{RuCl}_2\text{Ru[PET}_{3}\text{Ph}_2\text{Cl}]_2\) were dependent upon the solvent media and the temperature of pyrolysis. Thus, in propyl propanol at 50 or 120 °C, \([\text{PET}_{3}\text{Ph}_2\text{RuCl}_2\text{Ru[PET}_{3}\text{Ph}_2\text{Cl}]_2\) was formed \(\dagger\) whereas in methyl acetate at 50 °C, \([\text{PET}_{3}\text{Ph}_2\text{RuCl}_2\text{Ru[PET}_{3}\text{Ph}_2\text{Cl}]_2\) was produced \(\dagger\). Thus, by analogy with that work, the yellow solution obtained from the reaction of \([\text{RuCl}_2(\text{C}_{6}\text{H}_{5})_2]_2\) and \([\text{P(OMe)}_2\text{Ph}_2\text{Cl}]_2\) in methanol, which contains \([\text{P(OMe)}_2\text{Ph}_2\text{Cl}]_2\) \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph}_2\text{Cl})_2\text{Cl}]_2\) \(\dagger\) was reduced in volume and then pyrolysed at 120 °C for 12 h. The resulting bright yellow crystalline solid (1) was shown by e.s.r. and magnetic measurements to be diamagnetic and the far-infrared spectrum (400—200 cm\(^{-1}\)) was very similar to that of sulfur.

\(\dagger\) The diamagnetic complexes \([\text{RuCl}_2(\text{C}_{6}\text{H}_{5})_2]\) \([\text{RuCl}_2(\text{C}_{6}\text{H}_{5})_2]\) \([\text{P(OMe)}_2\text{Ph}_2\text{Cl}]_2\) \(\dagger\) have been synthesised by direct reaction of \(\text{RuCl}_2\) with \(\text{L}_2\) \(\dagger\). However, as written, these contain paramagnetic ruthenium(II) anions and therefore, it is more likely that they should be reformulated as \([\text{RuCl}_2(\text{C}_{6}\text{H}_{5})_2]\) \([\text{RuCl}_2(\text{C}_{6}\text{H}_{5})_2]\) \([\text{P(OMe)}_2\text{Ph}_2\text{Cl}]_2\) \(\dagger\). \(\dagger\)

† For details see Notices to Authors No. 7, in J.C.S. Dalton, 1976, Index issue (items less than 16 pp. are supplied as full-size copies).


† W. J. Sime and T. A. Stephenson, unpublished work.

\[\text{[P(OMe)}_2\text{Ph}_2\text{RuCl}_2\text{Ru[OMe]}_2\text{Cl}]_2\text{RuCl}_2\text{Ru[OMe]}_2\text{Cl}]_2,\] containing only a broad band at 260 cm\(^{-1}\), indicating that (1) probably contains a triple chloride bridge but no terminal chlorides. However, the infrared spectrum (400—400 cm\(^{-1}\)) revealed extra features not present in the spectrum of the ionic dimer, e.g., a broad band at 3 250 cm\(^{-1}\) and strong bands at 1 090, 920 and 855 cm\(^{-1}\), suggesting the presence of \(\text{Ph}_2\text{POH}\) and \(\text{Ph}_2\text{PO}^-\) groups \(\dagger\) in addition to \([\text{P(OMe)}_2\text{Ph}_2\text{Cl}]_2\). The same compound was obtained if the pyrolysis reaction was carried out at 60 °C. Although a full elemental analysis of (1) was undertaken, the compound was too insoluble and involatile for n.m.r. or mass spectrometry, or molecular weight studies. Therefore, an X-ray structural determination of (1) was undertaken, the results of which are described below. Final parameters are in Table 1. Structure-factor tables are deposited as Supplementary Publication No. SUP 21929 (5 pp., 1 microfiche). \(\dagger\) Selected bond lengths are given in Table 2, and mean values of chemically equivalent angles in Table 3. A view of the molecule, showing only one atom for each phenyl ring, is given in Figure 1.

DISCUSSION

Unlike the expected neutral dimer \([\text{P(OMe)}_2\text{Ph}_2\text{Cl}]_2\) \([\text{RuCl}_2\text{Ru[OMe]}_2\text{Cl}]_2\), (1) contains two methyl diphenyldiphosphinophosphinyl and four other oxyphosphorus ligands. The diamagnetism of the compound and the long \(\text{Ru} \cdots \text{Ru}\) distance \(3.425 \text{ Å}\), which indicate no direct metal—metal interaction, \(\dagger\) suggest a ruthenium(II) complex. One half of the dimer contains both methoxy-groups and interatomic distances suggest that a proton on O(1) interacts primarily with O(5). In the other half-molecule, there must formally be one \(\text{Ph}_2\text{PO}^-\) group and two \(\text{Ph}_2\text{POH}\) groups. The most plausible


arrangement is to place protons on O(2) and O(4), both of which interact with a negative charge on O(3). In two compounds, similar arrangements of atoms have been confirmed by X-ray analysis, and others probably exist [Figures 2 (ref. 15) and 3 (ref. 16)]. Pyrolysis of the yellow solution obtained from the and which analysed very well for \([\text{P(OEt)}\text{Ph}_2]_2\text{P(OH)}\text{Ph}_2\text{RuCl}_3\text{Ru}[\text{P(OH)}\text{Ph}_2]_2\text{P(Ph)}\text{PO}]\). The same compound (2) was also obtained if PCIPh$_2$ is refluxed with \([\text{RuCl}_3(\text{PPh}_3)]\) in aqueous ethanol whereas in hexane, earlier studies showed that \([\text{PCIPh}_2]_2\text{RuCl}_3\text{RuCl}(\text{PCIPh}_2)_2\) is formed. Crystals of (2) are orthorhombic.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>U$_{11}$</th>
<th>U$_{22}$</th>
<th>U$_{33}$</th>
<th>U$_{12}$</th>
<th>U$_{13}$</th>
<th>U$_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)</td>
<td>61</td>
<td>27</td>
<td>47</td>
<td>9</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Ru(2)</td>
<td>68</td>
<td>13</td>
<td>45</td>
<td>1</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>Cl(1)</td>
<td>32</td>
<td>27</td>
<td>50</td>
<td>13</td>
<td>27</td>
<td>9</td>
</tr>
<tr>
<td>Cl(2)</td>
<td>95</td>
<td>54</td>
<td>44</td>
<td>10</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>

a = 26.01 Å, b = 43.79 Å, c = 24.56 Å, space group P43d (No. 70). Photographs indicate a substantially disordered structure, and the calculated density (1.50 g/cm$^3$) indicates
disordered structure and space group $P4_3d$ (No. 70).

half a molecule per asymmetric unit (\(d_{l} = 1.50 \text{ g cm}^{-3}\) for \(Z = 16\)), suggesting that the molecules are disordered, about a two-fold axis or centre of symmetry.

Furthermore, if the yellow solution containing \([^\{P(\text{OEt})\text{Ph}_2\text{Cl}\}_3\text{RuCl}_4\text{Ru}[P(\text{OEt})\text{Ph}_2\text{Cl}]^+\] cation is treated

### Table 2

Selected bond lengths in (1). Estimated standard deviations are: \(\text{Ru}^-\text{Cl}, 0.015\); \(\text{Ru}^-\text{P}, 0.018\); \(\text{P}^-\text{O}, 0.05\); \(\text{P}^-\text{C}, 0.07\); and \(\text{O}^-\text{C}, 0.09 \text{ Å}\).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
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<tr>
<td>Ru(1)−Cl(1)</td>
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<td>Ru(1)−Cl(2)</td>
<td>2.484</td>
</tr>
<tr>
<td>Ru(1)−Cl(3)</td>
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<tr>
<td>Ru(1)−P(1)</td>
<td>2.258</td>
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<td>Ru(1)−P(2)</td>
<td>2.277</td>
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<tr>
<td>Ru(1)−P(3)</td>
<td>2.226</td>
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<tr>
<td>P(1)−O(1)</td>
<td>1.63</td>
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<tr>
<td>P(1)−O(14)</td>
<td>1.83</td>
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<td>P(1)−O(15)</td>
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<td>P(1)−O(16)</td>
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<td>P(1)−O(17)</td>
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<tr>
<td>O(1)−O(6)</td>
<td>2.66</td>
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<td>O(1)−O(6)</td>
<td>2.92</td>
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<tr>
<td>O(1)−O(6)</td>
<td>3.05</td>
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### Table 3

(a) Selected bond angles in (1). Estimated standard deviations are 0.5° for all angles given.

<table>
<thead>
<tr>
<th>Angle</th>
<th>Number</th>
</tr>
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<tbody>
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<td>Cl(1)−Ru(1)−Cl(2)</td>
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<td>Cl(1)−Ru(2)−Cl(2)</td>
<td>77.5</td>
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<td>Cl(1)−Ru(1)−Cl(3)</td>
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<td>Cl(1)−Ru(2)−Cl(3)</td>
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<tr>
<td>Cl(1)−Ru(1)−P(1)</td>
<td>92.7</td>
</tr>
<tr>
<td>Cl(1)−Ru(2)−P(1)</td>
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<tr>
<td>Cl(1)−Ru(1)−P(2)</td>
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<tr>
<td>Cl(1)−Ru(2)−P(3)</td>
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<tr>
<td>Cl(2)−Ru(1)−Cl(3)</td>
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<td>Cl(2)−Ru(2)−Cl(3)</td>
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<tr>
<td>Cl(2)−Ru(1)−P(1)</td>
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<td>Cl(2)−Ru(2)−P(1)</td>
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</tr>
<tr>
<td>Cl(2)−Ru(1)−P(2)</td>
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<tr>
<td>Cl(2)−Ru(2)−P(2)</td>
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<td>Cl(3)−Ru(2)−P(3)</td>
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<td>P(1)−Ru(1)−P(2)</td>
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<td>P(1)−Ru(2)−P(2)</td>
<td>90.5</td>
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<tr>
<td>P(1)−Ru(2)−P(3)</td>
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<tr>
<td>Ru(1)−Cl(1)−Ru(2)</td>
<td>87.9</td>
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<td>Ru(1)−Cl(2)−Ru(2)</td>
<td>88.6</td>
</tr>
<tr>
<td>Ru(1)−Cl(3)−Ru(2)</td>
<td>87.5</td>
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</tbody>
</table>

(b) Mean values of chemically distinct angles in (1)

### Bild 1

Structure of \([^\{P(\text{OEt})\text{Ph}_2\text{Cl}\}_3\text{RuCl}_4\text{Ru}[P(\text{OEt})\text{Ph}_2\text{Cl}]^+\] (1)

### Bild 2

Structure of \([^\{P(\text{OEt})\text{Ph}_2\text{Cl}\}_3\text{RuCl}_4\text{Ru}[P(\text{OEt})\text{Ph}_2\text{Cl}]^+\] (1)

### Bild 3

Structure of \([P(\text{S}_2\text{PMe}_2)\text{Ph}_2\text{PO}_3]H\] (ref. 16)

with an excess of lithium bromide before pyrolysis, the resulting yellow, crystalline solid (3) analysed very well for \([P(\text{OEt})\text{Ph}_2\text{Cl}]_3\text{RuBr}_3\text{Ru}[P(\text{OEt})\text{Ph}_2\text{Cl}]^+\] (Ph$_2$PO).

As expected, \([P(\text{OR})\text{Ph}_2\text{Cl}]_3\text{RuCl}_4\text{Ru}[P(\text{OR})\text{Ph}_2\text{Cl}]^+\)] (Ph$_2$PO).

\([\text{BPh}_4]\) (R = Me or Et) was recovered unchanged after pyrolysis. However, for \([P(\text{OEt})\text{Ph}_2\text{Cl}]_3\text{RuCl}_4\text{Ru}[P(\text{OEt})\text{Ph}_2\text{Cl}]_3\text{X} (X = \text{SCN}^-, \text{CN}^-, \text{or} [S_2\text{PM}_{2}]^+)\), pyrolysis gave yellow solids whose infrared spectra are identical with (2). This suggests that the first step is nucleophilic attack of \([\text{X}^-]\) on a co-ordinated alkoxycarbonyl group to give a \(\text{Ph}_2\text{PO}^-\) group and RX. This is presumably followed by stepwise hydrolysis of some of the \([\text{P(OR)}\text{Ph}_2\text{Cl}]_3\) groups, the partially hydrolysed product then precipitating out because of its insolubility. Attempts to make (1), (2), or (3) undergo further reactions or to synthesise the corresponding phosphonite complexes have proved unsuccessful to date.

**Experimental**

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Infra-red spectra were
recorded in the region 4000–200 cm⁻¹ on a Perkin-Elmer 225 and 557 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Magnetic measurements were made on a Faraday balance. Melting points were determined with a Kölfer hot-stage microscope and are uncorrected. Standard crystallographic calculations were performed at the Edinburgh Regional Computing Centre.¹⁸

Crystal Data.—C₄H₁₀Cl₂O₄P₂Ru₂, M = 1549, yellow monoclinic plates, a = 13.19(1), b = 21.98(2), c = 24.98(2) Å, β = 109.4(1)°, U = 6 831 Å², Dₐ = 1.48 g cm⁻³, Z = 4, Dₘ = 1.49 g cm⁻³. Space group P2₁/c (No. 14), Cu-Kα radiation, λ = 1.5418 Å, μ(Cu-Kα) = 65 cm⁻¹.

Structure Determination.—Data were collected from a single crystal, a plate of thickness 0.15 mm and cross-section 0.16 mm², using multiple film packs. Data for layers 0—5kl were collected by the equi-inclination Weissenberg method, and limited data for layers klh—2 by the precession method. The photographs were of poor quality, and suggested disorder in the crystal. The films were scanned using rotating-drum film scanners, the Weissenberg on an Optronics instrument, and the precession on a Saab. Merging of the data gave 1534 independent reflections significantly above background.

The positions of two independent ruthenium atoms, both having y ca. 0.25, were determined from the Patterson function, and the subsequent difference-Fourier synthesis (R 0.41) had significant pseudo-symmetry. The choice of three positions for chlorine atoms enabled all phosphorus and oxygen atoms to be found in subsequent difference syntheses. The phenyl groups could only be located approximately, and were refined as idealised groups with all C-C bonds 1.40 Å and all C-C-C angles 120°. At this stage the two terminal methyl groups were clearly indicated, but no attempt was made to locate hydrogen atoms. With phenyl groups constrained as above, and anisotropic thermal parameters for Ru and Cl only, the structure was refined treating the parameters in two large blocks, to convergence at R 0.11. Weights were of the form W = X Y with X = sinθ/0.3 for sin θ < 0.3, and 1.0 otherwise, and Y = 100/|F₀| for |F₀| < 100 and 1.0 otherwise. A final difference Fourier synthesis did not show any features above one-third the mean height of a carbon atom, and there were broad peaks near the worst determined phenyl rings.

def-Tri-μ-chloro-b-diphenylphosphino-bgi-tri(di diphenylphosphino acid)-ac-bis(ethyl diphenylphosphinato)diruthenium(II) * (1).—[(RuCl₂(C₄H₈O)₄)₂]¹³ (0.22 g) was refluxed with an excess of P(OEt)₂Ph₂ (0.50 ml) in methanol (10 ml) for 4 h under nitrogen to give a yellow solution. The solution was filtered to remove any unchanged starting material and then concentrated to a volume of ca. 5 ml. This solution was then pyrolysed in an evacuated, sealed tube at 120 °C for 12 h. The bright yellow crystals formed were filtered off, washed with methanol and diethyl ether, and dried in vacuo, m.p. >285 °C (Found: C, 56.6; H, 4.5; Cl, 6.5; P, 13.0; Ru, 11.0. Calc. for C₃₉H₁₆Cl₂O₄P₂Ru₂: C, 57.4; H, 4.5; Cl, 6.9; P, 12.0; Ru, 13.0%)

def-Tri-μ-chloro-b-diphenylphosphino-bgi-tri(di diphenylphosphino acid)-ac-bis(ethyl diphenylphosphinato)diruthenium(II) (2) —(a) Prepared as for (1) by reaction of [RuCl₂(C₄H₈O)₄]₂ and P(OEt)₂Ph₂ in ethanol followed by concentration and pyrolysis at 120 °C for 12 h, m.p. >225 °C (Found: C, 57.3; H, 4.6; Cl, 6.4; P, 11.9. Calc. for C₃₉H₁₆Cl₂O₄P₂Ru₂: C, 57.9; H, 4.6; Cl, 6.7; P, 11.8%). (b) [RuCl₂(PPPh₃)₂] (0.20 g) and PCIPh₂ (0.50 ml) were refluxed in an ethanol (25 ml)—water (5 ml) mixture. After a few minutes, the solution turned yellow and after 2 h a yellow solid had formed, shown by i.r. spectroscopy and m.p. to be identical with (2) (Found: C, 56.6; H, 4.5. Calc. for C₃₉H₁₆Cl₂O₄P₂Ru₂: C, 57.9; H, 4.6%). (c) [RuCl₂(C₄H₈O)₄] (0.02 g) was refluxed with excess of P(OEt)₂Ph₂ in ethanol under nitrogen for 4 h to give a yellow solution. An aqueous solution of KSCN was then added and the mixture allowed to stand for several days during which time the yellow solid tri-μ-chloro-hexakis(ethyl diphenylphosphinato)diruthenium(II) thiocyanate was deposited [ν(CN) 2030 cm⁻¹] (Found: C, 58.2; H, 5.1; N, 0.8). Calc. for C₃₉H₁₆Cl₂O₄P₂Ru₂S: C, 58.4; H, 5.1; N, 0.8%)

[(P(OEt)₂Ph₂)₂RuCl₂Ru(P(OEt)₂Ph₂)](SCN) (0.20 g) was then pyrolysed in n-propyl propionate (5 ml) at 120 °C to give the yellow solid (2).

In a similar fashion, pyrolysis of [(P(OEt)₂Ph₂)₂RuCl₂Ru(P(OEt)₂Ph₂)](SCN) (X = [CN]⁻ or [S₂PMe₂]⁻) gave only (2).

def-Tri-μ-bromo-b-diphenylphosphino-bgi-tri(di diphenylphosphino acid)-ac-bis(ethyl diphenylphosphinato)diruthenium(II) (3).—[(RuCl₂(C₄H₈O)₄)] (0.22 g) was refluxed with excess of P(OEt)₂Ph₂ (0.50 ml) for 4 h in ethanol to give a yellow solution. This was reduced in volume and an excess of LiBr (0.25 g) added. The mixture was then pyrolysed at 120 °C for 12 h and the resulting yellow crystals filtered off and washed with ethanol and diethyl ether, m.p. 220 °C (Found: C, 52.9; H, 4.3; Br, 13.9; P, 11.4. Calc. for C₃₉H₁₆Br₂O₄P₂Ru₂: C, 53.4; H, 4.3; Br, 14.0; P, 10.9%).

We thank Johnson Matthey Ltd. for loans of ruthenium trichloride, the S.R.C. for financial support (C. L. J., W. J. S.), the S.R.C. and Dr. M. Elder of the Atlas Computing Laboratory for the scanning of the Weissenberg photographs, Dr. W. D. S. Motherwell of Cambridge University for a molecular plotting program, Dr. G. Hunter of Dundee University for the magnetic measurements, and Dr. R. M. Paton for the e.s.r. measurements.

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* X-Ray' program system, Technical Report TR 192, Computer Science Center, University of Maryland, version of January 1974, implemented for the I.C.L. 4175 computer at the Edinburgh Regional Computing Centre.

SYNTHESSES AND REARRANGEMENT REACTIONS OF \([\text{RuCl}_2\text{L}_3\text{ or 4}]\)

COMPLEXES \((L=\text{P(OR)}_3, \text{P(OR)}_2\text{Ph}, \text{P(OR)}\text{Ph}_2)\)

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Summary: Reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\) with excess \(L\) in hexane gives either \([\text{RuCl}_2\text{L}_4]\) \((L=\text{P(OMe)}_3, \text{P(OMe)}_2\text{Ph})\) or \([\text{RuCl}_2\text{L}_3]\) \((L=\text{P(OMe)}\text{Ph}_2, \text{P(OEt)}\text{Ph}_2)\) which rearrange in polar solvents to the ionic complexes \([\text{L}_3\text{RuCl}_3\text{RuL}]\text{Cl} (L=\text{P(OMe)}_2\text{Ph}, \text{P(OMe)}\text{Ph}_2, \text{P(OEt)}\text{Ph}_2)\) and \([\text{Ru}_3\text{Cl}_5\text{L}_3]\text{Cl} (L=\text{P(OEt)}\text{Ph}_2, \text{P(OMe)}\text{Ph}_2)\).

Recently, we have shown that the monomeric tertiary phosphine complexes \([\text{RuCl}_2(\text{PR}_3)_3\text{ or 4}]\), made by exchange of \([\text{RuCl}_2(\text{PPh}_3)_4]\) with \(\text{PR}_3\) in non-polar solvents [1] undergo facile rearrangement reactions in solution as shown in the Scheme [2]. In an attempt to verify the generality of this rearrangement pattern, we now report the results of studies on exchange reactions of \([\text{RuCl}_2(\text{PPh}_3)_3]\)(I) with tertiary phosphites, phosphonites and phosphinites.

Thus, if (I) is refluxed with excess \(\text{P(OMe)}_3\) or \(\text{P(OMe)}_2\text{Ph}\) in hexane, yellow crystals \([\text{RuCl}_2\text{L}_4]\) are formed. Far ir studies suggest a cis/trans mixture for both compounds in the solid state but in solution, \(^{31}\text{P}\) nmr spectroscopy indicates that irreversible cis/ trans isomerisation readily occurs. Although the cis-isomers are then stable indefinitely at ambient temperature in solution, thermolysis or photolysis of \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]\) in \(\text{CH}_2\text{Cl}_2\) gives \([(\text{P(OMe)}_2\text{Ph})_3\text{RuCl}_3\text{Ru}(\text{P(OMe)}_2\text{Ph})_3]\text{Cl}^+\) isolated as its \(\text{BPh}_4^-\) salt. However, this does not occur for the \(\text{P(OMe)}_3\) complex. Reaction of (I) and excess \(\text{P(OMe)}_2\text{Ph}\) in methanol gives the
[Ru(P(OME)$_2$Ph)$_6$]$^{2+}$ cation$^\dagger$ which can also be isolated as a BPh$_4^-$ salt.

In contrast, reaction of (I) with excess P(OR)Ph$_2$ (R=Me, Et) in hexane gives orange solids of stoichiometry [RuCl$_2$(P(OR)Ph$_2$)$_3$], shown to be monomeric by molecular weight measurements in benzene. Variable temperature, proton decoupled $^{31}$P nmr studies indicate rapid intramolecular exchange of P(OR)Ph$_2$ groups at temperatures >160K (single resonance observed) but at lower temperatures, more signals are found eg. for [RuCl$_2$(P(OTEt)Ph$_2$)$_3$] in (CD$_3$)$_2$CO/C$_6$H$_5$CH$_3$ at ca 140K, two resonances at 141.1 (broadened doublet) and 167.3 ppm (broadened triplet) of relative intensity 2:1 are observed (cf the limiting $^{31}$P nmr spectra of [RuCl$_2$L$_3$](L=PPPh$_3$, PETPh$_2$)[1]) which is consistent with the square pyramidal geometry expected for a five coordinate d$^6$ complex [4].

Unlike [RuCl$_2$L$_4$] (L=P(OME)$_3$, P(OME)$_2$Ph), [RuCl$_2$(P(OR)Ph$_2$)$_3$] rapidly rearrange in polar solvents to give ionic complexes. For R=Me, the main product is [(P(OME)Ph)$_3$RuCl$_3$Ru(P(OME)Ph)$_2$]$_3^+$ which is consistent with the mechanism shown in the Scheme. However, for R=Et, the main rearrangement product based on $^{31}$P nmr, conductivity and analytical data is the trimeric cation [Ru$_3$Cl$_9$(P(OTEt)Ph$_2$)$_9$]Cl for which the cyclic structure (II) is tentatively proposed. $^{31}$P nmr studies indicate that

\[
2[RuCl_6(PR_3)_3] + 2PR_3 \rightarrow [R_3P \begin{array}{c} \text{Ru} \text{Cl} \text{Ru} \text{Cl} \text{Ru} \text{PR}_3 \\
R_3P \text{Cl} \text{PR}_3 \text{Cl} \text{Cl}
\end{array} + PR_3
\]
small amounts of \([\text{Ru}_3\text{Cl}_5(\text{P(OME)}\text{Ph}_2)_9]\)Cl and \([\text{RuCl}_3\text{Cl}_3\text{Ru}(\text{P(OEt)}\text{Ph}_2)_3]\)Cl⁺ respectively are also formed.

Reaction between (I) and excess P(OMe)Ph₂ in methanol gives an immediate red solution from which the \([\text{RuCl}(\text{P(OME)}\text{Ph}_2)_4]\)MeOH⁺ cation can be isolated by addition of NaBPh₄. With (I) and excess P(OEt)Ph₂ in ethanol, however, a red dimeric cation\([\left[\text{RuCl}(\text{P(OEt)}\text{Ph}_2)_4\right]_2]\) (BPh₄)₂ is isolated. On further refluxing, the red solutions turned yellow and \([\left[(\text{P(OME)}\text{Ph}_2)_3\text{RuCl}_3\text{Ru}(\text{P(OME)}\text{Ph}_2)_3\right]_\text{Cl}\) and \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph}_2)_9]\)Cl respectively are formed. Therefore, a possible rationalisation of the formation of (II) is by facile coupling \([\left[\text{RuCl}(\text{P(OEt)}\text{Ph}_2)_4\right]_2\text{Cl}_2\) and some unreacted \([\text{RuCl}_3(\text{P(OEt)}\text{Ph}_2)_3]\) accompanied by displacement of P(OEt)Ph₂. In contrast, rapid dimers of \([\text{RuCl}_2(\text{P(OME)}\text{Ph}_2)_3]\) to form the stable \([\text{P(OME)}\text{Ph}_2]_3\text{RuCl}_3\text{Ru}(\text{P(OMe)}\text{Ph}_2)\) Cl appears to be the preferred reaction.

Finally, no evidence has been found here for the formation of neutral dimers \([\text{L}_3\text{RuCl}_3\text{RuCL}_2]\) which is indicative of stronger Ru-P bonds in these alkoxy substituted phosphine complexes compared to those containing tertiary phosphines. In support of this, pyrolysis of \([\text{P(OR)}\text{Ph}_2)_3\text{RuCl}_3\text{Ru}(\text{P(OR)}\text{Ph}_2)_3]\)Cl at 120°C gives \([\text{P(OR)}\text{Ph}_2)_2\text{P(OH)}\text{Ph}_2]\text{RuCl}_3\text{Ru}(\text{P(OR)}\text{Ph}_2)_2(\text{Ph}_2\text{PO})(\text{R=Me,Et})\) with no cleavage of Ru-P bonds [5]

\[\text{of the formation of } [(\text{PET}_\text{2}\text{Ph})_3\text{RuCl}_3\text{RuCl}(\text{PET}_\text{2}\text{Ph})_2] \] by pyrolysis of \([\text{PET}_\text{2}\text{Ph})_3\text{RuCl}_3\text{Ru}(\text{PET}_\text{2}\text{Ph})_3\) Cl[6].


\[\text{These compounds have also been synthesised by reaction of } [\text{RuCl}_2\text{C}_7\text{H}_8]_n \]

with excess \text{L} in ethanol or methanol [3].
Further studies on these rearrangements and of reactions of the products are in progress.

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Preparation, X-Ray Crystal Structure Analysis, and Reactions of a Novel, Hydroxo-Bridged, Tetranuclear, \(\pi\)-Arene Ruthenium(II) Quadrivalent Cation
\[\{((\eta^4-C_8H_8)Ru(OH))_2J_2(\text{SO}_4)_2\cdot12\text{H}_2\text{O}\}\]

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Preparation, X-Ray Crystal Structure Analysis, and Reactions of a Novel, Hydroxo-Bridged, Tetrancular, π-Arene Ruthenium(II) Quadrivalent Cation \[ \text{[((} \eta^4-C_6H_4 \text{)}Ru(OH))_4\text{]}_2\text{SO}_4 \cdot 12\text{H}_2\text{O} \]

By Robert O. Gould,* C. Lynn Jones, Donald R. Robertson, and T. Anthony Stephenson*

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Summary Reaction of \[ \text{[((} \eta^4-C_6H_4 \text{)}RuCl)_4\text{]} \] with aqueous sodium carbonate (1:2 molar ratio) and excess of sodium sulphate gives the title compound (II) whose structure has been determined by X-ray diffraction; a mechanism of formation and some reactions of (II) are also outlined. \[ R = 0.11 \] based on all non-hydrogen atoms except the water molecules and the three oxygen atoms of each sulphate ion which do not lie on a three-fold axis.†

Recently, we reported that the reaction of \[ \text{[((} \eta^4-C_6H_4 \text{)}RuCl)_4\text{]} \] with an excess of aqueous sodium hydroxide gave the yellow triple hydroxy-bridged cation \[ \text{[((} \eta^4-C_6H_4 \text{)}Ru(OH))_3\text{]}_2\text{Ru(} \eta^4-C_6H_4 \text{)}\text{Cl}_3\text{H}_2\text{O} \] (I). The same compound is also formed using excess of aqueous sodium carbonate.

We now find that if \[ \text{[((} \eta^4-C_6H_4 \text{)}RuCl)_4\text{]} \] is treated with less sodium carbonate \[ \text{[((} \eta^4-C_6H_4 \text{)}Ru(OH))_2\text{]}^{2+}\] (ca. 1:1 molar ratio) and the resulting solution treated with excess of sodium sulphate, orange crystals are precipitated in low yield (ca. 25%) and these have been shown by X-ray analysis to be the novel tetrancular complex (II) containing both π-bonded benzene groups and hydroxido bridges.

Crystal data: \[ \text{C}_{60}\text{H}_{48}\text{O}_{6}\text{Ru}_2\text{S}_2\text{, M 1192, cubic, a = 12.862-} \]

(2) \[ A, U = 1889 \text{ Å}^2, Z = 2, D_m = 2.10, D_c = 2.14 \text{ g cm}^{-3} \]

space group \text{P}43m (no. 224). From precession photographs (Mo-\text{Kα radiation) 204 independent intensities were obtained using a Saab Mark II film scanner linked to a PDP-16 computer. The structure was solved by Patterson and difference Fourier syntheses and has been refined to.}

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by a full literature citation for this communication.
The structure consists of discrete cations with the formula $[([\eta^6-C_5H_5]Ru(OH)_3)_4]^{11+}$ and sulphate anions. The cations have crystallographic 4 $\overline{3}m$ ($D_d$) symmetry containing interpenetrating tetrahedra of ruthenium and oxygen atoms. Each ruthenium atom has bonds to three hydroxy groups of equal length (2.12 Å) and the O-Ru-O and Ru-O-Ru angles are 78.3 and 102.2° respectively. The arrangement of ruthenium and oxygen atoms may thus be described as a substantially distorted cube in which the Ru–Ru–O and O–O–O diagonals are 3.29 and 2.62 Å, respectively (see Figure) (cf. $\{\text{Me}_3\text{Pt(OH)}_3\}_2^+$. The ruthenium atoms in (II) are also bound to benzene rings, located 1.74 Å further out along the three-fold axes (Ru–C = 2.23 Å). The rings are, however, disordered with essentially equal site occupancy over two locations related by a 30° rotation about the axis. The sulphate ions in (II) are disordered on sites of $\overline{3}m$ ($D_d$) symmetry and only the half-occupied sites on the three-fold axes could be identified in the electron density maps.

The cations are centred at the points $\{\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\}$ and $\{\frac{3}{4}, \frac{3}{4}, \frac{3}{4}\}$ in the cell, and are each linked to four others by contacts of benzene rings (3.0 A) and to a further four by hydrogen bonds to sulphate ions from the OH groups (O–O ca. 2.6 Å). The resulting structure is very open, and contains channels with van der Waals diameters of about 3.2 Å parallel to each of the three crystallographic axes, and intersecting in pairs at the points $\{\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\}$, etc. Difference Fourier syntheses indicate broad, low regions of electron density in these channels and the water molecules are presumably randomly arranged there. Heating a powdered sample of (II) to 100 °C results in the reversible loss of water, also indicating that it is not tightly held in chemically discrete sites.

The probable mechanism of formation of (I) and (II) is shown in the Scheme. Thus, earlier it was suggested that in aqueous solution $[([\eta^6-C_5H_5]RuCl_4)_2]$ gave a mixture of $[([\eta^6-C_5H_5]RuCl(H_2O)_4)]^+$ and $[([\eta^6-C_5H_5]Ru(H_2O)_4)]^{11+}$ and therefore, in basic solution, successive deprotonation of the latter should give $[([\eta^6-C_5H_5]Ru(OH)(H_2O)_3)]^+$ and $[([\eta^6-C_5H_5]Ru(OH)(H_2O)_2)]^+$ respectively with the dihydroxo species favoured in strongly basic solutions. Because of the bridging propensity of hydroxyl groups and the desire of ruthenium(II) to exhibit six-co-ordination, it seems reasonable that $[([\eta^6-C_5H_5]Ru(OH)H_2O)]^+$ will tend to dimerise with concomitant elimination of water to form (I) and similarly, $[([\eta^6-C_5H_5]Ru(OH)(H_2O)O)]^+$ will tetrarmerise to form (II). The latter process is enhanced by addition of sulphate ion which removes the tetrameric cation from solution.

Support for the correctness of this mechanism comes from the observation that reaction of $[([\eta^6-C_5H_5]RuCl_4)_2]$ with either aqueous AgNO$_3$ or AgBF$_4$ (which produces the $[([\eta^6-C_5H_5]Ru(OH)Br)_2]^{2+}$ cation; with excess of Br the insoluble $[([\eta^6-C_5H_5]RuBr_3)]^3$ is precipitated. In contrast, with neutral Lewis bases, e.g. pyridine or $\gamma$-picoline (I) the double hydroxyl bridged cations $[([\eta^6-C_5H_5])_2Ru(OH)_2]^{2+}$ can be isolated.

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Preliminary Communication

Some $^5\eta$-Cyclohexadienyl Complexes of Ruthenium.

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Summary:— The compounds [(η$^5$C$_{6}H$_{6}$Y)Ru(PR$_3$(N-N))PF$_6$ (Y$^-$ = H$^-$, CN$^-$, \text{OH}$^-$; PR$_3$ = PMe$_2$Ph, PMePh$_2$; N-N = 1,10-phenanthroline, 2,2'-'bi-
pyridyl), [(η$^5$C$_6$Me$_3$H$_4$)Ru(PMe$_2$Ph)phen]PF$_6$ and[(η$^5$C$_{6}H$_{5}$Ru]η$^5$C$_{5}H$_{5}$] have been isolated and some evidence found for other unstable
cyclohexadienyl or 1,3 cyclohexadiene compounds on addition
of nucleophiles to a variety of cationic areneruthenium(II)
complexes.

Although reactions of nucleophiles with complexes containing
carbocyclic rings have been studied extensively, little work has been
published on such reactions with areneruthenium(II) compounds. This
is probably because, in most instances, addition to the coordinated
ring gave products which were too unstable to be isolated [1]. In
this note, we now report some results of our studies on the reactions
of nucleophiles with various cationic areneruthenium(II) compounds
where, in some instances, stable η$^5$-cyclohexadienyl complexes were
obtained.

Thus, if [(η$^6$-arene)RuCl$_2$]$_2$ (arene = C$_6$H$_6$, C$_6$Me$_3$H$_3$) is
stirred in methanol with excess 1,10-phenanthroline or 2,2'-'bi-
pyridyl (N-N) for ca 1 hour, and then NH₄PF₆ is added, the bright yellow solids [(η⁶-arene)RuCl(N-N)]PF₆ (I)⁺ are precipitated. All these compounds then reacted with tertiary phosphines in methanol to give the pale yellow dicationic complexes [(η⁶-arene)Ru(PR₃)(N-N)]PF₆ (II) (PR₃ = PMe₂Ph, PMePh₂). The analogous [(η⁵-C₅Me₅)RhCl(N-N)]PF₆ and [(η⁵-C₅Me₅)Rh(phen)(N-N)]PF₆ compounds have also been synthesised starting from [(η⁵-C₅Me₅)RhCl₂]²⁺.

Reaction of compounds (II) (arene = C₆H₆) with various nucleophiles Y⁻ (Y⁻ = H⁻, CN⁻, OH⁻) produced intensely coloured solutions from which the η⁵-cyclohexadienyl cationic compounds [(η⁵-C₆H₆Y)Ru(PR₃)(N-N)]PF₆⁺ were readily isolated. Similarly, [(η⁵-C₆H₃Ph)Ru(PMe₂Ph)(phen)]PF₆ reacted with NaBH₄ to give [(η⁵-C₆H₃Ph)Ru(PMe₂Ph)(phen)]PF₆ and, as for other methyl substituted arene compounds [2], nmr evidence suggested that nucleophilic attack has occurred at one of the unsubstituted positions.

Although reaction of compounds (I) with the above nucleophiles also produced rapid colour changes, facile decomposition occurred and no clean products could be isolated. This rapid decomposition reaction was a characteristic of other monocationic areneruthenium(II) compounds such as[(η⁶-C₆H₆RuCl₂)]PF₆ (L = PR₃, AsPh₃, etc) and[(η⁶-C₆H₆Ru(S₂PPh₂)PR₃]PF₆ on treatment with NaBH₄. Similar very unstable products have been reported [1] when [(η⁶-C₆H₆RuCl₂)₂ was reacted with either KCN or NaOH in d⁶-(CH₃)₂SO and here, H nmr studies indicated that

All these compounds have been fully characterised by elemental analyses, conductivity measurements, infrared, H and C nmr spectroscopy.
substituted η⁵-cyclohexadienyl compounds were initially formed.

For the mixed sandwich compound \( \eta^5\text{C}_6\text{H}_5\text{RuCl}_2 \), however, (made by reaction of \( \eta^6\text{C}_6\text{H}_6\text{RuCl}_2 \) with TICl \( \text{H} \)) small amounts of the neutral \( \eta^5\)-cyclohexadienyl complex \( \eta^5\text{C}_6\text{H}_5\text{RuC}_5\text{H}_5 \) could be isolated from the reaction mixture obtained on addition of \( \text{NaBH}_4 \).

\( ^1\text{H} \) nmr studies also indicated the formation of some \( \eta^5\text{C}_6\text{H}_5\text{OMe} \) on addition of \( \text{NaOMe} \), but with \( \text{NaOH} \) and \( \text{KCN} \), nmr studies suggested that ring displacement reactions were more important.

Finally, preliminary studies on the reaction of the triple hydroxide bridged compound \( \text{C}_6\text{H}_5\text{Ru(OH)}_3\text{RuC}_6\text{H}_5\text{BPh}_4 \) with \( \text{NaBH}_4 \) indicated that two hydride ions may have added to one benzene ring to produce a 1,3 cyclohexadiene rhenium compound. Similar double hydride ion additions have been observed for the \( \eta^6\text{C}_6\text{H}_6\text{Ru}^2+ \) cation forming \( \eta^6\text{C}_6\text{H}_6\text{Ru}^4\text{C}_6\text{H}_8 \) and in the reaction of \( \eta^6\text{C}_6\text{H}_6\text{RuCl}_2 \) with \( \text{NaBH}_4 \) in \( \text{d}^6-(\text{CH}_3)_2\text{SO} \), transient 1,3 cyclohexadiene complexes were detected by nmr spectroscopy [1].

Further studies on these and other cationic areneruthenium(II) compounds with a wider range of nucleophiles are now in progress.

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Ruthenium Complexes containing Group 5B Donor Ligands. Part 5.\textsuperscript{1}
Synthesis and Crystal and Molecular Structure of Acetone(carbonyl)-
chloro(trichlorostannio)bis(triphenylphosphine)ruthenium(II)—Acetone
(1/1)

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Ruthenium Complexes containing Group 5B Donor Ligands. Part 5.¹ Synthesis and Crystal and Molecular Structure of Acetone(carbonyl)-chloro(trichlorostannio)bis(triphenylphosphine)ruthenium(II)—Acetone (1/1)

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The lemon-yellow crystals (1) obtained by reaction of the red ‘carbonyl-containing’ ruthenium solution with SnCl₄ and PPh₃ in acetone have been shown to be [RuCl₂(SnCl₃)(C₅H₇CO)(PPh₃)₂(OCMe₃)₂]⁻ Me₂CO and not [Ru₂Cl₆(SnCl₃)₂(CO)₂(PPh₃)₆(OCMe₃)₂]⁻ as previously suggested. The crystals are monoclinic, space group P2₁/c with a = 11.950(3), b = 14.988(3), c = 24.316(2) Å, and β = 92.51(1)°. The structure has been solved with 3 601 diffraction data and refined to R 0.037. It is, however, possible to obtain (3) by warming (1) in benzene, but it readily loses SnCl₄ to give some (Ph₃P)(OC)ClRuCl₃Ru(CO)(PPh₃)₂.

Over 10 years ago one of us² reported that the reaction of the well known ‘carbonyl-containing’ red solution (i.e. ‘RuCl₃·xH₂O’ in ethanol treated with CO for 5 h) with a mixture of anhydrous tin(ii) chloride and triphenylphosphine in the presence of acetone gave a small yield of lemon-yellow crystals (1). On the basis of full elemental analyses (C, H, Cl, O, and Sn) and i.r. studies (v(CO) at 1 957 cm⁻¹ (Nujol); 1 701 and 1 661 cm⁻¹ (acetone)) this complex was tentatively formulated as [Ru₂Cl₃(SnCl₃)(CO)₂(PPh₃)₃(OCMe₃)₂]. In the absence of acetone only a mixture of products was formed and attempts to separate these by recrystallisation resulted in loss of SnCl₄ and the formation of cis-[RuCl₄(CO)₂(PPh₃)₂].

Recently, we have been studying the preparation and detailed mechanism of formation of various dimeric ruthenium(II) complexes containing both RuCl₃Ru and RuCl₃Ru bridging units. Some examples of those

synthesised in our laboratory are \([\{\text{RuCl}_3\text{Y} (\text{PPh}_3)_2\}]\), \([\{\text{Ph}_3\text{P}]_2\text{ClRuCl}_2\text{RuY} (\text{PPh}_3)_2\}]\cdot 2\text{Me}_2\text{CO}\), \([\{\text{Ph}_3\text{P}]_2\text{YClRuCl}_2\text{RuY} (\text{PPh}_3)_3\}]\), and \([\{\text{Ph}_3\text{P}]_2\text{YRuCl}_2\text{RuY} (\text{PPh}_3)_3\}]\cdot \text{BPh}_4\) \((\text{Y} = \text{CO} \text{ or } \text{CS})\).\(^{3,4}\) * In the light of these studies it was considered that two possible structures for (I) might be either the triple chloride-bridged (A) or the double chloride-bridged one (B) (or isomers of these complexes). However, the proton noise-decoupled \(^{31}\text{P}\) n.m.r. spectrum of (I) in \(\text{D}_2\text{O}\) at 303 K showed only one \(\text{PPh}_3\) resonance at 35.4 p.p.m. plus two broad weak signals arising from \(^{119}\text{Sn}\) and \(^{117}\text{Sn}\) satellites \((/\text{PSn} 250 \text{ Hz})\) which is not compatible with either structure (A) or (B). Therefore an X-ray structural determination of (I) was undertaken both to establish its formulation and to ascertain its detailed geometry.

RESULTS AND DISCUSSION

The most important distances and angles in (I) are given in Tables 2 and 3, based on the parameters in Table 1. A view of the molecule is given in the Figure. The molecule deviates only very slightly from \(\text{C}_6\text{m}\) symmetry; the maximum deviation of the atoms \(\text{Ru}, \text{Sn}, \text{Cl}(1), \text{Cl}(2), \text{O}(1), \text{C}(1), \text{O}(2), \text{C}(39), \text{C}(40),\) and \(\text{C}(41)\) from their best plane is 0.02 Å. Within this plane the short \(\text{Ru}-(\text{Cl}(1))\) bond is reflected in the large \(\text{Sn}-\text{Ru}-(\text{C}(1))\) and \(\text{Cl}(1)\)-\(\text{Ru}-(\text{C}(1))\) angles. Conversely, both \(\text{PPh}_3\) groups are substantially tilted away from the bulky \([\text{SnCl}_3^-]\) group. Within the latter the in-plane \(\text{Sn}-(\text{Cl}(2))\) bond is significantly shorter than the two out-of-plane bonds, and the distortion from \(\text{C}_6\text{m}(3m)\) local symmetry is marked in the angles.

The phenyl rings are staggered in three ways. The mean angles between the plane of a ring and the plane of C(33), and 82° for those at C(9) and C(21). These last rings lie in planes above and below the co-ordinated acetone molecule, and probably interact with it, since, for example, C(26) comes to within 3.15 Å of O(2). The other rings make larger Ru–P–C angles, and the only other outstandingly close contacts not involving hydrogen atoms are C(1)–C(16) and C(21)–C(34) (3.30 Å).

With the exception of the tin analysis figure, the

\* For detailed references to other ruthenium complexes of this type see ref. 3.


structure found for (1) is consistent with the $^{31}$P n.m.r. spectrum and all the experimental data published previously.\(^2\) Also the $\nu$(CO) and $^{31}$P n.m.r. values of 1661 and 1701 cm$^{-1}$ correspond to the carbonyl-stretching frequencies of co-ordinated and solvate acetone respectively (cf. \([\text{RuCl}_4(\text{PPh}_3)_2(\text{OClMe})_2]\), $\nu$(CO) at 1 656 cm$^{-1}$).\(^2\) There is also a strong band at 300 cm$^{-1}$ assigned to a $\nu$(SnCl) vibration.\(^5\)

### Table 2

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<th>Bond lengths (Å) for (1). Quantities related by the pseudo-symmetry are printed on the same line</th>
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### Table 3

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<td>O(2)–Ru–P(1)</td>
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### View of the molecule (1)

Although (1) is not a dimer, the complex \([\text{Ph}_3\text{P}](\text{OC})(\text{Cl}_2\text{Sn})\text{RuCl}_4\text{Ru}(\text{CO})(\text{PPh}_3)_2\) (3) can be synthesised by gently warming (1) in benzene for several hours and precipitating the product as a pale yellow powder with light petroleum (b.p. 60–80 °C) \(\text{cf. the formation of } (\text{Ph}_3\text{P})(\text{OC})\text{ClRuCl}_3\text{Ru}(\text{CO})(\text{PPh}_3)_2\) by heating \([\text{RuCl}_4(\text{CO})(\text{HOME})(\text{PPh}_3)_2]\) in dichloromethane–light petroleum (b.p. 60–80 °C).\(^4\) A closely related complex to (3), \([\text{OC}_2(\text{Cl}_2\text{Sn})\text{RuCl}_3\text{Ru}(\text{CO})_2]\), was obtained by reaction of \([\text{Ru}_2(\text{CO})_6]\) with SnCl$_4$.\(^6$

Unfortunately, (3) is not very stable in solution, readily eliminating a molecule of SnCl$_4$ to give some \([\text{Ph}_3\text{P}](\text{OC})\text{ClRuCl}_3\text{Ru}(\text{CO})(\text{PPh}_3)_2\) (\(^{31}$P n.m.r. evidence). Originally,\(^5\) the pale yellow solid obtained either by heating (1) in benzene or refluxing a mixture of the red solution, PPh$_3$, and SnCl$_4$ was assigned the formulation \([\text{Ru}_2\text{Cl}_4(\text{SnCl}_4)(\text{CO})(\text{PPh}_3)_2]\) on the basis of

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elemental analyses. However, a much better explanation is that the product generated under these conditions in 1966 was a mixture of [(Ph₃P)(OC)ClSn]RuCl₃Ru(OC)(PPh₃)$_2$ and [(Ph₃P)(OC)ClRuCl₃Ru(OC)(PPh₃)]. In fact, a 48:52 mixture of these two complexes gives excellent agreement with all the earlier analytical data (see Experimental section).

**EXPERIMENTAL**

Microanalyses were by the University of Edinburgh Chemistry Department (or taken from ref. 2) and the molecular weight was measured in CHCl₃ on a Mechrolab model 301A vapour-pressure osmometer (calibrated with benzil). Infrared spectra were recorded in the 250–600 cm⁻¹ region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Phosphorus-31 n.m.r. spectra were obtained on a Varian Associates XL-100 spectrometer operating in the pulse and Fourier-transform mode at 40.6 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H₃PO₄.

Acetone (carbonyl)chloro(triclorostannato)bis(triphénylphosphine)ruthenium(II) (1).—Acetone (1/1) (1).—This was prepared as described in ref. 2. (Found: C, 49.9; H, 4.1; Cl, 14.7; O, 6.4; Sn, 7.9. Calc. for C₉H₃_nO₃P₃Sn: C, 50.1; H, 4.1; Cl, 13.8; O, 14.7; Sn, 11.6%). Complex (1) was also obtained by the following modification of the method in ref. 2.

The 'red solution' (made from 0.50 g of 'RuCl₃(3H₂O)') (15 cm³) was treated with anhydrous SnCl₄ (1.50 g) in ethanol (5 cm³) followed by PPh₃ (1.00 g) in acetone (20 cm³).

To the resulting yellow-brown solution was added acetone (20 cm³) and the solution was allowed to stand overnight to deposit lemon-yellow crystals which were washed with acetone and diethyl ether, and dried in air (ν(CO) (Nujol) at 1857 cm⁻¹, 1701 and 1661 cm⁻¹ (acetone); ν(SnCl) at 300 cm⁻¹; ³¹P n.m.r. in CDCl₃ at 303 K, 35.4 p.p.m. (1/) [Re(P₃Sn) 270 Hz] and 40.7 (q) p.p.m. (JAB 25.5, δAB 183.1 Hz) assigned to [(Ph₃P)(OC)ClSn]RuCl₃Ru(OC)(PPh₃)].

When (1) was heated in benzene, or the 'red solution', SnCl₄, and PPh₃ in acetone under reflux, a pale yellow solid was deposited (see ref. 2).

Crystal Data for (1).—C₉H₃_nO₃P₃Sn, M = 1300, yellow monoclinic prisms, a = 11.950(3), b = 14.988(3), c = 24.916(2) Å, β = 95.51(1)°, U = 4458 Å³, Dm = 1.528, Z = 4, D₀ = 1.534 g cm⁻³, space group P2₁/c (no. 14), Mo-Kα radiation, λ = 0.71073 Å, μ(Mo-Kα) = 11.8 cm⁻¹.

**Structure Determination**—All the data were collected using a Nonius CAD-4 goniometer. Cell dimensions were obtained by refinement of 22 reflections with 0 ≤ a ≤ 15° (Mo-Kα). Two asymmetric units of data were collected with 2 ≤ θ ≤ 22°, using a crystal with a mean radius of 0.1 mm. No absorption corrections were applied. Symmetry-equivalent data were merged to give 5 671 independent data of which 3 601 with I > 3σ(I) were used to solve the structure. The Ru and Sn atoms were found by a Patterson synthesis, the P and Cl atoms in a difference-Fourier phased by these, and all the non-hydrogen atoms in the complex in a further cycle. The structure was partly refined before the unexpected second acetonate molecule was found. Refinement was carried out using large block least squares. In the last few cycles the Sn, Ru, Cl, and P atoms were given anisotropic thermal parameters, and fixed hydrogen atoms were entered in calculated positions (C–H bonds 1.0 Å, methyl hydrogens staggered with respect to the C–O bond in acetone, temperature factors equal to those of the atoms to which they are attached). Unit least-squares weights were used except for [Fₐ] > 120, where w = 120/[Fₐ].

In the last cycle no shift was greater than 0.3σ and wΔF was uniformly spread over ranges of sinθ and [Fₐ]. At convergence, R = 0.037. Positional parameters are given in Table 1, and structure factors and thermal parameters are in Supplementary Publication No. SUP 22154 (22 pp.).

The 'X-ray' 72 computer programs of Stewart et al.³ implemented at the University of Nijmegen Computer Centre were used for all the crystallographic calculations.

We thank Johnson, Matthey Ltd. for loans of ruthenium(III) trichloride, the S.R.C. for the award of a research studentship (to W. J. S.), Dr. A. S. F. Boyd for obtaining the ³¹P n.m.r. spectra, the University of Glasgow Chemistry Department for the use of their Mechrolab osmometer, and Dr. J. H. Noordik and Mr. J. Smits for help with the X-ray data collection.

[7/1160 Received, 4th July, 1977]

* X-Ray' program system, Technical Report TR 192, Computer Science Center, University of Maryland, version of June 1972.
DIAMMINE ($^6$-BENZENE)CHLORORUTHENIUM(II)HEXAFLUOROPHOSPHATE

(3/1) AMMONIUM HEXAFLUOROPHOSPHATE, [C$_6$H$_6$RuCl(NH$_3$)$_2$]$_3$(PF$_6$)$_3$^{-}

NH$_4$PF$_6$.

R.O. Gould, C.L. Jones, D.R. Robertson and T.A. Stephenson
Department of Chemistry, University of Edinburgh, Edinburgh,
EH9 3JJ, Scotland.

Preliminary information. Whilst synthesising the complex
[(η$^6$-C$_6$H$_6$)RuCl$_3$Ru(η$^6$-C$_6$H$_6$)]PF$_6$ by the method of Bennett and
Smith (1974) in order to compare it with the product isolated
by the reaction of [(η$^6$-C$_6$H$_6$RuCl$_2$)$_2$] and NH$_4$PF$_6$ in methanol
(Robertson and Stephenson 1976), we obtained a second product
from the reaction mixture whose analysis showed it to contain
a high nitrogen content (7.1%). An X-ray crystal structure
analysis of this material showed it to be the title compound.

Crystal data. MoKα(λ = 0.71073Å), μ(MoKα) 16.0 cm$^{-1}$,
hexagonal, a = 15.91(1), c = 9.09(1)Å, V = 1993 Å$^3$, D$_m$ = 2.27,
D$_c$ = 2.24 g cm$^{-3}$ Z = 2, F(000) = 1312, space group P6$_3$/m.

Intensity data, structure determination and refinement.
Intensity data were collected on precession photographs using
zirconium-filtered molybdenum radiation. From layers hkl 0-3
Table 1

Final positional and thermal parameters and their standard deviations (in parentheses).

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<th>site occupancy</th>
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*Anisotropic thermal parameters:

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Table 2

Bond distances(Å) and bond angles(°) with standard deviations

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Atoms marked with primes are related to those in the list by the symmetry operation 2, 1, 1. All distances and angles within the benzene are within three standard deviations of 1.39 Å and 120°.

Anions

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All angles within the anions are within three standard deviations of 90 or 180°.

and 0 > 2 k, 829 independent reflections were measured using a Saab Mark II Film Scanner to a limit θ = 25°. Of these, 738 data had I > 3o(I) and were taken as observed. No absorption corrections were made. The conditions for reflection (00k, k = 2n) do not distinguish between the space groups P6_3 and P6_3/m, but the centric group was strongly indicated by the intensity distribution.

The position of the ruthenium atom was determined from the Patterson function, and the other non-hydrogen atoms except P(2), N(2), F(5) and F(6) were found in a difference Fourier synthesis.

The remaining atoms were clearly indicated in a subsequent
difference Fourier synthesis, but implied that the NH$_4^+$ and PF$_6^-$ ions were disordered on sites of 3 (S$_6$) and 6 (C$_{3h}$) symmetry respectively. An unsuccessful attempt was made to refine the structure in the non-centric space group P6$_3$, and refinement was then completed in P6$_3$/m giving site-occupancy parameters of 0.5 for the atoms F(5) and F(6). In the last cycles of refinement, a weighting scheme $w = x \cdot y$ was introduced, with $x = \sin\theta/0.25$ for $\sin\theta < 0.25$ and otherwise 1.0, and $y = 65/|F_o|$ for $|F_o| > 65$ and 1.0 otherwise. Anisotropic thermal parameters were refined for the atoms Ru, Cl, and P(1). Hydrogen atoms were not included. In the last cycle of refinement, no shift exceeded 0.25 of an estimated standard deviation. The final R-value was 0.084. The atomic positional parameters, principal bond lengths and angles are given in Tables 1 and 2 respectively.

**Figure 1.** Projection of the cation along $b^*$

![Diagram of the cation](image)

**Comments.** The cation shown in Figure 1 is undistorted. Ignoring the distinction in the bond lengths from ruthenium to chlorine and nitrogen, the ion has C$_{3v}$ symmetry. Angles at ruthenium between nitrogen and chlorine atoms are all $84^\circ$,
Figure 2. Projection of a unit cell of the title compound along c. The PF$_6^-$ ion at $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$ is shown in one of the two observed orientations. Otherwise, only atoms on or above the mirror planes at $x, y, \frac{1}{4}$ and $x, y, \frac{3}{4}$ are shown.
while each of these atoms makes angles with the carbon atoms of the ring of $93^\circ$, $119^\circ$ and $157^\circ$. The packing of the ions is shown in Figure 2. Probable hydrogen bonds occur between atoms of type N(1) and the Cl of another cation ($3.43\text{	extmu}A$) and between atoms of type N(1) and F(1)(3.14\text{	extmu}A). The disorder of the ammonium ions is hardly surprising, as each N(2) is simultaneously $3.01\text{	extmu}A$ from six atoms of type F(2) and $3.06\text{	extmu}A$ from six atoms of type F(4). In either orientation of the second $\text{PF}_6^-$ ion, each F(5) is $3.14\text{	extmu}A$ from an atom of type N(1).

Acknowledgement Standard crystallographic calculations made use of the computer programs XRAY (1974) and ORTEP (Johnson 1965) at the Edinburgh Regional Computing Centre and the Computing Centre of the Catholic University, Nijmegen. Support by the SRC is acknowledged for (CLJ.DRR) and we thank Johnson Matthey Ltd., for loans of ruthenium trichloride.

References

'X-Ray' program system, Technical Report TR192, Computer Science Center, University of Maryland, version of January 1974, implemented for the I.C.L. 4175 computer at the Edinburgh Regional Computing Centre.

Received: 18 August 1977
Synthesis and Crystal and Molecular Structure of Benzyltriphenylphosphonium Bicyclo[2.2.1]hepta-2,5-diene-carbonyltrichlororuthenate(II) and Benzyltriphenylphosphonium Carbonylpentachlororuthenate(III)—Dichloromethane (1/2)

ROBERT O. GOULD,* LENA RUIZ-RAMIREZ, T. ANTHONY STEPHENSON,* and MARY A. THOMSON

Chemistry Department, University of Edinburgh, Edinburgh EH9 3JU and Crystallography Laboratory, The Catholic University, Nijmegen, The Netherlands

The reaction of \([\text{Ru}(	ext{CO})_2\text{Cl}_2(\text{C}_2\text{H}_4)]_2\) with an excess of \(\text{Ph}_3\text{PCH}_2\text{Cl}\) and \(\text{HCl}\) in degassed acetone gives the orange complex \([\text{Ph}_3\text{PCH}_2\text{Cl}]_2\text{Ru}([\text{Ru}(	ext{CO})_2\text{Cl}_2(\text{C}_2\text{H}_4)])_2\) \((1)^1\) and a red solution from which \([\text{Ph}_3\text{PCH}_2\text{Cl}]_2\text{Ru}([\text{Ru}(	ext{CO})_2\text{Cl}_2])_2.2\text{CH}_2\text{Cl}_2\) \((2)\) may be isolated by work-up with dichloromethane. Strong e.s.r. signals indicate that \((2)\) is a ruthenium(II) compound. After removal of \((2)\), further precipitation gave a mixture of products containing \([\text{Ru}(	ext{CO})_2\text{Cl}_2]_2\), \([\text{Ru}((\text{H}_2\text{O})(\text{CO})\text{Cl}_2])_2\) \(^{2-}\), and cis-\([\text{Ru}([\text{CO}])_2\text{Cl}_4]_2\) \(^{2-}\), indicated by i.r. evidence (cf. the work of Colton and Farthing).\(^8\)

Table 1 Crystal Data

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<tr>
<th>Compound</th>
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<th>(2)</th>
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<tbody>
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<td>Empirical formula</td>
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<td>(Pbn)</td>
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<tr>
<td>(a) /Å</td>
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<td>13.913(10)</td>
</tr>
<tr>
<td>(b) /Å</td>
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</tr>
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<td>(c) /Å</td>
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<tr>
<td>(\beta) (^o)</td>
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<td>1010</td>
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Crystal data for \((1)\) and \((2)\) are summarised in Table 1. Data were collected on a Nonius CAD4 diffractometer using monochromatised Mo K\(\alpha\) radiation. The structures were solved by the heavy atom method, and refined to \(R = 0.045\) for \((1)\) and 0.083 for \((2)\). Hydrogen atoms were included in calculated positions and not refined; all other atoms were found and refined isotropically, except the Ru, P, and Cl atoms, which were given anisotropic temperature factors. The geometries of the cations of the two structures are almost identical. Distances and angles for the anions are given in Table 3, and the anions are shown in Figure 1.

The anion of \((1)\) is essentially octahedral, with facial Cl ligands, as suggested by its \(^1\)H \((\text{ref. } 1)\) and \(^{13}\)C \((\text{ref. } 2)\) spectra. The anion of \((2)\) is disordered on a site of \(2\) \((C_2)\) symmetry such that the carbonyl group appears to be superimposed on Cl(3). This disorder is, however, not so extensive as that reported for \([\text{Ru}([\text{CO}])_2\text{Cl}_4]\).\(^8\)

Table 3 Distances and angles in the complex anions; \(X(1)\) and \(X(2)\) represent the mid points of the \(C(2)-C(3)\) and \(C(5)-C(6)\) bonds, respectively; primed atoms are related to unprimed by the symmetry operation \(-x, y, z/2\)

<table>
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<tr>
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<td>92(2)</td>
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Technique used: X-Ray diffraction

References: 11

Tables: 8

Figure 2: Perspective view of the cation of \((1)\), showing the numbering scheme

References cited in this synopsis:


*To receive any correspondence (Edinburgh address).
Synthesis, Crystal and Molecular Structure of Benzyltriphenylphosphonium Bicyclo[2.2.1.]hepta-2,5-diene-carbonyltrichlororuthenate(II) and Benzyltriphenylphosphonium carbonylpentachlororuthenate(III) - dichloromethane (1/2).


Chemistry Department, University of Edinburgh, Edinburgh EH9 3JJ and Crystallography Laboratory, The Catholic University, Nijmegen, The Netherlands.

Reaction of \(\left[\text{RuCl}_2\text{CO(C}_7\text{H}_8\right]_2\)} with \(\text{Ph}_3\text{(PhCH}_2\text{)PCl/HCl}\) in acetone gave \(\text{Ph}_3\text{(PhCH}_2\text{)P}\left[\text{RuCl}_3\text{CO(C}_7\text{H}_8\right]\)} \(\sim\) shown to have an octahedral anion with a facial arrangement of chloride ligands. Crystals are monoclinic, space group \(\text{P2}_1/\text{c}\) with \(a = 12.471(5), b = 18.176(2), c = 14.181(4)\text{Å}, \beta = 109.84(4)^\circ\), and contain one formula per asymmetric unit. Work up of the filtrate gave a small amount of the paramagnetic red solid \(\text{Ph}_3\text{(PhCH}_2\text{)P}_2\text{[Ru(CO)Cl}_3\text{]}\). \(\text{ZCH}_2\text{Cl}_2\) \(\sim\) Crystals are orthorhombic, space group \(\text{Pbcn}\) with \(a = 13.913(10), b = 18.401(9), c = 20.965(9)\text{Å}\), and contain one-half formula per asymmetric unit. The structures were solved with 2859 and 1010 diffractometer data respectively, and refined to \(R = 0.045\) and 0.083. The octahedral anion in \(\sim\) is disordered about a 2-fold axis.

Several years ago,\(^1\) it was reported that reaction of \(\left[\text{RuCl}_2\text{CO(C}_7\text{H}_8\right]_2\)} with an excess of \(\text{Ph}_3\text{PhCH}_2\text{PCl/HCl}\) on degassed

acetone for several days gave the orange complex \( \text{Ph}_3\text{PhCH}_2\text{P}^- \) \[ \text{RuCl}_3\text{CO(C}_7\text{H}_8\text{)} \] \(-\). This represented the first example of an anionic diene complex of ruthenium. A detailed study of the \( ^1\text{H} \) and \( ^{13}\text{C} \) nmr spectra indicated that the stereochemistry of this anion had a facial arrangement of chloride groups, at least in solution.

After removal of compound \( \sim \) from the reaction mixture, a red solution was left. Work up of this red solution using dichloromethane in the final stages (see experimental section) gave a small amount of a red crystalline solid \( \sim \). As for compound \( \sim \), the ir spectra of \( \sim \) showed a single carbonyl band at 1994 cm\(^{-1}\) and the many bands associated with the \( \text{Ph}_3\text{PhCH}_2\text{P}^+ \) cation but no bands characteristic of norbornadiene. There was also a band at 1270 cm\(^{-1}\) indicative of the presence of some dichloromethane of solvation. The compound gave a conducting solution in dichloromethane and exhibited strong esr signals suggesting an anionic ruthenium(III) complex. The X-ray structural analyses reported below confirm the structure of \( \sim \) and show \( \sim \) to be \( \text{Ph}_3\text{PhCH}_2\text{P}^- \) \[ \text{Ru(CO)Cl}_5 \] \( \cdot \) \( \text{2CH}_2\text{Cl}_2 \).

**CRYSTAL DATA**

These are summarised in Table 1 for \( \sim \) and \( \sim \). Unit cell parameters and intensity data for both compounds were obtained with a Nonius CAD4 diffractometer using monochromatised Mo-\( K\alpha \) radiation. Cell parameters were refined using 25 reflections with


TABLE 1  CRYSTAL DATA

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mathcal{C}<em>{53}^{13} \text{H}</em>{30}^{13} \text{Cl}<em>{3} \text{OP}</em>{2} \text{Ru} )</th>
<th>( \mathcal{C}<em>{53}^{13} \text{H}</em>{48}^{13} \text{Cl}<em>{9} \text{OP}</em>{2} \text{Ru} )</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula space group</td>
<td>( \mathcal{C}<em>{53}^{13} \text{H}</em>{30}^{13} \text{Cl}<em>{3} \text{OP}</em>{2} \text{Ru} )</td>
<td>( \mathcal{C}<em>{53}^{13} \text{H}</em>{48}^{13} \text{Cl}<em>{9} \text{OP}</em>{2} \text{Ru} )</td>
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<tr>
<td>( a / \AA )</td>
<td>12.471(5)</td>
<td>13.913(10)</td>
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<td>( b / \AA )</td>
<td>18.176(2)</td>
<td>18.401(9)</td>
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<td>( c / \AA )</td>
<td>14.181(4)</td>
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<td>( \beta /^\circ )</td>
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</table>

\( \theta \) about 15°. For 2, crystals were badly formed, and the number of observations represents only 40% of reflections actually measured \( \theta \leq 20° \), while for 1, 75% of the measured intensities \( \theta \leq 22° \) were significant at the 3σ level. No. absorption corrections were applied.

STRUCTURE SOLUTION AND REFINEMENT

The structure of 1 was solved readily by Patterson and Fourier techniques. For 2, the position of the ruthenium atom was readily determined on a special position of symmetry 2 (\( C_{2} \)).
contributing only to reflections with \( h + k = 2n \). The imposed pseudosymmetry could be broken by assigning as chlorine atoms only two symmetry related pairs of peaks on a difference Fourier corresponding to a fragment of an octahedron. In subsequent difference Fourier syntheses, all non-hydrogen atoms were located, including an unexpected molecule of dichloromethane solvent. In the anion, one chloride atom and the carbonyl group are disordered over a pair of sites related by a two-fold rotation.

In both structures, hydrogen atoms were inserted in calculated positions (C-H = 1.10 \( \text{Å} \), geometry idealised to tetrahedral or trigonal as appropriate) and were not refined. In the final cycles of refinement, by full matrix least squares, anisotropic temperature factors were assigned to P, Cl, and Ru atoms. The weighting scheme for \( \hbar \) was \( \tilde{w} = 56/F_0^2 \) for \( F_0^2 > 56 \) and 1.0 otherwise. For \( \tilde{\hbar} \), a scheme of the form \( \tilde{w} = 1/(\sigma_F^2 + 0.001|F_0|) \) was used, where \( \sigma_F \) is based on counting statistics. At convergence, \( R \) was 0.045 for \( \hbar \) and 0.083 for \( \tilde{\hbar} \).

Fractional co-ordinates for \( \hbar \) and \( \tilde{\hbar} \) are listed in Table 2. Thermal parameters, co-ordinates of calculated hydrogen positions and the tables of structure factors are given as Tables 5-8 at the end of this paper. The numbering scheme is given in Figures 1 and 2. The major distances and angles are given in Table 3, and other, chemically averaged distances and angles are in Table 4. In so far as possible, the arrangement of the tables and the numbering scheme indicate chemically similar features in the two structures.
Figure 1. Perspective views of the anions of 1 and 2, showing the numbering scheme.

Figure 2. Perspective view of the cation of 1, showing the numbering scheme.
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<th>$10^4 y$</th>
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<th>$10^4 y$</th>
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Solvent

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| C1(5)      | 3583(8)   | 2985(5)   | 2603(5)   |

*These atoms have a site occupancy of 0.5.*

3306
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### TABLE 4

Summary of subsidiary distances and angles. Mean \( \sigma \) values are based on the e.s.d.'s from least squares, \( \sigma \) (mean) values are from the spread of the \( n \) chemically equivalent values. Distances are given in \( \AA \) and angles in degrees.

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DISCUSSION

As expected, the anion in 1 is essentially octahedral, with the chloride ligands facial. The geometry of the norbornadiene ligand is similar to that in trans-[Ru(C$_7$H$_8$)(C$_5$H$_3$NH$_2$)$_2$Cl$_2$]$_3$ where Ru-X is 2.069 Å, X-Ru-X is 70.0°, and the angle corresponding to Cl(3)-Ru-C(1) is 156.5°. An example with chloride ions trans to double bonds is given by cis-[Ru(C$_8$H$_{12}$)(CO)(MeCN)Cl$_2$]$_4$ with the cyclooctadiene ligand allowing a much larger X-Ru-X angle (84.4°), a Cl-Ru-X angle at 175.6°, and a mean Ru-Cl of 2.395 Å.

The carbonylpentachlororuthenate(III) anion has been synthesised previously by several investigators. Thus, Halpern et al.$^5$ showed that aqueous solutions of (NH$_4$)$_3$[RuCl$_6$] containing 1-7 mol dm$^{-3}$ HCl absorb carbon monoxide at 65-80°C to give deep red solutions from which the air stable solid (NH$_4$)$_2$[Ru(CO)Cl$_5$] (ν$_{CO}$ 2059 cm$^{-1}$) was isolated. It was suggested that it was formed by reaction of the intermediate [Ru(H$_2$O)Cl$_5$]$_2^-$ anion with carbon monoxide. Later Colton and Farthing$^6$ and Cleare and Griffith$^7$ showed that the [Ru(CO)Cl$_5$]$_2^-$ anion was formed as the first product in the reaction between ruthenium trichloride and formic acid/hydrochloric acid mixtures but extended reaction led to the formation of green [Ru(H$_2$O)(CO)Cl$_4$]$_2^-$, then orange [Ru(CO)$_2$Cl$_4$]$_2^-$ and finally pale yellow [Ru(CO)$_3$Cl$_3$]$_2^-$ anions.

Likewise, in this work, although the first precipitate \( \text{CO} \) (after removal of compound 1) had a single \( \text{CO} \) band in its IR spectrum at 1994 cm\(^{-1}\) (cf. \( \text{Cs}_2\text{Ru(CO)Cl}_5 \) \( \text{CO} \) 2038 cm\(^{-1}\) \( \text{CO} \) further precipitation gave a product with several bands in the \( \text{CO} \) region at 2046, 1994, and 1950-1930s (broad). By comparison with the values cited in reference 6, this would indicate that this is a mixture containing the \( [\text{RuCOCl}_5]^{-} \), \( [\text{RuH}_2\text{(CO)Cl}_4]^{-} \), and \( \text{cis-[Ru(CO)Cl}_3]^{-} \) anions.

The crystal structure of a compound containing the \( [\text{Ru(CO)Cl}_3]^{-} \) anion does not seem to have been previously reported. A preliminary study of \( \text{Cs}_2\text{Ru(CO)Cl}_5 \) showed that the anion was required to have \( m\overline{3}m \) (O) symmetry, indicating complete disorder of the \( \text{CO} \) group over six sites. In \( \text{Cs}_2\text{Ru(CO)Cl}_5 \), the crystallographic \( 2m \text{ (C}_2 \text{)} \) symmetry causes the carbonyl group to be randomly disordered over two sites, and the parameters determined are thus of low accuracy, especially since the \( C, Cl, \) and \( O \) half atoms appear with apparent \( C-Cl \) of 0.67\( \text{Å} \), and \( Cl-O \) of 0.56\( \text{Å} \), considerably less than the resolution of the data. The Ru-Cl(1) (trans to Cl) bond length is similar to that (2.333\( \text{Å} \)) in \( \text{Cs}_2\text{RuCl}_3\text{H}_2\text{O} \), where the crystallographic two-fold axis lies along the unique bonds of the ion and there is no disorder.

It is interesting that this Ru(III) anion is apparently formed by reaction of the Ru(II) diene anion 1 with \( \text{conc HCl} \) in the presence of excess chloride ion. This is evident from the fact that reaction of \( [\text{RuCl}_2\text{CO(diene)}]_2 \) (diene = \( \text{C}_7\text{H}_8 \), \( \text{C}_8\text{H}_{12} \)) with excess \( \text{Ph}_3\text{PHCH}_2\text{PCl/HCl} \) in acetone under reflux gave much higher

yields of \( \text{[Ph}_3\text{PCH}_2\text{P}_2] \text{[Ru(CO)Cl}_5] \) and no anionic diene complexes were isolated. A related example of the synthesis of a Ru(III) anion by reaction of a Ru(II) compound with \( \text{MX}_1/\text{HCl} \) is the formation of \( \text{Ph}_4\text{As}[\text{RuCl}_4\text{(PPh}_3)_2\text{(Me}_2\text{CO)}_2] \) by reaction of \( \text{[RuCl}_2\text{(PPh}_3)_2\text{]} \) with excess \( \text{Ph}_4\text{AsCl} \)/HCl in acetone. Although the detailed mechanism of this oxidation process is unknown, it is possible that Ru(IV) hydride intermediates may be involved.

Finally, Berch and Davison have shown that the red solution (made by passing CO through an ethanolic solution of \( \text{RuCl}_3\text{H}_2\text{O} \), for several hours) contains some of the chlorocarboxyl anions of ruthenium(II) and (III) discussed in refs. 6 and 7. Furthermore, they present evidence that the \( \{\text{[RuCl}_2\text{CO(diene)}]_2\} \) compounds are only formed from reaction of diene with the ruthenium(III) chlorocarboxyl anion \( \text{[Ru(CO)Cl}_5]^{2-} \). Hence, it seems that the unusual reaction scheme shown below involving conversion of Ru(III) to Ru(II) by reaction with diene and then Ru(II) to Ru(III) by reaction with \( \text{MX}_1/\text{HCl} \) is applicable.

\[
\text{Ru(CO)Cl}_5^{2-} \xrightarrow{\text{HCl/Cl}^-} \text{C}_7\text{H}_8 \xrightarrow{\text{EtOH}} \{\text{[RuCl}_2\text{CO(C}_7\text{H}_8)]_2\} \]  

\[
\text{II} \xrightarrow{\text{HCl/Cl}^-} \text{[RuCl}_3\text{CO(C}_7\text{H}_8\text{)}]}
\]

As noted previously, however, the product obtained is very sensitive to the cation used since reaction of \( \text{[RuCl}_2\text{CO(C}_7\text{H}_8\text{)}]_2 \) and \( \text{Ph}_4\text{AsCl/HCl} \) in acetone under reflux gave \( \text{[Ph}_4\text{As}_2\text{RuCl}_2\text{CO}]_2 \). Presumably, \( \text{[Ru(CO)Cl}_5]^{2-} \) is initially formed and then, as in refs. 6 and 7 undergoes reduction with the additional CO group being abstracted from the solvent.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany and the University of Edinburgh Chemistry Department. IR spectra were recorded in the region 4000-250 cm\(^{-1}\) on a Perkin Elmer 257 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Conductivity measurements were made on a Portland electronics conductivity bridge (model 310) and mps were determined with a Kofler hot-stage microscope and are uncorrected.

Benzyltriphenylphosphoniumcarbonylpentaachlororuthenate(III)-dichloromethane(1/2).

A suspension of the complex \(\text{[RuCl}_2\text{Co(C}_7\text{H}_8\text{)]}_2\) (1.0g) was shaken in degassed acetone (100 cm\(^3\)) under nitrogen for 5 days with an excess of benzyltriphenylphosphonium chloride (2.8g) and concentrated hydrochloric acid (1.0 cm\(^3\)). The resulting orange \(\text{Ph}_3\text{PhCH}_2\text{P[RuCl}_3\text{Co(C}_7\text{H}_8\text{)]}\) was filtered off and purified as described elsewhere.\(^1\) Concentration of the remaining dark red solution under vacuo gave more of the anion \(\text{1}^+\). After filtering off this product, the solution was further concentrated and then a mixture of dichloromethane - light petroleum (bp 110 - 120°C) was added to precipitate the red crystalline solid (2) mp > 230°C (but at 120-125°C, loss of solvent occurs) \[\text{Found: C, 53.6; H, 4.1; Cl, 18.7; P, 6.7. Calc. for C}_{53}\text{H}_{48}\text{Cl}_{10}\text{P_Ru: C, 53.8; H, 4.1; Cl, 27.0; P, 5.2%}\]. However Calc. for \((\text{Ph}_3\text{PhCH}_2\text{P})_2\text{[RuCl}_5\text{Co]}\), Cl, 17.5; P, 6-17.

\(\nu_{\text{CO}}\) 1994 cm\(^{-1}\); \(\nu_{\text{RuCl}}\) 320 cm\(^{-1}\) (nujol) \(\Gamma(0.001 \text{ mol dm}^{-3})\) in \(\text{CH}_2\text{Cl}_2 = 26.0 \text{S cm}^2\text{ mol}^{-1}\).

On leaving the solution to stand, more reddish-brown solid was precipitated. The IR spectrum (nujol mull) showed several carbonyl bands at 2016\(^w\), 1994 and 1950 - 1930 cm\(^{-1}\) attributed to and the Ru(II) anions mentioned in the text.
Compound 2 was also prepared by refluxing [RuCl₂CO(diene)]₂ (0.10g) (diene = C₇H₈, C₈H₁₂) in degassed acetone under nitrogen with Ph₃PPhCH₂PCl (0.28g) and conc HCl (0.30 cm³) for ca 4h. Concentration of the solution and addition of CH₂Cl₂ - light petroleum (bp 110-120°C) gave a red precipitate. [Found: C, 53.1, H, 4.1%] ν̄ CO 1994 cm⁻¹ (nujol).

We thank Johnson Matthey Ltd., for loans of ruthenium trichloride and the S.R.C. (MAT) and the National A. University of Mexico (LRR) for research studentships. Standard crystallographic calculations were performed using the programs of X-ray 72.
Table 5. Structure factors for (1). Columns are $l, 10/F_0, 10 F_c$. 
Table 6. Structure factors for (2).
Columns are $1, 10/F_0, 10/F_C$. 
Table 7. Fractional co-ordinates of hydrogen atoms in (1) and (2). The atom given is that to which the hydrogens are joined.

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3342
Table 8. Temperature factors for (1) and (2).
All values are $10^3\overline{u}$ in $\AA^2$.

A. Anisotropic temperature factors.

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B. Isotropic temperature factors.

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Preliminary communication

ELECTROCHEMICAL STUDIES ON TRIPLE-BRIDGED DI-RUTHERENIUM(II) COMPOUNDS

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D.R. ROBERTSON, W.J. SIME and T.A. STEPHENSON*
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)
(Received February 20th, 1978)

Summary

Voltammetric studies on [(PR₃)₂ClRu³⁺Cl₃Ru³⁺Y(PR₃)₂] (PR₃ = PPh₃ or Ptol₃, Y = CO or CS) show a reversible one-electron oxidation to form [(PR₃)₂ClRu³⁺Cl₃Ru³⁺Y(PR₃)₂]⁺ whereas the corresponding oxidation of di-ruthenium(II) mono-cations [(PR₃)₃RuCl₂Ru(PR₃)₃]⁺ (PR₃ = P(OMe)Ph₂ or PMe₂Ph), [(C₆H₅)RuCl₂Ru(C₆H₅)]⁺ and [(C₆H₅R₃)Ru(OH)$_3$Ru(C₆H₅R₃)]⁺ (R = H or Me) is more difficult and also irreversible. For the (RuCl₂Ru)²⁺ moiety, the redox series z = 1, 2, 3 is established.

Chatt and Hayter characterised the first triple chloro bridged ruthenium(II) dimers, [Ru₂Cl₃(PR₃)₂]Cl, in 1961 [1], and there have been scattered subsequent examples [2]. In recent years a variety of triple bridged di-ruthenium(II) complexes have been synthesised including the thiocarbonyl complexes and their carbonyl analogues, I and II [3,4] and the μ-trichloro and μ-trihydroxy di-arenes, III and IV [5,6].
Interestingly, \([\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_4]\) is readily oxidised by HCl to the mixed oxidation state complex \([\text{Ru}_2\text{Cl}_5(\text{CS})(\text{PPh}_3)_3]\) [3], which has one confirmed analogue \([\text{Ru}_2\text{Cl}_5(\text{P-n-Bu}_3)_3]\) [7] and we have now isolated a di-ruthenium(III) complex \([\text{Ru}_2\text{Cl}_6(\text{AsPh}_3)_3]\) [8]. Thus in such phosphine and arsine systems the common -RuCl₃Ru- bridging unit displays a sequence of oxidation levels, which suggests that in an individual complex the various levels might be accessible by one-electron transfer at an electrode.

\[
(\text{RuCl}_3\text{Ru})^+ = (\text{RuCl}_3\text{Ru})^{2+} = (\text{RuCl}_3\text{Ru})^{3+} \tag{1}
\]

Cyclic voltammetry (CV) and linear alternating current voltammetry (acV) of I and II in CH₂Cl₂/0.5 M n-Bu₄NClO₄ now establish that these complexes readily undergo oxidation at a stationary platinum electrode. For example \([\text{Ru}_2\text{Cl}_4(\text{CO})(\text{PPh}_3)_4]\) exhibits a well-defined wave at +0.56 V vs. Ag/AgI (Fig. 1), satisfying all the criteria of a one-electron fully-reversible diffusion-controlled step. No further oxidation is observed before the solvent limit (approximately +1.5 V) and the complex resists reduction until an irreversible multi-electron process at -1.65 V. Qualitatively identical behaviour is found for the other carbonyl and thiocarbonyl complexes and the results are summarised in Table 1.

Initial attempts to prepare \([\text{Ru}_2\text{Cl}_4\text{Y}(\text{PR}_3)_4]^+\) salts by chemical oxidation of I and II using I₂ or cerium(IV) led to product mixtures. However, \([\text{Ru}_2\text{Cl}_4(\text{CO})(\text{PPh}_3)_4]^+\) has now been generated as a stable CH₂Cl₂ solution by controlled potential electrolysis (+1.0 V) on a platinum gauge electrode at -45°C, although the cation decomposes rapidly at room temperature. A market colour change from orange to brown accompanies the oxidation. Spectroscopic characterisation and attempts to isolate crystalline salts following electrosynthesis at low temperatures are now in progress.

![Fig. 1. Oxidation of \([\text{Ru}_2\text{Cl}_4(\text{CO})(\text{PPh}_3)_4]\) (CV = cyclic voltammogram, acV = linear alternating current voltammogram, vs. Ag/AgI in 0.5 M n-Bu₄NClO₄/CH₂Cl₂).](image-url)
TABLE 1
Cyclic Voltammetry and Linear Alternating Current Voltammetry for Carboxyl and Thio-carboxyl Di-Ruthenium(II) Complexes

<table>
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<th>Complex</th>
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<td>$[\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_2]$</td>
<td>+0.55 r</td>
<td>CH$_2$Cl$_2$, As/AgI</td>
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<td>+0.56 r</td>
<td>CH$_2$Cl$_2$, As/AgI</td>
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<td>+1.05 i</td>
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<td>+1.02 i</td>
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$r$ = reversible wave, $E_{1/2}(CV) = E_p(\text{acV}), \Delta E_{pp}(CV) \sim 60$ mV; $i$ = irreversible wave, $E_{1/2}(CV)$ measured at 85% $I_p$ (anodic scan). $^b$SCN$^-$ salt gives identical results.

In contrast to I and II, $[\text{Ru}_2\text{Cl}_3(\text{PR}_3)_2]$BPh$_4$ complexes (PR$_3$ = P(OMe)Ph$_2$ or PMe$_2$Ph [9,10]) in CH$_2$Cl$_2$ each undergo an irreversible oxidation (with no CV return wave); an additional irreversible one-electron wave of similar CV height is observed at more positive potentials. Evidently the initially formed di-cation is unstable and reacts very rapidly to form an as yet unidentified oxidizable species. No reduction is observed to at least $-2.0$ V.

The diarene systems III and IV have been examined by CV in acetonitrile/0.3 M n-Bu$_4$NCIO$_4$. In common with the previous cationic complexes they undergo a well-defined but irreversible oxidation at fairly positive potentials. Further irreversible waves are observed which again are due to unknown species arising by rapid reaction of the first-formed oxidation product.

The predicted capacity for oxidation is best demonstrated by the uncomplicated behaviour of the neutral complexes I and II, although only the first step can be observed. Interestingly the second redox couple (but not the first) has been identified previously in the case of harder supporting ligands since the mixed-valence species $[\text{Ru}_2\text{Cl}_3(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ru}_2\text{Cl}_3(\text{NH}_3)_6]^{2+}$ undergo reversible one-electron oxidation, although their reduction is ill-defined and almost inaccessible [11,12]. Taken together, these observations establish that electrode-reversible one-electron transfers do connect the three oxidation levels of the bridged di-ruthenium system, as in eq. 1.

In I and II replacement of CO by CS has a negligible effect on the oxidation potential, although replacement of Ptol$_3$ by the less electron-donating PPh$_3$ causes a consistent increase of 0.1 V. These results, and the absence of a ready second step suggest localised oxidation of the harder Cl(PR$_3$)$_2$Ru centre takes place to generate a true mixed-valence Ru$^{2+,3+}$ complex rather than an extensively delocalised Ru$^{3+,5+}$ radical. However, X-ray studies on the analogous but symmetrically ligated $[\text{Ru}_2\text{Cl}_5(\text{PBu}_3)_4]$ gave no evidence of differing ruthenium valencies [13], and further evidence is required to specify the degree of metal—metal interaction in the various systems$^*$. 

$^*$Similar considerations apply to formally mixed oxidation state complexes such as $[\text{I}(\text{NH}_3)_2\text{Ru}6(\text{pyrazine})\text{Ru}(\text{NH}_3)_2]^{1+}$ which have been extensively discussed as models for intramolecular electron-transfer theory [19].
A striking aspect of the present results is the loss of reversibility accompanying the shift to higher oxidation potentials in the case of the cationic complexes (e.g. compare [RuCl₂Cl₄(CO)(PPh₃)₄] and [Ru₂Cl₃(PMe₂Ph)₆]⁺). This may be correlated with the tendency of the preferred oxidation level to match the number of chloride ligands in the complexes as generally isolated. Thus the mono-cations [Ru₂Cl₃L₆]⁺ and [Ru₂Cl₄L₅]⁺, where L represents any soft neutral ligand, probably represent stable limits; [Ru₂Cl₃L₆]²⁺ species are only formed at more positive potentials and decompose rapidly, as evidenced by our electrochemical studies. Clearly, complexes of stoichiometry [Ru₂Cl₄L₄] provide the best chance of realizing the complete redox sequence (eq. 1) within one molecule, and a variety of these are now to be examined.

In EAN terms such a sequence ranges from 36 valence electrons (18 per Ru) to 34, permitting the formation of a metal—metal bond. Systematic spectroscopic and structural changes are known to accompany similar redox series in double- and single-bridged iron and manganese compounds [14,15], and comparison of the variously bridged clusters is of considerable interest. In the (RuCl₃Ru)⁺ complexes the Ru—Ru distance might indeed contract upon oxidation (from ca. 3.4 Å [16,17]), since [Ru₂Cl₅(P-n-Bu₃s)]⁻ has an internuclear separation of 3.12 Å [13], and in diamagnetic [Ru₂(S₃CNMe₂)₃]⁺ the relatively unconstrained ruthenium(III) —ruthenium(III) bond length is 2.79 Å [18]. However [Ru₂Cl₃(AsPh₃)₆] is paramagnetic (μeff (293 K) 1.95 per Ru). Hopefully the present investigation will provide more coherent data on this point.

Acknowledgement

We thank Johnson—Matthey Ltd for loans of ruthenium trichloride and the SRC for research studentships (DRR, WJS).

References

8. T.A. Stephenson, unpublished work.
RUTHENIUM COMPLEXES CONTAINING GROUP 5B DONOR LIGANDS VI* SYNTHESIS
AND REARRANGEMENT REACTIONS OF VARIOUS [RuCl\textsubscript{2}L\textsubscript{3or4}] COMPLEXES [L = P(OMe)\textsubscript{3}, P(OMe)\textsubscript{2}Ph, P(OR)Ph\textsubscript{2}(R = Me, Et)]

W.J. SIME and T.A. STEPHENSON*
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

Summary

Reaction of [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] with an excess of L in hexane gives either
[RuCl\textsubscript{2}L\textsubscript{4}] (L = P(OMe)\textsubscript{3}, P(OMe)\textsubscript{2}Ph) or [RuCl\textsubscript{2}L\textsubscript{3}] (L = P(OMe)Ph\textsubscript{2}, P(OEt)Ph\textsubscript{2}).

In polar solvents, [RuCl\textsubscript{2}(P(OMe)\textsubscript{2}Ph)\textsubscript{4}] and [RuCl\textsubscript{2}(P(OMe)Ph\textsubscript{2})\textsubscript{3}] rearrange to
the ionic dimers [Ru\textsubscript{2}Cl\textsubscript{3}L\textsubscript{6}]Cl whereas [RuCl\textsubscript{2}(P(OEt)Ph\textsubscript{2})\textsubscript{3}] converts to
the ionic trimer [Ru\textsubscript{3}Cl\textsubscript{5}(P(OEt)Ph\textsubscript{2})\textsubscript{9}]Cl. Reaction of [RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}] with
excess of P(OR)Ph\textsubscript{2} in alcohols first generates the red [RuCl(P(OMe)Ph\textsubscript{2})\textsubscript{4}]\textsuperscript{+}
and [Ru\textsubscript{2}Cl\textsubscript{2}(P(OEt)Ph\textsubscript{2})\textsubscript{8}]\textsuperscript{2+} cations respectively which can be isolated as
their BPh\textsubscript{4} salts, and later, the yellow [Ru\textsubscript{2}Cl\textsubscript{3}(P(OMe)Ph\textsubscript{2})\textsubscript{6}]\textsuperscript{+} and
[Ru\textsubscript{3}Cl\textsubscript{5}(P(OEt)Ph\textsubscript{2})\textsubscript{9}]\textsuperscript{+} cations are formed. These various rearrangement
processes have been extensively studied by variable temperature \textsuperscript{31}P -\textsuperscript{1}H NMR spectroscopy and an overall mechanism of rearrangement for the various
[RuCl\textsubscript{2}L\textsubscript{3and 4}] compounds in solution is proposed.

* For Part V, see ref 1.
Introduction

Recently, we have shown that the monomeric tertiary phosphine complexes \([\text{RuCl}_2(\text{PR}_3)_3 \text{ or } 4]\), made by exchange of \([\text{RuCl}_2(\text{PPh}_3)_4]\) with \text{PR}_3 in non-polar solvents [2] undergo facile rearrangement reactions in solution as shown in Scheme 1 [3]. In an attempt to verify the generality of this rearrangement pattern, we now report the full results [4] of studies on exchange reactions of \([\text{RuCl}_2(\text{PPh}_3)_3]\) (I) with tertiary phosphites, phosphonites and phosphinites.

Results and Discussion

a) Preparation of monomeric neutral complexes

On refluxing compound (I) with an excess of \text{P(OMe)}_3 in hexane, a yellow crystalline solid analysing for \([\text{RuCl}_2(\text{P(OMe)}_3)_3 \text{ or } 4]\) was deposited. The far ir spectrum (400-200 cm\(^{-1}\)), containing a strong band at 340 cm\(^{-1}\) assigned to \(\nu(\text{RuCl})\) from trans chloride groups, [5] and bands at 306 and 295 cm\(^{-1}\) assigned to \(\nu(\text{RuCl})\) vibrations from chloride groups trans to phosphorus [5] indicated a cis/trans isomer mixture in the solid state. However, the \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectra in CDCl\(_3\) at both 213 and 298K consisted of a singlet at 5129.4 ppm and the \(^1\text{H}\) nmr spectrum in CDCl\(_3\) at 301K showed a symmetrical quintet centred at 3.845 (cf similar resonance patterns for trans-[\text{Rh(P(OMe)}_3)_3 \text{ or } 4-XY])^+ cations [\(X = Y = \text{Br}^–; \ X = \text{H}^–, \ Y = \text{Br}^–; \ X = \text{Me}^–; \ Y = \text{I}^–\)][6]). Thus, these results indicate that rapid, irreversible rearrangement to the trans isomer occurs in solution.

The compound \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]\) was also prepared by this method and its far ir spectrum, containing bands at 324, 308 and 291 cm\(^{-1}\) again indicated the presence of both cis and trans isomers in the solid state. The \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum in CDCl\(_3\) at 213K contained a singlet at 5150.5 ppm (trans isomer) and two triplets at 166.6 and 149.4 ppm (\(^2J_{\text{pp}}\) 44.0 Hz)(cis isomer). On warming to 298K the triplets disappeared and did not reappear.
when the solution was recooled. Therefore, as for $[\text{RuCl}_2(\text{P}^\text{OMe}_3)_4]$,
an irreversible cis to trans isomerisation process takes place in
solution.

In contrast, reaction of $[\text{RuCl}_2(\text{PPh}_3)_3]$ with an excess of $\text{P(OR)Ph}_2$
($R = \text{Me}, \text{Et}$) in hexane produced orange-brown crystals analysing closely
for $[\text{RuCl}_2(\text{P(OR)Ph}_2)_3]$. The far ir spectra contained a strong band at
337 cm$^{-1}$ ($R = \text{Me}$), 328 cm$^{-1}$ ($R = \text{Et}$) indicating the presence of trans
chloride groups. The compounds dissolved in many common polar solvents
but rapidly rearranged (see below). However, they were soluble and stable
in benzene or toluene and osmometric molecular weight-measurements in
benzene at 294K indicated that the complexes are monomeric. The $^{31}\text{P-}^1\text{H}$
nmr spectra in $\text{C}_6\text{D}_6$ at 298K showed a sharp singlet at 149.5 ppm ($R = \text{Me}$),
144.7 ppm ($R = \text{Et}$) indicating that the tertiary phosphinite groups were
magnetically equivalent at this temperature. Possibilities to explain
this equivalence include a trigonal bipyramidal structure (IIa) or more
likely, a square pyramidal or weakly solvated octahedral structure (IIb)
in which facile scrambling of axial and equatorial $\text{P(OR)Ph}_2$ ligands renders
them equivalent on the nmr timescale, (cf the $^{31}\text{P-}^1\text{H}$ nmr spectra of
$[\text{RuCl}_2(\text{PR}_3)_3]$ ($\text{PR}_3 = \text{PPh}_3$, $[2,7] \text{P(p-tolyl)}_3$ $[9]$) at ambient temperatures).

In support of the latter conclusion, the $^{31}\text{P-}^1\text{H}$ nmr spectrum of
$[\text{RuCl}_2(\text{P})\text{OEt}(\text{Ph})_2)_3]$ in $(\text{CD}_3)_2\text{CO/toluene}$ at 140K consisted of two broad
resonances at 167.3 and 141.1 ppm of relative intensity 1:2 and these
nmr changes were concentration independent and reversible with temperature.
Thus, although no spin-spin couplings were resolved (probably because of
viscosity effects at this temperature), these resonances can be ascribed
respectively to the expected triplet and doublet pattern for the "frozen-out"
$[\text{RuCl}_2(\text{P(OEt)Ph}_2)_3]$ structure (IIb). The observed averaged position
(146.5 ppm at 193K in $(\text{CD}_3)_2\text{CO/toluene}$) and that calculated on the basis

*X-ray structural data shows that most five coordinate $d^6$ complexes have
an essentially square pyramidal structure $[7]$ and this is supported by
recent theoretical arguments.$[8]$
of the low temperature spectrum at 140K (149.8 ppm) provides further support for the correctness of the above interpretation of this nmr data.

This scrambling process producing equivalence of all the phosphinite groups of $[\text{RuCl}_2(\text{P(OEt)Ph}_2)_3]^-$ is much more facile than the corresponding process for $[\text{RuCl}_2(\text{PPh}_3)_3]$ (see refs [2] and [7]). This is attributed to two factors viz the less bulky ligands and the fact that the resonances for the different phosphinite groups of $[\text{RuCl}_2(\text{P(OEt)Ph}_2)_3]$ are much closer to each other than are the PPh$_3$ groups in $[\text{RuCl}_2(\text{PPh}_3)_3]$. The ligand P(OMe)Ph$_2$ is less bulky than either P(OEt)Ph$_2$ or PPh$_3$ and consequently, the $^{31}\text{P}$--$^1\text{H}$ nmr spectrum of $[\text{RuCl}_2(\text{P(OMe)Ph}_2)_3]$ at 140K in (CD$_3$)$_2$CO/toluene only contained a broad resonance at 147.0 ppm.

b) Rearrangement of monomeric species in polar solvents

The compound $[\text{RuCl}_2(\text{P(OMe)}_3)_4]$ appeared stable in polar solvents, being recovered unchanged both after refluxing in methanol for 6 hours or irradiating with ultraviolet light. The compound $[\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]$ did not rearrange on leaving at room temperature in methanol but after refluxing this solution for one hour, a yellow conducting solution was obtained. Addition of NaBPh$_4$ then precipitated a pale yellow solid whose $^{31}\text{P}$--$^1\text{H}$ nmr spectrum in CDCl$_3$ at 298K contained a singlet at 168.7 ppm and also an AB$_2$ pattern ($v_A$ 159.6 ppm; $v_B$ 170.4 ppm; $J_{AB}$ 58.4 Hz). On refluxing for a further hour the $^{31}\text{P}$--$^1\text{H}$ nmr spectrum of the product showed only the singlet. This corresponds to $[\text{RuCl}_2\text{(P(OMe)}_2\text{Ph})_6]\text{BPh}_4$, prepared earlier [10] by reaction of $[\{\text{RuCl}_2(\text{C}_7\text{H}_8)\}_n]$ with P(OMe)$_2$Ph in methanol. The AB$_2$ pattern must arise from an intermediate ionic product containing three phosphonite groups per ruthenium. Possibilities include $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_3(\text{Solv})_2]\text{BPh}_4$ or $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_3(\text{Solv})_2](\text{BPh}_4)_2$ but it was impossible to differentiate further between these formulations because
of the inability to separate this intermediate from the ionic dimer.

A similar cationic intermediate has been observed on reaction of 
\[ \text{[RuCl}_2(\text{PETPh}_2)_3] \] with \text{PETPh}_2 in ethanol for short periods, together 
with some \[ \text{[Ru}_2\text{Cl}_3(\text{PETPh}_2)_6] \text{Cl}[3] \].

In contrast, dissolving \[ \text{[RuCl}_2(\text{P(OMe)Ph}_2)_3] \] in \text{CH}_2\text{Cl}_2 produced 
initially a bright yellow solution which gradually became paler in 
colour and also increased in conductivity, reaching a maximum of 29\mu\text{mho} 
(specific conductivity) for a \( 10^{-3} \text{ dm}^{-3} \text{ mol. solution after ca 4 hours,} \)
which indicated the formation of a 1:1 electrolyte. The addition of 
\text{NaBPh}_4 then precipitated \[ \text{[Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6] \text{BPh}_4 \], synthesised earlier 
by reaction of \[ \{\text{[RuCl}_2(\text{C}_7\text{H}_8)\}_n \] and \text{P(OMe)Ph}_2 in methanol [10]. This 
rearrangement reaction has also been studied by \( ^{31}\text{P}-{^1}\text{H} \) nmr spectroscopy.

Thus at 183K in \( (\text{CD}_3)_2\text{CO/CH}_2\text{Cl}_2 \), the spectrum consisted of a broad 
signal at 144 ppm ([RuCl}_2(\text{P(OMe)Ph}_2)_3]) and a sharp singlet at 139.4 ppm 
due to the rearranged product \[ \text{[Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6] \text{Cl}. \] As the temperature 
was raised, the signal at 144 ppm sharpened and decreased in intensity whilst the 
signal at 139.4 ppm increased in intensity, such that at 303K, almost 
all of the monomer had been converted to the ionic dimer. The rearrangement 
was irreversible since cooling the mixture had no effect on the intensity 
ratios observed at ambient temperature.

Unlike the \[ \text{[RuCl}_2(\text{P(OMe)Ph}_2)_4] \] rearrangement process, no intermediate 
products were observed, but an expansion of the spectrum when the sample 
was recooled to 213K showed a number of weak peaks at the base of the 
singlet at 139 ppm (Fig. 1). After the sample was allowed to stand at 
room temperature for 48 hours, the spectrum, rerun at 213K, contained 
no resonance due to the monomer but the weak peaks at the base of the singlet 
were still present. These are attributed to a small amount of another 
rearrangement product. (see below).
When \([\text{RuCl}_2(\text{P}[\text{OEt}]\text{Ph}_2)_3]\) was dissolved in \(\text{CH}_2\text{Cl}_2\), the initial bright yellow solution also became progressively paler, the conductivity of a \(10^{-3}\) \text{dm}^{-3} \text{ mol. solution increasing to a maximum of 30 mho over a period of ca 24 hours. Again, the rearrangement has been studied by \(^{31}\text{P} - \text{H}\) nmr spectroscopy and, although much slower, followed a similar pattern to that of \([\text{RuCl}_2(\text{P}[\text{OMe}]\text{Ph}_2)_3]\), namely, irreversible conversion of the monomer to an ionic species. However, there is one very important difference here in that the rearrangement product (A) was not the triple bridged ionic dimer, \([\text{Ru}_2\text{Cl}_3(\text{P}[\text{OEt}]\text{Ph}_2)_6]\)Cl, since the \(^{31}\text{P} - \text{H}\) nmr spectrum at 213K in CDCl\(_3\) was not a singlet but a complicated multiplet consisting of at least 20 lines. (Fig. 2). Leaving the sample in solution for 3 days and then rerunning the spectrum at 213K showed that all of the monomer had been converted to (A). On warming to 303K, the multiplet collapsed to a broad resonance centred at ca 135 ppm which suggested that rapid intramolecular scrambling of all the P(OEt)Ph\(_2\) groups was taking place at this temperature. Subsequent recooling to 213K gave the original sharp multiplet shown in Fig. 2 and this remained unaltered, even after leaving the solution for 12 weeks. The addition of either NaBPh\(_4\) or NH\(_4\)PF\(_6\) gave a pale yellow solid but addition of AsPh\(_4\)Cl.HCl gave no precipitate, implying that the phosphorus containing species present is only cationic in nature. This was verified by running the \(^{31}\text{P} - \text{H}\) nmr spectrum in CDCl\(_3\) at 213K of the BPh\(_4^-\) salt which consisted of an identical multiplet to that shown in Fig. 2. Therefore (A) cannot be for example \([\text{Ru}_2\text{Cl}_3(\text{P}[\text{OEt}]\text{Ph}_2)_6][\text{RuCl}_3(\text{P}[\text{OEt}]\text{Ph}_2)_3]\). Furthermore, samples of (A) with counteranions BPh\(_4^-\) or PF\(_6^-\), prepared on several different occasions and run in a variety of different solvents eg (CD\(_3\))\(_2\)CO, CDCl\(_3\), (CD\(_3\))\(_2\)CO/CH\(_2\)Cl\(_2\), all displayed the same \(^{31}\text{P} - \text{H}\) nmr spectrum at 213K, suggesting that the product is a single species and not a mixture.
It is interesting to note that reaction of \([\{\text{RuCl}_2(C_7H_8)\}_n]\) with 
\(\text{P(OEt)}\text{Ph}_2\) was earlier reported to give on addition of \(\text{NaBPh}_4\), the ionic 
dimer \([\text{RuCl}_2\text{P(OEt)}\text{Ph}_2]_6\text{BPh}_4\) (based on analytical and \(^1\text{H}\) nmr data)[10].

On repeating this reaction, we found that the \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum of 
the product in \(\text{CDCl}_3\) at 213K was the same as that shown in Fig. 2. In 
contrast, the \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum of the product from the \([\{\text{RuCl}_2(C_7H_8)\}_n]/\text{P(OME)}\text{Ph}_2\) reaction was a singlet at all temperatures, indicating the 
formation of the \([\text{RuCl}_2\text{P(OME)}\text{Ph}_2]_6\) \(^{+}\) cation.

The ir spectrum (4000-400 cm\(^{-1}\)) of (A) \([\text{BPh}_4^-\) salt] was identical to 
that of \([\text{RuCl}_2\text{P(OEt)}\text{Ph}_2]_3\) except for the additional bands due to the 
anion and, therefore, this suggested that no change in the \(\text{P(OEt)}\text{Ph}_2\) 
groups has occurred during the rearrangement process. The narrow range 
of chemical shifts (ca 10 ppm) observed in the \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum of 
(A) is also consistent with the non-formation of Ru-P(O)Ph\(_2\) or Ru-P(OH)Ph\(_2\) 
linkages.\(^{+}\) Further support for this conclusion is the absence of ethanol 
or ethyl chloride in the \(^1\text{H}\) nmr spectrum or g.l.c. trace of a 3 day old 
solution of \([\text{RuCl}_2\text{P(OEt)}\text{Ph}_2]_3\) in \(\text{CDCl}_3\) and the close similarity of the 
ethyl region of the \(^{13}\text{C}-\{^1\text{H}\}\) nmr spectra of (A) in \(\text{CDCl}_3\) and \([\text{RuCl}_2\text{P(OEt)}\text{Ph}_2]_3\) in \(\text{C}_6\text{D}_6\) (see experimental section).

Since no free \(\text{P(OEt)}\text{Ph}_2\) was observed in the \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum 
on rearrangement of \([\text{RuCl}_2\text{P(OEt)}\text{Ph}_2]_3\) to (A) in various solvents, (A) 
must still contain an average of three \(\text{P(OEt)}\text{Ph}_2\) groups per Ru atom.

Conductivity measurements in both \(\text{CH}_2\text{Cl}_2\) and acetone were consistent with 
the presence of the a 1:1 electrolyte (see experimental section). Furthermore, the molecular weight of the \(\text{BPh}_4^-\) salt in \(\text{CHCl}_3\) was found to be 1350 
and thus, for a 1:1 electrolyte, the actual molecular weight would be 
2700. As a check on the validity of this conclusion the molecular weight

\(^{+}\)For \([\text{Ni}(\eta^5\text{C}_5\text{H}_5}\{(\text{P(OEt)}\text{)}_3}\{(\text{PO(OEt)}\text{)}_2\})\), the \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum shows two 
doublets centred at 6147.5 \(\text{P(OEt)}_3\) and 85.8 ppm \(\text{PO(OEt)}_2\), a separation of 
of $\left[ \text{Ru}_2\text{Cl}_3(\text{P}(\text{OMe})\text{Ph}_2)_6 \right] \text{BPh}_4$ in CHCl$_3$ was found to be 1003; required for 1:1 electrolyte 962. Support for the high molecular weight of (A) also came from the far ir spectrum of the BPh$_4^-$ salt which contained bands at 314 and ca 260 cm$^{-1}$, indicating the presence of both terminal and bridging chloride groups.

On the basis of all this data, compound (A) is best formulated as containing the trimeric ruthenium(II) cation $\left[ \text{Ru}_3\text{Cl}_5(\text{POEt})\text{Ph}_2\right]^{+}$ [calculated mol. wt. of BPh$_4^-$ salt = 2870] and analytical data for salts of the various counterions are also reasonably consistent with this formulation. Two possible structures which fit most of these experimental observations are (IIIa) and (IIIb). However, the linear structure (IIIa) can be readily eliminated on the basis that facile intramolecular scrambling of all P(POEt)Ph$_2$ groups in such a structure is impossible. The closed structure (IIIb) containing one terminal chloride group, one double chloride bridge, two single chloride bridges and three P(POEt)Ph$_2$ groups per ruthenium is much more feasible when trying to explain the fluxional nature of (A) and Scheme 2 indicates how it is possible to rationalise this facile intramolecular scrambling process in terms of a structure such as (IIIb). This, in (1a), terminal chloride (i) positioned on Ru(1) can form a bond with Ru(2) with the subsequent breaking of bond(s), to form (2a) in which the terminal chloride is now on Ru(3) or bond(z) to form (3a) in which the chlorides (i) and (iii) have interconverted. Similarly, (2a) and (4a) can rearrange intramolecularly, and so on, with the result that all the phosphinite groups become equivalent when such rearrangement processes are sufficiently rapid on the nmr time scale.

This is not the first example of a trimeric ruthenium(II) complex. For example, reaction of a carbonylated solution of "RuCl$_3\cdot$H$_2$O" in methanol with MeCS$_2$NET$_2$ gave a minute quantity of golden-brown crystals, shown by X-ray analysis to be $\left[ \text{Ru}_3(S_2\text{CNET}_2)_4(\text{CO})_3\text{Cl}_2 \right]$ (IV) [12]. Trinuclear iron
compounds of stoichiometry [Fe₃(CO)₆S₅SR]₂ have also been reported [13] and one of the proposed structures (V) for these 1:1 electrolytes is very similar to that of (IIIb).

Unfortunately, extensive recrystallisation attempts on (A) have failed to produce crystals suitable for an X-ray analysis and therefore unequivocal evidence for both the composition and detailed structure of (A) is still lacking.

On the basis of structure (IIIb), (assuming a regular octahedral geometry around each Ru ion), it might have been expected that the ³¹P- {¹H} nmr spectrum of (A) would have consisted of an AB₂ pattern arising from atoms P₂, P₁, P₃ superimposed on an ABC pattern of twice the intensity arising from atoms P₄, P₅, P₆ and P₇, P₈, P₉. Several attempts have been made to fit such a theoretical pattern of lines to the observed pattern shown in Fig. 2, using the computer simulation program LAOCOON, but unfortunately, these attempts were not successful. For several reasons, however, this failure does not necessarily invalidate the correctness of structure (IIIb). First, as stated above, the theoretical nmr pattern was formulated on the basis of a regular octahedral environment around each Ru ion, but it is quite likely that small deviations from regular geometry might occur, sufficient to destroy, for example, the postulated magnetic equivalence of the two ABC sets or the equivalence of atoms P₁ and P₃ in the supposed AB₂ set. Thus, the expected ³¹P- {¹H} nmr spectrum of (IIIb) might more realistically be a superposition of three slightly different ABC subsets ie 9 coupling constants and 9 chemical shifts would then be required to completely define this spin system. Another difficulty is the quality of the experimental spectrum. Thus, although 20 lines can be counted, the combination of narrow spectral width (ca 10 ppm), low temperature (producing some viscosity broadening), and complexity of signals, imply that it is highly likely that many over-
lapping resonances are present (NB a single ABC spin system can generate a maximum of 15 lines). Therefore, in this situation, insufficient unambiguous experimental information is available to completely solve this nmr problem.

Nevertheless, although the structure is not completely proven by nmr spectral analysis, the wide range of chemical and spectroscopic evidence does, in our view, strongly support the formulation of (A) as \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph}_2)_9]\)\(X = \text{Cl}^-, \text{BPh}_4^-, \text{PF}_6^-\) with structure (IIIb).

Finally, the weak peaks appearing at the base of the singlet (Fig. 1) correspond very closely to those in Fig. 2 and are therefore considered to arise from the presence of a small amount of \([\text{Ru}_3\text{Cl}_5(\text{P(OMe)}\text{Ph}_2)_9]\)Cl.

c) Reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\) (I) with L in polar solvents

Reaction of compound (I) with excess of L (L = P(OMe)_3, P(OMe)_2Ph) in methanol produced the previously known \([10,14][\text{RuL}_6]^{2+}\) complexes readily isolated as BPh_4^- salts. In contrast, refluxing (I) with an excess of P(OMe)Ph_2 in methanol for a short time gave a deep red solution which gradually, over a period of two hours, turned yellow in colour. Addition of NaBPh_4 to the yellow solution produced \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)}\text{Ph}_2)_6]\)BPh_4, but addition of NaBPh_4 to the initial red solution gave a red solid which analysed closely for \([\text{RuCl}(\text{P(OMe)}\text{Ph}_2)_4]^-\)BPh_4 (VI). The mullir spectrum of (VI), in which there was no evidence of a coordinated solvent molecule, contained, in addition to bands due to P(OMe)Ph_2 and BPh_4-, a band at 290 cm^{-1} attributed to \(\nu(\text{RuCl})\) of a chloride ion trans to phosphorus. This complex slowly rearranged to the ionic dimer in chlorinated solvents but was stable in acetone and therefore, \(^{31}\text{P} - {1^1}\text{H} \) nmr spectra were studied in \((\text{CD}_3)_2\text{CO}\) over a range
of temperatures. (Fig. 3). At 173K (Fig. 3a), several resonances were observed \textit{viz} a singlet at 139.1 ppm due to the presence of some 

\[ \text{Ru}_2\text{Cl}_3(\text{P(OME)Ph}_2)_6\text{BPh}_4 \] in the sample, a singlet at 110.9 ppm due to free \text{P(OME)Ph}_2, two multiplets at 157 and 140 ppm and sharp resonances resembling two triplets centred at 123 ppm. As the temperature was raised, the broad multiplets at 157 and 140 ppm coalesced to a broad hump at 148 ppm which on further warming sharpened up to a peak at 148.5 ppm (Fig. 3b and c). The resonance at 123 ppm also collapsed on warming and at 213K a broad peak at 124.0 ppm was observed (Fig. 3c). At 333K, (Fig. 3d) the peaks at 148.5 and 124.0 ppm disappeared and a broad resonance at 136 ppm appeared. No change in the singlet due to free \text{P(OME)Ph}_2 occurred up to 213K but at 333K, it had broadened considerably and shifted to higher frequency.

In the spectrum obtained at 173K (Fig. 3a), it appeared initially that the resonances at 157 and 140 ppm on the one hand and at 123 ppm on the other might arise from two different species. On examining the spectra at higher temperatures, the observed coalescence of the multiplets at 157 and 140 ppm to a resonance at 148 ppm indicates that they arise from the same species and that each peak corresponds to the same number of \text{P} atoms in that species. However, as the temperature is further raised the resonances at 148 and 123 ppm then coalesced to a resonance midway between them which implies that they also arise from the same species and correspond to the same number of \text{P} atoms. Cooling the solution restores the spectrum to that shown in Fig. 3a. Hence, it appears that the multiplets at 157, 140 and 123 ppm are produced by \text{P} atoms in intensity ratio 1;1;2 respectively and belong to a single species which is most probably 

\[ \text{RuCl}(\text{P(OME)Ph}_2)_4 \]\(^+\). Structures consistent with two magnetically equivalent and two non-equivalent \text{P} atoms are (VIa) with the sixth position of the octahedral complex in solution occupied by a solvent.
molecule or (VI b) with no coordinated solvent.

Unfortunately all attempts to reproduce the spectrum at 173K (Fig. 3a) assuming an ABC2 spin system and using computer simulation techniques have proved unsuccessful since no combination of chemical shift and coupling constant data could simulate the symmetrical pattern centred at 123 ppm.† However, a precedent exists in the literature for the occurrence of unexpected 31P-(1H) nmr spectra in a related complex at low temperature [15]. Thus, for cis-[FeH2(P(OMe)2Ph)4](VII), the 31P-(1H) nmr spectrum at 210K consisted of the expected A2B2 pattern (Fig. 4). However, as the temperature was lowered, the triplets broadened but at 187K they sharpened up again to give more complex patterns with the lower frequency resonance sharpening up more rapidly than the one at higher frequency. In fact, at 150K, the shape of the lower frequency resonance is virtually identical to that observed in Fig. 3a.

The explanation offered by Meakin et al [15] is that the bulky P(OMe)2Ph ligands interact in such a way as to reduce the symmetry of the molecule below that shown in (VII) and that the ligands motions are sufficiently restricted such that the reduction of symmetry is maintained on the nmr time scale at these low temperatures. In support of this interpretation, the solid state structure of [FeH2(P(OEt)2Ph)4] differs appreciably from the idealised C2v symmetry shown in (VII) and this distortion is attributed more to interligand interactions than crystal packing effects.

By comparison of the spectra in Fig. 4 with those in Fig. 3, it seems probable that such a situation also occurs for [RuCl(P(OMe)Ph2)4].† In the latter case, a frozen-out ABC2 spectrum was not observed at higher temperatures because of rapid intramolecular scrambling processes and at lower temperatures the equatorial phosphinite groups in (VI a) [and P1 and

†The other two multiplets at 157 and 140 ppm are much broader and it is difficult to tell whether or not they match the simulated spectra.
$P_2$ of (VI b) are in different chemical environments so that two multiplets are observed in contrast to the one for the equatorial phosphonite groups of $[\text{FeH}_2(\text{P(OMe)}_2\text{Ph})_4]$. The equivalence of the equatorial tertiary phosphinite groups of $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_2]_2^+$ at 193K can best be explained by invoking the dynamic equilibrium shown in equation (1). Loss of the solvent molecule occurs to form a 5 coordinate intermediate in which there is no facile overall rearrangement at this low temperature. Recombination of the solvent molecule trans to the other equatorial ligand then causes the two equatorial ligands to become equivalent on the nmr timescale. At higher temperatures further scrambling of axial and equatorial ligands via a pseudorotation process is proposed. Some intermolecular exchange with free P(OMe)Ph$_2$ also starts to occur at higher temperatures suggesting the equilibrium shown in equation (2) is becoming of some importance and a small additional resonance is observed at 141 ppm (Fig. 3d) which may be due to the cation $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_2]_3(\text{Solv})_2^+$. Furthermore, the addition of excess P(OMe)Ph$_2$ inhibited the formation of $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_2]_4(\text{Solv})_2^+$ but not $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_2]_3(\text{Solv})_2^+$ + P(OMe)Ph$_2$ (2) $[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}_2\text{Ph})_6]_6^+$ in CH$_2$Cl$_2$ whereas the addition of Cl$^-$ to an acetone solution of $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_2]_4$ BPh$_4$ caused a colour change from red to yellow and rerunning the spectrum at 298K showed that all the resonances except those due to $[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}_2\text{Ph})_6]_6$ BPh$_4$ and free P(OMe)Ph$_2$ had disappeared. Finally conductivity measurements on an acetone solution of $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_2]_4$ BPh$_4$ indicated the presence of a 1:1 electrolyte.
The reaction between compound (I) and excess of P(OEt)Ph₂ in ethanol, as for P(OMe)Ph₂, produced initially a red solution which slowly turned yellow in colour. Addition of NaBPh₄ to the yellow solution gave [Ru₃Cl₅(P(OEt)Ph₂)₉]BPh₄ and from the red solution a red solid analysing for [RuCl(P(OEt)Ph₂)₄]BPh₄ was obtained. However, the ³¹P⁻¹H] nmr spectra of this compound at various temperatures in (CD₃)₂CO contained several different features from those of [RuCl(P(OMe)Ph₂)₄]BPh₄. At 173K (Fig. 5a), the spectrum contained a multiplet centred at 135 ppm due to the presence of some [Ru₃Cl₅(P(OEt)Ph₂)₉]BPh₄, a singlet (not shown) at 110.1 ppm due to free P(OEt)Ph₂, and two triplets at 148.1 and 119.0 ppm (Jpp 29.2 Hz). As the temperature was raised, the triplets broadened (Fig 5b) and at 298K coalesced to a broad peak superimposed on the resonance at 135 ppm due to the trimer (Fig. 5c). The triplets, which reappeared on cooling the solution to 173K must arise from the double chloride bridged dimer [Ru₂Cl₂(P(OEt)Ph₂)₈](BPh₄)₂ (VIII) since a monomer would, as in the case of [RuCl(P(OMe)Ph₂)₄]⁺, be expected to give a more complicated spectrum. The presence of such a dimer in the solid state is suggested by a broad band at 270 cm⁻¹ in the far ir spectrum which was not observed for [RuCl(P(OMe)Ph₂)₄]BPh₄. However, the collapse and coalescence of the triplets at higher temperatures is not consistent with retention of this dimeric structure in solution, and it would suggest that the dimer is cleaved to produce the monomer [RuCl(P(OEt)Ph₂)₄]⁺ as the temperature is raised (cf the ³¹P⁻¹H] nmr spectra of compounds (VII) (Fig. 3) and (VIII) (Fig. 5) at 213K and above). Furthermore, conductivity measurements on (VIII) at 298K in acetone indicated the presence of a 1:1 electrolyte. No evidence for exchange with free P(OEt)Ph₂ was observed since the resonance at 110.1 ppm remained sharp at all temperatures and no additional resonance which could be attributed to [RuCl(P(OEt)Ph₂)₃(Solv)]⁺ appeared in the spectrum at
298K. However, addition of excess P(OEt)Ph$_2$ inhibited rearrangement to [Ru$_{3}$$\text{Cl}_{5}(\text{P(OEt)Ph}_{2})_{9}]$BPh$_4$ in CH$_2$Cl$_2$ whereas addition of Cl$^-$ to an acetone solution of [Ru$_{2}$$\text{Cl}_{2}(\text{P(OEt)Ph}_{2})_{8}]$ (BPh$_4$)$_2$ caused a colour change from red to yellow but the rearrangement process was slower than for [RuCl(P(OMe)Ph$_2$)$_4$]BPh$_4$.

d) Mechanism of rearrangement of [RuCl$_2$L$_{3or4}$] species

It is of interest to conclude this paper by briefly examining possible mechanisms of rearrangement for the various [RuCl$_2$L$_{3or4}$] compounds discussed above, particularly with reference to the mechanism proposed earlier [3] (Scheme 1) to rationalise the behaviour of various [RuCl$_2$(PR$_3$)$_{3or4}$] compounds in solution.

First, no evidence has been found in this work for the formation of the neutral dimers [Ru$_2$Cl$_4$L$_5$] [L = P(OMe)$_3$, P(OMe)$_2$Ph, P(OR)$_2$ (R = Me, Et)] which can presumably be attributed to the stronger Ru-P bonds found in these alkoxy substituted phosphine complexes compared to those containing most tertiary phosphines. Further support for this conclusion comes from the observation that unlike [RuCl$_2$(PMe$_2$Ph)$_4$][16] and [RuCl$_2$(PET$_2$Ph)$_3$][2], dissolving [RuCl$_2$(PMe$_2$Ph)$_4$] in non-polar solvents does not give any [Ru$_2$Cl$_4$(PMe$_2$Ph)$_5$] and this can be attributed to the well-known high affinity of PMe$_2$Ph for Ru(II) [17].

In an attempt to obtain such compounds, solutions containing [Ru$_2$Cl$_3$(P(OMe)Ph$_2$)$_6$]Cl were pyrolysed at 120$^\circ$C for 12 hours since a similar reaction with [Ru$_2$Cl$_3$(PET$_2$Ph)$_6$]Cl gave [Ru$_2$Cl$_4$(PET$_2$Ph)$_5$][18]$^\dagger$. However, X-ray structural analysis showed the product to be the unusual neutral dimer [(P(OMe)Ph$_2$)$_2$(P(OH)Ph$_2$)RuCl$_3$Ru(P(OH)Ph$_2$)$_2$$(PPh$_2$O)] in which O-R bond rupture rather than Ru-P bond cleavage had occurred [19]. Similarly, pyrolysis of solutions containing the [Ru$_3$Cl$_5$(P(OEt)Ph$_2$)$_9$]$^+$ cation gave

$^\dagger$Similarly, pyrolysis of [Ru$_2$Cl$_3$(PR$_3$)$_6$]Cl (PR$_3$ = PMe$_2$Ph, PET$_2$Ph) gives [Ru$_2$Cl$_4$(PR$_3$)$_5$] but even at 400K, [Ru$_2$Cl$_3$(PMe$_2$Ph)$_6$]Cl was recovered unchanged, [16], again demonstrating the strength of the Ru-PMe$_2$Ph bonds.
[\(\text{(P(OEt)Ph}_2\text{)}_2\text{(P(OH)Ph}_2\text{)}\text{RuCl}_3\text{Ru}(\text{P(OH)Ph}_2\text{)}_2\text{(PPh}_2\text{O})\text{]}^{19}\).]

As for \([\text{RuCl}_2\text{(PR}_3\text{)}_3\text{Cl}]^+\), both \([\text{RuCl}_2\text{(P(OMe)_2Ph)}_4]\) and \([\text{RuCl}_2\text{(P(OMe)Ph}_2\text{)}_3]\) rearranged to the ionic dimers \([\text{Ru}_2\text{Cl}_3\text{L}_6]\text{Cl}\) when dissolved in polar solvents. The observation of an ionic intermediate \([\text{RuCl}(\text{P(OMe)}_2\text{Ph})_3(\text{solv})_2]^+\) (or \([\{\text{RuCl}(\text{P(OMe)}_2\text{Ph})_3(\text{solv})\}_2]^2+\)) strongly suggests that the mechanism of formation of \([\text{Ru}_2\text{Cl}_3\text{(P(OMe)}_2\text{Ph})_6]\text{Cl}\) involves prior dissociation of \(\text{Cl}^-\) from the neutral monomer followed by coupling of this cation with more of the neutral monomer (see Scheme 3). A similar ionic intermediate \([\text{RuCl}(\text{PETPh}_2\text{)}_3(\text{solv})_2]^+\) (or \([\{\text{RuCl}(\text{PETPh}_2\text{)}_3(\text{solv})\}_2]^2+\)) has been observed in the formation of \([\text{Ru}_2\text{Cl}_3(\text{PETPh}_2\text{)})\text{Cl}\) from \([\text{RuCl}(\text{PETPh}_2\text{)}_3]\). [3]

However, with \([\text{RuCl}_2\text{(P(OEt)Ph}_2\text{)}_3]\) in polar solvents, the major rearrangement product is the ionic trimer \([\text{Ru}_3\text{Cl}_5\text{(P(OEt)Ph}_2\text{)}_9]\text{Cl}\) (III b). A rationalisation of all these results is obtained by postulating the formation of a labile, double-bridged cationic intermediate \([\text{L}_3\text{ClRuCl}_2\text{Ru}](\text{solv})-\text{L}_3]^+\) by coupling of \([\text{RuCl}_2\text{L}_3]\) and \([\text{RuCl}_2\text{L}_3(\text{solv})]^+\). This can then either rearrange in intramolecular fashion (pathway a) to generate the triple chloride bridged species or combine with another molecule of \([\text{RuCl}_2\text{L}_3]\) (pathway b) to give the ionic trimer (Scheme 3). The factors which determine the preferred pathway a or b are not understood at present and further work with a wider range of ligands to try and establish these factors is now in progress.

However, it is gratifying that similar double bridged cations \([\text{L}_3\text{(OH)}\text{-Ru(OH)}_2\text{RuL}_3]\]^+ which rearrange to \([\text{L}_3\text{Ru(OH)}_3\text{RuL}_3]\]^+ (L = PMe_2Ph, PMePh_2, P(OMe)Ph_2) have recently been postulated by Ashworth et al [20] and such species are probably key intermediates in the mechanism of formation of other triple-bridged cations.

*Note that in ref [19], on the basis of analytical and \(^1\text{H}\) nmr data, we and others [10] assumed that the product from the reaction of \([\{\text{RuCl}_2\text{(C}_7\text{H}_8\text{)}_2\}\_2]\) and \(\text{P(OEt)Ph}_2\) in ethanol was \([\text{Ru}_2\text{Cl}_3\text{(P(OEt)Ph}_2\text{)}_6]\text{Cl}\) but \(^{31}\text{P}^{-1}\text{H}\) nmr studies now show it to be \([\text{Ru}_3\text{Cl}_5\text{(P(OEt)Ph}_2\text{)}_9]\text{Cl}\).

†For example, a similar mechanism to that shown in Scheme 3, which involves the double bridged, cationic intermediate \([(\text{arene})\text{XRuX}_2\text{Ru}(\text{solv})\text{arene}]^+\) can be proposed to explain the formation of the triple bridged ionic cations \([\text{areneRuX}_2\text{Ruarene}]^+\) (X = Cl\(^-\), \(\text{OH}^-\), \(\text{OR}^-\)) [21].
Finally, the observations that addition of excess P(OR)Ph₂ (R = Me, Et) to CH₂Cl₂ solutions of [RuCl(P(OMe)Ph₂)₄]BPh₄ (VI) and [Ru₂Cl₂(P(OEt)Ph₂)₈]-(BPh₄)₂ (VIII) respectively inhibited the formation of [Ru₂Cl₃(P(OMe)Ph₂)₆]-BPh₄ and [Ru₃Cl₅(P(OEt)Ph₂)₉]BPh₄, whereas addition of Cl⁻ to acetone solutions of (VI) and (VIII) accelerated the formation of these species, supports the mechanism shown in Scheme 3.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department, B.M.A.C. and A. Bernhardt, West Germany. Molecular weights were determined on a Mechrolab Vapour Pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the region 4000-250 cm⁻¹ on Perkin Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the region 400-200 cm⁻¹ on a Beckman RIIC IR 720 far ir. spectrometer using pressed Polythene discs. Hydrogen-1 nmr spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable temperature attachment and carbon-13 nmr spectra on a Varian CFT-20 spectrometer operating at 20 MHz (¹³C chemical shifts are quoted in ppm to high frequency of TMS). Phosphorus-31 nmr spectra were obtained on a Varian Associates XL100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m to high frequency of 85% H₃PO₄. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Conductivity measurements were made at 303K using a model 310 Portland Electronics conductivity bridge. Conductivity vs concentration data were obtained over a range of concentrations (2 x 10⁻³ to 5 x 10⁻³ dm⁻³ mol) and a plot of \( \Lambda_e \) (equivalent conductance) against \( C^\frac{1}{2} \) (concentration in equivalents dm⁻³) gave a straight line which on extrapolation to \( C^\frac{1}{2} = 0 \) gave \( \Lambda_o \). A subsequent plot of \( \Lambda_o - \Lambda_e \) vs \( C^\frac{1}{2} \) gave a straight line whose slope is a function
of the ionic charges [22]. Thus, the slopes obtained for various samples were compared with those for known 1:1 and 2:1 electrolytes and hence the electrolyte type could be determined.

Materials

Ruthenium trichloride trihydrate (Johnson Matthey); triphenylphosphine (Aldrich); trimethylphosphite (Fisons); dimethylphenylphosphonite, methyldiphenylphosphinite, ethyldiphenylphosphinite (Maybridge); sodium tetraphenylborate (BDH); ammonium hexafluorophosphate (Alfa). [RuCl₂(PPh₃)₃] was prepared as described earlier [23].

All reactions were carried out in degassed solvents under a nitrogen atmosphere. s(singlet); t(triplet); pt(pseudotriplet); q(quintet); mt(multiplet); br(broad); sh(shoulder); st(strong); w(weak); m(weak).

Proposed ν(RuCl) bands underlined.

Dichlorotetrais(trimethylphosphine)ruthenium(II):- The compound [RuCl₂(PPh₃)₃] (0.20g) was refluxed with P(OMe)₃ (0.40 cm³) in hexane (20 cm³) for one hour. The solution was cooled and the yellow crystals obtained were filtered off and recrystallised from CH₂Cl₂/hexane (yield 0.63g 45%) m.p. 145-147°C

[Found: C, 21.6; H, 5.4%; Calc. for C₁₂H₃₆Cl₂O₂P₂Ru: C, 21.6;
H, 5.4%] far ir spectrum: 340st, 306st, 295st, 284m, 274m, 260w, 210st, ¹H nmr (CDCl₃ at 301K) 3.84 ppm (q) ¹³P-{¹H} nmr (CDCl₃ at 298K) 129.4(s) ppm.

Dichlorotetrais(dimethylphenylphosphonite)ruthenium(II):- The compound [RuCl₂(PPh₂)₂] (0.20g) was refluxed with P(OMe)₂Ph (0.40 cm³) in hexane (20 cm³) for 3 hours to give yellow crystals which were filtered off and recrystallised from CH₂Cl₂/hexane (0.125g 75%) m.p. 158-160°C [Found: C, 45.0; H, 5.2%; Calc. for C₃₂H₄₄Cl₂O₂P₂Ru: C, 45.0; H, 5.2%] far ir spectrum 324st, 308m, 291st, 257sh, 214st; ¹H nmr (CDCl₃ at 301K) 3.45 (q), 7.20 (mt) ppm ¹³P-{¹H} nmr (CDCl₃ at 213K) 150.5(s), 166.6(t), 149.4(t) [²J pp 44.0 Hz]
Dichlorotris(methylidiphenylphosphinite)ruthenium(II):- The compound
\[ \text{[RuCl}_2\text{(PPh}_3\text{)}_3] \] (0.20g) was refluxed with \( \text{P(OMe)_2Ph} \) (0.20 cm\(^3\)) in hexane
(20 cm\(^3\)) for 3 hours. The resulting orange-brown solid was filtered off
and washed with hexane (0.168g, 95%) m.p. 164-166\(^\circ\)C [Found: C, 56.5, H, 4.6,
Cl, 8.7%, M(C\(_6\)H\(_6\)) 834. Calc. for C\(_{39}\)H\(_{39}\)Cl\(_2\)O\(_3\)P\(_2\)Ru:- C, 57.0; H, 4.7;
Cl, 8.7% M 820] far ir spectrum 337st, 290at, 280sh. \(^1\)H nmr (C\(_6\)D\(_6\) at 301K)
2.90(pt) 6.9-7.70(mt) ppm \(^31\)P-\(^1\)H nmr (C\(_6\)D\(_6\) at 298K) 149.5(s) ppm;
(toluene/(CD\(_3\))\(_2\))CO at ca 140K) 147.0(br) ppm \(^13\)C-\(^1\)H nmr (C\(_6\)D\(_6\) at 318K)
singlets at 134.3 and 54.8 ppm.

Dichlorotris(ethyldiphenylphosphinite)ruthenium(II) was similarly prepared
from \[ \text{[RuCl}_2\text{(PPh}_3\text{)}_3] \] and \( \text{P(OEt)_2Ph} \) (0.160g, 66%) m.p. 155-157\(^\circ\)C [Found:
C, 58.1; H, 5.2; Cl, 8.1%, M(C\(_6\)H\(_6\)) 925. Calc. for C\(_{42}\)H\(_{45}\)Cl\(_2\)O\(_3\)P\(_2\)Ru:- C,
58.3, H, 5.2, Cl, 8.2% M 862] far ir spectrum 328st, 298w, 286st, 272m,
253m, 234m, 214m; \(^1\)H nmr (C\(_6\)D\(_6\) at 301K) 0.78(t), 3.40(br) [\(^3\)J\(_{HH}\) 7.0 Hz],
6.90-7.70 (mt) ppm. \(^31\)P-\(^1\)H nmr (C\(_6\)D\(_6\) at 298K) 144.7 (s) ppm (toluene/(CD\(_3\))\(_2\)-
CO at ca 140K) 141.1 (br), 167.3 (br) ppm \(^13\)C-\(^1\)H nmr (C\(_6\)D\(_6\) at 318K) singlets
at 134.3, 64.5 and 16.1 ppm.

[Hexakis(dimethylphenylphosphonite)ruthenium(II)]tetraphenylborate:- The compound
\[ \text{[RuCl}_2\text{(PPh}_3\text{)}_3] \] (0.20g) was refluxed with \( \text{P(OMe)_2Ph} \) (0.40 cm\(^3\)) in
methanol (20 cm\(^3\)) for 3 hours to give a very pale yellow solution which
was cooled and then NaBPh\(_4\) (0.25g) added. A white solid precipitated which
was filtered off and recrystallised from CH\(_2\)Cl\(_2\)/MeOH to give colourless
crystals of the complex m.p. 209-211\(^\circ\)C [Found: C, 65.2; H, 6.0%; Calc.
for C\(_{96}\)H\(_{106}\)B\(_2\)O\(_2\)P\(_2\)Ru: C, 65.5; H, 6.0%]

[Chlorotetrakis(methylidiphenylphosphinite)ruthenium(II)]tetraphenylborate:-
The compound \[ \text{[RuCl}_2\text{(PPh}_3\text{)}_3] \] (0.20g) was refluxed with \( \text{P(OMe)_2Ph} \) (0.20 cm\(^3\))
in methanol (20 cm\(^3\)) for 5m to give a deep red solution and the solution
then filtered to remove any unreacted starting material. Addition of NaBPh\(_4\)
(0.25g) gave a red precipitate, recrystallised from (CH\(_3\))\(_2\)CO/MeOH m.p. 96-98\(^\circ\)C
[Found: C, 68.3; H, 5.3, Cl, 3.6% Calc. for C_{76}H_{72}B_{10}Cl_{4}P_{4}Ru:: C, 69.1;
H, 5.4; Cl, 2.7%] Conductivity in (CH{sub 3}){sub 2}CO at 303K. Slope of $\nu_o - \nu_c$ vs C{sup 1/2} plot = 140 (for [Ru_{2}Cl_{3}(P(OMe)Ph){sub 6}]BPh{sub 4}, slope = 155; for [Ru(ηC_{6}H_{6})-(
NH{sub 3})_{3}](PF_{6})_{2}, slope = 350) far ir spectrum 290st, 275sh, {sup 1}H nmr
((CD{sub 3}){sub 2}CO at 301K) 3.15 (pt), 6.80-7.20 (mt) ppm {sup 31}P nmr [(CD{sub 3}){sub 2}CO at
173K] 123 (mt), 140 (mt), 157 (mt) ppm. (see Fig. 3a)

[Di-$\mu$-chlorobis[tetrakis(ethyldiphenylphosphinite)ruthenium(II)]]tetrphenyl-
borate was prepared similarly by reaction of [RuCl_{2}(PPh){sub 3}] with excess
P(OEt)Ph{sub 2} in ethanol, m.p. 91-93°C [Found: C, 69.6; H, 5.8; Cl, 2.6% Calc.
for C_{160}H_{160}B_{10}Cl_{10}P_{6}Ru_{2}: C, 69.8; H, 5.8; Cl, 2.6%]. Conductivity in
(CH{sub 3}){sub 2}CO at 303K. Slope of $\nu_o - \nu_c$ vs C{sup 1/2} plot = 175. Far ir spectrum
270st (br); {sup 1}H nmr [(CD{sub 3}){sub 2}CO at 301K)] 1.25 (t), 3.40 (br) [J{sub HH} 7.0 Hz],
6.80 - 7.20 (mt) ppm. {sup 31}P-(1H) nmr [(CD{sub 3}){sub 2}CO at 173K] 119.0 (t), 148.1 (t) ppm
(J{sub PP} 32.5 Hz) (see Fig. 5a)

[Tri-$\eta$-chlorohexakis(methylidiphenylphosphinite)diruthenium(II)]tetrphenyl-
borate:- The compound [RuCl_{2}(PPh){sub 3}](0.20g) was refluxed with P(OMe)Ph{sub 2}
(0.20 cm{sup 3}) in methanol (20 cm{sup 3}) for 3 hours to give a yellow solution.
Addition of NaBPh{sub 4} (0.20g) then produced a pale yellow solid which was
filtered off and recrystallised from CH_{2}Cl_{2}/MeOH m.p. 202-204°C. The same
compound was also obtained by adding NaBPh{sub 4} to a solution of [RuCl_{2}(P(OMe)-
Ph{sub 2})_{3}] dissolved in methanol. [Found: C, 63.6; H, 5.1% M(CHCl{sub 3}) 1003.
Calc. for C_{102}H_{98}B_{10}Cl_{10}P_{6}Ru:: C, 63.6; H, 5.1% M(for 1:1 electrolyte) 962.]
Conductivity in (CH{sub 3}){sub 2}CO at 303K. Slope of $\nu_o - \nu_c$ vs C{sup 1/2} plot = 155. Far
ir spectrum 295st, 260st (br), 228w. {sup 1}H nmr (CDCl{sub 3} at 301K) 2.95 (pt) 6.90-7.10 (mt)
ppm. {sup 31}P-(1H) nmr (CDCl{sub 3} at 298K) 138.6 (s) ppm {sup 13}C-(1H) nmr (CDCl{sub 3} at 318K)
singlets at 136.5, 125.4, 121.3 (Ph); 133.7, 129.8, 127.0 (BPh{sub 4}), 55.2 (Me) ppm.
[Tri-\(\mu\)-chlorohexakis(dimethylphenylphosphonite)diruthenium(II)]tetrphenylborate:– The compound \(\text{[RuCl}_2\left(\text{P\{OMe\}_2\text{Ph}\}_4\right)}\) (0.20g) was refluxed in methanol (30 cm\(^3\)) for 3 hours to give a yellow solution. Addition of NaBPh\(_4\) then precipitated a very pale yellow solid which was filtered off and washed with methanol; m.p. 186-188°C [Found: C, 52.3; H, 5.3% C\(_{72}\)H\(_{86}\)B\(_6\)Cl\(_3\)O\(_6\)P\(_4\)Ru\(_{12}\); Calc. for C\(_{72}\)H\(_{86}\)B\(_6\)Cl\(_3\)O\(_6\)P\(_4\)Ru\(_{12}\): C, 52.4; H, 5.2%] \(^1\)H nmr (CDCl\(_3\)) at 301K 3.45(q), 700-7.20(mt) ppm. \(^{31}\)P–\(^1\)H nmr (CDCl\(_3\)) at 298K 168.7 (s) ppm.

\{1,2, 1,3-\(\mu\)-chboro, -2,3-di-\(\mu\)-chloro, 1, chloro-cyclo tris(ethyldiphenyl-phosphinonet)diruthenium(II)]tetrphenylborate:– The compound \(\text{[RuCl}_2\left(\text{PPh}_3\right)_3}\) (0.20g) was refluxed with P(OEt)Ph\(_2\) (0.20 cm\(^3\)) in ethanol (20 cm\(^3\)) for 4 hours to give a pale yellow solution. Addition of NaBPh\(_4\) (0.20g) precipitated the complex as a pale yellow solid which was filtered off and washed with ethanol m.p. 174-176°C [Found: C, 60.1; H, 5.2; Cl, 6.3; P, 8.7%; M(CHCl\(_3\)) 1095] 1350 Calc. for C\(_{150}\)H\(_{155}\)B\(_{15}\)Cl\(_{9}\)O\(_9\)P\(_9\)Ru\(_{15}\); C, 62.7; H, 5.2; Cl, 6.3; P, 9.7% M (1:1 electrolyte), 1435. Conductivity in (CD\(_3\))\(_2\)CO at 303K. Slope of \(\chi_0 - \chi_c\) vs C\(^2\) plot = 140. Far IR spectrum 314m, 288sh, 272sh, 260s(br), 256sh, 242sh \(^1\)H nmr (CDCl\(_3\)) at 301K 1.18(t) 2.96(br) \(^3\)J\(_{HH}\) 7.0 Hz, 7.00 - 7.30(mt) ppm \(^{31}\)P–\(^1\)H nmr (CDCl\(_3\)) at 213K 135(mt) ppm (see Fig. 2) \(^{13}\)C–\(^1\)H nmr (CDCl\(_3\)) at 318K single at 136.5, 125.5, 121.4(Ph); 133.9, 129.8, 126.8 (BPh\(_4\)); 64.5 (CH\(_2\)); 16.0 (CH\(_3\)) ppm.

The corresponding \(\text{[Ru}_3\text{Cl}_5\left(\text{P\{OEt\}_2\text{Ph}\}_9\right)}\text{PF}_6\) was obtained by addition of NH\(_4\)PF\(_6\) to the pale yellow solution. [Found: C, 54.2; H, 5.0% Calc. for C\(_{126}\)H\(_{135}\)C\(_5\)F\(_{10}\)O\(_{10}\)P\(_{10}\)Ru\(_{3}\): C, 56.1; H, 5.1%].

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References


(IIa)

(IIb)

(IIIa)

(IIIb)
(IV) \((S-S^- = S_2\text{CNEt}_2)\)

(V)
Fig. 1. $^{31}$P-$^1$H nmr spectrum of the rearrangement products of 
$[\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3]$ in $(\text{CD}_3)_2\text{CO/CH}_2\text{Cl}_2$ at 213K.

Fig. 2. $^{31}$P-$^1$H nmr spectrum of the ionic rearrangement product of 
$[\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_3]$ in CDCl$_3$ at 213K.

Fig. 3. $^{31}$P-$^1$H nmr spectra of $[\text{RuCl}(\text{P(OMe)}\text{Ph}_2)_4]B\text{Ph}_4$ in $(\text{CD}_3)_2\text{CO}$ at 
 a) 173K  b) 193K  c) 213K  d) 333K.

Fig. 4. $^{31}$P-$^1$H nmr spectra of cis-$[\text{FeH}_2(\text{P(OMe)}_2\text{Ph})_4]$ in 50% CH$_2$Cl$_2$-50% 
CHF$_2$Cl at various temperatures (reproduced from ref [15]).

Fig. 5. $^{31}$P-$^1$H nmr spectra of $[\text{Ru}_2\text{Cl}_2(\text{P(OEt)}\text{Ph}_2)_6](B\text{Ph}_4)_2$ in $(\text{CD}_3)_2\text{CO}$ 
at a) 173K  b) 213K  c) 298K.
$$2[\text{RuCl}_2(\text{PR}_3)_2] + 2\text{PR}_3 \rightleftharpoons 2[\text{RuCl}_2(\text{PR}_3)_3]$$

$$\text{(PR}_3 = \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PEtPh}_2, \text{PET}_2\text{Ph}, \text{PClPh}_2)$$

SCHEME 1
Scheme 2
[RuCl\(_2\)\(_4\)] \xrightarrow{-L} [RuCl\(_2\)\(_3\)] \xrightarrow{+L} [RuCl\(_2\)\(_3\)\((\text{solv})\)]^+ \xrightarrow{dimerise} [{\{\text{RuCl}_3\text{solv}\}}_{\text{2}^+}]^2^+

polar solvent

(-Cl)

\[ \text{Scheme 3} \]
RUTHENIUM COMPLEXES CONTAINING GROUP 5B DONOR LIGANDS
PART VII* REARRANGEMENT REACTIONS OF SOME RUTHENIUM (II) COMPLEXES CONTAINING TRIPHENYLPHOSPHINE, TRI-p-TOLYLPHOSPHINE OR ETHYLDIPHENYLPHOSPHINE LIGANDS.

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Summary
As for [RuCl₂(PPh₃)₃], carbonylation of [RuCl₂(PR₃)₃]
[PR₃ = P(p-tolyl)₃, PETPh₂] in N,N¹-dimethylformamide (dmf) gives [Ru(CO)Cl₂(dmf)(PR₃)₂] (II). For PR₃ = PETPh₂, rearrangement of (II) in various solvents gives inseparable mixtures (³¹P evidence) but for PR₃ = P(p-tolyl)₃ [Ru₂(CO)₂Cl₄-
{P(p-tolyl)₃}₃] is obtained. Reaction of [Ru(CO)Cl₂(dmf) -
{P(p-tolyl)₃}₂] with [RuCl₂(P(p-tolyl)₃)₃] (1:1 mol ratio) gives [Ru₂(CO)Cl₄(P(p-tolyl)₃)₄] whereas reaction of [Ru(CO)Cl₂(dmf) -
{PPh₃}₂] with [RuCl₂(P(p-tolyl)₃)₃] gives [Ru₂(CO)Cl₄(PPh₃)₂-
{P(p-tolyl)₃}₂]. Reaction of [RuCl₂(P(p-tolyl)₃)₃] with CS₂ gives the related [Ru₂Cl₄(CS)₅(P(p-tolyl)₃)₄] and
[({RuCl₂(CS)₅P(p-tolyl)₃}₂] whereas [RuCl₂(PETPh₂)₃] and CS₂ produce [RuCl₂(S₂CPEtPh₂)(PETPh₂)₂]CS₂ and [Ru₂Cl₄(CS)₂(PETPh₂)₃].

*For Part VI, see ref 1.
Introduction

Earlier, it was shown that reaction of [RuCl₂(PPh₃)₃] with CS₂ gave the triple chloride bridged complex [Ru₂Cl₄(CS)(PPh₃)₄], together with smaller amounts of [Ru(n²-CS₂)Cl(PPh₃)₃]Cl, [{RuCl₂(CS)(PPh₃)₂}₂] and [Ru₂Cl₄(CS)₂(PPh₃)₃] (various isomers). Later, the compounds [Ru₂(Y)Cl₄(PPh₃)₄] were synthesised in high yield by means of an intermolecular coupling reaction of [RuCl₂(PPh₃)₃] and [Ru(Y)Cl₂(dmf)(PPh₃)₂] (Y = CO, CS). [3]

In this paper we now report on our attempts to utilise both these methods to synthesise analogous compounds with other tertiary phosphines such as tri-p-tolylphosphine and ethyldiphenylphosphine and also to synthesise mixed tertiary phosphine complexes [Ru₂(CO)Cl₄(PR₃)₂(PR₃')₂].

Results and Discussion

a) Tri-p-tolylphosphine complexes:

Reaction of "RuCl₃.3H₂O" with an excess of P(p-tolyl)₃ in methanol, reported to give [RuCl₂{P(p-tolyl)₃}₄] [4], repeatedly produced dark purple crystals of [RuCl₂{P(p-tolyl)₃}₃] (I)†. The ³¹P-{¹H} nmr spectrum of (I) in CH₂Cl₂/(CD₃)₂CO at 190K consisted of a doublet at δ 25.1 ppm and a triplet at 74.3 ppm (²Jpp 28.0Hz) (relative intensity 2:1) plus a weak singlet at 28.8 ppm due to (p-tolyl)₃PO. As the temperature was raised the doublet and triplet collapsed and at 298K coalesced to a broad singlet at 39.9 ppm. These nmr changes were concentration independent and reversible with temperature, and, taken in conjunction with the ir spectrum which contained a band at 320 cm⁻¹, (indicative of a trans Cl-Ru-Cl arrangement),

†The reason for this is probably the high pH of the commercial "RuCl₃.3H₂O" used which favours formation of the tris species.
suggest a structure analogous to that of \([\text{RuCl}_2(\text{PPh}_3)_3]\) [5] which is undergoing rapid intramolecular exchange of \(\text{P}(\text{p-tolyl})_3\) groups at ambient temperature.

When compound (I) was refluxed in \(\text{CS}_2\) for a short time, a red solution was obtained, but in contrast to the analogous reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\), no \([\text{Ru}(\text{n}^2-\text{CS}_2)\text{Cl}(\text{Pp-toly})_3)_3]\)Cl was deposited [6,2]. Addition of light petroleum (b.p. 60-80°C), however, precipitated a pink solid analysing closely for the double chloride bridged complex \([\{\text{RuCl}_2(\text{CS})\{\text{P}(\text{p-tolyl})_3\}_2\}_2]\). The ir spectrum contained a band at 1290 cm\(^{-1}\) (\(\nu_{\text{CS}}\)) and the \(^{31}\text{P}-^{1}\text{H}\) nmr spectrum in \(\text{CDCl}_3\) at 298K consisted of a strong singlet at 6 29.5 ppm together with weaker singlets at 28.5 ppm \([\{\text{P}(\text{p-tolyl})_3\}_2\text{PO}]\) and 42.5 ppm. The peaks at 29.5 and 42.5 ppm are possibly due to different isomeric forms of \([\{\text{RuCl}_2(\text{CS})\{\text{P}(\text{p-tolyl})_3\}_2\}_2]\). The remaining solution on standing for 6 hours deposited an orange solid whose \(^{31}\text{P}-^{1}\text{H}\) nmr spectrum in \(\text{CDCl}_3\) at 298K displayed two AB quartets at 6 47.6 and 34.6 ppm and which analysed for the triple chloride bridged complex \([\text{Ru}_2\text{Cl}_4(\text{CS})\{\text{P}(\text{p-tolyl})_3\}_4]\). (\(\nu_{\text{CS}}\) 1292 cm\(^{-1}\)).

Treatment of \([\text{RuCl}_2\{\text{P}(\text{p-tolyl})_3\}_3]\) with CO in \(\text{N,N-}
\text{dimethylformamide (dmf)}\) readily gave \([\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})\{\text{P}(\text{p-tolyl})_3\}_2]\) (II) whose i.r. spectrum showed \(\nu_{\text{CO}}\) 1935 cm\(^{-1}\), \(\nu_{\text{RuCl}}\) 340 cm\(^{-1}\) and a broad band at 1645 cm\(^{-1}\) due to coordinated dmf and whose \(^{31}\text{P}-^{1}\text{H}\) nmr spectrum at 298 K in \(\text{CDCl}_3\) contained a singlet at 32.3 ppm. Therefore, \([\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})\{\text{P}(\text{p-tolyl})_3\}_2]\) has an analogous structure to \([\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})\{\text{PPh}_3\}_2]\) with trans phosphines and trans chlorides [3].
Reaction of compound (II) with compound (I) (1:1 molar ratio) in ethanol then gave the triple chloride bridged dimer. \([\text{Ru}_2(\text{CO})\text{Cl}_4\{\text{P(toly}-\text{yl)}_3\}_4]\) whose \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum in CDCl\(_3\) at 298 K contained the expected two AB quartets at \(\delta\) 47.6 and 38.8 ppm. As for \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})\{\text{PPh}_3\}_2]\) [3], recrystallisation of compound (II) from methanol gave \([\text{Ru(CO)}\text{Cl}_2(\text{MeOH})\{\text{P(toly}-\text{yl)}_2\}_2]\), and shaking the latter in CH\(_2\)Cl\(_2\) for several days produced a yellow brown solid, whose \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum in CDCl\(_3\) at 298 K, showed it to contain the three possible geometrical isomers of \([\text{Ru}_2(\text{CO})_2\text{Cl}_4\{\text{P(toly}-\text{yl)}_3\}_3]\) (see experimental section and ref [3]).

An attempt to synthesise the mixed tertiary phosphine complex \([\{\text{PPh}_3\}_2\text{ClRuCl}_3\text{RuCO}\{\text{P(toly}-\text{yl)}_3\}_2]\) by reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\) with \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})\{\text{P(toly}-\text{yl)}_3\}_2]\) gave an orange solid but its \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum showed a large number of resonances in the region 46-50 ppm indicating a mixture of products. A possible explanation is that during the coupling process, dissociation of PPh\(_3\) from \([\text{RuCl}_2(\text{PPh}_3)_3]\) occurs and this can then displace P(toly)_3 from the initially formed product \([\{\text{PPh}_3\}_2\text{ClRuCl}_3\text{RuCO}\{\text{P(toly}-\text{yl)}_3\}_2]\) to give, in addition, the compounds \([\{\text{PPh}_3\}_2\text{ClRuCl}_3\text{RuCO}\{\text{P(toly}-\text{yl)}_3\}_n\{\text{PPh}_3\}_2-n]\) \((n = 0, 1)\).

However, this side reaction does not occur in the reaction between \([\text{RuCl}_2(\text{P(toly)}_3)_3]\) and \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})\{\text{PPh}_3\}_2]\) since an orange solid which analysed for \([\text{Ru}_2(\text{CO})\text{Cl}_4\{\text{PPh}_3\}_2(\text{P(toly)}_3)_2]\) and whose \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum in CDCl\(_3\) at 298 K contained only two AB patterns at \(\delta\) 48.0 and 40.2 ppm was obtained.
Finally, the attempted coupling reactions of \([\text{RuCOCl}_2(\text{dmf})(\text{PR}_3)_2]\) (\(\text{PR}_3 = \text{PPh}_3, \text{P}(p\text{-tolyl})_3\)) with other \([\text{RuCl}_2\text{L}_3]\) (L = \(\text{P(OME)}\text{Ph}_2, \text{P(OEt)}\text{Ph}_2\)) were completely unsuccessful. This is not surprising since earlier studies [1] have shown that these tertiary phosphinite complexes contain very strong Ru-P bonds and hence the formation of \([(\text{P(OR)}\text{Ph}_2)_2\text{ClRuCl}_3\text{Ru(CO)}-\text{(PR}_3)_2]\) is completely inhibited. Instead, the reaction products obtained in acetone were unreacted \([\text{RuCOCl}_2(\text{dmf})(\text{PR}_3)_2]\), \([\text{Ru}_2(\text{CO})_2\text{Cl}_4(\text{PR}_3)_3]\), and either \([\text{Ru}_2\text{Cl}_3(\text{P(OME)}\text{Ph}_2)_6]\)\text{Cl} or \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph}_2)_9]\)\text{Cl} (i.e. the rearrangement products of \([\text{RuCl}_2(\text{P(OR)}\text{Ph}_2)_3]\) in polar solvents [1].

b) Ethyldiphenylphosphine complexes:

When green\([\text{RuCl}_2(\text{PETPh}_2)_3]\) (prepared by reaction of \([\text{RuCl}_2(\text{PPh}_3)_4]\) with excess PETPh2 in hexane [5a]) was shaken in \(\text{CS}_2\) for one hour, a red-pink solid was produced which analysed closely for the expected \("[\text{Ru}(\eta^2-\text{CS}_2)\text{Cl}(\text{PETPh}_2)_3]\)Cl.\text{CS}_2". The ir spectrum contained a strong band at \(1515 \text{ cm}^{-1}\) which as for \([\text{Ru}(\eta^2-\text{CS}_2)\text{Cl}(\text{PPh}_3)_3]\)\text{Cl}\text{CS}_2 [2,6] is associated with a \(\text{CS}_2\) solvate. This was proved by dissolving the complex in \(\text{CH}_2\text{Cl}_2\) and reprecipitating with light petroleum (bp 60-80°C) to give a product analysing for \"[\text{Ru}(\eta^2-\text{CS}_2)\text{Cl}(\text{PETPh}_2)_3]\)\text{Cl}\" (III) whose ir spectrum no longer contained the band at \(1515 \text{ cm}^{-1}\). Ir bands at 1115 and 995 cm\(^{-1}\) which could be attributed to the \(\eta^2-\text{CS}_2\) group [7] were also present. The \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum of (III) in CDC\(_3\) at 298 K consisted of an AMX pattern \([\nu_\text{A} 41.1 \text{ ppm, } \nu_\text{M}, 34.0 \text{ ppm; } \nu_\text{X} 9.2 \text{ ppm; } J_{\text{AM}} 28.9 \text{ Hz, } J_{\text{AX}} 3.7 \text{ Hz, } J_{\text{MX}} 9.2 \text{ Hz}]\) indicating that the compound contained three
magnetically inequivalent PETPh₂ groups. However, the low values of \( J_{AX} \) and \( J_{MX} \) together with the fact that compound (III) gave non-conducting solutions in \( \text{CH}_2\text{Cl}_2 \) and acetone strongly suggests that it should be reformulated as \([\text{RuCl}_2(\text{S}_2\text{CETPh}_2)\text{PETPh}_2]_2\) containing the \( \text{Ph}_2\text{Etp}^+\text{-CS}_2^- \) zwitterion ligand.† The related compound "[Ir(\( n^2\text{CS}_2 \))(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4" has recently been shown to be \([\text{Ir}(S_2\text{CPPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BPh}_4\) by X-ray analysis and these authors then suggested that "[Ru(\( n^2\text{CS}_2 \))\text{Cl}(\text{PPh}_3)_3]\text{Cl}" also probably contained a \( \text{PPh}_3^+\text{-CS}_2^- \) ligand [8]. Unfortunately, this \( \text{PPh}_3 \) complex is too insoluble for \( ^{31}\text{P} \) nmr studies.

†The peaks at 1115 and 995 cm\(^{-1}\) in the ir spectrum of (III) can probably be attributed to the \( v_{\text{CS}_2}(\text{asym}) \) stretching vibrational mode of the \( \text{PETPh}_2^+\text{-CS}_2^- \) ligand [7].
Dissolving \([\text{RuCl}_2(\text{S}_2\text{CEtPh}_2)(\text{PETPh}_2)_2]\) in methanol produced a conducting purple solution which on standing for several hours gradually turned blue in colour and eventually green, the latter change being most likely due to oxidation to a Ru(III) species. Addition of NaBPh\(_4\) to the purple solution gave a purple solid which analysed quite well for \([\text{RuCl(MeOH)}(\text{S}_2\text{CEtPh}_2)(\text{PETPh}_2)_2]\)BPh\(_4\) (IV). The \(\text{^31P}_{-}(^1\text{H})\) nmr spectrum of (IV) in CDCl\(_3\) at 298 K, which showed an AMX pattern \(v_A\) 44.6 ppm, \(v_M\) 29.0 ppm, \(v_X\) 16.4 ppm; \(J_{AM}\) 28.0 Hz, \(J_{AX}\) 3.5 Hz \(J_{MX}\) 11.3 Hz] was consistent with this formulation and either of the structures shown. Unfortunately, no solid could be isolated from the blue solution formed on further rearrangement of (IV).

A small amount of \([\text{RuCl}_2(\text{S}_2\text{CEtPh}_2)(\text{PETPh}_2)_2]\)CS\(_2\) was also formed on refluxing \([\text{RuCl}_2(\text{PETPh}_2)_3]\) in CS\(_2\) for several hours. After filtering off this material, an orange solution remained which on standing deposited a non-conducting orange solid. Its ir spectrum contained a strong band at 1295 cm\(^{-1}\) \((v_{CS})\) whilst its \(\text{^31P}_{-}(^1\text{H})\) nmr spectrum at 298 K in CDCl\(_3\) consisted predominantly of a singlet at \(\delta\) 49.2 ppm and an AB pattern centred at 36.8 ppm, attributed to one isomer of the triple bridged dimer \([\text{Ru}_2\text{Cl}_4(\text{CS})_2(\text{PETPh}_2)_3]\) (see earlier). The spectrum also contained a weak resonance at 43.4 ppm (singlet) due to some unreacted \([\text{RuCl}_2(\text{PETPh}_2)_3]\) (see ref [5a]) and other weak singlets at 48.4 and 37.8 which might arise from the presence of some \([\{\text{RuCl}_2(\text{CS})(\text{PETPh}_2)_2\}_2]\). The spectrum also contained a small multiplet at 18.0 ppm of unknown origin.
Treatment of \([\text{RuCl}_2(\text{PETPh}_2)_3]\) with CO in dmf readily gave
\([\text{Ru(CO)Cl}_2(\text{dmf})(\text{PETPh}_2)_2]\) (II) whose ir and \(^{31}\text{P}-\{^1\text{H}\}\) spectra indicated that the compound had the same structure as
\([\text{Ru(CO)Cl}_2(\text{dmf})(\text{PR}_3)_2]\) (PR$_3$ = PPh$_3$, P(p-tolyl)$_3$) Like these compounds, the coordinated dmf molecule could be replaced by methanol although in this instance, recrystallisation of (II) (PR$_3$ = PETPh$_2$) from MeOH or CH$_2$Cl$_2$/MeOH always produced mixtures of \([\text{Ru(CO)Cl}_2(\text{dmf})(\text{PETPh}_2)_2]\) and \([\text{Ru(CO)Cl}_2(\text{MeOH})(\text{PETPh}_2)_2]\), indicating that the dmf group was more strongly complexed than for the PPh$_3$ and P(p-tolyl)$_3$ compounds.

In less polar solvents such as methylene chloride, (II) (PR$_3$ = PETPh$_2$) behaved in a similar manner to its PPh$_3$ and P(p-tolyl)$_3$ analogues except that the rate of rearrangement was much slower and, that the products could not be isolated in pure form. Identification of the products was therefore based mainly on the \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectra of the resulting mixtures.

Thus when \([\text{Ru(CO)Cl}_2(\text{dmf})(\text{PETPh}_2)_2]\) was shaken in CH$_2$Cl$_2$ for 10 hours and the solvent then removed under vacuo, a yellow solid (with \(\nu_{\text{CO}}\) 2040 w, 1970s br, 1928 m cm$^{-1}$) was obtained. The \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum of this mixture at 213 K in CDCl$_3$
(Fig. 1a) consisted of a strong singlet at $\delta$ 32.6 (dmf solvate), a weak doublet at 18.7 ppm, a weak broad resonance at ca. 35 ppm, an AB pattern centred at 41.2 ppm (J$_{AB}$ 26.6 Hz; $\delta_{AB}$ 70.0 Hz) superimposed on some weak resonances and another broad resonance at ca. 54.5 ppm. On raising the temperature to 308 K, the position of the singlet from the unreacted dmf solvate moved to 31.4 ppm (Fig. 1b), the broad resonance at 35.3 ppm sharpened into a triplet (with J$_{pp}$ 25.7 Hz) and the
doublet at 18.7 ppm ($J_{pp}$ 25.5 Hz) also sharpened. The AB quartet became more intense as were the additional peaks superimposed upon it (ca. 37-44 ppm) and the resonance at 53.5 ppm became a sharp singlet.

When [Ru(CO)Cl$_2$(dmf)(PETPh$_2$)$_2$] was shaken in benzene for 24 hours and the solvent removed, the ir spectrum of the yellow-orange product showed a broad band at 1950 cm$^{-1}$. The $^{31}$P-(1H) nmr spectrum of this material in CDCl$_3$ at 213 K (Fig. 2) showed no evidence for the AB pattern observed in the spectrum of the product obtained from rearrangement in CH$_2$Cl$_2$. However, the resonances at ca. 37 to 44 ppm were increased in intensity and the previously weak resonance at 53.5 ppm now exhibited three singlets at 55.2, 54.9 and 54.7 ppm. The doublet at 18.9 ppm and the broadened triplet at ca. 34 ppm were also more intense. A singlet from unreacted dmf solvate appeared at 32.9 ppm and other weak signals were observed at ca. 32, 26 and 20 ppm.

The resonances at 37 to 44 ppm together with the signals at ca. 54 ppm may be assigned to the three possible geometrical isomers of [Ru$_2$(CO)$_2$Cl$_4$(PETPh$_2$)$_3$] (cf ref [3]) which are the major rearrangement products in benzene. The AB quartet observed in the $^{31}$P-(1H) nmr spectrum of the CH$_2$Cl$_2$ reaction at 41.2 ppm can be assigned to the ionic species [Ru$_2$(CO)$_2$Cl$_3$(PETPh$_2$)$_4$]Cl (cf [Ru$_2$(CO)$_2$Cl$_3$(PPh$_3$)$_4$]Cl whose $^{31}$P-(1H) nmr spectrum showed an AB quartet at 40.6 ppm [3]). The weak singlets at ca. 32, 26 and 20 ppm probably correspond to isomers of the double halide bridged complex [{Ru(CO)Cl$_2$-(PETPh$_2$)$_2$}]$_2$. 
During the formation of [Ru₂(CO)₂Cl₄(P₃R₃)₃] from "Ru(CO)Cl₂(P₃R₃)₂", free tertiary phosphine will be liberated. In the case of PPh₃, this was observed in the ³¹P-{¹H} nmr spectrum as either free PPh₃ (-6 ppm) and/or Ph₃PO (29 ppm). However, in reactions of [Ru(CO)Cl₂(dmf)(PETPh₂)₂], no free PETPh₂ (-15.5 ppm) or Ph₂EtPO (35 ppm) was observed. Instead, [Ru(CO)Cl₂(PETPh₂)₃] (doublet and triplet at 18.9 and 35.3 ppm respectively) was formed, probably by direct reaction of [Ru(CO)Cl₂dmf(PETPh₂)₂] with PETPh₂.

Finally, an attempt to prepare [Ru₂(CO)Cl₄(PETPh₂)₄] by reaction of [Ru(CO)Cl₂(dmf)(PETPh₂)₂] and [RuCl₂(PETPh₂)₃] in acetone (1:1 molar ratios) produced a bright orange solid (νCO 1960 br). However, the ³¹P-{¹H} nmr spectrum of this material in CDCl₃ at 213 K consisted of peaks corresponding to [Ru(CO)Cl₂(PETPh₂)₃], [Ru₂Cl₄(PETPh₂)₅] (see ref [5a]) together with two AB resonances centred at 48.5 ppm (J_AB 40.1 Hz), 8_AB 191.3 Hz) and 39.4 ppm (J_AB 26.2 Hz; δ_AB 139.5 Hz) attributed to the triple bridged [Ru₂(CO)Cl₄(PETPh₂)₄]. Unfortunately, attempts to separate these compounds were unsuccessful.

Experimental

Microanalyses were by BMAC and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000-250 cm⁻¹ on Perkin Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Phosphorus-31 nmr spectra were obtained on a Varian Associates XL100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H₃PO₄.
Melting points were determined with a Köfler hot stage microscope and are uncorrected.

Materials

Ruthenium trichloride trihydrate (Johnson Matthey), carbon monoxide (Air products) carbon disulphide (Fisons). Tri-p-tolylphosphine and ethyldiphenylphosphine were prepared by standard literature methods. The compounds \([\text{RuCl}_2(\text{PR}_3)_3]\) \((\text{PR}_3 = \text{PPh}_3\text{[9]}\text{PETPh}_2\text{[5a]})\) and \([\text{Ru(CO)}\text{Cl}_2\text{dmf(PPh}_3)_2]\) \([10]\) were prepared as described earlier. All reactions were carried out in degassed solvents and, except for carbonylation reactions, under a nitrogen atmosphere. s(singlet); d(doublet), t(triplet), q(quartet), br(broad).

Tri(p-tolylphosphine)Complexes

Dichlorotris(tri-p-tolylphosphine)ruthenium(II):- The compound "RuCl$_3$H$_2$O" (0.50g) was refluxed with an excess of tri-p-tolylphosphine (2.50g) in methanol (25 cm$^3$) for 16h. The dark purple crystals obtained were filtered off and washed with diethyl ether (yield 75%) m.p. 138-140°C [Found C 69.7; H, 5.8% Calc for C$_{63}$H$_{63}$Cl$_2$P$_3$Ru:- C, 69.7; H, 5.8%] ν(RuCl) 320 cm$^{-1}$. $^{31}$P-{$_1$H} nmr [CH$_2$Cl$_2$/(CD)$_3$CO at 190 K] 74.3 (t), 25.1 (d) ppm ($^2$J$_{pp}$ 28.0 Hz); at 298 K, 39.9 (s) ppm.
Carbonyl[di(chloro)(N,N-dimethylformamide)bis(tri-p-tolylphosphine)]ruthenium(II):--

Carbon monoxide was bubbled through a suspension of \([\text{RuCl}_2\{\text{P(p-tolyl)}_3\}_3]\) (0.40g) in N,N-dimethylformamide (4.0 cm\(^3\)) for several minutes to give a yellow solution. Diethylether (5 cm\(^3\)) was then added, the solution shaken for one hour and the resulting yellow solid filtered off and dried in vacuo (Yield 85%): m.p. 173-175\(^{\circ}\)C. [Found: C, 62.6; H, 5.7; N, 1.6% Calc for \(\text{C}_{46}\text{H}_{49}\text{Cl}_2\text{NO}_2\text{P}_2\text{Ru}\): C, 62.6; H, 5.5; N, 1.6%]. \(\nu_{\text{CO}}\) 1935, \(\nu_{\text{CO}}\) (dmf) 1645; \(\nu\) (RuCl) 340 cm\(^{-1}\). \(\delta_{1\text{H}}\) nmr [CDCl\(_3\) at 298 K] 32.3 (s) ppm.

Tri-\(\mu\)-chloro-a-carbonyl-g-chlorotetrakis(tri-p-tolylphosphine)-diruthenium(II):--

The compounds \([\text{RuCl}_2\{\text{P(p-tolyl)}_3\}_3]\) (0.10g) and \([\text{Ru(CO)}\text{Cl}_2\text{(dmf)}-\{\text{P(p-tolyl)}_3\}_2]\) (0.08g) were refluxed together in ethanol (20 cm\(^3\)) for 6 h to give an orange solution. On cooling, an orange solid formed which was filtered off and dried in vacuo (Yield ca 80%); m.p. 155-157\(^{\circ}\)C [Found: C, 63.1; H, 5.3% Calc for \(\text{C}_{85}\text{H}_{84}\text{Cl}_4\text{OP}_4\text{Ru}_2\): C 64.2, H, 5.3%] \(\nu_{\text{CO}}\) 1975 cm\(^{-1}\). \(\delta_{1\text{H}}\) nmr [CDCl\(_3\) at 298 K] 47.6 (q) and 38.8 (q) ppm [\(\delta_{1\text{P}}\) 38.2, \(\delta_{1\text{P}^2}\) 25.1; \(\delta_{1\text{P}^3}\) 73.0; \(\delta_{1\text{P}^4}\) 97.5 Hz].

Tri-\(\mu\)-chloro-a-carbonyl-g-chloro-bc-bis(triphenylphosphine)-h1bis(tri-p-tolylphosphine)diruthenium (II) was obtained similarly from \([\text{RuCl}_2\{\text{P(p-tolyl)}_3\}_3]\) and \([\text{Ru(CO)}\text{Cl}_2\text{(dmf)}(\text{PPh}_3)_2]\) [Found: C, 67.5; H, 5.1% Calc for \(\text{C}_{79}\text{H}_{72}\text{Cl}_4\text{OP}_4\text{Ru}_2\): C 67.6; H, 5.1%] \(\nu_{\text{CO}}\) 1975 cm\(^{-1}\) \(\delta_{1\text{H}}\) nmr [CDCl\(_3\) at 298 K] 48.0 (q) and 40.2 (q) ppm [\(\delta_{1\text{P}}\) 34.2, \(\delta_{1\text{P}^2}\) 25.1; \(\delta_{1\text{P}^3}\) 83.2, \(\delta_{1\text{P}^4}\) 99.1 Hz].
Tri-μ-chloro-αq-dicarbonyl-b-chloro-tris(tri-p-tolylphosphine) diruthenium (II):

The complex [Ru(CO)Cl₂(MeOH)]₂[P(p-tolyl)₃]₂, prepared by recrystallisation of [Ru(CO)Cl₂(dmf)[P(p-tolyl)₃]₂] from methanol was shaken in CH₂Cl₂ for 4 days. The resultant solution was reduced in volume and light petroleum (bp 60-80°C) added to precipitate the complex as a yellow brown solid. νCO 1960 cm⁻¹. ³¹P-{¹H}nmr (CDCl₃ at 298K)-3 isomers a)
50.5 (s), 41.5 (q) ppm [J(PP) 25.5; δ(PP) 24.3 Hz]
b) 51.3 (s), 40.0 (q) ppm [J(PP) 24.9; δ(PP) 133.6 Hz]
c) 52.2 (s), 38.9 (q) ppm [J(PP) 26.1; δ(PP) 170.2 Hz].

Di-μ-chlorobis[chloro(thiocarbonyl)]bis(tri-p-tolylphosphine) ruthenium (II):— The complex [RuCl₂[P(p-tolyl)₃]₃] (0.25g) was refluxed in CS₂ (15 cm³) for 5 min to give a red solution which was cooled, filtered and reduced in volume (to ca. 5 cm³). Addition of light petroleum (bp 60-80°C) then precipitated a pink solid which was filtered off and dried in vacuo (Yield ca 15%) [Found: C, 62.5; H, 5.2% Calc for C₈₆H₅₈Cl₄P₄Ru₂S₂: C, 62.6; H, 5.1%] νCS 1290 cm⁻¹. ³¹P-{¹H}nmr [CDCl₃ at 298K] 29.5 (s), 42.5 (s) ppm. The remaining solution on standing for 6h deposited tri-μ-chloro-α-chloro-γ-(thiocarbonyl)tetraakis-(tri-p-tolylphosphine)diruthenium(II) as an orange solid which was filtered off and dried in vacuo (Yield ca. 30%); m.p. 160-162°C [Found: C, 64.2; H, 5.4%; Calc for C₈₅H₅₈Cl₄P₄Ru₂S: C, 63.6; H, 5.3%] νCS 1292 cm⁻¹ ³¹P-{¹H}nmr [CDCl₃ at 298 K] 47.6 (q) and 34.6 (q) ppm [J(P¹P²) 37.9, J(P³P⁴) 25.1; δ(P¹P²) 80.9, δ(P³P⁴) 74.9 Hz].
Ethylidiphenylphosphine Complexes

[Dichlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS\(^1\)-ruthenium(II)] carbodisulphide: Shaking the compound [RuCl\(_2\)(PETPh\(_2\))\(_3\)](0.20g) in carbon disulphide (20 cm\(^3\)) for one hour produced a red-pink solid which was filtered off (Yield 70%) m.p. 170-172\(^\circ\)C [Found: C, 55.1; H, 4.7% Calc for C\(_{44}H_{45}Cl_2P_3RuS_4\): C, 54.6; H, 4.6%] \(\nu(CS_2)\) 1515 cm\(^{-1}\); \(\nu(Ph_2Et^P-CS_2)\) \(\text{asym} 1115, 995 \text{ cm}^{-1}\). Dissolving this solid in CH\(_2\)Cl\(_2\) and reprecipitating with light petroleum (bp 60-80\(^\circ\)C) gave dichlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS\(^1\)-ruthenium (II) [Found: C, 57.1; H, 5.0% Calc for C\(_{43}H_{45}Cl_2P_3RuS_2\): C, 57.9; H, 5.0%] \(\nu(Ph_2Et^P-CS_2)\) \(\text{asym} 1115, 995 \text{ cm}^{-1}\) \(31^P-(^1H)\) \(\text{nmr} [\text{CDCl}_3 \text{ at } 298 K] \text{ AMX pattern,} \) \(\nu_A 41.1; \nu_M 34.0; \nu_X 9.2 \text{ ppm} [J_{AM} 28.9, J_{AX} 3.7, J_{MX} 9.2 \text{ Hz}].\) A small amount of the above complex was also produced, together with an orange solution, on refluxing [RuCl\(_2\)(PETPh\(_2\))\(_3\)] in CS\(_2\) for 3h. On standing for 2 days, or alternatively, by addition of light petroleum (bp 60-80\(^\circ\)C) to the orange solution, an orange solid was precipitated, consisting mainly of tri-u-chloro(chloro)bis(thiocarbonyl)tris(ethyldiphenylphosphine)diruthenium(II) \(\nu_{CS} 1295 \text{ cm}^{-1}\). \(31^P-(^1H)\) \(\text{nmr} [\text{CDCl}_3 \text{ at } 298 K] 49.2 \text{ (s) and} 36.8 \text{ (q) ppm} [J(PP) 35.7, \delta(PP) 84.1 \text{ Hz}].\)

Chlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS\(^1\)-(methanol)ruthenium(II)tetrphenylborate: The complex [RuCl\(_2\)(S\(_2\)CPETPh\(_2\))(PETPh\(_2\))\(_2\)] was dissolved in methanol to give a purple solution. Addition of NaBPh\(_4\) then precipitated the complex as a purple solid which was filtered off, m.p. 120-122\(^\circ\)C [Found: C, 66.3; H, 5.4% Calc for C\(_{68}H_{69}BClOP_3RuS_2\): C 67.7; H, 5.7%] \(\nu(Ph_2Et^P-CS_2)\) \(\text{asym} 1115, 980 \text{ (br), 850 (br)} \text{ cm}^{-1}\) \(31^P-(^1H)\) \(\text{nmr} [\text{CDCl}_3 \text{ at } 298 K] \text{ AMX pattern} \)
$\nu_A$ 44.6; $\nu_M$, 29.0; $\nu_X$ 16.3 ppm [J$_{AM}$ 28.0; J$_{AX}$ 3.5; J$_{MX}$ 11.3 Hz].

Carbonyldi(chloro)(N,N-dimethylformamide)bis(ethylidiphenylphosphine)ruthenium(II): - The compound [RuCl$_2$(PETPh$_2$)$_2$] (0.15g) was suspended in N,N-dimethylformamide (1.5 cm$^3$) and warmed gently in a very slow stream of carbon monoxide to deposit some yellow crystals. The solution was then cooled in ice, diethyl ether added, the complex filtered off and washed with diethyl ether, pentane and dried in vacuo at 40$^\circ$C; (Yield ca. 80% m.p. 167$^\circ$ (decomp) [Found: C, 54.6; H, 5.3; Cl, 10.2; N, 2.1% Calc for C$_{32}$H$_{37}$Cl$_2$NO$_2$P$_2$Ru: C, 54.8; H, 5.3; Cl, 10.1; N, 2.0%] $\nu_{CO}$ 1928; $\nu_{CO}$(dmf) 1641, $\nu$(RuCl) 327 cm$^{-1}$ 31P-{ $^1$H}nmr [CDCl$_3$ at 213 K] 32.8 (s) ppm; at 308K, 31.5 (s) ppm.

Reaction of [Ru(CO)Cl$_2$(dmf)(PETPh$_2$)$_2$] in methylene chloride solution: - [Ru(CO)Cl$_2$(dmf)(PETPh$_2$)$_2$] was shaken in CH$_2$Cl$_2$ for 10 hours. Light petroleum (bp 60-80$^\circ$C) was added to the resulting yellow solution and most of the solvent removed to precipitate a pale yellow powder. This solid was filtered and washed with diethyl ether. The 31P-{ $^1$H} nmr spectrum of this mixture (Fig. 1) has been discussed.

Reaction of [Ru(CO)Cl$_2$(dmf)(PETPh$_2$)$_2$] in benzene solution: - [Ru(CO)Cl$_2$(dmf)(PETPh$_2$)$_2$] was shaken in benzene for 24 hours. The solvent was then removed under vacuo to give an orange oil which was dissolved in CH$_2$Cl$_2$ (ca. 2.0 cm$^3$). Light petroleum (bp 60-80$^\circ$C) was then added slowly to give a yellow-orange solid which was filtered and washed with pentane. The 31P-{ $^1$H}nmr spectrum of this mixture (Fig. 2) has been discussed.
Reaction of $[\text{Ru(CO)}\text{Cl}_2\text{(dmf)}(\text{PETPh}_2)_2]$ with $[\text{RuCl}_2(\text{PETPh}_2)_3]$.-

The compounds $[\text{Ru(CO)}\text{Cl}_2\text{(dmf)}(\text{PETPh}_2)_2]$ (0.07g) and $[\text{RuCl}_2(\text{PETPh}_2)_3]$ (0.08g) (1:1 mol ratios) were refluxed in acetone (ca. 30 cm$^3$) for 5 hours. The solution was cooled and concentrated to ca. 5 cm$^3$. An excess of light petroleum (bp 60-80°C) was then added and the resulting orange solid filtered. The $^{31}\text{P-}^{1}\text{H}\text{nmr}$ spectrum showed the material to be a mixture of compounds (see earlier).

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References


Fig. 1  $^{31}$P-$^1$H nmr spectra in CDCl$_3$ of the product obtained on shaking $[\text{Ru(CO)Cl}_2(\text{dmf})(\text{PETPh}_2)_2]$ in CH$_2$Cl$_2$ a) at 213K
b) 308K

Fig. 2  $^{31}$P-$^1$H nmr spectrum in CDCl$_3$ at 213 K of product obtained on shaking $[\text{Ru(CO)Cl}_2(\text{dmf})(\text{PETPh}_2)_2]$ in C$_6$H$_6$. 
Ruthenium Complexes containing Group 5B Donor Ligands Part 8. Reaction of \([\text{Ru}_2(Y)\text{Cl}_4(\text{PPh}_3)_4]\) (Y = CO, CS) and \(\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}_2\) with various \(L\) \(L = \text{P(OR)}\text{Ph}_2\) \((R = \text{Me, Et})\), \(\text{P(OMe)}_2\text{Ph}\) and of \([\text{RuCl}_2\text{L}_3\text{ or 4}]\) with Carbon Monoxide.

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Reaction of \([\text{Ru}_2\text{YCl}_4(\text{PPh}_3)_4]\) (Y = CO, CS) with excess of \(L\) in benzene leads to facile bridge cleavage and ligand exchange to give mixtures of \([\text{RuYCl}_2\text{L}_3]\) and \([\text{RuCl}_2\text{L}_3\text{ or 4}]\) \(L = \text{P(OR)}\text{Ph}_2\) \((R = \text{Me, Et})\), \(\text{P(OMe)}_2\text{Ph}\). These monosubstituted carbonyl and thiocarbonyl compounds can also be synthesised by carbonylation of \([\text{RuCl}_2\text{L}_3\text{ or 4}]\) and reaction of \(\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}_2\) with excess of \(L\) respectively. In alcohols, \([\text{RuYCl}_2(\text{P(OR)}\text{Ph}_2)_3]\) rearrange to \([\text{Ru}(\text{Y})\text{Cl}(\text{P(OMe)}\text{Ph}_2)_3]\) and \(\{\text{Ru}(\text{Y})\text{Cl}(\text{P(OMe)}\text{Ph}_2)_3\}_2\) \(2^+\) respectively, whereas \([\text{Ru}(\text{Y})\text{Cl}_2(\text{P(OMe)}_2\text{Ph})_3]\) is recovered unchanged. Structures are assigned to these compounds mainly on the basis of \(^1\text{H}\) and \(^31\text{P}-(^1\text{H})\) nmr studies.

In previous papers, successful high yield syntheses of the triple chloride bridged complexes \([\text{Ru}_2(\text{Y})\text{Cl}_4(\text{PR}_3)_4]\) \((Y = \text{CO, CS}; \text{PR}_3 = \text{PPh}_3, \text{P(p-tolyl)}_3)\); which involved either direct reaction of \([\text{RuCl}_2(\text{PR}_3)_3]\) with \(\text{CS}_2\) or intermolecular coupling of \([\text{Ru}(\text{Y})\text{Cl}_2(\text{dmf})(\text{PR}_3)_2]\) with \([\text{RuCl}_2(\text{PR}_3)_3]\) \((1:1\text{ mol ratio})\) have been reported.\(^{1-3}\) Using the latter method, a pure sample of the mixed tertiary phosphine complex \([\text{P(p-tolyl)}_3)_2\text{ClRuCl}_3\text{Ru(CO)}(\text{PPh}_3)_2]\) was also obtained by reaction of
[\text{RuCl}_2(\text{P-tolyl})_3]_3 \text{ with } [\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})(\text{PPh}_3)_2]_2 \text{ and an isomeric mixture of } [\text{Ru}_2(\text{CO})\text{Br}_2\text{Cl}_2(\text{PPh}_3)_4] \text{ compounds has been generated.}^3

However, attempts to extend this method to the synthesis of other tertiary phosphine, phosphinite or phosphonite complexes of type [\text{Ru}_2(\text{Y})\text{Cl}_4\text{L}_4] \text{ have not been very successful.}^1 \text{ Thus, for example, although } ^{31}\text{P}-^{1}H \text{ nmr studies did indicate that some } [\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PETPh}_2)_4] \text{ was formed in the reaction of } [\text{RuCl}_2(\text{PETPh}_2)_3] \text{ with } [\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})(\text{PETPh}_2)_2], \text{ substantial amounts of other rearrangement products such as } [\text{Ru}(\text{CO})\text{Cl}_2(\text{PETPh}_2)_3] \text{ and } [\text{Ru}_2\text{Cl}_4(\text{PETPh}_2)_5] \text{ were also obtained and separation of these proved impossible.}^1

In this paper, the results of our attempts to prepare the compounds [\text{Ru}_2(\text{Y})\text{Cl}_4\text{L}_4] [L = \text{P(OR)}\text{Ph}_2, (R = \text{Me, Et}), \text{P(OMe)}_2\text{Ph}] \text{ by direct exchange of } L \text{ with } [\text{Ru}_2(\text{Y})\text{Cl}_4(\text{PPh}_3)_4] \text{ are described, together with a study of the reactions of various } [\text{RuCl}_2\text{L}_3 \text{ or } 4] \text{ compounds with carbon monoxide and of } [\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}_2] \text{ with various } L .

\text{Results and Discussion}

Reaction of [\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4] \text{ with an excess of } \text{P(OMe)}\text{Ph}_2 \text{ in benzene under reflux produced after lh., a bright yellow solution, which on addition of light petroleum (bp 60-80°C), yielded a yellow solid (A). The } ^{31}\text{P}-^{1}H \text{ nmr spectrum of (A) at 298 K in } C_6D_6 \text{ contained a singlet at 149.8}^6 \text{ (due to } [\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3])^4 \text{ and a doublet and triplet at 114.9 and 138.5}^6 \text{ respectively (Jpp = 29.6 Hz)} \text{ from } [\text{Ru}(\text{CO})\text{Cl}_2(\text{P(OMe)}\text{Ph}_2)_3] \text{ (see below). The ir spectrum of (A) contained a band at 1972 cm}^{-1} \text{ (v}_{\text{CO}}).}

Clearly, in addition to ligand exchange, facile bridge cleavage has also occurred as shown in the equation. The reaction was repeated using a 1:4 molar ratio of [\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4] \text{ to } \text{P(OMe)}\text{Ph}_2 \text{ which gave the same products, together with much unreacted starting material, thus indicating that the first step in this reaction is that of bridge cleavage.}
Unfortunately, chromatographic techniques failed to separate the two compounds and fractional recrystallisation proved impossible as it was found that both species rearranged in polar solvents (see later).

However, a pure sample of \([\text{Ru(CO)}\text{Cl}_2(\text{P(OMe)}\text{Ph}_2)_3]\) could be prepared by bubbling CO through a solution of \([\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3]\) in cold benzene. The ir spectrum, as for (A), contained a CO absorption band at 1972 cm\(^{-1}\) and, in addition, bands at 312 and 286 cm\(^{-1}\), consistent with \(\nu(\text{RuCl})\) vibrations from a chloride \textit{trans} to CO and a chloride \textit{trans} to phosphorus respectively.\(^5\) The \(^{31}\text{P}-\(^1\text{H}\) nmr spectrum exhibited an identical doublet and triplet pattern to that found for (A) whilst the \(^1\text{H}\) nmr spectrum at 30K in \(\text{C}_6\text{D}_6\) consisted of a triplet and doublet at 3.19 and 2.84\(^8\) respectively of intensity ratio 2:1. These results are consistent with structure (1), \((\text{Y} = \text{CO})\) containing \textit{cis} chloride groups and two magnetically equivalent and one non-equivalent \(\text{P(OMe)}\text{Ph}_2\) groups.

Likewise, although reaction of \([\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4]\) with an excess of \(\text{P(OMe)}\text{Ph}_2\) produced an inseparable mixture of \([\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3]\) and \([\text{Ru(CO)}\text{Cl}_2(\text{P(OMe)}\text{Ph}_2)_3]\), the latter could be prepared in a pure state by direct reaction of \([\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3]\) with CO in benzene. The \(^{31}\text{P}-\(^1\text{H}\), \(^1\text{H}\) nmr spectra (Tables 1 and 2 respectively) and ir spectrum (\(\nu_{\text{CO}} 1980 \text{ cm}^{-1}\); \(\nu(\text{RuCl}) 302, 279 \text{ cm}^{-1}\)) were also consistent with structure (1). This compound had been previously synthesised by reaction of \([\text{Ru(CO)}_2\text{Cl}_2]_n\) with \(\text{P(OMe)}\text{Ph}_2\) in ethanol, although in other instances, only mixtures of \([\text{Ru(CO)}\text{Cl}_2\text{L}_3]\) and \([\text{Ru(CO)}_2\text{Cl}_2\text{L}_2]\) \((\text{L} = \text{P(OMe)}\text{Ph}_2, \text{P(OMe)}_2\text{Ph})\) were produced by this route.\(^6\) Reaction of \([\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4]\) with excess \(\text{P(OMe)}_2\text{Ph}\) also gave a mixture of \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]\) and \([\text{Ru(CO)}\text{Cl}_2(\text{P(OMe)}_2\text{Ph})_3]\). However, in this case, neither of the compounds readily rearrange in polar solvents and, therefore, recrystallisation from \(\text{CH}_2\text{Cl}_2/\text{methanol}\) produced initially white crystals of \([\text{Ru(CO)}\text{Cl}_2(\text{P(OMe)}_2\text{Ph})_3]\) and later, yellow crystals of \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]\) were deposited.
Again spectroscopic data (Tables 1 and 2) indicated that the monocarbonyl complex had structure (1).

The reaction of CO with \([\text{RuCl}_2(\text{P(OME)}_2\text{Ph})_4]\) in cold \(\text{CH}_2\text{Cl}_2\) or benzene gave only starting material, but under reflux, a mixture of products was obtained. Spectroscopic evidence revealed the main product to be \([\text{Ru(CO)}\text{Cl}_2(\text{P(OME)}_2\text{Ph})_3]\) (1) together with small amounts of other monocarbonyl isomers and/or dicarbonyl species. The dicarbonyl complexes \([\text{Ru(CO)}_2\text{Cl}_2\text{L}_2]\) \([L = \text{P(OR)}_2\text{Ph}, \text{P(OR)}_2\text{Ph} (R = \text{Me, Et})]\) have, in fact, been previously prepared by addition of excess \(L\) to carbonylated solutions of "RuCl\(_3\)\(_2\)H\(_2\)O" in 2-methoxyethanol.\(^6\) As for \([\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4]\), reactions of \([\text{Ru}_2\text{Cl}_4(\text{CS})\text{(PPh}_3)_4]\) with \(\text{P(OR)}_2\text{Ph}\) gave an inseparable mixture of \([\text{RuCl}_2(\text{CS})(\text{P(OR)}_2\text{Ph})_3]\) and \([\text{RuCl}_2(\text{P(OR)}_2\text{Ph})_2]\) \((R = \text{Me, Et})\). However, \([\text{RuCl}_2(\text{CS})(\text{P(OR)}_2\text{Ph})_3]\) could be obtained in pure state by reaction of the double chloride bridged complex \([\text{RuCl}_2\text{(CS)(PPh}_3)_2]\) \(^2\) with \(\text{P(OR)}_2\text{Ph}\). For \([\text{RuCl}_2\text{(CS)(P(OMe)}_2\text{Ph})_3]\), the \(^3\text{P}-\{^1\text{H}\}\) nmr spectrum at 298 K in \(\text{C}_6\text{D}_6\) contained a triplet and doublet at 131.9 and 115.8 \(\delta\) respectively \((^2\text{J}_{\text{pp}} = 29.7 \text{ Hz})\) and ir spectral bands were observed at 1275 cm\(^{-1}\) \((\nu_{\text{CS}}\), 315 and 286 cm\(^{-1}\) \((\nu\text{RuCl})\). The \(^1\text{H}\) nmr spectrum in CDCl\(_3\) at 301 K consisted of a triplet and doublet at 3.23 and 3.14 \(\delta\) respectively of intensity ratio 2:1. Similar spectral data were obtained for \([\text{RuCl}_2\text{(CS)(P(OEt)}_2\text{Ph})_3]\) consistent with structure (1) \((Y = \text{CS})\).

The mixture produced in the reaction between \([\text{Ru}_2\text{Cl}_4(\text{CS})\text{(PPh}_3)_4]\) and excess of \(\text{P(OMe)}_2\text{Ph}\) could be separated by recrystallisation from \(\text{CH}_2\text{Cl}_2\)/methanol to give white crystals of \([\text{RuCl}_2\text{(CS)(P(OMe)}_2\text{Ph})_3]\), shown by ir and nmr spectroscopy to have structure (1).

As mentioned earlier, difficulties arose when trying to separate mixtures of \([\text{Ru}(\text{Y})\text{Cl}_2(\text{P(OR)}_2\text{Ph})_3]\) and \([\text{RuCl}_2(\text{P(OR)}_2\text{Ph})_2]\) because of the facile rearrangement reactions of both species in polar solvents (see ref.4 for a detailed discussion of the rearrangement reactions of \([\text{RuCl}_2(\text{P(OR)}_2\text{Ph})_2]\) compounds). Thus, dissolving \([\text{Ru}(\text{Y})\text{Cl}_2(\text{P(OMe)}_2\text{Ph})_3]\)
(Y = CO,CS) in methanol and adding NaBPh₄ gave colourless crystals analysing for [Ru(Y)Cl(P(OMe)Ph₂)₃]BPh₄ (Table 3). The mull ir spectra contained no evidence for coordinated solvent molecules but did have strong bands at ca. 300 cm⁻¹ attributable to terminal ν(RuCl) vibrations. The ³¹P⁻¹H) nmr spectra at both 213 and 298 K consisted of a singlet indicative of monomeric structures in which all the tertiary phosphinite groups were equivalent. Possibilities to explain this equivalence include a trigonal bipyramidal structure (2a), or more likely,* a square pyramidal or weakly solvated octahedral structure (2b), in which facile scrambling of axial and equatorial phosphinite ligands renders them equivalent on the nmr timescale. This conclusion was supported by the ¹H nmr spectra at 301 K which exhibited a single broad resonance at 2.97 δ. Furthermore, for each compound, conductivity measurements in CH₂Cl₂ were consistent with the presence of a 1:1 electrolyte in solution (see experimental section).

Dissolving [Ru(Y)Cl₂(P(OMe)Ph₂)₃] in ethanol containing NaBPh₄ also slowly deposited colourless crystals analysing for [Ru(Y)Cl(P(OEt)Ph₂)₃]BPh₄. However, in contrast to [Ru(Y)Cl(P(OMe)Ph₂)₃]BPh₄, the ³¹P⁻¹H) nmr spectra at 213 K showed complicated multiplet patterns at ca. 118 δ (see Fig , Y = CO). These spectra were not consistent with monomeric structures, since at 213 K, by analogy with the P(OMe)Ph₂ results, facile intramolecular

* X-ray structural data shows that most five coordinate d⁶ complexes have an essentially square pyramidal structure⁷ and this is supported by recent theoretical arguments.⁶
scrambling would still be expected. Therefore the existence of dimers in solution at this temperature is probable and furthermore, the complexity of the nmr patterns suggested the presence of more than one isomer.

For \( Y = \text{CO} \), cooling the sample to 198 K caused the resonance at 120.0 δ to decrease in intensity whilst the remainder of the spectrum remained unchanged, but on warming to 298 K the entire multiplet pattern collapsed to a single resonance at 119.0 δ. These results strongly indicated that the resonance at 120.0 δ was due to the monomeric cation \([\text{Ru(CO)}\text{Cl}(\text{P(OEt)}\text{Ph}_2)_3]^+\) which increased in concentration as the temperature was raised and the dimer dissociated. Indeed, conductivity measurements at 298 K in CH\(_2\)Cl\(_2\) were consistent with the presence of a 1:1 electrolyte. However, the presence of a dimeric structure in the solid state for both \( Y = \text{CO} \) and CS was supported by the occurrence of a broad band at 270 cm\(^{-1}\) and the absence of one at 300 cm\(^{-1}\) in their far infrared spectra. These appear to be the first cationic halide bridged Ru(II) carbonyl (and thiocarbonyl) complexes to be reported although several related neutral species such as \([\{\text{Ru}(Y)\text{Cl}_2(\text{PR}_3)_2\}^+]\) \([Y = \text{CO; PR}_3 = \text{PPh}_3,^9 \text{PMe}_2\text{Ph},^10 \text{Y = CS; PR}_3 = \text{PPh}_3,^2,11 \text{P(p-tolyl)}_3^1\] have been synthesised.

It should be noted that this behaviour of \([\{\text{Ru(CO)}\text{Cl}(\text{P(OEt)}\text{Ph}_2)_3\}^+]\)\(-\text{BPh}_4\)_2 in solution is analogous to that found for \([\{\text{RuCl}(\text{P(OEt)}\text{Ph}_2)_4\}^+]\)\(-\text{BPh}_4\)_4. This tendency of the P\((\text{OEt})\text{Ph}_2\) complexes to form dimeric species, compared to the corresponding P\((\text{OME})\text{Ph}_2\) complexes, which appear

* The possibility of frozen-out monomeric structures at this temperature (due to the bulkier P\((\text{OEt})\text{Ph}_2\) groups) seems unlikely in view of the fact that the \(^{31}\text{P}-^{1}\text{H}\) nmr spectrum of \([\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_3]\) is still a sharp singlet at 213 K.\(^4\)
to exist entirely as monomers, (also see ref. 4), must be attributed to
an electronic rather than a steric effect, since the smaller P(OMe)Ph₂
compounds would be expected to dimerise preferentially.

This tendency of [Ru(Y)Cl₂(P(OR)Ph₂)₃] to readily lose a chloride
ion in methanol to generate either five coordinate monomers or six
coordinate dimeric cations is unusual but not without precedent. Thus,
recently, [MX₂(dppp)₂] [M = Ru, Os; X = Cl,Br; dppp = Ph₂P(CH₂)₃PPh₂]
compounds were shown to lose a halide ion in boiling alcohol to give the
five coordinate cations [MX(dppp)₂]⁺, isolated as PF₆⁻ or BPh₄⁻ salts.¹²,¹³
Steric effects were clearly important here since the corresponding compounds
with smaller diposphines Ph₂P(CH₂)ₙPPh₂ (n = 1,2) showed no tendency to
lose halide ion. Similarly when [Ru(Y)Cl₂(P(OMe)₂Ph)₃] were dissolved
in methanol, no cationic complexes were generated and this can probably
be mainly attributed to the smaller steric requirements of the tertiary
phosphonite group.

Experimental

Microanalyses were by the University of Edinburgh Chemistry
Department. Infrared spectra were recorded in the region 4000-250 cm⁻¹
on Perkin Elmer 457 and 225 grating spectrometers using Nujol and
hexachlorobutadiene mulls on caesium iodide plates and in the region
400-200 cm⁻¹ on a Beckman RIIC IR 720 far i.r. spectrometer using pressed
polythene discs. ¹H nmr spectra were obtained on a Varian Associates
HA-100 spectrometer and ³¹P nmr spectra (proton noise decoupled) on a
Varian Associates XL-100 spectrometer operating in the Pulse and Fourier
Transform mode at 40.5 MHz. Chemical shifts are reported in ppm to high
frequency of 85% H₃PO₄. Conductivity measurements were made at 298 K
using a model 310 Portland Electronics conductivity bridge. As described
earlier,⁴ plots of λ₀-λ vs C¹ gave a straight line whose slope is a
function of the ionic charges. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Materials

Ruthenium trichloride trihydrate (Johnson Matthey); carbon monoxide (Air Products); P(OR)\textsubscript{2} \text{Ph}_2 (R = Me, Et), P(OMe)_2\text{Ph} [Maybridge]. Sodium tetraphenylborate (BDH). \[ \text{[Ru}_2(\text{Y})\text{Cl}_4(\text{PPh}_3)_4] (Y = \text{CO, CS}), \]
\[ \text{[RuCl}_2(\text{CS})(\text{PPh}_3)_2]_2, \text{[RuCl}_2\text{L}_3] \text{[L = P(OR)\text{Ph}_2(R = Me, Et)}^4, \text{and } \]
\[ \text{[RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]_4 \text{ were prepared as described earlier.} \]

\text{[P-}^{1}\text{H} \text{ and } ^1\text{H nmr data are given in Tables 1 and 2 respectively; analytical data in Table 3. All reactions were carried out in degassed solvents and, apart from carbonylation reactions, under an atmosphere of nitrogen. The proposed } \nu(\text{RuCl}) \text{ vibrational bands are underlined.}

\text{Carbonyl(dichloro)tris(methylidiphenylphosphinite)ruthenium(II): Carbon monoxide gas was bubbled through a solution of } \text{[RuCl}_2(\text{P(OMe)}_2\text{Ph})_3] \text{ in benzene for } 1 \text{ m. The resulting pale yellow solution was reduced in volume and light petroleum (bp. 60-80°C) added. A pale yellow solid precipitated which was filtered off and washed with light petroleum (bp. 60-80°C); mp. 128-130°C; } \nu_{\text{CO}} \text{ 1972 cm}^{-1}; \text{ far } \text{ir spectrum 312, 286, 275, 233 cm}^{-1}. \text{ A similar method was used to prepare}

\text{Carbonyl(dichloro)tris(ethylidiphenylphosphinite)ruthenium(II) from}
\[ \text{[RuCl}_2(\text{P(OEt)}_2\text{Ph})_3] \text{ as a white solid; m.p. 203-205°C; } \nu_{\text{CO}} \text{ 1980 (strong), 1935 (weak) cm}^{-1}; \text{ far } \text{ir spectrum 302, 279, 260, 238 cm}^{-1}. \]

\text{Carbonyl(dichloro)tris(dimethylphenylphosphonite)ruthenium(II): The complex}
\[ \text{[Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4] (0.20 g) \text{ was refluxed with excess of P(OMe)_2\text{Ph}} \]
\[ \text{(0.40 cm}^3) \text{ in benzene (30 ml) for 1h. The resulting yellow solution was reduced in volume to ca 10 ml and light petroleum (bp 60-80°C) added. The yellow solid which precipitated was filtered off and recrystallisation from CH}_2\text{Cl}_2/\text{MeOH produced colourless crystals of the complex;}
]
\[ \nu_{\text{CO}} 1985 \text{ cm}^{-1}; \nu(\text{RuCl}) 305, 280 \text{ cm}^{-1}. \]
The remaining yellow solution deposited after several days yellow crystals of \([\text{RuCl}_2(\text{P(OMe)_2}Ph)_2]^{-}\).
Similarly, \textit{dichloro(thiocarbonyl)tris(dimethylphenylphosphonite)ruthenium(II)} was prepared as colourless crystals from \([\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_4]\); m.p. 149-151°C; \[ \nu_{\text{CS}} 1305 \text{ cm}^{-1}; \nu(\text{RuCl}) 312, 274 \text{ cm}^{-1}. \]

\textit{Dichloro(thiocarbonyl)tris(methylidiphenylphosphinite)ruthenium(II)}:
The complex \([\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2]^{-}\) (0.20 g) was refluxed with \(\text{P(OMe)_2Ph}_2\) (0.30 ml) in benzene (30 ml) for 1 h. The resulting yellow solution was reduced in volume to ca 10 ml and light petroleum (b.p. 60-80°C) was added to precipitate the complex as a yellow solid which was filtered off, washed with light petroleum (b.p. 60-80°C) and dried in vacuo; m.p. 110-112°C; \[ \nu_{\text{CS}} 1275 \text{ cm}^{-1}; \] far ir spectrum 315, 286, 272, 233 cm\(^{-1}\).

Similarly, \textit{dichloro(thiocarbonyl)tris(ethylidiphenylphosphinite)ruthenium(II)} was prepared as a yellow solid; \[ \nu_{\text{CS}} 1295 \text{ cm}^{-1}; \] far ir spectrum 305, 280, 265 cm\(^{-1}\).

\textit{Carbonyl(chloro)tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate}:
The complex \([\text{Ru(CO)}\text{Cl}_2(\text{P(OMe)}\text{Ph}_2)_3]\) (0.20 g) was dissolved in methanol (15 ml) containing \(\text{NaBPh}_4\) (0.20 g). After 24 h, white crystals of the complex were deposited; m.p. 193-195°C; \[ \nu_{\text{CO}} 1975 \text{ cm}^{-1}; \nu(\text{RuCl}) 303 \text{ cm}^{-1}. \] Conductivity at 298 K in \(\text{CH}_2\text{Cl}_2\): slope of \(\Lambda_0-\Lambda\) vs \(\text{C}^2\) = 148 (for \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)_2Ph}_2)_6]\) \(\text{BPh}_4\), slope = 165). In the same way, \textit{chloro(thiocarbonyl)tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate} was prepared as white crystals; m.p. 174-176°C; \[ \nu_{\text{CS}} 1285 \text{ cm}^{-1}; \nu(\text{RuCl}) 301 \text{ cm}^{-1}; \] conductivity at 298 K in \(\text{CH}_2\text{Cl}_2\): slope of \(\Lambda_0-\Lambda\) vs \(\text{C}^2\) = 156.

\textit{(Bis)[carbonyl(chloro)tris(ethylidiphenylphosphinite)ruthenium(II)]tetraphenylborate}:
The complex \([\text{RuCl}_2(\text{CO})(\text{P(CEt)_2Ph}_3)]\) (0.20 g) was dissolved in ethanol (15 ml) containing \(\text{NaBPh}_4\) (0.20 g). Over a period of 3 days white crystals of the complex were deposited; m.p. 198-200°C;
$v_{CO}$ 1660 cm$^{-1}$; far ir spectrum 270, 262, 263, 256 cm$^{-1}$. Conductivity in CH$_2$Cl$_2$ at 298 K slope of $A_0 - A$ vs $c^2$ = 198. Likewise, [RuCl$_2$(CS)(P(OEt)Ph)$_2$]$_3$ dissolved in ethanol containing NaBPh$_4$ produced bis[chloro(thiocarbonyl)tris(ethylidiphenylphosphinite)ruthenium(II)]tetraphenylborate: m.p. 112-114°C; $v_{CS}$ 1285 cm$^{-1}$; $v$(RuCl) 270 cm$^{-1}$.

We thank Johnson-Matthey Ltd., for loans of ruthenium trichloride trihydrate, the S.R.C., for support (W.J.S.), and Dr. A.S.F. Boyd and Mr. J.R.A. Millar for obtaining the $^{31}$P and $^1$H nmr spectra respectively.

References


L = P(O\text{Me})\text{Ph}_2, P(O\text{Et})\text{Ph}_2, P(O\text{Me})_2\text{Ph}

Y = CO, CS

(1)

(2a)

(2b)
<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>T/K</th>
<th>δ (ppm)</th>
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<tr>
<td>Ru(CO)Cl₂(P(OMe)Ph₂)₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>138.5 (t)</td>
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<td>(Jpp 29.6 Hz)</td>
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<td></td>
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<td>114.9 (d)</td>
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<tr>
<td>Ru(CO)Cl₂(P(OST)Ph₂)₃</td>
<td>CDCl₃</td>
<td>298</td>
<td>135.4 (t)</td>
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<td></td>
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<td>(Jpp 30.0 Hz)</td>
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<td>115.1 (d)</td>
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<tr>
<td>Ru(CO)Cl₂(P(OMe)₂Ph)₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>157.4 (t)</td>
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<td>(Jpp 37.3 Hz)</td>
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<td>144.0 (d)</td>
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<td>RuCl₂(CS)(P(OMe)Ph)₂₃</td>
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<td>131.9 (t)</td>
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<td>(Jpp 29.7 Hz)</td>
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<td>115.8 (d)</td>
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<tr>
<td>RuCl₂(CS)(P(OST)Ph)₂₃</td>
<td>C₆D₆</td>
<td>298</td>
<td>130.0 (t)</td>
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<td>(Jpp 29.7 Hz)</td>
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<td>112.7 (d)</td>
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<td>RuCl₂(CS)(P(OMe)₂)Ph₃</td>
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<td>AB₂ pattern;</td>
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<td>νₐ 152.6</td>
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<td></td>
<td>νₐ 143.4 (Jpp 35.7 Hz)</td>
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<td>125.4 (s)</td>
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<tr>
<td>[Ru(CO)Cl(P(OMe)Ph₂)₃]BPh₄</td>
<td>CDCl₃</td>
<td>213</td>
<td>120.0 (s)</td>
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<td>122.7-115.2</td>
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<tr>
<td>[RuCl(CS)(P(OMe)Ph₂)₃]₂BPh₄</td>
<td>CDCl₃</td>
<td>213</td>
<td>123.0 (s)</td>
</tr>
<tr>
<td>[RuCl(CS)(P(OST)Ph₂)₃]₂(BPh₄)₂</td>
<td>CDCl₃</td>
<td>213</td>
<td>120.0-114.4</td>
</tr>
</tbody>
</table>

s, singlet; d, doublet; t, triplet.

a Multiplet ranging over values stated.
### Table 2

Hydrogen-1 nmr data for some Ruthenium compounds at 301 K

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<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Phenyl $^a$</th>
<th>Methylene Resonances</th>
<th>Methyl $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(CO)$_2$(P(OMe)Ph)$_2$</td>
<td>CD$_6$</td>
<td>6.90-8.40</td>
<td>-</td>
<td>3.19 (t) (N=11.5 Hz) 2.84 (d) ($^{2}J_{PH}=11.5$ Hz)</td>
</tr>
<tr>
<td>Ru(CO)$_2$(P(OEt)Ph)$_2$</td>
<td>CDCl$_3$</td>
<td>7.20-8.10</td>
<td>3.20-3.60 $^b$</td>
<td>0.97 (t), 0.87 (t) ($^{3}J_{HH}=7.0$ Hz)</td>
</tr>
<tr>
<td>Ru(CO)$_2$(P(OMe)$_2$Ph)</td>
<td>CDCl$_3$</td>
<td>7.10-7.80</td>
<td>-</td>
<td>3.94 (t) (N=11.0 Hz) 3.69 (t) (N=11.0 Hz) 3.61 (d) ($^{2}J_{PH}=11.5$ Hz)</td>
</tr>
<tr>
<td>RuCl$_2$(CS)(P(OMe)Ph)$_2$</td>
<td>CDCl$_3$</td>
<td>6.80-8.00</td>
<td>-</td>
<td>3.23 (t) (N=11.2 Hz) 3.14 (d) ($^{2}J_{PH}=11.5$ Hz)</td>
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<tr>
<td>RuCl$_2$(CS)(P(OEt)Ph)$_2$</td>
<td>CDCl$_3$</td>
<td>7.00-8.20</td>
<td>3.30-3.56 $^b$</td>
<td>0.91 (t) 0.88 (t) ($^{3}J_{HH}=7.0$ Hz)</td>
</tr>
<tr>
<td>RuCl$_2$(CS)(P(OMe)$_2$Ph)</td>
<td>CDCl$_3$</td>
<td>7.20-7.80</td>
<td>-</td>
<td>4.04 (t) (N=11.2 Hz) 3.71 (t) (N=11.2 Hz) 3.73 (d) ($^{3}J_{PH}=11.3$ Hz)</td>
</tr>
<tr>
<td>[Ru(CO)Cl(P(OMe)Ph)$_2$]$_2$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>6.90-7.50</td>
<td>-</td>
<td>2.97 $^b$</td>
</tr>
<tr>
<td>[Ru(CO)Cl(P(OEt)Ph)$_2$]$_2$(BPh$_4$)$_2$</td>
<td>CDCl$_3$</td>
<td>6.90-7.50</td>
<td>3.22</td>
<td>0.79</td>
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<tr>
<td>[RuCl(CS)(P(OMe)Ph)$_2$]$_2$BPh$_4$</td>
<td>CDCl$_3$</td>
<td>6.95-7.50</td>
<td>-</td>
<td>2.97 $^b$</td>
</tr>
</tbody>
</table>

(d) - doublet  (t) - triplet  
N = |$J$(PH) + $J$(PH)$_1$|

$^a$ Multiplet between stated values.  $^b$ Broad resonance
### Table 3

Analytical data for some new ruthenium(II) carbonyl and thiocarbonyl complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>% Found</th>
<th>% Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>( \text{Ru} (\text{CO}) \text{Cl}_2 \text{(P(OMe)\text{Ph}_2)}_3 )</td>
<td>56.4</td>
<td>4.5</td>
</tr>
<tr>
<td>( \text{Ru} (\text{CO}) \text{Cl}_2 \text{(POEt\text{Ph}_2)}_3 )</td>
<td>57.8</td>
<td>5.1</td>
</tr>
<tr>
<td>( \text{Ru} (\text{CO}) \text{Cl}_2 \text{(P(OMe)\text{Ph})}_3 )</td>
<td>42.3</td>
<td>4.5</td>
</tr>
<tr>
<td>( \text{RuCl}_2 \text{(CS) (P(OMe)\text{Ph}_2)}_3 )</td>
<td>56.0</td>
<td>4.6</td>
</tr>
<tr>
<td>( \text{RuCl}_2 \text{(CS) (POEt\text{Ph}_2)}_3 )</td>
<td>57.1</td>
<td>5.0</td>
</tr>
<tr>
<td>( \text{RuCl}_2 \text{(CS) (P(OMe)\text{Ph})}_3 )</td>
<td>41.4</td>
<td>4.6</td>
</tr>
<tr>
<td>( [\text{Ru} (\text{CO}) \text{Cl (P(OMe)\text{Ph}_2)}_3 ] \text{BPH}_4 )</td>
<td>67.6</td>
<td>5.3</td>
</tr>
<tr>
<td>( [\text{Ru} (\text{CO}) \text{Cl (POEt\text{Ph}_2)}_3 ]_2 (\text{BPH}_4)_2 )</td>
<td>68.8</td>
<td>5.6</td>
</tr>
<tr>
<td>( [\text{RuCl(CS) (P(OMe)\text{Ph}_2)}_3 ] \text{BPH}_4 )</td>
<td>66.9</td>
<td>5.2</td>
</tr>
<tr>
<td>( [\text{RuCl(CS) (POEt\text{Ph}_2)}_3 ]_2 (\text{BPH}_4)_2 )</td>
<td>67.9</td>
<td>5.5</td>
</tr>
</tbody>
</table>
$^{31}P-{^1}H$ nmr spectrum of $\left\{ \text{Ru(CO)}\text{Cl(PEt}_{3}\text{Ph}_2)_{3}} \right\}_2 \left\{ \text{BPh}_4 \right\}_2$ in CDCl$_3$ at 213 K
chemical shift (p.p.m.)

120.02

121.25
Cationic, Neutral and Anionic Complexes of Ruthenium(II) containing \( \eta^6 \)-Arene Ligands.

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Summary

Reaction of \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]\) with an excess of CsCl/HCl in ethanol gives the first anionic arene complex of ruthenium Cs[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_3](\text{II}) although in aqueous solution this readily loses a chloride ion to give \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2(\text{H}_2\text{O})]\) and reactions with various Lewis bases give the compounds \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\text{L}] (\text{L} = \text{C}_5\text{H}_5\text{N}, \text{Me}_2\text{SO}, \text{PR}_3\text{ etc})\). Reaction of \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]\) with \text{NH}_4\text{PF}_6 in methanol gives high yields of the triple chloride bridged complex \([\text{Ru}_2(\text{C}_6\text{H}_6)\text{Cl}_3]\text{PF}_6(\text{III})\) which, although stable in \text{MeNO}_2, readily undergoes bridge cleavage reactions in water and \text{Me}_2\text{SO}. Reaction of (III) with various Lewis bases produces the new monomeric, ruthenium(II), arene cations \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\text{L}]\text{PF}_6 (\text{L} = \text{C}_5\text{H}_5\text{N}, \text{Et}_2\text{S}, \text{AsPh}_3, \text{PR}_3\text{ etc})\).
Introduction

In recent years, some reactions of the unusual $\eta^6$-arene complexes $\{(\text{arene})_2\}_2$ (arene = C$_6$H$_6$, C$_6$H$_5$OMe, p- and m-C$_6$H$_4$Me$_2$, C$_6$H$_5$Me, 1,3,5-C$_6$H$_3$Me$_3$, p-MeC$_6$H$_4$CHMe$_2$; X = Cl or Br) have been investigated by several workers [1-7]. In particular, bridge cleavage reactions with a variety of Lewis bases to give the neutral, monomeric complexes $[\text{Ru}(\text{arene})X_2L]$ ($L = \text{PR}_3$, P(OR)$_3$, AsR$_3$, C$_5$H$_5$N etc) are well documented [1-3].

In this paper, we now report the full results [8] of the formation of the benzene anion $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_3]^{-}$ and the triple chloride bridged cation $[\text{C}_6\text{H}_3\text{RuCl}_3\text{RuC}_6\text{H}_3]^{+}$ from $[\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]$, together with details of the reactions of these compounds with various Lewis bases.

Results and Discussion

a) Synthesis and reactions of Cs[Ru(C$_6$H$_6$)Cl$_3$]

As reported earlier [9], reaction of the compound $[\{\text{Ru(CO)}\text{Cl}_2\}((\text{C}_7\text{H}_8))_2]$ (C$_7$H$_8$ = bicyclo [2.2.1] hepta-2,5-diene) with MCl/HCl ($M = \text{Ph}_3^-$ (PhCH$_2$)$_2$P$^+$, Cs$^+$) in degassed acetone gave a high yield of the first anionic diene complex of ruthenium M[Ru(CO)Cl$_3$(C$_7$H$_8$)]. An attempt has now been made to synthesise the first anionic $\eta^6$-arene ruthenium complex using a similar preparative route. Thus, shaking $[\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]$(I) with a mixture of excess CsCl and concentrated HCl in ethanol for several days gave an orange powder analysing closely for Cs[Ru(C$_6$H$_6$)Cl$_3$] (II) although it was always difficult to obtain this complex completely free of CsCl. The null i.r. spectrum of (II) indicated the presence of coordinated benzene and contained a broad band at 280 cm$^{-1}$ assigned to terminal $\nu$(RuCl) stretching vibration(s). Since compound (II) possesses $C_{3v}$ symmetry, two $\nu$(RuCl) bands were expected and thus, the broad band at 280 cm$^{-1}$
might contain both the \( a_1 \) and e vibrational modes or a weak band at 298 cm\(^{-1}\) could be assigned to one of the \( \nu(RuCl) \) bands. Unfortunately, attempts to make the corresponding \([Ru(C_6H_6)X_2]^{-} (X = Br, I)\) anions, either by reaction of \([Ru(C_6H_5Cl)X_2]^{-}\) or Cs[\(Ru(C_6H_6)Cl_3\)] with \( X^- \) were unsuccessful, only \([Ru(C_6H_5)X_2]^{-}\) being recovered from the reaction mixture in each case.

As expected, Cs[\(Ru(C_6H_6)Cl_3\)] was more soluble in water than \([Ru(C_6H_5)Cl_2]^{-}\) and an aqueous solution of (II) was highly conducting (eg. for a 10\(^{-3}\) mol dm\(^{-3}\) solution, \( \nu_m = 374 \text{ S cm}^2 \text{ mol}^{-1} \)). Unfortunately the unavoidable presence of a small amount of CsCl, together with the fact that \(^1\)H nmr studies on (II) in aqueous solution indicated that extensive dissociation of chloride ion occurred meant that no firm conclusion about electrolyte type could be drawn from these conductivity measurements.

The \(^1\)H nmr spectrum of Cs[\(Ru(C_6H_6)Cl_3\)] in D\(_2\)O consisted of a single \( \eta^6-C_6H_6 \) resonance at 6.40\(\delta\) whereas that of \([Ru(C_6H_5)Cl_2]^{-}\) in D\(_2\)O showed two coordinated benzene resonances at 6.39(vs) and 6.50(w)\(\delta\) which previous workers have assigned to either the aqua complexes \([Ru(C_6H_6)Cl(D_2)O]_2]^+\) and \([Ru(C_6H_5)(D_2)O]^{2+}\) respectively or to a combination of one of these cations and the neutral complex \([Ru(C_6H_6)Cl(D_2)O][\_1]\). It is therefore

* Zelonka and Baird [1] quoted the resonance positions for \([Ru(C_6H_5)Cl_2]^{-}\) in D\(_2\)O at 5.93 and 6.03\(\delta\). The discrepancy between their work and the chemical shifts given above probably arises from the fact that these chemical shifts are relative to an external TMS capillary whereas in ref [1] they are with respect to an internal TMS lock. Support for this explanation comes from the shift to high frequency observed for the co-ordinated \( \eta^6-C_6H_6 \) resonance in the \(^1\)H nmr spectrum of \([Ru(C_6H_5)Cl(PMe_2Ph)]\) when run in CDCl\(_6\) with respect to an external TMS capillary (5.95\(\delta\)) as opposed to an internal TMS reference (5.35\(\delta\)). Also, the difference between the chemical shifts of the two \( \eta^6-C_6H_6 \) resonances of \([Ru(C_6H_5)Cl_2]^{-}\) in D\(_2\)O is very similar with respect to both the external TMS reference (0.11\(\delta\)) and the internal TMS lock (0.10\(\delta\)).
very likely that the signal at 6.405 observed for (II) in D₂O is due to
an aqua complex formed by displacement of chloride ion, and by reference
to the reactions of (II) with Lewis bases, (see below), this aqua complex
is probably the neutral [Ru(C₆H₅)Cl₂(D₂O)]. In an attempt to suppress
this dissociation process and obtain the ¹H nmr spectrum of (II), large
amounts of CsCl/HCl were added to the D₂O solution of (II). Unfortunately,
the residual water peak became more intense and shifted to higher
frequencies (from 5.20 to 5.90δ), thus obscuring any new ⁶-C₆H₆ resonance,
and furthermore, slow precipitation of [{Ru(C₆H₅)Cl₂₂}₂] also occurred.

Earlier, Ph₃(PhCH₂)₃P[Ru(CO)Cl₃(C₇H₈)] was shown to be a good
precursor for synthesising a wide range of anionic complexes of the
type Ph₃PhCH₂P[Ru(CO)Cl₃L₂] (L = AsPh₃, C₅H₅N, Me₂S etc) via displa-
cement of diene [10]. Attempts, however, to synthesise the unknown fac-
[RuCl₃L]⁻ anions by reaction of Cs[Ru(C₆H₅)Cl₃] with excess of various
L gave only neutral complexes. Thus, either shaking or gently refluxing
(II) with excess of pyridine in methanol gave a yellow solution, and the
orange solid isolated from this by concentration followed by precipitation
with diethyl ether analysed very closely for [Ru(C₆H₅)Cl₂(C₅H₅N)]. The
compound was insoluble in most deuterated solvents except d⁶-Me₂SO and
its ¹H nmr spectrum in this solvent showed broad resonances at ca. 7.3
and 8.3δ (C₅H₅N) plus two ⁶-C₆H₆ resonances at 5.65 and 5.90δ. The
latter was assigned to the d⁶-Me₂SO complex [Ru(C₆H₅)Cl₂(d⁶-Me₂SO)],
(reported in ref [1] to have an ⁶-C₆H₆ ¹H nmr resonance at 5.93δ)
and this was verified by synthesising [Ru(C₆H₅)Cl₂(Me₂SO)], either by
refluxing [Ru(C₆H₅)Cl₂(C₅H₅N)] or Cs[Ru(C₆H₅)Cl₃] with excess Me₂SO in
methanol. In contrast, prolonged refluxing of (II) in neat pyridine
gave a mixture of [Ru(C₆H₅)Cl₂(C₅H₅N)] and the well-known [11] trans-
[RuCl₂(C₅H₅N)₄].
The products from the reaction of compound (II) and tertiary phosphines were dependent both on the reaction conditions and the nature of the phosphine. Thus, if (II) was shaken with excess PR₃ in methanol (PR₃ = PPh₃, PMe₂Ph, PMePh₂) the previously reported [1-3] monomeric complexes [Ru(C₆H₆)Cl₂(PR₃)] were formed. Similarly, [Ru(C₆H₆)Cl₂(SbPh₃)] was prepared by shaking (II) and excess SbPh₃ in methanol. However, under reflux conditions, the reaction with tertiary phosphines resulted in loss of the benzene ring from Cs[Ru(C₆H₆)Cl₃]. For example, refluxing (II) with excess of PMe₂Ph in methanol gave cis-[RuCl₂(PMe₂Ph)₄], previously synthesised either by reaction of excess PMe₂Ph with [RuCl₂(PPh₃)₃] in degassed light petroleum (bp 60 - 80°C) or with mer-[RuCl₃(PMe₂Ph)₃] in hexane [12]. In CH₂Cl₂, cis-[RuCl₂(PMe₂Ph)₄] readily rearranged to [Ru₂Cl₃(PMe₂Ph)₆]Cl[12]. In contrast, refluxing (II) with excess PPh₃ in methanol gave [RuCl₂(PPh₃)₃], previously prepared by refluxing "RuCl₃·xH₂O" with excess of PPh₃ in methanol [13].

Hence, although the complex Cs[Ru(C₆H₆)Cl₃] is in itself of interest in so much as it represents the first anionic arene complex of ruthenium, the lability of the coordinated benzene group is very much less than that of the diene in [Ru(CO)Cl₃(C₇H₈)]⁻. Thus, loss of chloride ion from [Ru(C₆H₆)Cl₃]⁻ occurs much more readily than loss of the C₆H₆ ring and therefore, little is to be gained by using the [Ru(C₆H₆)Cl₃]⁻ anion rather than [[Ru(C₆H₆)Cl₂]²⁻] as a starting material.

b) Synthesis of [C₆H₆RuCl₃RuC₆H₆]PF₆

As reported earlier by Bennett and Smith [3], the reaction of [[Ru(C₆H₆)Cl₂]²⁻] with hot water gave an orange solution from which NH₄PF₆ slowly precipitated in ca 40% yield, an orange solid identified as [Ru₂(C₆H₆)Cl₃]PF₆ (IIIA). In our hands, however, this reaction produced only low variable yields (ca. 12%) of (IIIA) plus, on one
occasion, a further product (see experimental section) shown by X-ray analysis [14] to be \([\text{Ru}(\text{NH}_3)_2(\text{C}_6\text{H}_6)\text{Cl}]_3(\text{PF}_6)_3\)\(_\text{NH}_4\text{PF}_6\). Since the \([\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}]_3^+\) cation is isoelectronic with \([\text{Rh}_2\text{Cl}_3(\text{C}_5\text{Me}_5)_2]^+\), which was isolated in high yield from reaction of \([\{\text{RhCl}_2(\text{C}_5\text{Me}_5)\}_2]\) with NaBPh\(_4\) in methanol [15], a similar preparative route for (III) has been examined. Thus, stirring the dark red-brown \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}]_2\) in methanol at ambient temperature with a slight excess of NH\(_4\text{PF}_6\) for 24h gave, in high yield, (\(>90\%\)) a dark orange-yellow solid which analysed quite well for \([\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}]_3\text{PF}_6\) (IIIb). No apparent reaction occurred in the absence of NH\(_4\text{PF}_6\) or if methanol was replaced by acetone.

The null ir spectrum of (IIIb) confirmed the presence of PF\(_6^-\) and in the Far ir spectrum two intense bands at 276, 264 cm\(^{-1}\) were observed, indicative of bridging \(\nu(\text{RuCl})\) vibrations (cf in ref [3], \(\nu(\text{RuCl})\) of (IIIa) quoted at 265 cm\(^{-1}\)). Compound (IIIb) gave conducting solutions in MeNO\(_2\) with values characteristic of 1:1 electrolytes [16] (eg. for a 10\(^{-3}\) mol dm\(^{-3}\) solution, \(\nu_m = 82\) S cm\(^{2}\) mol\(^{-1}\)) and this was supported by \(\nu_0 - \nu_C vs C^\frac{1}{2}\) plots over a range of concentrations which had a slope characteristic of 1:1 electrolytes (see experimental section).

The \(^1\)H and \(^{13}\)C-\(^1\)H nmr spectra of (IIIb) in d\(^3\)-MeNO\(_2\) at ambient temperature both showed a single sharp resonance for the \(\eta^6\text{-C}_6\text{H}_6\) groups at 5.905 and 82.0 ppm respectively, indicating that the dimeric unit remained intact in this solvent.

However, in other solvents such as D\(_2\)O and d\(^6\)-Me\(_2\)SO, more than one \(\eta^6\text{-C}_6\text{H}_6\) resonance was observed. Thus, the \(^1\)H nmr spectrum of (IIIa or b) in D\(_2\)O contained two \(\eta^6\text{-C}_6\text{H}_6\) resonances at 6.35 and 6.486 of comparable intensity [3], only a single resonance for (IIIa) in D\(_2\)O at 6.045 was reported. As discussed earlier, the difference in chemical shift is probably due to the different references used but the observation of only one signal for (IIIa) in ref [3] is puzzling.
intensity. These resonance positions are virtually identical to those found for \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]^-\) dissolved in D$_2$O [6.39 and 6.50δ — see section a)] indicating facile bridge cleavage has occurred as shown in the equation.

\[
\begin{align*}
\text{Cl} & \quad \text{Ru} \quad \text{Cl} \quad \text{Ru} \quad \text{Cl} \\
\text{Solvent} & \quad \text{Cl} \quad \text{Ru} \quad \text{Solvent} \quad \text{Cl} \\
\text{Solvent} & \quad \text{Cl} \quad \text{Ru} \quad \text{Cl}
\end{align*}
\]

In d$^6$-Me$_2$SO, three singlets were observed in the $^1$H nmr spectrum of (IIIb) at 5.95(vs), 6.15(w) and 6.50(s) δ which corresponded closely to the quoted positions of the $^6$-C$_6$H$_6$ resonances for the species [Ru-(C$_6$H$_6$)$_2$Cl$_2$(d$^6$-Me$_2$SO)]$^+$(5.93δ), [Ru(C$_6$H$_6$)Cl(d$^6$-Me$_2$SO)$_2$]$^+$(6.12δ) and [Ru(C$_6$H$_6$)(d$^6$-Me$_2$SO)$_3$]$^{2+}$(6.475) [1]. The relative intensities of these signals suggested that the monocation has reacted further with d$^6$-Me$_2$SO to give the dication.

As discussed elsewhere [17] for the closely related [Ru$_2$Cl$_3$L]$^+$ cations, (L = PR$_3$, P(OR)$_2$Ph$_2$, P(OR)$_2$Ph), the most likely mechanism of formation of [Ru$_2$(C$_6$H$_6$)$_2$Cl$_3$]$^+$ is by intermolecular coupling of the weakly solvated monomers [Ru(C$_6$H$_6$)Cl$_2$(solvent)]$^+$ and [Ru(C$_6$H$_6$)Cl(solvant)$_2$]$^+$, the monomers being formed by reaction of \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]^-\) with either methanol or hot water.* These may then couple to give the triple chloride bridged cation directly, or on the basis of evidence from earlier work with ruthenium ethyldiphosphaphosphinite complexes [17], via the cationic, double chloride bridged solvated intermediate \([\{\text{C}_6\text{H}_6\}^-\text{ClRuCl}_3\text{Ru(solvant)}\text{(C}_6\text{H}_6)\}]^+\) which then rearranges readily to (III) (Scheme).

*Unfortunately, the solubility of \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]^-\) in methanol is too low to obtain $^1$H nmr evidence for the formation of methanolate monomers although, of course, there is no doubt that analogous monomeric species are readily formed in D$_2$O and d$^6$-Me$_2$SO.
The low solubility of the PF$_6^-$ salt of [Ru$_2$(C$_6$H$_5$)$_2$Cl$_3$]$^+$ in either methanol or water, together with the desire of ruthenium (II) to achieve six strong bonds is presumably the driving force for the combination of these intermediates.

Attempts to prepare other triple halide bridged cations [Ru$_2$- (arene)$_2$X$_3$]$^+$ (arene = 1,3,5-C$_6$H$_3$Me$_3$; X = Cl$^-$; arene = C$_6$H$_6$, X = Br$^-$, I$^-$, SCN$^-$) by reaction of [Ru(arene)X$_2$]$^+_2$ with NH$_4$PF$_6$ in methanol were however unsuccessful, only [Ru(arene)X$_2$]$^+_2$ being isolated from the reaction mixture. This failure probably stems from the very insoluble nature of these [Ru(arene)X$_2$]$^+_2$ compounds which prevents formation of appreciable amounts of methanolate monomers.

c) Reactions of [Ru$_2$(C$_6$H$_5$)$_2$Cl$_3$]PF$_6$

Originally, it was hoped that this high yield synthesis of [Ru$_2$(C$_6$H$_5$)$_2$Cl$_3$]PF$_6$ (III) might provide a general route to the preparation of complexes such as [RuCl$_2$L]$^+_2$ (L = C$_5$H$_5$N, Me$_2$SO, RCN etc) via displacement of $\eta^6$-C$_6$H$_6$ groups. However, as discussed above, the tendency of (III) to generate monomers by facile bridge cleavage proved greater than the desire to undergo replacement of the coordinated benzene rings. Thus, refluxing compound (III) with excess of pyridine in ethanol for ca 4h gave an orange solution which on standing under nitrogen for a further 24h deposited an orange crystalline solid. On the basis of analytical data, together with $^1$H nmr, ir and conductivity studies, this was best formulated as the monomeric cation [Ru(C$_6$H$_5$)$_2$Cl(C$_5$H$_5$N)$_2$]PF$_6$. Concentration of the remaining filtrate gave the non-conducting orange-solid trans-[RuCl$_2$(C$_5$H$_5$N)$_4$]. Attempts to retain the chloride bridges but induce replacement of $\eta^6$-C$_6$H$_6$ groups for pyridine by photolysis of the same reaction mixture also proved unsuccessful, only [Ru(C$_6$H$_5$)$_2$Cl(C$_5$H$_5$N)$_2$]PF$_6$ and trans-[RuCl$_2$(C$_5$H$_5$N)$_4$] being isolated.
Reaction between compound (III) and Et₂S gave two compounds identified as \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}(\text{Et}_2\text{S})_2]\)PF₆ and \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2(\text{Et}_2\text{S})]\). This bridge cleavage reaction also occurred with tertiary phosphines and arsines when (III) was shaken in methanol with excess of the ligand for short reaction times and this provided a route to the previously unknown cationic tertiary phosphine complexes \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}(\text{PR}_3)_2]\)PF₆ (PR₃ = PPh₃, PMe₂Ph, PMePh₂).

The reaction of (III) with excess of PR₃ under reflux conditions sometimes produced loss of the \(\eta^6\)-C₆H₆ groups. For example, refluxing (III) with excess of PPh₃ in methanol gave a mixture of \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}(\text{PPh}_3)_2]\)PF₆ and \([\text{RuCl}_2(\text{PPh}_3)_3]\). In contrast, refluxing (III) with excess of PMe₂Ph in methanol gave a yellow solution from which only the triple chloride bridged complex \([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\)PF₆ was isolated. As discussed earlier [12,17], this cation was most likely formed by rearrangement reactions of cis-[RuCl₂(PMe₂Ph)₄], itself formed by bridge cleavage and \(\eta^6\)-C₆H₆ displacement from (III) by PMe₂Ph.

In conclusion, although reactions of \([\text{Ru}_2(\text{C}_6\text{H}_6)\text{Cl}_3]\)PF₆ do not provide a route to the synthesis of new triple chloride bridged cations \([\text{Ru}_2\text{Cl}_3\text{L}_6]^+\), the facile bridge cleavage reaction does give a convenient synthetic route to new \(\eta^6\)-C₆H₆ cationic compounds of type \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]\)PF₆. Recent work has shown that similar facile bridge cleavage reactions occur with other triple chloride bridged complexes. For example, reaction of \([\text{Ru}_2\text{YCl}_4(\text{PPh}_3)_4]\) (Y = CO, CS) with excess of P(OR)Ph₂ (R = Me, Et) in benzene gave a mixture of \([\text{Ru}(\text{Y})\text{Cl}_2(\text{P(OR)Ph}_2)_3]\) and \([\text{RuCl}_2(\text{P(OR)Ph}_2)_3]\) [18].

In view of this, it is surprising that the closely related \([\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]^+\) cations do not undergo bridge cleavage reactions with excess of PR₃ [19], although this may be a result of the strong electron donating ability of the coordinated PR₃ groups which inhibits bridge cleavage by other nucleophiles (cf the inertness of \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2(\text{PR}_3)]\) compounds
towards nucleophilic attack on the ring [1]).

Experimental

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000-250 cm\(^{-1}\) on a Perkin Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the region 400-200 cm\(^{-1}\) on a Beckman RII C IR 720 far ir spectrometer using pressed polythene discs. Hydrogen-1 nmr spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and \(^{13}\)C-{\(^1\)H} nmr spectra on a Varian XL100 spectrometer operating at 25.2 MHz (\(^{13}\)C chemical shifts quoted in ppm to high frequency of SiMe\(_4\)).

Conductivity measurements were made at 298K using a model 310 Portland Electronics conductivity bridge. As described earlier [17], plots of \(\sqrt{\nu} - \sqrt{c}\) vs C\(^\frac{1}{2}\) gave a straight line whose slope is a function of the ionic charges [20]. Melting points were determined with a Kófner hot-stage microscope and are uncorrected.

Materials

Ruthenium trichloride hydrate (Johnson Matthey); cyclohexa-1,3-diene, ammonium hexafluorophosphate and triphenylarsine (Ralph Emanuel Ltd); caesium chloride, triphenylphosphine and sodium tetraphenylborate (B.D.H.); methylidyphenylphosphine and dimethylphenylphosphine (Maybridge): nitromethane, pyridine, acetonitrile and mesitylene (Fisons); dimethylsulphoxide (Hopkins and Williams); triphenylstibine (Kodak). \([\{\text{Ru}(\text{C}_6\text{H}_5)\text{Cl}_3\}_2\}\) and \([\{\text{Ru}(\text{C}_6\text{H}_3\text{Me})\text{Cl}_3\}_2\}\) were prepared as described earlier [1,3] from "RuCl\(_3\)\(\times\)H\(_2\)O", cyclohexa-1,3-diene (or cyclohexa-1,4 diene) or 1,3,5-trimethylcyclohexa-1,4-diene respectively. \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{X}_2\}_2\}\) (X = Br, I, SCN) were prepared by treating aqueous solutions of \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_3\}_2\}\) with an excess of LiX.
Analytical and conductivity data for the various compounds are given in Table 1 and Hydrogen-1 nmr data are listed in Table 2. Diagnostic ir bands are listed for each compound. All reactions were carried out in degassed solvents under an atmosphere of nitrogen and a medium pressure.

Hanovia 1L mercury U.V. lamp was used for the photochemical reaction.

Caesium(benzene)(trichloro)ruthenate(II): The compound \( \{\text{Ru(}C_6H_6\text{)}\text{Cl}_2\text{}\}_{2} \) (0.20g, 0.40 mmol) was shaken in ethanol (25 cm\(^3\)) with an excess of caesium chloride (0.40g) and concentrated hydrochloric acid (5 cm\(^3\)) for 5 days. The resulting orange suspension was decanted off and washed with methanol and diethyl ether mp. 270°C (decomp) (Yield 0.31g, 95%) \( \nu(\text{RuCl}) 280 \text{ cm}^{-1} \).

Benzene(dichloro)pyridine ruthenium(II): The compound Cs[\( \text{Ru(}C_6H_6\text{)}\text{Cl}_3\)] (0.10g; 0.23 mmol) was shaken in methanol (10 cm\(^3\)) with excess of pyridine (1.0 cm\(^3\)) for ca 4h. Concentration of the resulting yellow solution and addition of diethyl ether gave an orange solid mp. 245°C (decomp) (0.07g, 86%) \( \nu(\text{RuCl}) 280 \text{ cm}^{-1} \).

Benzene(dichloro)triphenylphosphine ruthenium(II): The compound Cs[\( \text{Ru(}C_6H_6\text{)}\text{-Cl}_3\)] (0.10g; 0.23 mmol) was shaken with excess of PPh\(_3\) (0.10g; 0.40 mmol) in methanol for ca 3h to give a dark red crystalline solid mp. 182°C (0.11g, 91%) \( \nu(\text{RuCl}) 295, 280 \text{ cm}^{-1} \).

Benzene(dichloro)methyldiphenylphosphine ruthenium(II): mp. 197°C (0.09g, 82%) \( \nu(\text{RuCl}) 290, 270 \text{ cm}^{-1} \); benzene(dichloro)dimethylphenylphosphine-ruthenium(II) mp. 175°C (0.07g; 78%) \( \nu(\text{RuCl}) 290, 275 \text{ cm}^{-1} \); benzene-(dichloro)triphenylstibine ruthenium(II) mp. 220-222°C \( \nu(\text{RuCl}) 290, 269 \text{ cm}^{-1} \) and benzene(dichloro)dimethylsulphoxide ruthenium(II) mp. 211°C \( \nu(\text{RuCl}) 291, 272 \text{ cm}^{-1} \) were similarly prepared.
\(\text{Cis-dichlorotetrakis(dimethylphenylphosphine)ruthenium(II)}\): The compound \(\text{Cs} [\text{Ru(CH}_3\text{C}_6\text{H}_5\text{Cl}_3] (0.10g; 0.23 \text{ mmol})\) was refluxed in methanol with excess \(\text{PMe}_2\text{Ph} (0.50 \text{ cm}^3)\) for 6h. The resulting yellow solution on standing gave a yellow, crystalline solid mp. 126°C (0.13g; 82%) \(\nu(\text{RuCl}) 288, 241 \text{ cm}^{-1}\).

\(\text{Tri-μ-chlorobis[(benzene)ruthenium(II)]hexafluorophosphate:}\) Method A:

The complex \([\{\text{Ru(CH}_3\text{C}_6\text{H}_5\text{Cl}_2]\}_2\] (0.20g; 0.40 mmol) was heated under reflux with water (10 \text{ cm}^3) for 2h. The orange solution was filtered and treated with a saturated aqueous solution of \(\text{NH}_4\text{PF}_6\). After several days the orange precipitate was filtered off and washed with water and methanol mp. 255°C (decomp) (0.03g; 12%). On leaving the filtrate for another 7 days, another orange crystalline solid was deposited which was characterised by X-ray analysis \([14]\) as \([\text{Ru(NH}_3]_2(\text{C}_6\text{H}_5\text{Cl})_3(\text{PF}_6)_3\text{NH}_4\text{PF}_6\) \(\nu(\text{RuCl}) 285 \text{ cm}^{-1}; \nu(\text{NH}) 3180, 3250, 3320, 3370 \text{ cm}^{-1}; \delta(\text{NH}) 1615, 1630 \text{ cm}^{-1}; \nu(\text{Ru-N}) 421, 440, 455 \text{ cm}^{-1}\). Unfortunately, subsequent attempts to prepare this latter compound were unsuccessful.

Method B: The complex \([\{\text{Ru(CH}_3\text{C}_6\text{H}_5\text{Cl}_2\}_2\] (0.20g; 0.40 mmol) was stirred in methanol (25 \text{ cm}^3) with excess of \(\text{NH}_4\text{PF}_6 (0.16g; 1.00 \text{ mmol})\) for 24h. The orange-yellow solid was filtered off and washed with water, methanol and diethyl ether mp. 280°C (decomp) (0.22g; 90%) \(\nu(\text{RuCl}) 264, 276 \text{ cm}^{-1}\).

Conductivity in \(\text{MeNO}_2\) at 298K. Slope of \(\lambda - \lambda_c\) vs \(C^2\) plot = 207; for \([\text{Ru}_2\text{C}_1\text{Cl}(\text{PMe}_2\text{Ph})_6]\text{PF}_6\), slope = 190. \(13^\text{C} \text{-}\{1^\text{H}\}\text{nmr in d}^3\text{-MeNO}_2\) at 303K. 82.0 ppm (singlet). The compound is insoluble in \(\text{CHCl}_3, \text{CH}_2\text{Cl}_2, \text{benzene}\) and very sparingly soluble in acetone.

\(\text{Benzene(chloro)bis(pyridine)ruthenium(II)hexafluorophosphate:}\) The complex \([\text{Ru}_2(\text{CH}_3\text{C}_6\text{H}_5\text{Cl})_3\text{PF}_6 (0.09g; 0.14 \text{ mmol})\) was refluxed in ethanol (30 \text{ cm}^3) with pyridine (0.40 \text{ cm}^3) for ca 6h. The yellow solution on standing for 24h gave a yellow crystalline solid mp. 227-229°C (0.05g; 66%) \(\nu(\text{RuCl})\)
285 cm$^{-1}$. Concentration of the filtrate from this reaction gave an orange solid 
trans-dichlorotetakis(pyridine)ruthenium(II) mp. 255°C (decomp) (0.03g; 24%) $\nu$(RuCl) 338 cm$^{-1}$.

Benzenechloro(diethylsulphide)ruthenium(II): The complex $[\text{Ru}_2(C_6H_6)_2Cl_3]PF_6$ (0.10g; 0.16 mmol) was refluxed in ethanol (30 cm$^3$) with Et$_2$S- (0.20 cm$^3$) for ca 3h. The orange solution was filtered and concentrated by evaporation of solvent under vacuo. The orange precipitate obtained was recrystallised from acetone/diethyl ether mp. 225°C (decomp) $\nu$(RuCl) 283, 265 cm$^{-1}$). The filtrate from the above reaction gave an orange crystalline solid on standing for 24h identified as benzene(chloro)bis-
(diethylsulphide)ruthenium(II)hexafluorophosphate mp. 175°C, $\nu$(RuCl) 290 cm$^{-1}$.

Benzenechlorobis(triphenylphosphine)ruthenium(II)hexafluorophosphate:
The complex $[\text{Ru}_2(C_6H_6)_2Cl_3]PF_6$ (0.20g; 0.32 mmol) was shaken in methanol (20 cm$^3$) with excess of PPh$_3$ (0.20g; 0.80 mmol). The red precipitate was filtered off from the yellow solution, recrystallised from CH$_2$Cl$_2$/hexane and identified as $[\text{Ru}(C_6H_6)Cl_2(PPh_3)]$. Addition of diethyl ether and hexane to the yellow filtrate gave the yellow crystalline product mp. 172°C (0.11g, 41%), $\nu$(RuCl) 290 cm$^{-1}$. Similar reactions gave the yellow solids benzenechlorobis(triphenylarsine)ruthenium(II)hexafluoro-
phosphate mp. 142°C, $\nu$(RuCl) 310 cm$^{-1}$; benzenechlorobis(methyldiphenyl-
phosphine)ruthenium(II)hexafluorophosphate mp. 158°C $\nu$(RuCl) 292 cm$^{-1}$ and benzenechlorobis(dimethylphenylphosphine)ruthenium(II)hexafluoro-
phosphate mp.209-211°C, $\nu$(RuCl) 298 cm$^{-1}$.

Tri-µ-chlorobis[tris(dimethylphenylphosphine)ruthenium(II)]hexafluorophosphate:
The compound $[\text{Ru}_2(C_6H_5)_2Cl_3]PF_6$ (0.20g; 0.32 mmol) was refluxed in methanol (20 cm$^3$) with excess of PMe$_2$Ph (1 cm$^3$) for 5h. Addition of diethyl ether to the yellow solution gave a yellow crystalline solid mp. 238-239°C (0.37g, 92%).
Acknowledgements

We thank Johnson Matthey Ltd. for loans of ruthenium trichloride, the SRC (DRR) and the University of Edinburgh (TA) for financial support, and Dr. A.S.F. Boyd and Mr. J.R.A. Millar for running $^{13}\text{C}$ and $^{1}\text{H}$ nmr spectra.
References

### Table 1

Analytical and Conductivity Data for some $\eta^6$-Areneruthenium(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found %</th>
<th>Calculated %</th>
<th>$\sqrt{\chi_n}^a$</th>
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</thead>
<tbody>
<tr>
<td>Cs[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl$_3$]</td>
<td>16.9 1.4 - 25.2</td>
<td>17.2 1.4 - 25.5</td>
<td>37.4$^b$</td>
</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl$_2$($\eta^5$C$_5$H$_5$N)]</td>
<td>40.4 3.3 4.6 -</td>
<td>40.1 3.3 4.3 -</td>
<td></td>
</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl$_2$(PPh$_3$)$_2$]</td>
<td>56.6 4.3 - -</td>
<td>56.3 4.1 - -</td>
<td></td>
</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl$_2$(PMePh$_2$)$_2$]</td>
<td>49.9 4.1 - -</td>
<td>50.7 4.2 - -</td>
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<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl$_2$(Me$_2$SO)]</td>
<td>28.8 3.6 - -</td>
<td>29.2 3.2 - -</td>
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</tr>
<tr>
<td>[RuCl$_2$(PMe$_2$Ph)$_4$]</td>
<td>52.4 6.1 - -</td>
<td>53.0 6.1 - -</td>
<td>30.0$^c$</td>
</tr>
<tr>
<td>[Ru$<em>2$(C$</em>{6}$H$_{5}$)$_2$Cl$_3$]PF$_6$</td>
<td>23.8 1.9 - 16.2</td>
<td>23.6 1.9 - 17.4</td>
<td>82.0</td>
</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl($\eta^5$C$_5$H$_5$N)$_2$]PF$_6$</td>
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</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl($\eta^5$C$_5$H$_5$N)$_2$]PF$_6$</td>
<td>31.5 4.6 - -</td>
<td>31.2 4.8 - -</td>
<td>64.0</td>
</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl(PPh$_3$)$_2$]PF$_6$</td>
<td>56.7 4.2 - -</td>
<td>57.1 4.1 - -</td>
<td>78.0</td>
</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl(AsPh$_3$)$_2$]PF$_6$</td>
<td>51.6 3.7 - -</td>
<td>51.9 3.7 - -</td>
<td>75.0</td>
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<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl(PMe$_2$Ph)$_2$]PF$_6$</td>
<td>41.3 4.4 - -</td>
<td>41.5 4.4 - -</td>
<td>72.0</td>
</tr>
<tr>
<td>[Ru($\eta^6$C$<em>{6}$H$</em>{4}$)Cl(PMe$_2$Ph)$_2$]PF$_6$</td>
<td>50.5 4.8 - -</td>
<td>50.6 4.2 - -</td>
<td>67.0</td>
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<tr>
<td>[Ru$_2$Cl$_3$(PMe$_2$Ph)$_2$]PF$_6$</td>
<td>44.9 5.1 - -</td>
<td>44.9 5.2 - -</td>
<td>74.0</td>
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<tr>
<td>[Ru(NH$<em>3$)$<em>2$(C$</em>{6}$H$</em>{4}$Cl)$_3$]PF$_6$</td>
<td>16.3 2.9 7.1 -</td>
<td>16.1 3.0 7.3 -</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Equivalent conductivities (S cm$^2$ mol$^{-1}$) measured in nitromethane (unless stated) at 10$^{-3}$ mol dm$^{-3}$ concentration $^b$ measured in H$_2$O $^c$ measured in CH$_2$Cl$_2$ - rearranges to [Ru$_2$Cl$_3$(PMe$_2$Ph)$_2$]Cl.
### TABLE 2

Hydrogen-1 nmr data for some $\eta^6$-Areneruthenium(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$^6\text{C}_6\text{H}_6$ Resonances</th>
<th>Other Resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[^{\text{Ru}(\text{C}_6\text{H}_6\text{)}\text{Cl}_2]_2^{\text{dMe}_2\text{SO}}}$</td>
<td>D$_2$O$^b$</td>
<td>6.39$^c$, 6.50$^c$</td>
<td>7.30, 8.80 (pyridine)</td>
</tr>
<tr>
<td>Cs[$\text{Ru}(\text{C}_6\text{H}_6\text{)}\text{Cl}_3]^{\text{dMe}_2\text{SO}}$</td>
<td>D$_2$O$^b$</td>
<td>6.40$^c$</td>
<td></td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{C}_5\text{H}_5\text{N})]^{\text{dMe}_2\text{SO}}$</td>
<td>CDC1$_3$</td>
<td>5.65, 5.90$^d$</td>
<td>7.30, 8.80 (pyridine)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{Me}_2\text{SO})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.90</td>
<td>ca 2.70 (br) (Me$_2$SO)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{PPPh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.40</td>
<td>7.50 (PPPh$_3$)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{PMePh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.40</td>
<td>7.65 (Ph); 1.95 (d) ($^2\text{J}_{\text{PPh}}$ 12.0 Hz) (Me)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{PMe}_2\text{Ph})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.35</td>
<td>7.50 (Ph); 1.85 (d) ($^2\text{J}_{\text{PPh}}$ 12.0 Hz) (Me)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{SbPh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.68</td>
<td>8.03 (Ph); 2.48 (d) ($^2\text{J}_{\text{PPh}}$ 12.0 Hz) (Me)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{AsPh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.50</td>
<td>7.40–7.60 (AsPh$_3$)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{Et}_2\text{S})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.70</td>
<td>2.90 (q); 1.35 (t) (Et$_2$S)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}_2(\text{C}_5\text{H}_5\text{N})]^{\text{dMe}_2\text{SO}}$</td>
<td>CDC1$_3$</td>
<td>5.90</td>
<td>6.35$^c$, 6.48$^c$</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}(\text{Et}_2\text{S})]^{\text{dMe}_2\text{CO}}$</td>
<td>D$_2$O$^b$</td>
<td>6.16</td>
<td>7.45, 8.00, 8.85 (pyridine)</td>
</tr>
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<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}(\text{PPPh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.95</td>
<td>3.00 (q); 1.45 (t) (Et$_2$S)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}(\text{PMePh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.52</td>
<td>7.30 (PPPh$_3$)</td>
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<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}(\text{PMe}_2\text{Ph})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.75</td>
<td>7.20–7.60 (Ph); 1.60 (t) (Me)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}(\text{AsPh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.87</td>
<td>7.50 (Ph); 1.64 (t); 2.12 (t) (Me)</td>
</tr>
<tr>
<td>[Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}(\text{AsPh})]^{\text{CDC1}_3}$</td>
<td>CDC1$_3$</td>
<td>5.66</td>
<td>7.40–7.60 (AsPh$_3$)</td>
</tr>
</tbody>
</table>

$^d$ (doublet), $^t$ (triplet), $^q$ (quartet)

$^a$ Unless specified, reference is TMS (internal lock); $^b$ With respect to external TMS capillary; $^c$ See text for assignment of these resonances

$^d$ From [Ru($\text{C}_6\text{H}_6\text{)}\text{Cl}(\text{dMe}_2\text{SO})]^{\text{dMe}_2\text{SO}}$
Some reactions of the $\left[ (\eta^6-C_6H_6)Ru(OH)_3Ru(\eta^6-C_6H_6) \right]^+$ cation

D.R. Robertson and T.A. Stephenson*
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

Summary: Reaction of $\left[ (\eta^6-C_6H_6)Ru(OH)_3Ru(\eta^6-C_6H_6) \right]BPh_4$ (I) with aqueous solutions of $NH_4PF_6$ gives $[Ru(NH_3)_3C_6H_6]PF_6$ (II) whereas refluxing (I) in ROH ($R = Me, Et$) produced the triple alkoxide-bridged cations $[\eta^6-C_6H_6]Ru(OR)_3Ru(\eta^6-C_6H_6)]BPh_4$ (III); in contrast, no reaction between (I) and various tertiary phosphines was observed.

Recently, we reported that reaction of $\left[ \{Ru(C_6H_6)Cl_2 \}_2 \right]$ with an excess of either aqueous sodium hydroxide or carbonate gave the triple hydroxy-bridged cation $\left[ (C_6H_6)Ru(OH)_3Ru(C_6H_6) \right]Cl.3H_2O [1,2]$. However, although $[Ru_2(C_6H_6)_2(OH)_3]BPh_4$ (I) can be readily isolated by addition of $NaBPh_4$ to aqueous solutions of the chloride salt, attempts to trap-out the $PF_6^-$ salt by addition of excess of $NH_4PF_6$ gave, after several days, a yellow nitrogen-containing solid (ca. 40% yield). On the basis of elemental analysis, conductivity measurements in nitromethane, i.e. and $^1H$ nmr spectral studies, this is best formulated as the trisammine dication $[Ru(NH_3)_3(C_6H_6)]PF_6$ (II). A related complex to (II), namely, $[Ru(NH_3)_2(C_6H_6)Cl]PF_6$ has been obtained in small yield from the reaction of $\left[ \{Ru(C_6H_6)Cl_2 \}_2 \right]$ with hot water, followed by addition of $NH_4PF_6$ [3]. Presumably, (II) is formed from the reaction of $[Ru_2(C_6H_6)_2(OH)_3]^+$ with ammonium ion which can act as a weak acid, protonating the $OH^-$ bridges to form the trisquaqua intermediate $[Ru(H_2O)_3^{-}(C_6H_6)]^{2+}$, which could then undergo replacement of water by ammonia groups (cf. the related reactions of $[Ru_2(OH)_3(PMe_2Ph)]^{2+}$ with acids in various solvents (S) which gave $[RuS_3(PMe_2Ph)]^{2+}$ species [4]).
If (I) is refluxed in methanol for 3 hours, a yellow crystalline solid (III) is deposited on cooling. The ir spectrum of (III) shows no bands at ca 3500 cm\(^{-1}\) (νOH) but a strong band at 1050 cm\(^{-1}\) indicates the presence of -O\(_\text{Me}\) groups (cf Ti(\text{OME})\(_4\)) with ν(O-C) 1032 cm\(^{-1}\) [5]). Since the \(^1\)H nmr spectrum in (Cd\(_3\))\(_2\)CO consists of BPh\(_4^-\) multiplets at ca 6.90 and 7.30, a \(\eta^6\)-C\(_6\)\(_6\) peak at 5.48 and a singlet at 4.42 (assigned to -O\(_\text{Me}\) protons) in the intensity ratio 20; 12; 9 respectively, (III) is formulated as the triple methoxide bridged complex \(\text{[(C}_6\text{H}_6)\text{Ru(OMe)}_3\text{Ru(C}_6\text{H}_6)]B\text{Ph}_4^-\). This formulation is supported by elemental analyses and detailed conductivity measurements in nitromethane indicating a 1:1 electrolyte.

Similarly, \([\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OEt})_3]\text{BPh}_4^-\) was obtained by refluxing (I) in ethanol. Again, the mechanism of formation presumably involves protonation of the \(\text{OH}^-\) bridges by the weak acid ROH to form the \([\text{Ru}(\text{H}_2\text{O})_3(\text{C}_6\text{H}_6)]^{2+}\) cation which could then react rapidly with \(\text{OR}^-\) to give monomeric alkoxide compounds such as \([\text{Ru}(\text{H}_2\text{O})(\text{C}_6\text{H}_6)\text{OR}]^+\) and \([\text{Ru}(\text{H}_2\text{O})(\text{C}_6\text{H}_6)(\text{OR})_2]\). As discussed elsewhere for the analogous \([\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}_3]^+\) [6] and \([\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]^+\) [7] cations, facile intermolecular coupling reactions of these solvated monomers would then give the \([\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OR})_3]^+\) cations.

These alkoxide cations could also be synthesised by reaction of \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]\) with freshly prepared NaOR (R = Me, Et) in alcoholic solvents, and, unlike the corresponding \([\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3]^+\), their PF\(_6^-\) salts are readily isolated by addition of NH\(_4\)PF\(_6\) to the above reaction mixtures.

Finally, although the analogous \([\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}_3]^+\) cation undergoes facile bridge cleavage reactions with a variety of Lewis bases to give monomeric compounds of type \([\text{Ru}(\text{C}_6\text{H}_6)_2\text{ClL}]\text{PF}_6^-\), \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\text{L}]\) and/or \([\text{RuCl}_2\text{L}_4]\) (L = C\(_5\)N, Et\(_2\)S, \((\text{CH}_3)_2\)SO, PR\(_3\) etc) [1,6], \([\text{Ru}_2(\text{C}_6\text{H}_6)_2(\text{OH})_3]\text{BPh}_4^-\) does not react with excess of tertiary phosphines in acetone, even under
reflux conditions for prolonged periods, (cf \{\text{Pt(OH)}(\text{PR}_3)_2\}_2(\text{BF}_4)_2 also
does not react with more \text{PR}_3 [8]), the only product isolated being

$$[\text{Ru}_2(\text{C}_2\text{H}_6)_2(\text{OH})_3\text{BPh}_4(\text{CH}_3)_2\text{CO}].$$

Further studies on a wider range of these triple bridged hydroxo
and alkoxide ruthenium(II) arene complexes are now in progress.

Acknowledgement

We thank Johnson-Matthey Ltd. for loans of ruthenium trichloride
and the SRC (DDR) for a research studentship.
References


BY T. A. STEPHENSON, E. BANNISTER, AND G. WILKINSON.

A number of molybdenum(II) carboxylates have been obtained by the interaction of mono- and di-carboxylic acids with hexacarbonylmolybdenum. The monocarboxylates appear to have a dimeric structure involving both bridging and chelating carboxylate groups. The corresponding benzene-
sulphonate and diphenylphosphinate are reported.

Monocarboxylates of Molybdenum(II).—The compounds of stoichiometry Mo(O·COR)₂
(where R = Me, Et, Prⁿ, Prᵗ, C₆H₁₁, C₇H₁₅, C₅F₇, C₆H₅, m-C₆H₄Me, C₆H₄OH, and C₆H₄F) have been prepared; the acetate¹ and benzoate² have been briefly described previously. Hexacarbonylmolybdenum was heated, either alone or in diethylene glycol dimethyl ether (diglyme), with the carboxylic acid together with a small amount of its anhydride if available. The compounds are all yellow solids and some of them form very fine needle-like crystals. They are thermally quite stable, and the alkyl carboxylates can be sublimed unchanged in a vacuum at temperatures exceeding 300°. The solubility depends on the nature of the carboxylate group but the lower alkyl carboxylates are insoluble in hydrocarbon and halogenated solvents; they are sparingly to moderately soluble in acetone or tetrahydrofuran but the solutions turn brown and eventually blue on exposure to air.

Although a polymeric structure involving tetrahedral molybdenum(II) and bridging acetate groups is a possibility,¹ and would be in keeping with the low solubility of the compounds, they appear to be dimeric with both bridging and chelating carboxylate groups and tetrahedrally co-ordinated molybdenum(II). Evidence for the dimeric structure is two-fold. First, the perfluorobutyrte is sufficiently soluble (and the solutions sufficiently air-stable) in cold acetone, cold benzene, and boiling toluene to allow the molecular weight to be determined by both osmometric and ebulliometric methods. The salicylate is also dimeric in cold acetone (osmometric method). Conductivity measurements on solutions of the perfluorobutyrte in acetone and nitrobenzene and of ary1 carboxylates in acetone show that the solutions are non-conducting, e.g., for the perfluorobutyrte in acetone \( \Lambda_{\text{osm}} = 4.6 \text{ ohm}^{-1} \text{ cm}^{2} \text{ mole}^{-1} \).

Secondly, a single-crystal X-ray-diffraction study of molybdenum(II) acetate³ is sufficiently advanced to substantiate the dimeric geometry of the molecule. All the carboxylates are diamagnetic, and this is consistent with tetrahedral co-ordination by oxygen for a \( d^{4} \) configuration of molybdenum(II), as in (I).

\[ \text{R-C} \quad \text{Mo} \quad \text{O} \quad \text{C} \quad \text{R} \quad \text{Mo} \quad \text{O} \quad \text{C} \quad \text{R} \] (I)

Infrared Spectra.—It is well known that there are no reliable infrared criteria for distinguishing between chelating and bridging carboxylate groups, and even in the present compounds, where it is clear that for the first time both types of group are present on the same metal atom, there is no obvious splitting of the symmetric and asymmetric carboxylate stretching frequencies (Table 1). The assignment of the asymmetric stretch in the aryl carboxylates is complicated by a strong band at 1525—1475 cm.⁻¹ due to skeletal in-plane vibrations.⁴ However, all the carboxylates have strong bands in the region where bridging carboxylate groups are known to absorb, as in chromium(II), copper(II), and

² Abel, Singh, and Wilkinson, J., 1959, 3097.
³ Lawton and Mason, personal communication.
basic beryllium acetate, or in the rhenium, rhodium, palladium, and ruthenium carboxylates. The alkyl carboxylates have a splitting of the asymmetric stretching frequency of ca. 8–18 cm\(^{-1}\). This splitting can be attributed either to a slight difference in the force constants for the chelating and bridging carboxylate groups or to solid-state interactions within the lattice. The insolubility or instability of alkyl carboxylates in suitable organic solvents prevents the examination of solution spectra; although some of the aryl carboxylates are soluble without decomposition for short periods in acetone, chloroform, or methanol, these solvents are not satisfactory in the 1500–1450 cm\(^{-1}\) region. Only the perfluorobutryrate can be studied in both benzene solution and in the solid state, and here there is no splitting at all, even with the grating instrument. It seems reasonable, therefore, to conclude that there is little if any difference between the spectra of chelating and bridging carboxylate groups, and that any small differences observed in solid-state spectra are equally well attributed to crystal effects.

**Chemical Properties.**—The carboxylates appear to be stable indefinitely in the absence of air. On exposure to moist air, molybdenum(II) acetate turned green over a period of weeks and after some months became dark blue, losing acetic acid. The blue material has a strong infrared band at 940–970 cm\(^{-1}\), and appears to be "molybdenum blue." The higher alkyl carboxylates are rather more sensitive to moist air than is the acetate. The perfluorobutryrate is more stable, and even when exposed to air for over a year showed little sign of decomposition other than a green coating on the crystals. The compound is soluble in ethanol, methanol, dichloromethane, benzene, and toluene, the solutions being insensitive to air for periods of several hours. The aryl carboxylates are also fairly stable in the solid state in air, but their solutions in organic solvents decompose within 30 minutes.

The acetate reacts with dry hydrogen chloride at temperatures above ca. 130°, a brown material being obtained. The dark brown product from the reaction at ca. 250° analyses approximately as molybdenum dichloride (ca. 98% MoCl\(_2\)), but we have never been able to obtain a material entirely free from carbon, hydrogen, or oxygen. The substance is clearly not the usual yellow "molybdenum dichloride," Mo\(_6\)Cl\(_{12}\). It has some reactions which could be expected of the true dichloride. Thus it dissolves, leaving a small residue, however, in hot pyridine and hot isoquinoline to give very air-sensitive yellow and blood-red solutions, respectively. The solid is stable in air, and is insoluble in, and unaffected by, water and concentrated hydrochloric acid.

The acetate and other alkyl carboxylates react with triphenylphosphine, pyridine, piperidine, and other donor ligands. The adducts are often insoluble, and are all air- and

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8 Morehouse, Powell, Stephenson, and Wilkinson, unpublished work.
moisture-sensitive and impossible to purify. However, the acetate is soluble in pyridine from which yellow crystals can be obtained; these are diamagnetic, have the empirical formula MoO(CO)\(_{3}\)py, and have an infrared spectrum showing strong carboxylate bands at 1410 and 1500 cm\(^{-1}\), as well as characteristic pyridine bands.\(^9\) We have been unable to determine the molecular weight but it seems reasonable to assume that pyridine has merely added to the dimeric acetate to give a pentaco-ordinate molybdenum(II) complex. A similar benzoate complex can also be obtained. Both compounds are air-sensitive, the solutions in pyridine turning red. When a solution of the acetate in pyridine is allowed to stand in moist air, a reddish-brown powder is deposited. This is completely insoluble in all common organic solvents except dimethyl sulphoxide and dimethylformamide, which give deep yellow solutions, and, to a very limited extent, nitrobenzene and nitromethane. The infrared spectrum of this material shows evidence for pyridine, but no water, OH, pyridinium, or acetate bands. Analyses correspond closely to an empirical formula MoO\(_4\)py. A material of very similar analysis and identical spectroscopic properties can be obtained by addition of pyridine to an ethanolic solution of molybdenum oxotrichloride. In both materials, a simple band at ca. 950 cm\(^{-1}\) can be assigned to Mo=O stretching. It seems likely that the other oxygen atoms are present as oxo-bridges in a highly polymeric structure.

Dicarboxylates of Molybdenum(II).—The interaction of hexacarboxylmolybdenum with dicarboxylic acids under strictly anhydrous conditions gives green powders of composition Mo(O-CO\(_2\)\(_n\)-CO(O), where \(n = 3\) or 4, while, in the presence of small amounts of water, green hydrates, Mo(O-CO\(_2\)\(_n\)-CO(O))H\(_2\)O, are obtained for \(n = 2, 3,\) or 4. The substances are quite insoluble in organic solvents like acetone or alcohol, but they dissolve in warm dimethylformamide or dimethyl sulphoxide giving greenish-yellow solutions which decompose quite rapidly. The solids are also quite unstable, turning brown after ca. 15 minutes, although the succinate remained green for several days and its hydrate for about an hour. The infrared spectra of the anhydrous and hydrated compounds are similar except for bands due to water in the latter compound (at 3300 and ca. 1650 cm\(^{-1}\)). Strong bands in the 1400—1500 cm\(^{-1}\) region are due to asymmetric and symmetric carboxylate stretches, while an additional broad band at 1700—1725 cm\(^{-1}\) is probably due to the unco-ordinated carboxylate group.

**Experimental**

Microanalyses and molecular weights were by the Microanalytical Laboratory, Imperial College. Infrared spectra were taken on a Perkin-Elmer model 21 and a Grubb-Parsons Spectromaster grating instruments, using Nujol, and hexachlorobutadiene mulls. Magnetic measurements were made by the standard Gouy method. Molybdenum was determined by ignition to molybdenum trioxide at 500—525\(^\circ\)C, or gravimetrically as the oxinate.

All preparations were carried out under nitrogen. Analytical data are collected in Table 2.

Monocarboxylates.—(1) For the acetate, propionate, butyrate, and perfluorobutyrate, an excess of acid, together with a small amount of its anhydride where available, and hexacarboxylmolybdenum (ca. 2 g.) were heated under reflux (below 150\(^\circ\)) until gas evolution ceased.

(2) For all other acids, the hexacarbonyl and the acid (in a 1:2:2 mole ratio) were dissolved in the minimum amount of diglyme (dried by molecular sieves and freshly distilled) and heated at ca. 150\(^\circ\) until gas evolution ceased.

For the acetate, benzoate, \(\beta\)-fluorobenzoate, and cyclohexane carboxylate, yellow crystals separated during the reaction. The crystals were collected, washed with warm alcohol, then anhydrous ether, and dried in vacuo. In other cases, the reaction mixture was cooled to 0\(^\circ\) for several hours, after which the crystals were collected, washed several times with light petroleum (b. p. 60—80\(^\circ\)), and dried in vacuo at 130\(^\circ\). The perfluorobutyrate was recrystallised from hot toluene. For the octanoate, the diglyme was removed in vacuo and the residue thoroughly extracted with ether and dried.

## Table 2.

### Analyses of molybdenum(II) carboxylates and related compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Found (%)</th>
<th>Required (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Acetate</td>
<td>C,H_3MoO_5</td>
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<td>2-9</td>
</tr>
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<td>C,H_3MoO_4</td>
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<td>5-2</td>
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<td>Isobutyrate</td>
<td>C,H_3MoO_4</td>
<td>35-7</td>
<td>5-2</td>
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<tr>
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<td>C,H_3MoO_4</td>
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<td>6-5</td>
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<tr>
<td>Octanoate</td>
<td>C_6H_10MoO_4</td>
<td>49-5</td>
<td>7-9</td>
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<tr>
<td>Perfluorobutyrate</td>
<td>C_3F_7MoO_4</td>
<td>18-9</td>
<td>—</td>
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<tr>
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<td>2-3</td>
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<tr>
<td>Succinate</td>
<td>C_6H_12MoO_6</td>
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<td>3-4</td>
</tr>
<tr>
<td>Succinate hydrate</td>
<td>C_6H_12MoO_6</td>
<td>51-6</td>
<td>3-9</td>
</tr>
<tr>
<td>Benzenesulphonate</td>
<td>C_6H_12MoO_6</td>
<td>36-0</td>
<td>2-8</td>
</tr>
<tr>
<td>Diphenylphosphinate</td>
<td>C_6H_12MoO_6</td>
<td>54-2</td>
<td>4-0</td>
</tr>
<tr>
<td>Succinate hydrate</td>
<td>C_6H_12MoO_6</td>
<td>22-9</td>
<td>2-2</td>
</tr>
<tr>
<td>Adipate</td>
<td>C_6H_12MoO_6</td>
<td>28-0</td>
<td>5-7</td>
</tr>
<tr>
<td>Adipate hydrate</td>
<td>C_6H_12MoO_6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Glutarate hydrate</td>
<td>C_6H_12MoO_6</td>
<td>24-1</td>
<td>3-2</td>
</tr>
</tbody>
</table>

* Found: F, 10-3. C_6H_12MoO_4 requires F, 10-2\%.

In addition to the data given in Table 1, the carboxylates had the bands expected from the aliphatic or aromatic groups present. For the perfluorobutyrate (requires M, 1044): found by Mechrolab Osmometer (at 37°) in acetone, 1025; in benzene, 1020; by ebulloscopy in toluene, 1020. For the salicylate (requires M, 744): found by osmometer in acetone, 720.

**Dicarboxylates.**—Method (2) was used in all cases, but with an excess (ca. 10\%) of hexacarboxymolybdenum. When the solid dicarboxylate began to separate from the diglyme reaction mixture, the heating was stopped and the mixture was cooled to 0°. The green precipitate was collected, washed with acetone and anhydrous ether, and analysed immediately.

When the diglyme and the apparatus were not specially dehydrated, the product was the hydrated dicarboxylate. The anhydrous complexes were obtained only under strictly anhydrous conditions and using diglyme distilled over sodium directly into the reaction flask.

The diphénylphosphinate, which is assumed to be similar to the carboxylates but with OCO replaced by OPO, was obtained by method (2) as a salmon-pink powder; it was washed thoroughly with ether and dried in vacuo. Similarly, interaction with benzenesulphonic acid gave a greenish-grey powder. The analytical results are given in Table 2.

**Pyridine Adducts.**—(1) To molybdenum acetate or benzoate (ca. 2 g.) was added, in a nitrogen atmosphere, excess of pyridine (dried, redistilled, and deoxygenated (ca. 5 ml.)); after warming to dissolve the crystals, the yellow solution was allowed to cool and the large yellow plate-like crystals were collected, rinsed with pyridine and then ether, and, after being dried in vacuo (ca. 15 min.), were analysed immediately. The acetae, m. p. 130—140° (decomp.) (Found: C, 37-2; H, 3-8; N, 4-6; Mo, 34-3. C,H_11,MoO_4 requires C, 36-8; H, 4-1; N, 4-8; Mo, 32-7\%), and the benzoate (Found: C, 54-4; H, 4-1; N, 3-4; Mo, 25-4. C,H_11,MoO_4 requires C, 54-6; H, 3-6; N, 3-4; Mo, 23-0\%) were prepared.

(2) A warmed solution of the acetae (2 g.) in pyridine was filtered and allowed to stand in air for ca. 12 hr. The red, semicrystalline powder was collected, washed several times with pyridine, then light petroleum (b. p. 60—80°), and dried in vacuo at 80° for several hours (yield ca. 0-5 g.) (Found: C, 24-1; H, 2-3; N, 5-6; Mo, 42-3. C,H_11,MoO_4 requires C, 25-1; H, 2-1; N, 5-8; Mo, 40-2\%).

We thank the Climax Molybdenum Company for gifts of hexacarboxymolybdenum.

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Carboxylates of Palladium, Platinum and Ruthenium

By Sheila M. Morehouse, A. R. Powell, J. P. Heffer, T. A. Stephenson and G. Wilkinson

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During extended studies on platinum metal carboxylates, we have not only confirmed the original Russian findings on rhodium(II) acetate as in recently published work, but have encountered other novel features.

Palladium(II) acetate can be obtained as brown crystals from the interaction of slightly acid solutions of palladium nitrate with acetic acid or by dissolving palladium sponge in hot glacial acetic acid containing a deficiency of nitric acid. The propionate can be obtained similarly and benzoate, pentafluoropropionate and trifluoroacetate by exchange reactions with the acetate. An unusual feature of the propionate is that in benzene solutions at 37°C, molecular weights with intermed are obtained.

It seems reasonable to assume that the trimer has its normal square planar co-ordination and that the trimer-monomer system is one involving bidentate and chelate groups for the former, and different groups for the latter, viz.,
The trimers are readily cleaved by nitrogen, phosphorus, oxygen and sulphur donor ligands to give yellow crystalline monomeric species such as Pd
\[(OCOCH_3)_2(C_5H_5N)_2\]. The low dipole moment of such species indicates trans-configurations and they have a band at 1700 cm\(^{-1}\) arising from a singly bound carboxylate group in contrast to the absorption of bridge or chelate carboxylate groups at ca. 1600 and 1425 cm\(^{-1}\).

A similar platinum(II) acetate has been obtained by careful reduction with formic acid of solutions of hexahydroxyplatinate(IV) in acetic acid. From chloroform it gives purple crystals [Found: O, 19.3; C-CH\(_3\) (Kuhn-Roth), 17.46; M, 950 ± 2 (acetone and chloroform 37°, Mechrolab Osmometer). Required for [Pt(OCOCH\(_3\))\(_2\)]: O, 20.43; C-CH\(_3\), 17.3%; M, 940]. It forms green adducts with nitrogen donor ligands.

The interaction of acetic acid-acetic anhydride mixtures with hydrated ruthenium trichloride gives a paramagnetic brown crystalline powder, insoluble in organic solvents but soluble in water to give yellow solutions containing chloride ion and cation which can be precipitated by tetraphenylborate. The brown material appears to be \[\text{Ru}_2(OCOCH}_3\)_4Cl\] and the cation, \[\text{Ru}_2(OCOCH}_3\)_4OH\]^+; the former thus appears to have both Ru\(^{II}\) and Ru\(^{III}\) with acetate bridges similar to dimeric carboxylates of Cr, Cu, Rh and Re.\(^1\,\^2\)

A deep-green solution is also formed which contains a carbonyl-ruthenium acetate, having weak carbonyl stretching frequencies at 2062 and 1988 cm\(^{-1}\); the interaction of ruthenium trichloride with excess concentrated formic acid gives also a carbonyl complex containing formate and chloride, as orange crystals.

Received December 12, 1963

References

667. Carboxylates of Palladium, Platinum, and Rhodium, and their Adducts

By T. A. Stephenson, (Mrs.) S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson

- The interaction of palladium(II) nitrate with acetic and propionic acids produces the brown carboxylates Pd(OCOR)$_2$; the benzoate, trifluoroacetate, and pentafluoropropionate are obtained via exchange reactions. Although the fluoro-carboxylates are monomeric, the other compounds are trimers in solution at 37°C.

The interaction of the carboxylates with various amines, triphenylphosphate and triphenylarsine gives complexes of the type trans-[Pd(OCOR)$_2$L$_2$] with unidentate carboxylate groups.

Diacetatoplatinum(II) was obtained by the reduction of an acetic acid solution of hexahydroxyplatinum(IV) with formic acid. It is trimeric, not isomorphous with [Pd(OCOMe)$_2$]$_3$, and does not undergo cleavage reactions with donor ligands.

Studies on rhodium(II) carboxylates$^1$ have been confirmed and extended.

**Palladium Carboxylates.**—Diacetatopalladium(II) can be obtained as brown crystals from the interaction of slightly acid solutions of palladium(II) nitrate with glacial acetic acid, or by dissolving palladium sponge suspended in hot glacial acetic acid, by the addition of the minimum quantity of nitric acid. The propionate can be made directly in the same way, while the benzoate, trifluoroacetate, and pentafluoropropionate can be obtained from the acetate by exchange reactions.

An unusual feature of the acetate and propionate is that in benzene solution at 37°C, osmometric determinations show that they are trimeric, whereas ebulloscopically in benzene (80°C) they are monomeric. Attempts to study the trimer–monomer equilibrium by infrared, absorption, and high-resolution nuclear magnetic resonance spectral measurements over a temperature range were unsuccessful since the spectra of the two species appear to show no features that are characteristic (single peak only).

On the other hand, the benzoate is trimeric at 37°C (osmometer) and remains trimeric when its molecular weight is measured ebulloscopically in both benzene (80°C) and chlorobenzene (132°C), while the two fluoro-carboxylates are both monomeric in ethyl acetate at 37°C.

The absorption spectrum of the acetate in benzene or toluene solution (280—1000 mµ) shows a single broad charge-transfer band (ε ~1000) at 394 mµ, although a stronger band below 280 mµ is indicated. Solid-state reflectance spectra of the acetate (750—1000 mµ) showed weak peaks at 730, 820, and 910 mµ whilst the propionate had peaks at 760, 823, and 920 mµ; since these bands were not observed in solutions (0.1 M) a value of <1 is indicated. The longest wavelength d–d band in PtCl$_4^{2-}$ that is assigned to a singlet–triplet transition occurs$^2$ at 565 mµ, and substitution of ammonia for chloride shifts all the bands to shorter wavelengths. Since the carboxylate group produces a stronger ligand field than chloride, it seems unlikely that the weak bands here are due to d–d transitions in these d$^8$ spin-paired species; any d–d bands in the 300—700 mµ region are obscured by the broad charge-transfer band.

The carboxylates are stable indefinitely in air. They are soluble in a number of organic solvents, but decompose when warmed with alcohols, giving palladium metal; prolonged boiling in other solvents gives the same result.

The lability of palladium oxygen bonds is confirmed by the ease with which the carboxylate groups can be wholly or partially replaced by various mono-, bi-, and tetra-
dentate ligands. Thus, the acetate and propionate react in the cold with acetylacetone or with salicylaldehyde to give well-known compounds of the type PdL₂, and with bisacetylace-tone-ethylenedi-imine and bissalicylaldehyde-ethylenedi-imine to produce the completely substituted Pd(ENbisacac) and Pd(ENbisal). With various nitrogen donors, triphenylphosphine and triphenylarsine (a large excess required for complete reaction), yellow crystalline monomeric adducts of the type [Pd(OCOR)₂L₂] are obtained (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>ω₂</th>
<th>ω₁</th>
<th>Separation Δ(ω₂ − ω₁)</th>
<th>Difference (adduct)</th>
<th>Difference (carb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(OCCOPh₂)₂]</td>
<td>1557</td>
<td>1404</td>
<td>163</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Pd(OCCOPh₂)(Ph₂P)]</td>
<td>1623</td>
<td>1319</td>
<td>304</td>
<td>56</td>
<td>85</td>
</tr>
<tr>
<td>[Pd(OCCOPh₂)(Ph₂As)]</td>
<td>1626</td>
<td>1325</td>
<td>301</td>
<td>59</td>
<td>79</td>
</tr>
<tr>
<td>[Pd(OCCOPh₂)(py)]</td>
<td>1609</td>
<td>1342 and/or 1323</td>
<td>≥261</td>
<td>36</td>
<td>≥62</td>
</tr>
<tr>
<td>[Pd(OCCOEO₂)₂]</td>
<td>1572</td>
<td>1456</td>
<td>116</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Pd(OCCOCF₃)(Ph₂P)]</td>
<td>1684</td>
<td>1393</td>
<td>291</td>
<td>112</td>
<td>63</td>
</tr>
<tr>
<td>[Pd(OCCOCF₃)(OSMe₂)]</td>
<td>1681</td>
<td>1408</td>
<td>273</td>
<td>109</td>
<td>48</td>
</tr>
<tr>
<td>[Pd(OCCO₂F₂)]</td>
<td>1587</td>
<td>1431</td>
<td>136</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Pd(OCCO₂F₂)(Ph₂As)]</td>
<td>1672</td>
<td>1372</td>
<td>306</td>
<td>111</td>
<td>59</td>
</tr>
<tr>
<td>[Pd(OCCO₂F₂)(py)]</td>
<td>1578</td>
<td>1425</td>
<td>173</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Pd(OCCO₂F₂)(Et₂N)]</td>
<td>1618</td>
<td>1359 and/or 1311</td>
<td>≥259</td>
<td>23</td>
<td>≥69</td>
</tr>
<tr>
<td>[Pd(OCCO₂F₂)(Me₂NH)]</td>
<td>1602</td>
<td>1427</td>
<td>173</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>[Pd(OCCO₂Me₂)(py)]</td>
<td>1584</td>
<td>1353, 1307</td>
<td>≥281</td>
<td>34</td>
<td>≥74</td>
</tr>
<tr>
<td>[Pd(OCCO₂Me₂)(Et₂N)]</td>
<td>1626</td>
<td>≤1377</td>
<td>≥312</td>
<td>(−)</td>
<td>(−)</td>
</tr>
<tr>
<td>[Pd(OCCO₂Me₂)(Me₂NH)]</td>
<td>1582</td>
<td>≤1370</td>
<td>≥321</td>
<td>(−)</td>
<td>(−)</td>
</tr>
<tr>
<td>[Pd(OCCO₂Me₂)(py)]</td>
<td>≤1626</td>
<td>1377, 1361, 1314</td>
<td>≥239</td>
<td>≤26</td>
<td>≥57</td>
</tr>
</tbody>
</table>

* Among bands in the ω₁ region is the CH₃ rock (ca. 1330). * Band obscured by absorption due to Et₂N, Et₂NH, py, or bipy.

The compounds with nitrogen ligands are the most stable; the triphenylphosphine adducts dissociate and decompose readily in warm solvents making measurement of molecular weights impossible. A determination of the dipole moment of the diethyamine complex indicated a trans-configuration, and the other complexes are presumably also trans with the exception of the 2,2'-bipyridyl complex [Pd(OCCO₂Me₂)(bipy)] which, since it is monomeric, must have cis-carboxylate groups.

The fluoro-carboxylates dissolve in warm acetone and yield well-defined air-stable orange-red crystalline complexes of the composition [Pd(OCOR)₂Me₂CO]₂, these are dimeric in ethyl acetate at 37° and presumably have a structure of type I. Their infrared

spectra show strong bands at 1650 cm⁻¹ (CF₃ complex) and 1653 cm⁻¹ (C₂F₃ complex) with weaker shoulders at 1626 and 1629 cm⁻¹, respectively, one of which can be assigned to the co-ordinated CO (acetone), and the other to ω₂ of the unidentate carboxylate. This is comparable with the shift of the carbonyl band to lower frequencies (compared to free acetone) in, say, the boron trifluoride-acetone complex ³ (1714 → 1640 cm⁻¹). A further strong band around 1540 cm⁻¹ can be assigned to ω₂ of the bridged carboxylates.
For the propionate and acetate, molecular weights indicating dissociation of the trimers and corresponding to [Pd(OCOR)\_2(Me\_2CO)\_2] were obtained in boiling acetone, but crystalline adducts could not be isolated. Interaction of the acetate and trifluoroacetate with dimethyl sulfoxide yielded brown oils. Washing with diethyl ether produced the yellow-brown powder [Pd(OCOCF\_3)\_2(Me\_2SO)\_2] (the acetate complex could not be solidified). Dissolution of these oils in aqueous acidified tetraphenyl arsonium chloride solution gave the salt of the anion [PdCl\_4(Me\_2SO)\_2]^-. The infrared spectra contained a strong band at 1148 cm\(^{-1}\) (former) and 1124 cm\(^{-1}\) (latter) assigned to the SO stretching mode \(^4\) (i.e., S-bonded). Palladous chloride shaken with aqueous dimethyl sulfoxide followed by acidified tetraphenyl arsonium chloride produced the anion, further shaking of the original solution giving orange crystals of [PdCl\_2(Me\_2SO)\_2] (prepared by Cotton \textit{et al.})\(^4\). Precipitation of the anion is inhibited in alkaline solution, suggesting that the hydroxy-compound is an intermediate. No precipitation occurred with tetraethyl (or methyl)-ammonium salts but with n-butyltriphenylphosphonium bromide it did, showing that the physical size of the cation is an important factor.

The carboxylate adducts containing nitrogen also dissolved in water, whereas the phosphorus (and arsenic) adducts were completely insoluble. Furthermore, addition of halogen ions to these aqueous solutions produced immediate precipitation of the corresponding halogeno-complex. Thus, the compound [PdBr\_3(\text{Et}_\_2\text{NH})\_2] was prepared from the acetate complex and potassium or tetramethylammonium bromide. The compound is a non-electrolyte in nitromethane, and precipitation is again inhibited in alkaline solution.

\textit{Infrared Spectra.}—Previous work \(^5\) has shown that, since the acetate ion possesses low symmetry (C\(_2\)), no marked differences in spectra are to be expected for the various types of co-ordinated structure possible. However, the effect on the frequency of changing the metal is different for each structural type. Nakamoto \textit{et al.}\(^5\) have shown that for a series of \(\alpha\)-amino-acid complexes, bonded through only one oxygen, the antisymmetric COO\(^-\) stretching frequency (\(\omega_1\)) increased and the symmetric COO\(^-\) stretching frequency (\(\omega_2\)) decreased as the M-O bond became stronger. Similar trends were also found in edta complexes,\(^5\) the conclusion being that the shift in frequency is due to a breakdown in the equivalence of the C-O bonds so that the spectrum of the complex resembles more closely that of the acid. For symmetrical co-ordination of the carboxylate ion, Nakamoto \textit{et al.}\(^5\) showed that both \(\omega_1\) and \(\omega_2\) shifted in the same direction when the metal was changed. For the present compounds, it seems reasonable to assume that the palladium atom has its normal square planar co-ordination, the trimers having both bridging and chelate groups, and the monomers only chelate groups (II, III). Separation values of \(\omega_1\) and \(\omega_2\) comparable to that of the free ion support these symmetrically co-ordinated structures, e.g., for sodium acetate \(^5\) 164 cm\(^{-1}\).

However, infrared spectra (Table I) show that, with one exception (the diethylamine acetate complex), in their adducts of the type [Pd(OCOR)\_2L\_2] (in compounds where ligand bands do not interfere with the assignment of \(\omega_2\) and in spite of ambiguities in assigning \(\omega_1\) in several instances) \(\omega_2\) increases and \(\omega_1\) decreases compared with the original carboxylates. Similar variations of the COO\(^-\) stretching frequency bands have been observed with organotin carboxylates when the compounds are melted or dissolved in non-polar solvents (conversion from co-ordination polymers containing bridged groups into monomolecular species resembling organic esters being the explanation offered)\(^6\),\(^6\) and in the cleavage of bridged carboxylate systems such as rhodium carbonyl acetate and phthalate with pyridine and triphenylphosphine.\(^7\) Hence, unidentate carboxylate co-ordination as in (IV) rather than chelation is indicated. Why the acetate and propionate adducts contain several bands in the \(\omega_1\) region, whereas the fluoro-carboxylates have only one, is unknown; the rhodium carbonyl carboxylate adducts also contain several.

In the compound Pd(OCORMe)\_2(\text{Et}_\_2\text{NH})\_2, the decrease of 18 cm\(^{-1}\) in \(\omega_2\) can be attributed to intramolecular hydrogen bonding between the NH hydrogen and the unco-ordinated
oxygen of the carboxylate group. A similar effect is observed in nickel acetate tetrahydrate, where an X-ray structural analysis 8 indicates monodentate co-ordination, but a comparison with the free ion shows a lowering of $\omega_2$ and a decrease in the separation $^8$ between $\omega_1$ and $\omega_2$. This is attributed to hydrogen bonding (with water molecules) tending to equate the C-O bond lengths $^8$ (1.29 $\pm$ 0.02 and 1.31 $\pm$ 0.02 Å), thus compensating for the asymmetry produced through monodentate co-ordination.

Finally, although several investigators have shown that $\omega_2$ is more sensitive than $\omega_1$ to changes in the metal, $^9$ the decrease in $\omega_1$ in this system, for the alkane- and arenecarboxylates, is larger than the increase in $\omega_2$ and can only be attributed to the change in the mode of carboxylate bonding. Further evidence of this effect comes from the work on organotin carboxylates (Table 2) and the cleavage of rhodium carbonyl carboxylates; the explanation is at present unknown.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solid state (bridging)</th>
<th>Dissolved state (CCl4)</th>
<th>Difference $\omega_2$ (soln.) $-$ $\omega_1$ (soln.)</th>
<th>Difference $\omega_2$ (solid) $-$ $\omega_1$ (solid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethyltin acetate</td>
<td>1572</td>
<td>1412</td>
<td>1655</td>
<td>1302</td>
</tr>
<tr>
<td>Triisobutyltin acetate</td>
<td>1572</td>
<td>1410</td>
<td>1647</td>
<td>1300</td>
</tr>
<tr>
<td>Trihexyltin acetate</td>
<td>1570</td>
<td>1408</td>
<td>1650</td>
<td>1304</td>
</tr>
<tr>
<td>Trimethylnitauurate</td>
<td>1567</td>
<td>1410</td>
<td>1642</td>
<td>1302</td>
</tr>
</tbody>
</table>

In the fluoro-carboxylates, the decrease in $\omega_1$ is less than the increase in $\omega_2$, but here the strong positive inductive effect of the fluoro-group will accentuate the initial asymmetry of the carboxylate group just as variation of metal-oxygen bond strength does, thus accounting for a large increase in $\omega_2$.

Diacetatoplatinum(II).—Diacetatoplatinum(II) was obtained by careful reduction with formic acid of solutions of hexahydroxoplatinate(IV) in acetic acid. From chloroform, purple crystals were obtained, which are triclinic in acetone, or chloroform at 37° (osmometer), and trimeric ellipsoidically in benzene (80°C) and chlorobenzene (132°C). However, X-ray powder photographs of platinum and palladium acetates show that the compounds are not isomorphous, and therefore it is probable, but not necessarily so, that the compounds also have different molecular structures.

Attempts to prepare similar monomeric adducts with nitrogen and phosphorus donors produced compounds of uncertain compositions and very high molecular weights, e.g., with diethylamine a deep green solution was produced, with an analysis close to the formula \[ \text{[Pt}_3(\text{OCOC}_2\text{H}_5)_6(\text{Et}_2\text{NH})_4] \]. The absorption spectrum of the acetate in benzene solution (deep red) shows two charge-transfer bands at 519 $\text{m}_{\mu}$ ($\varepsilon = 2000$) and 402 $\text{m}_{\mu}$ ($\varepsilon = 1940$). However, the solid-state reflectance spectrum (350–1000 $\text{m}_{\mu}$) is completely different, showing a weak band at 925 $\text{m}_{\mu}$, a broad band 567 $\text{m}_{\mu}$ and indications of another charge-transfer band at 350 $\text{m}_{\mu}$ (cf. solid and solution spectra for palladous acetate, which are virtually identical).

The infrared spectrum contains strong bands at 1562 ($\omega_2$), 1429 ($\omega_1$), and 689 $\text{cm}^{-1}$ (COO$^{-}$ deformation band). Thus, the retention of a trimeric structure at 132°, non-isomorphism of powder photographs, and inability to cleave the acetate are clear evidence for a difference in structure between these platinum metal carboxylates. Metal-metal interaction is a possible explanation of the intense coloration and stability of diacetatoplatinum.

Rhodium Carboxylates.—The original Russian findings on rhodium(II) acetate hydrate have been confirmed as in recently published work. $^{10}$ The formate, propionate, and trifluoroacetate have also been prepared by the action of the appropriate acid upon rhodium hydrous oxide. All these carboxylates readily react with donor-type ligands such as triphenylphosphine, piperidine, etc., which replace the two water molecules of the dimer. These adducts were prepared in alcoholic solutions and recrystallised from a variety of solvents as pure crystalline species, for which complete analytical figures were obtained.
The "extremely insoluble" pyridine complex prepared by Johnson et al.\textsuperscript{10} from anhydrous rhodium acetate was prepared via the hydrate and could be recrystallised from chloroform and petroleum.

A 10\textsuperscript{3} molar aqueous solution of rhodium propionate hydrate has a molecular conductivity of 285 mhos and is acidic (cf. copper acetate hydrate which also ionises in aqueous solution\textsuperscript{11}) suggesting the equilibrium

\[ \text{[Rh(OOCET)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{3}]} \leftrightarrow [\text{Rh(OOCET)\textsubscript{2}(OH)\textsubscript{3}]}^{2+} + 2H^+ \]

Proton magnetic resonance spectra showed the compounds to be diamagnetic; this indicates that despite the formal bivalence of the rhodium, the \(d^7\) configuration is absent.

Infrared spectra showed strong bands corresponding to \(\text{\(\nu\)}\) and \(\text{\(\pi\)}\): rhodium formate hydrate 1587 (\(\text{\(\nu\)}\)), 1430 (\(\text{\(\pi\)}\)), \(\Delta\nu 157 \text{ cm}^{-1}\); rhodium propionate hydrate 1570 (\(\text{\(\nu\)}\)), 1420 (\(\text{\(\pi\)}\)), 150 cm.\textsuperscript{-1}; rhodium acetate hydrate 1580 (\(\text{\(\nu\)}\)), 1430 (\(\text{\(\pi\)}\)), \(\Delta\nu 150 \text{ cm}^{-1}\).

**EXPERIMENTAL**

Micro-analyses and molecular weight determinations (Mechrolab osmometer at 37\textdegree, and ebullioscopic) were made by the Microanalytical Laboratory, Imperial College. Infrared spectra were measured on a Grubb-Parsons spectrometer grating instrument in Nujol and hexachlorobutadiene mulls. Visible spectra were obtained with a Perkin-Elmer model 350 spectrophotometer and, in reflectance, with a Unicam S.P. 700 spectrophotometer. X-Ray powder photographs of palladium and platinum acetates in Lindemann glass tubes were taken with a Philips camera type PW 104 (11-46 cm. diam. with nickel-filtered copper radiation; ca. 3 hr. exposure).

Analyses of palladium compounds are given in Table 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (%)</th>
<th>Required (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}</td>
<td>21-4 3-1 28-5</td>
<td>714 benzene 21-4 2-7 28-5 675 (trimer) 225</td>
</tr>
<tr>
<td>Pd(EtCO\textsubscript{2})\textsubscript{2}</td>
<td>28-6 4-0 25-1</td>
<td>767 benzene 28-6 4-4 25-3 759 (trimer) 253</td>
</tr>
<tr>
<td>Pd(PhCO\textsubscript{2})\textsubscript{2}</td>
<td>47-8 3-2 18-4</td>
<td>1023 benzene 48-0 2-9 18-3 1047 (trimer) 1010</td>
</tr>
<tr>
<td>Pd(CF\textsubscript{3}CO\textsubscript{2})\textsubscript{2}</td>
<td>14-8</td>
<td>31-5 332</td>
</tr>
<tr>
<td>Pd(C\textsubscript{6}F\textsubscript{5}CO\textsubscript{2})\textsubscript{2}</td>
<td>16-9</td>
<td>25-2 434</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}Py\textsubscript{2}</td>
<td>43-4 4-3 7-4 10-7</td>
<td>509 benzene 43-8 4-2 7-3 10-7 383</td>
</tr>
<tr>
<td>Pd(PhCO\textsubscript{2})\textsubscript{2}Py\textsubscript{2}</td>
<td>56-3 4-3 5-6 12-8</td>
<td>418 chloroform 56-8 3-9 5-5 12-6 507</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}quin\textsubscript{2}</td>
<td>54-5 4-7 5-8 13-3</td>
<td>492</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}(NH\textsubscript{3})\textsubscript{2}</td>
<td>39-0 7-7 7-6 17-4</td>
<td>379 benzene 38-9 7-6 7-5 17-3 371</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}(N\textsubscript{2}Et\textsubscript{2})</td>
<td>6-6 14-5 24-7</td>
<td></td>
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<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}bipy</td>
<td>7-3 17-3</td>
<td>348 chloroform</td>
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<tr>
<td>Pd(PhCO\textsubscript{2})\textsubscript{2}(2,2'-AsPh\textsubscript{2}2)</td>
<td>61-9 4-0 6-8</td>
<td>977 benzene 62-4 4-2 6-7 961</td>
</tr>
<tr>
<td>Pd(PhCO\textsubscript{2})\textsubscript{2}(2,2'-PPh\textsubscript{2}2)</td>
<td>68-3 4-9 7-4</td>
<td>68-7 4-5 7-3 68-3</td>
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<td>Pd(MeCO\textsubscript{2})\textsubscript{2}(2,2'-Ph\textsubscript{2}2)</td>
<td>64-4 5-0 8-8</td>
<td>64-1 4-8 8-5 64-1</td>
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<tr>
<td>Pd(PhCO\textsubscript{2})\textsubscript{2}(2,2'-Ph\textsubscript{2}2)</td>
<td>65-5 5-2 8-3</td>
<td>64-9 5-2 8-2 64-9</td>
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<tr>
<td>Pd(CF\textsubscript{3}CO\textsubscript{2})\textsubscript{2}(2,2'-AsPh\textsubscript{2}2)</td>
<td>50-9 3-3</td>
<td>10-7 954</td>
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<tr>
<td>Pd(CF\textsubscript{3}CO\textsubscript{2})\textsubscript{2}(2,2'-Ph\textsubscript{2}2)</td>
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<td>10-4 1070</td>
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<tr>
<td>Pd(CF\textsubscript{3}CO\textsubscript{2})\textsubscript{2}MeCO\textsubscript{2}</td>
<td>21-7 1-9</td>
<td></td>
</tr>
<tr>
<td>Pd(C\textsubscript{6}F\textsubscript{5}CO\textsubscript{2})\textsubscript{2}MeCO\textsubscript{2}</td>
<td>22-9 2-1</td>
<td>912</td>
</tr>
<tr>
<td>Pd(C\textsubscript{6}F\textsubscript{5}CO\textsubscript{2})\textsubscript{2}MeSO\textsubscript{2}</td>
<td>20-0 2-8</td>
<td>19-6 2-5</td>
</tr>
</tbody>
</table>

* Ebullioscopic. † quin = isoquinoline. ‡ S: Found, 12-9; Required, 13-1.
Diacetatopalladium(II).—Palladium sponge (10 g.) was boiled gently under reflux with a solution of glacial acetic acid (250 ml.) and concentrated nitric acid (6 ml.) until evolution of brown fumes ceased. A small residue of palladium should remain undissolved; if not, a little more sponge should be added and boiling continued until no trace of brown fumes is observed. This procedure is necessary to avoid contamination of the product with PdNO₂₃OAc. The boiling brown solution is filtered and allowed to cool whereupon most of the complex separates as orange-brown crystals [m. p., 205° (decomp.)] which are washed with acetic acid and water and air-dried; the pale reddish-brown acetic acid mother-liquor may be used for further preparations. The yield is virtually quantitative. Large crystals of the compound can be prepared by dissolving it in warm benzene, mixing the solution with half its volume of glacial acetic acid, and allowing the benzene to evaporate slowly at room temperature.

The diacetato-complex has also been prepared by the addition of glacial acetic acid to a warm aqueous solution of palladous sulphate. The product contains small amounts of impurities (or mixed complex) and always leaves an insoluble pink or brown residue when dissolved in benzene.

The compound is soluble in chloroform, methylene dichloride, acetone, acetonitrile, and diethyl ether, but is insoluble in water and petroleum and decomposes when warmed with alcohols, in which it is also insoluble. It dissolves in aqueous potassium iodide to give PdI₂(s) and a red solution of PdI₂⁺, but is insoluble in aqueous solutions of sodium chloride, nitrite, and acetate. It is soluble with decomposition in aqueous hydrochloric acid to give PdCl₂⁻. X-Ray data are given in Table 4.

<table>
<thead>
<tr>
<th>Table 4</th>
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<tr>
<td>X-Ray values for palladium and platinum acetates</td>
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<tr>
<td><strong>Palladous acetate</strong></td>
</tr>
<tr>
<td>d</td>
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<td>ing)</td>
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<tr>
<td>8.087</td>
</tr>
<tr>
<td>7.099</td>
</tr>
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<td>6.521</td>
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<tr>
<td>5.864</td>
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<td>5.546</td>
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<td>4.962</td>
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<tr>
<td>4.794</td>
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<tr>
<td>4.503</td>
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<tr>
<td>4.131</td>
</tr>
<tr>
<td>3.715</td>
</tr>
<tr>
<td>3.598</td>
</tr>
<tr>
<td>3.370</td>
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</tbody>
</table>

Dipropionatopalladium(II).—This complex was obtained in virtually quantitative yield in a similar way, by using propionic acid and palladium sponge; it had m. p. 161—165°. The orange-brown compound has properties very similar to those of the diacetate complex, but is somewhat more soluble in cold organic solvents.

Dibenzoatopalladium(II).—A benzene solution of palladium diacetate and benzoic acid (mole ratio 1 : 3) was evaporated on a steam-bath and the residue washed with acetone or diethyl ether to remove benzoic acid. Recrystallisation from benzene gave the complex as a yellowish brown solid, m. p. 220° (decomp.). It is soluble in chloroform and toluene, but decomposes on warming with alcohols.

Di(trifluoroacetato)palladium(II).—A trifluoroacetic acid (ca. 15 ml.) solution of diacetatopalladium (0.8 g.) was evaporated on a steam-bath and the evaporation repeated with a further quantity (ca. 7 ml.) of acid. The residual complex was dried in vacuo (40°) to a brown powder, m. p. 210° (decomp.). It is soluble in ether and acetone, but insoluble in benzene, chloroform, and trifluoroacetic acid.

Di(pentafluoropropionato)palladium(II).—Like the di(trifluoroacetato)palladium(II) the complex is a brown powder, m. p. 195° (decomp.). Its solubility properties resemble those of the di(tri-fluoroacetato)-complex.

Diacetatobis(pyridine)palladium(II).—Diacetatopalladium(II) was dissolved in pyridine and the solution warmed (80°); chilling in ice gave pale yellow crystals of the complex, m. p. 185°
(decomp.), which were recrystallised from cold benzene. The compound is soluble in water as well as in organic solvents.

**Diacetato-2,2'-bipyridylipalladium(II)**.—Diacetatopalladium(II) (0.56 g.) in benzene (50 ml.) was added slowly to 2,2'-bipyridyl (0.4 g.) in benzene (10 ml.) with stirring. The mustard-coloured precipitate was washed with petroleum and recrystallised from benzene–dichloromethane to give the pale yellow complex, m. p. 195° (decomp.); it is soluble in water and ethanol, but insoluble in acetone and benzene.

**Dibenzoatobisbipyridinedipalladium(II)**.—Dibenzoatopalladium(II) (0.3 g.) in benzene was shaken with an excess (ca. 6 ml.) of pyridine and the white precipitate of the complex, m. p. 185°, were washed with diethyl ether and dried in vacuo at room temperature.

**Diacetatobisisquinolinedipalladium(II)**.—A solution of isoquinoline (3 ml.) in diethyl ether (5 ml.) was added to diacetatopalladium(II) (0.3 g.) in benzene (5 ml.); the pale yellow complex, m. p. 205° (decomp.), was dried in vacuo. It is insoluble in water and benzene, but dissolves in warm nitromethane.

**Diacetobis(diethylamine)palladium(II)**.—A solution of diacetatopalladium(II) (0.5 g.) in diethylamine (ca. 10 ml.) was filtered and evaporated to give pale yellow crystals of the complex, which were recrystallised from petroleum (b. p. 40–60°); it had m. p. 125°, soluble in water, ethanol, ether, petroleum, and benzene. By using the refraction method, the dipole moment was calculated from the dielectric constant (ε) measured with a heterodyne-beat capacitance meter; it was found to be zero within the limits of error.

**Diacetatobis(triethylamine)palladium(II)**.—Diacetatopalladium(II) (0.2 g.) in triethylamine (ca. 10 ml.) was warmed, filtered, and chilled to 0° for 1 hr. The lemon yellow crystals of the compound, m. p. 75° (decomp.), were dried in vacuo and analysed immediately. It is soluble in organic solvents, but the solutions decompose rather quickly, especially on warming, making a molecular weight determination impossible.

**Diacetatobis(triphenylphosphine)palladium(II)**.—Diacetatopalladium(II) (0.04 g.) in benzene was treated with an excess of triphenylphosphine (ca. 0.07 g.) in benzene. Addition of petroleum (60–80°) to the resulting pale yellow solution gave on shaking slowly yellow crystals of the complex, m. p. 135–136°, which were washed with petroleum and dried in vacuo (40°). It is sparingly soluble in cold solvents; when warmed with benzene, the initial yellow solution rapidly became red and then brown, depositing metallic palladium; attempts to isolate the red species failed.

**Dipropionatobis(triphenylphosphine)palladium(II)**.—This was prepared in the same way as the corresponding diacetate-complex, it is a pale yellow complex, m. p. 147–148°, which decomposes rapidly in solution in warm solvents such as benzene and ethyl acetate.

**Dibenzoatobis(triphenylphosphine)palladium(II)**.—This was prepared in the same way as the corresponding diacetate-complex, giving very pale yellow crystals m. p. 192–193°. It dissolves in warm benzene to give a yellow solution; low osmometric molecular weights (~500, req. 800) indicate some dissociation.

**Dibenzoatobis(triphenylarsine)palladium(II)**.—This was prepared in the same way as the triphenylphosphine complex, but with an excess of triphenylarsine, to give bright yellow crystals, m. p. 198–199°.

**Di(trifluoroacetato)bis(triphenylarsine)palladium(II)**.—The trifluoroacetato-complex (0.03 g.), suspended in benzene (ca. 7 ml.), and a large excess of triphenylarsine (0.15 g.) were shaken together until the solid had almost disappeared. The pale yellow solution was filtered, and petroleum (b. p. 100–120°) was added slowly to give bright yellow crystals of the complex, m. p. 192–193°, which were washed with petroleum (b. p. 30–40°) and dried in vacuo. The compound is insoluble in water, but soluble in benzene, acetone, and chloroform, etc.

**Di[pentfluorophosphonato]bis(triphenylarsine)palladium(II)**.—Prepared in the same way as the corresponding trifluorooraceto-complex. It formed bright yellow crystals, m. p. 204–205°.

**Di(trifluoroacetato)(acetone)palladium(II)**.—The bis(trifluoroacetato)-complex was dissolved in warm acetone to give a reddish-yellow solution, which when cooled gave the orange-red crystalline complex, m. p. 183° (decomp.). It is soluble in warm ethyl acetate (decomposing rapidly), but insoluble in acetone, benzene, chloroform, and ether. The bispentfluorophosphonato-complex gave a similar complex, m. p. 180° (decomp.).

**Ditrifluoroacetatobis(dimethyl sulfoxide)palladium(II)**.—Dimethyl sulfoxide was added dropwise to a suspension of ditrifluoroacetopalladium(II) in benzene. The resulting yellow
solution was filtered, the benzene removed (<45° in vacuo), and the residual oil washed several times with excess of diethyl ether to give a yellow-brown powder, m. p. 100° (decomp.).

_Tetraphenylarsornium Trichlorodimethyl sulfoxide) palladate(II)._—Diacetatopalladium(II) in benzene was shaken for several hours with excess of dimethyl sulfoxide. After removal of the benzene, the residual oil (or that from the corresponding trifluoroacetate reaction) was dissolved in water and filtered into a concentrated acidified (hydrochloric acid) solution of tetraphenylarsornium chloride. The lemon-yellow crystalline salt, m. p. 190° (decomp.) was washed with water, dried in a desiccator, and finally re Washed with ether (Found: C, 46.0; H, 4.0; Cl, 16.1; O, 2.5; S, 4-6. C_{86}H_{20}AsCl_{4}OPdS requires C, 46.3; H, 3.8; Cl, 15.8; O, 2.4; S, 4.7%). The salt is a 1:1 electrolyte in nitromethane.

Infrared spectrum: 1471w, 1343s, 1389w, 1333vw, 1309vw, 1176vw, 1124s (S=O, S-bonded), 1078m, 1020m, 995m, 965w, 930w (w, broad), 746s, 741s, 694m, and 685s cm^{-1}. An identical material was obtained by shaking palladium(II) chloride with a 1:1 mixture of dimethyl sulfoxide and water for several minutes, filtering the mixture, and then adding a concentrated aqueous solution of acidified tetraphenylarsornium chloride. When the original solution was shaken for ca. 30 min., orange crystals of [PdCl_4(OSMe_2)_2] were obtained; they were washed with water and ether and dried; they had m. p. 190° (decomp.) (Found: Cl, 21.3. Calc. for C_{86}H_{20}Cl_{6}O_{2}Pd_2: Cl, 21.2%). The infrared spectrum is identical to that previously reported.12

_Dichromobis(diethylamine)palladium(II)._—Diacetatobis(diethylamine)palladium(II) was added to a warm concentrated aqueous solution of potassium bromide. The immediate yellowish-green precipitate was filtered off, washed several times with water, dried in a desiccator, and then re Washed with ether; it had m. p. 180° (decomp.) (Found: C, 23.9; H, 5.25; Br, 39.8; N, 6.7. Calc. for C_{86}H_{20}Br_{2}N_{2}Pd: C, 23.2; H, 5.3; Br, 38.7; N, 6.8%). The compound is a non-electrolyte in warm nitromethane.

_Diacetoplatinum._—Sodium hexahydroxyplatinate, Na_2Pt(OH)_6 (10 g.), was slowly added with shaking to concentrated nitric acid (25 ml.) and the mixture heated until the solid had dissolved. Most of the acid was removed by heating the flask over a free flame until a brown syrup containing crystals of sodium nitrate remains. Glacial acetic acid (30 ml.) was added and the mixture boiled until the nitrate crystals had become white; the solution was cooled and filtered and the sodium nitrate crystals washed with acetic acid. The filtrate and washings were transferred to another flask and boiled by swirling over a free flame until only a thick orange-brown syrup remained; this treatment expelled most of the nitric acid. A further 30 ml. of acetic acid was added and a 20:80 mixture of 90% formic acid and glacial acetic acid was added slowly with swirling to the boiling solution until no further brown fumes were evolved. At this stage, the solution became dark brown and further addition of the formic acid caused it suddenly to become bright green. The formic acid mixture was now added a few drops at a time with vigorous boiling, whereupon the colour gradually turned to bright ultramarine blue and, with the addition of further formic acid, to deep purple. Crystals of the complex were suddenly precipitated at this point, but were always contaminated with a little platinum black. The solution was cooled and the precipitate washed with cold acetic acid. It should be noted that at every stage in this reduction with formic acid, the solution must be kept boiled and well stirred for some time after every small addition of reducing agent; addition of an excess causes rapid deposition of platinum black. After the brown fumes from the nitric acid ceased to form, about 4—5 ml. of the formic acid solution were required to give the maximum yield.

The crude purple crystals were extracted with chloroform and the filtered solution mixed with half its volume of glacial acetic acid and set aside to evaporate at room temperature, the resulting large crystals of the acetate were collected, washed with water, and dried in air.

The yield varied considerably; in some experiments most of the platinum was recovered as the acetate but in others the purple solutions gave no crystals. The compound gave almost black crystals, m. p. 245° (decomp.) (Found: O, 19.3; Pt, 64.0; C=CH_3 (Kuhn Roth), 17-5%; M (osmometer) at 37° acetone and chloroform, 950 ± 2; (ebullioscopically) in benzene, 837; chlorobenzene, 886. C_{86}H_{20}O_{2}Pt requires O, 20.4; Pt, 62.3; C=CH_3, 17.3%; M, 940 (trimers).

The compound is soluble in chloroform, benzene, and toluene, giving purple solutions.

_Rhodium Carboxylates._—The rhodium carboxylates were prepared by refluxing rhodium hydrous oxide in an excess of formic, acetic, or propionic acid and ethanol. The yellow solution
gradually turned amber and then green. The solution was cooled, and the dark green powder that was precipitated was filtered off. The products were recrystallised from methanol or water and were stable up to 240°.

The trifluoroacetorhodium(ii) complex was prepared by the action of trifluoroacetic acid on the hydrous oxide followed by extraction of the reaction mixture with dichloromethane. The blue-green product was recrystallised from benzene.

**Diacetopyridinerhodium(ii)**. Pyridine was added dropwise to a cold, methanolic solution of the trifluoroacetorhodium complex (mole ratio 2:1), and the product was obtained as dark red crystals, which after recrystallisation from chloroform and petroleum had m. p. 225° (decomp.) (Found: C, 36-4; H, 3-7; N, 4-8; O, 21-6. Calc. for C₉H₁₄NO₃Rh: C, 36-0; H, 3-7; N, 4-7; O, 21-3%).

**Dipropionatopyridinerhodium(ii) and diformatopyridinerhodium(ii)**. These were similarly prepared, the propionate complex being recrystallised from cyclohexane and petroleum and the formate complex from dichloromethane. The *propionate*-complex (Found: C, 40-8; H, 4-6; N, 4-8; O, 19-7%). C₉H₁₄NO₃Rf requires C, 40-3; H, 4-6; N, 4-8; O, 19-7%; the formate complex (Found: C, 31-6; H, 3-5; N, 5-4. Calc. for C₉H₁₄NO₃Rf: C, 31-0; H, 2-6; N, 5-2%); m. p. 145° (decomp.). This compound was first prepared by Chernyaev et al. who assigned it the composition [PyHRf(NOOC₂H₅)₂].

**Diacetato(triphenylphosphine)rhodium(ii)**. This complex was prepared by the addition of triphenylphosphine in diethyl ether to a cold methanolic solution of the diacetato-complex. The orange powder that was immediately precipitated, was recrystallised from chloroform (Found: C, 54-8; H, 4-6. C₂₃H₂₂O₄PRh requires C, 54-6; H, 4-8%).

**Dipropionato(triphenylphosphine)rhodium(ii)**. This complex was similarly prepared from the propionate-complex and was recrystallised from cyclohexane [Found: C, 56-4; H, 4-9; O, 12-2%; M (ehullisopic in benzene), 992. C₂₃H₂₂O₄PRh requires C, 56-4; H, 4-9; O, 12-5%; M, 1023 (dimer)].

**Diformalato(triphenylphosphine)rhodium(ii)**. This complex was similarly prepared from the diformal-complex; it was recrystallised from chloroform and petroleum giving orange crystals, m. p. 165° (decomp.) (Found: C, 52-8; H, 4-6. C₂₃H₂₂O₄PRh requires C, 52-6; H, 3-8%).

**Dipropionatoisquinolinorhodium(ii)**. Isoquinoline in diethyl ether was added to a cold, methanolic solution of dipropionorhodium(ii). Dark red crystals formed immediately and were recrystallised from cold benzene and petroleum (Found: C, 48-3; H, 4-9; N, 3-6; O, 16-9. C₂₃H₂₂O₄NO₃Rf requires C, 47-6; H, 4-5; N, 3-7; O, 16-9%).

**Di[(trifluoroacetato)pyridinerhodium(ii)]**. Pyridine was added dropwise to a cold ethanolic solution of di[(trifluoroacetato)rhodium(ii)]. Red crystals formed, and were recrystallised from dichloromethane (Found: C, 26-5; H, 2-1. C₂₃H₁₆F₃NO₃Rf requires C, 26-4; H, 1-2%).

We thank the Hercules Powder Company for financial assistance (T. A. S., S. M. M.).

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Johnson, Mathew and Co. Ltd., Wembley. [Received, November 18th, 1964.]
NEW RUTHENIUM CARBOXYLATE COMPLEXES

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(Received 22 January 1966)

Abstract—The interaction of hydrated ruthenium trichloride with carboxylic acid–acid anhydride mixtures gives crystalline complexes of formula [Ru$_3$(OCOR)$_6$Cl], (R = Me, Et, nPr), where the ruthenium atoms have formal oxidation states of II and III.$^{(1)}$ These complexes have high magnetic moments over the temperature range 300-100°K and appear to be the first spin-free complexes of ruthenium to be prepared. Other less well-defined ruthenium carboxylates are described.

The interaction of hydrated ruthenium (III, IV) oxide with glacial acetic acid was claimed to give$^{(2)}$ the binuclear complex [Ru$(OCOMe)_{2}$OH(H$_2$O)$_2$]$_2$, which on hydrolysis yielded [Ru$_3$(OCOMe)$_6$(OH)$_2$(H$_2$O)$_3$] and [Ru$_2$(OCOMe)$_6$(OH)$_2$(H$_2$O)$_3$]$_2$. Other products from the same reaction were [Ru$(OCOMe)_{2}$OH]$_2$ and [Ru$_2$(OCOMe)$_6$OH]; with formic acid, the basic trinuclear complex, [Ru$_3$(OCOH)$_6$(OH)$_2$]HCO$_2$·5H$_2$O, was obtained. Our attempts to repeat this work have, however, proved unsuccessful. By reduction of ruthenium tetroxide with acetaldehyde in anhydrous acetic acid–carbon tetrachloride mixtures, Martin$^{(3)}$ obtained [Ru$_3$(OCOMe)$_6$(OH)$_2$]OCOMe·7H$_2$O analogous to the trinuclear basic complexes of chromium and iron (III). The chlorides of the latter have recently been reformulated [M$_3$(OCOMe)$_6$O(H$_2$O)$_3$]Cl·xH$_2$O,$^{(4)}$ (M = Fe, Cr); hence the ruthenium complex is probably

[Ru$_3$(OCOMe)$_6$O(H$_2$O)$_3$]OCOMe·5H$_2$O.

Interaction of this complex with pyridine followed by the addition of chloroplatinic acid in dilute hydrochloric acid gave [Ru$_3$(OCOMe)$_6$(py)$_3$Cl[PtCl$_4$]·7H$_2$O$.^{(5)}$

In the present paper we report the interaction of hydrated ruthenium trichloride and oxide with carboxylic acid–acid anhydride mixtures.

RESULTS

Carboxylatoruthenium chlorides

The interaction of commercial hydrated “ruthenium trichloride” with carboxylic acid–acid anhydride mixtures on refluxing in a stream of oxygen for several hours gave carboxylates of the unusual stoichiometry Ru$_2$(OCOR)$_6$Cl. The acetate is insoluble in common organic solvents save hot methanol, but the solubility increases with the length of the alkyl chain (cf., rhenium chlorocarboxylates$^{(6)}$). Thus, the propionate is soluble in warm methanol and ethanol and the n-butyrate in cold methanol, ethanol, warm acetone and hot n-butyric acid. The first two are soluble

$^{(1)}$ Preliminary note: Chem. Ind. 544 (1964).
$^{(2)}$ A. W. M. Mond, J. chem. Soc. 1247 (1930).
in hot water, giving yellow-brown solutions; the n-butyrate sparingly so. The addition of tetraphenylboron ion to these aqueous solutions (which had a conductivity corresponding to that of a 1:1 electrolyte) gave fairly unstable orange precipitates, (1:1 electrolytes in acetone and nitrobenzene), of stoichiometry \([\text{Ru}_2(\text{OCOR})_2(\text{OH})_2\text{H}_2\text{O}]\,[\text{BPh}_4],\) (R = Me, Et). The i.r. spectra of these solids contain bands in the hydroxy region, not found in either sodium tetraphenylboron or the original complexes while the aqueous solutions from which they are obtained are acidic, suggesting that hydrolysis of the carboxylates occurs. Since the tetraphenylborate salt of the acetate complex has the same magnetic moment as the original chloride, the co-ordination of both hydroxo and aquo groups is necessary to maintain the same oxidation state for ruthenium. The acetate and n-butyrate are also completely ionized in methanol. Thus, molecular weights in this solvent confirm the binuclear structure of the complexes.

**Magnetic moments.** Assuming that the carboxylate groups are bridging between the metal atoms (see later) then, in a binuclear ion \([\text{Ru}_2(\text{OCOR})_4]^{1+},\) one ruthenium atom must be in the formal oxidation state II and the other III. All known complexes of ruthenium (II), \(d^8\) are octahedral and diamagnetic; those of ruthenium (III), \(d^5\), are spin-paired with a magnetic moment of \(\sim 2\text{B.M.}\) (provided the compound is magnetically dilute). The present compounds should therefore have given a low value of \(\mu_{\text{eff}}\). However, the values found for all three complexes in the solid state as \(\text{Ru}_2(\text{OCOR})_4\text{Cl},\) in solution in methanol, and for the tetraphenylborate salt of the acetate in nitrobenzene, were between 2·7 and 3·4 B.M. per ruthenium atom (or 4·4-6·6 B.M. per dimer) (Table 1).

**Table 1.—Magnetic data for ruthenium chlorocarboxylates**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>T(^\circ)K</th>
<th>(10^6\chi_M) (corr) (cgs)</th>
<th>(\mu_{\text{eff}}) B.M.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}_2(\text{OCOMe})_2\text{Cl}])</td>
<td>Gouy (solid state)</td>
<td>298</td>
<td>3446</td>
<td>2·88</td>
</tr>
<tr>
<td>([\text{Ru}_2(\text{OCOE})_2\text{Cl}])</td>
<td>NMR (MeOH)</td>
<td>294</td>
<td>3596</td>
<td>2·72</td>
</tr>
<tr>
<td>([\text{Ru}_2(\text{OCOPr})_2\text{Cl}])</td>
<td>Gouy (solid state)</td>
<td>292</td>
<td>3169</td>
<td>2·76</td>
</tr>
<tr>
<td>([\text{Ru}_2(\text{OCOMe})_2(\text{OH})_2\text{H}_2\text{O}],[\text{BPh}_4])</td>
<td>NMR (MeOH)</td>
<td>294</td>
<td>4789</td>
<td>3·37</td>
</tr>
<tr>
<td>([\text{Ru}_2(\text{OCOMe})_2(\text{OH})_2\text{H}_2\text{O}],[\text{BPh}_4])</td>
<td>Gouy (PhNO(_2))</td>
<td>292·5</td>
<td>3965</td>
<td>3·06</td>
</tr>
</tbody>
</table>

* From spin-only formula and per Ru atom.

It is impossible to correlate these very high values with the presence in the complexes of only one unpaired electron and hence if the stoichiometry is indeed correct, a spin-free system must be invoked. If the empirical formula were \([\text{Ru}_2(\text{OCOR})_4\text{Cl}],\) this could accommodate the magnetic moment (i.e. 3 unpaired electrons from oxidation states III and IV, \(d^4\), giving \(\sim 4\text{ B.M. per molecule}) and the fact that the preparation reaction is facilitated by oxygen. The carbon, hydrogen and chlorine percentages are very similar for both formulations, but there is a 2 per cent difference in the oxygen figure. However, analyses correspond well to the formula \(\text{Ru}_2(\text{OCOR})_4\text{Cl};\) furthermore, there are no bands in the 1000-650 cm\(^{-1}\) region corresponding to either Ru—O or Ru—O stretching vibrations.

Another feature of the magnetic properties of these compounds is that there is apparently very little ferro- or antiferromagnetic interaction in the temperature range
300–100°K. Thus, the acetate has a \( \mu_{\text{eff}} \) of 2.88 B.M. per ruthenium atom at 298°K, 2.71 B.M. at 105.7°K, no dependence of susceptibility on field strength, and a reasonable adherence to the Curie–Weiss Law \( (\theta = 20^\circ) \) (Table 2). This suggests that the metal–metal distance in these systems is large enough to prevent direct orbital overlap, the small depression in moment possibly arising from superexchange interactions via the carboxylate bridges (cf. \( \text{Cu(HCOO)}_2 \cdot 4 \text{H}_2\text{O} \)). Hence, in methanolic solution, the complexes may have co-ordination of the ruthenium atom by the oxygen atoms of carboxylate groups with the remaining co-ordination site occupied by a solvent molecule. The i.r. spectra of the propionate, before and after crystallization from methanol were identical and together with the analytical data show that there is no co-ordinated solvent in the solid.

| Table 2.—Variation of \( \chi_M \) (corr) and \( \mu_{\text{eff}} \) with temperature for [Ru(OCOMe)_4Cl] |
|-----------------|-----------------|-----------------|-----------------|
| \( T^\circ\text{K} \) | \( 10^6 \chi_M \) (corr), (cgs) | \( \frac{1}{\chi_M} \) (corr) | \( \mu_{\text{eff}} \) B.M.* |
| 298             | 3446            | 291·2           | 2·88            |
| 273             | 3752            | 266·8           | 2·87            |
| 255             | 4000            | 250·0           | 2·87            |
| 228             | 4416            | 227·1           | 2·85            |
| 208             | 4824            | 207·7           | 2·84            |
| 191·5           | 5224            | 191·7           | 2·84            |
| 166·5           | 5854            | 171·0           | 2·80            |
| 143·5           | 6633            | 150·9           | 2·77            |
| 105·7           | 8578            | 116·8           | 2·71            |

* Per Ru atom.

In the solid state, the structure of \( \text{Ru}_2(\text{OCOR})_4\text{Cl} \) could be ionic, or less likely, it could be polymeric involving single chlorine bridges between ruthenium atoms of adjacent carboxylate bridged dimers. The far i.r. spectrum of the acetate shows two sharp bands at 403 and 341 cm\(^{-1} \) which could be assigned to M–O and M–Cl stretching modes respectively. However, these occur in the region found for terminal M–Cl stretching vibrations of other second and third row transition metal complexes(7) and the Ru–Cl–Ru stretching mode would thus be expected to occur at a lower frequency. Attempts to prepare the corresponding bromides \( \text{Ru}_2(\text{OCOR})_4\text{Br} \), where a shift of the 341 cm\(^{-1} \) band to lower frequencies would be expected if this were due to a metal-halogen stretching-mode were unsuccessful.

Infra-red and electronic spectra. Apart from \(-\text{CH}\) stretches, the i.r. spectra contain no bands above 1500 cm\(^{-1} \). In the 1500–1400 cm\(^{-1} \) region, there are several bands assignable to antisymmetric \((\omega_2)\), symmetric \((\omega_1)\) carboxyl stretching and \(-\text{CH}\) bending vibrations. Thus, the separation between \( \omega_2 \) and \( \omega_1 \) is very small (\( \leq 80 \) cm\(^{-1} \)) suggesting symmetrically co-ordinated carboxylate groups.(8) Other characteristic bands such as the \(-\text{CH}_3\) deformation (1350 cm\(^{-1} \)) and OCO deformation (\( \sim 690 \) cm\(^{-1} \)) frequencies are readily assigned.

(7) M. KATO, H. B. JONASSEN and J. C. FANNING, Chem. Rev. 64, 99 (1964), and references therein.
The electronic absorption spectra of all three complexes and the tetraphenylborate salt of the acetate in aqueous or methanolic solution are almost identical, each having a single symmetrical band at 422–25 μ (ε = 750) (acetate); 1040 (propionate); 830 (μ-butyrate). In addition, there are weak inflexions at ~550 μ, which may be due to d-d transitions, e.g. acetate, 525 (ε = 12); propionate, 535 (ε = 16). Below 350 μ, there are charge-transfer bands at ~310, 280 μ (ε > 2000). The solid state reflectance spectra of the acetate, both before and after dissolution in methanol are identical, showing a single broad band at 464 μ.

Reactions with donor ligands. The compounds react with several nitrogen and phosphorus donors to give a mixture of products. The products from interaction with pyridine have been separated as acetone-soluble green solids of composition \([\text{Ru}(\text{OCOR})_2\text{py}_2]\), and less soluble yellow solids \([\text{Ru}(\text{OCOR})_2\text{py}_3]\) (R = Me, Et). Both types are non-electrolytes; in solution, the yellow species rapidly turn green especially on warming. The i.r. spectra of the yellow complexes suggest monodentate carboxylate co-ordination and they are presumably octahedral ruthenium (II) species. In the green complexes, a lower value of \(\omega_2 - \omega_1\) suggests symmetrical co-ordination. Similar complexes of iron (II) have been prepared by the action of pyridine on anhydrous ferrous acetate. The tetrakispyridine complex is converted to the bis-pyridine complex at 100°.

Other ruthenium carboxylates

In addition to the brown crystalline powders, emerald-green solutions were produced on refluxing ruthenium trichloride with carboxylic acid–acid anhydride mixture for several hours. On removal of the solvent from the acetic acid reactions, or by addition of excess diethylether, a very soluble (methanol, ethanol and water) dark-green powder was obtained, consistently close in analyses to \([\text{Ru}(\text{OCOMe})_2\text{H}_2\text{O}]_2\). However, it always contained ~3 per cent chlorine together with weak bands in the i.r. spectrum at 2062 and 1988 cm\(^{-1}\) presumably due to carbon monoxide. The interaction in the absence of acetic anhydride gave a material with no bands in the i.r. at 2000 cm\(^{-1}\) but on re-evaporating this to dryness with acetic anhydride weak carbonyl peaks were again evident.

Attempts to remove the impurities included solvent extraction, high vacuum sublimation, recrystallization (too soluble) and chromatography on cellulose, silica and acid-washed alumina. The last method removed the carbonyl bands (although ~2 per cent chlorine was still present) but also trimerized the complex, changing its chemical properties, i.r. and absorption spectra. The carbonyl impurity could also be removed by careful reprecipitation by ether from a concentrated warm methanol solution, the analysis remaining unchanged (but still containing 2 per cent chlorine). Refluxing for a short period with excess silver acetate in methanol then removed the chlorine, the product having the same i.r. spectrum as the original but the closest formulation was now \([\text{Ru}_4(\text{OCOMe})_{4-5}\text{H}_2\text{O})_{4-5}]\). This material was virtually diamagnetic (0.7 B.M.), a non-electrolyte in methanol and water with acetate bands in the i.r. at 1538 (\(\omega_2\)) and 1418 (\(\omega_1\)) indicating symmetrical co-ordination. Precipitation from warm methanol gave a methanolic species (i.r.) which slowly reverted to the original species on standing in air.

After Ru₂(OCOMe)₄Cl was removed, another portion of the green solution was refluxed for several more days in oxygen. It became bluer in colour, and finally deposited a very insoluble greenish-black powder, containing no chlorine. Its i.r. spectrum showed extremely weak carbonyl peaks, no co-ordinated water and bands at 1661, 1515 cm⁻¹ (ω₁) and 1389, 1309 cm⁻¹ (ω₂), indicative of both symmetrical and unsymmetrical acetate groupings. The analysis corresponds to [Ru₂(OCOMe)₆] (cf. the mixed ferrous-ferric complex [Fe₄(OCOMe)₆]) but this is probably a coincidence.

In order to avoid the formation of carbonyl species, the acid anhydride was omitted but the use of pure carboxylic acid alone led to the formation of dark-green solutions and insoluble black precipitates, both of which contained much chlorine (~10–20 per cent) and gave meaningless analyses. Attempts to separate the components of the dark-green solutions which are chemically and spectroscopically different from the emerald-green solutions obtained with anhydride present failed.

In order to eliminate complications due to chloride, hydrous ruthenium oxide was refluxed in an acetic acid–acetic anhydride mixture for ~3 hr in oxygen. From the emerald-green solution a dark-green product was obtained which showed weak carbonyl bands in the i.r. at 2062 and 1988 cm⁻¹ (the impurity which caused them could be removed by ether reprecipitation) and had empirical formula [Ru₂(OCOMe)₄(H₂O)]₆·₄. Similarly, with propionic acid–propionic anhydride, a material very close in analysis to [Ru₂(OCOMe)₆(H₂O)]₈·₄ was obtained. With acetic acid alone, a dark-green solution was obtained giving a very soluble greenish-black solid (no carbonyl bands) which analysed for [Ru₂(OCOMe)₆OH·(H₂O)]₂ (practically the only combination of ruthenium, acetate and water which was not found). Attempts to separate and purify these very soluble species have been unsuccessful.

**EXPERIMENTAL**

Microanalyses and molecular weight determinations (Mechrolab osmometer, 37%) were by the Microanalytical Laboratory, Imperial College, and A. Bernhardt, Mülheim. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected. Infra-red spectra were taken in Nujol and hexachlorobutadiene mulls, using a Grubb-Parsons grating “Spectromaster” instrument. Electronic spectra were obtained using a Perkin–Elmer Model 350 spectrophotometer and in reflectance, on a Unicam SP 700 spectrophotometer. Bulk susceptibility measurements were made by the standard Gouy method. The magnetic susceptibilities of solutions were determined by Gouy solution and the NMR method, using tetramethylsilane as the reference and a Willmad concentric tube. The spectra were recorded on a Varian Model 43100 at 56.6 Mc/s. Molar conductivities (Ω cm⁻¹) are for 0.001 M solutions.

The “ruthenium trichloride trihydrate” (Johnson–Matthey Ltd.) used in this work is a mixture of hydrated trichloride, tetrachloride and various polynuclear species. However, the use of ruthenium (III) chloro complexes, obtained by evaporating the commercial “trichloride” to dryness several times with concentrated hydrochloric acid, gave the same products.

Interaction of hydrated ruthenium “trichloride” with an acetic acid–acetic anhydride mixture

Commercial “RuCl₃3H₂O” (1 g) was gently refluxed with a mixture of glacial acetic acid (35 ml) and acetic anhydride (7 ml) in a slow stream of oxygen. After ~1 hr, the initial brown solution had become dark green. The solution was cooled, filtered and the black residue (which partially dissolved in hot water giving a green solution) was discarded. Refluxing was then continued for ~5–6 hr until the solution became emerald-green in colour. After cooling, reddish-brown microcrystals of tetraacetatodiruthenium (II, III) chloride were removed, washed with glacial acetic acid, followed by small

portions of methanol and diethyl ether, and dried in vacuo (40°) [0-6 g, m.p. 230° (decomp.)] [Found: C, 20-5; H, 2-6; Cl, 7-5; O, 27-0 per cent; M (methanol), 244. C₆H₅ClO₄Ru₄ requires C, 20-2; H, 2-5; Cl, 7-5; O, 26-9 per cent; M (for 1:1 electrolyte), 238]; \( \Lambda \), water 127, methanol 100. The same compound can also be obtained in a nitrogen atmosphere but it is necessary to reflux the mixture for \(~15\) hr to produce an emerald-green solution.

On vacuum evaporation of the emerald-green solution, the material obtained gave analyses consistently close to [Ru(OCOME)₃H₂O]₄⁺ [Found: C, 19-9; H, 4-1; O, 33-3; M (methanol) 460. C₆H₅O₂Ru requires C, 20-2; H, 3-4; O, 33-6 per cent; M (dimer), 476]. It also contained \(~3\) per cent chlorine and carboxyl-containing impurities. The latter could be removed by reprecipitation of the material from warm methanol with ether. [Found: C, 20-0; H, 3-8; O, 33-1; M (methanol) 500]. The chlorine could be removed by refluxing a methanol solution of the material with silver acetate; m.p. \(250°\) (decomp.). The product then had [Found: C, 21-7; H, 3-5; O, 33-9. [Ru(OCOME)₄(H₂O)₄]₂⁺ requires C, 21-8; H, 3-3; O, 33-9 per cent].

Reflexing the green solution in oxygen for several days still gave a product with analyses close to [Ru(OCOME)₃H₂O]₄⁺, e.g. after 4 days in oxygen, a turquoise-blue powder was precipitated out by ether [Found: C, 20-6; H, 3-3; O, 33-5 per cent]. Finally, \(~6\) days an insoluble greenish-black powder was deposited [Found: C, 24-4; H, 3-3. C₆H₅H₂O₄Ru₄ requires C, 24-1; H, 3-0 per cent].

Interaction of hydrated ruthenium oxide with an acetic acid–acetic anhydride mixture

Hydrated ruthenium oxide (0-5 g) obtained by addition of sodium hydroxide to the aqueous solution of ruthenium(III) chloro-complexes, was gently refluxed with a mixture of glacial acetic acid (35 ml) and acetic anhydride (7 ml) in a stream of oxygen for \(~3\) hr. The resulting emerald-green solution was evaporated. The product was dissolved in methanol, precipitated with ether to remove the carboxyl-containing impurities and dried in vacuo (60°) for several hours; m.p. \(250°\) (decomp.). [Found: C, 21-7; H, 3-5; O, 33-4 per cent]. The material appears to be identical to the purified product obtained from the interaction of the trichloride with acetic acid and acetic anhydride. The closest formulation is [Ru₂(OCOME)₆(H₂O)₁₁]₂⁺.

Tetracarboxytriruthenium (II, III) chloride

As for the acetic acid, using the trichloride (1 g), propanic acid (35 ml) and propionic anhydride (7 ml). Again, the reaction was stopped after \(~1\) hr and the initial precipitated material removed. The resulting dark brown micro-crystals of the complex were well-washed with acid and ether and dried in vacuo [0-65 g; m.p. \(>270°\) (decomp.)]. [Found: C, 27-4; H, 3-9; Cl, 7-1; O, 24-0; M (methanol), 331. C₁₆H₁₅ClO₄Ru₄ requires C, 27-1; H, 3-8; Cl, 6-7; O, 24-1 per cent; M (for 1:1 electrolyte), 265]; \( \Lambda \) (methanol), 67.

Although the emerald-green filtrate obtained from this reaction was not extensively investigated, it also contains weak carboxyl bands in its i.r. spectrum at 2062 and 1988 cm⁻¹ with extra bands arising from the \(-C₆H₅\) grouping.

Interaction of hydrated ruthenium oxide with a propionic acid–propionic anhydride mixture

As for the acetic acid reaction, giving an emerald-green solution. The product, reprecipitated from methanolic solution to remove the carboxyl-containing impurities, was dried in vacuo (60°) for several hours; m.p. \(280°\) (decomp.). [Found: C, 28-7; H, 4-2; O, 29-4. [Ru₄(OCOE)₆(H₂O)₁₁] requires C, 29-0; H, 4-5; O, 30-0 per cent].

Tetra-n-butytriruthenium (II, III) chloride

As for above, using the trichloride (1 g), n-butylic acid (35 ml) and n-butylic anhydride (10 ml). No attempt was made to remove impurities after \(~1\) hr since the complex is soluble in hot n-butylic acid. Instead, after formation of the emerald-green solution (\(~6\) hr), the mixture was filtered while still hot and then cooled at 0° overnight, when dark brown crystals of the complex were deposited. These were recrystallized from hot n-butylic acid, washed with diethyl ether and dried in vacuo (0-6 g) m.p. \(>270°\) (decomp.). [Found: C, 33-0; H, 5-0; Cl, 6-2; O, 21-9; M (methanol), 290. C₂₀H₂₃ClO₄Ru₄ requires C, 32-8; H, 4-9; Cl, 6-0; O, 21-8 per cent; M (for 1:1 electrolyte), 294]; \( \Lambda \) (methanol) 95.

The reaction must be stopped as soon as the emerald-green solution is formed. If left overnight, it turns dark green and no brown crystals are deposited on cooling.
Tetraphenylborates of the acetate and propionate

Addition of an excess concentrated aqueous solution of sodium tetraphenylboron to strong aqueous solutions of the acetate or propionate gave immediate orange-brown crystalline precipitates. These were centrifuged, washed several times with small portions of distilled water, followed by petroleum (60-80°) and were finally dried in an evacuated desiccator for several hours. For the acetate [Found: C, 49.1; H, 4.7; O, 17.4; M (acetone), 374. C_{25}H_{25}BO_{4}Ru requires C, 49.0; H, 4.4; O, 17.4 per cent; M, (for 1:1 electrolyte), 367]; A (acetone), 97, (nitrobenzene), 18. For the propionate, [Found: C, 51.2; H, 5.2; O, 16.7; M (acetone), 373. C_{25}H_{25}BO_{4}Ru requires C, 51.0; H, 4.9; O, 16.5 per cent; M, (for 1:1 electrolyte), 388]. The analyses on different batches of products were essentially identical. The test for chloride was negative. The formulation [Ru_{2}(OCOR)_{3}(OH)_{2}O](BPh_{4}) is the only formula which fits the analysis for both the acetate and propionate and is consistent with the presence of hydroxy bands in the i.r., the acidic pH of the aqueous solution and the magnetic data. The acetate has bands in the i.r. at 3509(sh), 3425 cm\(^{-1}\); the propionate at 3528 and 3413 cm\(^{-1}\) and both have a weak band at \(~1600\) cm\(^{-1}\) attributed to the HOH bending vibration. There are no carboxylate vibrations in the i.r. \(>1500\) cm\(^{-1}\). Left in air, the solids slowly turn dark brown with no apparent charge in the i.r. spectra. They are soluble in acetone, methanol, nitrobenzene but the solutions darken over several hours and decompose immediately on warming, making recrystallization impossible.

Interaction of the chlorocarboxylates with pyridine

The acetate or propionate was warmed on a steam bath with excess dried pyridine (in air or nitrogen) giving initially a yellow-brown solution which quickly turned dark green. Removal of the excess pyridine gave a mixture of yellow and green complexes. Careful extraction with acetone left a residue of pure yellow dicarboxylato-tetrakispyridineruthenium (II) which was carefully washed with more acetone, then petroleum (30-40°) and dried in an evacuated desiccator. For the acetate, m.p. 190° (decomp.). [Found: C, 53.3; H, 4.8; N, 10.2; O, 11.5; M (methanol), 376. C_{25}H_{25}N_{4}O_{2}Ru requires C, 53.7; H, 5.5; N, 10.4; O, 11.9 per cent; M, 536]. For the propionate, m.p. 210° (decomp.) [Found: N, 10.3; O, 11.5; C_{25}H_{25}N_{4}O_{2}Ru requires N, 9.9; 11.3 per cent]. The acetone solution of the green solid (plus some yellow) was left to stand for several days in air in order to convert all of the yellow to the green material. The solvent was removed, the product washed with petroleum (30-40°) and dried in an evacuated desiccator to give the very soluble green dicarboxylato-bis(pyridine)ruthenium (II) complexes. For the acetate, m.p. >240° (decomp.) [Found: 6.9; O, 16.5; M (methanol), 388. C_{25}H_{25}N_{4}O_{2}Ru requires N, 7.4; O, 16.9 per cent, M, 378]. For the propionate, m.p. >260° (decomp.), [Found: N, 7.3; C_{25}H_{25}N_{4}O_{2}Ru requires N, 6.9 per cent]. None of the complexes contained chlorine. They are all very soluble, the green complexes especially, in acetone, alcohols and in water. The low value for the molecular weight of Ru(OCOME\textsubscript{2}py\textsubscript{4}) is probably due to the fact that the solution turned green during the measurements.

Infra-red spectra (\(\omega, \omega_{1}\) cm\(^{-1}\)): [Ru(OCOME\textsubscript{2}py\textsubscript{4}), 1585, 1319; [Ru(OCOEt\textsubscript{2}py\textsubscript{4}), 1587, 1348; [Ru(OCOME\textsubscript{2}py\textsubscript{4}), 1577, 1538, 1410; [Ru(OCOEt\textsubscript{2}py\textsubscript{4}), 1575, 1538, 1408.

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Acetato complexes of palladium(II)

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We have reported\(^{12}\) the preparation of palladium(II) carboxylates and a number of monomeric adducts of the type \([\text{Pd} (\text{OCOR})_2 L_2]\) (R = Me, Et, CF\(_3\); \(L = \text{Ph}_2 \text{P}, \text{py}\)), the latter being obtained by the action of the ligand \(L\) in large excess (>1:4 mole ratio) on \([\text{Pd}(\text{OCOR})_2]_2\). By using ratios of only 1:2 we have now prepared complexes of the type \([\text{Pd} (\text{OCOCH}_3)_2 L_2]\) (\(L = \text{Ph}_2 \text{As}, \text{Ph}_2 \text{P}\)). These dimeric complexes may be assigned a structure in which there are both bridged and unidentate carboxylate groups. Corresponding halogeno complexes of the type \([\text{Pd} (\text{Cl})_2 L_2]\) of amines, phosphines or sulphides are well known\(^{13}\) and are usually isolated in the \(\text{trans}\) form although the thio-bridged complex \([\text{Pd} (\text{PPr}_3)_2 (\text{S})_2 \text{Cl}_2]\) can be isolated in the \(\text{cis}\) form. The only other carboxylate complexes of similar structure are the acetone adducts\(^{13}\) of palladium trifluoroacetate and perfluoropropionate, \([\text{Pd}(\text{OCOR})_2 \text{Me}_2 \text{CO}]\). The new complexes are insufficiently soluble in benzene to allow the dipole moments to be determined, so that we cannot determine whether the \(\text{cis}\) or \(\text{trans}\) forms are the most stable. The i.r. data in Table I confirm the presence of both bridging and unidentate groups; the position of the carboxylate bands has been discussed previously\(^{13}\) in some detail.

| Table I.—Infrared spectra of palladium(II) carboxylate complexes (cm\(^{-1}\) in nujol mulls) on Grubb-Parsons grating “Spectromaster” |
|-----------------|-----------------|-----------------|-----------------|
| **Compound**    | **Bridge** \(\omega_2\) | **Bridge** \(\omega_1\) | **Unidentate** \(\omega_2\) | **Unidentate** \(\omega_1\) |
| \([\text{Pd} (\text{COMe})_2 \text{PPh}_3]_2\) | 1580 | 1411 | 1629 | 1314 |
| \([\text{Pd} (\text{COMe})_2 \text{AsPh}_3]_2\) | 1582 | 1410 | 1631 | 1314 |
| \([\text{Pd} (\text{OCOCF}_3)_2 \text{Me}_2 \text{CO}]_2\) | 1541 | 1429 | 1650 or | |
| \([\text{Pd} (\text{OCOCF}_3)_2 \text{PPh}_3]_2\) | 1543 | 1414 | 1653 or | 1362 |
| \([\text{Pd} (\text{OCOCF}_3)_2 \text{py}]_2\) | 1543 | 1414 | 1629* | 1634 |


Attempts to prepare similar complexes from palladium(II) benzoate were unsuccessful, the products being only the monomeric adducts. Further an attempt to isolate the pyridine adduct of the acetate failed since the orange material first obtained decomposed quite rapidly.

The complex \([\text{Pd} (\text{OCOCH}_3)_2 \text{PPh}_3]_2\) reacts readily with additional triphenylphosphine, the bridge cleaving to give \(\text{trans-}[\text{Pd} (\text{OCOCH}_3)_2 (\text{PPh}_3)]\): similarly the triphenyl arson complex can be cleaved with pyridine to give \(\text{Pd} (\text{OCOCH}_3)_2 \text{py}_2\). In no case is there any evidence for mixed ligand complexes.

**Experimental**

Analyses and molecular weights (Mechrolab Osmometer) by the Microanalytical Laboratory, Imperial College.

*Triphenylphosphine acetato palladium(II)-\(\mu_4\)-acetato-triphenylphosphine acetato palladium(II)*

To palladium (II) acetate (0.08 g) in benzene (20 ml) was added triphenylphosphine (0.04 g). To the resulting red solution was added diethyl ether when orange crystals of the complex were precipitated. These were washed with ether and dried in vacuum (40°); yield essentially quantitative.
m.p., 140–141°. (Found: C, 54·0; H, 4·5; O, 13·3%; M(CHCl₃), 914. C₉₃H₇₀O₃Pd requires C, 54·2; H, 4·3; O, 13·2%. M(dimer), 974.) The compound is soluble in dichloromethane and chloroform, but is insoluble in ethanol, tetrahydrofuran and ether. It decomposes rapidly in warm benzene and turns black when exposed to moist air for several days. The corresponding triphenylarsonine complex was prepared analogously, using 0·06 g AsPh₃, as orange-red crystals. (Found: C, 50·6; H, 4·2; O, 12·25%; M(CHCl₃), 1020. C₉₃H₇₁AsO₃Pd C, 49·7; H, 4·0; O, 12·1%. M(dimer), 1060.) The compound is soluble in dichloromethane, chloroform and in ethanol and is evidently stable in air.

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A BASIC ACETATO COMPLEX OF TUNGSTEN

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Although monocarboxylates of chromium and molybdenum have been prepared and adequately characterised by several investigators (1), few references to tungsten carboxylates are to be found. With salicylic acid, the complexes

\[ \text{WOCI} \left( \text{OC}_6\text{H}_4\text{CO}_2 \right) \left( \text{OC}_6\text{H}_4\text{CO}_2\text{H} \right) \] (2) and \[ \text{WBr}_2 \left( \text{OH} \right) \left( \text{OC}_6\text{H}_4\text{CO}_2\text{H} \right) \left( \text{Et}_2\text{O} \right) \] (3) have been reported; benzoic, palmitic acid etc give 4:1 adducts with \text{WOCI}_4 (4) and 6:1 adducts with \text{WCl}_6 (5). In the present communication we wish to report the first acetate complex of tungsten.

Prolonged refluxing of tungsten hexacarbonyl with an acetic acid/acetic anhydride mixture under dry nitrogen gives a deep yellow-brown solution. (cf the corresponding reaction with \text{Mo(CO)}\text{6} which rapidly deposits yellow crystals of \[ \text{Mo(OOCCH}_3\text{)}_2 \] (6)). Distillation of the solvent under reduced pressure followed by dissolution in dry deoxygenated methanol, filtration and redistillation gives a microcrystalline yellow-brown solid (m.p.120\textdegree(d)). It is important to carry out the reaction under nitrogen; in air the only product appears to be "tungsten blue". The freshly prepared product is completely soluble in water, ethanol and methanol; insoluble in dichloromethane, acetone, benzene, ethers etc. However, in acetic acid solution, exposure to oxygen produces slow precipitation of a deep yellow material which is completely insoluble in methanol but soluble in water. Its infrared spectrum is identical to that of the original product except for the growth of bands at 820 and 890 cm\textsuperscript{-1}, suggestive of oxygen bridges and \( \text{W} = \text{O} \) groups respectively (7a). In
the solid state, the complex appears quite stable although after several weeks storage in a desiccator, the material is not completely resoluble in methanol.

Attempts to sublime the compound under vacuo (up to 150°) and to obtain a mass spectrum were unsuccessful. However, the attempted purification of the product on cellulose and silica thin layer chromatography plates produces no observable separation which suggests that only one complex is present. This conclusion is supported by the consistency of the analytical data obtained for several preparations of the complex.

For example: I  C, 17.9; H, 2.7; W, 50.7; O (by difference) 28.7%

II  C, 18.6; H, 2.7; W, 51.1; O (by difference) 27.6%

III  C, 18.9; H, 2.9%.

Sample I was obtained by ethereal treatment of the original solution; samples II and III as described above. A close fit to I is \([W_3(OCOCH_3)_8O(OH)H_2O]\)
requiring C, 17.9; H, 2.5; W, 51.2; O, 28.4% Mwt, 1075; for II and III
\([W_3(OCOCH_3)_8O(OH)CH_3OH]\) requiring C, 18.7; H, 2.6; W, 50.6; O, 28.1%
Mwt 1088. The empirical formulae \([W(OCOCH_3)_2]\) requiring C, 15.9; H, 2.0;
W, 61.0; O, 21.1% or \([W(OCOCH_3)_3]\) requiring C, 19.9; H, 2.5; W, 51.0;
O, 26.6% are not consistent with the analytical data.

The formulation of the compound as a trinuclear species containing eight acetato groups, hydroxy and solvent groups and possibly a trigonally coordinated oxide ion is supported by both chemical and spectroscopic evidence. This is as follows:-

a) Osmometric molecular weight measurements in methanolic solution at 37°
gives 976 and 1040 (for samples I and III respectively).

b) A Kuhn Roth analysis (CH₃% arising from C-CH₃ grouping only) on sample
III gives 12.1%; \([W_3(OCOCH_3)_8O(OH)CH_3OH]\) requires 11.1%.

c) Conductivity measurements show the freshly prepared complex to be a
non-electrolyte in ethanol, slightly ionized in methanol (\(\Lambda_{0.001M} = 22\ \text{cm}^2\ \text{ohm}^{-1}\ \text{mole}^{-1}\)) and a 1:1 electrolyte in water (\(\Lambda_{0.001M} = 123\ \text{cm}^2\ \text{ohm}^{-1}\ \text{mole}^{-1}\)).
Treatment of a concentrated aqueous solution with $\text{AsPh}_4\text{ClHCl}$ produces a small amount of a flocculent yellow precipitate indicating the presence of an anionic tungsten complex in aqueous solution (cf the behaviour of copper acetate hydrate (8) in aqueous media).

d) Oxidation state determinations (oxidation to $\text{W(VI)}$) with an excess of ceric sulphate followed by back titration with ferrous ammonium sulphate give an overall oxidation state for the tungsten of $3.5 \pm 0.2$.

e) The compound is diamagnetic suggesting either direct metal-metal interaction as in $\text{K}_2\text{W}_2\text{Cl}_9$ (7b) or possibly the presence of a trigonally coordinated oxide ion as in $[\text{Cr}_3(\text{OCOCH}_3)_6\text{O(H}_2\text{O})_3]\text{Cl}_5\text{H}_2\text{O}$ (9).

f) The detailed infrared spectrum of the complex is quite instructive. The spectrum contains no carbonyl bands, unmistakable evidence for both symmetric (chelate and/or bridged) and unidentate coordination of acetato groups (Table 1) (10) and a strong broad band at 3500-3300 cm$^{-1}$ characteristic of an $\text{-OH}$ stretching vibration. The latter could conceivably arise from either hydroxy and/or solvent groups in the complex.

| TABLE 1 |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Symmetric       | Unidentate      | Symmetric       | Unidentate      |
| $(\text{CH}_3\text{CO}_2^-) \text{ cm}^{-1}$ | $(\text{CH}_3\text{CO}_2^-) \text{ cm}^{-1}$ | $(\text{CH}_3\text{CO}_2^-) \text{ cm}^{-1}$ | $(\text{CH}_3\text{CO}_2^-) \text{ cm}^{-1}$ |
| $\nu_2$         | $\nu_1$         | $\nu_2$         | $\nu_1$         |
| 1530            | 1430            | 1630            | 1300            | 100             | 330             |


g) Treatment of the compound with trifluoroacetic acid, trichloroacetic acid and dry redistilled pyridine produces complexes of uncertain composition and high molecular weights (cf platinum acetate (10) with the following common infrared characteristics:

(i) Retention of the bands associated with symmetrically coordinated acetato groups;
(ii) Disappearance of the bands attributed to unidentate acetato groups and replacement by the characteristic bands of the ligand used (cf treatment of the \([Cr_3(OCOCH_3)_6O(H_2O)_3]^+\) cation with pyridine etc giving \([Cr_3(OCOCH_3)_6O(py)_3]^+\) (1));

(iii) Retention of the strong broad band at 3500–3300 cm\(^{-1}\) suggesting the presence of strongly bound hydroxy as well as solvent groups.

Two of the several possible structures consistent with the above observations are shown in Fig. 1.

**FIG. 1**

Possible structural types for basic tungsten acetate \((S = H_2O, CH_3OH)\)

In an attempt to clarify the detailed structure of this complex and hopefully to obtain a suitable crystal for X-ray studies, further work is now in progress on the preparation of some aryl and higher alkyl carboxylates of tungsten and on the purification and characterisation of various acetate adducts.

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Five- and Six-co-ordinate Tertiary Phosphine Complexes of Bis(diphenyl-phosphinodithioato)palladium(II)

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Five- and Six-co-ordinate Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II)

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The interaction of Pd(S$_2$PPh$_3$)$_2$ with tertiary phosphines to give both 1:1 (for PPh$_3$, PEt$_3$PPh$_2$, PMe$_2$Ph, and PEt$_3$) and 1:2 (for PMe$_2$Ph and PEt$_3$) adducts is described. i.r. spectra and molecular-weight evidence suggest that in the solid state, these are genuine five- and six-co-ordinate palladium(II) complexes respectively. Conversion between two five-co-ordinate isomers has been followed in the solid state by i.r. spectroscopy and tentative conclusions have been made about the stereochemistry of these isomers. In solution, i.r. evidence suggests that the 1:1 adducts may exist as a mixture of solvated square pyramidal species although the presence of a trigonal bipyramidal structure cannot be discounted. In solution, the 1:2 complexes rapidly dissociate to the 1:1 adducts and can be stabilised only by addition of excess of tertiary phosphine.

Although examples of five-co-ordinate complexes are becoming much more common throughout the periodic table,$^1$ the number of established five-co-ordinate complexes of palladium(II) is still rather small. Apart from complexes prepared by using 'umbrella-type' polynuclear ligands such as P(o-C$_6$H$_4$PPh$_3$)$_2$ etc. (ref. 2), few stable species have been isolated.$^3$ Six-co-ordinate complexes of palladium(II) are very rare, the only definite example being [Pd(diarasine)$_2$)$_2$], an X-ray analysis$^4$ of which showed the presence of trans-iodide ions. There is evidence, however, that the action of solvents and excess of halide ions on complexes such as [Pd(phen)$_2$]$^{2+}$ and Pd$_2$X$_4$$^{2-}$ (X = Cl or Br) give additional co-ordination.$^5$

Here, the interaction of tertiary phosphines with bis(diphenylphosphinodithioato)palladium(II) to give 1:1 and sometimes 1:2 adducts is described. These appear to be genuine five- and six-co-ordinate complexes and a detailed examination of their i.r. spectra, coupled with some molecular weight and n.m.r. results, has enabled tentative conclusions to be drawn about both the geometries of these complexes and their interconversions in solution and the solid state.

RESULTS

Preparation of Bis(diphenylphosphinodithioato)palladium(II).—Many complexes of phosphinodithioates with both main group and transition metal ions have been prepared.$^8$ The previously unknown compound Pd(S$_2$PPh$_3$)$_2$ is readily obtained as diamagnetic red crystals by treatment of a benzene solution of palladium(II) acetate with a slight excess of diphenylphosphinodithioc acid [Ph$_2$P(S)SH]. The complex is insufficiently soluble for molecular-weight measurements but mass spectral data at 160° show the highest peak to be at $m/z$ 604, as expected for a monomeric structure. This conclusion is supported by the monomeric structure of the corresponding nickel complex,$^7$ and by an i.r. spectrum (Figure 1a). No bands corresponding to acetate or free acid are found but the characteristic bands of the Ph$_4$PS$_2^-$ group are present. Comparison with the i.r. spectrum of Cs(S$_2$PPh$_3$)$_2$H$_2$O (Figure 1b) and earlier work,$^4$ indicating $C_{5v}$ symmetry for the ligand suggests that

![Figure 1: Mull i.r. spectrum (800—450 cm.$^{-1}$) of (a) Pd(S$_2$PPh$_3$)$_2$ and (b) Cs(S$_2$PPh$_3$)$_2$H$_2$O](image)

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The I.r. spectrum of (B) as a complex (Figure 2a) and of PdCl(PPh3)(Ph) (Figure 2b) and (PdCl(PPPh3))(PPPh3) (Figure 2c) shows a peak at 550 cm⁻¹ which is assigned to the Pd-Cl vibration. This peak is also observed in the spectrum of the ligand (PPPh3) which is explained by the formation of a five-coordinate adduct. The small peak at 460 cm⁻¹ is not observed in the figures and is assigned to a four-coordinate complex such as (1). The lack of this peak in the spectrum of the complex suggests that there is no additional coordination. The assignment of the bands in the figures is based on the observation that the band at 460 cm⁻¹ is strong support for simple addition of PPPh3 to form a five-coordinate adduct, rather than cleavage of a phosphine-phosphine bond to form a four-coordinate complex such as (1).
cleavage of the Pd–O bonds to give trans-[Pd(OOCF₃)₂(AsPh₃)]⁺ with unidentate carboxylate co-ordination (v₁, 1684; v₂, 1393; Δ, 291 cm⁻¹).  

Examination of the i.r. spectrum of (B) dissolved in benzene, dichloromethane (800—460 cm⁻¹), and particularly carbon disulphide where solvent absorptions do not interfere (800—460 cm⁻¹) (Figure 3a) shows that the structure of the complex has changed. In particular, the three bands at 498, 485, and 478 cm⁻¹ are replaced by a broad singlet at 460 cm⁻¹ whilst the region 750—660 cm⁻¹ is simplified. The relative intensities of the two bands at 624 and 638 cm⁻¹ and those at 605, 612, and 621 cm⁻¹ also change. These differences might be interpreted as being due to solid-state splittings or, conversely, solvent broadening, except for the following observations. In precipitation of (B) from these solutions, a pale yellow flocculent material is initially observed which on trituration is rapidly converted splitting of the three strong bands connected with the phenyl ring vibrations. However, these initial weak bands do not occur in the null spectrum of the orange solid (B), prepared either by precipitation from solution (Figure 2a) or by simply washing the yellow solid (C) with diethyl ether or acetone. In fact, if (C) is prepared and placed between caesium iodide plates on an i.r. machine for 16 min. without Nujol and then a Nujol null of the resultant orange product is measured, it is identical to that in Figure 2a. Thus, this strongly suggests that the extra weak bands at 728 and 672 cm⁻¹ arise from partial interaction of (C) with Nujol. The remainder of (C) is then rapidly converted into (B) but the amount which 'interacts' with the Nujol is not converted but remains in equilibrium with (B). Support for this conclusion is the extra weak band at 673 cm⁻¹ in the i.r. spectrum of (B) in carbon disulphide (indicative of some solvent interaction?) and the observation that although

into (B). If the precipitation is carried out in a cold solution, and the pale yellow product (C) is filtered off rapidly, washed with cold light petroleum (b.p. 100—120°) and an i.r. spectrum (Nujol) is run immediately, the spectrum shown in Figure 3b is obtained. This is identical to the solution spectra of (B) except for the absence of a weak band at 673 cm⁻¹ (which is not from CS₃) and the relative intensities of the triplet at 605, 612, and 621 cm⁻¹. Furthermore, if this null is left in the i.r. machine and the spectrum is run in the 750—600 cm⁻¹ region every 2 min. (Figure 4), conversion of (C) into (B) is complete in ca. 10 min. This change was also followed by monitoring the conversion of the singlet at 450 cm⁻¹ in (C) into the triplet in (B) (ca. 10 min.). (C) can also be isolated as above from a 1:1 molar ratio of (A) and triphenylphosphine in benzene. If left on a glass sinter, this is rapidly converted into (B) (especially if still moist with ether) without evidence for any free triphenylphosphine. This clearly indicates that the process is one of isomerisation and not conversion of say a 1:2 into a 1:1 adduct (see later).

Another important observation can be drawn from the conversion of (C) to (B). As is shown very clearly in Figure 4, the first change in the 750—660 cm⁻¹ region is the growth of two weak bands at 728 and 672 cm⁻¹, followed by

when heated, (C) rapidly gives (B), a solution of (B) in carbon disulphide, benzene, or methylene chloride clearly does not give any of (B) when heated. There is also an extra strong band at 1180 cm⁻¹ in the carbon disulphide solutions of (B), not found in carbon disulphide itself. This is superimposed on a weak band arising from the Ph₃PS₂⁺ group. A similar band (1193 cm⁻¹) is found in [Pd(PPh₃)₂CS₂] and other π-bonded carbon disulphide complexes and is assigned to the non-ring C=S stretching vibration (i.e. bonding of carbon and one sulphur atom occurs). However, on evaporation of the solvent, the crystals remaining are identical to those of (B) precipitated from benzene solution, which show no strong band at ca. 1200 cm⁻¹.

Although evidence, therefore, suggests that some solvation probably occurs in solution, the i.r. spectrum of (C) precipitated from benzene and from carbon disulphide solutions are identical (1000—1090 cm⁻¹). Since two strong bands at 1520—1500 cm⁻¹ are expected for an S-coordinated carbon disulphide molecule, this indicates that (C) is a genuine five-co-ordinate complex and not a six-co-ordinate solvate.


Finally, although when cooled solutions of (B) produce a distinctive and reversible colour change from orange to pale yellow, i.r. studies (1500–450 cm\(^{-1}\)) in carbon disulphide have detected no differences between the solutions at a variety of temperatures. \(^1\)H N.m.r. studies at various temperatures in dichloromethane also show no significant differences (apart from some slight broadening at lower temperatures) but in view of the complexity of the phenyl region this is perhaps not surprising. Unfortunately, the complex is not sufficiently soluble to observe a \(^31\)P resonance (only 11% P). Therefore, from these studies the following conclusions can be drawn. (a) Two genuine five-coordinate isomers (B) and (C) can be isolated from this reaction and the solid-state conversion of (C) into (B) can be followed by i.r. spectroscopy. 
(b) Reversible colour changes in solution, as a function of temperature, indicate the existence of several species in solution, which can not be differentiated by either i.r. or n.m.r. measurements.
(c) Neither (B) nor (C) exist in solution although i.r. studies show that the monomeric complexes in solution are very similar to the unstable yellow solid (C). The observation of some partial ‘interaction’ of (C) with Nujol and the additional bands at 1180 and 673 cm\(^{-1}\) in carbon disulphide suggest that solvation effects are important in solution.
(d) There is no evidence for formation of a 1:2 complex.

Reaction of Triethylphosphine with Pd\([\text{S}_2\text{PPh}_3]_2\) – Treatment of a suspension of (A) in benzene with a deficiency of triethylphosphine (< 1 mol.) gives an orange solution from which orange crystals of Pd\([\text{S}_2\text{PPh}_3]_2(\text{PET}_{3})\] can be isolated. The complex is diamagnetic, and very soluble in diethyl ether, carbon disulphide, and benzene; it is non-conducting in the last-named solvent. Molecular-weight measurements in benzene at 37° give a value of 770 ± 78 required for monomer. Mass-spectral studies show only triethylphosphine and its fragmentation pattern. The mull i.r. spectrum of the orange solid (Figure 5a) can be readily analysed, assigning \(v_1\) 652 cm\(^{-1}\); \(v_2\) 538 cm\(^{-1}\); \(\Delta\), 114 cm\(^{-1}\). In carbon disulphide, the i.r. is again quite different (Figure 5b). The triplet in the mull at 492, 484, and 475 cm\(^{-1}\) is replaced by a broad singlet at 488 cm\(^{-1}\) and the strong bands in the 780–600 cm\(^{-1}\) region are much simpler. The relative intensities of the triplet at 602, 612, and 621 cm\(^{-1}\) also change slightly and there is an extra weak band at 674 cm\(^{-1}\). Again, an extra strong band occurs at 1177 cm\(^{-1}\) which suggests some interaction between carbon disulphide and the 1:1 complex: on removal of solvent, this band disappears. Evaporation of the solution and addition of cold, light petroleum (b.p. 100–120°) gives a pale yellow solid but, unfortunately, it has proved impossible to obtain an i.r. spectrum of this solid since it immediately turns orange when dried. As for the solutions of the triphenylphosphine complex, variation of the temperature produces similar reversible colour changes. Again, i.r. studies (1000–450 cm\(^{-1}\)) on the solutions at a variety of temperatures show no apparent differences.

If an excess of triethylphosphine is added to either (A) or the 1:1 complex in a minimum volume of benzene, the solution turns lemon-yellow and when set aside deposits pale yellow crystals of Pd\([\text{S}_2\text{PPh}_3]_2(\text{PET}_{3})\]. A Nujol mull (Figure 6a) shows \(v_1\) 650 cm\(^{-1}\); \(v_2\) 560 cm\(^{-1}\); \(\Delta\), 90 cm\(^{-1}\). For reasons discussed earlier, this is strong support for the formation of a six-coordinate complex containing symmetrically co-ordinated Ph\(_3\)PS\(_2\) groups. Comparison with the 1:1 complex shows \(v_2\) has increased by 22 cm\(^{-1}\) whereas \(v_1\) is virtually unchanged. A possible reason for this may be that since \(v_1\) involves in-phase and \(v_2\) out-of-phase vibrations of the FS\(_2\) group, then any change in these P–S bonds, due to the extra co-ordination of a triethylphosphine molecule, should influence \(v_1\) more than \(v_2\). The mass spectrum of the 1:2 complex at 190° contains good evidence for Pd\([\text{S}_2\text{PPh}_3]_2(\text{PET}_{3})\]{(highest m/e 605)} and triethylphosphine.

Although the 1:2 complex is quite air-stable, in solution (PhH, C\(_8\)) it rapidly turns orange and an immediate i.r. spectrum indicates that substantial conversion into the 1:1 complex has occurred (Figure 6b). After 15 min., \(v_2\) of the 1:2 complex further decreases and after 30 min. it has almost disappeared. Removal of the solvent and extraction with diethyl ether then gives the orange 1:1 complex. The 1:2 complex can, however, be partially stabilised in solution in the presence of excess of triethylphosphine. It then exists in equilibrium with the 1:1 complex and free triethylphosphine. When this solution is cooled, an increase in the intensity of the 560 cm\(^{-1}\) band with respect to that at 538 cm\(^{-1}\) occurs, indicating that the formation of the 1:2 complex is favoured at lower temperatures; heat reverses this trend. Because of these complicated equilibria in solution, attempts to determine the isomeric form(s) of this 1:2 complex have so far been unsuccessful.

Reaction of Complex (A) with Dimethylphenylphosphine and
Ethylidiphenylphosphine.—Neither of these reactions has been as thoroughly studied as those with triphenyl- and triethyl-phosphine. Reactions of (A) with these phosphines have been examined mainly to see whether both 1 : 1 and 1 : 2 complexes are formed.

Reaction of (A) with a slight excess of dimethylphenylphosphine gives an orange solution which upon removal of the solvent gives an orange oil from which with some difficulty, an orange-yellow solid can be isolated. This has an analysis which is consistent with the formula [Pd(S₂PPh₃)₂(PMe₃-Ph)]; the mull i.r. spectrum (Figure 7a) is analogous to that of the triethylphosphine complex with νₚ 650 cm⁻¹; νₚ, 559 cm⁻¹; Δ, 91 cm⁻¹. A weak band at 540 cm⁻¹ suggests the presence of a small amount of the 1 : 1 complex. On dissolution of the complex in benzene, the band at 559 cm⁻¹ rapidly decreases with the accompanying growth of the band at 540 cm⁻¹ (Figure 7b). Removal of the solvent gives the 1 : 1 complex with νₚ 645 cm⁻¹; νₚ, 540 cm⁻¹; Δ, 105 cm⁻¹.

In contrast, reaction of (A) with an excess of ethylidiphenylphosphine leads to the isolation of a yellow solid which has an analysis consistent with the formula [Pd(S₂PPPh₃)₂(PET₃Ph)]. From a Nujol mull, the following assignment can be made, νₚ 664 cm⁻¹; νₚ, 539 cm⁻¹; Δ, 107 cm⁻¹. If an excess of ethylidiphenylphosphine is added to a benzene solution of the 1 : 1 complex, no band appears in the i.r. spectrum at ca. 560 cm⁻¹, confirming that no prior formation of the 1 : 2 complex occurs.

**Reaction of (A) with other Lewis Bases.**—Attempts to prepare similar adducts with such Lewis bases as triphenylarsine, pyridine, and az′-bipyridyl have been completely unsuccessful. Also, treatment of either trans-[PdCl₂(AsPh₃)] or trans-[Pd(OC₃)₂(AsPh₃)] with a slight excess of diphenylphosphinodithioc acid has produced only Pd[S₃PPh₃]₂. Addition of an excess of triphenyl phosphite to (A) in benzene solution does, however, give an orange solution. Removal of the solvent gives an orange oil but on attempted solidification with diethyl ether, this decomposes to (A) and triphenyl phosphite.

**DISCUSSION**

All the evidence presented here is consistent with the formation of five- and six-co-ordinate complexes of palladium(II). This is supported by recent work by Fackler et al., in which 1 : 1 adducts between methylidiphenylphosphine and platinum(II) and palladium(II)-dithio-complexes have been characterized, mainly by n.m.r. studies, although in some cases by the isolation of solid products. A brief mention is also made of the precipitation from solution of what may be six-co-ordinate species when excess of methylidiphenylphosphine is added to platinum(II) complexes of ring-substituted dithio-benzoates, but no details are given.

In a recent paper by Fackler and his co-workers, it is reported that both Pd[S₂CO₂Ph₂] and Pd[S₂P(OET)₂] give 1 : 1 adducts with methylidiphenylphosphine but, on addition of an excess of phosphine, C-O cleavage occurs (promoted in some as yet unknown way by the phosphine) to give the four-co-ordinate [Pd(S₂CO₂(PMe₃Ph₂)] and [Pd(S₂P(OET)] respectively. Such cleavage reactions are, of course, impossible in Pd[S₃PPh₃] but the ready formation of six-co-ordinate adducts here does suggest that this may be an important prior step in elimination reactions of xanthate and phosphate complexes.

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Possible Structures of the $1:1$ Complexes.—The potential nonrigidity of five-co-ordinate complexes has been extensively discussed and many examples of five-co-ordinate molecules in which positional changes occur as relatively low-energy processes are known. The preferred structure adopted for the ground-state configuration of such complexes will depend on a variety of factors, the relative importance of which is by no means understood. Blundell and Powell have listed some of these factors. From their results and those of other workers, these authors conclude that for five-co-ordinate palladium(II) and platinum(II) complexes, a square pyramidal (SP) structure is favoured in the absence of steric requirements of the ligands or strong multiple-bonded metal–ligand bonds.

For $\text{[Pd(S}_2\text{PPh}_3)_2(\text{PR}_3)]$, six structures (Figure 8) can be drawn based on the idealized extremes of trigonal bipyramidal (TBP) and SP geometries. However, in the molecules themselves considerable distortions are expected, either by twisting or bending of the $\text{Pd-S}$ bonds. Therefore, in view of these expected ready interconversions and the range of structures possible, it is unrealistic at present to attempt to assign any specific structure in Figure 8 to either (B) or (C).

![Figure 8 Possible idealized geometries for $\text{[Pd(S}_2\text{PPh}_3)_2(\text{PR}_3)]$](image)

However, it seems reasonable to use the conclusions of Blundell and Powell, coupled with these experimental observations, tentatively to infer approximate structures for these complexes. The steric requirements of the ligands do not exclude any of the structures given in Figure 8 although structure (IV) contains rather strained $\text{Pd-S}$ bonds. This is confirmed by building molecular models based on undistorted TBP and SP geometries, with various bond lengths taken from the literature.$^\dagger$

The large size of the ligands and the ability of both the tertiary phosphine and the diphenylphosphinodithioato groups to act as effective π-acceptors should enhance repulsive effects, both between bonding electron pairs and the ligands themselves. The larger these repulsions, the more a TBP structure should be favoured.$^\star$

Molecular models show, in fact, that the TBP structures (II)–(IV) are significantly less sterically crowded than the SP ones (V)–(VII). Therefore, assuming that these steric factors outweigh ligand-field stabilization effects in this instance, it is tentatively concluded that the stable isomer (B) has an approximate TBP geometry. X-ray studies on $\text{[Pd(S}_2\text{PPh}_3)_2(\text{PPh}_3)]$ are now in progress to test this hypothesis.

The close similarity of the i.r. spectrum of the unstable isomer (C) to the species in solution, plus the evidence indicating that the latter but not the former is probably partially solvated, suggest that (C) has an approximate SP structure. This can rapidly isomerize to a TBP structure in the solid state but in solution such an isomerisation is inhibited by solvent interaction (?). Further support for solvation of the $1:1$ adducts in solution is obtained from the preparation and dissociation of $1:2$ complexes with certain phosphines. Thus, addition of an excess of phosphine to the $1:1$ complex in solution gives the $1:2$ complex which can then be isolated. This is quite stable in the solid state but on redissolution the $1:1$ complex is rapidly reformed. A good explanation of these observations is prior solvation of the $1:1$ complex, displacement of solvent by excess of phosphine, and then displacement of phosphine by excess solvent.

Molecular models of structures (V)–(VII) show that it is relatively easy to add another $\text{PR}_3$ molecule ($\text{PET}_3$ or $\text{PMe}_3\text{Ph}$) to form either cis- [(V) (VII)] or trans- (VII) complexes, but it is impossible to predict from these models which will be sterically more stable. With $\text{PET}_3\text{Ph}$ and $\text{PPh}_3$ it is impossible to incorporate another phosphine molecule into these structures. This indicates that steric factors play an important role here, but the inability to prepare similar adducts with arsenic and nitrogen donors confirms that electronic factors are also important.

The best explanation suggested by these results for the reversible colour changes observed as a function of temperature for the $1:1$ complexes in solution is the existence of a mixture of solvated approximate SP complexes (V)–(VII) the concentrations of which vary reversibly with temperature. However, Fackler et al.$^{11}$ have a different explanation, based on n.m.r. changes of the ethyl groups as a function of temperature for $\text{[Pt(S}_2\text{P(OEt})_2(\text{PMePh}_3)]}$. They suggest that a solution equilibrium exists between TBP and solvated SP complexes. In view of the negative n.m.r. evidence obtained here (due to the complexity of the phenyl region), it is difficult to disprove these conclusions but if our explanation for the solid-state isomerisation of (C) to (B) is correct (i.e. SP $\rightarrow$ TBP), then it seems surprising that similar changes are not observed in the solution i.r. spectra if Fackler's explanation is correct.

However, although the authors strongly favour the

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$^\star$ By approximate, it is meant structures resembling idealised TBP more than SP (or vice versa).

$^\dagger$ Using framework molecular models, 1 inch = 1 Å with $\text{Pd-P}$, 2.3 Å (2.34 (avg) Å in $\text{[Pd(PMe}_3\text{Ph}_3)]}$; $\text{Pd-S}$, 2.2–4 Å (calculated from covalent radii, 2.14 Å; ca. 2.4 Å in $\text{[Ru(S}_2\text{CNEt}_3)]}$; $\text{P-C}$, 1.80 Å and remainder from X-ray analysis of $\text{[Ni(S}_2\text{PPh}_3)]}$


$^{13}$ B. D. Faithful, unpublished work.
conclusions reached in this section, it must be stressed that these are speculative and that alternative explanations for the results obtained can be formulated.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College, or A. Bernhardt, West Germany. Molecular weights were determined on a Mechrolab Vapour Pressure Osmometer (model 301A), calibrated with benzil. Infrared spectra were recorded in the region 4000—400 cm⁻¹ on a Perkin-Elmer model 125 spectrometer. Conductivity measurements were made on a Mullard conductivity bridge; magnetic susceptibilities were determined by the Faraday method. N.m.r. spectra were obtained on a Bruker Spectrospin HFX3 at 90 MHz and mass spectra were measured on an AEI MS9 mass spectrometer.

Materials.—Palladium(ii) chloride (Johnson Matthey); triphenylphosphine, triphenylarsine, dimethylphenylphosphine (B.D.H.); triethylphosphine (B. Newton Main). Ethylidiphenylphosphine was prepared from chlorodiphenylphosphine and ethyl Grignard. Palladium(ii) acetate and its triphenylphosphine and —arsine complexes were prepared as described previously. Diphenylphosphinodithioic acid was prepared by the method of ref. 16 from reaction of benzene with P₂S₂ in the presence of aluminium trichloride. The product was purified by low-temperature recrystallisation (—60°) from diethyl ether (m.p. 52—54°: lit., 54—56°). The caesium salt was made by mixing equimolar quantities of caesium carbonate and diphenylphosphinodithioic acid in a 1:1 ethanol—water mixture and evaporating the solution to dryness.

Bis(diphenylphosphinodithioato)palladium(ii).—Palladium(ii) acetate (1.30 g) was dissolved in warm benzene (45 ml); the solution was cooled and then added slowly to a stirred solution of diphenylphosphinodithioic acid (2.80 g) in benzene (35 ml). The yellow-brown acetate solution immediately turned deep cherry-red and after ca. 2 min. red crystals of the complex were deposited; these were recrystallised from hot benzene, washed with diethyl ether, and dried in vacuo (3.90 g, 90%), m.p. 332—333° (Found: C, 47.9; H, 3.6; F, 10.4; S, 22.6%. C₃₂H₂₃P₂S₂ requires C, 47.6; H, 3.3; F, 10.2; S, 21.1%). The compound is only soluble in hot benzene and dichloromethane.

Bis(diphenylphosphinodithioato)(triphenylphosphine)palladium(ii).—The complex (0.10 g) (A) was suspended in benzene (10 ml) and an excess of triphenylphosphine (1.10 g) was added to it. The suspension immediately dissolved to give an orange solution. Light petroleum (b.p. 100—120°) was then added until the first signs of a yellow precipitate appeared. Then, light petroleum (b.p. 60—80°) was added to give a pale yellow flocculent precipitate which, on trituration, was converted into a crystalline orange precipitate which was filtered off, washed with diethyl ether, and dried in vacuo at 40° for several hours (0.12 g, 84%), m.p. 188—189° (Found: C, 58.1; H, 4.3; F, 11.2; S, 18.6; Pd, 12.9%. C₃₂H₃₄P₂S₂ requires C, 58.1; H, 4.0; F, 10.7; S, 14.8; Pd, 12.3%).

The same compound (B) was obtained either by heating under reflux solutions of equimolar quantities of (A) and triphenylphosphine or by treatment of trans-[PdCl₂(PPh₃)₂] or trans-[Pd(OAc)₃(PPh₃)₂] with an excess of diphenylphosphinodithioic acid. This pale yellow solid (C) could be stabilised by carrying out the precipitation at —60° and washing the product with cold, light petroleum (b.p. 100—120°).

Molecular weight of (B).—(a) Osmometric in benzene at 37°. For 0.032 g. of (B), found 889; for 0.056 g. found 913; for 0.069 g., found 804.

(b) X-Ray method. Suitable crystals were obtained from benzene—diethyl ether. The dimensions of the unit cell were obtained from zero-layer precession photographs, with zirconium-filtered Mo-Kα radiation. The cell chosen was triclinic and possessed the d spacings: d₁₀₀ = 9.65, d₁₀₁ = 12.20, d₀₀₁ = 16.95 Å giving U = 1996 Å³. Dc (1.42) indicated that z = 2. This gave M = 854, compared with the calculated monomeric value of 867.

Bis(diphenylphosphinodithioato)(triphenylphosphine)palladium(ii).—The complex Pd[(C₃₂H₃₄P₂S₂)₋₂] (0.20 g.) was suspended in benzene (10 ml) and triethylphosphine (0.06 ml) was added to give an orange solution. Unchanged (A) was filtered off and the solvent was removed under reduced pressure to give an orange oil. Diethyl ether (15 ml) was then added to the oil which was shaken thoroughly and filtered. Removal of the solvent under reduced pressure followed by careful washing of the product with light petroleum (b.p. 60—80°) gave an orange crystalline solid which was dried in vacuo at 40° for several hours (0.20 g., 83%), m.p. 138° (Found: C, 50.5; H, 5.1; P, 12.9; Pd, 10.2; S, 18.6. C₃₂H₃₄P₂S₂ requires C, 49.8; H, 4.8; P, 12.9; Pd, 14.8; S, 17.7%).

Osmometric molecular weight in benzene: for 0.0544 g. of compound found, 758: monomer requires 723.

Bis(diphenylphosphinodithioato)(bis(triethylphosphine)palladium(ii).—The complex Pd[(C₃₂H₃₄P₂S₂)₋₂] (0.20 g.) was suspended in benzene (5 ml.) and a slight excess of triethylphosphine (ca. 0.20 ml) was added to it to give a lemon—yellow solution. When the mixture was set aside, pale yellow crystals of the complex were rapidly deposited; these were washed with with diethyl ether and dried in vacuo at 40° for several hours (0.19 g., 71%), m.p. 114—115° (Found: C, 51.1; H, 6.2; P, 14.8; S, 13.8. C₃₂H₃₄P₂S₂ requires C, 51.4; H, 6.0; P, 14.7; S, 15.2%). The same complex was isolated upon addition of an excess of triethylphosphine to a solution of the 1:1 adduct in benzene.

Although quite air-stable, the complex rapidly dissociates in solution to form the 1:1 complex.

Bis(diphenylphosphinodithioato)(bis(dimethylphosphine)palladium(ii).—As for the triethylphosphate complex, Pd[(C₃₂H₃₄P₂S₂)₋₂] (0.20 g.), and methylidiphenylphosphine (ca. 0.25 ml.) in benzene (10 ml.) gave an orange solution. Removal of the solvent under reduced pressure gave an oil which was washed with a variety of ethers without success. However, redissolution of the oil in acetone and immediate removal of the solvent under reduced pressure gave an orange-yellow crystalline solid, which was washed with light petroleum (b.p. 60—80°) and dried in vacuo (0.15 g., 55%), m.p. 62—65° (Found: C, 54.6; H, 5.2. C₂₉H₂₁P₂S₂ requires C, 54.5; H, 4.8%). Dissolution of the 1:2 complex in benzene and removal of the solvent gave a small yield of orange-red crystals of the 1:1 complex (m.p. 48—52°) (Found: C, 52.1; H, 4.4. C₂₉H₂₁P₂S₂ requires C, 51.7; H, 4.2%).

Bis(diphenylphosphinodithioato)ethylidiphenylphosphine)palladium(ii).—As for the other complexes, Pd[(C₃₂H₃₄P₂S₂)₋₂] (0.20 g.) and ethyldiphenylphosphine (0.5 ml.) in benzene

(10 ml.) gave an orange solution. Removal of the solvent under reduced pressure gave an orange oil which was difficult to solidify. However, addition of benzene (4 ml.) followed by an excess of light petroleum (b.p. 100—120°) (20 ml.) to it and storage at 0° for 24 hr. gave a yellow precipitate which was washed with ether and dried in vacuo (0.22 g., 81%), m.p. 65—70° [Found: C, 55.9; H, 4.8%; C₃₃H₃₃P₃PdS₄ requires C, 55.7; H, 4.3%].

Reaction of (A) with other Lewis Bases.—When an excess of triphenylphosphite was added to a suspension of (A) in benzene, an orange solution was formed. Removal of the solvent under reduced pressure gave an orange oil which when washed with diethyl ether gave (A) and free triphenylphosphite.

With (A) and an excess of triphenylnarsine, pyridine or az'-bipyridyl, reaction at room temperature or under reflux in benzene produced no evidence for any adduct formation. When trans-[Pd(OAc)₄(AsPh₃)₂] or trans-[PdCl₄(AsPh₃)₂] in benzene was treated with an excess of diphenylphosphino-dithioic acid, red crystals of (A) were rapidly deposited.

We thank Johnson Matthey Ltd., for a loan of palladium-(II) chloride.

[91639 Received, September 25th, 1969]
Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II). A Correction

By (Miss) J. M. C. Alison and T. A. Stephenson*

(Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ)

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Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II). 
A Correction

By (Miss) J. M. C. ALISON and T. A. STEPHENSON (Department of Chemistry, University of Edinburgh, Edinburgh EH9 3J)

Summary. The 1:1 and 1:2 tertiary phosphine adducts of Pd(S$_2$PPh$_3$)$_2$, originally formulated as five- and six-coordinate complexes, respectively, are probably both four-coordinate.

Recently evidence was reported for 1:1 and 1:2 tertiary phosphine adducts of Pd(S$_2$PPh$_3$)$_2$ which were tentatively formulated as five- and six-coordinate complexes, respectively. Further work on these and the isomorphous platinum(II) complexes has now indicated that this formulation is incorrect and that the "six-coordinate" complexes are in fact four-coordinate ionic species (I) and the "five-coordinate" complexes are probably the four-coordinate species (II).

\[ \begin{array}{c}
\text{Ph}_2\text{PS}^+ \\
\text{R}_3\text{P} \quad \text{S} \quad \text{PPh}_2
\end{array} \quad \begin{array}{c}
\text{Ph}_2\text{PS}_2^- \\
\text{R}_3\text{P} \quad \text{S} \quad \text{PPh}_2
\end{array} \]

(II)

\[ M = \text{Pd, Pt} \]

The evidence for the revised structures is as follows: (a) As discussed previously, the 1:2 complexes rapidly dissociate to 1:1 complexes in benzene and carbon disulphide. However, in more polar solvents such as dichloromethane the 1:2 complexes are stabilized and conductivity measurements (Table 1) are consistent with those expected for 1:1 electrolytes in this solvent.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent conductivities (25°) of some 1:1 and 1:2 complexes in CH$_2$Cl$_2$</td>
</tr>
<tr>
<td>Compounds</td>
</tr>
<tr>
<td>Bo$_2$NCIO$_4$</td>
</tr>
<tr>
<td>Pd(S$_2$PPh$_3$)$_2$(PET$_3$)$_2$</td>
</tr>
<tr>
<td>Pd(S$_2$PPh$_3$)$_2$(PMe$_2$Ph)$_2$</td>
</tr>
<tr>
<td>Pd(S$_2$PPh$_3$)$_2$(PMe$_3$Ph)$_2$</td>
</tr>
<tr>
<td>Pt(S$_2$PPh$_3$)$_2$(PET$_3$)$_2$</td>
</tr>
<tr>
<td>Pt(S$_2$PPh$_3$)$_2$(PMe$_2$Ph)$_2$</td>
</tr>
<tr>
<td>Pt(S$_2$PPh$_3$)$_2$(PMe$_2$Ph)$_2$</td>
</tr>
<tr>
<td>Pt(S$_2$PPh$_3$)$_2$(PMe$_3$Ph)$_2$</td>
</tr>
</tbody>
</table>

| *cm$^3$/ohm cm$^{-1}$ mole$^{-1}$. |

(b) Addition of an excess of tertiary phosphine to the 1:1 complexes (non-electrolytes) in CH$_2$Cl$_2$ produces an increase in conductivity consistent with the formation of 1:1 electrolytes (Table 1).

(c) $^1$H n.m.r. data on 1:2 platinum(II) complexes of Me$_2$P and Me$_3$P in deuteriochloroform (Table 2) indicate a cis-arrangement of tertiary phosphine groups (no virtual coupling$^a$).

(d) An X-ray structural analysis$^a$ on [Pd(S$_2$PPh$_3$)$_2$(PET$_3$)$_2$] is sufficiently advanced to verify the authenticity of structure (I). The mill and solution i.r. spectra of these 1:2 complexes are identical, suggesting the same species is retained in solution, and this is supported by $^1$H n.m.r. and conductimetric data.

The reformulation of the 1:2 complexes as the ionic species (I) and their ready interconversion with the 1:1 complexes casts doubt on the validity of the five-coordinate structure postulated earlier for the latter.$^1$ No direct evidence is yet available to support (II) (a crystal structure of Pt(S$_2$PPh$_3$)$_2$(PPh$_3$)$_2$ is in progress) but an analogous structure has been postulated by Tebbe and Müetters$^4$ for 1:1 tertiary phosphine complexes of palladium(II) difluorodithiophosphate on the basis of i.r. and $^{19}$F n.m.r. evidence.

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H n.m.r. data (methyl region) for some platinum tertiary phosphine complexes in CDCl$_3$</td>
</tr>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>[Pd(S$_2$PPh$_3$)$_2$(PMe$_2$Ph)$_2$]</td>
</tr>
<tr>
<td>[Pt(S$_2$PPh$_3$)$_2$(PMe$_3$Ph)$_2$]</td>
</tr>
<tr>
<td>[Pt(S$_2$PPh$_3$)$_2$(PMe$_2$Ph)$_2$]</td>
</tr>
<tr>
<td>$^* + 0-01.$</td>
</tr>
</tbody>
</table>

If (II) is correct, the best explanation for the "isomers" of [Pd(S$_2$PPh$_3$)$_2$(PPh$_3$)$_2$]$^a$ is probably different orientations of the unidentate diphenylphosphinodithioato-group with respect to the bulky triphenylphosphin ligand.

Finally, preliminary studies on tertiary phosphine complexes of platinum(II) dithiocarbamates$^5$ suggest that 1:1 and 1:2 adducts with analogous structures to (I) and (II) are formed.

We thank the Science Research Council for an award (to J.M.C.A.) and Johnson-Matthey Limited for a loan of palladium(II) chloride.

(Rceived, June 22nd, 1970; Com. 984.)

3. C. A. Beevers and A. Fraser, to be published.
Metal Complexes of Sulphur Ligands. Part II,\(^1\) Reaction of Bis(diphenylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group V\(_8\) Atoms

By (Miss) J. M. C. Alison, T. A. Stephenson,\(^*\) and (in part) R. O. Gould, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of Pt\((\text{S}_2\text{PPh}_3)_2\) with tertiary phosphines (PPh\(_3\), PMePh\(_3\), PMeMePh) gives crystalline 1:1 and 1:2 adducts. With triphenylarsine or triphenylstibine, only 1:1 adducts can be isolated and with pyridine, i.r. evidence indicates that the 1:1 adduct is only stable in solution in the presence of an excess of pyridine. As reported earlier for the analogous palladium compounds, the 1:2 adducts rapidly dissociate to the 1:1 compounds in non-polar solvents (benzene or carbon disulphide); however, it is now found that they can be stabilised in more polar solvents (dichloromethane or nitromethane). Conductivity measurements in the latter suggest that these 1:2 adducts have a four-co-ordinate ionic structure and this is confirmed by an X-ray analysis of [Pd\((\text{S}_2\text{PPh}_3)_2\)\(\text{PPh}_3\)]. An X-ray analysis on [Pd\((\text{S}_2\text{PPh}_3)_2\)\(\text{PPh}_3\)] suggests a four-co-ordinate monomeric structure for the 1:1 compounds with uni- and bi-dentate co-ordination of dithiocarbamides. Finally, an empirical i.r. method for distinguishing unidentate, bidentate and tri-dentate modes of co-ordination of the diphenylphosphinodithioato-group to platinum and palladium is discussed.

Recently, one of us reported\(^2\) that the compound Pd\((\text{S}_2\text{PPh}_3)_2\) reacted with tertiary phosphines to give both 1:1 and 1:2 adducts. On the basis of earlier studies, interpreted by analogy with previous studies on 1:1 and 1:2 Lewis base adducts with palladium carboxylates,\(^3\) these dithiocarbamides were tentatively formulated as examples of five- and six-co-ordinate palladium(II) respectively. The former was consistent with earlier studies by Fackler et al.\(^4\) on the reactions of other palladium (and platinum) dithiocarbamides \(M(\text{S-S})_2\) \((M = \text{Pd or Pt}; \ (\text{S-S})_2 = \text{RCS}_2, \text{ROCS}_2, \text{Et}_2\text{NCS}_2, \text{and} \ (\text{EtO})_2\text{PS}_2\) with methylphenylphosphine, in which 1:1 adducts were characterised and formulated as five-co-ordinate compounds on the basis of \(\text{H} \) n.m.r. studies. A brief mention was also made of the precipitation from solution of what may be six-co-ordinate species when an excess of methylphenylphosphine was added to platinum(II) compounds of ring substituted dihydrobenzoates, but no details were given.

Here, additional evidence is presented which shows that the above interpretation is incorrect and that the 1:1 and 1:2 tertiary phosphine adducts of Pd\((\text{S}_2\text{PPh}_3)_2\) should be reformulated as the four-co-ordinate compounds (I) and (II) respectively. In addition, the results of a detailed investigation of the reaction of ligands containing Group V\(_8\) atoms with the isomorphous Pt\((\text{S}_2\text{PPh}_3)_2\) are presented. These lend support to the conclusions drawn from the palladium study. Analogous structures have also recently been postulated by Terbe and Muetertees\(^5\) for tertiary phosphate complexes of palladium(II) difluoroanithiolophosphate on the basis of i.r. and \(\text{F} \) n.m.r. studies.

In Part III of this series,\(^6\) the results of a re-investigation of the reactions between tertiary phosphines and platinum(II) dithiocarbamates, xanthates, and dithiophosphates will be discussed. The evidence strongly suggests that reactions of all platinum (and palladium) dithiocarbamate compounds with tertiary phosphines can be rationalised in terms of the formation and, in the case of xanthate and dithiophosphate, of the rearrangement reactions of four-co-ordinate 1:1 and 1:2 adducts of type (I) and (II) respectively.

\[
\begin{align*}
\text{Ph}_2\text{S}(\text{S}^2\text{PPh}_3) & \quad (\text{I}) \\
\text{R}_3\text{P} \text{S}(\text{S}^2\text{PPh}_3) & \quad (\text{II})
\end{align*}
\]

RESULTS AND DISCUSSION

Reaction of either potassium tetrachloroplutinate(II) or platinum(II) acetate with a six-fold excess of diphenylphosphinodithioic acid readily gives orange crystals of Pt\((\text{S}_2\text{PPh}_3)_2\). This compound is isomorphous with the corresponding palladium and nickel salts (X-ray structural analysis of the latter\(^7\) confirms the structure is a square planar monomer), the mass spectrum at \(150^\circ\) shows the highest group of peaks corresponds to Pt\((\text{S}_2\text{PPh}_3)_2\) and the i.r. spectra (800—400 cm\(^{-1}\)) of the three compounds are almost identical. The compounds are non-conducting in dichloromethane.

Reaction of a suspension of Pt\((\text{S}_2\text{PPh}_3)_2\) in benzene with tertiary phosphines (1:1 molar ratios) rapidly gives bright yellow solutions, from which lemon-yellow compounds of stoichiometry \(\text{Pt}(\text{S}_2\text{PPh}_3)_2\text{PPh}_3\) \((\text{PPh}_3 = \text{PPh}_3, \text{PMePh}_2, \text{PMeMePh})\) can be isolated, either by


\(^3\) J. M. C. Alison and T. A. Stephenson, to be published.


precipitation with light petroleum or by removal of solvent under reduced pressure. Molecular weight measurements in chloroform show them to be monomeric. The $^1$H n.m.r. spectra of [Pt(S$_2$PPh$_2$)$_2$(PR$_3$)] (PR$_3$ = PMe$_2$Ph or PMe$_3$Ph) (Table 1) in carbon disulphide or deuterochloroform consists, in the methyl region, of a triplet of doublets which confirms direct co-ordination of the tertiary phosphine to platinum, rather than reaction with the dithio-ligand. For comparison, the chemical shifts and coupling constants of methylidiphenylphosphine adducts of other platinum dithioacids are given in Table 1. The close similarity of these

\begin{table}[h]
\centering
\caption{1\lowercase{H} N.m.r. data [methyl region (phos)] for some platinum and palladium tertiary phosphine complexes at 301 K}
\begin{tabular}{|c|c|c|c|}
\hline

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$\tau$</th>
<th>Multiplicity and J values$^8$</th>
<th>$^\dagger$</th>
<th>$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(S$_2$PPh$_2$)$_2$(PMe$_3$Ph)]</td>
<td>CS$_2$</td>
<td>7-69</td>
<td>11-4 38-0</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$PPh$_2$)$_2$(PMe$_2$Ph)]</td>
<td>CDCl$_3$</td>
<td>7-07</td>
<td>11-3 37-5</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$CNCE$_2$(PMe$_3$Ph)]</td>
<td>CDCl$_3$</td>
<td>7-72</td>
<td>10-0 38-0</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$CNE$_2$(PMe$_3$)]</td>
<td>CDCl$_3$</td>
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<td>11-0 41-0</td>
<td>9-3 38-0</td>
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</tr>
<tr>
<td>[Pt(S$_2$CNE$_2$(PMe$_3$)]</td>
<td>CDCl$_3$</td>
<td>7-64</td>
<td>11-2 41-0</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$PPh$_2$)$_2$(PMe$_2$Ph)]</td>
<td>CS$_2$</td>
<td>8-08</td>
<td>11-3 38-0</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$PPh$_2$)$_2$(PMe$_3$Ph)]</td>
<td>CDCl$_3$</td>
<td>7-99</td>
<td>13-2 49-5</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$PF$_2$)$_2$(PMe$_3$)]</td>
<td>CDCl$_3$</td>
<td>8-27</td>
<td>12-6 49-0</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$PF$_2$)$_2$(PMe$_3$)]</td>
<td>CDCl$_3$</td>
<td>8-66</td>
<td>10-0 39-0</td>
<td>9-3 38-0</td>
<td></td>
</tr>
<tr>
<td>[Pt(S$_2$PF$_2$)$_2$(PMe$_3$)]</td>
<td>CDCl$_3$</td>
<td>7-99</td>
<td>13-2 49-5</td>
<td>9-3 38-0</td>
<td></td>
</tr>
</tbody>
</table>

\hline
\end{tabular}
\end{table}

slowly reverts to Pt(S$_2$PPh$_2$)$_2$ and triphenylarsine whereas, in the absence of an excess of triphenylstibine, the stibine complex immediately dissociates in solution. Reaction of Pt(S$_2$PPh$_2$)$_2$ with an excess of pyridine in carbon disulphide gives a lemon-yellow solution but attempts to isolate a solid complex only resulted in recovery of the starting material. However, on the basis of solution i.r. studies (see later) there is probably a 1:1 adduct present in solution. In contrast, there is no reaction under any conditions between Pd(S$_2$PPh$_2$)$_2$ and triphenylarsine, triphenylstibine, or pyridine. With Ni(S$_2$PPh$_2$)$_2$, an excess of pyridine readily gives the green, crystalline 1:2 adduct [Ni(S$_2$PPh$_2$)$_2$(C$_6$H$_5$N)$_2$]. A very recent X-ray structural analysis$^8$ has shown this to be an octahedral complex with a trans-arrangement of pyridine ligands and bidentate diphenylphosphinothioato-groups.

If, however, a suspension of Pt(S$_2$PPh$_2$)$_2$ in benzene is shaken with an excess of any tertiary phosphine, the initial yellow solution rapidly becomes colourless and removal of solvent under reduced pressure gives white powders of stoichiometry [Pt(S$_2$PPh$_2$)$_2$(PR$_3$)] (PR$_3$ = PPh$_3$, PMe$_2$Ph, or PMe$_3$Ph). This is to be contrasted with the behaviour of Pd(S$_2$PPh$_2$)$_2$, which forms 1:2 adducts in benzene solution with PEt$_3$, PPh$_3$, and PMe$_2$Ph but not with PEt$_2$Ph or PPh$_3$. As reported earlier for the palladium complexes,$^2$ the platinum 1:2 adducts are also unstable in non-polar solvents such as benzene and carbon disulphide, readily dissociating to the 1:1 complexes. This process can be monitored by watching the growth in the i.r. spectrum of a band characteristic of the 1:1 adduct (ca. 540 cm$^{-1}$) and the loss of one characteristic of the 1:2 compound (ca. 560 cm$^{-1}$). As in the case of the palladium complexes, only the addition of an excess of tertiary phosphine can partially stabilise the 1:2 adducts in these solvents.

However, in more polar solvents such as chloroform, dichloromethane, and nitromethane, the platinum 1:2 adducts are stabilised. The mull and solution i.r. spectra are identical, suggesting that the same species is retained in these solvents and, on removal of solvent, the 1:2 compound is recovered. Furthermore, conductivity measurements in dichloromethane and nitromethane (Table 2), both on the 1:2 compounds and on the 1:1 compounds plus an excess of phosphine, are consistent with those expected for 1:1 electrolytes. In addition, a molecular weight determination of [Pt(S$_2$PPh$_2$)(PMe$_3$Ph)$_2$]S$_2$PPh$_2$ in chloroform gives a value of half that required for a monomeric complex, indicating a 1:1 electrolyte in this solvent.

It is interesting to note that although no evidence is found for the formation of [Pt(S$_2$PPh$_2$)(AsPh$_2$)$_2$]S$_2$PPh$_2$ in benzene solution, addition of an excess of triphenylarsine to a dichloromethane solution of [Pt(S$_2$PPh$_2$)$_2$](AsPh$_2$) produces a lightening of colour and an appreciable increase in conductivity (Table 2). The
maximum value of $\Lambda_{9000}$ found (ca. 11) would suggest ca. 30–40% conversion into an ionic species in this solvent. However, on removal of solvent, the i.r. spectrum of the residue contains no band at ca. 560 cm$^{-1}$ and the compound on dissolution is non-conducting. Clearly, the triphenylarsine 1:2 adduct is only partially stabilised in fairly polar solvents.

The $^1$H n.m.r. data for $[\text{Pt(S$_2$PPh$_3$)}(\text{PR$_3$})_2]_2$S$_2$PPh$_3$ (PR$_3$ = PMe$_3$Ph or PMePh$_3$) (Table 1) are very similar to those of the 1:1 compounds, although the coupling constants are slightly larger and the methyl resonances occur at a slightly higher field.

Similarly, conductivity measurements on the palladium complexes (Table 2) confirm the ionic nature of the 1:2 adducts. The palladium compounds (P$\ell_3$, PMe$_3$Ph, and PMePh$_3$) are completely stabilised in nitromethane; in dichloromethane and chloroform they are slightly dissociated, as shown by the presence of a weak band at ca. 540 cm$^{-1}$ (cf. the corresponding platinum compounds, which are completely stabilised in these solvents). Furthermore, although there is no evidence for the formation of palladium 1:2 complexes of PPh$_3$ or P$\ell_3$Ph in benzene solution, addition of an excess of these phosphines to dichloromethane solutions of the corresponding 1:1 adducts produces a lightening of colour and an increase in conductivity (Table 2). The values of $\Lambda$ found indicate an appreciable amount of an ionic species is present. However, although the solution i.r. spectra of these mixtures contain a weak band at ca. 560 cm$^{-1}$, all attempts to isolate an ionic species gave only the 1:1 compounds.

Thus, the non-electrolyte six-co-ordinate structure suggested earlier must be discarded and the 1:2 adducts of both palladium and platinum reformulated on the evidence given here as the four-co-ordinate ionic compounds (II). Confirmation of the authenticity of structure (II) has now been established by means of a two-dimensional X-ray diffraction study on [Pd(S$_2$PPh$_3$)$_2$]$_2$S$_2$PPh$_3$.

The reformulation of the 1:2 compounds as the ionic species (II) and their ready interconversion with the 1:1 complexes casts doubt on the validity of the five-co-ordinate structure postulated earlier for the latter. An X-ray structural analysis of [Pd(S$_2$PPh$_3$)$_2$P($\ell_3$)] is now sufficiently advanced to verify the unusual structure (I) containing four-co-ordinate palladium and bidentate and unidentate diphenylphosphinothioato-groups. The Figure shows the squire-planar arrangement about the palladium atom and the distinction between the unidentate and bidentate ligands. The non-co-ordinating sulphur atom, S(4), is 3.3 Å below the plane, and more than 3.5 Å from the palladium atom.

The heavy atoms of bis(diphenylphosphinothioato)triphenylphosphinepalladium(II) projected into the best plane of Pd, S(1), S(2), S(3), P(1), and P(3); bond lengths and angles are shown.

**Infrared Spectra.**—In an earlier paper, the mode of bonding of the diphenylphosphinothioato-ligand to palladium was inferred from the position and separation of the asymmetric ($v_1$) and symmetric ($v_2$) PS$_2$-stretching frequencies. At the time, it was considered that this approach was valid and completely analogous to the situation found in carboxylate complexes. However, such an approach is now considered unsuitable in view of the fact that, in the Ph$_2$PS$_2$ group,

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### Table 2

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<tr>
<th>Solvent</th>
<th>Compound</th>
<th>Conc. (10$^{-3}$mol)</th>
<th>$\Lambda_+$ excess of $\text{PR}_3$</th>
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<td>CH$_2$Cl$_2$</td>
<td>PPh$_3$, AsCl, HCl</td>
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<td>[Ni(S$_2$PPh$_3$)$_2$]</td>
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<td>1.7</td>
</tr>
</tbody>
</table>

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* C. A. Bevans and A. Fraser, to be published.

10 Miss J. M. C. Alison and R. O. Gould, to be published.

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the similar energies of \( \nu_1 \) and \( \nu_2 \) to the many other vibrations of the same symmetry class will surely lead to extensive coupling of these vibrations. This in turn will invalidate any arguments based on the expected shifts of uncoupled \( \nu P_{2} \) vibrations with changes in the mode of co-ordination.

Nevertheless, careful examination of the i.r. spectra of these platinum and palladium complexes (these are reproduced from 800 to 250 cm\(^{-1} \) in the Experimental section) suggest that the presence of certain bands appears to be diagnostic of unidentate, bidentate, and ionic co-ordination of the diphenylphosphinodithioate group to these metals. For the reason given above, no attempt has been made to assign these characteristic bands to any specific mode of vibration, although it is suggested that they probably contain an appreciable contribution from \( \nu P_{2} \) stretching frequencies. In Table 3, the two characteristic bands are given for each mode of bonding. In addition, the Table contains a number of examples taken from these studies, in order to show the similarity of \( \nu P_{2} \) in carbon disulphide shows bands at 573 and 540 cm\(^{-1} \), indicating the presence of a 1 : 1 complex of type (I).

Although the two isomers of \([MS_{2}PPPh_{2}PPh_{3}](M = Pd \text{ or } Pt)\) have different null i.r. spectra, the differences stem from changes in the region ca. 500 and 700 cm\(^{-1} \) (see reference 2 for details of the palladium compounds). The characteristic bands of 'bidentate' and 'unidentate' co-ordination remain unchanged (Table 3). Therefore, it is suggested that the best explanation for the isomers of \([MS_{2}PPPh_{2}PPh_{3}]\) is probably different orientations of the unidentate diphenylphosphinodithioate-group with respect to the bulky triphenylphosphine ligand. This is expected to produce changes in the i.r. spectra in regions associated with phenyl vibrations of both tertiary phosphine and dithio-ligand (ca. 500 and 700 cm\(^{-1} \)) but little change in the vibrations associated with the actual mode of bonding. Clearly, there is no need to invoke a five-coordinate low-temperature form to explain the spectral changes. Unfortunately, the low-temperature platinum isomer is not sufficiently crystalline for X-ray analysis and therefore direct proof of this theory is not possible.

Dissolution of either isomer in carbon disulphide gives identical i.r. solution spectra. These are very similar to that of the null spectrum of the low temperature form, except for the additional weak band in the former at 673 cm\(^{-1} \) (palladium) and 675 cm\(^{-1} \) (platinum), the intensity of which increases with concentration. A possible explanation for these observations is that solvation of a common intermediate occurs in solution. This intermediate is very similar in structure to the low-temperature isomer which is formed on removal of solvent. Apparently, the latter is kinetically inert for platinum, but rapidly converts to the room-temperature form for palladium.

Finally it should be noted that for \([Ni(S_{2}PPPh_{2})_{2}(C_{6}H_{4}N)_{2}]\) the 'bidentate' bands occur at 632 and 570 cm\(^{-1} \). Similarly, preliminary studies on diphenylphosphinodithioato-complexes of rhodium, ruthenium, and osmium indicate, in certain instances, some variation in the higher-energy band positions compared to those given in Table 3. However, in all compounds examined to data, the lower energy band positions are very similar to those given in Table 3. By analogy with carboxylate complexes, where \( \nu_1 \) is much more sensitive to changes in the metal than \( \nu_2 \), this might suggest that the higher energy band possesses appreciable \( \nu_1 \) character and the lower \( \nu_2 \) character.

In spite of these variations, it is hoped that this diagnostic method will prove invaluable in future studies, both for analysing the structure of diphenylphosphinodithioato complexes and for following the structural interconversions which are feature of the dithiocarboxylic complexes so far considered.

**Experimental**

Microanalyses were by the Analytical Laboratory, Edinburgh University, and by A. Bernhardt, West Germany.

12 D. J. Cole-Hamilton and T. A. Stephenson, unpublished work.
Molecular weights were determined in dry ethanol-free chloroform at 37° on a Mechrolab Osmometer (model 301A), calibrated with benzil. I.r. spectra were recorded in the region 4000-250 cm⁻¹ on a Perkin-Elmer model 457 and 225 Spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Spectra are listed for each compound (800-250 cm⁻¹). Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. N.m.r. spectra were obtained on a Perkin-Elmer model RS10 60 MHz spectrometer and a Varian Associates HA100 spectrometer. Mass spectra were measured on an AE1 MS20 spectrometer. M.p.s were determined with a Kofer hot-stage microscope and are uncorrected.

Materials.—Palladium(II) chloride and potassium tetrachloroplatinate(II) (Johnson-Matthey); triphenylphosphine and dimethylphenylphosphine (B.D.H.), triphenylarsine (Emanuel), triphenylstibine (Koch-Light), triethylphosphine (B. Newton Main); ethylidiphosphine and methylidiphosphine were prepared by the Grignard method. Diphosphinophosphoridithioic acid and its caesium salt were prepared as described previously.¹

**Platinum Compounds**

*Bis(diphenylphosphinidithioato)platinum(II).—* Potassium tetrachloroplatinate(II) (1.81 g, 4.4 mmol) in a minimum volume of hot water (30 ml) was shaken for 72 h with an excess of diphosphinophosphoridithioic acid (5.70 g, 22.8 mmol) in ethanol (30 ml) to give a pale orange precipitate. After washing with water and ethanol, this was recrystallised from hot benzene (or dichloromethane) giving bright orange crystals of the complex which were washed with diethyl ether and dried in vacuo (2.5 g, 84%), m.p. 298-300° (Found: C, 41.9; H, 2.9; P, 8.8; S, 20.0. C₁₂H₁₀P₂S₂ requires C, 41.6; H, 2.8; P, 8.9; S, 18.5%).

An alternative method of preparation* is by reaction of platinum(II) acetate and excess diphosphinophosphoridithioic acid in benzene to give an immediate orange precipitate, purified as above.

The compound is fairly soluble in dichloromethane, chloroform, and hot benzene; sparingly soluble in acetone and ethanol; insoluble in water, ethers, and hexane; v max (Nujol) 745, 718, 709, 685, 619, 601, 571, 485, 463, 454, 306, 296.

*Bis(diphenylphosphinidithioato)(triphenylphosphine)-platinum(II).—* (a) Bright yellow form. Pt(S₂PPh₃)₂ (0.10 g, 0.15 mmol) was suspended in benzene (10 ml) and shaken with triphenylphosphine (0.04 g, 0.15 mmol) for ca. 20 min to give a lemon-yellow solution. Light petroleum (b.p. 100-120') was then added to the solution giving a flocculent off-white precipitate which on_trituration was rapidly converted into a crystalline bright yellow product. This was filtered off, washed with more petroleum (b.p. 60-80'), and dried in vacuo at 40° for several hours (0.12 g, 99%). m.p. 122° (Found: C, 53.0; H, 3.8; P, 9.7; S, 13.5. C₂₅H₂₁P₂S₂ requires C, 52.8; H, 3.7; P, 9.7; S, 13.4%).


(b) Pale yellow form. A solution of the above product in carbon disulphide was cooled to ca. 200 K and on addition of an excess of light petroleum (b.p. 100-120') a pale yellow solid was obtained, washed with cold light petroleum (b.p. 60-80') and air-dried, m.p. 109-110° (Found: C, 52.6; H, 3.6. C₂₅H₂₁P₂S₂ requires C, 52.8; H, 3.7%).

V max (Nujol) 745, 706, 690, 648, 621, 612, 603, 570, 549, 531, 512, 495, 450, 435, 400, 365, 300, 230, 208; V max (C₅S₂, pale and bright-yellow isomers) 745, 706, 690, 675 (variable), 648, 623, 612, 603, 570, 540, 530, 512, 495, 490.

Both the bright and pale yellow complexes are soluble in dichloromethane and chloroform; sparingly soluble in carbon disulphide, benzene, and acetone and insoluble in ethanol and xylene.

*Bis(diphenylphosphinidithioato)triphenylarsine)platinum(II).—* A suspension of Pt(S₂PPh₃)₂ (0.22 g, 0.31 mmol) in benzene (15 ml) was treated with an excess of triphenylarsine (0.5 g, 1.00 mmol) and shaken for 1 h. Removal of the solvent under vacuum and treatment of the resulting oil with light petroleum (b.p. 60-80') gave a bright yellow precipitate which was washed carefully with light petroleum to remove free triphenylarsine and then dried in vacuo (0.29 g, 91%), m.p. 166° (Found: C, 50.7; H, 3.5. C₂₅H₂₁AsP₂S₂ requires C, 50.5; H, 3.5%). Attempts to obtain a pale yellow isomer by cooling the pale disulphide with dichloromethane solutions of the above product were unsuccessful: v max (Nujol) 759, 748, 708, 689, 645, 628, 612, 603, 571, 539, 485, 475, 468, 445, 440, 392, 342, 335, 330, 315, 305, 275.

*Bis(diphenylphosphinidithioato)triphenylstibineplatinum(II).—As above, shaking Pt(S₂PPh₃)₂ (0.22 g, 0.31 mmol) and a large excess of triphenylstibine (2.0 g, 5.7 mmol) in benzene. Solvent removal under vacuum and treatment with dichloromethane and ethanol gave the product as a bright yellow powder. Excess of triphenylstibine was removed by repeated washing with light petroleum (b.p. 60-80') (0.18 g, 55%), m.p. 130-132° (Found: C, 48.2; H, 3.4. C₂₅H₂₁P₂S₂ requires C, 48.2; H, 3.4%).


*Bis(diphenylphosphinidithioato)(dimethylphenylphosphine)platinum(II).—* A suspension of Pt(S₂PPh₃)₂ (0.23 g, 0.32 mmol) was shaken in benzene (20 ml) with dimethylphenylphosphine (0.05 ml, 0.30 mmol) under nitrogen for 2 h. After removal of any unreacted Pt(S₂PPh₃)₂, solvent was removed under vacuum and the residue treated with light petroleum (b.p. 40-60') to give a pale yellow product (0.26 g, 95%), m.p. 156-158° (Found: C, 46.3; H, 3.7%; M (Osmometric in CHCl₃), 790 (0.02 g ml⁻¹). 953 (0.11 g ml⁻¹). C₂₅H₂₁P₂S₂ requires C, 46.2; H, 3.7%; M, 831).

v max (Nujol) 745, 718, 712, 709, 690, 645, 623, 615, 605, 571, 539, 483, 471, 460, 443, 368, 360, 325, 305, 285, 265.

*Bis(diphenylphosphinidithioato)(methylidiphosphinophosphate)platinum(II).—Method as above, Pt(S₂PPh₃)₂ (0.24 g, 0.32 mmol) and methylidiphosphinophosphine (0.07 ml, 0.30 mmol) giving a pale yellow product (0.31 g, 98%), m.p. 206-209° (Found: C, 49.9; H, 3.9%; M (Osmometric in CHCl₃), 767 (0.02 g ml⁻¹). 964 (0.04 g ml⁻¹). C₂₅H₂₁P₂S₂ requires C, 49.7; H, 3.7%; M, 833).

v max (Nujol) 740, 720, 709, 690, 645, 621, 612, 603, 571, 541, 510, 488, 455, 430, 430, 365, 360, 312, 305, 260.

(Diphenylphosphinidithioato)bisp(triphenylphosphine)-
Diphenylphosphinodithioate.—Pt(S₂P₃H₅)₂
(0.11 g, 0.16 mmol) in dichloromethane or benzene (20 ml) on
shaking for 15 min with excess triphenylphosphine
(0.20 g, 0.75 mmol) gave a colourless solution. Removal
of solvent under vacuum gave a semi-crystalline mass
which, on trituration with light petroleum (b.p. 40–60°)
gave an off-white powder (0.09 g, 55%). m.p. 69–70°
(Found: C, 61.0; H, 4.3; P, 10.4; S, 10.7; C₉H₉P₂S₄ requires
C, 60.7; H, 4.2; P, 10.4; S, 10.8%).

The compound is soluble in dichloromethane and chloro-
form; largely dissociated to Pt(S₂P₃H₅)₂P in benzene;
carbon disulphide, and insoluble in light petroleum; νmax
(Nujol) 743s, 720s, 698s, 695s, 655m, 615w, 603w, 573w,
545s, 515s, 497s, 487s, 445w, 425w, 361m, 310m, 292w, 275w.

(Diphenylphosphinodithioato)bis(dimethylphos-
phinophosphine)platinum(ii) Diphosphinodithioato
diphenylphosphine-platinum(ii).—Method as above,
except under nitrogen, Pt(S₂P₃H₅)₂ (0.23 g, 0.32 mmol)
and excess dimethylphosphine (0.12 ml, 0.70 mmol)
gave a white powder, m.p. 110°
(Found: C, 49.5; H, 4.4; P, 11.4; S, 12.8%; M [Osmo-
metric in CHCl₃], 577 (0.004 g ml⁻¹), 430 (0.009 g ml⁻¹).
C₉H₉P₂S₄ requires C, 49.8; H, 4.3; P, 12.7; S, 13.2%; M
[for 1:1 electrolyte], 485); νmax (Nujol) 745s, 720m,
710m, 698sh, 690s, 656s, 615w, 603w, 570s, 502s, 485s,
470w, 450w, 432m, 365m, 312w, 305w.

(Diphenylphosphinodithioato)bis(methylphos-
phinophosphine)platinum(ii) Diphosphinodithioato
diphenylphosphine-platinum(ii).—Method as above,
except with methylphosphine (0.20 ml, 0.85 mmol) in
dichloromethane giving a white powder (0.22 g, 78%), m.p. 62–64°
(Found: C, 54.6; H, 3.9; C₉H₁₀P₂S₄ requires C, 54.9; H,
4.2%); νmax (Nujol) 740s, 720m, 710m, 690s, 655m, 650w,
605s, 571s, 502s, 421m, 459m, 450m, 430w, 365m, 310w.

(Diphenylphosphinodithioato)bis(dimethylphos-
phinophosphine)platinum(ii) Tetraphenylborate.—
[Pt(S₂P₃H₅)₂(PMe₃H₅)]₂S₂P₃H₅ (0.10 g, 1.1 mmol) in a
minimum volume of acetone (3 ml) was treated with a
concentrated aqueous solution of sodium tetraborionate
(1.0 g, 3.3 mmol). The immediate white precipitate was
filtered off, washed thoroughly with distilled water,
and then recrystallised from dichloromethane–light petroleum
(b.p. 60–80°), m.p. 161–165°
(Found: C, 60.5; H, 5.0; C₉H₁₀P₂S₁₃ requires C, 60.0; H,
5.0%); νmax (Nujol) 790m, 755w, 745s, 740s, 730s, 720s,
708s, 698s, 685m, 625w, 615w, 605m, 575s, 490m,
480m, 450m, 435w, 370m, 310m, 290w.

(Bis(diphenylphosphinathionate)platinum(ii) Chloride.—
[Pt(S₂P₃H₅)₂(PMe₃H₅)]₂S₂P₃H₅ was shaken in dichloromethane with an excess
of Biorad anion exchange resin (AG-1-X10; 200–400
mesh; Cl⁻ form) for several hours. Filtration, removal
of solvent, and trituration with light petroleum (b.p.
60–80°) gave a white powder, m.p. 180–188°
(decomp.)
(Found: C, 44.2; H, 4.2; Cl, 4.6; C₉H₁₀Cl₂P₂S₄ requires
C, 44.5; H, 4.2; Cl, 4.7%); νmax (Nujol) 745s, 728s, 716s,
710s, 708s, 690s, 615w, 603w, 575s, 490m, 485m, 460m,
440w, 370m, 310m, 280w.

Bis(1,2-bis(diphenylphosphinethionate)platinum(ii)
Bis(diphenylphosphinodithioate).—Pt(S₂P₃H₅)₂
(0.20 g, 0.30 mmol) suspended in benzene with an excess of 1,2-
bis(diphenylphosphinothionate) (1.0 g, 2.5 mmol) gave
an immediate white precipitate, m.p. 245–248°
(decomp.)
(Found: C, 50.6; H, 4.6; C₈H₁₂P₂S₄ requires C, 61.2;
H, 4.6%); νmax (Nujol) 743s, 725m, 709s, 695s, 675w,
Nickel Compounds

*Bis(diphenylphosphinodithioato)nickel(ii)* was prepared as described elsewhere; \( ^\text{13} \nu_{\text{max}} \) (Nujol) 740s, 709s, 685s, 619w, 601w, 573s, 485m, 463w, 464w, 342m.

*Bis(diphenylphosphinodithioato)bis(pyridine)nickel(ii).* Ni\(\text{S}_2\text{PPh}_3\)_2 was suspended in chloroform and an excess of dry pyridine added dropwise. Immediate reaction occurred to give a deep yellow-green solution which on standing for several minutes deposited the pale green crystalline *product*. This was filtered, washed well with diethyl ether, and air-dried m.p. 160° (decomp.) (Found: C, 57.4; H, 4.2; N, 3.7. Calc. for \( \text{C}_{28}\text{H}_{36}\text{N}_{2}\text{NiP}_{2}\text{S}_4 \): C, 57.1; H, 4.2; N, 3.8%); \( \nu_{\text{max}} \) (Nujol) 760s, 750s, 745s, 720w, 705s, 700s, 690s, 645w, 632s, 612s, 570s, 488m, 480m, 460m, 450w, 360s, 308w.

We thank Johnson-Matthey Ltd., for a loan of palladium-(ii) chloride and the S.R.C. for an award (to J. M. C. A.).

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NOVEL CARBOXYLATION PRODUCTS OF RUTHENIUM(II)

DITHIOACID COMPLEXES

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Edinburgh EH9 3JY

(Received 20 June 1972)

Dialkyl(aryl)phosphinodithioato complexes of ruthenium of type
\[ \text{[Ru(S}_2\text{PR}_2)_2\text{L}_2] \] (I) \((R = \text{Me, Et, Ph}; \ L = \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph, P(OPh)}_3)\)
can be prepared by reaction of \[ \text{[RuCl}_2\text{ or } 3 \text{L}_3 \text{ or } 4] \] (1,2,3) with the sodium salt of
the appropriate dithioacid. Unlike \[ \text{[Ru(S}_2\text{CNR}_2)_2\text{L}_2] (R = \text{Me, Et}; \ L = \text{PPh}_3, \text{PMePh}_2)\],
shown to be unreactive to Lewis bases such as carbon monoxide and
pyridine (4), compounds I undergo various interesting reactions. These
include ligand exchange, giving mixed complexes such as \[ \text{[Ru(S}_2\text{PR}_2)_2(P\text{R'}_3)}\]-
\((P\text{OPh)}_3\)
and carbonylation under mild conditions to give phosphine
carbonyls.

\[ \text{L} \]

\[ \text{L} \]

\[ \text{I} \]
For $L = \text{PMe}_2\text{Ph}$, carbonylation (1 atm.) of I in refluxing ethanolic solution leads to two products $\left[\text{Ru}(S_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})\text{CO}\right]$ (II) and $\left[\text{Ru}(S_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})_2\text{CO}\right]$ (III) which are readily separated by the new technique of dry column chromatography (5). $^1\text{H}$ n.m.r. studies on II indicate, in every case, a cis arrangement of ligands (4 inequivalent $R$ groups). (Table). Analysis of the $^1\text{H}$ n.m.r. and infrared spectra of III suggests a six co-ordinate structure with unidentate and bidentate dithio groups, and trans PMe$_2$Ph ligands. The $^1\text{H}$ n.m.r. also indicates a dynamic structure at higher temperatures ($> 60^\circ$) with rapid "flipping" of dithio groups, although a detailed study is made complicated by the slow dissociation of a PMe$_2$Ph ligand to give $\left[\text{Ru}(S_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})\text{CO}\right]$.

Low temperature carbonylation of $\left[\text{Ru}(S_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})_2\right]$ gives a third complex, also of formula $\left[\text{Ru}(S_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})_2\text{CO}\right]$ which readily converts in solution to a mixture of II and III. The structure of this compound is not easy to determine from spectroscopic data. The most likely formulation is a six co-ordinate complex containing both unidentate and bidentate dithio groups with cis PMe$_2$Ph ligands but a seven co-ordinate ruthenium (II) complex with two bidentate dithio groups cannot be ruled out on the evidence at present available. Full confirmation of the structure of this complex now awaits the results of an X-ray analysis. For $L = \text{PMePh}_2$, PPh$_3$ etc., carbonylation of I, even under very mild conditions, gives only
<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
<th>$\tau$ Value ($S_2PMe_2$)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\tau$ Value (Me phosphine)</th>
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</thead>
<tbody>
<tr>
<td>Ru($S_2PMe_2$)$_2$(PPh$_3$)$_2$</td>
<td>28&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.33&lt;sup&gt;c&lt;/sup&gt;</td>
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<td></td>
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<td>-60</td>
<td>7.69&lt;sup&gt;c&lt;/sup&gt; 8.85&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
</tr>
<tr>
<td>Ru($S_2PMe_2$)$_2$(PMePh$_2$)$_2$</td>
<td>60&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.39&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.00&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.39&lt;sup&gt;d&lt;/sup&gt;</td>
<td>8.04&lt;sup&gt;e&lt;/sup&gt;</td>
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<td></td>
<td>-60</td>
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<td>8.04&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$</td>
<td>65&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.01&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.38&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>28&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>8.38&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>-40</td>
<td>7.69&lt;sup&gt;c&lt;/sup&gt; 8.14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.30&lt;sup&gt;e&lt;/sup&gt; 8.45&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ru($S_2PMe_2$)$_2$(POPh$_3$)$_2$</td>
<td>60&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>0</td>
<td>7.94&lt;sup&gt;c&lt;/sup&gt; 8.33&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
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<tr>
<td>Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$CO</td>
<td>55&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7.84&lt;sup&gt;c&lt;/sup&gt;, 7.97&lt;sup&gt;c&lt;/sup&gt;, 8.06&lt;sup&gt;c&lt;/sup&gt;, 8.40&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.07&lt;sup&gt;f&lt;/sup&gt;</td>
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<td></td>
<td>-10&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>8.07&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>-30</td>
<td>7.81&lt;sup&gt;c&lt;/sup&gt;, 7.95&lt;sup&gt;c&lt;/sup&gt;, 8.03&lt;sup&gt;c&lt;/sup&gt;, 8.35&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.06&lt;sup&gt;f&lt;/sup&gt; 8.09&lt;sup&gt;f&lt;/sup&gt;</td>
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<tr>
<td>Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$CO</td>
<td>28</td>
<td>8.11&lt;sup&gt;c&lt;/sup&gt; 8.91&lt;sup&gt;c&lt;/sup&gt;</td>
<td>7.86&lt;sup&gt;h&lt;/sup&gt; 7.89&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> $J_{PH} = 12.5$ Hz  
<sup>b</sup> coalescence temperature  
<sup>c</sup> Doublet  
<sup>d</sup> Broad hump  
<sup>e</sup> Second order spectrum (7) with $J_{PH} + J_{PH'} = 8.5$ Hz  
<sup>f</sup> Doublet, $J_{PH} = 10.0$ Hz  
<sup>g</sup> Broadened doublet  
<sup>h</sup> 1:2:1 triplet with virtual coupling constant ($7) = 3.5$ Hz.

$[Ru(S_2PR$_2$)_2LCO]$, a reflection, presumably, of the strong affinity of PMe$_2$Ph for ruthenium (II) (6).

Analysis of the room temperature n.m.r. spectra of I is inconclusive in determining their stereochemistry since the methyl phosphine pattern could be interpreted as indicating either cis phosphines with a large $J_{pp}$ or trans phosphines with a low $J_{pp}$ (7). However, variable temperature $^1H$ n.m.r.
studies unequivocally confirm cis phosphines in every case (with restricted rotation around the metal-phosphorus bond at low temperature) and that scrambling of the R groups on the sulphur ligands occurs at higher temperature (Table). The most likely explanation for this averaging process is a rapid inversion of configuration between the two possible enantiomers of I, a phenomenon well documented in other chelate complexes of transition metals(8), although not previously reported for octahedral complexes of ruthenium(II). Preliminary results of a full kinetic line shape analysis suggest a solvent assisted bond rupture mechanism for this inversion process. In the case of compounds II, no inversion of configuration is found, even at 60°C.

Acknowledgment

We thank Johnson-Matthey Ltd. for a loan of ruthenium trichloride, the University of Edinburgh for an award (DJCH) and Drs. R.K. Harris and R.M. Lyden-Bell for helpful discussions.

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5. B. Loev and M.M. Goodman, Chem. and Ind., 2026 (1967).
Metal Complexes of Sulphur Ligands. Part III.† Reaction of Platinum(II) NN-Dialkyldithiocarbamates, O-Ethyl Dithiocarbonate (Xanthate), and OO'-Diethyl Dithiophosphate with Tertiary Phosphines

By (Miss) J. M. C. Allison and T. A. Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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Metal Complexes of Sulphur Ligands. Part III. Reaction of Platinum(II) N,N-Dialkylthiocarbamates, O-Ethyl Dithiocarbonate (Xanthate), and OO’-Diethyl Dithiophosphinate with Tertiary Phosphines

By (Miss) J. M. C. Alison and T. A. Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Evidence is presented to show that the reaction of all M(S-S)₄ compounds [M = Pt, Pd; (S-S) = -SₓCNRₓ (R = Me, Et), -SₓCOR (R = Et, PhCHₓ), -SₓP(OEt)ₓ, and -SₓPRₓ (R = Me, Et, Ph)] with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate compounds of formulae [M(S-S)₂PR₃] and [M(S-S)(PR₃)₂] with unidentate/bidentate (III) and ionic/bidentate (IV) co-ordination respectively. All the ionic compounds readily revert to the [M(S-S)₂PR₃] complexes in the presence of non-polar solvents via nucleophilic attack by (S-S)⁻ on the metal. In addition, for (S-S)⁻ = -SₓCOR, -SₓP(OEt)ₓ, nucleophilic attack can also occur on a co-ordinated alkoxy group to give the novel compounds [(R’₄P)₂MSₓCO] (I) and [(R’₄P)₂MSₓP(O)OEt] (II) respectively.

For [M(S-S)(PR₃)₂] compounds containing -SₓCNRₓ, the presence of excess PR₃ catalyses the reaction between dithiocarbamate ion and dichloromethane, giving CHₓ(SₓCNRₓ)₂ and [M(SₓCNRₓ)(PR₃)₂]Cl₂H₂O. These conclusions are based on extensive physico-chemical studies and, in particular, the use of variable temperature ¹H n.m.r. spectroscopy.

Recently, it was reported² that the reaction of tertiary phosphines with M(S-S)₄ [1:1 molar ratio] [M = Pt, Pd; (S-S) = -SₓCNRₓ, -SₓCOR, -SₓP(OEt)ₓ, and -SₓPRₓ] gave the complexes [M(S-S)₂PR₃] which were formulated as five-co-ordinate compounds on the basis of ¹H n.m.r. data. A brief mention was also made of the precipitation from solution of what may be six-co-ordinate species when an excess of methylhexaphosphine was added to platinum(II) compounds of ring-substituted dithiobenzothioles but no further details were given. It was also stated² that ‘diethylthiocarbamate complexes of palladium(II) and platinum(II) react only slowly (hours) with excess methylhexaphosphine to produce what appears to be phosphine co-ordinated substitution products’ but a footnote added that ‘these reactions have not been characterised completely to date’. When excess tertiary phosphine was added to these xanthate and dithiophosphinate adducts, further reaction occurred to give the novel complexes [(R’₄P)₂MSₓCO] (I) and [(R’₄P)₂PdSₓP(O)OEt] (II) respectively,² for which no convincing mechanism of formation was suggested.

Other studies, however, on tertiary phosphine complexes of M(S-S)₄ [M = Pd, Pt; R = Ph, Et, Me] and Pd(SₓPFₓ)₄ have suggested that the 1:1 and 1:2 adducts formed possess four-co-ordinate square planar structures of type (III) and (IV) respectively and these structural assignments have been confirmed by X-ray analyses on [Pd(SₓPPhₓ)₂PPhₓ] and [Pd(SₓPPhₓ)₃(PE₄ₓ)₂SₓPPhₓ].² In view of these latter results, it was therefore of some interest to re-examine and extend some of the work reported in publications ²–⁴; the results of this investigation are presented in this paper.

RESULTS AND DISCUSSION

Complexes of Stoichiometry [Pt(SₓCNRₓ)₂PR₃].—Reaction of Pt(SₓCNRₓ)₂ with either PPhₓ or PMePhₓ (1:1)

molar ratio) in carbon disulphide gives deep lemon-yellow solutions immediately from which crystalline yellow solids of stoichiometry \([\text{Pt(S}_2\text{CNET}_3)_2\text{PR}_3]\) can be readily isolated. These are non-conducting, diamagnetic, and quite stable both in solid and solution state. For \(\text{PR}_3 = \text{PMePH}_2\), the \(^1\text{H}\) n.m.r. at \(301\) K is identical to that reported earlier by Fackler et al.\(^2\) (Table 1). In a further note,\(^3\) these authors state that the p.m.r. behaviour of methylidiphenylphosphinebis-(NN-diethylthiocarbamato)platinum(II) is essentially i.e. a single methyl resonance at room temperature, broadening and splitting into two equivalent resonances at lower temperature (Table 1).

All these observations are analogous to those observed for the variable-temperature \(^1\text{H}\) n.m.r. spectra exhibited by \([\text{Pt(S}_2\text{P(OEt)}_3)_2\text{PMePH}_2]\), \([\text{Pt(S}_2\text{PMe}_3)_2\text{PR}_3]\) (\(\text{PR}_3 = \text{PPH}_2\), \(\text{PMePH}_2\), \(\text{etc.}\)) and the variable-temperature \(^{19}\text{F}\) n.m.r. spectrum of \([\text{Pt(S}_2\text{FP}_2)_2\text{PMeCH}_2\text{H}_3]\). In all cases, the temperature dependence is completely reversible, indicating that no gross chemical change has occurred. Furthermore, the close similarity of the activation energies for the temperature-dependent re-action manifested by these \(1:1\) adducts of \(\text{S}_2\text{P(OEt)}_2\), \(\text{S}_2\text{PMe}_2\), and \(\text{S}_2\text{CNR}_2\) (estimated from the coalescence temperature by standard methods)\(^9\) (Table 2) is indicative of a common mechanism to produce averaging of the protons attached to the dithioacid ligands. This strongly suggests that for \((\text{S}^{1} \text{S}^{2}=\text{S}_2\text{CNR}_2)\), the observed temperature dependence is not due to restricted rotation about the C–N bond as found, for example, in dithiocarbamate esters\(^10\) (Table 2). A full line-shape analysis for all compounds of type \([\text{M(S}^{1} \text{S}^{2} \text{R}_2]\text{[ER']}_2]\) (\(\text{E} = \text{P, As, Sb}\)) is at present in progress to ascertain accurate rate data and will be published later.

The observation of magnetically inequivalent alkyl groups at low temperature for \([\text{Pt(S}_2\text{CNR}_2)_2\text{PR}_3]\) is inconsistent with the square pyramidal structure (V)

independent of temperature from room temperature to \(-70^\circ\text{C}\) in \(\text{CS}_2\). However, we find that the room-temperature n.m.r. spectrum in \(\text{CDCl}_3\) or \(\text{CS}_2\) is deceptively simple, since on cooling, the \(\text{CH}_2\) quartet at \(\tau = 8.26\) starts to broaden at \(300\) K, coalesces at \(320\) K and, at \(213\) K, exhibits a limiting spectrum of two broadened signals (with some unresolved fine structure) centred at \(\tau = 6.37\) and \(6.17\) (separation \(20\) Hz). Likewise, the single \(\text{CH}_3\) triplet resonance (at \(8.89\)) starts to broaden at \(230\) K and, at \(213\) K consists of an overlapping doublet of triplets centred at \(\tau = 8.82\) and \(8.79\) (separation \(6\) Hz)\(^*\) (Table 1).

Similarly, \([\text{Pt(S}_2\text{CNET}_3)_2\text{PPH}_2]\) (Figure 1) exhibits a single \(\text{CH}_2\) quartet (at \(8.41\)) and \(\text{CH}_3\) triplet (at \(8.89\)) at \(301\) K; at \(203\) K it has two broadened quartets at \(\tau = 8.57\) and \(8.32\) (separation \(26\) Hz) and an overlapping doublet of triplets at \(\tau = 8.96\) and \(8.88\) (separation \(8\) Hz). A study of the reaction between \([\text{Pt(S}_2\text{CNET}_3)_2\text{PMePH}_2]\) (1:1 molar ratios) was also made. Although a pure, solid product could not be isolated by this method, solution studies were consistent with the results discussed above.

\* The discrepancy between this behaviour and that reported in ref. 3 may be due to the smaller limiting separation observable on a \(60\) MHz instrument (3.6 Hz for the \(\text{CH}_2\) resonance) in addition to the failure to observe the temperature dependence of the \(\text{CH}_2\) quartet in the earlier study.

postulated earlier for the low-temperature form,\(^3\) since the alkyl groups in (V) will be magnetically equivalent, even allowing for restricted rotation about the C–N bond. Although the low-temperature spectrum is not incompatible with the five-co-ordinate trigonal-bipyramidal structure (VI), we suggest that a better explanation for the temperature-dependent n.m.r. spectra of all the compounds of formula \([\text{M(S}^{1} \text{S}^{2} \text{R}_2]\text{[ER']}_2]\) is the presence of an equilibrium of type (I) between two n.m.r. equivalent four-co-ordinate complexes. At higher temperatures, rapid interchange of bidentate and unidentate dithio-ligands produces an averaging of the magnetic nuclei attached to the dithio-ligands whereas at lower temperatures, intramolecular rearrangement becomes


## Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>T/K</th>
<th>Dithio-ligand</th>
<th>CH$_3$ (PR$_3$) $^c$</th>
<th>Others $^e$</th>
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</thead>
<tbody>
<tr>
<td>Ph$_3$(PhCH$_3$)PS$_2$CNEt$_2$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>CH$_3$ $^a$</td>
<td>8-86(3) $^a$</td>
<td>Ph, 2-0-3(0-10)</td>
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<td>CDCl$_3$</td>
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<td>8-70(3)</td>
<td>6-40(2)</td>
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<tr>
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<td>CDCl$_3$</td>
<td>301</td>
<td>8-80(12)</td>
<td>6-41(8)</td>
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<tr>
<td>Pt(S$_2$CNEt$_2$)$_2$(PMePh$_2$)</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8-90(6)</td>
<td>5-26(8)</td>
<td>7-72(3) Ph, 2-2-2(6-10)</td>
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<tr>
<td>[Pt(S$_2$CNEt$_2$)(PMePh$_2$)$_2$]S$_2$CNEt$_2$</td>
<td>CDCl$_3$</td>
<td>213</td>
<td>8-32(6)</td>
<td>8-76(6)</td>
<td>6-37(4) $^i$</td>
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<td>CDCl$_3$</td>
<td>6-66(12) (s)</td>
<td>8-80(6)</td>
<td>6-57(2) $^i$</td>
<td>8-00(3) Ph, 2-6(10)</td>
</tr>
<tr>
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<td>133</td>
<td>6-81(6) (s)</td>
<td>6-46(6) (s)</td>
<td>8-30(3) (s)</td>
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<tr>
<td>Pt(S$_2$CNMe$_2$)$_2$(PPh$_2$)$_2$Cl$_2$H$_2$O</td>
<td>CDCl$_3$</td>
<td>213</td>
<td>8-76(3) (s)</td>
<td>6-39(3) (s)</td>
<td>8-10(3) Ph, 2-6(15)</td>
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<tr>
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<td>301</td>
<td>8-76(3)</td>
<td>6-42(2) Ph, 2-6(15)</td>
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<td>8-76(3)</td>
<td>6-68(2) Ph, 2-6(15)</td>
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<td>CDCl$_3$</td>
<td>301</td>
<td>8-72(3)</td>
<td>6-38(2) Ph, 2-6(15)</td>
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<tr>
<td>[Pt(S$_2$CNMe$_2$)(PMePh$_2$)$_2$]BPh$_4$</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8-84(3)</td>
<td>6-55(2) Ph, 2-6(15)</td>
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<tr>
<td>[Pt(S$_2$CNMe$_2$)(PMePh$_2$)$_2$]ClCl$_2$H$_2$O</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8-76(3)</td>
<td>6-22(2) Ph, 2-6(15)</td>
<td></td>
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<tr>
<td>Pt(S$_2$CNMe$_2$)(PPh$_2$)$_2$Cl$_2$H$_2$O</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8-76(3)</td>
<td>6-22(2) Ph, 2-6(15)</td>
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<tr>
<td>Pt(S$_2$CNMe$_2$)(PPh$_2$)$_2$ClCl$_2$H$_2$O</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8-76(3)</td>
<td>6-22(2) Ph, 2-6(15)</td>
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<td>8-10(3) Ph, 2-6(15)</td>
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<td>8-89(12)</td>
<td>6-00(8) $^i$ Ph, 2-6(15)</td>
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<td>[Pt$_2$(S$_2$P(OEt)$_2$)$_2$]BPh$_4$</td>
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<td>223</td>
<td>8-71(6)</td>
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<td>Pt(S$_2$P(OEt)$_2$)$_2$PCPh$_3$</td>
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<td>5-88(2) $^i$ Ph, 2-6(15)</td>
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<tr>
<td>Pt(S$_2$COOH)$_2$PPh$_3$</td>
<td>CDCl$_3$</td>
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<tr>
<td>[Pt(S$_2$COOH)$_2$PPh$_3$]BPh$_4$</td>
<td>CDCl$_3$</td>
<td>183</td>
<td>8-62(6) (s) (br) 5-46(4) (s) (br) Ph, 2-6(15)</td>
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<td></td>
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</tbody>
</table>

$s$ (singlet); $d$ (doublet); $b$ (broad).

$^a$ $\pm$ 0-01. $^b$ Triplet of doublets unless otherwise stated. $^c$ Phenyl resonance; complex multiplet. $^d$ $\pm$ 0-2 Hz. $^i$ $\pm$ 0-5 Hz. $^f$ Triplet unless otherwise stated (J$_{CH,PH}$, 7-0 Hz). $^i$ Quartet unless otherwise stated (J$_{CH,CH}$, 7-0 Hz). $^k$ Numbers in parentheses indicate normalised integrated intensities. $^l$ Two resonances of total intensity [ ] $^m$ Since H$_2$PPh$_2$, type spectrum, coupling constant is $J_{PH} + J_{Pr}$. $^n$ Value is concentration dependent. $^o$ Complex multiplet. $^p$ Pt(S$_2$P(OEt)$_2$)$_2$ + excess AsPh$_3$ in situ. $^q$ Not recorded since an excess of AsPh$_3$ present. $^r$ Overlapping doublet of quartets with J$_{CH,PH}$, 7-0 Hz. J$_{CH,PH}$, 9-4 Hz.
sufficiently slow for the ‘frozen-out’ n.m.r. spectrum to be observed.*

It should be noted that for (S-S)\(^{-}\) = \(\text{S}_{2}\text{CNR}_{2}\), the limiting low-temperature spectra are not completely consistent with those expected for the frozen-out structure (VII). Even assuming that rotation about the Pt-S and C-N bonds of the unidentate dithio-group is sufficiently rapid to average \(R^{1}\) and \(R^{2}\), \(R^{3}\) and \(R^{4}\) are magnetically inequivalent and three resonances of intensity ratio 1:1:2 are theoretically expected, whereas only two resonances are observed.

**Table 2**

Free-energy of activation and coalescence temperature \((T_{c}/K)\) obtained from \(1^H\) n.m.r. spectra for various sulphur compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_{c}/K)</th>
<th>(\Delta G^{*}_{f,c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pt}(\text{S}<em>{2}\text{P(OEt)}</em>{2})\text{PPH}_{3})</td>
<td>238</td>
<td>52.3</td>
</tr>
<tr>
<td>(\text{Pt}(\text{S}<em>{2}\text{PMe}</em>{2})\text{PPH}_{3})</td>
<td>263</td>
<td>56.1</td>
</tr>
<tr>
<td>(\text{Pt}(\text{S}<em>{2}\text{CNET}</em>{2})\text{PPH}_{3})</td>
<td>243</td>
<td>52.8</td>
</tr>
<tr>
<td>(\text{Pt}(\text{S}<em>{2}\text{CNET}</em>{2})\text{PMePh}_{2})</td>
<td>253</td>
<td>51.2</td>
</tr>
<tr>
<td>(\text{Pt}(\text{S}<em>{2}\text{CNET}</em>{2})\text{PMePh}_{2})</td>
<td>230</td>
<td>45.6</td>
</tr>
<tr>
<td>(\text{Pt}(\text{S}<em>{2}\text{CNET}</em>{2})\text{PMePh}_{2})</td>
<td>223</td>
<td>66.7</td>
</tr>
<tr>
<td>(\text{Pt}(\text{S}<em>{2}\text{CNET}</em>{2})\text{PMePh}_{2})</td>
<td>243</td>
<td>64.4</td>
</tr>
</tbody>
</table>

* \(\pm 1\) K, \(\pm 1.0\) kJ mol\(^{-1}\). * Measured on CH\(_2\) quartets. * C.f. 2-lithium \(\text{EtSCSNET}_{2}\) \(\Delta G^{*}_{f,c}\) \(69.8\) kJ mol\(^{-1}\) \(\Delta G^{*}_{f,c}\) \(69.8\) kJ mol\(^{-1}\).

However, the atoms (S and P) inducing the magnetic inequivalence in \(R^{3}\) and \(R^{4}\) are well removed (six bonds) from these groups, so that the separation between the \(R^{3}\) and \(R^{4}\) resonances may well be too small to be resolved, particularly at 213 K where machine line-broadening is also appreciable. A similar inconsistency is found for the square-planar compounds \(\text{[Ni}(\text{S}_{2}\text{CNR}_{2})\text{Cl}(\text{PR}_{3})]\) \(^{12}\)

(VIII) \(\text{Pt}^{2+}\) (one R resonance at 213 K) \(^{13}\) and even in compounds such as \(\text{Me}_{2}\text{NCOS(SiH)}_{3}\) where the magnetic inequivalence is produced by atoms (S and O), four bonds removed from the methyl protons, the separation at 301 K of the two methyl groups is only 12 Hz.\(^{14}\)

* A similar conclusion has recently been reached by Powell and Chandy\(^{16}\) for those compounds on the basis of detailed variable-temperature \(\text{1}^H\) n.m.r. studies on the related complexes \(\text{[Pt(PMePh)(X-Y)]}\) \(\text{[X-Y] = SNSp}_{2}\text{S-COMe}\). In addition Davis et al.\(^{17}\) invoke a similar mechanism for interconversion processes in molybdenum dialkylidithiocarbamates.

† As pointed out by a referee, we have assumed that the essential feature of the solid-state structure (viz. the unidentatobidentate co-ordination) is retained in solution, but this assumption is strongly supported by both the characteristic chemical shifts of the two CH\(_2\) quartets for the dithiocarbamate compounds and by the characteristic i.r. bands for the dithiophosphinate compounds.

‡ Note added in proof: An X-ray structural analysis of \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{PMePh}_{2}\) by J. M. C. Alister and R. O. Gould is now sufficiently advanced to show unequivocally that the structure in the solid state is also of type III.

Although we are unable to rule out unequivocally the presence of a five-co-ordinate trigonal bipyramidal structure to explain the low-temperature \(\text{1}^H\) n.m.r. data, there is a substantial amount of evidence which supports the interpretation given in equation (I). This is as follows. (i) There is a very close similarity of chemical shifts and coupling constants (for the methyl phosphine \(\text{1}^H\) n.m.r. resonance at 301 K) for all the dithio-compounds \(\text{[Pt}(\text{S}_{2}\text{CNR}_{2})\text{PMePh}_{2}\)\(^{1,2,5}\), which is indicative of a similar structure and the X-ray analysis of \(\text{[Pt}(\text{S}_{2}\text{PPh}_{2})\text{PMePh}_{2}\)\(^{7}\), isomorphous with the corresponding platinum complex) shows this to be of type (III).† ‡ Furthermore, for \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{PMePh}_{2}\) the position of the low-field CH\(_{2}\) quartet (\(\tau = 6.17\)) is intermediate between those found for the \(\text{[Pt}(\text{S}_{2}\text{PPh}_{2})\text{PMePh}_{2}\) and bidentate \(\tau = 6.40\) in \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{dethiophosphinato carbamate groups, suggesting that it probably arises from a unidentate group.}

(ii) For the \(\text{S}_{2}\text{PPh}_{2}\) compounds reported earlier,\(^{1}\) both room- and low-temperature isomeric forms of \(\text{[Pt}(\text{S}_{2}\text{PPh}_{2})\text{PMePh}_{2}\) \((M = Pt, Pd)\) can be isolated. However, the characteristic i.r. bands of 'bidentate' and 'unidentate' dithiophosphinato co-ordination\(^{1}\) remain unchanged which suggests that a structure of type (III) persists at all temperatures.

(iii) Reaction of either \(\text{[Pt}(\text{S}_{2}\text{CNR}_{2})\text{PMePh}_{2}\) with an excess of tertiary phosphine gives anionic species containing the \(\text{[Pt}(\text{S}_{2}\text{S}_{2}\text{CNR}_{2})\text{PR}_{3}\) \(^{+}\) cation (see later) which is indicative of stepwise cleavage of metal-sulphur bonds by tertiary phosphine.

Therefore, all this evidence suggests (to us) that a structure of type (III) is more feasible than a five-co-ordinate formulation; however, as in all interpretations, utilising 'sporting' methods, a degree of uncertainty naturally remains.

**Platinum(ii) NN-Dialkyldithiocarbamates with an Excess of Tertiary Phosphine.**—If a suspension of \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{PMePh}_{2}\) in acetone is treated with an excess of PMePh\(_{2}\), a pale yellow solution is formed from which pale yellow crystals are rapidly precipitated. This compound has an analysis consistent with the formula \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{PMePh}_{2}\)\(^{-}\) \(\text{S}_{2}\text{CNET}_{2}\) \(2\text{H}_{2}\text{O}\) (but not in co-ordinated dithiocarbamate groups) and the ready synthesis of \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{PMePh}_{2}\)\(^{-}\) \(\text{S}_{2}\text{CNET}_{2}\). The ionic formulation is confirmed by the presence of additional i.r. bands corresponding to those found in \(\text{NaS}_{2}\text{CNET}_{2}\text{H}_{2}\text{O}\) (but not in co-ordinated dithiocarbamate groups) and the ready synthesis of \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{PMePh}_{2}\)\(^{-}\) \(\text{S}_{2}\text{CNET}_{2}\). As noted earlier\(^{1}\) for the i.r. \(\text{PR}_{3}\) complexes of \(\text{[Pt}(\text{S}_{2}\text{PPh}_{2})\) this complex also readily dissociates to \(\text{[Pt}(\text{S}_{2}\text{CNET}_{2})\text{PMePh}_{2}\) \(\text{S}_{2}\text{CNET}_{2}\) in the presence of nonpolar solvents. In this instance, the increased nucleophilicity of \(\text{S}_{2}\text{CNET}_{2}\) compared to \(\text{S}_{2}\text{PPh}_{2}\) enhances this tendency. Thus, although the

13 J. A. McCleverty, personal communication.
ionic complex is insoluble in benzene, a yellow solution slowly forms with time and \([\text{Pt}(\text{S}_2\text{CNET}_2)_2\text{PMePh}_2]\) is isolated. Even in diethyl ether, a suspension of the ionic complex turns deep yellow (24 h) and the neutral compound is recovered.

The \(^1\text{H}\) n.m.r. spectrum of the ionic compound in CDCl\(_3\) is of some interest (Figure 2). At room temperature, a deep yellow solution is formed and although the integration of \(^{\text{S}_2}\text{CNET}_2\) to PMePh\(_2\) protons is correct for \(\text{[Pt}(\text{S}_2\text{CNET}_2)\text{PMePh}_2])\text{S}_2\text{CNET}_2\) p.o., the equilibrium lies well to the right-hand side of equation (2). This is evident since the position of the CH\(_2\) quartet at \(\tau = 6-26\)

\[
\text{[Pt}(\text{S}_2\text{CNRe})_2\text{PMePh}_2]\text{S}_2\text{CNRe} \rightleftharpoons \text{[Pt}(\text{S}_2\text{CNRe})_2\text{PMePh}_2] + \text{PMePh}_2
\]

is identical to that found for \([\text{Pt}(\text{S}_2\text{CNET}_2)\text{PMePh}_2]\) at room temperature and since there is a further quartet

of lower intensity centred at \(\tau = 6-09\), which we attribute to the ionic complex. In addition, the methyl phosphine resonance is a broad singlet at \(\tau = 8-16\) [cf. \(\text{[Pt}(\text{S}_2\text{CNET}_2)\text{PMePh}_2]\) a triple of doublets centred at \(\tau = 7-72\), indicative of rapid exchange between free and bound phosphine.

However, on cooling, the solution becomes progressively paler and the \(^1\text{H}\) n.m.r. shows the growth of the quartet at \(\tau = 6-09\), accompanied by a decrease in intensity of the quartet at \(\tau = 6-26\). At 273 K, the two quartets are of comparable intensity but at 263 K, the low-field quartet starts to broaden, whilst the one at high-field remains sharp. At 253 K, a single broad resonance is observed and further lowering of temperature to 213 K produces two quartets at \(\tau = 6-37\) (bidendate) and 5-77 (ionic) (separation 60 Hz). In addition, the methyl phosphine resonance sharpens such that at 213 K, a strong doublet, centred at \(\tau = 8-09\) with weak \(^{\text{S}_2}\text{CNET}_2\) satellites is observed [cf. \(\text{[Pt}(\text{S}_2\text{PPPh}_2)\text{PMePh}_2])\text{S}_2\text{PPPh}_2\) with a triple of doublets at \(\tau = 7-99\)]. Raising of the temperature to 301 K shows the process is reversible, the pale yellow solution once more becoming deep yellow.

Thus, down to ca. 265 K, the \(^1\text{H}\) n.m.r. changes signify a shift to the left-hand side of equation (2). A similar observation was made earlier \(^{15}\) for \([\text{Pd}(\text{S}_2\text{PPPh}_2)\text{PEt}_3])\text{S}_2\text{PPPh}_2\) where the intensity of the 560 cm\(^{-1}\) r.f. band (characteristic of a 1:2 compound) increased with respect to the 540 cm\(^{-1}\) band (characteristic of a 1:1 compound) as the temperature was lowered. In this instance, an estimate of the equilibrium constant for (2) can be computed from the \(^1\text{H}\) n.m.r. data. This gives \(K = 3000\) \(\text{K} \cdot \text{mol}^{-1}\), \(\Delta H = 60 \text{kJ mol}^{-1}\), \(\Delta S = 191 \text{J K}^{-1} \text{mol}^{-1}\). Below 265 K, the \(^1\text{H}\) n.m.r. changes are interpreted as a slowing down of the exchange between ionic and bidendate dithiocarbamate groups such that at 213 K, the spectrum corresponds to that expected for a "frozen-out" ionic structure of type (IV) [cf. \(\text{[Pd}(\text{S}_2\text{PPF}_2)\text{PPh}_2])\text{S}_2\text{PF}_2\); the absence at 213 K of a quartet at \(\tau = 6-17\) shows that the equilibrium lies completely to the right-hand side of (2) at this temperature. From the coalescence temperature (ca. 250 K), an estimate of the activation energy for the interchange of ionic and bidendate groups can be obtained (Table 2).

Similarly, reaction of \(\text{Pt}(\text{S}_2\text{CNRe})_2\) and an excess of PMePh\(_2\) in acetonitrile gives a crystalline sample of \(\text{Pt}(\text{S}_2\text{CNRe})_2\text{PMePh}_2\). Detailed \(^1\text{H}\) n.m.r. studies in CDCl\(_3\) show the same phenomenon as above, namely, a methyl \(\text{(-S}_2\text{CNRe})_2\) resonance at \(\tau = 6-71\) at 301 K, corresponding to \(\text{[Pt}(\text{S}_2\text{CNRe})_2\text{PMePh}_2])\) and when the temperature is lowered, the growth of a peak at \(\tau = 6-63\) (1:2 complex), followed by broadening (ca. 220 K) and splitting into two equivalent resonances at \(\tau = 6-65\) and 6-39 (213 K). Analysis of the higher-temperature region gives \(K = 3000\) \(\text{K} \cdot \text{mol}^{-1}\), \(\Delta H = 69 \text{kJ mol}^{-1}\), \(\Delta S = 181 \text{JK}^{-1} \text{mol}^{-1}\) and, from the coalescence temperature, an estimate of the activation energy for ionic-bidendate ligand exchange can be obtained (Table 2). All attempts to synthesise \(\text{[Pt}(\text{S}_2\text{CNET}_2)\text{PPPh}_2])\text{S}_2\text{CNET}_2\) have been unsuccessful, the only product isolated being \(\text{[Pt}(\text{S}_2\text{CNET}_2)\text{PPh}_3])\) [cf. the \(\text{Pd}(\text{S}_2\text{PPPh}_2)\text{PPh}_3\) system].\(^{16}\)

If the reactions between Pt(S\(_2\)CNET\(_2\))\(_2\) and an excess of \(\text{PR}_3\) are carried out in dichloromethane solution, the initial pale yellow solutions slowly decolourise during several hours, the qualitative rate of decolourisation being \(\text{PMePh}_2 \approx \text{PMePh}_2 > \text{PPPh}_3\). This phenomenon is accompanied by a steady increase in conductivity, the value finally corresponding to that expected for a 3:1 electrolyte. Concentration of the solution and addition of diethyl ether gives white microcrystalline solids (A). The \(^1\text{H}\) n.m.r. of these compounds are similar to those expected for \(\text{[Pt}(\text{S}_2\text{CNRe})_2\text{(PR}_3)_2])\text{S}_2\text{CNRe}_2\) (with averaging of ionic and bidendate dithiocarbamate groups) (Table 1).

except that integration of all these compounds shows that there are insufficient diethiocarbamate protons for this formulation. In fact, the $^1H$ n.m.r. spectra are consistent with the formulation $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]X$ (where X is an anion not containing protons), except for the presence of an additional weak resonance in the region 6–8. The position of this resonance depends on solvent, solute concentration, and temperature; lowering the temperature or increasing the concentration or the solvent polarity shifts the peak to lower field, phenomena indicative of the presence of a hydrogen-bonded species. The diethiocarbamate ethyl resonance is temperature independent and has a chemical shift compatible with bidentate co-ordination. We suggest that the species arising from prolonged reaction of $\text{Pt}(\text{S}_2\text{CNEt}_2)_2$ and an excess of $\text{PR}_3$ in dichloromethane are the compounds $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$ (A); we have amassed considerable evidence to support this rather surprising conclusion.

The solid (A) reacts with NaBP$_4$ or NH$_4$PF$_6$ in acetone–methanol solution to give the compounds $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]Y$ (Y = BP$_4$ −, PF$_6$ −) which have been fully characterised by $^1H$ n.m.r., analyses, and conductivity measurements (Tables 1, 4, and 3 respectively). An interesting feature of the $^1H$ n.m.r. of these compounds is the upfield shift (ca. 0.2 p.p.m.) of both $\text{S}_2\text{CNET}_2$ and $\text{PR}_3$ resonances in the BP$_4$ −, compared to the PF$_6$ − and Cl − compounds. Similar observations have been made for the $[\text{Pt}(\text{S}_2\text{PMec}_2)(\text{PR}_3)_2]Y$ series and we suggest that this is a consequence of a ring-current effect in the BP$_4$ − complex which is, of course, absent in the other compounds. Evidence for a water molecule is based on the appearance of very weak OH stretches and bends in the m.i.r. spectra of compounds (A), the presence of oxygen (established by direct analysis and ESCA measurements), and the similarity of the position of the hydrogen-bonded resonance to that recently reported for $\text{Co}(\text{CO})_2(\text{PPh}_3)_2\text{H}_2\text{O}\text{Cl}^−$ (7–4).17 We suggest that the water molecule is hydrogen-bonded to the cation since addition of chloride ion produces no change in its resonance position. The presence of chloride ion is confirmed by direct analysis, ESCA *, measurements, and the fact that after treating (A) with a chloride anion-exchange resin for several days, the $^1H$ n.m.r., i.r. spectra, and m.p. are unchanged.

The chloride ion can only arise, of course, from the dichloromethane used in this reaction. A careful examination of the ethereal filtrate results in the isolation of an organoethano-compound, shown by elemental analysis, mass, and $^1H$ n.m.r. spectroscopy to be $\text{CH}_2\text{S}_2\text{CNEt}_2$ (B). This compound has been recently prepared in high yield by refluxing sodium diethylthiocarbamate with anhydrous dichloromethane.18 We find that, unless both solvent and sodium salt are scrupulously dried, only very small amounts of (B) can be isolated. However, a more convenient method of preparation is by shaking a mixture of NaS$_2$CNEt$_3$·3H$_2$O, CH$_2$Cl$_2$ (solvent grade), and any tertiary phosphate for 12 h. The reason why the addition of $\text{PR}_3$ facilitates the formation of (B) is not at present clear. The $^1H$

### Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. (10$^{−3}$m)</th>
<th>$\Lambda$ *</th>
</tr>
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<tbody>
<tr>
<td>$\text{Ph}_3\text{AsCl.HCl}$</td>
<td>9.8</td>
<td>55.3</td>
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<td>$\text{Bu}_3\text{SiO}$</td>
<td>10.1</td>
<td>22.7</td>
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<td>$[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$</td>
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<td>$[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$</td>
<td>1.8</td>
<td>36.6</td>
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<td>$[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$</td>
<td>1.4</td>
<td>36.6</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$</td>
<td>1.0</td>
<td>36.6</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$</td>
<td>0.6</td>
<td>36.6</td>
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<tr>
<td>$[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$</td>
<td>0.2</td>
<td>36.6</td>
</tr>
</tbody>
</table>

* In $\Omega^−$ cm$^2$ mol$^{−1}$.

The mechanism of formation of (A) is most likely via prior formation of $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PMePh}_3)_2]\text{S}_2\text{CNEt}_2$. Support for this hypothesis comes from a study of the behaviour of $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PMePh}_3)_2]\text{S}_2\text{CNEt}_2$ in CH$_2$Cl$_2$. The initial deep yellow solution, containing a mixture of 1:2:1:1 compounds, and free PMePh$_3$, slowly decolourises, a change accompanied by a steady rise in conductivity (Table 5). Removal of the solvent and addition of diethyl ether gives a precipitate of $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PMePh}_3)_2]\text{CHCl}_3$ and the ethereal filtrate contains CH$_2$(S$_2$CNET)$_2$. Similarly, in CHCl$_3$ (plus ethanol stabiliser) the solution also decolourises and (A) is formed. In this instance, the nature of the organic side-products has not been investigated. This is to be contrasted with the behaviour of $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PMePh}_3)_2]\text{S}_2\text{CNEt}_2$ in ethanol-free CHCl$_3$ and CDCl$_3$ (see earlier), where only nucleophilic attack of S$_2$CNET$_2$ on the platinum ion occurs. At this juncture, it is not obvious (to us) why ethanol has such a profound effect on the current of the reaction.

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* We thank Dr. M. Barber and Mr. P. Swift of A.E.I. Scientific Apparatus Ltd. for these measurements.

Finally, prolonged reaction of Pt(S₂CNMe₂)₃ and an excess of PR₃ in CH₂Cl₂ followed by precipitation with diethyl ether gives a mixture of [Pt(S₂CNMe₂)(PR₃)₃]-Cl₂H₂O and CH₂(S₂CNMe₂)₂. The latter, which can be extracted with benzene, is best prepared by shaking a mixture of Na₂S₂CNMe₂, CH₂Cl₂, and a tertiary phosphine (PPh₃, PMePh₂, and PMe₂Ph were successfully used). Without the phosphine, the only product is tetramethylthiuram disulphide. Again, the room-temperature ¹H n.m.r. shows two CH₃ resonances, which coalesce formulated as five-co-ordinate species.² We suggest that these should be reformulated as four-co-ordinate compounds of type (III) on the basis of the detailed arguments given above for the related dithiocarbamate complexes. For comparison, we have made the triphenylphosphine and triphenylarsine analogues of these compounds and variable-temperature ¹H n.m.r. studies for S₂P(OEt)₂ parallel those reported earlier for the PMePh₂ derivative (Tables 1 and 2). For [Pt-(S₂COEt)₂PPh₃] in C₅₂H₄₂, coalescence of the CH₃ triplet occurs at 188 K, but even at 173 K, the limiting spectrum has not been reached.

The reaction of either M(S-S)₂ or [M(S-S)₂PR₃] [M = Pt, Pd; (S-S)⁻ = S₂COEt, S₂COCH₂Ph, S₂P(OEt)₂] with an excess of PR₃ is of considerable interest. Fackler and Seidel⁴ have studied the former in some detail and have convincingly demonstrated that the final products are the novel compounds [(R₃P)₂MS₂CO] (I) and [(R₄P)₂PdS₂P(O)OEt] (II) respectively and that for the xanthate reaction, xanthate esters are also formed. At that time, neither the detailed mechanism nor the role played by tertiary phosphines in these rearrangement reactions were understood. In this final section, we would therefore like to present evidence which rationalises these rearrangement reactions within the context of the overall mechanistic framework developed in this paper and in earlier work¹ for the reaction of platinum and palladium dithioacetic complexes with tertiary phosphines.

We suggest that the reaction of platinum (or palladium) xanthates with PR₃ is as given by the Scheme below, namely stepwise cleavage of metal–sulphur bonds to give the ionic 1 : 2 complex, followed by nucleophilic attack of the xanthate anion on the alkoxy-group of the co-ordinated xanthate to give the neutral dithiocarbamate complex and a xanthate ester. A similar scheme involving the ionic intermediate [M(S₂P(OEt)₂)(PR₃)₂] is also possible.
(S₂P(OEt)₂) would explain the formation of [(R'₃P)₂MS₂-P(O)(OEt)]. This mechanism accounts for all the experimental observations made by Fackler and Seidel. For example, the observation that platinum compounds undergo the rearrangement more readily than palladium and that carbon disulphide inhibits the reaction relative to chloroform is readily explicable in terms of the tendency of platinum to form the ionic 1:2 adducts more easily than palladium (cf. earlier S₂PPh₃ studies) and the requirement of a fairly polar solvent to promote both the formation and stabilisation of the ionic intermediate. The fact that the ethyl group is eliminated less readily than the benzyl group is consistent with the greater stability of the benzylcarbonyl ion generated in the transition state.

However, it is also possible to give more direct experimental proof for such a reaction scheme. On reaction of Pt(S₂COEt)₂ and an excess of PPh₃ in CH₂Cl₂, immediate decolourisation, accompanied by a rapid increase in conductivity occurs (with a maximum value corresponding to ca. two-thirds of that expected for a 1:1 electrolyte). This is followed by a steady decrease and the isolation of (1) (Table 5). In nitromethane, the maximum value corresponds closely to that expected for a 1:1 electrolyte but again the readings decrease steadily with time (Table 5) and attempts to isolate the ionic species have been unsuccessful. For example, addition of an excess of light petroleum (b.p. 40–60 °C) within 20 s of mixing, give a precipitate of [Pt(S₂COEt)₂PPh₃] together with a small amount of [(PPh₃)₂PtS₂CO]. This clearly demonstrates that both nucleophilic attack of S₂COEt on a platinum–phosphorus bond and on a co-ordinated alkoxo-group are ready reactions. Presumably, lowering the polarity of the solution by addition of light petroleum facilitates attack on the metal. Although the ionic intermediate with xanthate as counter anion is too labile to be isolated, addition of NaBPh₄ to an acetone–methanol solution of Pt(S₂COEt)₂ and an excess of PPh₃ (within 30 s of mixing) gives a precipitate of [Pt(S₂COEt)₂PPh₃]BPh₄, which has been fully characterised by ¹H n.m.r., analysis, and conductivity measurements (Tables 1, 3, and 4).

Similarly, reaction of Pt(S₂P(OEt)₂) with an excess of PPh₃ in CH₂Cl₂ produces rapid decolourisation and the conductivity of the final solution corresponds to that of a 1:1 electrolyte (Table 3). Although in this instance, the conductivity readings are quite steady with time, all attempts to isolate the ionic species either by rapid removal of solvent or precipitation with diethyl ether have given only the rearranged product [(PPh₃)₃Pt-S₂P(O)(OEt)] together, in the latter case, with some [(Pt(S₂P(OEt)₂)₂PPh₃). However, it is possible to isolate and characterise [Pt(S₂P(OEt)₂)₂(PPh₃)]BPh₄ (Tables 1, 3, and 4) by addition of an excess of NaBPh₄ to an acetone–methanol mixture of the same reagents. It should be noted that for xanthate and dithiophosphate, there is no evidence here, or elsewhere,¹⁸ for side-reactions with chlorinated solvents.

**Conclusion.** Reaction of platinum (and palladium) dithioacid compounds with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate adducts of type (III) and (IV). For (S–S) = S₂PR₂ (R = Me, Et, Ph, and probably F), the ionic 1:2 compounds readily revert to the 1:1 compounds in nonpolar solvents by means of nucleophilic attack by S₂PR₂ on the metal. Similar processes occur for S₂P(OEt)₂, S₂CO, and S₂CN₂ but, in addition, competing nucleophilic attack on a co-ordinated alkoxo-group occur with the first two anions and on chlorinated solvents (catalysed by free PR₃) for the latter anion.

Although we have not investigated the dithiocarbamate adducts reported earlier, the very recent brief mention of essentially planar PtS₆P co-ordination for [Pt(S₂CC₆H₄-iPr)₂PPh₃] with the dangling sulphur atom 3.58 Å from the platinum(II) ion (cf. in Pd(S₂PPh₂)₂-PPh₃ > 3.5 Å away) suggests these compounds also conform to the general pattern.

**Experimental.** Microanalyses were by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Analytical data for many of the new compounds are given in Table 1. i.r. spectra were recorded in the region 4000—200 cm⁻¹ on a Perkin-Elmer 225 Grating Spectrometer, using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. ³¹P N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Mass spectra were measured on an A.E.I. MS9 mass spectrometer and conductivity measurements on a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

**Materials.**—Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson Matthey): triphenylphosphine, dimethylphenylphosphine, sodium diethylidithiocarbamate (B.D.H.); sodium dimethylidithiocarbamate (Ralph Emanuel). The other tertiary phosphines were prepared by standard literature methods.

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NN-Dialkyldithiocarbamate Complexes.—Bis(NN-dimethylldithiocarbamate)platinum(II). Potassium tetrachloroplatinate(II) in a minimum volume of hot water was mixed with an ethanolic solution of an excess of sodium NN di
 methylldithiocarbamate and shaken for 24 h. The yellow product was washed with water and ethanol and air-dried, m.p. 305–308°C (Found: C, 16.8; H, 2.9; N, 6.3. Calc. for C₁₉H₁₄N₂P₂S₂: C, 16.6; H, 2.8; N, 6.4%). Bis(NN-dialkyldithiocarbamate)platinum(II) ¹⁰ (m.p. 245–250°C) was prepared in the same way using K₂[P₄Cl₆] and Na₂S₄N₄Et₂
H₂O.

Bis(NN-dimethylldithiocarbamate) palladium(II).¹⁰ Palladium(II) acetate ²¹ was dissolved in benzene—dichloromethane and shaken for several hours with an ethanol solution containing an excess of Na₂S₄N₄Et₂H₂O. The yellow precipitate was filtered off, washed with water and ethanol, and air-dried (Found: C, 20.6; H, 3.3; N, 7.5. Calc. for C₁₉H₁₄N₂P₂S₂: C, 20.8; H, 3.5; N, 8.1%).

Bis(NN-dialkyldithiocarbamate)(triphenylphosphosphate)platinum(II). Bis(NN-dialkyldithiocarbamate)platinum(II) was suspended in carbon disulphide and treated with triphenyl
phosphine (< 1 : 1 molar ratio). An orange-yellow solution was immediately formed, together with unchanged Pt(S₄N₄Et₂)₂; the later was removed by filtration. Partial removal of the solvent followed by cooling (290 K) gave the yellow crystalline product. This was washed with diethyl ether and dried in vacuo. Bis(NN-dialkyldithiocarbamate)methylphenylphosphate platinum(II) was prepared in the same way, using a deficiency of PMe₃H under nitrogen. Preparation of the PMe₃H compound was complicated by the side—reaction between the phospine and CS₂.²² These products are soluble in chloroform, dichloromethane, carbon disulphide, and benzene; and insoluble in ethanol, near dimethyl sulphoxide.

(NN-Dialkyldithiocarbamate)(bis(methylphenylphosphine)platinum(II). NN-Dialkyldithiocarbamate. Pt(S₄N₄Et₂)₂ (0-90 mmol) in acetonitrile (5 ml) was treated with an excess of methylphenylphosphine (1-0 ml, 4-0 mmol) to give an immediate yellow solution from which yellow crystals of the product rapidly separated. These were washed with light petroleum (b.p. 40–60°C) and dried in vacuo (40°C). (NN-Dialkyldithiocarbamate)(bis(methylphenylphosphine)platinum(II) NN-dialkyldithiocarbamate was made by the same method. These compounds are very unstable, readily rearranging to form [Pt(S₄N₄Et₂)₂(PMe₃H)] and free PMe₃H on prolonged exposure to benzene, diethyl ether, or acetone. Attempts to make the corresponding triphenylphosphine and dimethylphenylphosphine ionic species were unsuccessful. The former gave only [Pt(S₄N₄Et₂)₂PPh₃] and the latter an intractable oil.

(NN-Dialkyldithiocarbamate)(bis(methylphenylphosphine)platinum(II) chloride monohydrate. Method (A). Pt(S₄N₄Et₂)₂ in dichloromethane (dried over MgSO₄) was treated with a three-fold excess of PMe₃H under nitrogen. The initial yellow solution slowly became colourless (ca. 1–2 h) and concentration in vacuo followed by addition of an excess of diethyl ether gave a white microcrystalline precipitate of the product. This was washed with diethyl ether and dried in vacuo (40°C).

Method (B). The same compound was also made by prolonged exposure of [Pt(S₄N₄Et₂)(PMe₃H)] to dichloromethane. The initial deep yellow solution slowly became colourless (ca. 2 h) and concentration of the solution followed by addition of an excess of diethyl ether gave the product. In addition, solvent removal from the ethereal filtrates in methods (A) or (B) gave an oil which, on trituration with light petroleum (b.p. 60–80°C), gave a white crystalline solid characterised as methylene bis(NN-dialkyldithiocarbamate), m.p. 70–71°C (Found: C, 42.6; H, 7.2; N, 9.0. Calc. for C₁₉H₁₄N₂S₄: C, 42.6; H, 7.1; N, 9.0%). Another method of preparation is to shake a mixture of Na₂S₄N₄Et₂H₂O, dichloromethane (not scrupulously dried), and a tertiary phosphine (PPh₃, PMe₃H, or PMe₂Ph) for 24 h. Solvent removal and trituration of the resulting oil with light petroleum (b.p. 60–80°C) gave the product characterised by m.p. and mass ¹⁰ and H n.m.r. spectroscopy. The same compound was also formed (but in lower yield) when the reaction was carried out in the absence of PMe₂Ph. Complexes [Pt(S₄N₄Et₂)(PPh₃)]Cl₂H₂O (PPh₃ = PMe₃H, PMe₂Ph) were also made by the procedure outlined in method (A), together with some CH₂(S₄N₄Et₂).

(NN-Dialkyldithiocarbamate)(bis(methylphenylphosphine)platinum(II) chloride monohydrate. Method A. The method used was exactly as for the preparation of [Pt(S₄N₄Et₂)(PMe₃H)]Cl₂H₂O, using a suspension of Pt(S₄N₄Et₂)(PMe₃H)₃Cl₂H₂O and a three-fold excess of PMe₃H. Precipitation with either diethyl ether or light petroleum (b.p. 60–80°C) gave a mixture of [Pt(S₄N₄Et₂)(PMe₃H)]Cl₂H₂O and CH₂(S₄N₄Et₂). The latter was removed by careful washing with benzene, and the remaining crystalline product was washed with diethyl ether and dried in vacuo (40°C). From the benzene washings, methylbenzene(NN-dialkyldithiocarbamate) was isolated (m.p. 93–96°C) (Found: C, 33.7; H, 5.3; N, 10.9. C₁₉H₁₄N₂S₂ requires C, 33.1; H, 5.1; N, 10.6%). The compound was also made by shaking a mixture of Na₂S₄N₄Et₂H₂O, CH₂Cl₂, and tertiary phosphine (PPh₃, PMe₃H, or PMe₂Ph) mass spectrum: 254 [CH₂(S₄N₄Et₂)]. 166 [Me₂Nc₆H₄S₂], and 88 [Me₂NCS⁻]” (cf. ref. 18).

In the absence of tertiary phosphine, only tetramethylthiuram disulphide (Found: C, 30.8; H, 5.0; N, 11.7%) and Na₂S₄N₄Et₂ were detected.

Method (B). From [Pt(S₄N₄Et₂)(PMe₃H)]S₄N₄Et₂H₂O, the deep yellow solution slowly becoming colourless. Precipitation with diethyl ether and extraction of CH₂(S₄N₄Et₂) with benzene gave the white product:

[Pt(S₄N₄Et₂)(PPh₃)]Cl₂H₂O (PPh₃ = PMe₃H, PMe₂Ph, PMe₃Ph) and [Pd(S₄N₄Et₂)(PMe₃H)]Cl₂H₂O were also made by the procedure outlined in method (A), together with some CH₂(S₄N₄Et₂).

(NN-Dialkyldithiocarbamate)(bis(methylphenylphosphine)platinum(II) tetraphenylborate. [Pt(S₂N₄Et₂)](PMe₃H)Cl₂H₂O was dissolved in methanol and treated with a concentrated acetone solution of NaPB₃H. The white precipitate of the product was washed with water and light petroleum (b.p. 60–80°C) and dried in vacuo (40°C). The same compound was also obtained by reaction between [Pt(S₂N₄Et₂)(PMe₃H)]S₂N₄Et₂ and NaPB₃H in ethanol.

Similarly, the complexes [Pt(S₂N₄R₉)(PPh₃)]BP₃H (R = Me, Et; PPh₃ = PMe₃H, PMe₂Ph, PMe₃Ph) were prepared from [Pt(S₂N₄R₉)(PPh₃)]Cl₂H₂O and an excess of NaPB₃H. (NN-Dialkyldithiocarbamate)(bis(methylphenylphosphine)platinum(II) hexafluorophosphate. [Pt(S₂N₄Et₂)](PMe₃H)₆F₆.

Cl₂H₂O in acetone-methanol was added to an aqueous solution of ammonium hexafluorophosphate to give a white colloidal precipitate. Partial removal of solvent in vacuo gave a white powder which was washed with water and light petroleum (b.p. 60–80°C) and dried in vacuo (40°C). [Pt(S₂CNMe₂)(PMe₃)₄]PF₆ and [Pt(S₂CNEt₂)₂(PPh₃)₄]PF₆ were also prepared by this method.

OO'-Diethyl Dithiophosphate Complexes.—Bis(0-ethyl dithiophosphate)platinum(ii) was prepared as described earlier (m.p. 124°C) [Found: C, 17.2; H, 3.5. Calc. for C₁₂H₁₆O₁₅P₁₃S₂: C, 17.0; H, 3.6%).

Bis(00'-diethyl dithiophosphate)(triphenylphosphine)platinum(ii). Pt([S₂P(OEt)₂]₂) was shaken with triphenylphosphine (1:1 molar ratio) in dichloromethane to give a lemon-yellow solution. Slow evaporation of the solvent in the presence of an excess of light petroleum (b.p. 40–60°C) gave yellow crystals of the product. [Pt([S₂P(OEt)₂]₂)₅AsPh₃] was prepared in situ by reaction of Pt([S₂P(OEt)₂]₂)₅ and an excess of AsPh₃ in CDCl₃.

O-Ethyl dithiophosphatebis(triphenylphosphine)platinum(ii). Pt([S₂P(OEt)₂]₅)PPh₃ (ca. 1:3 molar ratios) were refluxed in CHCl₃ for ca. 3 h during which time the initial yellow solution slowly became colourless. Removal of solvent and addition of diethylether gave a white product. Reaction of Pt([S₂P(OEt)₂]₅) and an excess of PPh₃ in CH₂Cl₂ rapidly gave a colourless conducting solution, presumably containing the ionic [Pt([S₂P(OEt)₂]₅)(PPh₃)₂]SO₄·2H₂O, but removal of solvent by a stream of nitrogen and washing with light petroleum (b.p. 40–60°C) was sufficient to cause rearrangement to ([PPh₃]₂Pt([S₂P(OEt)₂]₅)₂).

OO'-Diethyl dithiophosphatebis(triphenylphosphine)platinum(ii) tetraphenylborate. [Pt([S₂P(OEt)₂]₅)] in methanol was treated with an excess of triphenylphosphine in a minimum volume of acetone, followed by addition of an aqueous solution of NaBPh₄. The white precipitate was well washed with water and diethylether and dried in vacuo (40°C).

O-Ethyl Dithiocarbonate Complexes.—Bis(o-ethyl dithiocarbonate)(triphenylphosphine)platinum(ii). Pt([S₂COEt]₂)₅ and PPh₃ (1:1 molar ratio) were shaken in a minimum volume of CH₂Cl₂ to give a lemon-yellow solution. Trituration with an excess of light petroleum (b.p. 40–60°C) gave a pale yellow crystalline precipitate which was washed with diethylether and dried in vacuo (40°C). The same product (contaminated with a small amount of [Pt([S₂COEt]₂)(PPh₃)₅]) was also obtained by reaction of Pt([S₂COEt]₂) with an excess of PPh₃ in CH₂Cl₂ followed by immediate addition of an excess of light petroleum (b.p. 40–60°C).

Dithiocarbonatebis(triphenylphosphine)platinum(ii)-chloroform. Pt([S₂COEt]₂) was shaken with an excess of PPh₃ in dichloromethane to give a colourless conducting solution. Partial removal of solvent and addition of light petroleum (b.p. 60–80°C) gave a white precipitate, which was non-conducting when redissolved in CH₂Cl₂ (m.p. 256°C) [Found: C, 49.2; H, 3.3. Calc. for C₃₃H₃₅Cl₅O₄P₁₃S₂: C, 49.1; H, 3.3%].

O-Ethyl dithiocarbonatobis(triphenylphosphine)platinum(ii) tetraphenylborate. Pt([S₂COEt]₂) in acetone-methanol was treated with an excess of PPh₃ in a minimum volume of acetone, followed immediately by addition of an aqueous solution of NaBPh₄. The resulting white precipitate was well washed with water and diethylether and dried in vacuo (40°C).

We thank Johnson-Matthey Ltd. for loans of potassium tetrachloroplatinate(ii) and palladium(ii) chloride, the S.R.C. for an award (to J. M. C. A.), Professor J. I. G. Cadogan, Dr. R. O. Gould, and Dr. D. Leaver for helpful discussions, and Mrs. M. Groves and Mr. J. Miller for obtaining the variable-temperature 1H n.m.r. spectra.

[2] Received, 21st June, 1972

NEW DITHIOACID COMPLEXES OF MOLYBDENUM

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(Received 19 March 1973)

Although a number of papers have appeared in recent years on the synthesis of dialkyldithiocarbamates, dialkyldithiophosphates, difluorodithiophosphinates and alkylidithiocarbonates (xanthates) of molybdenum, most of the reported compounds contain the molybdenum ion in formal oxidation states IV, V or VI, e.g. \([\text{MoO(S}_2\text{P(OEt)}_2\text{)}_2]\), \([\text{Mo}_2\text{O}_3\text{(S}_2\text{COEt})_4]\) and \([\text{Mo}_2\text{O}_2\text{(S}_2\text{CNEt})_2\text{]}\) (1). Only a few examples of low-valent dithioacid molybdenum compounds are known, e.g. \([\text{Mo(NO)}_2\text{(S}_2\text{CNR})_2\text{]}\) (2), \([\text{Mo(CO)}_n\text{(S}_2\text{CNR})_2\text{]}\) (n = 2, 3) (3) and \([\text{Mo(CO)}_2\text{(PPh}_3\text{)(S}_2\text{CNR})_2\text{]}\) (4). A versatile method of synthesis of low-valent, binuclear molybdenum halides e.g. \(\text{Mo}_2\text{Cl}_4^{-}\), \(\text{Mo}_2\text{Cl}_8^{-}\) is by direct replacement of acetate ion by halide ion in molybdenum (II) acetate (5). In this preliminary communication, we wish to report the results of a study of the reactions of molybdenum (II) acetate with a number of dithioacid anions.

a) O-ethylidithiocarbonate: Treatment of molybdenum (II) acetate (6) with potassium ethylxanthate in degassed methanol leads to the precipitation of a red crystalline solid analysing closely for \([\text{Mo(S}_2\text{COEt})_2]\) (A) [Found: C, 21.0; H, 2.8; S, 37.5, Mwt (acetone) 671; Required: C, 21.2; H, 2.9; S, 37.6% Mwt(dimer) 680]. Although analytical data is not sufficient to unequivocally distinguish this formulation from oxy species such as \([\text{Mo}_2\text{O}_3\text{(S}_2\text{COEt})_4]\) (B) [Required: C, 19.9; H, 2.8; S, 35.4%], a careful
### Table

**Spectral parameters for various molybdenum xanthate complexes**

<table>
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<tr>
<th>Colour</th>
<th>[Mo(_2)(S(_2)COEt(_4)] (\text{red})</th>
<th>[Mo(_2)O(_3)(S(_2)COEt(_4)] (\text{dark green})</th>
<th>[Mo(_2)(S(_2)COEt(_4))py(_2)] (\text{red})</th>
<th>[MoO(S(_2)COEt(_2))py(_2)] (\text{light brown})</th>
</tr>
</thead>
<tbody>
<tr>
<td>i.r. spectra</td>
<td>1260m, 1200vs, 1150s (1300 - 700\text{cm}^{-1})</td>
<td>1284vs, 1242vs, 1120s, 1047vs, 1032s</td>
<td>1295m, 1225m, 1120m, 1180vs, 1145vs</td>
<td>1220vs, 1120s, 1065m, 1040m, 1015m</td>
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<tr>
<td>(40-15)x 10(^3) cm(^{-1})</td>
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<td>31.7 (10,000)</td>
<td>34.3 (10,000)</td>
<td>37.4</td>
</tr>
<tr>
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<td>in acetone</td>
<td>in chloroform</td>
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<td>solid state reflectance</td>
</tr>
<tr>
<td>(\text{H m.n.r.})</td>
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<td>in deuterobenzene</td>
<td>in deuterochloroform</td>
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<td>8.54T (CH(_3))</td>
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<td>(1.15T, 2.59T) (C(_5)H(_5)N)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>


\(^b\) From F.W. Moore and M.L. Larson, Inorg. Chem. 6 998 (1967)

\(^c\) Nujol mulls.

\(^d\) KBr discs

\(^e\) Band energy maximum \(10^3\) cm\(^{-1}\)

\(^f\) Maximum molar extinction coefficients \(10^3\) mol\(^{-1}\) cm\(^{-1}\).
comparison of the colour, i.r., 
'H n.m.r. and electronic spectra of A and B (Table) confirms that they are quite different compounds. Furthermore, A reacts readily with various donor ligands L (L = pyridine, 4-picoline, triethylarsine etc) giving dimeric red-brown compounds of formula [Mo(S₂COEt)₂L]₂ with similar 
'H n.m.r. and electronic spectral parameters to A. In contrast, B reacts with pyridine to give the light brown [MoO(S₂COEt)₂(py)] with different spectral properties from the pyridine adduct of A (Table).

Therefore, all the evidence suggests compound A has the "acetate-type" structure (7) shown below *, although, unlike the acetate (6) but like the recently reported trifluoroacetate dimer (8), the xanthate dimer is relatively stable in solution and readily forms stable base adducts.

\[ \text{S} \quad \text{S} \]
\[ \text{S} \quad \text{S} \]
\[ \text{S} \quad \text{S} \]
\[ \text{S} \quad \text{S} \]
\[ \text{Mo} \quad \text{Mo} \]

\[ \begin{array}{c}
\alpha \\
\beta 
\end{array} \]

b) Monothiobenzaote: Reaction of molybdenum (II) acetate with ammonium monothiobenzaote in degassed methanol gives a red precipitate of [Mo(SOCPh₂)₂]₂. (C)

[Found: C, 45.1; H, 2.7; S, 17.4; Mo, 25.7; Required: C, 45.2; H, 2.7; S, 17.2; Mo, 26.3%] shown to be dimeric by mass spectral analysis.

* A recent reference in a paper by J. M. Burke and J. P. Fackler Jr. Inorg. Chem., 11, 3000 (1972) reveals that L Ricard (as reported at the XIVth International Conference on Co-ordination Chemistry, Toronto, Canada, 1972) has independently synthesised Mo₂(S₂COEt)₄ and confirmed the acetate-type structure (with a Mo-Mo distance of 2.12A).
As for the xanthate complex, reaction occurs readily in solution with various donor ligands but removal of solvent only regenerates starting material. Comparison of the i.r. spectrum of C with other monothiobenzoate complexes (9) suggests substantial interaction of the metal with both oxygen and sulphur (ν<sub>CO</sub> 1465 cm<sup>-1</sup>; ν<sub>CS</sub> 960 cm<sup>-1</sup>) which is consistent with either of the structures shown below (cf. the structure of [Ni(PhCOS)<sub>2</sub>]<sub>2</sub>EtOH (10) with ν<sub>CO</sub> 1508 cm<sup>-1</sup>; ν<sub>CS</sub> 958 cm<sup>-1</sup> (9)).

(c) N,N<sup>1</sup>-Dialkylthiocarbamates:— Reaction of molybdenum (II) acetate in a degassed minimum volume of methanol with excess NaS<sub>2</sub>CNR<sub>2</sub> (R = Et, Pr) gives immediate crystalline green precipitates which analyse closely for [Mo(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (D). Unfortunately, it was impossible to obtain molecular weights because of the very rapid oxidation to purple [Mo<sub>2</sub>O<sub>3</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>4</sub>]. However, if the same starting materials are reacted in either ethanol solution or left for extended periods in very dilute methanol solution, green solids also of formula [Mo(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub>]<sub>n</sub> (E) are obtained but these have a more complicated <sup>1</sup>H n.m.r. spectra than compounds D. In fact, <sup>1</sup>H n.m.r. studies confirm that in carefully degassed solvents, compound D slowly converts to compound E at room temperature. Furthermore, compound E is then more stable towards oxidation than compound D. A recent note by Weiss et al. (11) reporting an X-ray analysis on the product from the reaction of molybdenum (II) acetate with ammonium di-n-
propyldithiocarbamate in ethanol reveals that the product is a dimeric molybdenum (IV) complex with bridging sulphido groups and a "carbene" ligand. We therefore suggest that compound E (R = Et, iPr) also possesses this structure whereas the labile intermediate D has an acetate-type structure!

Further work is now in progress in attempts to analyse the n.m.r. spectra and the detailed mechanism of this interesting reaction.

(d) Diphenylphosphinodithioate:— The reactions of this ligand with molybdenum (II) acetate are also very sensitive to the reaction conditions. Preliminary studies indicate that with $\text{Mo}_2(\text{OCOCH}_3)_4$ and excess $\text{NH}_4\text{S}_2\text{PPh}_2$ in ethanol, incomplete substitution of acetate occurs giving a very insoluble orange precipitate of composition $[\text{Mo}(\text{OCOCH}_3)[\text{S}_2\text{PPh}_2]^n]_n$ (F). However, if $[\text{Mo}_2(\text{OCOCH}_3)_4]$ is reacted with diphenylphosphinodithioic acid in benzene or F is treated with $\text{HS}_2\text{PPh}_2$ in benzene, a very insoluble green compound of formula $[\text{Mo}(\text{S}_2\text{PPh}_2)^2]_n$ is formed. Neither of these compounds appear to exhibit $\nu\text{Mo} = \text{O}$ or $\nu\text{Mo-O-Mo}$ vibrations in their i.r. spectra although such bands slowly appear on prolonged exposure of the compounds to air.

Clearly, reactions of molybdenum (II) acetate with dithioacid ligands exhibit a diversity of behaviour comparable to that found with halogen acids. Work is now in progress to determine the precise nature of the products
formed, particularly as a function of such variables as solvent, temperature, time of reaction etc.

Acknowledgement

We thank the S.R.C. for an award (DFS)

References


Metal Complexes of Sulphur Ligands. Part IV.¹ Reaction of Bis(dialkylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group Va Atoms

By David F. Steele and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ
Metal Complexes of Sulphur Ligands. Part IV. Reaction of Bis(dialkylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group Va Atoms

By David F. Steele and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of the complexes $\text{[Pt(S}_2\text{PR}_3)_2]$ (R = Me or Et) with tertiary phosphines gives four co-ordinate complexes $\text{[Pt(S}_2\text{PR}_3)_2\text{PR}_3]^+ \text{ and } \text{[Pt(S}_2\text{PR}_3)_2\text{PR}_3]^+ \text{ and } \text{[Pt(S}_2\text{PR}_3)_2\text{PR}_3]^+ \text{ and } \text{[Pt(S}_2\text{PR}_3)_2\text{PR}_3]^+$ Variable-temperature H n.m.r. studies of the neutral complexes indicate rapid unidentate-bidentate exchange at ambient temperatures and a full line-shape analysis of this process for complexes of general type $\text{[Pt(S}_2\text{S}_2\text{ER}_3]^+ \text{ [(S}_2\text{S}_2\text{CNR}_2]^+ \text{ or } \text{S}_2\text{P(OEt)}_2]^+ \text{ or } \text{S}_2\text{PMe}_2]$; E = P or As) suggests a concerted mechanism in which both bond-breaking and bond-making steps are important. For the complex $\text{[Pd(S}_2\text{PMe}_2)_2]$, the ionic complexes are too unstable to be isolated in pure form because of facile rearrangement to the neutral complexes. However, addition of either NaBPh$_4$ or NaPF$_6$ to solutions containing the ionic species provides a general method of synthesising the complexes $\text{[M(S}_2\text{P}_2\text{PR}_3)_2\text{X]} (M = \text{Pt or Pd}; \text{R} = \text{Me or Ph}; X = \text{BPh}_4^-$ or $ \text{PF}_6^-$). For $M = \text{Pt and X} = \text{BPh}_4^-$, these complexes readily react with $\text{Ph}_3\text{AsY}$ (Y = Cl, Br, or I) giving $\text{Ph}_3\text{AsBPh}_4$ and $\text{[Pd(S}_2\text{P}_2\text{Me}_2)_2\text{PR}_3]^+ \text{Y]}$. However, for the complexes $\text{[Pd(S}_2\text{P}_2\text{PR}_3)_2\text{BPh}_4}$ (R = Me or Ph) dissolution in $\text{CH}_2\text{Cl}_2$-EtOH, $\text{CH}_2\text{Cl}_2$-EtOH (Y = Cl or Br), or in acetone containing added halide ion produces rapid rearrangement to give $\text{[Pd(S}_2\text{S}_2\text{PR}_3)\text{Y(PPh}_3)]$. This rearrangement does not occur for $X = \text{PF}_6^-$ and a tentative mechanism involving a labile $\pi$- or $\sigma$-bonded phenyl group is suggested. Finally, an empirical i.r. method for distinguishing unidentate, bidentate, and ionic modes of co-ordination of the dimethylphosphinodithioato-group to platinum and palladium is briefly discussed.

In Parts II$^2$ and III$^1$ of this series it was shown that the reaction of the complexes $\text{[M(S}_2\text{S}_2\text{S)_2]} (M = \text{Pt or Pd}; \text{S}_2\text{S})^- = \text{S}_2\text{PPh}_3, \text{S}_2\text{CNMe}_2, \text{S}_2\text{COR}, \text{or } \text{S}_2\text{P(OEt)}_2$ with tertiary phosphines occurs by stepwise cleavage of metal-sulphur bonds to generate four-co-ordinate adducts $\text{[M(S}_2\text{S}_2\text{S}_2\text{PR}_3]^+}$ and $\text{[M(S}_2\text{S}_2\text{S}_2\text{PR}_3]^+ \text{(S}_2\text{S)}^-}$ with unidentate-bidentate and bidentate-ionic dithio-ligand co-ordination respectively. Similar results were briefly reported by Tebbe and Muetterties$^3$ for the complex $\text{[Pd(S}_2\text{PF}_3)_2]}$. It has also been demonstrated that the ionic complexes readily reverted to $\text{[M(S}_2\text{S}_2\text{S}_2\text{PR}_3]^+}$ when dissolved in non-polar solvents via nucleophilic attack by $\text{(S}_2\text{S)}^-$ on the metal.$^1,2$ Furthermore, variable-temperature$^1$H n.m.r. studies on the platinum 1 adducts of the dithiocarbamato- and dithiophosphato-complexes indicated rapid interchange of the unidentate-bidentate dithio-ligands at ambient temperature, whereas at lower temperatures, intramolecular rearrangement became sufficiently slow for the 'frozen-out' n.m.r. spectrum to be observed.$^1$ Activation energies for these processes were estimated from the coalescence temperatures by a standard method (see table 2, ref. 1).

However no activation energies could be obtained for the $\text{[M(S}_2\text{PPh}_3)_2\text{S}_2\text{S}_2\text{S}_2\text{PR}_3]}$ complexes$^2$ since phenyl groups are not amenable to such$^1$H n.m.r. temperature studies. Therefore, in order to rectify this deficiency, and also to investigate the effect on complex reactivity of varying the substituent $\text{R}$, we have carried out a study of the reactions of the complexes $\text{[M(S}_2\text{P}_2\text{PR}_3)_2]} (M = \text{Pt or Pd}; \text{R} = \text{Me or Et})$ with ligands containing Group Va atoms and the results are reported below.


RESULTS AND DISCUSSION

**Complexes of Stoichiometry [M(S₂PR₃)₂]⁻.—** Reaction of the complex [Pt(S₂PMe₃)₂] with tertiary phosphines (1 : 1 molar ratio) in benzene or chloroform gave immediate yellow solutions from which complexes of stoichiometry [Pt(S₂PMe₃)₂PR₃] were readily isolated by concentration and precipitation with pentane. These complexes are diamagnetic (sharp ¹H n.m.r. signals) and non-conducting in dichloromethane. For the complex

This process is reversible and is in accordance with the facile unidentate–bidentate exchange process suggested earlier (equation 1).

Although the activation energy at a coalescence temperature of 263 K has already been quoted in Table 2 (ref. 1) for the complex [Pt(S₂PMe₃)₂PPh₃], a full line-shape analysis has now been performed on the complexes [Pt(S₂PMe₃)₂ER₃] (ER₃ = PPh₃, PPh₂C₆H₄F₅, or AsPh₃) as well as [Pt(S₂CNMe₂)₂PPh₃] and [Pt(S₂P(OEt)₂)₂PPh₃]

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>CH₃(dithio-ligand)</th>
<th>CH₃(PR₃)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(S₂PMe₃)₂]⁻</td>
<td>CH₂Cl₂</td>
<td>7-99</td>
<td>8-09(5)</td>
<td>Ph 2-8(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₃]⁻</td>
<td>CH₂Cl₂</td>
<td>7-96(2)</td>
<td>8-10(2)</td>
<td>Ph 2-2—2-5(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>7-79(3)</td>
<td>8-03(3)</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂AsPh₃]⁻</td>
<td>CH₂Cl₂</td>
<td>7-96(2)</td>
<td>8-10(2)</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₃]⁻</td>
<td>CH₂Cl₂</td>
<td>7-98 a [3]</td>
<td>7-63 a</td>
<td>Ph 2-0(4)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>7-96 a [18]</td>
<td>8-04 a</td>
<td>Ph 2-0(4)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>7-94 a [5]</td>
<td>7-67 a</td>
<td>Ph 2-7(2)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>7-92 a [18]</td>
<td>8-08 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CH₂Cl₂</td>
<td>7-99(2)</td>
<td>8-09 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CH₂Cl₂</td>
<td>8-14(1)</td>
<td>8-14 a</td>
<td>Ph 2-7(6)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CH₂Cl₂</td>
<td>8-04(2)</td>
<td>8-20 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>8-41(3)</td>
<td>8-14 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>8-40(5)</td>
<td>8-20 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>8-40(5)</td>
<td>8-20 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>8-43(3)</td>
<td>8-20 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>7-91(1)</td>
<td>8-14 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>8-40(3)</td>
<td>8-14 a</td>
<td>Ph 2-7(5)</td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂PPh₂C₆H₄F₅]⁻</td>
<td>CDCl₃</td>
<td>8-00(2)</td>
<td>8-14 a</td>
<td>Ph 2-7(5)</td>
</tr>
</tbody>
</table>


[Pt(S₂PMe₃)₂]⁻, an excess of tertiary phosphine was required in order to obtain the 1 : 1 adducts free of starting material. Similar conditions are necessary to isolate a pure sample of [Pt(S₂PMe₃)₂AsPh₃]. However, with PE₃ and AsEt₃ (for M = Pt) the products are too soluble to be satisfactorily isolated and, although treatment with ammonia and pyridine did indicate some reaction in solution, efforts to isolate a solid complex only resulted in recovery of the starting material. In contrast, the palladium complex does not react with arsenic- or nitrogen-donor ligands (cf. [Pd(S₂PPh₂)₂]).

Like the analogous complexes [M(S₂S)₂ER₃]⁺, these 1 : 1 adducts apparently undergo a rapid intramolecular rearrangement reaction, since, at ambient temperatures, all the complexes exhibited a single doublet for the dimethylphosphinodithioate methyl protons (with J₉≈ 13-0 Hz), whereas, at lower temperatures, coalescence occurred, followed (in some instances) by the growth of two pairs of doublets of intensity ratio 1 : 1 (Table 1).

In order to obtain more accurate activation energies, and also the enthalpies and entropies of activation for these rearrangement processes. These data are given in Table 2. For the complexes [Pt(S₂PMe₃)₂PR₃]⁻ (PR₃ = PPh₃ or PMe₃) and all the palladium 1 : 1 adducts, the rate of rearrangement was too rapid to obtain any kinetic parameters (single doublet even at 200 K). This

\[
\begin{array}{c}
\text{R}_3 \text{E} \\
\text{M} \\
\text{S} \\
\text{S}
\end{array}
\]

\[
\rightarrow
\begin{array}{c}
\text{R}_3 \text{E} \\
\text{M} \\
\text{S} \\
\text{S}
\end{array}
\]

(1)

* Whilst this work was in progress, complete characterisation of the complexes [M(S₂PR₃)₂]⁻ (M = Ni, Pd, or Pt; R = Me, Ph, F, CF₃ or OEt) was reported (R. G. Cavell, W. Byers, E. D. Day, and F. M. Watkins, Inorg. Chem., 1972, 11, 1998), although no reactions of the complexes were discussed.
latter observation is in accordance with the increased lability of palladium substitution reactions compared to those of platinum.\(^4\)

A comparison of Table 2 with the activation energies derived from coalescence-temperature measurements (Table 2, ref. 1) shows reasonable agreement. For all the 1:1 complexes studied, the rate of rearrangement was concentration independent, indicating a wholly intramolecular process, and for the complex \(\text{[Pt(S}_{2}\text{P} \text{(OEt)}_{2}]_{2} \text{PPh}_{3}\) activation parameters obtained in \(\text{CH}_{2}\text{Cl}_{2}\) and \(\text{CH}_{2}\text{Cl}_{2}-\text{CS}_{2}\) (1:1) were very similar, indicating the absence of a solvent-assisted bond-rupture mechanism. However, examination of the data for the \(\text{S}^2\text{PMe}_{3}\) reveals that the rate of rearrangement is dependent on the ligand \(\text{ER}_{3}\). The relative rates are in the order \(\text{PMe}_{3}\text{Ph} \sim \text{PMe}_{2}\text{Ph} \rightarrow \text{PPh}_{3}\text{C}_{6}\text{H}_{5} \sim \text{PPh}_{3} > \text{AsPh}_{3}\), clearly indicating that cleavage of the metal-sulphur bond \(\text{trans}\) to \(\text{ER}_{3}\) is an important factor in the rate-determining step. However, another important observation is that, although for \(\text{ER}_{3} = \text{PPh}_{3}\), the free energies of activation for complexes with different dithio-ligands are quite similar (54—57 kJ mol\(^{-1}\)), the enthalpies of activation for the \(\text{S}_{2}\text{CNPh}_{3}\) and \(\text{S}_{2}\text{P(OEt)}_{2}\) complexes (29 and 33 kJ mol\(^{-1}\) respectively) are much lower than that for the \(\text{S}_{2}\text{PMe}_{3}\) complex (64 kJ mol\(^{-1}\)). This is compensated for by the more unfavourable entropy terms in the first two complexes, although the large error limits incurred in determining \(\Delta S^\ddagger\) mean that such small differences must be treated with some caution. Since other studies indicate that the order of ligand-field strengths for these dithio-ligands is \(\text{S}_{2}\text{CNPh}_{3} > \text{S}_{2}\text{P(OEt)}_{2} > \text{S}_{2}\text{PR}_{3}\),\(^5\) then the lower enthalpy values for the stronger nucleophiles suggest that the bond-making process is also involved in the rate-determining step. A concerted mechanism involving a transition state such as (I) is also favoured by the small negative

\[
\text{[R\text{F}
\begin{array}{c}
\text{S} \\
\text{S}
\end{array}
\begin{array}{c}
\text{M} \\
\text{S}
\end{array}
\text{S} \\
\text{S}
\]
\]

entropy values [a dissociative mechanism would give rise to a positive entropy term]\(^6\) and the tendency for

\(\text{Pt}^\text{II}\) substitution reactions to occur by associative mechanisms.\(^4\)

For completion, the complexes \(\text{[Pt(S}_{2}\text{P} \text{Ph}_{3}]_{2}\) and \(\text{[Pt(S}_{2}\text{P} \text{(OEt)}_{2}]_{2} \text{PPh}_{3}\) were also prepared. The \(\text{H}^1\) n.m.r. spectra of both complexes consist of a doublet of quartets (CH\(_2\)) and a doublet of triplets (CH\(_3\)) (see Experimental section), indicating rapid unidenate-bidentate exchange in the latter complex at room temperature which is still fast even at 203 K.

**Complexes of Stoichiometry** \(\text{[M(S}_{2}\text{P} \text{Me}_{3}]_{2} \text{ER}_{3}\)\(^2\). Reaction of the complex \(\text{[Pt(S}_{2}\text{PMe}_{3}]_{2}\) with an excess of \(\text{PR}_{3}\) (\(\text{PR}_{3} = \text{PPh}_{3}\) or \(\text{PMe}_{3}\)) in methanol followed by light petroleum addition gave the pale yellow complexes \(\text{[Pt(S}_{2}\text{PMe}_{3}]_{2} \text{PPh}_{3}\) \(\text{[Pt(S}_{2}\text{PMe}_{3}]_{2}\) \(\text{PMe}_{3}\). The stability of these complexes with respect to rearrangement to \(\text{[Pt(S}_{2}\text{PMe}_{3}]_{2}\) \(\text{PR}_{3}\), by means of nucleophilic attack by \(\text{S}_{2}\text{PMe}_{3}\) on the platinum-phosphorus bond, depends on the \(\text{PR}_{3}\) group. For \(\text{PR}_{3} = \text{PPh}_{3}\), even recrystallisation from a polar solvent such as acetone gave only the 1:1 adduct, whereas for \(\text{PR}_{3} = \text{PMe}_{3}\), the complex could be recrystallised from chloroform or even benzene without any

---

**Table 2**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>(E^\ddagger) (kJ mol(^{-1}))</th>
<th>(\Delta H^\ddagger) (kJ mol(^{-1}))</th>
<th>(\Delta S^\ddagger) (J K(^{-1}) mol(^{-1}))</th>
<th>(\Delta G^\ddagger) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{[Pt(S}<em>{2}\text{PMel}]</em>{2} \text{AsPh}_{3})</td>
<td>(\text{CH}<em>{2}\text{Cl}</em>{2})</td>
<td>154.0</td>
<td>56.0</td>
<td>9.0</td>
<td>57.0</td>
</tr>
<tr>
<td>(\text{[Pt(S}<em>{2}\text{PMel}]</em>{2} \text{Cl}_{2})</td>
<td>(\text{CH}<em>{2}\text{Cl}</em>{2})</td>
<td>198.0</td>
<td>56.0</td>
<td>10.0</td>
<td>55.0</td>
</tr>
<tr>
<td>(\text{[Pt(S}<em>{2}\text{P(OEt)}</em>{2}]<em>{2} \text{Cl}</em>{2})</td>
<td>(\text{CH}<em>{2}\text{Cl}</em>{2})</td>
<td>188.0</td>
<td>56.0</td>
<td>10.0</td>
<td>56.0</td>
</tr>
<tr>
<td>(\text{[Pt(S}<em>{2}\text{CNPh}</em>{3}]<em>{2} \text{PPh}</em>{3})</td>
<td>(\text{CH}<em>{2}\text{Cl}</em>{2})</td>
<td>200.0</td>
<td>34.0</td>
<td>10.0</td>
<td>55.0</td>
</tr>
<tr>
<td>(\text{[Pt(S}<em>{2}\text{CNPh}</em>{3}]<em>{2} \text{Cl}</em>{2})</td>
<td>(\text{CH}<em>{2}\text{Cl}</em>{2})</td>
<td>208.0</td>
<td>36.0</td>
<td>10.0</td>
<td>54.0</td>
</tr>
</tbody>
</table>

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However, when the reaction of the complexes [M(S₂PMe₃)₂] and an excess of PR₃ (ca. 1:3 mole ratio) in dilute methanol solution was followed by immediate addition of either sodium tetrathionate or hexa-
fluorophosphate, precipitation of the ionic complexes [M(S₂PMe₃)₂(PR₃)₂]X (X = BPh₄⁻ or PF₆⁻) occurred. A similar reaction between the complex [Pd(S₂PPh₃)₂] and PPh₄ also resulted in formation of the previously unisolable [Pd(S₂PPh₃)₂(PPh₃)₂]⁺ cation as its BPh₄⁻ (or PF₆⁻) salt. An interesting characteristic of the ¹H n.m.r. spectra of the BPh₄⁻ salts is that the resonances of both the S₂PMe₃ and PR₃ protons were shifted to ca. 0-2–0-4 upfield with respect to the corresponding PF₆⁻ salts (Table 1). We suggest that this is a consequence of a ring-current effect in the BPh₄⁻ complexes which produces additional shielding of these methyl protons (cf. the [Pt(S₂CNr₂)₂(PR₃)₂]X (X = BPh₄⁻ or PF₆⁻) series).¹

Reaction of the platinum triphenylphosphine tri-
phenylborate complexes with P₃AsCl₂ (Y = Cl, Br, or I) in chloroform led to immediate precipitation of the very insoluble P₃AsBPh₄ and the isolation of [Pt(S₂PMe₃)₂-
(PPh₃)₂]Cl from the filtrate. These complexes are quite stable in solution, exhibiting no tendency to rearrange to neutral 1:1 adducts.

The corresponding complexes [Pd(S₂PR₃)₂(PPh₃)₂]BPh₄ (R = Me or Ph) behave in a different manner. Dissolution in chlorinated solvents such as CH₂Cl₂ or CHCl₃ (containing ethanol stabiliser) produced a rapid decrease in the conductivity of the solutions which turned orange-yellow and, after concentration and pentane addition, gave the neutral complexes [Pd(S₂PR₃)₂Cl]PPh₄. The corresponding bromo-complexes were obtained if the BPh₄⁻ salts were dissolved in CH₂Br₂ or CH₃Br₂ containing ca. 2% ethanol. In the absence of ethanol, the BPh₄⁻ salt was recovered unchanged, whereas addition of a few drops of alcoholic potassium hydroxide solution enhanced the rate of formation of the neutral complex. It would thus appear that the function of ethanol in this and similar rearrangement reactions is to provide traces of base in order to facilitate formation of halide ion from the solvent. Rearrangement of the BPh₄⁻ complex also occurs in acetone solution containing added halide ion.

However, the presence of BPh₄⁻ ion also appears essential for facile rearrangement to occur since, when the complex [Pd(S₂PR₃)₂(PPh₃)₂]PPh₆ was dissolved in halogenated solvents or in acetone with an excess of halide present, the ionic species was recovered unchanged. The rearrangement is also confined to the PPh₄ complexes, since we found no evidence for rearrangement for [Pd(S₂PMe₃)₂(PMe₃)₂]BPh₄ when dissolved in chloro-
form. For the ionic platinum phosphate complexes, irrespective of the nature of the counter-anion, no rearrangement occurred, even after heating under reflux in chloroform–ethanol for 3 days. The arson complex [Pd(S₂PMe₃)₂(AsPh₃)₂]BPh₄ did, however, react with halogenated solvents (as indicated by a decrease in conductivity), but no pure product could be isolated. This difference in behaviour between the platinum and palladium complexes is readily explicable in terms of the greater lability of palladium(II) complexes coupled with the lower stability of these ionic palladium(II) species, as established in earlier studies.¹,² Earlier work² has also revealed that the ionic platinum triphenylarsine complex is only stabilised by the presence of a large anion.

The role of the BPh₄⁻ ion and the reason why only this ion promotes the rearrangement reaction is not really understood. However, evidence exists in the literature both for formation of π-bonded BPh₄⁻ complexes by displacement of tertiary phosphines or phosphites and for formation of metal–phenyl σ-bonds via fission of a boron–carbon bond.³ Therefore it is not unreasonable to postulate that a similar process might occur here, giving a labile π- or σ-bonded phenyl intermediate such as (IIa) or (IIb) followed by displacement by a stronger nucleo-
phile such as halide ion. At present, insufficient evidence is available to distinguish between these two possibilities.

I.r. Studies.—In earlier work with diphenylphosphino-
dithioates,² an empirical correlation was established between the mode of co-ordination of the dithio-group and the presence of certain i.r. bands. Thus, bidentate

<table>
<thead>
<tr>
<th>Complex</th>
<th>Unidentate</th>
<th>Bidentate</th>
<th>Ionic</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(S₂PMe₃)₂]</td>
<td>572s</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂(PPh₃)₂]</td>
<td>572w</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂AsPh₃]</td>
<td>572w</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pd(S₂PMe₃)₂(PMe₃)₂]</td>
<td>570w</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pd(S₂PMe₃)₂(PMe₃)₂]</td>
<td>570w</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂(PPh₃)₂]S₂PMe₃</td>
<td>572w</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂(PPh₃)₂]BP₄*</td>
<td>575w</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂(PPh₃)₂]PF₆*</td>
<td>572w, sh</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pd(S₂PMe₃)₂(PMe₃)₂]PF₆*</td>
<td>570w</td>
<td>570w</td>
<td></td>
</tr>
<tr>
<td>[Pt(S₂PMe₃)₂(PPh₃)₂]Cl</td>
<td>570w</td>
<td>570w</td>
<td></td>
</tr>
</tbody>
</table>

* Ionic region masked by BPh₄⁻ vibrations at 605s, 612m, and 925w cm⁻¹.


---

TABLE 3

Characteristic bands (650–550 cm⁻¹) for determining the mode of co-ordination of the dimethylphosphino-
dithioate-group to palladium(II) and platinum(II) ions
These diagnostic band positions were then used to infer the types of bonding in other \( \text{S}_2\text{PPh}_2 \) complexes. Similarly for the \( \text{S}_2\text{PMe}_2 \) complexes, careful examination of the region 650–550 cm\(^{-1}\) also reveals that certain bands appear diagnostic of the different types of coordination (Table 3). For the reason discussed earlier,\(^4\) i.e. extensive coupling of vibrations in these low-symmetry complexes, no attempt has been made to assign these bands to any specific mode of vibration, although they probably contain an appreciable contribution from \( \text{S}_2\) stretching frequencies. There appears to be only one characteristic band in this region and comparison of the direction of shift of this band on change in coordination mode with those found earlier for \( \text{S}_2\text{PPh}_2 \) complexes\(^2\) suggests that this is the higher-energy band. A band at 505 cm\(^{-1}\) in the complex \( \text{Pt}(\text{S}_2\text{PMe}_2)_2 \) can be assigned to the lower-energy band (corresponding to the 570 cm\(^{-1}\) band in \( \text{S}_2\text{PPh}_2 \) complexes). Unfortunately in all the adducts reported here, any change in the position of this latter band was masked by strong ligand vibrations.

**EXPERIMENTAL**

Microanalyses were carried out by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were measured in dry acetone at 37 °C on a Perkin-Elmer–Hitachi osmometer calibrated with benzil. Analytical data for all the new complexes are given in Table 4. I.r. spectra were recorded in the region 4000–200 cm\(^{-1}\) on a Perkin-Elmer 255 grating spectrometer using Nujoj mulls on caesium iodide plates. \(^1\)H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Mass spectra were obtained on an AEI MS9 mass spectrometer and conductivity measurements on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

**Materials.—**Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson Matthey); triphenylphosphate, dimethylphenylphosphate (B.D.H.); triphenylarsine (Ralph Emanuel). Triphenylphosphine and triphenylarsine were recrystallised from ethanol before use. Methylidiphosphine was made by the Grignard method from chlorodiphosphine. Sodium dimethyl- and diethyl-phosphinodithioates were made by standard methods.\(^6\) Triethylarsine and pentfluorophenyl(diphenyl)phosphine were kindly supplied by Dr. D. I. Nichols. Operations involving free tertiary phosphines (other than \( \text{PPh}_3 \)) were carried out under an atmosphere of nitrogen.

\(^1\)H N.m.r. Variable-temperature Studies.—The variable-temperature unit on the HA 100 spectrometer was used with methanol as a calibrant. Spectra were run at 5 K intervals in the range 313–200 K. Spectra were simulated using a computer program based on that of Nakagawa.\(^8\) The exchange process was considered for the purpose of computation as consisting of \( n \) two-site exchanges, where \( n \) is the multiplicity of the resonance being monitored. The single-

**Table 4**

Analytical data for some platinum(II) and palladium(II) dithio-complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>M.p.(°C)</th>
<th>Found (%)</th>
<th>Calc (%)</th>
<th>A *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(S₂PMe₂)₂PPh₂</td>
<td>211–214</td>
<td>C: 37-0 H: 3-7</td>
<td>C: 37-0 H: 3-8</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂)₂PMe₂</td>
<td>214-219</td>
<td>C: 40-0 H: 5-0</td>
<td>C: 40-0 H: 5-4</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂)₂PMe₂Br</td>
<td>219-221</td>
<td>C: 43-0 H: 5-5</td>
<td>C: 43-0 H: 5-6</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PPh₂</td>
<td>222-226</td>
<td>C: 46-0 H: 4-6</td>
<td>C: 46-0 H: 4-8</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PMe₂</td>
<td>226-229</td>
<td>C: 49-0 H: 5-2</td>
<td>C: 49-0 H: 5-3</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂)₂PF₆</td>
<td>232-235</td>
<td>C: 52-0 H: 5-8</td>
<td>C: 52-0 H: 6-1</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PF₆</td>
<td>235-238</td>
<td>C: 54-0 H: 6-8</td>
<td>C: 54-0 H: 7-0</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PF₆</td>
<td>238-241</td>
<td>C: 57-0 H: 7-6</td>
<td>C: 57-0 H: 7-8</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PF₆</td>
<td>241-244</td>
<td>C: 60-0 H: 8-2</td>
<td>C: 60-0 H: 8-4</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PF₆</td>
<td>244-247</td>
<td>C: 63-0 H: 8-8</td>
<td>C: 63-0 H: 9-0</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PF₆</td>
<td>247-250</td>
<td>C: 65-0 H: 9-4</td>
<td>C: 65-0 H: 9-6</td>
<td>0-60</td>
</tr>
<tr>
<td>Pt(S₂PMe₂Cl)₂PF₆</td>
<td>250-253</td>
<td>C: 68-0 H: 10-0</td>
<td>C: 68-0 H: 10-2</td>
<td>0-60</td>
</tr>
</tbody>
</table>

*In O-1 cm⁻¹ mol⁻¹; measured in CH₂Cl₂ (10⁻⁸) at 298 K. ** Experimental molecular weight (acetone). ° Calc. molecular weight.

line simulated spectra were then superimposed with suitable weighting for intensities and the results plotted out on the line printer; e.g., a doublet was considered as two two-site exchanges of intensity ratio 1:1.

Experimental spectra were fitted to the computed spectra by finding the best fit between the ratio of maximum to minimum heights in the multiplet and the life-times so obtained were used to construct Arrhenius plots in which straight lines were fitted by the least-squares method. Broadening of the lines due to effects other than exchange (e.g., increased viscosity and lower solubility at lower temperatures) had to be taken into account, otherwise values of the life-times particularly at lower temperatures were artificially enhanced. This was accomplished by measuring the natural linewidth at both the high- and low-temperature limits and then using these different values in the regions near these limits. A similar technique has been used elsewhere. Final activation parameters, obtained by the usual methods, are shown in Table 2 along with assessed error limits.

**Bis(dimethylphosphinodithioato)platinum(II).** — Potassium tetrachloroplatinate(II) (500 g, 12.0 mmol) in a minimum volume of hot water was shaken with an excess of sodium dimethylphosphinodithioato dihydrate (4.40 g, 24.0 mmol) for several minutes. The immediate yellow-orange precipitate which formed was filtered off, washed with water, methanol, and diethyl ether and recrystallized from chloroform (Yield 4-25 g, 80%). (Found: C, 10-7; H, 2-6. Calc. for C_{12}H_{12}P_{2}S_{2}: C, 10.3; H, 1.0%). The same compound was prepared independently by Cavell et al. and the electronic, i.r., and mass spectra are thoroughly discussed in their paper.

**Bis(dimethylphosphinodithioato)(triphenylphosphine)platinum(II).**—The complex [Pt(S_{2}PMe_{2})] was suspended in benzene or chloroform and treated with a 1:1 molar ratio of triphenylphosphine. On warming gently, a yellow solution was formed which was filtered, concentrated, and the product precipitated by addition of pentane. The yellow complex was recrystallized from chloroform-pentane. In a similar manner, bis(dimethylphosphinodithioato)(methyldiphenylphosphine)platinum(II), bis(dimethylphosphinodithioato)(dimethylphenylphosphine)platinum(II), and bis(dimethylphosphinodithioato)(pentafurorophenyl(diphenylphosphine)platinum(II)) were prepared.

**Bis(dimethylphosphinodithioato)(triphenylarsine)platinum(II).**—A suspension of [Pt(S_{2}PMe_{2})] in benzene or chloroform was treated with an excess of triphenylarsine. On concentration and addition of pentane, the complex was precipitated as a yellow powder which was filtered, washed with light petroleum, and air-dried. The products with triethylarsine and triethylphosphine were too soluble to isolate and with pyridine and ammonia only starting material was isolated on removal of the solvent.

**Bis(dimethylphosphinodithioato)platinum(II) and (Tetraphenylborate).** — A suspension of the complex [Pt(S_{2}PMe_{2})] in methanol was gently warmed with excess of triphenylphosphine (ca. 1:3 molar ratio), then filtered, and a concentrated methanolic solution of sodium tetraphenylborate added, giving an immediate pale yellow precipitate. Recrystallisation from acetone gave the crystalline product. The same method was used to prepare all the complexes [M(S_{2}PMe_{2})(PR_{3})] X (X = Br{sub 2}H_{5}, or PF{sub 6} ; M = Pt or Pd) listed in Table 4, and also [Pt(S_{2}PMe_{2})(AsPr_{3})] Br{sub 4} and [Pt(S_{2}PMe_{2})(PF{sub 6})] Br{sub 4}. However, for M = Pd and PR_{3} = PPh_{3}, reaction in very concentrated methanolic

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**Bis(dimethylphosphinodithioato)(triphenylphosphine)platinum(II) was prepared as for the complex [Pt(S_{2}PMe_{2})]PF{sub 6}.**

1H N.m.r. spectrum (301 K): τ 2-60 (phenyl multiplet); 8-06 (CH_{2}, f_{J=0-11}, 11-0 Hz); and 8-82 (CH_{2}, f_{J=0-11}, 7-0 Hz, f_{J=0-11}, 21-0 Hz). On cooling, some broadening of the CH_{2} and CH_{2} resonances at 203 K occurred indicating still rapid unidentate–bidentate exchange at this temperature. I.r. spectrum (650—550 cm{sup -1}): 590s and 572w, sh cm{sup -1}.

**Bis(dimethylphosphinodithioato)platinum(II).** — Method (A). Palladium(II) acetate was dissolved in benzene-acetone and heated under reflux for 2 h with a slight excess of sodium dimethylphosphinodithioato dihydrate in methanol. On cooling, the dark red-brown crystalline powder was filtered off and washed with water, methanol, and diethyl ether (Found: C, 13-9; H, 3-4. Calc. for C_{12}H_{12}P_{2}S_{2}: C, 18-3; H, 3-4%).

**Method (B).** Palladium(II) chloride was suspended in acetone and heated under reflux for 3 h with an excess of NaS_{2}PMe_{2}2H_{2}O. The resulting orange-red solution was filtered and, on cooling, deposited the orange-red crystalline product which was purified as before.

Although the products formed by these methods are different in colour they had the same i.r. and mass spectra and behaved in the same way with tertiary phosphines. Spectral parameters are reported elsewhere.

**Bis(dimethylphosphinodithioato)(triphenylphosphine)platinum(II).** — A suspension of the complex [Pt(S_{2}PMe_{2})] in benzene was treated with an excess of triphenylphosphine (ca. 1:2 molar ratio). On warming gently, a dark red solution was obtained which, on addition of pentane, precipitated the orange-yellow product which was recrystallized from chloroform. A similar method was used to make the complexes [Pd(S_{2}PMe_{2})(F_{2}PMePh)] and [Pd(S_{2}PMe_{2})(PF_{3}Ph)].

**Bis(dimethylphosphinodithioato)bis(triphenylphosphine)platinum(II).** — A suspension of the complex [Pt(S_{2}PMe_{2})] in a small amount of methanol was treated with triphenylphosphine (1:4 molar ratio). The mixture was boiled for 2 min, filtered, and then an excess of diethyl ether was added. The resulting yellow-buff precipitate was filtered off, washed with light petroleum, and dried in vacuo (40 °C). (Dimethylphosphinodithioato)bis(methyldiphenylphosphine)platinum(II) dimethylphosphinodithioato was prepared in a similar manner. The ionic triphenylphosphine complex readily reverted to [Pt(S_{2}PMe_{2})PF_{6}] on attempted recrystallisation; in contrast, the ionic methyldiphenylphosphine complex was unchanged, even on recrystallisation from such non-polar solvents as benzene or chloroform. Attempts to prepare pure samples of the corresponding palladium complexes proved unsuccessful; only mixtures of 1:1 and 1:2 adducts were formed which rapidly reverted to the pure 1:1 complexes even in acetone.

**Bis(dimethylphosphinodithioato)bis(triphenylphosphine)platinum(II) and (Tetraphenylborate).** — A suspension of the complex [Pt(S_{2}PMe_{2})] in methanol was gently warmed with excess of triphenylphosphine (ca. 1:3 molar ratio), then filtered, and a concentrated methanolic solution of sodium tetraphenylborate added, giving an immediate pale yellow precipitate. Recrystallisation from acetone gave the crystalline product.

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solution using a large excess of triphenylphosphine gave instead a yellow crystalline precipitate of tetraakis(triphenylphosphine)palladium(0), m.p. 103—105 °C (lit., 14 100—105 °C) (Found: C, 74.7; H, 5.1. Calc. for C73H58P2Pd: C, 75.1; H, 5.2%).

(Dimethylphosphinodithioato)bis(triphenylphosphine)platinum(II) Chloride.—The complex [Pt(S2PMe3)(PPh3)2]—BPh4 (0.20 g) was dissolved in chloroform (10 cm3) and treated with Ph4AsClHCl (0.07 g) (1:1 mole ratio) in chloroform (5 cm3). The mixture was stirred for 10 min, the precipitate of Ph4AsBPh4 filtered off, the solution concentrated, and diethyl ether—pentane added to precipitate the complex as a white powder, which was recrystallised from chloroform—pentane. The complexes [Pt(S2PMe3)(PPh3)2]Y (Y = Br− or I−) were made in similar manner.

Chloro(dimethylphosphinodithioato)triphenylphosphinepalladium(II).—The complex [Pd(S2PMe3)(PPh3)2]BPh4 was dissolved in chloroform (containing ethanol stabiliser), warmed briefly, and then set aside (ca. 5—10 min) until the conductivity of the solution was very low (ca. 0.6 μΩ−1). Precipitation with pentane then gave the orange yellow product, which was recrystallised from benzene—pentane. The same complex was obtained much more slowly from dichloromethane solution.

Bromo(dimethylphosphinodithioato)triphenylphosphinepalladium(II) was prepared in analogous fashion using CHBr3 or CH2Br2 plus ethanol (ca. 2%) as solvent, the reaction taking ca. 30 min for completion. The complex [Pd(S2PPh2)(Cl)PPh3] was similarly prepared from [Pd(S2PPh2)(PPh3)2]BPh4 and chloroform.

We thank Johnson Matthey Ltd. for loans of potassium chloroplatinate(II) and palladium(II) chloride, the S.R.C. for an award (to D. F. S.), and the Atlas Computer Laboratory for a copy of their Shape Function program.

[3/539 Received, 13th March, 1973]

Metal Complexes of Sulphur Ligands. Part V.¹,² Dialkyl-, Diaryl-phosphinodithioato-and \( \mu/N\)-Dialkyldithiocarbamato-complexes of Ruthenium(II)

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Complexes of general formula \([\text{Ru}((S-S)_2L_2)]((S-S)^- = -S_2PR_2 (R = \text{Me}, \text{Et}, \text{Ph}), -S_2CNMe_2; \quad L = \text{PPh}_3, \text{PMe}_3\text{Ph}, \text{PMePh}_2, \text{P(OEt)}_2 \text{etc.}\) have been synthesised by the reaction of various ruthenium(II) and (III) tertiary phosphine and phosphate complexes with Na(S-S). For \((S-S)^- = -S_2PR_2\), these compounds are readily carbonylated to give the monokarbynyls \([\text{Ru}((S-S)_2)_{L}((CO))].\) However, the dicarbynyls can be synthesised directly, from ruthenium carbonyl halides and NaS-S-PR_2. Although the corresponding dithiocarbamates are resistant to carbonylation, \(\text{all these compounds undergo ligand exchange reactions with ligands of greater basicity (L') to give either [Ru(S-S)_2L'] and/or [Ru(S-S)_2L'_{1.2}].}\) All these complexes have been thoroughly examined by l.r., mass, and \(^1\)H n.m.r. spectroscopy and the latter indicates a cis-configuration. Most of these compounds also show temperature variable \(^1\)H n.m.r. spectra, attributable to facile interconversion of optical enantiomers (for the \(-S_2PR_2\) compounds), restricted rotation about the \(-CN\) bond (for the \(-S_2CNMe_2\) compounds), and, in some cases, hindered rotation about the ruthenium–phosphorus bonds.

Finally, for \([\text{Ru}((S-S)_2)_{L}((PMe_3\text{Ph}))],\) carbonylation gives, in addition to \([\text{Ru}((S-S)_2)_{L}((PMe_3\text{Ph}))_{(CO)}],\) two isomers of formula \([\text{Ru}((S-S)_2)_{L}((PMe_3\text{Ph}))_{(CO)}].\) The structures of these complexes have been established by \(^{1}\)H, \(^{31}\)P n.m.r. and double resonance studies and a general mechanism of carbonylation for these compounds is proposed.

In Parts I—IV of this series, the results of a thorough investigation of the reactions of the square-planar \([M(S-S)_2] \text{compounds [M = Pt, Pd; (S-S)^- = -S_2PR_2 (R = Me, Et, Ph), -S_2CNR_2 (R = Me, Et), -S_2COEt, and -S_2P(OEt)_2 with ligands containing Group Va donor atoms (L') have been presented.}\) A detailed analysis, utilising X-ray diffraction, spectroscopic, and chemical techniques, revealed that reaction occurs by stepwise cleavage of the metal–sulphur bonds of one dithio-ligand, giving the compounds \([M(S-S)_2L] \text{and [MS(S-S)] (S-S) with unidentate–bidentate and bidentate–ionic co-ordination respectively. In addition, these compounds were shown to exhibit several different types of intra- and inter-molecular rearrangement reactions, depending on the nature of the dithioligand, the solvent, and the temperature at which the reactions were studied.}\)

In view of these unusual results, it was decided to extend the investigation to a study of other platinum metal dithiocarbamate complexes and in this and the following papers, we wish to report the full results of our recent ruthenium–sulphur studies. Later papers will discuss related investigations into rhodium– and osmium–sulphur chemistry.

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RESULTS AND DISCUSSION

Although there has recently been an increasing interest in the chemistry of ruthenium as well as in the chemistry of complexes of sulphur-containing ligands with various metals, research into ruthenium complexes containing dithiolato ligands has been confined to relatively few papers and most of these have been concerned with complexes containing NN-dialkyl dithio-carbamato-groups. Thus, complexes such as [Ru(S₂CNRR')₃] (R = R' = Me, Et, Bu,⁶ R = Me, R' = PhCH₂), [Ru(S₂CN(PhCH₂)(CO)₂]Cl,⁸ [Ru(S₂CN(CH₂))₂CO] (R = Me, Et),⁸ [Ru(S₂CNR₂)₂(CO)] (R = Me, PhCH₂),⁹ [Ru(S₂CNR₂)₂(PPh₂)] (R = Me, Et, Ph),⁹ [Ru(S₂CN(Ph)(Me₂SO)]₄,¹⁰ [Ru(S₂CNR₂)₂(S₂CNPh₂)] (R = R' = Me, Et; R = Me, R' = Ph),¹¹ and [RuNO(S₂CNCH₃)] (R = Me, Et)¹² have all been reported but the last is the only example to date of a ruthenium compound containing a danging dithiolato group. Related 1,2-dithiole complexes of ruthenium of type [Ru(S₂C(Ph₃)₄)(CO)]₂(ER₃)ₙ (n = 2, 0; E = P, As) have also been recently reported.¹³

In contrast, apart from brief references to the synthesis of [Ru(S₂PR₂)] (R = Et,¹⁴ Ph,¹⁵) no investigation of ruthenium dialkyl (or diaryl) phosphinodithioates has been made.

By analogy with our earlier palladium and platinum studies,¹⁶ our first attempts to synthesise a range of ruthenium dithiolato compounds were made either by reacting tertiary phosphines directly with [Ru(S₂PR₂)] or by refluxing an ethanolic solution of RuCl₃·H₂O, Na₂S₂PR₂, and PMe₃Ph. In both cases, the main product was [Ru(S₂PR₂)], which provides an effective demonstration of the substitutional inertness of the ruthenium(III) (d⁵) co-ordination sphere in this instance. Therefore, we tried another method, which has been successfully used to prepare other metal dithiolato complexes; namely, direct reaction between metal halogeno-complexes and an alkali metal salt of the appropriate dithiolato.

\[ \text{C₅H₅Fe(CO)}₂\text{Cl} + \text{NaS₂CNMe₂} \rightarrow \]

Thus, when [RuCl₃(PPh₃)₃] or [RuCl₃(PPh₃)₂MeNO₂],¹⁷ [RuCl₃(PPh₃)₃],¹₈ [RuCl₃(PPh₃)₂PMe₃][,¹₉]

* Shorter reaction times with stoichiometric amounts of NaS₂PR₂ give paramagnetic species which have not been completely characterised to date.


or mer-[RuCl₃(PMe₆Ph₃)] are gently refluxed in ethanol with an excess of NaS₂PR₂ (R = Me, Et, Ph) for ca. two hours and the solutions are precipitated. This form of ruthenium chloride red or orange crystals of composition [Ru(S₂PR₂)]₂L (L = tertiary phosphine) are precipitated. Simpler compounds are formed using acetone or methanol as solvent, except for [RuCl₃(PMe₆Ph₃)]Cl in methanol when a red solid, believed to be of composition [RuCl₃(PMe₆Ph₃)]₂S₂PR₂ is precipitated. Similar compounds can be obtained by pyrolys of [RuCl₃(PR₃)]₂S₂PR₂ (cf. the pyrolysis of [RuCl₃(PPh₃)₂C]Cl giving [RuCl₃(PPh₃)₂C]Cl) and these will be discussed in more detail in a later publication.¹³ In this instance, the dimer is readily separated from [Ru(S₂PR₂)]₂(PMe₆Ph₃) by the technique of dry column chromatography.²² For [RuCl₃(PPh₃)] and NaS₂PPh₃, [Ru(S₂PR₂)]₂(PPh₃) is only obtained in pure form in the presence of an excess of triphenylphosphine; with no added triphenylphosphine, analytical and molecular weight data (see Experimental section) indicate that a mixture of [Ru(S₂PR₂)]₂(PPh₃) and [Ru(S₂PR₂)₂PPh₃] is probably formed. (cf. the formation of mono- and bis-carbonyldithio-carbamato-ruthenium complexes ⁸ and [RuCl₃(PPh₃)] (n = 3 or 4) ¹⁰ by slight changes in the experimental conditions.) However, by reaction in the presence of an excess of sulphur (an efficient tertiary phosphine scavenger), pure [Ru(S₂PR₂)]₂(PPh₃) can be isolated.

Compounds (A) have been characterised by elemental analyses (Table 1) and the usual spectroscopic methods (see later), and the monomeric formulation confirmed by osmometry and by an X-ray analysis on [Ru(S₂Ph₂)₃(PMe₆Ph₃)]. The compounds are non-electrolytes and diamagnetic (by Evans’ method),²⁰ and exhibit sharp H. m.r. resonances. However, exposure of the solutions to air rapidly produces broadening of the n.m.r. signals which is attributed to facile oxidation to paramagnetic ruthenium(III) species. The rate of oxidation, which can be substantially reduced by


For details see: B. Leov and M. M. Goodman, Chem. and Ind., 1967, 2926.

addition of an excess of tertiary phosphone, is also dependent on the nature of L, a qualitative order being PPh₃ > PMePh₃ > PMe₃Ph. The solvent medium is also important, since studies indicate that increasing the percentage of CDCl₃ in CDCl₃–CS₂ mixtures increases the rate of oxidation.

In the reaction of [RuCl₂(P(OPh)₃)₃] with an excess of Na₂P₃R₂, the product formed depends critically upon both reaction time and solvent medium. Thus, interpretation, the ¹H n.m.r. spectrum of the mixture shows two sets of ethyl resonances of approximate intensity 3 : 1 (the ratio varied from sample to sample) attributable to the mono- and bis-ethoxy phosphite complexes respectively. The experimental carbon and hydrogen percentages for the mixture are also in good agreement with calculated data based on this ratio.

Further refluxing (24 h) gives a yellow solution from which no solid product could be isolated but a mass

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M. p. (°C)</th>
<th>Found %</th>
<th>Required %</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(P(OPh)₃)]</td>
<td>Red-brown</td>
<td>139 – 142</td>
<td>54.7 4.7</td>
<td>61.8 a</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(PMePh₂)]</td>
<td>Orange</td>
<td>279 – 280(d)</td>
<td>57.8 5.0</td>
<td>47.9 5.1</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(PMe₃Ph)]</td>
<td>Orange</td>
<td>212(d)</td>
<td>38.3 5.2</td>
<td>38.3 5.4</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(PMe₃Ph)]</td>
<td>Orange</td>
<td>215 – 216(d)</td>
<td>49.3 4.6</td>
<td>75.3 ± 0.8</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(PMe₃Ph)]</td>
<td>Orange</td>
<td>214 – 215</td>
<td>49.3 4.9</td>
<td>49.3 5.4</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(PMe₃Ph)]</td>
<td>Orange</td>
<td>214</td>
<td>59.1 5.4</td>
<td>59.1 5.5</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(PMe₃Ph)]</td>
<td>Red</td>
<td>164 – 166(d)</td>
<td>39.1 5.0</td>
<td>39.1 5.0</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₃(PMe₃Ph)]</td>
<td>Red</td>
<td>204 – 206</td>
<td>42.8 5.5</td>
<td>42.8 5.5</td>
</tr>
</tbody>
</table>

| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Yellow | 160 – 162 | 42.8 5.5 | 42.8 5.5 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 182 – 184 | 51.7 4.7 | 51.7 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |
| trans-[Ru(S₂CNMe₂)₃(PMe₃Ph)] | Orange | 234 – 235 | 44.4 4.7 | 44.4 4.7 |

* Molecular weight measured osmotically at 37° in benzene. * Molecular weight from parent ion peak (¹⁰⁶Ru isotope) in mass spectrum. * Sublimes at 180 °C. * Configuration C. * Configuration D. / Sublimes at 170 °C.

in refluxing ethanol for one hour, reaction with an excess of Na₂P₃Me₂ gives a sample of [Ru(S₂PMe₂)₃(P(OPh)₃)]₂. However, if refluxing is continued for a further hour, a mixture of products is obtained which proved impossible to separate by chromatographic or sublimation techniques. However, the mass spectrum of the mixture reveals the parent ion and fragmentation pattern. Peaks expected for [Ru(S₂PMe₂)₃(P(OEt)₃)OPh₃]₂ together with a peak at m/e 780 [¹⁰⁶Ru isotope] which can only arise from the species [Ru(S₂PMe₂)₃(P(OEt)₃)OPh₃]₂ since there is no way of obtaining a fragment of this mass number by degradation of [Ru(S₂PMe₂)₃(P(OEt)₃)OPh₃]. Consistent with this interpretation, the ¹H n.m.r. spectrum of the resultant oil shows peaks attributable to [Ru(S₂PMe₂)₃(P(OEt)₃)OPh₃]₂, together with a number of other tertiary phosphite compounds (see Experimental section). However, if the reaction between [RuCl₂(P(OPh)₃)] and excess Na₂P₃Me₂ is carried out in refluxing methanol, even for comparatively short reaction times, a pure sample of [Ru(S₂PMe₂)₃(P(OPh)₃)]₂ can be isolated and phenol and trimethyl phosphite can be identified in the filtrate. All these phosphite compounds are more resistant to oxidation in solution than the corresponding tertiary phosphite complexes.

Muecktteres et al.²³ have reported that triphenyl phosphinite, when co-ordinated to ruthenium, does not suspended.

appear to undergo transesterification by alcohols, whereas such reactions readily occur with the free ligands. Therefore, at first sight, the transesterification of the tertiary phosphine groups in [Ru(S₂PR₂)₆(CO)₆] appears surprising. However, since the starting material has four phosphines per ruthenium and the product only two, then two must be released during the reaction, presumably as free tertiary phosphine. This free triphenylphosphine may then be transesterified giving, in the case where methanol is solvent, trimethylphosphine. The trimethylphosphine, being a stronger nucleophile than its triphenyl analogue (as well as less bulky), can then replace the co-ordinated P(OPh)₃ groups to give [Ru(S₂PR₂)₆(P(OMe)₃)]₆. This conclusion is supported by the observation that [Ru(S₂PR₂)₆(P(OPh)₃)]₆ may be recovered unchanged after refluxing in degassed methanol for 24 h. Presumably the ease of formation of the P(OMe)₃ complex, compared with the P(OEt)₃ complex, is a reflection of the greater nucleophilicity of the methoxide ion compared to the ethoxide ion.

Finally, reaction of mer-[RuCl₆(PMe₃)₃] with an excess of Na₃S₂CNMe₃ gives [Ru(S₂CNMe₃)(PMe₃)]₆, analogous to the triphenylphosphine complex reported elsewhere.

Reactions of [Ru(S-S)₆L₄] Complexes.—All the compounds of type (A) readily react with carbon monoxide under very mild conditions to give the monocarbonyl species [Ru(S₃PR₃)₆L₄(CO)] (B). For L = PPh₃, AsPh₃; R = Me, the same compounds are also formed by prolonged interaction of cis-[RuCl₄(CO)₂]₄ with Na₃S₂CNMe₃. In contrast, in agreement with earlier work, attempted carbylation of the corresponding [Ru(S₃CNMe₃)₆(PR₃)₄] compounds (PR₃ = PMe₃, PPh₃), even under pressure, gives only unchanged starting material. Furthermore, attempts to displace the remaining L group from [Ru(S₃PR₃)₆L₄(CO)] to give [Ru(S₃PR₃)₆CO]₄ have also proved unsuccessful. However, the dicarbonyl complexes [Ru(S₃PR₃)₆CO]₄ (R = Me, Ph) have been synthesised from C₆H₅[RuCl₆]·2CO and from [Ru(CO)₄]₂, Ph₃PS₄H combinations respectively. Similarly, reaction of [Ru(S₃CNMe₃)₆] with tetramethylium disulphide gives the previously characterised [Ru(S₃CNMe₃)₆(CO)]₄. A small amount of this product is also formed by prolonged reaction of cis-[RuCl₄(CO)₂(PPh₃)]₄ with Na₃S₂CNMe₃. Although [Ru(S₃CNMe₃)₆(CO)]₄ does not react with PR₃, the corresponding [Ru(S₃PR₃)₆(CO)]₄ are readily converted to [Ru(S₃PR₃)₆(PC₃R₃)]₄. Thus, it appears that the products [Ru(S₃PR₃)₆L₄(CO)] are thermodynamically very stable, being readily formed from

[Ru(S₃PR₃)₆L₄] or [Ru(S₃PR₃)₆(CO)]₄, whereas with (S-S) = S₂CNMe₃ no evidence has been found for the mixed species. For L = PMe₃, reaction of [Ru(S₃PR₃)₆(PMe₃)] and carbon monoxide gives, in addition to [Ru(S₃PR₃)₆(PMe₃)CO]₄, two other complexes which both analyse for [Ru(S₃PR₃)₆(PMe₃)CO]. Compounds of this type have not been observed with other tertiary phosphines. A detailed spectroscopic analysis of these compounds, together with proposed structures and a possible general mechanism for these carbonylation reactions are presented later in this paper.

All the [Ru(S-S)₆L₄] compounds undergo ligand exchange reactions with other phosphorus ligands of greater basicity. Thus, for [Ru(S₃PR₃)₆L₄] where L = PPh₃ or PMe₃, reaction with PMe₃ gives [Ru(S₃PR₃)₆L₄]; similarly, both L groups are displaced by L' when L = PF₃, L' = PPh₃ and also with [Ru(S₃CNMe₃)₆(PC₃R₃)] and an excess of PPh₃, [Ru(S₃CNMe₃)₆(PMe₃)] is exclusively formed. These results can be readily rationalised on the basis that the compounds [Ru(S-S)₆L₄] are both sterically and electronically favoured compared with the mixed ligand complexes [Ru(S-S)L₄]. However, when the phosphine complexes are treated with P(OPh)₃, steric effects become more important. Thus, [Ru(S₃PR₃)₆(PMe₃)₂] and P(OPh)₃, give only the mixed ligand complex [Ru(S₃PR₃)₆(PMe₃)(P(OPh)₃)], whereas with [Ru(S-S)₆(PPh₃)] (S-S = S₂CNMe₃), both [Ru(S-S)₆(PPh₃)(P(OPh)₃)] and [Ru(S-S)₆(P(OPh)₃)] can be isolated, the amount of each depending on the conditions employed. This is presumably because there is a fine balance between the large difference in basicity of PPh₃ and P(OPh)₃ (which will favour the bis-phosphine complex) and the greater steric crowding in the bis-phosphine complex compared to the mixed phosphine-phosphate species.

Spectroscopic Properties of Dithioacids Complexes.—
(a) Infrared spectra. The i.r. spectra of all the complexes reported are rather complicated, showing absorptions due to the tertiary phosphine or phosphate groups, as well as the phosphinodithioate ligands. However, a recent paper from this laboratory indicates that for platinum and palladium(II) diphosphinodithioate complexes there appears to be an empirical i.r. method of distinguishing between bidentate, monodentate, and tridentate co-ordination of the S₂Ph₂ group. Thus, bidentate co-ordination is characterised by two bands at 603.570 cm⁻¹, ionic, 650.650 cm⁻¹; and unidentate, 645.540 cm⁻¹. Similarly, platinum and palladium(II) dimethylphosphinodithioates have characteristic bands at 570–585 cm⁻¹ (bidentate); 610 cm⁻¹ (ionic); and 600 cm⁻¹ (unidentate). In this instance, the lower energy band (ca. 500 cm⁻¹) is masked by strong ligand vibrations.

An examination of Table 2 reveals that all the [Ru]...
(S₂PR₃)₂L and [Ru(S₂PR₃)₂LL⁻] complexes contain only i.r. absorptions characteristic of bidentate S₂PR₃ co-ordination. Similarly, in spite of complications arising from the presence of carbonyl bending modes (3)(CO) in the region 600–600 cm⁻¹, all the compounds of type [Ru(S₂PR₃)₂L(CO)] and [Ru(S₂PR₃)₂(CO)] show only 'bidentate' S₂PR₃ co-ordination. The latter also have two ν(CO) bands indicating a cis-configuration. For the compounds [Ru(S₂PR₃)₂(PMe₃Ph)CO], in addition to the 'bidentate' bands, there are absorptions at 645,549 cm⁻¹ (S₂PPh₃) and ca. 600 cm⁻¹ (S₂PMes), indicative of unidentate co-ordination only for the tertiary phosphine, parent ion peaks together with fragmentation patterns corresponding to loss of carbonyl, loss of tertiary phosphine, and loss of both carbonyl and phosphine groups are observed. There are also metastable ions corresponding to the loss of carbonyl groups and, in some cases, doubly positively charged species [Ru(S₂PR₃)₂L]²⁺ are observed. For the [Ru(S₂PR₃)₂(PMe₃Ph)CO] complexes, exactly the same parent ion and fragmentation pattern is observed as for [Ru(S₂PR₃)₂(PMe₃Ph)CO] due to ready loss of a PMe₃Ph group. The phosphine complexes containing a carbonyl group give more complicated mass spectra.

**Table 2**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bidentate</th>
<th>Unidentate</th>
<th>ν(CO)(cm⁻¹)</th>
<th>3(3)(CO)(cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Ru(S₂PMe₃)₂(PPh₃)₂]</td>
<td>583</td>
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<td></td>
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</tr>
<tr>
<td>cis-[Ru(S₂PMe₃)₂(PMe₃Ph)₂]</td>
<td>583</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₃)₂(PMe₃Ph)₃]</td>
<td>589</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PMes)₂(PPh₃)₂]</td>
<td>589</td>
<td></td>
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</tr>
<tr>
<td>cis-[Ru(S₂PMes)₂(PMe₃Ph)₂]</td>
<td>589</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PMes)₂(PMe₃Ph)₃]</td>
<td>589</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PMes)₂(PMe₃Ph)CO]</td>
<td>589</td>
<td>579</td>
<td>600</td>
<td>1933 (1945)²</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMes)₂(PMe₃Ph)CO]²⁻</td>
<td>589</td>
<td>598</td>
<td>1939, 7299, (1940)²</td>
<td>569</td>
</tr>
<tr>
<td>[Ru(S₂PMe₃)₂(PMe₃Ph)CO]</td>
<td>589</td>
<td>598</td>
<td>1961, 1944, (1967)²</td>
<td>569</td>
</tr>
<tr>
<td>[Ru(S₂PMe₃)₂(PMe₃Ph)CO]²⁻</td>
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<td>598</td>
<td>1984, 1970, 1970</td>
<td>569</td>
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<tr>
<td>cis-[Ru(S₂PMe₃)₂(PMe₃Ph)CO]</td>
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<tr>
<td>cis-[Ru(S₂PMe₃)₂(PMe₃Ph)CO]²⁻</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PMes)₂(PMe₃Ph)CO]</td>
<td>581</td>
<td>598</td>
<td>1985, 1938</td>
<td>563</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMes)₂(PMe₃Ph)CO]²⁻</td>
<td>581</td>
<td>598</td>
<td>1945, 1969, 1970</td>
<td>569</td>
</tr>
<tr>
<td>cis-[Ru(S₂PPh₃)₂(PPh₃)₂]</td>
<td>605, 572, 568</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PPh₃)₂(PMe₃Ph)₂]</td>
<td>605, 570</td>
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<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PPh₃)₂(PMe₃Ph)₃]</td>
<td>611, 573</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PPh₃)₂(PMe₃Ph)CO]</td>
<td>611, 579</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PPh₃)₂(PMe₃Ph)CO]²⁻</td>
<td>607, 556</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>cis-[Ru(S₂PPh₃)₂CO]</td>
<td>608, 565</td>
<td></td>
<td></td>
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</tbody>
</table>

* Measured in CHCl₃ solution. ² Configuration C. ³ Configuration D. ⁴ Measured in CDCl₃ solution.

The presence of a carbonyl bending vibration in this region is a complicating factor. However, in spite of this, the data in Table 2 clearly indicate the generality of these empirical methods for distinguishing between different types of S₂PR₃ co-ordination in platinum metal complexes.

(b) Mass spectra. The complexes of formula [Ru(S₂PR₃)₂(PR₃)₂] are all of high m.p. and decompose at low enough temperatures to make it impossible to obtain mass spectra for these complexes. However, the phosphine-phosphite and bis-phosphite compounds are more volatile and excellent mass spectra may be recorded at ca. 440 K. These consist of well defined parent ion peaks together with fragmentation patterns e.g. the spectrum of [Ru(S₂PMe₃)₂(P(OPh₃)₃)] (Table 3) which shows successive loss of methyl groups and oxygen atoms from the phosphite groups.

The carbonyl-containing compounds [Ru(S₂PR₃)₂L(CO)] and [Ru(S₂PR₃)₂(PMe₃Ph)CO] are also more volatile than their bis-phosphine parent compounds and thus give reasonable mass spectra. For L = (c) ¹H N.m.r. spectra. (i) Complexes of formula [Ru(S₂PR₃)₂L₃]. For L = PMe₃Ph₂ or PMe₃Ph, the room temperature resonance arising from the methyl groups on the phosphines (a H₃PPH₃) are second-order type
spectrum \( n = 3 \) or 6 \(^{20}\) consists of a sharp doublet with a broad hump situated between the doublet \(^\star\) (see Table 4).

**Table 4**

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<th>Mass no. of (^{103})Ru peak</th>
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<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^-)</td>
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<tr>
<td>662</td>
<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^+)</td>
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<tr>
<td>635 (metastable)</td>
<td>690 (\rightarrow) 662 (\rightarrow) 635</td>
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<tr>
<td>597</td>
<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^-)</td>
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<tr>
<td>569</td>
<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^+)</td>
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<tr>
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<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^+)</td>
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<tr>
<td>476</td>
<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^-)</td>
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<tr>
<td>432 (metastable)</td>
<td>662 (\rightarrow) 537 (\rightarrow) 476</td>
</tr>
<tr>
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<tr>
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<td>352</td>
<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^-)</td>
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<tr>
<td>331</td>
<td>([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^+)</td>
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\(^\star\) All peaks show the characteristic ruthenium isotopic pattern.

Figure 1b). Comparison with other similar ruthenium tertiary phosphine complexes is of interest. Thus, for \(\text{trans}[\text{RuCl}_2\text{L}(\text{PMe}_2\text{Ph})_2]\), the \(^1\text{H}\) n.m.r. spectrum consists of a 'virtually' coupled 1,2,1 triplet from the \(\text{trans}\) phosphines and a doublet arising from the \(\text{cis}\) phosphine, due to the fact that in this compound \(J(\text{PP})(\text{trans})\) is very large and \(J(\text{PP})(\text{cis})\) is effectively zero. \(^{20}\) However, in some complexes, where the \(\text{cis}\)-phosphines are in equivalent chemical environments similar in shape to those observed here for \([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^-\) (L = PMe_2Ph, PMePh_2). This however is not true in every case, e.g. the \(\text{cis}\)-phosphines in \(\text{cis}[\text{RuCl}_2\text{L}(\text{PMe}_2\text{Ph})_2]\) (which are also in equivalent chemical environments) give rise to a single sharp doublet \(^{20}\) \([\text{i.e.} J(\text{PP})\text{ is effectively zero}]. Thus, the pseudo-triplet pattern could arise either from \(\text{cis}\)-phosphines with a relatively large \(J(\text{PP})\) or \(\text{trans}\) phosphines with a relatively low \(J(\text{PP})\) \(^{20}\) and hence no definitive conclusion about stereochemistry can be drawn from these peak contours at room temperature.

However, on cooling the PMe_2Ph complex, the methyl resonance signal broadens and at 250 K consists of two pseudo-triplets separated by ca. 13 Hz (Figure 1c); raising the temperature reverses the process. The

![Diagram](image_url)

**Figure 2** Diagrammatic representation of \(\text{cis}\)-configuration for \([\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\text{(OPh)}_3\text{CO}]^-\)

best explanation for these observations is that the complex has a \(\text{cis}\)-configuration and at lower temperatures rotation about the ruthenium–phosphorus bond is slowed down sufficiently for the inequivalence of the chemical environments of the two methyl groups (a and b) to be seen in the n.m.r. spectrum (Figure 2). This phenomenon has also been noted for the \(\text{trans}\) phosphines of \(\text{cis}[\text{RuCl}_2\text{L}(\text{PMe}_2\text{Ph})_2]\). \(^{29}\) If \(A = \text{PMe}_2\text{Ph}\) had a \(\text{trans}\)-configuration, then the two methyl groups on the one PMe_2Ph ligand would be in identical chemical environments, giving rise to one resonance, irrespective of the rate of rotation about the ruthenium–phosphorus bond. For \(L = \text{PMe}_2\text{Ph}\), the similarity of the shape of the pseudo-triplet to that for \(L = \text{PMe}_2\text{Ph}\), and for \(L = \text{P}(\text{OMe})_3\), the close similarity of the observed second-order spectrum with that obtained for \(\text{cis}[\text{PtX}_2\text{L}(\text{P}(\text{OMe})_3)_2]\) \(^31\) is further evidence for \(\text{cis}\)-stereochemistry in these compounds.

However, full confirmation of \(\text{cis}\) stereochemistry for all these tertiary phosphine and phosphite complexes comes from an examination of the low temperature \(^1\text{H}\) n.m.r. spectra of the methyl groups of the \(\text{S}_2\text{PMe}_2\) ligands. For \(\text{cis}[\text{Ru}(\text{S}_2\text{PMe}_2)\text{L}_2]\), two types of inequivalent dithiocarbamoyl methyl groups (c and d in Figure 2) are present, which should give two signals, each split into a doublet by the \(^31\text{P}\) nuclei, whereas for \(\text{trans}\) stereochemistry only one doublet should be observed. Experimentally, the low temperature \(^1\text{H}\) n.m.r. spectra of all the bis-phosphine and -phosphite compounds consists of two doublets, indicative of \(\text{cis}\)-stereochemistry,


at least at low temperature.* (See Figure 1c and Table 5.)

However, on warming to room temperature or above, these two doublets first coalesce and then sharpen to a single doublet [with a very similar J(PH)] (Figure 1a and Table 5). This process, which occurs at different rates for different L, is completely reversible. At first sight, these observations are consistent with either a reversible cis-trans isomerism or a rapid interconversion of the two possible optical enantiomers of the cis compounds at elevated temperatures. There are several reasons why the latter explanation is preferred. First, the shape of the resonance due to the methyl groups on the phosphines remains almost unchanged throughout the temperature changes whereas cis-trans isomerism should produce large changes in J(PP) and hence in the shape of this resonance.  

In general, it has been found that the more stable isomers of ruthenium complexes have a cis-configuration and that quite often on heating, the trans isomer undergoes an irreversible conversion to the cis isomer.  

This is the reverse of the behaviour found in these complexes. Furthermore, the related [Ru(S_2PR_2)(CO)] complexes, which have a cis configuration in both solid and solution state [two ω(CO)], show no evidence for formation of the trans isomer at higher temperatures (no change in i.r. spectra). Finally, the high temperature doublet is approximately halfway between the positions of the low temperature doublets, irrespective of L (Table 5). This phenomena is characteristic of a process such as rapid inversion which averages the two chemical environments of methyl groups c and d but not of an interconversion of geometrical isomers where it is extremely unlikely that the chemical shift of the methyl groups of the trans isomer will always coincide with the mean of those of the cis isomer.

Therefore, all the evidence suggests that the variation in H n.m.r. spectra of the complexes cis-[Ru(S_2PR_2)L_2] with temperature is due to the facile interconversion of optical isomers and the mechanism of this process is discussed in detail in Part VI.4

The chemical shifts of the methyl resonances of the dithio-ligands are also of interest in that the position of the lower field doublet remains almost unaltered by changing L whereas that of the higher field doublet is very sensitive to changes in L, varying from τ 8-08 (L = P(OMe)_3) to τ 8-94 (L = PPh_3) (Table 5). A possible explanation of this is that the lower field doublet arises from the methyl groups anti to the phosphorus ligands (d in Figure 2) and the higher field doublet from the methyl groups c syn to the phosphorus ligands. Then, the syn methyl groups will be influenced by the ring currents of the phenyl rings on the phosphine, causing them to be more shielded than the anti methyl groups which would account for their higher field position. Furthermore, increasing the number of phenyl groups on the tertiary phosphine will lead to increased shielding of the syn methyls, making them resonant at even higher fields. Similar effects have been observed in the compounds [M(S-S)-(PR_2)_2]BPPh_4 (M = Pt, Pd) (S-S = S_2PR_2, S_2CNR) where the R and R' resonances are shifted τ ca. 0-2—0-4 upfield with respect to their positions in the corresponding PF_6— and Cl—salts, 3,5 and also in recent studies on the interaction of benzene with arsenic, antimony, and bismuth diethiocarbamates.  

For L = P(OPPh)_3, the higher field doublet resonates at τ 8-35. This is lower than that in the PPh_3 complex, presumably because the phenyl groups are further away from the syn methyl groups, producing less efficient shielding.

(A) Complexes of formula [Ru(S_2PR_2)_2L(CO)] and [Ru(S_2PR_2)_2LL']. In all the [Ru(S_2PR_2)_2L(CO)] complexes the methyl group(s) of the phosphorus ligand produce a single doublet at high temperature in the H n.m.r., an observation consistent with either cis or trans stereochemistry. However, for L = PMe_2Ph,

Figure 3 Diagrammatic representation of cis-configuration for [Ru(S_2PMe_2)LL']. (a). L = PMe_2Ph, L' = P(OPh)_3; (b). L = P(OMe)_3, L' = CO; (c). L = PPh_3, L' = P(OPh)_3.

cooling produces broadening and then splitting into two overlapping doublets, a fact attributable to a cis-configuration and to slow rotation about the ruthenium—phosphorus bond at low temperatures. For the compounds [Ru(S_2PR_2)_2LL'], the methyl groups on the phosphine exhibit a single sharp doublet, which is temperature invariant [except for R = Ph, L = PMe_2Ph, L' = P(OPh)_3] (Table 5). However, as for the [Ru(S_2PR_2)L_2] compounds, examination of the S-PMe_2 resonances provides an unequivocal demonstration of cis-stereochemistry. If the complexes [Ru(S_2PMe_2)LL'] or [Ru(S_2PMe_2)L(CO)] had a trans configuration, the methyl groups of the dithiocarbamates would occupy two different chemical environments either syn to the ligand L or syn to L' (or CO), which would give rise to two signals each split into a doublet by coupling with a 31P nucleus. For a cis configuration, all four methyl groups will be in different chemical environments (Figure 3) and four resonances (each a doublet) should appear in the H n.m.r. spectrum.

At low temperature, the H n.m.r. spectra of all these complexes (with the exception of [Ru(S_2PMe_2)(P(OPh)_3)] and [Ru(S_2PMe_2)[P(OMe)_3]CO]) consists of four doublets arising from the S-PMe_2 groups.

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* X-Ray analysis has confirmed the cis-configuration for [Ru(S_2PPh_3)(PMe_2Ph)] 4 and the related compounds [Ru(HCS)S_2[PPh_3]] 32 and [Ru(pyS)(PPh_3)] 33 (pyS = pyridine-2-thiolato) also possess cis stereochemistry in the solid state.

---

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<th>Temp. ($T_\text{e}$/$K$)</th>
<th>Dithioligand (Me groups) $\tau$ Value $\times [$/P(Ph)]$ $\tau$ Value $\times [$/P(Ph)]$</th>
<th>Me(phenyl ligand) $\tau$ Value $\times [$/P(Ph)]$</th>
<th>Phenyl groups $\tau$ Value $\times [$/P(Ph)]$</th>
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* Doublet. + \(\pm 0.01\) Hz. ¥ Coalescence temperature of dithiocarbamoyl methyl resonances. ¥ Coalescence temperature of methyl groups attached to phosphorus ligands. ¥ H\(_2\)PPH\(_2\) Type spectrum (pseudo-triplet). ¥ \([PFH]\) in parentheses \(\pm 0.02\) Hz. ¥ Doublet. ¥ \([PFH]\) in parentheses \(\pm 0.02\) Hz. ¥ Two doublets superimposed. ¥ Coalescence of inner doublets. ¥ Doublet from coalescence of outer doublets. ¥ Coalescence temperature for outer doublets. ¥ Broadened doublet superimposed on broad signal. ¥ Coalescence temperature for doublets at \(\tau 8.05, 8.41\) and \(7.96, 8.41\). ¥ Virtually-coupled 1,2,1 triplet. ¥ Methyl singlet (acetone) at \(7.86\). ¥ Singlet. ¥ Singlet from coalescence of peaks at \(7.13\) and \(7.37\). ¥ Coalescence temperature for resonances at \(7.13\) and \(7.37\).

For [Ru(S\(_5\)PMMe\(_3\)](PMe\(_3\)Ph)(P(OMe)\(_3\))], the two higher field doublets are superimposed (Table 5). These two resonances presumably arise from the methyl groups deep to the phosphine and thus to the phosphite ligands (e and f respectively—Figure 3a). In this instance, although the PMMe\(_3\)Ph group has fewer phenyl rings than P(OMe)\(_3\), those on the phosphite are further removed from the methyl group f by the presence of the oxygen atoms, thus producing similar shielding effects and hence identical chemical shifts for e and f. This conclusion is supported, in part, by the observation that the chemical shifts of the methyl groups (c) in the bis-PMe\(_3\)Ph and bis-P(OMe)\(_3\) complexes are fairly close, being \(\tau 8.14\) and \(8.35\) respectively.

For [Ru(S\(_5\)PMMe\(_3\)](P(OMe)\(_3\))], the two lower field doublets are superimposed (i.e. g and h in Figure 3b). This is not unexpected since the chemical shifts of the low field doublets in the bis-P(OMe)\(_3\) and bis-carbonyl compounds occur at \(\tau 7.89\) and \(7.86\) respectively (Table 5). In support of this interpretation, heteronuclear phosphorus–hydrogen spin decoupling experiments confirm that the two methyl groups attached to different phosphorus atoms are accidentally superimposed.

The methyl resonances of the dithio-digands of the cis-[Ru(S\(_5\)PMMe\(_3\)](L(CO))] and cis-[Ru(S\(_5\)PMMe\(_3\)](CO))] complexes, are temperature invariant up to ca. 330 K (although measurements on cis-[Ru(S\(_5\)PMMe\(_3\)](PPH\(_3\))-CO]) at higher temperatures in chlorobenzene indicate similar behaviour to that described below for [Ru(S\(_5\)PMMe\(_3\)](PPH\(_3\))(P(OMe)\(_3\)). However, those of the [Ru(S\(_5\)PMMe\(_3\)](L\(_7\))] compounds show marked changes at lower temperatures. For example, on warming [Ru(S\(_5\)PMMe\(_3\)](PPH\(_3\))(P(OMe)\(_3\))], the four methyl doublets present at low temperature (Figure 4a) begin to broaden, the inner two coalescing at \(\tau 280\) K (Figure 4b) and the outer two continuing to broaden until at \(320\) K the spectrum consists of a slightly broadened doublet superimposed on a broad signal which represents the coalesced peak of the outer doublets (Figure 4c). At even higher temperatures (in chlorobenzene), the spectrum consists of two doublets situated halfway between the original inner and outer doublet positions respectively (Figure 4d) (Table 5). This behaviour is attributed to the facile interconversion of optical isomers at higher temperatures, the different coalescence temperatures for the two pairs of doublets being due to their different separations.

![Figure 4](image-url)

Figure 4 Variable temperature \(^1\)H n.m.r. spectrum of [Ru(S\(_5\)PMMe\(_3\)](PPH\(_3\))(P(OMe)\(_3\))]: (a) 233 K in CH\(_2\)Cl\(_2\); (b) 283 K in CH\(_2\)Cl\(_2\); (c) 310 K in CH\(_2\)Cl\(_2\); (d) 363 K in CH\(_2\)Cl.
in ascending order of chemical shift (Figure 4a). This is based on the fact that methyl groups e and g are closer to the PPh₃ group (which has the greater shielding effect) than are f and h. These conclusions are supported by the fact that irradiating the phosphorus spectrum at 40 481 Hz collapses the doublets labelled e and g whereas irradiation at 40 482 Hz decouples f and h. This confirms that the methyl groups giving rise to resonances e and g are attached to the same phosphorus atom whereas those giving rise to resonances f and h are attached to the other phosphorus atom. Thus at higher temperature, the chemical environments of groups h,e and of g,f are interchanged but there is no exchange between any of the other environments.* A possible interpretation of these observations is presented in Part VI.

(iii) Complexes of formula [Ru(S₂CNMe₃)₂L₂]. It was reported earlier⁹ that the H n.m.r. spectrum of [Ru(S₂CNMe₃)₂(PPh₃)₂]·MeCO shows S₂CNMe₃ methyl resonances at 7-18 and 7-30 (with an intensity ratio of 1:2). The authors concluded that the structure was trans, attributing the methyl group splitting to different orientations of the methyl groups, which they suggested is probably caused by steric effects emanating from the bulky PPh₃ groups. However, on repeating this experiment (in both cold and refluxing acetonitrile), we have obtained a crystalline yellow solid, analysing for [Ru(S₂CNMe₃)₂(PPh₃)₂]·MeCO, whose n.m.r. spectrum contains two methyl resonances of the same intensity at 7-06 and 7-25; there is also a peak at 7-86 (acetone). This spectrum is consistent with a cis-configuration. Similarly, for [Ru(S₂CNMe₃)₂(PMe₂Ph)₂], prepared from mer-[RuCl₃(PMe₂Ph)₂], the low temperature H n.m.r. spectrum consists of two pseudo-triplets (PMe₂Ph groups) and two singlets (S₂CNMe₃ groups) which is indicative of a cis-configuration. At higher temperatures, coalescence to a single pseudo-triplet occurs at ca. 250 K and the methyl doublet coalesces to a singlet at ca. 300 K. A similar behaviour is observed at 318 K for the bis-PPh₃ complex (Table 5). For these compounds, coalescence of the pseudo-triplets is attributed to the onset of free rotation around the Ru-P bonds. However, the process equilibrating the methyl groups at higher temperatures is probably due to facile -CN bond rotation rather than inversion of optical isomers. This conclusion is based on the results of a kinetic line shape analysis on the compound [Ru(S₂CNMe₃)₂(PPh₃)₂(P(OPh)₃)] which reveals different activation parameters for the rates of exchange of the two sets of methyl groups. This is discussed in more detail in Part VI.

Finally, the reaction of cis-[Ru(S₂CNMe₃)₂(PPh₃)₂] with an excess of PMe₂Ph in ethanol gives two products which both analyse for [Ru(S₂CNMe₃)₂(PMe₂Ph)₂]. The H n.m.r. spectrum of the more soluble species (71% yield) is identical to that obtained from mer-

* Note added in proof: In support of this conclusion, homonuclear double resonance experiments (S. Forsen and R. A. Hoffman, J. Chem. Phys. 1965, 39, 2892) confirm that exchange only occurs between groups h, e and g, f respectively.

[RuCl₃(PMe₂Ph)₃] and Na₂S₂CNMe₃ (i.e. the cis isomer). However, the H n.m.r. spectrum of the minor product (21%), which is temperature invariant up to 315 K, has a single sharp peak at 7-20 (S₂CNMe₃ groups) and a broader peak of the same intensity at 8-27 (PMe₂Ph groups), indicative of a trans configuration. On further heating, this compound rearranges irreversibly to the cis isomer. Therefore, in this instance, there is evidence for the irreversible trans → cis isomerism found elsewhere.¹⁶,⁴⁹ and on this evidence, it is also possible to interpret the H n.m.r. spectrum of [Ru(S₂CNMe₃)₂(PPh₃)₂] observed earlier⁹ as a 50:50 cis-trans mixture of isomers with the trans methyl resonance accidentally superimposed on one of the cis methyl resonances.

Mechanism of Carboxylation of cis-[Ru(S₂PR₃)₂(PMe₂Ph)₂].—When cis-[Ru(S₂PR₃)₂(PMe₂Ph)₂] (A) (R = Me, Ph) is carboxylated in refluxing ethanol or acetonitrile for a prolonged period, a mixture of cis-[Ru(S₂PR₃)₂(PMe₂Ph)CO] (B) and [Ru(S₂PR₃)₂(PMe₂Ph)CO] (C) is always formed although these can be separated by dry column chromatography. However, when C is redissolved, partial rearrangement to B slowly occurs whereas if the reaction of A and CO is carried out in the presence of an excess of sulphur, only B is formed. Conversely, reaction of A and CO in the presence of an excess of PMe₂Ph gives pure C. In addition, another complex of formula [Ru(S₂PR₃)₂(PMe₂Ph)CO] (D) may be isolated if the carboxylation reaction is carried out in the cold for a very short time (ca. one minute). In solution, D slowly and irreversibly gives first B and then some of C. This process can be monitored by both H n.m.r. (since all the compounds have different spectra) or by observing the change in ν(CO) position with temperature: ν(CO)(D) = 1984; ν(CO)(B) = 1948; ν(CO)(C) = 1946 cm⁻¹ (all measured in CCl₄). Measurement of the rate of loss of the carboxyl band intensity for D gives a rate constant for this rearrangement reaction of 1.7 × 10⁻⁴ s⁻¹ at 325 K (k₂ = 65 min) and also confirms that the process is first order with respect to D.

Thus, these observations are consistent with the carboxylation mechanism shown below: viz. facile formation of D followed by a slower conversion to B which then undergoes a partial reversible rearrangement to C. It now only remains to determine the structures of C and D in order to establish the stereochemical pathway of the mechanism.

Assuming that ruthenium(II) retaining its usual six-co-ordinate stereochemistry;† we therefore have unidentate and bidentate S₂PR₃ groups;‡ there are four possible isomers for compounds of formula [Ru(S₂PR₃)₂(PMe₂Ph)CO] (Figure 5). For R = Me, the

† A reasonable assumption since to our knowledge only one ruthenium(II) seven-co-ordinate compound has been claimed, i.e. [RuCl₃(CO)(MeCSET)₂]⁻.⁴⁹

‡ This is suggested by the i.r. spectra of C and D (see earlier)[⁵⁰] and the i.r. spectra of C and D (see earlier)[⁵¹] of [Ru(NO)(S₂CNMe₃)]⁻.⁴⁹

room temperature ¹H n.m.r. spectrum of C consists of two doublets (from the $S_2PMe_2$ groups) and a 1,3,3,1 quartet for the $PMe_2Ph$ groups (i.e. two overlapping

![](image)

\[
[Ru(S_2PR_2)_{3}(PMe_2Ph)_{3}] + CO \xrightarrow{\text{fast}} [Ru(S_2PR_2)_{3}(PMe_2Ph)_{3}CO] \\
(\text{A})
\]

\[
[Ru(S_2PR_2)_{3}(PMe_2Ph)_{3}] + CO \xrightarrow{\text{slow}} [Ru(S_2PR_2)_{3}(PMe_2Ph)_{3}CO] \\
(\text{B})
\]

\[
[Ru(S_2PR_2)_{3}(PMe_2Ph)_{3}CO] + PMe_2Ph \xrightarrow{\text{slow}} [Ru(S_2PR_2)_{3}(PMe_2Ph)_{3}CO] \\
(\text{C})
\]

Figure 5 Possible isomeric forms for $[Ru(S_2PR_2)_{3}(PMe_2Ph)_{3}]$ assuming bidentate and unidentate $S_2PR_2$ coordination

1,2,1 'virtually-coupled' triplets as is seen for $R = Ph$ (Table 5). At higher temperatures, these collapse to a single triplet although a detailed observation of this process is obscured (for $R = Me$) by the increased tendency to rearrange to compound B at these higher temperatures. In contrast, the two $S_2PMe_2$ doublets are almost temperature invariant, except for a slight broadening at ca. 330 K which again is obscured because of the facile rearrangement to B at this temperature. Examination of Figure 5 reveals that this n.m.r. spectrum corresponds to that expected for structure (I) i.e. trans $PMe_2Ph$ groups with slow exchange of uni/bidentate $S_2PR_2$ groups. Assignment of this structure to C would also account for the similarity in the position of $\nu$(CO) to that observed for B (Table 2) since in each case the carbonyl group is situated trans to a sulphur atom of a bidentate dithiacid ligand.

The ¹H n.m.r. spectrum of D ($R = Me$), which is temperature invariant from 220 to 320 K (although over longer periods, it slowly converts to a mixture of B and C) consists of fourteen lines (Figure 6). By means of heteronuclear spin decoupling experiments it can be shown that the four phosphorus atoms in the molecule are all in inequivalent chemical environments and this is confirmed by measuring the proton noise decoupled ³¹P n.m.r. spectrum of the complex (Figure 7). The decoupling studies (see Figure 6) also indicate that the 14 line ¹H n.m.r. spectrum is comprised of 8 doublets (with four of the doublets partially superimposed). NB: The irradiation frequencies given in Figure 6 are different from the frequencies of the phosphorus nuclei obtained from the Fourier transform

![Image](image)

Figure 6 ¹H N.m.r. spectrum of $[Ru(S_2PMe_2)_{3}(PMe_2Ph)_{3}]CO$ (D) [methyl region] at 273 K; irradiating at 40 482 120 Hz decouples 1 and 1', at 40 480 770 Hz decouples 2 and 2', at 40 478 777 Hz decouples 3 and 3', and at 40 477 700 Hz decouples 4 and 4' (note Assignments of 2 and 2', 3 and 3', 4 and 4' are arbitrary)

![Image](image)

Figure 7 ³¹P N.m.r. spectrum of $[Ru(S_2PMe_2)_{3}(PMe_2Ph)_{3}]CO$ (D) gives $J(p,p_1) 0-0$; $J(p,p_2) 7-6$; $J(p,p_3) 0-0$; $J(p,p_4) 10-0$; $J(p,p_1) 14-9$; $J(p,p_2) 32-6$ Hz. Chemical shifts are in p.p.m. to high frequency of $85\% \ H_2PO_4$. cf. $[Ru(S_2PMe_2)_{3}(CO)]_2 + 92-6 \ [Ru(S_2PMe_2)_{3}(PMe_2Ph)]_2 + 88-1$ and $+ 21-4$

* A recent note (S. D. Robinson and M. F. Uettley, Chem. Comm., 1972, 1047) reports the synthesis of the analogous $[Ru(CO)Me]_2(PPh_3)CO$ compound with uni/bidentate acetato-groups but the detailed stereochemistry is not given. Added in proof: In the full paper (J. C. S. Dalton, 1973, 1912) the analogous carbonylato-complex is arbitrarily assigned a structure of type (I).
latter are directly measured on the XL 100 machine and these have slightly different reference frequencies. Thus, all the methyl groups are in inequivalent chemical environments, and there is restricted rotation (even at 320 K) about the Ru-P bonds. This n.m.r. evidence is, in fact, compatible with a seven-co-ordinate complex with only bidentate dithiocarb acid groups. However, addition of methyl iodide to a dichloromethane solution of D produces an immediate increase in conductivity. A similar increase is observed for $[\text{Pt}(\text{S}_2\text{PMe}_2\text{Ph})_2(\text{PMe}_2\text{Ph})]$ (where un/bidentate co-ordination is well established) and compound C, but with $[\text{Pt}(\text{S}_2\text{PMe}_2\text{Ph})]$ and $[\text{Ru}(\text{S}_2\text{PMe}_2\text{Ph})]$ there is no change. This conductivity increase is attributed to the formation of the complex $[\text{Ru}(\text{S}_2\text{PMe}_2\text{Ph})(\text{MeS}_2\text{PMe}_2\text{Ph})(\text{PMe}_2\text{Ph})_2\text{CO}]$ by methylation of the uncoordinated sulphur atom. Furthermore, the $^1\text{H}$ n.m.r. spectrum of the conducting solution is not significantly different from that of D, except for extra signals at $6.96$ (SMe group) and $7.93$ (excess of MeI) which strongly suggests that MeI is not reacting with a bound sulphur atom of a labile seven-co-ordinate species.

Examination of Figure 5 indicates that neither structure (I) (already assigned to C) nor structure (IV) (which has a plane of symmetry making the PMe$_2$Ph groups equivalent) fit the $^1\text{H}$ and $^{31}\text{P}$ n.m.r. data. However, (II) and (III) are both possible structures since in both cases hindered rotation about the ruthenium-phosphorus bonds is reasonable on steric grounds and furthermore the ruthenium atom is potentially a chiral centre and thus, no matter how rapid the rotation about the Ru-S bond of the unidentate $^2\text{S}_2\text{PMe}_2$ ligand, the two Me groups will always remain inequivalent. However, (III) would be expected to have a v(CO) band in a similar position to that found in compounds B and C since the CO group is trans to a sulphur atom of a bidentate $^2\text{S}_2\text{PPh}_2$ ligand whereas (II) should have a higher v(CO) since the CO group is trans to a stronger $\pi$ acceptor ligand and hence back donation into the $\pi^*$ orbitals of the CO group will be reduced. The latter is experimentally the case (Table 2) and hence structure (II) is preferred.

The heteronuclear decoupling information given in Figure 6 determines which sets of methyl protons in D are attached to phosphorus atoms 1-4 which are labelled in the order they occur in the $^{31}\text{P}$ n.m.r. spectrum (Figure 7). Assuming structure (II) is more feasible than (III), then these phosphorus atoms can be assigned as follows: P$_1$ and P$_2$ belong to the $^2\text{S}_2\text{PMe}_2$ groups and P$_3$ and P$_4$ to the PMe$_2$Ph groups. This assignment is based on the chemical shifts of the $^{31}\text{P}$ nuclei compared to those in $[\text{Ru}(\text{S}_2\text{PMe}_2\text{Ph})(\text{CO})_2]$ and $[\text{Ru}(\text{S}_2\text{PMe}_2\text{Ph})(\text{PMe}_2\text{Ph})]$ (see Figure 7) together with the fact that the lower field methyl doublets (which correspond to the $^2\text{S}_2\text{PMe}_2$ methyl resonances) are decoupled by irradiating at frequencies corresponding to phosphorus atoms P$_1$ and P$_2$. In $[\text{Ru}(\text{S}_2\text{PMe}_2\text{Ph})(\text{PMe}_2\text{Ph})(\text{CO})]$, the separation between the methyl dithiocarb acid group syn to PMe$_2$Ph and that syn to CO is 33 Hz, which is close in value to the separation of the methyl groups 1 and 1' attached to P$_1$ (44 Hz). In contrast, those attached to P$_3$ (2 and 2') are only separated by 6 Hz. We therefore assign P$_1$ to the phosphorus atom of the bidentate $^2\text{S}_2\text{PMe}_2$ group and P$_2$ to the unidentate $^2\text{S}_2\text{PMe}_2$ group. Finally, since P$_3$ couples to P$_1$ whereas P$_4$ does not (Figure 7) it seems likely that P$_3$ is more nearly trans to P$_1$ than is P$_4$ and therefore P$_3$ and P$_4$ are assigned accordingly [see Figure 5, structure (II)].

The stereochemical pathway of the carbonylation mechanism is given in Figure 8. Thus, D is formed by cleavage of the weakest Ru-S bond i.e. that trans to a PMe$_2$Ph group. This is consistent with the bond lengths found in cis-[Ru(S$_2$PMe$_2$Ph)$_2$(PMe$_2$Ph)]$_2$, where the Ru-S bonds trans to the PMe$_2$Ph groups are ca. 0.2 Å longer than those trans to another sulphur atom. This, incidentally, is another reason why structure (II) rather than (III) is preferred for D since to form the latter the Ru-S bond trans to a sulphur atom must be broken. Next, the combination of two high trans effect ligands such as CO and PMe$_2$Ph situated trans to each other, together with the favourable energy change associated with the conversion of unidentate to bidentate $^2\text{S}_2\text{PMe}_2$ co-ordination, results in the expulsion of a PMe$_2$Ph group and the formation of B. Finally, the high affinity of PMe$_2$Ph for ruthenium(ii) is demonstrated by its attack on the Ru-S bond trans to PMe$_2$Ph to give C. As was inferred earlier for the ligand exchange reactions of $[\text{Ru}(\text{S}_2\text{PR}_2)_2(\text{CO})_2]$ compounds, these favourable electronic changes are reinforced by favourable steric changes on progressing from A to D to B to C. The inability of cis-[Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)(CO)] to give cis-[Ru(S$_2$PR$_2$)$_2$(CO)$_2$] is presumably a reflection
of the fact that the favourable steric change is more
than offset by the unfavourable electronic change of
replacing a Ru–PMe₂Ph bond with a Ru–CO bond.
This rationale is supported by the fact that cis-[Ru(S₂-
PMe₂Ph)(CO)]₂ reacts with an excess of PMe₂Ph, even
in the presence of CO, to give C and with an excess of
PPh₃ to give cis-[Ru(S₂PMe₂Ph)(PPh₃)CO]. The failure
to observe compounds of type C or D with ligands other
than PMe₂Ph is probably due to the smaller trans
effects (tertiary phosphines) and nucleophilicities (tertiary
phosphines) towards ruthenium(II) of these other
ligands compared to PMe₂Ph, although, doubtless, a
similar mechanism of carbonylation is applicable.
It is also reasonable to postulate a similar mechanistic
scheme for formation of the mixed ligand species
[Ru(S₂PPh₂)₂LL'] although, again, no intermediates
of type D (or C) have been observed.
Finally, the unsuccessful attempts to carbonylate
the cis-[Ru(S₂CNRe₂)₂LL'] complexes are probably due to
the stronger nucleophilicity of S₂CNRe₂ compared to
S₂PR₂ (see reference 1), preventing formation of a comp of type D.

EXPERIMENTAL

Microanalyses were by the National Physical Laboratory,
Teddington, A. Bernhardt, West Germany, and the Uni-
versity of Edinburgh Chemistry Department. Molecular
weights were determined on a Perkin-Elmer–Hitachi 115
osmometer at 37°. I.r. spectra were recorded in the
region 4000–250 cm⁻¹ on a Perkin-Elmer 457 grating
spectrometer using Nujol mulls on caesium iodide plates.
Solution spectra were run in potassium bromide cells.
Mass spectra were obtained on an A.E.I. MS9 spectrometer
and conductivity measurements on a Portland electronics
310 conductivity bridge. H N.m.r. spectra and solution
magnetic moments (Evans' method) were obtained on a
Varian Associates HA 100 spectrometer and 31P n.m.r.
spectra on a Varian XL 100 spectrometer operating in the
Pulse and Fourier Transform mode at 40–5 MHz. Hetero-
nuclear decoupling experiments were carried out on the
HA 100 spectrometer using a second radio frequency
field provided by the Schlumberger FS 30 frequency
synthesiser. M.p.s were determined with a Kohler hot-
stage microscope and are uncorrected.

Materials. —Ruthenium trichloride trihydrate (Johnson
Matthey); triphenylphosphate, dimethylphenylphosphate;
triphenyl phosphite (B.D.H.); methyltriphenylphosphine
(Strem); P₂Et₃Ph was made by a standard literature
method; carbon monoxide (Air products); Na₂S₂CNMe₂
2H₂O (Ralph Emanuel). Sodium diethyl- and di-
ethylphosphinothioates were prepared as described earlier
and ammonium diphenylphosphinodithioate from Ph₂-
PH₂S and ammonia in benzene. Operations involving
free tertiary phosphines and phosphites [with the exception
of (PO(OEt)₂P₂Ph₃ and PPh₃] were carried out under nitrogen.
The various ruthenium(II) and (III) tertiary phosphine
and phosphite complexes which were used as starting
materials were synthesised by published methods.

cis-Bis{diphenylphosphinodithioato)b(is(triphenylphos-

*The one possible exception is with [Ru(S₂PMe₂Ph)(P(OMe)₂Ph)]₂ where carbonylation gives a transient species with ν(CO) 1987
cm⁻¹ (type D1) but unfortunately this could not be separated from
starting material.

phine)ruthenium(II). —[RuCl₂(PPh₃)₂] (0.10 g), NH₄S₂P₂Ph₃
(0.20 g), and PPh₃ (0.20 g) were shaken in acetone (25 ml)
for 30 min and then the resulting red crystals filtered off,
flushed with water, acetone and n-pentane (yield: 0.10 g,
85%). However, if the reaction was carried out in the
absence of an excess of PPh₃, the resulting red crystalline
precipitate gave a consistently low analysis for the bis-
phosphine complex [Found: C, 60.1; H, 4.2; (Ru(S₂PMe₂Ph-
PPh₃)₂] requires C, 64.1; H, 4.5%; and bis(diphenylphos-
phinodithioato)(triphenylphosphine)ruthenium(II), 0.5: acetone
requires C, 58.6; H, 4.3%]. Furthermore, the molecular
weight of the product in benzene, over a short period of
time, decreased from 697 to 649, values indicative of the
facile dissociation of [Ru(S₂PMe₂Ph)(PPh₃)₂] (M, 1125) to
[Ru(S₂PMe₂Ph)₂PPh₃] (M, 801) and free PPh₃ in solution.
However, by refluxing a mixture of [RuCl₂(PPh₃)$_2$] (0.10 g),
NH₄S₂P₂Ph₃ (0.12 g), and sulphur (0.063 g) in acetone, a
pure sample of [Ru(S₂PMe₂Ph)₂PPh₃] (0.06 g; 72%) was
isolated [Found: C, 58.1; H, 4.1%].

cis-Bis(dimethylphosphinodithioato)b(is(triphenylphos-
phinodithioato)ruthenium(II). —[RuCl₂(PPh₃)₂MeNO₂]
(0.04 g), Na₂S₂PMe₂ (0.04 g), and PPh₃ (0.04 g) were shaken overnight
in ethanol (10 ml). The resultant brown crystalline
precipitate was filtered off, washed with water, ethanol, and
n-pentane to give red-brown needles of the complex
(0.04 g, 90%). The same compound was also prepared
from [RuCl₂(PPh₃)₂] (0.25 g) and Na₂S₂PMe₂ (0.15 g) in
acetone solution (0.21 g, 92%). Similarly, cis-bis(diethyl-
phosphinodithioato)b(is(triphenylphosphine)ruthenium(II) was
prepared from [RuCl₂(PPh₃)₂] (0.25 g) and Na₂S₂PET₃
(0.12 g).

cis-Bis(dimethylphosphinodithioato)b(is(ethyl)diphenylphos-
phinodithioato)ruthenium(II). —[RuCl₂(PEt₃Ph)₂]
was shaken in ethanol for 12 h with a three-fold excess of Na₂S₂PMe₂
to give the orange crystalline complex (73%).

The compounds tabulated below were prepared by
the following general method. The starting materials were
refluxed in ethanol for the time shown and then the solution
cooled and filtered. The crystals obtained were washed
with water, ethanol, n-pentane and dried in vacuo (40°).

If [RuCl₂(PMe₃Ph)₄] Cl (0.60 g) and Na₂S₂PMe₂ (0.50 g)
are refluxed in methanol (15 ml) for 24 h, an orange crystal-
line solid is precipitated. Dissolution in a minimum volume
of benzene and chromatography on a dry alumina column
gives an orange and a red band. The orange band was
extracted with diethyl ether, evaporated to dryness, and
recrystallised from CH₂Cl₂-n-pentane giving cis-[Ru-
(S₂PMe₂Ph)(PMe₃Ph)] (0.10 g, 20%). The red band was
also eluted with diethyl ether, evaporated to dryness, and
recrystallised from CH₂Cl₂-n-pentane to give [RuCl₂(PMe-
₃Ph)₂S₂PMe₂] (0.07 g, 11%) [Found: C, 56.1; H, 5.0%
Required C, 56.0; H, 5.0%]. cis-Bis(dimethylphosphino-
dithioato)b(is(methyl)diphenylphosphine)ruthenium(II) may also
be prepared by the reaction of cis-[Ru(S₂PMe₂Ph)(PPh₃)₂]
(0.05 g) with PMe₃Ph (0.10 ml) in refluxing ethanol (15 ml)
for 12 h. Cooling the solution gives orange crystals of the
complex (0.03 g; 70%). cis-Bis(dimethylphosphinodithio-
ato)b(is(dimethyl)diphenylphosphine)ruthenium(II) may be
prepared in two other ways: (a) cis-[Ru(S₂PMe₂Ph)(PMe-
₃Ph)] (0.05 g) and PMe₃Ph (0.05 ml) were refluxed in
ethanol (20 ml) for 4 h. Cooling the solution and partial

removal of solvent gave orange crystals of the complex which were filtered off, washed with n-pentane, and dried in vacuo (0.02 g; 48%); (b) cis-[Ru(S₂P₄Me₄)₂(PPh₃)₂] (0.10 g) and PMe₃Ph (0.03 ml) were refluxed in acetone for 1 h. Removal of the solvent gave an orange oil from which the product was obtained by recrystallisation from CH₂Cl₂-n-pentane (0.05 g; 70%).

Reaction of [RuCl₃(P(OPh)₃)₃] (0.05 g) and Na₂S₂P₂Me₄ (0.48 g) in ethanol (25 ml) under reflux for 5 h gave a yellow solution. The solution was filtered hot, concentrated, and allowed to crystallise overnight to give a yellow solid. Mass spectrum: m/e 876, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂OEt]⁺; 828, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂OEt]⁺; 780, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺; etc. ¹H N.M.R. spectrum (223 K): [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂OEt]⁺, τ 7.89 (2.5); 8.20 (2.5) [S₂P₂Me₄]; τ 6.08; 8.97 (6.0) [Et group]; [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺, τ 7.91, 8.13 [S₂P₂Me₄]; τ 5.93; 8.80 (6.0) [Et group] intensity ratio 6:1: Found C: 42.9, H: 4.9. [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺ requires C, 43.9; H, 4.8. [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺ requires C, 43.7; H, 5.4. For 6:1 ratio, calculated analysis is C, 42.9; H, 4.9%.

Reactions of [RuCl₃(P(OPh)₃)₃] with Na₂S₂P₂Me₄ in refluxing ethanol for 24 h shows, on solvent removal, an oil with mass spectral peaks m/e 828, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂OEt]⁺; 780, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂OEt]⁺; 732, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺; 684, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺; etc. cis-Bis(dimethylphosphinodithiao)(triarylphosphine)(triphenylphosphine)rhodium(II). cis-[RuCl₃(P(OPh)₃)₂] (0.50 g) and Na₂S₂P₂Me₄ (0.30 g) were refluxed in methanol (30 ml) for 3 h. The resultant yellow solution was filtered hot, and, after concentrated, allowed to slowly crystallise at 273 K for 10 days. The orange crystals so formed were washed with water, methanol, and n-pentane (0.08 g; 28%). On further solvent removal from the filtrate, an oily white solid was obtained which on recrystallisation was identified as phenol (by its HH N.M.R. spectrum). The ruthenium complex rapidly decomposed on air exposure to give a black solid.

cis-[RuCl₃(S₂P₂Me₄)₂(PPh₃)₂] (0.08 g) and P(OPh₃) (0.05 ml) were refluxed in ethanol (15 ml) for 3 h. The solution was cooled and the precipitated orange solid was washed with ethanol and n-pentane (yield, 0.03 g, 35%). The yellow filtrate was allowed to crystallise overnight to give a sample of cis-Bis(dimethylphosphinodithiao)(dimethylphosphine)(triphenylphosphine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(PPh₃)₂] (0.20 g) was refluxed with P(OPh₃) (1.2 ml) in ethanol for 1 h. Then, after concentration and standing for two days at 273 K, orange crystals were deposited which were filtered off and washed with ethanol and n-pentane (0.10 g; 39%).

cis-Bis(diphenylphosphinodithiao)(dimethylphenylphosphine)(triphenyl phosphine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(PPh₃)₂] (0.20 g) and P(OPh₃) (0.03 ml) were shaken in dichloromethane (20 ml) for 7 days. After filtration and addition of n-pentane, the resultant orange solution was concentrated until orange crystals were deposited. These were filtered off and washed with n-pentane (0.07 g; 29%).

cis-Bis(dimethylphosphinodithiao)(carbonyl(triphenylphosphine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(PPh₃)₂] (0.10 g) and P(OPh₃) (0.40 g) were carbonylated in refluxing ethanol for two hours. The resulting orange solution was evaporated to dryness and the residue recrystallised from CH₂Cl₂-light petroleum (b.p. 60-80) to give orange crystals of the complex (0.03 g, 41%).

Reactions of [RuCl₃(P(OPh)₃)₃] with Na₂S₂P₂Me₄ in refluxing ethanol for 24 h shows, on solvent removal, an oil with mass spectral peaks m/e 828, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂OEt]⁺; 780, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂OEt]⁺; 732, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺; 684, [Ru(S₂P₂Me₄)₂(P(OPh)₃)₂]⁺; etc. cis-Bis(dimethylphosphinodithiao)(triphenylarsine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(PPh₃)₂] (0.08 g) and Na₂S₂P₂Me₄ (0.09 g) were refluxed in acetone (25 ml) for 4 days with no apparent reaction. The mixture was then shaken for 3 weeks to give an orange solid and a white precipitate. After filtration, the solution was evaporated to dryness and the resulting orange oil chromatographed on a dry silica column using benzene as eluant. One orange band was observed and the central portion of this band was extracted with diethyl ether. The resulting yellow solution was evaporated to dryness and the residue recrystallised from CH₂Cl₂-light petroleum (b.p. 60-80) to give orange crystals of the complex (0.08 g, 73%).

cis-[RuCl₃(S₂P₂Me₄)₂(PPh₃)₂] (0.08 g) and P(OPh₃) (0.05 ml) were refluxed in CH₂Cl₂ for 10 min and recrystallised from CH₂Cl₂-hexane gave yellow crystals of cis-Bis(dimethylphosphinodithiao)(carbonyl(triphenylarsine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(POPh₃)₂] (0.07 g) in refluxing acetone for 4 h gave, after recrystallisation from CH₂Cl₂-n-pentane, yellow crystals of cis-Bis(dimethylphosphinodithiao)(carbonyl(triphenylphosphine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(P(OPh)₃)₂] (0.08 g) and Na₂S₂P₂Me₄ (0.05 g) were shaken in dichloromethane (20 ml) for 8 days with no apparent reaction. The mixture was then shaken for 3 weeks to give an orange solid and a white precipitate. After filtration, the solution was evaporated to dryness and the resulting orange oil chromatographed on a dry silica column using benzene as eluant and washing off the orange band with diethyl ether. Evaporation of the ether solution and recrystallisation from CH₂Cl₂-n-pentane gave the orange complex (0.03 g, 61%).

cis-Bis(dimethylphosphinodithiao)(carbonyl(methyl)diphenylphosphine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(PPh₃)₂] (0.10 g) was carbonylated in cold CH₂Cl₂ for one minute. The yellow-orange solution was evaporated to dryness and the product recrystallised from CH₂Cl₂-n-pentane to give the orange crystalline complex (0.03 g, 37%). Similarly, carbonylation of cis-[RuCl₃(S₂P₂Me₄)₂(PMe₃)₃] (0.05 g) in CH₂Cl₂ for 10 min and recrystallisation from CH₂Cl₂-hexane gave yellow crystals of cis-Bis(dimethylphosphinodithiao)(carbonyl(triphenylarsine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(POPh₃)₂] (0.07 g) in refluxing acetone for 4 h gave, after recrystallisation from CH₂Cl₂-n-pentane, yellow crystals of cis-Bis(dimethylphosphinodithiao)(carbonyl(triphenylphosphine)rhodium(II). cis-[RuCl₃(S₂P₂Me₄)₂(P(OPh)₃)₂] (0.08 g) and Na₂S₂P₂Me₄ (0.09 g) were refluxed in acetone (25 ml) for 4 days with no apparent reaction. The mixture was then shaken for 3 weeks to give an orange solid and a white precipitate. After filtration, the solution was evaporated to dryness and the resulting orange oil chromatographed on a dry silica column using benzene as eluant and washing off the orange band with diethyl ether. Evaporation of the ether solution and recrystallisation from CH₂Cl₂-n-pentane gave the orange complex (0.03 g, 61%).
cis-Bis(dimethylphosphinothiato)carbonyl(dimethylphenylphosphine)rhodium(II), \( \text{(D).} \) — cis-[Ru(S\(_2\)P\(_2\)Ph\(_4\))] \( \text{C}(0-20 \text{ g}) \) was carboxylated for one minute in cold \( \text{CH}_3\text{Cl}_2 \). Then, pentane was added and the resulting orange solution evaporated to dryness and the orange solid collected without further purification (0-21 g, 100%).

**cis-Bis(dimethylphosphinothiato)bis(carbonyl)rhodium(II),** \( \text{(C).} \) — cis-[Ru\( \text{PMe}_2\)(C\(_O\)\(_2\))\(_2\)] \( \text{C}(0-50 \text{ g}) \) and Na\( \text{S}_2\text{PMe}_2\) \( \text{(0-60 \text{ g})} \) were refluxed in ethanol (20 ml) for six hours to give a yellow solution. After filtration, this was cooled giving yellow crystals which were washed with water, ethanol, and n-pentane (0-14 g, 39%).

**cis-Bis(dimethylphosphinothiato)bis(carbonyl)rhodium(II),** \( \text{(B).} \) — cis-[Ru\( \text{S}_2\text{PMe}_2\)(C\(_O\)\(_2\))\(_2\)] \( \text{C}(0-50 \text{ g}) \) and Na\( \text{S}_2\text{PMe}_2\) \( \text{(0-60 \text{ g})} \) were refluxed in tetrahydrofuran for 18 h. The resulting yellow solution was evaporated to dryness, the residue extracted with diethyl ether and crystallised at 273 K to give the yellow **product**.

**cis-Bis(dimethylidithiocarbamato)bis(triphenylphosphine)rhodium(II),** \( \text{Acetonitrile.} \) — [Ru\( \text{Cl}_2\)(PPh\(_3\))\(_2\)] \( \text{(0-26 g) and NaS}_2\text{CNMe}_2\cdot2\text{H}_2\text{O (0-15 g) were shaken in acetonitrile (25 ml) for two days. The solution was then filtered and the orange crystals washed with water, diethyl ether and dried in vacuo at 40°C.} \)

**trans-Bis(dimethylidithiocarbamato)bis(dimethylphenylphosphine)rhodium(II),** \( \text{(C).} \) — cis-[Ru\( \text{S}_2\text{CNMe}_2\)(PPh\(_3\))\(_2\)] \( \text{(0-20 g) was refluxed with PMe}_2\text{Ph (0-15 ml) in ethanol (20 ml) for 12 h. The resulting yellow solution was filtered hot and allowed to crystallise. The first crop of yellow crystals was filtered off, washed with ethanol and n-pentane to give the desired product (0-03 g, 21%). The yellow filtrate later deposited more crystals shown to be cis-[Ru\( \text{S}_2\text{CNMe}_2\)(PMe\(_2\)Ph\(_2\))] \( \text{(0-10 g, 71%).} \)

**cis-Bis(dimethylidithiocarbamato)bis(triphenylphosphine)rhodium(II),** \( \text{[RuCl}_2\text{(P(OPh\(_3\))_3)] (0-20 g) and NaS}_2\text{CNMe}_2\cdot2\text{H}_2\text{O (0-16 g) were refluxed in ethanol (15 ml) for one hour. The resulting yellow solution was filtered hot and on cooling gave yellow crystals of the product (0-08 g, 41%).} \)

**cis-Bis(dimethylidithiocarbamato)bis(carbonyl)rhodium(II),** \( \text{[RuCl}_2\text{(P(OPh\(_3\))_3)] (0-20 g) and NaS}_2\text{CNMe}_2\cdot2\text{H}_2\text{O (0-20 g) were refluxed in ethanol (20 ml) for seven days. The resulting pale yellow solution was filtered, chromatographed on a dry alumina column with benzene, and the yellow band extracted with diethyl ether. Re-
moval of solvent and recrystallisation from hexane gave the product (0.001 g. 2%).

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Metal Complexes of Sulphur Ligands. Part VI.\textsuperscript{1,2} Studies of Facile Optical Isomerism Reactions in Dimethylphosphinodithioato-complexes of Ruthenium(II)

By David J. Cole Hamilton and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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Metal Complexes of Sulphur Ligands. Part VI.1,2 Studies of Facile Optical Isomerism Reactions in Dimethylphosphinodithioato-complexes of Ruthenium(ii)

By David J. Cole-Hamilton and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Rate constants and associated activation parameters for the optical isomerisation reactions of cis-[Ru(S2PMe2)2L2] (L = PPh3, PMePh2, PMe2Ph, P(OH)3, P(OPh)3), cis-[Ru(S2PMe2)2(PPh3)2[P(OH)3]], and cis-[Ru(S2PMe2)2(PPh3)2(CO)] have been determined by line-shape analyses of their temperature-dependent 1H n.m.r. spectra. Consideration of various bond-rupture and twist mechanisms for this inversion process strongly suggests that the only mechanism compatible with the overall experimental data is one involving a solvent-assisted cleavage of a ruthenium–sulphur bond trans to L.

For the analogous cis-[Ru(S2CNMe2)2L2] (L = PPh3, PMePh2, P(OH)3) and cis-[Ru(S2CNMe2)2(PPh3)] complexes, line shape studies suggest that their temperature dependent 1H n.m.r. spectra arise from restricted rotation about the CN bonds and not a facile inversion process.

In Part V of this series,1 the preparation, reactions, and spectroscopic properties of the compounds cis-[Ru(S2PR2)2L2] (L = tertiary phosphine or phosphite) were presented and discussed. In that paper, the variation with temperature of the 1H n.m.r. spectra of these compounds and some of their derivatives was noted and ascribed to rapid interconversion of the two possible optical enantiomers, rather than a reversible cis-trans isomerism. A great deal of interest has been shown in recent years in the mechanism of interconversion of optical isomers of metal complexes and, in particular, of the nature of the first step in the reaction. However, most of the publications on this topic have been confined to studies of tris-chelate complexes,3a and relatively few have discussed detailed mechanisms of optical isomerism in complexes of type cis-[M(chelate)2X2].3b Furthermore, with the exception of a very recent note on variable temperature 1H n.m.r. studies of [Ru(S2CNRR)] (R = Me, R' = PhCH2),4 this paper represents the only other published work on the facile interconversion of optical isomers in ruthenium chemistry.

Two main first-step mechanisms involving either a twist of the molecule or rupture of a metal ligand bond have been postulated. In this paper, presentation of the kinetic results is followed by a consideration of these various methods of optical inversion in an attempt to determine which mechanism is most energetically feasible for these compounds.

RESULTS

(i) Dimethylphosphinodithioato-complexes.—Typical variable-temperature 1H n.m.r. spectra for the compounds of Part V, D. J. Cole-Hamilton and T. A. Stephenson, preceding paper.


Type cis-[Ru(S2PMe2)2L2] are illustrated in Figure 1 (Part V) for cis-[Ru(S2PMe2)2(PMe2Ph)] and the proton resonance positions in the fast and slow exchange limits for other compounds of this type are given in Table 5 (Part V). These spectra all show two -S2PMe methyl doublets at low temperatures and a single doublet at higher temperatures. Thus, these n.m.r. changes, which are independent of complex concentration, are amenable to a detailed kinetic line-shape analysis and some of the results obtained from this are presented graphically (Figure 1) and the rates and calculated activation parameters at 298 K listed in Table 1.

For the mixed ligand complexes cis-[Ru(S2PMe2)2LL'] (L = tertiary phosphine, L' = tertiary phosphite) and cis-[Ru(S2PMe2)2(L)2(CO)], four methyl doublets are expected although in some instances, two of the doublets are accidentally superimposed. For cis-[Ru(S2PMe2)2(PPh3)] (L' = P(OPh)3) (where four methyl doublets are observed at low temperatures) inversion rates and activation parameters were determined by separate line shape analysis on the exchange of the inner methyl doublets g and f and the outer doublets e and h (see Figure 3, Part V, for stereochemical assignment of these methyl groups). The close similarity of the calculated values for these rates and activation parameters (see Table 1) indicates that the same kinetic process is probably responsible for the interchange of the chemical environments of these two sets of methyl protons. For cis-[Ru(S2PMe2)2(PPh3)CO], the activation parameters given in Table 1 were calculated by using rate data obtained from the exchange of both the inner and outer doublets respectively which again suggests that a common kinetic process is in operation.

From Table 1, several other points of importance emerge which must be considered when contemplating possible mechanisms of inversion. For example, Table 1 reveals

3 For detailed references see N. Serpene and D. G. Bickley in Progr. Inorg. Chem., 1972, 17 (Part II) (a) pp. 416—500, (b) 600—542.

Table 1

Rates and activation parameters obtained by line shape analysis for the inversion process \(cis-\Delta \rightleftharpoons cis-\Delta\) in some ruthenium(II) dimethylphosphinodithioate complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(\log_{10} k_{\text{obs}})</th>
<th>(E_a)</th>
<th>(\Delta H_{\text{obs}})</th>
<th>(\Delta S_{\text{obs}})</th>
<th>(\Delta G_{\text{obs}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CDCl_3</td>
<td>3.63 ± 0.02</td>
<td>49.6 ± 1</td>
<td>47.1 ± 1</td>
<td>-13 ± 3</td>
<td>52.8 ± 0.1</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CDCl_3</td>
<td>2.78 ± 0.02</td>
<td>60.6 ± 2</td>
<td>56.0 ± 2</td>
<td>3 ± 7</td>
<td>57.1 ± 0.2</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CDCl_3</td>
<td>2.33 ± 0.04</td>
<td>67.8 ± 2</td>
<td>65.5 ± 2</td>
<td>17 ± 3</td>
<td>60.2 ± 0.2</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CDCl_3</td>
<td>1.61 ± 0.12</td>
<td>62.0 ± 1</td>
<td>59.6 ± 1</td>
<td>-15 ± 4</td>
<td>63.6 ± 0.1</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CH_2Cl_2</td>
<td>1.21 ± 0.06</td>
<td>67.7 ± 2</td>
<td>67.7 ± 1</td>
<td>0 ± 4</td>
<td>67.2 ± 0.1</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CH_2Cl_2</td>
<td>1.04 ± 0.12</td>
<td>126 ± 4</td>
<td>123.5 ± 4</td>
<td>171 ± 10</td>
<td>72.7 ± 0.1</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CH_2Cl_2</td>
<td>0.41 ± 0.01</td>
<td>73 ± 2</td>
<td>71 ± 2</td>
<td>2 ± 7</td>
<td>70 ± 6</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CH_2Cl_2</td>
<td>0.19 ± 0.05</td>
<td>47.9 ± 4</td>
<td>44.9 ± 4</td>
<td>-62 ± 15</td>
<td>63.6 ± 0.4</td>
</tr>
<tr>
<td>(cis-[Ru(S_2PMe_2Ph)_2]^{2+})</td>
<td>CH_2Cl_2</td>
<td>-1.62 ± 0.08</td>
<td>121.8 ± 4</td>
<td>119 ± 4</td>
<td>83.8 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

* Units of \(k\), s\(^{-1}\).
* Units of kJ mol\(^{-1}\).
* Units of K\(^{-1}\) mol\(^{-1}\).
* Obtained from analysis of exchange of outer doublets d and h.
* For \(cis-[Ru(S_2PMe_2Ph)_2]^{2+}\), no scrambling of methyl groups at 330 K.
* Obtained from analysis of exchange of inner and outer doublets.

That the rate and the associated activation parameters are dependent on the solvent media in which the measurements are made. For \(cis-[Ru(S_2PMe_2Ph)_2]^{2+}\), measurements in C_6H_6, C_6H_5Cl and CDCl_3 respectively (Figure 2) show an increasing inversion rate accompanied by a substantial decrease in \(\Delta H^*\) and \(\Delta S^*\) values, particularly on changing from C_6H_6 to C_6H_5Cl (or CDCl_3).

In addition, measuring the inversion rate (by line-shape analysis) at 301 K for C_6H_6/CDCl_3 solutions of \(cis-[Ru(S_2PMe_2Ph)_2]^{2+}\), in which the CDCl_3 component is increased from 0 to ca. 40%, reveals a first order dependence of activation for this averaging process are estimated to be 57.4 and 58.6 kJ mol\(^{-1}\) respectively. Comparison with

![Figure 1](https://example.com/figure1.png)

**Figure 1** Arrhenius plots (log_{10}k vs. 1/T) for various \(cis-[Ru(S_2PMe_2Ph)_2]^{2+}\) compounds in CDCl_3:
- □, L = PhPh;
- ■, L = PMePh_2;
- △, L = P(OMe)_3;
- ○, L = PMePh;
- ●, L = P(OPh)_2

on CDCl_3 concentration (Figure 3). In a given solvent (CDCl_3), the inversion rate is also dependent on the group L, the relative order being PhPh > PPh_2 > P(OMe)_3 > PCh_2Ph > P(OPh)_2 > CO. It is also of interest that the rate of oxidation of \(cis-[Ru(S_2PMe_2Ph)_2]^{2+}\) as a function of L and solvent composition (see Part V) parallels these inversion rates in a semi-quantitative manner.

Finally, for the compounds \(cis-[Ru(S_2PR_2Ph)_2]^{2+}\) (R = Me, Ph) the two pseudo-triplets arising from the PPh_2 methyl groups at low temperature in CDCl_3 are separated by 13 and 8 Hz, and these coalesce at ca. 278 and 273 K respectively. From this data, the free energies

![Figure 2](https://example.com/figure2.png)

**Figure 2** Arrhenius plots (log_{10}k vs. 1/T) for \(cis-[Ru(S_2PMe_2Ph)_2]^{2+}\) in various solvents:
- ○, in CDCl_3;
- △, in C_6H_5Cl;
- ■, in C_6H_6

![Figure 3](https://example.com/figure3.png)

**Figure 3** Rate of inversion of \(cis-[Ru(S_2PMe_2Ph)_2]^{2+}\) (0.015 g ml\(^{-1}\)) in C_6H_6/CDCl_3 solution at 301 K as a function of CDCl_3 concentration

\( \Delta G^* \) obtained from the "S\textsubscript{2}PM\textsubscript{3}e\textsubscript{2} signals of cis-[Ru(S\textsubscript{2}PM\textsubscript{3}e\textsubscript{2})\textsubscript{2}(PM\textsubscript{3}e\textsubscript{2}Ph\textsubscript{2})] by line shape analysis at 273 K (63.4 \text{ \textdegree}K \text{ mol}^{-1}) indicates that these PM\textsubscript{3}e\textsubscript{2}Ph methyl protons are not averaged by the inversion process, since the observed \( \Delta G^* \) is lower than that of the inversion process. Therefore, the only reasonable explanation for these n.m.r. changes is to postulate rapid rotation at higher temperatures about the ruthenium–phosphorus bonds.

(ii) NN-Dimethylidithiocarbamoato-complexes. — For cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})\textsubscript{2}L\textsubscript{2}] (L = PM\textsubscript{3}e\textsubscript{2}Ph, PPh\textsubscript{3}, P(OPh\textsubscript{3})\textsubscript{3}), the low temperature \( \text{H} \) n.m.r. spectra consists of two "S\textsubscript{2}CNMe\textsubscript{2} methyl singlets which coalesce at higher temperatures signals are independent of each other and the best explanation of this that we can offer is that these n.m.r. changes are produced by fast rotation about the "CN bond of the "S\textsubscript{2}CNMe\textsubscript{2} groups syn to the PPh\textsubscript{3} and P(OPh\textsubscript{3})\textsubscript{3} groups respectively and not by a facile inversion process. In support of this conclusion, the two sets of activation parameters found for the PPh\textsubscript{3}-P(OPh\textsubscript{3})\textsubscript{3} complex are reasonably similar to those found for the bis-PPh\textsubscript{3} and bis-P(OPh\textsubscript{3})\textsubscript{3} compounds respectively. The large difference in \( \Delta S^* \) values for the "CN bond rotation process is tentatively attributed to substantial differences in the degree of solvation of the PPh\textsubscript{3} and P(OPh\textsubscript{3})\textsubscript{3} complexes, which might

### Table 2

Rates and activation parameters obtained by line shape analysis for the interchange of methyl groups in some ruthenium(ii) NN-dimethylidithiocarbamoato-complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>( \log k_{298}^b )</th>
<th>( E_a^b )</th>
<th>( \Delta H^*_{298}^b )</th>
<th>( \Delta S^*_{298}^b )</th>
<th>( \Delta G^*_{298}^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})\textsubscript{2}(PM\textsubscript{3}e\textsubscript{2}Ph\textsubscript{2})]</td>
<td>C\textsubscript{6}D\textsubscript{6}</td>
<td>0.71 \pm 0.01</td>
<td>94.0 \pm 2</td>
<td>0.15 \pm 2</td>
<td>75 \pm 7</td>
<td>0.94 \pm 0.02</td>
</tr>
<tr>
<td>cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})\textsubscript{2}(PPh\textsubscript{3})]</td>
<td>C\textsubscript{6}D\textsubscript{6}</td>
<td>0.22 \pm 0.02</td>
<td>102 \pm 2</td>
<td>0.12 \pm 2</td>
<td>105 \pm 6</td>
<td>8 \pm 0.07</td>
</tr>
<tr>
<td>cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})\textsubscript{2}(P(OPh\textsubscript{3})\textsubscript{3})]</td>
<td>C\textsubscript{6}D\textsubscript{6}</td>
<td>0.01 \pm 0.02</td>
<td>79 \pm 2</td>
<td>0.12 \pm 2</td>
<td>76 \pm 3</td>
<td>3 \pm 0.07</td>
</tr>
<tr>
<td>cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})(PPh\textsubscript{3})(P(OPh\textsubscript{3})\textsubscript{3})]</td>
<td>C\textsubscript{6}D\textsubscript{6}</td>
<td>0.23 \pm 0.01</td>
<td>109 \pm 2</td>
<td>0.12 \pm 2</td>
<td>120 \pm 3</td>
<td>7 \pm 0.07</td>
</tr>
<tr>
<td>cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})(PPh\textsubscript{3})(P(OPh\textsubscript{3})\textsubscript{3})]</td>
<td>C\textsubscript{6}D\textsubscript{6}</td>
<td>0.17 \pm 0.05</td>
<td>57 \pm 3</td>
<td>0.12 \pm 2</td>
<td>60 \pm 11</td>
<td>3 \pm 0.07</td>
</tr>
</tbody>
</table>

* Units of \( h^b \). s^b. | Units of \( k \) mol\(^{-1}\). | Units of \( J \text{ K}^{-1} \) mol\(^{-1}\). Obtain from exchange of high field pair of singlets.

### Table 3

Assignment of methyl group stereoechemisries for cis-\( \Delta [(S\textsubscript{2}PM\textsubscript{3}e\textsubscript{2})\textsubscript{2}LL\textsubscript{2}] \) after twisting and bond rupture operations

<table>
<thead>
<tr>
<th>Methyl group stereocemistries</th>
<th>Syn (to L)</th>
<th>Anti (to L)</th>
<th>Syn (to L')</th>
<th>Anti (to L')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syn (to L)</td>
<td>Anti (to L)</td>
<td>Syn (to L')</td>
<td>Anti (to L')</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>h</td>
<td>f</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>h</td>
<td>f</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>h</td>
<td>f</td>
<td>g</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>h</td>
<td>f</td>
<td>g</td>
<td></td>
</tr>
</tbody>
</table>

* \( \Delta \) and \( \Lambda \) Isomers defined on basis of rules suggested by I.U.P.A.C. commission (see Inorg. Chem., 1970, 9, 1). See Figure 4 for assignment of e, g, and h groups in cis-\( \Lambda \) isomer. * By variable temperature \( \text{H} \) n.m.r. studies for cis-[Ru(S\textsubscript{2}PM\textsubscript{3}e\textsubscript{2})(PPh\textsubscript{3})(P(OPh\textsubscript{3})\textsubscript{3})] see Part V. * See Figures 4 and 5. * These twist operations are sterically impossible since they produce a configuration in which a "S\textsubscript{2}PM\textsubscript{3}e\textsubscript{2} group would have to span trans-positions.

(see Table 5, Part V). The rates and activation parameters at 298 K for this process are given in Table 2. The room temperature \( \text{H} \) n.m.r. spectrum of cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})(PPh\textsubscript{3})(P(OPh\textsubscript{3})\textsubscript{3})] consists of three methyl singlets of intensity ratio 1:2:1 indicating accidental superposition of two of the methyl resonances. At higher temperatures, the highest field singlet at \( \tau = 7.37 \) and one of the superimposed resonances at \( \tau = 7.13 \) coalesce to give a signal at \( \tau = 7.13 \) (\( T_c = 318 \text{ K} \)) whilst the lowest field signal at \( \tau = 6.86 \) and the remaining resonance at \( \tau = 7.13 \) broaden considerably and move towards each other (see Table 5, Part V). Thus, the high field pair of singlets and the low field pair of singlets are undergoing exchange and the rates and activation parameters at 298 K for these exchange processes are given in Table 2. This data clearly shows that although the rates are fairly similar at 298 K, the activation parameters are very different. This can only mean that the kinetic processes exchanging these two sets of methyl arise as a consequence of replacing phenyl with phenoxo groups.

Finally for cis-[Ru(S\textsubscript{2}CNMe\textsubscript{2})(PM\textsubscript{3}e\textsubscript{2}Ph\textsubscript{2})], the estimated free energy of activation for averaging the two pseudopotentials of the PM\textsubscript{3}e\textsubscript{2}Ph methyl groups is 34.0 \text{ \textdegree}K \text{ mol}^{-1} (at \( T_c = 253 \text{ K} \)) which is again attributed to rapid rotation at higher temperatures about the ruthenium–phosphorus bonds.

**DISCUSSION**

Possible Mechanisms of the Inversion Process in Dimethylphosphinidithioato-complexes.—The possible mechanisms for the inversion process in these complexes will now be considered with intramolecular twisting mechanisms.

(i) Bailar (or trigonal) twist. In this mechanism,

the three atoms comprising one face of these octahedral complexes are rotated through 120° about the imaginary three-fold axis \( i-C_3 \) whilst keeping the opposite face fixed. In the complexes \( \text{cis-[Ru(S}_{2}\text{PMe}_{3}l_{2}ll'] } \), there are four such axes as illustrated in Figure 4 and diagrams of the complex as viewed along these axes are given in Figure 5. The positions of the methyl groups e, f, g, and h shown in these Figures are consistent with the detailed assignments made in Part V for \( L = \text{PPh}_{3} \), \( L' = \text{P(OPh)}_{3} \) and the starting configuration arbitrarily chosen is designated \( \text{cis}-\Delta \) on the basis of rules suggested by the recent I.U.P.A.C. commission.\(^7\)

The problem is now to consider the effect of a trigonal twist around each axis in turn (clockwise and anti-clockwise) in order to determine if such a process gives the optical isomer and also interchanges only the chemical environments of the methyl groups e, f, g, and h respectively. Examination of Figure 5a and Table 3 shows that rotation about the \( i-C_3(1) \) axis in a clockwise direction gives the \( \text{trans} \) isomer whereas an anticlockwise twist gives the \( \text{cis}-\Delta \) isomer. However, the \( \text{S}_{2}\text{PMe}_{3} \) methyl groups will finish in the same chemical environment as they started and hence this twisting motion predicts inversion without any scrambling of methyl resonances. Rotation about \( i-C_3(2) \) or \( i-C_3(3) \) in a clockwise direction is impossible because it leads to a configuration in which a \( \text{S}_{2}\text{PMe}_{3} \) group would have to span \( \text{trans} \) positions. Anticlockwise rotation about these axes gives the optical isomer together with scrambling of all methyl groups. Hence, if this were the inversion mechanism, a single methyl resonance should be observed at elevated temperatures and careful experiments with \( \text{cis-[Ru(S}_{2}\text{PMe}_{3}l_{2}l=	ext{P(OPh)}_{3}l_{2}]} \) and \( \text{cis-[Ru(S}_{2}\text{PMe}_{3}l_{2}l=	ext{P(OPh)}_{3}l_{2}CO]} \) (see Part V) show that this is not the case.\(^7\)

Finally, rotation about

\(^7\) For details see *Inorg. Chem.*, 1970, 9, 1.

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**Figure 4** Labelling of the four imaginary three-fold axes \( i-C_3 \) for the \( \text{cis}-\Delta-[\text{Ru(S}_{2}\text{PMe}_{3}l_{2}ll'] } \) complex: \( i-C_3(1) \), axis through plane of atoms \( S_1lS_2lS_3 \); \( i-C_3(2) \), axis through plane of atoms \( L'lS_1lS_2 \); \( i-C_3(3) \), axis through plane of atoms \( S_1lL'lL' \); \( i-C_3(4) \), axis through plane of atoms \( S_1lL'lS_2 \).

**Figure 5** Bailer (trigonal) twists for a \( \text{cis}-\Delta-[\text{Ru(S}_{2}\text{PMe}_{3}l_{2}ll'] } \) compound about the four \( i-C_3 \) axes in clockwise (+) and anticlockwise (−) directions. For ease of interpretation, the direction of the P–Me bonds are drawn as the same as those of the Ru–L (or L') bonds to which they are syn or anti.


(i) Råy-Dutt (or rhombic) twist. For cis-[Ru(S₂PMe₃)₂L₂], this inversion mechanism can be visualised as follows.

(ii) Cleavage of a ruthenium-sulphur bond. Since the activation energies for the optical isomerism of the compounds cis-[Ru(S₂PMe₃)₂L₂] depend on the ligand L, it seems reasonable, at first sight, to postulate that the inversion mechanism might involve dissociation of a phosphorus ligand to give a square pyramidal or trigonal bipyramidal intermediate followed by recombination as the optical isomer. However, if this were the mechanism, then a ¹H n.m.r. spectrum of a mixture of two complexes containing different L groups should show scrambling of all the methyl resonances of the S₂PMe₃ groups. This is not the case for a mixture of cis-[Ru(S₂PMe₃)₂[PPh₃]₂] and cis-[Ru(S₂PMe₃)₂(PMe₃)₂] in CDCl₃ which shows only the unchanged methyl resonances.

(iii) Cleavage of a ruthenium-phosphorus bond. Since the activation energies for the optical isomerism of the compounds cis-[Ru(S₂PMe₃)₂L₂] depend on the ligand L, it seems reasonable, at first sight, to postulate that the inversion mechanism might involve dissociation of a phosphorus ligand to give a square pyramidal or trigonal bipyramidal intermediate followed by recombination as the optical isomer. However, if this were the mechanism, then a ¹H n.m.r. spectrum of a mixture of two complexes containing different L groups should show scrambling of all the methyl resonances of the S₂PMe₃ groups. This is not the case for a mixture of cis-[Ru(S₂PMe₃)₂[PPh₃]₂] and cis-[Ru(S₂PMe₃)₂(PMe₃)₂] in CDCl₃ which shows only the unchanged methyl resonances.

(i) Råy-Dutt (or rhombic) twist. For cis-[Ru(S₂PMe₃)₂L₂], this inversion mechanism can be visualised as follows. The two L groups remain fixed while the two chelate rings rotate in their planes in different directions through an angle of 90° about axes which are perpendicular to their respective planes and pass through the ruthenium ion. For cis-[Ru(S₂PMe₃)₂L₂] this does not produce any scrambling of the methyl resonances and so this twisting mechanism can also be discarded.

(ii) Cleavage of a ruthenium-sulphur bond. Since the activation energies for the optical isomerism of the compounds cis-[Ru(S₂PMe₃)₂L₂] depend on the ligand L, it seems reasonable, at first sight, to postulate that the inversion mechanism might involve dissociation of a phosphorus ligand to give a square pyramidal or trigonal bipyramidal intermediate followed by recombination as the optical isomer. However, if this were the mechanism, then a ¹H n.m.r. spectrum of a mixture of two complexes containing different L groups should show scrambling of all the methyl resonances of the S₂PMe₃ groups. This is not the case for a mixture of cis-[Ru(S₂PMe₃)₂[PPh₃]₂] and cis-[Ru(S₂PMe₃)₂(PMe₃)₂] in CDCl₃ which shows only the unchanged methyl resonances.

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1 H n.m.r. spectral patterns of the two components. Furthermore, the ¹H n.m.r. spectrum of a mixture of cis-[Ru(S₂PMe₃)₂(PMe₃)₂] and free PMe₃PH in CDCl₃ at ca. 330 K indicates no exchange of free and bound phosphine. Thus, cleavage of a ruthenium-phosphorus bond may be eliminated as a possible first step in the inversion process.

(iv) Complete dissociation of a dithioacid group. If this was an important process, then a mixture of the two compounds cis-[Ru(S₂PR₃)₂L₂] and cis-[Ru(S₂PR₃)₂L₂] should give some of the mixed species cis-[Ru(S₂PR₃)₂(S₂PR₃)₂L₂] under exchange conditions. This does not occur and therefore, the racemisation mechanism cannot involve complete dissociation of a dithioacid ligand.

(v) Cleavage of a ruthenium-sulphur bond. In the symmetrical complexes cis-[Ru(S₂PR₃)₂L₂], there are two types of ruthenium-sulphur bond; those which are trans to another sulphur atom and those trans to a phosphorus ligand. If optical isomerism occurred via cleavage of a ruthenium-sulphur bond trans to another sulphur atom, then the activation energy for the reaction would be relatively insensitive to changes in L.

Therefore, it is necessary next to consider inversion mechanisms arising from initial cleavage of a ruthenium-ligand bond.

(iii) Cleavage of a ruthenium-phosphorus bond. Since the activation energies for the optical isomerism of the compounds cis-[Ru(S₂PMe₃)₂L₂] depend on the ligand L, it seems reasonable, at first sight, to postulate that the inversion mechanism might involve dissociation of a phosphorus ligand to give a square pyramidal or trigonal bipyramidal intermediate followed by recombination as the optical isomer. However, if this were the mechanism, then a ¹H n.m.r. spectrum of a mixture of two complexes containing different L groups should show scrambling of all the methyl resonances of the S₂PMe₃ groups. This is not the case for a mixture of cis-[Ru(S₂PMe₃)₂[PPh₃]₂] and cis-[Ru(S₂PMe₃)₂(PMe₃)₂] in CDCl₃ which shows only the unchanged methyl resonances.

* The transfer influence of a ligand is defined as the extent to which that ligand weakens the bond trans to itself in the equilibrium state of the substrate.

† This does not necessarily mean that step (1) is rate-determining since for consecutive reactions of the type shown in Figure 6, (assuming steady state conditions), it can be shown that the overall rate expression involves a first order dependence on CDCl₃ concentration irrespective of the size of the relative rate constants of sub-steps (1) and (2).
with the size of L, there is a good correlation between rate and the trans influence of L as established independently by H. n.m.r. and i.r. studies.\textsuperscript{13} cis.PPh₃ > PMePh₃ > PMe₂Ph > P(OMe)₃ \simeq P(OPh)₃ > CO.

This provides a reasonable explanation of the observed rate dependence if either sub-step (1) and/or sub-step (2) are contributing to the overall rate. The anomalous position of P(OMe)₃ compared with trans influence predictions could perhaps be explained by its small steric size having different effects in sub-steps (1) and (2) which we tentatively suggest below are associative and dissociative processes respectively.

![Diagram of proposed solvent-assisted bond rupture mechanism](image)

Figure 6 Proposed solvent-assisted bond rupture mechanism for the optical isomerisation reaction \textit{cis}-\textit{A}→(Ru(S₂PMe₂)₂L₂) \rightarrow cis-\textit{A}'(Ru(S₂PMe₂)₂L₂)' (Y = CDCl₃ or C₂H₂Cl₂). (For clearer presentation, after step (2), the molecule is rotated by 90° in an anticlockwise direction about the L--Ru--Y axis.)

Therefore, the overall mechanism depicted in Figure 6 is able to account for many of the experimental observations. However, there still remains the question of the relative importance of sub-steps (1) and (2) in the inversion rates of these bis-L₉, -LL', and -LCO complexes [it can be assumed that sub-step (3) is always rapid] and the nature of the activation parameters for these sub-steps. An explanation for the large change in activation parameters, which occurs on changing from CDCl₃ (or C₂H₂Cl₂) to C₆H₆ is also required. Although with the information at present available, it is impossible to provide completely satisfactory (or unambiguous) answers, we nevertheless feel that some speculation on these matters is justified in this instance.

From Table 1, the activation parameters for cis-[Ru(S₂PMe₂)₂(PPh₃)CO] in C₆H₆ are \( \Delta H^\# \), 119.3 kJ mol\(^{-1}\); \( \Delta S^\# \), 119 JK\(^{-1}\) mol\(^{-1}\). In terms of the proposed mechanism, step (1) must involve cleavage of the Ru–S bond \textit{trans} to PPh₃ (highest trans influence ligand) and step (2), that of the Ru–S bond \textit{trans} to CO. Furthermore, it is reasonable to expect the rate of step (1) to be comparable to that in \textit{cis}→[Ru(S₂PMe₂)₂(PPh₃)CO]. This compound has overall activation parameters of 47.1 kJ mol\(^{-1}\) (\( \Delta H^\# \)) and -19 JK\(^{-1}\) mol\(^{-1}\) (\( \Delta S^\# \)) in CDCl₃. However, since the overall rate constant is considerably higher for the bis-PPh₃ compound, compared to the phosphine carbonyl complex, this can only mean that the observed rate and activation parameters for \textit{cis}→[Ru(S₂PMe₂)₂(PPh₃)CO] correspond mainly to the rate and activation parameters of step (2). Thus, in this instance, step (2) is characterised by large positive \( \Delta H^\# \) and \( \Delta S^\# \) values. For ligands of higher trans influence than CO, it is reasonable to infer much lower \( \Delta H^\# \) values for step (2) but \( \Delta S^\# \) should remain fairly insensitive to the nature of L (or L') on this view for \( \Delta H^\# \) and \( \Delta S^\# \) would be consistent with a dissociative mechanism\textsuperscript{14} for step (2) in which bond-breaking of the Ru–S bond \textit{trans} to L' is the rate-determining step.

However, because the \( \Delta S^\# \) term for (2) is probably fairly insensitive to the nature of L, this suggests that the inversion rates for all the bis-L₉ compounds in CDCl₃ (or C₂H₂Cl₂) must have an appreciable contribution from sub-step (1) since they all have activation parameters in the range 47 to 71 kJ mol\(^{-1}\) (\( \Delta H^\# \)) and 17 to -19 JK\(^{-1}\) mol\(^{-1}\) (\( \Delta S^\# \)). Thus, it seems reasonable to propose that in solvents such as CDCl₃ and C₂H₂Cl₂, step (1) is characterised by relatively low \( \Delta H^\# \) values and negative \( \Delta S^\# \) values. These values are indicative of an associative process which is to be expected for a solvent-assisted bond rupture step.

For \textit{cis}→[Ru(S₂PMe₂)₂(PPh₃)P(OPh)₃], the activation parameters are found to be \( \Delta H^\# \), 44.8 kJ mol\(^{-1}\); \( \Delta S^\# \), -62 JK\(^{-1}\) mol\(^{-1}\) and again step (1) must involve cleavage of the Ru–S bond \textit{trans} to PPh₃ and step (2) that of the Ru–S bond \textit{trans} to P(OPh)₃. In this instance, the overall rates of inversion for the bis-PPh₃ and bis-P(OPh)₃ compounds are more comparable than that estimated for the bis-CO compound (no exchange even at 330 K). Therefore, although step (2) is probably slower than (1), we propose that both steps contribute to the observed rate.

The overall rate decrease, accompanied by substantial increases in \( \Delta H^\# \) and \( \Delta S^\# \), which is observed when \textit{cis}→[Ru(S₂PMe₂)₂(PMe₂Ph)₃] is examined in C₂H₆ rather than CDCl₃ (or C₂H₂Cl₂) is explicable on the basis that in such a poor solvating medium, step (1) not only becomes considerably slower because it is no longer a solvent-assisted process but it also becomes dissociative in nature. However, the similarity of the high temperature n.m.r. spectrum of \textit{cis}→[Ru(S₂PMe₂)₂(PPh₃)₃] in C₆H₆ and C₂H₂Cl₂ (two methyl doublets) is consistent with retention of the same overall inversion mechanism.

Finally, the apparent inability of the corresponding cis-[Ru(S₂CNMe₂)₂L₂] compounds to undergo inversion, even at elevated temperatures, is consistent with the stronger nuclophilicity of S₂CNR₂ compared to S₂PR₂, which will lead to prohibitively high activation energies for sub-steps (1) and (2).

EXPERIMENTAL

All the compounds used in the line shape studies were prepared as described earlier.¹

Kinetic Line Shape Analysis.—¹H N.m.r. spectra were measured on a Varian Associates HA 100 Spectrometer with variable temperature attachment. Accurate temperatures were determined using the separation of the two resonances of methanol (low temperature) and ethylene glycol (high temperature). Spectra were simulated using a computer programme based on that of Nakagawa.¹² The exchange process was considered for the purpose of computation as consisting of n two site exchanges where n is the multiplicity of the resonance being monitored. The single line simulated spectra were then superimposed with suitable weighting for intensities and the results plotted out on the line printer. Thus, in this work, a doublet is considered as two two-site exchanges of intensity ratio 1:1. The experimental spectra were fitted to the computed spectra either by finding the best fit between the ratio of maximum to minimum heights in the doublets (above and below coalescence) or the width of the signal at half height (around coalescence). Spin-spin relaxation times (T₂) were obtained for each compound by measurement of peak width at half height under slow exchange conditions. The same value of T₂ was used for all line shape calculations on a given compound because, for L = PMe₃Ph and P(OME)₃, the widths at half height in the slow and fast exchange limits differed by less than 0.25 Hz.

Lifetimes obtained by these fitting procedures were then used to construct Arrhenius plots (log₁₀k vs.1/T) in which straight lines were fitted by the least squares method. Activation parameters at 298 K, calculated from standard equations are shown in Tables 1 and 2 together with assessed error limits.

We thank Johnson-Matthey Ltd., for loans of ruthenium trichloride, the University of Edinburgh for an award (to D. J. C. -H.), Mr. J. Miller for obtaining the variable temperature ¹H n.m.r. spectra, and the Atlas Computer Laboratory for a copy of their Shape Function programme.

[3/1496 Received, 16th July, 1973]
Metal Complexes of Sulphur Ligands. Part VII. Reaction of mer-Tri-chlorotris(dimethylphenylphosphine)rhodium(III) with N,N-Dimethyldithiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and O-Ethyl Dithiocarbonate (Xanthate) Ligands

By David J. Cole-Hamilton and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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1974
Metal Complexes of Sulphur Ligands. Part VII. Reaction of mer-Tri-chloroaluminium(dimethylphenylphosphine)rhodium(III) with NN-Dimethyl-di-thiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and O-Ethyl Dithiocarbonate (Xanthate) Ligands

By David J. Cole-Hamilton and T. Anthony Stephenson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reactions of the complex mer-[RhCl4(PMe3Ph)3] (I), with excess of (S-S)-ion [S-S]- = S2CNMe2, S-2PMe2, S2PPh2, S2COEt] have been thoroughly studied. On shaking in methanol for 10 min, the complexes mer-[RhCl4(S-S)(PMe3Ph)3] (IV), are formed which contain a unidentate dithio-acid group. Recrystallisation of complexes (IV) from non-polar solvents gives trans-[RhCl4(S-S)(PMe3Ph)3] (II). For (S-S) = S2PMe2 or S2PPPh, further recrystallisation gives small amounts of the cis-cis-cis-isomers (VII). Conversely, for (S-S) = S2CNMe2 or S2COEt, recrystallisation of complexes (IV) with NaBH4 in methanol gives some mer-[RhCl4(S-S)(PMe3Ph)3] (III) as well as (II). However, reaction of complex (I) with excess of (S-S) heated under reflux in ethanol for 60 min, followed by addition of Y (Y = BPh4- or PF6-) to the filtrates, gives high yields of cis-[Rh2Cl6(S-S)2Y2] (III) and (VII) respectively. In contrast, reaction of complex (I) with KSCN and ethylene gives mer-[RhCl3(S2CNMe2)(PPh3)2] (XIV), K[RhCl3(S2CO)(PMe3Ph)2] (XII), and trans and cis-RhCl3(S2CO)(PPh3)(PMe3Ph)2 (XIII) and (XIIIIII) respectively, which can be separated by chromatography. The complexes have been characterised by elemental analyses and lr. and n.m.r. spectroscopy (H and MP), and a detailed mechanism for the overall reaction is postulated.

Previous papers in this series have been concerned with an examination of dithio complexes of palladium, platinum, and ruthenium, and, in particular, those complexes with ligands containing Group VB donor atoms (L) have been thoroughly studied. All these metals are characterised by the possession of a stable bivalent oxidation state and, in addition, form complexes which are fairly labile. Thus, with palladium and platinum, complexes of the type [M(S-S)2] and [M(S-S)L2] (S-S) are formed, which exhibit (to date) seven different types of intra- and inter-molecular rearrangement reactions which can be monitored by various spectroscopic techniques. Complexes formed with ruthenium of type cis-[Ru(S-S)2L2] also exhibit rearrangement reactions, which have been interpreted as arising from facile interconversion of optical enantiomers via ruthenium-sulphur bond rupture [for (S-S) = S2PMe2] and rotation about the C=S bond at elevated temperatures for (S-S) = S2CNMe2.

In view of these results it was decided to extend our studies to rhodium, where complexes of the bivalent oxidation state are comparatively rare and where, in general, complexes are less labile than those formed with ruthenium. The results of this detailed investigation are presented below.

RESULTS AND DISCUSSION

Because of our previous success in generating dithio complexes by replacement of chloro-groups in various ruthenium-(II) and -(III) tertiary phosphine and phosphite complexes by reactions with various alkali-metal dithio-acid salts, we decided to use the same methods in this work. This method has already been employed with some success for the synthesis of other complexes of rhodium containing dithio-acid ligands, viz.: [Rh2S2(PR3)2] (R = Ph, Et, or F); [Rh2S2(CNPh)2] (R = Me, Et, or Ph); [Rh2S2(OR)2] (R = Ph or PhCH3); [Rh2S2(OEt)2] (R = Me or Et); [Rh2S2(OCNMe2)2] (R = Ph); [Rh2S2(OCNPh)2] (R = Ph); [Rh2S2(OCNPh)2] (R = Ph); [Rh2S2(OCNPh)2] (R = Ph);

The alternative method of preparing these complexes, namely by direct reaction of free ligand with complexes

References

TABLE 1

Analytical data for some rhodium complexes

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<th>Complex</th>
<th>Colour</th>
<th>M.p. (°C)</th>
<th>Found (%)</th>
<th>Calc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*trans-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂</td>
<td>(II)</td>
<td>Orange</td>
<td>207-208</td>
<td>39.9</td>
</tr>
<tr>
<td>*cis-[Rh₂(S₂CNMe₂)(PMe₂Ph)]₄</td>
<td>(III)</td>
<td>Yellow</td>
<td>178-180</td>
<td>58.7</td>
</tr>
<tr>
<td>*cis-[Rh₂(S₂CNMe₂)(PMe₂Ph)]PF₆</td>
<td>(IV)</td>
<td>Orange</td>
<td>204-206</td>
<td>34.8</td>
</tr>
<tr>
<td>*mer-[Rh₂Cl₂(S₂CNMe₂)(PMe₂Ph)]₂PF₆</td>
<td>(V)</td>
<td>Yellow</td>
<td>158-178</td>
<td>64.1</td>
</tr>
<tr>
<td>*trans-[Rh₂(S₂CNMe₂)(PMe₂Ph)]₂PF₆</td>
<td>(VI)</td>
<td>Yellow</td>
<td>152-175</td>
<td>62.4</td>
</tr>
<tr>
<td>*trans-[Rh₂(S₂CNMe₂)(PMe₂Ph)]₂PF₆</td>
<td>(VII)</td>
<td>Yellow</td>
<td>&gt;230</td>
<td>43.3</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₁PF₆</td>
<td>(III)</td>
<td>Yellow</td>
<td>62.1</td>
<td>5.6</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₁PF₆</td>
<td>(IV)</td>
<td>Yellow</td>
<td>110-112</td>
<td>63.8</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₁PF₆</td>
<td>(V)</td>
<td>Orange</td>
<td>128-130</td>
<td>47.3</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₁PF₆</td>
<td>(VI)</td>
<td>Orange</td>
<td>208-210</td>
<td>48.3</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₁PF₆</td>
<td>(VII)</td>
<td>Yellow</td>
<td>72-73</td>
<td>57.2</td>
</tr>
<tr>
<td>*mer-[Rh₂Cl₂(S₂CO)(PMe₂Ph)]₂PF₆</td>
<td>(IX)</td>
<td>Yellow</td>
<td>195</td>
<td>34.9</td>
</tr>
<tr>
<td>*trans-[Rh₂Cl₂(S₂CO)(S₂COEt)(PMe₂Ph)]₂PF₆</td>
<td>(XII)</td>
<td>Orange</td>
<td>150-153</td>
<td>40.5</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(S₂CO)(S₂COEt)(PMe₂Ph)]₂PF₆</td>
<td>(XI)</td>
<td>Yellow</td>
<td>172-173</td>
<td>40.5</td>
</tr>
<tr>
<td>*trans-[Rh₂Cl₂(S₂CO)(S₂COEt)(PMe₂Ph)]₂PF₆</td>
<td>(XII)</td>
<td>Orange</td>
<td>165-177</td>
<td>40.6</td>
</tr>
<tr>
<td>*mer-[Rh₂Cl₂(S₂CO)(S₂COEt)(PMe₂Ph)]₂PF₆</td>
<td>(XIII)</td>
<td>Yellow</td>
<td>120-123</td>
<td>46.4</td>
</tr>
</tbody>
</table>

* In Ω⁻¹ cm² mol⁻¹; measured in MeNO₂ at 298 K; conc. (10⁻⁴M) in parentheses.  A Mixture of cis- and trans-isomers (¹H n.m.r. evidence).

TABLE 2

I.r. spectra (cm⁻¹) of various rhodium dithio-acid complexes (shoulders in italics)

<table>
<thead>
<tr>
<th>Complex</th>
<th>υ(RhCl)</th>
<th>Dithio-acid ligand absorptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>*mer-[RhCl₂(PMe₂Ph)]</td>
<td>(I)</td>
<td>339, 313, 273</td>
</tr>
<tr>
<td>*mer-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂</td>
<td>(II)</td>
<td>339, 319</td>
</tr>
<tr>
<td>*mer-[RhCl₂(S₂COEt)(PMe₂Ph)]</td>
<td>(III)</td>
<td>339, 319</td>
</tr>
<tr>
<td>*trans-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂</td>
<td>(IV)</td>
<td>332, 320</td>
</tr>
<tr>
<td>*cis-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂</td>
<td>(V)</td>
<td>340, 330</td>
</tr>
<tr>
<td>*trans-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂</td>
<td>(VI)</td>
<td>339, 319</td>
</tr>
<tr>
<td>*cis-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂</td>
<td>(VII)</td>
<td>332, 320</td>
</tr>
<tr>
<td>*mer-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂BF₄</td>
<td>(VIII)</td>
<td>339, 319</td>
</tr>
<tr>
<td>*trans-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂BF₄</td>
<td>(IX)</td>
<td>339, 325</td>
</tr>
<tr>
<td>*cis-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂BF₄</td>
<td>(X)</td>
<td>320</td>
</tr>
<tr>
<td>*mer-[RhCl₂(S₂CNMe₂)(PMe₂Ph)]₂BF₄</td>
<td>(XI)</td>
<td>342</td>
</tr>
<tr>
<td>*mer-[RhCl₂(S₂CO)(PMe₂Ph)]</td>
<td>(XII)</td>
<td>312</td>
</tr>
<tr>
<td>*mer-[RhCl₂(S₂CO)(S₂COEt)(PMe₂Ph)]₂</td>
<td>(XIII)</td>
<td>320</td>
</tr>
<tr>
<td>*cis-[RhCl₂(S₂CO)(S₂COEt)(PMe₂Ph)]₂</td>
<td>(XIV)</td>
<td>312</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₂PF₆</td>
<td>(XV)</td>
<td>312</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₂PF₆</td>
<td>(XVI)</td>
<td>312</td>
</tr>
<tr>
<td>*cis-[Rh₂Cl₂(PPh₃)(PMe₂Ph)]₂PF₆</td>
<td>(XVII)</td>
<td>312</td>
</tr>
</tbody>
</table>

* υ(CN) (S₂CNMe₂) (refs. 12 and 36).  * Band for unidentate S₂PMe₄ (refs. 5 and 6).  * υ(C=O) (S₂COEt): D. Coucouvanis, Progr. Inorg. Chem., 1970, 11, 305 and refs. therein.  * Bands for bidentate S₂PMe₄ (refs. 5 and 6).  * Bands for bidentate S₂PMe₄ (refs. 5 and 6).  * Band for bidentate S₂PMe₄ (refs. 5 and 6).  * Band for bidentate S₂PMe₄ (refs. 5 and 6).
already containing the dithio-acid ligands, has also been used, but less frequently, e.g. in the preparation of \[\text{Rh}(\text{S}_2\text{PF}_6)(\text{CO})\text{L}] \text{(L = PH}_3, \text{AsPH}_3, \text{or SbPH}_3)\] from \[\text{Rh}(\text{S}_2\text{PF}_6)(\text{CO})\text{L}\text{a} \text{and L}.\]

In this work, reaction of the complex mer-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[I], with an excess of alkali-metal or ammonium dithio-acid salt under reflux for 1 h led to formation of several different products in every case. These products were separated by fractional recrystallisation or dry-column chromatography, or, in general, Na\text{S}_2\text{CNMe}_2\text{H}_2\text{O} was shaken in methanol for 10 min, the orange methanol-insoluble [RhCl\text{S}\text{CNMe}_2\text{PMMe}_2\text{Ph}],[\text{PMMe}_2\text{Ph}],[IV], was formed, but on recrystallisation from dichloromethane–hexane this was converted into (II). When (IV) was shaken in methanol with a mixture of NaBPh_4 and PMMe_2Ph for 24 h, (II) was again formed together with a new complex [RhCl\text{S}\text{CNMe}_2\text{PMMe}_2\text{Ph}],[\text{PMMe}_2\text{Ph}],[BPh],[V], Attempts to prepare the latter directly from complex (I) by reaction with Na\text{S}_2\text{CNMe}_2\text{H}_2\text{O}, NaBPh_4, and PMMe_2Ph proved abortive;

### Table 3

<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>Dithio-ligand</th>
<th>Methyl groups of phosphate</th>
<th>Phenyl groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>mer-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[I]</td>
<td>301</td>
<td>6:83 (s)</td>
<td>8:64 (t)</td>
<td>11:0 (s)</td>
</tr>
<tr>
<td>mer-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[IV]</td>
<td>301</td>
<td>7:62 (d)</td>
<td>13:0 (s)</td>
<td>11:0 (s)</td>
</tr>
<tr>
<td>trans-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[II]</td>
<td>301</td>
<td>6:54 (s)</td>
<td>8:66 (t)</td>
<td>11:0 (s)</td>
</tr>
<tr>
<td>cis-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[III]</td>
<td>301</td>
<td>7:62 (d)</td>
<td>13:0 (s)</td>
<td>11:0 (s)</td>
</tr>
<tr>
<td>cis-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[II]</td>
<td>301</td>
<td>6:54 (s)</td>
<td>8:66 (t)</td>
<td>11:0 (s)</td>
</tr>
<tr>
<td>cis-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[III]</td>
<td>301</td>
<td>7:62 (d)</td>
<td>13:0 (s)</td>
<td>11:0 (s)</td>
</tr>
<tr>
<td>trans-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[VI]</td>
<td>301</td>
<td>7:60 (s)</td>
<td>8:66 (t)</td>
<td>11:0 (s)</td>
</tr>
</tbody>
</table>

s = Singlet, d = doublet, t = triplet, and q = quartet.

* Since \(H_2\text{S}_2\text{PH}_4\) type spectrum, coupling constant is \(J_{\text{HH}} + J_{\text{HH}}\) in Hz. * \(J_{\text{HH}}\) in Hz. * \(J_{\text{CH}_2\text{CH}_2}\) in Hz. * Pseudo-doublet. / Measured in (CD)_2CO. * Spectrum obtained from mixture of cis- and trans-isomers.

each was synthesised as the sole product by slight changes in the conditions of reaction. Analytical data for all these new complexes are given in Table 1 and spectroscopic properties in Tables 2 and 3.

**NN-Dimethylidithiocarbamate-complexes.**— Heating complex (I) under reflux with an excess of Na\text{S}_2\text{CNMe}_2\text{H}_2\text{O} in ethanol for 1 h led to formation of two products. These were readily separated, since one of them, [RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[II], is insoluble in cold ethanol whereas the other is very soluble. After removal of complex (II), the other was precipitated in high yield as a yellow crystalline complex by addition of excess of NaBPh_4 or NH_2PF_6. The latter salts are strongly conducting in CH_2Cl_2 and analyse for \[\text{Rh}(\text{S}_2\text{CNMe}_2\text{PMMe}_3\text{Ph})\text{Y}\text{Y}{(\text{III}; \text{Y} = \text{BPH}_4\text{ or PF}_6\text{)}}\]. Long reaction times in ethanol led exclusively to product (III) on addition of Y.

However, when a suspension of complex (I) and instead, the yellow conducting solid [RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[BPh],[VI] formed which, on setting aside in CDCl_3 for 48 h, reverted to (I) and free PMMe_2Ph.

Finally, when the complex mer-[RhCl\text{S}\text{CNMe}_2\text{PMMe}_3\text{Ph}],[BPh],[was used instead of (I) long-term reaction in ethanol under reflux with excess of Na\text{S}_2\text{CNMe}_2\text{H}_2\text{O}, followed by addition of NaBPh_4, gave two ionic complexes, both of formula \[\text{Rh}(\text{S}_2\text{CNMe}_2\text{PMMe}_2\text{Ph}],[\text{PMMe}_2\text{Ph}],[\text{BPh}],[\text{III}] and (VI), together with very small amounts of \[\text{Rh}(\text{S}_2\text{CNMe}_2\text{PMMe}_3\text{Ph}],[\text{BPh}],[\text{IV}]. Similar complexes \[\text{Rh}(\text{S}_2\text{CNMe}_2\text{PMMe}_2\text{Ph}],[\text{PMMe}_2\text{Ph}],[\text{PF}],[\text{IV}\text{a}].

**Diphenyl- and Dimethyl-phosphinodithioato-complexes.**— When complex (I) was heated under reflux in ethanol for 60 min with an excess of NH_2SPh_2, addition of excess of NaBPh_4 or NH_2PF_6 led to precipitation of the

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expected \( \text{[Rh}(\text{S}_2\text{PPh}_3\text{)}\text{PMe}_2\text{Ph})\text{]}\text{Y} \) (III; \( Y = \text{BPPh}_3^{-} \) or \( \text{PF}_6^{-} \)). In addition, very small amounts of an ethanol-insoluble complex analysing for \( \text{[RhCl}(\text{S}_2\text{PPh}_3\text{)}\text{PMe}_2\text{Ph})\text{]} \) (VII), were obtained. However, when the reaction was carried out using \( \text{Na}_2\text{S}_2\text{PMe}_2\cdot\text{H}_2\text{O} \), the analogous complexes were not formed; instead, a red solid of uncertain composition was obtained which exhibited variable analyses (carbon and hydrogen) each time the reaction was attempted. The \( ^1\text{H} \) n.m.r. spectrum of this material contained only broad peaks, which were temperature invariant. The broadness of these signals probably arises from a paramagnetic impurity since the substance exhibited a weak e.s.r. signal (cf. the preparation of \( \text{[RhCl}(\text{PPh}_3\text{)}\text{]} \)). The complex \( \text{[Rh}(\text{S}_2\text{PMe}_2\text{)}\text{PMe}_2\text{Ph})\text{]}\text{BPPh}_3 \), (III), was, however, prepared as a yellow microcrystalline solid either by excluding oxygen completely from the reaction in ethanol or by reaction of \( \text{[RhCl}(\text{PMe}_2\text{Ph})\text{]} \) with excess of \( \text{Na}_2\text{S}_2\text{PMe}_2\cdot\text{H}_2\text{O} \) in acetonitrile, followed by addition of \( \text{NaBPPh}_3 \). The compound is, in fact, stable both in the solid state and in solution; however, a red solution is rapidly formed when the compound is dissolved in ethanol or methanol in the presence of excess of \( \text{Na}_2\text{S}_2\text{PMe}_2\cdot\text{H}_2\text{O} \) and air.

Short-term reactions between complex (I) and \( \text{Na}_2\text{S}_2\text{PMe}_2\cdot\text{H}_2\text{O} \) or \( \text{NH}_2\text{S}_2\text{PPh}_3 \) also differed slightly from one another. The dimethylphosphinodithioato behavior was the same as the \( \text{NN}-\text{dimethylthiocarbamato-} \) ion, giving, after shaking for 10 min in methanol, orange \( \text{[RhCl}(\text{S}_2\text{PMe}_2\text{)}\text{PMe}_2\text{Ph})\text{]} \) (IV), which, on recrystallisation from deuteriochloroform–hexane, gave \( \text{[RhCl}(\text{S}_2\text{PMe}_2\text{)}\text{PMe}_2\text{Ph})\text{]} \). Recrystallisation from the latter of hot toluene gives mainly (II), together with a small amount of another complex; (VII), with the same analytical data but different spectral properties. In contrast, shaking complex (I) and \( \text{NH}_2\text{S}_2\text{PPh}_3 \) in ethanol for 10 min gave only \( \text{[RhCl}(\text{S}_2\text{PPh}_3\text{)}\text{PMe}_2\text{Ph})\text{]} \). (II). The latter complex had different spectral properties from (VII), although recrystallisation from hot ethanol gave small amounts of (VII).

Finally, attempts to prepare the complex \( \text{[RhCl}(\text{S}_2\text{PMe}_2\text{)}\text{PMe}_2\text{Ph})\text{]}\text{BPPh}_3 \) by reaction between \( \text{[RhCl}(\text{S}_2\text{PMe}_2\text{)}\text{PMe}_2\text{Ph})\text{]} \) (IV), \( \text{NaBPPh}_3 \), and \( \text{PMe}_2\text{Ph} \) in methanol yielded only \( \text{[Rh}(\text{O})\text{PMe}_2\text{Ph})\text{]}\text{BPPh}_3 \) (VIII) \(^{25}\) or, if oxygen was excluded, a mixture of \( \text{[RhCl}(\text{S}_2\text{PMe}_2\text{)}\text{PMe}_2\text{Ph})\text{]}\text{BPPh}_3 \) (IX) \(^{25}\) and \( \text{[RhCl}(\text{S}_2\text{PMe}_2\text{)}\text{PMe}_2\text{Ph})\text{]} \), (II). Compound (VIII) was also formed as the sole product from reaction of \( \text{[Rh}(\text{S}_2\text{PMe}_2\text{)}\text{]}\), \( \text{PMe}_2\text{Ph} \), and \( \text{NaBPPh}_3 \).

O-Ethyl Dithiocarbonate (Xanthate) and Dithiocarbonate Complexes.—The reaction of \( \text{K}_3\text{COEt} \) with complex (I) led to an even wider range of products than those found with the other dithio-ligands, since there is the added possibility of attack on a co-ordinated xanthate ligand by a nucleophile to yield dithiocarbonate-complexes [equation (I)].

Thus, when complex (I) was heated under reflux in ethanol with excess of \( \text{K}_3\text{COEt} \) for 60 min, no fewer than four different complexes, which were separated by dry-column chromatography, were isolated. Analytical and spectroscopic analyses indicated the formulations \( \text{[RhCl}(\text{S}_2\text{CO})\text{PMe}_2\text{Ph})\text{]} \) (X), \( \text{[K[RhCl}(\text{S}_2\text{CO})\text{PMe}_2\text{Ph})\text{]} \) (XI), and two isomers of \( \text{[Rh}(\text{S}_2\text{CO})\text{PMe}_2\text{Ph})\text{]} \), (XII) and (XIII). However, when the reaction was carried out in a less-polar solvent such as acetone or ethanol–chloroform, none of these products was obtained but, instead, orange \( \text{[RhCl}(\text{S}_2\text{CO})\text{PMe}_2\text{Ph})\text{]} \), (II), was isolated.

As for \( \text{S}_2\text{CNMe}_2 \), shaking complex (I) and \( \text{K}_3\text{COEt} \) in methanol for 10 min gave the dark orange \( \text{[RhCl}(\text{S}_2\text{CO})\text{PMe}_2\text{Ph})\text{]} \), (IV), which, on recrystallisation from hot methanol or chloroform–hexane. This interconversion was also affected by heating (IV) to its melting point (120–123 °C), whereupon \( \text{PMe}_2\text{Ph} \) was evolved and the orange residue consisted largely of compound (II).

Finally, when complex (IV); \( \text{S}_2\text{CO} \) was shaken in ethanol with excess of \( \text{NaBPPh}_3 \) for several weeks, a small amount of \( \text{[RhCl}(\text{S}_2\text{CO})\text{PMe}_2\text{Ph})\text{]}\text{BPPh}_3 \), (V), was deposited. The latter complex was also prepared in high yield by reaction of (I) and \( \text{K}_3\text{COEt} \) (1 : 1 molar ratio) in methanol heated under reflux for 60 min, followed by addition of \( \text{NaBPPh}_3 \). Longer reaction times (5 h) gave yellow solutions from which compounds (X) and (XIII) were isolated.

Spectroscopic Properties of the Dithio-acid Complexes.—I.r. spectra. Group theory predicts three i.r.-active \( \nu(\text{RhCl}) \) stretching vibrations for complex (I) and Brookes and Shaw \(^{21}\) assign these to the peaks at 339, 313, and 273 cm\(^{-1}\), with the band at lowest energy arising (predominantly) from the stretch of the rhodium–chloride bond \textit{trans} to a \text{PMe}_2\text{Ph} group. Thus, analysis of the Rh–Cl stretching region of some of these new complexes should yield information about their structures. Also, earlier work in this and other laboratories suggests that the position of the sulphur-ligand absorption bands should give some information about the mode of bonding of the dithio-acid group.

For each of the complexes (IV), the \( \nu(\text{RhCl}) \) region was similar to that of (I) (Table 2) except that the lowest band had disappeared, indicating that the chloride ion \textit{trans} to phosphine has been replaced. This


Compounds shown in broken square brackets were not isolated.
is in agreement with the larger trans-labilising effect of PMe₂Ph compared to chloride ion and with the results of other exchange reactions carried out by Brookes and Shaw. In addition, for \((S-S)^-\) = \(S_4\)PMe₄ the absorption at 601 cm⁻¹, 5,6 and for \((S-S)^-\) = \(S_4\)CNEt the position of \(v(CN)\) below 1 470 cm⁻¹, 15,36 both suggest that the sulphur ligands are co-ordinated through only one sulphur atom.

Since there was little change in the \(v(RhCl)\) region from complexes (IV) to (II), and since all the dithioligand absorptions now have characteristic frequencies for bidentate co-ordination (see Table 2), it seems reasonable to infer that the chloro-groups remain mutually trans and that chelation of the dithioligand occurs with concomitant loss of a PMe₂Ph group. From an i.r. standpoint, there was very little difference between the \(v(RhCl)\) region or between the \(v(PS)\) region for complexes (II) and (VII), although other parts of their i.r. spectra and their \(^1\)H n.m.r. spectra are substantially different (see later).

The remaining complexes all appeared to contain only chelated dithio-groups and had only one or no \(v(RhCl)\) bands and, hence, little stereochemical information can be gleaned from i.r. studies. N.m.r. spectroscopy has, however, proved an invaluable tool in assigning structures to all these complexes.

**N.m.r. spectra.** The only differences between \(^1\)H n.m.r. spectra of complexes (IV) and (I) were that dithioligand resonances occurred in the former and that positions of the triplet and doublet arising from the phosphine groups were very slightly different (Table 3), presumably because of different shielding effects of the dithioligands from that of chloride ion. In agreement with the i.r. data, this confirms the structure of these complexes (Scheme), since if either of the other chloride ions had been replaced the plane of symmetry passing through the three phosphorus atoms would have been removed and, because of hindered rotation about the rhodium-phosphorus bonds, two triplets would arise from the methyl groups of the mutually trans phosphine ligands (cf. cis-[RuCl₂(CO)₂(PMe₂Ph)₃]).

In fact, \(^1\)H n.m.r. spectra of the complexes \([V; \ (S-S)^-\) = \(S_4\)CNEt] and (X) did show two triplets arising from the trans-phosphine groups, indicating that there is no plane of symmetry through these phosphines and hence (V) is assigned the structure shown in the Scheme. Further evidence that complex \([V; \ (S-S)^-\) = \(S_4\)CNEt] has the structure shown stems from the fact that, at 301 K, there were two resonances arising from methyl groups on the dithiocarbamato-ligand which can only be explained if there is no plane of symmetry perpendicular to the S₂CN plane in the molecule and if rotation about the C-N bond is hindered. Since the two resonances remained sharp up to 320 K, it appears that free rotation about the C-N bond is not occurring.

A 'pseudo-doublet' is a sharp doublet with additional signal intensity situated between the doublet. This spectral pattern is indicative of a small, but non-zero, \(J_{PP} \) value when compared to \(|J_{HH} + J_{PH}|\). A

even at this temperature. Complex (X) is most probably formed from \([V; \ (S-S)^-\) = \(S_4\)COEt] by attack of a previously displaced chloride ion on the co-ordinated O-ethyl dithiocarbonate-group.

Complexes (II) showed only one dithioligand resonance in each case, together with one \(H_3 PP'P'^{\prime} \) pseudo-doublet * which arises from the PMe₂Ph groups. Since \(J_{PP} \) was small and there was only one phosphine methyl resonance, the phosphine groups must be mutually cis and the phosphorus atoms must lie on the plane of symmetry of the molecule. The sulphur ligand must also have planes of symmetry both in the S-Rh-S plane and also perpendicular to it since, if any of these were absent, either the complex with \((S-S)^-\) = \(S_4\)CNEt or \(S_4\)PMe₄ would give rise to two dithioligand resonances. Thus, the only possible structure for these complexes is that with trans-chloride groups (as suggested by i.r. studies).

Since \(^1\)H n.m.r. spectra of the complex \([VII; \ (S-S)^-\) = \(S_4\)PMe₄] contained no triplet pattern, the complex cannot contain trans-PMe₂Ph groups. The only possible structure for this isomer is one containing cis-chlorides and -phosphines. This structure would exhibit four phosphine methyl doublets but only two were observed (Table 3). This could be due to fast rotation about the metal-phosphorus bonds at room temperature but, since solutions used for this n.m.r. study were very weak [because of the small yield of (VII)], it is possible that further small splittings were obscured by the high noise level. Further support for the correctness of this cis-cis-cis-isomer formulation for complex (VII) comes from recent studies of the isomerisation reaction of \([RuCl₂(CO)₂(EPh₃)₃]\) (E = P or As) where recrystallisation of trans-[RuCl₂(CO)₂(EPh₃)₃] gives the more stable cis-cis-cis-isomer.

The \(^1\)H n.m.r. spectrum of complex (XI) consisted of broad peaks in the phenyl region, together with a single sharp triplet at \(\tau \) 8.22. This can only occur if the phosphine groups are mutually trans ('virtually coupled' triplet with large \(J_{PP} \)). A possible mode of formation of this rather unusual complex is by attack of potassium chloride, formed from reaction of (I) and K₂CO₃ on (X). The PMe₂Ph group released could then attack (XI) to reproduce (X) with loss of potassium chloride. Since both complexes were found in the reaction mixture, it seems probable that in the presence of excess of KCl and PMe₂Ph an equilibrium is set up between the two complexes.

\(^1\)H N.m.r. spectra of the two complexes (XII) and (XIII) both contained quartet and triplet signals in positions expected for an OEt group, but the pattern arising from the methyl groups on the two phosphines

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was quite different in each case. Complex (XII) exhibited a single 'virtually coupled' triplet indicative of trans-phosphines, whereas (XIII) showed four doublets which suggests that the two phosphine groups are mutually cis and in different chemical environments and that there is hindered rotation about the rhodium-phosphorus bonds. A similar phosphine methyl pattern is observed for one isomer of the complex [Ru(S₂PMe₂)_2(PMe₂Ph)]^−. For complex (XIII), the proton-noise-decoupled ^{31}P n.m.r. spectrum showed two resonances (indicating the phosphorus atoms are magnetically inequivalent) each split into a doublet of doublets by coupling to the rhodium-103 nucleus and the other phosphorus atom. The ^{103}Rh n.m.r. spectrum of complex (XIII) was also measured by decoupling the proton spectrum. Each peak arising from a methyl group in the ^{1}H n.m.r. spectrum was rather broad (2-3 Hz) due to ^{103}Rh-^{1}H coupling and, hence, irradiation in the rhodium range of frequencies sharpened some of the signals but not others. In this way, the rhodium spectrum may be seen to consist of four resonances, i.e., a doublet of doublets arising from coupling to two inequivalent phosphorus atoms. The only structure consistent with all this information is that shown in the Scheme.

Complexes (III) [(S-S) = S₂CNMe₂; Y = BPh₄^− or PF₆^−; (S-S) = S₂PMe₂; Y = BF₄^−] all had low-temperature ^{1}H n.m.r. spectra consistent with cis-phosphines and hindered rotation about the rhodium-phosphorus bonds, namely two resonances corresponding to the methyl groups on the dithio-ligands and two pseudo-doublets arising from the phosphine methyl groups. The ^{1}H n.m.r. spectrum of the complex cis-[Rh(S₂PMe₂)_2(PMe₂Ph)]^−(BF₄^−) was temperature invariant in chlorobenzene up to 360 K, but above this temperature all the peaks began to broaden and the solution darkened, indicating that decomposition had probably occurred. Thus, unlike the related cis-[Ru(S₂PMe₂)_2(PMe₂Ph)]^− complex, the inversion process cis-Δ ← cis-Δ is very slow on the n.m.r. time scale. The complexes cis-[Rh(S₂CNMe₂)_2(PMe₂Ph)]^+ (Y = BPh₄^− or PF₆^−) both gave rise to a single doublet in the proton-noise-decoupled ^{31}P n.m.r. spectrum due to coupling with the ^{103}Rh nucleus and this coupling was found to be temperature invariant in each case. In contrast, the ^{1}H n.m.r. spectrum of the PF₆^− salt showed marked variations with temperature giving only a singlet for the S₂CNMe₂ resonance and a doublet for the phosphine methyl resonance at 300 K. However, the way in which this equivalence of the phosphine methyl groups is realised is rather strange since, on raising the temperature, rather than broadening of the signals followed by coalescence into a broad peak which then sharpens to a single resonance [the established pattern for dynamic mechanism involving, for example, C=N bond rotations or optical isomerisations (see refs. 1 and 6)], the resonances gradually moved closer together without broadening until they were coincident. Further elevation of the temperature did not affect the spectrum. Unpublished work indicates that the complex cis-[Os(S₂CNMe₂)_2(PMe₂Ph)]^+ shows similar variable-temperature ^{1}H n.m.r. spectra.

The only type of mechanism that could give rise to this behaviour is one in which the chemical environments of the two methyl groups on one phosphine ligand become more equivalent at higher temperatures, without any exchange of methyl groups between the two environments (since no coalescence phenomenon was observed). One such mechanism could arise from the fact that at low temperatures (when rotation about the metal-phosphorus bond is slow) there will be one or more preferred discrete orientations of the phosphine moiety with respect to the rest of the complex. These preferred orientations will be determined by a combination of steric and electronic factors. Since there is no symmetry element of the complex that incorporates the metal-phosphorus bond, under these conditions the environments of the two methyl groups on one phosphine ligand will be different and two different signals will therefore be seen in the ^{1}H n.m.r. spectrum.

Now, when the orientation of the phosphine ligand differs from that preferred, each methyl group will be in a different chemical environment from that in the preferred configuration. Thus, as the temperature is raised and the rate of rotation about the metal-phosphorus bond is increased, each methyl group will spend less time in its preferred environment and more in other environments. Its chemical shift will then be an average of the chemical shifts of each environment, weighted according to the amount of time spent in each environment. When, at higher temperatures, the phosphine group is rotating freely, each methyl group will spend an equal amount of time in all environments; hence, the average environment of each is the same and a single resonance is expected. This argument applies to both the phosphine ligands in the complex since they are related to one another by rotation about the two-fold axis and, hence, whatever happens to one phosphine group will be exactly analogous to what happens to the other.

* Closer examination of the phosphine methyl region in the ^{1}H n.m.r. spectra of the complexes cis-[Ru(S₂CNMe₂)_2(PMe₂Ph)]^− and cis-[Ru(S₂PMe₂)_2(PMe₂Ph)]^− reveals that exactly the same type of behaviour occurs and not, as previously recorded, a coalescence behaviour. However, for the phosphine methyl groups of the complex cis-[Ru(S₂PMe₂)_2(PMe₂Ph)]^−, coalescence does occur as previously stated and this can be attributed to exchange of the environments of the methyl groups on different phosphine groups by means of the facile optical-isomerisation process discussed in these papers. Then, the discrepancy between the activation energy (ΔG‡) for this inversion reaction, as calculated by lineshape analysis of methyl resonances of the dithio-ligands (i.e. 63-4 kJ mol⁻¹) and that calculated from the coalescence temperature of the pseudo-triplets arising from the phosphine methyl groups (67-4 kJ mol⁻¹) is explicable on the basis that the coalescence approach assumes a small linewidth compared with the separation of the peaks. In this case, the assumption is invalid since the linewidth of each pseudo-triplet is ca. 126-0 Hz and their separation only ca. 136-0 Hz.

** J.C.S. Dalton

D. J. Cole-Hamilton and T. A. Stephenson, unpublished work.
It is important to note that exchange of the elements of the methyl groups does not occur in this process since, although at different times, each may occupy the same position relative to the non-phosphorus part of the molecule, their environment with respect to the orientation of the other methyl group and the phenyl group attached to the phosphorus atom will always be different.

Finally, the ionic complexes formed by long-term reaction between (I; \( I = PMe_3Ph \)) and Na\(_2\)C\(_{6}\)CNMe\(_2\).2H\(_2\)O are, as expected, geometrical isomers of \([\text{Rh}(\text{S}_2\text{CNe}_2\text{Ph})_2(\text{PMe}_3\text{Ph})_2]Y\). Thus, \( ^{1}H \) n.m.r. spectra of complexes (VI; \( Y = BPh_4^− \) or PF\(_6^− \)) consisted of one \( ^{13}C \) resonance and a 'virtually coupled' triplet phosphine methyl resonance, whereas (III), which could not be satisfactorily separated from the trans-isomer, had two \( ^{13}C \) resonances and one pseudo-doublet phosphine resonance in each case. The fact that the trans-isomer is formed more readily when the phosphine is PMe\(_3\)Ph rather than PMe\(_3\)Ph can presumably be attributed to the greater steric size of PMe\(_3\)Ph. It should be noted at this point that the analogous complex \([\text{Rh}(\text{S}_2\text{CNe}_2\text{Ph})_2(\text{PPh}_3)_2]BF_4 \) has been assigned a 

\[ \text{trans-stereosymmetry} \] and, although no evidence is cited to support this assignment, the result is consistent with the still greater steric size of triphenylphosphine. Thus, this combination of i.r. and n.m.r. studies, together with the various interconversions of complexes noted earlier, can be used to suggest a probable stereochemical path for the overall reaction between complex (I) and the various dithio-acid ligands and this is outlined in the Scheme.

**Conclusion.**—The reactions between \( \text{mer-}[\text{RhCl}_2(\text{PMe}_3\text{Ph})_3] \) (I), and the various dithio-acid ligands can be seen to proceed in a stepwise manner and, as expected, the oxidation state of three is maintained in all the complexes formed. The latter are indeed much less labile than their ruthenium analogues, but this is probably due mainly to the fact that many of them are ionic. Hence, the positive charge on the metal atom will tend to make the metal–ligand bonds stronger and it is probably this fact, rather than any large intrinsic differences in lability of the coordination spheres of rhodium(III) and ruthenium(II), which accounts for the difference in behaviour. It is very probable that re-arrangements of the dithio-acid ligands with \( \text{mer-}[\text{RuCl}_2(\text{PMe}_3\text{Ph})_3] \) also proceed as above, but the combination of such factors as the tendency to form ruthenium(II) complexes under the reducing conditions present, the greater lability of ruthenium compared to rhodium, and the paramagnetism of most ruthenium(III) species make satisfactory characterisation of any ruthenium(III) intermediate a difficult task.

**EXPERIMENTAL**

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4 000–250 cm\(^{-1}\) on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. \(^1\)H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer and \(^{31}\)P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform mode at 40-5 MHz (\(^{31}\)P chemical shifts are given in p.p.m. to high frequency of 85\% H\(_2\)PO\(_4\)). Heteronuclear-decoupling experiments were carried out on the HA-100 spectrometer using a second radio-frequency field provided by a Schlumberger FS30 frequency synthesiser. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Köfler hot-stage microscope and are uncorrected.

Rhodium trichloride trihydrate (Johnson, Matthey Ltd), dimethylphenylphosphine (B.D.H.), methylidyphenylphosphine (Strem), Na\(_2\)C\(_{6}\)CNMe\(_2\).2H\(_2\)O (Ralph Emanuel), and K\(_3\)S\(_2\)COEt (B.D.H.) were obtained as indicated. Sodium dimethylphosphonidotrioxide was prepared as described earlier \(^{21}\) and ammonium diphenylphosphonodiohexane from Ph\(_3\)P=O.H \(^{22}\) and ammonia in benzene. The complexes \( \text{mer-}[\text{RhCl}_2(\text{PMe}_3\text{Ph})_3] \) (I), \( \text{fac-}[\text{RhCl}_2(\text{PMe}_3\text{Ph})_3] \), and \( \text{mer-}[\text{RhCl}_2(\text{PMe}_3\text{Ph})_3] \) were synthesised by published methods.\(^{21}\)

**Preparations.**—trans-Dichloro\((N\text{N-dimethylthiodi-carbamato)bis(dimethylphenylphosphine)rhodium(III)}\), (II), and cis-bis\((N\text{N-dimethylthiodi-carbamato)bis(dimethylphenylphosphine)rhodium(III)}\) tetraphenylborate, (III). Complex (I) (0.25 g) and excess of Na\(_2\)C\(_{6}\)CNMe\(_2\).2H\(_2\)O (0.25 g) were heated under reflux in ethanol (20 cm\(^3\)) for 60 min and the resulting orange solution was cooled and filtered. The residue was washed with ethanol to remove sodium chloride and then with ethanol and pentane to give the orange solid (II) (0.07 g, 30\%).

The yellow filtrate was treated with excess of NaBPh\(_4\) in ethanol, and the resulting yellow precipitate filtered off, washed with water, ethanol, and pentane, and then re-crystallised from dichloromethane–ethanol to give complex (III) (0.20 g, 51\%). \(^{31}\)P n.m.r. spectrum of (III) in CDCl\(_3\); 4.5 p.p.m. (doublet, \( J_{\text{P–P}} 112 \text{ Hz} \)). When complex (I) and Na\(_2\)C\(_{6}\)CNMe\(_2\).2H\(_2\)O were heated under reflux in ethanol for 16 h, only (III) (0.35 g, 92\%) was isolated on addition of NaBPh\(_4\).

cis-Bis\((N\text{N-dimethylthiodi-carbamato)bis(dimethylphenylphosphine)rhodium(III)}\) hexafluorophosphate, (III), was similarly prepared except that excess of NH\(_4\)PF\(_6\) was added to the yellow ethanolic solution. No immediate precipitation occurred but large orange crystals were deposited when the solution was left for 3 days. They were filtered off, washed with water, ethanol, and pentane to give complex (III) (0.30 g, 98\%). \(^{31}\)P n.m.r. spectrum in CDCl\(_3\); 4.57 (doublet, \( J_{\text{P–P}} 114 \text{ Hz} \)); 147.2 p.p.m. (heptet, \( J_{\text{P–P}} 727 \text{ Hz} \)).

cis- and trans-Bis\((N\text{N-dimethylthiodi-carbamato)bis(dimethylphenylphosphine)rhodium(III)}\) tetraphenylborate, (II), and (VI). These complexes were prepared as above, by heating under reflux \( \text{mer-}[\text{RhCl}_2(\text{PMe}_3\text{Ph})_3] \) (0.20 g) and excess of Na\(_2\)C\(_{6}\)CNMe\(_2\).2H\(_2\)O (0.15 g) in ethanol (20 cm\(^3\)) for 16 h. Addition of NaBPh\(_4\) then gave an immediate yellow precipitate consisting of a mixture of the cis- and trans-isomers (III) and (VI) (\(^1\)H n.m.r. and analytical evidence). On setting aside the filtrate, yellow microcrystals of the pure trans-isomer (VI) were deposited. Total yield 90\% (cis: trans ratio ca. 1:5:1:0).

Similarly, cis- and trans-\( \text{[Rh}(\text{S}_2\text{CNe}_2\text{Ph})_2(\text{PMePh}_3)_2]PF_6 \).


(III) and (VI), were prepared from mer- [RhCl₃(PMe₃)₂] and Na₂SnCNMe₄·2H₂O followed by addition of excess of NH₄PF₆. The yellow crystals that separated first were the pure trans-isomer (VI) (H n.m.r. evidence). Later batches were orange and consisted of a mixture of cis- and trans-isomers. Total yield ca. 70%.

mer-Dichloro(NN-dimethylthiocarbamato)(dimethylphenylphosphine)rhodium(III), (IV). A suspension of the orange solid (IV) was filtered off and washed with water, methanol, and pentane (0-25 g, 98%). Recrystallisation from dichloromethane-hexane gave trans-[RhCl₃(S₂CNMe₄)]·(PMe₃)₂, (II).

cis-Chloro(NN-dimethylthiocarbamato)(dimethylphenylphosphine)rhodium(III) tetracyanoethylene, (V). The complex mer-[RhCl₃(S₂CNMe₄)]·(PMe₃)₂ (0-23 g), NaBP₄ (0-36 g), and PMe₃ (5-0 g) were shaken in methanol for 24 h under nitrogen atmosphere. The resulting mixture of orange solid was washed with methanol to leech out the yellow solid. On cooling, this solution gave yellow crystals which were recrystallised from methanol to give (V) (0-20 g, 55%). The remaining orange solid, which was insoluble in hot ethanol, was trans-[RhCl₃(S₂CNMe₄)]·(PMe₃)₂, (II).

cis-cis-cis-Dichlorobis(dimethylphenylphosphine)(diphenylphosphinodithioato)rhodium(III), (VII), and cis-cis-bis(dimethylphenylphosphine)bis(diphenylphosphinodithioato)rhodium(III) tetracyanoethylene, (III). Complex (I) (0-30 g) and excess of NH₄PF₆ (0-40 g) were heated under reflux in ethanol (20 cm³) for 60 min. Filtration of the hot solution left a very small amount of orange crystals of (VII), which were purified by washing with water, methanol, and pentane. The orange filtrate was treated with excess of NaBP₄ to give an immediate orange precipitate (III), which was recrystallised from dichloromethane-methanol to remove any NH₄BF₄ (0-46 g, 80%). The complex cis-[RhCl₃(PMe₃)₂] (0-30 g) (II), was similarly prepared except that the orange filtrate was treated with excess of NH₄PF₆ and the complex separated slowly as large orange crystals (0-40 g, 80%). The BP₄⁻ salt was also obtained in a pure state by dissolving the PF₆⁻ salt in methanol and adding excess of NaBP₄.

cis-Bis(dimethylphenylphosphine)bis(dimethylphosphinodithioato)rhodium(III) tetracyanoethylene, (III). Complex (I) (0-30 g) and Na₂SnPM₃H₂O (0-35 g) were heated under reflux in degassed ethanol (20 cm³) for 1 h with dry oxygen-free nitrogen continuously bubbling through the mixture. The resulting orange solution was cooled (under a nitrogen atmosphere) and NaBP₄ (0-20 g) added. The resulting yellow solid was filtered off under a nitrogen atmosphere and washed with water, ethanol, and pentane (yield 0-90 g, 61%). Omission of nitrogen from the reaction gave a red solution from which a red solid was precipitated by addition of excess of NaBP₄. This material had different analyses from ostensibly the same preparation, e.g. C, 51-2; H, 5-6 and C, 37-3; H, 4-7%. However complex (III) was prepared by treating under reflux fac-[RhCl₃(PMe₃)₂] (0-07 g) and excess of Na₂SnPM₃H₂O (0-06 g) in acetonitrile (50 : 50 v/v) (25 cm³) for 60 min. By evaporating to dryness, dissolving in CH₂Cl₂, filtering off excess of Na₂SnPM₃H₂O, again evaporating to dryness, dissolving in methanol, and adding excess of NaBP₄, complex (III) was obtained as yellow microcrystals.

cis-Dichlorobis(dimethylphenylphosphine)(diphenylphosphinodithioato)rhodium(III), (VII). This complex was prepared by shaking (I) (0-30 g) and Na₂SnPM₃H₂O (0-20 g) in methanol (40 cm³) for 10 min (0-41 g, 90%). Recrystallisation from deuterochloroform-hexane gave trans-dichlorobis(dimethylphenylphosphine)(diphenylphosphinodithioato)rhodium(III), (II).

Reactions. — mer-[RhCl₃(S₂CNMe₄)]·(PMe₃)₂, (IV), with NaBP₄ and PMe₃. Complex (IV) (0-32 g), NaBP₄ (0-32 g), and PMe₃ (0-10 cm³) were shaken in glass beakers under nitrogen atmosphere for 2 days to give a yellow precipitate of cis-dichlorotetrakis(dimethylphenylphosphine)rhodium(III) tetracyanoethylene, (IX), purified by washing several times with water, methanol, diethyl ether, and pentane (yield 0-43 g, 80%), m.p. 145—147 °C (Found: C, 64-1; H, 6-3). Calc. for CsH₈B₁₅Cl₃Ru: C, 64-3; H, 6-1%). The same complex was also formed by reaction of a mixture of (I), Na₂SnPM₃H₂O, NaBP₄, and PMe₃. ¹H N.m.r. spectrum (CH₃Cl₂) (253 K): 8 26-26 (triplet) (J₉/₉ + J₂/₂) 48 : 8-94 (doublet) (J₉/₉ + J₂/₂) 40 Hz) 810-80 (singlet); Ph resonance at 7-7-8-9. Complex (IX) rearranged to (I) and free PMe₃ on standing in CDC₁₂ for 48 h.

When the reaction between complex (IV), NaBP₄, and PMe₃ was carried out in the presence of air, the white solid cis-tetrakis(dimethylphenylphosphine)dicarbonylrhodium(II) tetracyanoethylene, (IV), was formed (0-40 g, 80%) (ν(O—O) at 841, 860 cm⁻¹; ν(C=C) at 841, 870 cm⁻¹ for [Ru(CO)₂(PMe₃)]₂ClO₄).¹ The same complex was formed when [Rh(S₂CNMe₄)] was treated with PMe₃ in the presence of NaBP₄, m.p. 129—130 °C (Found: C, 66-2; H, 6-6. Calc. for CsH₈B₁₅Cl₃Ru: C, 66-8; H, 6-4%). ¹H N.m.r. spectrum (CH₃Cl₂) (300 K): 8 88-88 (triplet) 8 J₂/₂ + J₉/₉ 7 8-99 (doublet) (J₉/₉ + J₂/₂) 8 Hz; Ph resonance at 7-2-7-6.

Potassium O-ethyl dithiocarbonate (xanthate) with complex (I). Complex (I) (0-30 g) and excess of K₂CO₃ (0-30 g) were heated under reflux in ethanol for 60 min and the resulting yellow solution settled hot in order to remove potassium chloride. It was then evaporated to dryness and the yellow oil dissolved in CH₂Cl₂. Excess of K₂CO₃ was filtered off and the solution allowed to stand whereupon yellow needle-shaped crystals of potassium dichlorobis(dimethylphenylphosphine)(dithiocarbamato)rhodium(II), (XI), were deposited (0-02 g, 7%). These were filtered off and recrystallised from dichloromethane-methanol. The yellow filtrate was placed on an alumina dry column and eluted with CH₂Cl₂ to give two poorly resolved bands. The first band was extracted with diethyl ether and then hexane added. Slow evaporation of these solutions gave crystals in each
case. The first yellow band gave trans-bis(dimethylphenylphosphine)(dithiocarbanato)(O-ethyl dithiocarbanato)rhodium(III), (XII) (0-05 g, 17-5%). The second yellow band gave 1-mer-
chlorotris(dimethylphenylphosphine)(dithiocarbanato)rhodium(III), (X) (0-05 g, 16%), and the second yellow band yielded cis-bis(dimethylphenylphosphine)(dithiocarbanato)(O-ethyl dithiocarbanato)rhodium(III), (XIII) (0-10 g, 35%). $^{31}$P N.m.r. spectrum of complex (XIII) in CDCl$_3$: 9-13 (doublet of doublets), 0-46 p.p.m. (doublet of doublets): $J_{PF}$ 118, $J_{HF}$ 110, $J_{HF}$ 18 Hz.

When the initial ethanolic solution was allowed to evaporate slowly, the first product to crystallise out was (XIII) (0-20 g, 70%). Then a mixture of complexes (XIII) and (X) were deposited followed by small amounts of pure (X) (0-05 g, 16%). When complex (I) (0-30 g) and K$_3$COEt (0-08 g, 1:1-05 molar ratio) were heated under reflux in ethanol for 5 h and the resulting yellow solution worked-up as before, two bands were eluted containing (X) (0-05 g, 16%) and (XIII) (0-02 g, 7%). However, when complex (I) (0-30 g) and excess of K$_3$COEt (0-30 g) were shaken in acetone (25 cm$^3$) for 16 h and the resulting orange solution evaporated to dryness (after removing KCl by filtration), recrystallisation of the orange oil from dichloromethane–hexane gave orange crystals of trans-di-
chlorobis(dimethylphenylphosphine)(O-ethyl dithiocarbanato)rhodium(III), (I) (0-20 g, 72%). This complex was also prepared by carrying out the same reaction in a solution of ethanol–chloroform heated under reflux and working up the orange solution in the same way. Reaction of complex (II) with K$_3$COEt gave (XIII).

When complex (I) (0-30 g) and K$_3$COEt (0-30 g) were shaken in methanol (25 cm$^3$) for 10 min the orange complex mer-
chlorotris(dimethylphenylphosphine)(O-ethyl dithiocarbanato)rhodium(III), (IV) (0-30 g, 88%) was deposited. Recrystallisation of this complex from methanol (or chloroform–hexane) gave trans-[RhCl$_3$(S$_2$COEt)($^3$Me$_2$P$_2$)$_3$], (II). Finally, when the complex mer-[RhCl$_3$(S$_2$COEt)($^3$Me$_2$P$_2$)$_3$], (IV) (0-12 g), was shaken for 4 weeks in ethanol (20 cm$^3$) with NaBPh$_4$ (0-12 g), a small amount of orange mer-
chlorotris(dimethylphenylphosphine)(O-ethyldithiocarbon-
ate)rhodium(III) tetraphenylborate, (V), was deposited (0-02 g, 9-5%). However, this complex was also prepared in high yield by reaction of (I) (0-37 g) with K$_3$COEt (0-09 g, 1:1 molar ratio) in methanol (20 cm$^3$) heated under reflux for 60 min followed by addition of excess of NaBPh$_4$.

Recrystallisation of the resulting yellow solid from dichloromethane–methanol gave (V) as orange microcrystals (0-45 g, 80%).

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REATIONS OF PLATINUM (II) AND PALLADIUM (II) XANTHATES
WITH XANTHATE IONS

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It is now well established that when reaction occurs between \([\text{Ni}(S-S)_2]\)
\((S-S) = S_2\text{CNR}_2, \ S_2\text{COR}, \ S_2\text{P(OR)}_2, \ S_2\text{PR}_2\) etc and most nitrogen or phosphorus donor ligands \((L)\), either five co-ordinate \([\text{Ni}(S-S)_2L]\) and/or six co-ordinate \([\text{Ni}(S-S)_2L_2]\) adducts are formed, depending on the nature of the ligand used \((1)\). Furthermore, it has been shown that reaction of \(\text{NiCl}_2\cdot 6\text{H}_2\text{O}, \ \text{NaS}_2\text{COEt and Me}_3\text{PhNCl}\) gives the dark green complex \(\text{Me}_3\text{PhN[Ni(S_2COEt)_3]}\) which was assigned a six co-ordinate octahedral structure on the basis of electronic spectral evidence \((2)\).

In contrast, the reaction of the isomorphous \([\text{M}(S-S)_2]\) complexes \((\text{M}=\text{Pd, Pt})\) with tertiary phosphines occurs by stepwise cleavage of metal-sulphur bonds to generate the four co-ordinate compounds \([\text{M}(S-S)_2PR'_3]\) and \([\text{M}(S-S)(PR'_3)_2]\) \((S-S)\) which exhibit unidentate/bidentate and bidentate/ionic modes of bonding of the dithiophosgene groups respectively \((3)\).

In this preliminary communication, we wish to report the results of reactions between various platinum (II) and palladium (II) xanthates with xanthate ion which provides further evidence for the substantial differences in chemistry exhibited by the elements in this triad.
Results and Discussion

Reaction of $[\text{Pt}(S_2\text{COEt})_2]$ with excess $\text{Ph}_4\text{AsS}_2\text{COEt}$ in dichloromethane followed by addition of diethylether gave the yellow crystalline solid $\text{Ph}_4\text{As}[\text{Pt}(S_2\text{COEt})_3]$ (I) (Table). This compound can also be prepared by reaction of $[\text{Pt}(S_2\text{COEt})_2]$ with excess $\text{KS}_2\text{COEt}$ in acetone followed by addition of methanolic $\text{Ph}_4\text{AsCl.HCl}$. An X-ray structural analysis of (I) is now sufficiently advanced to show that unlike the nickel analogue, the platinum (II) ion remains four co-ordinate by binding to one bidentate and two unidentate xanthato groups (4). The complex $\text{Ph}_4\text{As}[\text{Pt}(S_2\text{CO}^\text{1Pr})_3]$ (II) can be similarly prepared. The close similarity of the mull and solution infrared spectra of these compounds, together with the similarity between their electronic spectra and those of well-established square-planar platinum (II) complexes strongly suggests that the four co-ordinate structure is retained in solution.

Further evidence for this statement comes from the low temperature (233K) $^1\text{H}$ n.m.r. spectrum of (I) in CDCl$_3$ which consists of two sharp methyl triplets at $\tau$8.55 and $\tau$8.72 of relative intensity 1:2. Two overlapping methylene quartets centred at $\tau$5.57 are also observed. Similarly for (II) at 223K, two sharp doublets were observed for the methyl protons at $\tau$8.53 and 8.71 also of relative intensity 1:2. The $^{19}\text{F}$ n.m.r. spectrum of a related compound $n-(\text{C}_3\text{H}_7)_4\text{N}[\text{Pd}(S_2\text{PF}_2)_3]$ at 209K also shows two doublets of relative intensity 1:2 with P-F coupling constants consistent with bidentate and unidentate co-ordination of the $S_2\text{PF}_2$ group respectively (5).

On warming (I) to higher temperatures (303K), broadening of the methyl signals occurs and these n.m.r. changes are reversible. For (II), the two methyl doublets also broaden. For the $[\text{Pd}(S_2\text{PF}_2)_3]^-$ ion, the $^{19}\text{F}$ n.m.r. spectrum at ambient temperatures consist of a single broad doublet. These
observations are indicative of a unidentate-bidentate scrambling process at higher temperatures \([\text{cf. } [\text{M}(S-S)_2\text{PR}_3^1]]\) complexes (3)). Unfortunately, because of decomposition before the coalescence temperatures of compounds (I) and (II) are reached, it appears unlikely that useful kinetic information can be extracted from the available data.

**TABLE**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found %</th>
<th>Required %</th>
<th>(\lambda^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})_3])</td>
<td>112</td>
<td>41.9</td>
<td>3.8</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})^1\text{Pr})_3])</td>
<td>117-119</td>
<td>43.9</td>
<td>4.2</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})(\text{S}_2\text{COEt})])</td>
<td>141</td>
<td>42.5</td>
<td>3.1</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})(\text{S}_2\text{COEt})]^1\text{Pr})])</td>
<td>122-124</td>
<td>42.8</td>
<td>3.2</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})(\text{S}_2\text{COME})])</td>
<td>155</td>
<td>47.8</td>
<td>3.6</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{As})_2[\text{Pt}(\text{S}_2\text{CO})_2])</td>
<td>136-138</td>
<td>41.5</td>
<td>3.1</td>
</tr>
<tr>
<td>((\text{Ph}_4\text{As})_2[\text{Pt}(\text{S}_2\text{CO})_2])</td>
<td>255-258(d)</td>
<td>52.1</td>
<td>3.9</td>
</tr>
</tbody>
</table>

\(\lambda^a\) Equivalent conductivity (Scm² mol⁻¹) for 10⁻³ M solutions in nitromethane at 298K.

 Attempted recrystallisation of (I) from either dichloromethane or chloroform solutions gives an orange-yellow crystalline compound (III) containing extra infrared bands at 1678(m), 1600(s), 1576(m) cm⁻¹. These values are reasonably close to the characteristic frequencies reported for the dithiocarbonato ion in \([\text{Pt}(\text{S}_2\text{CO})(\text{PMePh}_2)_2]\) (1696(s), 1681(sh), 1615(s) cm⁻¹) (6) and analytical data confirms that (III) is \(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})(\text{S}_2\text{COEt})]\) (Table). A similar compound
Ph₄As[Pt(S₂CO)(S₂CO²Pr)] (IV) is formed from (II) either by recrystallisation from CH₂Cl₂ or CHCl₃ or by leaving methanol/ether or acetone solutions of (II) to stand for 24 hours.

Reaction of [Pd(S₂COEt)₂] with excess KS₂COEt in acetone followed by filtration into a methanolic solution of Ph₄AsCl. HCl gives a bright orange-yellow precipitate with an infrared spectrum almost identical to that of (III) and this formulation was confirmed by elemental analysis. However, when the same reaction is carried out in methanol, a very small yield of a buff coloured powder with an infrared spectrum almost identical to (I) was obtained. These observations suggest that the palladium trisxanthato complex rearranges very readily to the dithiocarbonate complex which is consistent with the expected lability of Pd-S compared to Pt-S bonds.

A possible mechanism of formation of these various species which is consistent with the above evidence is outlined in the Scheme. Thus, initial nucleophilic attack of xanthate ion on a M-S bond gives the trisxanthato complex and this is followed by intramolecular generation of adithiocarbonate group accompanied by the formation of a xanthate ester. A related rearrangement process has been described elsewhere (7).

\[
\text{viz. } \begin{array}{c}
(R₃P)₂ \quad \text{S} \\
M \quad \text{C} \quad \text{O} \quad \text{R} \\
S₂COR \quad \text{S} \quad \text{C} \quad \text{O}
\end{array} \quad \rightarrow \quad \begin{array}{c}
(R₃P)₂ \quad \text{M} \\
\text{S} \quad \text{C} \quad \text{O} \\
+RS₂COR
\end{array}
\]

Finally, attempts to prepare trisxanthato anionic complexes for R = PhCH₂ or R = Me have proved unsuccessful. For the former, the only compound which could be isolated at all ratios of [Pt(S₂COCH₂Ph)₂] to KS₂COCH₂Ph (1:5 to 1:1) was the complex (Ph₄As)₂[Pt(S₂CO)₂]. (V). The infrared spectrum of this yellow crystalline solid showed no bands between 1200 - 1300 cm⁻¹ (xanthate) but strong absorptions at 1690(sh), 1670(m), 1590(s), 1574(s) cm⁻¹ indicative
of dithiocarbonato ligands. Confirmation of this formulation was obtained by reaction of (V) with excess PPh₃ which gave [PPh₃]₂Pt(S₂CO) (cf., the reaction of [Pt(S₂CS)₂]²⁻ with PMePh₂ giving [(PMePh₂)₂Pt(S₂CS)] (8)). The same compound is obtained from the reaction between Ph₄As[Pt(S₂CO)(S₂COEt)] and PPh₃.

**SCHEME**

For [Pt(S₂COMe)₂] and KS₂COMe, (1:5 molar ratio), the only product isolated was the bis-dithiocarbonato anion (V). However, when a 1:1 or 1:2 molar ratio was used, orange-yellow crystals of Ph₄As[Pt(S₂CO)(S₂COMe)] were deposited.

Work is now in progress on attempts to synthesise the related species [M(S-S)₃]⁻ (S-S = S₂CNR₂, S₂P(OR)₂ etc) and also mixed dithioacid anionic compounds of platinum and palladium (II).
Acknowledgement

We thank Johnson-Matthey Ltd. for loans of potassium tetrachloroplatinate (II) and palladium (II) chloride and the S.R.C. for awards (M.C.C.; D.F.S.)

References


3. For detailed references, see D.F. STEELE and T.A. STEPHENSON J.C.S. Dalton, 2124 (1973).


Metal Complexes of Sulphur Ligands. Part IX.† Synthesis of Dimethylphosphinodithioato-complexes of Ruthenium(II) containing Bidentate Donor Ligands

By David J. Cole-Hamilton, T. Anthony Stephenson,* and Donald R. Robertson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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Metal Complexes of Sulphur Ligands. Part IX.¹ Synthesis of Dimethylphosphinodithioato-complexes of Ruthenium(II) containing Bidentate Donor Ligands

By David J. Cole-Hamilton, T. Anthony Stephenson,* and Donald R. Robertson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

The tris(chelate) complexes \([\text{Ru}(S_2\text{PMe}_2)_2(\text{diene})]\) \(\{\text{diene} = \text{bicyclo}[2.2.1]\text{hepta}-2,5\text{-diene (nbd)}\) or cyclo-octa-1,5-diene (cot)\} have been synthesised by the reaction of \([\{\text{RuCl}_2(\text{diene})\}_2]\) with \(\text{Na}[S_2\text{PMe}_2]_2\cdot\text{H}_2\text{O}\) in either ethanol or \(\text{NN}-\text{dimethylformamide}\). The labile diene moiety is readily replaced by various chelating ligands to give \([\text{Ru}(S_2\text{PMe}_2)_2(L-L)]\) \(\{L-L = \text{Ph}_2\text{P}[\text{CH}_2]_2\text{PPh}_3\text{ (dpppe), Ph}_2\text{PCH}_2\text{PPh}_4\text{ (dppm), C}_6\text{H}_4(\text{AsMe}_2)_2\text{ (pdma)}\}\). For \(L-L = \text{pdma, trans-}[\text{Ru}(S_2\text{PMe}_2)_2(\text{pdma})_2]\) is also formed. Unlike the corresponding \(\text{cis-}[\text{Ru}(S_2\text{PMe}_2)_2(L-L)]\) \(\{L = \text{PR}_3\text{ or P(OR)}_3\}\), all the tris(chelate) complexes exhibit very slow rates of optical inversion and this evidence is used to tentatively propose a modified inversion mechanism of that postulated earlier.

In a recent paper² we proposed that the temperature-variable \(^1\text{H}\) n.m.r. spectra of complexes of the type \(\text{cis-}[\text{Ru}(S_2\text{PMe}_2)_2(L-L)]\) \(\{L = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{PMe}_2\text{PMe}_2\text{Ph, P(OMe)}_3\text{ or P(OPh)}_3\}\) are best explained in terms of rapid inter-


conversion of the two possible optical isomers of these complexes and that, at least for cis-\([	ext{Ru}(S_2\text{PMe}_2)_2(L-L')]\) \([L = \text{PPh}_3; \quad L' = \text{P(OPh})_3\text{ or CO}]\) in solvating media (DCM or PhCl) the mechanism of these inversion processes involves initial \(S_2\) solvent (Y)-assisted cleavage of the Ru=S bond trans to L, followed by exchange between uni- and bi-dentate sulphur ligands and finally recombination of a unidentate \([\text{Me}_2\text{PS}_2]^-\) group with concomitant loss of solvent to form the optical isomer [Scheme 1(a)]. In a non-solvating media \(\text{C}_6\text{H}_6\) the mechanism is essentially the same except that the first step is dissociative with no solvent participation. Furthermore, on the basis of the calculated activation parameters, we postulated that the exchange of unidentate sulphur ligands occurs via a dissociative mechanism irrespective of the solvent. We have now synthesised some tris(chelate) complexes \([\text{Ru}(S_2\text{PMe}_2)_2(L-L')]\) \([L-L = \text{bicyclo-[2.2.1]hepta-2,5-diene (nbd), cyclo-octa-1,5-diene (cot), Ph}_2\text{P(CH}_2)\text{PPH}_2 \text{(dppe), Ph}_2\text{PCH}_2\text{PPH}_2 \text{(dppp), or C}_6\text{H}_4\text{(AsMe}_2)\text{(pdma)}\] and examined their variable-temperature \(\text{H}\) n.m.r. spectra. These studies provide more insight into possible mechanisms of the inversion process and the nature of the seven-co-ordinate intermediate.

RESULTS AND DISCUSSION

The reaction between \([\text{RuCl}_2(\text{diene})]_n\) (diene = nbd or cot) and \(\text{Na}[\text{S}_2\text{CNMe}_2]\) in hot \(\text{NN-dimethylformamide}\) has recently been shown to produce \([\text{Ru}(\text{S}_2\text{CNMe}_2)_2(\text{diene})]_n\) in high yield.\(^3\) We have found that \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(\text{diene})]\) may be prepared in analogous fashion using \(\text{Na}[\text{S}_2\text{PMe}_2]_2\text{H}_2\text{O}\) and furthermore that the diene moity is labile, being readily replaced by CO or PPh$_3$ to give the known cis-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2(L)]_n\) complexes \(^4\) \((L = \text{CO or PPh}_3)\). Reaction of \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(\text{diene})]\) in ethanol with chelating ligands also causes exchange producing \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(L-L')]\) \([L-L = \text{Ph}_2\text{P(CH}_2)\text{PPH}_2 \text{(dppe), Ph}_2\text{PCH}_2\text{PPH}_2 \text{(dppp), or C}_6\text{H}_4\text{(AsMe}_2)\text{(pdma)}\), although when excess of pdma was used a complex of formula \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(\text{pdma})_2]_n\) was formed. This may be converted into \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(\text{pdma})]\) by recrystallisation from toluene. These tris(chelate) complexes may also be isolated in low yield by prolonged reaction of trans-\([\text{RuCl}_2(L-L')]_2\) and \(\text{Na}[\text{S}_2\text{PMe}_2]\) heated under reflux in ethanol.

**Scheme 1** Possible solvent (Y)-assisted bond-rupture mechanism for inversion of cis-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2(L-L')]\): (a) cis attack by solvent; (b) trans attack by solvent.

**Spectroscopic Properties of \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(L-L')]\):**

- **I.r. spectra.** The i.r. spectra of the complexes \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(L-L')]\) all showed absorptions arising from the chelating L-L' ligands and from the \([\text{Me}_2\text{PS}_2]^-\) groups. The bidentate nature of the latter is indicated in every case by the position of \(\nu(\text{PS})\) between 580 and 590 cm$^{-1}$.\(^4\) However for \([\text{Ru}(\text{S}_2\text{PMe}_2)_2(\text{pdma})_2]_n\) the only peak in the region 500--700 cm$^{-1}$ was a sharp absorption at 600 cm$^{-1}$ with a shoulder at 595 cm$^{-1}$ which suggests that both \([\text{Me}_2\text{PS}_2]^-\) groups are probably bound through only one sulphur atom.\(^5\) This observation is supported by \(\text{H}\) n.m.r. data (see below).

- **\(\text{H}\) n.m.r. spectra.** In all these tris(chelate) complexes the stereochemistry of the molecules is constrained to be cis and, although for \(L-L' = \text{Nbd}\) the signals from the diene protons were difficult to see and for dppe only the phenyl resonances were clearly seen (on account of the low intensity and complicated nature of the \(\text{H}\) n.m.r. signals arising from the expected \(\text{H}_2\text{PPH}_2\)/\(\text{H}_2\text{PCH}_2\) spin system), the resonances arising from \(L-L'\) in the other complexes were readily distinguished and are all consistent with cis stereochemistry (Table 1). Thus, for \(L-L' = \text{Nbd}\), signals are assigned as arising from four olefinic protons.
high positive values found for \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) (Table 2) could be explained either by sub-step (i) or (iii) in the mechanism shown in Scheme 1(a) being slow and rate determining. That is either the chelating ligands have low trans influences, thus making step (iii) slow (as was proposed for cis-[Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](PPh\(_3\))CO] and cis-[Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](CO)\(_3\))\(_2\)) or they prevent the solvent from entering the co-ordination sphere for steric reasons, thus making step (i) dissociative and slow (as is found for cis-[Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](PMePh\(_2\)) in a non-co-ordinating medium such as benzene).

The literature available on the trans influences of these ligands is somewhat erratic since, although dienes all appear to have low trans influences, dppe can apparently exhibit either a low or a high trans influence depending on how it is measured whereas pdma always appears to exhibit a high trans influence. Hence, at least for [Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](pdma))], the observed low rate of inversion

### Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>[Me(_2)PS(_2)](Me group)</th>
<th>L-L*</th>
<th>Phenyl or phenylene group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru<a href="nbd">S(_2)PMe(_2)Ph(_2)</a>]</td>
<td>7-78 (12-0), 8-15 (13-0)</td>
<td>5-90, 6-18, 8-70*</td>
<td>6-36, 7-90</td>
</tr>
<tr>
<td>Ru<a href="cot">S(_2)PMe(_2)Ph(_2)</a>]</td>
<td>7-80 (13-0), 8-75 (12-0)</td>
<td>8-24, 8-60 (s)</td>
<td>8-20 (d)</td>
</tr>
<tr>
<td>Ru<a href="dppe">S(_2)PMe(_2)Ph(_2)</a>]</td>
<td>7-85 (13-0), 8-88 (12-0)</td>
<td>5-03 (t), (10-0)</td>
<td>2-9-28</td>
</tr>
<tr>
<td>Ru<a href="pdma">S(_2)PMe(_2)Ph(_2)</a>]</td>
<td>7-65 (13-0), 8-20 (12-0)</td>
<td>8-24 (s)</td>
<td>8-20 (d)</td>
</tr>
<tr>
<td>trans-Ru<a href="pdma">S(_2)PMe(_2)Ph(_2)</a>]</td>
<td>8-46 (12-0)</td>
<td>2-9-28</td>
<td></td>
</tr>
</tbody>
</table>

* \( \tau \) = Singlet, \( t \) = triplet.
* Doubles: \( f(\text{PH}) \) in parentheses (±0·2 Hz).
* See text for assignments.
* \( \text{C}_8\text{H}_5 \) Protons too weak for accurate measurement.

### Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>( \log_{10}(k/s^{-1}) )</th>
<th>( E^\ddagger ) ( \text{kJ mol}^{-1} )</th>
<th>( \Delta H_{298}^\ddagger ) ( \text{kJ mol}^{-1} )</th>
<th>( \Delta S_{298}^\ddagger ) ( \text{kJ mol}^{-1} )</th>
<th>( \Delta G_{298}^\ddagger ) ( \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru<a href="dppe">S(_2)PMe(_2)Ph(_2)</a>]</td>
<td>PhCl</td>
<td>( 32 \pm 0-30 )</td>
<td>( 118 \pm 7 )</td>
<td>( 110 \pm 9 )</td>
<td>( 65 \pm 20 )</td>
<td>( 91 \pm 4 )</td>
</tr>
<tr>
<td>cis-Ru<a href="PPh(_3)">S(_2)PMe(_2)Ph(_2)</a>CO</td>
<td>PhCl</td>
<td>( 1-60 \pm 0-08 )</td>
<td>( 128 \pm 2 )</td>
<td>( 110 \pm 3 )</td>
<td>( 65 \pm 20 )</td>
<td>( 91 \pm 4 )</td>
</tr>
<tr>
<td>cis-Ru<a href="PMePh(_2)">S(_2)PMe(_2)Ph(_2)</a></td>
<td>PhCl</td>
<td>( 1-01 \pm 0-04 )</td>
<td>( 69 \pm 2 )</td>
<td>( 65 \pm 20 )</td>
<td>( 91 \pm 4 )</td>
<td></td>
</tr>
<tr>
<td>cis-<a href="PMePh(_2)">Ru(S(_2)PMe(_2)Ph(_2)</a>]</td>
<td>C(_8)H(_5)</td>
<td>( 0-04 \pm 0-12 )</td>
<td>( 126 \pm 4 )</td>
<td>( 123 \pm 5 )</td>
<td>( 170 \pm 11 )</td>
<td>( 72 \pm 7 )</td>
</tr>
</tbody>
</table>

* See ref. 2.

Finally, [Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](pdma)] gave rise to a well resolved AA'BB' type set of signals in the phenylene region, a sharp singlet from the pdma methyl groups at \( \tau 8-02 \), and a sharp doublet from the methyl groups of the [Me\(_2\)PS\(_2\)] ligands (\( \tau 8-46 \)). This spectrum was temperature invariant (233–333 K) and this is best explained if the two [Me\(_2\)PS\(_2\)] ligands are both undifferentiated and mutually trans since, if they were cis, two resonances would be expected from the methyl groups of the pdma ligands.

**Mechanistic Implications.**—In Part VI of this series \(^2\) we proposed that complexes [Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](L)] invert by the solvent-assisted bond-rapture mechanism [Scheme 1(a)]. At first sight there seems no reason why the same mechanism of inversion should not apply for the tris(chelate) complexes [Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](L)]. Thus for [Ru(S\(_2\)PMe\(_2\)Ph\(_2\)](dppe)] the very low rate constant and the

* All the other tris(chelate) complexes have even slower inversion rates and thus insufficient data could be obtained for Arrhenius plots.
leaving sulphur atom and the attacking solvent molecule are in the two axial positions. In these pentagonal bipyramids L and L' may either be adjacent to one another in the plane of the pentagon or may be separated by a sulphur atom and after cleavage of the Ru-S bond either L or L' may be trans to the co-ordinated solvent molecule.* Examination of the seven-co-ordinate intermediate in the last mechanism outlined in Scheme 1(b) reveals that L and L' are separated by a sulphur atom, and therefore if L and L' were joined together (as in a chelate molecule) any inversion mechanism involving this

![Scheme 2: Postulated mechanisms of inversion for cis-[Ru(S₂PMe₂)₂(μ-L)]⁺](image)

seven-co-ordinate species would be very unfavourable on steric grounds as is experimentally observed.†

Thus we tentatively propose that the mechanism of inversion of complexes cis-[Ru(S₂PMe₂)₂L₂] and cis-[Ru(S₂PMe₂)₂(μ-L)] in solvating media (CDCl₃ or PhCl) is shown in Scheme 2(a), whereas in a non-solvating medium and for [Ru(S₂PMe₂)₂(μ-L)] the mechanism is as in 2(b). However, although the mechanisms shown in Scheme 2 accommodate all the observations we have made in this paper and earlier work,² we cannot entirely rule out the possibility that different mechanisms of inversion operate for these different tris(chelate) complexes; e.g. for L-L = diene or dpdm the mechanism may be that shown in Scheme 1 (a) where the low trans influences of these ligands are responsible for their very slow inversion rates, whereas for L-L = dppe or pdma their low inversion rates may be attributable to the steric constraints expected for a rigid bidentate ligand on the basis of the mechanism shown in Scheme 2(a).

**Experimental**

Microanalyses were by the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the

* If any of the sulphur atoms takes up a position trans to Y the mechanisms which result can all be shown to disobey the principle of microscopic reversibility.

† It should also be pointed out that this seven-co-ordinate intermediate is the least sterically hindered of the ones shown in Scheme 1.

region 4,000–250 cm⁻¹ on a Perkin-Elmer 457 grating spectrometer using Nujol mulls on caesium iodide plates. Mass spectra were obtained on an A.E.I. MS9 spectrometer and ¹H n.m.r. spectra on a Varian Associates HA-100 spectrometer with variable-temperature attachment. Accurate temperatures were determined using the separation of the two resonances of ethylene glycol. Spectra were simulated using a computer program based on that of Nakagawa.⁷ The exchange process was considered for the purpose of computation as consisting of two two-site exchanges of equal intensity and separated by the coupling constant of the doublets. Computed spectra were plotted on the

line printer and experimental spectra were fitted to them by finding the best fit between the ratio of maximum to minimum heights in the doublets. Spin–spin relaxation times (T₂) were obtained by measurement of the peak widths at half height under slow-exchange conditions. Life-times obtained by this fitting procedure were then used to construct an Arrhenius plot (log T₂ against 1/ T) to which a straight line was fitted by the least-squares method. Activation parameters at 298 K were obtained from standard equations. Analytical data for the new complexes are given in Table 3. M.p.s were determined on a Kölfer hot-stage microscope and are uncorrected.

**Materials.**—Ruthenium trichloride trihydrate (Johnson Matthey), bicyclo[2.2.1]hepta-2,5-diene (nbd) (Koch-Light), cyclo-octa-1,5-diene (cot) (Ralph Emanuel), and o-phenylenebis(dimethylarsine) (pdma) (Aldrich) were obtained as indicated. 1,2-Bis(diphenylphosphino)methane (dpdm), 1,2-bis(diphenylphosphino)ethane (dppe), sodium dimethylphosphinothioate, and ruthenium(II)-containing starting materials were prepared by standard literature methods. Operations were carried out under nitrogen and in degassed solvents.

(Bicyclo[2.2.1]hepta-2,5-diene)bis(dimethylphosphinothioato) ruthenium(II).—(a) The complex [(RuCl₂(nbd))₂]₈ (0-20 g) and Na₂(S₂PMe₂)₂·2H₂O (0-40 g) were heated under


reflux in ethanol (25 cm³) for 5 h. After filtration and cooling, the complex precipitated as orange crystals (0-20 g, 60%).

(b) The complex ([RuCl₄(dppp)]₄) (0-26 g) was added to a hot solution of Na[S₂PMe₅]₂·2H₂O (0-29 g) in NN-dimethylformamide (8 cm³). After cooling and addition of water, the brown solid was filtered off and recrystallised from aqueous acetone as orange crystals (0-17 g, 41%).

(Cyclo-octa-1,5-dime)bis(dimethylphosphinodithioato)ruthenium(II) was similarly prepared from ([RuCl₄(cot)]₄)₈ (0-28 g) and Na[S₂PMe₅]₂·2H₂O (0-29 g) as orange crystals.

[1,2-Bis(diphenylphosphino)ethane]bis(dimethylphosphinodithioato)ruthenium(II).—(a) The complex [Ru(S₂PMe₅)₂(cot) (nbdl)] (0-11 g) was heated under reflux with dppp (0-10 g) in acetone for 24 h. Cooling and concentrating the solution then afforded the complex as orange crystals which were recrystallised from CH₂Cl₂-n-hexane (0-10 g, 58%).

(b) The complex trans-[RuCl₄(dppp)]₂ (0-20 g) and Na[S₂PMe₅]₂·2H₂O (0-20 g) were heated under reflux in ethanol (25 cm³) for 24 h. The solution was filtered hot to remove excess of trans-[RuCl₄(dppe)]₂ and NaCl and, on cooling, the complex precipitated as orange crystals (0-06 g, 39%).

<table>
<thead>
<tr>
<th>Table 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical data for some ruthenium complexes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M.p. (°C)</th>
<th>M *</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(S₂PMe₅)₂(cot)]</td>
<td>Orange</td>
<td>167—170</td>
<td>443 ± 1 (443)</td>
</tr>
<tr>
<td>[Ru(S₂PMe₅)₂(dppp)]</td>
<td>Orange</td>
<td>184—186</td>
<td>460 ± 1 (460)</td>
</tr>
<tr>
<td>[Ru(S₂PMe₅)₂(nbdl)]</td>
<td>Orange</td>
<td>228—230</td>
<td>749 ± 1 (749)</td>
</tr>
<tr>
<td>[Ru(S₂PMe₅)₂(pdma)]</td>
<td>Orange</td>
<td>230—233</td>
<td></td>
</tr>
<tr>
<td>trans-[Ru(S₂PMe₅)₂(pdma)]</td>
<td>Pink</td>
<td>238—240</td>
<td>444 ± 1 (444)</td>
</tr>
<tr>
<td></td>
<td>(decomp.)</td>
<td></td>
<td>47-7 4-8</td>
</tr>
<tr>
<td></td>
<td>(decomp.)</td>
<td></td>
<td>47-5 4-8</td>
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<tr>
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<td>(decomp.)</td>
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<td>28-8 4-3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>31-3 4-9</td>
</tr>
</tbody>
</table>

* Molecular weight from parent-ion peak (¹⁹⁵Ru isotope) in mass spectrum; calculated values are given in parentheses.

(20 cm³) for 5 h. The orange crystals were filtered off and washed with water, ethanol, and n-pentane (0-15 g, 80%).

trans-Bis(dimethylphosphinodithioato)bis(1-phenylenebis-(dimethylarsine))ruthenium(II).—The complex [Ru(S₂PMe₅)₂(cot) (nbdl)] (0-05 g) and pdma (0-2 cm³) were heated under reflux in ethanol (10 cm³) for 10 min. The pink crystals were filtered off and washed with water, ethanol, and n-pentane (0-085 g, 97%). Recrystallisation from boiling toluene gave orange crystals of the product in 100% yield.

We thank Johnson, Matthey Ltd. for loans of ruthenium trichloride, the University of Edinburgh for an award (to D. J. C-H), and the Atlas Computer Laboratory for a copy of their shape-function program.
Preliminary Communication

REACTION OF PALLADIUM DIENE AND 2-PHENYL AZOPHENYL COMPLEXES WITH SOME SULPHUR-CONTAINING NUCLEOPHILES

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(Received December 10th, 1975)

Summary

The syntheses of \([\text{PdX}(S-S)]_2\) \([X = \text{Cl}, \text{Br}; (S-S)^- = \text{S}_2\text{CNR}_2, \text{S}_2\text{COR}]\)
via \([\text{C}_8\text{H}_8\text{PdCl}_2]\) or \([\text{PhN}_2\text{C}_8\text{H}_4\text{Pd(OCOCH}_3)\])_2\) are reported and some
reactions of these compounds are described.

The activation of olefins towards nucleophilic attack by coordination to
palladium(II) is now well established and of commercial importance. Extensive
studies on reactions of \([\text{dienenPdCl}_2]\) complexes with various nucleophiles
containing oxygen or nitrogen donor atoms (e.g. \(^{-}\text{OR}, \text{OCOR}, \text{NH}_2\text{R etc.}\)
show that, usually, attack on one of the coodinated double bonds occurs to
give substituted alkenyl complexes [1].

We now report that the reaction between \([\text{C}_8\text{H}_8\text{PdCl}_2]\) \((\text{C}_8\text{H}_8 = 1,5\text{-cycol}
\text{octadiene})\) and S-containing nucleophiles such as \(N, N^\prime\)-dialkyl- and O-alkyl-thio-
carbamate anions \((S-S^-)\) \(1 : 1\) molar ratios) leads, in contrast, to complete
diene displacement with formation of compounds of empirical formula
\([\text{PdCl}(S-S)]_n^{**}\). Molecular weight measurements in chloroform reveal that
\(n = 2\) and thus, these compounds are best formulated with the square planar,
chloride bridged structure (I). With excess \((S-S)^-\), \([\text{Pd}(S-S)_2]\) is formed.
The probable mechanism of formation is given in eq. 1.

As outlined in Scheme 1 for \((S-S)^- = \text{S}_2\text{CNR}_2\), these dimers prove to be
excellent precursors for a variety of reactions. For example, the chloride
bridges are readily cleaved by a wide range of Lewis bases \((L)\) to give the
monomeric \([\text{PdCl(S}_2\text{CNR}_2]L\) \((\text{II})\) \((L = \text{PPPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{C}_5\text{H}_5\text{N, CO}
\text{etc.})\). For \(L = \text{tertiary phosphine}, \) these complexes can also be synthesised
by reaction of \([\text{PdCl}_2(\text{PR}_3)]_2\) with either \(\text{Me}_2\text{SnCl(S}_2\text{CNR}_2)\) \([3]\) or \(\text{Na}(S-S)
((S-S)^- = \text{S}_2\text{CNR}_2 [3,4], \text{S}_2\text{COR} [4], \text{S}_2 \text{PR}_2 [4] )\) but, with weaker Lewis

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*To whom correspondence should be addressed.
**With the exception of \(\text{CF}_3\text{S}^- [2]\), this appears to be the first reported reaction between anionic
sulphur-containing nucleophiles and \([\text{dienenPdCl}_2]\) compounds.
bases in the coordination sphere, only [Pd(S—S)₂] are formed by this route. Reaction of II with AgBF₄ in tetrahydrofuran, followed by addition of another Lewis base (L') and NaNB₄ readily gives the mixed ligand complexes [Pd(S₂CNR₂)LL']B₄H₁₄ (III) (e.g. L = PPh₃, L' = AsPh₃, C₅H₅N etc). Similarly, reaction of I with Ph₃PCH₂PCI/HCl gives the anionic Ph₃PCH₂P[PdCl₂(S₂-CNR₂)]⁻ (IV). The related [Pd(S₂COR)₃]⁻ has been described elsewhere [5].

SCHEME 1. (i) L = PPh₃, AsPh₃, SbPh₃, C₅H₅N, CO etc.; (ii) L = PPh₃; L' = AsPh₃, C₅H₅N etc.; (iii) M = Ph₃PCH₂P⁺; (iv) X = Br, I, 'SPh; (v) L = PPh₃, X = 'SPh; L = PPh₃, X = Br; (vi) (S—S) = 'S₂'Me₂; S₆COEt.
The chloride bridges in I can be readily exchanged for Br\(^{-}\), I\(^{-}\), PhS\(^{-}\) (X\(^{-}\)) by treatment with the corresponding lithium or sodium salt, giving [PdX-(S\(_2\)CNR\(_2\))]\(_2\) (V). The compound V with X = Br can also be prepared from the (2-phenylazophenyl)dithiocarbamato complex (Z) by treatment with bromine, the 2-phenylazophenyl ligand being removed as 2-bromoazobenzene. The complexes Z are readily obtained by reaction of the known acetate complex Y [6] with Et\(_4\)N(S\(_2\)CNR\(_2\)) (1:2 molar ratio) (eq. 2).

![Chemical Structure](image)

The related thiol bridged complex [Pd(S-t-Bu)(S\(_2\)CNEt\(_2\))]\(_2\) has been synthesised by reaction of [Pd(S-t-Bu)(S\(_2\)CS-t-Bu)]\(_2\) [7] with Et\(_2\)NH [8]. Reaction of these compounds with PMePh\(_2\) is reported to give [Pd(S-t-Bu)(S–S)PMePh\(_2\)]\(_n\), originally formulated from \(^1\)H NMR studies as five coordinate dimers [8] *. However, we have found that reaction of [Pd(SPh)(S\(_2\)CNMe)]\(_2\) with PPh\(_3\) gives the red, crystalline monomeric [Pd(SPh)(S\(_2\)CNMe)PPh\(_3\)] (VI).

Finally, preliminary studies indicate that reaction of [PdCl(S\(_2\)CNR\(_2\))]\(_2\) with other dithiocarbamato anions gives the mixed [Pd(S\(_2\)CNR\(_2\))(S–S)] (VII) complexes (S–S = S\(_2\)PR\(_2\), S\(_2\)COR)** and reactions of these compounds with Lewis bases are now in progress.

Acknowledgement

We thank Johnson—Matthey Ltd for loans of palladium(II) chloride and the S.R.C. (M.C.C.) and the University of Edinburgh (R.C.D.) for research studentships.

References


* Very recently, Professor Fackler (private communication) has suggested that these compounds might be monomeric but unfortunately, they could isolate no solids to confirm this statement unequivocally.
** All the compounds reported in this note have been characterised satisfactorily by elemental analyses, molecular weight determinations and \(^1\)H NMR spectroscopy.
Preliminary communication

REACTION OF $\left[ \eta^6 \cdot C_6 H_6 \text{RuCl}_2 \right]_2$ AND $\left[ \eta^5 \cdot C_5 \text{Me}_5 \text{RhCl}_2 \right]_2$ WITH SOME SULPHUR-CONTAINING NUCLEOPHILES

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(Received December 27th, 1975)

Summary

The dithioaciden ligand complexes $\left[ \eta^6 \cdot C_6 H_6 \text{Ru(S}_2 \text{PR}_2)_2 \right]_2$, $\left[ \eta^5 \cdot C_5 \text{Me}_5 \text{Rh(S}_2 \text{S})_2 \right]$, $\left[ \eta^5 \cdot C_5 \text{Me}_5 \text{Rh(S}_2 \text{S})_2 \text{CNR}_2 \right]$, $\left[ \eta^5 \cdot C_5 \text{Me}_5 \text{RhCl}(\text{S}_2 \text{CNMe}_2) \right]$ and $\left[ \eta^5 \cdot C_5 \text{Me}_5 \text{Rh(S}_2 \text{PMe}_2)(\text{S}_2 \text{CNMe}_2) \right]$ have been synthesised by reaction of $\left[ \eta^6 \cdot C_6 H_6 \text{RuCl}_2 \right]_2$ and $\left[ \eta^5 \cdot C_5 \text{Me}_5 \text{RhCl}_2 \right]_2$ respectively with Na(S–S).

In recent papers, the synthesis of the complexes cis-[Ru(S–S)$_2$ diene] [(S–S)$^-\!\!-\!\!-$S$_2$ CNR$_2$ [1,2], $^-\!\!-\!\!-$S$_2$ PR$_2$ [2]; diene = 1,5-C$_8$ H$_{12}$, C$_7$ H$_8$] by reaction of [RuCl$_3$(diene)]$_n$ with Na(S–S) have been described. In this note, we wish to report the results of the related reactions between $\left[ \eta^6 \cdot C_6 H_6 \text{RuCl}_2 \right]_2$ (I) and various sulphur containing nucleophiles. Although the reactions of I with various monodentate nucleophiles have been described [3,4], the only other published work involving reaction with potential bidentate nucleophiles is that of Ph$_2$ P(CH$_2$)$_n$ PPh$_2$ ($n = 1, 4$) giving $\left[ \eta^6 \cdot C_6 H_6 \text{RuCl}_2 \text{Ph}_2 \text{PCH}_2 \text{PPh}_2 \right]$ and $\left[ (\eta^6 \cdot C_6 H_6 \text{RuCl}_2)_2 \text{Ph}_2 \text{PCH}_2 \text{PPh}_2 \right]$ with mono- and bi-dentate coordination respectively [3].

*To whom correspondence should be addressed.
Reaction of I with NaS₂PR₂ in water (1:2 molar ratio) gives monomeric complexes of formula \([\eta^6-C₆H₆\text{Ru}(S₂PR₂)₂]\) (R = Me, Ph, OMe, OEt). \(^1\text{H}\) and \(^{31}\text{P}\) NMR studies reveal that these compounds are best formulated with mono- and bi-dentate ligands [structure (II)], e.g. for \(-S₂PMe₂\), the \(^1\text{H}\) NMR spectrum at 303 K consists of three doublets of relative intensity (2; 1; 1) \((^2J(\text{PH}) \text{ 12.0 Hz})\) in addition to a singlet at \(δ 5.88 \text{ ppm (}\eta^6-C₆H₆\)). However, although they are stereochemically rigid at room temperature, ready decomposition in solution as indicated by the appearance of free benzene (\(^1\text{H}\) and \(^{31}\text{C}\) NMR) and \(-S₂PR₂\) (\(^{31}\text{P}\) NMR) prohibits a detailed examination of possible rearrangement processes in these complexes. Furthermore, reaction of I with dialkyldithiocarbamate and \(O\)-alkyldithiocarbonate anions gives paramagnetic products containing no coordinated benzene.

![Diagram](III)

Therefore, since I does not give a very wide range of arene complexes containing dithioacetic ligands, we have investigated similar reactions with the isoelectronic \([\eta^5-C₅Me₅\text{RhCl₂}]₂\) (III) \([5]\). Thus; III reacts with \(-S₂PR₂\) (1:1 mole ratio) (R = Me, Ph) to give \([\eta^5-C₅Me₅\text{Rh}(S₂PR₂)₂]\) (IV). Unlike I, however, III reacts with the stronger nucleophiles \(-S₂\text{CNR₂}\) and \(-S₂\text{COR}\), without loss of the \(π\)-bonded ring, to give the analogous \([\eta^5-C₅Me₅\text{Rh}(S-S₂)]\) (IV). NMR studies at ambient temperature confirm the presence of inequivalent dithioacetic ligands in all these compounds and variable temperature studies at higher temperatures reveal that interconversion of mono- and bi-dentate dithioacetic ligands occurs. A detailed kinetic line-shape analysis of this process is now in progress. Reaction of III with NaS₂CNMe₂ (1:1 mole ratio) gives \([\eta^5-C₅Me₅\text{RhCl(S₂CNMe₂)}]\), from which the mixed dithioacetic complex \([\eta^5-C₅Me₅\text{Rh}(S₂PMe₂)(S₂CNMe₂)}]\) * can be synthesised. NMR studies show the latter to have bidentate \(-S₂\text{CNMe₂}\) and unidentate \(-S₂PMe₂\) groups.

Acknowledgement

We thank Johnson—Matthey Ltd for loans of ruthenium trichloride and rhodium trichloride and the S.R.C. (D.R.R.) for a research studentship.

*All the compounds reported in this note have been characterised satisfactorily by elemental analyses and molecular weight determinations.
References

SYNTHESIS AND CHARACTERISATION OF PLATINUM (II) AND PALLADIUM(II)
COMPLEXES CONTAINING DITHIOACID AND OTHER LIGANDS

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(Received 25 November 1975)

In previous papers, we have reported the results of the reactions of various tertiary phosphines, arsines and stibines (L) with the square planar [M(S-S)_2] compounds (M=Pd, Pt; S=S_2PR_2, S_2COR and S_2P(OR)_2]. In particular, a study of the various rearrangement reactions exhibited by the products [M(S-S)_2L] and [M(S-S)L_2]Y (Y=S-S^-, BPh_4^-, Cl^-, PF_6^-) has been described (i). One reaction was the conversion of [Pd(S_2PR_2)_2(PPh_3)_2]BPh_4 (R=Me, Ph) to [PdX(S_2PR_2)PPh_3] when dissolved in either CH_2Cl_2 or CHX_3 (X=Cl, Br)(i). Unfortunately, this particular rearrangement appears to be confined to compounds containing a combination of Pd, PPh_3, S_2PR_2 and BPh_4^- and thus does not provide a general method of synthesising the series [MX(S-S)PR_3]^-.

Although [NiX(S-S)PR_3]^- [S-S^- = S_2CNR_2(2, 3), S_2COR(4)] compounds have recently been reported, [PdX(S_2PR_2)PPh_3] represented the first palladium complex of this type. In this preliminary communication, we report the results of our attempts to find a general synthetic route to palladium (II) and platinum (II) complexes of this type and also, some reactions of these compounds.

Our initial efforts to develop a general synthetic method were largely unsuccessful. Thus, in contrast to the preparation of [NiX(S_2CNR_2)PR_3]^- (2, 3), reaction of PdCl_2 (or K_2PtCl_4), PR_3 and NaS_2CNR_2.3H_2O (or NaS_2PR_2) gave only [M(S-S)_2]. Similarly, although reactions of [Pd(S_2PR_2)_2PR_3] with excess AgX (X=Cl, Br, I, SCN) in acetone readily gave [PdX(S_2PR_2)PR_3], the corresponding exchange reactions with [Pt(S-S)_2PR_3]^- (S-S^- = S_2PR_2, S_2CNR_2) were very inefficient and produced only low yields of the required product (especially for S-S^- = S_2CNR_2).
### TABLE 1

Analytical Data for some Platinum (II) and Palladium (II) Dithioacid Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found 0/o</th>
<th>Required 0/o</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[PtCl(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph\textsubscript{2}]</td>
<td>37.2</td>
<td>4.1</td>
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<tr>
<td>[PtCl(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph]</td>
<td>29.4</td>
<td>4.0</td>
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<tr>
<td>[Pt(S\textsubscript{2}CNET\textsubscript{2})(S\textsubscript{2}PM\textsubscript{2}Ph)PM\textsubscript{2}Ph\textsubscript{2}]</td>
<td>36.0</td>
<td>4.5</td>
</tr>
<tr>
<td>[PdCl(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph]</td>
<td>36.4</td>
<td>5.0</td>
</tr>
<tr>
<td>[PdBr(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph]</td>
<td>33.2</td>
<td>4.3</td>
</tr>
<tr>
<td>[PdI(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph]</td>
<td>30.3</td>
<td>4.1</td>
</tr>
<tr>
<td>[PdCl(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph]</td>
<td>33.0</td>
<td>4.0</td>
</tr>
<tr>
<td>[PdBr(S\textsubscript{2}PM\textsubscript{2}Ph)PM\textsubscript{2}Ph]</td>
<td>26.7</td>
<td>5.8</td>
</tr>
<tr>
<td>[PdI(S\textsubscript{2}PM\textsubscript{2}Ph)PM\textsubscript{2}Ph]</td>
<td>24.3</td>
<td>3.5</td>
</tr>
<tr>
<td>[PdCl(S\textsubscript{2}CNET\textsubscript{2})(PM\textsubscript{2}Ph)PPh\textsubscript{3}]PPh\textsubscript{4}</td>
<td>67.8</td>
<td>6.0</td>
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<tr>
<td>[PdCl(S\textsubscript{2}CNET\textsubscript{2})(PM\textsubscript{2}Ph)(CF\textsubscript{3}H\textsubscript{5}N\textsubscript{3})]PPh\textsubscript{4}</td>
<td>63.6</td>
<td>5.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Molecular weight measured osmometrically at 37\textdegree in chloroform
\textsuperscript{b} Molecular weight from parent ion peak (106\textsuperscript{105}Pd or 195\textsuperscript{195}Pt isotope) in mass spectrum

### TABLE 2

\textsuperscript{1}Hnmr Data in CDCl\textsubscript{3} at 300K for some Platinum (II) and Palladium (II) Dithioacid Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>\textsubscript{6} value \textsuperscript{a}</th>
<th>Dithio ligand</th>
<th>Methyl groups of phosphine \textsuperscript{c}</th>
<th>Phenyl groups</th>
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<tr>
<td></td>
<td>CH\textsubscript{3}\textsuperscript{b}</td>
<td>CH\textsubscript{2}\textsuperscript{b}</td>
<td>CH\textsubscript{3}\textsuperscript{b}</td>
<td>CH\textsubscript{2}\textsuperscript{b}</td>
</tr>
<tr>
<td>[PtCl(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph\textsubscript{2}]</td>
<td>1.26(t), 1.19(t)</td>
<td>3.64(q), 3.47(q)</td>
<td>2.16(t, d)\textsuperscript{d}</td>
<td>7.32-7.82(m)</td>
</tr>
<tr>
<td>[PtCl(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph]</td>
<td>1.28(t), 1.25(t)</td>
<td>3.66(q), 3.55(q)</td>
<td>1.83(t, d)\textsuperscript{g}</td>
<td>7.32-7.86(m)</td>
</tr>
<tr>
<td>[Pt(S\textsubscript{2}CNET\textsubscript{2})(S\textsubscript{2}PM\textsubscript{2}Ph)(PM\textsubscript{2}Ph\textsubscript{2})]</td>
<td>1.29(t), 1.21(t)</td>
<td>3.68(q), 3.50(q)</td>
<td>2.29(t, d)\textsuperscript{h}</td>
<td>7.32-7.80(m)</td>
</tr>
<tr>
<td>[PdCl(S\textsubscript{2}CNET\textsubscript{2})PM\textsubscript{2}Ph]</td>
<td>1.24(t), 1.22(t)</td>
<td>3.72(q), 3.62(q)</td>
<td>1.80(d)</td>
<td>7.38-7.90(m)</td>
</tr>
<tr>
<td>[PdCl(S\textsubscript{2}PM\textsubscript{2}Ph)PM\textsubscript{2}Ph]</td>
<td>1.25(t), 1.22(t)</td>
<td>3.70(q), 3.59(q)</td>
<td>1.95(d)</td>
<td>7.35-7.80(m)</td>
</tr>
<tr>
<td>[PdCl(S\textsubscript{2}PM\textsubscript{2}Ph)PM\textsubscript{2}Ph]</td>
<td>2.00(d)</td>
<td>1.77(d)</td>
<td>7.32-7.80(m)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{d} = doublet; \textsuperscript{t} = triplet; \textsuperscript{q} = quartet; \textsuperscript{m} = multiplet

\textsuperscript{a} J = 6 \text{ Hz} \textsuperscript{b} \text{J} = 2 \text{ Hz} \textsuperscript{c} \text{J} = 3 \text{ Hz} \textsuperscript{d} \text{J} = 5 \text{ Hz} \textsuperscript{e} \text{J} = 7 \text{ Hz} \textsuperscript{f} \text{J} = 7 \text{ Hz} \textsuperscript{g} \text{J} = 8 \text{ Hz} \textsuperscript{h} \text{J} = 10 \text{ Hz}
However, we have found that reaction of the halide bridged dimers \([MX_2(PR_3)_2]_2\) (M=Pd; X=Cl, Br, I; PR_3=PMe_2Ph; M=Pt; X=Cl; PR_3=PMe_2Ph, PMePh_2) with various alkali metal dithioacid salts \(\text{S}_2PR_2^-, \text{S}_2\text{CN}R^-, \text{S}_2\text{COR}\) in 1:2 molar ratio in acetone (Pd) or acetone/CH_2Cl_2 (Pt) provides an excellent general method of synthesising a wide range of these compounds +.

All compounds have been characterised by elemental analyses (Table 1), infrared and ^1^H nmr spectroscopy (Table 2) and, in several instances, the monomeric nature of the products have been established by mass spectroscopy and/or osmometric molecular weight measurement in chloroform (Table 1).

\[
\begin{align*}
R & \\
NC & \\
S & \\
M & \\
PR_3 & \\
X & \\
\end{align*}
\]

(1)

Full confirmation of structure (1) is obtained from the ^1^H nmr spectra of the diethylidithiocarbamato derivatives which show two magnetically inequivalent ethyl groups at ambient temperature. As expected for a structure of this type, the \(\text{S}_2PMe_2\) compounds show only one methyl resonance from the dithioacid group.

These compounds prove to be useful starting materials for a variety of reactions. For example, reaction of \([\text{PtCl}(\text{S}_2\text{CNET}_2)\text{PMePh}_2]\) with Na\(\text{S}_2\text{PMe}_2\) gives the mixed dithio complex \([\text{Pt}(\text{S}_2\text{CNET}_2)(\text{S}_2\text{PMe}_2)\text{PMePh}_2]\) shown by ^1^H nmr spectroscopy (Table 2) to have structure (II). Unlike the corresponding

\[
\begin{align*}
\text{Et}_2\text{NC} & \\
S & \\
\text{Pt} & \\
\text{S} & \\
\text{PMe}_2 & \\
\text{PMePh}_2 & \\
\end{align*}
\]

(II)

\[
\begin{align*}
\text{Et}_2\text{NC} & \\
\text{Pd} & \\
\text{S} & \\
\text{S} & \\
\text{PMe}_2\text{Ph} & \\
\text{PMe}_2\text{Ph} & \\
\end{align*}
\]

(III)

+ Very recently, N Sonoda and T Tanaka, Inorg Chim Acta 12 261 (1975) have independently reported the synthesis of the related \([\text{PdCl}(\text{XYCNR}_2)PR_3]\) (R=Me, Et; PR_3=PMePh_2, PPh_3, PMe_2Ph; X=S, Y=Se) by reaction of \([\text{PdCl}_2(PR_3)_2]\) with Me_2SnCl(XYCNR_2). \([\text{PdCl}(\text{S}_2\text{CNR}_2)PR_3]\) (R=Me, Et; PR_3=PPh_3, PMePh_2) are also briefly described.
[Pt(S₂CNEt₂)₂PMeph₂] (5) and [Pt(S₂PMe₂)₂PMeph₂] (I), this compound is stereochemically rigid even at 330K. As expected, reaction of [PtCl(S₂PMet₂)⁻PMeph₂] with NaS₂CNEt₂·3H₂O gives Pt(S₂CNEt₂)⁺, indicating the greater nucleophilicity of S₂CNEt₂ compared to S₂PMet₂. Attempts to make a wider range of mixed dithio and diseleno complexes of platinum (II) and palladium (II) are now in progress.

Finally, reaction of [PdCl(S₂CNEt₂)PMeph₂] with AgBF₄ in tetrahydrofuran produces a white precipitate of AgCl and a yellow solution thought to contain the solvated cation [Pd(THF)(S₂CNEt₂)PMeph₂]⁺. Addition of various ligands (L) to this solution followed by treatment with NaBPh₄ readily gives the mixed ligand complexes [Pd(S₂CNEt₂)(PMeph₂)L] BPh₄⁻ (III) (L=PMep₃, C₅H₅N etc). Extension of this reaction to a wider range of ligands is also in progress.

Acknowledgement

We thank Johnson-Matthey Ltd for loans of potassium tetrachloroplatinate (II) and palladium (II) chloride and the S.R.C. for an award (M.C.C.).

References

Crystal and Molecular Structure of Bis(\(\text{NN}\)-diethylselenocarbamato)-
seelenium(II)

By Robert O. Gould, C. Lynn Jones, W. John Savage, and T. Anthony Stephenson, Department of
Chemistry, University of Edinburgh, Edinburgh EH9 3JJ
Crystal and Molecular Structure of Bis(NN-diethylselenocarbamato)-selenium(II)


Crystals of the title compound (II) are monoclinic, space group $P2_1/n$, with $a = 6.707(5)$, $b = 9.978(6)$, $c = 25.41(1)$ Å, $\beta = 90.75(5)^\circ$. Except for the terminal methyl groups, the molecules are planar with non-crystallographic $C_{2v}$ ($mm$) symmetry. There are two types of Se-Se bond of length 2.45 and 2.80 Å. The structure was solved by a combination of direct and heavy-atom methods from 1 890 photographic data. It was refined by least-squares techniques to $R$ 0.08.

In an attempt to prepare bis(NN-diethylselenocarbamoyl)diselenide (I), an aqueous solution of sodium diethylselenocarbamate was allowed to react with atmospheric oxygen.¹ Two products were obtained by fractional crystallisation of the resulting orange solid from ethanol–chloroform: bis(NN-diethylselenocarbamato)selenium(II) (II), and bis(NN-diethylseleno-

carbamoyl)selenium(II) (III). The crystal structure of (II) is reported here.

\[
\begin{align*}
\text{Et}_2\text{N}\text{C(Se)=Se-SeC(Se)=NET}_2 & \quad \text{(I)} \\
\text{Et}_2\text{N-C(Se)=Se-SeC(Se)=NET}_2 & \quad \text{(II)} \\
\text{Et}_2\text{N-C(Se)=SeC(Se)=NET}_2 & \quad \text{(III)} \\
\text{Et}_2\text{N-C(Se)=SeC(Se)=NET}_2 & \quad \text{(IV)}
\end{align*}
\]

EXPERIMENTAL

Crystal Data. - \(\text{C}_{13}\text{H}_{38}\text{N}_{2}\text{Se}_{2}\), \(M = 563\), orange monoclinic needles, \(a = 6.707(5)\), \(b = 9.978(6)\), \(c = 25.41(1)\) Å, \(\beta = 90.75(5)\), \(U = 1700\) Å\(^2\), \(D_m = 2.17\), \(Z = 4\), \(D_a = 2.20\) g cm\(^{-3}\). Space group \(P2_1/n\) (non-standard setting of \(P2_1/c\), No. 14). \(\text{Cu-K} \alpha\) radiation, \(\lambda = 1.5418\) Å; \(\mu(\text{Cu-K} \alpha) = 144\) cm\(^{-1}\).

Structure Determination. - Data for layers 0—5\(h\) were collected on multi-film packs, by the equi-inclination Weissenberg method. The crystal chosen was approximately cylindrical, elongated along [100] with a mean cross-sectional area of 0.08 mm\(^2\). The intensities of 1890 unique reflections were obtained by use of a Saab rotating-drum film scanner. No absorption corrections were applied.

The positions of the selenium atoms were found unambiguously by the MULTAN procedure,\(^5\) and the remaining atoms were located by successive difference-Fourier syntheses. Refinement of interlayer scale factors and the positions and isotropic temperature factors of the selenium atoms led to \(R = 0.13\). No attempt was made to locate hydrogen atoms. For the final refinement cycles, all positional parameters, isotropic thermal parameters for the ethyl carbon atoms and anisotropic for all others, and a single scale factor were varied. Weights were of the form \(W = 1/Y\), where \(X = \sin \theta/0.22\) for \(\sin \theta < 0.22\) and 1.0 otherwise, and \(Y = 150/|F|_{o}\) for \(|F|_o > 150\) and 1.0 otherwise. The final \(R\) was 0.08.

Final atomic parameters are given in the Table, and intramolecular distances and angles in Figure 1. Among the atoms found, there are no intermolecular distances <3.6 Å. Structure factor tables are deposited as Supplementary Publication No. SUP 21657 (4 pp., 1 microfiche).\(^6\) All standard crystallographic calculations were done by use of the 'X-Ray '72' program system\(^7\) at the Edinburgh Regional Computing Centre.

DISCUSSION

The projection of a molecule on its best plane is shown in Figure 2. Within experimental error, the molecules have \(C_j\) (m) symmetry; excluding terminal methyl groups, they are planar with \(C_{\alpha}\) symmetry, the maximum deviation from the plane being 0.4 Å [C(7)]. The corresponding bis(NV-diethylthiocarbamato)selenium(II) (IV) has been reported.\(^8\) Its molecular structure is very similar: mean Se–S distances in (IV)

![Figure 1](image1.png)

![Figure 2](image2.png)

\(\text{Et}_2\text{N-C(Se)=SeC(Se)=NET}_2\) and \(\text{Et}_2\text{N-C(Se)=SeC(Se)=NET}_2\) are 2.52 and 2.76 Å, while in (II) the mean Se–Se distances are 2.46 and 2.82 Å. As would be expected,

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\(^*\) See Notice to Authors No. 7 in J.C.S. Dalton, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)


the difference between the two bonds in the SeSe₄ system is much less than that in the SeS₄ system. Similarly, the angles about the central atom are significantly nearer 90° in (II) than they are in (IV). The structures have very similar cell dimensions, but (IV) forms orthorhombic crystals, space group P₂₁₁. If the atom co-ordinates of (IV) are transformed to 1/4 + z, 3/4 – x, 1 – y, the two molecules may virtually be superimposed, as may the two projections down the shortest axis of the entire structure. Clearly there is little difference in energy between the two packing arrangements, and this may explain the high thermal parameters for terminal groups, and the disorder found in (IV).²

Brøndmo et al.⁵ distinguish three classes of structures for complexes of sulphur(II), selenium(II), and tellurium(II) with bidentate dithio- and related ligands. Classes (I) and (II) both have four-co-ordinate structures with two long and two short bonds, but in class (I) two bidentate ligands form a discrete complex molecule, while in class (II) the ligands are bridging and the ‘intermolecular’ bonds are particularly long. Both compounds (II) and (IV) are examples of class (I), while bis(diethyldiselenophosphinato)selenium(II)⁶ is in class (II). In terms of their arguments, the diselenocarbamate ligand should thus have a greater donor capacity than the diselenophosphinate ligand. This distinction is well established for the sulphur analogues where, for example, the Ni–S bonds in bis(diethylidithiocarbamato)nickel(II) (2.202 Å)⁷ are significantly shorter than those in bis(dimethylidithiocarbamato)nickel(II) (2.240 Å).⁸

We thank the S.R.C. for financial support (of C. L. J. and W. J. S.) and Professor E. A. V. Ebsworth and Dr. D. W. H. Rankin for encouragement and discussion.

[5] Received, 12th September, 1975

Metal Complexes of Sulphur Ligands. Part 10.\textsuperscript{1} Reaction of \textit{mer}-
Trichlorotris(dimethylphenylphosphine)osmium(\textit{iii}) with Dimethyldithiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and \textit{O}-
Ethyl Dithiocarbonate Ligands

By David J. Cole-Hamilton and T. Anthony Stephenson,\textsuperscript{*} Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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\textbf{DALTON TRANSACTIONS}

1976
Metal Complexes of Sulphur Ligands. Part 10.\textsuperscript{1} Reaction of mer-Trichlorotris(dimethylphenylphosphine)osmium(III) with Dimethylthiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and O-Ethyl Dithiocarbonate Ligands

By David J. Cole-Hamilton and T. Anthony Stephenson,\textsuperscript{*} Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reactions of the complex \textit{mer}-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}] (1) with excess of \textit{S-S}⁻ ion (S-S⁻ = S\textsubscript{2}CNMe\textsubscript{2}⁻, S\textsubscript{2}PMesse⁻, or S\textsubscript{2}COPh⁻) have been thoroughly studied. For [S\textsubscript{2}CNMe\textsubscript{2}⁻], refluxing in methanol for 90 min gives a high yield of cis-[Os(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}CNMe\textsubscript{2})] (2), whereas shaking in methanol gives \textit{mer}-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}-(S\textsubscript{2}CNMe\textsubscript{2})] (3). Reaction of (3) with Na[S\textsubscript{2}CNMe\textsubscript{2}]-2H\textsubscript{2}O in refluxing ethanol gives (2) together with small amounts of face-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}CNMe\textsubscript{2})] (5) and fac-[Os(OEt)(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}CNMe\textsubscript{2})] (6), whereas with K[S\textsubscript{2}COEt] these three complexes and cis-[Os(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}CNMe\textsubscript{2})] (4) are formed. Similarly, for \textit{S-S}⁻ = S\textsubscript{2}PMesse⁻ or S\textsubscript{2}COPh⁻, reaction with (1) in refluxing ethanol gives cis-[Os(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}PR\textsubscript{2})] [R = Me (7) or Ph (8)]. However, shaking in methanol gives paramagnetic \textit{mer}-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}PR\textsubscript{2})] [R = Me (9) or Ph (10)]. Recrystallisation of (9) from boiling benzene gives trans-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}PMesse)] (11), whereas prolonged standing in cold benzene gives a purple oil containing the cation [OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}PMesse)] (12) together with (1) and brown crystalline \textit{mer}-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}PMesse)] (13). Carbonylation of (7) in refluxing ethanol in the presence of sulphur gives cis-[Os(OC)(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}PMesse)] (14) together with a brown oil containing PMessePhS and a complex of probable formula [Os(OC)(PMe\textsubscript{3}Ph)\textsubscript{2}(S\textsubscript{2}PMesse)] (15). In the presence of PMessePh, carbonylation of (7) gives [Os(OC)(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}PMesse)] (16) whereas in cold CH\textsubscript{2}Cl\textsubscript{2}-C\textsubscript{6}H\textsubscript{6} a different isomeric form of [Os(OC)(PMe\textsubscript{3}Ph)\textsubscript{2}(S\textsubscript{2}PMesse)] (17) is produced. In contrast, reaction of (1) with K[S\textsubscript{2}COEt] under all conditions gives only \textit{mer}-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}(S\textsubscript{2}COEt)] (18). The complexes have been characterised by elemental analyses and mass, i.r., and n.m.r. spectroscopy (\textit{H} and 31P), and detailed mechanisms for the overall reaction and the carboxylation of (7) are postulated.

In Part 7 of this series\textsuperscript{3} the investigation of the reactions of \textit{mer}-[RhCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}] with dithiocarbamates gave considerable insight into the possible nature of some of the paramagnetic intermediates which might be formed in the preparation of cis-[Ru(PMe\textsubscript{3}Ph)\textsubscript{2}(S\textsubscript{2}PR\textsubscript{2})] (R = Me or Ph) from \textit{mer}-[RuCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}]\textsuperscript{3}. However, because of the stability of rhodium(III) complexes with respect to reduction to Rh\textsuperscript{II}, no information could be gleaned about the step at which reduction to Ru\textsuperscript{II} occurs or the nature of any ruthenium(III) intermediates. It was therefore felt, since osmium has stable oxidation states of both \textit{II} and \textit{III} and is also less labile than ruthenium in both of these oxidation states,\textsuperscript{4} that an investigation of the reactions of \textit{mer}-[OsCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}] with dithiocarbamates might shed some extra light on the mechanism of formation of cis-[Ru(PMe\textsubscript{3}Ph)\textsubscript{2}(S\textsubscript{2}PR\textsubscript{2})] from \textit{mer}-[RuCl\textsubscript{3}(PMe\textsubscript{3}Ph)\textsubscript{3}].

With the exception of a very recent paper on osmium dialkylthiocarbamates and \textit{O}-alkyl dithiocarbamates,\textsuperscript{5} very little work has been published on osmium

complexes containing dithioacetal ligands. Earlier examples include the synthesis of [Os(S₂CNMe₂)₃] from the reaction of [NH₄]₂[OsCl₆] with Na[S₂CNMe₂], a brief mention of [OsO₂(S₂CNMe₂)₂] and [OsCl(bipy)₂(S₂CNMe₂)] (bipy = 2,2'-bipyridyl) from the interaction of [OsCl(bipy)] and K[S₂CN(CH₂)₂].

Analytical data for the new complexes are given in Table 1 and spectroscopic properties in Tables 2–4.

**Dimethylthiocarbamato-complexes**.—When complex (1) was heated under reflux with excess of Na[S₂CNMe₂]-2H₂O in ethanol for 90 min, a yellow complex of composition [Os(PMe₂Ph)₂(S₂CNMe₂)₂] (2) was isolated in

### Table 1

**Analytical data for some osmium dithioacetal complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M.p. (°C)</th>
<th>Found</th>
<th>Calc.</th>
<th>%\text{FeCl}_3</th>
<th>B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>mer-[OsCl₃(PMe₂Ph)(S₂PMe₃)]</td>
<td>Yellow</td>
<td>140–142</td>
<td>39.8</td>
<td>4.9</td>
<td>39.0</td>
<td>4.9</td>
</tr>
<tr>
<td>mer-[OsCl₃(PMe₂Ph)(S₂PPh₂)]</td>
<td>Red</td>
<td>207–210</td>
<td>32.6</td>
<td>4.3</td>
<td>32.6</td>
<td>4.3</td>
</tr>
<tr>
<td>trans-[OsCl₂(PMe₂Ph)(S₂PMe₃)]</td>
<td>Orange</td>
<td>198–200</td>
<td>39.9</td>
<td>4.7</td>
<td>39.8</td>
<td>4.7</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₂Ph)(S₂PMe₃)]</td>
<td>Yellow</td>
<td>140–150</td>
<td>42.6</td>
<td>5.3</td>
<td>42.7</td>
<td>5.1</td>
</tr>
<tr>
<td>fac-[OsCl(PMe₂Ph)(S₂CNMe₂)]</td>
<td>Yellow</td>
<td>172–174</td>
<td>42.4</td>
<td>5.2</td>
<td>42.5</td>
<td>5.1</td>
</tr>
<tr>
<td>fac-[OsCl₂(Et)(S₂CNMe₂)]</td>
<td>Yellow</td>
<td>206–210</td>
<td>41.5</td>
<td>5.2</td>
<td>41.5</td>
<td>5.2</td>
</tr>
<tr>
<td>fac-[OsCl₂(PMe₃)(S₂CNMe₂)]</td>
<td>Orange</td>
<td>123–125</td>
<td>42.5</td>
<td>5.2</td>
<td>42.6</td>
<td>5.0</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂CNMe₂)]</td>
<td>Orange</td>
<td>189–190</td>
<td>33.5</td>
<td>4.9</td>
<td>33.5</td>
<td>4.9</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂PPh₂)]</td>
<td>Orange</td>
<td>238</td>
<td>40.5</td>
<td>4.5</td>
<td>40.6</td>
<td>4.5</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂CO)]</td>
<td>Yellow</td>
<td>122–174</td>
<td>37.5</td>
<td>4.9</td>
<td>37.4</td>
<td>4.8</td>
</tr>
<tr>
<td>fac-[OsCl₂(PMe₃)(S₂CO)]</td>
<td>Yellow</td>
<td>84–86</td>
<td>37.1</td>
<td>4.6</td>
<td>37.2</td>
<td>4.6</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂CO)]</td>
<td>Yellow</td>
<td>129–132</td>
<td>25.8</td>
<td>3.8</td>
<td>25.7</td>
<td>3.8</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂CO)]</td>
<td>Yellow</td>
<td>155–165</td>
<td>34.0</td>
<td>4.7</td>
<td>33.9</td>
<td>4.6</td>
</tr>
</tbody>
</table>

* Obtained in CH₃Cl at 301 K by Evans' method. 1 B.M. ≈ 9.27 × 10⁻⁶ A m⁻¹. * Decomposition.

### Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>υ(OsCl)</th>
<th>Dithioacetal ligand absorptions</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>mer-[OsCl₃(PMe₂Ph)(S₂PMe₃)]</td>
<td>350v, 312s, 270m</td>
<td>600v, 312s, 270m</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>mer-[OsCl₃(PMe₂Ph)(S₂PPh₂)]</td>
<td>350v, 312s, 270m</td>
<td>600v, 312s, 270m</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>mer-[OsCl₃(PMe₃)(S₂PMe₃)]</td>
<td>350v, 312s, 270m</td>
<td>600v, 312s, 270m</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>trans-[OsCl₂(PMe₂Ph)(S₂PMe₃)]</td>
<td>300v, br</td>
<td>600v, 312s, 270m</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>fac-[OsCl₂(PMe₃)(S₂PMe₃)]</td>
<td>348v</td>
<td>600v, 312s, 270m</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>fac-[OsCl₂(PMe₃)(S₂PPh₂)]</td>
<td>350v, 312s, 270m</td>
<td>600v, 312s, 270m</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>fac-[OsCl₂(PMe₃)(S₂CO)]</td>
<td>350v, 312s, 270m</td>
<td>600v, 312s, 270m</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂PMe₃)]</td>
<td>583v</td>
<td>583v, 571 vs *</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂PPh₂)]</td>
<td>580v, 571 vs *</td>
<td>580v, 571 vs *</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂CO)]</td>
<td>602s, 570 vs *</td>
<td>602s, 570 vs *</td>
<td>1 040 vs *</td>
</tr>
<tr>
<td>cis-[OsCl₂(PMe₃)(S₂CNMe₂)]</td>
<td>602s, 570 vs *</td>
<td>602s, 570 vs *</td>
<td>1 040 vs *</td>
</tr>
</tbody>
</table>


**RESULTS AND DISCUSSION**

It is reported that mer-[OsCl₃(PMe₂Ph)₃] can be prepared either by reaction of OsO₄ with PMe₂Ph in hydrochloric acid, or, in low yield, by refluxing [NH₄]₂[OsCl₆] with excess of PMe₂Ph in 2-methoxyethanol. We have found that quantitative yields of the complex are obtained in the latter reaction by addition of concentrated HCl to the mixture and by prolonging the reflux for 16 h. The reactions of mer-[OsCl₃(PMe₂Ph)₃] (1) with various dithioacetal anions are described below.

* R. A. Bois, University Microfilms, 72–14, 064 (Chem. Abst., 1972, 77, 10888T).

80% yield and the remaining solution was shown (by t.l.c.) to contain small quantities of three other coloured compounds together with some white tetramethylthiuram disulphide. Shaking the two reactants in methanol for 10 min produced a single yellow complex of formula [OsCl(PMe₂Ph)(S₂CNMe₂)] (3), white S₈(S₂CNMe₂)₂, and a very small quantity of (2). When, however, this latter reaction was carried out in the presence of excess of PMe₂Ph, the previously known, pale yellow, complex [OsCl₃(PMe₂Ph)₃] was isolated and this was

oxidised quantitatively to mer-[OsCl₃(PMe₂Ph)₃] and PMe₂PhO on standing in CDCl₃ (cf. the reaction of

<table>
<thead>
<tr>
<th>TABLE 3</th>
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<tbody>
<tr>
<td>Main peaks in the mass spectrum of mer-[OsCl(PMMe₂Ph)₃(S₂CNMe₂)] (3) at 200 °C</td>
</tr>
</tbody>
</table>
|m/e of 185Os peak 

| 705 | [OsCl₂(PMMe₂Ph)₃(S₂CNMe₂)]⁺ |
| 761 | [OsCl₂(PMMe₂Ph)₃(S₂CNMe₂)]⁺ |
| 768 | [OsCl₂(PMMe₂Ph)₃(S₂CNMe₂)]⁺ |
| 520 | [OsCl₂(PMMe₂Ph)₃(S₂CNMe₂)]⁺ |
| 485 | [OsCl₂(PMMe₂Ph)₃(S₂CNMe₂)]⁺ |
| 458 | 705 → 570 |
| 354 | [OsCl₂(PMMe₂Ph)₃(S₂CNMe₂)]⁺ |
| 328 | 570 → 354 |

* All the peaks showed the characteristic osmium isotopic pattern.  Metastable.

[RhCl₂(PMMe₂Ph)₄]⁺ with CDCl₃ to give mer-[RhCl₂(PMMe₂Ph)₃]⁺.

Refluxing ethanol in the absence of excess of PMe₂Ph to produce, after 90 min, (2) together with the three other coloured complexes obtained earlier. In this instance, (2) was only obtained in 50% yield.

Reaction of (3) with K[S₂COEt] in refluxing ethanol again produced several compounds, four of which were the same as those obtained from the reaction of (3) with Na[S₂CNMe₂]:2H₂O and the fifth was an orange compound of higher Rf value than the others. In this case, the five compounds were separated on a dry alumina column and, after recrystallisation, shown to have the following composition in decreasing order of Rf value: [Os(PMMe₂Ph)₃(S₂CNMe₂)(S₂COEt)] (4), [OsCl₂(PMMe₂Ph)₃(S₂CNMe₂)] (5) [but with different spectral properties from (3)], [Os(OEt)(PMMe₂Ph)₃(S₂CNMe₂)] (6), and a red oil which was not successfully recrystallised or identified.

The stereochemistries of these complexes are discussed later but it is of interest to note that, although reaction of (3) with Na[S₂CNMe₂]:2H₂O does give rise

<table>
<thead>
<tr>
<th>TABLE 4</th>
</tr>
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<tbody>
<tr>
<td>Hydrogen-1 n.m.r. data for various osmium(II) dithioacids complexes (in CDCl₃)</td>
</tr>
<tr>
<td>Complex</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>mer-[OsCl(PMMe₂Ph)₃(S₂PMMe₂)]</td>
</tr>
<tr>
<td>mer-[OsCl(PMMe₂Ph)₃(S₂CNMe₂)] (3)</td>
</tr>
<tr>
<td>fac-[OsCl(PMMe₂Ph)₃(S₂CNMe₂)] (5)</td>
</tr>
<tr>
<td>fac-[Os(OEt)(PMMe₂Ph)₃(S₂CNMe₂)] (6)</td>
</tr>
<tr>
<td>mer-[OsCl₂(PMMe₂Ph)₃(S₂COEt)] (18)</td>
</tr>
<tr>
<td>mer-[OsBr₂(PMMe₂Ph)₃(S₂COEt)] (19)</td>
</tr>
<tr>
<td>cis-[Os(PMMe₂Ph)₂(S₂PMMe₂)] (7)</td>
</tr>
<tr>
<td>cis-[Os(PMMe₂Ph)₂(S₂CNMe₂)] (8)</td>
</tr>
<tr>
<td>cis-[Os(PMMe₂Ph)(CO)(PMMe₂Ph)₂(S₂PMMe₂)] (14)</td>
</tr>
<tr>
<td>cis-[Os(PMMe₂Ph)(CO)(PMMe₂Ph)₂(S₂CNMe₂)] (15)</td>
</tr>
<tr>
<td>Os(CO)(PMMe₂Ph)(S₂PMMe₂)</td>
</tr>
<tr>
<td>Os(CO)(PMMe₂Ph)(S₂CNMe₂)</td>
</tr>
<tr>
<td>Os(CO)(PMMe₂Ph)(S₂CNMe₂)</td>
</tr>
<tr>
<td>Os(CO)(PMMe₂Ph)(S₂CNMe₂)</td>
</tr>
</tbody>
</table>

s = singlet, d = doublet, t = triplet, q = quartet.

* ± 0.001.  † J(PH) in Hz.  ‡ Since H₂PPH₂ type spectrum, coupling constant is J(PH) + J(PH) in Hz.  § Broad singlet.

Attempts to prepare complexes of formula [Os(PMMe₂Ph)₃(S₂CMMe₂)] by shaking (3) with Na[S₂CMMe₂]:2H₂O in the presence of excess of PMe₂Ph were unsuccessful, giving only unchanged starting material. However, (3) did react with Na[S₂CMMe₂]:2H₂O in to the formation of (2), the yield of (2) (50%) is not as high as from the reaction of mer-[OsCl₃(PMMe₂Ph)₃] (1) with Na[S₂CMMe₂]:2H₂O (80%). Thus, although (3)

10 For details see B. Loev and M. M. Goodman, Chem. and Ind., 1967, 2026.
may be an intermediate in the formation of (2) from (1), a parallel path which does not involve (3) as an intermediate must also be operating to form (2). The mechanistic implications of this observation are discussed later.

**Diphenyl- and Dimethyl-phosphinodithioato-complexes.**

As for dithiocarbamate, reactions of (1) with excess of Na[S$_2$PMe$_3$] or NH$_4$[S$_2$PPh$_2$] in refluxing ethanol led to the formation of orange solutions from which crystalline complexes of formula [Os(PMe$_3$Ph)$_4$(S$_2$PPh)$_2$]$_2$ [R = Me (7) or Ph (8)] may be isolated in high yield. Solutions of these complexes rapidly turn green in the presence of air and, as with cis-[Ru(PMe$_3$Ph)$_4$(S$_2$PMe$_3$)$_2$], broadening of the previously sharp $^1$H n.m.r. signals is observed, indicating that oxidation to a paramagnetic species is probably occurring. Again as for the ruthenium complexes, sharp peaks appeared in these spectra after several weeks but these clearly arise from non-metal-containing decomposition products since the ruthenium and osmium spectra were superimposable and one of the doublets in the spectrum is assignable to PMe$_3$PhS. During one of the preparations of (7), a pale yellow solid was also isolated. This is the well known [OsCl$_2$(PMe$_3$Ph)$_2$]Cl which is formed when (1) is heated under reflux in aqueous ethanol.

As with mer-[RhCl$_2$(PMe$_3$Ph)$_3$], shaking (1) with excess of Na[S$_2$PMe$_3$] or 2H$_2$O in methanol produced a complex of formula [OsCl$_2$(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$] (9). In this case, the complex is purple and a reaction time of 90 min (cf. 10 min for Rh) was required for complete conversion. The analogous complex [OsCl$_2$(PMe$_3$Ph)$_3$(S$_2$PPh)$_2$] (10) was also prepared by reaction of (1) in CH$_2$Cl$_2$ with a methanolic solution of Na[S$_2$PPh$_2$], followed by evaporation of the CH$_2$Cl$_2$ and collection of the methanol-insoluble product. Since (10) is more difficult to prepare than (9) and less amenable to $^1$H n.m.r. studies, its reactions were not investigated further but those of (9) were studied in some detail.

Thus, (9) was recovered unchanged when it was recrystallised rapidly from dichloromethane-n-hexane in the cold (cf. the facile formation of trans-[RhCl$_2$(PMe$_3$Ph)$_3$] on recrystallisation of mer-[RhCl$_2$(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$], but when the solution was warmed and allowed to stand quantitative conversion into red mer-[OsCl$_2$(PMe$_3$Ph)$_3$] occurred, whilst prolonged reaction (9) with PMe$_3$Ph in cold CH$_2$Cl$_2$ produced a yellow solution from which [OsCl$_2$(PMe$_3$Ph)$_3$]Cl was isolated. Recrystallisation of (9) from boiling benzene in air gave a red complex of formula [OsCl$_2$(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$] (11) together with some PMe$_3$PhO, whereas when (9) was allowed to stand in cold benzene for 2 weeks, three compounds were isolated from the resulting brown solution by fractional crystallisation with n-hexane. These were a purple strongly conducting oil, which is thought to contain the cation [OsCl(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$]$^+$ (12), a brown crystalline solid of formula [OsCl(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)] (13), and mer-[OsCl$_2$(PMe$_3$Ph)$_3$] (1). Longer reaction times in cold benzine (4 weeks) produced only (13) and (1). Finally, shaking (9) in acetonitrile for several days again produced a highly conducting purple oil, as well as (1), but, in this instance, no (13).

As in the case of cis-[Ru(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$] [Os(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$] (7) reacted with carbon monoxide under mild conditions. Thus, reaction of (7) with CO in refluxing ethanol, in the presence of a small amount of elemental sulphur, produced a complex of formula [Os(CO)$_2$(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$] (14) together with a brown oil which contained (i.r. and n.m.r. evidence) both PMe$_3$PhS and a complex with two cis-CO groups of probable formula [Os(CO)$_3$(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_2$] (15). When the carbonylation reaction was carried out in the presence of excess of PMe$_3$Ph, a yellow crystalline complex of formula [Os(CO)$_2$(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_3$] was exclusively formed. Finally, reaction of (7) with CO in cold CH$_2$Cl$_2$ gave another yellow complex, probably also of formula [Os(CO)$_2$(PMe$_3$Ph)$_3$(S$_2$PMe$_3$)$_3$], which rapidly becomes green on air exposure and whose structure will be discussed later.

**O-Ethyl Dithiocarbonato-complexes.**—The reaction of (1) with K[Co(CO)$_3$] is rather different from those with the other dithiocarboxylic acids studied since both refluxing the reactants in ethanol for 1 h or shaking them in methanol for 10 min produced only one complex which has the formula [OsCl(PMe$_3$Ph)$_3$(S$_2$COEt)] (18). Attempts to persuade this complex to react further with either K[Co(CO)$_3$] or Na[CNMe$_2$] or 2H$_2$O were abortive yielding only unchanged starting materials in both cases. An attempt to prepare the complex [Os(PMe$_3$Ph)$_3$(S$_2$COEt)] by reaction of mer-[OsBr$_2$(PMe$_3$Ph)$_3$] with K[Co(CO)$_3$] was also fruitless since, although no solid product could be isolated, a $^1$H n.m.r. spectrum of the resulting orange oil indicated that [OsBr$_2$(PMe$_3$Ph)$_3$(S$_2$COEt)] (19) was the only identifiable product.

**Spectroscopic Properties of the Dithiocarboxylates.**

**I.r. spectra.** Like mer-[RhCl$_2$(PMe$_3$Ph)$_3$], mer-[OsCl$_2$(PMe$_3$Ph)$_3$] has three i.r.-active $\nu$(OsCl) stretching vibrations and these are assigned to the absorptions at 350, 312, and 270 cm$^{-1}$ (Table 2). Again, by analogy with the rhodium complex, the band of lowest energy (270 cm$^{-1}$) is assigned as arising predominantly from the Os=Cl bond to the highest $\nu$(trans)-influence ligand (PMe$_3$Ph). Then, the two absorptions at 350 and 312 cm$^{-1}$ are assigned as arising predominantly from the symmetric ($\nu_{\text{sym}}$) and asymmetric ($\nu_{\text{asym}}$) Cl=Os=Cl stretching vibrations. Although the exact assignment of these two absorption frequencies to $\nu_{\text{sym}}$ and $\nu_{\text{asym}}$ is not possible, since in a molecule of this size mixing with other vibrations of the same symmetry will occur, this region may be used as a 'fingerprint' in assigning stereochemistries to related molecules.

Analysis of the $\nu$(OsCl) region of [OsCl$_2$(PMe$_3$Ph)$_3$(S$_2$PR$_3$)] (R = Me or Ph) (Table 2) indicates that in both cases the chloride ion is trans to phosphine has been removed, as expected in view of the greater $\nu$(trans) influence of PMe$_3$Ph compared to chloride. This fact, coupled with the observations that absorptions in the $\nu$(PS)

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region indicate that only unidentate $[\text{S}_2\text{PR}_2]^-$ groups are present and that $[\text{RhCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ has a meridional configuration,\textsuperscript{9} leads to the conclusion that complexes (9) and (10) have the structure shown in Scheme 1. The complex $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ (11) has a strong absorption at 300 cm$^{-1}$ indicative of a trans-OsCl$^2$ arrangement.

The similar $\nu$(OsCl) of complexes (13), (3), and (18), all of which have formula $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{S})]$ ($S^\text{-}$ $S^\text{-}$ = $\text{S}_2\text{PMe}_2^-$, $\text{S}_2\text{CNMe}_2^-$, and $\text{S}_2\text{COEt}^-$ respectively), indicate that these complexes probably have a common stereochemistry. Since the other isomer of $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (6) has a lower $\nu$(OsCl), it is likely that here the chloride ion is trans to a phosphine group.

Scheme 1  Proposed mechanism for the reaction of mer-$[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3]$ (1) with $[\text{S}-\text{S}]^-$ (complexes shown in broken square brackets were not isolated).  (i) $\sim$ Cl$^-$; (ii) $\sim$ PMe$_2$Ph; (iii) + S$^-$; (iv) $[\text{S}-\text{S}]^-$.
whilst the other complexes (13), (3), and (18) have a meridional configuration (see Scheme 1). The other complexes, apart from those containing CO, all have dithiocarbamates characteristic of bidentate coordination (Table 2) and little information as to their stereochemistries can be gleaned from their i.r. spectra, although the presence of a ν(CO) stretching vibration at 1300 cm⁻¹ in [OsO(CO)(PMe₃Ph)(S₂CNMe₃)] (6) is in the region expected for an ethoxy-group directly bound to a metal (1000–1100 cm⁻¹).²

For the carbonyl-containing species, although the 500–700 cm⁻¹ region in their i.r. spectra is complicated by the presence of carbonyl bending modes, it can be seen from Table 2 that the two complexes of formula [OsO(CO)(PMe₃Ph)(S₂PMc₃)] (16 and 17) as well as [OsO(CO)(PMe₃Ph)(S₃PMc₃)] (15) probably contain both uni- and bi-dentate S₃PMc₃ groups and that (16) has the two CO groups in a cis configuration [having two ν(CO)]. The higher value of ν(CO) for (17) compared to the other two monocarbonyl complexes indicates that the CO group in (17) may be trans to PMe₃Ph (cf. [Ru(CO)(PMe₃Ph)(S₃PMc₃)] (D) in ref. 3). Finally, the absence of a peak at 600 cm⁻¹ in the i.r. spectrum of [OsO(CO)(PMe₃Ph)(S₃PMc₃)] indicates that this complex probably does not contain the S₂PMc₃⁺ groups.

**Mass spectra.** The mass spectra of [OsO(CO)(PMe₃Ph)(S₂PMc₃)] (14) and [OsO(CO)(PMe₃Ph)(S₂PMc₃)] (16) were identical since (16) readily loses PMe₃Ph at high temperatures to form (14). Their mass spectra showed well defined, intense, osmium isotope patterns which correspond to [OsO(CO)(PMe₃Ph)(S₂PMc₃)]⁺ (608), *OsO(CO)(PMe₃Ph)(S₃PMc₃)]⁺ (580), *Os(S₂PMc₃)⁺ (442), and [Os(PMe₃Ph)(S₃PMc₃)]⁻ (290), as well as several weaker patterns corresponding to loss of metal groups and large metastable-ion signals at m/e 560 and 347 which correspond to loss of CO from [OsO(CO)(PMe₃Ph)(S₃PMc₃)] and of PMe₃Ph from [OsO(CO)(PMe₃Ph)(S₃PMc₃)] respectively.

The mass spectrum of [OsCl(PMe₃Ph)(S₂CNMe₃)] (3) is also of interest since it not only showed the parent ion and fragmentation pattern corresponding to this complex, but also those for two other complexes, [Os(PMe₃Ph)(S₂CNMe₃)] (2) and [OsCl(PMe₃Ph)(S₂CNMe₃)] (9) (Table 3). Since there is no evidence for (2), or an isomer of (2), in the ¹H n.m.r. spectrum of (3) and since the relative intensities of the mass-spectral signals arising from these two complexes are comparable in two different samples, it seems likely that (2) is formed from (3) under the extreme conditions present in the mass spectrometer (200 °C). However, since the intensities of the mass-spectral signals arising from [OsCl(PMe₃Ph)(S₂CNMe₃)] (9) vary considerably relative to those of (3) from one sample to another, it is likely that this complex is an impurity in (3). This is quite possible since the mode of preparation of (3) is similar to that of (9), and the presence of this osmium(III) impurity might also explain the broadness of the signals observed in the ¹H n.m.r. spectrum of (3) (see below).

**Hydrogen-¹ n.m.r. spectra.** The ¹H n.m.r. spectra of mer-[[OsCl₂(PMe₃Ph)₂(S₂PR₃)] (R = Me (9) or Ph (10)] and of trans-[[OsCl₂(PMe₃Ph)₂(S₂PMc₃)] (11) all showed ill defined contact-shifted resonances from which very little structural information may be obtained. These spectra are indicative of paramagnetic species, and solution magnetic moments obtained by Evans' method may lie well within the range expected for one unpaired electron and are consistent with the formulation of these complexes as containing OsIII. However, the structures of (9), (10), and (11) as indicated by their i.r. spectra are consistent with those of the analogous diamagnetic rhodium(II) complexes as well as with their modes of preparation, which involve replacement of the most labile chloride ion in (1) by a unsubstituted [S-S]⁻ ligand [(9) and (10)] followed by chelation of this dithiocarbamate ligand with concomitant loss of phosphine to form (11) (see Scheme 1). The remaining complexes are all diamagnetic and gave rise to sharp n.m.r. signals from which their structures in solution may be unequivocally assigned (Table 4). The methyl groups on the phosphine ligands of [OsX(PMe₃Ph)(S-S)] (X = Cl, S-S = S₂PMc₃ (13) or S₂COEt (18); X = Br, S-S = S₂COEt (19)] gave rise to two virtually coupled triplets and a sharp doublet in their ¹H n.m.r. spectra. This, together with only one methyl doublet from the S₂PMc₃⁺ group of (13), confirms that these complexes have the meridional structure shown in Scheme 1.

At low temperature, the ¹H n.m.r. spectra of [OsX(PMe₃Ph)(S₂CNMe₃)] (X = Cl (5) or OEt (6)] consisted of two pseudo-doublets and a sharp doublet arising from the phosphine methyl groups as well as a sharp singlet from the dithiocarbamate methyl groups. For (6), there were also a quartet and a triplet arising from the OEt group. This indicates that the complexes do not contain mutually trans phosphine groups and hence must have a facial configuration (Scheme 1). Then, the phosphines trans to the sulphur atoms are chemically equivalent giving rise to the pseudo-doublets, and there are two such pseudo-doublets since there is no plane of symmetry through the Os-P bonds. The phosphine trans-X is unique, giving rise to a single methyl doublet.

The ¹H n.m.r. spectrum of [OsCl(PMe₃Ph)(S₂CNMe₃)] (3) is more difficult to interpret since, although immediately after the solution was made up the resonances were relatively sharp, they rapidly broadened. This is presumably because the complex is rapidly oxidised in air or because a paramagnetic impurity is present in the

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* Numbers in parentheses refer to m/e of the ¹⁹Os peak.

† A 'pseudo-doublet' is a sharp doublet with additional signal intensity situated between the doublet. This spectral pattern is indicative of a small, but non-zero, J(PP) value when compared to J(PH) + J(PP).¹⁴

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solution.* Complex (3) is assigned a mer configuration on the basis of heteronuclear-decoupling studies and because it is different from (5) which is definitely the fac isomer. Irradiation in the $^{31}$P resonance region produced sharpening of the slightly broad singlets at $\delta$ 1.80 and 1.68 p.p.m. which indicates that these are separate resonances with some P-H coupling. Irradiation at a different frequency in the same region decoupled the doublet at $\delta$ 1.34 p.p.m. to a singlet and thus it is most likely that the $^1$H n.m.r. spectrum of the phosphine methyl groups is similar to those of the mer complexes (13), (18), and (19) and that (3) also has this mer configuration.

The low-temperature $^1$H n.m.r. spectra of [Os(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] $[S^-S^- = S_2PMe_3^-]$ (7), $S_2PPh_3^-$, (8), or $S_2CNMe$_2$-$ (2)$ are all consistent with cis stereochemistry, although the non-equivalence of the methyl groups of (8) was not seen even at 213 K. As for cis-[Ru(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] (3) the two doublets arising from the $[S_2PMe_3^-]$ groups of (7) broadened and coalesced on warming, but in this case the coalescence temperature was ca. 328 K and the fast-exchange limit was not reached in CDCl$_3$. The two pseudo-doublets from the phosphine methyl groups also coalesced on warming to give a sharp signal at higher temperatures. This behaviour is again attributed to rapid interconversion of the two possible optical isomers of (7) $^{15}$ and rates together with related activation parameters for the inversion in CDCl$_3$ and C$_6$H$_6$ are given in Table 5. Since there is negligible difference in $\Delta H^\ddagger$ for the inversion on changing the solvent from CDCl$_3$ to C$_6$H$_6$, it is unlikely that a doublets from the phosphine methyl groups gradually moved together without broadening. This behaviour is similar to that found for cis-[Ru(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] $^{3,15}$ and cis-[Rh(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] (14) and cis-[Ru(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] $^{2}$ and cannot be explained in terms of a metal-centred inversion, but rather by separate processes involving increases in the rates of rotation about the C-C=N bonds of the $[S_2CNMe^-]$ ligands and coincidental equivalence of the signals from different rotamers at higher temperatures.

The low-temperature $^1$H n.m.r. spectrum of [Os(CO)$_2$(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] (14) consisted of six doublets arising from the six inequivalent methyl groups in the molecule indicating cis stereochemistry (see Scheme 2). However, on warming, the two doublets arising from the methyl groups on the phosphine (c and c') became coincident, but also, more surprisingly, two of the dithioacetyl doublets (b and b') move together until at ca. 283 K they were exactly coincident. The large doublet so formed broadened on further heating, which presumably indicates that the chemical shifts of these two doublets are no longer identical. Phosphorus-31 decoupling studies indicate that these two doublets arise from two methyl groups attached to the same phosphorus atom (presumably with one of the methyl groups syn to CO), and the only explanation for this behaviour appears to be that small structural changes occur on warming the complex and these give rise to different shielding effects on the two methyl groups at different temperatures.†

The presence of a triplet from the methyl groups of the phosphines and two doublets from the $[S_2PMe_3^-]$ methyl groups in the $^1$H n.m.r. spectrum of [Os(CO)$_2$(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] (16) is consistent with a structure containing trans phosphines, as shown in Scheme 2, provided that there is free rotation about the metal–phosphorus bonds. For the analogous [Ru(CO)$_2$(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$] (complex C, Figure 8 in ref. 3) the $^1$H n.m.r. spectrum indicates that rotation about the Ru–P bonds is slow at room temperature. Another important difference between these two complexes is that, whereas at elevated temperatures the ruthenium complex readily loses PMe$_3$Ph to give cis-[Ru(CO)(PMe$_3$Ph)(S$_2$CNMe$_2$)$_2$]$^{3}$ (16) may be kept in solution at 323 K for several hours or may be recovered unchanged on recrystallisation from CH$_2$Cl$_2$–C$_6$H$_6$. This is presumably a reflection of the greater inertness of Os$^\ddagger$ compared to Ru$^{11}$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E^\ddagger$</th>
<th>$\Gamma$</th>
<th>$\Delta H^\ddagger$</th>
<th>$\Delta S^\ddagger$</th>
<th>$\Delta G^\ddagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>91.5 ± 4</td>
<td>90.5 ± 4</td>
<td>72 ± 8</td>
<td>70.1 ± 0.2</td>
<td>74.1 ± 0.1</td>
</tr>
<tr>
<td>C$_6$H$_6$</td>
<td>91.0 ± 4</td>
<td>90.4 ± 4</td>
<td>57 ± 12</td>
<td>74.1 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

* A weak c.s.r. signal was observed in the solid, but since its position is not reproducible it is probably due to a small amount of paramagnetic impurity rather than to any inherent paramagnetism of the compound itself. The nature of this impurity is unclear although the presence of OsCl$_3$(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$ in the mass spectrum of (3) (Table 3) could indicate that OsCl$_3$(PMe$_3$)$_2$(S$_2$CNMe$_2$)$_2$ is the impurity, but this could also be formed in the mass spectrometer.

† Since the four-membered rings in cis-[Ru(PMe$_3$)$_2$(S$_2$PET$_4$)$_2$] are not planar in the solid state, it may be that this is also the case at low temperature for cis-[Os(CO)(PMe$_3$Ph)(S$_2$CNMe$_2$)$_2$], but on warming the inversion of these rings occurs which fortuitously causes equal shielding effects of the two methyl groups on one $[S_2PMe_2^\text{-}]$ ligand at 283 K.

The other isomer of \([\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_3)_2]\) (17) gave rise to seven doublets in the \(^1\text{H}\) n.m.r. spectrum and, apart from small changes in chemical shift, this spectrum was temperature invariant up to 323 K and again showed no detectable decomposition at this temperature. Phosphorus-31 decoupling studies indicate that the doublet at \(\delta 1.74\) p.p.m., which has twice the intensity of the other doublets, is composed of two accidentally degenerate resonances from methyl groups.

\[
\begin{array}{c}
\text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_3)_2] \\
\text{in the presence of sulphur}
\end{array}
\]

show that it consists of a mixture of (14), \text{PMe}_2\text{PhS}, and complex (15) whose n.m.r. spectrum is given in Table 4. The best interpretation of this spectrum is that the complex contains one \text{PMe}_2\text{Ph} ligand, in which the methyl groups are inequivalent, and two \([\text{S}_2\text{PMe}_3]^-\) ligands in one of which the methyl groups are inequivalent whilst in the other they are equivalent. We assign this complex the structure shown in Scheme 2.

![Scheme 2 Proposed mechanism of carbonylation of cis-\[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_3)_2\] (7). (i) CO; (ii) \text{PMe}_2\text{Ph}](7)

on different phosphine ligands. Thus, all the methyl groups in this complex are inequivalent, and in view of the similarity of preparation of this complex and that of \([\text{Ru(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_3)_2]\) (complex D, Figure 8 in ref. 3) as well as the similarity in their spectroscopic properties (17) is assigned the structure shown in Scheme 2.

Finally, \(^{31}\text{P}\) decoupling studies on the \(^1\text{H}\) n.m.r. spectrum of the brown oil obtained from carbonylation of because this fits the evidence and is the most likely dicarbonyl to be formed from further carbonylation of \text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_3)_2] (14). It is also the only isomer with no plane of symmetry through the Os-P bond in which there is a methyl group \textit{syn} to \text{PMe}_2\text{Ph} on the bidentate \([\text{S}_2\text{PMe}_3]^-\) ligand, which is required to explain the large shift to low frequency of one of these methyl groups (e'). Since the osmium atom in this complex is a chiral centre, the two methyl groups of the
unidentate \([\text{S}_2\text{PMe}_2]^–\) ligand would be expected to be inequivalent [as in (17)], but in this case it appears that the chemical-shift difference is only very small.

**Stereochemical Path for Conversion of mer-[OsCl\(_2\)(\text{PMe}_3\text{Ph})\(_2\)] into cis-[Os(PMe_3\text{Ph})_2(S-S)]**.—Since the only complex obtainable from the reaction of (1) with \([\text{S}_2\text{COEt}]^–\) is mer-[OsCl(PMe_3\text{Ph})_2(S-S)], it is clear that this complex does not react with \([\text{S}_2\text{COEt}]^–\) and that the chloride ion in this complex is inert. This indicates that the sulphur atom of the \([\text{S}_2\text{COEt}]^–\) moiety has a low trans effect and is not able to stabilise the chloride ion trans to it to any large extent. Although little information is available on the trans effects of sulphur-containing ligands, work on the reactions of fac-[Cr(NO)(\text{OH})\(_3\)(S-S)] \([\text{S}-\text{S}]^–=\text{S-CN}\text{R}_2^–, \text{S-COR}^–, \text{S-PR}_2^–\) with Lewis bases has shown that the trans effects of these dithiocarbamates are low but of comparable magnitude. Thus, since mer-[OsCl(PMe_3\text{Ph})_2(\text{CNMe}_2\text{CNMe}_2)] \((3)\) reacts with \(\text{S}-\text{S}^–\) to give cis-[Os(PMe_3\text{Ph})_2(\text{CNMe}_2\text{CNMe}_2)] \((\text{S}-\text{S}^–=\text{S-CNMe}_2^–\text{S})\) \((4)\), the mechanism of these reactions cannot involve direct displacement of chloride ion by \(\text{S}-\text{S}^–\). However, since fac-[OsCl(PMe_3\text{Ph})_2(\text{CNMe}_2\text{CNMe}_2)] \((5)\) is also obtained from these reactions, it is probable that they proceed by isomerisation of \((3)\) to give \((5)\) followed by displacement of Cl by \(\text{S}-\text{S}^–\) since in the fac isomer the chloride ion is trans to the high trans-effect ligand, PMe_3Ph. The formation of fac-[Os(OEt)(PMe_3\text{Ph})_2(\text{CNMe}_2\text{CNMe}_2)] \((6)\) is then explained as arising from interaction of \((5)\) with solvent ethanol and loss of HCl gas.

As has already been noted, the reaction of (1) with \(\text{Na}(\text{CNMe}_2\text{CNMe}_2)\cdot 2\text{H}_2\text{O}\) gives higher yields of \(2\) than does the corresponding reaction of (3). This can only mean that another path which does not involve \(3\) as an intermediate is operative in the formation of \(2\) from \(1\). This path probably involves ionosum(III) intermediates with the reduction to Os\(^{II}\) occurring as the last step (see Scheme 1).

Since mer-[OsCl(PMe_3\text{Ph})_2(\text{CNMe}_2\text{CNMe}_2)] \((13)\) is only formed on prolonged standing of mer-[OsCl_2(PMe_3\text{Ph})_2(\text{CNMe}_2\text{CNMe}_2)] \((9)\) in non-polar solvents and since no \((13)\) but only a purple ionic oil and \((1)\) are formed from \((9)\) in polar solvents, it seems likely that the formation of cis-[Os(PMe_3\text{Ph})_2(\text{S-S})^–](\text{S-S}^–=\text{S-PR}_2^–) \((7)\) from \((1)\) in refluxing ethanol does not involve \((13)\) as an intermediate but rather goes by the path which involves osium(III) cations. Then, the purple ionic oil probably contains [OsCl(PMe_3\text{Ph})_2(\text{S-S})]^+ \((12)\), and the formation of \((1)\) on allowing \((9)\) to stand in polar or non-polar solvents is easily explained since the chloride ion released in the formation of \((12)\) from \((9)\) might then attack \((9)\) to release \([\text{S}_2\text{PMe}_2]^–\) and give mer-[OsCl(PMe_3\text{Ph})_2] \((1)\).

It still remains to explain why neither of the paths shown in Scheme 1 is open to the reaction of \((1)\) with \([\text{S}_2\text{COEt}]^–\) in refluxing ethanol. The latter is thought to be excluded because the strongly reducing nature of \([\text{S}_2\text{COEt}]^–\) causes reduction to Os\(^{II}\) before [OsCl(PMe_3\text{Ph})_2(\text{S-S})] \((18)\) can react with more \([\text{S}_2\text{COEt}]^–\). Since it is well documented that the ease with which isomerisations of complexes occur is dependent on the substituents in the molecule,\(^{29}\) we propose that mer-[OsCl(PMe_3\text{Ph})_2(\text{S-S})] \((18)\) isomerises less readily to its fac isomer than does \((3)\) and that, in fact, harsher conditions than refluxing in ethanol are required to effect this isomerisation for \((18)\) and thus to allow further reaction to occur.

**Experimental**

Microanalyses were by the University of Edinburgh Chemistry Department. l.r. spectra were recorded in the 250–4000 cm\(^{-1}\) region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Solution spectra were recorded in potassium bromide cells. Mass spectra were obtained on an A.E.I. MS9 spectrometer and conductivity measurements on a Portland Electronics 310 conductivity bridge. Hydrogen-1 n.m.r. spectra and solution magnetic moments (Evans' method) \(^{10}\) were obtained on a Varian Associates HA-100 spectrometer and \(^{2}P\) n.m.r. spectra on a Varian XL-100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz \((^{2}P\) chemical shifts are given in p.p.m. to high frequency of \(80.7%\) \(\text{H}_2\text{PO}_4\)). Kinetic line-shape analysis on cis-[Os(PMe_3\text{Ph})_2(\text{S-S})] \((14)\) was made as described elsewhere.\(^{15}\) Heteronuclear-decoupling experiments were carried out on the HA-100 spectrometer using a second radio-frequency field provided by a Schumberger FS30 frequency synthesiser. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

**Materials.**—Ammonium hexachloro-oso-nitrate (Evans, Matthey Ltd.), carbon mono-oxide (Air Products), dimethyl-phenylphosphine (B.D.H.), Na(\text{CNMe}_2\text{CNMe}_2)\cdot 2\text{H}_2\text{O} (Ralph Emanuel), and K(S-S)OEt (B.D.H.) were obtained as indicated. Sodium dimethylphosphinodithioate, and sodium and ammonium diphenylphosphinodithioate were prepared as described earlier.\(^{4}\) All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere unless otherwise stated.

**Preparations.**—mer-Trichlororidris(dimethylphenylphosphine)osmium(III).—The salt \([\text{NH}_3]\text{Cl}[\text{OsCl}_2\text{(2.0 g)}\) and PMe_3Ph (3 cm\(^3\)) were heated under reflux in 2-methoxy-ethanol (50 cm\(^3\)) containing concentrated HCl (5 cm\(^3\)) for 16 h. The resulting red solution was filtered hot to remove \([\text{NH}_3]\text{Cl} and allowed to crystallise. The red crystals were collected and washed with water, ethanol, and n-pentane (3.0 g, 93%).

mer-Tribromoridris(dimethylphenylphosphine)osmium(III). The complex mer-[OsCl_2(PMe_3Ph)_2] \((0.35 \text{ g})\) and LiBr (2.0 g) were heated under reflux in ethanol (20 cm\(^3\)) for 36 h and allowed to cool. The resulting purple needles were filtered off and washed with water, ethanol, and n-pentane (0.30 g, 72%).

mer-Dichlororidris(dimethylphenylphosphine)(diaryl-phosphinodithioate)osmium(III).—Solutions of (1) \((0.15 \text{ g})\) in \(\text{CH}_2\text{Cl}_2\) \((15 \text{ cm}^3)\) and \(\text{Na}(\text{S-PPh}_2\text{)}} \((0.20 \text{ g})\) in methanol \((10 \text{ cm}^3)\) were mixed and after passing nitrogen the purple solution was evaporated to half its volume. The purple

product was collected and washed with water, methanol, and n-pentane (0.10 g, 51%).

Mer-Dichlorotris(dimethylphenylphosphine)(dimethyl-
phosphonodithioato)osmium(II) (9). Complex (1) (0.30 g) and
Na[S,PMe]_2·2H_2O (0.30 g) were shaken in methanol (25 cm³) for 90 min. The resulting purple crystals were
collected and washed with water, methanol, and n-pentane (0.31 g, 92%). Slow recrystallisation of (9) from CH_2Cl_2-
CH_3Cl gave red crystals of (1).

Mer-Bromotris(dimethylphenylphosphine)(O-ethyl dithiocarboxato)osmium(II) (10). To a mixture of
K[S,COE] (0.10 g) in methanol (15 cm³) for 10 min as yellow crystals (0.22 g, 66%).

Mer-Chlorotris(dimethylphenylphosphine)(dimethyl-
phosphonodithioato)osmium(II) (13). The complex mer-
[OCl,Cl(PMe,Ph),]Cl (9) was dissolved in benzene (5 cm³) and allowed to stand in air for 2 weeks.

Cis-(Dimethylidithiocarborato)bis(dimethylphenylphosphine)(O-ethyl dithiocarboxato)
mer-Bromotris(dimethylphenylphosphine)(dimethyl-
phosphonodithioato)osmium(II) (11). This complex was
prepared by refluxing mer-[OCl,Cl(PMe,Ph),]Cl (9) in benzene (10 cm³) for 30 min and evaporating to near
dryness. The red needles were collected and washed with n-pentane (0.063 g, 97%).

Cis-Bis(dimethylphenylphosphine)(bis(dimethylphosphino-
dithioato)osmium(II) (7). Complex (1) (0.60 g) and Na[S,PMe]_2·2H_2O (0.50 g) were heated under reflux in ethanol
(25 cm³) for 60 min. The orange solution was cooled with nitrogen bubbling through it and the resulting orange
crystals were collected and washed with water, ethanol, and n-pentane (0.40 g, 66%). On one occasion, the filtrate
deposited a small quantity of yellow [OCl,Cl(PMe,Ph),]Cl.

Similarly prepared were cis-bis(dimethylphenylphosphine-
bis(diphenylphosphinodithioato)osmium(II) (8) from (1) (0.15 g) and [NH,][S,PPh] (0.20 g) as orange crystals (0.10 g; 50%) and cis-bis(dimethylidithiocarborato)bis(dimethyl-
phenylphosphine)osmium(II) (2) from (1) (0.10 g) and Na-
[S,Cl,S,Me]_2·2H_2O (0.10 g) in ethanol (10 cm³) for 90 min,
as yellow crystals (0.08 g, 80%). A thin-layer chromatograph
of the filtrate from (2) (toluene on alumina) showed four weak bands, one of which corresponded to (2).

Complex (2) was also prepared by the reaction of mer-[OsCl-
(PMe,Ph),]Cl (3) (0.026 g) with Na[S,Cl,S,Me]_2·2H_2O (0.62 g) in refluxing ethanol (5 cm³) for 90 min, the yellow
solid crystallising out on cooling (0.01 g, 37%). T.l.c.
(toluene on alumina) of the resulting solution showed four
bands of approximately equal intensity, identical in Rf values and colours to those obtained from the reaction of
(1) with Na[S,Cl,S,Me]_2·2H_2O. Thus, the total yield
of (2) was 75%.

cis-(Dimethylidithiocarborato)bis(dimethylphenylphosphine)(O-ethyl dithiocarboxato)
mer-Chlorotris(dimethylphenylphosphine)(dimethyl-
phosphonodithioato)osmium(II) (13). The complex mer-
[OCl,Cl(PMe,Ph),]Cl (9) (0.10 g) and K[S,COE] (0.07 g) were heated under reflux in ethanol (15 cm³) for 60 min and the orange
solution was evaporated to dryness. The resulting orange
crystal could not be recrystallised.

cis-Carboxyl(dimethylphenylphosphine)bis(dimethyl-
phosphinodithioato)osmium(II) (14). The complex cis-[Os-
PMe,Ph),]Cl (7) (0.10 g) and sulphur (0.01 g) were heated under reflux in ethanol (15 cm³), with CO bubbling,
for 30 min. The yellow solution was cooled, filtered through celite, and evaporated to dryness. The resulting yellow
oil was recrystallised from CH_2Cl_2-C_6H_4 to give a brown oil which contained (15), (14), and PMPeS. The yellow
supernatant was decanted and allowed to crystallise to give the product as yellow crystals (0.04 g, 47%).

Carbonylbis(dimethylphenylphosphine)bis(dimethylphosphinodithioato)osmium(II) (16). The complex cis-[Os-
PMe,Ph),]Cl (7) (0.10 g) and PMPePh (0.20 cm³) were carbonylated in refluxing ethanol (15 cm³) for 30 min. On
cooling, the resulting yellow solution gave yellow crystals
of the product (0.07 g, 97%).

Carbonylbis(dimethylphenylphosphine)bis(dimethylphosphinodithioato)osmium(II) (17). The complex cis-[Os-PMe-
Ph),]Cl (7) (0.05 g) was carbonylated in CH_2Cl_2-
C_6H_4Cl (1:1 v/v) at room temperature for 2 min. The solvent
was evaporated by passing nitrogen and the yellow solid
was collected in quantitative yield.

We thank Johnson, Matthey Ltd for generous loans of ammonium hexachloro-osmate(iv), the University of Edin-
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and Mr. J. R. A. Millar for obtaining the 11P and 31N. n.m.r.
spectra respectively.
Metal Complexes of Sulphur Ligands. Part 11. Reactions of Platinum(II) and Palladium(II) Dithiocarbonates with Dithiocarbonate Ions

By Margaret C. Cornock, Robert O. Gould, C. Lynn Jones, John D. Owen, David F. Steele, and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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Metal Complexes of Sulphur Ligands. Part 11.1 Reactions of Platinum(II) and Palladium(II) Dithiocarbamates with Dithiocarbonate Ions

By Margaret C. Cornock, Robert O. Gould, C. Lynn Jones, John D. Owen, David F. Steele, and T. Anthony Stephenson.1 Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JL

Reaction of the complexes \([\text{Pt}(S_x\text{COR})_2]\) with \(K[S_x\text{COR}](R = \text{Et or Pr})\) followed by addition of \([\text{AsPh}_3]\) \(\text{Cl}\) generates \([\text{AsPh}_3][\text{Pt}(S_x\text{COR})_2]\). Variable-temperature \(\text{H}^1\) n.m.r. studies indicate rapid undentate–bidentate exchange at ambient temperature. Attempted recrystallisation from \(\text{CH}_3\text{Cl}_2\) or \(\text{CD}_3\text{Cl}_2\) results in an intramolecular rearrangement to give \([\text{AsPh}_3][\text{Pt}(S_x\text{COR})_2]\). Reaction of \([\text{Pd}(S_x\text{COEt})_2]\) with \(K[S_x\text{COEt}]\) gives \([\text{AsPh}_3][\text{Pd}(S_x\text{CO})(S_x\text{COEt})]\) as the main product. Reaction of \([\text{Pt}(S_x\text{CO})_2]\) with \(K[S_x\text{COR}](R = \text{Me}, \text{Et}, \text{Pr}\text{, or CH}_3\text{Ph})\) and \(\text{AsPh}_3\) \(\text{Cl}\) generates \([\text{AsPh}_3][\text{Pt}(S_x\text{CO})(S_x\text{COEt})_2]\) or \([\text{AsPh}_3][\text{Pt}(S_x\text{CO})_2]\), both of which give \([\text{Pt}(S_x\text{CO})_2]\) on addition of various Lewis bases \(L\) \((L = \text{PPh}_3, \text{PMMe}_3, \text{Pr}, \text{PC}_{2}H_4\text{PPPh}_2, \text{PC}_{2}H_4\text{PPPh}_3)\). The salt \([\text{AsPh}_3][\text{Pt}(S_x\text{CO})_2]\) is shown by X-ray diffraction analysis to have square-planar stereochemistry with one b- and two uni-dentate \([S_x\text{COEt}^-]\) groups. The crystals are monoclinic, space group \(P2_1/c\) with \(a = 9.95, b = 14.26, c = 25.82\) \(\text{Å}\), \(\beta = 99.3^\circ\).

It is now well established that when reaction occurs between \([\text{Ni}(S_x\text{S})_2]\) \((S_x = \text{S}, \text{CNR})\), \([S_x\text{COR}^-], [S_x\text{PR}_3^-], [S_x\text{PR}_2\text{OR}]^-\), \(M\text{NR})_2, \text{etc.}\) and most nitrogen- or phosphorus-donor ligands \(L\) either five-co-ordinate \([\text{NiL}(S_x\text{S})_2]\) and/or six-co-ordinate \([\text{NiL}_2(S_x\text{S})_2]\) adducts are formed, depending on the nature of the ligand used.2 Furthermore, it has been shown that reaction of \(\text{NiCl}_2\cdot6\text{H}_2\text{O}, \text{Na[S}_x\text{COEt}]\), and \([\text{NMMe}_3\text{Ph}]\) \(\text{Cl}\) gives the dark green complex \([\text{NMMe}_3\text{Ph}][\text{Ni}(S_x\text{COEt})_2]\) which was assigned a six-co-ordinate octahedral structure on the basis of electronic-spectral evidence 3 and preliminary X-ray studies.4 In contrast, some of the earlier papers in this series 5 have shown that the reaction of the isomorphous \([M(S_x\text{S})_2]\) complexes \((M = \text{Pd or Pt})\) with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate the four-co-ordinate square-planar complexes \([M(\text{PR}_3)_2(S_x\text{S})_2]\) and \([M(\text{PR}_3)_2(S_x\text{S})][S_x\text{S}]\) which exhibit undentate–bidentate and bidentate–ionic modes of bonding of the dithiocarbamate groups respectively.

In this paper, we report the full results 6 of reactions between various platinum(II) and palladium(II) dithiocarbamates with dithiocarbonate ion which provide further evidence for the substantial differences in chemistry exhibited by nickel on the one hand and palladium and platinum on the other.

RESULTS AND DISCUSSION

Reaction of \([\text{Pt}(S_x\text{CO})_2]\) with excess of \([\text{AsPh}_3]\) \(\text{Cl}\) in dichloromethane followed by the addition of diethyl ether gave a yellow crystalline solid which was a 1:1 electrolyte in nitromethane and analysed closely for \([\text{AsPh}_3][\text{Pt}(S_x\text{CO})_2]\) (I). This complex could also be prepared by treating \([\text{Pt}(S_x\text{CO})_2]\) with excess of \(\text{AsPh}_3\) \(\text{Cl}\).


K[S₂COT2Et] in acetone followed by addition of methanolic
AsPh₃]Cl·HCl. An X-ray structural analysis of (1)
(see below) shows that, unlike the nickel analogue, the
platinum(II) ion remains four-co-ordinate and square
planar by binding to one bidentate and to two undentate
dithiocarbamate groups [c.f. [Au(S₂CNEt)₃]²⁻]. The
complex [AsPh₄]²[Pt(S₂COPPh)₃] (2) could be similarly
prepared. Furthermore, the close similarity of the null
and solution i.r. spectra of these complexes together
with the similarity between their electronic spectra and
those of well established square-planar platinum(II)
complexes strongly suggests that this four-co-ordinate
structure is retained in solution.

Further evidence for this statement comes from the
low-temperature (233 K) ¹H n.m.r. spectrum of (1) in
again this change was reversible. Hence, these observa-
tions are indicative of a facile intramolecular undentate–
bidentate scrambling process at higher tempera-
tures, similar to that already proposed to explain the
temperature-dependent n.m.r. changes of the neutral
[M(PR₃)₂(S-S)] complexes. Unfortunately, because of
decomposition and irreversible rearrangement pro-
cesses which occur before the coalescence temperatures
of complexes (1) and (2) could be reached (> 320 K)
(see below), useful kinetic information was not obtained
from the limited data available.

Crystal Data for [AsPh₄][Pt(S₂COT2Et)₃] (1).—C₃₄H₅₅
AsO₆Pt₅S₆, M = 542, yellow monoclinic needles, a =
9.95(1), b = 14.26(1), c = 25.82(2) Å, β = 99.3(2)°,
U = 3 615 Å³, Dₐ = 1.70, Z = 4, Dₚ = 1.73 g cm⁻³.

TABLE I
Fractional co-ordinates (× 10⁶) and thermal parameters (× 10³/Å²) for (1). Mean standard deviations for atomic
positions are: Pt, 0.003; As, 0.007; S, 0.02; O, 0.03; C, 0.08; ring centres, 0.03 Å.

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* Anisotropic thermal parameters

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<th>U₃₃</th>
<th>U₁₂</th>
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CDCl₃ which consisted of two sharp triplet at
δ 1.45 and 1.28 p.p.m. of relative intensity 1 : 2. Two
overlapping methylene quartets centred at δ 4.43 p.p.m.
were also observed. Similarly, for (2) at 223 K, two
sharp doublets were observed for the methyl protons at
δ 1.47 and 1.29 p.p.m. of relative intensity 1 : 2, in
addition to a weak multiplet at δ 4.50 p.p.m. from
the methine protons. The ¹⁹F n.m.r. spectrum of a related
complex [NPh₃]²[Pd(S₂PF₂)₃] at 209 K also shows two
doublets of relative intensity 1 : 2 with P-F coupling
constants consistent with bi-and uni-dentate co-ordination
of the [S₂PF₂]⁻ groups respectively.⁸

On warming (1) to higher temperatures (303 K),
broadening of the methyl signals occurred and these
n.m.r. changes were reversible and concentration
independent. For (2), the two methyl doublets also
broadened on raising the temperature. For the [Pd-
(S₂PF₂)₂]²⁻ ion, the ¹⁹F n.m.r. spectrum at ambient
temperature consisted of a single broad doublet and
Space group P2₁/c, No. 14; Cu-Kα radiation, λ =
1.5418 Å, μ(Cu-Kα) = 119 cm⁻¹.

Structure determination. Considerable difficulty was
experienced in choosing a suitable crystal. Layers
60—5l were eventually collected by the equi-inclination
Weissenberg method using multiple film packs. Inten-
sities were estimated photometrically, using a Saab
rotating-drum film scanner, and I 292 independent data
were taken as significant above background. No absorp-
tion corrections were made. From the Patterson
function, positions could be assigned to the platinum and
arsenic atoms. Subsequent difference-Fourier syntheses
gave approximate positions for the sulphur and oxygen
atoms. Carbon atoms were generally ill defined, and
alternative positions were tried for ethyl groups. Ideal-
ised phenyl rings, with C-C 1.40 Å, were fitted to regions

of electron density near the arsenic atom, and these were refined as groups. Layer scale factors were initially allowed to refine, but were fixed in the last few cycles when the platinum and arsenic atoms were given anisotropic thermal parameters. Reflections were given unit weight except for those with $|F_o| > 125$, which were given a weight of $125/|F_o|$. At convergence, by full-matrix refinement, $R$ was 0.12. Final values of the fractional co-ordinates and thermal parameters are given in Table 1, and the table of structure factors is deposited as Supplementary Publication No. SUP 21964 (4 pp.).

**Description of the structure.** Distances and angles relating to the co-ordination of the platinum atom are given in Table 2, and a view of the complex anion is shown in the Figure. The co-ordination of the platinum is essentially planar, the maximum deviation from the plane of Pt(1), S(1), S(2), S(4), S(5) being 0.18 Å. The unco-ordinated sulphur atoms of the unidentate groups are almost at the maximum possible distance from Pt(1), and lie 0.9 and 0.6 Å from the plane of co-ordination. There are no other platinum–sulphur distances of less than 5 Å. The oxygen atoms of these molecules approximate very roughly to axial ligands, but are still >3 Å from the platinum. They both lie 1.5 Å from the plane of co-ordination, but make angles of ca. 60 or 120° at Pt(1) with the co-ordinated sulphur atoms. Within the very large standard deviations of the determination, the arsenic co-ordination and the geometry of the dithiocarbonate groups are normal.

Thus, crystallographic and spectroscopic evidence clearly show that these tris(dithiocarbonato)platinum(II) anions contain both bi- and uni-dentate dithiocarbonate groups in both the solid and solution states. Although several main-group dithiocarbonates such as $[\text{NET}_4]^{-}[\text{Cd}(\text{S}_2\text{COEt})_4]$ and $[\text{NET}_4][\text{Te}(\text{S}_2\text{COEt})_3]$ have recently been shown to possess five-co-ordinate structures with two bi- and one uni-dentate O-ethyl dithiocarbonate groups, complexes (1) and (2) are two of the few examples of transition-metal complexes shown unequivocally to

| Table 2 |
| Bond lengths (Å) and angles (°) for the platinum co-ordination in (1) |

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Angles</th>
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<td>Pt(1)–S(1)</td>
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<td>Pt(1)–S(5)</td>
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<td>Pt(1)–Pt(5)</td>
<td>2.289(18)</td>
</tr>
</tbody>
</table>

* For details see Notices to Authors No. 7, J.C.S. Dalton, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).


**Scheme 1** Proposed intramolecular mechanism for conversion of $[\text{M}(\text{S}_2\text{COR})_3]^-$ into $[\text{M}(\text{S}_2\text{CO})(\text{S}_2\text{COR})]^-$.  

contain unidentate dithiocarbonate groups. Other recent possible examples are \( \text{[M(PPh}_3\text{)]}_2\text{(S}_2\text{COEt)}_2 \) (M = Pd or Pt),\textsuperscript{11} \( \text{[Pd(1-3-γ,γ-dimethylallyl)(PMe}_2\text{Ph})(\text{S}_2\text{COMe})]_2 \)\textsuperscript{12} and \( \text{[RhCl}_2\text{(PMe}_3\text{Ph)}_2\text{(S}_2\text{COEt)}_2 \)\textsuperscript{13}.

Attempted recrystallisation of (1) from either dichloromethane or chloroform solutions gave an orange-yellow crystalline complex (3) containing extra i.r. bands at 1 678 cm\(^{-1}\), 1 600 cm\(^{-1}\), and 1 576 cm\(^{-1}\). These values are reasonably close to the characteristic frequencies reported for the dithiocarbonate ion in \( \text{[Pt(PMe}_2\text{Ph)}_2\text{(S}_2\text{CO)}]_2 \)\textsuperscript{14} at 1 690 cm\(^{-1}\), 1 681 cm\(^{-1}\), and 1 615 cm\(^{-1}\) \textsuperscript{14} and \( \text{[Rh(PMe}_2\text{Ph)}_2\text{(S}_2\text{CO)}]_2 \)\textsuperscript{14} at 1 670 cm\(^{-1}\) and 1 698 cm\(^{-1}\) \textsuperscript{14} and analytical data confirm that (3) is \( \text{[AsPh}_4\text{][Pt(S}_2\text{CO)}]_2\text{(S}_2\text{COEt)}_2 \). A similar complex \( \text{[AsPh}_4\text{][Pt(S}_2\text{CO)}_2\text{(S}_2\text{COEt)}_2 \) (4) was formed from (2) either by recrystallisation from CH\(_2\)Cl\(_2\) or CHCl\(_3\) or by leaving methanol-diethyl ether or acetone solutions of (2) to stand for 24 h.

Reaction of \( \text{[Pd(S}_2\text{COEt)}_2 \) with excess of K\( \text{[S}_2\text{COEt)}_2 \) in acetone followed by filtration into a methanolic solution of \( \text{[AsPh}_4\text{][Cl-HCl]} \) gave a bright orange-yellow precipitate with an i.r. spectrum almost identical to that of (3) and the formulation \( \text{[AsPh}_4\text{][Pd(S}_2\text{CO)}_2\text{(S}_2\text{COEt)}_2 \) was confirmed by elemental analyses. However, on carrying out the same reaction in methanol, a very small yield of a buff powder with an i.r. spectrum almost identical to (1) was obtained. These observations suggest that the \( \text{[Pd(S}_2\text{COEt)}_2 \) anion rearranges very rapidly to \( \text{[Pd(S}_2\text{CO)}_2\text{(S}_2\text{COEt)}_2 \) which is consistent with the known lability of Pd-S compared to Pt-S bonds.

A possible mechanism of formation of these various species which is consistent with the above evidence is outlined in Scheme 1. Thus, initial nucleophilic attack


\textsuperscript{14} J. M. Burke and J. P. Fackler, jun., \textit{Inorg. Chem.}, 1972, 11, 2744.


from the reactions of \([\text{AsPh}_4][\text{Pt}(\text{S}_2\text{CO})_2(\text{S}_2\text{COET})]\) and excess of \(L\).

For \([\text{Pt}(\text{S}_2\text{COME})_2]_2\) and \(K[\text{S}_2\text{COME}]\) \((1:5\) molar ratio), the only product isolated was the bis(dithiocarbonato)anion (5). However, when \(1:1\) or \(1:2\) molar ratios were used, orange-yellow crystals of \([\text{AsPh}_4][\text{Pt}(\text{S}_2\text{CO})_2(\text{S}_2\text{COME})]\) were deposited. Presumably, the inability to isolate the \([\text{Pt}(\text{S}_2\text{COCH}_2\text{Ph})_2]^-\) and \([\text{Pt}(\text{S}_2\text{COME})_2]^-\) anions is a reflection of the great stability of the benzylcarbonyl cation generated in the transition state in the mechanism shown in Scheme I and of the high nucleophilicity of the \([\text{S}_2\text{COME}]^-\) group. The final step in formation of (5) is probably intermolecular attack of \([\text{S}_2\text{COR}]^-\) on the co-ordinated alkoxy-group in \([\text{Pt}(\text{S}_2\text{CO})_2(\text{S}_2\text{COR})]^-\).

Finally, reactions of \([\text{Pt}(\text{S}_2\text{S})_2]_-\) \((\text{S}_2\text{S}^2- = \text{S}_2\text{PMe}_2^-\)
\([\text{S}_2\text{PPPh}_2^-\)
\([\text{S}_2\text{CNET}_2^-\) with \(\text{Na}[\text{S}-\text{S}]\) under similar conditions gave only starting materials and, unlike the recent synthesis of \([\text{NbBu}_3][\text{Zn}(\text{S}_2\text{CNR}_3)_2(\text{S}_2\text{CNMe}_2)]\)
\((\text{R} = \text{Me or Et})\) by reaction of \([\text{Zn}(\text{S}_2\text{CNR}_3)_2]\) and \([\text{NbBu}_3][\text{S}_2\text{CNMe}_2]\), no reaction was observed between \([\text{Pd}(\text{S}_2\text{CNET}_2)_2]\) and \([\text{NbBu}_3][\text{S}_2\text{CNEt}_2]\) or \([\text{Pt}(\text{S}_2\text{CNMe}_2)_2]\).

**EXPERIMENTAL**

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the 250—4 000 cm\(^{-1}\) region on Perkin-Elmer 225 and 457 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Conductivity measurements were made on a Solartron Electronics 310 conductivity bridge in nitromethane at 298 K. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Electronic spectra were recorded on a Unicam SP 800 spectrophotometer using unmatched silica cells. Melting points were determined with a Kölfer hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(I) and palladium(II) chloride (Johnson Matthey Ltd.), \([\text{AsPh}_4]\)\(\text{Cl}\) \((\text{Koch Light Ltd.})\), PPh\(_3\) and \(K[\text{S}_2\text{COET}]\) (B.D.H.) were used as obtained. The salts \(K[\text{S}_2\text{COR}]\) \((\text{R} = \text{Me, Pr}^\text{I},\) or \(\text{CH}_2\text{Ph})\) were synthesised as described in ref. 2a and \([K(\text{S}_2\text{COR})_2]\) \((M = \text{Pd or Pt})\) as described earlier. Operations were carried out under nitrogen and in degassed solvents.

**Tetrachloroplatinato(i) and palladato(ii) chloride** (Johnson Matthey Ltd.), \([\text{AsPh}_4]\)\(\text{Cl}\) \((\text{Koch Light Ltd.})\), PPh\(_3\) and \(K[\text{S}_2\text{COET}]\) (B.D.H.) were used as obtained. The salts \(K[\text{S}_2\text{COR}]\) \((\text{R} = \text{Me, Pr}^\text{I},\) or \(\text{CH}_2\text{Ph})\) were synthesised as described in ref. 2a and \([K(\text{S}_2\text{COR})_2]\) \((M = \text{Pd or Pt})\) as described earlier. Operations were carried out under nitrogen and in degassed solvents.

**Tetrachloroplatinato(i) and palladato(ii) chloride** (Johnson Matthey Ltd.), \([\text{AsPh}_4]\)\(\text{Cl}\) \((\text{Koch Light Ltd.})\), PPh\(_3\) and \(K[\text{S}_2\text{COET}]\) (B.D.H.) were used as obtained. The salts \(K[\text{S}_2\text{COR}]\) \((\text{R} = \text{Me, Pr}^\text{I},\) or \(\text{CH}_2\text{Ph})\) were synthesised as described in ref. 2a and \([K(\text{S}_2\text{COR})_2]\) \((M = \text{Pd or Pt})\) as described earlier. Operations were carried out under nitrogen and in degassed solvents.

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solution. Removal of solvent gave a yellow oil which yielded a white solid on addition of diethyl ether. This was filtered off and washed with water, methanol, and diethyl ether, m.p. 258—259 °C (Found: C, 54.9; H, 3.9). Calc. for C_{27}H_{36}OP_2PtS_2: C, 54.8; H, 3.7%. v(C=O) (S,C=O) at 1 690 cm\(^{-1}\) and 1 615 cm\(^{-1}\) (mull). The same product was obtained from the reaction of [AsPh_3][Pt(S,C=O)(S,C=OEt)] and excess of Ph_3P in dichloromethane.

_Dithiocarbamatobis(dimethylphenylphosphinophosphate)platinum(II)_

—Excess of PMe_3Ph was added to a suspension of [AsPh_3]_2[Pt(S,C=O)] in dichloromethane and the mixture shaken for ca. 1 h. The resulting pale yellow solution was filtered to remove unchanged starting material and the filtrate was concentrated. Addition of diethyl ether then gave a white solid which was filtered off and washed with water, methanol, and diethyl ether (Found: C, 36.6; H, 4.1). Calc. for C_{27}H_{36}OP_2PtS_2: C, 36.2; H, 3.9%. v(C=O) (S,C=O) at 1 670 cm\(^{-1}\) and 1 505 cm\(^{-1}\) (mull). Similarly, [1,2-bis(di-phenylphosphino)ethane](dithiocarbanato)platinum(II) was obtained from [AsPh_3][Pt(S,C=O)] and Ph_3PC_{2}H_{4}PPPh_2, m.p. 262—265 °C (Found: C, 47.2; H, 3.5). Calc. for C_{27}H_{36}OP_2PtS_2: C, 47.3; H, 3.5%. v(C=O) (S,C=O) at 1 690 cm\(^{-1}\) and 1 620 cm\(^{-1}\) (mull).

Crystallographic calculations were made using the X-Ray 74 system.\(^{19}\)

We thank Johnson, Matthey Ltd. for loans of potassium tetrachloroplutinate(II) and palladium(II) chloride, the S.R.C. for support (to M. C. C., C. L. J., J. D. O., and D. F. S.), Mr. J. C. MacKay for experimental assistance, and Dr. W. D. S. Motherwell of Cambridge University for a plotting program.

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Metal Complexes of Sulphur Ligands. Part 12.¹ Synthesis, Characterisation, and Reactions of Palladium(II) and Platinum(II) Complexes of Type [MX(PR₃)(_S–S_)] (X = halide, S–S⁻ = [S₂PR₂]⁻, [S₂CNR₂]⁻, or [S₂COR]⁻)

By Margaret C. Cornock and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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1977
Metal Complexes of Sulphur Ligands. Part 12.1 Synthesis, Characterisation, and Reactions of Palladium(ii) and Platinum(ii) Complexes of Type [MX(PR$_3$)$_2$(S−S)] (X = halide, S−S = [S$_2$PR$_3$]−, [S$_2$CN$_2$R$_2$]−, or [S$_2$COR]−)

By Margaret C. Cornock and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JY

Reaction of [Pd(PR$_3$)$_2$(S$_2$CPPh$_3$)$_2$] (PR$_3$ = PPh$_3$ or PMe$_2$Ph) with excess of AgX in acetone (X = Cl, Br, I, or SCN) leads to facile replacement of the unidentate [S$_2$CPPh$_3$]− group by X− to give [PdX(PR$_3$)$_2$(S$_2$CPPh$_3$)$_2$]. Similar reactions with [Pt(PR$_3$)$_2$(S−S)$_2$] (S−S = [S$_2$CPPh$_3$]− or [S$_2$CN$_2$Et$_2$]−) are not very efficient and a better general method for synthesising [MX(PR$_3$)$_2$(S−S)] complexes (M = Pd or Pt; X = Cl, Br, or I; S−S = [S$_2$PM$_2$Ph$_2$]−, [S$_2$CN$_2$Et$_2$]−, [S$_2$CN$_2$R$_2$]−, or [S$_2$COEt]−) is by reaction of equimolar amounts of [MX(PR$_3$)$_2$]$_2$ and alkali-metal dithioaceto salts. The complexes (MX(PR$_3$)$_2$(S−S)) have been characterised by elemental analyses and molecular-weight, 1H n.m.r., and I.r. measurements and some of their reactions have been investigated.

In previous papers in this series 2 the results of the reactions of various tertiary phosphines, arsines, and stibines (I) with the square-planar [M(S−S)$_2$] complexes {M = Pd or Pt; S−S = [S$_2$PR$_3$]−, [S$_2$COR]−, [S$_2$CN$_2$R$_2$]−, or [S$_2$P(OOR)$_2$]−} have been reported. In particular, a study of the various rearrangement reactions exhibited by the products [M(S−S)$_2$]L and [M(S−S)L]$_2$ (Y = [BPh$_4$]−, [Cl]−, or [PF$_6$]−) has been described. One reaction was the conversion of [Pd(PPh$_3$)$_2$(S$_2$PR$_3$)] [BPh$_4$] (R = Me or Ph) into [PdX(PPh$_3$)(S$_2$PR$_3$)] when dissolved in either CH$_2$Cl$_2$ or CHX$_4$ (X = Cl or Br). Unfortunately, this particular rearrangement was confined to complexes containing a combination of Pd, PPh$_3$, [S$_2$PR$_3$]−, and BPh$_4$− and thus does not provide a general method of synthesising the series [MX(PR$_3$)$_2$(S−S)] (X = halide).

Although [NiX(PR$_3$)$_2$(S−S)] (S−S = [S$_2$CN$_2$R$_2$]− (refs. 3–5) or [S$_2$COR]− (ref. 6)) complexes have recently been reported, [PdX(PPh$_3$)(S$_2$PR$_3$)] represented the first palladium complex of this type. In this paper, we report the full results 7 of our attempts to find a general synthetic route to palladium(ii) and platinum(ii) complexes of this type, and also some reactions of these complexes.

RESULTS AND DISCUSSION

In contrast to the method of preparation of [NiX(PR$_3$)$_2$(S$_2$CN$_2$R$_2$)] 3–5 reaction of PdCl$_2$ (or K$_2$[PtCl$_4$]), PR$_3$, and Na$_2$S$_2$CR$_2$Na$_2$·3H$_2$O (or Na$_2$S$_2$PR$_3$·2H$_2$O) gave only [M(S−S)$_2$]$_2$. However, reactions of [Pd(PR$_3$)$_2$](S−S) with excess of AgX (X = Cl, Br, I, or SCN) in acetone readily gave high yields of the required [PdX(PR$_3$)$_2$(S−S)$_2$] by replacement of the unidentate [S$_2$PR$_3$]− group by X− under mild conditions. Unfortunately, this method cannot be used to prepare the analogous [PdX(PR$_3$)$_2$(S$_2$CN$_2$R$_2$)] because of the inability to isolate the corresponding [Pd(PR$_3$)$_2$(S$_2$CN$_2$R$_2$)$_2$] complexes. Furthermore, the corresponding exchange reactions with [Pt(PR$_3$)$_2$(S−S)$_2$] (S−S = [S$_2$PR$_3$]− or [S$_2$CN$_2$R$_2$]−) were very inefficient and produced only low yields of the required products [PtX(PR$_3$)$_2$(S−S)] (especially for S−S = [S$_2$CN$_2$R$_2$]−) even on prolonged refluxing. Presumably, this is a reflection of the high lability of Pd–S

5 J. P. Fackler, jun., personal communication.
compared to Pt–S bonds and the fact that diithiocarbamates form stronger bonds to platinum than phosphinodithioates.

However, an excellent general method of synthesising a wide range of these complexes is by careful reaction of the well known halide-bridged dimers \([\text{MX}_4(\text{PR}_3)_2]\)

and in several instances the monomeric nature of the products was established by mass spectroscopy and/or osmometric molecular-weight measurements in chloroform or acetone (Table 1).

The i.r. spectra of these complexes show bands characteristic of bidentate dithioacido co-ordination (see Experimental section). However, full confirmation of structure (1) was obtained from the \(^1\text{H}\) n.m.r. spectra of the dialkyldithiocarbamato-derivatives which showed two magnetically inequivalent alkyl groups at ambient

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<th>Complex</th>
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* Molecular weight measured osmotically at 37°C in acetone. * From carbonpeak \(^{133}\text{Pt}\) or \(^{195}\text{Pt}\) isotope in mass spectrum. * Cl, 8.2 (Calc.: 8.3%). * Measured osmotically at 37°C in chloroform. \(^*\) 1, 24.8 (Calc.: 24.5%). * Cl, 6.9 (Calc.: 6.1%).

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<th>Table 2</th>
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Hydrogen-1 n.m.r. data in CDCl\(_3\) at 301 K for some palladium(I) and platinum(I) dithioacido complexes \(\delta^a/\text{p.p.m.}\)

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<tr>
<th>Complex</th>
<th>Dithio-ligand</th>
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\(M = \text{Pd, X = Cl, Br, or I, PR}_3 = \text{PM}_{2}\text{Ph}; M = \text{Pt, X = Cl, PR}_3 = \text{PM}_{2}\text{Ph or PM}_{3}\text{Ph} \) with various alkali-metal dithioacido salts \([\text{S}_2\text{PM}_{2}Cl]{^+}^{-}; \text{[S}_2\text{CNET}_{3}]^{-}; \text{[S}_2\text{CNPr}_{4}]^{-}; \text{[S}_2\text{COET}]^{-}\) in 1:2 molar ratio in acetone (Pd) or acetonitrile (Pt).* All these complexes were characterised by elemental analyses (Table 1) and i.r. and \(^1\text{H}\) n.m.r. spectroscopy (Table 2).

* Recently, N. Sonoda and T. Tanaka, *Iwog. Chim. Acta* 1976, 261 have independently reported the synthesis of the related \([\text{PdCl}(\text{PR}_3)\text{C}(\text{XYCNNR})]_2\) (\(R = \text{Me or Et}; \text{PR}_3 = \text{PM}_{2}\text{Ph, PP}_{2}\text{Ph or PM}_{3}\text{Ph}; X = \text{S}; Y = \text{Se}) by reaction of \([\text{PdCl}(\text{PR}_3)\text{C}]_2\) with \(\text{SnMe}_{3}\text{Cl}(\text{XYCNNR})\). The complexes \([\text{PdCl}(\text{PR}_3)\text{C}(\text{XYCNNR})]_2\) (\(R = \text{Me or Et}; \text{PR}_3 = \text{PP}_{2}\text{Ph or PM}_{2}\text{Ph}\)) are also briefly described.
temperature. As expected for a structure of this type, the $[S_2PMe_3]^-$ complexes exhibited only one methyl resonance from the dithiocarbamato group (Table 2). Up to 330 K (the limit of our studies) the $^1$H n.m.r. spectra of the dithiocarbamato-complexes were temperature invariant. However, Fackler$^8$ showed that, at $>390$ K, magnetic equivalence of the alkyl groups was obtained and he ascribed this to the onset of facile rotation about the $-\text{CN}$ partial double bond.

The observation of magnetically inequivalent dithiocarbamato-alkyl groups in complexes (1) at ambient temperature indicates that our earlier explanation$^9$ of the apparent magnetic equivalence of $R^2$ and $R^4$ in $[\text{Pt}(PR''_3)_{3}[S_2CNR_2]_2]$ (2) at low temperature [namely that the atoms (S and P) inducing the magnetic inequivalence in $R^2$ and $R^4$ are well removed (six bonds) from these groups so that the separation between the $R^2$ and $R^4$ resonances may well be too small to be resolved] is clearly incorrect. Furthermore, unlike $[\text{NiX(PR''_3)(S_2CNR_2)}]$ where the inability to observe magnetically inequivalent dithiocarbamato-alkyl groups at ambient temperature is ascribed to facile phosphine$^4$ or halide exchange,$^5$ there is no evidence of facile phosphine exchange in $[\text{Pt(PMePh}_2][S_2CNET_2]_2]$ since in the $^1$H n.m.r. spectrum between 213 and 301 K the $\text{PMePh}_2$ group showed a sharp triplet of doublets centred at

$$\delta = 2.28 \text{ p.p.m.} \text{ [with} \frac{3}{J(\text{PtH})} = 38.0 \text{ and} \frac{5}{J(\text{PH})} = 10.0 \text{ Hz}]^8$$

This is also evident from the $^{31}$P n.m.r. spectra of $[\text{Pt}(\text{PMePh}_2)(S_2CNPh)]_2$ (Figure) which show that $\frac{1}{J(\text{PtP})}$ remains practically invariant from 218 to 338 K. These spectra also provide good evidence that the solid-state structure (3) is maintained in solution with $\frac{2}{J(\text{PtP}^3)} = 276.6 \text{ Hz} \text{ (}^{31}\text{P at 87.8 p.p.m.})$ and $\frac{3}{J(\text{PtP}^3)} = 103.3 \text{ Hz} \text{ (}^{31}\text{P at 87.1 p.p.m.) at 218 K \text{ [cf.} [\text{Pt}(\text{PPh}_3)_2][\text{PF}_6]_2\frac{2}{J(\text{PtP})} = 254.7 \text{ Hz}; \text{ S}_2PPh}_2, 92.1 \text{ p.p.m.}]$. At 338 K rapid intramolecular scrambling of univalent and bidentate $[\text{S}_2PPh}_2]^-$ groups produced, as expected, an averaged signal at 70.5 p.p.m. with $\frac{3}{J(\text{PtP}^3)} = 191.0 \text{ Hz}$. This evidence confirming the retention of the four-co-ordinate square-planar structure in solution strongly suggests that the apparent magnetic equivalence of $R^2$ and $R^4$ in (2) at low temperature can only be produced by the fortuitously similar electronic effects of the $PR'_3$ and $[S_2CNR_2]^-$ groups.

Reaction of excess of $\text{Na}[\text{S}_2\text{CNR}_2]-3\text{H}_2\text{O} \text{ R = Et or Pr'}$ with $[\text{MCl}_4(PR''_3)]_2$ gave $[\text{M}(\text{S}_2\text{CNR}_2)_2]$, whereas excess of $\text{Na}[\text{S}_2\text{PMe}_3]-2\text{H}_2\text{O}$ gave the well known $\text{M}([PR''_3]_2[S_2\text{PMe}_3])_2$. The difference in behaviour is again presumably a reflection of the higher nucleophilicity of $[\text{S}_2\text{CNR}_2]^-$ compared to $[S_2\text{PMe}_3]^-$.

In contrast, reaction of $[\text{MX}_2(PR''_3)]_2$ with silver carboxylates gives the dimeric $[\text{MX}(\text{O}_2\text{CR})(PR''_3)]_2$ (1 : 2 molar ratio)$^9$ and $[\text{M(O}_2\text{CR})_2(PR''_3)_2]_2$ (1 : 4 molar ratio)$^{10}$ respectively.

The complexes $[\text{MX}(PR''_3)(S-S)]$ are useful starting materials for a number of reactions. For example, reaction of $[\text{P}Cl(\text{PMePh}_2)(S_2\text{CNH}_2)$_2$]_2$ with $\text{S}_2\text{PMe}_3$, $2\text{H}_2\text{O}$ gave the mixed dithio-complex $[\text{Pt}(\text{PMePh}_2)(S_2\text{CNH}_2$_2$)(S_2\text{PMe}_3)]_2$. The i.r. spectrum of this complex had bands at 600 and $1530 \text{ cm}^{-1}$ indicative of indeterminate $[\text{S}_2\text{PMe}_3]^-$ (ref. 2) and bidentate $[\text{S}_2\text{CNH}_2$_2$]$ co-ordination$^{11}$ respectively. The $^1$H n.m.r. spectrum (Table 2) confirmed structure (4) with bidentate $[\text{S}_2\text{CNH}_2$_2$]$ and indeterminate $[\text{S}_2\text{PMe}_3]^-$ groups. Unlike the corresponding reaction of $[\text{P}Cl(\text{PMePh}_2)(S_2\text{CNH}_2$_2$)]_2$ and $[\text{Pt}(\text{PMePh}_2)(S_2\text{PMe}_3)]_2$, this complex is stereochemically rigid even at 330 K. In contrast, reaction of $[\text{P}Cl(\text{PMePh}_2)(S_2\text{PMe}_3)]_2$ with $\text{Na}[\text{S}_2\text{CNH}_2$_2$]-3\text{H}_2\text{O}$ gives $[\text{Pt}(\text{S}_2\text{CNH}_2$_2$)]_2$, indicating the greater nucleophilicity of $[\text{S}_2\text{CNH}_2$_2$]$ compared to $[S_2\text{PMe}_3]^-$.

Finally, reaction of $[\text{P}Cl(\text{PMePh}_2)(S_2\text{CNH}_2$_2$)]_2$ with

Ag[BF₄] in tetrahydrofuran (thf) produces a white precipitate of AgCl and a yellow solution which probably contains the solvated cation [Pd(thf)(PMe₅Ph)(S₂CNEt₂)]⁺. Addition of various ligands (L) to this solution followed by treatment with Na[BPh₄] then gave the mixed-ligand cationic complexes [PdL(PMe₅Ph)(S₂CNEt₂)][BPh₄]⁻ (L = PPh₃ or C₅H₅N) which, as expected, showed magnetically inequivalent ethyl groups in their ¹H n.m.r. spectra at ambient temperature (Table 2). The related mixed-ligand complex [Pt(AsPh₃)(PFP₃)(S₂PMe₅)][BPh₄] can be synthesised by reaction of [Pt(PFP₃)(S₂PMe₅)]₂, AsPh₃, and Na[BPh₄].

**Experimental**

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the 250–4000 cm⁻¹ region on a Perkin-Elmer 457 grating spectrometer using NaCl and nujol and chlorobenzene diene mulls on calcium iodide plates. Conductivity measurements were made on a Portland Electronics 310 conductivity bridge. Hydrogen-¹ n.m.r. spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe, and ³¹P n.m.r. spectra on a Varian XL-100 spectrometer operating in the pulse and Fourier-transform modes at 40.0 MHz (³¹P chemical shifts quoted in p.p.m. to high frequency of 85% H₃PO₄). Mass spectra were obtained on an A.E.I. MS9 spectrometer. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson, Matthey Ltd.), triphenylphosphine, sodium diethyldithiocarbamate, and sodium tetraphenylborate (B.D.H.), dimethylphenylphosphine and methyl-diphenylphosphine (Maybridge Chemical Company) were obtained as indicated. The compounds Na[S₂PMe₅]⁻2H₂O, [PdX₂(PMe₅Ph)]⁺ (X = Cl, Br, or I), [PtCl₂(PFP₃)]⁺, [Pd(PFP₃)(S₂PPh₂)], [Pd(PMe₅Ph)(S₂PPh₂)]⁺, [Pt(PFP₃)(S₂PPh₂)]⁺, and [Pt(PMe₅Ph)-(S₂PPh₂)]⁺ were synthesised as described earlier.

Infrared bands diagnostic of bidentate [S₂PPh₂], [S₂PMe₅]⁻, and [S₂CN]⁻ co-ordination ⁴ are listed for each complex.

**Palladium Complexes.—**Diphenylphosphinodithiobis(thiocyanato)(triphosphine)palladium(II). The complex [Pd(PFP₃)(S₂PPh₂)]⁺ and Ag(SCN)⁻ (1:6 molar ratio) were shaken together in acetic acid for 1 hour after which the solution was filtered to remove insoluble silver salts. Removal of solvent in vacuo then yielded a yellow solid which was recrystallised from benzene–light petroleum (b.p. 60–80 °C), m.p. 216–218 °C, ν(PS₂) at 603 and 570 cm⁻¹, ν(CN) at 2 100 cm⁻¹. Similarly, bromo(diphenylphosphinodithioato)(triphosphine)palladium(II), m.p. 211–213 °C, ν(PS₂) at 600 and 570 cm⁻¹, diphenylphosphinodithioato(iodo)(triphosphine)palladium(II), ν(PS₂) at 603 and 570 cm⁻¹, dimethylphenylphosphinodithioato(iodo)palladium(II), ν(PS₂) at 602 and 570 cm⁻¹, and dimethylphenylphosphinodithioato(thiocyanato)thiophosphinodithioato(palladium(II)), ν(PS₂) at 603 and 572 cm⁻¹ were prepared by reaction of [Pd(PR₃)(S₂PPh₂)]⁺ with the appropriate silver salt.

Chloro(dimethylphenylphosphine)(dimethylphosphinodithioato)palladium(II). The salt Na[S₂PMe₅]⁻2H₂O (0.03 g) was added to an acetone solution of [PdCl₂(PMe₅Ph)]⁺ (0.10 g) (2:1 molar ratio) and the mixture shaken for 2 hours. The resulting cloudy yellow solution was filtered through Celite to give a bright yellow filtrate. Removal of solvent gave a yellow solid which was recrystallised from acetone–light petroleum (b.p. 60–80 °C), ν(PS₂) at 570 cm⁻¹, ν(PdCl) at 340 cm⁻¹. Similarly, bromo(dimethylphenylphosphine)(dimethylphosphinodithioato)palladium(II), ν(PS₂) at 570 cm⁻¹, and dimethylphenylphosphinodithioato(dimethylphosphinodithioato)iodopalladium(II), m.p. 258–250 °C, ν(PS₂) at 570 cm⁻¹ were prepared from [PdBr₂(PMe₅Ph)]⁺ and [Pd(PMe₅Ph)]⁺ respectively.

Chloro(diethylthiocarbamato)(dimethylphenylphosphine)palladium(II). The complex [PdCl₂(PMe₅Ph)]⁺ and Na[S₂CNEt₂]⁻3H₂O (1:2 molar ratio) were shaken in acetone for ca. 1 hour to give a white precipitate of sodium chloride and a yellow solution. After filtering through Celite, the filtrate was evaporated to dryness to give a yellow-orange solid which was recrystallised from acetone–light petroleum (b.p. 60–80 °C), m.p. 162–164 °C, ν(CN) at 1 530 cm⁻¹, ν(PdCl) at 300 cm⁻¹. Similarly, bromo(diethylthiocarbamato)(dimethylphenylphosphine)palladium(II), m.p. 164–166 °C, ν(CN) at 1 530 cm⁻¹, and diethylthiodicarbamato(dimethylphenylphosphine)iodopalladium(II), m.p. 145–147 °C, ν(CN) at 1 530 cm⁻¹, were prepared from [PdBr₂(PMe₅Ph)]⁺ and [Pd(PMe₅Ph)]⁺ respectively, and chloro(di-isopropylidithiocarbamato)(dimethylphenylphosphine)palladium(II), ν(CN) at 1 500 cm⁻¹, was obtained from [PdCl₂(PMe₅Ph)]⁺ and Na[S₂CNEt₂]⁻3H₂O. Likewise, reaction of [PdCl₂(PMe₅Ph)]⁺ and K[S₂COEt] (1:2 molar ratio) gave chloro(dimethylphenylphosphine)(O-diethylthiocarbamato)iodopalladium(II), m.p. 148–150 °C (decomp.), ν(CO) at 1 260 cm⁻¹, ν(PdCl) at 300 cm⁻¹.

Diethylthiocarbamato(dimethylphenylphosphine)(triphenylphosphine)palladium(II) tetrabromoborate. The complex [PdCl₂(PMe₅Ph)(S₂CNEt₂)]⁺ (0.10 g) and Ag[BF₄]⁻ (0.04 g) in tetrahydrofuran were shaken together to give a white precipitate of AgCl and an orange solution. After filtering through Celite, an excess of triphenylphosphine was added to the filtrate to give a pale yellow solution. Removal of the solvent in vacuo produced a yellow oil. Methanol was then added to give a white solid (unchanged PPh₃) and a yellow solution which was filtered into a methanolic solution of Na[BPh₄] to give the pale yellow product, m.p. 78–80 °C, ν(CN) at 1 525 cm⁻¹, λ(1×10⁻³ mol dm⁻³) in CH₂Cl₂ = 38.0 S cm mol⁻¹.

**References**

Platinum Complexes.—Diphenyolphosphinodithioato(thiocyanato)(triphenylphosphine)platinum(II). The complex [Pt(PPh₃)(S₂PPh₂)₂] and an excess of Ag(SCN) in acetone were heated under reflux for 2 h. After filtration and removal of solvent, the pale yellow solid was dissolved in a minimum volume of benzene and precipitated with light petroleum (b.p. 60—80 °C) to give the pale yellow product, ν(PS₂) at 600 and 570 cm⁻¹, ν(CN) at 2100 cm⁻¹. Similarly, bromo(diphenylphosphinodithioato)(triphenylphosphine)platinum(II) was prepared from [Pt(PPh₃)(S₂PPh₂)₂] and AgBr, ν(PS₂) at 600 and 570 cm⁻¹.

Dimethylphosphinodithioato(triphenylarsine)(triphenylphosphine)platinum(II) tetraphenylborate. The complex [Pt(PPh₃)(S₄PMe₂)₂] was dissolved in acetone–methanol and a slight excess of AsPh₃ was added followed immediately by an excess of Na[BPh₄]. Removal of acetone then gave an off-white precipitate which was washed with methanol and light petroleum (b.p. 60—80 °C), ν(PS₂) at 574 cm⁻¹.

Chloro(diethylidithiocarbamato)(methyldiphenylphosphine)platinum(II). The salt Na[S₂CNET₂]·3H₂O (0.045 g) was dissolved in acetone, added to [PtCl₄(PMePh₃)] (0.10 g) in dichloromethane (2:1 molar ratio), and the mixture shaken for 1 h. A white precipitate of sodium chloride formed together with a yellow solution. After filtration, evaporation of the solution almost to dryness followed by addition of light petroleum (b.p. 60—80 °C) gave a pale yellow precipitate which was washed with water, methanol, and diethyl ether, ν(CN) at 1534 cm⁻¹, ν(PtCl) at 310 cm⁻¹. Similarly, chloro(diethylidithiocarbamato)(dimethylphosphinodithioato)(triphenylphosphine)platinum(II) was prepared from [[PtCl₄(PMePh₃)] and Na[S₂CNET₂]·3H₂O, m.p. 110—115 °C, ν(CN) at 1530 cm⁻¹, and chloro(dimethylphosphinodithioato)(methylidiphenylphosphine)platinum(II) was obtained from [[PtCl₄(PMePh₃)] and Na[S₂PMe₂]·2H₂O, ν(PS₂) at 573 cm⁻¹.

Diethylidithiocarbamato(dimethylphosphinodithioato)(methylidiphenylphosphine)platinum(II). The complex [PtCl₃(PMePh₃)(S₂CNET₂)] (0.06 g) and Na[S₂PMe₂]·2H₂O (0.02 g) were shaken in acetone–dichloromethane for ca. 1 h. A white precipitate of NaCl was then filtered off and the yellow filtrate was evaporated almost to dryness. Addition of diethyl ether–pentane gave a yellow solid which was washed with water, methanol, and diethyl ether, ν(CN) at 1530 cm⁻¹, ν(PS₂) at 600 cm⁻¹.

We thank Johnson, Matthey Ltd. for loans of potassium tetrachloroplatinate(II) and palladium(II) chloride, the S.R.C. for support (to M. C. C.), Professor J. P. Fackler, jun., for furnishing results prior to publication, Dr. A. S. F. Boyd for obtaining the ⁸¹P n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Mechemlab osmometer.

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Metal Complexes of Sulphur Ligands. Part 13.¹ Reaction of Dichloro-(η-cyclo-octa-1,5-diene)-palladium and -platinum Complexes with some Sulphur-containing Nucleophiles

By Margaret C. Cornock and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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Reaction of Dichloro-(η-cyclo-octa-1,5-diene)-palladium and -platinum Complexes with some Sulphur-containing Nucleophiles

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Reaction of $[\text{Pd}(\text{C}_8\text{H}_{12})\text{Cl}_2]$ (C$_8$H$_{12}$ = cyclo-octa-1,5-diene) with equimolar amounts of various alkali-metal dithiocarbamates $([\text{S}_{2}\text{CNEt}_2]$-, $[\text{S}_2\text{C(OEt)}_2]$-, or $[\text{S}_2\text{PMe}_3]$-) gives the chloride-bridged dimers $([\text{PdCl}(\text{S}_2\text{S})_2])$ (1). Metathetical reactions of these give the corresponding $([\text{PdCl}(\text{S}_2\text{CNEt}_2)]_2 (X = \text{Br}^-$ or $[\text{SpH}^-]$). Cleavage of these complexes with Lewis bases gives $[\text{PdCl}(\text{S}_2\text{S})_2\text{L}]$ (2: $L = \text{PPPh}_3$ [S-$\eta^-$] = $[\text{S}_2\text{CNEt}_2]$-, $[\text{S}_2\text{COEt}]^-$, or $[\text{S}_2\text{PMe}_3]$-; $L = \text{AsPh}_3$, $\text{SbPh}_3$, or $\text{C}_8\text{H}_{12}$, [S-$\eta^-$] = $[\text{S}_2\text{CNEt}_2]$-) and with $[\text{MCl}]$ $[\text{M} = \text{PdCl}(\text{C}_8\text{H}_{12})\text{Cl}]$ gives $[\text{M}(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{PMe}_3)]_2$ 2H$_2$O gives $[\text{Pd}(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{PMe}_3)]_2$ (4a) which partially disproportionates in solution to $[\text{Pd}(\text{S}_2\text{CNEt}_2)]_2$ and $[\text{Pd}(\text{S}_2\text{PMe}_3)]_2$ Complex (4a) reacts with $\text{PPPh}_3$ to give $[\text{Pd}(\text{PPPh}_3)(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{PMe}_3)]_2$ (5a) which possesses bidentate $[\text{S}_2\text{CNEt}_2]$- and unidentate $[\text{S}_2\text{PMe}_3]$- groups. In contrast, reaction of $[\text{Pt}(\text{C}_8\text{H}_{12})\text{Cl}_2]$ and $\text{Na}[\text{S}_2\text{CNEt}_2]$·3H$_2$O (1:1 mol ratio) gives $[\text{PtCl}(\text{S}_2\text{CNEt}_2)]_2$·C$_8$H$_{12}$ (6a) which in turn reacts with $\text{PPPh}_3$ to give $[\text{Pt}(\text{PPPh}_3)(\text{S}_2\text{CNEt}_2)]_2$·C$_8$H$_{12}$ and with excess of $\text{PPPh}_3$ to give $[\text{Pt}(\text{PPPh}_3)(\text{S}_2\text{CNEt}_2)]_2$·C$_8$H$_{12}$·H$_2$O. Reaction of (6a) and $\text{Na}[\text{S}_2\text{PMe}_3]$·2H$_2$O gives $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{PMe}_3)]_2$ (4b) which on treatment with $\text{PPPh}_3$ gives $[\text{Pt}(\text{PPPh}_3)(\text{S}_2\text{CNEt}_2)(\text{S}_2\text{PMe}_3)]_2$ (5b).

The activation of olefins towards nucleophilic attack by co-ordination to palladium(ii) and platinum(ii) is now well established and of commercial importance. Extensive studies on reactions of $[\text{M}(\text{diene})\text{Cl}_2]$ complexes (M = Pd or Pt) with various nucleophiles containing oxygen- or nitrogen-donor atoms (e.g. $[\text{OR}]^-$, $[\text{O}_2\text{CR}]^-$, $\text{NRH}_2$, etc.) show that, usually, attack on one of the co-ordinated double bonds occurs to give substituted alkynyl complexes. In contrast, in the only previously reported reaction of $[\text{M}(\text{diene})\text{Cl}_2]$ complexes with sulphur-containing nucleophiles, reaction of $[\text{Pt}(\text{C}_8\text{H}_{12})\text{Cl}_2]$ with $\text{Ag}[\text{SCF}_3]$ gives $[\text{Pt}(\text{C}_8\text{H}_{12})(\text{SCF}_3)]_2$ whereas with $[\text{Pd}(\text{C}_8\text{H}_{12})\text{Cl}_2]$ the norbicyclyl derivatives $[\text{Pd}_{\text{C}}(\text{C}_8\text{H}_{12})(\text{SCF}_3)]_2$ and $[\text{Pd}(\text{C}_8\text{H}_{12})(\text{SCF}_3)]_2$ are obtained.

In this paper, we report the full results of reactions between $[\text{M}(\text{C}_8\text{H}_{12})\text{Cl}_2]$ (M = Pd or Pt; $\text{C}_8\text{H}_{12}$ = cyclo-octa-1,5-diene) and various dithiocarbamates where quite different behaviour from that previously observed with other nucleophiles has been found.

RESULTS AND DISCUSSION

(a) Palladium Complexes.—Addition of an acetone solution of $\text{Na}[\text{S}_2\text{CNEt}_2]$·3H$_2$O to $[\text{Pd}(\text{C}_8\text{H}_{12})\text{Cl}_2]$ in methylene chloride (1:1 mol ratio) gave an orange solution from which an orange solid of empirical formula $([\text{PdCl}(\text{S}_2\text{CNEt}_2)]_2$ was isolated. With excess of $\text{Na}[\text{S}_2\text{CNEt}_2]$·3H$_2$O, the well known $[\text{Pd}(\text{S}_2\text{CNEt}_2)]_2$ was obtained. Molecular-weight measurements in chloroform indicated that $n = 2$ and thus this complex was formulated with the square-planar chloride-bridged structure (1). Further evidence for this formulation came from the far-i.r. spectrum which showed a strong band at 300 cm$^{-1}$ [bridging $\nu$(PdCl)], not present in $[\text{PdBr}(\text{S}_2\text{CNEt}_2)]_2$ which can be prepared either by reaction of $[\text{PdBr}_2(\text{C}_8\text{H}_{12})]$ with $\text{Na}[\text{S}_2\text{CNEt}_2]$·3H$_2$O (1:1 mol ratio) or by reaction of $[\text{PdCl}(\text{S}_2\text{CNEt}_2)]_2$ with excess of lithium bromide. Similarly, the chloride


$\text{Cu}$ J. P. Fackler, jun., personal communication.


bridges in (1) were readily exchanged for [SPh]⁻ by treatment with Na[SPh] to give {PdCl(S₂CNMe₂)₂}. The ¹H n.m.r. spectra of these complexes (Table 1), which showed magnetically equivalent ethyl groups, also support the proposed structure (1). However, with [Pd(C₈H₁₂)Cl₂] and Na[S₂CNMe₂]·2H₂O, the only product isolated was [Pd(S₂CNMe₂)₂] which can almost certainly be attributed to the high insolubility of [Pd(S₂CNMe₂)₂].

The analogous [[PdCl₂(S₂COEt)₂]] was similarly prepared by reaction of [Pd(C₈H₁₂)Cl₂] and K₂[S₂COEt] chloride bridges in [[PdCl₂(S₂CNMe₂)₂]] were readily cleaved by a wide range of Lewis basis (L) to give the monomeric [[PdCl₂(S₂CNMe₂)₂]L] (L = PPh₃, AsPh₃, SbPh₃, or C₆H₆).

As reported elsewhere, these complexes (for L = tertiary phosphine) can also be synthesised by reaction of [[PdCl₂(PR₃)₂]] and either SnMe₃Cl(S₂CNMe₂) or Na[S₂CNMe₂]·2H₂O. However, with weaker bases in the palladium co-ordination sphere, only [[Pd(S₂CNMe₂)₂]L] were formed by this route. As found earlier for [PdX₂(PMe₂Ph)(S₂CNMe₂)] (X = Cl, Br, or I), all these complexes showed two magnetically inequivalent ethyl groups at ambient temperature in their ¹H n.m.r. spectra (Table 1) confirming structure (2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Dithio ligand</th>
<th>CH₃⁻</th>
<th>CH₃⁺</th>
<th>Other ligand resonances</th>
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<tr>
<td>[PdCl(S₂CNMe₂)₂]</td>
<td>CH₃⁻</td>
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<tr>
<td>[PdCl₂(S₂COEt)₂]</td>
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<td>4.87 (q)</td>
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<td>[PdBr(S₂CNMe₂)₂]</td>
<td>CH₃⁻</td>
<td>1.18 (t)</td>
<td>3.58 (q)</td>
<td>7.38–7.80 (m)</td>
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<tr>
<td>[PdCl₂(S₂CNMe₂)₂]</td>
<td>CH₃⁻</td>
<td>1.24 (t), 1.18 (t)</td>
<td>3.71 (q), 3.56 (q)</td>
<td>7.40 (t), 7.82 (t), 8.82 (d)</td>
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<tr>
<td>[PdCl₂(PPh₃)(S₂CNMe₂)]</td>
<td>CH₃⁻</td>
<td>1.13 (t), 1.07 (t)</td>
<td>3.60 (q), 3.46 (q)</td>
<td>6.90–8.00 (m)</td>
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<td>[PdCl₂(NCMe₂)(S₂CNMe₂)]</td>
<td>CH₃⁻</td>
<td>1.29 (t), 1.28 (t)</td>
<td>3.59 (q), 3.66 (q)</td>
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<td>[PdCl₂(PMe₂)(S₂CNMe₂)]</td>
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<td>1.47 (t)</td>
<td>4.87 (q)</td>
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<td>CH₃⁻</td>
<td>1.14 (t), 1.12 (t)</td>
<td>3.61 (q), 3.59 (q)</td>
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<td>[PdCl₂(PPh₃)(S₂CNMe₂)]</td>
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<td>2.03 (d), 1.75 (d)</td>
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<td>5.32 (d), 7.00–7.80 (m)</td>
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<td>3.60 (q)</td>
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<td>CH₃⁻</td>
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<td>[PdCl₂(S₂CNMe₂)₄]</td>
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<td>3.60 (q), 3.45 (q)</td>
<td>7.20–7.80 (m)</td>
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<td>[PdCl₂(S₂CNMe₂)₄]</td>
<td>CH₃⁻</td>
<td>1.30 (t), 1.27 (t), 1.90 (d)</td>
<td>3.67 (q), 3.47 (q)</td>
<td>7.20–7.70 (m)</td>
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</table>

* s = Singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. ** /CH₃/CH₂ 7.0 Hz. † Broad. ‡ Phenyl resonances. § /PPh₃ 13.0 Hz. ¶ Methylene. § /PH₃ 14.0 Hz. ¶ Solution gave resonances at 2.02 (d) [[Pd(S₂PMesp)₂]] and at 1.27 (t) and 3.71 (q) p.p.m. [[Pd(S₂CNMe₂)₂]]. ¶ Very broad due to superimposition of some [Pd(PPh₃)₂(S₂CNMe₂)].

(1:1 mol ratio). However, unlike [[PdCl₂(S₂CNMe₂)₂]], this orange-red solid slowly turned brown on standing and rapidly decomposed when heated in methylene chloride. Reaction of [Pd(C₈H₁₂)Cl₂] with equimolar amounts of Na[S₂PMesp]·2H₂O in CH₂Cl₂·Me₂CO also gave an immediate red solution but this rapidly turned brown precipitating an intractable brown material of unknown composition. However, although attempts to isolate a compound from the red solution were unsuccessful, reactions of the red solution (see below) strongly suggest that [[PdCl₂(S₂PMesp)₂]] is initially formed. With excess of Na[S₂PMesp]·2H₂O, [Pd(S₂PMesp)₂] was readily isolated. In the Scheme, the probable mechanism of formation of these chloro-bridged dimers is outlined. Presumably, the difference in behaviour compared to oxygen and nitrogen nucleophiles is the class (b) (soft-base) character of the sulphur ligands and the consequent affinity for Pd.²

In common with other halide-bridged dimers, e.g. [[(RhCO₂)₂Cl]₄]¹⁰ these complexes were excellent precursors for a variety of reactions. For example, the complexes showed two magnetically inequivalent ethyl groups at ambient temperature in their ¹H n.m.r. spectra (Table 1) confirming structure (2).

Carbon mono-oxide also reacted with [[PdCl₂(S₂CNMe₂)₂]] in methylene chloride to give a yellow solution. Unfortunately, on solvent removal, only the original orange dimer was isolated. Attempts to record the ¹H n.m.r. spectrum of the expected [[PdCl₂(CO)₂(S₂CNMe₂)₄]] in CDCl₃ even under 1 atm of CO also failed, presumably due to ready loss of CO and reformation of (1).

Reaction of \([\text{Pd}^{(\text{PH})_{2}}(2\text{S}_{2}\text{CNET})_{2}]\) with \(\text{PPh}_{3}\) gave the red, crystalline, monomeric \([\text{Pd}^{(\text{PH})_{2}}(2\text{S}_{2}\text{CNET})_{2}]\) whose \(^{1}H\) n.m.r. spectrum shows the magnetically inequivalent ethyl groups expected for a structure of type (2). Earlier, Andrews et al.\(^{12}\) synthesised \([\text{M}^{+}\text{Bu}^{+}(2\text{S}_{2}\text{CNET})_{2}]\) (M = Pd or Pt) by reaction of \([\text{M}^{+}\text{Bu}^{+}(2\text{S}_{2}\text{CSBu})_{2}]\) with \(\text{NET}_{2}H\).\(^{13}\) Reaction of these complexes with \(\text{PMePh}_{3}\) was reported to give \([\text{M}^{+}\text{MePh}_{3}(2\text{S}^{+}\text{Bu})_{2}(\text{S}-\text{S})_{2}]\) originally tentatively formulated from \(^{1}H\) n.m.r. studies (since solid materials could not be isolated) as five-co-ordinate dimers\(^{13}\) but recently reformulated\(^{5}\) as four-co-ordinate monomers of structure (2).

Reaction of \([\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{COEt})_{2}]\) with excess of \(\text{PPh}_{3}\) in methylen chloride gave a yellow solution from which the yellow solid \([\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{COEt})_{2}]\) was isolated. Treatment of the red solution (formed by reaction of \([\text{Pd}^{+}(\text{CS}_{2}\text{H}_{2})_{2}]\) and \(\text{Na}^{+}\text{S}_{2}\text{PMe}_{2}^{-}\cdot 2\text{H}_{2}\text{O}\)) with excess of \(\text{PPh}_{3}\) gave an orange solution from which an orange crystalline solid was obtained. The i.r. spectrum showed the presence of \(\text{PPh}_{3}\) and a band at 580 cm\(^{-1}\) assigned to a bidentate \(\text{S}_{2}\text{PMe}_{2}^{-}\) group.\(^{9}\) The complex analysed for \([\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{PMe}_{2})_{2}]\) which strongly suggests that the red solution contains \([\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{PMe}_{2})_{2}]\).

Hence, the order of stability of the chloride-bridged dimers is \([\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{CNET})_{2}] > [\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{COEt})_{2}] > [\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{PMe}_{2})_{2}]\) and this can be correlated with the established order of \(\text{Pd}-\text{S}\) bond strengths, i.e. \(\text{S}_{2}\text{CNET}^{-} > \text{S}_{2}\text{COEt}^{-} > \text{S}_{2}\text{PMe}_{2}^{-}\).\(^{9}\)

A typical reaction of halide-bridged dimers is reaction with halide ion to give anionic complexes, e.g. \([\text{NMe}_{4}]^{-}\cdot \text{[Rh}^{+}\text{(CO)}_{2}\text{Cl}]^{-}\) from reaction of \([\text{Rh}^{+}\text{(CO)}_{2}\text{Cl}]^{-}\) with chloroform.

Since the chloride bridges in \([\text{Pd}^{+}\text{Cl}(2\text{S}_{2}\text{CNET})_{2}]\) can be cleaved with excess of \(\text{S}_{2}\text{PMe}_{2}^{-}\) ion to give \([\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}]\), the dimer was treated with \(\text{Na}^{+}\text{S}_{2}\text{PMe}_{2}^{-}\cdot 2\text{H}_{2}\text{O}\) in an attempt to synthesise \([\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}]\) (4a). However, the \(^{1}H\) n.m.r. spectrum in \(\text{CDCl}_{3}\) of the orange-yellow product contained more signals than expected for (4a). Comparison with the \(^{1}H\) n.m.r. spectra of \([\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}]\) and \([\text{Pd}^{+}\text{(S}_{2}\text{PMe}_{2})_{2}]\) showed that both these products were present in solution. Hence, the remaining signals centred at 1.25 (t), 2.12 (d), and 3.65 (q) p.p.m. (Table I) were assigned to (4a).

Support for this conclusion came from the observation that mixing equimolar amounts of \([\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}]\) and \([\text{Pd}^{+}\text{(S}_{2}\text{PMe}_{2})_{2}]\) in \(\text{CDCl}_{3}\) at 301 K gave the same \(^{1}H\) n.m.r. spectrum. The equilibrium shown in equation (I) was established after ca. 1 h and lies predominantly to the right-hand side.

\[
[\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}][\text{Pd}^{+}\text{(S}_{2}\text{PMe}_{2})_{2}] + [\text{Pd}^{+}\text{(S}_{2}\text{PMe}_{2})_{2}] \rightleftharpoons 2[\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}][\text{Pd}^{+}\text{(S}_{2}\text{PMe}_{2})_{2}]
\] (1)

Similarly, Fackler\(^{5}\) recently showed that mixing \([\text{Ni}^{+}\text{(S}_{2}\text{CN}^{(\text{CH}_{2})_{2}}\text{Ph})_{2}]\) and \([\text{Ni}^{+}\text{(S}_{2}\text{CN}^{(\text{Bu})_{2}}\text{Bu})_{2}]\) in \(\text{CDCl}_{3}\) produced extra resonances in the \(^{1}H\) n.m.r. spectrum ascribed to the mixed complex \([\text{Ni}^{+}\text{(S}_{2}\text{CN}^{(\text{CH}_{2})_{2}}\text{Ph})_{2}]^{+}\cdot [\text{S}_{2}\text{CN}^{(\text{Bu})_{2}}\text{Bu}]^{-}\). In contrast, the \(^{1}H\) n.m.r. spectrum of a mixture of \([\text{Pt}^{+}\text{(S}_{2}\text{CNET})_{2}][\text{Pt}^{+}\text{(S}_{2}\text{PMe}_{2})_{2}]\) in \(\text{CDCl}_{3}\) at 301 K showed no evidence for the formation of \([\text{Pt}^{+}\text{(S}_{2}\text{CNET})_{2}]^{+}\cdot [\text{S}_{2}\text{PMe}_{2}]^{-}\), which can again be attributed to the decreased lability of \(\text{Pt}^{-}\text{S}\) compared to \(\text{Pd}^{-}\text{S}\) and \(\text{Ni}^{-}\text{S}\) bonds. In accordance with this, \([\text{Pt}^{+}\text{(S}_{2}\text{CNET})_{2}]^{+}\cdot [\text{S}_{2}\text{PMe}_{2}]^{-}\) (4b) (see later) does not disproportionate at ambient temperature and showed the expected three signals centred at 1.30 (t), 2.06 (d), and 3.55 (q) p.p.m. (Table I).

Addition of an excess of \(\text{PPh}_{3}\) to a suspension of \([\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}]^{+}\cdot [\text{S}_{2}\text{PMe}_{2}]^{-}\) in benzene produced a yellow solid analysing closely for \([\text{Pd}^{+}\text{(S}_{2}\text{CNET})_{2}]^{+}\cdot [\text{S}_{2}\text{PMe}_{2}]^{-}\) (5a). The i.r. spectrum of (5a) was virtually identical with that of \([\text{Pt}^{+}\text{(S}_{2}\text{CNET})_{2}]^{+}\cdot [\text{S}_{2}\text{PMe}_{2}]^{-}\) (5b) indicating unidentate \(\text{S}_{2}\text{PMe}_{2}^{-}\) (v(PS) at 605 cm\(^{-1}\)) and bidentate \(\text{S}_{2}\text{CNET}^{-}\) (v(CN) at 1615 cm\(^{-1}\)).\(^{14}\) Co-ordination. However, although the \(^{1}H\) n.m.r. spectrum of the platinum complex was completely consistent with structure (6) (Table I), that of the palladium complex contained small additional resonances superimposed on some of those of (5a). These appear to correspond to


reaction of [PtMe(C₈H₁₂)][PF₆] with an equimolar amount of Na₃S₂CNET₄·3H₂O. This then reacts with PPh₃ and AsPh₃ (I) to give the soluble neutral complexes [PtMe(L)(S₂CNET₄)] plus free cyclo-octa-1,5-diene which is consistent with the behaviour expected for a complex with structure (6b). These complexes were also prepared by reaction of [PtMe(C₈H₁₂)L][PF₆] with an equimolar amount of Na₃S₂CNET₄·3H₂O. Similarly, reaction of [PtCl₂(S₂CNET₄)]C₈H₁₂ with PPh₃ (1 : 1 mol ratio) readily gave [Pt(PPh₃)(S₂CNET₄)] and free C₈H₁₂ was also detected supporting our formulation (6a). As expected, the ³¹P n.m.r. spectrum of the latter complex showed magnetically inequivalent ethyl groups at ambient temperature. With excess of PPh₃ in methylene chloride, [Pt(PPh₃)(S₂CNET₄)]·Cl·H₂O was isolated and this was identical in spectroscopic properties to the product obtained earlier by prolonged reaction of [Pt(S₂CNET₄)] with an excess of PPh₃ in methylene chloride. The related [Pt(PMe₃)₂(S₂CNET₄)]·Cl·H₂O has also been prepared by reaction of [PtCl₂(PMe₃)₂] with Na₃S₂CNET₄·3H₂O.

Hence, unlike reactions of [M(diene)Cl₂] (M = Pd or Pt) with various oxygen- and nitrogen-containing nucleophiles which give the same type of product, their behaviour with [S₂CNET₄]⁻ is quite different giving [PtCl₂(S₂CNET₄)] and [PtCl₂(S₂CNET₄)]Cl·C₈H₁₂ respectively. This difference in behaviour is presumably a consequence of the weaker palladium–olefin, than platinum–olefin bonds involved with the insolvibility of complex (6a).

Reaction of (6a) with Na₃S₂CNET₄·3H₂O gave [Pt(S₂CNET₄)] and free C₈H₁₂. Therefore, (6a) was treated with an equimolar amount of Na₃S₂CNET₄·2H₂O in acetonitrile–methylene chloride to give a yellow solid shown by analysis and i.r. and ¹H n.m.r. spectroscopy (Table 1) to be [Pt(S₂CNET₄)(S₂CNET₄)] (6b). Unlike [Pt(PMe₃)(S₂CNET₄)] (4a) reported earlier in this paper, there was no evidence for disproportionation into [Pt(S₂CNET₄)] and [Pt(S₂CNET₄)]·Cl·H₂O when dissolved in solution at 301 K. Reaction of (6b) with PPh₃ in benzene gave the pale yellow solid [Pt(PPh₃)(S₂CNET₄)(S₂CNET₄)] (5b) which, like the analogous [Pt(PMe₃)(S₂CNET₄)(S₂CNET₄)] reported elsewhere, has unidentate [S₂CNET₄]⁻ and bidentate [S₂CNET₄]⁻ co-ordination (i.r. and ¹H n.m.r. evidence) and is stereochemically rigid even at 303 K.

**Experimental**

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzoic. Infrared spectra were recorded in the 250—4000 cm⁻¹ region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on calcium iodide plates. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(ii) and palladium(ii) chloride (Johnson, Matthey Ltd.) and PPh₃, Na₃S₂CNET₄·3H₂O, K₃S₂CNET₄, and [AsPh₃]Cl·HCl (B.D.H.) were used as received. The compounds Na₃S₂CNET₄·2H₂O, [Pt(C₈H₁₂)L][PF₆], and [Pt(C₈H₁₂)Cl₂] (10) and [Pt(C₈H₁₂)Cl₂] (9) were synthesised as described earlier. Analytical data for the new complexes are given in Table 2 together with i.r. bands diagnostic of 13. L. E. Manzer, *J.C.S. Dalton*, 1974, 1535.


the mode of co-ordination of \([\text{S}_2\text{CNET}_2]^\text{−}\) (ref. 14) and \([\text{S}_2\text{PMe}_3]^\text{−}\) (ref. 8).

**Palladium Complexes.** — Di-\(\mu\)-chloro-bis[diethyldithiocarbamate]palladium(II). The salt \(\text{Na}_4[\text{S}_2\text{CNET}_2]_2\cdot3\text{H}_2\text{O}\) (0.30 g) in acetonite was added to a methylene chloride solution of \([\text{PdCl}_2(\text{S}_2\text{CNET}_2)_{2}]_2\) (0.36 g) to give a white precipitate (\(\text{NaCl}\)) and an orange solution. The solution was stirred for 30 min until it became deep orange and was then filtered through Celite. Solvent was removed in vacuo and a mixture of methylene chloride (15 cm\(^3\)) and water (15 cm\(^3\)) was added to the residue. The volume of the methylene chloride layer was then reduced and diethyl ether was added.

**Chloro(diethyldithiocarbamato)(triphenylphosphine)palladium(II).** Addition of excess of PPh\(_3\) to a methylene chloride solution of \([\text{PdCl}_2(\text{S}_2\text{CNET}_2)_{2}]_2\) resulted in a colour change from orange to yellow. The volume of solution was then reduced and diethyl ether was added to give a yellow solid. This was filtered off, washed with water, methanol, and diethyl ether, and dried in air, \(\text{v}(\text{CN})\) at 1.535 cm\(^{-1}\), chloro(diethyldithiocarbamato)(triphenylarsine)palladium(II), \(\text{v}(\text{CN})\) at 1.535 cm\(^{-1}\), and chloro(diethyldithiocarbamato)(pyridine)palladium(II), \(\text{v}(\text{CN})\) at 1.535 cm\(^{-1}\), were similarly

<table>
<thead>
<tr>
<th>Complex</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Others</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{PdCl}_2(\text{S}_2\text{CNET}<em>2)</em>{2}]_2)</td>
<td>21.0</td>
<td>3.5</td>
<td>4.7</td>
<td>Cl, 12.1</td>
<td>29.7</td>
<td>3.5</td>
<td>4.8</td>
<td>Cl, 12.3</td>
</tr>
<tr>
<td>([\text{PdBr}_2(\text{S}_2\text{CNET}<em>2)</em>{2}]_2)</td>
<td>18.2</td>
<td>3.0</td>
<td>4.1</td>
<td>18.0</td>
<td>3.0</td>
<td>4.2</td>
<td>18.0</td>
<td>3.0</td>
</tr>
<tr>
<td>([\text{Pd}(\text{SPh})_2(\text{S}_2\text{CNET}<em>2)</em>{2}]_2)</td>
<td>36.2</td>
<td>4.0</td>
<td>3.8</td>
<td>36.4</td>
<td>4.1</td>
<td>3.9</td>
<td>36.4</td>
<td>4.1</td>
</tr>
<tr>
<td>([\text{PdCl}_2(\text{S}<em>2\text{COET})</em>{2}]_2)</td>
<td>14.1</td>
<td>1.9</td>
<td>14.1</td>
<td>1.9</td>
<td>14.1</td>
<td>1.9</td>
<td>14.1</td>
<td>1.9</td>
</tr>
<tr>
<td>([\text{PdCl}(\text{PPPh}_3)(\text{S}_2\text{CNET}_2)])</td>
<td>50.0</td>
<td>4.3</td>
<td>2.3</td>
<td>50.0</td>
<td>4.5</td>
<td>2.5</td>
<td>50.0</td>
<td>4.5</td>
</tr>
<tr>
<td>([\text{Pd}(\text{AsPh}_3)(\text{S}_2\text{CNET}_2)])</td>
<td>46.2</td>
<td>4.2</td>
<td>1.9</td>
<td>46.4</td>
<td>4.2</td>
<td>2.3</td>
<td>46.4</td>
<td>4.2</td>
</tr>
<tr>
<td>([\text{Pd}(\text{SPh})_2(\text{S}_2\text{CNET}_2)])</td>
<td>42.8</td>
<td>3.8</td>
<td>1.8</td>
<td>43.0</td>
<td>3.9</td>
<td>2.2</td>
<td>43.0</td>
<td>3.9</td>
</tr>
<tr>
<td>([\text{Pd}(\text{SPh})_2(\text{S}_2\text{CNET}_2)])</td>
<td>42.8</td>
<td>3.8</td>
<td>1.8</td>
<td>43.0</td>
<td>3.9</td>
<td>2.2</td>
<td>43.0</td>
<td>3.9</td>
</tr>
<tr>
<td>([\text{Pd}(\text{SPh})_2(\text{S}_2\text{CNET}_2)])</td>
<td>42.8</td>
<td>3.8</td>
<td>1.8</td>
<td>43.0</td>
<td>3.9</td>
<td>2.2</td>
<td>43.0</td>
<td>3.9</td>
</tr>
<tr>
<td>([\text{Pd}(\text{SPh})_2(\text{S}_2\text{CNET}_2)])</td>
<td>42.8</td>
<td>3.8</td>
<td>1.8</td>
<td>43.0</td>
<td>3.9</td>
<td>2.2</td>
<td>43.0</td>
<td>3.9</td>
</tr>
</tbody>
</table>

* Molecular weight measured osmotically at 37 °C in chloroform; calculated values are given in parentheses.

**Table 2**

**Analytical data for some palladium(II) and platinum(II) dithiocarbamate complexes**

**Analyses (%)**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{PdCl}_2(\text{S}_2\text{CNET}<em>2)</em>{2}]_2)</td>
<td>(69%) (579)</td>
<td>(74%) (668)</td>
</tr>
<tr>
<td>([\text{PdBr}_2(\text{S}_2\text{CNET}<em>2)</em>{2}]_2)</td>
<td>(70%) (658)</td>
<td>(72%) (658)</td>
</tr>
<tr>
<td>([\text{Pd}(\text{SPh})_2(\text{S}_2\text{CNET}_2)]_2)</td>
<td>(71%) (658)</td>
<td>(72%) (658)</td>
</tr>
</tbody>
</table>

**Di-\(\mu\)-bromo-bis[diethyldithiocarbamato]palladium(II)** was prepared in the same way by reaction of \([\text{PdBr}_2(\text{H}_2\text{PPh}_3)]\) and \(\text{Na}_4[\text{S}_2\text{CNET}_2]_2\cdot3\text{H}_2\text{O}\) (1:1 mol ratio), \(\text{m}p \ 210–212 \ ^\circ\text{C}, \text{v}(\text{CN}) \ 1153 \ \text{cm}^{-1}\). Alternatively, \([\text{PdBr}_2(\text{S}_2\text{CNET}_2)]_2\) was precipitated by shaking \([\text{PdCl}_2(\text{S}_2\text{CNET}_2)_{2}]_2\) with excess of lithium dibromide in acetonite for 24 h. The solvent was then removed and the residue was extracted into methylene chloride.

Addition of diethyl ether gave an orange powder which was filtered off, washed with water, methanol, and diethyl ether, and dried in air.

**Di-\(\mu\)-phenylthio-bis[diethyldithiocarbamato]palladium(II)**. Sodium benzenethioniate in acetonite was added to a methylene chloride solution of \([\text{PdCl}_2(\text{S}_2\text{CNET}_2)_{2}]_2\), stirred for 30 min, and then filtered through Celite. Removal of solvent and addition of methylene chloride-cyclohexane gave an orange-red powder which was filtered off, washed with water, methanol, and diethyl ether, and dried in air, \(\text{m}p \ 228–230 \ ^\circ\text{C}, \text{v}(\text{CN}) \ 1150 \ \text{cm}^{-1}\).

**Di-\(\mu\)-chloro-bis[O-ethyl dithiocarbamato]palladium(II)**. The salt \(\text{K}_2[\text{S}_2\text{COET}]\) (0.08 g) in acetonite was added to a methylene chloride solution of \([\text{PdCl}_2(\text{H}_2\text{PPh}_3)_{2}]\) (0.14 g) to give an orange solution and a white precipitate (KCl). After stirring for 30 min, the solution was filtered through Celite and evaporated to dryness. Recrystallisation from methylene chloride-diethyl ether gave the dark orange product which is unstable and darkens in colour over 24 h. Prepared by reaction of \([\text{PdCl}_2(\text{S}_2\text{CNET}_2)_{2}]_2\) with \(\text{AsPh}_3\), \(\text{SbPh}_3\), and \(\text{C}_6\text{H}_4\text{N}\) respectively.

**Chloro(diethyldithiocarbamato)(phenylthio)(triphenylphosphine)palladium(II)**. An excess of PPh\(_3\) was added to a methylene chloride solution of \([\text{PdCl}_2(\text{S}_2\text{CNET}_2)_{2}]_2\) and shaken for 15 min. Addition of hexane and slow evaporation of the methylene chloride resulted in the formation of the red crystalline product, \(\text{m}p \ 178–179 \ ^\circ\text{C}, \text{v}(\text{CN}) \ 1150 \ \text{cm}^{-1}\).

**Chloro(dimehyldithiosphodithioato)(triphenylphosphine)palladium(II)**. The salt \(\text{Na}_2[\text{S}_2\text{PMe}_3]_2\cdot2\text{H}_2\text{O}\) (0.09 g) in acetonite was added to a methylene chloride solution of \([\text{PdCl}_2(\text{H}_2\text{PPh}_3)_{2}]\) (0.14 g) to give a dark red solution. An excess of PPh\(_3\) was then immediately added giving an orange solution. This was filtered through Celite and the volume of filtrate was reduced. Addition of diethyl ether-pentane gave an orange crystalline solid which was removed by filtration and washed with water, methanol, and diethyl ether, \(\text{m}p \ 203–205 \ ^\circ\text{C}, \text{v}(\text{PS}) \ 578 \ \text{cm}^{-1}\).
Benzyl(triphenyl)phosphonium dichloro(diethylidithiocarbamoato) palladate(ii). The complex \([\text{PdCl}(\text{S}_2\text{CNET}_2)_2] \) (0.28 g) in acetonitrile was shaken with excess of \([\text{PPPh}_3(\text{CH}_3\text{Ph})]\)Cl (1.00 g) and concentrated hydrochloric acid (1 cm³) for 24 h. The solvent was then removed in vacuo and the product was extracted into methylene chloride. Addition of light petroleum (b.p. 60–80 °C) precipitated a yellow-orange solid which was filtered off, washed with water, methanol, and diethyl ether, and dried in air, m.p. 168–170 °C, ν(CN) at 1 522 cm⁻¹. 

Teitaphenylarsensouimium dichloro(diethylidithiocarbamoato)palladate(ii) was prepared similarly by reaction of \([\text{PdCl}(\text{S}_2\text{CNET}_2)_2]\) with excess of \([\text{AsPh}_3]\)CHCl in acetonitrile, ν(CN) at 1 522 cm⁻¹. 

(Diethylidithiocarbamoato)(dimethylphosphinidithioato)palladium(ii). An excess of Na[S₂PMe₂]·2H₂O in acetonitrile was added to an acetone solution of \([\text{PdCl}(\text{S}_2\text{CNET}_2)_2]\) to give a pale orange solution and a white precipitate (NaCl). Removal of solvent after 15 min, followed by extraction with methylene chloride and addition of diethyl ether, gave an orange solid which was filtered off and washed with water, methanol, and diethyl ether, ν(CN) at 1 515 and ν(PS₃) at 578 cm⁻¹. 

(Diethylidithiocarbamoato)(dimethylphosphinidithioato)(triphosphine)palladium(ii). Excess of triphenylphosphine was added to a suspension of \([\text{Pd}(\text{S}_2\text{CNET}_2)_2]\)·(S₂PMe₂) in benzene to give a yellow solution. The volume was reduced in vacuo and addition of diethyl ether–pentane gave a yellow crystalline solid which was filtered off and washed with water, methanol, and diethyl ether, ν(CN) at 1 515 and ν(PS₃) at 605 cm⁻¹. 

Platinum Complexes. — trans-μ₁,₂-γ,₅-6-γ-Cyclo-octa-1,5-diene-bis[chloro(diethylidithiocarbamoato)palladium(ii)]. The salt Na[S₂CNET₂]·3H₂O (0.11 g) in acetonitrile was added to a methylene chloride solution of \([\text{Pt}(\text{C}_6\text{H}_5\text{Cl})_2]\) (0.19 g) to give an immediate white precipitate (NaCl) and a yellow solution. On further stirring, a yellow precipitate was formed and after 1 h this was filtered off, washed with water to remove NaCl, then with methanol and diethyl ether, and dried in air, m.p. 190–192 °C, ν(CN) at 1 550 cm⁻¹. 

Chloro(diethylidithiocarbamoato)(triphenylphosphine)palladium(ii). Triphenylphosphine (0.07 g) was added to a suspension of \([\text{PdCl}(\text{S}_2\text{CNET}_2)_2]\)·(S₂PMe₂) (0.11 g) in methylene chloride to give a pale yellow solution. Removal of some solvent and addition of diethyl ether–pentane gave a yellow precipitate which was filtered off and washed with water, methanol, and diethyl ether, and dried in air, m.p. 191–194 °C, ν(CN) at 1 530 cm⁻¹. 

(Diethylidithiocarbamoato)bis(triphenylphosphine)palladium(ii) chloride–water (1/1). An excess of PPPh₃ was added to a suspension of \([\text{PdCl}(\text{S}_2\text{CNET}_2)_2]\)·(S₂PMe₂) in methylene chloride to give a colourless solution. After removal of some solvent, addition of diethyl ether–pentane gave a white precipitate which was washed with water, methanol, and diethyl ether, m.p. 174–175 °C, ν(CN) at 1 550 cm⁻¹. 

(Diethylidithiocarbamoato)bis(dimethylphosphinidithioato)palladium(ii) chloride–water (1/1). Excess of Na[S₂CNET₂]·3H₂O in acetonitrile was added to cis-[PtCl₂(PMe₂Ph)₂] in methylene chloride and shaken for 15 min to give a very pale yellow solution and a white precipitate (NaCl). Removal of solvent and addition of methylene chloride–diethyl ether gave a white solid which was washed with water, methanol, and diethyl ether, and dried in air. The same complex was reported elsewhere by the prolonged interaction of \([\text{Pt}(\text{S}_2\text{CNET}_2)_2]\) and PMe₂Ph in methylene chloride. 

We thank Johnson, Matthey Ltd, for loans of potassium tetrachloroplatinate(ii) and palladium(ii) chloride the S.R.C. for support (to M. C. C.). Professor J. P. Fackler, jun., for furnishing results prior to publication, and the Department of Chemistry, Glasgow University, for the use of their Mechromat osmometer.
Metal Complexes of Sulphur Ligands. Part 14.¹ Reaction of Palladium(II) and Platinum(II) Dithioacid Complexes with Tertiary Phosphinites, and the Crystal and Molecular Structure of Dimethylphosphinodithioato-(diphenylphosphinito)(diphenylphosphinous acid)palladium(II)

By Margaret C. Cornock, Robert O. Gould, C. Lynn Jones, and T. Anthony Stephenson.* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

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Metal Complexes of Sulphur Ligands. Part 14.1 Reaction of Palladium-(ii) and Platinum(ii) Dithiocarb Complexes with Tertiary Phosphinites, and the Crystal and Molecular Structure of Dimethylphosphinodithioato-(diphenylphosphino) (diphenylphosphinonic acid) palladium(ii)

By Margaret C. Cornock, Robert O. Gould, C. Lynn Jones, and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Prolonged reaction of [Pd(S₂PMe₃)₂] with excess PPh₃(OR) (R = Me or Et) in either methane chloride or benzene gives the four-coordinate complex [Pd(S₂PMe₃)(PPh₃O)(PPh₃OH)] (1a) shown by spectroscopic evidence and X-ray structural analysis to contain the symmetrical hydrogen-bonded P₃H₉OH₂ ligand. Crystals of (1a) are monoclinic, space group P2₁/m, with a = 6.86(1), b = 22.12(2), c = 9.69(1) Å, β = 91.15(2)°. The acidic hydrogen atom links two equivalent diphenylphosphite groups with O···O 2.41 Å. Similar complexes [M(S-S)(PPh₃O)(PPh₃)(OH)] (M = Pd, S-S = [S₂PMe₃]₂-, [S₂CNMe₂]₂-, M = Pt, S-S = [S₂PMe₃]₂-) have been prepared by reaction of [M(S-S)] with PPh₃(OR) or, for M = Pd, by reaction of [PdCl₂(PPh₃O)(PPh₃OH)] with the appropriate dithiocarb anion (1:2 molar ratio). A careful study of the [Pt(S₂CNMe₂)(PPh₃O)(OMe)] reaction has resulted in the isolation of the intermediates [Pt(S₂CNMe₂)(PPh₃O)(OMe)]X (X = [B₆H₆]⁻ or Cl⁻) and [Pt(S₂CNMe₂)(PPh₃O)(PPh₃)(OMe)] (3) and a mechanism of formation of [Pt(S₂CNMe₂)(PPh₃O)(PPh₃)(OH)] (1b) involving both nucleophilic attack on a P=O bond and subsequent hydrolysis of a P=O bond is proposed. In contrast, reaction of [M(S₂CO)₂(PPh₃)] with PPh₃(OR) gives [M(S₂CO)₂(PPh₃)(OR)] (M = Pd or Pt), although [Pd(S₂CO)(PPh₃)](PPh₃OH) can be synthesised from [PdCl₂(PPh₃O)(PPh₃OH)] and K₂(S₂CO) (1:2 molar ratio).

In some of the earlier papers in this series 2 the results of the reactions of various tertiary phosphines (L) with the square-planar [M(S-S)L₄] complexes [M = Pd or Pt; S-S = [S₂PR₃]⁻, [S₂CNMe₂]⁻, or [S₂P(OR)₃]⁻] have been reported. These studies clearly show that reaction occurs by stepwise cleavage of metal-sulphur bonds to generate the four-coordinate square-planar complexes [M(S-S)L₄] and [M(S-S)L₄][S-S] which exhibit unidentate-bidentate and bidentate-ionic bonding of the dithioacids groups respectively. In addition, for these ionic [S₂COR]⁻ and [S₂P(OR)₂]⁻ complexes, nucleophilic attack can also occur on a co-ordinated alkoxy-group to give [M(S₂CO)L₄] and [M(S₂P(OR)₂)O(L₄)] respectively.

In this paper, we now report the results of reactions between palladium(ii) and platinum(ii) dithioacids and tertiary phosphinites PPh₃(OR) (R = Me or Et) in which, on the basis of earlier work, both hydrolysis of the P=O group 3 and/or nucleophilic attack on the P=O group ⁴ might be expected to play a significant role.

RESULTS AND DISCUSSION

Addition of an excess of PPh₃(OMe) to a methylene chloride solution of [Pd(S₂PMe₃)₂] immediately gave a highly conducting solution which slowly decreased in conductivity when the solution was left to stand for 24 h. This decrease in conductivity was accompanied by a colour change from orange-yellow to pale yellow, and on addition of diethyl ether to a pale yellow, non-conducting, crystalline precipitate (1a) was obtained. The ¹H n.m.r. spectrum of this product contained in addition to the phenyl multiplet, a sharp doublet at δ 8.97 p.p.m. (2/3 (OH) 12.0 Hz (relative intensity 10:3) assigned to the methyl protons of the [S₂PMe₃]⁻ ligand but no signals between 3 and 4 p.p.m. which could be assigned to the methoxy-group of the phosphinite. The same complex was formed by using PPh₃(OC₃) or by carrying out the reactions in benzene which both eliminates the possible participation of chloride ion in these reactions (cf. the reaction of [M(S₂CNMe₂)(PPh₃)] with CH₂Cl₂ which gave [M(S₂CNMe₂)(PPh₃)Cl] and CH₂(S₂CNMe₂)Cl ⁵) and suggests that either hydrolysis and/or nucleophilic attack on the P=O group ⁶ might be expected to play a significant role.

Complex (1a) analysed closely for [Pd(S₂PMe₃)(PPh₃O)(PPh₃OH)] and is monomeric in chloroform at 37 °C. However, all attempts to observe the ¹H n.m.r. signal of the acid hydrogen on the co-ordinated diphenylphosphinic acid proved unsuccessful (cf. related studies on [MX(PPh₃O)(PPh₃OH)] (M = Pt or Pd; X = Cl or Br) ⁷) although Beaulieu et al. ⁸ found such a signal at δ 13.43 p.p.m. for [PtH(PPh₃)(PPh₃OH)] (PPh₃OH). The i.r. spectrum of (1a) shows several bands in the P=O stretching region (850-1100 cm⁻¹). However, the three strong bands at 850, 895, and 944 cm⁻¹ are also observed for the starting material [Pd(S₂PMe₃)₂] while that at 1100 cm⁻¹ corresponds to a band usually observed in phenylphosphine complexes ⁹ and can therefore be assigned to a ligand absorption. Thus, the remaining

2 For detailed references, see D. F. Steele and T. A. Stephenson, J. C. S. Dalton, 1973, 2124.
peak at 1010 cm⁻¹ is assigned to a ν(PO) stretching mode. The peak at 582 cm⁻¹ is consistent with bidentate coordination of the [S₂PMe₄]⁻ group. The absence of ν(OH) in the normal region of the i.r. spectrum (ca. 3200 cm⁻¹) is consistent with a symmetrical hydrogen-bonded system of the type first postulated by Dixon and Rattray in [[MX(PPh₃)₂][PPh₃(OH)]], etc., and later confirmed by an X-ray structural analysis on the related [[Pd(SCN)(PPh₃)][PPh₃(OH)]]₂⁺.

Further evidence for the validity of this statement is based on the ³¹P n.m.r. spectrum (proton decoupled) of (1a) which shows the expected AX₂ pattern with resonances centred at 8.45.04 (δ = [S₂PMe₄]⁻) and 83.20 p.p.m. (δ = [S₂PMe₄]⁻) respectively, and the fact that reaction of [[PdCl(PPh₃)(PPh₃(OH))]₂] with Na[S₂PMe₄]·2H₂O (1 : 2 molar ratio) in methylene chloride gave (1a) in high yield. However, unequivocal proof of the solid-state structure of (1a) is given by the results of an X-ray analysis which is reported in detail below. An analogous complexes [M(S-S)₂][PPh₃][PPh₃(OH)] (M = Pd, S[S₂PMe₄]⁻ or [S₂PMe₄]⁻; M = Pt, S = [S₂PMe₄]⁻ or [S₂PMe₄]⁻) were prepared by prolonged reaction of [M(S-S)₂] with excess of PPh₃(OR) in methylene chloride and fully characterised by elemental analyses, and i.r., ¹H and ³¹P n.m.r. spectroscopy (see Experimental section). The palladium complexes were also synthesised by reaction of [[PdCl(PPh₃)(PPh₃(OH))]₂] with either NH₄[S₂PPh₃] or Na[S₂PMe₄]·3H₂O (1 : 2 molar ratio).

Crystal Data for (1a). — C₇₀H₁₂O₈P₄P₄S₂PMe₄, M = 634, pale yellow monoclinic needles, a = 8.80 (1), b = 22.12 (2), c = 9.69 (1) Å, β = 111.52 (2), U = 1308 Å³, Dₘ = 1.50, Z = 2, Dc = 1.64 g cm⁻³. Space group P2₁/m (No. 13), Cu-Kα radiation, λ = 1.5418 Å, μ(Cu-Kα) = 88.7 cm⁻¹.

Structure Determination. — Data for layers 0–4kl were collected on multilamp packs by the equi-inclination Weissenberg method. Intensities were evaluated by the Photocan Service of the Atlas Computing Laboratory, and 228 independent reflections were measured above background. The crystal was a needle elongated along [100] with a length of 0.8 mm and a cross-section of 0.2 mm². Cylindrical absorption corrections were applied to the data.

The data were put on a common scale statistically, and the position of the Pd atom was found from a Patterson summation; all the other non-hydrogen atoms were located in two subsequent difference-Fourier syntheses, and the space group was confirmed as P2₁/m rather than the non-centric P2₁. The phenyl rings were constrained to be planar with all C–C distances 1.40 Å and all C–C–C angles 120°, and the model was refined isotropically with separate layer-scale factors and unit weights. For the last few cycles, only a single overall scale factor was refined, the palladium, phosphorus, and sulphur atoms being given anisotropic temperature factors, and a weighting scheme (w = 30/[F₀]) for |F₀| > 30 and otherwise w = 1) was applied. In the last cycle no shifts were greater than 0.1 times the estimated standard deviation, and the final R was 0.077. Hydrogen atoms could not be reliably located.

Final atomic parameters are given in Table 1, and the principal interatomic distances and angles in Table 2.

| Table 1 |
|-------------------|------------------|------------------|------------------|
| Fractional co-ordinates and thermal parameters (all ×10⁴) |                      |
|                      |                  |
| (1a)                                          |
|                      |                  |
|                      |                  |
|                      |                  |

The structure-factor table is deposited as Supplementary Publication No. SUP 22091 (4 pp., 1 microfiche).

Description of the Structure. — The structure of (1a) is monomeric with crystallographic m(C₄) symmetry. The co-ordination of palladium is very nearly square planar, and is illustrated in Figure 1. The Pd atom is less than 0.04 Å from the plane determined by P(1), S, P(1'), and S', and the co-ordination distances and angles are normal for complexes of Pd²⁺ with sulphur- and phosphorus-containing ligands. Figure 2 shows the projection of the complex into its symmetry plane. The dithiophosphinate ligand possesses a molecular plane of symmetry perpendicular to this, but inclined at an angle of 12.9°.

* For details see Notice to Authors No. 7, J. C. S. Dalton, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).
to the co-ordination plane. One result of this is that C(14) is only 3.56 Å from the Pd atom at (1 + x,y,z).

The diphenylphosphino ligands are symmetry related; this requires the hydrogen atom to lie symmetrically between the two oxygen atoms. The plane

**TABLE 2**

Interatomic distances (Å) and angles (°) in (1a). Primed atoms are related to unprimed ones by the operation 

\[ x, y, z \rightarrow x, -y, z \].

Estimated standard deviations are given only when atoms in the phenyl rings are not involved.

<table>
<thead>
<tr>
<th>Distance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd–S</td>
<td>2.40(3)κ</td>
</tr>
<tr>
<td>Pd–P(1)</td>
<td>2.29(4)κ</td>
</tr>
<tr>
<td>S–P(2)</td>
<td>2.00(6)κ</td>
</tr>
<tr>
<td>P(1)–O</td>
<td>1.54(15)κ</td>
</tr>
<tr>
<td>P(1)–C(1)</td>
<td>1.800κ</td>
</tr>
<tr>
<td>P(2)–C(13)</td>
<td>1.79(6)κ</td>
</tr>
<tr>
<td>O–O'</td>
<td>1.54(4)κ</td>
</tr>
<tr>
<td>O–C(11)</td>
<td>1.32(11)κ</td>
</tr>
<tr>
<td>O–C(12)</td>
<td>1.32(11)κ</td>
</tr>
<tr>
<td>O–C(13)</td>
<td>1.32(11)κ</td>
</tr>
</tbody>
</table>

Intermolecular contacts less than 3.5 Å are listed.

**Figure 1** Projection of (1a) on to the co-ordination plane

slightly distorted from \( m \) symmetry; the planes of the two phenyl rings are inclined at 63 and 50° respectively to the Pd(1), P(1), O(1) plane, and at 85° to one another. A smaller rotation of the ligands would make the O(1) ···

* A "pseudo-triplet" pattern consists of a sharp doublet with a broad hump situated between the doublet and signifies a relatively large \( J(PP) \) compared to the \( J(PH) + J(P'H) \) value [cf. cis-[Ru(S4PMe3)4(PMe3PPh3)].

**Figure 2** Projection of (1a) on to the symmetry plane

products formed during the reaction of \([M(S4CNEt)2]2\) with \( \text{PPh}_3(\text{OMe}) \) were carefully examined. Thus, reaction of \([M(S4CNEt)2]2\) with excess of \( \text{PPh}_3(\text{OMe}) \) in methanol followed either immediately (Pt) or within 30 min (Pd) by addition of \( \text{Na}[\text{BPPh}_3] \) gave a precipitate of \([M(S4CNEt)2][\text{PPh}_3(\text{OMe})]_2[\text{BPPh}_3] \). Complexes (2) were characterised by elemental analyses, conductive measurements in methylene chloride which are indicative of 1:1 electrolytes, \( ^{1}H \) n.m.r. spectra which show the presence of a 'pseudo-triplet' \( ^{1}H \) n.m.r. spectra which show the presence of a 'pseudo-triplet' for the methoxy-groups with \( ^{3}J(\text{PH}) + ^{4}J(\text{PH}) = 12.0 \text{ Hz} \) and magnetically equivalent ethyl groups, and \( ^{31}P \) n.m.r. spectra which for M = Pt shows the expected 1:4:1 triplet \( ^3J(\text{PtP}) = 3749.0 \text{ Hz} \) indicative of magnetically equivalent phosphorus-bonded \( \text{PPh}_3(\text{OMe}) \) groups. These results clearly show that, as in the case of tertiary

\[ ^{1}H \text{ cis-[MCi(4,4,4-NPAO)(OMe)]_2 (M = Pd or Pt) with \( J(PH) + J(P'H) = 12.0 \text{ Hz} \).} \)

\[ ^{10} \text{ D. J. Cole-Hamilton and T. A. Stephenson, } \textit{J.C.S. Dalton}, 1974, 739. \]

\[ ^{11} \text{ D. A. Couch, S. D. Robinson, and J. N. Wingfield, } \textit{J.C.S. Dalton}, 1974, 1309. \]
phosphines, the initial rapid increase in conductivity on mixing [M(S₂CNE₄)₂] and PPh₃(OR)₂ due to the formation of \([M(S₂S)₂][PPh₃(OMe)]₂\) presumably by stepwise cleavage of metal-sulphur bonds.

However, rather surprisingly, treatment of a methylene chloride solution of (2; \(M = Pt\)) with Na[S₂CNE₄]·3H₂O in acetone led after 3 d only to the recovery of the starting materials. Hence, because of the strong possibility that the presence of the large anion was inhibiting further reaction of the cation, (2) was treated with an equimolar amount of \([AsPh₄][Cl]HCl\) which precipitated the very insoluble \([AsPh₄][BPh₄]_2\) and left a methylene chloride solution containing \([Pt(S₂CNE₄)(PPh₃(OMe))]_2Cl\). This solution was divided into three parts which were treated as described below.

One portion of this solution was treated with an equimolar amount of Na[S₂CNE₄]·3H₂O which gave an immediate precipitate of sodium chloride. The conductivity of the filtered solution was then monitored over a period of 3 d and found to decrease steadily. At the end of this period, evaporation of the solvent and addition of diethyl ether gave a non-conducting microcrystalline pale yellow solid (3). The \(^1H\) n.m.r. spectrum of (3) consisted of a doublet at \(3.87\) \([PPh₃(OMe)]\), two closely spaced quartets at \(3.52\) and \(3.56\), a triplet at \(1.23\) p.p.m. \([S₂CNE₄]^{-}\), and a multiplet in the aromatic region. The \(^31P\) n.m.r. spectrum (proton decoupled) in CDCl₃ at 223 K consisted of two doublets at \(38.89\) and \(94.14\) p.p.m. (relative intensity \(ca. 1: 1\)) with \(J(pp') 28.0\) Hz, indicative of a cis arrangement of different phosphorus-containing ligands bound to Pt\[^{11}\]. Each of the doublets exhibited platinum satellites with \(J(pp') 3 264.8\) and \(4 212.3\) Hz respectively, confirming directly bonded phosphorus atoms in each ligand. The i.r. spectrum showed a strong \(\nu(PO)\) stretch at \(1 050\) cm\(^{-1}\) with \(\nu(CN)\) at \(1 530\) cm\(^{-1}\) indicative of bidentate \([S₂CNE₄]^-\) coordination. All this spectroscopic information together with the analytical data is consistent with the formulation of (3) as \([Pt(S₂CNE₄)(PPh₃(OMe))(PPh₃(OMe))]\). By analogy with the complex \([Ni(C₅H₅)₂[P(OEt₃)]_2\) \([PO(OEt₃)]_2\] which shows two doublets centred at \(147.5\) \([P(OEt₃)]_2\) and \(85.8\) p.p.m. \([P(OEt₃)]_2\), the position of the PPh₃(OMe) resonance for \([Pt(S₂CNE₄)(PPh₃(OMe)(PPh₃(OMe))]_2[BPh₄]^-\) \(94.20\) p.p.m. the resonance at \(94.14\) p.p.m. is assigned to PPh₃(OMe) and that at \(38.89\) p.p.m. to \([PPh₃(OMe)]^-\).

Complex (3) was also isolated by reaction of \([Pt(S₂CNE₄)]_2\) and excess of PPh₃(OMe) in methylene chloride for only 10 min, followed by precipitation by addition of diethyl ether-pentane. Thus, these experiments clearly demonstrate that ionic \([Pt(S₂CNE₄)(PPh₃(OMe))]^-\) \([S₂CNE₄]^-\) readily rearranges to (3) by nucleophilic attack of \([S₂CNE₄]^-\) on a co-ordinated PPh₃(OMe) group.

Related studies of nucleophilic attack on co-ordinated alkoxysilanes ligands are well documented.\(^{4,12,15}\

Another portion of the \([Pt(S₂CNE₄)]_2[PPh₃(OMe)]_2[Cl]_2\) solution was treated with an equimolar amount of Na[S₂CNE₄]·3H₂O together with a few drops of PPh₃(OMe) and, after filtering off the sodium chloride precipitate, the solution was left to stand for 2 d. Removal of solvent from the non-conducting solution then gave a very pale yellow microcrystalline solid readily identified as \([Pt(S₂CNE₄)(PPh₃(OH))(PPh₃(OMe))]\) (1b). This complex was also formed if a methylene chloride solution of \([Pt(S₂CNE₄)(PPh₃(OMe))]_2\) (3) was treated with a small amount of PPh₃(OMe) for a prolonged period, whereas in the absence of free PPh₃(OMe) only (3) was recovered from solution.

Thus, these studies indicate that (3) is slowly converted into (1b), probably by displacement of the co-ordinated PPh₃(OMe) group by free PPh₃(OH) and subsequent formation of the stable six-membered Pt\[^{13}\][PPh₃OH]Pt[PPh₃] ring structure. Evidence for the generation of some PPh₃(OMe) under these conditions comes from H n.m.r. studies on PPh₃(OMe)-CDCl₃ solutions which show the appearance of methanol and the concomitant disappearance of methoxy-resonances on prolonged standing. Conductivity studies on PPh₃(OMe)-CH₂Cl₂ solutions indicate that PPh₃(OMe) is not \([PPh₃(OH)]^-\) is formed under these conditions. Furthermore, these observations are consistent with earlier studies which indicate that tertiary phosphinites undergo more ready hydrolysis when not co-ordinated to a transition metal.\(^{16}\) Similar displacement reactions of co-ordinated PPh₃(OR) by free PPh₃(OH) are also proposed.\(^{13}\) To explain the formation of \([Pt[PPh₃(OH)]_2[PPh₃(OMe)]_2\) from \([Pt[PPh₃(OMe)]_2[PPh₃(OH)]_2\) and free PPh₃(OMe) when left in ethanol for 4 d.

When the methylene chloride solution of \([Pt(S₂CNE₄)]_2[PPh₃(OMe)]_2[Cl]_2\) was treated with only a few drops of PPh₃(OMe) and left for several days (1b) was again isolated, whereas in the absence of PPh₃(OMe) some of (3) was produced. However, the rate of decrease in conductivity in both these solutions was much slower compared to those containing \([S₂CNE₄]^-\) ion which is simply a reflection of the greater nucleophilicity of \([S₂CNE₄]^-\) compared to Cl⁻ ion.

A summary of the reactions involved in the formation of \([M(S₂CNE₄)(PPh₃(OMe)(PPh₃(OMe))]\) is given in the Scheme and, to our knowledge, this represents only the second example of a system where both nucleophilic attack on a P–OR bond and subsequent hydrolysis of a P–OR bond play an essential role in determining the product composition (see ref. 18 for the other example). It is expected that a similar mechanism would explain the formation of \([M(S₂PR₃)(PPh₃(OMe)(PPh₃(OMe))]\) from \([M(S₂PR₃)]_2\) and excess of PPh₃(OR) but attempts to confirm this have not been completely successful. For


example, reaction of [Pd(S₂PPh₂)₂] and PPh₃(OMe) in methanol followed by addition of Na[BPh₄] gave a pale yellow precipitate but this rapidly turned brown (cf. the analogous [Pd(S₂PPh₂)(PPh₃)(BPh₄)], which also rapidly decomposed in the solid state). However, treatment of [Pd(S₂PPh₂)₂] with PPh₃(OMe) in methylene chloride followed by solvent removal after ca. 10 min and addition of diethyl ether gave a pale yellow non-conducting solid whose ¹H n.m.r. spectrum was consistent with the formulation [Pd(S₂PPh₂)(PPh₃(OCH₃))]

between palladium(II) and platinum(II) alkyl dithiocarbonates and PPh₃(OR) because of the presence of two types of alkynyl group which might undergo nucleophilic attack. Thus, reaction of [Pd(S₂COPr)₂]₂ in methylene chloride with excess of PPh₃(OEt) gave an immediate red conducting solution which slowly turned yellow accompa-}

SPECTRAL DATA OF [Pd(S₂CO)(PPh₃(OEt))₃] PRODUCED, *e.g.* displacement of PPh₃(OEt) by free PPh₃(OH). However, [Pd(S₂COPr)₃](PPh₃(OH)) can be readily synthesised by reacting of [[PdCl₂(PPh₃(OEt))₃] with K[S₂COPr] (1:2 molar ratio).

EXPERIMENTAL

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzal. Infrared spectra were recorded in the 250—4000 cm⁻¹ region on a

* The multiplet appears to consist of a 1:3:3:1 quartet of "pseudo-triplets" with ¹J(HH) 7.0 Hz and ¹J(PH) + ¹J(PH) of 6.5 Hz, whereas for cis-[PdCl₂(PPh₃(OEt)]₃ a quartet of overlapping virtual-coupling doublets is observed with ¹J(HH) = ¹J(PH) + ¹J(PH) of 7.0 Hz.

Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge. Hydrogen-I n.m.r. spectra were obtained on Varian Associates HA-100 and EM360 spectrometers, 1H n.m.r. spectra on a Varian XL100 spectrometer recorded in the pulse and Fourier transform modes at 40.5 MHz (1H chemical shifts quoted in p.p.m. to high frequency of 85% H$_3$PO$_4$. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson, Matthey Ltd), Na$_2$S$_2$CNEt$_2$[H$_2$O], Na[BPH$_4$], and [AsP$_3$H$_3$][CHCl$_3$ (B.D.H.), and PPH$_4$(OMe) and PPH$_4$(OEt) (Maybridge Chemical Company) were obtained as indicated. The compounds Na$_2$S$_2$PMe$_3$: 2H$_2$O, [NH$_4$][S$_2$PMe$_3$], K[S$_2$COPF$_4$], [M$_2$(S$_2$CNEt)$_4$]: [M(S$_2$CNEt)$_3$] (R = Me$_3$ or Ph$_2$), and [M(S$_2$COPF$_4$)$_3$] (M = Pd or Pt) were synthesised as described earlier. Solvents were used as purchased.

Infrared bands diagnostic of [SP$_3$PH$_4$]: $^{13}$[SP$_3$PMe$_3$]:, and [S$_2$CNEt$_2$]: bidentate-coordination are listed for each record, and unless otherwise stated, 1H n.m.r. spectra were recorded in CDC$_2$Cl$_4$ at 301 K and 400 MHz n.m.r. spectra (proton decoupled) in CDCl$_4$ at 303 K. Relative intensities are given in parentheses and s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and p = pseudo-triplet.

**Palladium Complexes. —Dimethylphosphinodithioate(diphenyolphosphino)phosphine(hydrogen)acetylacetonato)(diphenylphosphino)acid)palladium(II).**

**Method (A).** An excess of PPH$_4$(OMe) or PPH$_4$(OEt) was added to a methylene chloride solution of [PD(S$_2$PMe$_3$)$_4$] and the solution was left to stand for 24 h. The resulting pale yellow solution was then reduced in volume and diethyl ether was added to give an off-white microcrystalline precipitate. The product was filtered off, washed with diethyl ether, and dried in air, m.p. 225–227 °C (decomp.), v(PS$_3$) at 582 cm$^{-1}$, v(PO) at 1 010 cm$^{-1}$ (Found: C, 49.1; H, 4.3; P, 14.3; Pd, 16.1; S, 10.3%; M (in CHCl$_3$) 350. Calc. for C$_{58}$H$_{68}$O$_2$P$_4$PdS$_4$: C, 52.7; H, 4.6. Calc. for C$_{52}$H$_{56}$O$_2$P$_4$PdS$_4$: C, 52.9; H, 4.6%).

**Method (B).** [Pd(S$_2$PMe$_3$)PPh$_4$O][PPh$_4$(OH)]. The salt Na$_2$S$_2$PMe$_3$:2H$_2$O (0.036 g) in acetone was added to a methylene chloride solution of [PdCl$_2$(PPh$_4$O)(PPh$_4$(OH))]$_4$ (0.13 g) (2 : 1 molar ratio) and the resulting pale yellow solution was shaken for 30 min. After filtering through Celite to remove sodium chloride, addition of diethyl ether gave an off-white precipitate which was filtered off and washed with water, methanol, and diethyl ether. The complex [Pd(S$_2$COPF$_4$)][PPh$_4$(OH)] was similarly precipitated using K[S$_2$COPF$_4$] (1 : 2 molar ratio) as Na$_2$S$_2$PMe$_3$:2H$_2$O. v(PO) at 1 020 cm$^{-1}$ (Found: C, 51.5; H, 4.5). Calc. for C$_{56}$H$_{62}$O$_2$P$_4$PdS$_4$: C, 52.1; H, 4.3% was similarly prepared using K[S$_2$COPF$_4$] (1 : 2 molar ratio) as Na$_2$S$_2$PMe$_3$:2H$_2$O. v(PO) at 1 020 cm$^{-1}$ (Found: C, 51.5; H, 4.3%).

The following complexes were prepared similarly using [Pd(S$_2$PPh$_4$O)][PPh$_4$(OMe)] and [Pd(S$_2$CNEt$_2$)PPh$_4$O][PPh$_4$(OMe)]. Diphosphinodithioate(diphenyolphosphinodithioato)(diphenylphosphino)phosphinic acid acid) palladium(II), m.p. 184–185 °C, v(PS$_3$) at 620 and 573 cm$^{-1}$, v(PO) at 1 009 cm$^{-1}$ (Found: C, 50.8; H, 4.3. Calc. for C$_{58}$H$_{68}$O$_2$P$_4$PdS$_4$: C, 52.7; H, 4.4%).

**Method (C).** [Pd(S$_2$PMe$_3$)PPh$_4$O][PPh$_4$(OH)]. The salt Na$_2$S$_2$PMe$_3$:2H$_2$O (0.036 g) in acetone was added to a methylene chloride solution of [PdCl$_2$(PPh$_4$O)(PPh$_4$(OH))]$_4$ (0.13 g) (2 : 1 molar ratio) and the resulting pale yellow solution was shaken for 30 min. After filtering through Celite to remove sodium chloride, addition of diethyl ether gave an off-white precipitate which was filtered off and washed with water, methanol, and diethyl ether. The complex [Pd(S$_2$COPF$_4$)][PPh$_4$(OH)] was similarly precipitated using K[S$_2$COPF$_4$] (1 : 2 molar ratio) as Na$_2$S$_2$PMe$_3$:2H$_2$O.

The compound [Pd(S$_2$COPF$_4$)][PPh$_4$(OH)] was similarly prepared using K[S$_2$COPF$_4$] (1 : 2 molar ratio) as Na$_2$S$_2$PMe$_3$:2H$_2$O.

The following complexes were prepared similarly from [M(S$_2$CNEt)$_3$] (R = Me$_3$ or Ph$_2$), and [M(S$_2$COPF$_4$)$_3$] (M = Pd or Pt) were synthesised as described earlier. Solvents were used as purchased.

Infrared bands diagnostic of [SP$_3$PH$_4$]: $^{13}$[SP$_3$PMe$_3$]:, and [S$_2$CNEt$_2$]: bidentate-coordination are listed for each record, and unless otherwise stated, 1H n.m.r. spectra were recorded in CDC$_2$Cl$_4$ at 301 K and 400 MHz n.m.r. spectra (proton decoupled) in CDCl$_4$ at 303 K. Relative intensities are given in parentheses and s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and p = pseudo-triplet.
[Pt(S₂CNEt₂)₂] and PPh₃(OMe). NN-Diethylthiocarbamato(diphenylphosphinophenyl)diphenylphosphinophenyl acid)platinum(II), m.p. 242—244 °C, ν(CN) at 1 530 cm⁻¹, ν(PO) at 1 090 cm⁻¹, Found: C, 46.9; H, 4.4; N, 1.9%; M (in CHCl₃) 768. Calc. for C₃₆H₃₅NO₃P₂PtS₂: C, 46.7; H, 4.2; N, 1.9%; M 766. Hydrogen-1 n.m.r. spectrum: 1.20 (t, 6), 3.53 (q, 4) ([S₂CNEt₂])²⁻ [J(2H)] 7.0 Hz, and 7.20—7.90 p.p.m. (m, 20) (Ph). It was also obtained by addition of PPh₃(OMe) to a methylene chloride solution of [Pt(S₂CNEt₂)(PPh₃)(OMe)]Cl⁻ and leaving for several days, by reaction of the same solution with Na[S₂CNEt₂]·3H₂O and PPh₃(OMe) (formed more rapidly), or by reaction of a methylene chloride solution of [Pt(S₂CNEt₂)(PPh₃)(OMe)] with PPh₃(OMe) for 24 h.

(20:1) Diethylthiocarbamato(bis(methyl)diphenylphosphinophenyl)platinum(II) tetraphenylborate. An excess of PPh₃(OMe) was added to a suspension of [Pt(S₂CNEt₂)₂] in methanol to give a colourless solution. This was then added to a methanolic solution of Na[BPh₄] to give a sticky white precipitate which on trituration with diethyl ether gave a white microcrystalline solid, m.p. 156—158 °C, ν(CN) at 1 532 cm⁻¹, ν(PO) at 1 030 cm⁻¹, λ (1×10⁻² mol dm⁻³ in CH₂Cl₂) 420 S cm² mol⁻¹ (Found: C, 60.6; H, 5.1; N, 1.3.). Calc. for C₃₆H₃₅NO₃P₂PtS₂: C, 60.3; H, 5.1; N, 1.3%. N.m.r. spectra: ¹H, 1.10 (t, 6), 3.33 (q, 4) ([S₂CNEt₂])₂⁻ [J(2H)] 7.0 Hz, 6.27 (p, 10) * [PPh₃(OMe)] [¹H(PH) + ¹H(PO)] 12.0 Hz), and 6.80—7.90 p.p.m. (m, 40) (Ph); ³¹P, 94.20 p.p.m. (t) [¹H(Pt) 3 749.0 Hz].

NN-Diethylthiocarbamato(diphenylphosphinophenyl)methyl diphenylphosphinophenylplatinum(II). An excess of PPh₃(OMe) was added to a methylene chloride solution of [Pt(S₂CNEt₂)₂]. Partial removal of solvent after 10 min and addition of diethyl ether—pentane gave a very pale yellow solid which was filtered off, washed with diethyl ether and pentane, and dried in air, m.p. 205—207 °C, ν(CN) at 1 530 cm⁻¹, ν(PO) at 1 050 cm⁻¹ (Found: C, 47.5; H, 4.4; N, 1.9%. Calc. for C₃₆H₃₅NO₃P₂PtS₂: C, 47.4; H, 4.3; N, 1.8%). N.m.r. spectra: ¹H, 1.23 (t, 6), 3.52 (q, 4) ([S₂CNEt₂])²⁻ [J(2H)] 7.0 Hz, 3.87 (d, 3) [PPh₃(OMe)] [¹H(PH)] 12.0 Hz, and 7.00—7.90 p.p.m. (m, 20) (Ph); ³¹P (in CDCl₃ at 228 K), 38.80 (t, 1) * [PPh₃(OMe)] [¹H(Pt) 3 264.8, ¹H(PF) 27.7 Hz] and 94.14 p.p.m. (t, 1) [PPh₃(OMe)] [¹H(Pt) 4 212.3, ¹H(PF) 28.0 Hz].

This complex was also synthesised by reaction of Na[S₂CNEt₂]·3H₂O (0.05 g) with a methylene chloride solution of [Pt(S₂CNEt₂)(PPh₃)(OMe)]Cl⁻ (0.17 g) (made in situ by reaction of [Pt(S₂CNEt₂)(PPh₃)(OMe)]₃[BPh₄] with [AsPh₃]-Cl-HCl). The mixture was left for 3 d and then slow evaporation of the solvent gave the product as a microcrystalline pale yellow solid. If the solution of [Pt(S₂CNEt₂)(PPh₃)(OMe)]Cl⁻ was left for several days some of this product could be identified on solvent removal. (Dithiocarbamato)bis(ethyl diphenylphosphinophenyl)platinum(II). This complex was prepared as for the corresponding palladium complex starting from [Pt(S₂COCl)₂] and PPh₃(OMe), m.p. 190—192 °C, ν(CO)([S₂COCl]²⁻) at 1 690s, 1 618s, and 1 686w cm⁻¹ (Found: C, 46.6; H, 4.0%. Calc. for C₃₆H₃₄O₃P₂PtS₂: C, 46.6; H, 4.0%).

All the standard crystallographic calculations were made at the Edinburgh Regional Computing Centre using the X-Ray '74' system.

We thank Johnson, Matthey Ltd. for loans of potassium tetrachloroplatinate(II) and palladium(II) chloride, the S.R.C. for support (to M. C. C. and C. L. J.), Dr. A. S. F. Boyd for obtaining the ³¹P n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Meckrolab osmeter.

[6/2161 Received, 23rd November, 1976]
Preliminary communication

SYNTHESSES AND CHARACTERISATION OF SOME TRIPHENYLICYANOBORATE COMPLEXES OF RHODIUM(III), RUTHENIUM(II) AND PALLADIUM(II)

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Summary

The triphenylcyanoborate (N-bonded) complexes \([\eta^5-(C_5Me_5)Rh(S-S)-NCBPh_3]\) \((S-S^- = S_2PMe_2, \overline{S_2PPPh_2, \overline{S_2CNMe_2}})\), \([\eta^6-(C_6H_6)Ru(S_2PPPh_2)-NCBPh_3]\) and \([\text{Pd}(S_2CNEt_2)(PMe_2Ph)(NCBPh_3)]\) have been synthesised and characterised by both spectroscopic and X-ray structural methods.

Recently the syntheses of \([\eta^5-(C_5Me_5)Rh(S-S)_2] \) (I) and \([\eta^5-(C_5Me_5)RhCl-(S-S)] \) (II) \((S-S^- = S_2CNMe_2, \overline{S_2PR_2 \ (R = Me, Ph)}\)) by treatment of \([\eta^5-(C_5Me_5)RhCl_2] \) with Na(S-S) in 1/4 and 1/2 molar ratios, respectively were reported [1]. Treatment of II with methanol followed by addition of NaBPh_4 gives the solvated cations \([\eta^5-(C_5Me_5)Rh(S-S)(MeOH)] \) BPh_4 which are very useful precursors for generating a range of cations \([\eta^5-(C_5Me_5)Rh(S-S)L] \) BPh_4 (III: L = PPh_3, PMePh_2, AsPh_3, C_5H_5N, CO, etc.) However, attempts to synthesise \([\eta^5-(C_5Me_5)Rh(S-S)(C_2(CN)_4)] \) BPh_4 by treatment of II with excess tetracyanoethylene in methanol, followed by addition of NaBPh_4 to the result-
ing orange-yellow solutions gave non-conducting yellow solids (IV: S=S = (a) \( S_2PMe_2 \); (b) \( S_2PPh_2 \); (c) \( S_2CNMe_2 \)). The analytical data (C, H, N) of IV are, however, consistent with the formulation \( [\eta^5-(C_5Me_5)Rh(S=S)NCBPh_3] \), e.g. found for IVc: C, 60.7; H, 5.7; N, 4.6. Calcd.: C, 61.3; H, 5.7; N, 4.5%.

Additional evidence for the formulation of IV as zwitterionic complexes containing the triphenylcyanoborate anion is based on spectroscopic data. For example, the infrared spectra of all these compounds contain a C—N stretching frequency band at ca. 2180 cm\(^{-1}\), indicative of nitrile rather than isonitrile coordination of the \( -\text{NCBPh}_3 \) group [2], and all show bands characteristic of bidentate coordination of the dithiocarbamid ligands. The mass spectrum of IVc has a peak at \( m/e \) 626 corresponding to \( [\eta^5-(C_5Me_5)Rh(S_2CNMe_2)NCBPh_3]^{+} \) together with a fragmentation pattern consistent with this formulation. Furthermore, the \(^1\)H NMR spectrum of IVc in CDCl\(_3\) at 303 K has the expected three signals at \( \delta \) 1.79 (C\(_5\)Me\(_5\)), 3.17 (\( -S_2CNMe_2 \)) and 7.21 ppm (\( -\text{NCBPh}_3 \)) of relative intensity 5/2/5.

However, unequivocal proof of the solid state structure of IV comes from a preliminary X-ray structural analysis of IVa. Crystals of the complex from methanol are monoclinic, space group \( P2_1/n \) with cell parameters \( a = 24.013 \pm 0.006 \AA \), \( b = 9.368 \pm 0.002 \AA \), \( c = 14.678 \pm 0.001 \AA \), \( \beta = 106.70 \pm 0.01^\circ \), \( Z = 4 \) and \( \rho = 1.329 \) kg m\(^{-3}\). Data were collected to \( \theta = 40^\circ \) on a Nonius CAD4 diffractometer using filtered Cu-K\(_\alpha\) radiation. A Patterson map allowed ready location of the Rh atom, which yielded phases with which a Fourier map was calculated. As the Rh atom appeared on the glide plane at \( y = 1/4 \), superimposed mirror images of the structure resulted. Further inspection of the Patterson map allowed the Rh atom to be placed just off the plane and, together with the sulphur atoms, a map phased on these three revealed much of the centre of the molecule. A difference Fourier synthesis based on this extra information allowed the complete structure to be determined. Refinement of the structure with data to \( \theta = 30^\circ \) (838 reflections) gives a conventional \( R \)-factor of 0.07. Further refinement with all measured data is in progress. The structure of the central region of the molecule is shown in Fig. 1 whilst Table 1 lists the bond lengths and angles. No density other than diffraction ripple round the Rh atom has been detected on difference Fourier maps. Refinement of the two enantiomorphic

![Fig. 1. View of the molecular geometry of \( \{\eta^5-(C_5Me_5)Rh(S_2PMe_2)NCBPh_3\} \) (IVa). For clarity only the central part of the molecule is shown.](image)
TABLE 1

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>Bond angle (°)</th>
</tr>
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<tr>
<td>Rh–S(1)</td>
<td>2.41(1)</td>
</tr>
<tr>
<td>Rh–S(2)</td>
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</tr>
<tr>
<td>Rh–N–C</td>
<td>168.9(2.8)</td>
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<tr>
<td>Rh–N</td>
<td>167.6(2.6)</td>
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<tr>
<td>Rh–N–C–Me₅⁺</td>
<td>87.0(5)</td>
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<tr>
<td>Rh–S(1)–P</td>
<td>86.5(4)</td>
</tr>
<tr>
<td>N–C</td>
<td>1.81</td>
</tr>
<tr>
<td>N–Rh–S(1)</td>
<td>91.7(1.0)</td>
</tr>
<tr>
<td>C–B</td>
<td>1.58(5)</td>
</tr>
<tr>
<td>S(1)–Rh–S(2)</td>
<td>82.0(3)</td>
</tr>
<tr>
<td>S(1)–P</td>
<td>2.01(1)</td>
</tr>
<tr>
<td>N–Rh–C–Me₅⁺</td>
<td>123.0</td>
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<tr>
<td>S(2)–P</td>
<td>2.01(1)</td>
</tr>
<tr>
<td>S(1)–Rh–C–Me₅⁺</td>
<td>125.7</td>
</tr>
</tbody>
</table>

Torsion angle about C–N: -30.0°

*R*Distance to the centre of gravity of the pentamethylocyclopentadienyl ring.

(Rh–S₂) moieties gave R-factors of 0.39 and 0.50, the latter one being disregarded as incorrect.

Only two papers describing transition metal complexes of triphenylcyanoborate have been found in the literature (viz. \(\eta^5:(C_5H_5)M(PPh_3)_2NCBPh_3\) (M = Fe, Ru) [3], \(\eta^5:(C_5H_5)Ru(PPh_3)_2CNBPPh_3\) [3] and \((PPh_3)CuNCBPh_3\)_n CHChCl [2] and all these compounds have been prepared by means of direct reaction with NaBPh₃CN.

In this work, the BPh₃CN⁻ anion is generated in situ, possibly by reaction of hydrogen cyanide with BPh₄⁻. Earlier studies on C₅(CN)₄ have shown that hydrogen cyanide is readily released on reaction with alkoxide ions in the presence of certain catalysts [4].

Finally, it should be noted that this rather unusual reaction is not confined to rhodium. Thus, reaction of \(\eta^6:(C_6H_6)Ru(S_2PPh_2)Cl\) with a methanolic solution of C₅(CN)₄ and NaBPh₄ gives \(\eta^6:(C_6H_6)Ru(S_2PPh_2)NCBPh_3\) and \(\{Pd(S_2CNEt_2)(PMe_2Ph)Cl\}\) on treatment with AgBF₄/THF, (which gives \(\{Pd(S_2CNEt_2)(PMe_2Ph)(THF)\}\)¹ [5]), followed by C₅(CN)₄ and NaBPh₄ in methanol gives \(\{Pd(S_2CNEt_2)(PMe_2Ph)NCBPh_3\}\).

Acknowledgment

We thank Johnson–Matthey Ltd. for loans of rhodium trichloride, ruthenium trichloride and palladium chloride, the S.R.C. for research studentships (MCC, DRR) and the Physics Department of Edinburgh University for the use of their X-ray facilities.

References

REATIONS OF [RuCl₂L₃] (L = P(OMe)Ph₂, P(OEt)Ph₂) AND
[RuCl₂L₄] (L = P(OMe)₂Ph, PMe₂Ph, PMePh₂) WITH VARIOUS
DITHIOACID LIGANDS

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(Received 28 March 1977)

Reactions of [RuCl₂L₃] (L = PPh₃, PEtPh₂) and mer-
[RuCl₃(PMe₂Ph)₃] with various dithioacid ligands have previously
been reported. In all cases, the products obtained were the
six coordinate ruthenium(II) complexes [Ru(S-S)₂L₂] [S-S⁻ =
S₂PR₂ (R = Me, Et, Ph), S₂CNR₂ (R = Me, Et, Ph), S₂COMe] containing
bidentate dithioacid groups and, in most instances, cis tertiary
phosphine ligands. (1)

In this preliminary communication, we now report the
reactions of more [RuCl₂L₃] (L = P(OMe)Ph₂, P(OEt)Ph₂) (2) and
[RuCl₂L₄] (L = P(OMe)₂Ph (2), PMe₂Ph (3), PMePh₂ (4)) compounds with
various alkali metal dithioacid salts [S₂PR₂ (R = Me, Ph), S₂CNR₂
(R = Me, Et)]. Again, the final products are [Ru(S-S)₂L₂] (I)
but in some instances, several intermediate products can be
isolated and on the basis of this evidence, a general reaction
mechanism for the formation of (I) is proposed.

Thus, reaction of [RuCl₂L₄] (L = P(OMe)₂Ph, PMePh₂)
with all the dithioacid ligands above give compounds of type
(I) and no intermediate products are observed. However, when
[RuCl₂(PMe₂Ph)₄] is shaken with Na₂PMe₂H₂O in benzene, a
yellow solid analysing for [RuCl(S₂PMe₂)(PMe₂Ph)₃] (II) is
obtained. The 3¹P-{¹H} nmr spectrum of (II) at 213K in CDCℓ₃
consists of an AB₂ pattern [A, 20.4, B, 16.1 ppm; δ(AB) 174.2,
J(AB) 33.0 Hz] due to the three PMe₂Ph groups and a singlet at
94.0 ppm due to the S₂PMe₂ ligand. The ¹H nmr spectrum at
213K in CDCℓ₃ consists of two overlapping 'pseudo-doublets.'

†A 'pseudo-doublet' is a sharp doublet with additional signal
intensity situated between the doublet. This spectral pattern
is indicative of a small, but non-zero, J(P-H¹) value when
compared to |J(PH) + J(PH¹)| (6).
at 1.886 and three doublets at 1.19, 1.60 and 2.1786. This information is consistent with structure (II). Thus the 'pseudo-doublets' arise from the methyl groups of the two PMe₂Ph ligands trans to \( ^{-}S_2PMe_2 \) and the doublet at 1.606 from the other PMe₂Ph group (cf. fac - [OscI(S₂CNMe₂)(PMe₂Ph)₂] (5)). The other two doublets (which decouple at the same phosphorus frequency) are from the inequivalent methyl groups of the \( ^{-}S_2PMe_2 \) ligand.

![Structure (II)](image)

If (II) is dissolved in methanol, a red conducting solution is obtained and addition of NaB₄Ph gives red crystals analysing for \([\text{Ru}(S_2PMe_2)(PMe₂Ph)]_3\text{BPh}_4\) (III). A band at 580 cm⁻¹ in the infrared spectrum of (III) suggests bidentate coordination of the \( ^{-}S_2PMe_2 \) group (7) and conductivity studies in dichloromethane indicate a 1:1 electrolyte. The \( ^{31}\text{P}^{-}({}^1\text{H}) \) nmr spectrum of (III) at 213K in CDCl₃ consists of a doublet at 32.4 ppm (PMe₂Ph) and a quartet at 110.3 ppm (\( ^{-}S_2PMe_2 \)) [J(PP) 3.6Hz]. The \( ^1\text{H} \) nmr spectrum at 213K in CDCl₃ also indicates that rapid intramolecular scrambling of the PMe₂Ph groups is occurring since it consists of a 'pseudo-triplet' at 1.378 (PMe₂Ph) and a doublet at 1.828 (\( ^{-}S_2PMe_2 \)). This information is consistent with a monomeric, five coordinate structure and a preliminary X-ray structural analysis (8) on the related \([\text{Ru}(S_2PPh_2)(PMe₂Ph)]_3\text{BPh}_4\) complex indicates a square pyramidal structure (III).

![Structure (III)](image)

* A 'pseudo-triplet' pattern consists of a sharp doublet with a broad hump of comparable intensity situated between the doublet and signifies a relatively large J(PP') compared to the \( |J(\text{PH}) + J(\text{PH}^1)| \) value of cis-[Ru(S₂PMe₂)₂(PMe₂Ph)₂] (1).
Prolonged reaction of [RuCl₂(PMe₂Ph)₄] with NaS₂PR₂·2H₂O gives the previously reported cis-[Ru(S₂PMe₂)₂(PMe₂Ph)₂] (1).

Similar results to those above have been obtained for the reaction of [RuCl₂{P(OR)Ph₂}₃] (R=Me, Et) with NaS₂PR₂ (R=Me, Ph), and a reaction sequence for the formation of complexes cis-[Ru(S-S)₂L₂] from [RuCl₂L₃or₄] is outlined in the Scheme.

The complex containing one unidentate and one bidentate dithioacid ligand has not been isolated for the S₂PR₂ series. However, reaction of [RuCl₂(P(OME)Ph₂)₃] with NaS₂CNMe₂·2H₂O in benzene gives a yellow solid analysing closely for [Ru(S₂CNMe₂)₂(P(OME)Ph₂)₃]. Shaking this complex in dichloromethane for 12 hours then gives quantitative yields of [Ru(S₂CNMe₂)₂(P(OME)Ph₂)₂].

Reaction of [RuCl₂(P(OME)Ph₂)₃] and NaS₂CNMe₂·2H₂O in methanol however, produces initially a red solution containing the [Ru(S₂CNMe₂)₃(P(OME)Ph₂)]⁺ cation which on further reaction also gives [Ru(S₂CNMe₂)₂(P(OME)Ph₂)₂].

Further reactions of these monomeric ruthenium(II) tertiary phosphine, phosphinite and phosphonite complexes with a wide range of ligands are now in progress.

Acknowledgement

We thank Johnson-Matthey Ltd for loans of ruthenium trichloride, the S.R.C. for an award (W.J.S.) and Dr. A.S.F. Boyd for obtaining the 31P nmr spectra.

References

1. For detailed references see D.J. COLE-HAMILTON and T.A. STEPHENSON, J.C.S. Dalton, 739 (1974)


Metal Complexes of Sulphur Ligands. Part 15. Reaction of Bis[\((\eta^-\text{arene})\text{dichlororuthenium}\)] and Bis[\(\text{dichloro}(\eta^-\text{pentamethylcyclopentadienyl})\text{metal}\)] Complexes of Rhodium and Iridium with Various Dithioacid Ligands

By Donald R. Robertson and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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1978
Metal Complexes of Sulphur Ligands. Part 15.\textsuperscript{1} Reaction of Bis[(\textit{\textgamma}-arene)dichlororuthenium\textsuperscript{+}] and Bis[dichloro(\textit{\textgamma}-pentamethylcyclopentadienyl)metal] Complexes of Rhodium and Iridium with Various Dithioacido Ligands

By Donald R. Robertson and T. Anthony Stephenson,\textsuperscript{*} Department of Chemistry, University of Edinburgh, Edinburgh EH3 3JY

Reaction of the complexes \{[Ru(\textit{\textgamma}-arene)Cl\textsubscript{2}]\textsubscript{2} (1) \textit{arene} = C\textsubscript{6}H\textsubscript{6} or C\textsubscript{5}H\textsubscript{5}Me and \{[M(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl\textsubscript{2}]\textsubscript{2} (2) \textit{M} = Rh or Ir\} with excess of various dithioacids anions gives monomeric [Ru(\textit{\textgamma}-arene)(S-S)]\textsubscript{2} (3): S-S\textsuperscript{-} = [S\textsubscript{2}PPh\textsubscript{2}\textsuperscript{-}] or [S\textsubscript{2}CNMe\textsubscript{2}\textsuperscript{-}] or [S\textsubscript{2}CNMe\textsubscript{2} \textsubscript{2} \textsuperscript{-} or [S\textsubscript{2}PMe\textsubscript{2}\textsubsuperscript{2} \textsuperscript{-}]. Analytical data together with i.r. and \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{31}P n.m.r. studies show that these complexes contain both bin- and uni-dentate dithioacido ligands both in the solid state and in solution. For \{[M(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)\textsubscript{2}(S\textsubscript{2}CNMe\textsubscript{2})\textsubscript{2}] (M = Rh or Ir) and \{[Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)(S\textsubscript{2}COEt\textsubscript{2})\textsubscript{2}] in solution at higher temperatures, however, kinetic line-shape analysis indicates the occurrence of uni- and bi-dentate dithioacido exchange probably via a dissociatively controlled intramolecular mechanism.

Reaction of (1) \textit{arene} = C\textsubscript{6}H\textsubscript{6} and (2) \textit{M} = Rh with \{S-S\textsuperscript{-} = \textsuperscript{1} : \textsuperscript{1} mol ratio\} gives [Ru(\textit{\textgamma}-C\textsubscript{6}H\textsubscript{6})Cl(S\textsubscript{2}PPh\textsubscript{2})] and [Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl(S-S)] (5): S-S\textsuperscript{-} = \{S\textsubscript{2}PMe\textsubscript{2}\textsubscript{2} \textsuperscript{-} or [S\textsubscript{2}CNMe\textsubscript{2} \textsubscript{2} \textsuperscript{-} or [S\textsubscript{2}PMe\textsubscript{2}\textsubsuperscript{2} \textsuperscript{-}]. In methanol, (5) S-S\textsuperscript{-} = \{S\textsubscript{2}CNMe\textsubscript{2} \textsuperscript{-} gives the solvated cation [Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)(HOMe)(S\textsubscript{2}CNMe\textsubscript{2})\textsubsuperscript{+}] which reacts with various Lewis bases (L) to give [Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)(S\textsubscript{2}CNMe\textsubscript{2})(L)](PF\textsubscript{6})(L = PPh\textsubscript{3}, PMe\textsubscript{3}, CO, AsPh\textsubscript{3}, or C\textsubscript{6}H\textsubscript{6}N). Similar complexes can also be made by reaction of [Ru(\textit{\textgamma}-arene)Cl\textsubscript{2}(NC\textsubscript{3}H\textsubscript{5})] or [Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl(PPh\textsubscript{3})] with \{S-S\textsuperscript{-} \textsuperscript{1} : \textsuperscript{1} mol ratio\} and excess of Na[BPh\textsubscript{4}]. However, reaction of [5; S-S\textsuperscript{-} = \{S\textsubscript{2}CNMe\textsubscript{2} \textsuperscript{-} with excess of Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}PPh\textsubscript{2}(dppe) or Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{2}PPh\textsubscript{2}(dppm) in methanol gives the dimeric cation \{[Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)(S\textsubscript{2}CNMe\textsubscript{2})(dppm)] or [dppm])\} (7) and with C\textsubscript{6}H\textsubscript{6}Na and Na[BPh\textsubscript{4}] in methanol the cyanotriphenylborate complex \{[Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)(NC\textsubscript{6}H\textsubscript{6})(BPh\textsubscript{3})] \{S\textsubscript{2}CNMe\textsubscript{2} \textsuperscript{-} \} (8) is formed.

In previous papers on dithioacido complexes of the rarer platinum metals ruthenium,\textsuperscript{6,8} rhodium,\textsuperscript{7} and osmium,\textsuperscript{8} we have examined the reactions of mer-[MCl\textsubscript{3}(PMe\textsubscript{3}Ph\textsubscript{2})] and various ruthenium(tl) tertiary phosphate, phosphinite, phosphonite, and phosphinate complexes with dithioacids ligands, and also the reaction with \{[RuCl\textsubscript{2}-(diene)]\textsubscript{2} which gave the complexes cis-[Ru(diene)\textsubscript{2}(S\textsubscript{2}PMe\textsubscript{2})\textsubscript{2} (diene = bicyclo[2.2.1]hept-2,5-diene or cyclo-octa-1,5-diene).

In this paper, we report the full results\textsuperscript{9} of reactions of the related \{[Ru(\textit{\textgamma}-arene)Cl\textsubscript{2}] \{\textit{arene} = C\textsubscript{6}H\textsubscript{6} or C\textsubscript{5}H\textsubscript{5}Me\} and \{[M(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl\textsubscript{2}] \{\textit{M} = Rh or Ir\} complexes with some dithioacids anions. Although several reactions of (1) with unidentate Lewis bases have been reported,\textsuperscript{10,11} this is only the second study involving ligands capable of bidentate co-ordination. Earlier\textsuperscript{10} reaction of (1) with Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}PPh\textsubscript{2} (dppm) gave [Ru(\textit{\textgamma}-C\textsubscript{6}H\textsubscript{6})Cl\textsubscript{2}(dppm)] with the dppm ligand bound in a unidentate fashion whereas with Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}PPh\textsubscript{2} (dppb) the dimer [Ru(\textit{\textgamma}-C\textsubscript{6}H\textsubscript{6})Cl\textsubscript{2}(dpdb)] with a bridging dpdb group was formed. Similarly, with (2; \textit{M} = Rh, Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{3}PPh\textsubscript{2} (dppe) gave [Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl\textsubscript{2}(dppe)] and \{[Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl\textsubscript{2}] \{dppb\} with excess 1: 1 mol ratios of (2): dppe respectively. The complex \{[Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl\textsubscript{2}(dppe)]\textsuperscript{+} then reacted readily with \textsubscript{14}NH\textsubscript{4}[PF\textsubscript{6}] in ethanol to give [Rh(\textit{\textgamma}-C\textsubscript{5}H\textsubscript{5}Me)Cl(dppe)][PF\textsubscript{6}]\textsuperscript{12}

RESULTS AND DISCUSSION

Reaction of (1) \textit{arene} = C\textsubscript{6}H\textsubscript{6} in aqueous media with an excess of Na[S\textsubscript{2}P\textsubscript{3}R\textsubscript{2}] (R = Me, OMe, or OEt) or \textsubscript{14}NH\textsubscript{4}[S\textsubscript{2}PPh\textsubscript{2}] gave an immediate colour change from orange to deep red, and, after extraction with diethyl ether or methylene chloride, red crystalline solids were isolated. On the basis of analytical and molecular-weight data\textsuperscript{+} together with \textsuperscript{1}H and \textsuperscript{31}P n.m.r. (Tables I and 2 respectively) and i.r. studies (Experimental section) these solids are best formulated as monomeric [Ru(\textit{\textgamma}-C\textsubscript{6}H\textsubscript{6})(S\textsubscript{2}P\textsubscript{3}R\textsubscript{2})\textsubscript{2}] (3) with one bi- and one uni-
dentate $[S_2PR_4]^{-}$ group. Thus, the positions of $\nu(\text{PR}_3)$
in the i.r. spectra of the methyl- and phenyl-substituted $[S_2PR_4]^{-}$ complexes were diagnostic of the presence of both bi- and uni-dentate co-ordination (see refs. 13 and 14). Furthermore, the $^{1}H$ n.m.r. spectrum in CDCl$_3$ at 301 K of $[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$ consisted of a singlet at 8 5.88 p.p.m. due to the co-ordinated benzene ring and three doublets of relative intensity $2:1:1$ at 2.10, 1.95, and 1.89 p.p.m. respectively.

**Table 1**

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<th>Complex</th>
<th>Dithio-ligand</th>
<th>$\eta$-Arene</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$</td>
<td>2.10 (d) (12.0)</td>
<td>5.88 (s)</td>
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<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PPh_3)_3]$</td>
<td>1.86 (d) (12.0)</td>
<td>1.92 (d) (12.0)</td>
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<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PPh_3)_3]$</td>
<td>2.16 (d) (12.0)</td>
<td>2.21 (s)</td>
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<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$</td>
<td>4.15 (m)</td>
<td>5.76 (s)</td>
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<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$</td>
<td>3.75 (d) (14.0)</td>
<td>2.31 (s)</td>
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<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$</td>
<td>1.92 (d) (12.0)</td>
<td>2.00 (d)</td>
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</tr>
<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$</td>
<td>2.16 (d) (12.0)</td>
<td>3.75 (d)</td>
<td></td>
</tr>
</tbody>
</table>

$s$ = Singlet, $d$ = doublet, and $m$ = multiplet.

- $^{1}H$ N.M.R. data for various ruthenium(II) dithioacid complexes at 301 K.

**Table 2**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T$/K</th>
<th>$[S_2PR_4]$</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$</td>
<td>298</td>
<td>85.9 (s), 68.9 (s)</td>
<td>24.6 (d) (16.5)</td>
</tr>
<tr>
<td>$[\text{Ru}(\eta^3-\text{C}_3\text{H}_5)(S_2PPh_3)_3]$</td>
<td>298</td>
<td>88.0 (d) (16.5)</td>
<td>122.9 (d) (19.0)</td>
</tr>
<tr>
<td>$[\text{Rh}(\eta^3-\text{C}_3\text{H}_5)(S_2PPh_3)_3]$</td>
<td>343</td>
<td>103.9 (d) (10.1), 57.5 (d) (3.6)</td>
<td>34.9 (d) (11.3)</td>
</tr>
<tr>
<td>$[\text{Rh}(\eta^3-\text{C}_3\text{H}_5)(S_2PMe_3)_3]$</td>
<td>343</td>
<td>103.9 (d) (10.1), 57.2 (d) (3.6)</td>
<td>34.9 (d) (11.3)</td>
</tr>
</tbody>
</table>

- Phosphorus-31 n.m.r. data (proton-noise decoupled) for various ruthenium(II) and rhodium(III) dithioacid complexes in CDCl$_3$.

- $^{1}$H N.M.R. data for various ruthenium(II) dithioacid complexes at 301 K.
\(^{31}\)P n.m.r. spectra of the \([S_2PMe_3]^–\) and \([S_2PPb_3]^–\) complexes at 303 K each showed two resonances consistent with structure (3).

Thus, this spectroscopic evidence indicated stereochemical rigidity of these complexes in solution at ambient temperature, i.e. no rapid scrambling of the position also readily occurred on warming the freshly prepared solutions and, therefore, no detailed investigation could be undertaken of any fluxional processes which might be exhibited by these complexes in solution.

Furthermore, attempts to synthesise the related

<table>
<thead>
<tr>
<th>Complex</th>
<th>(T/K)</th>
<th>Dithio-ligand</th>
<th>(\tau-C_\text{Me}_8)</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2PMe_3)]_2)</td>
<td>343</td>
<td>2.02 (d) (12.6) [4]</td>
<td>1.71 (s) [5]</td>
<td></td>
</tr>
<tr>
<td>301</td>
<td>1.8-2.3 (m) [b] [4]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>273</td>
<td>2.11 (d) (12.5) [2]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.99 (d) (12.5) [1]</td>
<td></td>
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<tr>
<td>1.93 (d) (12.5) [1]</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>301</td>
<td>7.1-8.0 (m) [4]</td>
<td>1.52 (s) [3]</td>
<td></td>
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<tr>
<td>357</td>
<td>3.65 (s) [2], 3.16 (s) [2]</td>
<td>1.73 (s) [5]</td>
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<td></td>
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<tr>
<td>387</td>
<td>3.62 (s) [2], 2.80 (s) [2]</td>
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<tr>
<td>253</td>
<td>4.17 (d) (7.0) [4], 3.65 (7.0) [4]</td>
<td>1.75 (s) [16]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>301</td>
<td>4.12 (d) (7.0) [4], 3.61 (7.0) [4]</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1.20 (m) (7.0) [12], 1.75 (s) [16]</td>
<td></td>
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<td></td>
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<tr>
<td>343</td>
<td>4.13 (br), 3.68 (br), 1.29 (t) (7.0)</td>
<td>1.75 (s) [16]</td>
<td></td>
<td></td>
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<tr>
<td>359</td>
<td>3.77 (br), 1.29 (t) (7.0)</td>
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</tr>
<tr>
<td>301</td>
<td>4.03 (s) [1], 4.00 (s) [1]</td>
<td>1.79 (s) [5]</td>
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</tr>
<tr>
<td>45.0 (q), 4.48 (q) (7.0) [4], 1.33 (t) (7.0) [6]</td>
<td>1.78 (s) [16]</td>
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</tr>
<tr>
<td>301</td>
<td>1.33 (t) (7.0) [6]</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2COMe)_2])</td>
<td>301</td>
<td>3.20 (s)</td>
<td>1.73 (s) [5]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2COMe)]_2)</td>
<td>301</td>
<td>3.21 (s) [2], 2.00 (d) (13.0) [2]</td>
<td>1.79 (s) [5]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2COMe)]_2)</td>
<td>301</td>
<td>8.0 (m), 7.1 (m) [10], 1.78 (s) [16]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)_2](S_2COMe]_2)</td>
<td>301</td>
<td>4.05 (s) [1], 3.28 (s) [2]</td>
<td>1.78 (s) [5]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>301</td>
<td>2.20 (s)</td>
<td>1.78 (s) [5]</td>
<td>6.7-7.3 (m)</td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>301</td>
<td>1.69 (d) (13.0) [3], 1.32 (d) (4.0) [16]</td>
<td>1.92 (d) (10.0) [3], 7.0-7.5 (m) [10]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>1.54 (d) [16]</td>
<td>8.23 (d), 1.29 (m) [28]</td>
<td>7.0-7.4 (m) [20]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>301</td>
<td>2.35 (s) [6]</td>
<td>2.01 (s) [16]</td>
<td>2.10 (m) (10.0) [3]</td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>301</td>
<td>3.21 (d) (13.0) [2]</td>
<td>1.32 (d) (4.0) [16]</td>
<td>6.7-7.5 (m) [40]</td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>2.95 (s) [6]</td>
<td>1.34 (d) (4.0) [16]</td>
<td>6.7-7.7 (m) [40]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>2.12 (d) (12.5) [3], 0.75 (d) (13.0) [1]</td>
<td>1.60 (d) (4.0) [16]</td>
<td>2.34 (d) (4.0) [3], 7.0-7.5 (m) [10]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>2.05 (s) (12.5) [6], 0.75 (d) (13.0) [1]</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>0.89 (d) (12.5) [3]</td>
<td>1.48 (d) (4.0) [5], 0.75 (d) (13.0) [1]</td>
<td>2.04 (d) (10.0) [3], 6.7-7.5 (m) [10]</td>
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</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>3.17 (s) [2]</td>
<td>1.79 (s) [5]</td>
<td>6.7-7.5 (m) [5]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>3.90 (s) [2], 3.28 (s) [2]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>357</td>
<td>3.23 (s) [2], 2.36 (s) [2]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ir}(\tau-C_\text{Me}_8)(S_2CNMe)]_2)</td>
<td>402</td>
<td>3.17 (s) [br], 2.47 (s) [br]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(t\) = Triplet, \(q\) = quartet.

* In CDCl₃ unless otherwise stated. ¹ J(PH) (in Hz) values are given in parentheses. Numbers in square brackets indicate normalised integrated intensities. ² In chlorobenzene. ³ J(CH₃CH₃) in Hz. ⁴ In (CD₃)₂SO. ⁵ Contaminated by some \([\text{Rh}(\tau-C_\text{Me}_8)(SMeO)(S_2CNMe)]_2\) [PF₆] (integration not exact). ⁶ J(PH)(CMe₆) in Hz. ⁷ Methyl resonance of PF₆. ⁸ Pyridine resonance: others masked by phenyl resonances. ⁹ In (CD₃)₂CO. ¹° Intensity includes aromatic resonances from other ligands. ¹¹ CH₃ protons in p-n-dpp too weak for accurate measurement. ¹² Silicon oil capillary as external reference. ¹³ ABM₂ system with J(AB) 14.0 Hz, 8(AB) 19.5 Hz. ¹⁴ ABM₄ system with J(AB) 14.0 Hz, 8(AB) 16.4 Hz.

uni- and bi-dentate \([S_2PR_2]^–\) groups was observed \([c_{13}^{13} \text{P}([\text{PR}_2'](S_2PR_2)]\). However, on leaving as a solid in air for \(R = \text{Me}\) or in solution (all \(R\)) for several days some decomposition occurred as indicated by the appearance of free benzene in the \(^1\)H n.m.r. spectra and of \([S_2PR_2]^–\) ion in the \(^{31}\)P n.m.r. spectra. Decomplexes \([\text{Ru}(\tau-C_\text{Me}_8)(S-S)]\) \((S-S = [S_2COR])\) or \([S_2CNR_2]^–\) by the same methods were unsuccessful. Instead, greenish brown paramagnetic solids were obtained which contained no co-ordinated benzene ring (n.m.r. evidence) and therefore were not investigated further, although most probably mixtures of species.
such as [Ru(\text{S}_2\text{CNR}_2)_2], [Ru\text{Me}(\text{S}_2\text{CNR}_2)_2]\text{Cl}_2, \text{etc.} were formed.

In an attempt to retain the arene ring, the methyl-substituted arene dimer \([\text{Ru}(\text{S}_2\text{CNR}_2)_2]\text{Cl}_2\text{Me}_2\) was treated with Na\text{S}_2\text{CNR}_2 and K\text{S}_2\text{COR} but again ring displacement accompanied chloride-ion substitution in each case. However, with the less nucleophilic \([\text{S}_2\text{PR}_3]^-\) (R = Me or Ph), \([\text{Ru}(\text{S}_2\text{CNR}_2)_2]\text{S}_2\text{PR}_3\text{Me}_2\) were isolated and characterised as above (Tables 1 and 2). For R = Me, the complex is more stable than \([\text{Ru}(\text{S}_2\text{CNR}_2)_2]\text{S}_2\text{PR}_2\text{Me}_2\) since it can be heated to 320 K in CDCl₃ without decomposition, although no fluxional behaviour was observed up to this temperature.

Since the reactions of (1) with dithioacid ligands did not generate a very wide range of stable \(\pi\)-bonded benzene ruthenium(II)-sulphur complexes, it was decided to investigate the reactions of the isoelectronic \([\text{Rh}(\text{S}_2\text{CNR}_2)_2]\text{Cl}_2\text{Me}_2\) (2) with these ligands because earlier studies \(^{12}\) had indicated the inertness of the Rh-\text{C}_5\text{Me}_5 bond towards a range of nucleophiles. Thus (2) was dissolved in either water or methyl cyano and treated with an excess of \([\text{S-S]}^- = [\text{S}_2\text{PR}_3]^-\), \([\text{S}_2\text{PR}_3]\text{Me}_2^-\), \([\text{S}_2\text{CNR}_2]\text{Me}_2^-\), \([\text{S}_2\text{CNMe}_2]\text{Me}_2^-\), \([\text{S}_2\text{COMe}_2]^-\), or \([\text{S}_2\text{COEt}]^-\) to give either orange-red solutions which could be extracted with ethyl ether or methylene chloride or orange-red precipitates directly which were readily recrystallised. From analytical and molecular-weight data and i.r. and n.m.r. spectroscopy (Tables 2–4) these products were formulated as monomeric of \([\text{Rh}(\text{S}_2\text{CNR}_2)_2]\text{S}_2\text{PR}_3\text{Me}_2\) in CDCl₃ consisted of a singlet at \(\delta 1.71\) p.p.m. (from the \text{C}_5\text{Me}_5 ring) and a rather complicated multiplet between 1.8 and 2.3 p.p.m. On cooling, this multiplet was resolved into three
doublets of relative intensity 2:1:1 at 2.11, 1.93, and 1.90 p.p.m. respectively \(\delta 7.25 \text{ Hz}\) as expected for structure (4a; R = Me). On warming the solution, the doublets broadened and coalesced at 333 K giving a single doublet centred at 2.02 p.p.m. \(\delta 7.25 \text{ Hz}\) (Table 3). This phenomenon, which is concentration independent and reversible with temperature, suggested that rapid intramolecular scrambling of dithioacid
groups \(\text{see equation (1)}\) was occurring at higher temperatures \(\text{cf.}^{16} [\text{Pt(Pr} \text{R}_3\text{)}_2]\text{S}_2\text{PR}_3\text{Me}_2\). The fluxional behaviour of this complex was also monitored by \(\text{\textsuperscript{31}P}\)
n.m.r. spectroscopy (Table 2). At ambient temperatures the spectra consisted of two sharp resonances which broadened on warming. Although coalescence of the peaks was not achieved in CDCl₃ [because of their large separation (1 474 Hz) and the low boiling point of CDCl₃], use of chlorobenzene as solvent produced a single ³¹P n.m.r. resonance, indicative of fast uni- and bi-dentate [S₂PMe₃]⁻ exchange at 405 K.

For [Rh(η-C₆H₅)(S₂CNMe₃)]⁺, the ¹H n.m.r. spectrum in CDCl₃ at ≤ 301 K consisted of two singlets of equal intensity at 8 3.58 and 3.15 p.p.m. (from [S₂CNMe₃]⁻) in addition to the singlet at 1.73 p.p.m. from the C₆H₅ ring. Here the two methyl groups on the bidentate

Interestingly, for [Rh(η-C₆H₅)S₂CN_{Et₂}²⁺], the ¹H n.m.r. spectrum in CDCl₃ at 253 K for the methylene region consisted of an overlapping doublet of quartets centred at 8 4.17 p.p.m. and a multiplet centred at 3.66 p.p.m. which was readily analysed as arising from an ABM₃ spin system (Table 3). On increasing the temperature to 343 K, the doublet first became a single quartet and then broadened, whereas for the multiplet

<table>
<thead>
<tr>
<th>Complex</th>
<th>ln(½τ) [s⁻¹]</th>
<th>Ε [kJ mol⁻¹]</th>
<th>ΔH [kJ mol⁻¹]</th>
<th>ΔS [kJ mol⁻¹]</th>
<th>ΔG [kJ mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(η-C₆H₅)S₂CNMe₃]⁺</td>
<td>-0.74</td>
<td>86.3 ± 6</td>
<td>83.8 ± 6</td>
<td>30.5 ± 43</td>
<td>74.7 ± 7</td>
</tr>
<tr>
<td>[Rh(η-C₆H₅)S₂COE₃]⁺</td>
<td>-1.63</td>
<td>81.1 ± 3</td>
<td>80.6 ± 3</td>
<td>28.8 ± 20</td>
<td>77.0 ± 3</td>
</tr>
</tbody>
</table>

= 72.0 kJ mol⁻¹ (T = 359 K). * Obtained from monitoring methylene resonances. * ΔG = 75.2 ± 3 kJ mol⁻¹ (T = 381 K for methylene resonances). * T > 402 K.

data given in Table 5 are rather large, especially for the ΔS^1 values, comparisons with kinetic data obtained for the related [Pt(S-S)Cl] complexes 13 are of interest. In the latter, the negative ΔS^1 values and the dependence of rate on both dithioacetic acid and L group were interpreted in terms of an aromatic intramolecular mechanism. In this instance, the positive ΔS^1 values indicate an essentially dissociative intramolecular process which is consistent with other kinetic studies on rhodium(II) complexes. 17

For completion, the analogous [Ir(η-C₅Me₅)(S₂CNMe₂)] was synthesised from [[Ir(η-C₅Me₅)(Cl)] 18 and an excess of Na[S₂CNMe₂]·2H₂O. A line-shape analysis performed on the 1H n.m.r. spectra of this complex gave the kinetic parameters shown in Table 5. Again, an essentially dissociative, intramolecular exchange process was suggested (positive ΔS^1 value) and the considerably larger ΔG^∞ value compared to the rhodium analogue was in keeping with the more inert co-ordination sphere expected for a third-row compared to a second-row transition-metal complex belonging to the same triad. Finally, the excellent agreement between ΔG^∞ and ΔG^∞ (T_c = coalescence temperature) for these complexes provided a good internal check on the validity of this line-shape data.

\[ \text{S-S}^* = \{\text{S₂CNMe₂}^2\}^{\cdot\cdot\cdot}\text{[S₂PMe₅]}^{\cdot\cdot\cdot}\text{[S₂PPh₂]}^{\cdot\cdot\cdot} \]

If (2; M = Rh) was treated with either Na[S₂CNMe₂]·2H₂O, Na[S₂PMe₅]·2H₂O, or [NH₄][S₂PPh₂] in a 1:2 mol ratio, then the monomeric complexes [Rh(η-C₅Me₅)Cl(S-S)] (5) were formed. Similarly, reaction of (1; arone - C₆H₆) with [NH₄][S₂PPh₂] (1:2 mol ratio) in methanol gave [Ru(η-C₅Me₅)Cl(S₂PPh₂)], although with Na[S₂PMe₅]·2H₂O only [Ru(η-C₅Me₅)(S₂PMe₅)] could be isolated. Attempts to make [Rh(η-C₅Me₅)Cl(S₄COR)] were also unsuccessful due to the formation of inseparable mixtures whose i.r. spectra indicated the formation of some dithiocarbonate [S₂CO]⁺ as well as alkyl dithiocarbonate complexes.

The above complexes have been fully characterised by analytical data, i.e. [ν(PS₄) and ν(CN) positions], and 1H and 31P n.m.r. studies (Tables 2–4). For example, the 31P n.m.r. spectrum of [Rh(η-C₅Me₅)Cl(S₂PMe₅)] in CDCI₃ at 298 K contained a doublet at 87.6 p.p.m. [3](RhP) 10.8 Hz [cf. [Rh(η-C₅Me₅)(S₂PMe₅)] whose 31P n.m.r. spectrum at 233 K had two doublets at 83.9 [3](RhP) 10.1] and 57.5 p.p.m. [3](RhP) 3.6 Hz]. This clearly showed that the higher-frequency resonances were due to bidentate [S₂PMe₅]⁻ groups and that these could also be differentiated from tridentate [S₂PMe₅]⁻ groups by virtue of their larger [3](RhP) coupling constants. Similarly, for [Pt(PMe₅)Ph₃] (S₂PPPh₂), it was found that at 218 K the 31P n.m.r. signal of the bidentate [S₂PPPh₂]⁻ group was a triplet at 87.8 p.p.m. [3](PtP) 276.6 Hz and the unidentate [S₂PPPh₂]⁻ group gave a triplet at 57.1 p.p.m. [3](PtP) 105.3 Hz. 18 Further examples include [Ru(η-C₅Me₅)Cl(S₂PPPh₂)] (31P n.m.r. at 298 K showed a singlet at 91.7 p.p.m. compared to [Ru(η-C₅Me₅)](S₂PPPh₂), singlet at 85.9 and 68.9 p.p.m.) and [Pt(PPh₅)₂] (S₂PPPh₂)(PF₆) whose 31P n.m.r. spectrum had a triplet at 92.1 p.p.m. [3](PtP) 254.7 Hz) from the bidentate [S₂PPPh₂]⁻ group. 19

Thus, 31P n.m.r. chemical shifts and coupling constants (where appropriate) in these [S₂PR₂]⁻ complexes are, like ν(PS₄) values, 12,14 diagnostic of the type(s) of co-ordination present. The complexes [Rh(η-C₅Me₅)Cl(S-S)] (6) were useful starting materials for synthesising a variety of complexes. Thus, reaction of (6; S-S⁻ = [S₂CNMe₂]⁻) in methanol with an excess of either LiBr, NaI, or KSCN led to replacement of the chloride group to give [Rh(η-C₅Me₅)(S₂CNMe₂)] (X = Br⁻; I⁻; or SCN⁻), whereas reaction with Na[S₂PMe₅]·2H₂O (1:1 mol ratio) in methyl cyanide gave the mixed dithiocarbamate [Rh(η-C₅Me₅)(S₂CNMe₂)(S₂PMe₅)] (6). The i.r. spectrum of this complex had bands at 1524 and 600 cm⁻¹ indicative of bidentate [S₂CNMe₂]⁻ (ref. 19) and unidentate [S₂PMe₅]⁻ co-ordination 12 respectively. Like the analogous [Pt(PR₃)(S₂CNMe₂)(S₂PMe₅)] (PR₃ = PMe₅ or PPh₃), 1H n.m.r. studies show that (6) is stereochemically rigid at elevated temperatures, a fact attributed to the low nucleophilicity of [S₂PMe₅]⁻ compared to [S₂CNMe₂]⁻. Similarly, reaction of (5; S-S⁻ = [S₂CNMe₂]⁻) with [NH₄][S₂PPh₂] and

K[S₂COME] (1:1 mol ratio) gave [Rh(η-C₅Me₅)(S₂CNMe₂)(S₂COME)] and [Rh(η-C₅Me₅)(S₂CNMe₂)(S₂COME)] respectively. Again, i.r. studies on [Rh(η-C₅Me₅)(S₂CNMe₂)(S₂PPh₂)] clearly indicated unidentate [S₂PPPh₂]⁻ [ν(PS₄)] at 646 and 535 cm⁻¹ 14 and bidentate [S₂CNMe₂]⁻ [ν(CN)] at 1520 cm⁻¹ 10 coordination. For [Rh(η-C₅Me₅)(S₂CNMe₂)(S₂COME)] the


value of ν(CN) (1530 cm⁻¹), together with the position of
the methyl singlet (3.28 p.p.m.) in its ¹H n.m.r.
spectrum (which compared favourably with those in
[Rh(γ-C₅H₅)Cl(S₂CNMe₂)] (3.32) and [Rh(γ-C₅H₅)
(S₂CNMe₂)(S₂PMe₅)] (3.21 p.p.m.)), also supported bi-
dentate [S₂CNMe₂]⁻ co-ordination.

If [Rh(γ-C₅H₅)Cl(S₂CNMe₂)] was dissolved in methanol
a conducting solution was obtained and addition of
Na[BPh₄] precipitated solvated [Rh(γ-C₅H₅)Cl][OMe]-
(S₂CNMe₂)[BPh₄]. The latter was then used as a pre-
cursor for synthesising a range of cationic complexes
of the type [Rh(γ-C₅H₅)(S₂CNMe₂)L][BPh₄] (L = PPh₃,
PMe₂Ph₂, CO, AsPh₃, or C₅H₅N). Similarly, reaction
of [Rh(γ-C₅H₅)Cl(S₂PPh₂)] and [Ru(γ-C₅H₅)Cl(S₂PPh₂)]
in alcoholic media with excess of L followed by addition
of [NH₄][PF₆] gave the analogous [Rh(γ-C₅H₅)(S₂PPh₂)L]-
[PF₆] (L = PMe₂Ph₂ or PPh₃) and [Ru(γ-C₅H₅)-
(S₂PPh₂)L][PF₆] (L = PPh₃, PMe₂Ph₂, PO(Me)₂, SbPh₃,
or C₅H₅N) respectively. Alternatively, this type of
complex could be prepared by shaking either [Ru(arene)-
Cl₂(NC₅H₅)] (arene = C₅H₅, or C₅H₅Me)¹⁰, Na[S₂PMe₅]·
2H₂O (or [NH₄][S₂PPh₂]) (1 : 1 mol ratio), and excess of
Na[BPh₄] in ethanol to give [Rh(γ-C₅H₅)(PPh₃)(S₂S)]·
[BPh₄].

All these complexes, which are 1 : 1 electrolytes in
methylen chloride, have been fully characterised by
elemental analyses, and i.r. (which showed bidentate
dithiocarbac co-ordination), ¹H, and, in certain cases,
³¹P n.m.r. spectroscopy (Tables 2-4). For example, the
³¹P n.m.r. spectrum of [Rh(γ-C₅H₅)(PPh₃)(S₂PMe₅)]-
[BPh₄] in CDCl₃ at 298 K consisted of an overlapping
doublet of doublets at δ 103.3 p.p.m. (bidentate
[S₂PMe₅]⁻ resonance) due to the fortuitously similar
values of ³¹/P(RhP) 9.2 and ³¹/P(PPh₃) 9.7 Hz, and a doublet
of doublets at 35.9 p.p.m. (PPh₃) with ¹/J(RhP) 144.8
and ³¹/J(PPh₃) 9.7 Hz.

Attempts to make related cationic complexes by
reaction of (5; S⁻⁻ = [S₂CNMe₂]⁻), a large anion, and
potentially bidentate ligands such as 2,2'-bipyridyl,
1,10-phenanthroline, and cyclo-octa-1,5-diene were
unsuccessful. However, treatment of (5; S⁻⁻ =
[S₂CNMe₂]⁻) with an excess of dppe in methanol, followed
by addition of Na[BPh₄] to the resulting yellow solution,
gave a yellow precipitate which analysed closely for the
dimer [(Rh(γ-C₅H₅)(S₂CNMe₂))(dppe)][BPh₄]₂.
Support for this formulation came from the conductivity
value in methylene chloride which was considerably
higher than the values found earlier, and elsewhere,¹⁰ for
1 : 1 electrolytes containing similar anions. The i.r.
spectrum indicated bidentate [S₂CNMe₂]⁻ co-ordination,
and the ¹H n.m.r. spectrum integrated for one dppe to
two [S₂CNMe₂]⁻ to two C₅H₅ groups. Furthermore,
the small doublet splitting of 3.0 Hz of the latter resonance,
resulting from coupling of a phosphorus ligand to the C₅H₅
protons, indicated that only one P atom was bound to
each rhodium atom. On the basis of this evidence the
complex was formulated with structure (7) (cf.¹² the
related [(Rh(γ-C₅H₅)Cl₂)(dppe)][BPh₄]). Likewise (5; S⁻⁻ =
[S₂CNMe₂]⁻) reacted with excess of dppm and Na[BPh₄]
in methanol to give [(Rh(γ-C₅H₅)(S₂CNMe₂)(dppm))-]
[BPh₄]₂ and [Rh(γ-C₅H₅)(S₂PPh₂)(dppm)]·

In view of the above studies, a surprising reaction
occurred when (5; S⁻⁻ = [S₂PMe₅]⁻, [S₂PPh₂]⁻, or
[S₂CNMe₂]⁻) were treated with C₅H₅(CN)₄ in methanol,
followed by addition of Na[BPh₄]. Instead of the
expected [Rh(γ-C₅H₅)(C₅H₅(CN)₄)(S⁻⁻)][BPh₄], yellow
cyanotriphenylborate anion was based on spectroscopic
data. Thus, the i.r. spectra of all complexes (8) con-
tained a CN stretching band at ca. 2 180 cm⁻¹, indicative
of cyanide rather than isocyanide co-ordination of the
[BPh₄(CN)]⁻ group and all showed bands characteris-
tic of bidentate co-ordination of the dithiocarb ligands.
The mass spectrum of (8; S⁻⁻ = [S₂CNMe₂]⁻) had a
peak at m/e 628 corresponding to [Rh(C<sub>4</sub>Me<sub>5</sub>)(NCBP<sub>2</sub>H<sub>3</sub>)(S<sub>CN</sub>Me<sub>3</sub>)]<sup>+</sup> together with a fragmentation pattern consistent with this formulation. Furthermore, the <sup>1</sup>H n.m.r. spectrum of (8; S–S<sup>–</sup> = [S<sub>CN</sub>Me<sub>3</sub>]<sup>–</sup>) in CDC<sub>3</sub> at 303 K had the expected three signals at 1.79 (s) (C<sub>4</sub>Me<sub>3</sub>), 3.17 (s) ([S<sub>CN</sub>Me<sub>3</sub>]<sup>–</sup>), and 7.0–7.5 (m) p.p.m. (PH<sub>3</sub>BCN) of relative intensity 1:2:5:

However, unequivocal proof of the solid-state structure of (8; S–S<sup>–</sup> = [S<sub>CN</sub>Me<sub>3</sub>]<sup>–</sup>) came from a preliminary X-ray structural analysis which showed a Rh–N distance of 2.00 Å. In fact, only a few examples of transition-metal complexes of cyanotriphenylborate have been found in the literature (viz. M=[C<sub>5</sub>H<sub>5</sub>N]= (NCBP<sub>2</sub>H<sub>3</sub>)<sup>–</sup>) (M = Fe or Ru) and [Ru(C<sub>5</sub>H<sub>5</sub>N)= (NCBP<sub>2</sub>H<sub>3</sub>)<sup>–</sup>]. and [Cu(NC<sub>5</sub>H<sub>5</sub>N)=(NCBP<sub>2</sub>H<sub>3</sub>)<sup>–</sup>]) and [C<sub>4</sub>N] and all these were prepared by means of direct reaction with Na(BPh<sub>3</sub>)(CN). Here, the (BPh<sub>3</sub>)(CN)<sup>–</sup> anion was generated in situ, possibly by reaction of hydrogen cyanide with BPh<sub>3</sub><sup>+</sup>. Since earlier studies on C<sub>4</sub>N<sub>4</sub> have shown that HCN was readily released on its reaction with alkoxide ions in the presence of certain catalysts.

However, it should be noted that this rather unusual reaction is not confined to rhodium. Thus, reaction of [Ru(C<sub>5</sub>H<sub>5</sub>N)= (NCBP<sub>2</sub>H<sub>3</sub>)<sup>–</sup>] with a methanolic solution of C<sub>4</sub>N<sub>4</sub> and Na(BPh<sub>3</sub>) gave [Ru(C<sub>5</sub>H<sub>5</sub>N)= (NCBP<sub>2</sub>H<sub>3</sub>)<sup>–</sup>][Na(BPh<sub>3</sub>)(C<sub>4</sub>N)]. Also, [PdCl(PhMePh)]= (S<sub>CN</sub>Et<sub>3</sub>)<sup>2</sup>] on treatment with Ag(BPh<sub>3</sub>)<sup>–</sup>-tetrahydrofuran (thf) (which gave [Pd(PhMePh)(S<sub>CN</sub>Et<sub>3</sub>)(thf)]) followed by C<sub>4</sub>N<sub>4</sub> and Na(BPh<sub>3</sub>) in methanol gave [Pd(NC<sub>5</sub>H<sub>5</sub>N)(PhMePh)= (S<sub>CN</sub>Et<sub>3</sub>)(S<sub>CN</sub>Et<sub>3</sub>)].

Finally, by analogy with earlier studies on complexes of type cis-[Pd(PPh<sub>3</sub>)(S<sub>CN</sub>Me<sub>3</sub>)]<sup>2</sup>] (M = Ru or Os), which undergo ready cleavage of M=S bonds with CO to give complexes such as [M(CO)(PPh<sub>3</sub>)(S<sub>CN</sub>Me<sub>3</sub>)]<sup>2</sup>] containing a unidentate [S<sub>CN</sub>Me<sub>3</sub>]<sup>–</sup> linkage, it was hoped to generate [Rh(C<sub>5</sub>H<sub>5</sub>N)(S<sub>CN</sub>Me<sub>3</sub>)]<sup>2</sup>] containing two unidentate [S<sub>CN</sub>Me<sub>3</sub>]<sup>–</sup> ligands by reaction of [Rh(C<sub>5</sub>H<sub>5</sub>N)(S<sub>CN</sub>Me<sub>3</sub>)]<sup>2</sup>] with various L in non-polar solvents. However, even in benzene with PPh<sub>3</sub>Me, the only product isolated was [Rh(C<sub>5</sub>H<sub>5</sub>N)(PPh<sub>3</sub>Me)(S<sub>CN</sub>Me<sub>3</sub>)]<sup>2</sup>] indicating that the loss of the unidentate [S<sub>CN</sub>Me<sub>3</sub>] group here is always the preferred process. This complex, which was fully characterised by analytical and spectroscopic data (see Table 3), showed no evidence for bidentate–ionic diiodooxo exchange up to 343 K (cf. the related [Pt(PR<sub>3</sub>)(S–S)][S–S]= [S<sub>CN</sub>Me<sub>3</sub>]<sup>–</sup> (ref. 27) or [S<sub>CN</sub>Me<sub>3</sub>]<sup>2</sup>] (ref. 13)).

**EXPERIMENTAL**

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab model 301A vapour.

* Very recently, some platinum complexes containing both NCBP<sub>2</sub>H<sub>3</sub> and CNBP<sub>2</sub>H<sub>3</sub> linkages have been prepared, both by reaction of the cyanocyclohexene complexes with BPh<sub>3</sub> and by reaction of [PdCl(PhMePh)= (S<sub>CN</sub>Et<sub>3</sub>] with Na(BPh<sub>3</sub>)(CN).

† Hydrogen-1 spectral data for other rhodium(ii) diiodooxo complexes are given in the Supplementary Publication.

Pressure osmometer calibrated with benzyl. Infrared spectra were recorded in the 250—4000 cm<sup>-1</sup> region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Conductivity measurements were made on a Portland Electronics 310 conductivity bridge at 298 K. Hydrogen-l n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable temperature probe and on a Varian EM-360 spectrometer. Phosphorus-31 n.m.r. spectra (proton-noise decoupled) were obtained on a Varian XL-100 spectrometer operating in the pulse and Fourier-transform modes at 60.5 MHz (31P chemical shifts quoted in p.p.m. to high frequency of 85% H<sub>2</sub>PO<sub>4</sub>), and 13C n.m.r. spectra (proton-noise decoupled) on a Varian CFT-20 spectrometer operating at 20 MHz (13C chemical shifts quoted in p.p.m. to high frequency of SiMe<sub>3</sub>) Mass spectra were recorded on an A.E.I. MS8 spectrometer. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. The kinetic line-shape analysis was carried out as detailed in ref. 13 and (AG<sub>r</sub>)<sup>°</sup> calculated by use of equation (2) (where T<sub>r</sub> = coalescence temperature and k<sub>r</sub> = rate constant at temperature T<sub>r</sub> = (πΔν/2k<sup>–</sup>) where Δν = separation of peaks in the absence of exchange.

Analytical, molecular weight, and conductivity data are given in Supplementary Publication No. SUP 22220, and in n.m.r. data for ruthenium, and selected rhodium and iridium complexes in Tables 1 and 3, and in n.m.r. data in Table 2. Infrared bands diagnostic of the mode of coordination of [S<sub>CN</sub>Me<sub>3</sub>] (ref. 13) and [SPh<sub>3</sub>]<sup>–</sup> ligands are listed for the various complexes (b = bidentate, u = unidentate, i = ionic). Finally, all the reactions under reflux were carried out in degassed solvents under an atmosphere of nitrogen.

Ruthenium Complexes.—(γ-Benzene)bis(dimethylphosphinodithiocarboxyl) ruthenium(ii). The complex ([Ru(C<sub>5</sub>H<sub>5</sub>N)= (NCBP<sub>2</sub>H<sub>3</sub>)<sup>–</sup>]<sup>2</sup>] (0.20 g, 0.4 mmol) was dissolved in water with gentle warming. Excess of Na(S<sub>CN</sub>Me<sub>3</sub>)=2H<sub>2</sub>O (0.55 g, 5.84(b) cm<sup>–3</sup>) was then added to the orange solution, producing an immediate colour change to deep red. Extraction with diesel oil, followed by separation and drying over anhydrous sodium sulphate gave a red ether solution. Concentration of this solution gave a dark red crystalline precipitate, m.p. 140 °C (decomp.), ν(P<sub>S</sub>) at 603(u) and 584(b) cm<sup>–1</sup>. (γ-Benzene)bis(OO’-diethyl dithiophosphato)-ruthenium(ii) was similarly prepared as a dark red crystalline solid, m.p. 110 °C (decomp.), from [Ru(C<sub>5</sub>H<sub>5</sub>N)= (NCBP<sub>2</sub>H<sub>3</sub>)<sup>–</sup>](ref. 13) and Na[S<sub>CN</sub>Me<sub>3</sub>](OMe<sub>3</sub>)<sup>–</sup>. A similar preparation gave an orange oil on concentration of the
ether solution. This was dissolved in the minimum volume of methanol and addition of water then precipitated slowly an orange crystalline solid, m.p. 132 °C (decomp.).

(η-Benzene)bis(diphenylphosphinothiadiato)rhodium(ii). The product from reaction of [Ru(η-C5H5)Cl]2 and excess of [NH4][S2PPh2] in water was extracted with methylene chloride. Addition of light petroleum (b.p. 60—80 °C) to this solution then gave a brick-red solid. m.p. 176 °C, v(PS) at 643 and 548(u) and 610 and 575(b) cm⁻¹.

Bis(dimethylphosphinothiadiato)(η-mesitylene)rhodium(ii), red, m.p. 145 °C (decomp.), v(PS) at 601(u) and 585(b) cm⁻¹, and bis(dimethylphosphinothiadiato)(η-mesitylene)rhodium(ii), orange-red, m.p. 186 °C, v(PS) at 647 and 541(u), and 604 and 580(b) cm⁻¹, were prepared as above using [Ru(η-C5H5)Cl]2 and an excess of Na[S2PMe2]2H2O or [NH4][S2PPh2] respectively, the products precipitating directly from the aqueous media.

(η-Benzene)chlorodiphenylphosphinothiadiato)rhodium(ii). The complex [Ru(η-C5H5)Cl]2 (0.20 g, 0.4 mmol) was stirred in methanol (15 cm³) with [NH4][S2PPh2] (0.21 g, 0.8 mmol) (1:2 mol ratio) for several hours. After removal of solvent, the residue was recrystallised from methylene chloride–hexane to give a red solid, m.p. 190 °C (decomp.), v(PS) at 608 and 587(b) cm⁻¹.

(η-Benzene)dimethylphosphinothiadiato)pyridinerruthenium(ii) tetraphenylborate. The complex [Ru(η-C5H5)Cl]2(NCCH4)2 (0.066 g, 0.2 mmol), Na[S2PMe2]2H2O (0.097 g, 0.2 mmol), and excess of Na[BPh4] (0.12 g, 0.4 mmol) were shaken in acetone (25 cm³) for 3 h. A white precipitate of NaCl was filtered off and the orange solution was concentrated at ca. 5 °C. Addition of diethyl ether then gave a yellow precipitate which was washed with warm water and diethyl ether and recrystallised from methylene chloride–hexane, m.p. 220 °C (decomp.), v(PS) at 628(b) cm⁻¹.

Similarly prepared were (diphenylphosphinothiadiato)(η-mesitylene)pyridinerruthenium(ii) tetraphenylborate from [Ru(η-C5H5)Cl]2(NCCH4)2, [NH4][S2PPh2], and Na[BPh4] as a yellow solid, m.p. 199 °C (decomp.), v(PS) at 604 and 580(b) cm⁻¹ and (diphenylphosphinothiadiato)(η-mesitylene)pyridinerruthenium(ii) tetraphenylborate, v(PS) at 628(b) cm⁻¹, from [Ru(η-C5H5)Cl]2(NCCH4)2, Na[S2PMe2]2H2O, and Na[BPh4].

(η-Benzene)bis(dimethylphosphinothiadiato)(triphenylphosphine)rhodium(ii) hexafluorophosphate. The complex [Ru(η-C5H5)Cl][S2PPh2] (0.09 g, 0.2 mmol) was shaken in ethanol with excess of triphenylphosphine (0.10 g, 0.4 mmol) and [NH4][PF6] (0.06 g, 0.4 mmol) for several hours. The solvent was removed, the residue dissolved in acetone, and the solution filtered. Addition of diethyl ether then gave a yellow precipitate which was washed with warm water then diethyl ether and dried in air, m.p. 215 °C (decomp.), v(PS) at 605 and 580(b) cm⁻¹. The following complexes were prepared similarly: [Ru(η-C5H5)-(PMePh2)[S2PPh2]][PF6], m.p. 129 °C, v(PS) at 602 and 580(b) cm⁻¹; [Ru(η-C5H5)-POMe3][S2PPh2][PF6], m.p. 190 °C, v(PS) at 603 and 580(b) cm⁻¹; [Ru(η-C5H5)-S2PPh2][SbPh3][PF6], m.p. 211 °C, v(PS) at 600 and 577(b) cm⁻¹; and [Ru(η-C5H5)[NCCH4][S2PPh2]][PF6], m.p. 202 °C, v(PS) at 605 and 580(b) cm⁻¹.

(η-Benzene)cyanophenylrhodium(ii)bis(dimethylphosphinothiadiato)rhodium(ii). The complex [Ru(η-C5H5)Cl][S2PPh2] (0.09 g, 0.2 mmol) dissolved in methanol on addition of tetracyanoethylene (0.12 g, 1.0 mmol) to give a yellow solution. Addition of excess of Na[BPh4] to this solution then gave a yellow precipitate, m.p. 210 °C (decomp.), v(PS) at 602 and 580(b) cm⁻¹.

Rhodium Complexes.—Bis(dimethylphosphinothiadiato)(η-pentamethylcyclopentadienyl)rhodium(iii). The complex [Ru(η-C5H5)Cl]2 (0.12 g, 0.2 mmol) was dissolved in water (20 cm³) by warming and excess of Na[S2PMe2]2H2O (0.28 g, 1.5 mmol) added to the filtered solution. The resulting dark red solution was extracted with methylene chloride, and the organic layer separated and dried over anhydrous Na2SO4. Hexane was then added and the methylene chloride allowed to evaporate off slowly giving a red crystalline solid, m.p. 181 °C, v(PS) at 600(u) and 588(b) cm⁻¹. Bis(dimethylphosphinothiadiato)(η-pentamethylcyclopentadienyl)rhodium(iii), m.p. 214 °C (PS) at 648 and 539(u), and 603 and 575(b) cm⁻¹, was similarly prepared from [Ru(η-C5H5)Cl]2 (0.12 g) and [NH4][S2PPh2] (0.42 g).

Bis(dimethylthiostibocarbamate)(η-pentamethylcyclopentadienyl)rhodium(iii). The complex [Ru(η-C5H5)Cl]2 (0.12 g, 0.2 mmol) was dissolved in water (20 cm³). Addition of excess of Na[S2CNMe2]2H2O (0.28 g, 1.6 mmol) gave a red precipitate which was recrystallised from methylene chloride–light petroleum (b.p. 60—80 °C), m.p. 218 °C. Bis(diethylthiophosphocarbamate)(η-pentamethylcyclopentadienyl)rhodium(iii), m.p. 223 °C, was similarly prepared from [Ru(η-C5H5)Cl]2 (0.12 g) and Na[S2CNMe2]2H2O (0.33 g).

Bis(O-ethyl dithiocarbamate)(η-pentamethylcyclopentadienyl)rhodium(iii). The complex [Ru(η-C5H5)Cl]2 (0.12 g, 0.2 mmol) was dissolved in water (20 cm³). Addition of excess of K[SCOMe] (0.23 g, 1.6 mmol) gave an oily bright orange precipitate which was extracted from aqueous solution by diethyl ether. The orange ether solution was then concentrated to dryness and the residue recrystallised from acetonitrile–water. Bis(O-ethyl dithiocarbamate)(η-pentamethylcyclopentadienyl)rhodium(iii), m.p. 120 °C, was similarly prepared from [Ru(η-C5H5)Cl]2 (0.12 g) and excess of K[S2COEt] (0.26 g).

Chloro(dimethylthiocarbamate)(η-pentamethylcyclopentadienyl)rhodium(iii). The complex [Ru(η-C5H5)Cl]2 (0.12 g, 0.2 mmol) was dissolved in methyl cyanide (20 cm³), Na[S2CNMe2]2H2O (0.072 g, 0.4 mmol) added (1:2 molar ratio), and the solution stirred for several hours. After filtering to remove NaCl, the solution was evaporated to dryness and the residue recrystallised from methylene chloride–hexane, m.p. 273 °C, v(PS) at 270 cm⁻¹. Chloro(dimethylthiocarbamate)(η-pentamethylcyclopentadienyl)rhodium(iii), v(PS) at 588(b) cm⁻¹ and v(PS) at 265(b) cm⁻¹, and chloro(dimethylphosphinothiadiato)(η-pentamethylcyclopentadienyl)rhodium(iii), m.p. 247 °C, v(PS) at 603 and 574(b) cm⁻¹, v(PS) at 270 cm⁻¹, were similarly prepared using Na[S2PMe2]2H2O and [NH4][S2PPh2] respectively and recrystallising from chloroform–light petroleum (b.p. 60—80 °C).

Bromo(dimethylthiocarbamate)(η-pentamethylcyclopentadienyl)rhodium(iii). The complex [Rh(η-C5H5)Cl][S2CNMe2] was shaken with excess of lithium bromide for several hours in methanol. The solution was then evaporated to dryness and the residue extracted with methylene chloride. After filtering through Celite and adding hexane, slow evaporation of methylene chloride gave a dark red crystalline precipitate, m.p. 235 °C. The analogous [Ru(η-C5H5)Cl][S2CNMe2], m.p. 247 °C, and [Ru(η-C5H5)-(SCN)][S2CNMe2], m.p. 151 °C, v(CN) at 2 095 cm⁻¹, were similarly prepared from [Ru(η-C5H5)Cl][S2CNMe2] and NaI or K[SCN] respectively.
(Dimethylthiocarbamato)(dimethylphosphinodithioato)-(η-pentamethylycyclopentadieny)rhodium(III). The complex
[Rh(η-C₅Me₅)Cl(S₂CNMe₂)] (0.153 g, 0.4 mmol) and Na-[S₂PMe₂]₂H₂O (0.074 g, 0.4 mmol) (1 : 1 mol ratio) were
stirred in methanol with sodium chloride for 3 h. The solution was
filtered to remove NaCl, concentrated to dryness, and the residue crystallised from methylene chloride-pentane,
m.p. 157 °C, ν(PS₄) at 600 cm⁻¹. Similarly, (dimethyl
thiocarbamato)(diphenylphosphinodithioato)-(η-pentamethylycyclopentadieny)rhodium(III), m.p. 224 °C, ν(PS₄) at 646
and 535 (cm⁻¹), and (dimethylthiocarbamato)(O-methyl
dithiocarbamato)-(η-pentamethylycyclopentadieny)rhodium(III), m.p. 181 °C, were prepared from [Rh(η-C₅Me₅)Cl(S₂CNMe₂)]
and [NH₄][S₂P₂Ph₂] or K[S₂COMe] respectively.

(Dimethylthiocarbamato)(methanol)-(η-pentamethylycyclopentadieny)rhodium(III) tetraphenylborate. The complex
[Rh(η-C₅Me₅)Cl(S₂CNMe₂)] was dissolved in methanol and addition of excess of Na[BPh₄] precipitated an orange
solid, m.p. 197 °C.

(Dimethylthiocarbamato)-(η-pentamethylycyclopentadieny)(trisphenylphosphine)rhodium(III) tetraphenylborate. Method
A. The complex [Rh(η-C₅Me₅)Cl(PPh₃)] (0.11 g, 0.2 mmol) was washed in ethanol with excess of Na-[S₂
CNMe₂] (2H₂O) (0.09 g, 0.5 mmol) and Na[BPh₄] (0.17 g, 0.6 mmol) for 24 h. The resulting orange solid was filtered
off and washed thoroughly with warm water, ethanol, and diethyl ether, m.p. 205 °C. The analogous [Rh(η-C₅Me₅)
[PPh₃][S₂PMe₂]][BPh₄], m.p. 216 °C (decomp.), was prepared by the same method, using [Rh(η-C₅Me₅)Cl(PPh₃)]
and excess of Na[S₂PMe₂] (2H₂O) ν(PS₄) at 573 (cm⁻¹).

Method B. The complex [Rh(η-C₅Me₅)Cl(S₂CNMe₂)] (0.085 g, 0.2 mmol) was dissolved in methanol and excess of
PPh₃ (0.13 g, 0.6 mmol) added. The solution became orange-yellow on gentle warming and addition of Na[BPh₄] gave
an orange crystalline product on cooling. Similar methods were used to prepare the analogous [Rh(η-C₅Me₅)
(PMe₂Ph)[S₂CNMe₂]Cl][PF₆], [Rh(η-C₅Me₅)(NCS)₂
(S₂CNMe₂)][BPh₄], m.p. 97 °C, and [Rh(AsPh₃)(η-C₅Me₅])
(S₂CNMe₂)][BPh₄], m.p. 192 °C.

Carbonyldimethylthiocarbamato)-(η-pentamethylycyclopentadieny)rhodium(III) tetraphenylborate. The complex
[Rh(η-C₅Me₅)Cl(S₂CNMe₂)] (0.10 g, 0.25 mmol) was
dissolved in methanol (50 cm³) and carbon monoxide bubbled through the solution for 4 h. Addition of Na[BPh₄] to the
resulting yellow solution gave a crystalline yellow solid, m.p. 183 °C, ν(CO) at 2 070 cm⁻¹.

(Diphenylphosphinodithioato)(methylene)diphenylphosphine)-(η-pentamethylycyclopentadieny)rhodium(III) hexafluorophosphate. The complex [Rh(η-C₅Me₅)Cl(S₂P₂Ph₂)] (0.10 g, 0.2 mmol) was dissolved in methanol (15 cm³). On addition of several drops of PMe₂Ph₂, the solution became yellow and addition of excess of [NH₄][PF₆] then gave an orange-yellow crystalline solid, ν(PS₄) at 603 and 577 (cm⁻¹). (Diphenylphosphinodithioato)-(η-pentamethylycyclopentadieny)(trisphenylphosphine)rhodium(III) hexafluorophosphate was similarly prepared, m.p. 214 °C, ν(PS₄) at 603 and 577 (cm⁻¹).

μ-[1,2-Bis(diphenylphosphino)ethane]-bis(dimethylthiocarbamato)-(η-pentamethylycyclopentadieny)rhodium(III) bis
tetraphenylborate. The complex [Rh(η-C₅Me₅)Cl(S₂CNMe₂)] (0.08 g) was dissolved in methanol. Addition of
excess of Ph₃PCH₂CH₂PPh₃ (dppe) (0.15 g) accompanied by gentle warming gave a yellow solution from which a
yellow solid was precipitated on addition of Na[BPh₄], m.p. 217 °C. The complex [Rh(η-C₅Me₅)[S₂P₃Ph₂][PPh₃][BPh₄]], m.p. 200 °C, was similarly prepared. μ-[1,2-Bis(diphenylphosphino)ethane]-bis(dimethylphos
phinodithioato)-(η-pentamethylycyclopentadieny)rhodium(III) bis
tetraphenylborate, ν(PS₄) at 603 and 577 (cm⁻¹), was also prepared as above from [Rh(η-C₅Me₅)Cl(S₂P₂Ph₂)], dppe,
and Na[BPh₄].

(Dimethylphosphinodithioato)(methylene)diphenylphosphine)-(η-pentamethylycyclopentadieny)rhodium(III) dimethylphosphinodithioato. The complex [Rh(η-C₅Me₅)[S₂PMe₂]] was dissolved in benzene and several drops of PMe₂Ph₂ were added to give a yellow solution which, on standing, deposited a yellow crystalline solid, m.p. 226 °C, ν(PS₄) at 610 (i) and 575 (b) cm⁻¹.

(Cyanorphenylborato)(dimethylthiocarbamato)-(η-pentamethylycyclopentadieny)rhodium(III). The complex [Rh(η-C₅Me₅)Cl(S₂CNMe₂)] (0.10 g, 0.25 mmol) was dissolved in methanol (10 cm³) and treated with tetracyanoethylene (0.13 g, 1.0 mmol). On gentle warming a yellow solution was formed which on treatment with Na[BPh₄] gave an orange-yellow crystalline solid on cooling, m.p. 221 °C, ν(CN) at 2180 cm⁻¹. The analogous complexes [Rh(η-C₅Me₅)(NCBPh₃)[S₂PMe₂]], m.p. 225 °C, ν(CN) at 2180, ν(PS₄) at 577 (cm⁻¹), and [Rh(η-C₅Me₅)(NCBPh₃)[S₂P₂Ph₂]], m.p. 257 °C, ν(CN) at 2180, ν(PS₄) at 603 and 577 (cm⁻¹), were prepared from C₅CN₄Na[BPh₄] and [Rh(η-C₅Me₅)Cl(S₂P₂Ph₂)] or [Rh(η-C₅Me₅)Cl(S₂P₂Ph₂)] respectively.

Iridium Complexes.—Bis(dimethylthiocarbamato)-(η-pentamethylycyclopentadieny)iridium(III). The complex
[[Ir(η-C₅Me₅)[Cl][Cl]],[13] (0.16 g, 0.2 mmol) was dissolved in methyl cyanide (20 cm³) together with Na[S₂CNMe₂] (2H₂O)
(0.28 g, 1.6 mmol) and the resulting yellow solution stirred for 2 h. After filtering off NaCl, the filtrate was evaporated to dryness and the residue extracted with methylene chloride. Excess of Na[S₂CNMe₂] (2H₂O) was filtered off and addition of hexane gave the yellow product, m.p. 242 °C. Bis(dimethylphosphinodithioato)-(η-pentamethylycyclopentadieny)
iridium(III), ν(PS₄) at 602 (u) and 590 (b) cm⁻¹, was similarly prepared from [[Ir(η-C₅Me₅)[Cl][Cl]]] and excess of
Na[S₂PMe₂] (2H₂O).

We thank Johnson, Matthey Ltd. for generous loans of ruthenium, rhodium, and iridium trichlorides, the S.R.C. for support (to D. R. R.), Dr. A. S. F. Boyd for obtaining the ¹H and ¹³C n.m.r. spectra, Mr. J. R. A. Millar for the ¹H and ¹³C n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Mechrolab spectrometer.

[7/1880 Received, 5th July, 1977]
Metal Complexes of Sulphur Ligands. Part 16. Reaction of mer-Tri-chlorotris(dimethylphenylphosphine)ruthenium and Dichlorotris(triphenylphosphine)ruthenium with Sodium and Ammonium Monothio-benzoates, and the Crystal and Molecular Structure of (4-Amino-2- imino-4-methylpentane)bis(dimethylphenylphosphine)bis(monothio- benzoato)ruthenium(ii)

By Robert O. Gould, T. Anthony Stephenson, and Mary A. Thomson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JY

Reaction of \( [\text{RuCl}_3(\text{PPPh}_3)_3] \) with an excess of Na[SOCPH] or [NH₄][SOCPH] in either acetone or methanol and mer-[RuCl₃(PE₅Ph₃)] with Na[SOCPH] in acetone gives six-co-ordinate \([\text{Ru(SOCPH)}_2(\text{PR})_2] \) \( \text{PR} = \text{PPPh}_3 \) (1) or \( \text{PME}_5\text{Ph} \) (2) shown by i.r. and \(^{31} \text{P} \) n.m.r. studies to contain trans- and cis-PR₃ groups respectively. Support for these conclusions comes from the reactions of (1) and (2) with various Lewis bases which give \([\text{Ru(SOCPH)}_2(\text{PR})_2L] \) \( \text{PR} = \text{PPPh}_3, L = \text{CO or NH}_3 \) (3a); \( \text{PR} = \text{PME}_5\text{Ph}, L = \text{CO}, \text{NH}_3, \text{or NH}_3\text{Et} \) (3b), shown by spectroscopic methods to have trans-S-bonded \([\text{SOCPH}^-] \) groups with trans-PPPh₃, trans-L (3a), and cis-PME₅Ph, cis-L (3b) groups respectively. In contrast, reaction of mer-[RuCl₃(PE₅Ph₃)] with excess of [NH₄]-[SOCPH] in acetone gives a nitrogen-containing product (4) shown by X-ray analysis to be \([\text{Ru(SOCPH)}_2 \{\text{HNC(Me)}\text{CH}_2\text{CMe}_3\text{NH}_2\} \text{(PMe}_5\text{Ph)}_2] \). The crystals are orthorhombic, space group \( Pna_2_1 \), with \( a = 23.899(2), b = 11.163(1), \) and \( c = 13.989(3) \AA \). Finally, a mechanism of formation of (4) is suggested involving condensation of the diamine complex (3b) with mesityl oxide.

In Parts 5 and 6 of this series the reaction of various tertiary phosphine complexes of ruthenium(III) and ruthenium(II) with dithiocarbamoyl ligands was reported to give the six-co-ordinate \([\text{Ru(S-S)}_2(\text{PR})_2] \) (S-S = \([\text{S}_2\text{PR}_2^- \) or \( \text{S}_2\text{CNR}_2^- \) ). Detailed variable-temperature \(^{1} \text{H} \) n.m.r. studies indicated a cis configuration in most instances (mixture of enantiomers), and the rates of interconversion of these enantiomers were measured and a general mechanism of rearrangement deduced. Some reactions of these complexes with Lewis bases such as carbon monoxide were also examined.

We now report the results of the reaction of mer-[RuCl₃(PE₅Ph₃)] and [RuCl₃(PPPh₃)] with sodium and ammonium monothio-benzoates where, to our initial surprise, the nature of the cation sometimes plays an important role in determining the form of the reaction product. The reactions of the products with some unidentate Lewis bases were also examined.

RESULTS AND DISCUSSION

When [RuCl₃(PPh₃)₃] was heated under reflux with an excess of Na[SO₄Ph] or [NH₄][SO₄Ph] in either acetone or methanol solvent an orange-yellow non-conducting solid of composition [Ru(SO₄Ph)₃(PPh₃)₂]

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Mull i.r. spectra of various monothiobenzoate complexes of ruthenium(II)</td>
</tr>
<tr>
<td>Compounds</td>
</tr>
<tr>
<td>[Na(SO₄Ph)]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(PPh₃)₂]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(NH₄)₃]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(CO)₂]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(PMe₂Ph)₂]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(PMe₂Ph)₃]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(NH₂Et)₂]</td>
</tr>
<tr>
<td>[H(NC)(Me₃)CH]</td>
</tr>
<tr>
<td>C₆H₅NH₂₃(PMe₂Ph)₂</td>
</tr>
<tr>
<td>1660 (ν(CN)(imine))</td>
</tr>
<tr>
<td>1585 (ν(NH₄³))</td>
</tr>
</tbody>
</table>

† Low values of ν(CO) attributed to intramolecular hydrogen bonding between the carbonyl groups and the amine group (see text).

Identification of the positions of the C-O and C-S stretching frequencies in the i.r. spectra is the best way of determining the mode of bonding of the monothiobenzoate ligand. Earlier, Savant et al.5 assigned these vibrations in Na[SO₄Ph] to the bands at 1500 and 960 cm⁻¹ respectively and then, by comparison with these values, elucidated the mode of bonding in a series of metal monothiobenzoate complexes. Thus, for bidentate co-ordination both ν(CO) and ν(CS) remain almost unaffected but, as the interaction through sulphur becomes more important than that through oxygen, ν(CS) decreases and ν(CO) increases. Hence, examination of Table 1 clearly shows that only bidentate [SO₄Ph]¹ co-ordination is present in complexes (1) and (2).

Although the ¹H n.m.r. spectrum of (1) is of no use for obtaining structural information, the ³¹P-{¹H} spectrum (singlet at δ 59.9 p.p.m.) indicates that only a single isomer which contains magnetically equivalent phosphines is formed. The ¹H n.m.r. spectrum of complex (2) in CDCl₃ at 300 K (methyl region) consists of a strong 'pseudo-triplet' † at δ 1.42 p.p.m. and a much weaker 'virtually coupled' triplet at 1.57 p.p.m. By comparison with earlier studies, these patterns are indicative of the presence of two isomers containing cis- and trans-PMe₂Ph groups respectively. Furthermore, phosphorus-31 decoupling studies confirm that these two signals arise from different species, and in keeping with this the ³¹P-{¹H} n.m.r. spectrum of (2) at 303 K consists of a strong resonance at δ 39.0 p.p.m. and a very weak signal at 4.6 p.p.m.

Table 2

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen-¹ H n.m.r. data in CDCl₃ for some ruthenium(II) monothiobenzoate complexes</td>
</tr>
<tr>
<td>Complex</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(PMe₂Ph)₂]</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(NH₄)₃(PMe₂Ph)₂]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(CO)₂(PMe₂Ph)₃]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(PMe₂Ph)₃]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(NH₂Et)₂]</td>
</tr>
<tr>
<td>[Ru(SO₄Ph)₃(HNC(Me₃)CH)₂C₆H₅NH₂₃(PMe₂Ph)₂]</td>
</tr>
<tr>
<td>&amp; 1.31(s), 1.21(s)</td>
</tr>
</tbody>
</table>

* s = Singlet, d = doublet, t = triplet, ppt = pseudo-triplet, and m = multiplet. † Phenyl resonances. * Overlapping doublets of doublets. † Phenyl resonances. * Overlapping doublets of doublets.

the reddish brown product [Ru(SO₄Ph)₃(PMe₂Ph)₂] (2). These complexes were characterised by elemental analysis, and i.r. (Table 1). ¹H n.m.r. (Table 2), and ³¹P n.m.r. spectroscopy, and their monomeric nature was established by mass spectroscopy and osmometric molecular-weight measurements in chloroform. * The analogous [Ru(SO₄Me)₃(PPh₃)₂] has been very briefly reported elsewhere. * A 'pseudo-triplet' pattern consists of a sharp doublet with a broad hump of comparable intensity situated between the doublet, and signifies a relatively large (³¹P) compared to the [³¹P(ph₂) + ³¹P(ph³)] value (ref. * cit. [Ru(SO₄Me)₃(PMe₂Ph)₂]).

Variable-temperature ¹H n.m.r. studies on (2) reveal that at lower temperatures the 'pseudo-triplet' signal broadens and at 260 K the spectrum consists of two 'pseudo-triplets' centred at δ 1.32 and 1.46 p.p.m. This behaviour, which is concentration-independent and

reversible with temperature, is analogous to that observed earlier for \( [\text{M}(\text{S} \text{PM} \text{Me}_2 \text{Ph})_2] \) (\( \text{M} = \text{Ru}^2,^3 \text{ or Os}^7 \)) and is likewise attributed to rapid interconversion on the n.m.r. time scale of two optical isomers of \( \text{Ru}^+ \) [see equation (1)]. As expected for an isomer containing \( \text{PM} \text{Me}_2 \text{Ph} \) groups, there is no apparent change in the shape of the 'virtually coupled' triplet at \( \delta 1.57 \) p.p.m. on changing the temperature.

Further information about the detailed structures of complexes (1) and (2) has been obtained from an examination of their reactions with carbon monoxide. Thus, reaction with carbon monoxide gave lemon-yellow and pale cream products respectively which both analysed for \([\text{Ru}(\text{SOCPh})_2 \text{L}_2(\text{PF}_3)_2]\) \( \text{L} = \text{CO}; \text{PF}_3 = \text{PF}_3 \) (3a) or \( \text{PM} \text{Me}_2 \text{Ph} \) (3b). The Nujol i.r. spectra of both these complexes revealed that an increase in the \( \nu(\text{CO}) \) (SOCPh) and a decrease in the \( \nu(\text{CS}) \) band positions, compared to those of (1) and (2), had occurred (Table 1) indicative of unidentate co-ordination of the \( \text{SOCPH}^+ \) groups through sulphur in both cases. However, the i.r. spectrum of (3a) contained only a single terminal \( \nu(\text{CO}) \) absorption band at 1950 cm\(^{-1}\) whereas that of (3b) had two \( \nu(\text{CO}) \) bands at 2025 and 2005 cm\(^{-1}\) suggesting \( \text{trans} \) and \( \text{cis} \) carbyl-group arrangements respectively.

The \( ^1\text{H} \) n.m.r. spectrum of (3b) \( \text{L} = \text{CO} \) in CDCl\(_3\) (methyl region) at 240–300 K exhibited a single 'pseudo-triplet' pattern at \( \delta 1.80 \) p.p.m. and the \( ^3\text{P}(^1\text{H}) \) n.m.r. spectrum at 303 K contained a singlet at \( \delta -10.8 \) p.p.m. This large change in \( ^3\text{P} \) n.m.r. chemical shift on going from (2) to (3b) suggests that geometrical isomer postulated earlier for the major isomer of complex (2) [equation (1)] and with the expected most ready point of cleavage in (2), viz. the Ru–O rather than the Ru–S bonds.

The \( ^3\text{P}(^1\text{H}) \) n.m.r. spectrum of complex (3a; \( \text{L} = \text{CO} \)) consists of a singlet at \( \delta 84.8 \) p.p.m. The relatively small change in \( ^3\text{P} \) n.m.r. chemical shifts on going from (1) to (3a) \( \text{L} = \text{CO} \) together with the i.r. data given above is consistent with a structure containing trans-carsbonyls, \( \text{trans-PPF}_3 \), and \( \text{trans-S-bonded [SOCPh]^+} \) groups. In support of this conclusion, the reaction of all-trans-\([\text{RuCl}_4(\text{CO})_2(\text{PF}_3)_2] \) and \([\text{NH}_4][\text{SOCPh}] \) in acetone under reflux also gave a high yield of complex (3a; \( \text{L} = \text{CO} \)).

Therefore, this evidence strongly suggests that complex (1) has a structure with trans-\( \text{PPF}_3 \) groups (cf. the minor isomer of \([\text{Ru}(\text{SOCPH})_2(\text{PM} \text{Me}_2 \text{Ph})_2] \). Presumably, the larger size of the \( \text{PPF}_3 \) groups facilitating formation of \( \text{trans} \) rather than \( \text{cis} \) isomers, allied with the high \( \text{trans} \) effect of \( \text{PM} \text{Me}_2 \text{Ph} \) groups favours a \( \text{cis} \) rather than a \( \text{trans} \) configuration, is the main reason for this difference in stereochemistry between complexes (1) and (2).

Further support for this conclusion is that reaction of (1) with gaseous ammonia gives a yellow solid of composition \([\text{Ru}(\text{SOCPH})_2(\text{NH}_3)_2(\text{PF}_3)_2] \). Again, i.r. studies indicate the presence of unidentate \( S \)-bonded \( \text{SOCPH}^+ \) groups (Table 1) and the \( ^3\text{P}(^1\text{H}) \) n.m.r. spectrum shows a singlet at \( \delta 46.3 \) p.p.m. consistent with structure (3a; \( \text{L} = \text{NH}_3 \)). In contrast, reaction of complex (2) with ammonia yields a product \textit{in situ} whose \( ^1\text{H} \) n.m.r. spectrum in CDCl\(_3\) exhibits a 'pseudo-triplet' at \( \delta 1.75 \) p.p.m. and whose \( ^3\text{P}(^1\text{H}) \) n.m.r. spectrum contains a singlet at 23.7 p.p.m. Unfortunately, attempts to isolate a solid product in the latter case were unsuccessful although with \( \text{NH}_2\text{Et} \), complex (2) gave the yellow-brown solid \([\text{Ru}(\text{SOCPH})_2(\text{NH}_2\text{Et})_2(\text{PM} \text{Me}_2 \text{Ph})_2] \) whose \( ^1\text{H} \) and \( ^3\text{P} \) n.m.r. spectra were also consistent with structure (3b; \( \text{L} = \text{NH}_2\text{Et} \)). Thus, the low sensitivity of the position of the \( ^3\text{P} \) n.m.r. resonance signals to a change in Lewis base for the \( \text{PPF}_3 \) compared to the \( \text{PM} \text{Me}_2 \text{Ph} \) complexes adds further support to the structural assignments made above.

Unlike the reactions of \([\text{RuCl}_4(\text{PF}_3)_2] \) with either \([\text{NH}_3][\text{SOCPH}] \) or \( \text{Na}[\text{SOCPH}] \) in methanol or acetone which yielded the same product (1), the reaction of meso-\([\text{RuCl}_4(\text{PM} \text{Me}_2 \text{Ph})_2] \) with \([\text{NH}_4][\text{SOCPH}] \) in acetone, either

\[ ^7 \text{D. J. Cole-Hamilton and T. A. Stephenson, } \text{J.C.S. Dalton, 1976, 2366.} \]

at ambient temperature or under reflux, did not give
(2) but, instead, an orange-brown non-conducting solid
(4) containing 3.3% nitrogen. The i.r. spectrum of (4)
showed a small increase in the position of the band
assigned to ν(CO) (1530 cm⁻¹) and a decrease in that for
ν(CS) (935 cm⁻¹), compared to the values for complex
(2), which again suggests the presence of undentate S-bonded [SOCPh]⁻ groups. The mass spectrum of (4),
like that of (2), shows a strong peak at m/e 662 (¹⁰⁶Ru
isotope) corresponding to [Ru(SOCPh)₂(PMe₂Ph)₃]⁺ and
the same fragmentation pattern for m/e values >100
which correspond to loss and subsequent breakdown of
[SO(t)CPh]⁻ and PMe₂Ph groups. However, a number of
extra peaks compared to (2) appear at m/e 97, 58, 42,
and 15.

The ¹H n.m.r. spectrum of (4) is quite different to (2)
comprising, at 300 K in CDCl₃, for δ values <5 p.p.m.,
two doublets [J(P)] 8.0 Hz] centred at 1.86 and 1.43
p.p.m. and three singlets at 2.31, 1.58, and 1.06 p.p.m.
On decreasing the temperature, the doublets first broaden and then at 250 K each is resolved into two
doublets (see Table 2) indicative of the presence of four
magnetically inequivalent methyl groups. The three
singlet resonances show no significant variation with
temperature. The ³¹P-¹H n.m.r. spectrum at 303 K in
CDCl₃ consists of an AB pattern centred at δ 19.9 p.p.m.
[J(PP) 32.9 Hz, δ(PP) 251.7 Hz] suggesting two magnetically inequivalent PMe₂Ph groups. Furthermore,
the magnitude of the coupling constant suggests a cis
orientation of these groups.⁹

A suitable single crystal of (4) was selected of dimen-
sions 0.3 x 0.1 x 0.05 mm, and an X-ray structural
analysis (see below) showed it to contain a co-ordinated
4-amino-2-imino-4-methylpentane molecule.

Crystal Data for (4).—C₇₆H₆₅N₁₈O₆P₂Ru₂, M = 765,
reddish-brown prismatic crystals, a = 23.899(2), b =
11.163(1), c = 13.889(3) Å, U = 3.705 Å³, Dₘ = 1.34,
Z = 4, D₀ = 3.72 g cm⁻³, F(000) = 1592, space group
Pnma (no. 63), Cu-Kα radiation, λ = 1.5418 Å, μ(Cu-
Kα) = 56.2 cm⁻¹.

Structure determination. Photographic equi-inclina-
tion Weissenberg data were collected for layers h0→8l
and k0→6. Cell dimensions were determined by the
x₁-x₂ splitting method applied to 23 zero-layer re-
fections with Θ > 75°. All the films were scanned by the S.R.C. Microdensitometer Service and, after merging,
249 independent data were obtained, significant above
background. No absorption corrections were applied.
The x and y co-ordinates of the ruthenium atom were
readily determined from the Patterson function.
The subsequent difference Fourier, phased with these
coordinates and an arbitrary z, is pseudo-centric, and some
difficulty was experienced in choosing suitable S and P
co-ordinates to break this symmetry. Eventually, all the
non-hydrogen atoms were found. The structure was
refined by block-diagonal least squares. In the last
few cycles a weighting scheme was used of the form

$$W = X^2$$

with

$$X = (\sin \theta)/0.3$$

for \(\sin \theta < 0.3\) and 1.0 otherwise, and

$$Y = 35/[F_0]$$

for \(F_0 > 35\) and 1.0 otherwise. Ruthenium, S, and P atoms were given anisotropic temperature factors, but hydrogen atoms were
not included in the refinement. At convergence, R =
0.065. Final values of fractional parameters are given
in Table 3. A structure-factor table, thermal para-
$$\text{FIGURE A perspective view of (4)}$$

deviations from ideal octahedral angles about the
ruthenium atom. In the imino-amino-ligand the amine
C(32)-N(1) bond [1.333(26) Å] is a significant 0.15 Å
shorter than the amine C(31)-N(2) distance [1.482(26) Å]
and the Ru-N(1) bond length [2.151(15) Å] is 0.12 Å
shorter than the Ru-N(2) distance [2.271(15) Å]. Similarly,
in [Cu{HNC(Me)CH₂CMMe₂NH₂}_{12}]N₂O₃, made by
reaction of Cu(NO₃)₂ and ammonia in acetone, X-ray
analysis⁹ showed C-NH 1.30, C-NH₂ 1.31, Cu-NH
1.98, and Cu-NH₂ 2.01 Å.

An interesting feature of the structure is the orienta-
tion of the [SO(t)CPh]⁻ ligands, which brings the carbonyl oxygenes within hydrogen-bonding distances (2.870 and
2.861 Å) of the amine nitrogen. In one case this results
in the Ru atom being non-coplanar with the SOC
group: Ru=S(1)-C(9)=O(1) 14°. Such hydrogen bonding
presumably lends stability to the molecule and may

1975, 97, 4021 and refs. therein.

explain the unexpectedly low value of the w(CO) wave-number (1 530 cm⁻¹) in the i.r. spectrum of (4) and also in that of [Ru(SOCPh)₂(NH₂Et)₂(PMe₂Ph)₂] (Table 1).

### Table 3

Atomic positional parameters (× 10⁴) for (4) with estimated standard deviations in parentheses

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>1 574.6(4)</td>
<td>665.3(10)</td>
<td>5 600</td>
</tr>
<tr>
<td>P(1)</td>
<td>2 062.2(2)</td>
<td>793.4(9)</td>
<td>5 786(4)</td>
</tr>
<tr>
<td>P(2)</td>
<td>1 345.2</td>
<td>1 660.4</td>
<td>4 604(4)</td>
</tr>
<tr>
<td>S(1)</td>
<td>681.2</td>
<td>318.4</td>
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<td>S(2)</td>
<td>2 373.2</td>
<td>1 955.4</td>
<td>4 824(4)</td>
</tr>
<tr>
<td>O(1)</td>
<td>1 098.3(5)</td>
<td>2 174.1(2)</td>
<td>4 162(9)</td>
</tr>
<tr>
<td>O(2)</td>
<td>2 196(6)</td>
<td>474.1(3)</td>
<td>3 680(12)</td>
</tr>
<tr>
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Similarly in the i.r. spectra of both [Ni(O₂CMe)₂]⁴⁺[H₄O]⁺ and [Pd(O₂CMe)₂[NH₂Et]₂]⁺ the low value of v(ν max(CO)) is attributed to intramolecular hydrogen bonding between the uncoordinated oxygens of the carboxylate groups and water or amine groups respectively.

The three singlets in the ¹H n.m.r. spectrum are assigned to gem-methyl groups (δ 1.06 p.p.m.), the imino-C-methyl group (1.58 p.p.m.), and to the methylene protons (2.31 p.p.m.) (cf. the related signals in [Ni(NHC₃Me)₂CH₂C₂Me₂NH₃⁺][BF₄]⁻). There is also a weak broad resonance at 5.80 p.p.m. which may be due to the hydrogens bound to nitrogen. If the solid-state structure of (4) is retained in solution, four magnetically inequivalent methyl groups are expected (and observed) in the ¹H n.m.r. spectrum because the bidentate ligand is both asymmetric and has a puckered conformation. At higher temperatures averaging of the signals from the methyl groups on the same phosphorus atoms occurred probably because of ready inversion of the chelate ring on the n.m.r. time scale. In the mass spectrum of (4) the additional peaks m/z <100 correspond to the fragmentation pattern of the 4-amino-2-imino-4-methylpentane molecule (Scheme 1) and we have observed the same pattern in the mass spectrum of [Ni(NHC₃Me)₂CH₂C₂Me₂NH₃⁺][BF₄]⁻. In neither spectrum however is the parent-ion peak observed at m/z 114 and attempts to isolate such a molecule in the free state, either by displacement from (4) with various Lewis bases or protonation of (4) with gaseous HCl, were unsuccessful (although with CO, [Ru(SOCPh)₂(CO)₂(PMe₂Ph)₂] (3b)

![Scheme 1](image)

**Scheme 1** Fragmentation pattern of the 4-amino-2-imino-4-methylpentane molecule

was obtained. This failure is not surprising because of the known instability of compounds containing imine groups which readily rearrange or polymerise.¹⁴

Finally, it is of some interest to speculate briefly on possible mechanisms for this reaction. As mentioned


earlier, [Ru(SOCPh)$_3$(NH$_3$)$_2$(PMe$_3$)$_2$] can be prepared in situ and this readily reacts with either acetone or mesityl oxide at room temperature to give high yields of (4). This strongly suggests that the reaction path involves initial formation of [Ru(SOCPh)$_3$(PMe$_3$)$_2$] (2) followed by reaction with ammonia to give the diammine species. Since reaction of [Ru(SOCPh)$_3$(PMe$_3$)$_2$] (2) with either [NH$_3$][PF$_6$] or [NH$_3$][SOCPh] in acetone did not give any (4), it is clear that, in the original preparation of (4), deprotonation of the ammonium ion by the free PMe$_3$Ph released in the reaction is a key step in the formation of this diammine complex. A possible method of condensing mesityl oxide (the self-condensation product of acetone) with the diammine complex to give (4) is shown in Scheme 5.

This is similar to a mechanism proposed elsewhere to explain the formation of ruthenium imine complexes from reaction of ruthenium ammine and various organic carbonyl-containing compounds. An added attraction of the mechanism shown in this Scheme is that cis-ammine groups are essential for formation of the imino-amino chelating ligand and therefore this provides a good rationale for the inability to form the corresponding species starting from either [RuCl$_3$(PPh$_3$)$_2$] or [Ru(SOCPh)$_3$(NH$_3$)$_2$(PPh$_3$)$_2$] (3a).

However, attempts to condense acetone (or mesityl oxide) with [Ru(SOCPh)$_3$(NH$_3$)$_2$(PMe$_3$)$_2$] or ethylmethyl ketone with [Ru(SOCPh)$_3$(NH$_3$)$_2$(PMe$_3$)$_2$] were also unsuccessful suggesting that steric constraints are another important consideration.

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzoic. Infrared spectra were recorded in the range 250-4000 cm$^{-1}$ region on a Perkin-Elmer 557 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe, and proton-noise-decoupled $^1$H n.m.r. spectra on a Varian XL 100 spectrometer operating in the pulse and Fourier-transform modes at 40.5 MHz ($^1$H chemical shifts quoted in p.p.m. to high frequency of 85% H$_2$PO$_4$). Mass spectra were obtained on an A.E.I. MS9 spectrometer. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Crystallographic calculations were made using the 'X-ray '72' system as implemented at the Edinburgh Regional Computing Centre. Ruthenium(III) trichloride trihydrate (Johnson, Matthey Ltd.), carbon monoxide (Air Products), triphenylphosphine (B.D.H.), dimethylphenylphosphine (Maybridge Chemical Company), and monothiobenzoic acid (Aldrich) were obtained as indicated. The salts [NH$_3$][SOCPh] and Na[SOCl] were prepared by reaction of PhCOH with ammonia gas in benzene and Na$_2$CO$_3$ in water respectively. The complexes [RuCl$_3$(PMe$_3$)$_2$]$_2$ mer-[RuCl$_3$(PMe$_3$)$_2$], and all-trans-[RuCl$_3$(CO)$_2$(PPh$_3$)$_2$] were prepared as described earlier. All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere.

**Bis(monothiobenzoato)bis(triphenylphosphine)ruthenium(III)**.—The compounds [RuCl$_3$(PPh$_3$)$_2$] (0.20 g) and Na[SOCl] (0.40 g) were heated under reflux in degassed acetone (50 cm$^3$) for 3 h. The resulting orange-yellow product was filtered off and washed with acetone and diethyl ether (0.15 g, 88%), m.p. 218–220°C (Found: C, 65.7; H, 4.7. Calc. for C$_{39}$H$_6$O$_2$P$_3$RuS$_2$: C, 66.7; H, 4.4%). The same product can also be obtained by reaction of [NH$_3$][SOCPh] with [RuCl$_3$(PPh$_3$)$_2$]. $^1$H n.m.r. spectrum in CDCl$_3$ at 303 K: δ 5.99 (s) p.p.m.

**Diamminebis(monothiobenzoato)bis(triphenylphosphine)**—

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**Ruthenium**

1978

**ruthenium** (11).—Ethanol (20 cm³) was saturated with ammonia gas and then [Ru(SOCPh)₄(PPh₃)₂] (0.10 g) was added. The suspension was stirred at room temperature for 3 h and the resulting bright yellow *product* was filtered off and washed with acetone and diethyl ether (0.09 g, 86%), m.p. 205—208 °C (Found: C, 64.5; H, 5.0; N, 2.7.

Cal. for C₂₅H₂₆N₂O₆P₂RuS₄: C, 64.4; H, 4.9; N, 3.0%)

**3P**-**(H)** n.m.r. spectrum in CDCl₃ at 303 K: δ 48.3 (s) p.p.m.

**Dicarboxyldi(monothiobenzoato)bis(triphenylphosphine)-ruthenium** (11).—Method (a). The complex [Ru(SOCPh)₄(PPh₃)₂] (0.10 g) was suspended in ethanol (50 cm³) and heated under reflux under carbon monoxide gas for 3 h. The bright yellow *product* was separated from starting material by dissolving it in dichloromethane, filtering, and recrystallising the product, m.p. 235—239 °C (Found: C, 65.2; H, 4.7. Cal. for C₂₃H₁₉O₄P₂RuS₄: C, 65.3; H, 4.2%)

**3P**-**(H)** n.m.r. spectrum in CDCl₃ at 303 K: δ 42.8 (s) p.p.m.

Method (b). The compounds all-trans-[RuCl₂(CO)₄] (0.05 g) and [NH₄][SOCPh] (0.05 g) were heated under reflux in acetone (50 cm³) for 2 h. The resulting bright yellow solution was filtered while hot, the volume was reduced, and light petroleum (b.p. 40—60 °C) was added. The lemon-yellow *product* was then filtered off.

**Bis(dicarboxyldi(monothiobenzoato)bismonothiophenolphosphate)bismonothiobenzoato**-ruthenium (11).—The compounds mer-[RuCl₂(PMe₃Ph)₂] (0.20 g) and Na[SOCPh] (0.20 g) were heated under reflux in acetone (50 cm³) for 3 h. The solution was filtered while hot, the volume was reduced, and water was added to yield a red-brown *precipitate* which was filtered off and dried in vacuo over calcium chloride (0.17 g, 70%), m.p. 256—171 °C (Found: C, 55.5; H, 5.0%; M(CHCl₃) 636. Calc. for C₄₅H₃₂N₄O₈P₂RuS₄: C, 55.3; H, 4.9%; M 651)

**3P**-**(H)** n.m.r. spectrum in CDCl₃ at 303 K: δ 39.0 (s) and 4.6 (m) p.p.m. The complex can also be prepared as above using Na[SOCPh] or [NH₄][SOCPh] in methanol as solvent.

**Diamminebis(dicarboxyldi(monothiobenzoato)bismonothiophenolphosphate)bismonothiobenzoato**-ruthenium (11).—The complex [Ru(SOCPh)₄(PMe₃Ph)₂] (0.20 g) was dissolved in chloroform (10 cm³) and ammonia gas was bubbled through the solution at room temperature for 10 min to give a yellow-brown solution. The product was not isolated but was identified by **1H** and **3P** n.m.r. studies using a sample prepared in CDCl₃ (see Discussion section). Attempts at isolation were unsuccessful.

**3P**-**(H)** n.m.r. spectrum in CDCl₃ at 303 K: δ 23.7 (s) p.p.m.

**Dicarboxyldi(monothiobenzoato)bismonothiophenolphosphate)bismonothiobenzoato**-ruthenium (11).—The complex [Ru(SOCPh)₄(PMe₃Ph)₂] (0.10 g) was dissolved in ethanol (30 cm³) and then carbon monoxide gas was bubbled through the solution at room temperature for 1 h to give a pale yellow solution. The volume of the solution was reduced and it was cooled over ice to yield a pale cream crystalline *powder* which was filtered off and dried in vacuo (0.06 g, 51%), m.p. 153—155 °C (Found: C, 53.8; H, 4.6. Calc. for C₂₅H₂₆N₂O₆P₂RuS₄: C, 54.2; H, 4.5%).

**3P**-**(H)** n.m.r. spectrum in CDCl₃ at 303 K: δ 10.8 (s) p.p.m.

**Bis(dimethylphenylphosphine)bismethyaminebismonothiobenzoato**-ruthenium (11).—The complex [Ru(SOCPh)₄(PMe₃Ph)₂] (0.10 g) was heated under reflux in chloroform (20 cm³) with ethylamine (0.50 cm³; 70% aqueous solution) for 1 h. Ethanol (10 cm³) was then added and the chloroform was evaporated off to yield a yellow-brown crystalline *powder* which was filtered off and washed with cold ethanol (0.10 g, 93%), m.p. 177—180 °C (Found: C, 54.0; H, 6.0; N, 3.7. Cal. for C₃₃H₃₆N₂O₆P₂RuS₄: C, 58.1; H, 6.2; N, 3.8%).

**3P**-**(H)** n.m.r. spectrum in CDCl₃ at 303 K: δ 22.3 (s) p.p.m.

(4-Amino-2-imino-4-methylpentane)bisdimethylphenylphosphinebismonothiobenzoato)ruthenium (11).—Method (a). The compounds mer-[RuCl₂(PMe₃Ph)₂] (0.30 g) and [NH₄][SOCPh] (0.30 g) were dissolved in the minimum volume of acetone (20 cm³) and the solution was filtered and left standing at room temperature under nitrogen for 72 h, after which time clear orange-brown *crystals* were removed from the flask. The complex was also prepared by refluxing the above reaction mixture in acetone (50 cm³) for 2 h, reducing the volume of the solution, and then cooling it in ice to yield a yellow *powder* which was filtered off and recrystallised from chloroform (0.26 g, 72%), m.p. 208—210 °C (Found: C, 54.4; H, 5.6; N, 3.3%; M(CHCl₃) 724. Calc. for C₃₃H₃₆N₂O₆P₂RuS₄: C, 56.5; H, 6.0; N, 3.7%; M 765)

Method (b). The complex [Ru(SOCPh)₄(PMe₃Ph)₂] (0.10 g) in chloroform (10 cm³) was treated with ammonia gas to give the diammine complex in situ (see earlier). Acetone (30 cm³) was then added and the solution was left to stand for 3 h at room temperature when the complex was obtained as a yellow powder as in method (a). Similarly, [Ru(SOCPh)₄(PMe₃Ph)₂] (0.10 g) in chloroform (10 cm³) treated with ammonia gas and then with mesityl oxide (5 cm³) yielded the complex after standing at room temperature. The complex was also obtained in both cases when the solutions were heated under reflux. **3P**-**(H)** n.m.r. spectrum in CDCl₃ at 303 K: δ 19.9 (q) p.p.m. [J(PP) 32.0 Hz, J(PP) 251.7 Hz]

We thank Johnson, Matthey Ltd. for loans of ruthenium trichloride, the S.R.C. for support (to M. A. T.), Dr. A. S. F. Boyd for obtaining the **3P** n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.

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Metal Complexes of Sulphur Ligands Part 17. Reaction of Palladium(II) and Platinum(II) Monothiobenzoates with Various Lewis Bases and Further Studies on the Related Dioxo- and Dithioacid Complexes.

by John A. Goodfellow, T. Anthony Stephenson* and (in part) Margaret C. Cornock, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

Reaction of palladium(II) acetate with an excess of mono-
thiobenzoic acid in benzene gives \([\text{Pd(PhCOS)}_2]_n\)
formulated as a sulphur bridged polymer \((n \geq 3)\) on the basis of infrared and molecular weight studies. In contrast, various forms of \([\text{Pt(PhCOS)}_2]_n\) are obtained by reaction of Na\(_2\)PtCl\(_4\) and Na[PhCOS] in ethanolic or aqueous media. All these materials, however, react with an excess of various Lewis bases L or L-L \([L = \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{AsPh}_3, \text{SbPh}_3, \text{C}_5\text{H}_5\text{N}; \text{L-L} = 2,2'-\text{bipyridyl, Ph}_2\text{P(\text{CH}_2)}_x\text{PPh}_2 (x = 1,2)]\) to give the neutral monomeric \([\text{M(PhCOS)}_2L_2]\) or \([\text{M(PhCOS)}_2(L-L)]\) compounds which contain unidentate PhCOS\(^-\) groups. For \(L = \text{PMePh}_2, \text{PMe}_2\text{Ph}, ^1\text{H}\) and \(^{31}\text{P}\) nmr studies indicate a trans configuration whereas the related [Pd(MeCO\(_2\))\(_2\)(PR\(_3\))\(_2\)] complexes have a cis configuration. Unlike the related carboxylato and dithioacid compounds, however, no evidence has been found here for either the neutral 1:1 or ionic 1:2 complexes \([\text{M(PhCOS)}_2L]_n\) or \([\text{M(PhCOS)L}_2][\text{PhCOS}]\) respectively.
The reaction of \([M(S-S)_2]\) compounds \((M = \text{Pd, Pt}; S-S = \text{S}_2\text{PR}_2, \text{S}_2\text{P(OR)}_2, \text{S}_2\text{CNR}_2, \text{S}_2\text{COR})\) with various tertiary phosphines\(^2\) and phosphinites\(^3\) has been discussed in detail in earlier parts of this series and some work on the reactions of \([\text{Pd(RCO}_2\text{'})_2]_n\) with various Lewis bases has also been published.\(^4,5\) In this paper, we now report on the reactions of \([M(\text{PhCOS})_2]_n\) compounds \((M = \text{Pd, Pt})\) with various Lewis bases and compare the results with those of the related dithio- and dioxoacid compounds.

Results and Discussion

Dropwise addition of monothiobenzoic acid to a benzene solution of palladium(II) acetate gave an immediate red-brown precipitate of palladium(II) monothiobenzoate, obtained in higher yield by further treatment of the filtrate with light petroleum (bp 60-80\(^\circ\)C). The platinum complex was best obtained, albeit in low yield, by prolonged shaking at room temperature of a mixture of \(\text{Na}_2\text{PtCl}_4\) and an excess of \(\text{Na}[\text{PhCOS}]\) in ethanol and then filtering off the insoluble products. Although the platinum species was not sufficiently soluble for molecular weight studies, osmometric molecular weight measurements on the palladium complex in chloroform at 37\(^\circ\)C over a range of concentrations (1.0 - 4.0g dm\(^{-3}\)) produced concentration-dependent molecular weights varying from 1100 to 1700 respectively. Similar concentration-dependent association phenomena have been observed for various metal thiophosphinate and selenophosphinate complexes in benzene or chloroform and ascribed to differing amounts of ligand bridge formation.\(^6\) Since X-ray structural analyses have shown that both \([\text{Pd(MeCO}_2\text{'})_2]_3\)\(^7\) and \([\text{Pd(PhCS}_2\text{'})_2]_3\)\(^8\) are trimeric in the solid state, (although of quite different molecular structure),\(^†\) and ebullioscopic

\(^†\)Palladium(II) dithiobenzoate has a stacked trimeric structure in the solid state but osmometric molecular weight measurements in benzene\(^9\) reveal a monomeric structure in solution, whereas palladium(II) acetate has a cyclic trimeric structure which osmometric molecular weight studies in benzene at 37\(^\circ\)C\(^4\) indicate is retained in solution.
molecular weight studies on \([\text{Pd(PhCO}_2\text{)}_2]_3\) indicate a trimer, \(^4\) it seems reasonable to expect that \([\text{Pd(PhCOS)}_2]_n\) would also possess at least a trimeric structure in the solid state.

As discussed elsewhere, \(^10\) the most useful method for establishing the mode of bonding of the monothiobenzoate group is infrared spectroscopy. Thus, Savant et al \(^10\) showed that in \(\text{Na[PhCOS]}\) , \(\nu_{\text{CO}}\) 1500, \(\nu_{\text{CS}}\) 960 cm\(^{-1}\). Furthermore, when PhCOS\(^-\) acts as a bidentate ligand and the bonding in the M-O and M-S linkages is more or less symmetrical, then \(\nu_{\text{CO}}\) and \(\nu_{\text{CS}}\) are expected to remain almost unaffected eg for \([\text{Ru(PhCOS)}_2(\text{PPh}_3)_2]\) \(\nu_{\text{CO}}\) 1500, \(\nu_{\text{CS}}\) 965 cm\(^{-1}\). \(^1\) However, as the interaction with the metal through sulphur increases and that through oxygen decreases, it is expected that \(\nu_{\text{CO}}\) will increase and \(\nu_{\text{CS}}\) will decrease in energy. Thus, for \([\text{Pd(PhCOS)}_2]_n\) strong bands are observed at 1670 and 875 cm\(^{-1}\) (broad) suggesting a strong Pd-S interaction and at best a very weak Pd-O interaction. \(^{++}\)

Without X-ray structural information, the exact structure of this monothiobenzoate compound must remain a matter of conjecture and unfortunately, all attempts to date to grow single crystals have been unsuccessful. However, the infrared spectrum of \([\text{Pd(PhCOS)}_2]_n\) is similar to that of \([\text{Hg(PhCOS)}_2]_n\) \(\nu_{\text{CO}}\) 1630, \(\nu_{\text{CS}}\) 912 cm\(^{-1}\) for which a polymeric sulphur bridged structure has been suggested. \(^10\) A polymeric sulphur bridged structure has also been suggested for the very insoluble, red-brown \([\text{Pd(OSCNR}_2)]_2\) \(_n\) compounds. \(^11\)

For \([\text{Pt(PhCOS)}_2]_n\), strong bands were also observed in the i.r. spectrum at 1660 and 880 cm\(^{-1}\) but, in addition, strong peaks appeared at 1595, 1575 and 920 cm\(^{-1}\). These latter bands could also be attributed to \(\nu_{\text{CO}}\) and \(\nu_{\text{CS}}\) vibrations respectively of PhCOS\(^-\) groups and again suggest

\(^{++}\) For PhCOSH, \(\nu_{\text{CO}}\) = 1690 cm\(^{-1}\) but the absence of a band at 2560 cm\(^{-1}\) (\(\nu_{\text{SH}}\)) shows that no free monothiobenzoic acid is present here.
appreciable Pt-S and weak Pt-O interactions. The presence of these additional peaks might signify either that the overall structure is different from that of the palladium compound or that the material consists of several rather insoluble compounds of stoichiometry \([\text{Pt(PhCOS)}_2]_n\) one of which has the same structure as \([\text{Pd(PhCOS)}_2]_n\). There is a precedent for the first suggestion since both platinum(II) acetate and aryldithiocarboxylates have been shown by X-ray analysis to have different molecular structures from the corresponding palladium compounds.*

However, further work has shown that the latter suggestion is more likely and that the reaction products here are very sensitive to both the reaction conditions and work-up procedure. Thus, work-up of the filtrate from the \(\text{Na}_2\text{PtCl}_4/\text{Na[PhCOS]}\) reaction in ethanol gave a yellow solid, (which analysed quite closely for \([\text{Pt(PhCOS)}_2\text{EtOH}]_n\)), whose ir spectrum showed strong peaks at 1590, 1570 and 920 cm\(^{-1}\) but only weak peaks at 1660 and 880 cm\(^{-1}\). Additional peaks occurred at 1530 and 950 cm\(^{-1}\). Reaction of \(\text{Na}_2\text{PtCl}_4\) and \(\text{Na[PhCOS]}\) in aqueous solution also produced several products (see experimental), one of which contained strong bands in its ir spectrum at 1530 and 950 cm\(^{-1}\) and weak peaks at 1590, 1570 and 920 cm\(^{-1}\). Furthermore, in a closely related study, it has recently been shown that reaction of \(\text{K}_2\text{PdCl}_4\) with \(\text{Me}_2\text{CS}_2\text{H}\) produced several structural variations of \([\text{Pd(MeCOS)}_2]_2\) which exhibit different multiplicities of ligand vibrations in their ir spectra.\(^{14}\)

Without X-ray structural analyses, further speculation on the structure of these various compounds is unwarranted although by analogy with \([\text{Ni(PhCOS)}_2]_2\)\(^{2-}\) EtOH, \(v_{\text{CO}}\ 1508;\ v_{\text{CS}}\ 958 \text{ cm}^{-1}\)\(^{15}\) the platinum compound with ir bands

*Platinum(II) acetate has a tetrameric structure containing strong metal-metal interactions\(^{12}\) whereas platinum(II) dithiocumate has a dimeric structure with strong metal-metal bonds.\(^{13}\) The ir spectrum of \([\text{Pt(PhCOS)}_2]_2\) indicates that it has a similar dimeric structure.\(^{13}\)
at 1530 and 950 cm$^{-1}$ may also have a dimeric structure with bridging PhCOS$^{-}$ groups.†

Although complete characterisation of these [M(PhCOS)$_2$]$_n$ compounds has not proved possible, all these materials react with an excess of a variety of Lewis bases (L) in either benzene or dichloromethane to give monomeric, non-conducting compounds of stoichiometry [M(PhCOS)$_2$L$_2$] (M = Pd, Pt; L = PPh$_3$, PMe$_2$Ph, PMe$_2$Ph, AsPh$_3$, SbPh$_3$, C$_5$H$_5$N). The ir spectra of all these compounds show $\nu_{CO}$ bands between 1550 - 1600 cm$^{-1}$ and $\nu_{CS}$ bands between 900 - 940 cm$^{-1}$ (Table 1) indicative of strong M-S and weak M-O interactions. (cf [Ru(CO)$_2$(PMe$_2$Ph)$_2$(PhCOS)$_2$] $\nu_{CO}$(PhCOS) 1600, 1570; $\nu_{CS}$ 945 cm$^{-1}$, which has S-bonded PhCOS$^{-}$ groups$^1$). Furthermore, the electronic spectra of these compounds are similar to those of other well established square planar M(II) complexes, and this fact, together with the ir evidence suggests they have structure (1) and/or (2).††

![Diagram](image)

(1) (2)

Examination of the $^{31}$P and $^1$H nmr spectra of the compounds [M(PhCOS)$_2$L$_2$] (L = PMe$_2$Ph, PMePh$_2$) has enabled the isomeric form to be established.

† In fact Oro et al.$^{16}$ reported that reaction of PdCl$_2$ with Na[PhCOS] in water gave [Pd(PhCOS)$_2$]$_2$ ($\nu_{CO}$ 1530 cm$^{-1}$) which was dimeric in benzene. In our hands, however, reaction of Na$_2$PdCl$_4$ and Na[PhCOS] in water gave a material with strong peaks in its ir spectrum at 1660 and 880 cm$^{-1}$ plus very weak peaks at 1590 and 920 cm$^{-1}$.

†† [Pd(PhCOS)$_2$(C$_5$H$_5$N)$_2$] has been briefly reported elsewhere$^{16}$ although the $\nu_{CO}$ band was assigned to a peak at 1700 cm$^{-1}$ which was not found in the ir spectrum of our sample.
Thus, the $^{31}$P-$^1$H nmr spectra in each instance, showed either a singlet (Pd) or a 1,4,1 triplet (Pt) ($J_{ptP} \approx 2600$ Hz) indicative of a single isomer with directly bonded PR$_3$ groups. The $^1$H nmr spectra showed a "virtually-coupled" triplet pattern for the methyl resonances of the phosphine indicative of the trans structure (2).$^{17}$ A trans configuration has also been established by $^1$H nmr studies for $[\text{Pd(pyr)₂}(\text{PMe₂Ph})₂]$ (pyrm = N-pyrrolidin-1-ylmonothiocarbamate).$^{18}$

Earlier,$^4$ the analogous $[\text{Pd(MeCO}_₂]_₂(\text{Et}_₂\text{NH}_₂]$ was also assigned the trans configuration (3) on the basis of dipole moment measurements. However, clearly the isomer formed here depends on the Lewis base used since the $^1$H nmr spectra of $[\text{Pd(MeCO}_₂]_₂(\text{PR}_₃)_₂]$ ($\text{PR}_₃ = \text{PMe₂Ph, PMePh₂}$) made by reaction of $[\text{Pd(MeCO}_₂]_₂]$ with excess $\text{PR}_₃$, both show a "pseudo-doublet* pattern for the methyl resonance indicative of the cis-configuration (4). The $^{31}$P-$^1$H nmr spectrum of $[\text{Pd(MeCO}_₂]_₂(\text{PMe₂Ph})₂]$ showed a singlet at 5.3$^5$ consistent with only one isomer in solution. For $[\text{Pt(CF}_₃\text{CO}_₂]_₂(\text{PMe₂Ph})₂]$, however, made by reaction of $[\text{PtCl}_₂(\text{PMe₂Ph})₂]$ with $[\text{Ag(CF}_₃\text{CO}_₂])$, the $^1$H nmr spectrum showed a "virtually-coupled" triplet pattern indicating the trans structure (3).$^{19}$

![Diagram](image)

The compound $[\text{Pd(MeCO}_₂]_₂\text{bipy}]$ (bipy = 2,2'-bipyridyl) reported earlier$^4$ must of course have the cis configuration (4). Similarly, reaction of $[\text{M(PhCOS)}_₂]_n$ with various bidentate Lewis bases (L-L) gave the mono-

*A "pseudo-doublet" is a sharp doublet with additional signal intensity situated between the doublet. This spectral pattern is indicative of a small but non-zero $J_{pp}$ value when compared to $|J_{\text{PP}} + J_{\text{PH}}'|$. 


meric, non-conducting compounds \([M(PhCOS)_{2}(L-L)] \) \((M = \text{Pd, Pt}; (L-L) = \text{bipy, Ph}_2P(\text{CH}_2)_2\text{PPh}_2, \text{Ph}_2P(\text{CH}_2)_2\text{PPh}_2)\) which must have the \textit{cis}\-configuration \((1)\)

An interesting feature here is the big difference between the positions of the \(^{31}\text{P}\) nmr resonances in \([M(PhCOS)_{2}(\text{Ph}_2P\text{CH}_2\text{PPh}_2)]\) \((-37.3^\circ\text{Pd} -49.1^\circ\text{Pt}\) and \([M(PhCOS)_{2}(\text{Ph}_2P(\text{CH}_2)_2\text{PPh}_2)]\) \((57.0^\circ\text{Pd}, 45.8^\circ\text{Pt}\)\). This big difference between \(^{31}\text{P}\) nmr chemical shifts in 4 and 5 membered phosphorus ring compounds has been found elsewhere\(^\text{20}\) but an acceptable explanation has not yet been suggested.

Comparison of the platinum-phosphorus coupling constants in the various compounds indicates that the \textit{trans}\-influence of the PhCOS group is slightly lower than that of \(\text{PMe}_2\text{Ph}\) or \(\text{PMePh}_2\), but considerably greater than chloride. Thus, \textit{trans}\-[\(\text{Pt}(\text{PhCOS})_{2}(\text{PMe}_2\text{Ph})_{2}\)] and \textit{trans}\-[\(\text{Pt}(\text{PhCOS})_{2}(\text{PMePh}_2)_{2}\)] have \(^1J_{\text{PtP}}\) values of 2546 and 2655 Hz respectively compared to 2761 and 3018 Hz in \textit{cis}\-[\(\text{Pt}(\text{PhCOS})_{2}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)\)] and \textit{cis}\-[\(\text{Pt}(\text{PhCOS})_{2}(\text{Ph}_2P(\text{CH}_2)_2\text{PPh}_2)\)] respectively. The compounds \textit{cis}\-[\(\text{PtCl}_2(\text{PMe}_2\text{Ph})_{2}\)] and \textit{cis}\-[\(\text{PtCl}_2(\text{PMePh}_2)_{2}\)] have \(^1J_{\text{PtP}}\) values of 3549 and 3616 Hz respectively.\(^\text{21}\)

In contrast to the reaction of \([\text{Pd(MeCO}_2]_2\) with stoichiometric amounts of \(\text{EPh}_3\) \((E = \text{P, As})\) which gave the dimeric compounds \([\text{Pd(MeCO}_2]_2EPh}_3\) \((5)^5\) and of\([M(S-S)]_{2}\) with \(\text{PR}_3\) which gave the monomeric compounds \([M(S-S)]_{2}\text{PR}_3\) \((6)^\text{**}\) attempts to obtain the analogous \([M(\text{PhCOS})_{2}\text{L}_n]\) have been unsuccessful. Thus, reaction of \([M(\text{PhCOS})_{2}]\) with stoichiometric amounts of \(\text{L}\) only led to the isolation of \([M(\text{PhCOS})_{2}\text{L}_2]\) and unreacted \([M(\text{PhCOS})_{2}]_n\). Furthermore, monitoring the reaction between \([\text{Pd}(\text{PhCOS})_{2}]\)\(^\text{**}\) This structure \((6)\) has now been established by X-ray analyses for \([\text{Pd}(S_2\text{PPh}_2)_2\text{PPh}_3\{\text{Pt}(S_2\text{CC}_6\text{H}_5\text{C}_6\text{H}_5)_2\text{PMePh}_2\}]\), \([\text{Pt}(S_2\text{CNE}_2)_2\text{PPh}_3]\), \([\text{Pt}(S_2\text{CO}_2)_2\text{PPh}_3]\) and \([\text{Pt}(S_2\text{CO}_2)_2\text{PPh}_3]\)\(^25\)
and small amounts of PMePh₂ in benzene confirmed that only the bis-
phosphine complex was generated in spectroscopically detectable amounts.

For \([\text{Pd(MeCO}_2]_2\text{AsPh}_3\text{]}_2\), only one methyl resonance is observed in
the \(^1\text{H}\) nmr spectrum at ambient temperature. On cooling to 223K, the
singlet splits into two resonances of equal intensity consistent with that
expected for structure (5). Similar temperature variable \(^1\text{H}\) nmr spectra
have been observed elsewhere for \([\text{Pd(RCO}_2]_2\text{PMe}_2\text{Ph}]_2\) (5), [made by reaction
of \([\text{PdCl}_2\text{(PMe}_2\text{Ph})]_2\) with \([\text{Ag(RCO}_2]_2\) (1:4 mole ratio)] and attributed to
facile scrambling of terminal and bridging carboxylato groups by a
solvent assisted ring-opening mechanism.\(^{26}\) Attempts to synthesise pure
samples of \([\text{Pd(MeCO}_2]_2\text{PR}_3\text{]}_2\) (PR₃ = PMe₂Ph, PMePh₂) by reaction of
\([\text{Pd(MeCO}_2]_2\text{]}_3\) with stoichiometric amounts of PR₃ were unsuccessful,
giving inseparable mixtures of the dimers and \([\text{Pd(MeCO}_2]_2\text{(PR}_3\text{)}_2\) .
Furthermore, unlike \([\text{Pd(MeCO}_2]_2\text{(PPh}_3\text{)}_2\] which rearranged to \([\text{Pd(MeCO}_2]_2\text{-}
P\text{Ph}
\text{PPh}_3\text{]}_2\) when left in benzene for 12 hours, \([\text{Pd(MeCO}_2]_2\text{(PR}_3\text{)}_2\] (PR₃ = PMe₂-
Ph, PMePh₂) were recovered unchanged from benzene solution. This
reluctance to lose a PR₃ group can be correlated with the higher
basicity and smaller size of these alkyl substituted phosphines compared
to PPh₃ (cf rearrangement of \([\text{PdX}_2\text{L}_2\] to \([\text{PdX}_2\text{L}_2\] which takes place far
more readily for \(X = \text{I}^−\) than for \(X = \text{Cl}^−\).\(^{26}\)
Unlike the reactions of \([M(S-S)_2]\) with excess \(PR_3\) in polar solvents which gave the ionic complexes \([M(S-S)(PR_3)_2](S-S)\)^2, no ionic species have been detected in any reactions of \([M(PhCOS)_2]_n\). Thus reaction of \([M(PhCOS)_2]_n\) with various \(L\) in acetone led to no increase in the conductivity of the solution and only the neutral \([M(PhCOS)_2L_2]\) were isolated from the reaction mixture. In contrast, reaction of \([Pd(MeCO_2)_2]_3\) with an excess of \(PR_3\) in acetone did produce a highly conducting solution.

However, only the neutral \([Pd(MeCO_2)_2(PR_3)_2]\) were isolated from the reaction mixtures and attempts to 'trap out' an ionic species by addition of Ph\(_4\)AsClHCl or NaBPh\(_4\) were unsuccessful. By analogy with the reaction of \(K_2PtCl_4\) with \(PR_3\) in water which gives initially \([M(PR_3)_4]^-\) [\(MC_14\)] and then rearranges to \([MC_12(PR_3)_2]\), the ionic species here are probably \([Pd(PR_3)_4][Pd(MeCO_2)_4]\).

![Diagram](image)

Finally, contrary to earlier reports,\(^{28}\) there is some very recent evidence for the formation of neutral 1:2 dithioacid compounds \([M(S-S)_2-L_2]^-\). Thus, Fackler\(^{25}\) has shown by X-ray analysis that the reaction product from \([Pt(S_2CN^\text{Bu}_2)_2]\) treated with excess PMe\(_2\)Ph in acetone/diethylether is the neutral monomer \([Pt(S_2CN^\text{Bu}_2)_2(PMe_2Ph)_2]\) (8) with trans monodentate bonded \(-S_2CN^\text{Bu}_2\) ligands. However, in solution, even at low temperatures, this compound rapidly rearranges to an ionic species of structure (7). Clearly the nature of the product isolated by reaction of \([M(S-S)_2]\) with excess \(PR_3\) is very sensitive to such variables as the nature of the phosphine, the dithioacid, the solvent used and the method of
Thus, reaction of \([M(S_2PR_2)_2]\) with an excess of \(PR_3\) such as PMe$_2$Ph, PEt$_3$, PPh$_3$ etc appear to give only ionic compounds as shown by the X-ray structural analysis of \([Pd(S_2PPh_2)(PET_3)_2](S_2PPh_2)\)\[^{22,32}\] together with the observation of identical mull and solution ir spectra.\[^{22,33}\]

A reexamination of the ir spectra of the dithiocarbamate compounds prepared as reported in Ref. 28 also confirms that these are genuine ionic species \([Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2\) (\(R = Me, Et\)) in the solid state and not neutral \([Pt(S_2CNR_2)_2](PMePh_2)_2\) which rapidly rearrange to the ionic species in solution.\[^{++}\]

However, reaction of \([M(S_2PPh_2)_2]\) with the more bulky phosphines P$^n$(octyl)$_3$ and P$^n$Bu$_3$ give yellow solids whose mull ir spectra contain strong bands at ca 540 cm$^{-1}$, indicative of unidentate $S_2$PPh$_2$ coordination \[^{22}\] but no bands at 560 or 570 cm$^{-1}$ characteristic of ionic or bidentate $S_2$PPh$_2$ ligands.\[^{22}\] These products are very unstable, readily rearranging in solution to give the ionic \([M(S_2PPh_2)(PR_3)_2]S_2PPh_2\) compounds.

Conclusion: Although the reaction of \([Pd(MeCO_2)_2]_3\) with various Lewis bases \(L\) gives both the 1:1 and 1:2 adducts \([Pd(MeCO_2)_2L]_2\) and \([Pd(MeCO_2)_2L]_2\) and likewise, with \([M(S-S)]_2\), reaction with tertiary phosphines gives \([M(S-S)_2PR_3]\), \([M(S-S)(PR_3)_2](S-S)\) or \([M(S-S)_2(PR_3)_2]\), reaction of \([M(PhCOS)]_n\) with a variety of Lewis bases gives only the neutral \([M(PhCOS)]_2L\) or \([M(PhCOS)](L-L)\).

\[^{++}\] Similarly with \([Ni(S-S)]_2\) where it is well established that the five and six coordinate adducts \([Ni(S-S)_2]_2\) and \([Ni(S-S)_2L]_2\) respectively are readily formed with a range of nitrogen donor ligands, \[^{26}\] very recent work has shown that reaction of \([Ni(S_2COR)]_2\) (\(R = Et, tBu\)) with PBu$_n$ gives the red, square-planar \([Ni(S_2COR)](PBu_3)\) containing unidentate xanthate groups.\[^{30}\] Also, reaction of \([Ni(S_2POMe)]_2\) with Ph$_2$PC$_2$H$_4$AsPh$_2$ gives \([Ni(S_2POMe)(Ph_2PC$_2$H$_4$AsPh$_2)]S_2C_6H$_4$, probably via the ionic intermediate \([Ni(S_2POMe)](Ph_2PC$_2$H$_4$AsPh$_2)]S_2C_6H$_4\).\[^{31}\]

\[^{++}\] Thus, \(v_{CN}\) in the ir spectra (mull and KBr disc) of these compounds and of \([Pt(S_2CNR_2)(PMePh_2)_2]\) \((Y = BPH$_4$, PF$_6$, Cl$^-)\) \[^{28}\] occur at ca 1560 cm$^{-1}$ (bidentate $S_2CNR_2$ coordination)\[^{34}\] whereas in \([Pt(S_2CN$_4$Bu$_2)_2(PMePh_2)]\) \(v_{CN} = 1465 \text{ cm}^{-1}\) (unidentate $S_2CNR_2$ coordination).\[^{34}\]
Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour pressure osmometer (model 301) calibrated with benzil. Infrared spectra were recorded in the 250-4000 cm\(^{-1}\) region on a Perkin-Elmer 557 grating spectrometer using Nujol and Hexachlorobutadiene mulls on caesium iodide plates. Electronic spectra were recorded on a Unicam SP800 spectrophotometer using unmatched silica cells. Hydrogen-1-nmr spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a variable temperature probe and proton noise-decoupled \(^{31}\)P nmr spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform modes at 40.6 MHz (\(^{31}\)P chemical shifts quoted in ppm to high frequency of 85% \(\text{H}_3\text{PO}_4\)). Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298K. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Palladium(II) chloride, potassium tetrachloroplatinate(II) (Johnson Matthey Ltd), monothiobenzoic acid (Aldrich), triphenylphosphine (BDH), dimethylphenylphosphine, methylidiphenylphosphine (Maybridge Chemical Company) were obtained as indicated. Na[PhCOS]\(^{1}\), Ph\(_2\)PCH\(_2\)PH\(_2\), \(^{35}\)Ph\(_2\)P-(CH\(_2\))\(_2\)PPh\(_2\), \(^{36}\)[Pd(OCOMe)\(_2\)]\(_3\), \(^4\)[Pd(OCOMe)\(_2\)AsPh\(_3\)]\(_2\) and [Pt(S\(_2\)CN\(_2\))\(_2\)](PMePh\(_2\))\(_2\)Y (Y = S\(_2\)CN\(_2\), Cl\(^-\), BPh\(_4\), PF\(_6\)\(^-\)) \(^{28}\) were prepared as described earlier. Analytical data and characteristic IR bands for various monothiobenzoate compounds are given in Table 1 and \(^1\)H and \(^{31}\)P-\(^1\)H{nmr} data for selected monothiobenzoate and acetate compounds in Table 2.

Reactions involving tertiary phosphines were carried out under a nitrogen atmosphere.
Bis(monothiobenzoato)palladium(II):— The compound palladium(II) acetate (0.40g) was dissolved in a minimum volume of cold benzene (30ml) and monothiobenzoic acid (2.0ml) added in dropwise fashion to the resulting red-brown solution to give an immediate red-brown precipitate. Complete precipitation was induced by the addition of an excess of light petroleum (bp 60-80°C). The product was then filtered off, washed with diethylether to remove any free PhCOSH, and then dried under vacuo at 40°C mp 118-121°C (yield 0.30g) [Found C, 43.3; H, 2.7; M(CHCl₃) 1125 (0.90g dm⁻³) 1504 (2.08g dm⁻³), 1672 (4.08g dm⁻³) Calc. for C₁₄H₁₀O₂PdS₂; C, 44.2; H, 2.6%; M 380 (monomer)] IR spectrum (nujol mull):— 1670vs (νCO), 875vs (νCS). Bis(monothiobenzoato)platinum(II):— The compound Na₂PtCl₄ (0.50g), (prepared by passing K₂PtCl₄ down a cation ion exchange column) was suspended in an ethanol (25ml)/water(5ml) mixture and treated with Na[PhCOS] (0.40g) dissolved in ethanol (40ml). This mixture was shaken at room temperature for 5 days and then, the resulting yellow-brown precipitate filtered off, washed with ethanol and dried in vacuo at 40°C mp 194°C (decomp) [Found: C, 35.6; H, 2.2; Calc for C₁₄H₁₀O₂PtS₂; C, 35.8; H, 2.1%] IR spectrum (nujol mull):— 1660s, 1595s, 1575s (νCO); 920s, 880s (νCS).

The remaining red filtrate was evaporated almost to dryness and then treated with an excess of light petroleum (bp 60-80°C) to give a yellow precipitate which was washed with more light petroleum and dried in vacuo at 40°C. [Found: C, 38.3; H, 2.6 Calc for [Pt(PhCOS)₂- EtOH]ₙ C, 37.3; H, 3.1%] IR spectrum (nujol mull) 1660w, 1590vs, 1570-1520vs (broad) cm⁻¹ (νCO); 950-920vs (broad), 880w cm⁻¹ (νCS).

If Na₂PtCl₄ (1.00g) was dissolved in hot water (15ml) and treated with an aqueous solution (40ml) of Na[PhCOS] (2.00g), a brown precipitate is produced. After filtering, extracting into dichloromethane and drying over MgSO₄ for 12 hours, the solution was filtered, solvent
partially removed and excess light petroleum (bp 60–80°C) added to give a pinkish solid [Found C, 40.6; H, 2.6%] IR spectrum (nujol mull) 1580w, 1530vs (ν\text{CO}); 950vs, 920w (ν\text{CS}).

On leaving the aqueous solution which remained after removal of the brown solid, a yellow solid precipitated out after two days which was filtered off and dried under vacuo. [Found, C, 38.1; H, 2.4%] IR spectrum (nujol mull) 1660s, 1590–1520vs (broad) (ν\text{CO}); 950–920 vs (broad); 880w cm\(^{-1}\) (ν\text{CS}).

Qualitative analysis showed that none of these platinum mono-thiobenzoate complexes contained any chlorine.

**General method of preparation of \([M(\text{PhCOS})_2L_2]\) and \([M(\text{PhCOS})_2(L-L)]\) compounds:** The compounds \([M(\text{PhCOS})_2]_n\) (M = Pd, Pt) were dissolved or suspended in benzene or dichloromethane and treated with an excess of Lewis base (L). After shaking for 2–3 hours, the volume was reduced and light petroleum (bp 60–80°C) added to precipitate out the products. These were filtered off, washed with diethyl ether and dried under vacuo at 40°C.

For \(\text{L = SbPh}_3\) or \(\text{AsPh}_3\), the dichloromethane solutions were heated for 2–3 hours to induce complete reaction and the compounds then crystallised out containing one molecule of dichloromethane of solvation. For the bidentate ligands (L–L), an excess of ligand was avoided in order to help prevent complete displacement of the monothio benzoate groups.

**cis-Bis(acetato)bis(dimethylphenylphosphine)palladium(II):** The compound \([\text{Pd(OCOMe)}_2]_3\) in benzene was treated with an excess of dimethylphenylphosphine under nitrogen to give a yellow solution. Addition of light petroleum (bp 60–80°C) gave a cream crystalline precipitate which was washed with diethyl ether and light petroleum (bp 60–80°C) and air-dried

[Found:– C, 47.8; H, 5.8% Calc for C\(_{20}\)H\(_{28}\)O\(_4\)P:– C, 48.0; H, 5.6%] IR spectrum (mull) vsym (CO\(_2^–\)) 1590, vsym 1330 cm\(^{-1}\).
cis-Bis(acetato)bis(methyl(diphenylphosphine)palladium(II) was similarly prepared from [Pd(OCOMe)$_2$]$_3$ and an excess of PMePh$_2$. [Found; C, 57.5; H, 5.1% Calc for C$_{30}$H$_{32}$O$_4$P$_2$Pd: C, 57.7, H, 5.1%] IR spectrum (mull) v$_{asym}$ (CO$_2^-$) 1580; v$_{sym}$ 1315 cm$^{-1}$.

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References


25. J.P. Fackler Jr., personal communication.


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<td>C 56.5</td>
<td>H 3.9</td>
<td>1045</td>
<td>1590s, 1560s</td>
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<td>yellow</td>
<td>175</td>
<td>C 52.3</td>
<td>H 3.7</td>
<td>1160</td>
<td>1590s, 1560s</td>
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<td>129</td>
<td>C 53.5</td>
<td>H 3.9</td>
<td>1160</td>
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<td>280(decomp)</td>
<td>54.8</td>
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<td>brown</td>
<td>194-196</td>
<td>C 61.4</td>
<td>H 4.3</td>
<td>M 61.3</td>
<td>1595s, 1560s</td>
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<td>C 61.9</td>
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<td>228</td>
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<sup>a</sup> Molecular weight measured osmotically at 37°C in chloroform

<sup>b</sup> Partially masked by strong PMe<sub>2</sub>Ph vibration at 900 cm<sup>-1</sup>
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<tr>
<th>Complex</th>
<th>δ value (1H nmr) $^a$</th>
<th>Ph</th>
<th>δ $^b$</th>
<th>J$_{PtP}$ (Hz)</th>
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<tr>
<td></td>
<td>Me (carboxylate)</td>
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<td>[Pd(PhCOS)$_2$(PMe$_2$Ph)$_2$]</td>
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<td>45.8(t)$^{13017.8}$</td>
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$s =$ singlet, $pd =$ pseudo doublet, $t =$ triplet, $m =$ multiplet

$^a$ ±0.01 $^b$ ±0.05 $^c$ 2$J_{PH}$ + 4$J_{PH}$ = 7.0Hz $^d$ CH$_2$ resonance 2$J_{PH}$ 10.0Hz

$^e$ CH$_2$ resonance $^f$ 2$J_{PH}$ + 4$J_{PH}$ = 11.0Hz $^g$ At 223K $^h$ 2$J_{PH}$ 28.0Hz $^i$ 1.4.1 triplet $^j$ Too insoluble to determine splitting pattern
Metal Complexes of Sulphur Ligands Part 18

Reaction of $[\text{RuCl}_2\text{L}_3]$ and 4

$L = \text{PR}_3$, $\text{P(OR)}_2\text{H}_2$, $\text{P(OR)}_2\text{Ph}$ with various Dithioacid Ligands.

By Wilma J. Sime and T. Anthony Stephenson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JH.

Reaction of the compounds $[\text{RuCl}_2\text{L}_4]$ ($L = \text{P(OMe)}_2\text{H}$, $\text{PMePh}_2$)
and $[\text{RuCl}_2\text{(PETH}_2)_3]$ with various alkali metal dithioacid salts gives, under all conditions, the complexes $[\text{Ru}(\text{S-S})_2\text{L}_2]$ [S-S$^-$ = S$_2$PR$_2$(R$^1$ = Me, Ph), $S_2\text{COME}$, $S_2\text{CNR}_2$ (R = Me, Et)].

In contrast the products of reaction of cis-$[\text{RuCl}_2\text{(PMe}_2\text{Ph)}_4]$ and $[\text{RuCl}_2\text{(P(OR)}_2\text{H}_2)_3]$ (R = Me, Et) with these dithioacid anions are very sensitive to reaction conditions. For example, shaking with Na[S$_2$PR$_2$] in benzene gives the yellow complexes $[\text{RuCl}(\text{S}_2\text{PR}_2)_2\text{L}_3]$ which readily rearrange to the red five coordinate cations $[\text{Ru}(\text{S}_2\text{PR}_2)_2\text{L}_3]^+$ in alcoholic media. In contrast, shaking with K[S$_2\text{COME}$] gives the six coordinate $[\text{Ru}(\text{S}_2\text{COME})_2\text{L}_3]$ (with mono-/bidentate $S_2\text{COME}$ coordination), which on heating, rearrange irreversibly to $[\text{Ru}(\text{S}_2\text{COME})_2\text{L}_2]$. Reaction of $[\text{RuCl}_2\text{(PMe}_2\text{Ph)}_4]$ with Na[S$_2$CNR$_2$]xH$_2$O for very short periods in ethanol gives the $[\text{Ru}(\text{S}_2\text{CNR}_2)(\text{PMe}_2\text{Ph})_4]^+$ cation whereas in benzene, $[\text{Ru}(\text{S}_2\text{CNR}_2)_2(\text{PMe}_2\text{Ph})_3]$ are formed. All these compounds have been fully characterized by elemental analyses, $^1\text{H}$ and $^{31}\text{P}$-$^1\text{H}$nmr spectroscopy and a general mechanism for the formation of $[\text{Ru}(\text{S-S})_2\text{L}_2]$ from $[\text{RuCl}_2\text{L}_3]$ and 4 compounds has been proposed.
Reactions of \( [\text{RuCl}_2\text{L}_3] \) (\( \text{L} = \text{PPh}_3, \text{PETPh}_2 \)) and \( \text{mer-}[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3] \) with various dithioacid ligands have previously been reported. In all cases, the products obtained were the six coordinate ruthenium(II) complexes \( [\text{Ru}(\text{S-S})_2\text{L}_2] \) \( \text{S-S}^- = \text{S}_2\text{PR}^1_2 \) \( (\text{R}^1 = \text{Me}, \text{Et}, \text{Ph}), \text{S}_2\text{CNR}^1_2 \) \( (\text{R} = \text{Me}, \text{Et}, \text{Ph}), \text{S}_2\text{COMe} \) containing bidentate dithioacid groups and, in most instances, cis tertiary phosphine ligands.

In this paper, we now report the reactions of more \( [\text{RuCl}_2\text{L}_3] \) \( (\text{L} = \text{P(OMe)Ph}_2^3, \text{P(OEt)Ph}_2^3, \text{PMePh}_2^5, \text{PMe}_2\text{Ph}_2^5, \text{PMe}_2\text{Ph}_2^5, \text{PMe}_2\text{Ph}_2^7) \) compounds with various alkali metal dithioacid salts \( \text{S}_2\text{PR}^1_2 \) \( (\text{R}^1 = \text{Me}, \text{Ph}), \text{S}_2\text{COMe}, \text{S}_2\text{CNR}^1_2 \) \( (\text{R}^1 = \text{Me}, \text{Et}) \). Again the final products were \( [\text{Ru}(\text{S-S})_2\text{L}_2] \) complexes but, in some instances, several intermediate products were isolated and characterised, and on the basis of this data, a general reaction mechanism for the formation of \( [\text{Ru}(\text{S-S})_2\text{L}_2] \) has been proposed.

Results and Discussion

a) Diphenyl- and dimethylphosphinodithioate complexes:— Prolonged reflux of \( [\text{RuCl}_2(\text{P(OR)Ph})_2] \) \( (\text{R} = \text{Me}, \text{Et}) \) with an excess of \( \text{Na} \text{S}_2\text{PMe}_2 \)-2\( \text{H}_2\text{O} \) in alcohol produced a brown solution from which, for \( \text{R} = \text{Me}, \) no solid could be isolated, but where for \( \text{R} = \text{Et} \) a small amount of red-brown crystals analysing for \( [\text{Ru}(\text{S}_2\text{PMe}_2^3)\text{P(OEt)Ph}_2^3] \) (Table 1) were obtained. The infrared spectrum contained a band at 588 cm\(^{-1} \) indicating bidentate coordination of the \( \text{S}_2\text{PMe}_2 \) group, \(^9\) and the \(^{31}\text{P} \) nmr spectrum in CDCl\(_3 \) at 303K (Table 2) consisted of two triplets at 140.76 and 86.70 ppm assigned to the phosphinite and \( \text{S}_2\text{PMe}_2 \) groups respectively. The \(^1\text{H} \) nmr spectrum at 301K contained a doublet at 1.43 ppm due to the methyl groups of \( \text{S}_2\text{PMe}_2 \) and resonances at 3.30 and 1.20 ppm from P(OEt)Ph\(_2 \). Unfortunately, at lower temperatures, the spectrum became very broad and
thus, the isomeric form could not be determined. Similarly, prolonged reaction of \( \text{cis-[RuCl}_2(\text{PMe}_2\text{Ph})_4] \) with Na[S\(_2\text{PMe}_2\)]\(2\text{H}_2\text{O} \) produced yellow crystals, shown by \(^{31}\text{P}\) and \(^1\text{H}\) nmr spectroscopy to be identical to those obtained from \( \text{mer-[RuCl}_3(\text{PMe}_2\text{Ph})_3] \) viz \( \text{cis-[Ru(S}_2\text{PMe}_2\text{)}_2(\text{PMe}_2\text{Ph})_2] \).

However, shaking \( \text{[RuCl}_2(\text{PMe}_2\text{Ph})_4] \) or \( \text{[RuCl}_2(\text{P[OR]}\text{Ph})_2)_3] \) in methanol \((R = \text{Me}) \) or ethanol \((R = \text{Et}) \) with Na[S\(_2\text{PMe}_2\)] \((R = \text{Me, Ph}) \) for a short time produced red, conducting solutions, which on addition of NaBPh\(_4\) precipitated red solids analysing closely for \( \text{[Ru(S}_2\text{PMe}_2\text{)}_2(\text{L}_3\text{)BPh}_4] \). The ir spectra contained bands at ca 580 cm\(^{-1}\) consistent with bidentate \( \text{S}_2\text{PMe}_2 \) coordination and conductivity measurements in acetone indicated 1:1 electrolytes (see experimental section). The latter result suggested monomeric structures in solution and this was supported by molecular weight studies in CHCl\(_3\) on \( \text{[Ru(S}_2\text{PMe}_2\text{)}_2(\text{PMe}_2\text{Ph})_3]BPh}_4\) (Table 1). The presence of a monomeric structure in the solid state has been confirmed by the results of a preliminary X-ray analysis on \( \text{[Ru(S}_2\text{PPh}_2\text{)}_2(\text{PMe}_2\text{Ph})_3]BPh}_4\). The cation has a distorted square pyramidal geometry as found (and predicted) for several other five coordinate ruthenium(II) complexes.

The \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum of \( \text{[Ru(S}_2\text{PMe}_2\text{)}_2(\text{PMe}_2\text{Ph})_3]BPh}_4\) in CDCl\(_3\) at 298K consisted of a doublet at 32.36\(\delta\) (\(^3J_{\text{PP}} = 3.6\) Hz) due to the \( \text{PMe}_2\text{Ph} \) groups which, because of facile intramolecular scrambling, are rendered equivalent and thus equally coupled to the \( \text{S}_2\text{PMe}_2 \) group, and a quartet at 110.31\(\delta\) due to the \( \text{S}_2\text{PMe}_2 \) group coupled equally to the three \( \text{PMe}_2\text{Ph} \) groups. Similarly, the \(^1\text{H}\) nmr spectrum at 301K consisted of a doublet (\(^2J_{\text{PH}} = 13\) Hz) due to the \( \text{S}_2\text{PMe}_2 \) methyl groups (equivalent because of facile \( \text{PMe}_2\text{Ph} \) scrambling) and a "pseudo-triplet" pattern from

\(^*\) A "pseudo-triplet" pattern consists of a sharp doublet with a broad hump situated between the doublet and signifies a relatively large \(J(PP)\) compared to the \( |J(PP)+J(\text{PH})| \) value (cf \( \text{cis-[Ru(S}_2\text{PMe}_2\text{)}_2(\text{PMe}_2\text{Ph})_2] \))
the PMe$_2$Ph methyl groups. Neither the $^{31}$P or $^1$H nmr spectra changed
on cooling to 213K indicating that intramolecular scrambling was still
rapid at these temperatures.

If [RuCl$_2$(P|OR|Ph)$_2$]$_3$ or [RuCl$_2$(PMe$_2$Ph)$_4$] were shaken with
Na[S$_2$PMe$_2$]$_2$H$_2$O in benzene, however, yellow non-conducting solids
analysing for [RuCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$] were obtained. These were fairly stable
in CHCl$_3$ or CH$_2$Cl$_2$, but in methanol or ethanol, red solutions containing
the [Ru(S$_2$PMe$_2$)$_3$]$^+$ cations were formed immediately. The $^{31}$P-($^1$H) nmr
spectrum of [RuCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$] at 213K in CDCl$_3$ consisted of an un-
symmetrical quartet centred at 93.90 ppm ($S_2$PMe$_2$ group) and an AB$_2$
pattern ($v_A$ 20.38; $v_B$ 16.06; $J_{AB}$ 33.0 Hz)(PMe$_2$Ph groups). At 298K, the AB$_2$
pattern broadened and a singlet appeared at 21.26 ppm corresponding to
[RuCl$_2$(PMe$_2$Ph)$_3$]Cl, formed presumably by the slow decomposition of
[RuCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$] in chlorinated solvents.

The $^1$H nmr spectrum at 233K in CDCl$_3$ contained two doublets at
1.19 and 2.17 ppm which both collapsed at the same $^{31}$P nmr frequency
(viz 95.5 ppm) indicating that they arise from the methyl groups of $S_2$PMe$_2$.
There was also a doublet at 1.60 (decoupling $^{31}$P nmr frequency = 19.5 ppm)
and a broad resonance at 1.88 due to the PMe$_2$Ph groups. At 298K, only a
broad resonance at 1.70 ppm was observed, indicating that, on the one hand,
all the PMe$_2$Ph groups and, on the other, the methyls of $S_2$PMe$_2$ had
become equivalent.

*The irradiation frequencies are different from the frequencies of the $^{31}$P nuclei obtained from the Fourier transform spectrum because the former
are obtained from the HA-100 spectrometer (with Schlumberger FS30 frequency
synthesiser attachment) whereas the latter were directly measured on the
XL100 spectrometer and these have slightly different reference frequencies.
This low temperature $^1$H nmr data is consistent with structure (1) in which the $^2$PMe$_2$ methyl groups are inequivalent; the doublet at 1.60$\delta$ is assigned to methyl groups (c) and (d) attached to the PMe$_2$Ph group trans to Cl$^-$ whereas the resonance at 1.88$\delta$ (two overlapping 'pseudo-doublets') is ascribed to the methyls on the two PMe$_2$Ph groups trans to the dithioacid ligand. The equivalence of all the tertiary phosphine methyl groups (and also Me(a) and Me(b)) at higher temperatures is readily rationalised by postulating facile Ru-S bond cleavage to generate five coordinate intermediates, followed by reformation to produce various six coordinate isomers (see Scheme 1).

Reaction between [RuCl$_2$(P(OMe)$_2$Ph)$_4$] and NaS$_2$PR$_2$ ($R^1$ = Me, Ph) under all these conditions, however, produced in both cases only [Ru(S$_2$PR$_2$)$_2$(P$_2$OMe$_2$Ph)$_2$]. The $^1$H nmr spectrum at 301K of [Ru(S$_2$PMe$_2$)$_2$P$_2$(OMe)$_2$Ph$_2$]$_n$ exhibited a "pseudo-triplet" pattern at 3.60$\delta$ and a broad resonance at 1.80$\delta$. As the temperature was lowered, the "pseudo-triplet" split into two and the broad resonance sharpened, such that at 213K, the spectrum contained two "pseudo-triplets" (decoupling to give two singlets at the same $^{31}$P nmr frequency) at 3.42 and 3.58$\delta$ and two doublets (also decoupling at the same $^{31}$P nmr frequency) at 1.71 and 2.12$\delta$. This low temperature spectrum is consistent with a cis-configuration and the mechanism of interconversion of optical isomers which occurred at higher temperatures is probably identical to that established earlier for other cis-[Ru(S$_2$PMe$_2$)$_2$L$_2$] complexes.$^{13}$

* A "pseudo-doublet" is a sharp doublet with additional signal intensity situated between the doublet. This spectral pattern is indicative of a small, but non-zero, $J_{PP}$ value when compared to $|J_{PH} + J_{PP}|$.$^{12}$
b) O-methylene dithiocarbonate complexes: Shaking \([ \text{RuCl}_2(\text{P}[\text{OR}]\text{Ph}_2)_3 ] \), (R = Me, Et) or \([ \text{RuCl}_2(\text{PMe}_2\text{Ph})_4 ] \), with excess \( \text{K}[\text{S}_2\text{COMe}] \) in methanol produced yellow, non-conducting solids analysing for \([ \text{Ru}(\text{S}_2\text{COMe})_2\text{L}_3 ] \). The ir spectra contained several bands in the region 1000-1200 cm\(^{-1} \) indicating the presence of coordinated \( \text{S}_2\text{COMe} \) groups and the \( ^{31}\text{P}-\{^1\text{H}\} \) nmr spectrum at 298K (for \( \text{L} = \text{PMe}_2\text{Ph} \)) consisted of an \( \text{AB}_2 \) pattern, confirming the presence of three \( \text{PMe}_2\text{Ph} \) groups. The \( ^1\text{H} \) nmr spectrum of this compound in \( \text{CDCl}_3 \) at 301K contained two resonances at 3.92 and 3.65\( \delta \) (\( \text{S}_2\text{COMe} \)) indicating the presence of both mono- and bi-dentate xanthate ligands. The spectrum also showed "pseudo-triplet" and doublet resonances in intensity ratio 2:1 (\( \text{PMe}_2\text{Ph} \) groups), (Table 3). The doublet could be assigned to a \( \text{PMe}_2\text{Ph} \) group trans to the monodentate dithio acid ligand and the "pseudo-triplet" to the two cis \( \text{PMe}_2\text{Ph} \) groups, each trans to a sulphur of the bidentate ligand.

If \([ \text{Ru}(\text{S}_2\text{COMe})_2(\text{P}[\text{OMe}]\text{Ph}_2)_3 ] \) was heated under reflux in the presence of \( \text{K}[\text{S}_2\text{COMe}] \), orange-yellow crystals of \([ \text{Ru}(\text{S}_2\text{COMe})_2(\text{P}[\text{OMe}]\text{Ph}_2)_2 ] \) were produced. The \( ^{31}\text{P}-\{^1\text{H}\} \) nmr spectrum in \( \text{CDCl}_3 \) at 298K consisted of a singlet at 146.51\( \delta \) while the \( ^1\text{H} \) nmr contained a singlet at 3.71\( \delta \) (\( \text{S}_2\text{COMe} \)) and a "pseudo-triplet" at 3.22\( \delta \) (\( \text{PMe}_2\text{Ph} \)) suggesting a cis configuration.

An intractable yellow oil was obtained from the reaction between \([ \text{RuCl}_2(\text{P}[\text{OMe}]\text{Ph}_2)_2 ] \) and excess \( \text{K}[\text{S}_2\text{COMe}] \) but shaking \([ \text{RuCl}_2(\text{PMePh}_2)_4 ] \) and \([ \text{RuCl}_2(\text{PEThPh}_2)_3 ] \) with excess of \( \text{K}[\text{S}_2\text{COMe}] \) in alcohol produced \([ \text{Ru}(\text{S}_2\text{COMe})_2\text{L}_2 ] \). For \([ \text{Ru}(\text{S}_2\text{COMe})_2(\text{PMePh}_2)_2 ] \), the \( ^{31}\text{P} \) and \( ^1\text{H} \) nmr spectra at both 218 and 298K were consistent with a cis-configuration. However, for \([ \text{Ru}(\text{S}_2\text{COMe})_2(\text{PEThPh}_2)_2 ] \), the \( ^{31}\text{P}-\{^1\text{H}\} \) nmr spectrum at 218K in \( \text{CDCl}_3 \) consisted of two singlets of equal intensity, at 50.32 and 44.31\( \delta \). As the temperature was raised, the singlet at 44.31\( \delta \) increased.
$^1$H nmr spectrum of [Ru($S_2CNMe_2$)$_2$(PMe$_2$Ph)$_4$]BPh$_4$ in CDCl$_3$ at 301K contained a singlet at 2.37δ, "pseudo-triplet" at 1.76δ and triplet at 1.27δ in the intensity ratio 1:2:2, assigned to the $S_2CNMe_2$ groups (P$_A$ and P$_B$) and the trans phosphines (P$_C$ and P$_D$) respectively.

The reaction between [RuCl$_2$(PMe$_2$Ph)$_4$] and Na[$S_2CNMe_2$]$_2$H$_2$O in benzene, however, produced a bright yellow non-conducting solid analysing for [Ru($S_2CNMe_2$)$_2$(PMe$_2$Ph)$_3$]. The $^{31}$P-{$^1$H} nmr spectrum in CDCl$_3$ at 298K exhibited an AB$_2$ pattern ($v_A = 14.19$; $v_B = 11.48$; $J_{AB} = 29.5$ Hz) and the $^1$H nmr spectrum under the same conditions contained two singlets at 3.49 and 2.90δ (assigned to mono- and bidentate $S_2CNMe_2$ groups respectively), two overlapping "pseudo-doublets" at 1.96δ arising from the two phosphine groups trans to bidentate $S_2CNMe_2$ and a doublet at 1.07δ from the phosphine ligand trans to the unidentate group.

This compound was also precipitated as yellow crystals on prolonged reaction of [RuCl$_2$(PMe$_2$Ph)$_4$] with Na[$S_2CNMe_2$]$_2$H$_2$O in methanol. The reaction presumably does not give [Ru($S_2CNMe_2$)$_2$(PMe$_2$Ph)$_2$] because of the insolubility of [Ru($S_2CNMe_2$)$_2$(PMe$_2$Ph)$_3$] in methanol.

When [RuCl$_2$(POMe$_2$Ph)$_3$] was shaken with an excess of Na[$S_2CNR_2$]$_2$H$_2$O (R$_1$ = Me, Et) in ethanol, cis-[Ru($S_2CNR_2$)$_2$(POMe$_2$PH)$_2$]$_2$ (isomer confirmed by $^{31}$P and $^1$H nmr evidence) was the major product, together with a small amount of the $[\text{Ru}(S_2CNR_2)(P\text{OMe}\\text{PH}_2)_3]^+$ cation which was trapped out by addition of NaBPh$_4$. In benzene, the major product was $[\text{Ru}(S_2CNMe_2)(P\text{OMe}\\text{Ph}_2)_3]$ shown by $^{31}$P nmr spectroscopy to partially convert to $[\text{Ru}(S_2CNMe_2)_2(P\text{OMe}\\text{Ph}_2)_2]$ in solution.

As for the other dithioacid ligands, treatment of [RuCl$_2$L$_4$] (L = PMePh$_2$, POMe$_2$Ph) and [RuCl$_2$(PETPh$_2$)$_3$] with Na[$S_2CNR_2$]$_2$H$_2$O under all conditions gave only [Ru($S_2CNR_2$)$_2$L$_2$]. All the $^{31}$P-{$^1$H} nmr spectra, (except $[\text{Ru}(S_2CNMe_2)_2(\text{PMePh}_2)_2]$ which was too insoluble for either $^{31}$P or $^1$H nmr studies), consisted of a singlet except those of $[\text{Ru}(S_2CNMe_2)_2(P\text{OMe}\\text{Ph}_2)_2]$ which contained
two singlets, the higher frequency signals decreasing in intensity as the temperature was raised from 213 to 298K. This suggested, as for [Ru($S_2$COMe)$_2$(PETPh)$_2$], an irreversible isomerisation, which was shown for [Ru($S_2$CNMe$_2$)$_2$(PETPh)$_2$] to be from the trans to the cis isomer by means of the relative intensities of the three $S_2$CNMe$_2$ methyl resonances in the $^1$H nmr spectrum at 301K, two of which are of equal intensity and much more intense than the third.

The $^1$H nmr spectra of the remaining complexes were all consistent with a cis stereochemistry. (See Table 3).

d) Proposed mechanism of formation of [Ru(S-S)$_2$L$_2$] from [RuCl$_2$L$_3$ or 4]

In view of the above results, in which several intermediates produced in the formation of [Ru(S-S)$_2$L$_2$] have been isolated, a reaction scheme for the formation of [Ru(S-S)$_2$L$_2$] from [RuCl$_2$L$_3$ and 4] can now be proposed, (Scheme 2).

Thus for [RuCl$_2$L$_3$](II) the initial step is probably replacement of one of the chloride ions by a dithioacid ligand to give the intermediate(III) followed by rapid attack of the dangling sulphur atom on the vacant coordination site to produce (IV). Complex (V) is stable in benzene when (S-S)$^-$ = $S_2$PR$_2^1$ but in alcohol, it loses chloride ion and converts to the cation (V) which can then react with more Na[$S_2$PR$_2^1$] to give (VI). However, (IV) is not stable in benzene in the presence of stronger nucleophiles such as $S_2$COMe and $S_2$CNR$_2^1$ which replace the chloride ion to produce (VI), although in polar solvents, for (S-S)$^-$ = $S_2$CNR$_2$ the initial step in this process is the formation of the cation (V). The final step in this mechanism is then attack of the free sulphur atom with the loss of L to give (VII).

For [RuCl$_2$L$_4$](I) the reaction with Na[$S_2$PR$_2^1$] follows the same path as
that of \([\text{RuCl}_2\text{L}_3]\) and it seems reasonable, therefore, to assume that loss of an L group occurs prior to reaction with the dithioacid ligand. However, reaction with Na[\(S_2\text{CNR}_2^1\)]\(\times\)\(\text{H}_2\text{O}\) in alcohol produced the cationic species (VIII) containing four L groups, which is probably formed by the rapid attack of the more nucleophilic \(S_2\text{CNR}_2^1\) ligand on \([\text{RuCl}_2\text{L}_4]\), which occurs prior to loss of L. Subsequent loss of L and reaction with \(S_2\text{CNR}_2^1\) yields (VI) which, because of its insolubility in alcohol, is precipitated out and further reaction does not occur. Treatment of \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) with K[\(S_2\text{COMe}\)] produced only (VI) and, therefore, as (VI) is formed by both pathways, it is not possible to determine which one is operative in this case.

Finally, the isolation of several intermediate products in the reactions of \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) and \([\text{RuCl}_2(\text{POR})\text{Ph}_3]\) \((\text{R} = \text{Me, Et})\) with dithioacid ligands, as opposed to the corresponding reactions of \([\text{RuCl}_2\text{L}_4]_2\) \((\text{L} = \text{PMePh}_2, \text{P(OMe)}_2\text{Ph})\) and \([\text{RuCl}_2(\text{PETPh}_2)_3]\), which yield only \([\text{Ru(S-S)}_2\text{L}_2]_2\), is presumably a reflection of the stronger Ru-P bonds in the former complexes. Hence the last step of the mechanism, which involves the cleavage of a Ru-P bond, is slow so that the intermediate complexes containing three phosphorus donor groups are fairly long-lived and can readily be isolated. On the other hand, for complexes containing weaker Ru-P bonds, the tendency to lose an L group is much greater and any intermediates will quickly rearrange to form \([\text{Ru(S-S)}_2\text{L}_2]_2\) (VII).

**EXPERIMENTAL**

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab Vapour Pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the region 4000-250 cm\(^{-1}\) on Perkin Elmer 457 and 225
grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. $^1$H nmr spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable temperature attachment. Heteronuclear decoupling experiments were carried out on this spectrometer using a radio frequency field provided by the Schlumberger FS30 frequency synthesiser. $^{31}$P nmr spectra (proton noise decoupled) were recorded on a Varian Associates XL-100 spectrometer operating in the Pulse and Fourier Transform mode at 40.5 MHz. Chemical Shifts are reported in p.p.m. to high frequency of 85% $\text{H}_3\text{PO}_4$. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Conductivity measurements were made at 298K using a model 310 Portland Electronics conductivity bridge. Conductivity vs concentration data were obtained over a range of concentrations ($2 \times 10^{-3}$ to $5 \times 10^{-3}$ dm$^{-3}$ mol) and a plot of $\mathcal{L}$ (equivalent conductance) against $C^\frac{1}{2}$ (concentration in equivalents dm$^{-3}$) gave a straight line which on extrapolation to $C^\frac{1}{2} = 0$ gave $\mathcal{L}_0$. A subsequent plot of $\mathcal{L}_0 - \mathcal{L}$ vs $C^\frac{1}{2}$ gave a straight line whose slope is a function of the ionic charges. Thus, the slopes obtained for various samples were compared with those for known 1:1 and 2:1 electrolytes and hence the electrolyte type could be determined.

Materials

Ruthenium trichloride trihydrate (Johnson Matthey); $\text{NaS}_2\text{CNR}_2\times\text{H}_2\text{O}$ (R = Me, Et; Ralph Emanuel) $\text{Na[S}_2\text{PMe}_2]\times\text{H}_2\text{O}$, $\text{NaS}_2\text{PPh}_2$, and $\text{K}[\text{S}_2\text{COMe}]$ were prepared by standard literature methods. The various [RuCl$_2$L$_3$ or L$_4$] complexes were prepared as described elsewhere.

Analytical data is given in Table 1, $^{31}$P and $^1$H nmr data in Tables 2 and 3 respectively. All reactions were carried out in degassed solvents under an atmosphere of nitrogen.
Diaryl(alkyl)phosphinodithioate complexes

Chloro(dimethylphosphinodithioato)tris(dimethylphenylphosphine)-
    ruthenium(II):- The compounds [RuCl₂(PMe₂Ph)₄] (0.20g) and Na[S₂PMe₂] -
    2H₂O (0.20g) were shaken in benzene (20ml) for 1h. The resulting yellow
    solution was filtered to remove any unreacted Na[S₂PMe₂]₂H₂O and the
    benzene removed to give the complex as yellow crystals which were
    washed with water and dried in vacuo m.p. 178-180°C. IR spectrum:-
    \( \nu \text{P=S} \) 600 cm⁻¹.

Chloro(dimethylphosphinodithioato)tris(methylidiphenylphosphinite)-
    ruthenium(II):- The compounds [RuCl₂(P(OMe)Ph₂)₃] (0.20g) and
    Na[S₂PMe₂]₂H₂O (0.20g) were shaken in benzene (20ml) for 1h., the
    resulting yellow solution filtered and reduced in volume to ca 5 ml.
    Addition of light petroleum (bp 60-80°C) then precipitated a yellow
    solid which was filtered off, washed with water and dried in vacuo
    m.p. 91-93°C; \( \nu \text{P=S} \) 595 cm⁻¹.

Similarly, chloro(dimethylphosphinodithioato)tris(ethyldiphenyl-
    phosphinite)ruthenium(II) was prepared from [RuCl₂(P(OEt)Ph₂)₃] m.p.
    116-118°C; \( \nu \text{P=S} \) 595 cm⁻¹.

(Dimethylphosphinodithioato)tris(dimethylphenylphosphine)-
    ruthenium(II)tetraphenylborate: - The compounds[RuCl₂(PMe₂Ph)₄] (0.20g)
    and Na[S₂PMe₂]₂H₂O (0.20g) were shaken in methanol (20ml) for 5m to
    give a red solution. After filtering to remove any unreacted Na[S₂PMe₂] -
    2H₂O, a solution of NaBPh₄ (0.20g) in methanol (5ml) was added and the
    red crystals formed were filtered off and washed with water and
    diethyl ether m.p. 149-151°C; \( \nu \text{P=S} \), 580 cm⁻¹. Conductivity in acetone;
    slope of \( \sqrt{I} \) - \( \sqrt{\text{C}} \) plot = 192. (For \[RuCl₂(P(OMe)Ph₂)₃\BPh₄\], slope = 155;
    for \[Ru(\eta-C₆H₆)(NH₃)₃\] (PF₆)₂', slope = 350). Similarly, reaction with
    Na[S₂PPh₂] produced red crystals of (diphenylphosphinodithioato)tris-
(dimethylphenylphosphine)ruthenium(II)tetrphenylborate m.p. 160-162°C; $\nu_{PS_2}^{O}$, 570 cm$^{-1}$.

(Dimethylphosphinodithioato)tris(methylidiphenylphosphinite)ruthenium(II)tetrphenylborate m.p. 184-186°C; $\nu_{PS_2}$ 580 cm$^{-1}$; conductivity in acetone, slope = 215 and diphenylphosphinodithioato-

tris(methylidiphenylphosphinite)ruthenium(II)tetrphenylborate m.p. 150-152°C; $\nu_{PS_2}$, 570 cm$^{-1}$ were prepared as red-brown and orange-brown solids respectively by shaking [RuCl$_2$(P(OMe)Ph$_2$)$_3$] with Na[S$_2$PR$_2$] in methanol for 5m., followed by addition of NaBPh$_4$ in methanol to the resulting red solutions. Similarly, (dimethylphosphinodithioato)tris(ethylidiphenylphosphinite)ruthenium(II)tetrphenylborate m.p. 116-118°C; $\nu_{PS_2}$ 580 cm$^{-1}$ and diphenylphosphinodithioato)tris-

(ethylidiphenylphosphinite)ruthenium(II)tetrphenylborate m.p. 174-176°C; $\nu_{PS_2}$, 570 cm$^{-1}$ were prepared as red-brown and orange-brown solids respectively.

Bis(dimethylphosphinodithioato)bis(ethylidiphenylphosphinite)-ruthenium(II):- The compounds [RuCl$_2$(P(OEt)Ph$_2$)$_3$] (0.20g) and Na[S$_2$PMe$_2$]2H$_2$O (0.20g) were refluxed in ethanol (20ml.) for 2h. to give a brown solution. On standing for 3 days, a small amount of yellow brown crystals were deposited m.p. 230°C; $\nu_{PS_2}$ 588 cm$^{-1}$.

Bis(dimethylphosphinodithioato)bis(dimethylphenylphosphonite)ruthenium(II):- The compounds [RuCl$_2$(P(OMe)$_2$Ph)$_4$] (0.20g) and Na[S$_2$PMe$_2$]2H$_2$O (0.20g) were refluxed in methanol (40ml.) for 1h to give a bright yellow solution. After reducing in volume to ca. 15ml. and leaving for 1h., yellow crystals were deposited, filtered off, washed with water and dried in vacuo m.p. 207-209°C; $\nu_{PS_2}$ 580 cm$^{-1}$. Similarly, bis(diphenylphosphinodithioato)bis

(dimethylphenylphosphonite)ruthenium(II) m.p. 211-213°C was prepared by reaction of [RuCl$_2$(P(OMe)$_2$Ph)$_4$] with Na[S$_2$PPh$_2$].
O-methylidithiocarbonate complexes

Bis(0-methylidithiocarbonate)tris(dimethylphenylphosphine)ruthenium(II):- The compounds \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) (0.20g) and \(\text{K}[\text{S}_2\text{COMe}]\) (0.20g) were shaken in methanol (30ml) for 2h. during which time lemon-yellow crystals of the complex were deposited. These were filtered off and washed with water and diethyl ether, m.p. 123-125°C. Both bis(0-methylidithiocarbonate)tris(methylidiphenylphosphinite)ruthenium(II), m.p. 111-113°C and bis(0-methylidithiocarbonate)tris(ethylidiphenylphosphinite)ruthenium(II) m.p. 106-108°C were prepared similarly from \([\text{RuCl}_2(\text{PO}(\text{OR})\text{Ph})_3]\) (R = Me, Et) respectively. Bis(0-methylidithiocarbonate)bis(methylidiphenylphosphinite)ruthenium(II):- The compound \([\text{Ru(S}_2\text{COMe})_2(\text{POMe})\text{Ph}_2)_3]\) (0.20g) was refluxed in \(\text{CH}_2\text{Cl}_2\) (20ml) containing \(\text{K}[\text{S}_2\text{COMe}]\) (0.05g) for 1h. to give an orange-yellow solution. Methanol (10ml) was added and the dichloromethane allowed to evaporate off over a period of 2 days to produce orange crystals m.p. 85-87°C.

Bis(0-methylidithiocarbonate)bis(methylidiphenylphosphinite)ruthenium(II):- The compounds \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) (0.20g) and \(\text{K}[\text{S}_2\text{COMe}]\) (0.20g) were shaken in methanol for 12h. The bright yellow solid obtained was filtered off and washed with water and diethyl ether m.p. 163-165°C. The complex bis(0-methylidithiocarbonate)bis(ethylidiphenylphosphinite)ruthenium(II) was prepared similarly as a yellow solid from \([\text{RuCl}_2(\text{PEtPh}_2)_3]\) m.p. 147-149°C.

N,N dialkyldithiocarbamate complexes

(Dimethylidithiocarbamate)tetrakis(dimethylphenylphosphine)ruthenium(II)-tetrabenzylborate:-- The compounds \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) (0.20g) and \(\text{Na}[\text{S}_2\text{CNMe}_2\text{]}_2\text{H}_2\text{O}\) (0.20g) were shaken in methanol for 5m. After filtering, \(\text{NaBP}_4\) (0.20g) was added, the white precipitate filtered off and washed with methanol and diethyl ether m.p. 154-156°C; \(\nu_\text{CN} 1525 \text{ cm}^{-1}\).
conductivity in \( \text{CH}_2\text{Cl}_2 \), slope of \( \nu - \frac{1}{\nu} \) vs. \( \text{C}_2 \) plot = 185. Similarly, (diethylthiocarbamato)tetrakis(dimethylphenylphosphine)ruthenium(II)-tetraphenylborate, \( \nu_{\text{CN}} \) 1492 cm\(^{-1}\), was prepared using Na[S\(_2\)CNET\(_2\)]\(3\)H\(_2\)O.

Bis(dimethylthiocarbamato)tris(dimethylphenylphosphine)ruthenium(II):- The compounds [RuCl\(_2\)(PMe\(_2\)Ph\(_4\)] (0.20g) and Na[S\(_2\)CNMe\(_2\)]2H\(_2\)O (0.20g) were shaken in benzene (20ml.) for 1h., the resulting yellow solution reduced in volume to ca 5ml. and light petroleum (bp 60-80°C) added to precipitate a yellow solid; \( \nu_{\text{CN}} \) 1510 cm\(^{-1}\). (Bis(dimethylthiocarbamato)tris(methylidiphenylphosphinite)ruthenium(II), was prepared similarly from [RuCl\(_2\)(POMe)\(_2\)Ph\(_3\)] m.p. 95-97°C; \( \nu_{\text{CN}} \) 1500 cm\(^{-1}\) (broad).

(Dimethylthiocarbamato)tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate:- The compounds [RuCl\(_2\)(POMe)\(_2\)Ph\(_3\)] (0.20g) and Na[S\(_2\)CNMe\(_2\)]2H\(_2\)O (0.20g) were shaken in methanol (20ml.) for 10m. to give an orange solution. The addition of NaBPh\(_4\) (0.20g) produced an orange-pink solid which was filtered off, leaving a yellow filtrate.

Recrystallisation of the solid from \( \text{CH}_2\text{Cl}_2\)/MeOH gave yellow crystals of [Ru\(_2\)Cl\(_3\)(POMe)\(_2\)Ph\(_6\)]BPh\(_4\) (identified by \( ^1\)H nmr) but on further standing, the remaining red solution gave red crystals of the complex; \( \nu_{\text{CN}} \) 1510 cm\(^{-1}\). The yellow filtrate on slowly evaporating to half its volume produced orange-yellow crystals of bis(dimethylthiocarbamato)bis(methylidiphenylphosphinite)ruthenium(II) m.p. 194-196°C; \( \nu_{\text{CN}} \) 1510 cm\(^{-1}\). Similarly, reaction with Na[S\(_2\)CNET\(_2\)]3H\(_2\)O gave (diethylthiocarbamato)tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate as red crystals, \( \nu_{\text{CN}} \) 1480 cm\(^{-1}\) and bis(diethylthiocarbamato)-bis(methylidiphenylphosphinite)ruthenium(II) as yellow crystals m.p. 170-172°C; \( \nu_{\text{CN}} \) 1482 cm\(^{-1}\).

Bis(dimethylthiocarbamato)bis(dimethylphenylphosphinite)ruthenium-(II):- The compounds [RuCl\(_2\)(POMe)\(_2\)Ph\(_4\)] (0.20g) and Na[S\(_2\)CNMe\(_2\)]2H\(_2\)O (0.20g) were refluxed in methanol for 1h. The solution was filtered and the solvent allowed to evaporate off slowly to give yellow crystals m.p. 178-180°C; \( \nu_{\text{CN}} \) 1520 cm\(^{-1}\). Reaction with Na[S\(_2\)CNET\(_2\)]3H\(_2\)O yielded
yellow crystals of bis(diethylthiocarbamato)bis(dimethylphenylphosphonite)ruthenium(II) m.p. 125-127°C; $\nu_{CN}$ 1482 cm$^{-1}$. The complexes bis(dimethylthiocarbamato)bis(methylidiphenylphosphine)ruthenium(II) m.p. 229-231°C; $\nu_{CN}$ 1515 cm$^{-1}$; bis(diethylthiocarbamato)bis(methylidiphenylphosphine)ruthenium(II), m.p. 84-86°C; $\nu_{CN}$ 1485 cm$^{-1}$; bis(dimethylthiocarbamato)bis(ethylidiphenylphosphine)ruthenium(II) m.p. 133-135°C; $\nu_{CN}$ 1515 cm$^{-1}$ and bis(diethylthiocarbamato)bis(ethylidiphenylphosphine)ruthenium(II) m.p. 152-154°C; $\nu_{CN}$ 1480 cm$^{-1}$ were all obtained as yellow solids by shaking [RuCl$_2$(PMePh$_2$)$_4$] (0.20g) and [RuCl$_2$(PEtPh$_2$)$_3$] (0.20g) respectively with Na[$S_2CNMe_2$]$_2$H$_2$O (0.20g) and Na[$S_2CNEt_2$]$_2$H$_2$O (0.20g) in methanol (30ml.). The complexes were filtered off and washed with water and diethyl ether.

We thank Johnson-Matthey Ltd for generous loans of ruthenium trichloride trihydrate, the S.R.C. for support (WJS), Dr. A.S.F. Boyd and Mr. J.R.A. Millar for obtaining the $^{31}$P and $^1$H nmr spectra respectively and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.
References


2. For detailed references, see D.J. Cole-Hamilton and T.A. Stephenson, J.C.S. Dalton, 1974, 739.


TABLE 1

Analytical data for some ruthenium(II) dithioacid complexes

<table>
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<tr>
<th>Complex</th>
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<th>% Calculated</th>
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<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[RuCl(S&lt;sub&gt;2&lt;/sub&gt;PMe&lt;sub&gt;2&lt;/sub&gt;)(P(OMe)Ph)&lt;sub&gt;2&lt;/sub&gt;]&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>5.0</td>
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<td>55.5</td>
<td>5.4</td>
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<td>[RuCl(S&lt;sub&gt;2&lt;/sub&gt;PMe&lt;sub&gt;2&lt;/sub&gt;)(PMe&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;3&lt;/sub&gt;]</td>
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<td>5.2</td>
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<td>5.6</td>
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<td>5.5</td>
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<td>5.9</td>
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<sup>a</sup> Measured osmotically at 37°C in CHCl<sub>3</sub>

<sup>b</sup> Half actual molecular weight since 1:1 electrolyte
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<th>Complex</th>
<th>T/K</th>
<th>$\delta^a$/ppm</th>
<th>Other resonances $^b$</th>
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<td>[RuCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$]</td>
<td>213</td>
<td>93.90$^c$</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 20.38, $\nu_B$, 16.06; $J</em>{AB}$ 33.0 Hz)</td>
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<td>[RuCl(S$_2$PMe$_2$)(POME$_2$Ph)$_3$]</td>
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<td>96.65$^d$</td>
<td>139.67$^d$</td>
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<td>[RuCl(S$_2$PMe$_2$)(P[OEt]Ph$_2$)$_3$]</td>
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<td>109.38$^d$</td>
<td>140.42$^d$</td>
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<tr>
<td>[Ru(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$]BPh$_4$</td>
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<td>110.31(q)</td>
<td>32.36(d) ($^3J_{PP} = 3.6$ Hz)</td>
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<td>[Ru(S$_2$PPh$_2$)(PMe$_2$Ph)$_3$]BPh$_4$</td>
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<td>104.28$^d$</td>
<td>32.29$^d$</td>
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<td>[Ru(S$_2$PMe$_2$)(P[OEt]Ph$_2$)_3]BPh$_4$</td>
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<td>111.58(q)</td>
<td>144.85(d) ($^3J_{PP} = 4.4$ Hz)</td>
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<td>[Ru(S$_2$PPh$_2$)(P[OEt]Ph$_2$)_3]BPh$_4$</td>
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<td>103.96$^d$</td>
<td>144.95$^d$</td>
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<td>[Ru(S$_2$PMe$_2$)(P[OEt]Ph$_2$)_3]BPh$_4$</td>
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<td>109.09(q)</td>
<td>141.53(d) ($^3J_{PP} = 4.7$ Hz)</td>
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<td>[Ru(S$_2$PPh$_2$)(P[OEt]Ph$_2$)_3]BPh$_4$</td>
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<td>102.52(q)</td>
<td>141.39(d) ($^3J_{PP} = 4.2$ Hz)</td>
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<tr>
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<td>140.76(t) ($^3J_{PP} = 6.0$ Hz)</td>
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<td>170.54(t) ($^3J_{PP} = 6.8$ Hz)</td>
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<td>[Ru(S$_2$PMe$_2$)(P[OEt]Ph$_2$)$_2$]</td>
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<td>89.47(t)</td>
<td>170.97(t) ($^3J_{PP} = 6.3$ Hz)</td>
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<td>[Ru(S$_2$COMe)$_2$(PMe$_2$Ph)$_3$]</td>
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<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 7.62; $\nu_B$, 10.61; $J</em>{AB}$ 30.3 Hz)</td>
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<td>[Ru(S$_2$COMe)$_2$(P[OEt]Ph$_2$)$_3$]</td>
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<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 136.70; $\nu_B$, 138.89; $J</em>{AB}$ 35.0 Hz)</td>
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<td>[Ru(S$_2$COMe)$_2$(P[OEt]Ph$_2$)$_2$]</td>
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<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 132.64; $\nu_B$, 135.06; $J</em>{AB}$ 34.8 Hz)</td>
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<tr>
<td>[Ru(S$_2$COMe)$_2$(P[OEt]Ph$_2$)$_2$]</td>
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<td>-</td>
<td>146.51(s)</td>
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<td>[Ru(S$_2$COMe)$_2$(PMMePh)$_2$]</td>
<td>218</td>
<td>-</td>
<td>30.89(s)</td>
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<td>[Ru(S$_2$COMe)$_2$(PETPh)$_2$]</td>
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<td>-</td>
<td>50.32(s)$^e$, 44.31(s)$^f$</td>
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<td>[Ru(S$_2$CNMe$_2$)(PMe$_2$Ph)$_4$]BPh$_4$</td>
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<td>-</td>
<td>6.02(t), -3.68(t) ($^2J_{PP} = 27.0$ Hz)</td>
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<td>-</td>
<td>5.12(t), -3.32(t) ($^2J_{PP} = 28.0$ Hz)</td>
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<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 14.19; $\nu_B$, 11.48; $J</em>{AB}$ 29.5 Hz)</td>
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**TABLE 2 (continued)**

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<th>T/K</th>
<th>$\delta^{a}/\text{ppm}$</th>
<th>Other resonances $^{b}$</th>
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<td>$[\text{Ru(S}_2\text{CNMe}_2\text{)}_2(\text{POMe})_2\text{Ph}_2\text{)}_3]$</td>
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<td>143.80$^d$</td>
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<td>-</td>
<td>145.47(s)</td>
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<td>$[\text{Ru(S}_2\text{CNET}_2\text{)}_2(\text{POMe})_2\text{Ph}_2\text{)}_3]\text{BPh}_4$</td>
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<td>145.54(s)</td>
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<td>31.40(s)</td>
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<td>-</td>
<td>54.42(s)$^e$, 45.76(s)$^f$</td>
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<td>-</td>
<td>54.11(s)$^e$, 45.82(s)$^f$</td>
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<td>$[\text{Ru(S}_2\text{CNMe}_2\text{)}_2(\text{POMe})_2\text{Ph}_2\text{)}_2]$</td>
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<td>176.15(s)</td>
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<td>-</td>
<td>176.64(s)</td>
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(s) - singlet; (d) - doublet; (t) - triplet; (q) - quartet

$^a$ Chemical shifts reported to high frequency of 85% $\text{H}_3\text{PO}_4$.

$^b$ Resonances from tertiary phosphine, phosphonite or phosponite ligands.

$^c$ Multiplet resembling unsymmetrical quartet.

$^d$ Broad.  $^e$ Decreases in intensity as temperature raised.

$^f$ Increases in intensity as temperature raised.
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<th>Dithioligand</th>
<th>Other resonances</th>
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<td>[RuCl(S₂PMe₂)(PMe₂Ph)]₃</td>
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<td>2.17(d), 1.19(d) (²JₚH 12.5 Hz)</td>
<td>1.60(d) (²JₚH 8.0 Hz)</td>
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<td>1.88 (7.28-7.36(m))</td>
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<td>3.20 (7.10-7.60(m))</td>
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<td>[RuCl(S₂PMe₂)(POMePh)]₃</td>
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<td>1.36(d) (²JₚH 12.0 Hz)</td>
<td>1.25(t) (³JHH 7.0 Hz)</td>
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<td>3.36 (7.20-7.40(m))</td>
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<td>1.52(d) (²JₚH 12.0 Hz)</td>
<td>1.37(pt) (N=8.0 Hz)</td>
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<td>6.96-7.50(m)</td>
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<td>3.12(pt) (N=11.5 Hz)</td>
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<td>1.19(t), 3.40</td>
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<td>1.36(d) (²JₚH 13.0 Hz)</td>
<td>1.20(t) (³JHH 7.0 Hz)</td>
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<td>(N=12.0 Hz)</td>
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<td>[Ru(S₂COMe)₂(PMe₂Ph)]₃</td>
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<td>1.83(pt) (N=8.0 Hz)</td>
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<td>1.19(d) (³JₚH 7.5 Hz)</td>
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<td>7.30-7.60(m)</td>
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<td>[Ru(S₂COMe)₂(P̄OMePh₂)₃]</td>
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<td>3.33(s), 3.46(s)</td>
<td>3.22(pt)(N=11.0Hz)</td>
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<td>3.10(d)(JₚH=10.5Hz)</td>
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<tr>
<td>[Ru(S₂COMe)₂(P̄OEtPh₂)₃]</td>
<td>301</td>
<td>2.96(s), 3.33(s)</td>
<td>3.00-3.40(m)c</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.26(m)d; 7.10-7.50(m)b</td>
</tr>
<tr>
<td>[Ru(S₂COMe)₂(P̄OMePh₂)₂]</td>
<td>301</td>
<td>3.71</td>
<td>3.22(pt)(N=11.0Hz)</td>
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<tr>
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<td>7.10-7.40(m)b</td>
</tr>
<tr>
<td>[Ru(S₂COMe)₂(PMePh₂)₂]</td>
<td>301</td>
<td>3.81(s)</td>
<td>1.88(pt)(N=7.5Hz)</td>
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<tr>
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<td>7.18(m)b</td>
</tr>
<tr>
<td>[Ru(S₂COMe)₂(P̄EtPh₂)₂]</td>
<td>301</td>
<td>3.72(s), 3.85(s)</td>
<td>2.30a, 0.60(m)</td>
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<td></td>
<td></td>
<td>7.18(m)</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph₄)BPh₄]</td>
<td>301</td>
<td>2.37(s)</td>
<td>1.76(pt)(N=6.5Hz)</td>
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<td>1.17(t)(N=5.0Hz)</td>
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<td>7.00-7.45(m)b</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph₄)BPh₄]</td>
<td>301</td>
<td>2.90(q), 0.82(t)(J₃H=7.0Hz)</td>
<td>1.72(pt)(N=6.5Hz)</td>
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<tr>
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<td></td>
<td></td>
<td>1.27(t)(N=5.0Hz)</td>
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<td>6.98-7.44(m)b</td>
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<tr>
<td>[Ru(S₂CNMe₂)₂(PMe₂Ph₃)]</td>
<td>301</td>
<td>2.90(s), 3.49(s)</td>
<td>1.96a, 1.07(d)(JₚH=8.0Hz)</td>
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<td>7.31(m)b</td>
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<tr>
<td>[Ru(S₂CNMe₂)₂(P̄OMePh₂)₂]</td>
<td>301</td>
<td>3.02(s), 3.10(s)</td>
<td>3.30(pt)(N=11.0Hz)</td>
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<td>7.20-7.60(m)b</td>
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<tr>
<td>Complex</td>
<td>T/K</td>
<td>Dithioligand</td>
<td>Other resonances</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>-----</td>
<td>-----------------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{CNMe}_2\text{)}_2\text{(P[OMe]Ph}_2\text{)}_2])</td>
<td>301</td>
<td>3.44(q); 3.60(q)</td>
<td>3.22(pt)(N=11.0Hz)</td>
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<tr>
<td></td>
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<td>1.05(t); 1.09(t)</td>
<td>7.20-7.60(m)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(^3\text{J}_{\text{HH}7.0\text{Hz}})</td>
<td></td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{CNMe}_2\text{)}_2\text{(PMePh}_2\text{)}_2])</td>
<td>301</td>
<td>3.57(^e) 1.07(t)(^f)</td>
<td>1.78(pt)(N=4.0Hz)</td>
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<tr>
<td></td>
<td></td>
<td>(^3\text{J}_{\text{HH}7.0\text{Hz}})</td>
<td>7.10-7.40(m)(^b)</td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{CNMe}_2\text{)}_2\text{(PETPh}_2\text{)}_2])</td>
<td>301</td>
<td>2.72(s)(^f)</td>
<td>0.56(m), 2.10(^g), 2.50(^g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.91(s), 3.11(s)</td>
<td>7.00-7.40(m)(^b)</td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{CNMe}_2\text{)}_2\text{(PETPh}_2\text{)}_2])</td>
<td>301</td>
<td>3.10-3.90(^h)</td>
<td>0.56(m), 2.10(^g), 2.50(^g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1(^i)</td>
<td>7.00-7.40(m)(^b)</td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{CNMe}_2\text{)}_2\text{(P[OMe]Ph}_2\text{)}_2])</td>
<td>301</td>
<td>2.91(s); 3.04(s)</td>
<td>3.48(t), 3.61(t)(N=7.5Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.30-7.50(m)(^b)</td>
</tr>
</tbody>
</table>

(s) - singlet  (d) - doublet  (t) - triplet  (pt) - pseudotriplet  (m) - multiplet

\(N = |J(\text{PH}) + J(\text{PH})|\)

\(^a\) Broad resonance  \(^b\) Phenyl group resonances  \(^c\) Overlapping quartets  \(^d\) Contains at least one triplet

\(^e\) ABM3 spin system-four overlapping quartets  \(^f\) Less intense than other two singlets and therefore assigned to less stable isomer.

\(^g\) Symmetrical multiplet  \(^h\) Several overlapping quartets.

\(^i\) At least two triplets at 1.01 and 1.18\(^\circ\) are observed.
Caption for Schemes

1. Possible rearrangements of $[\text{RuCl}(S_2\text{PMe}_2)L_3]$ at 298K


(* cis isomer for $L = \text{PMe}_2\text{Ph}$; trans isomer for $L = \text{P(OMe)}_2\text{Ph}$)
Scheme 1
\[
\begin{align*}
\text{(I)} & \xrightarrow{-L} \text{(II)} \xrightarrow{-L} \text{(III)} \\
\text{(VIII)} & \xrightarrow{-L} \text{(IV)} \xrightarrow{-\text{Cl}^-} \\
\text{(V)} & \xrightarrow{(S-S)^-} \\
\text{(VII)} & \xrightarrow{} \text{(VI)}
\end{align*}
\]

SCHEME 2