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

by

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D.Sc.
University of Edinburgh
1978
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ABSTRACT

In Part A, 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 trans-[\text{RuCl}_4(\text{EPh}_3)_2]^- have been fully characterised. Reaction of \([\{\text{Ru(CO)Cl}_2(C_7H_8)\}_2\] with MCl/HCl gave the first anionic Ru(II) diene complex \(\text{M}[\text{Ru(CO)Cl}_2(C_7H_8)]\) together with some \(\text{M}_2[\text{Ru(CO)Cl}_2]\) and diene displacement reactions on the former have been studied. Synthesis of the related \([\{\text{RuCl}_2(\text{CS})(\text{PR}_3)_2\}_2\] from \([\text{RuCl}_2(\text{PR}_3)_3]\) and CS_2 also gave the triple chloride bridged complex \([\text{RuCl}_4\text{CS}(\text{PR}_3)_4]\) \(\text{PR}_3 = \text{PPh}_3, \text{P}(p\text{-tolyl})_3\). 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 \([\text{Ru(CO)Cl}_2(\text{dmf})(\text{PR}_3)_2]\). Cyclic voltammetric studies showed that these dimers undergo reversible one electron oxidation steps. Self dimerisation of \([\text{RuCl}_2(\text{dmf})(\text{PR}_3)_2]\) \((\text{Y} = \text{CO}, \text{CS})\) 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 \([\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph})_6]\)Cl and \([\text{Ru}_2\text{Cl}_5(\text{P(OMe)Ph})_9]\)Cl gave the unusual dimers \([\text{P(OR)}\text{Ph}_2)_2\text{P(OH)Ph}_2\text{RuCl}_3\text{Ru(P(OH)Ph)}_2\text{PPh}_0]\).

In section 2), various reactions of the compounds \([\{\text{Ru(η-arene)Cl}_2\}_2]\) are described including the preparation of the triple bridged cations \(\text{[areneRu}_3\text{Ru arene]}^+ (\text{X} = \text{Cl}^-, \text{OH}^-, \text{OR}^-)\) and the novel \([\{\text{Ru(\eta-6,6)OH}\}_4]^4+\) cation, shown by X-ray analysis to have a cubane-like structure. Some stable substituted η⁵-cyclohexadienyl compounds \([\text{Ru(η}^5\text{C}_6\text{H}_5\text{Y})\text{(PMe}_2\text{Ph})-(\text{N-N})\text{PF}_6 (\text{Y} = \text{H}^-, \text{OH}^-, \text{CN}^-; \text{N-N} = 2,2\text{'bipy}, 1, 10 \text{phen})\) have been synthesised by reaction of \([\text{Ru(η}^6\text{-C}_6\text{H}_5\text{PMe}_2\text{Ph(N-N})\text{(PF}_6)_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, $^1$H and $^{31}$P-$^1$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


"Ruthenium complexes containing group 5B donor ligands. Part VIII. Reaction of [Ru$_2$(Y)Cl$_2$(PPh$_3$)$_2$] (Y = CO, CS) and [{RuCl$_2$(CS)PPh$_3$$_2$}] with various L [L = P(OR)P$_2$ (R = Me, Et), P(OMe)$_3$, Ph$_2$, and of [RuCl$_2$L$_2$] with carbon monoxide", W.J. Sime and T.A. Stephenson, J.C.S. Dalton, submitted for publication.


[64.] "Reactions of [RuCl₂(L)] (L = P(OMe)₂Ph₂, P(OEt)₂Ph₂) and RuCl₂(L₂) (L = P(OMe)₂Ph, PMe₂Ph, PMe₂Ph) with various dithioacid ligands". W.J. Sime and T.A. Stephenson, Inorg. Nuclear Chem. Letters, 1977, 12 311-314.


[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 dithioacid 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 [RuCl₂(L)₂] (L = PR₃, P(OR)₂PH, P(OR)₂Ph) with various dithioacid ligands". W.J. Sime and T.A. Stephenson, J.C.S. Dalton, 1978 000
SYNTHETIC, 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 "RuCl₃H₂O" 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 "RuCl₃H₂O" (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 "RuCl₃H₂O" 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 compound 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 [RuX₃L₁(EP₃₂)₂] (X = Cl, Br; E = P, As; L = RCN, Me₂SO, CS₂, CS, Me₂CO).

b) Displacement of methanol and one EP₃ group giving [RuX₃L₂(EP₃₂)] (L = Me₂S, 2,2'-bipyridyl(bipy), 1,10-phenanthroline(phen), C₅H₅N).

c) Complete displacement of methanol, EP₃ and X⁻ without reduction eg. [Ru(S₂PPh₂)₃].

d) Reduction to neutral ruthenium(II) complexes with or without complete displacement of EP₃ groups eg. [RuX₂L₂(EP₃₂)₂] (L = CO, C₇H₈, RCN) and [RuX₂L₄] (L = C₅H₅N, Me₂SO).

e) Reduction to cationic ruthenium(II) compounds when carried out in polar solvents eg. [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 \([\text{RuCl}_3\text{MeOH}(\text{EPPh}_3)_2]\) 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 = \(\text{CH}_2\text{Cl}_2\), \(\text{Me}_2\text{CO}\)) 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_2phen), \([\text{Ru}_2\text{Cl}_2(\text{Me}_2\text{phen})_4]\)\(_{\text{Cl}}\) 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 \([\text{PMe}_2\text{Ph})_2(\text{N-N})\text{ClRu}(\text{L})\text{RuCl}(\text{N-N})(\text{PMe}_2\text{Ph})_2]\)^2+ (L = pyrazine, 4,4'-bipyridyl),\(^3\) and a detailed study of their redox behaviour is planned (cf electrochemical studies on the related \([\text{bipy})_2\text{ClRu}(\text{L})\text{RuCl(bipy)}_2]\)^2+ etc\(^4\).

Reaction of \([\text{RuCl}_3\text{MeOH}(\text{EPPh}_3)_2]\) with \(\text{MCl/HCl}\) (\(\text{M} = \text{P}_{4}\text{As}^{+}, \text{Me}_{4}\text{N}^{+}\)) in acetone led to methanol displacement by halide ion to form \(\text{M}[\text{RuCl}_4(\text{EPPh}_3)_2]\) \((\text{E} = \text{P,As})\) which was shown to have a trans structure by esr and far infrared studies. The compound \((\text{E} = \text{P})\) 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 \textit{trans}-\([\text{RhCl(CO)}(\text{PPh}_3)_2]\) 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 \([\text{RuCl}_4(\text{PPh}_3)_2]^-\) anion \([3,4]\). By this method, \([\text{RuCl}_4-(\text{P[OPh]_3)_2}^-]\) \([4]\) and \([\text{RuCl}_4(\text{P(OMe)_2Ph})_2]^-\), 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 \([\text{RuCl}_4(\text{PPh}_3)_2]^-\) 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 \(\text{H}^+\) to generate the Ru(III) anion. Recent evidence
to support this conclusion is the observation of oxidative addition of
\(\text{H}_2\) to \([\text{RuH}(\text{Ph}_2\text{P[CH}_2\text{_3}P\text{PPh}_2\text{_2}MeOH}]\text{PF}_6\) to give the relatively stable Ru(IV)
trihydrido complex. \([\text{RuH}_3(\text{Ph}_2\text{P[CH}_2\text{_3}P\text{PPh}_2\text{_2}]\text{PF}_6\) which reacts with \(\text{Et}_3\text{N}\) to generate \([\text{RuH}_2(\text{Ph}_2\text{P[CH}_2\text{_3}P\text{PPh}_2\text{_2}]\text{PF}_6\) \([6]\).

The well-known compound \textit{trans}-\([\text{Rh}(\text{PPh}_3)_2\text{ClCO}]\), used to synthesise
the \([\text{RhCl}_4(\text{PPh}_3)_2]^-\) ion, was prepared by reaction of \([\text{Rh(CO)}_2\text{Cl}]_2\) with
excess of \(\text{PPh}_3\). It was reported in 1969 that reaction of \([\text{Rh(CO)}_2\text{Cl}]_2\) with
\(\text{PPh}_3\) \((1:2 \text{ molar ratio})\) gave \textit{trans}-\([\text{Rh(CO)}_2\text{ClPPh}_3]\) \([7]\). However, in making the
mixed ligand complexes \([\text{Rh(CO)}\text{ClPPh}_3\text{L}]\) \((\text{L} = \text{PMePh}_2, \text{P(C}_6\text{H}_{11})_3, \text{AsPh}_3, \text{etc})\) via this compound, we discovered that it should be reformulated as
the dimeric \(\text{[Rh(CO)Cl(PPh}_3\text{)]}_2\) complex \([6,7]\). Oxidative addition of \(\text{Cl}_2\) and
\(\text{MeI}\) 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 \([\text{Rh(CO)}_2\text{Cl}]_2\) as catalyst. A review of this work, in which a number of parallel studies were made in different countries has since been published.

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)}_2\text{Cl}_2(\text{C}_7\text{H}_8)\}_2\] (\(\text{C}_7\text{H}_8 = \text{norbornadiene}\)) with \(\text{Ph}_3(\text{PhCH}_2)\text{PCl/HCl}\) in acetone gave the first anionic Ru(II) diene complex, \(\text{Ph}_3(\text{PhCH}_2)\text{P}[\text{Ru(CO)}_2\text{Cl}_2(\text{C}_7\text{H}_8)]\) [5,13], whose structure was established by X-ray analysis [29], \(^1\text{H}\) [5,13] and \(^{13}\text{C}\) [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 \([\text{Ru(CO)}_2\text{Cl}_2(\text{C}_7\text{H}_8)]^{2-}\) [29]. In contrast, refluxing \([\{\text{Ru(CO)}_2\text{Cl}_2(\text{C}_7\text{H}_8)\}_2\)] with \(\text{Ph}_4\text{AsCl/HCl}\) in ethanol gave the Ru(II) dicarbonyl anion \(\text{cis-}[\text{Ru(CO)}_2\text{Cl}_4]^{2-}\) [5,13]. Rationalisation of these observations is now possible by reference to the established reaction of "\(\text{RuCl}_3\times \text{H}_2\text{O}\)" with \(\text{HCO}_2\text{H/HCl}\) mixtures, which gives first \([\text{Ru(CO)}_2\text{Cl}_5]^{2-}\), later \([\text{Ru(H}_2\text{O)}\text{COCl}_4]^{2-}\), then \([\text{Ru(CO)}_2\text{Cl}_4]^{2-}\) and finally the \([\text{Ru(CO)}_2\text{Cl}_3]^{-}\) anion. Presumably, a similar stepwise formation of \([\text{Ru(CO)}_2\text{Cl}_4]^{2-}\) from \([\text{Ru(CO)}_2\text{Cl}_5]^{2-}\) 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.

The \([\text{Ru(CO)}_2\text{Cl}_3(\text{C}_7\text{H}_8)]^{-}\) ion proved to be a useful starting material for the syntheses of several new ruthenium(II) anions of formulae \([\text{Ru(CO)}_2\text{Cl}_3\text{L}]^{-}\).
with larger bases such as AsPh$_3$, SbPh$_3$ and C$_5$H$_5$N, the neutral monomeric compounds [Ru(CO)Cl$_2$(C$_7$H$_8$)] were also formed and, on this basis, a mechanism of reaction was postulated which involved an intermediate 2-C$_7$H$_8$ complex. Evidence for the latter was obtained from hydrogenation studies, using [RhCl(PPh$_3$)$_3$] as catalyst [10,16]. Later it was found that reaction of [LuCOCl$_2$(C$_8$H$_{12}$)] (C$_8$H$_{12}$ = cyclo-octa-1,5-diene) with MeCN also gave the compound [Ru(CO)Cl$_2$(C$_8$H$_{12}$)MeCN] and X-ray analysis revealed a trans-OC-Ru-MeCN arrangement [22]. Detailed $^1$H nmr studies had shown earlier that this could not be the isomer formed from the [Ru(CO)Cl$_3$(C$_7$H$_8$)]$^-$ anion [10,16] and an explanation based on the different stereochemistries of the anion and [Ru(CO)Cl$_2$(C$_8$H$_{12}$)]$_2$ was therefore proposed [22].

Attempts to synthesise the anionic tertiary phosphine complexes [Ru(CO)Cl$_3$(PR$_3$)$_2$]$^-$ from [Ru(CO)Cl$_3$(C$_7$H$_8$)]$^-$ were however unsuccessful. Thus with PMe$_2$Ph (1:2 molar ratio), the only product obtained was [RuCl$_2$-(PMe$_2$Ph)$_2$(C$_7$H$_8$)], whereas PMePh$_2$ gave an inseparable mixture of [RuCl$_2$-(PMe$_2$Ph)$_2$(C$_7$H$_8$)] and [Ru(CO)Cl$_2$(PMe$_2$Ph)$_3$] ($^1$H and $^{31}$P nmr evidence). With PPh$_3$ (1:2 molar ratio), a mixture of products initially formulated as isomers of [(Ru(CO)Cl$_2$(PPh$_3$)$_2$)$_2$] was obtained [10,16] but, later, [21], detailed $^{31}$P nmr studies led to the reformation of these products as a mixture of [Ru(CO)Cl$_2$(PPh$_3$)$_2$]$_2$ (67%) and [(PPh$_3$)Cl(OC)RuCl$_3$Ru(CO)(PPh$_3$)$_2$] (33%) isomers. More recently the [Ru(CO)Cl$_3$(PPh$_3$)$_2$]$^-$ anion has been successfully synthesised by reaction of the methanolate [Ru(CO)Cl$_2$(MeOH)(PPh$_3$)$_2$] with AsPh$_4$ClHCl [21].

Another interesting related study was the reaction of MC1/HCl (M = Ph$_4$As$^+$, Ph$_3$(PhCH$_2$)$_2$P$^+$, Et$_4$N$^+$) with the major product from the reaction of [RuCl$_2$(PPh$_3$)$_3$] with CS$_2$. This had been reported earlier as [RuCl$_2$-(CS)(PPh$_3$)$_2$]$_2$] and, in keeping with this formulation, some of it reacted to give M[RuCl$_3$(CS)(PPh$_3$)$_2$], an example of the first and, until very
recently, only anionic thiocarbonyl complex [5,14]. However, the remainder of the "[RuCl₂(CS)(PPh₃)₂]₂" complex reacted very slowly with the MC1/HCl mixture (later it was shown that the presence of MC1 was not necessary) to give a sparingly soluble orange-brown solid. This was characterised by analytical, infrared and magnetic susceptibility measurements (μₑff = 2.0/dimer at 292K) as the mixed oxidation state, triple chloride bridged dimer [(PPh₃)Cl₂RuCl₃Ru(CS)(PPh₃)₂]₂Me₂CO (I) [14].

Careful separation of the "[RuCl₂(CS)(PPh₃)₂]₂" product by extraction with acetone revealed the presence of two thiocarbonyl complexes: namely the acetone soluble double-chloride bridged dimer [{RuCl₂(CS)(PPh₃)₂}]₂(II) (16%) and the acetone insoluble triple chloride bridged dimer [(PPh₃)₂ClRuCl₃Ru(CS)(PPh₃)₂] (III) (40%) [14], whose structure was verified by X-ray analysis. Thus, the formation of the mixed Ru(II)/Ru(III) dimer (I) by reaction of (III) with HCl is attributed to removal of a PPh₃ group as [Ph₃PH]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 "[RuCl₂(CS)(PPh₃)]" and [RuCl₂(PPh₃)₃] was believed to be the most feasible. The desire of compounds with d⁶ 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 "[RuCl₂(CS)(PPh₃)]" [14], but fortunately, the closely related solvated monocarbonyl complex [Ru(CO)Cl₂dmf(PPh₃)₂] (dmf = NN-dimethylformamide) had just been synthesised by carbonylation of [RuCl₂(PPh₃)₃] in dmf solution. [15] When this dmf solvate was heated under reflux in acetone

† In less basic solvents such as acetone, it had been well established that carbonylation of [RuCl₂(PPh₃)₃] gave the dicarbonyl complex [Ru(CO)₂Cl₂(PPh₃)₂] the isomer formed depending on the reaction conditions [1].
with \([\text{RuCl}_2(\text{PPh}_3)_3]\) (1:1 molar ratio), deep red crystals of \([(\text{PPh}_3)_2-\text{ClRuCl}_3\text{Ru(CO)(PPh}_3)_2]2\text{Me}_2\text{CO}\), 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, \([\text{RuCl}_2(\text{CS})\text{dmf}(\text{PPh}_3)_2]\) was synthesised by reaction of \([\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}]\) with \(\text{N,N}^-\text{-dimethylformamide}\) and direct proof of the coupling mechanism obtained since its reaction with \([\text{RuCl}_2(\text{PPh}_3)_3]\) 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 \([\text{Ru}_2(\text{CO})\text{Br}_2\text{Cl}_2(\text{PPh}_3)_4]\) was successfully accomplished, although an inseparable mixture of geometrical isomers was generated \([15,21]\).

The corresponding \([\text{Ru}_2(\text{CO})\text{Cl}_4\text{P(p-tol)}_3\text{P}]_4\) could also be synthesised by reaction of \([\text{Ru(CO)}\text{Cl}_2\text{dmf}[\text{P(p-tol)}_3\text{P}]_2]\) with \([\text{RuCl}_2[\text{P(p-tol)}_3\text{P}]_3]\) (1:1 mol ratio) and reaction of \([\text{RuCl}_2[\text{P(p-tol)}_3\text{P}]_3]\) with \(\text{CS}_2\) gave both \([\{\text{RuCl}_2(\text{CS})[\text{P(p-tol)}_3\text{P}]_2]\) and \([\text{Ru}_2\text{Cl}_4(\text{CS})[\text{P(p-tol)}_3\text{P}]_4]\). Furthermore, reaction of \([\text{RuCOCl}_2\text{dmf}(\text{PPh}_3)_2]\) and \([\text{RuCl}_2[\text{P(p-tol)}_3\text{P}]_3]\) gave a high yield of the mixed phosphine dimer \([(\text{PPh}_3)_2\text{CORuCl}_3\text{RuCl}[\text{P(p-tol)}_3\text{P}]_2]\). The reverse coupling reaction, however, between \([\text{RuCOCl}_2\text{dmf}[\text{P(p-tol)}_3\text{P}]_2]\) and \([\text{RuCl}_2(\text{PPh}_3)_3]\) gave a complicated mixture of products \((^3\text{P nmr evidence})\), probably because of facile phosphine exchange \([32]\). Nixon and Head \([16]\) have recently synthesised some mixed metal triple chloride bridged complexes \([(\text{PPh}_3)_2\text{ClRuCl}_3\text{RhCl}(\text{PPh}_3)(\text{PPh}_3)]\) by a related coupling reaction.

However, attempted coupling of \([\text{RuCl}_2(\text{PETPh}_3)_3]\) (see later) and \([\text{RuCOCl}_2\text{dmf}(\text{PETPh}_3)_2]\) (1:1 mol ratio) produced the following mixture of compounds: \([\text{Ru}_2\text{Cl}_4(\text{CO})(\text{PETPh}_3)_4]_4, [\text{Ru}_2\text{Cl}_4(\text{CO})_2(\text{PETPh}_3)_3], [\text{RuCl}_2\text{CO}(\text{PETPh}_3)_3]_3\) and \([\text{Ru}_2\text{Cl}_4(\text{PETPh}_3)_5]_5\) \((^3\text{P nmr evidence})\) 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 \([\text{RuYCl}_2S(\text{PR}_3)_2]\) (Y = CO, CS; PR\(_3\) = PPh\(_3\), P(p-tol)\(_3\); S = MeOH, dmf) to undergo self-dimerisation in low polarity solvents (with displacement of a PR\(_3\) group), giving the triple chloride bridged compounds \([\text{(PR}_3)_2\text{Cl}(Y)\text{RuCl}_3\text{Ru}(Y)(\text{PR}_3)_2]\) (IV). Three geometrical isomers are possible for (IV) and detailed 31P nmr studies indicated that all three were formed [21,32]. As mentioned earlier [21], this isomer mixture was also formed, along with some \([\{\text{Ru(CO)Cl}_2(\text{PPh}_3)_2\}_2]\), when the \([\text{Ru(CO)}_3\text{Cl}_2(\text{C}_7\text{H}_8)]^-\) anion was treated with PPh\(_3\) (1:2 mol ratio). A similar behaviour has been observed for reactions of \([\text{RuCl}_2(\text{PPh}_3)_3]\) with PF\(_3\), a 1:1 molar ratio giving \([\text{Ru}_2\text{Cl}_4(\text{PF}_3)_2(\text{PPh}_3)_3]\) and a 2:1 molar ratio \([\text{Ru}_2\text{Cl}_4(\text{PF}_3)(\text{PPh}_3)_4]\)^17 and analogous mechanisms of formation can be postulated [21].

Preliminary cyclic voltammetric and A.C. polarographic studies on \([\text{Ru}_2\text{YCl}_4(\text{PR}_3)_4]\) (Y = CO, CS; PR\(_3\) = PPh\(_3\), 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 \([\text{(PR}_3)_2\text{YRuCl}_3\text{RuCl}(\text{PR}_3)_2]^+\). Further oxidation and reduction steps showed irreversible behaviour indicative of rapid decomposition of these products [30].

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

Earlier [1] it had been reported that treatment of the "carbonyl-containing" red solution with a mixture of SnCl\(_2\) and PPh\(_3\) in acetone gave a small yield of lemon yellow crystals, which analysed for \([\text{Ru}_2(\text{CO})_2\text{Cl}_3-(\text{SnCl}_3)(\text{PPh}_3)_3\text{(Me}_2\text{CO})_2]\). 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\textsubscript{3} ligand. A more recent \textsuperscript{31}P-{\textsuperscript{1}H} nmr spectrum of the material was, however, inconsistent with either formulation since it revealed only one PPh\textsubscript{3} resonance \cite{27}. X-ray structural analysis then showed the compound to be a monomeric solvate [RuCO(Me\textsubscript{2}CO)Cl(SnCl\textsubscript{3})-(PPh\textsubscript{3})\textsubscript{2}]Me\textsubscript{2}CO(V) with \textit{trans} PPh\textsubscript{3} groups. If (V) was gently warmed in benzene, however, self-dimerisation accompanied by PPh\textsubscript{3} and SnCl\textsubscript{2} loss occurred and some [(PPh\textsubscript{3})SnCl\textsubscript{3}(CO)RuCl\textsubscript{3}Ru(CO)(PPh\textsubscript{3})\textsubscript{2}] was isolated. Unfortunately, this compound was not very stable in solution, readily eliminating another molecule of SnCl\textsubscript{2} to give some [Ru\textsubscript{2}(CO)\textsubscript{2}Cl\textsubscript{4}(PPh\textsubscript{3})\textsubscript{3}] \textsuperscript{31}P nmr evidence \cite{27}.

On the basis of the relative percentages of the various dimerisation products found in the RuCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{3}/CS\textsubscript{2}, Ph\textsubscript{3}(PhCH\textsubscript{2})(RuCl\textsubscript{3}CO(C\textsubscript{7}H\textsubscript{8}))/2PPh\textsubscript{3} and thermolysis reactions of [RuYCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] and [Ru(CO)Me\textsubscript{2}CO(SnCl\textsubscript{3})-(PPh\textsubscript{3})\textsubscript{2}]Me\textsubscript{2}CO it was concluded that self-dimerisation with phosphine loss to give [Ru\textsubscript{2}(Y)Cl\textsubscript{4}(PPh\textsubscript{3})\textsubscript{3}] occurred in low polarity solvents when the phosphine groups were \textit{trans} to each other in the monomeric precursor. When the phosphine ligands were \textit{cis}, however, dimerisation without phosphine loss occurred giving the double chloride bridged species [{(RuYCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2})}] \cite{21}. This difference is attributed to the high \textit{trans} influence of PPh\textsubscript{3}- and the consequent electronic instability of \textit{trans}-Ru(PPh\textsubscript{3})\textsubscript{2}- compared to \textit{cis}-Ru(PPh\textsubscript{3})\textsubscript{2}- arrangements.

Further support for these conclusions comes from the formation of [(AsPh\textsubscript{3})\textsubscript{2}ClRuCl\textsubscript{3}RuCl\textsubscript{2}(AsPh\textsubscript{3})] by heating [RuCl\textsubscript{3}MeOH(AsPh\textsubscript{3})\textsubscript{2}] (which contains \textit{trans} AsPh\textsubscript{3}) in benzene\textsuperscript{3} and the reported isolation of the double chloride bridged dimer [{(Ru(CO)Cl\textsubscript{2}(PM\textsubscript{e}Ph\textsubscript{2})\textsubscript{2})}] from a solution which contains the monomer [RuMeCOCl\textsubscript{2}(PM\textsubscript{e}Ph\textsubscript{2})\textsubscript{2}] with \textit{cis} PM\textsubscript{e}Ph\textsubscript{2} groups.\textsuperscript{18}

Preliminary work on self-dimerisation reactions of [RhCl\textsubscript{3}(solv)(PR\textsubscript{3})\textsubscript{2}] species to give either [Rh\textsubscript{2}Cl\textsubscript{6}(PR\textsubscript{3})\textsubscript{3}] and/or [Rh\textsubscript{2}Cl\textsubscript{6}(PR\textsubscript{3})\textsubscript{4}] can probably also be correlated with the isomeric form of the solvated monomer.\textsuperscript{3}
In contrast, in more polar solvents, chloride ion displacement is facilitated leading to formation of the triple chloride bridged cations \([\text{Ru}_2(Y)_2\text{Cl}_3(P\text{Ph}_3)_4]\)Cl. Well known analogues of these cations, namely \([\text{RuCl}_3\text{Ru}(PR)_3]_2\)Cl, had previously been prepared by reaction of "RuCl\(_3\)·H\(_2\)O" 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 \([\text{RuCl}_2(PR)_3]_4\) complexes. In fact, a detailed literature survey (in late 1973) revealed that, although the monomeric compounds \([\text{RuCl}_2L_3\) or 4\(]_L = \text{PHR}_2, \text{AsR}_3, \text{SbPh}_3, \text{C}_5\text{H}_5N \text{ etc} \) were well characterised, only two compounds of this type containing tertiary phosphines (namely \(\text{PPh}_3\) and \(\text{R}_3\)p-tolyl))\(^{21}\) had been synthesised. Earlier, it had been shown that, when \([\text{RuX}_2(PR)_3]_4\) \(X = \text{Cl,Br}\) 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 \([\text{Ru}_2\text{Cl}_3(PR)_6]_X \) were obtained; whereas in hexane (or light petroleum bp 60-80°C) neutral tertiary phosphine complexes were isolated. For \(\text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PEtPh}_2, \text{PEt}_{2}\text{Ph} \) and \(\text{PClPh}_2\), \([\text{Ru}_2\text{Cl}_3(PR)_4]_4, [\text{Ru}_2\text{Cl}_3(PR)_3]_2 \) and \([\text{PR}_3]_2\text{XRuX}_3\text{Ru}(\text{PR}_3)_3\) 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 \([\text{Ru}_2\text{X}_3(PR)_6]_X \) were always rapidly produced when the monomers were dissolved in polar solvents and this accounted for the difficulties in synthesising \([\text{RuX}_2(PR)_3]_4 \) or \(4\)
compounds. Only when bulky tertiary phosphines such as PPh$_3$ and P(p-tolyl)$_3$ were used are monomeric compounds isolated from "RuCl$_3$·H$_2$O", since here, steric constraints inhibited the associative rearrangement reactions. For these compounds variable temperature $^{31}$P nmr studies revealed the fluxional nature of the trisphosphine complexes [18,32] and showed that [RuCl$_2$(PPh)$_3$]$_4$ was best formulated as $[\text{RuCl}_2(\text{PPh}_3)_3 \cdot \text{PPh}_3]^{-}$ with one PPh$_3$ group trapped in the lattice [18]. In non-polar solvents, dimerisation of the $[\text{RuX}_2(\text{PR}_3)_3]_4$ compounds ($\text{PR}_3 = \text{PMePh}_2, \text{PETPh}_2$) readily occurred to produce the neutral triple halide bridged dimers $[(\text{PR}_3)_2 \cdot \text{RuX}_3 \cdot \text{Ru(PR}_3)_3]_4$.

Initially [18] it was believed that these rearrangement reactions involved formation of an unstable double halide bridged complex $[(\text{RuX}_2(\text{PR}_3)_3)_2]_2$ which then underwent further intramolecular rearrangement to generate either $[\text{Ru}_2\text{X}_4(\text{PR}_3)_5]$ with PR$_3$ loss or $[\text{Ru}_2\text{X}_3(\text{PR}_3)_6]X$ with halide ion displacement (Scheme 1).

![Scheme 1](image-url)
Later, however, the species thought to be \( \{ \text{RuCl}_2(\text{PETPh}_2)_3 \}_2 \) was reformulated as the cationic complex \([ \text{RuCl}(\text{PETPh}_2)_3(\text{EtOH})_2 ]\text{Cl} \) [21] and the mechanism of formation of \([ \text{Ru}_2 \text{X}_3(\text{PR}_3)_6 ]\text{X} \) is now believed to involve direct intermolecular coupling of \([ \text{RuX}(\text{PR}_3)_3(\text{Solv})_2 ]\text{X} \) and \([ \text{RuX}_2(\text{PR}_3)_3 ]\) for formation of \([ \text{Ru}_2 \text{X}_4(\text{PR}_3)_5 ]\), 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 phosphinites [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 \( \text{P(OR)}\text{Ph}_2 \) (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 \([ \text{RuCl}(\text{P(OMe)}\text{Ph}_2)_4 ]^+ \) and \([ \text{Ru}_2 \text{Cl}_2(\text{P(OEt)}\text{Ph}_2)_8 ]^{2+} \) 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 $[\text{L}_3\text{(OH)}\text{Ru(OH)}_2\text{RuL}_3]^+$ which rearranges to $[\text{L}_3\text{Ru(OH)}_3\text{RuL}_3]^+$ has recently been postulated by Ashworth et al. 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)Ph$_2$ 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 $[\text{Ru}_2\text{Cl}_4\text{L}_5]$ ($\text{L} = \text{P(OMe)}_3$, \text{P(OMe)}_2\text{Ph}, \text{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, $[\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph})_6]\text{Cl}$ was pyrolysed at 120°C for 12 hours since a similar reaction with $[\text{Ru}_2\text{Cl}_3(\text{PET})_6]\text{Cl}$ had given
X-ray analysis showed, however, that the unusual neutral dimer \([\text{RuCl}_3\text{(PEt}_2\text{Ph})_2\] \(\text{VI}\)) was formed [23]. The same compound was produced on pyrolysis of \([\text{RuCl}_3\text{(P(OMe)_Ph)}_2\text{]_6X} \ (X = \text{SCN}^-, \text{CN}^- \ etc)\) suggesting that nucleophilic attack of \(X^-\) on a coordinated alkoxy group to give a \(\text{Ph}_2\text{PO}^-\) group and \(\text{MeX}\), followed by stepwise hydrolysis of some of the \(\text{P(OMe)}_\text{Ph}_2\) groups probably occurred.

\[
\begin{align*}
\text{Ph}_2
\quad \text{MeO} \quad \text{P}_2
\quad \text{H} \quad \text{O} \quad \text{P}_2
\quad \text{MeO} \quad \text{P}
\quad \text{Cl} \quad \text{P}_2
\quad \text{O} \quad \text{H}
\end{align*}
\]

(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 \([\text{Ru}_3\text{Cl}_5\text{(P(OEt)_Ph)}_2\] \(\text{X} \ (X = \text{Cl}^-, \text{SCN}^-, \text{CN}^- \ etc)\) [23, 31].

In an attempt to synthesise neutral dimeric complexes containing \(\text{P(OR)}\text{Ph}_2\) or \(\text{P(OR)}_2\text{Ph}\) ligands, \([\text{Ru}_2\text{YCl}_4(\text{PPh}_3)_4\] \(Y = \text{CO,CS}\) were reacted with an excess of \(L\) in benzene. However, in every instance, PPh\(_3\) displacement was accompanied by facile bridge cleavage to give a mixture of monomeric compounds \([\text{RuCl}_2\text{L}_{3\text{or4}}\] and \([\text{Ru(Y)Cl}_2\text{L}_3\] [33]. The latter could also be synthesised by direct carbonylation of \([\text{RuCl}_2\text{L}_{3\text{or4}}\] [33]. In polar solvents these compounds (\(L = \text{P(OR)}\text{Ph}_2\) readily lost chloride ion and addition of \(\text{BPh}_4^-\) ion precipitated the cationic complexes \([\text{Ru(Y)Cl-)}_\text{P(OMe)}_\text{Ph}_2\] \(3\) \(\text{BPh}_4\) and \([\text{RuYCl}_2\text{(P(OE)}_\text{Ph}_2\] \(6\) \(\text{BPh}_4\) \(2\). In contrast, no cationic complexes were generated when \([\text{RuCl}_2\text{Y(POMe)}_2\text{Ph}_3\] was dissolved in methanol and this is attributed to the smaller steric require-
ments of the P(OMe)₂Ph groups. Similar changes have been observed for

\[ MX₂(Ph₂P(CH₃)₂PPh₀)₂ \] (M = Ru, Os; X = Cl, Br), which lose a halide ion in boiling alcohol to give

\[ MX(Ph₂P(CH₃)₂PPh₀)₂⁺ \] (for n = 3) but not when n = 1 or 2.²⁵

Finally, reaction of \([RuCl₂(PEtPh₂)₃]\) with CS₂ gave "[Ru(η²-CS₂)Cl(PEtPh₂)₃]Cl"", reformulated on the basis of ³¹P nmr and conductivity studies as \([RuCl₂(S₂CPPh₂)(PEtPh₂)₂]\) (VII) containing the Ph₂EtP⁺-CS₂-zwitterion ligand. In methanol, (VII) rearranged to the cationic

\[ [RuCl(MeOH)₅CPPh₂)(PEtPh₂)₂]^+ \] (VIII) isolated as its BPh⁻ salt.[32]

Further studies on reactions of CS₂ with other \([RuCl₂L₃or₄]\) compounds are now in progress.

(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 \([{Ru(arene)Cl₂}_2]\) complexes was started in 1974. The compound \([{Ru(η⁶-C₆H₆)Cl₂}_2]\) had been synthesised by dehydrogenation of 1,3 or 1,4 cyclohexadienes with "RuCl₃-xH₂O"²⁶ and later²⁷ this was extended to substituted 1,4 cyclohexadienes. The compounds underwent typical bridge cleavage reactions with a variety of Lewis bases, giving \([Ru(arene)Cl₂L]\) (L = PR₃, AsR₃, Me₂SO etc), although under more forcing conditions, arene ring displacement also occurred.²⁶,²⁷
It was found that reaction of \([\{\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}_2\}_2\]\) with CsCl/HCl in ethanol gave Cs[\(\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}_3\)] 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[\(\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}_3\)] with excess \(\text{L}\), gave either \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}_2\text{L}]\) \((\text{L} = \text{C}_5\text{H}_5-\text{N}, \text{Me}_2\text{SO}, \text{SbPh}_3 \text{ etc})\) or, under more forcing conditions, \([\text{RuCl}_2\text{L}_4]\) \((\text{L} = \text{C}_5\text{H}_5\text{N}, \text{PMe}_2\text{Ph etc})\)[34]. Clearly the lability of the coordinated arene group is much less than that of the diene in \([\text{Ru}(\eta^6-\text{C}_7\text{H}_8)\text{Cl}_3]\) and, thus, displacement of chloride ion occurs much more readily than loss of the benzene ring.

Reaction of\([\{\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{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 \([\eta^6-\text{C}_6\text{H}_6]\)\(\text{RuCl}_3\)\(\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\] \(\text{PF}_6\) \((\text{IX})\) \((40\% \text{ yield})\). 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 \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}(\text{NH}_3)_2]\) \(\text{PF}_6\) \((\text{IX})\) \(\text{NH}_4\text{PF}_6\) \([28]\).

Shaking \([\{\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}_2\}_2\]\) with excess of \(\text{NH}_4\text{PF}_6\) in methanol produced a higher yield of \((\text{IX})\) \((>90\%)\). Unfortunately, attempts to synthesise a range of new triple halide bridged complexes \([\text{L}_3\text{RuCl}_3\text{RuL}_3]\) \(\text{PF}_6\) \((\text{L} = \text{C}_5\text{H}_5\text{N}, \text{Me}_2\text{SO}, \text{Et}_2\text{S etc})\) by arene displacement from \((\text{IX})\) 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 \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{ClL}_2]\) \(\text{PF}_6\) \((\text{L} = \text{PR}_3, \text{C}_5\text{H}_5\text{N}, \text{AsPh}_3 \text{ etc})\) \([20,34]\).

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 \((\text{IX})\) is by intermolecular coupling of the solvated monomers \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}_{(\text{MeOH})}]\) and \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)-\text{Cl}_{(\text{MeOH})}]\)\(^+\). These could either form \((\text{IX})\) directly or via a cationic dimeric double bridged intermediate \([\{\eta^6-\text{C}_6\text{H}_6\}\text{ClRuCl}_2\text{Ru(MeOH)}(\eta^6-\text{C}_6\text{H}_6)]\)\(^+\),
which then rapidly rearranges to give (IX) (Scheme 3) \(\text{(cf formation of } [\text{Ru}_3\text{Cl}_5(\text{P}^{\text{OEt}}\text{Ph}_2)_9]\text{Cl) - section 1A) [34].}\)

Reaction of aqueous solutions of \([\text{Ru(arene)Cl}_2]\_2\) (arene = benzene, mesitylene) with an excess of either NaOH or Na$_2$CO$_3$ resulted in the isolation of the yellow triple hydroxo bridged compounds \([\text{areneRu(OH)}_3\text{Ruarene}]\text{Cl}_3\text{H}_2\text{O}\) (X). Treatment of aqueous solutions of (X) with NaBPh$_4$ readily gave the BPh$_4^-$ salt but addition of NH$_4$PF$_6$ led to the isolation of \([\text{Ru}(\eta\text{C}_6\text{H}_6)(\text{NH}_3)_3]\text{PF}_6\) \(\cdot\) \([20,25,35]\). 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

![Scheme 3](image)

phosphines for prolonged periods. \(\text{(cf. related studies with } [\text{Pt}_2(\text{OH})_2]$^{\text{(PR}_3)_4}(\text{BF}_4)_2$ and PR$_3^\text{I}).\) \(\text{28 In contrast, reaction of (X) with alcohols readily gave the triple alkoxo bridged complexes } [\text{areneRu(OR)}_3\text{Ruarene}]\text{-BPh}_4^-(\text{R} = \text{Me,Et}), \text{which could also be synthesised by reaction of } [\{\text{Ru(arene)Cl}_2]\_2] \text{ with NaOR}[35]. \text{A detailed study of the reactions of all these compounds is now in progress.}\) \(\text{29}\)}
If \([\{\text{Ru}^+\text{(C}_6\text{H}_6\text{Cl})_2\}^+_2]\) in water was treated with less sodium carbonate \([\text{Ru}^{2+}; \text{CO}_3^{2-}]\) 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 \([\{\text{Ru}(\eta^5-\text{C}_6\text{H}_6\text{OH})\}_{4}\}(\text{SO}_4)^2\text{H}_2\text{O}\) (XI) containing both \(\eta^5-\text{C}_6\text{H}_6\) 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 \([\text{Ru}_2(\eta^5-\text{C}_6\text{H}_6\text{OH})_2(\text{OH})_3]^+\) and, with LiBr, \([\text{Ru}_2(\eta^5-\text{C}_6\text{H}_6\text{(OH)Br})_2]^+\) was isolated as its \(\text{PF}_6^-\) salt. With nitrogen donor ligands such as pyridine, the dicationic dimer \([\text{Ru}(\eta^5-\text{C}_6\text{H}_6\text{(C}_5\text{H}_5\text{N})\text{Ru(\text{OH})}_2\text{Ru(C}_6\text{H}_6)(\text{OH})_2(\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 \([\text{Ru}(\eta^5-\text{C}_6\text{H}_6\text{(OH)(H}_2\text{O})_2]^+\) cation via deprotonation of a coordinated water molecule in \([\text{Ru}(\eta^5-\text{C}_6\text{H}_6\text{(OH)(H}_2\text{O})_2]^2+\) followed by direct tetramerisation to \([\text{Ru}(\eta^5-\text{C}_6\text{H}_6\text{OH})_4]^{4+}\) 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 \([\text{Ru}(\text{arene})\text{(OH)(H}_2\text{O})_2]^+\) and the neutral \([\text{Ru}(\text{arene})\text{(OH)(H}_2\text{O})_2]\), probably via a cationic double hydroxo bridged intermediate \([\text{arene(OH)Ru(OH)(H}_2\text{O)}\text{arene}]^{2+}\) (XII). Alternatively, (XII) could be formed by direct dimerisation of \([\text{Ru}(\text{arene})\text{(OH)(H}_2\text{O})_2]\) to \([\text{arene(OH)Ru(OH)(H}_2\text{O)}\text{arene}]^{2+}\) followed by deprotonation in more basic media. (cf \([\text{L}_3(\text{H}_2\text{O)}\text{Ru(OH)(H}_2\text{O)}\text{RuL}_3]^{2+}\) to \([\text{L}_3(\text{OH)Ru(OH)(H}_2\text{O)}\text{RuL}_3]^+\) 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 $\text{[Ru(C}_6\text{H}_6\text{Cl}(\text{N-N})]\text{PF}_6}$ ($\text{N-N} = 2,2^\text{1}-\text{bipyridyl}, 1,10\text{-phenanthroline}$), reaction of various nucleophiles with $\text{[Ru(\eta^6-C}_6\text{H}_6\text{)(PMe}_2\text{Ph}(\text{N-N})]\text{PF}_6}_2$ leads to the isolation of air-stable $\eta^5$-cyclohexadienyl complexes $\text{[Ru(\eta^5-C}_6\text{H}_6\text{Y)(PMe}_2\text{Ph}(\text{N-N})]\text{PF}_6} (\text{Y} = \text{H}^-, \text{OH}^-, \text{CN}^-)[26]$. Attempts to make various disubstituted cyclohexadiene complexes $\text{[Ru(\eta^4-C}_6\text{H}_6\text{YZ})(\text{PMe}_2\text{Ph})(\text{N-N})]} (\text{Y} = \text{H}^-; \text{Z} = \text{OH}^- \text{etc})$ from these are now in progress. There is also some $^1\text{H nmr evidence that two hydride ions might add to one of the benzene rings in the [Ru}_2(\eta_6\text{C}_6\text{H}_6\text{)(OH)}_3^+]$ 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 0,0; 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 \( \{ \text{Pd(OCOR)}_2 \}_2 \text{L}_2 \). 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 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, PMePh\(_2\)) 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, \(_n\text{Bu}, \text{i-Bu, Ph etc} \), made by direct reaction of \( \text{Mo}(\text{CO})_6 \) 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 "MoCl\(_2\)" and this was later substantiated by other workers.\(^\text{36}\)

These replacement reactions have been extended mainly by Cotton and coworkers,\(^\text{3}\) who synthesised a range of binuclear low valent molybdenum halides, such as \([\text{Mo}_2\text{Cl}_8]\) etc., from \([\text{Mo}_2(\text{OCOMe})_4]\).

The acetate groups in \([\text{Mo}_2(\text{OCOMe})_4]\) were later replaced by various dithioacid ligands giving \([\text{Mo}_2(S-S)_4]\) \((S-S^- = -\text{S}_2\text{COEt}, -\text{S}_2\text{CNPr}_2, -\text{S}_2\text{CN}^\text{Et}_2, -\text{S}_2\text{PPh}_2)\) and by monothiobenzoate ion to give \([\text{Mo}_2(\text{PhCO})_4]\). For \(S-S^- = -\text{S}_2\text{COEt}\), stable adducts \([\text{Mo}_2(S_2\text{COEt})_4]^{-}\) \((L = \text{C}_5\text{H}_5\text{N}, \text{AsEt}_3\text{ etc})\) were readily formed but with \([\text{Mo}_2(S_2\text{CNR})_4]\) rapid rearrangement to the "carbene" complex(XIII) occurred, followed by oxidation to \([\text{Mo}_2\text{O}_3-(S_2\text{CN})_4]\)[47]. The structure of (XIII) was established independently by Weiss et al.\(^\text{38}\) using X-ray crystallography.

\begin{equation}
\text{R}_2\text{N}^+\text{C}^-\text{Mo}^-\text{S}^-\text{S}\text{Mo}^-\text{S}^-\text{S}\text{C}^-\text{NR}_2^-
\end{equation}

(XIII)

Rather surprisingly, reaction of \(\text{W}(\text{CO})_6\) 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.\(^\text{39}\)

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 "RuCl\(_3\)\text{H}_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, 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 $[\text{Pd}(\text{S}_2\text{PPh}_2)_2(\text{PR}_3)_2]$ 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 \([M(S-S)_2]\) (S-S\(^-\) = S\(^2\)CNR\(_2\), S\(^2\)PR\(_2\), S\(^2\)P(OR)\(_2\), S\(^2\)COR) showed that this stepwise cleavage of M-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\(^2\)CNET\(_2\))\(_2\)(PMePh\(_2\))\] confirmed this conclusion and structure (XIV) has now been firmly established for various S-S\(^-\)ligands (see \[67\] for references). Characteristic ir bands for S\(^2\)PPh\(_2\)\[^44\] and S\(^2\)PMe\(_2\)\[^48\] compounds were also used to determine the mode of bonding.

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

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\] (M = 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 \([M(S-S)_2L]\) and \([M(S-S)L_2](S-S)\) were shown by \(^1\)H nmr (and later \(^{31}\)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 \([M(S-S)_2L]\) 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 \([\text{M}(S-S)L_2](S-S)\) compounds.

c) Slower intermolecular exchange of free and bound \(\text{PR}_3\) in \([\text{M}(S-S)_2\text{PR}_3]\).

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.

\[
\text{[M(S-S)(\text{PR}_3)_2](S-S)} \rightleftharpoons \text{[M(S-S)_2\text{PR}_3]} + \text{PR}_3 \quad (2)
\]

Some irreversible rearrangement reactions also occurred. For example, reaction of \([\text{M}(S_2\text{COR})_2]\) and \([\text{M}(S_2\text{P(OEt})_2)_2]\) with excess of \(\text{PR}_3\) gave the unusual products \([\text{M}(S_2\text{CO})(\text{PR}_3)_2]\) and \([\text{M}(S_2\text{P}(\text{O})(\text{OEt}))(\text{PR}_3)_2]\) 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 \(S_2\text{CO}^2-\) and \(S_2\text{P}(\text{O})(\text{OEt})^2-\) anions.

Another irreversible rearrangement occurred with the \(S_2\text{CNR}_2\) compounds in chlorinated solvents such as \(\text{CH}_2\text{Cl}_2\), giving the complexes \([\text{M}(S_2\text{CNR}_2)-\)

\((\text{PR}_3)_2\)ClH₂O and \(\text{CH}_2(\text{S_CNR}_2)_2\). Interestingly, no such rearrangement occurred with other dithioacid anions.

For \([\text{Pd}(\text{S}_2\text{PR}_2)(\text{PPh}_3)_2]\text{BPh}_4\) (\(R = \text{Me}, \text{Ph}\)) dissolution in \(\text{CH}_2\text{X}_2-\text{EtOH}\) or \(\text{CHX/EtOH} (X = \text{Cl}, \text{Br})\) produced rapid rearrangement, to give \([\text{Pd}(\text{PPh}_3)_2(\text{S}_2\text{PR}_2)]\), and this process was believed to involve a labile \(\pi\)- or \(\sigma\)-bonded phenyl group[48]. Unfortunately, this particular rearrangement was confined to compounds containing a combination of \(\text{Pd}, \text{PPh}_3, \text{S}_2\text{PR}_2\) and \(\text{BPh}_4^-\) and thus did not provide a general method of synthesising the series \([\text{MX}(\text{PR}_3)](\text{S-S})\). It was found later, however, that these compounds could readily be synthesised by reaction of \([\{\text{MX}_2(\text{PR}_3]\}_2]\) with alkali metal dithioacid salts (1:2 mol ratio). In contrast, reactions of carboxylate ions with these halide bridged dimers gave either \([\{\text{MX}(\text{OCOR})-\text{PR}_3\}_2]\) (1:2 mol ratio)\(^{42}\) or \([\{\text{M(OCOR)}_2\text{PR}_3\}_2]\) (1:4 mol ratio).\(^{32}\) These compounds were useful starting materials for the synthesis of the mixed dithioacid complexes \([\text{Pt}(\text{PR}_3)(\text{S}_2\text{CNET}_2)(\text{S}_2\text{PR}_2)]\) (shown to be stereochemically rigid up to 330K by \(^1\text{H} \text{nmr spectroscopy}) and the mixed ligand cations \([\text{PdL(PMePh)}(\text{S}_2\text{CNET}_2)]\text{BPh}_4\) (\(L = \text{PPh}_3, \text{C}_5\text{H}_5\text{N etc})\ [56,60]. With tetra-cyanomethylene, however, the unusual triphenylcyanoborate complex \([\text{Pd}(\text{S}_2-\text{CNET}_2)(\text{PMePh})](\text{NCBPh}_3)]\) was isolated [63,65].

A wider range of compounds of type \([\text{PdX}(\text{L})(\text{S-S})]\) (\(L = \text{AsPh}_3, \text{SbPh}_3, \text{C}_5\text{H}_5\text{N etc}) were made by cleavage of the halide bridged dimers \([\{\text{PdX(\text{S-S})}\}_2]\) (XVI) (\(\text{S-S}^- = \text{S}_2\text{CNET}_2, \text{S}_2\text{PMe}_2, \text{S}_2\text{COEt}\)). These were synthesised by reaction of \([\text{Pd}(\text{C}_8\text{H}_{12})\text{Cl}_2]\) with \(\text{S-S}^-\) (1:1 mol ratio), in contrast to previous reactions of this diene compound with nucleophiles, which gave substituted alkenyl compounds [54,61].

The corresponding \([\text{Pt}(\text{C}_8\text{H}_{12})\text{Cl}_2]\) with \(\text{S}_2\text{CNET}_2\) behaved differently, giving the insoluble diene bridged complex \([\{\text{PtCl}_2(\text{S}_2\text{CNET}_2)\}_2\text{C}_8\text{H}_{12}\}(\text{XVII})\), which was ascribed to stronger Pt-C bonds. Both (XVI) (\(\text{S}_2\text{CNET}_2\)) and (XVII)
however, reacted with NaS$_2$PMe$_2$.H$_2$.O to give the mixed dithioacid

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

Another unusual reaction of [M(S-S)$_2$] compounds was the reaction of

[Pt(S$_2$COR)$_2$] with K[S$_2$COR] to give the [Pt(S$_2$COR)$_3$]$^-$ anions (R = Et, $^1$Pr). Unlike the [Ni(S$_2$COEt)$_3$]$^-$ anion, which is six coordinate, X-ray analysis showed the [Pt(S$_2$COEt)$_3$]$^-$ to be square planar with two unidentate $^-$S$_2$COEt groups and $^1$H nmr studies indicated rapid intramolecular exchange of xanthato ligands at ambient temperature. Furthermore, slow irreversible rearrangement occurred in solution to give the [Pt(S$_2$CO)(S$_2$COR)]$^-$ anions, which reacted with various Lewis bases to give [Pt(S$_2$CO)L$_2$] (L = PPh$_3$, PMe$_2$Ph, $^3$P$_2$H$_2$.P(CH$_2$)$_2$.PPh$_2$)[52,59]

Finally, these versatile [M(S-S)$_2$] compounds reacted with excess of tertiary phosphinites (P(OR)Ph$_2$) to give [M(S-S)(PPh$_2$.O)(PPh$_2$.OH)] complexes (XVIII) shown by X-ray analysis to contain the symmetrically hydrogen-bonded Ph$_2$.POHOPPh$_2$ ligand.
A careful study of this reaction has enabled intermediates such as \([\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PPh}_2\text{OMe})_2]\) \(B\text{Ph}_4\) and \([\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{PPh}_2\text{O})(\text{PPh}_2\text{OMe})]\) to be isolated and a detailed mechanism of formation of (XVIII) has been proposed. With \([M(S_2\text{CO})^+\text{Pr}]_2\), however, only the compounds \([M(S_2\text{CO})(\text{PPh}_2\text{-OEt})_2]\) 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 \([\text{Ru}(\text{S-S})_2\text{L}_2]\) 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 \([\text{Ru}(\text{S_2PEt}_2)_2(\text{PMe}_2\text{Ph})_2]\) [43]. More recently it has been shown that under milder conditions of reaction, intermediates such as \([\text{RuCl}(\text{S-S})\text{L}_3]\), \([\text{Ru}(\text{S-S})\text{L}_3]^+\) and \([\text{Ru}(\text{S-S})_2\text{L}_3]\) can be trapped out and characterised by chemical and spectroscopic methods [64,68].

The complexes \([\text{Ru}(\text{S_2PR}_2)_2\text{L}_2]\) reacted with CO under very mild conditions to form the monocarbonyl species \([\text{Ru}(\text{S_2PR}_2)_2\text{LCO}]\) and underwent ligand exchange reactions with other phosphorus ligands \((\text{L'})\) of greater basicity to give either \([\text{Ru}(\text{S-S})_2\text{LL}']\) and/or \([\text{Ru}(\text{S-S})_2\text{L}'_2]\) [45,49]. Most of these compounds exhibited temperature variable \(^1\text{H} \text{nmr spectra attributed to facile interconversion of optical enantiomers (for } \text{S}_2\text{PR}_2 \text{ complexes) and restricted rotation about the -CN bond (for the } \text{S}_2\text{CNR}_2 \text{ 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 \(\text{trans to } \text{L}\)

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-$[\text{Ru(PhCOS)}_2(\text{PMe}_2\text{Ph})_2]$, 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 $[\text{Ru(PhCOS)}_2(\text{PMe}_2\text{Ph})_2(\text{HNC}(\text{Me})\text{CH}_2\text{CMe}_2\text{NH}_2)]$ (XIX) and a mechanism of formation involving condensation of $[\text{Ru(PhCOS)}_2(\text{PMe}_2\text{Ph})_2]^-$ (NH$_3$)$_2$ with mesityl oxide was suggested [66].

The tris(chelate) complexes $[\text{Ru(S}^\text{PMe}_2\text{Ph})_2\text{diene}]$ were synthesised by reaction of $[\text{RuCl}_2(\text{diene})]_n$ with Na[S$^\text{PMe}_2\text{Ph}]$$_2\text{H}_2\text{O}$ and the labile diene group readily replaced by various bidentate ligands such as Ph$_2$P(CH$_2$)$_n$PPh$_2$ ($n = 1,2$) and C$_6$H$_4$(AsMe$_2$)$_2$ [53]. In contrast, reaction of $[\text{Ru}($arene$)$Cl$_2$]$_2$ with $^-S_2$PR$_2$ gave the compounds $[\text{Ru($arene$)}(S_2$PR$_2)_2]^-$ which contain both uni- and bi-dentate $^-S_2$PR$_2$ ligands. Similar compounds $[\text{Rh}($C$_5$Me$_5$)$]($S-S)$_2]$ were made with a wider range of dithioacid ligands and kinetic line shape analysis studies indicated a dissociatively controlled uni-/bi-dentate exchange process for the latter compounds. Other compounds prepared included $[\text{Rh}($C$_5$Me$_5$)$\text{Cl}(S-S)]$, $[\text{Rh}($C$_5$Me$_5$)$]($S$_2$CNMe$_2$)$($S$_2$PMe$_2$)$_2]$ and $[\text{Rh}($C$_5$Me$_5$)$]($S$_2$CNMe$_2$)$_L$BPh$_4$ ($L =$ PPh$_3$, CO, AsPh$_3$, C$_5$H$_5$N etc) [55,65]. Reaction of $[\text{Rh}($C$_5$Me$_5$)$]($S-S)$\text{MeOH}$BPh$_4$ with C$_2$(CN)$_4$, however, gave the triphenyl-cyanoborate complexes $[\text{Rh}($nC$_5$Me$_5$)$]($S-S)$\text{NCBPh}_3]$ as verified by X-ray analysis for S-S = $^-S_2$PMe$_2$ [63,65].
Earlier, a variety of rhodium(III) dithioacid complexes had been synthesised starting from mer-[RhCl\(_3\)(PMe\(_2\)Ph)\(_3\)]. These included species such as [RhCl\(_2\)(S-S)(PMe\(_2\)Ph)\(_3\)], [RhCl\(_2\)(S-S)(PMe\(_2\)Ph)\(_2\)], [RhCl(S-S)-(PMe\(_2\)Ph)\(_3\)]BPh\(_4\) and [Rh(S-S)\(_2\)(PMe\(_2\)Ph)\(_2\)]BPh\(_4\). All these compounds were characterised by extensive spectroscopic studies and a detailed mechanism for the overall reaction postulated[51]. Similar studies on mer-[OsCl\(_3\)(PMe\(_2\)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 Et\(_2\)NC(Se)SeSeC(Se)N\(_2\) by the oxidation of NaSe\(_2\)CNET\(_2\), the two disproportionation products Et\(_2\)NC-(Se)Se-Se-Se-C(Se)N\(_2\) (XX) and Et\(_2\)N.C(Se)SeC(Se)N\(_2\) 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 tellurium(II) complexes of bidentate dithio and diseleno ligands.44

(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-Ramirez, 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.

I would also like to express my thanks to the many other members of the academic, technical and secretarial staff in Edinburgh who have helped me in the past nine years; the Science Research Council for financial assistance, the University of Edinburgh for the use of their facilities, Johnson Matthey Limited for generous loans of platinum metal compounds and last, but not least, my wife and children for their support while both carrying out the work and writing the thesis.
References Cited

3. T.A. Stephenson, unpublished work.


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


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

T. A. STEPHENSON and G. WILKINSON

(Received 5 August 1965)

Abstract—The interaction of triphenylphosphine, -arsine and -stibine with hydrated ruthenium trichloride in methanol leads to a variety of complexes such as [RuCl₂(PPh₃)₂], [RuCl₃(PPh₃)], [RuCl₃(PPh₃)₂CH₃OH], [RuCl₃(AsPh₃)CH₃OH] 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], [RuCl₄(CO)L₄] and [pyH][RuCl₄(CO)py] are described.

Although much information is available on the preparation and properties of tertiary phosphine and -arsine complexes of transition metals, relatively little exists for those of ruthenium. The insoluble hydrido-carbonyl species, [RuHCl(CO)(MPh₃)], (M = P, As), have been prepared by refluxing hydrated ruthenium trichloride with an excess of ligand in 2-methoxyethanol. A preliminary note by Vaska 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)], [RuBr₃(AsPh₃)₂CH₃OH] and [RuCl₃(PPh₃)₂CH₃OH] but detailed preparations are not available. The binuclear complexes [Ru₂Cl₄(PR₃)₂Cl] were obtained by the prolonged interaction of the phosphine with hydrated trichloride in boiling methanol (R = Et₃Ph, EtPh₂ etc.); although these complexes do not react with an excess of tertiary phosphine to give mononuclear complexes, [RuCl₂(PR₃)₄], analogous preparative methods using dimethylphenylarsine gave cis and trans-[RuCl₃(AsMe₂Ph₄)] (but not [Ru₂Cl₄(AsMe₂Ph₆)Cl]). The preparation of the mixed alkyl/aryl tertiary phosphine and arsine complexes [RuCl₃(P(As)Et₃Ph)], [RuCl₂(CO)(PEt₂Ph₃)], [RuHX(CO)(PEt₂Ph₃)] (X = Cl, Br, I), cis-[RuX₂(CO)₂(P(As)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 = Et₃, Et₄) by a variety of methods has been described. Complexes such as [RuCl₂(PEt₂Ph₂)L₂] (L₂ = bipy, o-phen) have been prepared by refluxing hydrated ruthenium trichloride with methanol and dimethylphenylarsine. The binuclear complex [Ru₂Cl₄(PEt₂Ph₃)] has been prepared by refluxing hydrated ruthenium trichloride with dimethylphenylarsine in methanol. The corresponding bromo complex has also been prepared by refluxing hydrated ruthenium bromide with dimethylphenylarsine in methanol.

(6) B. L. Shaw. Personal communication (1965).
were prepared via \([\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\)Cl and finally, the cis-dicarbonyl complexes \([\text{RuI}_2(\text{CO})_2\text{L}_2]\) (L = PPh\(_3\), AsPh\(_3\), SbPh\(_3\), py, CH\(_3\)CN 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 Ph\(_3\)P, Ph\(_3\)As and Ph\(_3\)Sb with hydrated ruthenium trichloride, (2) the utilization of the reaction, briefly reported by Chatt et al.\(^{(5a)}\) in order to prepare new mono- and dicarbonyl complexes of ruthenium (II) and (III) with various ligands.

Triphenylphosphine, -arsine and -stibine complexes

On passing carbon monoxide into a boiling solution of ethanolic commercial RuCl\(_3\)3H\(_2\)O for several hours, a deep red solution was formed,\(^{(5a)}\) addition of triethylphosphine (2 mole) then gave trans-\([\text{RuCl}_2(\text{CO})_2(\text{PEt}_3)_2]\). 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 = P, As, Sb) and \([\text{RuCl}_2(\text{CO})(\text{MPh}_3)_3]\) (M = As, 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 1) 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\(^{(6b)}\) 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 1).

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

pure cis-[RuCl₂(CO)₂(PPh₃)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)₂] (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)₂(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 PPh₃Et and PEt₃ 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; λ₀.001M = 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 (II) 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 Ph₃P and Ph₃As complexes of ruthenium (III) of formula \([\text{RuCl}_2(MPh}_3\text{)]\) by the method used\(^{(5)}\) by CHATT to obtain \([\text{RuCl}_2(\text{PET}_3\text{Ph})_3]\). 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 Ph₃P and hydrated ruthenium trichloride (6:1 mole ratio) was shaken in methanol at room temperature, dark-brown diamagnetic crystals of \([\text{RuCl}_2(\text{PET}_3\text{Ph})_3]\) 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:

\[\text{[RuCl}_2(\text{PPh}_3)_4] + \text{solvent} \Rightarrow \text{[RuCl}_2(\text{PPh}_3)_2(\text{solvent})_2] + 2\text{PPh}_3.\]

This dissociation is similar to that found for \((\text{Ph}_3\text{P})_3\text{RhCl}\);\(^{(9)}\) 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 \([\text{RuCl}_2(\text{CO})_2(\text{PET}_3\text{Ph})_2]\) (1988 cm\(^{-1}\)) suggests the same configuration (III). HAYTER\(^{(10)}\) has recently prepared similar complexes \([\text{RuCl}_2(\text{PHR}_2)_4]\) \((\text{R} = \text{Et}, \text{Ph})\) by refluxing the trichloride and excess ligand in ethanol for two hours.

When the methanolic solution of Ph₃P and ruthenium trichloride was refluxed under nitrogen instead of being shaken, red-brown crystals of empirical formula \([\text{RuCl}_2(\text{PPh}_3)_3]\) 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 \([\text{RuCl}_2(\text{C}_7\text{H}_8)(\text{PPh}_3)_2]\)\(^{(9)}\) were also obtained by interaction with CO and \(\text{C}_7\text{H}_8\) under very mild conditions. These facts suggest that in solution the solvated species \([\text{RuCl}_2(\text{PPh}_3)_2(\text{solvent})_2]\) is again present. In nitromethane, conversion to an ionized complex, which is possibly \([\text{RuCl}_2(\text{PPh}_3)_3]\)Cl or \([\text{RuCl}(\text{PPh}_3)_2]\text{MeNO}_3\)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 unstable to isolate pure salts from these solutions.

On shaking Ph₃P and ruthenium trichloride (2:1 mole ratio) in excess methanol for several days, green crystals of the complex [RuCl₃(PPh₃)₂CH₃OH], 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, [RuCl₆(PPh₃)₂C₂H₅OH] 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 [RuCl₆(PPh₃)₂(Me₂CO)] 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. F₃B.OCMe₃, νCO = 1640 cm⁻¹;(12) the other acetone bands are readily assigned.

The corresponding reactions with Ph₃As and Ph₃Sb do not give the same range of complexes. Thus, on refluxing ruthenium trichloride with excess Ph₃As(6:1 mole ratio), paramagnetic (1.79 BM) green crystals of [RuCl₆(AsPh₃)₂CH₃OH] were formed; these showed methanol bands in the 1000 cm⁻¹ region. On treatment with acetone, brown crystals of the acetone complex [RuCl₆(AsPh₃)₂(Me₂CO)] (νCO 1656 cm⁻¹) are obtained. With pyridine under very mild reaction conditions, the complex gives [RuCl₆(AsPh₃)(py)₂] suggesting that one of the Ph₃As groups is comparatively labile, especially in the presence of ligands having a lower trans-effect. It would also suggest that the Ph₃As groups are trans to each other.

The interaction of ruthenium trichloride and excess Ph₃Sb (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 [RuCl₆(SbPh₃)₃]. 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 [RuCl₆(PPh₃)₃]. In contrast to the reactions with Ph₃P and Ph₃As, no evidence was found for the formation of a hydrido-carbonyl complex containing Ph₃Sb on refluxing in 2-methoxyethanol.

By shaking the hydrated trichloride for several hours with excess lithium bromide and then treating the solution with Ph₃P and Ph₃As as discussed above, we have also prepared the corresponding bromides [RuBr₆(PPh₃)₄], [RuBr₆(PPh₃)₃], [RuBr₃(PPh₃)₂CH₃OH] (red–brown) and [RuBr₃(AsPh₃)₂CH₃OH] (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 trans-[RuBr₃(CO)₄(PPh₃)₂] and [RuBr₃(C₅H₈)(PPh₃)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-[RuCl₆(CO)₂py₂]. No evidence was found for the direct formation of [RuCl₆(CO)py₃] 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 [RuCl₆(CO)(diene)]; on warming these with excess pyridine, crystals of [RuCl₆(CO)py₃] 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)py₂]. Since (1) the infra-red spectrum contained pyridinium bands; (13) (2) a solution of the complex in nitromethane has the conductivity of a 1:1 electrolyte \( \Lambda_{\infty} = 87 \ \Omega^{-1} \text{cm}^{2} \text{mole}^{-1} \) 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 tetraphenylarsonium 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 "ageing" 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, \( \beta \)-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.

**Trihalostannane 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 [Ru₂Cl₄(SnCl₃)(CO)₂(PPh₃)₃] 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 \( \Lambda_{\infty} = 30 \ \Omega^{-1} \text{cm}^{2} \text{mole}^{-1} \) 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 [Ru₂Cl₄(SnCl₃)(CO)₂(PPh₃)₄]. If however, analogous reactions are carried out with acetone replaced by diethylether, no single product could be isolated. Attempts to separate the mixture of trihalostannate complexes by recrystallization resulted in the loss of stannous chloride with the formation of cis-[RuCl₄(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]²⁻.

New complexes of ruthenium (II) and (III) with triphenylphosphine

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 “Spectromaster” 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

Dichlorotetrakis(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.

Dibromotetrakis(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).

Dichlorotris(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, 5.65%; in 2-methoxyethanol (Found: C, 53.2; H, 4.3%).

cis-Dicarboxyl complexes of ruthenium (II):- cis-dichloro(dicarboxyldis(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) Dichlorotetakis(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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<th>Compound</th>
<th>m.p. (°C)</th>
<th>Found (%)</th>
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* Prepared by VASKA(3)
† 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 triphenylphosphate 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) (cacoetheline 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(2-picoline)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-Dicarbonyl complexes of ruthenium (II):- trans-dichloro(dicarbonyl)bis-(quinaline)ruthenium (II). To 5 ml of freshly-prepared red solution, excess quinaline (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)**

\[ [\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_4]\] 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 (ν_\text{CO} 1691 cm\(^{-1}\)). The same compound is deposited if the red solution, stannous chloride and phosphine (same quantities) are refluxed instead of shaken. It analyses for \([\text{Ru}_2\text{Cl}_3(\text{SnCl}_3)(\text{CO})_2(\text{PPh}_3)_4]\). The tin (II) (cacocethine test) was positive.

**Bis(tetramethylammonium)dicarbonyldichlorobis(trichlorostannate)rubenate (II).**\(^*\) (a) Dicarbonyldichlororuthenium (II) (0.3 g) was refluxed in 3M-hydrochloric acid (25 ml) with SnCl\(_2\)2H\(_2\)O (1.2 g) for 1 hr. Addition of NMe\(_4\)Cl (0.5 g) in water (5 ml) to the yellow solution precipitated the yellow complex (0.7 g, 75 percent); recrystallized from 3M-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 (\(\Lambda_{\text{g},0.01M} = 97 \Omega^{-1}\text{cm}^2\text{mole}^{-1}\)).

(b) (Me\(_4\)N\(_2\))[RuCl\(_2\)(SnCl\(_3\))]\(_2\)\(^*\) (0.5 g) was suspended in acetone (15 ml) and treated with carbon monoxide at 85 atm and 120°C 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°C) and air-dried (40 percent).

**Trichlorobis(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 percent).

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

**Trichlorobis(triphenylphosphine)(acetone)ruthenium (III).** [RuCl\(_3\)(PPh\(_3\))\(_2\)CH\(_3\)OH] 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 percent).

**Trichlorobis(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 percent). The complex has a magnetic moment of 1.74 BM.

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

**Trichlorobis(triphenylarsine)bis(pyridine)ruthenium (III).** [RuCl\(_3\)(AsPh\(_3\))\(_2\)CH\(_3\)OH] was gently warmed with dry pyridine to give a bright yellow solution. Addition of excess petroleum (100–120°C) precipitated an orange-yellow powder, recrystallized from an acetone/diethyl ether mixture as orange-brown crystals (65 percent).

**Pyridinium tetrachlorocarbonylpyridinyl 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°C) 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.

The compound is soluble in acetone, water, ethanol and nitromethane; insoluble in ethers and benzene.

**Tetraphenylarsoniumtetrachloro(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(triethylphosphate)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 [Ru₂Cl₄(PR₃)₆]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 RuCl₆³⁻ 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)

\[
\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + n(\text{C}_6\text{H}_5)_3\text{P} \xrightarrow{25^\circ \text{C.}} \text{N}_2 \text{ atm.} \quad 24 \text{ hours in methanol solution} \quad [\text{RuCl}_2\{\text{P(C}_6\text{H}_5)_3\}_4] + \text{other products}
\]

Checked by RICHARD SINGLER\* and ROBERT D. FELTHAM\*

Procedure

Ruthenium trichloride trihydrate (0.6 g., 2.2 mmole) 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 mmole) 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\(_{72}\)H\(_{60}\)Cl\(_2\)P\(_4\)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)

\[
\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + n(\text{C}_6\text{H}_5)_3\text{P} \xrightarrow{85^\circ \text{C.}, 3 \text{ hours N}_2 \text{ atm.}} \text{methanol soln.} \quad [\text{RuCl}_2\{\text{P(C}_6\text{H}_5)_3\}_3] + \text{other products}
\]

Checked by RICHARD HOLM†

Procedure

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

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† Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.
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 RuCl\(_3\cdot3\text{H}_2\text{O}\), 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 C\(_{56}\)H\(_{45}\)Cl\(_2\)P\(_3\)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 \([\text{RuCl}_2\{\text{P(C}_6\text{H}_5)\}_3\}_3\)\(^3\) 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\(^1\) at room temperature and pressure, and with norbornadiene\(^4\) to give, respectively, trans-[\(\text{RuCl}_2\text{(CO)}\text{(C}_6\text{H}_5)\text{)}\text{)}\text{)}\text{)}\text{)}\text{)}\text{]}\text{)}\text{)}\text{)]} and \([\text{RuCl}_2\text{(C}_7\text{H}_8)\text{(P(C}_6\text{H}_5)\text{)}\text{)}\text{)]}\text{)}\text{)}\text{)}\text{)]}\text{)}\text{)}\text{)}\text{]}\text{)}\text{)}\text{]}\text{)]. 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

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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 $M[RuCI_3(AsPh_3)_2]$ ($M=AsPh_4^+$, $(CH_3)_4N$; $X=Cl$, Br) and $M[RuCl_3(PR_3)_2]$ ($M=AsPh_4^+$, $(CH_3)_4N$; $PR_3=PPh_3$, $PEt_3$, $PMe_2Ph$). The preparation of $R_3PH[RuCl_3(PR_3)_2]$ ($PR_3=PEt_3$, $PEt_2Ph$) via an ethanolic carbonyl-containing ruthenium solution has been briefly mentioned (2).

Reaction of $[RuCl_3(LPh_3)_2CH_3OH]$ ($L=P$, As) (2) with a large excess of $MCI$ in acetone slowly forms red crystals of $M[RuCl_4(LPh_3)_2]$ (75-80% yield); with $[RuBr_3(AsPh_3)_2CH_3OH]$ (2) and $MBr$, purple acetone-soluble crystals of the bromo anion are readily isolated. The $PPh_3$ anion can also be obtained from the reaction of $[RuCl_2(PPh_3)_3$ or $4]$ (2) and $MCI$. As for $PEt_3$ and $PEt_2Ph$, the phosphonium salt of the $PMe_2Ph$ anion can be isolated as a dark brown crystalline material by treating an ethanolic carbonyl-containing ruthenium solution with $PMe_2Ph$ (35-40% yield); other products from this
reaction are \([\text{RuCl}_2 \text{CO}(\text{PMe}_2 \text{Ph})_3]\) 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 M[\text{RuCl}_4(\text{PR}_3)_2]. However, a more convenient method of preparing these anions in much higher yield is by treatment of M[\text{RuCl}_4(\text{PPh}_3)_2] with the appropriate phosphine when quantitative conversion to M[\text{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 \((\text{CH}_3)_4\text{N}[\text{RuCl}_4(\text{PPh}_3)_2]\) 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%. \(\text{C}_{40}\text{H}_{42}\text{Cl}_{14}\text{N}_{2}\)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 \([\text{RuCl}_3(\text{LPh}_3)_2\text{CH}_3\text{NO}_2]\) (L=P, 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 \([\text{RuCl}_4(\text{PMe}_2 \text{Ph})_2]^-\) ion using the NMR technique developed by Shaw et al (5) was unsuccessful because of the broadness of the methyl resonance (cf. mer-\([\text{RuCl}_3(\text{PMe}_2 \text{Ph})_3]\) (6)). However, the close similarity between the infrared spectra \((4000-200 \text{ cm}^{-1})\) of this paramagnetic ion and the diamagnetic \([\text{M}^{1}\text{Cl}_4(\text{PMe}_2 \text{Ph})_2]^-\) ions \((\text{M}^{1}=\text{Rh}, \text{Ir})\), shown by NMR (5,7) to
### TABLE 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T^a_K$</th>
<th>$\mu_{eff}(B.M.)$</th>
<th>$\Lambda (0.001M)cm^2 ohm^{-1} mole^{-1}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(CH_3)_4N[RuCl_4(AsPh_3)_2]$</td>
<td>292</td>
<td>2.21</td>
<td>67</td>
</tr>
<tr>
<td>$(CH_3)_4N[RuBr_4(AsPh_3)_2]$</td>
<td>295</td>
<td>1.84</td>
<td>73</td>
</tr>
<tr>
<td>$(CH_3)_4N[RuCl_4(PPh_3)_2]$</td>
<td>294</td>
<td>1.97</td>
<td>74</td>
</tr>
<tr>
<td>AsPh_4[RuCl_4(PPh_3)_2]</td>
<td>295</td>
<td>2.00</td>
<td>62</td>
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<tr>
<td>Me_2PhPH[RuCl_4(PMe_2Ph)_2]</td>
<td>293</td>
<td>2.10</td>
<td>60</td>
</tr>
<tr>
<td>AsPh_4[RuCl_4(PMe_2Ph)_2]</td>
<td>295</td>
<td>1.94</td>
<td>51</td>
</tr>
<tr>
<td>[RuCl_3(AsPh_3)_2CH_3NO_2]</td>
<td>295</td>
<td>2.00</td>
<td>4</td>
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</tbody>
</table>

$^a$ Measured at 295°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_2Ph 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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Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION A
Inorganic, Physical, and Theoretical Chemistry

1970
Some Anionic Ruthenium(III) and Rhodium(III) Complexes of Tertiary Monophosphines and Arsines

By T. A. Stephenson, Department of Inorganic Chemistry, University of Newcastle upon Tyne, NE1 7RU

Various methods of preparing ruthenium(III) anions of formula $\text{M}[[\text{RuCl}_6(\text{PR}_3)_6]_2]$ (M = Me$_4$N$^+$, Ph$_3$As$^+$; PR$_3$ = PPh$_3$, PMe$_2$Ph, PEt$_2$P(OPh)$_2$), and $\text{M}[[\text{RuX}_2(\text{AsPh}_3)_6]]$ (M = Me$_4$N$^+$, Et$_3$N$^+$, Ph$_3$As$^+$; X = Cl, Br) are described including one involving 'oxidation' of $\text{RuCl}_6(\text{PR}_3)_6$ by concentrated hydrochloric acid. Methods of synthesising the isomorphous complexes Ph$_3$As$^+$RbCl$_6[(\text{PR}_3)_6]\text{Rb}$ (PR$_3$ = PPPh$_3$, PMe$_2$Ph) via RhCl(PPh$_3$)$_4$ and trans-[RhClCO(PPh$_3$)$_4]$ 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 variety of the complexes of ruthenium(III) 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 $\text{RuBr}_3\text{CO}(\text{PPh}_3)_2$ (ref. 3). The only other ruthenium(III) carbonyl complexes are $\text{M}_2[[\text{RuCOCl}_4]$ [M = NH$_4^+$ (ref. 4), Cs$^+$ (ref. 5)], $\text{[Ru}2\text{CO}_5(\text{PhCH}_2\text{NCS})_2\text{Cl]}$ (ref. 6), and $\text{M}[\text{Ru}-\text{CO py]}$ (M = py$^+$, Ph$_3$As$^+$).$^7$

(b) The synthesis of $\text{RuCl}_6(\text{LPh}_3)_2\text{MeOH}$ (L = P, As)$^3$ obtained by treatment of $\text{RuCl}_6\text{H}_2\text{O}$ with a stoichiometric amount of triphenylphosphine in methanol and by heating $\text{RuCl}_6\text{H}_2\text{O}$ under reflux with an excess of triphenylarsine. The bromo-compounds can also be obtained; reaction with acetone gives $\text{RuCl}_6(\text{LPh}_3)_2\text{MeCO}$ and with pyridine $\text{RuCl}_6(\text{AsPh}_3)_2\text{py}$.$^7$

(c) Various methods for the preparation of the complexes $\text{Me}_3\text{NR}_{2}X$ (X = Cl, Br; L = As, P; R = alkyl and/or aryl) have been reported, culminating in a recent paper by Chatt et al.$^5$ in which a general preparative method has been given. Further papers have discussed the e.s.r.$^9$ and configurations$^{10}$ of these and other platinum-metal tertiary phosphine and arsine complexes.

(d) The binuclear complexes $\text{[RuCl}_6(\text{PR}_3)_6]_2$ and $\text{[RuCl}_6(\text{PR}_3)_6]$ (R = Pr$_3$, Bu$_4$) have been recently reported.$^{11}$ The former is formulated as a halogen-bridged dimer and the latter has been shown by X-ray analysis$^{12}$ to be analogous to the $\text{[RuCl}_6(\text{PR}_3)_6]\text{Cl}$ complexes (postulated to contain a triple chloride bridge)$^{13}$ with two chloride ions replacing two phosphine ligands to give a neutral complex with formal mixed oxidation states of (II) and (III).

(e) A brief report of the preparations of $\text{R}_2\text{PH}[\text{RuCl}_4-$

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$^4$ L. Vaska, Chem. and Ind., 1961, 1402.


the range expected for 1:1 electrolytes in this solvent.\(^4\) 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 \([\text{RuBr}_4(\text{PPh}_3)_2\text{MeOH}]\) and MBr was unsuccessful; the red-brown solids isolated contained no large cations (i.r. evidence) and were non-electrolytes in acetone and nitromethane solution. Treatment of a suspension of \(\text{Me}_2\text{N}[\text{RuCl}_4(\text{PPh}_3)_2]\) 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 \([\text{RuBr}_4(\text{PPh}_3)_2\text{H}_2\text{O}]\text{H}_2\text{O}\). This formulation was supported by the very low conductance (Table 1) 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 \([\text{RuCl}_4(\text{AsPh}_3)_2]\)\(^{2-}\) 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 \([\text{RuBr}_4(\text{AsPh}_3)_2]^{-}\) and \(\text{H}_2\text{O}\). 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 solvolytic attack and exchange reactions with other tertiary phosphines, clearly indicate the increased lability of the \(\text{PPh}_3\) 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 \([\text{RuX}_4(\text{PPh}_3)_2]\)\(^{-}\) (\(\text{X} = \text{SCN}^-, \text{I}^-, \text{etc}\)) by metathetical reactions. In contrast, similar reactions with \([\text{RhCl}_4(\text{PPh}_3)_2]\)\(^{-}\) readily produced \([\text{RhX}_4(\text{PPh}_3)_2]\)\(^{-}\) (\(\text{X} = \text{Br}^-, \text{SCN}^-\)) which did not undergo solvolysis.

A feature of the tetrachloroarsenoborane salts of the ruthenium(III) triphenylphosphine 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 (\(\text{cm}^{-1}\)) and 1220 cm\(^{-1}\) (\(\text{cm}^{-1}\)). The position of \(\text{cm}^{-1}\) indicated that the acetone was probably present as molecules of solvation and not co-ordinated, [cf. \(\text{cm}^{-1}\) in \([\text{RuCl}_4(\text{AsPh}_3)_2\text{Me}_2\text{CO}]\)]\(^7\); \(\text{cm}^{-1}\) 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 tetrachloroarsenoborane 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 \([\text{RuCl}_4(\text{PPh}_3)_2]^{2-}\) via \([\text{RuCl}_4(\text{PPPh}_3)_2]^{4-}\).\(^4\) There is only one example in the literature of a ruthenium(II) anionic complex containing a tertiary phosphine group: the rather strange \([\text{RuCl}_4(\text{PPh}_3)_2\text{Cl}]\) prepared by heating \([\text{RuCl}_4(\text{PEt}_3\text{Ph})_2\text{Cl}\] at 60\(^\circ\) in methyl acetate.\(^6\) At 120\(^\circ\) in this solvent, \([\text{RuCl}_4(\text{PEt}_3\text{Ph})_2\text{Cl}]\) is formed.\(^6\) However, the corresponding halogenocarbonyl anions \([\text{RuX}_4(\text{CO})_3]\) (\(\text{X} = \text{Cl}, \text{Br}\))\(^5\) as well as \([\text{M}[\text{RuX}_4(\text{CO})_3]\] \(\text{M} = \text{Cs}^+\) (refs. 5 and 19), \(\text{NH}_4^+\) (ref. 4); \(\text{X} = \text{Cl}, \text{Br}, \text{I}\) and \(\text{M}_2[\text{RuX}_4(\text{CO})_3]\text{H}_2\text{O}\) \(\text{M} = \text{Cs}^+\) (ref. 5); \(\text{NH}_4^+\) (ref. 20) are well known.

However, reaction of \([\text{RuCl}_4(\text{PPh}_3)_2]^{4-}\) with an excess of \(\text{Ph}_4\text{AsCl}\) in acetone produced orange crystals of \(\text{Ph}_4\text{As}[\text{RuCl}_4(\text{PPh}_3)_2(\text{Me}_2\text{CO})_2]\) identical to the product obtained from \([\text{RuCl}_4(\text{PPPh}_3)_2\text{MeOH}]\). With \(\text{Me}_2\text{NCl}\), 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 \(\text{Me}_2\text{NCl}\) to a portion of this then rapidly deposited orange \(\text{Me}_2\text{N}[\text{RhCl}_4(\text{PPh}_3)_4]\). 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 1) and had an analysis close to that for \(\text{H}_2\text{O}[\text{RuCl}_4(\text{PPh}_3)_4]\). However, an i.r. spectrum of the carefully dried compound contained no evidence for either hydrogen ion or aquo-groups and a better formulation may be \(\text{H}[\text{RuCl}_4(\text{PPh}_3)_4]\) (cf. \(\text{H}[\text{RuCl}_4(\text{ophen})]\) obtained by reduction of \([\text{RuCl}_4(\text{ophen})]\) with alcohol in the presence of hydrochloric acid).\(^2\)

The structure of these complexes may be similar to that postulated for \(\text{H}_2[\text{Ru}(\text{CN})_6]\)\(^2\) with hydrogen bonding between the hydrogen and chloride groups.

**Ruthenium(III) Anions of other Tertiary Monophosphines.**—Although the \(\text{PPh}_3\) 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 aliphatic group are unknown. Instead, refluxing methanolic \(^3\) or 2-methoxy-ethanolic \(^3\) solutions of \(\text{R}_2\text{P}\) and \(\text{RuCl}_4\text{xH}_2\text{O}\) gives \([\text{RuCl}_4(\text{PPPh}_3)_2\text{Cl}]\); in an acidified ethanolic solution

mer-RuCl$_2$(PPh$_3$)$_2$ is formed 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 RuCl$_2$[PEt$_3$]$_3$, by treatment of monomeric $^{23}$ RuCl$_2$- (PPh$_3$)$_3$ 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 [RuX$_2$(PMe$_2$Ph)$_2$] (X = Cl or Br) readily decomposes to give green [RuX$_2$(PMe$_2$Ph)$_3$], 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 color was discharged and very pale yellow crystals were deposited; these had an analysis which was consistent with the empirical formula [RuCl$_2$(PEt$_3$)$_3$]. The far-i.r. spectrum [no ν(RuCl) > 270 cm$^{-1}$], conductivity in nitromethane (A$_{0.001}$ = 49 ohm$^{-1}$ mole$^{-1}$ cm$^2$), and melting point were identical with those of a sample of [RuCl$_2$(PEt$_3$)$_3$]Cl, prepared from RuCl$_3$·H$_2$O, Et$_3$P, and 2-methoxyethanol.$^2$ A similar result was obtained when RuH$_2$(PMe$_2$Ph)$_4$ was treated with hydrochloric acid when [RuCl$_2$(PMe$_2$Ph)$_4$]Cl, and not the expected [RuCl$_2$(PMe$_2$Ph)$_3$], was isolated.$^{25}$ It is concluded, therefore, that although mononuclear halide complexes of ruthenium(II) with R$_3$P do exist, they are unstable with respect to the halogeno-bridged binuclear complex. The only exceptions are RuCl$_2$-[PPh$_3$]$_2$ and 4.

As briefly reported earlier,$^7$ treatment of a ruthenium carbonyl-containing solution with a large excess of Et$_3$P or Et$_3$PO gives immediate precipitation of green crystals of RPH[RuCl$_3$(PPh$_3$)$_2$]. This reaction has now been extended to the preparation of the phosphonium salt of Me$_3$P$^+$; reaction of an excess of Me$_3$P$^+$ with a cold freshly prepared 'red solution' produced a mixture of Me$_4$N[RuCl$_3$(PMe$_2$Ph)$_2$], (ca. yield 40%), RuCl$_2$CO-(PMe$_2$Ph)$_2$, and RuCl$_2$(CO)$_2$(PMe$_2$Ph)$_2$. The carbonyl complexes have been well characterised by previous workers.$^{26}$ Treatment of the phosphonium salts with MCl in a minimum volume of solvent then gave M[RuCl$_3$(PPh$_3$)$_2$] (M = Ph$_3$P$^+$ or Me$_3$N$^+$).

A more direct method of obtaining these salts is by treatment of $^4$M[RuCl$_4$(L$_3$P)$_2$] with an excess of neat tertiary phosphine for several days under nitrogen, when almost quantitative conversion into the corresponding tertiary phosphine anionic complex occurred. Care must be taken to avoid solvents in these exchange reactions because of ready solvolysis of all the anions; further, since the compounds are thermally unstable, heat must be avoided. The rate of exchange was also sensitive to whether Ph$_3$P or Ph$_3$As was being displaced and on the particular cation present. Qualitatively, this rate of exchange was found to be $^4$[RuCl$_4$(PPh$_3$)$_2$] $^+ >$ RuCl$_4$(AsP$_3$)$_2$ $^+$ and Ph$_3$As $^+ >$ Me$_3$N$^+$ for the same anion. This exchange reaction was also used to prepare the first tertiary phosphite complex of ruthenium(III). Treatment of Me$_4$N[RuCl$_4$(PPh$_3$)$_2$] with an excess of neat triphenyl phosphite for several months gave orange Me$_4$N[RuCl$_4$(PPh$_3$)$_2$].

Magnetic moments and conductivity data are given in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Lambda_{0.001}$ (cm$^2$ ohm$^{-1}$ mole$^{-1}$)</th>
<th>Solvent</th>
<th>$\mu_{eff}$ (BM)</th>
<th>$T$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_3$As<a href="Me$_2$CO">RuCl$_3$(AsP$_3$)$_2$</a>$_2$</td>
<td>50</td>
<td>MeNO$_2$</td>
<td>1.97</td>
<td>291</td>
</tr>
<tr>
<td>Me$_4$N[RuCl$_3$(AsP$_3$)$_2$]</td>
<td>30</td>
<td>CH$_2$Cl$_2$</td>
<td>2.21</td>
<td>292</td>
</tr>
<tr>
<td>Et$_3$N[RuCl$_3$(AsP$_3$)$_2$]</td>
<td>30</td>
<td>MeNO$_2$</td>
<td>2.10</td>
<td>293</td>
</tr>
<tr>
<td>Ph$_3$As<a href="Me$_2$CO">RuCl$_3$(PMe$_2$Ph)$_2$</a>$_2$</td>
<td>73</td>
<td>MeNO$_2$</td>
<td>2.00</td>
<td>294</td>
</tr>
<tr>
<td>Me$_4$N[RuCl$_3$(PMe$_2$Ph)$_2$]</td>
<td>73</td>
<td>MeNO$_2$</td>
<td>2.10</td>
<td>295</td>
</tr>
<tr>
<td>Ph$_3$As<a href="Me$_2$CO">RuCl$_3$(PPh$_3$)$_2$</a>$_2$</td>
<td>29</td>
<td>MeCO</td>
<td>2.3</td>
<td>293</td>
</tr>
<tr>
<td>Ph$_3$As[RuCl$_3$(PPh$_3$)$_2$]</td>
<td>29</td>
<td>MeNO$_2$</td>
<td>1.97</td>
<td>296</td>
</tr>
<tr>
<td>Ph$_3$As[RuCl$_3$(PET$_3$)$_2$]</td>
<td>37</td>
<td>CH$_2$Cl$_2$</td>
<td>1.84</td>
<td>295</td>
</tr>
<tr>
<td>Ph$_3$As[RuCl$_3$(PPh$_3$)$_2$]</td>
<td>37</td>
<td>MeNO$_2$</td>
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<td>37</td>
<td>MeNO$_2$</td>
<td>1.84</td>
<td>295</td>
</tr>
</tbody>
</table>

*a* Ph$_3$AsGHCl in CH$_2$Cl$_2$; $\Lambda_{0.001}$ = 48 cm$^2$ ohm$^{-1}$ mole$^{-1}$. *b* Prepared from RuCl$_3$(PPh$_3$)$_2$. *c* Prepared from RuCl$_3$(PPh$_3$)$_2$MeOH. *d* Prepared from RuCl$_3$(PMe$_2$Ph)$_2$. *e* From Ru$_3$(AsP$_3$)$_2$ MeOH. *f* From Me$_3$N$^+$ salt. *g* From phosphonium salt. *h* From Ph$_3$P


Solvolysis of Ruthenium(III) Anions.—When the red anionic complexes M[RuCl₄(LPh₃)] 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 Ph₄As⁺ 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 related systems. For example, persistent treatment of red H[RUCl₄]₂H₂O with alcohol gives a green solid and Griffith has suggested that these may be cis- and trans-isomers of the [RuCl₄(H₂O)]⁻ anion. A recent X-ray analysis of red Ph₄As[RuCl₄(H₂O)]H₂O has shown it to contain cis-aquo-groups. The brown complexes phenH[RuCl₄(phen)] and bipyH[RuCl₄(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 Et₃PO[RuCl₄(PEt₃)] 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 MCI to the solution, and, further, the addition of MCI to the green solids (from the [RuCl₄⁻(LPh₃)]⁻ anions) in acetone rapidly gave the original red complexes. Furthermore, the green complexes were found to be non-conducting in nitromethane and to contain no large cation (i.e., evidence); in fact, they had melting points and analyses identical to [RuCl₄(LPh₃)]⁻.MeNO₂, which was obtained by treating [RuCl₄(LPh₃)]⁻.MeOH with nitromethane. A similar behaviour was observed in acetonitrile solutions. Thus the red–green colour change can be ascribed to the equilibrium:

\[
[RuCl₄(LPh₃)]^{-} + S \rightleftharpoons [RuCl₄(LPh₃)S]^{+} + Cl^{-} \quad S = \text{MeNO}_₂, \text{MeCN}
\]

A similar behaviour has been found for the complexes M[IrX₄(SbPh₃)] (M = Na, K; X = Cl, Br) which on dissolution in methanol slowly gave [IrX₄(SbPh₃)]⁻.CH₂OH. Rather surprisingly, the i.r. spectra of the ruthenium complexes showed no evidence for solvent-coordination, 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 Et₄P anion led to isolation of a red-brown solid, nonconducting in dichloromethane and nitromethane and containing no large cation (i.e., 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 [RuCl₄(H₂O)]⁻ is treated with ethanol is probably due to the formation of green [RuCl₄(H₂O)]⁻(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 [RhCl₄(PMe₂Ph)]⁻, isolated as its phosphonium salt (2–3% yield) in the reaction of RhCl₃H₂O and Me₂P to give mer- and fac-[RhCl₄(PMe₂Ph)]. Reaction of the phosphonium salt with Ph₄AsCl,HCl then gave Ph₄As[RhCl₄(PMe₂Ph)]/Ph₄AsCl,HCl. Attempts to prepare this anion in larger yields by treatment of mer-[RhCl₄(PMe₂Ph)] with an excess of Me₂NCl 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(PPh₃)₃ in acetone was treated with a large excess of Ph₄AsCl,HCl, conversion into orange crystalline Ph₄As[RhCl₄(PPh₃)] occurred during several hours. As for the ruthenium anion, the complex crystallises out with two molecular equivalents of solvent acetone. With Me₂NCl, 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-(I) anion [RhCl₃(PPh₃)]⁻, analogous to the well-known [RhCl₃(CO)]⁻, with a stoichiometric quantity of Ph₄AsCl,HCl were unsuccessful; only the rhodium(III) anion and unchanged RhCl(PPh₃)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 trans-[RhCl(CO)(PPh₃)] with a large excess of Ph₄AsCl,HCl in an acetone–chloroform mixture. The main product was trans-[RhCl₃(CO)(PPh₃)]₃, previously obtained by direct interaction of chloride with trans-[RhCl₃(CO)]⁻(PPh₃)₃. Although carbonyl groups have been replaced in metal carbonyls by halide ion to give halogenocarbonyl 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 Me2PhP gave Ph4As•-[RuCl4(PMe2Ph)2]; however with Et2P and (PhO)3P, only the unchanged aryphosphine 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 chloro-anion with various lithium salts gave [RhX4(PPh3)2]- ions (X = Br- and SCN-) which were quite stable in solution. Unlike reactions of mer-[RhCl4(PMe2Ph)2] with lithium salts, which require 'triplet' indicative of trans-Me2PhP groups. The complex Ph4As•[RuCl4(PMe2Ph)2] 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 Ph4As+ ion at 351 and 339 cm. (3 ref. 31) to that reported by Shaw et al.21 Similar i.r. evidence suggests a trans-structure for the [RuCl4(PPh3)2]- ion and this has been recently substantiated by e.s.r. measurements9 on Et2PH[RuCl4(PPh3)2].

For the chloro-Ph4P and Ph4As 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(MCl) to be assigned and the ratio of ν(MCl) : ν(MBr) (1:25—1:30) is in the range found by other workers38 and supports these assignments. However, unlike mer-[MCl4(PR3)2](M = Ru,10 Rh,10 Ir,36 and Re36); R2 = R1 = 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 phosphine may be invalid for triphenylphosphine (and arsine) complexes. The reason for this presumably arises from the fact that Ph4P is a weaker σ-donor than Et4P or Me4Ph and that in octahedral complexes of the platinum metals, the trans-bond weakening effect of a ligand σ-donor to depend on its σ bond properties.39

Although far-i.r. evidence is, therefore, by no means conclusive, the ready exchange of Me2PhP, etc., for Ph4L

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>Ph4As•[RuCl4(PPh3)2]</td>
<td>358s, 338m, 32s, 319vs, 296m, *</td>
<td>311vs, *</td>
</tr>
<tr>
<td>Ph4As•[RuBr4(PPh3)2]</td>
<td>352s, 347m, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4(PPh3)2]</td>
<td>358s, 344m, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4Cl(PPh3)2]</td>
<td>357s, 347m, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuBr4Cl(PPh3)2]</td>
<td>354s, 341s, 322s, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuBr4Cl(PPh3)2]</td>
<td>360s, 354s, 326s, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4Cl(PPh3)2]</td>
<td>362m, 300m, 293m, 290m, 244m, 224m</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4C2H5(PPh3)2]</td>
<td>346w, 328s, 316w, 292m, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4C2H5(PPh3)2]</td>
<td>325s, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4C2H5(PPh3)2]</td>
<td>340s, *</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4C2H5(PPh3)2]</td>
<td>342w, 222m</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4C2H5(PPh3)2]</td>
<td>392m, 228m</td>
<td>296s</td>
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<tr>
<td>Ph4As•[RuCl4C2H5(PPh3)2]</td>
<td>338m, 320s, 272w, 220w</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>322m, 214w</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>344w, 372w, 228m</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>348s, 326s, 222m</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>316w, 307w, 22w</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>330s, 227w</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>392m, 323w, 227m</td>
<td>296s</td>
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<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>348m, 278w, 220w</td>
<td>296s</td>
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<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>352m, 225m</td>
<td>296s</td>
</tr>
<tr>
<td>Ph4As•[RuCl4PMe2Ph]</td>
<td>352m, 225m</td>
<td>296s</td>
</tr>
</tbody>
</table>

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.

Configuration of Ruthenium(III) and Rhodium(III) Anions...
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 phosphine, 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 Ph₄As[Rh(SCN)]₄(PPh₃)₂, the unsplit ν(CN) absorption (2105 cm⁻¹) is consistent with a trans-configuration. Comparison with the i.r. spectrum of the chloro-anion shows there is no additional band in the M-NCS range (780—860 cm⁻¹) but that a weak extra band occurs at 688 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). The region 690—720 cm⁻¹ is obscured by other bands due to the triphenylphosphine ligands.

Finally, X-ray powder photographs of Ph₄As[MCl₄(PPh₃)₂] (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 015) at 35°C. 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.I.C. Fourier spectrometer F.S. 520 with a Melinex beam divider and an effective resolution of 5 cm⁻¹ was also used to obtain

### Table 3

Analytical data for ruthenium(iii) and rhodium(iii) anions

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (%)</th>
<th>Required (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₄As[RuCl₃(PPh₃)₂][Me₂CO]</td>
<td>56-8</td>
<td>C: H: As: X: N: O: P</td>
</tr>
<tr>
<td>Me₄[N[RuCl₄(PPh₃)₂]</td>
<td>51-6</td>
<td>4-5</td>
</tr>
<tr>
<td>Pt₄[N[RuCl₄(PPh₃)₂]</td>
<td>53-9</td>
<td>5-5</td>
</tr>
<tr>
<td>Ph₄As[RuCl₃(PMe₂Ph)₂][Me₂CO]</td>
<td>63-6</td>
<td>4-8</td>
</tr>
<tr>
<td>Me₄[N[RuCl₄(PMe₂Ph)₂]</td>
<td>62-3</td>
<td>4-5</td>
</tr>
<tr>
<td>Pt₄[N[RuCl₄(PMe₂Ph)₂]</td>
<td>67-0</td>
<td>5-0</td>
</tr>
<tr>
<td>Ph₄As[RuBr₄(AsPh₃)₂][Me₂CO]</td>
<td>51-6</td>
<td>4-0</td>
</tr>
<tr>
<td>Me₄[N[RuBr₄(AsPh₃)₂]</td>
<td>43-2</td>
<td>4-0</td>
</tr>
<tr>
<td>Pt₄[N[RuBr₄(AsPh₃)₂]</td>
<td>44-0</td>
<td>5-4</td>
</tr>
<tr>
<td>Ph₄As[RuCl₄(AsPh₃)₂]</td>
<td>55-7</td>
<td>4-7</td>
</tr>
<tr>
<td>Me₄[N[RuCl₄(AsPh₃)₂]</td>
<td>53-2</td>
<td>4-7</td>
</tr>
<tr>
<td>Ph₄As[RuCl₄(PMe₂Ph)₂]</td>
<td>—</td>
<td>16-1</td>
</tr>
<tr>
<td>Me₄[N[RuCl₄(PMe₂Ph)₂]</td>
<td>36-2</td>
<td>7-6</td>
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<tr>
<td>Ph₄As[RuBr₄(PMe₂Ph)₂]</td>
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<tr>
<td>Me₄[N[RuBr₄(PMe₂Ph)₂]</td>
<td>50-7</td>
<td>4-0</td>
</tr>
<tr>
<td>Ph₄As[RhCl₄(PMe₂Ph)₂][Me₂CO]</td>
<td>62-7</td>
<td>4-5</td>
</tr>
<tr>
<td>Me₄[N[RhCl₄(PMe₂Ph)₂]</td>
<td>61-7</td>
<td>4-5</td>
</tr>
<tr>
<td>Ph₄As[RhBr₄(PMe₂Ph)₂][Me₂CO]</td>
<td>53-4</td>
<td>4-1</td>
</tr>
<tr>
<td>Me₄[N[RhBr₄(PMe₂Ph)₂]</td>
<td>53-2</td>
<td>4-2</td>
</tr>
</tbody>
</table>

* Found S: 11-1%; Required 10-3%.
* X = Cl or Br.
* From RuCl₃(PPh₃)₂CH₃OH.
* From RuCl₄(PPh₃)₂.
* From RuCl₄(PPh₃)₄.
* From RuCl₄(PPh₃)₅.

* From phosphonium salt
¢ From Pt₄[P anion.
¢ From Rh₄[P anion.
¢ From trans-RhCl₄(CO)(PPh₃)₂.

**Ruthenium Complexes**

**Tetraphenylassionium** Tetrahydroisotriphenylarsinyl ruthenium(iii) — Dicarbonate. — Trichlorobis(triphenylarsine)methanolate(ruthenium(iii)) (0-15 g) was suspended in solvent acetone (35 ml) and thoroughly shaken with tetraphenylassionium 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°C for several hours (0-27 g, 70%), m.p. 195°C (decomp.) (w dehydration) (1709 cm⁻¹; v₂ deformation) (1219 cm⁻¹). The complex exhibits a stable dichloromethane but decomposes in hot acetone.


Tetramethylammonium Tetrachlorobis(triphenylarsine)ruthenate(III).—This was prepared as for the Ph₄As⁺ salt with [RuCl₄(AsPh₃)₂MeOH] (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(III).—This was prepared as for the other salts from [RuCl₄(AsPh₃)₂MeOH] (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.

Diacetone.—Method (A). This was prepared as for the corresponding triphenylarsine salt from [RuCl₄(PPh₃)₂MeOH] (0·15 g.) and Ph₄AsCl,HCl (0·80 g.) in acetone (30 ml.); it was obtained as orange crystals (0·20 g., 79%), m.p. 207° [vco 1708 cm.⁻¹; υ₁ 1211 cm.⁻¹]. This product is more soluble in dichloromethane.

Dichlorotris(triphenylphosphine)ruthenium(II) with Hydrochloric Acid.—[RuCl₂(PPh₃)₃] (0·15 g.) dissolved under nitrogen in warm acetone (25 ml.) gave a yellow-brown solution to which Ph₄AsCl,HCl (0·60 g.) in acetonitrile (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° [vco 1708 cm.⁻¹; υ₁ 1216 cm.⁻¹]. The same product is formed if RuCl₃(PPh₃)₃ is used.

Tetraethylammonium Tetrachlorobis(triphenylarsine)ruthenate(III).—This was prepared as for the Ph₄As⁺ salt with [RuCl₄(PPh₃)₂MeOH] (0·15 g.) and Me₄NCl (0·60 g.) and gave orange crystals (0·12 g., 80%), m.p. 220° (decomp.). This compound is insoluble in dichloromethane.

Reaction of Dichlorotris(triphenylphosphine)ruthenium(II) with Hydrochloric Acid.—[RuCl₂(PPh₃)₃] (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., 80%), m.p. 122—125° (decomp.) [Found: C, 54·7; H, 5·0; Cl, 18·1%; H[RuCl₄(PPh₃)₂] requires C, 56·3; H, 4·2; Cl, 18·5%. A closer formulation is H₂O[RuCl₄(PPh₃)₂] (Requires C, 55·0; H, 4·2; Cl, 18·0; O, 2·0%) but the i.r. spectrum shows no evidence for aquo or hydroxonium groups; in view of the i.r. spectrum of [RuCl₄(L₄P₃)₂MeNO₃] (no evidence for MeNO₃), this may be inconclusive. An oxygen analyses was, in fact, obtained (5·5%) but the delay was considerable and some hydrolysis has probably occurred.

When a methanol (3 ml.) solution of Me₄NCl (0·60 g.) was added to the red-brown solution, orange crystals of tetramethylammonium tetrachlorobis(triphenylarsine)ruthenate(III) were slowly deposited (0·09 g., 68%), m.p. 220—222° (decomp.). The same compound can be obtained from RuCl₃(PPh₃)₃.

Tetraphenylarsonium Tetraethylammonium Tetrachlorobis(triphenylarsine)ruthenate(III).—Diacetone.—[RuBr₃(AsPh₃)₂MeOH] (0·30 g.) was suspended in acetone (35 ml.) and treated with concentrated hydrobromic acid (3 ml.) to give a deep red-brown solution. Ph₄AsBr (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, ethanol, and diethyl ether and then dried in vacuo at 40° for several hours (0·30 g., 66%), m.p. 180° (decomp.) [vco 1701 cm.⁻¹; υ₁ 1211 cm.⁻¹]. The compound can also be made by treating the corresponding chloro-salt 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° (vco 1700 cm.⁻¹). The compound is soluble in dichloromethane and nitromethane to give purple solutions; the latter rapidly turns red-brown.

Tetramethylammonium Tetrabromobis(triphenylarsine)ruthenate(III).—This was prepared as for the Ph₄As⁺ salt from [RuBr₃(AsPh₃)₂MeOH] (0·30 g.) and concentrated hydrobromic acid (3 ml.), Me₄NBr (0·80 g.) in an acetone (35 ml.)—methanol (6 ml.) mixture. A purple solution was obtained which upon removal of the solvent under reduced pressure gave a purple-black solid, which was washed with methanol and diethyl ether (0·20 g., 60%), m.p. 230—231° (decomp.) [Found: M(acetone) 608. Required, 553 (for 1:1 electrolyte)].

Reaction of Tetramethylammonium Tetrachlorobis(triphenylarsine)ruthenate(III) with Lithium Bromide.—Me₄N⁺[RuCl₄(AsPh₃)₂] (0·20 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. 230° (decomp.); its i.r. spectrum was identical with that of Me₄N[RuBr₄(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)₂H₂O] 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(triphenylarsine)ruthenate(III) with Lithium Bromide.—This was prepared as for the triphenylarsine complex from Me₄N[RuCl₄(PPh₃)₂] (0·30 g.) and lithium bromide (1·60 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, 26·6%; [RuBr₄(PPh₃)₂H₂O] 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)₃ is treated with a mixture of Me₄NBr and HBr.

Trichlorobis(triphenylarsine)(nitromethane)ruthenate(II).—Ph₄As[RuCl₃(AsPh₃)₂] (0·20 g.) was gently warmed with nitromethane (6 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%; C₁₇H₂₄As₂Cl₃NO₃Ru 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[RuCl₄(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 acetic acid with an excess of Me₄NCl regenerated red Me₄N[RuCl₄(AsPh₃)₂] (2 hr.).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>Description</th>
<th>Yield</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₃As[RuBr₃(AsPh₃)₂]</td>
<td>With methanol and water</td>
<td>Soluble</td>
<td>0.16 g.</td>
<td>78%</td>
</tr>
<tr>
<td>Ph₃As[RuCl₄(AsPh₃)₂]</td>
<td>With methanol and water</td>
<td>Soluble</td>
<td>0.16 g.</td>
<td>78%</td>
</tr>
</tbody>
</table>

**Tetrabromobis(triethylphosphine)ruthenate(iii).** —Ph₃As[RuCl₃(BrPh₃)₂] (0.10 g) was treated with neat Et₄P (1.0 ml) for 2 months to give a dark green solid which was washed with water and diethyl ether (0.06 g., 93%), m.p. 196—198° (decomp.).

**Tetramethylammonium Tetrachlorobis(triethylphosphine)ruthenate(iii).** —Me₄N[RuCl₄(PEt₃)₂] (0.10 g) was treated with neat triphenylphosphite (1.0 ml) for 3 months to give the crystalline orange complex; this was washed with diethyl ether and dried in vacuo at 40° (0.19 g., 95%), m.p. 158—160° (decomp.). The i.r. spectrum shows unmistakable evidence for (Ph₃PO)₂ ²⁺ [cf. RuCl₄(Ph₃PO)₂] plus an extra band at 940 cm⁻¹ (Me₄N⁺).

**Tetramethylammonium Tetrachlorobis(dimethylphenylphosphine)ruthenate(iii).** —Me₄N[RuCl₄(PPh₃)₂] (0.10 g) was prepared from Me₄N[RuCl₄(AsPh₃)₂] (1.0 g) and MeNO₂ (10 min.) gave the complex.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Preparation</th>
<th>Description</th>
<th>Yield</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Ph₃As[RuCl₃(BrPh₃)₂]</td>
<td>With methanol and water</td>
<td>Soluble</td>
<td>0.16 g.</td>
<td>78%</td>
</tr>
<tr>
<td>Ph₃As[RuCl₄(AsPh₃)₂]</td>
<td>With methanol and water</td>
<td>Soluble</td>
<td>0.16 g.</td>
<td>78%</td>
</tr>
</tbody>
</table>

**Tetramethylammonium Tetrachlorobis(dimethylphenylphosphine)ruthenate(iii).** —Method (A). —The phosphonium salt (0.30 g) was dissolved in acetic acid (10 ml) and an excess of Ph₃AsCl, HCl was added (120 g) to it, red-brown crystals of the complex (0.36 g., 90%), m.p. 215° (decomp.) were deposited.

**Method (B).** —Neat Me₄P (1.5 ml) was added to crushed Ph₃As[RuCl₄(PPh₃)₂] (0.15 g) which was then set aside at room temperature under nitrogen for 4 days. The excess complex was then decanted off and the red-brown complex was washed with acetonitrile and diethyl ether (0.10 g., 95%), m.p. 212° (decomp.). With Me₄N[RuCl₄(PPh₃)₂] and Me₄P, the i.r. spectrum after 4 days showed the presence of Ph₃P and indicating incomplete exchange. The complex is soluble in CH₂Cl₂ and MeNO₂ but insoluble in ethanol and water.

**Triphenylarsonium Tetrachlorobis(dimethylphenylphosphine)ruthenate(iii).** —This was prepared as for the Me₄PPh salt from Ph₃As[RuCl₄(PPh₃)₂] (0.15 g) and neat Et₄P (1.0 ml) during 6 days. The green-brown complex was washed with water and diethyl ether and dried in vacuo (0.09 g., 93%), m.p. 198° (decomp.). With the corresponding Ph₃As salt, 30 days are required to give the Et₄P salt. The complex was also prepared from Et₄P[RuCl₄(PEt₃)₂] and Ph₃AsCl, HCl in acetonitrile (m.p. 200° (decomp.)). The complex is soluble in CH₂Cl₂ and methanol to give green solutions which rapidly turn yellow-brown.

**Tetramethylammonium Tetrachlorobis(dimethylphenylphosphine)ruthenate(iii).** —This was prepared as the preceding complex from Me₄N[RuCl₄(PPh₃)₂] (0.20 g) and neat Et₄P (1.0 ml). The complex was obtained as green crystals (8 days) (0.13 g., 90%), m.p. 170° (decomp.). With the Ph₃As anion, ca. 15% conversion into the green Et₄P anion occurred during 30 days. The complex is very soluble and unstable in solution (e.g. in chloroform) and the green solution rapidly turns yellow-brown; the brown solid isolated contained no Me₄N⁺.
shaken for 1 hr. with Me$_4$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.).

Tetraphenylarsonium Tetrabromobis(triphenylphosphine)-rhodate(III)—Acetone.—A suspension of Ph$_4$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 dried in vacuo at 40° (0.09 g., 91%), m.p. 170° (decomp.) ($\nu$$_0$ 1705 cm.$^{-1}$; $\nu$$_0$ 1220 cm.$^{-1}$). The compound is very soluble in acetone and methanol.

Tetraphenylarsonium Tetraiodobis(dimethylphenylphosphine)rhodate(III).—This was prepared as for the corresponding ruthenium complex from the Ph$_3$P anion (0.15 g.) which was treated with neat Me$_2$P (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 Cl$_2$ showed methyl resonance (1:2:1 triplet) at $\tau$ 8.07 apparent coupling constant $J$(P—H) 4.1 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$_4$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$_3$(PMe$_2$Ph)$_3$].$^{31}$ 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.

[9/1574 Received, September 12th, 1969]
SYNTHESIS OF SOME RUTHENIUM(II)
ANIONIC COMPLEXES
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(Received 6 May 1971)

In spite of a wealth of information on coordination complexes of ruthenium (II), particularly with ligands such as PR₆, 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(P₂Et₂Ph)₆][RuCl₃(P₂Et₂Ph)₃] (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)C₇H₈] (M = Cs⁺, Ph₃BzP⁺) and the ruthenium (II) thiocarbonyl triphenylphosphine anion M[RuCl₃(CS)(PPh₃)₂] (M = Ph₄As⁺, Ph₃BzP⁺, Et₄N⁺).

(Ph₃BzP)[RuCl₃(CO)C₇H₈] was prepared by shaking [RuCl₂(CO)C₇H₈]₂ (3) 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. 177-186°).

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

C₃₃Cl₃H₃₀OP Ru 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

\[ ^1H \text{ nmr Spectrum of } (\text{Ph}_3BzP)[\text{RuCl}_3(\text{CO})_3\text{C}_7\text{H}_8] \]^a

<table>
<thead>
<tr>
<th>( \tau )</th>
<th>Ratio</th>
<th>Assignment</th>
<th>Assignmentb</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.38</td>
<td>20</td>
<td>Phenyl</td>
<td>phenyl</td>
</tr>
<tr>
<td>2.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.80</td>
<td>2</td>
<td>Doublet</td>
<td>methylene ((J_{p-H} 4.0 \text{Hz}))</td>
</tr>
<tr>
<td>4.78</td>
<td>2</td>
<td>Triplet</td>
<td>( \text{H}_2, \text{H}_6 )</td>
</tr>
<tr>
<td>5.48</td>
<td>2</td>
<td>Triplet</td>
<td>( \text{H}_2, \text{H}_6 )</td>
</tr>
<tr>
<td>5.80</td>
<td>1</td>
<td>Broad singlet</td>
<td>( \text{H}_1 )</td>
</tr>
<tr>
<td>6.34</td>
<td>1</td>
<td>Broad singlet</td>
<td>( \text{H}_4 )</td>
</tr>
<tr>
<td>8.71</td>
<td>2</td>
<td>Triplet</td>
<td>( \text{H}_7, \text{H}_8 )</td>
</tr>
</tbody>
</table>

\[ J_{\text{H}_7, \text{H}_8} = 1.25 \text{Hz}, \quad J_{\text{H}_7, \text{H}_4} = 1.50 \text{Hz}, \quad J_{\text{H}_2, \text{H}_6} = J_{\text{H}_6, \text{H}_6} = 4.5 \text{Hz}, \]

\[ J_{\text{H}_1, \text{H}_6} = J_{\text{H}_1, \text{H}_2} = 3.0 \text{Hz}, \quad J_{\text{H}_8, \text{H}_4} = J_{\text{H}_4, \text{H}_6} = 3.0 \text{Hz} \]

\(^a\) Measured in \( \text{CDCl}_3 \) \(^b\) 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 \textit{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 \([\text{RhCl}(\text{C}_7\text{H}_8)])-(\text{Ph}_3\text{P})\]) \((4 \text{ a, b})\), it is dissimilar \textit{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 $[\text{RuCl}_3(\text{CO})C_7\text{H}_8]^{-}$, only one isomer has been found. Furthermore, addition of free diene (to the $\text{Ph}_3\text{Bz}^+$ salt) or excess CsCl (to a $D_2O$ solution of the caesium salt) does not affect the nmr spectrum.

Rather surprisingly, attempts to prepare the $\text{Ph}_4\text{As}^+$ salt have resulted in the formation of the cis-$[\text{RuCl}_4(\text{CO})_2]^{2-}$ anion (with $\nu_{\text{CO}}$ 1940, 2030 cm$^{-1}$, nujol) compared to $\text{Cs}_2[\text{RuCl}_4(\text{CO})_2]$ (5) with $\nu_{\text{CO}}$ 1935 and 2036 cm$^{-1}$). An intermediate in this reaction appears to be the previously unknown trans-$[\text{RuCl}_4(\text{CO})_2]^{2-}$-anion ($\nu_{\text{CO}}$ 2010 cm$^{-1}$) which rapidly isomerises to the cis form.

Although it was expected that $[\text{RuCl}_3(\text{CO})C_7\text{H}_8]^{-}$ might prove an excellent precursor for a general synthesis of the series $[\text{RuCl}_3\text{CO}_3]^{-}$, 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 $[\text{RuCl}_2\text{CO}(\text{Ph}_3\text{P})_3]$. 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 $[\text{RuCl}_3(\text{CS})(\text{Ph}_3\text{P})_2]_2$ (6) with $\text{MCI/HCl}$ ($M = \text{Ph}_4\text{As}^+$, $\text{Ph}_3\text{Bz}^+$, $\text{Et}_4\text{N}^+$) 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 \(\text{Ph}_4\text{As}[\text{RuCl}_3(\text{CS})(\text{Ph}_3\text{P})_2]\))
\[2. (\text{CH}_3)_2\text{CO}; \text{Found; C, 62.8; H, 4.7; S, 2.6\%} \]
\[\text{C}_8\text{H}_{12}\text{AsCl}_3\text{O}_2\text{P}_2\text{SRu requires; C, 63.1; H, 4.9; S, 2.5\%}.\]
The diamagnetic complexes are 1:1 electrolytes (dichloromethane) and infrared spectra show the characteristic cation bands, triphenylphosphine and a thiocarbonyl band at 1272 cm\(^{-1}\) (nujol).

In other attempts to synthesise ruthenium (II) anions, reaction of \([\text{RuCl}_2(\text{Ph}_3\text{P})_2]\) acetone \((7)\) with \text{MCl}/\text{HCl} or \text{MCl} alone gave only the ruthenium (III) complexes \(\text{M}[\text{RuCl}_4(\text{Ph}_3\text{P})_2]\) \((\text{M} = \text{Ph}_4\text{As}^+, \text{Et}_4\text{N}^+)\) previously obtained by the reaction of \([\text{RuCl}_2(\text{Ph}_3\text{P})_3]\) or \([\text{RuCl}_3(\text{Ph}_3\text{P})_2\text{Cl}_6\text{OH}]\) with \text{MCl}/\text{HCl} \((8)\). With \([\text{RuCl}_2(\text{Me}_2\text{PhP})_2]\) \(\text{EtOH}\) \((9)\) and \text{MCl}/\text{HCl}, instead of the expected \([\text{RuCl}_3(\text{Me}_2\text{PhP})_3]^{-}\) anion, the well known \((10)\) \text{mer}-\([\text{RuCl}_3(\text{Me}_2\text{PhP})_3]\) was obtained. Finally, with \([\text{RuCl}_2\text{C}_7\text{H}_8]\) \((11)\) and \text{MCl}/\text{HCl}, the polymeric diene complex was recovered unchanged.

Acknowledgment

We thank Johnson-Matthey Ltd. for a loan of ruthenium trichloride and The National Institutes of Health for a fellowship. (E.S)

References

SYNTHESIS OF MIXED LIGAND CARBONYL COMPLEXES
OF RHODIUM(I) AND RHODIUM(III)

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(Received 18 May 1971)

Recently, the reaction of [RhCl(CO)]₂ with triphenylphosphine (1:2 molar ratio) to give the complex trans-[RhCl(CO)₅(PPh₃)] (Ia) has been reported (1). Further papers have discussed oxidative addition reactions of 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 binuclear monocarbonyl complex [RhCl(CO)(PPh₃)]₂ (Ib).

In this note, further evidence supporting the dimeric structure is presented and the synthesis and reactions of the mixed ligand complexes trans-[RhCl(CO)(PPh₃)L'] (II) (L' = AsPh₃, SbPh₃, C₆H₅N, Me₂S etc) are briefly discussed.

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 [RhCl(CO)(PPh₃)(AsPh₃)]: Found: C, 60.4; H, 4.1; As, 9.7; Cl, 9.2% \( \text{C}_{37} \text{H}_{30} \text{AsClO}_{2} \text{PPh}_3 \text{Rh} \) requires C, 60.5; H, 4.1, As, 10.2; Cl, 9.2% and infrared spectra which confirms the presence of both PPh₃ and L'.
layer chromatography on II ($L'$ = AsPh$_3$) reveals that this is not an equimolar mixture of [RhCl(CO)(PPh$_3$)$_2$] and [RhCl(CO)(AsPh$_3$)$_2$]. In fact, this compound can be recrystallised from an acetone/dichloromethane solution (unlike the SbPh$_3$ and C$_5$H$_5$N compounds, which readily decompose) and an osmometric molecular weight determination (in CHCl$_3$) 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 $\nu_{CO}$ (ca 1960 cm$^{-1}$) and $\nu_{RhCl}$ (ca 310 cm$^{-1}$) to those found for trans-[RhCl(CO)(PPh$_3$)$_2$] (6,7).

As expected, the chemistry of the mixed complexes is analogous to that established for trans-[RhCl(CO)(PPh$_3$)$_2$]. Thus II ($L'$ = AsPh$_3$) readily undergoes oxidative addition reactions to give the rhodium(III) compounds [RhClXY(CO)(PPh$_3$)(AsPh$_3$)] (XY = Cl$_2$, I$_2$, CH$_3$COCl, CH$_3$I etc.). With CH$_3$I, the infrared spectrum shows the acetyl complex [RhClI(CH$_3$CO)(PPh$_3$)(AsPh$_3$)] ($\nu_{CO}$ 1718 cm$^{-1}$) is also formed.

Further evidence for the revised formulation of "trans-[RhCl(CO)$_2$PPh$_3$]" 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 AsPh$_3$ or PPh$_3$ 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 $\nu_{CO}$ at 2010 cm$^{-1}$ and 2090 cm$^{-1}$. Removing the solvent or simply bubbling nitrogen through the solution regenerates I ($\nu_{CO}$ 1980 cm$^{-1}$). This behaviour is identical to that observed in toluene (5) and attributed to the equilibrium:-

\[
2 \text{cis-[RhCl(CO)$_2$PPh$_3$]} \overset{-2\text{CO}}{\rightarrow} \overset{+2\text{CO}}{\rightarrow} \text{[RhCl(CO)(PPh$_3$)$_2$]}
\]

d) Belluco et al (1) support their formulation of the compound as a on the observed position of $\nu_{RhCl}$ (295 cm$^{-1}$), which is in agreement with a chloride trans to a tertiary arylphosphine in a rhodium(I) complex (7). However, since $\nu_{RhCl}$ is assigned at 284, 274 cm$^{-1}$ and 303 cm$^{-1}$ in the bridged chloro
compounds $[\text{RhCl}(\text{CO})_2]_2$ and $[\text{RhCl}(\text{PPh}_3)_2]_2$ respectively (7), it is reasonable to expect that $\nu\text{RhCl}$ will occur for the mixed dimer $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ in the region 285-295 cm$^{-1}$.

e) Finally, the product from the reaction of I with $\text{Cl}_2$ (previously formulated as the dicarbonyl monomer $[\text{RhCl}_3(\text{CO})_2(\text{PPh}_3)]$ ($\nu\text{CO} 2111 \text{ cm}^{-1}$) (2)), reacts with $\text{AsPh}_3$ without evolution of carbon monoxide, to give $[\text{RhCl}_3(\text{CO})(\text{PPh}_3)(\text{AsPh}_3)]$ ($\nu\text{CO} 2102 \text{ cm}^{-1}$). Therefore, it is suggested that the rhodium(III) dicarbonyl compounds, reported in reference 2 should be reformulated as the binuclear rhodium(III) monocarbonyl complexes $[\text{RhClXY}(\text{CO})(\text{PPh}_3)]_2$.

Acknowledgment

We thank Johnson-Matthey Ltd. for a loan of rhodium trichloride and the Science Research Council for an award (to DFS).

References

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

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Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

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

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Evidence is presented which suggests that the compounds trans-[RhX(CO)4PPh3] (Ia) (X = Cl, Br, I), made from [RhCl(CO)4] and triphenylphosphine (1 : 2 molar ratio), should be reformulated as the dimeric complexes trans-[RhCl2(CO)3PPh3] (Ib). Similar compounds with X = SCN, COOMe are also described. Detailed i.r. solution studies of the preparative reaction for X = Cl are interpreted in terms of the initial formation of a labile intermediate cis-[RhCl2(CO)3PPh3] (III) (probably 2), followed by partial decarbonylation and isolation of (Ib) and a small amount of cis-[RhCl2(CO)3PPh3] (Ic). The compounds (Ib) undergo bridge cleavage reactions with various Lewis bases, giving [RhX(CO)(PPh3)L] (L = PPh3, PMePh2, P(C6H5)3, AsPh3, SbPh3, C6H5N, Me2S, etc.). With SbPh3 the five-co-ordinate complex [RhCl2(CO)3(SbPh3)]2 is also formed. The H n.m.r. of [RhCl2(CO)3(PMePh2)] shows only a singlet for the methyl resonance, indicative of easy phosphine exchange in a strongly coupled PP complex. As expected, [RhCl2(CO)3(PMePh3)] readily undergoes oxidative addition reactions, giving [RhCl2Zn(CO)2(PMePh3)] (X = Cl2, Br2, I2). However, pure [RhCl2(CH2)4(CO)(PMePh3)] can be synthesised by reaction of the acyl-alkyl mixture [RhCl2(CH2)4(CO)PPh3] (IV) and [RhCl2(CO)(PMePh3)] (V) (previously formulated as the single compound [RhCl2(CO)(CO2PPh3)] with AsPh3. Similarly, [RhCl2(CO)3(AsPh3)] (L = PPh3 or SbPh3) can be obtained. These compounds readily undergo isomerisation to the more stable acyl isomer. Finally, [RhCl2(CO)(PPh3)(AsPh3)] can also be prepared by reaction of trans-[RhCl2(CO)3PPh3] (originally formulated as trans-[RhCl2(CO)2(PPh3)] with AsPh3.

Recently the reaction of [RhCl2(CO)3] with triphenylphosphine (1 : 2 molar ratio) was reported to give the complex trans-[RhCl2(CO)3PPh3] with more PPh3 gave the well-known 6 trans-[RhCl2(CO)3PPh3]. Thus, by reacting other ligands L (L = AsPh3, SbPh3, PMePh2, C6H5N, etc.) with (Ia), we hoped to synthesise the mixed ligand complexes [RhX(CO)(PPh3)L] (II), which may be useful catalytic precursors for olefin hydroformylation, etc. (cf. trans-[RhCl2(CO)3PPh3] 7). Although some mixed ligand complexes containing tertiary phosphines have been recently reported, e.g. [HRh(PPh3)3(AsPh3)] 8 and [RhCl3(Bu)3[P(OMe)3]9 the only reported complex of type II is [RhCl2(PBu)2] (P(C6H5)3) made by reacting [RhCl2(PBu)2] with P(C6H5)3 (ten-fold excess) in toluene at 25° for 24 h. 10 In this instance, 100% conversion to the mixed ligand complex is observed. However, in all other systems investigated by this method, 10 the result has been either mixtures of [Rh(X)ClO2], [Rh(X)ClO2] and [Rh(X)ClO2] or completely exchanged products (i.r. evidence).

RESULTS AND DISCUSSION

(a) Reaction of I with Arsenic-, Nitrogen-, and Sulphur-containing Ligands.—Reaction of trans-[RhCl2(CO)3PPh3] with excess of L = AsPh3, C6H5N, PPh3,

CH3,C6H5NH2, 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 [RhCl2(CO)3PPh3] (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 PPh3, L, and CO. The compounds are non-electrolytes and diamagnetic. T.L.C. of (II; L = AsPh3) clearly shows that the observed single spot has an Rf value intermediate between that of the bis-phosphine and -arsine compounds, proving that the compound is not an equimolar mixture of trans-[RhCl2(CO)3PPh3] and trans-[RhCl2(CO)3AsPh3]. In fact this compound can be recrystallised from dichloromethane-acetone and appears indefinitely stable both in solid and solution state. In contrast, (II; L = C6H5N) 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 trans to PPh3) is assigned on the basis of the similarity of the positions of both υ(CO) (ca. 1960 cm⁻¹) and υ(RhCl) (ca. 310 cm⁻¹) to those found for trans-[RhCl2(CO)3PPh3]. 11, 12

As expected, [RhCl2(CO)3PPh3(AsPh3)] readily undergoes oxidative addition reactions, giving [RhCl2Zn(CO)2(PMePh3)] (X = Cl2, Br2, I2). For X = Cl2, I2, analytical and mass spectral data indicate the presence of some Cl2 solvate (ca. 0.25 mol/oxide). 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 AsP₃. After 4 h under reflux, a deeper brown solid is isolated with very weak bands at 2069, 1980 cm⁻¹ and a strong, broad band at 1712 cm⁻¹. This dark brown solid analyses closely for \( \text{[RhCl(CO)₃PPh₃]AsPPh₃} \cdot 0.5\text{CHCl₃} \) (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 ¹³ for the reaction of \( \text{trans-}[\text{RhXCO(PPh₃)}_2] \) with \( \text{CH₃I} \), viz. rapid oxidative addition of \( \text{CH₃I} \) giving initially \( \text{[RhXI(CH₃)CO(PPh₃)}_2] \), followed by a slower isomerisation to the acetyl complex \( \text{[RhXI(COCH₃)(PPh₃)}_2] \). Neither in this work nor in that reported by Wilkinson et al.¹³ has it been possible to separate the two isomers when prepared by this method (but see section f).

(b) Reformulation of ' \( \text{trans-}[\text{RhCl(CO)₃PPh₃}] \) '— Rather surprisingly, the reactions of ' \( \text{trans-}[\text{RhCl(CO)}_₃\text{PPh₃}] \) ' with \( \text{L} \) 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 ' \( \text{trans-}[\text{RhCl(CO)}_₂\text{PPh₃}] \) ' should be reformulated as the binuclear complex ' \( \text{trans-}[\text{RhCl(CO)}_₂\text{PPh₃}] \) '. (Ib, X = Cl).

Uguagliati et al.² support their formulation of the compound as (Ia) on the observed position of \( v(\text{RhCl}) \) (295 cm⁻¹), which is in agreement with that expected for a chloride atom \( trans \) to a tertiary arylphosphine in a rhodium(III) complex.¹² However, since \( v(\text{RhCl}) \) is assigned at 284, 274, and 303 cm⁻¹ in the bridged chloro compounds, \( \text{[RhCl(CO)}_₂\text{PPh₃}] \) and \( \text{[RhCl(PPh₃)}_₁ \) respectively,¹² it is reasonable to expect that \( \text{[RhCl(CO)}_₂\text{PPh₃}] \) will occur

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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 $\text{trans-}[\text{RhCl}([\text{CO}])_{2}(\text{PMe}_3)_2]$, where the analytical and molecular weight data unequivocally support the dimeric formulation. (Ib) ($X = \text{Cl}$) has also been recently prepared by reaction of $[\text{C}_6\text{H}_5\text{Rh}([\text{CO}])\text{PPh}_3]_2$ with HCl.\textsuperscript{16}

The complexes ' $\text{trans-}[\text{RhX}([\text{CO}])_2\text{PPh}_3]$ ' made by metathetical reactions on (Ia)\textsuperscript{9} can also be reformulated as the dimers (Ib) ($X = \text{Br}^{3}$, $I^{3}$, SCN, OCOME) (see Table). Examination of the i.r. spectrum of the thio cyanato-complex shows $\nu_{\text{CO}}$ 2135 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 complex has i.r. bands at 1572 and 1439 cm$^{-1}$, attributed to asymmetric ($\nu_a$) and symmetric ($\nu_s$) carboxylate stretching frequencies respectively [cf. $\nu_{\text{CO}}$ (OCOME) Me$_2$ 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 AsPh$_3$, etc., giving monomeric mixed ligand complexes $\text{[RhXCO(PPh)]_2}$ (Table). Examination of the i.r. spectrum of $[\text{Rh(NCS)}([\text{CO}])\text{PPh}_3](\text{AsPh}_3)$ ($\nu_{\text{CO}}$ 2064, $\nu_{\text{As}}$ 840 cm$^{-1}$) indicates that the thio cyanato 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 $[\text{Rh(OCOME)}([\text{CO}])\text{PPh}_3]\text{[AsPh}_3]$ has $\nu_{\text{CO}}$ 1606, $\nu_{\text{As}}$ 1323, $\Delta$ 283 cm$^{-1}$, indicative of unsymmetrical co-ordination and $\nu_{\text{CO}}$ (OCOME) PPh$_3$ made from $[\text{Rh(OCOME)}\text{PPh}_3]$ and excess PPh$_3$ with $\nu_{\text{CO}}$ 1610, $\nu_{\text{As}}$ 1325, $\Delta$ 285 cm$^{-1}$.\textsuperscript{8}

The compounds $\text{[RhXCO(PPh)]_2}(\text{AsPh}_3)$ can also be synthesised directly from $[\text{RhCl}([\text{CO}])\text{PPh}_3](\text{AsPh}_3)$ and LiX. Pure products are obtained with LiBr and LiSCN provided that short reaction times (5–20 min) are employed. Longer reaction times lead to contamination by rhodium(iii) species ($\nu_{\text{CO}} > 2000$ cm$^{-1}$).\textsuperscript{11} With 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 2024 cm$^{-1}$ (benzene) in addition to the strong, broad absorption at 1890 cm$^{-1}$. The compound giving rise to these weak absorptions can be removed by reflushing compound (Ib) in benzene for ca. 30 min, after which pure $\text{trans-}[\text{RhCl}([\text{CO}])\text{PPh}_3]_2$ ($\nu_{\text{CO}}$ 1890 cm$^{-1}$) is recovered (Deganello et al.\textsuperscript{2} note that their product ' Ia ' readily disproportionate to $\text{trans}[\text{RhCl}([\text{CO}])\text{PPh}_3]_2$ ($\nu_{\text{CO}}$ 1960 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 ' Ia ' at room temperature and has been assigned the structure ' cis- $\text{[RhCl}([\text{CO}])\text{PPh}_3]$ ' (IIIa).\textsuperscript{3} Poilblanc and Gallay\textsuperscript{15} observed similar behaviour, on carbonylation of (Ib) in toluene, to that reported here (i.e. two $\nu_{\text{CO}}$ 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 $[\text{RhCl}([\text{CO}])_2\text{PPh}_3]$ (1:2 molar ratio) were mixed. Attempts to isolate this species resulted in CO evolution (one CO/Rh) and formation of $\text{trans-}[\text{RhCl}([\text{CO}])\text{PPh}_3]_2$. We have also followed the i.r. changes of this reaction in benzene and confirm that the first step is the loss of $[\text{RhCl}([\text{CO}])_2\text{PPh}_3]$ carbonyl bands and the growth of two strong bands at 2090 and 2008 cm$^{-1}$. Then, concentration 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 1890 cm$^{-1}$.

Poilblanc et al.\textsuperscript{15} interpreted their observations in terms of equation (1) with the same postulated intermediate as Deganello et al.\textsuperscript{3} cis- $\text{[RhCl}([\text{CO}])_2\text{PPh}_3]$ (IIIa).

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

However, this infers that PPh$_3$ initially reacts with $[\text{RhCl}([\text{CO}])_2\text{PPh}_3]$ 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 PPh$_3$, (Ib) is cleaved giving $\text{trans-}[\text{RhCl}([\text{CO}])\text{PPh}_3]_2$. 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 cis- $\text{[RhCl}([\text{CO}])_2\text{PPh}_3]$ (IIb), probably with trans-addition of PPh$_3$ to minimise steric

\textsuperscript{13} For detailed references, see M. A. Jennings and A. Wojcicki, 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(OOCMe)CO(PPh₃)]₂ gives an orange solution with v(CO) 2094 and 2009; v(CO) 1570, ν₁ 1435, Δ 135 cm⁻¹, indicative of symmetrical acetate co-ordination, as expected for (IIIb) and not unidentate co-ordination as expected for (IIIa).

This could indicate either that v(CO) and v(RhCl) are the same for [RhCl(CO)(PPh₃)(AsPh₃)]₂ and (IIIb) and readily isomerised to (Ib) by warming in benzene. Although the i.r. spectrum is also consistent with the other cis-dicarbonyl isomer (Id) [and would possibly be more compatible with the observed v(CO) values than (Ic)] the observation that recarbonylation of a mixture of (Ib) and another dicarbonyl compound gives only the single product (IIIb) suggests that we can discount the formulation (Id). Reaction of [RhCl(CO)PPh₃]₂ 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)PPh₃]₂ with triphenylstibine (1:2 molar ratio) in benzene gives an orange solution which, on concentration and pentane addition, gives the yellow solid [RhCl(CO)(PPh₃)(SbPh₃)]²⁺. In addition, the filtrate contains another rhodium complex; the red-brown five-co-ordinate [RhCl(CO)(PPh₃)₂(SbPh₃)]²⁺. A better method of making this compound is to react benzene solutions of [RhCl(CO)PPh₃]²⁺, [RhCl(CO)(PPh₃)(AsPh₃)], or [RhCl(CO)(PPh₃)₂(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)₃] and some free PPh₃. Furthermore, in the absence of excess SbPh₃, [RhCl(CO)(PPh₃)(SbPh₃)₂] in benzene readily dissociates to [RhCl(CO)(PPh₃)(SbPh₃)] and SbPh₃ (cf. the behaviour of [RhCl(CO)(SbPh₃)₃]). This suggests that in solution the following complexes are present in equilibrium (equation (2)):

$$3[RhCl(CO)(PPh₃)(SbPh₃)] + 3SbPh₃$$

$$3[RhCl(CO)(PPh₃)(SbPh₃)] ⇌ [RhCl(CO)(PPh₃)₂] + 2RhCl(CO)(SbPh₃)₃ + PPh₃$$ (2)

[RhCl(CO)(SbPh₃)₃] can be prepared directly from [RhCl(CO)PPh₃] and excess SbPh₃ in benzene and also from trans-[RhCl(CO)AsPh₃]₂ and excess SbPh₃. The most interesting feature of this compound is the low position of v(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. The latter might provide an explanation for the stability of [RhCl(CO)\( \text{PPh}_3 \)] in benzene compared to dichloromethane. Although a more likely explanation is the low solubility of trans-[RhCl(CO)(\text{PPh}_3)\_2] in CH\(_2\)Cl\(_2\) (as compared to C\(_6\)H\(_6\)) which results in a shift of the equilibrium to the right hand side of equation (2).

Reaction of [RhCl(CO)(\text{SbPh}_3)\_2] with excess AsPh\(_3\) regenerates trans-[RhCl(CO)(AsPh\(_3\))] and trans-[RhCl(CO)(\text{SbPh}_3)\_2] gives [RhCl(CO)(\text{PPh}_3)(\text{AsPh}_3)]. This and similar reactions of [RhCl(CO)(\text{SbPh}_3)\_2] and [RhCl(CO)(\text{PPh}_3)\_2] are two members of a series containing five-co-ordinate rhodium(i) and triphenylstibine. A third is the cation [RhCl(CO)(\text{SbPh}_3)]\(^+\) recently prepared by Hieber et al. Reaction of trans-[RhCl(CO)(\text{PPh}_3)] with excess triphenylstibine gives an orange-yellow, soluble, compound of the unknown (RhCl(CO)(\text{PPh}_3)(\text{SbPh}_3)] complex but removal of solvent gives only trans-[RhCl(CO)(\text{PPh}_3)]. This and earlier work clearly indicates that, as SbPh\(_3\) groups are replaced by PPh\(_3\) and AsPh\(_3\), the stability of the five-co-ordinate rhodium(i) complexes decrease. Similarly, Westland concluded that palladium(ii) and platinum(ii) compounds of the kind [RhCl(CO)(\text{PPh}_3)] and [RhCl(CO)(\text{SbPh}_3)] are likely to exist in the solid state. However, the reasons why antimony donor ligands promote five-co-ordination in low-spin d\(_8\) complexes is not presently obvious although, doubtless, both steric and electronic factors play an important role, e.g., the longer rhodium-antimony bond distances allow more SbPh\(_3\) molecules to be packed around the rhodium atom.

All these results suggest that the only remaining six-co-ordinate rhodium(i) complex containing triphenylstibine [RhCl\(_2\)(\text{H}_2\text{O})\_2\text{CO} \text{(SbPh}_3\)] (C\(_6\)H\(_5\)O\(^-\) = acetylacetonate ion) is probably the five-co-ordinate [RhCl\(_2\)(\text{H}_2\text{O})\_2\text{CO} \text{(SbPh}_3\)] complex. The quoted analytical figures C, 54-5, H, 4-0, O, 3-7%, are intermediate between those required for [RhCl\(_2\)(\text{H}_2\text{O})\_2\text{CO} \text{(SbPh}_3\)] (C, 55-9, H, 4-0; O, 3-2; Sb 28-4%) and [RhCl\(_2\)(\text{H}_2\text{O})\_2\text{CO} \text{(SbPh}_3\)] (C, 53-5, H, 4-0; O, 5-1, Sb 26-0%). An antimony analysis is required to distinguish between these possibilities but the rarity of six-co-ordinate rhodium(i) complexes and the close similarity of the compound to [RhCl(CO)(\text{SbPh}_3)] and [RhCl(CO)(\text{PPh}_3)(\text{SbPh}_3)] strongly favours the five-co-ordinate bis-stibination formalism.

(d) Reaction of Complex (Ib) with Tertiary Phosphines. 
---Treatment of [RhCl(CO)(\text{PPh}_3)] with methylidanaphosphine or tricyclohexylphosphine (1:2 molar ratio) in acetone, followed by solvent removal and addition of ether gives the products [RhCl(CO)(\text{PPh}_3)L\_2] characterised by analysis, m.p., (Table), and i.r. spectra. The \(^1\)H n.m.r. spectra (methyl region) of [RhCl(CO)(\text{PPh}_3)(\text{PMePh}_3)] in deuteriochloroform shows only a single resonance (\(\delta 7.86\)). Similarly, examination of the n.m.r. spectrum of an equimolar mixture of trans-[RhClCO(PMePh\(_3\))]\_2 and trans-[RhClCO(PPh\(_3\))]\_2 (in CDC\(_3\)) shows a single methyl peak (\(\delta 7.82\)). In contrast, trans-[RhCl(CO)(\text{PMePh}_3)]\_2 in CDC\(_3\) shows the expected doublet of triplets \(\delta 7.84\) (J\(_{\text{Rh-Ph}}\) 1-0 Hz) centred at \(\delta 7.84\). Addition of trans-[RhCl(CO)(\text{PPh}_3)]\_2 to this solution gives a single resonance (\(\delta 7.82\)) at a minimum ratio (PMePh\(_3\) to PPh\(_3\)) of ca. 10:1. The same effect is observed when the n.m.r. spectrum of trans-[RhCl(CO)(\text{PMePh}_3)]\_2 is run in CS\(_2\).

The only explanation which appears applicable in this instance to explain the loss of P-H coupling is that given by Fackler et al. to explain the \(^1\)H n.m.r. spectra of compounds such as cis-[PdCl\(_2\)PMePh\(_3\)] and trans-[RhCl(CO)(PMePh\(_3\))]\_2, 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 CDC\(_3\) solution of [RhCl(CO)(\text{PPh}_3)(\text{PMePh}_3)] to \(-60^\circ\) 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 \(80^\circ\) 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)(PMePh\(_3\))]\_2 comes from either partial dissociation of the added [RhCl(CO)(\text{PPh}_3)] and/or some displacement of PMePh\(_3\) by PPh\(_3\) and consequent scrambling of phosphine groups in these labile, square-planar d\(_8\) compounds. The singlet found for trans-[RhCl(CO)(\text{PMePh}_3)] in CS\(_2\) could be the result of enhanced dissociation in this solvent compared to CDC\(_3\) due to the ready formation of 1:1 adducts between tertiary phosphines and CS\(_2\). For [RhCl(CO)(\text{PPh}_3)(\text{PMePh}_3)] in solution, the existence of an equilibrium of the type given by equation 3 would account for easy

\[
2[\text{RhCl(CO)(PPh}_3)] = \text{trans}-[\text{RhClCO(PMePh}_3)] + \text{trans}-[\text{RhClCO(PPh}_3)]
\]  

phosphine exchange processes and consequent P-H decoupling. There is more convincing evidence for the existence of this equilibrium for compounds [RhCl(CO)(\text{PPh}_3)]\_2. Reaction of [RhCl(CO)(\text{PPh}_3)] with tertiary phosphines (L = PMePh\(_3\) or PPh\(_2\)Ph) gives oils on solvent removal which on trituration with ethers or pentane gives a precipitate of trans-[RhCl(CO)(\text{PPh}_3)] and evidence in solution for [RhCl(CO)(\text{PPh}_3)]\_2. Similar results are found when using excess AsEt\(_3\) and Me\(_2\)SO. However, we suggest that for all the [RhCl(CO)(\text{PPh}_3)]\_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

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pentane, etc., gives pure samples of $[\text{RhCl}(\text{CO})\text{PPh}_3\text{L}]$ ($L = \text{AsPh}_3$ (t.i.c.), PMePh$_2$ (t.i.c.), SbPh$_3$, etc.) since these compounds are expected to be of similar low solubility in these solvents to that of trans-$[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$; postulated to be present in only low concentration. However, when L is a more alkylated phosphine, arsine, or an alkyl sulphonide, the mixed compounds (and $[\text{RhCl}(\text{CO})_{2}\text{L}_2]$) will be of higher solubility in pentane, etc., than trans-$[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$. 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 $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ in various solvents. As discussed in detail earlier, benzene, toluene and chloroform (in which $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ is soluble) contain a complex with two $\nu_{\text{CO}} > 2000 \text{ cm}^{-1}$, believed to be cis-$[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ (III) (with $n$ probably 2). However, carbonylation of a methanol suspension (or concentrated dichloromethane solution) of (Ib) gives a precipitate of trans-$[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ and $[\text{RhCl}(\text{CO})_{2}\text{L}_2]$ can be isolated from the solution, i.e., trans-$[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ is of much lower solubility in these solvents than cis-$[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$. Note that equation (3) predicts that the other product should be $[\text{RhCl}(\text{CO})_{2}X]$ but it is not inconceivable that this compound (at present unknown) might readily lose carbon monoxide and then dimerise (cf. $2[\text{RhCl}(\text{CO})_{2}\text{PPh}_3] \rightarrow [\text{RhCl}(\text{CO})_{2}\text{L}_2] + 2\text{PPh}_3$).

(c) Oxidative Addition Reactions of Complex (Ib).—The reformation of ‘trans-$[\text{RhX}(\text{CO})_{2}\text{PPh}_3]$’ as trans-$[\text{RhX}(\text{CO})_{2}\text{PPh}_3]$ also implies that the reported oxidative addition products $[\text{RhXYZ}(\text{CO})_{2}\text{PPh}_3]$ are incorrect. This is readily verified by an oxygen analysis on $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ (required 6:1; found 3:3%), which suggests that the compound should be reformulated as trans-$[\text{RhClX}(\text{CO})_{2}\text{PPh}_3]$ ($X = \text{Cl}, \text{PhI}, \text{CICOEt}, \text{etc.}$) are incorrect. This is readily verified by an oxygen analysis on $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ (required 6:1; found 3:3%), which suggests that the compound should be reformulated as trans-$[\text{RhClX}(\text{CO})_{2}\text{PPh}_3]$ ($X = \text{Cl}$, $Y = \text{Cl}$; required 0, 3:3%). The position of $\nu_{\text{RhCl}}$ 354 and 340 cm$^{-1}$ suggests trans-addition of the halogen. This compound is too insoluble for a molecular weight determination but it reacts with excess triphenylarsine (without CO evolution) giving $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3(\text{AsPh}_3)]$: with SbPh$_3$ a product close in analysis to $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3(\text{SbPh}_3)]$ but formed but partial reduction to $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3(\text{SbPh}_3)]$ also occurs. Triphenylarsine gives mainly trans-$[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$. Rather surprisingly, extended reaction with pyridine gives a sample of 1,2,6-$[\text{RhCl}(\text{C}_9\text{H}_8\text{N}_3)]$ (the isomeric form was confirmed by comparison with the i.r. spectrum of an authentic sample).

It is therefore suggested that with the exception of the methyl iodide reaction, the other oxidative addition products reported in ref. 3 should be reformulated as the dimeric compound (IV) (or isomers of this compound).

(f) Reaction of Complex (Ib) with Methyl Iodide.—Deganello et al.$^3$ report that the reaction of methyl iodide with $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ gives $[\text{RhCl}(\text{CO})_{2}\text{Me}_2\text{PPh}_3]$, probably via a labile intermediate $[\text{RhCl}(\text{C}_9\text{H}_8\text{Me}_2)(\text{CO})_{2}\text{PPh}_3]$. 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, $X = \text{Cl}$) (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.$^{12}$ we suggest that the terminal carbonyl stretch arises from compound (IV) ($YZ = \text{CH}_3\text{I}$, $X = \text{Cl}$), 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.$^4$, where rapid formation of an intermediate followed by a second slower rate determining step was observed.

The reaction of this mixture of isomers with an excess of L ($L = \text{AsPh}_3$, PPh$_3$, SbPh$_3$) in chloroform or dichloromethane gives, on immediate precipitation with pentane or ether, orange-yellow crystalline compounds, which are pure for $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ (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., $L = \text{AsPh}_3$, 2065s, 2056m, and 1980w cm$^{-1}$ (Nujol)); 2078s and 1980m cm$^{-1}$ (CHCl$_3$)). 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. Heck$^{32}$ reports the preparation of $[\text{RhCl}(\text{CH}_3\text{CO})(\text{PBu}_3)_2]$ which absorbs CO at 1 atm and 25$^\circ$ to give the acyl compound $[\text{RhCl}(\text{CO})(\text{C}_9\text{H}_8\text{Me}_2)_2]$ and Wilkinson et al.$^{33}$ by reaction of acetyl chloride with $[\text{RhCl}(\text{CO})_{2}\text{PPh}_3]$ at 6$,^\circ$ have isolated the compound $[\text{RhCl}(\text{CH}_3\text{CO})(\text{CO})_{2}\text{PPh}_3]$ in solution, this rapidly isomerises to $[\text{RhCl}(\text{CO})(\text{CO})_{2}\text{PPh}_3]$.

Graham et al.$^{34}$ also report the preparation of $[(\text{C}_9\text{H}_8\text{H}_2\text{RhCl}(\text{CH}_3\text{CO})(\text{PMe}_2\text{Ph}))\text{PPh}_3]$ by treatment of the acyl complex $[(\text{C}_9\text{H}_8\text{H}_2\text{RhBr}(\text{Ac})(\text{PMe}_2\text{Ph}))$ with NaPPh$_3$. The chloroiodo-compounds reported here are reasonably

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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\(_3\)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 [RhCl(CO)-(PPh\(_3\))(AsPh\(_3\))].

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

**CONCLUSION**

The reaction of [RhCl(CO)]\(_2\) with PPh\(_3\), originally reported by Vallarino,\(^6\) 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 mull 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.

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%) (vCO 1962; νRhCl 304 cm⁻¹). Attempts to recrystallise or prolonged standing in chloroform led to extensive decomposition. Bromocarbonyl(triphenylphosphine)pyridine)rhodium(t) (vCO 1966 cm⁻¹) was similarly prepared from the bromo-dimer. Chlorocarbonyl(triphenylphosphine)(p-toluidine)rhodium(t) (vCO 1980; νRhCl 301 cm⁻¹) and chlorocarbonyl(triphenylphosphine)(dimethyl sulphone)rhodium(t) (vCO 1965; νRhCl 310 cm⁻¹) were prepared in analogous manner to [RhCl(CO)(PPh₃)₂] and [RhCl(CO)PF₃] (vCO 2110, 2090 cm⁻¹) using [RhCl(CO)PPh₃]₂ and excess ethereal filtrate containing triphenylphosphine. An orange-yellow precipitate and an orange solution. The latter compound slowly loses dimethyl sulphone on exposure to air. Chlorocarbonyl(triphenylphosphine)rhodium(t)—[RhCl(CO)PPh₃]₂ (0·30 g, 0·55 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 solvent rapidly gave an orange-yellow solid which was washed with ether and dried in vacuo (0·80 g, 90%) (vRhCl 317 cm⁻¹). The same compound can be made by high yield in reaction of benzene solutions of either [RhCl(CO)PF₃]₂, [RhCl(CO)PF₃AsPh₃] or [RhCl(CO)PF₃(CH₂N)] with a four-fold excess of SbPh₃. Removal of solvent and addition of SbPh₃, gave the reddish-brown crystalline solid chlorocarbonyl(triphenylphosphine)bis(triphenylstibine)rhodium(t) (vCO 2065; νRhCl 317 cm⁻¹). The same can also be prepared from the reaction of trans-[RhCl(CO)(PPh₃)₂] and excess SbPh₃ in benzene (Found: C, 54.8; H, 3.7; Cl, 2.5; Sb, 31.2. Calc. for C₃₇H₃₀Cl₃Sb₃Rh: C, 56.2; H, 3.8; Cl, 2.7; Sb, 31.2. The same compound can also be prepared from the reaction of trans-[RhCl(CO)(PPh₃)₂] and excess SbPh₃ in benzene (Found: C, 54.8; H, 3.7; Cl, 2.5; Sb, 31.2. Calc. for C₃₇H₃₀Cl₃Sb₃Rh: C, 56.2; H, 3.8; Cl, 2.7; Sb, 31.2.

Chlorocarbonyl(triphenylphosphine)(methylidiphenylphosphine)rhodium(t)—[RhCl(CO)PPh₃]₂ (0·10 g, 0·11 mmol) was dissolved in dry acetone (15 ml) and methylidiphenylphosphine (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 (vCO 1963; νRhCl 308 cm⁻¹). T.l.c. showed a single spot with an Rₜ value slightly larger than trans-[RhCl(CO)PF₃]₂. Similarly, chlorocarbonyl(triphenylphosphine)(tricyclohexylphosphine)rhodium(t) (vCO 1950; νRhCl 310 cm⁻¹) was made in chloroform solution, precipitating the product with light petroleum (b.p. 60—80°).

Attempts to prepare [RhCl(CO)PF₃]₂ (L = PMe₃Ph, PEt₂Ph) by the same method gave only a precipitate of trans-[RhCl(CO)(PPh₃)₂] and yellow ethereal solutions containing [RhCl(CO)LC₃] (confirmed by comparison with authentic samples made by literature methods). Similarly, only trans-[RhCl(CO)(PPh₃)₂] was isolated from the reaction of [RhCl(CO)PPh₃]₂ with excess AsEt₃ or Me₃As. Carbynation of [RhCl(CO)PPh₃]₂—(a) In benzene, toluene, or chloroform. Reaction of the orange benzene solution with CO at room temperature gives an immediate lemon-yellow solution (vCO 2000 and 2008 cm⁻¹) which on removal of solvent in vacuo or purging with nitrogen reverts to [RhCl(CO)PPh₃]₂ (vCO 1980s, 2000 cm⁻¹, 2032 cm⁻¹). (b) In methanol suspension. [RhCl(CO)PPh₃]₂ 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)₂] (i.r. spectrum and analysis) (Found: C, 64.7; H, 4.4). Calc. for C₇H₈O₃P: C, 64.3; H, 4.3. Removal of solvent from the methanol 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)AsPh₃]₂. The same behaviour was observed in concentrated dichloromethane solution.

Rhodium(III) Compounds

trans-Di-μ-chloro-tetraiodocarbonylbis(triphenylphosphine)dirhodium(III).—Dry chlorine was bubbled through a suspension of trans-[RhCl(CO)PPh₃]₂ in dichloromethane for ca. 5 min. The solid dissolved completely giving an orange-yellow solution which on concentration in vacuo and addition of pentane precipitated the yellow product which was washed with ether and dried in vacuo (0·80 g, 90%) (vRhCl 317 cm⁻¹). The same compound can be made by high yield in the reaction of benzene solutions of either [RhCl(CO)PF₃]₂, [RhCl(CO)PF₃AsPh₃] or [RhCl(CO)PF₃(CH₂N)] with a four-fold excess of SbPh₃. Removal of solvent and addition of SbPh₃ gave a reddish-brown crystalline solid chlorocarbonyl(triphenylphosphine)bis(triphenylstibine)rhodium(t) (vCO 2065; νRhCl 317 cm⁻¹). The same compound can also be prepared from the reaction of [RhCl(CO)(PPh₃)₂] and excess SbPh₃, in benzene (Found: C, 54.8; H, 3.7; Cl, 2.5; Sb, 31.2. Calc. for C₃₇H₃₀Cl₃Sb₃Rh: C, 56.2; H, 3.8; Cl, 2.7; Sb, 31.2.

Chlorocarbonyl(triphenylphosphine)(methylidiphenylphosphine)rhodium(t)—[RhCl(CO)PPh₃]₂ (0·10 g, 0·11 mmol) was dissolved in dry acetone (15 ml) and methylidiphenylphosphine (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 (vCO 1963; νRhCl 308 cm⁻¹). T.l.c. showed a single spot with an Rₜ value slightly larger than trans-[RhCl(CO)PF₃]₂. Similarly, chlorocarbonyl(triphenylphosphine)(tricyclohexylphosphine)rhodium(t) (vCO 1950; νRhCl 310 cm⁻¹) was made in chloroform solution, precipitating the product with light petroleum (b.p. 60—80°). Attempt to prepare [RhCl(CO)PPh₃]₂ (L = PMe₃Ph, PPh₃) by the same method gave only a precipitate of trans-[RhCl(CO)(PPh₃)₂] and yellow ethereal solutions containing [RhCl(CO)LC₃] (confirmed by comparison with authentic samples made by literature methods). Similarly, only trans-[RhCl(CO)(PPh₃)₂] was isolated from the reaction of [RhCl(CO)PPh₃]₂ with excess AsEt₃ or Me₃As. Carbynation of [RhCl(CO)PPh₃]₂—(a) In benzene, toluene, or chloroform. Reaction of the orange benzene solution with CO at room temperature gives an immediate lemon-yellow solution (vCO 2000 and 2008 cm⁻¹) which on removal of solvent in vacuo or purging with nitrogen reverts to [RhCl(CO)PPh₃]₂ (vCO 1980s, 2000 cm⁻¹, 2032 cm⁻¹). (b) In methanol suspension. [RhCl(CO)PPh₃]₂ 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)₂] (i.r. spectrum and analysis) (Found: C, 64.7; H, 4.4). Calc. for C₇H₈O₃P: C, 64.3; H, 4.3. Removal of solvent from the methanol 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)AsPh₃]₂. The same behaviour was observed in concentrated dichloromethane solution.
acetyl form. A small amount of rhodium(i) complex (ν₀ 1980 cm⁻¹) is also present.

Reaction of the isomeric mixture [RhClII(CH₃)(CO)PPh₃]₂ and [RhClII(COCH₃)PPh₃]₂ with excess AsPh₃ in chloroform or dichloromethane followed by immediate precipitation with pentane gave the pure orange-yellow product [RhClII(CH₃)(CO)(PPh₃)(AsPh₃)] (ν₀ 2065 cm⁻¹). Similarly, reaction with L (L = PPh₃ or SbPh₃) gave [RhClII(CH₃)(CO)-PPh₃L]. In solution, these rapidly isomerise to the corresponding acyl isomer.

Trichlorotris(pyridine)rhodium(III).— [RhCl₃(CO)PPh₃]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°) 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 C₁₅H₁₆Cl₃N₃Rh: 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-[RhCl₃(C₅H₅N)]₃ indicates the latter has been formed.

We thank Johnson Matthey Ltd., for a generous loan of rhodium trichloride trihydrate, the S.R.C. for an award (to D. F. S.), and Drs. R. D. Gillard, D. Forster, R. J. Haines, and J. F. Nixon for helpful discussions.

[2/940 Received, 27th April, 1972]
NEW RUTHENIUM (III) AND (II) COMPLEXES CONTAINING TRIPHENYL-ARSINE, -PHOSPHINE AND OTHER LIGANDS

E.S. Switkes, L. Ruiz-Ramirez, T.A. Stephenson and (in part) J. Sinclair

Department of Chemistry, University of Edinburgh, Edinburgh, Scotland

(Received 21 March 1972)

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 Ru₅Cl₁₂²⁻ (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)

Ru₃(MPh₃)₂S (M = P, As; S = CH₃OH (1, 6), CH₃NO₂ (7)), the anions trans- [RuX₄L₂]⁻ (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 \( \text{RuX}_3 \left( \text{MPh}_3 \right)_2 \text{L} \) \( \text{L} = \text{RCN, (R = Me, Ph, PhCH}_2, \text{CH}_2 \text{= CH)} \), acetone \( \text{(1), T.H.F, Me}_2 \text{SO, CS}_2 \). The infrared spectra (ir.) of all the nitrile compounds contain a very weak \( \nu \text{CN} \) at ca. \( 2300 \text{ cm}^{-1} \), \( 50 \text{ cm}^{-1} \) higher than in the free ligands which suggest that bonding occurs through the nitrogen \( \text{(9)} \). The dimethylsulphoxide complexes have strong absorptions in the ir. spectra between \( 900-1000 \text{ cm}^{-1} \) suggestive of an O-bonded sulphoxide group (cf. \( \text{RuCl}_3 \left( \text{Me}_2 \text{SO} \right)_3 \) \( \text{(4)} \) ). The ir. of the \( \text{CS}_2 \) complexes contain a broad band at ca. \( 1510 \text{ cm}^{-1} \) indicating the presence of a linearly bonded \( \text{CS}_2 \) group. No bands due to thiocarbonyl \( \text{(ca. 1280-1330 cm}^{-1} \) or to \( \pi-\text{CS}_2 \) (ca. \( 1020 \text{ cm}^{-1} \) or \( 1120 \text{ cm}^{-1} \) linkages are present \( \text{(10)} \) and attempted recrystallisation of these complexes from benzene results in loss of \( \text{CS}_2 \) and formation of \( \text{RuX}_3 \left( \text{MPh}_3 \right)_2 \). Examination of the far ir. spectra of these compounds \( 400-200 \text{ cm}^{-1} \) indicates a similar configuration to that of the starting materials A and configuration I with trans halide \( (\nu \text{RuCl 347-299 cm}^{-1}) \) \( \text{(11)} \) 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], T4.60 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)₂CH₃CN (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 RuX\(_2\)(MPh\(_3\))\(_2\)C\(_7\)H\(_8\) are readily obtained. For M = P, the same compounds can be synthesised from RuX\(_2\)(PPh\(_3\))\(_3\) or \(\text{C}_7\text{H}_8\) (13). With carbon monoxide, reaction with RuCl\(_3\)(AsPh\(_3\))\(_2\)CH\(_3\)OH at room temperature gives trans-RuCl\(_2\)(CO)\(_2\)(AsPh\(_3\))\(_2\) \((\nu_{\text{CO}} 1993 \text{ cm}^{-1} [\text{CH}_2\text{Cl}_2])\). Comparison with earlier triphenylphosphine work (1, 14) suggests configuration IV.

Recrystallisation from hot benzene gives the cis isomer \((\nu_{\text{CO}} 2061 \text{ and } 1999 \text{ cm}^{-1})\) (1) (configuration V). Recrystallisation from cold CH\(_2\text{Cl}_2\)/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 (\(\nu_{\text{CO}}\) 2038, 1983, 1967sh 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 (6). With benzyl cyanide and \(M = P\), reaction under mild conditions gives RuX\(_3\)(PPh\(_3\))\(_2\)PhCH\(_2\)CN. However, under more vigorous 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 (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)\(_2\)]\(^+\) 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.

Acknowledgment

We thank Johnson-Matthey Ltd for a loan of ruthenium trichloride, the National Institutes of Health (ES) and the National A. University of Mexico (LR) for fellowships and the Department of Inorganic Chemistry, University of Newcastle for use of the Faraday balance.
References

# 10
Metal Compounds Containing Six-Electron and Seven-Electron Organic Ligands
T. A. STEPHENSON
University of Edinburgh

## 10.1 INTRODUCTION

## 10.2 ARENE–METALCARBONYL COMPLEXES

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## 10.3 CYCLOHEPTATRIENE AND CYCLOHEPTATRIENYL COMPLEXES

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10.5 MIXED SANDWICH COMPLEXES

10.5.1 Titanium, zirconium and hafnium
10.5.2 Vanadium, niobium and tantalum
10.5.3 Chromium, molybdenum and tungsten
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10.6 COMPLEXES OF LARGER RING TRIENES

10.6.1 Cyclo-octatriene complexes
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10.7 MISCELLANEOUS COMPLEXES

10.7.1 Cyclo-octatetraene complexes
10.7.2 1, 6-Methanocylodecapentaenechromiumtricarbonyl
10.7.3 Azulenium cation complexes

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 Winkler, ‘Metal π-Complexes’ Volume 1 by Fischer and Werner, ‘Olefin Complexes of the Transition Metals’ by Quinn and Tsai, ‘Organometallic Compounds’ Volume 2 by M. L. H. Green and articles by D. A. White entitled ‘Electrophilic and Nucleophilic attack on Organo-transition Metal Compounds’ and by Wheatley called ‘π-Complexes of Transition Metals with Aromatic Systems’.

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 \((C_5H_5)_2Ti(CO)_2\), 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 \([\text{arene}]V(CO)_4]^+\) cations (1) (arene = benzene, toluene, methyl-substituted benzenes etc.), obtained by direct reaction between the arene and \(V(CO)_6\) and isolated as the hexacarbonyl vanadate salt \([\text{arene}][V(CO)_6]\). Attempts to obtain the still unknown \((C_6H_6)V(CO)_3\) complex by reduction of this cation with NaBH₄, gave, instead the \(\pi\)-cyclohexadienyl derivative \([C_6H_7V(CO)_4]^+\). Similar methyl-substituted \(\pi\)-cyclohexadienyl derivatives were obtained by reduction of the methyl-substituted arene—vanadium compounds \([\text{Me}_nC_6H_{6-n}]V(CO)_4]^+\). 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 NaBH₄: Section 10.2.4). However, the author 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 \([C_6\text{Me}_6HRe(CO)_3]\) \(\text{Section 10.2.4); \[C_7H_7\text{PhCr(CO)}_3\]\(\text{Section 10.3.3); and}\) \([C_6H_5\text{PhCoC}_5H_5]\) \(\text{Section 10.5.5}\) for further discussion).

In a very recent paper, Davison and Reger have discussed the synthesis of \([\text{Me}_3C_6H_3V(CO)_3]^+\) by treatment of \([\text{Me}_3C_6H_3V(CO)_4]^+\) with NaI in THF. Reduction of this with NaBH₄ gave \([\text{Me}_3C_6H_3\text{V(CO)}_3\text{H}]\) (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 \([(\text{arene})\text{M(CO)}_3]\) (M = 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 hexacarbonyls, 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 \(\alpha, \beta, \gamma, \delta\)-tetraphenylporphinzinc \([\text{Zn(tpp)}]\)\(^{16}\), formulated by n.m.r. as \(\text{Zn(tpp)Cr(CO)}_3\) (3) and \(\text{Zn(tpp)Cr(CO)}_2\). Preliminary results indicated that similar complexes are formed with other \(\text{M(tpp)}\) complexes (M = 1st row transition metal).

(ii) Mixed iron-chromium complexes formed from phenyl-substituted ferrocene derivatives and Cr(CO)\(_5\), e.g.

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

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 \(\left[\text{Ph}_2\text{C}_4\text{H}_4\text{Cr(CO)}_3\text{Fe(CO)}_3\right]\) (6).
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\(^{21}\) reported that pyrolysis of \(N\)-methylpyridinium iodopentacarbonylchro–

miumtricarbonyl complex (7). However, on the basis of n.m.r. evidence, the same authors\(^{22}\) have reformulated the product as (1-methyl-1,2-dihydro-

dropyridine) chromiumtricarbonyl(0) (8). This can also be prepared by direct reaction of 1-methyl-1,2-dihydro-

ropyridine and \(\text{Cr}(\text{CO})_6\), and is the first of a new series of metal–carbonyl complexes of dihydropyridines.

\[ \text{Me} \begin{array}{c}
\text{Me} \\
\text{N} \\
\text{Cr(CO)}_3
\end{array} \quad (7) \]

\[ \begin{array}{c}
\text{Me} \\
\text{N} \\
\text{Cr(CO)}_3
\end{array} \quad (8) \]

(b) Reactions involving displacement of arene or carbonyl groups—A large amount of work on arene exchange reactions of \(\text{areneCr(CO)}_3\) complexes has been published by Strohmeier et al. in the period 1960–1964 but this work is excellently discussed elsewhere\(^{1a}\). 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 \(\text{S}_{\text{N}}2\) mechanism was suggested.

\[ \text{[arene W(CO)}_3\text{]} + 3(\text{MeO})_3\text{P} \rightarrow \text{fac [W(CO)}_3\text{]} (\text{MeO})_3\text{P} \quad (10.1) \]

A similar rate expression was observed earlier for the displacement of arene by \((\text{MeO})_3\text{P}\)\(^{24}\) and other ligands\(^{25}\) from \(\text{[arene Mo(CO)}_3\text{]}\) and the displacement of cycloheptatriene\(^{26}\) from \(\text{[C}_7\text{H}_8\text{M(CO)}_3\text{]}\) (\(\text{M} = \text{Cr}, \text{Mo}, \text{W}\)). 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

\[ \begin{array}{c}
\text{M(CO)}_3 \\
\text{(MeO)}_3\text{P}
\end{array} \quad (9) \]

(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 C7H8 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 elsewhere16 but recent examples include synthesis of various [areneCr(CO)2(OSR2)]27 complexes and a study of the kinetics of the reaction28 (10.2):

\[ [\text{C}_6\text{Me}_6\text{Cr(CO)}_2(\text{PhC}≡\text{CPh})] + \text{L} \rightarrow [\text{C}_6\text{Me}_6\text{Cr(CO)}_2\text{L}] + \text{Ph}_2\text{C}_2 \]  
(10.2)

with rate law \( k'[\text{C}_6\text{Me}_6\text{Cr(CO)}_2(\text{PhC}≡\text{CPh})] \), suggesting an S_N1 mechanism. Complete displacement occurs in the photolysis of dry methanolic solutions of \([\text{areneCr(CO)}_3]\) giving \([\text{Cr(OMe)}_3]_2 \)29.

(c) Electrophilic attack at the arene group — \([\text{Arene M(CO)}_3]\) 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) \(^1\text{H}\) n.m.r. studies of \([\text{arene M(CO)}_3]\) complexes by various workers between 1964 and 196930 have shown that the most obvious characteristic is the upfield shift of ring proton resonances upon complexation. A recent investigation30 has correlated these shifts with three effects, namely: withdrawal of \(\pi\)-electron density from the ring; the magnetic anisotropy of the \(-\text{Cr(CO)}_3\) 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 work30 on the observed direction of the metal-ring dipole moments in \([\text{(substituted arene)Cr(CO)}_3]\) complexes.

(ii) Infrared studies14,42,31 on the variation of \(\nu\text{CO}\) 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 studies32 on the effect of solvents on \(\nu\text{CO}\) shifts indicate that \(\pi\)-bonding between the metal and carbonyl groups increases in the sequence \(\text{Cr}<\text{Mo}<\text{W}\). Attempts to correlate the shifts of the CO bending modes and ring-metal stretching frequencies with electronic factors was unsuccessful33, 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 \([\text{tolueneCr(CO)}_3] \)34 (p; o; m = 46; 39; 15) is substantially different from that obtained by acetylation of free toluene (p; o; m = 92; 8; 0). A more recent example is found in the acetylation of some alkylbenzenechromiumtricarbonyls35, in which the percentage of product distribution was different from that of free benzene.
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 carbonyl groups in the o- and p-positions of conformer (10). An earlier communication by these and other authors\textsuperscript{36} 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\textsuperscript{37} 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\textsuperscript{37a} these viscosity effects have been refuted by Jackson \textit{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\textsuperscript{38–40} on mono-substituted benzenechromium tricarbonyls have established that the \textit{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\textsuperscript{30} have suggested that, in the eclipsed conformers, the effect of the magnetic anisotropy of the \(-\text{Cr(CO)}_3\) group will produce different chemical shifts at the starred and unstarred ring protons. Thus, if either conformer is \textit{preferred} in solution, there will be a differential shift of the two sets of ring protons.

\[
\begin{align*}
\text{OC} & \quad \text{Cr} & \quad \text{CO} \\
\text{X} & & \\
(10) & \quad \text{OC} & \quad \text{Cr} & \quad \text{CO} \\
\text{O} & & \\
(11) & \quad \text{OC} & \quad \text{Cr} & \quad \text{CO} \\
\text{OC} & \quad \text{Cr} & \quad \text{CO} \\
(12)
\end{align*}
\]

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\textsuperscript{41} are explained by invoking partial \textit{three point} bonding of the \(-M(\text{CO})_3\) moiety to the arene ring. However, the x-ray structures of \([\text{C}_6\text{H}_6\text{Cr(\text{CO})}_3]\)\textsuperscript{42} and others cited earlier\textsuperscript{36–40} 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 \textit{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 \(^43\) of Friedel–Crafts acetylation of \([C_6H_5Cr(CO)_3]\), 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 (\(\text{arene} = C_6H_6\) \(^42\), \(C_6M_6\) \(^44\)), the staggered orientation \((12)\) is adopted. A similar orientation is found in the \(-\text{Cr(CO)}_3\) derivatives of \(o-\) and \(m\)-toluate anions \(^45\) and this is attributed to the enhanced \(-\text{I}\) and diminished \(-\text{M}\) 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 \(^47\) based on n.m.r. evidence. A similar geometric arrangement has been found in both the orthorhombic \(^48\) and monoclinic \(^49\) forms of \([\text{phenanthrene Cr(CO)}_3]\).

In contrast to other electrophilic reagents, reaction with strong acids gave yellow protonated species \(\text{[areneCr(CO)}_3H]^+\) \(^50\) (characterised by \(\tau_{M-H} \approx 14\)).

Reaction of \([C_6Me_6M(CO)_3]\) (\(M = \text{Cr}, \text{Mo}, \text{W}\)) with SbCl\(_5\) in CH\(_2\)Cl\(_2\) \(^51\) gave \([C_6Me_6M(CO)_3Cl]SbCl_6\) the first characterised oxidation product of \([\text{areneM(CO)}_3]\) complexes (cf. \(\text{arene}\cdot M^{n+}\) systems; Section 10.4). These in turn readily gave \([M(CO)_3L_2Cl_2]\) (\(L = \text{PPh}_3, \text{AsPh}_3\)) and \([M(CO)_2D_2Cl]BPh_4\) (\(D = \text{bipy; o-phen; diarsine}\)) with mono- and bidentate ligands respectively. A related arene cation \([C_5H_5M(CO)C_6H_6]^+\) was reported earlier \(^52\). Reaction of \(\text{[(Me}_3C_6H_3)M(CO)_3]}\) (\(M = \text{Cr}, \text{Mo}\)) with mercuric halides in diethyl ether gave both 1:1 and 1:2 adducts \(^53\). 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{(13)} & \quad \begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{X}_2\text{Hg} \\
\text{OC} \\
\text{CO} \\
\text{CO}
\end{array} \\
\text{(14)} & \quad \begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{Me} \\
\text{X}_2\text{Hg} \\
\text{OC} \\
\text{CO} \\
\text{CO}
\end{array} \\
\quad \quad \left[\text{HgX}_3\right]^-
\end{align*}

(d) **Nucleophilic substitution of arene metal carbonyls** — Although nucleophilic attacks on benzenoid molecules are relatively rare reactions, it was demonstrated some years ago \(^54\) (by the facile reaction of \([\text{ClC}_6\text{H}_5\text{Cr(CO)}_3]\) with NaOCH\(_3\) to give \([\text{CH}_3\text{OC}_6\text{H}_5\text{Cr(CO)}_3]\)), that coordinated arenes have an enhanced reactivity towards nucleophiles. More recent kinetic studies of methoxide attack on \([\text{halogenobenzeneCr(CO)}_3]\) \(^55\) indicate a typical \(S_n2\) displacement mechanism and confirm the enhanced reactivity.

However, most nucleophilic substitutions in \([\text{areneM(CO)}_3]\) complexes have involved reactions in the aromatic side-chain. For example, although benzoic acid and \(\text{Cr(CO)}_6\) do not give \([\text{C}_6\text{H}_5\text{CO}_2\text{HCr(CO)}_3]\), this compound can be synthesised \(^54\) by alkaline hydrolysis, followed by acidification of \([\text{C}_6\text{H}_5\text{CO}_2\text{MeCr(CO)}_3]\). The rate of solvolysis of \([\text{C}_6\text{H}_5\text{CH}_2\text{ClCr(CO)}_3]\) is...
is a factor of \( c \cdot 10^5 \) 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 chromiumtricarbonyl complexes of benzoic acid esters\(^57\).

![Diagram](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\(^66\),

![Diagram](16) ![Diagram](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 \(\nu\text{CH} (2700-2800 \text{ cm}^{-1})\) 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.

\[ \text{(18)} \]

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

\[ \text{(19)} \]

and analytical data are consistent with formulation (19). Furthermore, in another communication\(^{71} \), Maitlis et al. note that the reaction of the rearranged ring contraction product of hexamethyl-Dewar-benzene (3) with \( \text{Fe(CO)}_5 \) gives hexamethylbenzene and ferrous chloride. With \( \text{Fe}_2(\text{CO})_9 \) and hexamethyl-Dewar-benzene, a compound of empirical
formula \([\text{Fe}_2\text{C}_{19}\text{H}_{16}\text{O}_7]\) has been obtained\(^72\), formulated on the basis of n.m.r. and i.r. evidence as (21). Earlier attempts\(^1\) to obtain \(\pi\)-bonded arene compounds have proved unsuccessful. A recent paper\(^73\) 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\(^74\) (\(\text{Me}_3\text{C}_6\text{H}_3\), \(m\)-\(\text{Me}_2\text{C}_6\text{H}_4\), \(\text{MeC}_6\text{H}_5\)) gives the unusual 'carbide' complexes \([\text{Ru}_6\text{C(CO)}_{17}]\) and \([\text{Ru}_6\text{C(CO)}_{14}(\text{arene})]\). N.M.R. studies\(^74\) and a preliminary x-ray structure determination\(^74\) 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 \(\text{Hg}[\text{Co(CO)}_4]_2\)? or \(\text{Co}_2\text{(CO)}_8\)? with \(\text{AlCl}_3\) and benzene
gives a salt, formulated as \[\{(C_6H_6)_2Co_3(CO)_2\}[Co(CO)_4]\](23). In a very recent note, reaction of norbornadiene with \[RC≡CH]Co_2(CO)_6\] (R = H, Ph) complexes in aromatic hydrocarbon solvents is reported as giving, as major products, compounds formulated as \[((\text{arene})Co_4(CO)_9\)]^{78} (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.

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 \([\text{MCl}_2(C_7\text{H}_7)_2]\) (M = Ti, Zr), obtained by direct interaction of \(\text{MCl}_4\) and \(C_7\text{H}_8\)^{79}. According to the authors, these compounds contain an anionic \(C_7\text{H}_7\) 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 \([C_7\text{H}_7\text{V}(\text{CO})_3]\)(25)^{80,81} and \([C_7\text{H}_7\text{VC}_7\text{H}_8]\)[\(\text{V}(\text{CO})_6\)]^{81} (see Section 10.5.2) by reaction of \(\text{V}(\text{CO})_6\) and \(C_7\text{H}_8\) 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.82.

\[
\text{Cycloheptatrienyl Complex} \\
\text{V} = \text{CO} \\
\text{CO}
\]  

(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 Kreiter83 have suggested as a possible 
exploration, 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 Mitchell84 have elegantly demonstrated 
that the signal obtained at ambient temperature is due to \(^{51}\text{V}-1\text{H}\) spin-spin 
 coupling and that the temperature dependence of the line shape reflects 
variations in the rate of \(^{51}\text{V}\) spin-lattice relaxation. The temperature-depen¬
dent behaviour of the high field resonance in \([\text{Me}_3\text{C}_6\text{H}_3\text{V}(\text{CO})_3\text{H}]\)13 
[very broad (\(~51\,\text{Hz}\)) at \(-20\,^{\circ}\text{C}\); narrower (\(~19\,\text{Hz}\)) at \(-52\,^{\circ}\text{C}\)] is also 
probably due to \(^{51}\text{V}-1\text{H}\) spin-spin coupling. However, the increase in 
complexity of the i.r. spectrum of \([\text{C}_7\text{H}_7\text{V}(\text{CO})_3]\) when dissolved in solution83, is not explicable 
in terms of coupling constants and may, in fact, reflect preferential solvation effects or a change in structure.

The compound \([\text{TaCl}_3(\text{C}_7\text{H}_7)_2]\)85 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 \(C_7\text{H}_7\) 
and \(C_7\text{H}_8\) 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.80 in 
1962 and this was later confirmed by the x-ray analysis87 of its tricarbonyl-
chromium derivative (26).
However, the standard method of preparation of \([C_7H_8M(CO)_3]\) is by direct reaction of \(C_7H_8\) with \(M(CO)_6\) \(^{88}\) (\(M = Cr, Mo\)); with \([CH_3CN)_3W(CO)_3]\) \(^{14}\), or with \([(C_5H_5N)_3Cr(CO)_3]\) and \(BF_3\) in ether\(^9\). 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 \([C_7H_7Cr(CO)_3]^+\) (28), (prepared by hydride abstraction from \([C_7H_8Cr(CO)_3]\) using \(Ph_3CBF_4\) \(^91\) or \(Et_3OBF_4\) \(^92\)) 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.\(^99,90\) and mass spectroscopy\(^93\) and the validity of this interpretation has been confirmed by an x-ray analysis\(^91\) of (29) (\(Y = Ph\)). 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-\(C_7H_7OCH_3Cr(CO)_3\)\(^90\). Use of \([(CH_3CN)_3Cr(CO)_3]\) and \(C_7H_7Y\) ligands provide a facile route to 7-endo-\(C_7H_7Y\) complexes\(^94\). By this means, compounds of \(C_7H_7CO_2Me\) (7-endo, 1 and 3 isomers)\(^95\), 7-endo-\(C_7H_7OR\) (\(R = Me, Et\) etc.)\(^94\) have been synthesised for the first time. Reaction of these compounds (and the 7-endo-\(C_7H_7Me\) complex) with \(Ph_3CBF_4\) leads to the stereospecific removal of the 7-exo-hydrogen atom and formation of the 7-Y-tropylium cations \([C_7H_6YCr(CO)_3]^+\) \(^94,95\) (30). In contrast, \(Ph_3CBF_4\) does not react with the 7-exo-\(C_7H_7Me\) 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\textsuperscript{96} have shown that, on reaction of \([\text{C}_7\text{H}_7\text{M(CO)}_3]^+\) (\(\text{M} = \text{Cr, Mo}\)) 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\textsuperscript{89} 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.

\[
\begin{array}{ccc}
\text{H, CHX}_2 & \rightarrow & \text{CH-CHY-CX}_2 \\
\text{Y-} & \rightarrow & \text{Cr(CO)}_3^- \\
\text{CH-CHY-CX}_2 & \rightarrow & \text{H}^- + \text{[C}_6\text{H}_6\text{Cr(CO)}_3] + \text{CHY}=\text{CX}_2
\end{array}
\]

The salt \([\text{C}_7\text{H}_6\text{CO}_2\text{MeCr(CO)}_3]^+\)\textsuperscript{[(30); \(\text{Y} = \text{CO}_2\text{Me}\)} also reacts with nucleophiles to give \([\text{RC}_7\text{H}_6\text{CO}_2\text{MeCr(CO)}_3]\)[(31); \(\text{R} = \text{OMe}\)]\textsuperscript{95}. 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\textsuperscript{95}. 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 \([\text{C}_7\text{H}_7\text{YMo(CO)}_3]\) have recently been presented\textsuperscript{97}. Considerable selectivity is found, depending on both the directive effect of \(\text{Y}\) and the nature of the entering group, i.e. with \(\text{Y} = \text{OMe}\), \(\text{MeO}^-\) 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 \(\text{Y}\) groups with a +\(\text{M}\) 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 −\(\text{M}\) effect direct more uniformly to position 2.

In contrast, the \([\text{C}_7\text{H}_7\text{Mo(CO)}_3]\)\textsuperscript{+} cation\textsuperscript{98} 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\textsuperscript{89, 91} 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 = Mo⁷⁷, 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 = Mo⁷⁷, W¹⁴) was reacted with NaC₅H₅. The product was the unexpected, orange [C₇H₇M(CO)₂C₅H₅], postulated to have structure (32) with an h⁵-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 workers⁹¹—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 h¹-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 h¹-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)$_3$ 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$_7$H$_7$ 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$_7$H$_7$Mo(CO)$_2$I] and C$_6$F$_5$MgBr gives [C$_7$H$_7$Mo(CO)$_2$C$_6$F$_5$] 105 (35) with a σ-bonded pentafluorophenyl group and a symmetrically bound C$_7$H$_7$ ring.

Kinetic studies on the displacement of C$_7$H$_8$ by monodentate Lewis bases from [C$_7$H$_8$M(CO)$_3$] complexes are discussed elsewhere (Section 10.2.3). Recent displacement reactions with bidentate ligands D (D = bipy; o-phen) in polar solvents (S) have given complexes [M(CO)$_3$D(S)], whereas in non-polar solvents, the carbonyl bridged binuclear complexes [M(CO)$_3$D]$_2$ are obtained$^{106}$. If the reaction is carried out in the presence of X$^-$ (X = Cl, Br, I etc.), the anionic compounds [M(CO)$_3$DX]$^-$ are obtained$^{107}$.

Finally, reaction of MOCl$_3$ (M = Mo, W) and C$_7$H$_8$ gives [MOCl$_2$(C$_7$H$_7$)$_2$]$^{79}$. 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$_7$H$_6$RMnC$_5$H$_5$]$^+$, which is discussed in Section 10.5.4.

10.3.5 Iron, ruthenium and osmium

Very little recent work concerning C$_7$H$_8$ and C$_7$H$_7$ complexes of this triad has appeared in the literature. Earlier work$^{26,108}$ has shown that reaction of Fe(CO)$_5$ and C$_7$H$_8$ gives [C$_7$H$_8$Fe(CO)$_3$] in which the triene is bound through only two double bonds (36). The free double bond could readily be hydrogenated, giving [C$_7$H$_{10}$Fe(CO)$_3$] (37). Reaction of the former with HBF$_4$ or the latter with Ph$_3$CBF$_4$ gives the cycloheptadienyl cation [C$_7$H$_9$Fe(CO)$_3$]$^+$BF$_4^-$ (38).
However, a cycloheptatrienyl iron complex has been prepared by treating $7\text{-C}_7\text{H}_7\text{OCH}_3\text{Fe(CO)}_3$ with HBF$_4$ to give CH$_3$OH and $[\text{C}_7\text{H}_7\text{Fe(CO)}_3] \text{BF}_4$. Although the room temperature $^1\text{H}$ n.m.r. shows a single resonance, the $v\text{CH}$ region of the i.r. is more complex than the corresponding Group VIA $[\text{C}_7\text{H}_7\text{M(CO)}_3]^+$ compounds and the fluxional structure (39) was postulated. Likewise if $[\text{C}_7\text{H}_9\text{Fe(CO)}_3]^+$ is treated with KI, the compound $[\text{C}_7\text{H}_7\text{Fe(CO)}_2\text{I}]$ is formed. Rather surprisingly, no variable temperature n.m.r. studies appear to have been reported on these compounds.

![Diagram](image)

Very recently, reaction of $[\text{h}^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]^-$ and $\text{C}_7\text{H}_7\text{BF}_4$ has been reported to give $[\text{h}^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]\text{[h}^1\text{-C}_7\text{H}_7]^+\text{. However, this has recently been reformulated as } [\text{h}^5\text{-C}_5\text{H}_5\text{Fe(CO)}\text{h}^3\text{-C}_7\text{H}_7]^+\text{, because of the close similarity of its variable temperature n.m.r. spectrum with those of } [\text{C}_7\text{H}_7\text{Mo(CO)}_2\text{C}_5\text{H}_5]^+\text{.}^\text{(42)}\text{ and } [\text{C}_7\text{H}_7\text{Co(CO)}_3]^+\text{.}^\text{(41)}\text{ (Section 10.3.6.)}

![Diagram](image)

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 RuCl₃ and C₇H₈ gives a polymeric compound [C₇H₈RuCl₂]ₙ,¹¹³ 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 cycloheptatrienyl, cyclo-octatriene or cyclo-octa-tetraene ring¹¹⁴ 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 [C₇H₇Co(CO)₃], prepared by photochemical reaction of Co₂(CO)₈ and C₇H₈. Variable temperature n.m.r. studies have recently confirmed the trihapto coordination of the C₇H₇ 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 [Rh(CO)₂(acac)] and cycloheptatriene gives the norbornadiene complex [C₇H₈Rh(acac)]¹¹⁵ 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 H\textsubscript{2}PtX\textsubscript{6} (X = Cl, Br) with C\textsubscript{7}H\textsubscript{8} gives a mixture of (C\textsubscript{7}H\textsubscript{7})\textsubscript{2}[PtX\textsubscript{6}] and C\textsubscript{7}H\textsubscript{8}PtX\textsubscript{2}. The triene ligand is readily displaced from the latter with pyridine, giving cis-[PtX\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}N)\textsubscript{2}], which would suggest h\textsuperscript{4}-C\textsubscript{7}H\textsubscript{8} coordination. However, unlike h\textsuperscript{4}-C\textsubscript{7}H\textsubscript{8}Fe(CO)\textsubscript{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 σ-phenyl aluminium compound TiCl\textsubscript{3}·AlCl\textsubscript{3}·AlCl\textsubscript{2}C\textsubscript{6}H\textsubscript{5}\textsuperscript{119} should be reformulated as the π-arene complex [(C\textsubscript{6}H\textsubscript{6})TiCl\textsubscript{2}(AlCl\textsubscript{3})\textsubscript{2}] and Russian workers\textsuperscript{120} have shown that, on warming [(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}Ti], black pyrophoric [(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}Ti] and biphenyl are the decomposition products.

Reaction of C\textsubscript{6}Me\textsubscript{6}, Al and AlCl\textsubscript{3} with MCl\textsubscript{4} (M = Ti, Zr) is reported to give the trinuclear cationic complexes [(C\textsubscript{6}Me\textsubscript{6})\textsubscript{3}M\textsubscript{3}Cl\textsubscript{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\textsubscript{6}Me\textsubscript{6}, Al and AlCl\textsubscript{3} gives instead the trinuclear cationic compounds (45) and in addition the binuclear [(C\textsubscript{6}Me\textsubscript{6}) NbCl\textsubscript{2}]\textsubscript{2}\textsuperscript{121} (46).

In contrast, a similar reaction with VCl\textsubscript{4} gives V(C\textsubscript{6}H\textsubscript{6})\textsubscript{2} which is readily air-oxidised to V(C\textsubscript{6}H\textsubscript{6})\textsuperscript{7+}. E.S.R. studies on the paramagnetic V(arene)\textsubscript{2} and the isoelectronic Cr(arene)\textsubscript{2}\textsuperscript{+} 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{122}. 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\textsubscript{10}H\textsubscript{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) C₁₀H₈ complexes. At higher lithium naphthalide/vanadium concentrations, reduction leads to disappearance of the e.s.r. signal¹²⁴,¹²⁵.

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 documented¹⁰,¹²⁶. 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 compounds¹²⁷. E.S.R. evidence for Cr(−I) and Cr(−II) bis-arene complexes is also available¹²⁴.

(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 1960¹²⁸ 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 biscyclopentadienyl 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, Fe⁰, 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 metallocene and arene compounds and by Rettig and Drago from n.m.r. work on metallocene 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 dₓ²–ᵧ², dₓᵧ < dₓz, 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 diarenechromium 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:

\[ C₆H₆ < Me₃C₆H₃ ≤ C₆H₅ – C₆H₅ ≤ C₆Me₆ \]

(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 [C₆H₆ Cr(CO)₅], the aromatic chemistry of Cr(C₆H₆)₂ is very limited. This is partly...
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. \( \text{[arene M(CO)_3]} \) 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 \( \text{RCOR}'(R = R' \text{ is H, Me, Ph etc.}) \), for example, gives the alcohols \( [\text{C}_6\text{H}_5\text{CrC}_6\text{H}_5\text{CRR'(OH)}] \) (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 \( \text{AlCl}_3 \) catalyst.

\[
\begin{align*}
\text{(47)} & \quad \begin{aligned}
\text{Cr} & - \text{C} - \text{R'} \\
& - \text{R} - \text{OH}
\end{aligned} \\
\text{(48)} & \quad \begin{aligned}
\text{Cr} & - \text{C} - \text{O} \\
& - \text{R}
\end{aligned}
\end{align*}
\]

More recently, it has been shown that, whilst \( n\)-BuLi alone does not metallate \( \text{Cr}(\text{C}_6\text{H}_6)_2 \)\(^{142}\), mettallation does occur in the presence of \( \text{NNNN}' \text{-tetramethylenediamine} \)\(^{143}\). By reaction of the resulting bis(lithiobenzene)-chromium with \( \text{Me}_3\text{SiCl} \)\(^{144}\), \[\text{Cr}(\text{C}_6\text{H}_5\text{SiMe}_3)_2\] (49) was synthesised. Evidence 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. carbonium 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 Cr(C₆H₆)₂ with ligands such as PF₃ have also been reported."}

10.4.4 Manganese, technetium and rhenium

It was reported in 1961 that the reaction of MnCl₂, PhMgBr and 2-butyne leads to cyclic condensation of the latter and the isolation of \([\text{Mn(C₆Me₆)₂}]^+\) in 11% yield as its tetraphenylborate salt. However, Fischer and Schmidt have been unable to reproduce this result and have obtained instead a 2% yield of \([\text{C₆H₆MnC₆Me₆}]^+\) isolated as its hexafluorophosphate salt. Reaction of this with LiAlH₄ leads to stereospecific attack on the unsubstituted benzene ring with formation of \([\text{C₆H₇MnC₆Me₆}]\) \(^1^{147}\).

In contrast, \([\text{Re(arene)₂}]^+\) (arene = C₆H₆ \(^1^{148}\), C₆Me₆ \(^1^{149}\)) can be synthesised by the reducing Friedel–Crafts reaction. A recent report \(^1^{149}\) 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 \([\text{C₆Me₆HReC₆Me₆}]\) (50) containing a π-cyclohexadienyl ring is obtained; it is very probable that, as in \([\text{C₆Me₆HRe(CO)₃}]\) \(^1^{10}\) (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 \([\text{Re(C₆Me₆)₂}]\) \(^2\) of apparent structure (51) is obtained. If this dimer is immediately sublimed onto a cold finger at \(-196°C\), appreciable amounts of monomeric, paramagnetic Re(C₆Me₆)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 Rh(C₅H₅)₂] \(^1^{150}\).

The behaviour of the \([\text{Tc(C₆Me₆)₂}]^+\) cation with reducing agents is analogous, except that only a trace of the dimer is obtained \(^1^{151}\).

\(\text{(50)}\)

\(\text{(51)}\)
10.4.5 Iron, ruthenium and osmium

By the standard reducing Friedel–Crafts reaction followed by hydrolysis in the presence of NH$_4$PF$_6$, the \([\text{M(arene)}_2](\text{PF}_6)_2\) complexes (\(\text{M} = \text{Ru}^{152,153}, \text{Os}^{152}\)) can be synthesised: in contrast, the \([\text{Fe(arene)}_2]^2+\) cations are obtained directly from the ferrous ion and arenes$^{154}$. 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)$_2$ compounds$^{149}$; Section 10.4.3] although the influence of steric factors on the rate of hydrolysis cannot be discounted. Hence, although \([\text{Fe(C}_6\text{H}_6)_2]^2+\) is too unstable hydrolytically to be isolated, the hexamethylbenzene cation is sufficiently stable to undergo stepwise reduction with dithionite ion to the monopositive \([\text{Fe(C}_6\text{Me}_6)_2]^+\) and the neutral \(\text{Fe(C}_6\text{Me}_6)_2\)^155. Very recently, reduction of the corresponding \([\text{Ru(C}_6\text{Me}_6)_2]^2+\) cation to \(\text{Ru(C}_6\text{Me}_6)_2\), using sodium in liquid ammonia, has been reported$^{153}$. 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 \(\text{Ru(C}_6\text{Me}_6)_2\) complex.

![Diagram](https://via.placeholder.com/150)

(52)

E.S.R. evidence$^{156}$ also suggests that \([\text{Fe(C}_6\text{Me}_6)_2]^+\) 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 authors$^{156}$ 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 $e_{2u}$. This assignment has been questioned by Anderson and Drago$^{137}$ who, on the basis of n.m.r. contact shift studies, suggest that the unpaired electron resides in the $e_{1g}$ molecular orbital (which is mainly associated with the metal). This would give rise to a $2E_{1g}$ ground state and a small dynamic distortion, whereas for a $2E_{2u}$ ground state, a large static distortion accompanied by large contact shifts (which are not found) would be expected.
The \([\text{Ru}(\text{C}_6\text{H}_6)_2]^{2+}\) 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 \(\text{Ph}_3\text{CBF}_4\) \(66\): 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 \([\text{C}_5\text{H}_5\text{CoC}_6\text{H}_6]^{2+}\) \(157\) (Section 10.5.6). Direct reaction of \(\text{RuCl}_3\times\text{H}_2\text{O}\) \(113\) and \(\text{OsCl}_3\) \(158\) with 1,3 cyclohexadiene gives the polymeric compounds \([\text{C}_6\text{H}_6\text{MCl}_2]_n\), in which the presence of diene co-ordination is suggested \(\text{cf.} \ [\text{C}_7\text{H}_8\text{RuCl}_2]_n \) \(113\) (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 \([\text{Ru}(\text{C}_{10}\text{H}_8)_2](\text{PF}_6)_2\) was synthesised\(159\). The only other naphthalene complex of ruthenium is the one obtained by reduction of \(\text{RuCl}_3(\text{DMPE})_2\ [\text{DMPE} = \text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2]\) with sodium naphthalide\(160\). The reduction product displays chemical properties corresponding to the \(\pi\)-arene formulation (53) but its spectroscopic properties\(160\) and structure\(161\) are consistent with the hydride structure (54). 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\(162\).

\[
(D\text{MPE})_2\text{Ru} \quad \text{(53)} \quad \leftrightarrow \quad (D\text{MPE})_2\text{RuH} \quad \text{(54)}
\]

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 \([\text{Co}(\text{C}_6\text{Me}_6)_2]^{3+}\) although this could not be isolated\(16\). The non-zero dipole moment for \(\text{Co}(\text{C}_6\text{Me}_6)_2\) and magnetic moment corresponding to one rather than the expected three unpaired electrons have been the subject of some discussion\(163\). As suggested for \(\text{Ru}(\text{C}_6\text{Me}_6)_2\) \(153\), 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-Dewar-benzene and \(\text{RhCl}_3\times\text{H}_2\text{O}\) leads to ring contraction and the formation of a pentamethylcyclopentadienylrhodium(III)chloride dimer (55) \(70\) rather than a \(\pi\)-hexamethylbenzenerhodium(III)chloride cation (56) \(164\).
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 [Rh{P(OMe)₃}₅]BPh₄. This decomposes in air to give the neutral complex [Rh{P(OMe)₃}₂BPh₄], shown by x-ray analysis to have structure (57) in which the BPh₄ group is π-bonded to the rhodium through an arene ring. A wider range of [RhL₂BPh₄] (L₂ = C₅H₁₀, C₇H₈, C₈H₁₂, C₈H₈ etc.) and the analogous [IrL₂BPh₄] (L₂ = C₈H₁₂, 1,5-hexadiene) compounds have since been characterised.

10.4.7 Nickel, palladium and platinum

A preliminary report on the synthesis of [Ni(C₆Me₆)₂]⁺⁺⁺ (n = 1, 2) has been given, 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 PdCl₂. A palladium–aluminium complex [PdAl₂Cl₇(C₆H₆)]₂ is produced, shown by preliminary x-ray work to have structure (58). It is suggested that, in order to conform with the 18-electron rule, each benzene ring behaves as a π-enyl system towards each palladium atom but no further evidence has been presented to support this speculative conclusion.
A recent paper\textsuperscript{169} reports that nickel (and Cu, Cr, Mn and Co) halides react with AlCl\textsubscript{3} in the presence of hydrocarbons to give compounds containing metal, AlCl\textsubscript{3} and hydrocarbon. However, empirical formulae such as [(C\textsubscript{6}H\textsubscript{6})\textsubscript{2}Ni(AlCl\textsubscript{3})\textsubscript{4.3}], [(C\textsubscript{6}H\textsubscript{6})\textsubscript{2}Co(AlCl\textsubscript{3})\textsubscript{3.5}] 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 [C\textsubscript{5}H\textsubscript{5}TiC\textsubscript{7}H\textsubscript{7}]\textsuperscript{176}. 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 [C\textsubscript{5}H\textsubscript{5}VC\textsubscript{7}H\textsubscript{7}] (Section 10.5.2) suggests structure (59) [M = Ti].

10.5.2 Vanadium, niobium, tantalum

At present, mixed sandwich compounds are known only for vanadium. Reaction of C\textsubscript{5}H\textsubscript{5}V(CO)\textsubscript{4} with C\textsubscript{7}H\textsubscript{8} gives [C\textsubscript{5}H\textsubscript{5}VC\textsubscript{7}H\textsubscript{7}]\textsuperscript{171}, shown by x-ray analysis\textsuperscript{172} to have structure (59) [M = V]. Electrochemical studies\textsuperscript{173}

\[
\text{(59)}
\]

of this compound indicated the formation of [C\textsubscript{5}H\textsubscript{5}VC\textsubscript{7}H\textsubscript{7}]\textsuperscript{+} and recently, by means of iodine oxidation, this has been isolated as its stable tri-iodide\textsuperscript{174}. Rather surprisingly, [C\textsubscript{5}H\textsubscript{5}VC\textsubscript{7}H\textsubscript{7}]I\textsubscript{3} has a magnetic susceptibility (\(\chi_M\)) of only 200 \times 10\textsuperscript{-6} c.g.s.u.\textsuperscript{174}, rather than the expected moment corresponding to \(\text{c. two unpaired electrons [cf. the isoelectronic [V(Me}_3\text{C}_6\text{H}_3)_2]I with }\chi_M = 3456 \times 10^{-6} \text{ c.g.s.u.; } \mu_{\text{eff}}(295 \text{ K}) = 2.87 \text{ BM}.\) A possible explanation of this low moment may be the loss of axial symmetry on oxidation due to
Jahn-Teller distortion etc.? [cf. \( \text{[Fe(C}_6\text{Me}_6)_2]^+ \); Section 10.4.5] but as yet the evidence is too scanty to draw any definite conclusions.

The compound \([\text{C}_7\text{H}_7\text{VC}_7\text{H}_8][\text{V(CO)}_6]\)\(^{81}\) 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 -triethyl groups (60) is based solely on spectroscopic evidence.

![Diagram](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) \([M = \text{Cr}]\) has recently been isolated in 20\% yield by reaction of \(\text{CrCl}_3\) with a mixture of NaC\(_3\)H\(_5\) and PhMgBr, followed by hydrolysis\(^{77}\). The corresponding molybdenum compound can be prepared either by reaction of MoCl\(_5\), i-C\(_3\)H\(_7\)MgBr, C\(_5\)H\(_5\)MgBr and 1,3-cyclohexadiene\(^{177}\) in ether or by lithium aluminium hydride reduction\(^{79}\) of \(\text{[C}_5\text{H}_5\text{Mo(CO)}\text{C}_6\text{H}_6]\)\(^{52}\) (see Section 10.2.3) in THF. In contrast, reduction of \(\text{[C}_5\text{H}_5\text{W(CO)}\text{C}_6\text{H}_6]\)\(^{52}\) with NaBH\(_4\)
in a water/methanol mixture gives the 1,3 cyclohexadiene tungsten carbonyl hydride complex \([\text{C}_5\text{H}_5\text{WH(CO)C}_6\text{H}_8]\) \(^{62}\). 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 \(\text{WCl}_6\), i-C\(_3\)H\(_7\)MgBr, C\(_5\)H\(_5\)MgBr and 1,3-C\(_6\)H\(_8\) in ether gives the diamagnetic hydrido compound \([\text{C}_5\text{H}_5\text{WH(C}_6\text{H}_6)\] \(^{177}\). This compound is isoelectronic with \([\text{C}_5\text{H}_5\text{ReH(C}_6\text{H}_6)\] \(^+\) (Section 11.5.4) and both probably have the structure (63) with non-parallel rings [cf. \((\text{C}_5\text{H}_5)\text{MoH}_2\)] \(^{63}\) (64).

Unexpectedly, attempted Friedel–Crafts acylation of \([\text{C}_5\text{H}_5\text{CrC}_6\text{H}_6]\) (and the corresponding manganese complex; Section 10.5.4) led to ring expansion and the formation of the substituted cycloheptatrienyl complex cations \([\text{C}_5\text{H}_5\text{MC}_7\text{H}_6\text{R}^+]\) \(^{64}\) [\(\text{R} = \text{Me, Ph}\)] \(^{176}\). The same compounds can be prepared by an exchange reaction between \([\text{C}_5\text{H}_5\text{CrC}_6\text{H}_6]\) and \(\text{C}_7\text{H}_6\text{R}^+\) \(^{180}\). The chromium compounds are readily reduced with alkaline dithionite solution to give \([\text{C}_5\text{H}_5\text{CrC}_7\text{H}_6\text{R}]\) \(^{176}\). The mechanism of this ring expansion reaction is unknown but it is suggested \(^{176}\) that the first step is probably attack of the acyl cation on the metal, followed by insertion into the \(\text{C}_6\) ring. A similar reaction with the molybdenum complex would be of interest in view of recent studies with \([\text{C}_5\text{H}_5\text{ReC}_6\text{H}_6]\), in which only competitive acetylation if the \(\text{C}_6\) and \(\text{C}_5\) rings is observed (Section 10.5.4) \(^{181}\).

More conventional methods of synthesising \([\text{C}_5\text{H}_5\text{MC}_7\text{H}_7]^+\) \(^{64}\) [\(\text{R} = \text{H}\)] \((n = 0, 1; \text{M} = \text{Cr}^{99}, \text{Mo}^{177}, \text{W}^{177})\) are also available (see References 2b and 182 for a summary of the chromium syntheses). Reaction of \([\text{C}_5\text{H}_5\text{CrC}_7\text{H}_7]\) with excess phenyl lithium \(^{180}\) gives a mixture of \([\text{C}_5\text{H}_5\text{CrC}_7\text{H}_6\text{C}_6\text{H}_5]\) \((65) [\text{Y} = \text{Ph}]\) (presumably an exo substituted triene complex) and \([\text{C}_5\text{H}_5\text{CrC}_7\text{H}_7]\). 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 \([\text{C}_5\text{H}_7\text{Cr(CO)}_3]\) (Section 10.3.3) and \([\text{C}_5\text{H}_5\text{FeC}_6\text{H}_6]\)^+] (Section 10.5.5). The unsubstituted triene complex \([\text{C}_5\text{H}_5\text{CrC}_7\text{H}_7]\) \((65) [\text{Y} = \text{H}]\) is also known \(^{183}\); from this, \([\text{C}_5\text{H}_5\text{CrC}_7\text{H}_7]\)
is obtained by catalytic dehydrogenation and $[\text{C}_5\text{H}_5\text{CrC}_7\text{H}_7]^+$ by atmospheric oxidation\textsuperscript{183}.

Finally, on reacting anhydrous CrCl$_3$, EtMgBr and C$_7$H$_8$ in an attempt to prepare Cr(C$_7$H$_8$)$_2$, the novel cycloheptatrienyl/1,3-cycloheptadiene complex $[\text{C}_7\text{H}_7\text{CrC}_7\text{H}_{10}]$ (66) was synthesised\textsuperscript{184}.

The sandwich compounds $[\text{C}_7\text{H}_7\text{M}(\text{CO})_2\text{C}_5\text{H}_5]$ (M = Mo, W) are fully discussed in Section 10.3.3.

10.5.4 Manganese, technetium and rhenium

As discussed in the last section, $[\text{C}_5\text{H}_5\text{MnC}_6\text{H}_6]$ (61) (M = Mn) undergoes ring expansion to $[\text{C}_5\text{H}_5\text{MC}_7\text{H}_6\text{R}]^+$ (64) on attempted Friedel–Crafts acylation\textsuperscript{176}. In contrast, acetylation of the corresponding $[\text{C}_5\text{H}_5\text{ReC}_6\text{H}_6]$ complex gives $[\text{C}_5\text{H}_5\text{ReC}_6\text{H}_5\text{COCH}_3]$ (16\%\%) and $[\text{C}_5\text{H}_4\text{COCH}_3\text{ReC}_6\text{H}_6]$ (18\%\%)\textsuperscript{181}. The cyclopentadienylarene compound can be protonated in aqueous HCl to give the hydrido cation $[\text{C}_5\text{H}_5\text{Re-H(C}_6\text{H}_6)]\text{Cl}$ (63) [cf. $[\text{C}_5\text{H}_5\text{W-H(C}_6\text{H}_6)]$; Section 10.5.3]\textsuperscript{181}.

The mass spectra of various mixed sandwich compounds namely $[\text{C}_5\text{H}_5\text{MC}_6\text{H}_6]$ (M = Cr, Mn), $[\text{C}_5\text{H}_5\text{MC}_7\text{H}_7]$ (M = 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\textsuperscript{185}.

10.5.5 Iron, ruthenium and osmium

The mixed sandwich complexes of this triad can be divided into two sections: arenecyclopentadienyliron 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\textsuperscript{186} have examined in detail the factors controlling the addition of nucleophiles (Y) $[Y = \text{H}^-, \text{Me}^-, \text{Ph}^-]$ to the substituted arenecyclopentadienyliron cations $[\text{C}_5\text{H}_5\text{FeC}_6\text{H}_n\text{R}_6-n]^+$ (67) (R = 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-Hexo $\sigma$-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$^{46}$, is improbable.

The arene/diene complexes $[\text{C}_6\text{H}_6\text{M}1,3-\text{C}_6\text{H}_8]$ ($\text{M} = \text{Fe, Ru}$) have been prepared, the former by photolysis of a mixture of FeCl$_3$, i-C$_3$H$_7$MgBr and 1,3-cyclohexadiene$^{187}$ and the latter either by reaction of $[\text{Ru}(\text{C}_6\text{H}_8)_2]$ (ClO$_4$)$_2$ with NaBH$_4$$^{66}$ or by irradiation of a mixture of $[\text{diene RuCl}_2]_n$ (diene = 1,5-cyclo-octadiene or norbornadiene), 1,3-C$_6$H$_8$ and i-C$_3$H$_7$MgBr$^{188}$.

Reaction of $[(\text{diene})\text{RuCl}_2]_n$ with cycloheptatriene and i-C$_3$H$_7$MgBr gives the mixed compounds $[(\text{diene})\text{RuC}_7\text{H}_8]$$^{188}$. Photolysis of a mixture of MCl$_3$ ($\text{M} = \text{Fe, Ru}$), 1,3,5-cyclo-octatriene and i-C$_3$H$_7$MgBr gives the compounds $[\text{C}_8\text{H}_{10}\text{MC}_8\text{H}_{10}]$, 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$^{188}$ (see Section 10.6.1 for further examples). Finally, in an earlier paper, the compounds $[\text{C}_8\text{H}_{12}\text{MC}_8\text{H}_{10}]$ $^{169}$ (73) ($\text{M} = \text{Fe, Ru}$) have been synthesised by reaction of MCl$_3$, 1,3,5-C$_8$H$_{10}$, 1,5-C$_8$H$_{12}$ and i-C$_3$H$_7$MgBr.

10.5.6 Cobalt, rhodium and iridium

The only recent work on mixed sandwich compounds in this triad is the synthesis of $[\text{Ph}_4\text{C}_4\text{Co}(\text{C}_7\text{H}_9)]^+$ (74) and $[\text{Ph}_4\text{C}_4\text{Co}(\text{arene})]^+$ (75) cations$^{190}$. 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 $N$-bromosuccinimide in methanol leads to endo hydride ion abstraction from these exo substituted compounds, whereas Ph$_3$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 arenecyclopentadienylcobalt cation $[C_5H_5CoC_6H_6]^{2+}$\textsuperscript{157} has been isolated as its PF$_6^-$ salt by double hydride abstraction from $[C_5H_5Co 1,3-C_6H_8]^{191}$ 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 $[C_8H_{10}M(CO)_3]$ (76) ($M = Cr, Mo, W$) gives $[C_8H_9M(CO)_3]^+$, assigned, on the basis of n.m.r. as the homotropylium structure (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 $C_8H_8^+$ 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.$C_8H_{10}MeC_3H_10$(72); Section 10.5.5]. Thus, one of the
products in the reaction of Fe$_3$(CO)$_{12}$ and 1,3,5-C$_8$H$_{10}$ is $[C_8H_{10}Fe(CO)_3]$, in which the triene has isomerised to give the diene complex (78)\(^{2c}\).

Finally, recent papers\(^{193}\) have reported the reaction of tetrafluorobenzobicyclo [2,2,2]octatriene (tetrafluorobenzobarrelene) with Fe$_3$(CO)$_{12}$, to give compounds of type LFe(CO)$_3$. Spectroscopic evidence (n.m.r. and Mössbauer\(^{193}\)) suggest structure (79) and this has recently been confirmed by x-ray analysis\(^{194}\).

10.6.2 Bicyclononatriene complexes

Here again, the only work not covered by an earlier review\(^2d\) is that of Grimme\(^{195}\) who, by reaction of bicyclo[6,1,0]nona-2,4,6-triene and \([(\text{THF})_3\text{Mo(CO)}_3]\) has synthesised $[C_9H_{10}\text{Mo(CO)}_3]$ (80). On heating at 125 °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 C₉H₁₀ olefins, such as 5-6-dimethylene-bicyclo[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 elsewhere²⁶. More recent studies have investigated the reaction of cyclododeca-1,5,9-trienes with rhodium¹⁹⁶, platinum¹⁹⁷, iron²⁶ 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 [C₈H₈Mo(CO)₃]¹⁹⁹ and [1,3,5,7-Me₄C₈H₄Cr(CO)₃]²₀₀ indicate that the —M(CO)₃ moiety interacts with six of the carbon atoms [cf. C₇H₈M(CO)₃; Section 10.3.3], as shown in (82). Earlier variable temperature 'H n.m.r. studies¹⁰¹,²⁰¹,²⁰² have indicated that these compounds are fluxional, showing a single resonance at room temperature and a complex spectrum below —30 °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
observed are very complex and apparently involve at least two distinct phases of intramolecular rearrangement\textsuperscript{203}. Protonation of the $[\text{C}_8\text{H}_8\text{Mo} (\text{CO})_3]$ complex\textsuperscript{201} gives the homotropylium cation $[\text{C}_8\text{H}_9\text{Mo} (\text{CO})_3]^+$ (\textsuperscript{77}) (see Section 10.6.1 for alternative synthesis), whereas carbonylation\textsuperscript{204} gives the $[\text{C}_8\text{H}_8\text{Mo} (\text{CO})_4]$ complex where the $\text{C}_8\text{H}_8$ ring is coordinated ‘diene-fashion’ (\textsuperscript{83}). Protonation of this results in CO evolution and the formation of (\textsuperscript{77}).

![Diagram](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 (\textsuperscript{84}) i.e. $(\text{h}^6-\text{C}_8\text{H}_8)\text{Fe(h}^4-\text{C}_8\text{H}_8)$.

![Diagram](84)

At room temperature the $^1\text{H}$ n.m.r. spectrum\textsuperscript{207} shows only a single peak and at $-84 ^\circ\text{C}$ a four line spectrum corresponding to a ‘frozen’ $\text{h}^6$-ring [by comparison with the spectra of $\text{C}_8\text{H}_8\text{M} (\text{CO})_3$] and a time-averaged $\text{h}^4$-ring. The equivalence of all protons of the $\text{h}^4$-ring between the coalescence temperature (c. $-40 ^\circ\text{C}$) and $-84 ^\circ\text{C}$ 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 $-35 ^\circ\text{C}$ suggests the presence of an internuclear rearrangement process transforming the $\text{h}^4$-ring to a $\text{h}^6$-ring (and vice versa) with consequent interconversion of the conformation of the two rings and interchange of all bonds.

10.7.2 1,6-Methanocyclodecapentaenechromiumtricarbonyl

The reaction of 1,6-methanocyclodecapentaene with $\text{Cr(CO)}_6$ 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 $\pi$-electron system of the free ligand is retained on coordination and this has been confirmed by a recent x-ray structure determination (\textsuperscript{85})\textsuperscript{210}. 
10.7.3 Azulenium cation complexes

For completion, readers are referred to the recent review by Churchill\(^2\) (literature coverage up to December 1968) in which references (all pre-1965) to complexes containing the azulenium ion $\text{C}_{10}\text{H}_9^+$ 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) 88, (f) 49, (g) 17, (h) 27 (New York: The Ronald Press Company)
4. Green, M. L. H. (1968). *Organometallic Compounds, Volume 2*, (a) 181, (b) 215, (c) 240 (London; Methuen)


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[RuCl$_3$CO(C$_7$H$_8$)] (M = Ph$_3$BzP$^+$, Cs$^+$)$^1$ [A]. 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 = Me$_2$S, Me$_2$SO, CH$_2$=CHCN (A/L 1/2 mole ratio), displacement of diene occurs giving the new anionic compounds Ph$_3$BzP[RuCl$_3$CO(L)]$_2$. Similar compounds are obtained for L = AsPh$_3$, SbPh$_3$, C$_5$H$_5$N together with neutral species of composition [RuCl$_2$CO(C$_7$H$_8$)]L, shown by detailed $^1$H NMR studies to have structure I. With an excess of SbPh$_3$, the well-known tris-stibine compound [RuCl$_2$CO(SbPh$_3$)$_3$]$^2$ is obtained. Reaction with PPh$_3$ (1/2 mole ratio) gives the dimeric carbonyl phosphine [RuCl$_2$CO(PPh$_3$)$_2$]; with an excess of PPh$_3$ bridge cleavage occurs to give [RuCl$_2$CO(PPh$_3$)$_3$]. In contrast, reaction with PMe$_2$Ph (1/2 or excess) gives only [RuCl$_2$(PMe$_2$Ph)$_2$CO(C$_7$H$_8$)] shown by $^1$H 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 Ph$_3$BzP[RuCl$_3$CO(N-N)] and [RuCl$_2$CO(N-N)$_2$]: with an excess of (N-N), small amounts of the new cationic species [RuClCO(N-N)$_2$]Cl are also obtained.

The analogous tertiary phosphine cations [RuCl$_2$(PPh$_3$)$_3$](N-N)$_2$ can be prepared by treatment of either [RuCl$_2$(PPh$_3$)$_3$]$_2$ or [RuCl$_3$(PPh$_3$)$_2$(N-N)$_2$]$_3$ with an excess of (N-N) in methanol. Small amounts of the dimeric chloro-bridged cations [Ru$_2$Cl$_2$(PPh$_3$)$_4$(N-N)$_2$]Cl$_2$ are also obtained. Similarly, with mer-[RuCl$_3$(PMe$_2$Ph)$_3$]$^4$ and excess (N-N), the orange crystalline cationic compounds [RuCl(PMe$_2$Ph)$_3$(N-N)]Cl·H$_2$O 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, $^1$H 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 \([\text{RuX}_2(\text{PR}_3)_3\) or \(4\)]{color} \(})

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(Received July 19th, 1973)

Since the preparation of \([\text{RuX}_2(\text{PPh}_3)_3]\) \(X = \text{Cl, Br}; n = 3, 4\) in 1966, numerous papers have been published on the reactions of these compounds with carbon, sulphur, nitrogen and oxygen donor ligands and on their usefulness as catalytic precursors in various olefin hydrogenation and oxidation reactions. A number of similar compounds of type \([\text{RuX}_2(\text{L}_4)\) containing phosphorus donor ligands \((\text{L} = \text{secondary phosphine}_5; \text{tertiary phosphite}_6; \text{L}_2 = \text{ditertiary phosphine}_7)\) have also been prepared, either by reaction between \(\text{RuX}_3\) and \(\text{L}\) 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 or 2-methoxyethanol gives only the lemon-yellow dimeric triply halide-bridged cations \([\text{Ru}_2\text{X}_3(\text{PR}_3)_6]^+\) \((\text{PR}_3 = \text{PMe}_2\text{Ph}, \text{PMe}_\text{Ph}_2, \text{PET}_\text{Ph}_2, \text{PET}_\text{Ph}_2, \text{PPr}_2\text{Ph}, \text{PBu}_2\text{Ph}, \text{PET}_3)\) which are not very useful starting materials in comparison with \([\text{RuX}_2(\text{PPh}_3)_3\) 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 \((\text{b.p.} 60-80^\circ)\) with an excess of tertiary phosphine, \(\text{e.g., PMe}_2\text{Ph}, \text{PMe}_\text{Ph}_2, \text{PET}_\text{Ph}_2, \text{PET}_\text{Ph}_2, \text{PPr}_2\text{Ph}, \text{PBu}_2\text{Ph}, \text{PET}_3\). 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 \(^{1}H\) NMR of \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) indicates a cis-configuration \((\text{cf. cis-}[\text{RuH}_2(\text{PMe}_2\text{Ph})_4]_9\).

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 \([\text{RuX}_2(\text{PR}_3)_3\) or \(4\) compounds, refluxing gently in ethanol \((\text{with a small amount of free phosphine in the case of the tris compounds})\) readily gives the ionic species. If the reactions between \([\text{RuX}_2(\text{PPh}_3)_4\) and
excess PR₃ are carried out in CH₂Cl₂ 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

Reprinted from
JOURNAL
OF
THE CHEMICAL SOCIETY
DALTON TRANSACTIONS
1973
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

A detailed investigation of the reactions of [RuX₂(EPh₃)₂]Cl₂MeOH (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 sulphoxide, dialkyl sulphides, carbon disulphide, sodium diphenylphosphinodithioate) oxygen (tetrahydrofuran, acetone, nitromethane) and carbon (norbornadiene, 1,5-cyclo-octadiene, carbon monoxide) donor atoms is presented. Five different types of behaviour towards these ligands are exhibited by (A): (1) displacement of methanol giving the ruthenium(III) compounds [RuX₂(EPh₃)₂L] (L = Me₂S, bipy, C₅H₅N; (2) complete displacement of methanol and one EPh₃ group giving [RuX₂(EPh₃)₃L] (L = Me₂S, bipy, C₅H₅N); (3) complete displacement of methanol, EPh₃ and X without reduction, e.g. [Ru(S₂P₂H₄)₂] (4) reduction to ruthenium(II) with or without complete displacement of EPh₃ groups, e.g. [Ru₂Cl₄(L)₂] (L = CO, C₅H₅N) and [Ru₂Cl₄L₂] (L = C₅H₅N, Me₂SO); (5) reduction to cationic ruthenium(II) compounds in methanol, e.g. [RuCl(PPh₃)(N-N)₂]Cl (N-N = bipy or phen). Several of these compounds can also be synthesised from [RuX₂(PPh₃)₃]. The complexes are characterised by elemental analyses, molecular weights, e.s.r., and magnetic measurements, and configurations tentatively suggested on the basis of detailed far-infrared [ruthenium(II)] and ¹H 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 [RuX₂(PPh₃)₂] (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 [Ru₃Cl₄(PPh₃)₂]Cl⁴ and the blue methanolic solutions of [RuCl₂(μ)(μ)₂]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-[RuX₂L₃] (L = PMe₂Ph, PPh₃, PO₃H₂, PPh₃, PPh₃)⁶ [RuX₃(EPh₃)₂] (L = E or As; S = MeOH,¹⁷ 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)₃(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)₂L]; (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 [RuX₃L₂] or [RuX₃(EPh₃)L₂]; (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 coordination 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)₂] and RCN, the compounds [RuCl₃(RCN)₂(PPh₃)₂] are readily obtained.²⁻³ From the blue solution of ruthenium(II) in methanol, the phenyl cyanide dimer [RuCl₂(PPh₃)₂] is isolated and halide bridge cleavage with Lewis bases gives [RuCl₂(PPh₃)L₂] (L = Pr₃, MeC₆H₄NH₂, CO, etc.)⁵ In contrast, reaction of the blue solution with succino- and glutaro-cyanides (L') gives brown insoluble compounds of approximate stoichiometry RuCl₄L'.⁵ Preparation of the blue solution in methyl cyanide gives [RuCl₄(MeCN)₄] which reacts further to produce [RuCl₄(MeCN)₄]₂ (L = PhNH₂, CO);⁵ [RuCl₄(MeCN)₂(CO)₂] is also obtained from [RuCl₄(CO)₂], and MeCN.²³ Cleavage of the halogenocarboxyl dimer [RuX₂(CO)₄]₂ with nitriles gives cis-[RuX₂(RCN)(CO)₃] (R = Et, Ph, CH₂=CH)¹⁴ and [RuCl₄(NO)(MeCN)] is obtained from the reaction of RuCl₄NO and MeCN.¹⁵

In recent years, a number of cationic ruthenium(II) compounds containing RCN ligands have also been reported. These include [RuH(PPh₃)(Et₂PC₆H₅-PEt₃)]¹⁶ [J₃-(MeCN)]RuCl₂(MeCN)₂HgCl₂,¹⁷ [RuH(CO)-(MeCN)₃(PPh₃)₂CO]ClO₄,¹⁸ [RuX₃(MeCN)(bipy)₂PF₆ (X = Cl⁻ or NO₃⁻)],¹⁹ and the series [Ru(NH₃)₄(RCN)]²⁺ and [Ru(NH₃)₄RCN]³⁺.²⁰ Several of the latter can be readily oxidised to the corresponding ruthenium(III) species [Ru(NH₃)₄RCN]³⁻.²¹ The only other ruthenium(III) nitrite compounds known (to us) are the recently reported [RuCl₆(PhSPr)²MeCN] and [RuCl₆(MeCN)₃]-MeCN.²²

We now report that reaction of excess of RCN with (A) in dichloromethane gives the crystalline compounds [RuX₃(EPh₃)₂RCN] (E = P or As; X = Cl or Br; R = Me, Ph, PhCH₂, or CH₂=CH). 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 1), and e.s.r. studies at 77 K. The values of μₑₑ (300 K) ranging from 1.80 to 2.00 B.M. are indicative of monomeric, spin-paired ruthenium(III) 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 [RuX₃L₂] compounds (L = PMe₂Ph, SmPh₂, 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.²³ 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. [RuCl₆(PhSPr)²MeCN)] w(CN) 2310 cm⁻¹].²⁶ As expected,²⁷ the HI 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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<td>1100</td>
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<td>[RuBr₃(PPh₃)(thf)]</td>
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<td>48.7</td>
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<td>Brown</td>
<td>&gt;300</td>
<td>45.3</td>
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<td>1100</td>
<td>45.3</td>
<td>3.2</td>
<td>687</td>
<td></td>
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</table>

* Osmometrically at 37°C (C₆H₆).  * Magnetic moment, measured by Faraday method (solid) at 294 K; in parentheses, as measured by Evans' method (solution) at 301 K.  * Measured in CHCl₃.  * Measured in CH₂Cl₂.  * 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 ν(RuX) vibrations can be assigned and the ratio of ν(RuCl) : ν(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 trans to the halide may be substantial. Thus, terminal ν(RuCl) are generally found in the region 347–299 (when trans to chlorine), 311–266 (trans to CO), 262–229 (trans to PR₃) and bridging chloride stretching frequencies are usually found below 250 cm⁻¹.²⁷,²⁸ There appear to be no ν(RuCl) below 300 cm⁻¹ but the presence in all these compounds of a strong ν(RuCl) band at ca. 330 cm⁻¹ is consistent with trans-chlorides, suggesting either configuration (I) or (II). Although it is impossible to distinguish unequivocally between these possibilities on the basis of far i.r. studies alone, the close similarity of the far i.r. spectra of [RuX₃(EPh₃)₂RCN] to those of [RuX₃(EPh₃)₂MeOH], together with the established trans* structure of the MX₄[EPh₃]⁺ anions (M = Rh or Ru), strongly suggests that the nitrile (and methanol) compounds have configuration (I).

Unlike [RuCl₃(PhSP̃)₂MeCN], which readily undergoes displacement of PhSP̃ by MeCN, giving [RuCl₃(PhCN₃)MeCN],²⁵ we have found no evidence for the formation of [RuX₃(EPh₃)₂(RCN)₃₋₄] (n = 0 or 1) by reaction of (A) with RCN. However, prolonged reaction of [RuX₃(PPh₃)₂MeOH] with RCN results in the formation of some [RuX₃(RCN)₂(PPh₃)]. A careful examination of the product for X = Cl, R = PhCH₂ confirms that it is identical to cis-[RuCl₂(PhCH₂CN)₂(PPh₃)] (ν(CN) 2209, 2243 cm⁻¹) obtained directly from [RuCl₃(PPh₃)].³ The ease of reduction depends on R and a qualitative order is found to be MeCN < PhCN < PhCH₂CN < CH₂CN. Under the same conditions no reduction products are found for E = 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. Refluxing for 5–10 min with an excess of pyridine in dichloromethane gives the crystalline compounds [RuX₃(EPh₃)₂(PPh₃)] (mentioned earlier for X = Cl, E = 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 EPh₃ and C₅H₅N is confirmed by i.r. spectroscopy and the strong ν(RuCl) band at ca. 340 cm⁻¹ (Table 3) is indicative.

* An X-ray structural analysis of AsPh₃[RuCl₃(PPh₃)₂]₂-Mn(CO) by A. Fraser, University of Edinburgh, confirms the trans-stereochemistry suggested earlier (ref. 8) and this compound is isomorphous with the corresponding ruthenium(III) anion.

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(RuCl) (cm⁻¹)</th>
<th>ν(RuBr) (cm⁻¹)</th>
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<tbody>
<tr>
<td>[RuCl₃(AsPh₃)₂(MeCN)]</td>
<td>347</td>
<td>329</td>
</tr>
<tr>
<td>[RuBr₃(AsPh₃)₂(MeCN)]</td>
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<td>299</td>
</tr>
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<td>249</td>
</tr>
<tr>
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<td>219</td>
</tr>
<tr>
<td>[RuCl₃(PPh₃)₂ppy]</td>
<td>262</td>
<td>249</td>
</tr>
<tr>
<td>[RuCl₃(AsPh₃)₂(bipy)]</td>
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<td>221</td>
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<tr>
<td>[RuBr₃(PPh₃)₂(bipy)]</td>
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<td>137</td>
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</tbody>
</table>

* Band energy (cm⁻¹). ¹ Maximum molar extinction coefficient (mol⁻¹ cm⁻¹). ² Oscillator strength (10⁻²) where f = 4.69 × 10⁻² ϵmax νmax and υmax = half band intensity width i.e. the width at ½ max. (cm⁻¹).
TABLE 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(RuX)</th>
<th>Other bands</th>
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<tr>
<td>[RuCl₂(PPh₃)₂(MeCN)]</td>
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<td>329s, 320s, 300w</td>
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<tr>
<td>[RuBr₂(PPh₃)₂(MeCN)]</td>
<td>334s</td>
<td>255w, 242m, 259w, 300w, 311s, 283w, 264w, 329s, 311s, 283w, 264w</td>
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<tr>
<td>[RuBr₂(PPh₃)₂(C₅H₅N)]</td>
<td>335s, 329s, 255w</td>
<td>329s, 320s, 300w, 311s, 283w, 264w, 329s, 311s, 283w, 264w</td>
</tr>
<tr>
<td>[Ru₂Cl₃(PPh₃)₄(MeOH)]</td>
<td>335s, 329s, 255w</td>
<td>329s, 320s, 300w, 311s, 283w, 264w, 329s, 311s, 283w, 264w</td>
</tr>
<tr>
<td>[Ru₂Br₂(PPh₃)₄(MeOH)]</td>
<td>335s, 329s, 255w</td>
<td>329s, 320s, 300w, 311s, 283w, 264w, 329s, 311s, 283w, 264w</td>
</tr>
</tbody>
</table>

These appear to be the first well characterised ruthenium(III) compounds containing both pyridine and tertiary phosphine (or arsenic) ligands although a number of ruthenium(III) pyridine complexes are known. These include mer-²³ and fac-²² [RuCl₃(py)₃], [RuCl₃(py)₃]Cl₃, pyH[RuCl₃(py)₃]²³ pyH[RuCl₃(CO)(py)]²² and a number of 2,2'-bipyridyl (and 1,10-phenanthroline) compounds such as [RuCl₄(py)₂(bipy)]²⁺ and [RuCl₄(py)₃(bipy)]Cl₃.²⁴

If [RuX₄(AsPh₃)₃(MeOH)] is refluxed with neat pyridine for ca. 20 minutes, [RuX₄(py)₃]²⁻ 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.²⁵ A comparison of the r.r. and ¹H n.m.r. spectra of our products with those given in ref. 35 confirms the trans-configuration.

In contrast, reaction of [RuX₄(AsPh₃)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-[RuX₄(py)₃]²⁻ and the other(s) are probably ruthenium(II) species (since sharp n.m.r. signals) containing both pyridine and triphenylphosphine. By reaction of [RuBr₂(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 [RuBr₂(PPh₃)₃(py)]²⁻. Longer reaction

times lead to precipitation of trans-[RuBr₂(py)₄]. Unfortunately, various attempts to obtain the corresponding chloro-compound from [RuCl₂(PPh₃)₂] and pyridine gave either [RuCl₂(PPh₃)(py)]₂, together with a small amount of [RuCl₂(py)]⁴ (H n.m.r., i.r., and analytical evidence) or, on longer reaction times, pure trans-[RuCl₂(py)]. Although [RuCl₂(PPh₃)(py)]₂ could not be satisfactorily separated from [RuCl₂(py)], a careful examination of the far i.r. of the mixture, in conjunction with that of [RuBr₂(PPh₃)(py)]₂ indicates υ(RuCl) 340 cm⁻¹, supporting the expected trans-configuration (VI). Rather surprisingly, in view of the normal reaction of [RuX₂(PPh₃)₂] with Lewis bases,³ no evidence has been found for the unknown [RuX₂(py)]₄ (PPh₃)₂, although the carbonyl analogues [RuX₂(CO)₂(py)]₄ (Py),⁴ cis-[RuX₂(CO)₂(py)]₄ (X = Cl, Br, I),³⁶ SnCl₂, and [RuCl₂(PPh₃)(py)]₂⁴ are well-established series of compounds.

Although trans-[RuX₂(py)]₄ and trans-[RuX₂(PPh₃)(py)]₂ 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 [RuBr₂(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 re-fluxed) give [RuX₂(EPh₃)(N-N)]Cl₂ are isolated, together with small amounts of the rather insoluble [Ru₂Cl₂(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 [RuX₂(PPh₃)(N-N)] and an excess of (N-N) in methanol.

In contrast, the reaction of [RuCl₂(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 stilbene [Ru(bipy)₂Cl₂]₄H₂O,⁴⁰ which we have also characterised by synthesis of the BPh₇⁻ salt. In addition, small amounts of purple [RuCl₂(H₂O)(bipy)₂]Cl₂H₂O previously synthesised in higher yields by several methods,⁴¹,⁴² can also be isolated. However, if a mixture of [RuCl₂(AsPh₃)(bipy)], bipyridyl, and sodium tetraphenylboron are refluxed in methanol, the only product is [RuCl₂(AsPh₃)(bipy)]BPh₃.

The detailed chemistry of these and other ionic ruthenium(II) 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 [RuX₃[(PPh₃)₂MeOH] and DMSO († 7-39) (cf. the facile dissociation of [RuX₃(PPh₃)₂MeOH]. Unfortunately, [RuBr₃(dmsol₄)] appears too insoluble for direct molecular weight measurements.

The three singlets at † 6-49, 6-52, and 6-61 do not decrease in intensity on addition of DMSO, indicating they do not arise from dissociation products of [RuBr₃(dmsol₄)]. The best explanation for these we can offer, at present, is to assign the † 6-49 resonance to the eight equivalent methyl groups in trans-[RuBr₃(dmsol₄)] (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-[RuBr₃(dmsol₄)], the higher resonance corresponding to the dmso ligands trans to the bromo-groups. Raising the temperature increases the intensity of the resonance at † 6-49 with respect to those at † 6-52 and 6-61. This is consistent with a report by James et al. who have recently synthesised [RuX₃(dmsol₄)] (X = Cl or Br) by reaction of RuX₃ 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 [RuCl₄(dmso)] from the reaction of [RuCl₂(AsPh₃)₂MeOH] and DMSO have proved so far to be unsuccessful. This can be attributed to the high solubility of [RuCl₄(dmso)] in DMSO and the consequent difficulty of removing the high boiling solvent without decomposition of the product.

However, heating [RuBr₃(dmso)] to 333 K in an n.m.r. tube and then cooling the solution to low temperature reveals an extra resonance at † 7-09 (241 K). On raising the temperature, this moves to higher field. Similarly, recrystallisation of [RuBr₃(dmso)] from hot CHCl₃-acetone solution gives a darker coloured material with additional i.r. bands at 1120, 930, and 920 cm⁻¹ (cf. ref. 46). In addition, the 1H n.m.r. (301 K) shows an extra weak peak at † 7-30 indicative of some O-bonded dmso. However, the analysis of the recrystallised product is ca. 3% too low in carbon for [RuBr₃(dmso)] and the resonance at † 6-49 has broadened considerably, suggesting that some oxidation of the product may have occurred. In fact, if solutions of [RuBr₃(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 [RuX₃(dmso)] is very critical in determining the isomeric composition of the product and further studies are in progress to unravel this interesting problem.

(b) *Diethyl Sulphides.*—Reaction of (A) with Me₂S in
CH₂Cl₂ gives [RuX₃(EPh₃)(Me₂S)₂]. The ¹H n.m.r. spectrum of [RuCl₃(AsPh₃)(Me₂S)₂] 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(PMe₂Ph₃)], [Ru(acac)₃]⁴⁷ and [Ru(S₂Ph₂Ph₃)₃] (see section d) whereas [RuBr₃AsPh₃(Me₂S)₂] 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)(Me₂S)₂] 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, possibly of [RuCl₃(PPh₃)₂Me₂S] and [RuCl₃(PPh₃)₃(Me₂S)₂], which we 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)₃] and Me₂S.

In contrast, reaction of [RuX₃(AsPh₃)₂Me₃OH] with an excess of Et₄S gives [RuX₃(AsPh₃)₂Et₄S] [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)₂Me₃OH] even short reaction times give a complicated mixture of products which could not be separated, even by dry column chromatography.⁴⁸

Reaction of Ph₃S with [RuCl₃(AsPh₃)₂Me₃OH] gives a brown solid which i.r. spectroscopy and analyses confirm contains no Ph₃S but is [RuCl₃(AsPh₃)₂]. These results suggest that the donor ability of organic sulphides in these compounds is Me₆S > Et₄S > Ph₃S but this does not necessarily reflect the intrinsic bonding ability of the sulphur atom towards ruthenium(II) since steric repulsions of EPh₃ groups will probably play an important role.

Although a number of ruthenium mono-, di-, and tri-sulphide compounds have been recently reported,⁴⁶,⁴⁸ these complexes represent the first examples of dialkyl sulphides and tertiary phosphines (or arsines) bonded to ruthenium(II) and (III).

(c) Carbon Disulphide.—Reaction of [RuCl₃(EPh₃)₂(Me₃OH)] 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 CS group. No bands due to thioacetyl (ca. 1280–1330 cm⁻¹) or ζ-CS₂ (ca. 1120 or 1020 cm⁻¹) linkages are present.⁵⁰ The compounds analysed 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)₂CS₂] is easily lost. Attempts to recrystallise the compound from CH₂Cl₂ or C₂H₆ give only [RuCl₃(AsPh₃)₂]. However, the CS₂ group is not lost from the solid even after prolonged drying in vacuo at 80° 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.⁵¹,⁵²

However, reaction of [RuBr₃(EPh₃)₂Me₃OH] 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 analyse for [RuBr₃(EPh₃)₂CS₂]. Shorter reaction times give a mixture of this compound and [RuBr₃(EPh₃)₂CS₂] (i.r. and analytical evidence). The reason for the nonformation of the thioacetyl complex for X = Cl is not understood. These represent the first carbon disulphide and thioacetylene complexes of ruthenium(II) although ruthenium(II) compounds such as [RuCl₃(AsPh₃)₂Cl₂]⁴⁹, [RuCl₂(AsPh₃)₃]⁵⁰, [RuCl₂(AsPh₃)₃]⁵¹, [RuCl₃(AsPh₃)₂]⁵¹ and [RuCl₃CS(PPh₃)₂]⁵² and [RuCl₃CS(PPh₃)₃]⁵² have recently been synthesised.

(d) Sodium Diphenylphosphinodithioate.—Reaction of [RuCl₃(AsPh₃)₂L] (L = Me₃OH or PhCH₂CN) with Na₃S₂PPh₃ in acetone produces the violet, crystalline compound [Ru₃S₄PPh₃]. The same compound is also prepared from Me₆N[RuBr₃(AsPh₃)₂2(Me₃CO)] (or 'Ru₃x₈H₂O') and Na₃S₂PPh₃. This compound is of interest in that its ¹H n.m.r. spectrum exhibits contact shifted ortho-, meta-, and para-protons at τ 3.45, 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(II) oxidation state. The corresponding [Ru₃S₄P(ECl)₃] is mentioned briefly, elsewhere,⁵⁵ but no preparative details have been given.

In contrast, reaction of [RuCl₃(AsPh₃)₂Me₃OH] with Na₃S₂PR₃ (R = Me or Et) gives the ruthenium(II) compounds trans-[Ru₃S₄PR₃(AsPh₃)₂]. The chemistry of these and related dithioacids of ruthenium(II) are discussed in detail elsewhere.⁵⁶

⁵⁵ T. A. Stephenson and E. S. Switkes, to be published.
⁵⁸ D. J. Cole-Hamilton and T. A. Stephenson, to be published.
Oxygen Ligands

If (A) is shaken in tetrahydrofuran (THF), displacement of methanol occurs and the compounds \([\text{Ru}(\text{EPh}_3)_2\text{MeOH}]\) 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.

\[\text{[RuX}_3\text{(AsPh}_3)\text{MeOH}]\] also loses the methanol group in CHCl\(_3\), CHCl\(_3\) or C\(_6\)H\(_6\) solution giving yellow-brown solutions. Addition of heptane gives brown solids, analysing closely for \([\text{RuX}_3\text{(AsPh}_3)\text{]}\), 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 \(v(\text{RuCl})\) 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 \([\text{RuCl}_6\text{(AsPh}_3)\text{MeOH}]\) in CHCl\(_3\) shows a 2 g value spectrum, \(g_1 = 2.52\), \(g_2 = 2.03\) in CHCl\(_3\) at 77 K, which indicates the presence of an axially symmetric complex such as (IX).

\[
\text{(IX)}
\]

The intensity of the e.s.r. signals, coupled with the normal magnetic moments found for the \([\text{RuX}_3\text{(EPh}_3)\text{MeOH}]\) compounds in both solid and solid 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. \([\text{RuCl}_6\text{(EPh}_3)\text{]}\) \((E = P, As)\) and the compounds \([\text{RuX}_3\text{(EPh}_3)\text{]}\) \((E = P, As)\) were mentioned by Vaska and Sloane \(^{58}\) but no preparative or other details about them are available.

In contrast, dissolution of \([\text{RuX}_3\text{(EPh}_3)\text{MeOH}]\) in acetone or nitromethane gives solvates which are surprisingly stable and which can be recrystallised without loss of solvent. The nitromethane compound \([\text{RuCl}_6\text{(PPh}_3)\text{MeNO}_3\text{]}\) is an excellent precursor for the synthesis of most of the chlorophosphate compounds reported in this paper. Its main advantage is the ease of preparation \textit{via} \(\text{AsPh}_3\[\text{RuCl}_4\text{(PPh}_3)\text{]}\) (which is prepared from \([\text{RuCl}_6\text{(PPh}_3)\text{]}\) \(^8\)). The methanol solvate can only be prepared in low yield (40%) and on a small scale from \(\text{RuCl}_6\text{H}_2\text{O} \) \((0.2 \text{g})\) and stoichiometric amounts of \(\text{PPh}_3\). Attempts to 'scale-up' this reaction (to 1.0 g of \(\text{RuCl}_6\text{H}_2\text{O} \)) gave only the reduced product \([\text{RuCl}_4\text{PPh}_3\text{]}\).


Carbon Donors

(a) \textit{Bicycle[2,2,1]hepta-2,5-diene} (Norbornadiene).—A number of ruthenium(II) diolefin compounds, such as \([\text{Ru}(\text{C}_7\text{H}_8\text{O})\text{]}\), \(^{60}\) \([\text{Ru}(\text{C}_7\text{H}_8\text{O})\text{]}\) \(^{55}\), and \([\text{Ru}(\text{C}_7\text{H}_8\text{O})\text{]}\) \(^{54}\), 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 \(\text{C}_7\text{H}_8\) in refluxing \(\text{CH}_2\text{Cl}_2\) produced no reaction. However, in refluxing benzene, crystallographic precipitates are obtained which analyse quite closely for \([\text{Ru}(\text{C}_7\text{H}_8\text{O})\text{]}\). For \(E = P\), the same compounds can be synthesised from \([\text{Ru}(\text{PPh}_3)\text{]}\) \(^{54}\) and \(\text{C}_7\text{H}_8\). Although the compounds are too insoluble for \(^{1}H\) n.m.r. studies, a careful examination of their far-i.r. spectra (Table 3) suggests that two \(v(\text{RuCl})\) vibrations occur at 278 and 253 cm\(^{-1}\) \((E = P)\). Thus, configuration (X) with \textit{trans}-chlorides is unlikely because of the low \(v(\text{RuCl})\) values. The other possibilities, i.e. where both chloride groups are \textit{trans} to the diene (XI) or where one chloride is \textit{trans} to the diene and the other is \textit{trans} to a phosphine (or arsine) (XII), cannot be distinguished on i.r. evidence alone, especially since earlier work \(^{55}\) indicates that olefins, tertiary phosphines, and arsines all have a similar \textit{trans} effect on \(v(\text{MC1})\) vibrations.

However, we have also prepared the corresponding \([\text{Ru}(\text{P}(\text{Me})\text{Ph}_2)\text{C}_7\text{H}_8\text{O}]\) \([\text{Ru}(\text{Cl})\text{]}\) \(277\) and 253 cm\(^{-1}\) \((E = P)\) and \(\text{PPh}_3\) and the \(^{1}H\) n.m.r. spectrum unequivocally shows \textit{trans}-\textit{PMe}_2\text{Ph}

\[\text{(XI)}\]

\[\text{(XII)}\]

The reaction of \([\text{RuCl}_4\text{(AsPh}_3)\text{MeOH}]\) with \(1,5\)-cyclo-octadiene in benzene gave only \([\text{RuCl}_4\text{(C}_7\text{H}_12)\text{]}\) \(^{60}\)}


\[\text{(XII)}\]
and attempts to prepare ethylene and diphenylacetylene complexes gave only \([\text{RuCl}_6(\text{AsPh}_3)_2]\).

(b) Carbon Monoxide.—The reaction of \([\text{RuCl}_6(\text{AsPh}_3)_2\text{MeOH})\] with carbon monoxide in dichloromethane results in the formation of a pale yellow, diamagnetic, monomeric solid which analyses for \(\text{trans-}[\text{RuCl}_4(\text{CO})_2(\text{AsPh}_3)_2]\) \((\nu(\text{CO}) 1993 \text{ cm}^{-1} \text{ (CH}_2\text{Cl}_2))\).

A similar product is obtained from \([\text{RuCl}_6(\text{PPh}_3)_2]\) \((\text{S = MeOH or MeNO}_2)\). This isomer \((E = P)\) has been prepared earlier \([\text{from RuCl}_6(\text{PPh}_3)_2\text{MeCN})\] \([\nu(\text{CN}) 334 \text{ cm}^{-1}]\). Recrystallisation of \((\text{XIII})\) from hot benzene gives the cis-isomer \([\nu(\text{CO}) 2061\) and 1999 cm\(^{-1}\)] whose far-i.r. spectrum \((E = P)\) shows \(\nu(\text{RuCl})\) bands at 300 and 275 cm\(^{-1}\) which is consistent with configuration \((\text{XIV})\) but not \((\text{XV})\). However, recrystallisation of \((\text{XIII})\)

\[(E = \text{As})\] from cold CH\(_2\text{Cl}_2\)-methanol solutions causes several carbonyl bands to develop. A band at 1943 cm\(^{-1}\) first appears and then the growth of further bands at 2036 and 1978 cm\(^{-1}\) occurs although the mixture still analyses for \([\text{RuCl}_6(\text{CO})_2(\text{AsPh}_3)_2]\). By analogy with the earlier \(\text{PPh}_3\) studies,\(^6^3\) the 1943 cm\(^{-1}\) band is assigned to the other trans-isomers \((\text{XVI})\) and the 2036, 1978 cm\(^{-1}\) bands to the cis-isomer \((\text{XVII})\). Similar results were found for \([\text{RuBr}_6(\text{CO})_2(\text{AsPh}_3)_2]\).

\[(\text{XVI})\]

\[(\text{XVII})\]

However, no evidence has been found for the formation of ruthenium(III) compounds such as the unknown \([\text{RuCl}_6(\text{AsPh}_3)_2\text{CO})\]. The compound \([\text{RuBr}_6(\text{PPh}_3)_2\text{CO})\] has been briefly reported\(^7\) but no further details are available.

The electronic spectra \((50 \text{ 000—12 000 cm}^{-1}\) 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 \(E = \text{P or As}\), 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 \([\text{RuX}_6]^{3-}\)

and various halogenobiopyridylruthenium(III) compounds.\(^6^5\) Hence, these can be assigned principally to \(X \rightarrow \text{Ru} \text{ charge transfer transitions.}\)

The more intense absorptions \(>30 000 \text{ cm}^{-1}\) 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 \([\text{cf. (Ru(NH}_3)_4\text{RCN})^{3+}\) with an absorption band at 31 500 cm\(^{-1}\) assigned to \(\text{RCN} \rightarrow \text{Ru charge transfer transitions})].\(^6^6\) 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 \((\text{model 115})\) at \(37^\circ\)C. i.r. spectra were recorded in the region \(4000—200 \text{ cm}^{-1}\) 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 \((\text{Evans’ method})\)\(^6^6\) were obtained on a Varian HA 100 spectrometer. Magnetic susceptibilities \((\text{solid})\) were measured on the Faraday balance at Newcastle University. E.s.r. measurements were performed on a Hiler & Watts ‘Microspin’ spectrometer operated at \(9-33 \text{ GHz}\) and employing \(100 \text{ kHz}\) 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-picryl-hydrazyl \((g = 2-0036)\) as reference. Conductivity measurements were made on a Portland Electronics conductivity bridge \((\text{model 310})\) and m.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

**Nitrogen Ligands**

(a) Nitrites.—Trichlorobis(triphenylarsine)\((\text{methyl cyanide})\)ruthenium(III). Trichlorobis(triphenylarsine)\((\text{methyl cyanide})\)ruthenium(III) \((9-10 \text{ g})\) was added to methyl cyanide \((5 \text{ ml})\) and the green suspension shaken for 1 h. The resulting dark green crystals were collected and recrystallised from \(\text{CH}_2\text{Cl}_2\)-pentane \((\text{Yield 76\% \ (\nu(\text{CN}) 2305 \text{ cm}^{-1})})\). Similarly, \([\text{RuBr}_6(\text{AsPh}_3)_2\text{MeCN})\] \((\nu(\text{CN}) 2310 \text{ cm}^{-1})\) was prepared and recrystallised \((78\%)\). The reaction of \([\text{RuCl}_6(\text{PPh}_3)_2\text{MeOH})\) with \(\text{MeCN}\) gave \([\text{RuCl}_6(\text{PPh}_3)_2\text{MeCN})\] \((\nu(\text{CN}) 2306 \text{ cm}^{-1})\) \((75\%)\) and the bromophenyl compound was similarly prepared \((\nu(\text{CN}) 2310 \text{ cm}^{-1})\) \((74\%)\).

Trichlorobis(triphenylarsine)\((\text{benzyl cyanide})\)ruthenium(III). \([\text{RuCl}_6(\text{AsPh}_3)_2\text{MeOH})\] \((3-0 \text{ g})\) was stirred for 24 h in dichloromethane \((40 \text{ ml})\) with an excess of benzyl cyanide \((1-0 \text{ ml})\) under nitrogen. The resulting green solution was reduced in volume and the addition of diethyl ether gave a green precipitate. Recrystallisation from \(\text{CH}_2\text{Cl}_2\)-heptane gave the bright green powder \((71\%) \ ((\nu(\text{CN}) 2300 \text{ cm}^{-1})\).


Trichlororuthenium(iii). As for [RuCl₃(AsPh₃)₂PhCN] except the reaction time was only 5 h. Recrystallisation from CHCl₃-pentane gave bright green microcrystals of the product (60%) [v(CN) 2310 cm⁻¹]. However, prolonged treatment gave cis-dichlorobis(triphenylphosphine)bis(benzyl cyanide)ruthenium(ii) as a crystalline pale green solid (yellow when powder) m.p. 168° (Found: C, 65-1; H, 4-1; N, 3-0). Calc. for C₃₈H₃₃Br₂N₄Ru: C, 73-1; H, 3-9; N, 7-9. The product is this same as that prepared from [RuCl₃(AsPh₃)₂] and benzyl cyanide. V [v(CN) 2260, 2243 cm⁻¹].

Trichlororuthenium(ii) chloride. [RuCl₃(AsPh₃)₂PhCN] (0-20 g) was dissolved in CHCl₃ (20 ml), an excess of phenyl cyanide 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 CHCl₃-pentane (71%) [v(CN) 2280 cm⁻¹]. The same product is obtained by stirring for 24 h. [RuBr₃(AsPh₃)₂PhCN] (70%) [v(CN) 2278 cm⁻¹] and [RuCl₃(PhCN)₃] (70%) [v(CN) 2280 cm⁻¹] were prepared by the same method. The corresponding [RuX₃(EPh₃)CH₂CHCN] were also prepared by this method [E = As, 75%; v(CN) 2305 cm⁻¹; E = P, 60%].

Pyridine. — Trichlororuthenylarsinobis(pyridine)ruthenium(iii). [RuCl₃(AsPh₃)₂MeOH] (0-20 g) and an excess of pyridine (0-4 ml) in CHCl₃ (10 ml) were gently refluxed for 5 min. Addition of light petroleum (p.b. 100—120°) gave an orange precipitate recrystallised from CHCl₃-pentane (58%). [RuBr₃(AsPh₃)(py)₂] and [RuX₃(PPh₃)(py)₂] were prepared in the same way (60%).

Trans-Dichlorotetakispyridinoruthenium(ii). [RuCl₃(AsPh₃)₂MeOH] (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.b. 100—120°) or CHCl₃-pentane, m.p. 270° (decomp.) (30%) (Found: C, 49-2; H, 4-1; N, 11-5%). The same compound was prepared from [RuCl₃(PPh₃)₃] and an excess of pyridine under the same conditions.

H N.m.r. (CDCl₃) τ 1-44(d), 2-40(t), 3-14(t) [C₆H₅N], and 2-6—2-9 (multiplet) [Ph₂P]. trans-[RuCl₂(py)₃]: τ 1-44(d) (the resonances at τ 2-40 and 2-90 are masked by those from [RuCl₃(PPh₃)(py)₂] (Found: C, 55-3; H, 4-3; N, 7-9. [RuCl₃(PPh₃)py] requires C, 59-1; H, 4-4; N, 6-3%).

(c) 2,2'-Bipyridyl. — Trichloro(bis(triphenylphosphine)(2,2'-bipyridyl)ruthenium(iii). [RuCl₃(AsPh₃)₂MeOH] (0-31 g) was stirred under nitrogen with a CHCl₃ solution (40 ml) containing an excess of 2,2'-bipyridyl (0-11 g). Concentration of the resulting dark red solution followed by heptane addition gave the brown product recrystallised from CHCl₃-heptane (80%). [RuBr₃(AsPh₃)(bipy)] and [RuCl₃(PPh₃)(bipy)] were similarly prepared (79%) and 90% yield respectively. The green solution was identified as the reduced species bis(triphenylphosphine)(2,2'-bipyridyl)ruthenium(ii). Dichloro(2,2'-bipyridyl)ruthenium(iii) dibromide m.p. 295—296° (Found: C, 57-6; H, 3-9; N, 3-9). C₃₈H₃₃Cl₂Br₄N₃Ru requires C, 58-6; H, 4-0; N, 3-40%. The same compound was also made from [RuBr₃(PPh₃)₃] (0-20 g) and 2,2'-bipyridyl (0-04 g) in CHCl₃ (15 ml) stirred under nitrogen for 30 min. [A (7 x 10⁻⁴m) in MeOH = 90 S cm⁻² mol⁻¹]. Similarly, [RuCl₃(PPh₃)(bipy)₂]Cl₂ was prepared from [RuCl₃(PPh₃)₃] and 2,2'-bipyridyl, m.p. 300° (Found: C, 63-7; H, 4-3; N, 3-2). Calc. for C₃₈H₃₃Cl₂N₃Ru: C, 64-0; H, 4-4; N, 3-2%. [A (7 x 10⁻⁴m) in MeOH = 88 S cm⁻² mol⁻¹].

Chloro(4,4'-dimethyl-2,2'-bipyridyl)ruthenium(iii) hydroxide. [RuCl₃(PPh₃)py] (0-10 g) was refluxed under nitrogen in methanol (100 ml) for 24 h with an excess of 2,2'-bipyridyl (0-04 g). Concentration of the resulting red solution and recrystallisation from acetone-pentane gave the orange product m.p. 235° (78%) (Found: C, 58-3; H, 4-3; N, 7-7. C₃₈H₃₃Cl₂N₃O₃Ru requires C, 59-7; H, 4-3; N, 7-7%). A (1 x 10⁻⁴m) in CHCl₃ = 29 S cm⁻² mol⁻¹). The same product was obtained from [RuCl₃(PPh₃)py] and an excess of bipyridyl in methanol (55%) (Found: C, 59-3; H, 4-3; N, 7-1%) together with some [RuCl₃(PPh₃)py]Cl₂ (35%).

The corresponding [RuCl₃(PPh₃)py]PF₆ was prepared from NH₄PF₆ and [RuCl₃(PPh₃)py]Cl₂. Refluxed in methanol m.p. 210° (Found: C, 51-9; H, 3-6; N, 6-5. C₃₈H₃₃Cl₂N₃O₃Ru requires C, 52-2; H, 3-5; N, 6-4%). Similarly [RuCl₃(PPh₃)(bipy)]BF₄, prepared m.p. 230° (Found: C, 73-1; H, 5-2; N, 5-5. C₃₈H₃₃BF₄N₃Ru requires 72-3; H, 4-9; N, 5-4%).

Chloro(2,2'-bipyridyl)ruthenium(iii) tetraphenylborate. [RuCl₃(AsPh₃)py] (0-10 g) was refluxed in methanol (100 ml) under nitrogen with an excess of sodium tetraphenylboron (0-10 g) and 2,2'-bipyridyl (0-04 g) for ca. 1 h. The resultant orange-red precipitate was filtered, well washed with water, light petroleum (p.b. 100—120°), and dried in vacuo at 40° (75%) (Found: C, 69-7; H, 4-6; N, 5-9. C₃₈H₃₃AsBF₄Ru requires C, 69-4; H, 4-7; N, 6-2%).

H [RuCl₃(AsPh₃)py] (0-30 g) was refluxed in methanol (24 ml) under nitrogen with an excess of 2,2'-bipyridyl (0-12 g) for 24 h, the resulting red solution contained a mixture of two compounds (t.l.c. evidence). The solvent
was removed and the residue washed with water leaving a purple material (20%) and an orange solution. The solution was concentrated almost to dryness 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 in m.p. > 300° (60%) [Found: C, 47.8; H, 4.2; N, 11.1. Calc. for C₃₃H₂₆(N₂O)₂Ru: C, 48.1; H, 4.8; N, 11.2%] [Λ (1 x 10⁴ m) in MeOH = 170 S cm² mol⁻¹]. The corresponding BF₄⁻ salt was also prepared [Ru(bpy)₃]BF₄ hexane, 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 in m.p. > 300° (Found: C, 45.7; H, 3.4; N, 10.2. Calc. for C₃₃H₂₂Cl₂N₂O₂Ru: C, 46.1; H, 3.8; N, 10.7%)] [Λ (6 x 10⁴ m) in CH₂Cl₂ = 7.0 ε cm⁻¹ mol⁻¹].

(d) 1,10-Phenanthrolines.—[RuX₂(Et₃P)₃(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-phenanthrolinato)ruthenium(II) chloride. [RuCl₃(PPh₃)(phen)] (10-9 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, 60.8; H, 3.7; N, 6.9. Calc. for C₃₃H₂₆Cl₄N₂P₃Ru requires C, 60.9; H, 3.7; N, 6.8%] [Λ(1 x 10⁴ m) in CH₂Cl₂ = 28.6 ε cm⁻¹ mol⁻¹]. The same product was obtained from the reaction of [RuCl₃(PPh₃)₂MeOH] and an excess of 1,10-phenanthroline in methanol (58%) together with some [RuCl₃PPh₃(phen)] (30%). When [RuCl₃(PPh₃)₂] and 1,10-phenanthroline were refluxed in methanol, [RuCl₃(PPh₃)₂(phen)]Cl (58%) and the yellow-brown powder [RuCl₃(PPh₃)₂(phen)]Cl were obtained, m.p. > 300° (25%) [Found: C, 64.8; H, 4.2; N, 3.1. Calc. for C₃₃H₂₈Cl₄N₂P₃Ru requires C, 64.7; H, 4.3; N, 3.1%] [Λ(7 x 10⁴ m) in MeOH = 11.5 ε cm⁻¹ mol⁻¹]. The latter compound was obtained in high yield (80%) by reaction of [RuCl₃(PPh₃)₂] and 1,10-phenanthroline in CH₂Cl₂.

Chloro(triphenylphosphine)bis(1,10-phenanthrolinato)ruthenium(II) hexafluorophosphate. A methanolic solution of [RuCl₃(PPh₃)₂(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. 213° (decomp.) (Found: C, 52.6; H, 3.4; N, 5.8. Calc. for C₃₃H₂₆F₆N₂P₃Ru requires C, 52.6; H, 3.4; N, 5.8%).

**Sulphur Ligands**

(a) Dimethyl Sulphoxide.—Trichlorobis(triphenylarsine)-
(dimethyl sulphonyl) ruthenium(III) [RuCl₃(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 (60%). I.r. spectrum (1350—1000 cm⁻¹) 1315m, (1190s, 1160w, 1080s, 1025s, 975s, 935m [v(δO)] 920s cm⁻¹. The same compound was prepared by shaking [RuCl₃(AsPh₃)₂MeOH] with neat dimethyl sulphonyl (DMSO) and filtering off the product after 5 min. A similar reaction with [H₂]dimethyl sulphonyl gave trichlorobis(triphenylarsine)((H₂)dimethyl sulphonyl) ruthenium(III). I.r. spectrum (1350—

800 cm⁻¹): [1190s, 1160w, 1080s, 1025s, 975m, [v(δO)] 850 cm⁻¹, [RuBr₃(AsPh₃)₂(dms)] and [RuX₃(PP₃)] were readily prepared from aqueous DMSO solutions by the method given above (ca. 70% yields).

**Dibromotetrasakis(dimethyl sulphonyl)ruthenium(II).** [RuBr₃(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 C₃₃H₂₆Br₂O₃AsRu₂: C, 16.7; H, 4.2; Br, 28.0; S, 22.3%]. I.r. spectrum (1350—750 cm⁻¹) 1304m, 1290w, 1080s [v(βO)] 1025vs, 978s, 942s cm⁻¹.

**Dibromotetrasakis(phenyl sulphonyl)ruthenium(II).** was prepared by the same method, m.p. 240° (decomp.) (80%) [Found: C, 17.6; D, 8.1; Br, 25.4. C₃₃H₂₅Br₂O₃AsRu₂ requires C, 16.0; D, 8.0; Br, 27.0%]. I.r. spectrum (1350—750 cm⁻¹) 1080vs, [v(βO)] 1020m, 1060m, 820s, 780m, 770s cm⁻¹.

(b) Dialkyl Sulphides.—Trichlorotriphenylarsinobis(dimethyl sulphide)ruthenium(III). [RuCl₃(AsPh₃)₂MeOH] (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%). [RuBr₃(Et₃P)₂(MeS)₂] (E = P or As) were obtained by the same method except longer reaction times (ca. 2 h) were needed for complete conversion (75%).

**Trichlorotriphenylphosphinobis(dimethyl sulphide)ruthenium(III)** was prepared as for the chloro-arsine compound, partial removal of solvent giving a dark green solid (32%). Concentration of the remaining red solution gave orange solids whose analyses and m.ps were variable, suggesting a mixture of [RuCl₃(Ph₃P)(MeS)₂] and [RuCl₃(PPh₃)₂(Ph₃S)₂]. However, reaction of [RuCl₃(PPh₃)₂] and an excess of Me₃S 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 dichlorotriphenylphosphinobis(dimethyl sulphide)ruthenium(II) [Found: C, 57.8; H, 4.6; Cl, 10-5. m, 986 (C₂H₄). C₃₃H₂₇Cl₂P₃Ru₂ requires C, 58.5; H, 5.1; Cl, 8.7%; M, 820]. H n.m.r.: phenyl multiplet (2.4—3.3); methyl singlet (8.8).**

**Trichlorobis(triphenylarsine)-(diethyl sulphide)ruthenium(III).** [RuCl₃(AsPh₃)₂MeOH] (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 [RuCl₃(AsPh₃)(Et₂S)]. [RuBr₃(AsPh₃)(Et₂S)] was similarly prepared (83%).

(c) Carbon Disulphide.—Trichlorobis(triphenylarsine)-(carbon disulphide)ruthenium(III). [RuCl₃(AsPh₃)₂MeOH] (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 Cl₂ group). [RuCl₃(PP₃)] was similarly prepared (70%).

**Tri bromobis(triphenylarsine)(thiocarbonylsulphur)ruthenium(III).** [RuBr₃(AsPh₃)₂MeOH] (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 (79%) (v (CS₂) 1295 cm⁻¹).

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

(d) Tris(diphenylphosphinothioato)ruthenium(II).* [RuCl₃(AsPh₃)₂MeOH] (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 an orange-red precipitate which was washed with water and diethyl ether, and dried in vacuo at 40°, m.p. 219—220° (Found: C, 50-5; H, 3-3. C₃₈H₃₈P₃RuS requires C, 50-9; H, 3-5%). The same compound is also prepared from [RuCl₂(AsPh₃)₂PhCH₂CN], Me₄N[RuBr₃(AsPh₃)₂] (acetone) or 'RuCl₂(AsPh₃)₃H₂O' and Na₂S₂P₂H₄.

Oxygen Ligands

(a) Tetrahydrofuran.—Trichlorobis(triphenylarsino) (tetrahydrofuran) ruthenium(t). [RuCl₃(AsPh₃)₂MeOH] (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 an orange-red precipitate which was washed with THF and air-dried (70%). The corresponding [RuBr₃(AsPh₃)₂(thf)] and [RuX₂(PPh₃)₂(thf)] were similarly prepared (ca. 65% yield).

(b) Acetone, nitromethane. The compounds [RuX₅(EPh₃)₅] (ν = acetone, MeNO₂) were prepared as for the THF adducts (see ref. 2 and 8) and for S = MeNO₂, from Ph₃As[RuX₅(EPh₃)₅] (acetone) (ref. 9).

Trichlorobis(triphenylarsino)ruthenium(II). [RuCl₃(AsPh₃)₂MeOH] 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).—Dichlorobis(triphenylarsino)(norbornadiene)ruthenium(t). [RuCl₂(AsPh₃)₂MeOH] (0.40 g) and an excess of C₇H₈ (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. 258—260° (Found: C, 57-8; H, 4-2; As, 16.4; Cl, 7-8. C₃₈H₃₈As₂Cl₂Ru requires C, 58-9; H, 4-4; As, 17-1; Cl, 8-1%). Similarly, [RuBr₂(AsPh₃)₂C₇H₈] was prepared (Found: C, 55-2; H, 4-0; As, 10-6; Br, 16-8. C₃₈H₃₈As₂Br₂Ru requires C, 53-5; H, 4-0; As, 10-5; Br, 16-6%). These compounds are very insoluble in all common solvents. [RuCl₃(PPh₃)₂C₇H₈] was prepared for the chloro-arsine compound from [RuCl₃(PPh₃)₂S] (S = MeOH or MeNO₂) and C₇H₈ m.p. 220° (60%) (Found: C, 65-6; H, 4-9. Calc. for C₃₈H₃₈Cl₂P₂Ru: C, 65-5; H, 4-8%) (see ref. 38). [RuBr₃(PPh₃)₂C₇H₈]*

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

C₇H₈ was similarly prepared (Found: C, 60-8; H, 4-9. C₃₈H₃₈Br₂P₂Ru requires C, 58-8; H, 4-4%). These compounds are also very insoluble in all common solvents.

Dichlorobis(dimethylphenylphosphino)(norbornadiene)ruthenium(t).—Ph₃BzPCl₂[RuCl₃CO(C₇H₈)] (0.20 g) was refluxed in CH₂Cl₂ (100 ml) under nitrogen with PMe₃Ph (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 Ph₃BzPCl and recrystallised from CH₂Cl₂-pentane, m.p. 247°. (Found: C, 51-0; H, 5-8, M(C₇H₈) 600. C₃₈H₃₈Cl₂P₂Ru requires C, 51-0: H, 5-5%; M, 520.) ¹H N.M.R. : δ = 6-70(2), 7-20(4), 8-50(2) [diene, 1:2:1 triplet].

Refluxing [RuCl₃(AsPh₃)₂MeOH] (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 [RuCl₃C₇H₈] (Found: C, 36-1; H, 4-3. Calc. for C₃₈H₃₈Cl₂Ru: C, 34-4; H, 4-3%) (see ref. 60).

(b) Carbon Monoxide.—trans-Dichlorodicyanobis(triphenylarsino)ruthenium(t) (Configuration XIII). Carbon monoxide was bubbled through an oxygen-free solution of [RuCl₃(AsPh₃)₂MeOH] (0-40 g) in CH₂Cl₂ (40 ml) for ca. 1 h. The solution was concentrated to dryness and the residue washed with acetone leaving a pale yellow solid, m.p. 230° (decomp.) (36%) (Found: C, 64-2; H, 3-6; Cl, 7-8; M(C₇H₈) 857. C₃₈H₃₈As₂Cl₂O₂Ru requires C, 54-2; H, 3-6; Cl, 8-4%; M, 814). ν(co) 2081v, 2036w, 1978v (Nujol) (assigned to configuration XVII) and ν(co) 1943 cm⁻¹ (Nujol) (assigned to configuration XVI). Similarly trans-[RuBr₃(CO)(AsPh₃)₂] (configuration XII) was prepared from [RuBr₃(AsPh₃)₂MeOH] m.p. 265° (decomp.) (60%) (Found: C, 48-8; H, 3-3. C₃₈H₃₈As₂Br₂Ru requires C, 49-1; H, 3-2%; ν(co) 1995 cm⁻¹ (CH₂Cl₂). Recrystallisation from CH₂Cl₂-methanol gave a mixture of isomers with ν(co) 2086, 1978 cm⁻¹ (Nujol) (assigned to configuration XVII) and ν(co) 1943 cm⁻¹ (Nujol) (assigned to configuration XVI). Similarly trans-[RuBr₃(CO)(AsPh₃)₂] (configuration XIII) was prepared from [RuBr₃(AsPh₃)₂MeOH] m.p. 265° (decomp.) (60%) (Found: C, 48-8; H, 3-3. C₃₈H₃₈As₂Br₂Ru requires C, 49-1; H, 3-2%; ν(co) 1995 cm⁻¹ (CH₂Cl₂). Recrystallisation from CH₂Cl₂-methanol gave a pinkish-tan product (Found: C, 49-0; H, 3-4%) with a number of carbonyl bands in the i.r. spectrum. ν(co) 2090v, 1980v cm⁻¹ (configuration XVII); 1940w (configuration XVI).
(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

Reprinted from JOURNAL OF THE CHEMICAL SOCIETY DALTONG TRANSACTIONS 1973
rhodium(i) diene complex \([\text{RhCl}(C_7H_8)(\text{PPh}_3)]\) (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 experiments 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 Ph₃(PPh₃)Cl 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 1

<table>
<thead>
<tr>
<th>(M = \text{PPh}_3(\text{PhCH}_2))</th>
<th>(M = \text{Cs}^+)</th>
<th>(\frac{X = \text{Cl}}{X = \text{Br}})</th>
<th>(X = \text{Cl})</th>
<th>Relative Fine</th>
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<td>4.78</td>
<td>4.89</td>
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<tr>
<td>5.48</td>
<td>6.02</td>
<td>2</td>
<td>Triplet (H(3)) and (H(6))</td>
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<tr>
<td>5.80</td>
<td>5.90</td>
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<td></td>
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<td>6.34</td>
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<td>8.71</td>
<td>8.78</td>
<td>8.20</td>
<td>2</td>
<td>Triplet (H(4))</td>
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</table>

\(^{a}\) See configuration (II). \(^{b}\) Measured in \(\text{CDCl}_3\). \(^{c}\) Measured in \(\text{D}_2\)O. \(^{d}\) \(J_{\text{Ph}} 14.0\) Hz. \(^{e}\) Shown by double-resonance experiments to be overlapping doublet of doublets.

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 experiments are also shown in Table 2.

### Table 2

<table>
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<tr>
<th>Irradiated at (\delta)</th>
<th>Resonance (\tau)</th>
<th>Assignment</th>
<th>Fine structure observed on irradiation</th>
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<td>6.34 H(4)</td>
<td>4.78</td>
<td>H(2), H(6)</td>
<td>Doublet</td>
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<tr>
<td>4.84 H(3)</td>
<td>3.00</td>
<td>H(1)</td>
<td>No change</td>
</tr>
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<td>5.80 H(1)</td>
<td>8.71</td>
<td>H(7), H(8)</td>
<td>Doublet</td>
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<tr>
<td>5.48 H(3) and H(5)</td>
<td>4.78</td>
<td>H(2), H(6)</td>
<td>Doublet</td>
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<tr>
<td>6.34 H(4)</td>
<td>6.34</td>
<td>H(2)</td>
<td>No change</td>
</tr>
<tr>
<td>5.80 H(2) and H(6)</td>
<td>5.48</td>
<td>H(3), H(5)</td>
<td>Doublet</td>
</tr>
</tbody>
</table>

| \(J_{\text{H(1)-H(2)}}\) = 1.25 Hz; \(J_{\text{H(2)-H(3)}}\) = 1.50 Hz; \(J_{\text{H(4)-H(6)}}\) = 1.90 Hz; \(J_{\text{H(6)-H(7)}}\) = \(J_{\text{H(5)-H(6)}}\) = 3.90 Hz. |

undergoing neither ligand exchange, isomerisation, nor oxidation 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 Ph₃(PPh₃)PCI and CsCl, the only product isolated was the acetone-insoluble \([\text{RuCl}_2\text{CO}(C_7H_8)]\). However, with Ph₃AsCl-HCl, reaction with \([\text{RuCl}_2\text{CO}(C_7H_8)]\), 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.r. and analytical evidence) under, ostensibly, the same reaction conditions.*

If, however, Ph₃AsCl-HCl and \([\text{RuCl}_2\text{CO}(C_7H_8)]\), were gently heated under reflux in acetone for ca. 1 h, a single product was obtained which analysed closely for cis-(Ph₃As)₂RuCl₂(CO)₂. In support of this formulation, the complex has a conductivity in dichloromethane characteristic of a 2:1 electrolyte \([\alpha(0.01\text{M}) 40 \Omega \text{cm}^2 \text{mol}^{-1}\] and its i.r. spectrum shows two v(CO) bands at 2 030 and 1 940 cm⁻¹ (Nujol), very close to those reported earlier for cis-C₅H₅[RuCl₂(CO)] [\(v(CO) 2 036\) and 1 935 cm⁻¹]. 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 is recommended.

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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⁺) or from some intramolecular rearrangement process. It is of interest that Robinson and Wilkinson also isolated a dicarbonyl complex, trans-[RuCl₂(CO)₂(quinoline)₂] by reaction of [RuCl₂CO(C₇H₈)]ₙ 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.

Benzylic(triphenyl)phosphonium (Bicyclo[2.2.1]hepta-2,5-diene)carbonyltrichlororuthenate(n).—A suspension of the complex [RuCl₂CO(C₇H₈)]ₙ (ref. 6) (0-40 g) was shaken in degassed acetone (50 cm³) for 5 days with an excess of benzylic(triphenyl)phosphonium chloride (1·10 g) and concentrated hydrochloric acid (0·50 cm³). The resulting orange solid was filtered, washed free of acid and excess of benzylic(triphenyl)phosphonium chloride with warm water, then with acetone, and recrystallised from dichloromethane-heptane (82%); m.p. 177—180 °C (Found: C, 57·8; H, 4·4; Cl, 15·8; O, 2·5; P, 4·7). Calc. for C₃₅H₃₀Cl₃OPRu: C, 58·2; H, 4·5; Cl, 15·6; O, 2·4; P, 4·6%. A(0·001m) 16·5 Ω cm² mol⁻¹ in CH₂Cl₂. Far i.r. spectrum (400—200 cm⁻¹): 385m; 350w; 330m; 314w; 303w; 281vs; 269w; 255w; 248; and 260s cm⁻¹.

Benzylic(triphenyl)phosphonium (Bicyclo[2.2.1]hepta-2,5-diene)tritromocarbonyltrichlororuthenate(n).—The salt Ph₂(PhCl₃)₆[RuCl₂CO(C₇H₈)] (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 acetone—diethyl ether addition then gave a brown microcrystalline solid (65%); m.p. 162 °C (Found: C, 48·4; H, 3·6; Br, 29·7. Calc. for Cs₂H₃₅Br₃OPRu: C, 48·7; H, 3·6; Br, 29·5%). A(0·001m) 25·4 Ω cm² mol⁻¹ in CH₂Cl₂. Far i.r. spectrum (400—200 cm⁻¹): 385m; 350w; 330m; 318w; 303m; 281vs; 269w; 255w; 248; and 260s cm⁻¹.

Caesium (Bicyclo[2.2.1]hepta-2,5-diene)carbonyltrichlororuthenate(n).—A suspension of the complex [RuCl₂CO(C₇H₈)]ₙ (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. 270 °C (decomp.) (Found: C, 21·2; H, 1·8; Cl, 22·8; O, 3·4. Calc. for Cs₃H₅₃Cl₄O₂Ru: C, 20·9; H, 1·8; Cl, 23·1; O, 3·5%). A(0·001m) 87·2 Ω cm² mol⁻¹ in methanol. Far i.r. spectrum (400—200 cm⁻¹): 326m; 280s; and 260s cm⁻¹.

Bis(tetraphenyl arsonium) cis-Dicarbonyltetrachlororuthenate(n).—The complex [RuCl₂CO(C₇H₈)]ₙ (0·23 g) was heated under reflux gently, under an atmosphere of nitrogen, in degassed acetone (50 cm³) with an excess of Ph₄AsCl-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 excess Ph₄AsCl 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 Cs₅H₆₃As₂Cl₄O₂Ru: C, 56·3; H, 3·7; Cl, 13·3%).

We thank Johnson, Matthey Ltd. for loans of ruthenium trichloride, and the National Institutes of Health (E. S. S.) and the National A. University of Mexico (L. R. R.) for fellowships.

[3/352 Received, 15th February, 1973]

New Thiocarbonyl Complexes of Ruthenium

By T. Anthony Stephenson,* Ellen S. Switkes, and (in part) Peter W. Armit, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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DALTON TRANSACTIONS

1974
New Thiocarbonyl Complexes of Ruthenium

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There are now a large number of publications discussing syntheses and characterisation of neutral complexes of ruthenium(II), 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(II) complexes containing these types of ligand. However, relatively few anionic ruthenium(II) complexes of this type have been prepared other than those containing nitrosyl, and more recently, carbonyl groups, e.g.\[ [RuCl_4(CO)_2]^{-}\] and \[ [RuCl_4(CO)]^{-}\] (\( X = \text{Cl, Br, or I} \)). In particular, only a few papers on anionic tertiary phosphine (or phosphite) complexes of ruthenium(II) appear to have been published, none of which involve 'conventional' methods of preparation; e.g. the well known complex \[ [RuCl_4L_4]^{-}\] on heating in methyl acetate at 60°C, gives \[ [RuCl_3L_3]^{-}\] (L = P(Et_2)Ph)). Similar diamagnetic complexes have been reported for the ligands L = P(OEt)_3, P(OMe)Ph_2, and P(OEt)_2Ph, obtained by direct reaction of RuCl_4 with L (although the authors inadvertently formulated them as \[ [RuCl_4L_2]^{-}\] anions, which would be paramagnetic). A recent note given results of a reinvestigation of the reaction between the complex \[ [RuCl_4(CO)]^{-}\] and methyl iodide which, instead of \[ [RuCl_4(PPh_3)I(Me)]^{-}\), gives \[ [RuCl_3PPh_3]^{-}\]. The same anionic complex could be made from \[ [RuCl_4(CO)]^{-}\] and methyl iodide.

Several years ago, one of us reported that a convenient synthesis of the ruthenium(III) anions \[ [RuCl_4L_2]^{-}\] (\( X = \text{Cl or Br; L = PPh_3, AsPh_3, etc.} \)) was through the use of this type of reaction to synthesise the first anionic ruthenium diene complexes \[ [RuX_2(CO)(C_5H_8)]^{-}\] (\( X = \text{Cl or Br; C_5H_8 = bicyclo[2.2.1]hepta-2,5-diene} \) via \[ [RuX_2(CO)]^{-}\])\[ [RuCl_4(CO)]^{-}\] \[ [RuCl_4(CO)(C_5H_8)]^{-}\] \[ [RuCl_4(CO)]^{-}\] \[ [RuCl_4(CO)(C_5H_8)]^{-}\]. These complexes are very useful precursors for the preparation of a range of new anionic complexes of type \[ [RuCl_4CO]^{-}\] (\( L = \text{AsPh_3, SbPh_3, py, Me_2S, CH_2CHCN, etc.} \)), although, to date, attempts to prepare tertiary phosphine anions by this method have been unsuccessful; instead complexes such as...
as [RuCl₂(CO)(PPh₃)₂] and [RuCl₂(PMe₂Ph)₂(C₇H₈)] are preferentially formed. However, another halide-bridged dimer already containing triphenylphosphine groups is [RuCl₂(CS)(PPh₃)₂]₂ (I), prepared by Gilbert et al. from [RuCl₂(PPh₃)₃] and CS₂. In the present paper, reactions of complex (I) with halide ion are described, together with results of a careful re-investigation of the [RuCl₂(PPh₃)₂]-CS₂ reaction. A preliminary account of the first part of this work has been presented elsewhere.

RESULTS AND DISCUSSION

In accordance with the method of Gilbert et al., the complex [RuCl₂(PPh₃)₃] in carbon disulphide was heated under reflux with 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(PPh₃)₂]Cl (ca. 8% yield). 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 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]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 (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 Ph₄AsCl·HCl for several days, slow conversion to a red crystalline precipitate of Ph₄As[RuCl₂(CS)(PPh₃)₂]Cl·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 thio-carbonyl band at 1272 cm⁻¹ (Nujol). Although they are not sufficiently soluble for either H or ³¹P n.m.r. studies, the presence of a strong i.r. band at 320 cm⁻¹ is characteristic of a trans-RuCl₂ arrangement, consistent with either structure (IIa) or (IIb).

At this juncture, the only discrepancy with the work of Gilbert 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]Cl (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); ³¹P n.m.r. studies revealed that (I) and (III) had quite different spectra and, finally, reaction of (III) and Ph₄AsCl·HCl did not give Ph₄As[RuCl₂(CS)(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 (³¹P n.m.r. evidence) and were readily separated by a few minutes shaking in degassed acetone.

By means of the liquid-diffusion method 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, has unequivocally established that

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


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complex (III) has the molecular composition \([\text{PPh}_3]_2\text{RuCl}_3\text{Ru}([\text{CS}])\text{PPh}_3\), i.e. a tri-\(\mu\)-chloro-complex with one \(\text{CS}\) 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 \(\text{C}_6\text{H}_5\)-\(\text{C}_6\text{D}_4\) 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 \(\text{CDCl}_3\), 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 trans-form favoured in benzene and the 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 \(\text{CDCl}_3\) suggests that this quartet arises from the \text{PPh}_3 groups numbered (3) and (4) which are cis to the thiocarbonyl group.

Complex (III) represents another example of the increasing number of ruthenium complexes which contain a RuCl\(_3\)Ru bridging unit. Earlier examples are \([\text{L}_2\text{RuCl}_3\text{RuL}_2]\text{Cl} (\text{L} = \text{PET}_{2}\text{Ph}, \text{etc.})\)\(^7\) (although this structure has not been verified by X-ray analysis), \([\text{RuCl}_3\text{RuL}_2]\text{Cl} (\text{L} = \text{PET}_{2}\text{Ph}),\text{R}_{\text{PET}_{2}\text{Ph}}\text{ClRuCl}_3\text{Ru}[\text{PET}_{2}\text{Ph}]_2\text{Cl}\) made by heating \([\text{RuCl}_3(\text{PET}_{2}\text{Ph})_2]\text{Cl}\) in methyl acetate at 120 °C,\(^{25}\) and the paramagnetic \((\text{PBu}_3)_2\text{ClRuCl}_3\text{RuClPBu}_3)\text{Cl}\) made from RuCl\(_3\) and PBu\(_3\).\(^{27}\) A very recent example is the complex \([\text{PPh}_3]_2\text{ClRuCl}_3\text{Ru}[\text{N}_2\text{B}_{10}\text{H}_8\text{SMe}_2])\text{PPh}_3\) made from \([\text{RuCl}_3(\text{PPh}_3)_2]\text{Cl}\) and molecular nitrogen by the novel technique of reverse osmosis,\(^{28}\) and closely related examples are \([\text{PPh}_3]_2\text{ClRuCl}_3\text{Ru}[\text{N}_2\text{B}_{10}\text{H}_8\text{SMe}_2])\text{PPh}_3\) and \([\text{CO}_2\text{SnCl}_3]\text{RuCl}_3\text{RuCl}[\text{CO}_3]\) made from Ru\(_3\)(CO)\(_{12}\) and SnCl\(_3\).\(^{30}\) Details of the structural relations of (III) to these complexes are presented in the following paper.\(^{25}\)

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 [equation (2)]. A related rearrangement reaction has been reported by Kang and Maitlis [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 \text{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 goldenes


yellow crystals were deposited. The i.r. spectrum of this material showed evidence of solvent acetone, thiacarbonyl [ν(CS) 1 900 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)₂ClRuCl₃Ru(CO)(PPh₃)₂]Me₂CO, (IV). The 3¹P n.m.r. spectrum of complex (IV) in CDCl₃ consists 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 35-5 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 ε 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 [RuCl₂(PPh₃)₃] or [RuCl₂(CS)]⁻.

* Note added in proof: These assignments are supported by the 3¹P n.m.r. spectrum in CDCl₃ at 298 K of the isomorphous [(PPh₃)₂ClRuCl₂Ru(CO)(PPh₃)₂]Me₂CO complex which has two AB quartets centred at 48-0 and 40-3 p.p.m.

(PPh₃)₃Cl. A speculative mechanism could involve elimination of P₃Cl₃ from the cationic complex (as demonstrated in ref. 20) with formation of the complex [RuCl₂(CS)(PPh₃)₃]. This five-co-ordinate species might then undergo dimerisation to give complex (I) or combine with unreacted 'RuCl₂(PPh₃)₂' to give (III). Such a mechanism (which is difficult to prove, particularly for these thiacarbonyl complexes) might explain why complex (III) was not observed by earlier workers. A similar mechanism involving intermediates such as [RuCl₂(N₂)(PPh₃)] and 'RuCl₂(PPh₃)₂' could also be invoked to explain formation of the complex [(PPh₃)₂ClRuCl₂Ru(N₂)(PPh₃)] from [RuCl₂(PPh₃)₃] and molecular nitrogen.

Finally, although (III) does not react with Ph₃AsCl,HCl to give a ruthenium(II) anionic complex, it does react slowly in acetone with concentrated hydrochloric acid to give a sparingly soluble orange-brown solid. This material is sharp melting (254 °C), non-conducting (CH₂Cl₂), and its i.r. spectrum was very similar to that of complex (III), except for ν(CS) at 1 303 and 1 297 cm⁻¹ and small differences in the far-i.r. region. However, the complex is paramagnetic (strong e.s.r. signals) and analysed closely (C, H, and Cl) for [(PPh₃)₂ClRuCl₂Ru(CS)(PPh₃)]₂Me₂CO, (V). This formulation is supported by the magnetic moment of 2-00 B.M. per dimer, obtained on a Faraday balance at 292 K [cf. ([PPh₃]₃ClRuCl₂RuCl₂[PBu₃]₃)₂ with μeff = 1-50 B.M. per dimer, and the formation of complex (V) from (III) is readily explained by invoking intermolecular displacement of a PPh₃ group by chloride ion.

It is hoped that current work on the reaction of other [RuX₄(PPh₃)]₃ (X = Cl or Br; PR₃ = PPh₃, PEt₃, Ph, 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 4 000—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 XL-100 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)₂ClRuCl₂Ru(CO)(PPh₃)]₂Me₂CO from reaction of [RuCl₂(CS)(PPh₃)]₂(dmf) and [RuCl₂(PPh₃)₃] (1:1 mole ratio) in acetone dmf = N,N-dimethylformamide.

were measured by Faraday (solid) and Evans' n.m.r. methods (solution). Conductivity measurements were obtained on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

Ruthenium(III) trichloride trihydrate (Johnson, Matthey Ltd), carbon disulphide (Fisons), tetraphenylarsonium chloride-hydrochloride (Koch-Light), tetraethylammonium chloride (B.D.H.), and benzyldiarylphosphinophenium chloride (Alfa Inorganics) were obtained as indicated. The complex [RuCl(CPPh3)3] was prepared as described earlier.[2]

Reaction of Dichlorotris(triphenylphosphine)ruthenium(II) with Carbon Disulphide.—The complex [RuCl(CPPh3)3] (0-19 g) was heated under reflux for 5 min in degassed CS2 (30 cm³) 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 CS2 of solvation [v(CS2) at 1515 cm⁻¹] but this was removed by gentle suction. The product was then identical (i.r. spectrum and analysis) to that reported earlier, i.e. [RuCl(CS2)(CPPh3)3]Cl (Found: C, 64-0; H, 4-2. Calc. for C24H36Cl2P3RuCl: C, 63-8; H, 4-4%).

The remaining red solution was concentrated on a rotary evaporator to ca. 5 cm³ and then treated with excess of diethyl ether to give a microcrystalline purple-red solid and a red solution. The solid was washed with degassed acetone 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(CS2)(CPPh3)3]Cl (i.r. evidence). Removal of benzene, followed by washing with diethyl ether, then gave di-μ-chloro-bis[chloro(triphenylphosphine)bis(triphenylphosphine)ruthenium(II), (I) (0-024 g, 16%), m.p. 165—166°C (decomp.), v(CS) at 1290 cm⁻¹ (Found: C, 60-3; H, 4-2; Cl, 9-3; P, 8-7; S, 4-2. M(m(C6H6)) 974. Calc. for C51H41ClP3Ru3S2: C, 60-0; H, 4-1; Cl, 9-5; P, 8-4; S, 4-3%. M 1480). This complex is completely soluble in benzene, dichloromethane, chloroform, and acetone, but rapidly oxidises in the latter giving a greenish brown solution. As reported earlier,[9] it appears stable to oxidation in the other solvents. The complex is non-conducting in dichloromethane and diamagnetic. 3P N.m.r. spectrum: (C6H6-C6D6) 24-4 (singlet) (s); 31-3 (singlet) (w); (CDCl3) 31-3 (singlet) p.p.m. I.r. spectrum (400—250 cm⁻¹) (Nujol): 330—3200 cm⁻¹; 260w cm⁻¹.

Removing the diethyl ether immediately from the remaining red solution and then adding excess of light petroleum (b.p. 60—80°C) gave a further pinkish red precipitate which, after washing well with acetone to remove any of the complex [RuCl(CS2)(CPPh3)3]Cl, left tris-μ-chloro-bis[chloro(triphenylphosphine)bis(triphenylphosphine)ruthenium(II)][thiocarbonylbis(triphenylphosphine)ruthenium(II)](I), [III] (0-057, 39%), m.p. 167—168°C, v(CS) at 1284 cm⁻¹ (Found: C, 60-7; H, 4-3; Cl, 9-4; P, 8-5; S, 2-3. M (in C6H6) 1423. Calc. for C51H41ClP3Ru3S2: C, 61-0; H, 4-2; Cl, 9-9; P, 8-6; S, 2-2%. M 1436). The same complex separated out in smaller yield when the diethyl ether solution was set aside for a few minutes. This complex is also completely soluble in benzene, dichloromethane, and chloroform, but only slightly soluble in acetone. Although the complex is quite stable in acetone suspension, it is rapidly oxidised in benzene and the other solvents. The complex is non-conducting (CH2Cl2) and diamagnetic. 3P N.m.r. spectrum: (C6H6-C6D6) 48-8 (quartet); 35-2 (quartet) (JPP, 38-1, JPP, 24-4, JPP, 124-9, JPP, 43-8); (CDCl3) 48-3 (quartet); 38-1 (quartet) p.p.m., JPP, 37-4. JPP, 24-6. δP, 94-0. δP, 54-9 Hz. I.r. spectrum (400—250 cm⁻¹) (Nujol): 318s; 368m; and 260m cm⁻¹.

The same products were also obtained by treating the initial CS2 solution (after filtering off [RuCl(η-CS2)(CPPh3)3]Cl) with light petroleum (b.p. 60—80°C). In this instance, both thiocarbonyl complexes were immediately precipitated and were separated by shaking with degassed acetone for 10—15 min. Under these conditions, complex (III) separates out with an acetone molecule of solvation [v(CO) at 1705, v(CC) at 1221 cm⁻¹] which can be removed by prolonged pumping at room temperature.

Finally, the relative percentages of the complexes [RuCl(η-CS2)(CPPh3)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 η-CS2 and mono(CS) complexes increase with time, whereas that of the bis(CS) complex decreases with time.

Preparations.— Tri-μ-chloro-μ-chloro(thiocarbonyl)(triphenylphosphine)ruthenium(II) [thiocarbonylbis(triphenylphosphine)ruthenate(II)]—acetone (1/1), (IV). Complex (I) was shaken in degassed acetone for several days to give a very small amount of golden-yellow crystals, m.p. 264°C (v(CS) at 1300, v(CO) at 1700 cm⁻¹) (Found: C, 53-5; H, 8-7. Calc. for C24H36Cl2P3Ru3S: C, 52-5; H, 3-7%).

1H N.m.r. spectrum (CDCl3): 2-9. Phenyl (phenyl). 7-9 (acetone). 13P N.m.r. spectrum (CDCl3): 48-1 (singlet), 37-7 (broad) [isomer (IVA)]; 50-2 (singlet), 35-5 p.p.m. (doublet) [isomer (IVB)]. I.r. spectrum (400—250 cm⁻¹) (Nujol): 3268s, and 259m cm⁻¹.

Tri-μ-chloro-μ-chloro(thiocarbonyl)(triphenylphosphine)ruthenium(III) [thiocarbonylbis(triphenylphosphine)ruthenate(II)]—acetone (1/2), (V). The acetone solvate of complex (III) (0-12 g) was suspended in degassed acetone (18 cm³) and shaken with concentrated hydrochloric acid (3-0 mol L⁻¹) for several days. The resulting orange-brown solid was then filtered off and washed with water, acetone, and light petroleum (b.p. 60—80°C) (0-07 g, 66%), m.p. 234°C (v(CS) at 1303, v(CO) at 1710, and v(CC) at 1233 cm⁻¹) (Found: C, 55-2; H, 4-2; Cl, 12-8. Calc. for C34H36Cl2O2P3Ru3S: C, 55-2; H, 4-3; Cl, 13-4%). The complex is sparingly soluble in CH2Cl2, non-conducting, gives strong e.s.r. signals (g = 2, 43, g = 1-75), and has a magnetic moment of 2-90 B.M. per dimer at 202 K (solid). I.r. spectrum (400—250 cm⁻¹) (Nujol): 339vs, 286m; and 260m cm⁻¹. The same complex was obtained using a mixture of Ph3AsCl, HCl and H2O.

Tetraphenylarsonium trichloro(thiocarbonylbis(triphenylphosphine)ruthenate(II))—acetone (1/2). Complex (I) (0-01 g) was dissolved in degassed acetone (60 cm³) and shaken with excess of Ph3AsCl, HCl (1/2 g) under an atmosphere of nitrogen for 5 days. The red crystals which formed were collected, washed with small amounts of ethanol and pentane, and dried in vacuo (40°C), m.p. 180—183°C, v(CS) at 1727, and v(CC) at 1712 cm⁻¹ (Found: C, 62-8; H, 4-7; S, 2-6. Calc. for C47H42AsClO2P3Ru3S: C, 63-1; H, 4-9; S, 2-5%). (10×10 mm) in CH2Cl2 = 34-8 Ω cm⁻¹ mol⁻¹.

Benzyldiarylphosphinophenium trichloro(thiocarbonylbis(triphenylphosphine)ruthenate(II)). Complex (I) (0-02 g) was dissolved in degassed acetone (60 cm³) and shaken with excess of Ph3PCl, CH2Cl2 (1-5 g) and concentrated hydrochloric acid (0-30 mol L⁻¹) for 5 days under an atmosphere of nitrogen for 5 days.
nitrogen. The red precipitate was then collected and washed with small amounts of acidified acetone to remove Ph₃PhCH₂PCl, then with acetone and pentane, m.p. 190-195 °C, ν(CS) at 1,272 cm⁻¹ (Found: C, 66.4; H, 4.7. Calc. for C₆₂H₅₂Cl₃P₃RuS: C, 65.9; H, 4.7%) [λ(10⁻⁴m) in CH₂Cl₂ = 20.1 cm² mol⁻¹].

**Tetraethylammonium trichlorothiocarbonyl bis(triphenylphosphine)ruthenate(II).** This complex was prepared as above using excess of Et₄NCl and a small amount of conc. HCl (Found: C, 58.1; H, 5.1; N, 1.9. Calc. for C₄₅H₃₉Cl₃NP₃RuS: C, 59.6; H, 5.6; N, 1.6%).

We thank Johnson, Matthey Ltd., for generous loans of ruthenium(III) 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 ³¹P n.m.r. spectra, and the Universities of Newcastle and Dundee, for use of their Faraday balances.

[3/2526 Received, 12th December, 1973]
SYNTHESSES OF DI- AND TRI-\(\mu\)-HALIDE COMPLEXES OF RUTHENIUM(II)-CONTAINING CARBONYL AND TERTIARY PHOSPHINE LIGANDS

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(Received May 2nd, 1974)

We have recently shown that the reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\) and carbon disulphide gives, in addition to the previously reported [1] di-\(\mu\)-chloro complex \([\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2]_2\) (I) and the \(\eta\)-CS\(_2\) cation \([\text{RuCl}(\eta\text{-CS}_2)(\text{PPh}_3)_3]\text{Cl}\) (II), the tri-\(\mu\)-chloro complex \([\text{PPh}_3]_2\text{ClRuCl}_3\text{Ru}(\text{CS})(\text{PPh}_3)_2]\) (III) which has been characterised by X-ray analysis [2] and \(^{31}\text{P}\) 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.

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\begin{align*}
\text{[} & \begin{array}{c}
\text{Ph}_3\text{P} \\
\text{Cl} \\
\text{CS} \\
\text{Cl} \\
\text{Ru} \\
\text{Ph}_3\text{P}
\end{array} & \begin{array}{c}
\text{Cl} \\
\text{CS} \\
\text{PPh}_3
\end{array} & \begin{array}{c}
\text{PPh}_3
\end{array} \\
\text{Ph}_3\text{P} & \text{Cl} & \text{CS} & \text{PPh}_3
\end{align*}
\xrightarrow{\Delta}\begin{align*}
\text{[} & \begin{array}{c}
\text{Cl} \\
\text{Ru} \\
\text{Cl} \\
\text{Ru} \\
\text{PPh}_3
\end{array} & \begin{array}{c}
\text{Cl} \\
\text{CS} \\
\text{PPh}_3
\end{array} & \begin{array}{c}
\text{PPh}_3
\end{array} \\
\text{PPh}_3 & \text{Cl} & \text{CS} & \text{PPh}_3
\end{align*} + \text{CS}
\]

(1)

Therefore, a speculative mechanism was suggested which involved formation of \([\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2]\) (probably via abstraction of \text{Ph}_3\text{PS} from (II)) and then, either dimerisation of this five coordinate intermediate to give (I) or combination with some unreacted \([\text{RuCl}_2(\text{PPh}_3)_3]\)* 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 \([\text{RuCl}_2\text{CO}(\text{PPh}_3)_2\text{dmf}]\) (\(\nu(\text{CO})\) 1911 cm\(^{-1}\); \text{dmf} = \(N,N'\)-dimethylformamide) [4] is gently refluxed in dichloromethane,

*Recent \(^{31}\text{P}\) 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 \([\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2]\) \(_2\) (I, \(Y = \text{CO}\)) \(\nu(\text{CO})\) 1960 (br) cm\(^{-1}\)) whereas if the dmf complex is refluxed with \([\text{RuCl}_2-(\text{PPh}_3)_3]\) in acetone (1/1 molar ratio), red crystals of the tri-\(\mu\)-chloro complex \([(\text{PPh}_3)_2\text{ClRuCl}_3\text{Ru(PO)(PPh}_3)_2]\) (III, \(Y = \text{CO}\)) \(\nu(\text{CO})\) 1951 cm\(^{-1}\)) are formed. This latter compound is isomorphous with the corresponding thiocarbonyl complex and the \(^{31}\text{P}\) proton decoupled NMR spectra in CDCl\(_3\) which consists of two AB quartets centred at 48.0* and 40.3 ppm. \((Y = \text{CO})\) and 48.3 and 36.1 ppm \((Y = \text{CS})\) respectively confirm that the same structure is retained in solution.

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

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 \(^{31}\text{P}\) NMR spectra.

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

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

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Reprinted from JOURNAL OF THE CHEMICAL SOCIETY DALTON TRANSACTIONS 1974
Reaction of Benzyltriphenylphosphonium Bicyclo[2.2.1]hepta-2,5-diene-carbonyltrichlororuthenate(II) with Lewis Bases

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A detailed investigation of the reactions of the salt [Ph₃(PhCH₂)P][RuCl₃(CO)(C₇H₈)] (I; C₇H₈ = bicyclo[2.2.1]hepta-2,5-diene) with ligands (L) containing Group Va or Vi donor atoms is presented. Several different types of behaviour are found, depending on both the nature and amount of added L. For L = Me₂S, Me₂SO, and CH₂=CH-CN, the salts [Ph₃(PhCH₂)P][RuCl₂(CO)₂L], (II), have been isolated in high yield, whereas for L = AsPh₃, SbPh₃, and C₅H₅N, a mixture of (II) and [RuCl₂(CO)L(C₇H₈)], (III), have been obtained ([I]: L = 1:2 molar ratio).

Reaction of complex (I) with excess of SbPh₃ gives (II), (III), and [RuCl₂(CO)(SbPh₃)₂], (IV). In contrast, reaction of complex (I) with PPh₃ (1:2 molar ratio) gives [RuCl₂(CO)(PPh₃)₂], (V), whereas with PMe₂Ph, only [RuCl₂(PMe₂Ph)₂(C₇H₈)], (VI), is isolated. A similar complex of type (VI) is formed with PMePh₂, together with some [RuCl₂(CO)(PMePh₂)₂], (IV), whilst with 2,2'-bipyridyl or 1,10-phenanthroline (L'), the complexes [RuCl₂(CO)(L')₂], (VII), and [Ph₃(PhCH₂)P][RuCl₂CO(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), M[RuX₃(CO)(C₇H₈)] (M = Ph₃(PhCH₂)P⁺ or Cs⁺; X = Cl or Br; C₇H₈ = γ-bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)).

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(III) complexes with ligands containing Group VB and VIB donor atoms, we have undertaken a detailed study of the reactions of \([\text{Ph}_3\text{PPh}_2\text{Cl}]\) [RuCl\(_4\)(CO)](C\(_2\)H\(_4\)), (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 \([\text{Ph}_3\text{PPh}_2\text{Cl}]\) [RuCl\(_4\)(CO)](C\(_2\)H\(_4\)), (I), was dissolved in dichloromethane and heated under reflux under a nitrogen atmosphere with either Me\(_2\)S, Me\(_2\)SO, or CH\(_2\)=CH-CN [(I) : L = 1 : 2 molar ratio] for ca. 12 h, complete displacement of the diene group occurred and yellow or orange crystalline complexes \([\text{Ph}_3\text{PPh}_2\text{Cl}]\) [RuCl\(_4\)(CO)L\(_2\)], (II), were isolated from the reaction mixture

\[
\begin{align*}
\text{CO} & \quad \text{Ru} \quad \text{Cl} \\
\text{(I)} & \quad \text{Me}_2\text{S} & \text{Me}_2\text{SO} & \text{CH}_2\text{=CH-CN}
\end{align*}
\]

in 75—80% yield on addition of diethyl ether. For L = Me\(_2\)S, the \(^{1}H\) n.m.r. spectrum (methyl region) consisted of a strong singlet at \(\tau = 7-37\) together with two very weak doublets (ca. 5 Hz separation) centred at \(\tau = 6-58\) and 7-37. 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 L = Me\(_2\)SO, the \(^{1}H\) n.m.r. spectrum revealed a strong singlet at \(\tau = 6-72\) attributed to isomer (IIa) or (IIb) and weak signals at \(\tau = 9-60\) and 7-39. The highest-field signal corresponds to free Me\(_2\)SO and the others to S-bonded Me\(_2\)SO (cf. \(\text{RuX}_2(\text{Me}_2\text{SO})_2\)) (refs. 5 and 6). The i.r. spectrum of this complex showed a strong band at 1 113 cm\(^{-1}\) assigned to S-bonded Me\(_2\)SO, but no bands which can be attributed definitely to O-bonded Me\(_2\)SO. The absence of the latter was confirmed by synthesis of the complex \([\text{Ph}_3\text{PPh}_2\text{Cl}]\) [RuCl\(_4\)(CO)][[\(\text{HC}\)=CH-CN], (III), x\(_m\)N at 1 108 cm\(^{-1}\)].

For L = CH\(_2\)=CH-CN, x\(_m\)N occurred at 2 245 cm\(^{-1}\), suggesting that bonding occurs through the nitrogen atom rather than the double bond (cf. \([\text{RuCl}_2(\text{PPh}_3)\text{Cl}]\) (CH\(_2\)=CH-CN), x\(_m\)N at 2 230 cm\(^{-1}\) (ref. 6)). The far-i.r. spectra of these complexes (see Experimental section) cannot unequivocally distinguish between isomer (IIa) (Cl trans to L and CO) and (IIb) (Cl trans to CO and Cl), but the similarity in properties between complexes (II) and \([\text{Ph}_3\text{PPh}_2\text{Cl}]\) [RuCl\(_4\)(CO)(L\(_2\)) \(\tau = 2,2\,'\)-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 \(^{1}H\) (ref. 2) and \(^{13}C\) m.r. studies. The latter shows diene resonances at 77-10, 64-84, 60-92, 50-40, 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 Et\(_2\)S, Ph\(_2\)S, CS\(_2\), MeCN, Ph\(_2\)CN, and PhCN were reacted under the same conditions with (I), but in all cases (I) was recovered unchanged. However, with L = AsPh\(_3\), SbPh\(_3\), or C\(_6\)H\(_4\)N \([\tau = 1 : 2 \text{ molar ratio}]\), reaction in CH\(_2\)Cl\(_2\) for 12 h, followed by addition of diethyl ether, also gave the complexes \([\text{Ph}_3\text{PPh}_2\text{Cl}]\) [RuCl\(_4\)(CO)L\(_2\)] (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 C\(_6\)H\(_4\) groups (\(^{1}H\) n.m.r. and i.r. evidence) and elemental analyses and molecular-weight determinations indicated the composition [RuCl\(_4\)(CO)(L)(C\(_6\)H\(_4\))]. (III). There are three geometrical isomers possible for (III). \(^{1}H\) N.m.r. spectra of all these complexes [Figure 1 (L = AsPh\(_3\)) and Table 1] consisted of seven diene resonances of relative intensity 1 : 1 : 1 : 1 : 1 : 1 : 2. This clearly eliminates isomer (IIc), where only five diene resonances should be observed. Homonuclear-decoupling experiments for L = AsPh\(_3\) indicated that the resonance at \(\tau = 6-34\) is coupled to the resonances at \(\tau = 5-60\) and 4-52 and that at \(\tau = 5-92\) is coupled to the peak at \(\tau = 4-25\). The signals at \(\tau = 6-92\) 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 vice versa) produce lower-field shifts than those of chloride ion, leads to the tentative assignments given in Table 1. Unfortunately, it is not possible to distinguish between isomer (IIa) and (IIb) on this evidence, even by careful comparison of \(^{1}H\) 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, 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 \(\nu_{\text{O}}\) in each case (ca. 2 000 cm\(^{-1}\)), suggests that the same isomer is always produced. On leaving the


complex [RuCl₂(CO)(AsPh₃)(C₅H₈)] in CDCl₃ for 48 h. Additional resonances appeared at ν = 325, 463, and 804, corresponding to free norbornadiene. This indicates that dissociation of the diene group in complexes (III) occurs slowly in solution and that intermolecular exchange (V). A similar complex ([RuCl₂(CO)(PET₃Ph₂)]₃) has been obtained by reaction of [RuCl₂(PET₃Ph₂)] with butyraldehyde. The i.r. spectrum of complex (V) showed several carbonyl bands (2029 m, 1993 s, 1960 s, br cm⁻¹) indicative of a mixture of isomers. The ³¹P n.m.r. spectrum 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)]₃, (IV) (ν₀₀ at 1948 cm⁻¹) was isolated, together with small amounts of (II) and (III). An orange-brown isomer of (IV) has been reported earlier (ν₀₀ at 1961 cm⁻¹) and was obtained by direct reaction of SbPh₃ with an ethanolic 'carbonyl-containing' ruthenium solution. Comparison of far-i.r. spectra indicates ν₀₀ₚ at 320 cm⁻¹ for the orange-brown isomer and <300 cm⁻¹ for the orange-red isomer. This evidence, together with similarity of the ν₀₀ positions to those of the two isomers established by ¹H n.m.r. methods for the complex [RuCl₂(CO)(PMe₂Ph₃)]₃, suggests that the orange-red isomer has configuration (IVa) and the other has configuration (IVb).

For L = PPh₃, 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)]₃).]

* Added in proof: However, this complex has now been synthesised by reaction of [RuCl₂(CO)(PPh₃)]₃ in dme and [RuCl₂(PPET₃Ph₂)] (1 : 1 molar ratio) in acetone (dme = NN-dimethylformamide).

Figure 1 ¹H n.m.r. spectrum (diene region) in CDCl₃ of the complex [RuCl₂(CO)(AsPh₃)(C₅H₈)]

Table 1

<table>
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<tr>
<th>L = AsPh₃, SbPh₃ or C₅H₅N</th>
<th>ν₀₀ (cm⁻¹)</th>
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* Also at 2100—2400 (spectrophilic). * Also at 2100—2400 (spectrophilic). * Also at 1900—2100, 2:30, and 2:42 (spectrophilic). * Pyridine. * Configuration (IIIa) or (IIIb). * Shown by double-resonance experiments on L = AsPh₃ to be an overlapping doublet of doublets. * Broad.

* Numbers in parentheses indicate normalised integrated intensities.
[(RuCl₂(PMe₂Ph)₂(C₇H₈)₂)₃]. (V). This is in contrast to the reaction between the complex [(RuCl₂(PPh₃)₂)₂] and CS₂, which produces both [(RuCl₂(CS)(PPh₃)₂)₂] and [(PPh₃)₂ClRuCl₂-Ru(CS)(PPh₃)₂]₄.

When complex (V) was reacted with excess of Ph₃P or when (I) was reacted directly with excess of Ph₃P, an orange solid was obtained which analysed for [RuCl₂(CO)(PMe₂Ph)₂(C₇H₈)] (IV), and whose i.r. spectrum contained carbonyl bands at 2 025m, 1 982m, and 1 945 cm⁻¹. One isomer of this complex has been previously reported with νₐ at 1 960 cm⁻¹.⁷ By analogy with related work on PMe₂Ph complexes,⁸ 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)

\[
\text{L=PMe₂Ph or PMePh₂, X=Cl or Br}
\]

gave a single product, which contained no carbonyl group. This complex is monomeric, non-conducting, and analysed [P₃(PhCH₂)₃][RuBr₃(CO)(C₇H₈)] and PMe₃Ph gave [RuBr₃(PMe₂Ph)(C₇H₈)], which had a very similar ¹H n.m.r. spectrum. The same complexes were also obtained by reaction of [RuX₂(PMe₂Ph)₃] and excess of CH₂Br in methanol. Related complexes [RuX₂(L)₂(C₇H₈)] (L = PPh₃, AsPh₃, X = Cl or Br), [RuH(X)L₂(diene)] [L = PPh₃, P(OR)₃, etc.],¹⁴ and [Ru(OH)₂(CO)₃(C₇H₈)] 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)² to its formal negative charge.

When complex (I) was heated under reflux with methylidenephosphine in CH₂Cl₂ (1 : 2 molar ratio), a pale yellow solid was isolated and shown by ¹H n.m.r. studies (Figure 2) to be a mixture of [RuCl₂(PMe₂Ph)(C₇H₈)] and [RuCl₂(CO)(PMe₂Ph)₃] (IV). Although attempts to separate this mixture of complexes by either t.l.c. or fractional recrystallisation were unsuccessful, the formulation of the mixture as 53% [RuCl₂(PMe₂Ph)(C₇H₈)] and 47% (IV) (from ¹H n.m.r. integration) is consistent with the analytical data. The ¹H n.m.r. spectrum of the diene complex was that expected for configuration (VI). For the complex [RuCl₂(CO)(PMe₂Ph)₃] the doublet and triplet pattern of resonances are indicative of either isomer (IVA) or (IVB). The position of ν₀₀ (1 938 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 PMe₂Ph is used, the same work-up procedure gave a yellow solid with a very similar i.r. spectrum.

![Figure 2](image_url)

**Figure 2** ¹H N.m.r. spectrum in CDCl₃ (δ 6-0—9-0) of the product mixture from the reaction of complex (I) with PMe₂Ph [(I) : PMe₂Ph = 1 : 2 molar ratio]

for [RuCl₂(PMe₂Ph)(C₇H₈)]. The ¹H 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

This instance, consistent with their i.r. measurements, but the observation of a closely ratio in 1,10-phenanthroline (phen) (L') \([I] : L' = 1:1\) molar ratio in \(CH_2Cl_2\) gave yellow precipitates which analysed closely for \([RuCl_4(CO)(L')]_2\). These precipitates are too insoluble for either molecular-weight or \(^1H\) n.m.r. measurements, but the observation of only one carbonyl band in their i.r. spectrum (e.g. for \(L' = \text{bipy}\), \(v_{CO}\) is at 1940 cm\(^{-1}\)) is consistent with a structure such as (VIIa) or (VIIb)

\[
\text{(VIIa)}
\]

\[
\text{(VIIb)}
\]

\[
\text{(VIIc)}
\]

[cf. \([RuCl_4(CO)(CH_2)]_2\), \(v_{CO}\) at 2045 cm\(^{-1}\)]. Work-up of the orange filtrates gave, in addition to \([Ph_3(PhCH_2)P][RuCl_4(CO)(L')]\), small amounts of orange solids which were reasonably close in analysis to \([Ph_3(PhCH_2)P][RuCl_4(CO)(L')][I] : L' = 1:1\) molar ratio). 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 \([\{RuCl_4(CO)(bipy)\}_n\] but contained two carbonyl bands in its i.r. spectrum at 1952 and 1918 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 \([RuCl_4(CO)(bipy)]_2\text{Cl}\) (cf. purple \([RuCl_4(H_2O)(bipy)]_2\text{Cl}_2\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 \(\text{PR}_3\), 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 \(CH_2\) 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 (this is very unlikely in the presence of free \(L\) and is not considered further); (ii) cleavage of the second ruthenium-olefin bond by \(L\) to give (IIa); (iii) displacement of the chloride ion \(\text{trans}\) to \(CO\) by the free double bond with formation of (IIIb); and (iv) displacement of the chloride ion \(\text{trans}\) to \(L\) by the free double bond with formation of (IIIa). If this mechanism is valid, then the percentage yields of complexes (IIa), (IIa), 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...
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 [Ph₃P][PhCH₂P][RuCl₃(CO)₂][Me₂S] 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 C₅H₅N (small bases) only complex (Ia) is formed [i.e. (ii) > (iii) or (iv)], whereas for L = AsPh₃, SbPh₃, and C₃H₅N (larger bases), a mixture of (IIA) and (III)

(a or b) is produced [i.e. (ii) < (iii) or (iv)]. The failure to observe reactions of complex (I) with bases such as Et₂S and PhCN can presumably be attributed to the inability of these weaker nucleophiles to cleave the ruthenium-olefin 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 (IIA) (22%) together with some [RuCl₃(CO)₂(Me₂S)] (20%) [νCO at 1 943 cm⁻¹, configuration (IV)]. The failure to isolate any diene complex here would suggest that even in benzene (ii) > (iii) or (iv), but that the tendency of the resulting anion to undergo further reaction with Me₂S is considerably enhanced in the less-polar solvent. For L = Me₂SO in benzene, only complex (IIA) 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, hydrogenolysis (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 τ 8-60, 8-74, and 8-90. These resonances are close to those found in this region for norbornene (τ 8-43, 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], C₅H₅N, 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)

Scheme 2

from (VIII) of a chloride ion trans to the PMe₂Ph 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 [RuCl₂(PMe₂Ph)₂(C₇H₈)] (VI), then appears to be a reasonable final step. The alternative site of attack (i.e. the chloride ion trans to CO) would give the complex [RuCl(CO)(C₇H₈)(PMe₂Ph)₂]Cl which might be favoured in more polar solvents. In fact, reaction of complex (I) and PMe₂Ph 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 PMe₂Ph for ruthenium(n) and the high trans-effect of CO combine to give the complex [RuCl₂(CO)(PMe₂Ph)(C₇H₈)], and this is followed by expulsion of CO by PMe₂Ph to give (VI). Both these mechanisms are consistent with results of earlier studies of ruthenium–phosphine chemistry which indicate that trans-R₃P–Ru–PR₃ arrangements are not formed via isomerisation of cis-Ru(PR₃)₃ arrangements. A possible way of distinguishing between mechanisms 2(a) or 2(b) is by means of hydrogenation experiments. Reaction of complex (I) and PMe₂Ph solutions with [RhCl₂(PPh₃)₂] and hydrogen gave solutions with additional strong ¹H n.m.r. signals at δ 8.29, 8.42, and 9.14. These resonances did not appear on reaction of hydrogen with dichloromethane solutions of [RhCl₂(PPh₃)₂], C₇H₈, and PMe₂Ph. Thus, the mechanism depicted in Scheme 2(a) involving an intermediate with a free olefin group is preferred.

For PMe₂Ph₂ a similar mechanistic path can be invoked to explain formation of the complex [RuCl₂(PMe₂Ph)₂(C₇H₈)]. However, in this instance, the lower affinity of PMe₂Ph₂ for ruthenium(n) might enable competing reaction steps to be more dominant as compared to the PMe₂Ph reaction, thus leading to formation of [RuCl₂(CO)(PMe₂Ph)₂], (IVa).

For L = PPh₂, a mechanism to explain formation of an isomeric mixture of [[RuCl₂(CO)(PPh₃)₂] and [RuCl₂(CO)(PPh₃)₂]] is presented in Scheme 3. It seems reasonable to postulate that the same intermediate (VIII) is first formed and then, since PPh₂ is a stronger nucleophile than EPh₃ (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 PPh₂ compared to the other ligands studied, together with the unfavourable cis-arrangement of these bulky groups in (IIa) (since PPh₂ has a larger ligand cone angle than EPh₃ on coordination to a metal), could readily lead to expulsion of a chloride ion, in order to relieve steric crowding, with formation of [RuCl₂(CO)(PPh₃)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 PPh₃ groups respectively. Similar rearrangements have been elegantly demonstrated for related complexes [IrH(CO)₂(PR₃)₂] (R = Ph or β-MeC₆H₄). 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(n) ions. Similar processes readily occur for [RuX₂(PR₃)₂] (X = Cl or Br; R₃ = Et₃Ph or Et₂Ph) to give the binuclear complexes [Ru₂X₂(PR₃)₆]X. Reaction of more PPh₃ with this isomeric mixture of [[RuCl₂(CO)(PPh₃)₂] complexes would then be expected to give an isomeric mixture of [RuCl₂(CO)(PPh₃)₂] complexes. However, a very recent paper reported the preparation of the yellow complex [RuCl₂(CO)(PPh₃)₂], (m.p. 250–263 °C) by recrystallis-

Scheme 3
ation of [RuCl₂(CO)(PPh₃)₂L] (L'' = NN-dimethylformamide or NN-dimethylacetamide) from CH₂Cl₂-MeOH. This monomeric complex [ν₀₀ at 1921 and 1931 (Nujol), 1940 cm⁻¹ (CH₂Cl₂)] is reported to isomerise in CH₂Cl₂ with the original 1940 cm⁻¹ carbonyl band being gradually replaced by a rather broad band at 1970 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 dimerisation of a monomeric intermediate such as [RuCl₄(CO)(PPh₃)₂], we re-examined this 'isomerisation' reaction. Our results indicate that the five-co-ordinate monomer is more correctly formulated as the six-co-ordinate complex [RuCl₆(CO)(PPh₃)₄(MeOH)]. This formulation is based on mass-spectral evidence, which indicates methanol, and the presence of an extra i.r. band at 1020 cm⁻¹ (cf. [RuCl₆(PPh₃)₄(MeOH)], 1012 cm⁻¹; [RuCl₆(PhSP₃)₂(MeOH)], 990 cm⁻¹ (ref. 27)) when compared with the i.r. spectrum of the complex ([RuCl₆(CO)(PPh₃)₄]). Elemental analyses quoted in ref. 26 are also consistent with this formulation (Found: C, 60-3; H, 4-5; Cl, 9-1. [RuCl₆(CO)(PPh₃)₄(MeOH)] requires C, 60-5; H, 4-5; Cl, 9-4%). Furthermore, on gentle heating under reflux of a CH₂Cl₂ solution of this yellow complex, an orange solution is formed from which a pale orange solid can be precipitated on addition of pentane. This complex contains no methanol but its i.r. spectrum [ν₀₀ at 1960 br cm⁻¹ (Nujol)] and m.p. [188—170 °C (decomp.)] are very similar to those reported by us for the most stable isomer of ([RuCl₆(CO)-P(Ph₃)₃)₄]). Finally, addition of methanol to a dichloromethane solution of the complex ([RuCl₆(CO)(PPh₃)₄] (prepared either from the diene anion or methanol complex) reprecipitates [RuCl₆(CO)(PPh₃)₄(MeOH)]. This is analogous to recrystallisation of the complex ([RuCl₆(CO)(PPh₃)₄] from ethanol-stabilised CHCl₃ which is reported to give some [RuCl₆(CO)₂(EOH)]-

Therefore, the information reported, but incorrectly interpreted, in ref. 26 provides good evidence for the feasibility of the mechanism outlined in Scheme 3. For L' = bipy and phen, a similar mechanism involving a five-co-ordinate intermediate [RuL₅(CO)L'] might also explain formation of ([RuCl₄(CO)(L')]₄ but, in this instance, more information is required to substantiate this speculative proposal.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Perkin-Elmer-Hitachi osmometer (model 115) at 37 °C. i.r. spectra were recorded in the region 4000—250 cm⁻¹ on Perkin-Elmer 225 and 457 grating spectrometers 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 and ¹³C and ³¹P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform mode at 25-2 and 40-5 MHz respectively. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected. Analytical data for the new ruthenium(ii) complexes are given in Table 2.

Preparations.—Benzyltriphenylphosphonium carbonyltetrachlorobis(dimethyl sulphide)ruthenate(ii), (II). This complex [Ph₃P(PhCH₂)₂][RuCl₄(CO)(C₂H₄)], (I) (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 20 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% v/v) (ν₀₀ at 1993 cm⁻¹): i.r. spectrum (400—250 cm⁻¹): 312s, 309, 295w, 285, 271m, and 249m 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)₂][Cl], addition of excess of diethyl ether gave a pale orange solid (52%) identified as [Ph₃P(PhCH₂)₂][RuCl₄(CO)(Me₂S₂)], (II). Concentration of the filtrate followed by pentane addition gave a yellow solid which was identified as carbonyldichlorotris(dimethyl sulphide)ruthenium(ii), (IV) (20%) (ν₀₀ at 1943 cm⁻¹). i.H N.m.r. spectrum (DCCl₃): +7-48 (singlet) (2) and +7-65 (singlet) (1) *; i.r. spectrum (400—250 cm⁻¹): 330; 319w, and 275m cm⁻¹.

Benzyltriphenylphosphonium carbonyltetrachlorobis(dimethyl sulphoxide)ruthenate(ii), (II). This complex was prepared from (I) 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%) (ν₀₀ at 1980 cm⁻¹) [A (0.0113) 18-6 Ω cm² mol⁻¹ in CH₂Cl₂]. i.r. spectrum (400—250 cm⁻¹): 319s; 305; 295w; 283w; and 260w cm⁻¹. The complex [Ph₃P(PhCH₂)₂][RuBr₃(CO)(Me₂SO)] was prepared as for the chloro-complex from [Ph₃P(PhCH₂)₂][RuBr₃(CO)(C₂H₄)] and Me₂SO to give a yellow crystalline solid (60%) (ν₀₀ at 1975, ν₁₀ at 1980 cm⁻¹). i.r. spectrum (400—250 cm⁻¹): 323w; 305s; and 280w 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%) (ν₀₀ at 1860, ν₁₀ at 2245 cm⁻¹). The same product was formed when an excess of acrylonitrile rather than 1:2 molar ratios were used [A(0.0019) 16-5 Ω cm² mol⁻¹ in CH₂Cl₂]. i.r. spectrum (400—250 cm⁻¹): 316m; 307m; 281w; and 271w cm⁻¹.

Benzyltriphenylphosphonium carbonyltetrachlorobis(triphenylarsine)ruthenate(ii), (II). Complex (I) (0-20 g) and triphenylarsine (0-20 g; 1:2 molar ratio) 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%) (v0 at 1 928 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

\[
[\text{Ph}_3(\text{PhCH}_2)_3P][\text{RuCl}_3(\text{CO})(\text{phen})] \quad \text{(II)}
\]

and (18%). (VI) 925—928 cm⁻¹. 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.

\[
[\text{Ph}_3(\text{PhCH}_2)_3P][\text{RuBr}_3(\text{CO})(\text{AsPh}_3)_2] \quad \text{(II)}
\]

and (18%) (vco cm⁻¹): 346; 332s; 320w; 270s; and 250 cm⁻¹. I.r. spectrum (400—
250 cm⁻¹): 355w; 330w; 320w; 270s; and 250 cm⁻¹. Treating the residual solution with pentane gave a yellow precipitate of (bicycle[2.2.1]hepta-2,5-
diene)cyanobis[chloro(triphenylstibine)ruthenium(II)] (III) (60%) which was recrystallised from dichloromethane-
pentane. This complex is more insoluble than the corresponding Ph₃As derivative in common organic solvents. Reaction of complex (I) (0-20 g) with excess of SbPh₃

### Table 2

<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></td>
<td></td>
<td>(M.p.)</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[Ph₃(PhCH₂)P][RuCl₃(CO)(Me₂S)_2] (II)</td>
<td>Orange</td>
<td>206 (decomp.)</td>
<td>50-5</td>
<td>4-2</td>
</tr>
<tr>
<td>[Ph₃(PhCH₂)P][RuCl₃(CO)(Me₂SO)₂] (II)</td>
<td>Yellow</td>
<td>184—185 (decomp.)</td>
<td>48-2</td>
<td>4-5</td>
</tr>
<tr>
<td>[Ph₃(PhCH₂)P][RuBr₃(Ph₃As)₂] (II)</td>
<td>Yellow</td>
<td>197—198 (decomp.)</td>
<td>49-3</td>
<td>5-3</td>
</tr>
<tr>
<td>[RuCl₃(CO)(AsPh₃)(C₅H₅N)] (III)</td>
<td>Pale</td>
<td>215—217</td>
<td>53-7</td>
<td>3-8</td>
</tr>
<tr>
<td>[RuCl₃(CO)(Ph₃P)(bipy)] (IV)</td>
<td>Orange</td>
<td>173—175</td>
<td>51-9</td>
<td>3-7</td>
</tr>
<tr>
<td>[RuCl₃(CO)(phen)] (IV)</td>
<td>Orange</td>
<td>163—165 (decomp.)</td>
<td>53-2</td>
<td>3-5</td>
</tr>
<tr>
<td>[RuCl₃(Ph₃P)(C₅H₅N)] (III)</td>
<td>Orange</td>
<td>195—196</td>
<td>47-5</td>
<td>3-5</td>
</tr>
<tr>
<td>[RuCl₃(CO)(C₅H₅N)] (III)</td>
<td>Yellow</td>
<td>215—217</td>
<td>52-1</td>
<td>3-8</td>
</tr>
<tr>
<td>[RuCl₃(CO)(Ph₃P)] (IV)</td>
<td>Orange</td>
<td>231—232</td>
<td>51-5</td>
<td>3-8</td>
</tr>
<tr>
<td>[RuCl₃(CO)(C₅H₅N)] (III)</td>
<td>Yellow</td>
<td>171—174</td>
<td>43-2</td>
<td>3-5</td>
</tr>
<tr>
<td>[RuCl₃(CO)(bipy)] (VII)</td>
<td>Yellow</td>
<td>&gt;280</td>
<td>36-6</td>
<td>2-1</td>
</tr>
<tr>
<td>[RuCl₃(CO)(phen)] (VII)</td>
<td>Yellow</td>
<td>&gt;280</td>
<td>37-9</td>
<td>2-3</td>
</tr>
<tr>
<td>[RuCl₃(Ph₃P)(Ph₃P)] (V)</td>
<td>Orange</td>
<td>168—172</td>
<td>50-8</td>
<td>4-2</td>
</tr>
<tr>
<td>[RuCl₃(Ph₃P)(Ph₃P)] (V)</td>
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<td>247</td>
<td>51-0</td>
<td>5-6</td>
</tr>
<tr>
<td>[RuBr₃(Ph₃P)(Ph₃P)] (VI)</td>
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<td>214—215</td>
<td>45-7</td>
<td>4-8</td>
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<tr>
<td>[RuCl₃(CO)(Me₂S)₂] (IV)</td>
<td>Yellow</td>
<td>200—202</td>
<td>22-3</td>
<td>4-7</td>
</tr>
</tbody>
</table>

* (H + D)% 1 Osmometrically in CHCl₃ (37 °C). 2 Obtained from (I): bipy = 1:1 molar ratio. 3 Osmometrically in C₄H₁₀ (37 °C).

give a yellow solid which, on recrystallisation from dichloromethane-pentane, gave microcrystals of (bicycle[2.2.1]-
hepta-2,5-diene)cyanobis[chloro(triphenylstibine)ruthenium(II)] (IV) [v0 at 1 948 cm⁻¹] was precipitated, m.p. 215—216 °C

\[
[\text{Ph}_3(\text{PhCH}_2)_3P][\text{RuCl}_3(\text{CO})(\text{Ph}_3\text{H}_2\text{N})_2] \quad \text{(II)}
\]

[Av (0-001m) 17-5 Ω⁻¹ cm² mol⁻¹ in CH₂Cl₂] and yellow [RuCl₃(CO)(C₅H₅N)(C₅H₅N)] (III) (60%) (vco at 2 010 cm⁻¹)

\[
[\text{Ph}_3(\text{PhCH}_2)_3P][\text{RuCl}_3(\text{CO})(\text{Ph}_3\text{H}_2\text{N})_2] \quad \text{(II)}
\]

were prepared from complex (I) and C₅H₅N (1:2 molar ratio) in CH₂Cl₂.

**Di-μ-chloro-bis[cyano]bis[chloro(triphenylphosphine)]-
ruthenium(II),** (V). Complex (I) (0-24 g) and triphenyl-
phosphine (0-20 g; 1:2 molar ratio) were dissolved in

\[
[\text{Ph}_3(\text{PhCH}_2)_3P][\text{RuCl}_3(\text{CO})(\text{Ph}_3\text{H}_2\text{N})_2] \quad \text{(II)}
\]

CH₂Cl₂ (100 cm³) and the solution heated under reflux
under a nitrogen atmosphere for 12 h. The resulting pale orange solution was extracted in volume and diethyl ether added to give a white precipitate of [Pb2(PhCH2)4]Cl2. The remaining solution was treated with pentane to give the pale orange solid (70%) (v00 at 2,029 m, 1,993s, and 1,960 cm⁻¹). ²³P N.m.r. spectrum (CDCl₃): 17-2 (singlet) (s); 25-5 (singlet) (s); 38-5 (multiplet) (w); 42-3 (multiplet) (w); and 52-0 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) [Found: C, 60-5; H, 4-4]. [RuCl₂(CO)₂(PMePh₂)₆] 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 CH₂Cl₂ (100 cm³) under a nitrogen atmosphere for 12 h and the resulting solution treated exactly as above, orange crystals of carbonyl dichlorobis(triphenylphosphine)ruthenium(II) (IV) (72%) were isolated, m. p. 160 °C [lit. for isomer [IVa] 70-72 °C] (Found: C, 66-3; H, 4-3; Calc. for C₄₅H₃₇Cl₂O₂Ru: C, 66-9; H, 4-9%) (v00 at 2,025m, 1,982 m, and 1,945 cm⁻¹). The same mixture of isomers was obtained by reaction of [RuCl₂(CO)(PMePh₂)₆]₂ with PPh₃ under the same conditions.

(Bicyclo[2.2.2]hepta-2,5-diene)dichlorobis(dimethylphenylphosphine)ruthenium(II) (VI). Complex (I) (0-20 g) was heated under reflux in CH₂Cl₂ (100 cm³) under a nitrogen atmosphere with PMe₂Ph (0-10 cm³) for ca. 12 h. Reduction in volume of the yellow solution followed by diethyl ether addition gave a white precipitate of [Pb2(PhCH2)4]Cl2. 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 PMe₂Ph was used. ¹H N.m.r. spectrum in CDCl₃: δ = 7-0 (protons 1, 4); 7-20 (2, 3, 5, 6); 8-50 (a, b); 2-00-2-60 (phenyl multiplet); and 7-74 (1: 2: 1 triplet, PMe₂Ph). I.r. spectrum (400-250 cm⁻¹): 305w; 277s; and 253 cm⁻¹. The complex [RuBr₂(PMePh₂)₂(C₆H₄)] was prepared in the same way from [Ph₂(PMePh₂)₆][RuBr₂(CO)₆(C₆H₄)] and PMe₂Ph as a yellow crystalline solid (65%). ¹H N.m.r. spectrum in CDCl₃: δ = 6-67 (protons 1 and 4); 7-12 (2, 3, 5, 6); 8-74 (a, b); 2-00-2-60 (phenyl multiplet); and 7-56 (1: 2: 1 triplet, PMe₂Ph).

Reactions.—Complex (I) and PMe₂Ph₂. Complex (I) (0-20 g) and PMe₂Ph₂ (0-10 cm³; 1: 2 molar ratio) were heated under reflux in CH₂Cl₂ (100 cm³) under a nitrogen atmosphere for ca. 12 h. Concentration of the solution followed by diethyl ether addition gave a white precipitate of [Pb2(PhCH2)4]Cl₂. Pentane addition to the residual yellow solution gave a pale yellow solid, shown by ¹H n.m.r. studies to be a mixture of complexes [RuCl₂(PMePh₂)₆(C₆H₄)] (VI) and [RuCl₂(CO)(PMePh₂)₆] (IV) (v00 at 1,938 cm⁻¹) (83 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 ¹H n.m.r. studies (Found: C, 59-3; H, 4-9. [RuCl₂(PMePh₂)₆(C₆H₄)] (63%) and [RuCl₂(CO)(PMePh₂)₆] (47%) requires C, 58-7; H, 4-9%). ¹H N.m.r. spectra in CDCl₃ (Figure 2): [RuCl₂(PMePh₂)₆(C₆H₄)] (VI) δ = 6-68 (protons 1, 4); 8-88 (2, 3, 5, 6); 8-98 (a, b); 2-00-2-60 (phenyl multiplet); 7-47 (1: 2: 1 triplet, PMe₂Ph₂); [RuCl₂(CO)(PMePh₂)₆] (IVa) 7-82 (triplet) (2) and 8-25 (doublet) (1).

When excess of PMe₂Ph₂ was used, the same work-up procedure gave a yellow solid (Found: C, 60-1; H, 5-3%). This material had a very similar i.r. spectrum to the solid obtained earlier, but contained an extra peak in its ¹H n.m.r. spectrum at 8-30. When the mixture was dissolved in CH₂Cl₂ (green solution) and precipitated on addition of diethyl ether, a yellow powder and orange crystals were obtained. The orange crystals were identical (i.r. and ¹H n.m.r. spectra) to [RuCl₂(PMePh₂)₆].

Complex (I) and 2,2'-bipyridyl (bipy). Complex (I) (0-20 g) and bipy (0-045 g; 1: 1 molar ratio) were heated under reflux in CH₂Cl₂ (100 cm³) under a nitrogen atmosphere for 12 h. The resulting yellow precipitate of [RuCl₂(CO)(bipy)₆] (v00 at 1,940 cm⁻¹) was filtered, then washed with CH₂Cl₂, methanol, and diethyl ether, and finally dried in vacuo at 40 °C (58%). This precipitate was insoluble in all common organic solvents. I.r. spectrum (400-250 cm⁻¹): 344m; 322w; and 278w cm⁻¹. The remaining orange solution was reduced in volume and diethyl ether added giving a white precipitate of [Pb2(PhCH₂)₄]Cl₂. The residual solution was treated with pentane to give an orange precipitate of benzyltriphenylphosphonium (2,2'-bipyridyl)carbonoyl trichlororuthenate(II) (20%) (v00 at 1,926 cm⁻¹), recrystallised from dichloromethane-pentane (30-001m 15-0 Ω cm⁻¹ mol⁻¹ in CH₂Cl₂). When the reaction was stopped after 1 h, the complex [RuCl₂(CO)(bipy)₆] was present but the solution only contained starting materials. When the complex [RuCl₂(CO)(bipy)₆] and [Pb2(PhCH₂)₄]Cl₂ were heated under reflux in CH₂Cl₂ for 12 h, a very small amount of [Pb2(PhCH₂)₄][RuCl₂(CO)(bipy)] was isolated from the solution. Using an excess of bipy, an orange precipitate (v00 at 1,952 and 1,918 cm⁻¹) analysing reasonably closely for [RuCl₂(CO)(bipy)₆] was obtained (Found: C, 40-6; H, 2-7; N, 7-9%). I.r. spectrum (400-250 cm⁻¹): 336w; 321m; 300w; and 276w cm⁻¹. The residual solution contained the complex [Pb2(PhCH₂)₄][RuCl₂(CO)(bipy)] (orange, contaminated by a very small amount of purple material (t.l.c. evidence). Similarly, reaction of complex (I) and 1,10-phenanthroline (1: 1 molar ratio) in CH₂Cl₂ gave an insoluble yellow precipitate of [RuCl₂(CO)(phen)₆] (57%) (v00 at 1,945 cm⁻¹) and orange [Pb2(PhCH₂)₄][RuCl₂(CO)(phen)] (20%) (v00 at 1,925 cm⁻¹) [λ (0-001m) 13-2 Ω cm⁻¹ mol⁻¹ in CH₂Cl₂].

Hydrogenation Experiments.—Complex (I) (0-20 g) and triphenylarsine (0-20 g; 1: 2 molar ratio) were heated under reflux in dichloromethane under a nitrogen atmosphere for 30 min. Then the complex [RhCl(PPh₃)₂] (0-05 g) was added to the reaction mixture and hydrogen passed through the solution under reflux for a further 2 h. Reduction in volume of a portion of this solution, followed by addition of diethyl ether, gave an orange solid identified as [Pb2(PhCH₂)₄][RuCl₂(CO)(AsPh₃)₆] (II). Treatment of the filtrate with pentane gave a yellow solid. This was a mixture (t.l.c. evidence), conducting, and its n.m.r. spectrum in CDCl₃ showed extra peaks at δ = 8-60, 8-74, and 8-90 (cf. norbornene: δ = 8-43, 8-68, 8-93, and 9-06). The mixture 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 [RuCl₂(CO)(AsPh₃)₆(C₄H₄)] and [Pb2(PhCH₂)₄][RuCl₂(CO)(AsPh₃)₆(C₄H₄)] (Found: C, 56-5; H, 4-3%). Similarly, when the reaction was repeated but the CH₂Cl₂ solution was simply

* We thank Dr. E. S. Switek for the preparation of this complex.
reduced in volume and a $^1$H n.m.r. spectrum obtained. Additional resonances occurred at $\tau$ 8-26, 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 $[\text{RhCl(PPh}_3)_3]$ and $\text{C}_7\text{H}_8$ or $[\text{RhCl(PPh}_3)_3]_2$, $\text{C}_7\text{H}_8$, and $\text{AsPh}_3$. Similarly, hydrogenation of dichloromethane solutions of complex (I), $\text{PMe}_2\text{Ph}$, and $[\text{RhCl(PPh}_3)_3]$ 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 $[\text{RhCl(PPh}_3)_3]_2$, $\text{C}_7\text{H}_8$, and $\text{PMe}_2\text{Ph}$ were treated with hydrogen under the same conditions.

We thank Johnson Matthey Ltd. for generous loans of ruthenium trichloride, the National A. University of Mexico for a fellowship (to L. R. R.), Dr. A. S. F. Boyd for obtaining the $^{31}$P and $^{13}$C n.m.r. spectra, and Mr. J. Miller for the $^1$H n.m.r. spectra.

[3/2521 Received, 10th December, 1973]
# 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 Cr(CO)₃ group coordinates either with the pyrrole or the benzene ring², whereas with 2-phenylpyrrole, Cr(CO)₆ and Mn₂(CO)₁₀, complex (1) is formed³. Migration of a Cr(CO)₃ group from a six- to a five-membered ring has been proposed to account for the ¹H n.m.r. spectral changes produced by addition of base to fluorene-chromium tricarbonyl⁴. Reaction of Cr(CO)₆ and Ph₂AsCH₂AsPh₂ in decane gives (2)⁵, whereas with tri(o-tolyl)phosphine and M(CO)₆ (M = Cr, Mo, W) complex (3) is produced⁶. Complexes of a/b/γ/δ-tetraphenyl-porphin and its metal chelates with Cr(CO)₃ have also been synthesised⁷.

Binuclear species [(arene)₂Cr₂(CO)ₙ]⁺ (n = 0, 1, 2, 3) have been detected in the mass spectra of arene–Cr(CO)₃ complexes⁸ and ionisation and appearance potential measurements reported⁹. Separation of an isomeric mixture of (2,3-dimethylnaphthalene)chromium tricarbonyl has been achieved by means of high-speed column liquid chromatography¹⁰. A normal-coordinate analysis of C₆H₆Cr(CO)₃ has been presented, incorporating a sixfold symmetry for the benzene ring¹¹. However, more recent low-temperature, x-ray and neutron-diffraction studies on C₆H₆Cr(CO)₃ indicate some distortion of the molecule, consistent with a threefold symmetry of the benzene ring¹².

More examples of carbonyl replacement in arene–Cr(CO)₃ complexes giving (arene)Cr(CO)₂X [X = SiHCl₃¹³, C(OMe)C₆H₅¹⁴, P(C₅H₄FeC₅H₅)₃¹⁵] have been reported. The factors influencing the ease of protonation in arene–Cr(CO)₃ and arene–Cr(CO)₂PPh₃ complexes have been discussed¹⁶, and a ¹H n.m.r. spectroscopic method of distinguishing between metal or ring attack by hydride ion on these compounds has also been outlined¹⁷. Several investigators have examined the effect of complexation of a Cr(CO)₃ group¹⁸ on arene ring substituent reactivity. Arene–M(CO)₃ compounds (M = Cr, Mo, W) are also effective homogeneous catalysts in promoting Friedel-Crafts-type reactions¹⁹ and the affinity of these compounds for halide ion is demonstrated by the ready formation of such compounds as (R₄N)₃[(CO)₃MX₃M(CO)₃] and (R₄N)₂[(CO)₃MX₃M(CO)₃] (X = F, Cl, Br, I, etc.)²⁰.

A wide range of nucleophilic addition reactions to [(arene)Mn(CO)₃]⁺ cations giving substituted cyclohexadienyl compounds has been reported²¹. In contrast, reaction with primary alkylamines gives arene–Mn(CO)₂CONHR complexes²². With (C₆H₅)₉-Meⁿ-CN Mn(CO)₃, oxidation with ceric ion liberates the cyano-arenes, C₆H₅-Meⁿ-CN, whereas thermal decomposition in polar solvents generates (arene)Mn(CO)₂CN²³. The latter undergo facile electrophilic attack on the coordinate cyano group, giving, for example, with Ph₃CBF₄, the [(arene)Mn(CO)₂CNCPh₃]⁺ cation²⁴.
Reaction of $\text{YCCo}_3(\text{CO})_9$ ($\text{Y} = \text{Fe, Me, Ph}$) and arenes gives $\text{YCCo}_3(\text{CO})_6$-(arene)$^{25}$ and full preparative and spectroscopic details for the compounds (arene)$\text{Co}_4(\text{CO})_9$ are now available$^{26}$.

8.3 CYCLOHEPTATRIPINE AND CYCLOHEPTATRIPINYL COMPLEXES

The preparation of $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3[L \equiv \text{PPh}_3, \text{P}(\text{OPh})_3]$ by photochemical reactions of $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3$ and L has been reported$^{27}$. In contrast, thermal reactions of $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_3$ with nitriles$^{28}$ or isocyanides$^{29}$ give $\text{fac-[X}_3\text{Cr}(\text{CO})_3\text{]}$.

Reaction of $(\text{C}_7\text{H}_7)\text{M}(\text{CO})_2\text{I}$ ($\text{M} = \text{Mo, W}$) with various tertiary phosphines and phosphites gives $(\text{C}_7\text{H}_7)\text{M}(\text{CO})_4\text{I}$ which, in some cases, appears to exist in two different isomeric forms$^{30}$. $^{13}\text{C}$ n.m.r. studies on $\text{L'}\text{M}(\text{CO})_3$ ($\text{M} = \text{Cr, Mo, W}; \text{L'} = \text{arene or triene}$) indicate stronger metal-triene than metal-arene bonds$^{31}$, e.g. $\text{YCCo}_3(\text{CO})_6$(triene) is readily synthesized from $\text{YCCo}_3(\text{CO})_6$(arene) and triene$^{25}$. An x-ray structure of (tropone)-chromium tricarbonyl reveals a non-planar ring and $h^6$ coordination$^{32}$. In contrast, structural and spectroscopic studies$^{34}$ on $[\text{H}_2\text{B}(3,5-\text{Me}_2\text{Pz})_2]\text{C}_7\text{H}_7$($\text{CO})_2\text{Mo}$ and related compounds indicate $h^3$-$\text{C}_7\text{H}_7$ bonding and stereochemical non-rigidity.

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

8.4 METAL–AREN E COMPLEXES

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

Normal-coordinate analysis of molecular vibrations has been performed for $\text{Cr(C}_6\text{H}_6)_2$ assuming $D_{6h}$ symmetry$^{45}$ and the calculated mean amplitudes show excellent agreement with electron-diffraction data$^{46}$. Convenient methods of synthesizing pure $\text{Cr(arene)}_2$ (arene = cumene, $m$-di-isopropylbenzene),
Cr(\text{arene})(\text{PF}_3)_3 (\text{arene} = \text{C}_6\text{H}_6, \text{C}_6\text{F}_6, \text{etc.}) and Fe(\text{C}_6\text{H}_6)(\text{PF}_3)_2 by co-condensation reactions have been reported recently by Timms et al.\(^{47}\); a new improved synthesis of [Fe(\text{C}_6\text{H}_6)_2](\text{PF}_6)_2 (79\% yield) via FeCl_3, AlCl_3 and benzene has been described also\(^{48}\). Isotopic hydrogen exchange in [Cr(\text{arene})_2]^{n+} (n = 0, 1) has been demonstrated by Russian workers\(^{49}\) and the rate constants for these reactions given.

A series of excellent papers by Green and co-workers on the reactions of [bis(\text{arene})molybdenum(0)] complexes has appeared. Treatment with tertiary phosphines or phosphites (L) gives \text{C}_6\text{H}_6\text{MoL}_3\(^{50}\) which, for \text{L} = \text{PMePh}_2 and \text{PMe}_2\text{Ph}, are readily protonated to give both \text{C}_6\text{H}_6\text{MoL}_3\text{H}^{+} and \text{C}_6\text{H}_6\text{MoL}_3\text{H}_2^{2+} cations\(^{50,51}\). Reaction with allyl chloride gives [(\text{arene})\text{Mo}(h^3-\text{C}_3\text{H}_5)\text{Cl}]_2 (4) which undergoes bridge cleavage with \text{PR}_3 giving (\text{arene})\text{Mo}(h^3-\text{C}_3\text{H}_5)(\text{PR}_3)\text{Cl}\(^{52,53}\). Reduction of this compound with NaBH_4 in the presence of excess \text{PR}_3 gives \text{C}_6\text{H}_6\text{Mo}(\text{PR}_3)_3, except for \text{R} = \text{Ph} when (\text{arene})\text{Mo}(\text{PPh}_3)_2\text{H}_2 is formed\(^{52,53}\). This dihydride reacts with nitrogen to form either (5) or (6) from which dinitrogen can be displaced by carbon monoxide to give (\text{arene})\text{Mo}(\text{PR}_3)_2\text{CO}\(^{52}\). Further reactions of (4) with butadiene, allylmagnesium chloride, 2,2'-bipyridyl, etc. have also been outlined\(^{51}\) and (4) is shown to act as a homogeneous catalyst for the polymerisation of dienes and related reactions\(^{54}\).

The compounds [(h^6-\text{arene})\text{RuX}_2]_2 (\text{arene} = \text{C}_6\text{H}_6; \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}\(^{55}\); \text{arene} = \text{C}_6\text{H}_5\text{Me}, p-\text{MeC}_6\text{H}_4\text{CHMe}_2, \text{etc.}; \text{X} = \text{Cl}\(^{56}\)) have also been fully characterised. Reaction with \text{PR}_3 gives (\text{arene})\text{RuX}_2\text{PR}_3\(^{55,56}\) and x-ray analyses\(^{56}\) of (\text{arene})\text{RuCl}_2(\text{PMePh}_2) (\text{arene} = \text{C}_6\text{H}_6, p-\text{MeC}_6\text{H}_4\text{CHMe}_2) 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 \text{arene} dimers also react with \text{R}_2\text{Hg} (\text{R} = \text{Me}, \text{Ph}) and then \text{PPh}_3, giving (h^6-\text{C}_6\text{H}_6)\text{Ru}(\text{R})\text{Cl}(\text{PPh}_3) and with tetra-allyltin to form (h^6-\text{C}_6\text{H}_6)\text{RuCl}-(h^3-\text{C}_3\text{H}_5)\(^{57}\); reaction with cyanide and hydride ion forms cyanocyclohexadienyl and 1,3-cyclohexadiene complexes respectively (\text{\textsuperscript{1}H n.m.r. spectral evidence})\(^{55}\).

Full details of the structures of \text{MH}(\text{C}_{10}\text{H}_{17})(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2) [\text{M} = \text{Ru}, \text{Os}] have now been reported\(^{58}\) 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(h⁶-C₅H₅) 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 [(h⁶-C₆H₆)RuCl₂]₂ and TiC₅H₅⁵⁷ and the related (h⁷-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)]₂BF₄ 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.

8.6 COMPLEXES OF LARGER RING TRIENES

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

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 and -triennyls; reaction of \(\text{Ru}_3\text{(CO)}_9\) with cyclododeca-1,5,9-triene; reactions of \(\text{Fe}_2\text{(CO)}_9\) with cis-(bicyclo[6,2,0]deca-2,4,6-triene), semi- and azabullvalene and iron, chromium and molybdenum compounds of anti-7,8-benzotricyclo[4,2,0,0]deca-3,7,9-triene.

8.7 MISCELLANEOUS COMPLEXES

Although none of the compounds exhibit \(h^6\) or \(h^7\) coordination, work on titanium, vanadium, zirconium, iron, ruthenium and osmium cyclo-octatetraenes may be included for completion.

References

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

By Peter W. Armit, Alan S. F. Boyd, and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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JOURNAL
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THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1975
Synthesis and Rearrangement Reactions of Dihalogenotris- (tertiary phosphine) ruthenium(ii) Compounds

By Peter W. Armit, Alan S. F. Boyd, and T. Anthony Stephenson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

The reactions of [RuCl4(PPPh3)4] with several tertiary phosphine ligands in various solvents have been examined. Whereas prolonged reaction in ethanol or dichloromethane leads to the well known ionic dimers [RuCl2L4]Cl⁻ (L = P(OPh)3, P(OMe)Ph, or PPh3), reaction in non-polar solvents such as hexane or light petroleum (b.p. 60–80 °C) produces neutral complexes. For L = P(OPh)3, [RuCl2(PPPh3)2] has been isolated although this readily converts to the triple chloride-bridged dimer ([P2Cl6RuCl4(PPPh3)4] in non-polar and [RuCl4(PPPh3)4]Cl in polar media. For L = P(OMe)Ph and PCIPh3 only [L2RuCl2RuCl2L2] can be isolated although 31P n.m.r. studies indicate the presence of [RuCl4(PPPh3)2] in the reaction mixture. For L = PPh3, cis-[RuCl4(PPPh3)4] is formed although this very readily rearranges to [RuCl4(PMe2Ph)3]. Preliminary studies indicate that similar compounds are formed from [RuBr2(PPPh3)]. All these compounds (including [RuCl4(PPPh3)2 and 3]) have been extensively studied by variable-temperature 31P n.m.r. spectroscopy and an overall mechanism for the rearrangement reactions of all tertiary phosphine complexes of type [RuX2L2 or 3] is proposed.

Thus, although some monomeric tertiary-phosphine halide complexes of RuII are known, 3 no general synthesis is available and this we set out to find.

RESULTS AND DISCUSSION

It has been shown that when [RuX2L4] (X = Cl or Br) are heated under reflux with excess of triaryl phosphites in dichloromethane, ethanol, or hexane the corresponding [RuX2L4] compounds [L = P(OPh)3, etc.] are produced. 19 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 [RuBr2(PPPh3)] were heated under reflux for prolonged periods with a six-fold excess of tertiary phosphine in either ethanol or dichloromethane the sole products were [RuX2L2]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(OPh)3, P(OMe)Ph, and PPh3 and PCIPh3, [RuX2L4], [RuX2L3], and [L2RuX2RuCl2] were formed, respectively. The mononuclear species undergo facile rearrangement in solution in a complex fashion which we have analysed mainly by 31P n.m.r. and far-i.r. (400–150 cm⁻¹) 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 [RuX2L2 or 3].
(a) \( L = \text{PPh}_3 \).—Although the compounds \([\text{RuX}_2(\text{PPh}_3)_5] (X = \text{Cl or Br}; x = 3 \text{ or } 4)\) were first reported in 1966, few studies have been made to ascertain the nature of the species present in solution (cf. the numerous studies on the related \([\text{RhCl}(\text{PPh}_3)_5])\). In the original paper reporting the preparation of these compounds, osmometric molecular-weight determinations in acetone on \([\text{RuCl}_2(\text{PPh}_3)_5]\) and \([\text{RuCl}_2(\text{PPh}_3)_4]\) 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); \( L = \text{PPh}_3 \)). Recent, spectrophotometric studies in deoxygenated benzene supported these conclusions showing that \([\text{RuCl}_2(\text{PPh}_3)_4]\) was completely dissociated in solution and that a \(10^{-3} \text{M}\) solution of \([\text{RuCl}_2(\text{PPh}_3)_5]\) was \(80\% \) dissociated at 298 K \((K \text{ for equation (2) was calculated to be } (2.7 \pm 0.6) \times 10^{-3} \text{ mol }^{-1})\)\.* We have now examined the variable-temperature proton-noise-decoupled \(^{31}\text{P}\) n.m.r. spectra of more concentrated solutions of these compounds \((ca. 0.01—0.1 \text{M})\) in an attempt to identify more directly the species present in solution.†

Thus, the spectrum of \([\text{RuCl}_2(\text{PPh}_3)_5]\) in deoxygenated CDC\(_2\)Cl\(_2\), at 290 K \((ca. 0.1 \text{M})\), consisted of two strong signals at 25.0 and 75.8 p.p.m. of relative intensity 2 : 1 \([\text{Figure } 1(a)]\). At 173 K in CH\(_2\)Cl\(_2\)-(CD\(_3\))\(_2\)CO these signals were resolved into a doublet and triplet pattern respectively \([\text{I} \text{H} \text{P} 30.3 \text{ Hz}]\) which is consistent with the square-pyramidal structure (I) established for the compound by X-ray analysis.\(^{23}\) In addition \([\text{Figure } 1(a)]\) there were some weak peaks centred at 56.0 p.p.m. which comprise an AB pattern \([\text{I} \text{H} \text{P} 42 \text{ Hz}, 8(\text{PPH}_3\text{}) 320 \text{ Hz}]\) and a small singlet at \(-7.3 \text{ p.p.m.} \) \((\text{free PPh}_3)\) also of relative intensity 2 : 1. On raising the temperature the intense signals first broadened and then coalesced \((ca. 250 \text{ K})\) and finally gave a sharp singlet \((>290 \text{ K})\) at 41.1 p.p.m.; the smaller peaks broadened and coalesced at slightly higher temperatures \((ca. 290 \text{ K})\), but the free PPh\(_3\) signal remained sharp to ambient temperature although it shifted slightly to lower field \([\text{see Figure } 1(b) \text{ and } (c)]\). On lowering the temperature, the spectrum shown in \([\text{Figure } 1(a)]\) was produced. In C\(_6\)D\(_6\)-toluene \((ca. 0.01 \text{M})\) at 220 K the same spectrum as in \([\text{Figure } 1(a)]\) was observed except that the AB pattern at 57.6 p.p.m. and the free PPh\(_3\) peak were much more intense in comparison to the \([\text{RuCl}_2(\text{PPh}_3)_5]\) signals \([\text{Figure } 1(d)]\). On addition of free PPh\(_3\) the AB pattern disappeared, indicating the resonances arise from a dissociation product of \([\text{RuCl}_2(\text{PPh}_3)_4]\) in rapid scrambling of equatorial and apical PPh\(_3\) groups above 200 K in \((I)\) probably via an intramolecular pseudo-rotation mechanism since the resonance linebands were not resolved.

\* 1 M = 1 mol dm\(^{-3}\).

† Although some of our results are very similar to those briefly reported by Caulton\(^{22}\) 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 \([\text{RuX}_2(\text{PR})_3] \text{ or } 4\) compounds in solution.


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

![Chemical structure](image)

the dissociation compound \([\text{RuCl}_2\text{(PPh}_3\text{)}_3] \text{Cl}\) and, like Caulton,\(^{22}\) we conclude that such a pattern is incompatible with a monomeric \([\text{RuCl}_4\text{(PPh}_3\text{)}_3] \text{Cl}\) species (only a \(^{31}\)P n.m.r. singlet is expected for tetrahedral or square-planar configurations and stabilisation of a cis-octahedral compound \([\text{RuCl}_2\text{(PPh}_3\text{)}_3\text{(solvent)}]_2\) is very unlikely in solvents such as CDCl₃ or toluene), but it is consistent with a dimeric structure of type (II).\(^*\)

Thus we suggest that equilibrium (2) should be re-formulated as (3).\(\dagger\) This equilibrium is analogous to

\[ 2\text{[RuCl}_2\text{L}_3] \leftrightarrow \text{[RuCl}_2\text{L}_2\text{]} + 2L \]  

that now established for the behaviour of \([\text{RhCl}_2\text{L}_2] \] \((L = \text{PPh}_3 \text{or } \text{P(C}_6\text{H}_4\text{Me/-}_3\text{)}_3\) in solution \(^{30}\) [equation (4)], although earlier spectrophotometric studies \(^{24}\) (for \(L = \text{PPh}_3\)) were erroneously interpreted in terms of equilibrium (6). Therefore, with the modification that there

\[ 2\text{[RhCl}_2\text{L}_3] \leftrightarrow \text{[RhCl}_2\text{L}_2\text{]} + 2L \]  

\[ \text{[RhCl}_2\text{L}_2\text{]} \leftrightarrow \text{[RhCl}_2\text{]} + L \]  

is a monomer–dimer, (3), and not a monomer–monomer equilibrium, (2), for \([\text{RuCl}_2\text{(PPh}_3\text{)}_3] \) in low polarity solvents, these \(^{31}\)P n.m.r. results are in excellent agreement with those of the recent spectrophotometric studies.\(^{21}\)

For \([\text{RuCl}_4\text{(PPh}_3\text{)}_3] \) \((\text{ca. } 0.1\text{m})\), \(^{31}\)P n.m.r. measurements show even at 153 K in CH₃Cl–(CD₃)₂CO (Figure 2) complete dissociation into \([\text{RuCl}_2\text{(PPh}_3\text{)}_3] \) and PPh₃. On raising the temperature coalescence of the two signals from \([\text{RuCl}_4\text{(PPh}_3\text{)}_3] \) 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 \([\text{RuCl}_4\text{(PPh}_3\text{)}_3] \) is reminiscent of that reported for ML₄ compounds \((\text{M} = \text{Ni, Pd, or Pt; } L = \text{PPh}_3, \text{etc.})\) \(^{34}\) which are substantially dissociated into ML₃ and L at ambient temperature. A suggestion made by Tolman et al.\(^{25}\) could also be valid here, namely that the tetrakis complex might be best represented as \([\text{RuCl}_2\text{(PPh}_3\text{)}_3\text{]}\text{Cl}_2\text{PPh}_3\] with one PPh₃ group trapped in the lattice. This suggestion is supported by the similar colours of \([\text{RuCl}_4\text{(PPh}_3\text{)}_3] \) \((\text{cf. } \text{[Ni(PPh}_3\text{)}_4] \text{and [Ni(PPh}_3\text{)}_3]\) \(^{28}\)

As noted earlier,\(^3\) solutions of \([\text{RuCl}_2\text{(PPh}_3\text{)}_3] \) are extremely sensitive to oxygen, rapidly changing from yellow-brown to green with the formation of Ph₃PO.

\[ \text{[RuCl}_2\text{(PPh}_3\text{)}_3] + 1.5\text{O}_2 \rightarrow 3\text{Ph}_3\text{PO} + \text{'RuCl}_2' \]  

Cenini et al.\(^{29}\) postulated the formation of an intermediate oxygen complex \([\text{RuCl}_6\text{(O)}\text{(PPh}_3\text{)}_3] \) during this process although no direct evidence has been found.

**Figure 2** \(^{31}\)P n.m.r. spectrum of \([\text{RuCl}_4\text{(PPh}_3\text{)}_3] \) \((\text{ca. } 0.1\text{m})\) in CH₃Cl–(CD₃)₂CO at 153 K

Therefore, we examined the \(^{31}\)P n.m.r. spectra of \([\text{RuCl}_4\text{(PPh}_3\text{)}_3] \) \((\text{and } 4) \) in the presence of small amounts of air. When the sealed tube was open to air for short periods, the CDCl₃ solution (at 308 K) turned greenish brown and the \(^{31}\)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(O(PPh₃)₃) 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 56.0


p.p.m.), but when excess of PPh₃ was present [or alternatively when solutions of [RuCl₂(PPh₃)₄] 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 [RuCl₂(PPh₃)₄] after air exposure. In CDCl₃ a peak at 48.1 p.p.m., whereas in CH₂Cl₂—CD₂Cl₂CO extra peaks at 48.1 and 38.8 p.p.m., were observed. For [RuCl₂(PPh₃)₃] 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 [RuCl₂(PPh₃)₅], [RuCl₂(O₂)(PPh₃)₃], a Ru(OPPh₃) complex, dimers such as (III) or (IV) with equivalent PPh₃ groups, or even a cationic RuIII 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 [(RuCl₂(PPh₃)₃)(OCMe₂)]ₙ, 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 [RuCl₂(PPh₃)₄] which would be facilitated in more polar solvents; namely loss of Cl⁻ to produce RuIII cations [equations (7) and (8)]. Spectrophotometric and conductometric studies on NN-dimethylformamide (dmf) solutions of [RuCl₂(PPh₃)₄] indicated that these types of equilibria were important in polar solvents but no cationic compounds were isolated.²¹ Also, [RuCl₂(PPh₃)₅] 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 [RuCl₂(PPh₃)₃] in MeNO₂ revealed an AB pattern centred 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 [RuCl₂(PPh₃)₃(O₂NMe)₃]Cl, (V), which is consistent with the spectrophotometric results²¹ and with the recent synthesis of compounds such as [RuCl₂(NCMMe₃)]PF₆] (L = PPh₃, etc.) via [RuCl₂(C₅H₅)(NCMe₃)]PF₆.²⁷

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 = PE₅Ph₃.—When [RuCl₂(PPh₃)₄] was heated under reflux with excess of PE₅Ph₃ in degassed hexane under nitrogen for ca. 18 h green crystals were deposited which analysed closely for the empirical formula [RuCl₂(PPh₃)₃]. Likewise, reaction with [RuBr₂(PPh₃)₃] gave green [RuBr₂(PPh₃)₃], whereas in 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>υ(RuX)</th>
<th>Other bands</th>
</tr>
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<tr>
<td>[RuCl₂(PPh₃)₃]</td>
<td>318s</td>
<td>298w, 294w, 275w, 268w, 257w, 235m, 250, 197m, 183m, 175w, 155w</td>
</tr>
<tr>
<td>[RuBr₂(PPh₃)₃]</td>
<td>299w</td>
<td>307s, 277w, 266m, 257m, 235w, 196m, 184w</td>
</tr>
<tr>
<td>[(RuCl₂(PPh₃)₃)(OCMe₂)]</td>
<td>223s, 250m</td>
<td>239, 290m, 280w, 267m, 260w, 239w, 224s, 216m, 196w, 192w, 182s, 154w</td>
</tr>
<tr>
<td>[RuCl₂(PPh₃)₅]</td>
<td>327s</td>
<td>296w, 272m(br), 246w, 173m(br)</td>
</tr>
<tr>
<td>[RuBr₂(PPh₃)₅]</td>
<td>322w</td>
<td>322w, 315w, 290w, 265m(br), 190w</td>
</tr>
<tr>
<td>[RuCl₂(PPh₃)₅]Cl</td>
<td>260m</td>
<td>296w, 269w, 208w, 180m</td>
</tr>
<tr>
<td>[RuBr₂(PPh₃)₅]Cl</td>
<td>312m, 260m(br)</td>
<td>300w, 260w</td>
</tr>
<tr>
<td>[RuCl₂(PPh₃)₅]Cl</td>
<td>311s, 248s</td>
<td>291m, 264w, 217w, 155w</td>
</tr>
<tr>
<td>[RuBr₂(PPh₃)₅]Cl</td>
<td>310s, 260s</td>
<td>319w, 299m, 217w</td>
</tr>
<tr>
<td>[RuCl₂(PPh₃)₅]Cl</td>
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<tr>
<td>[RuCl₂(C₅H₅)(PPh₃)]</td>
<td>318s, 290m</td>
<td>308</td>
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<tr>
<td>[RuCl₂(PMe₅Ph₃)]</td>
<td>292s</td>
<td>358w, 341s, 282s, 248, 234vs, 189w</td>
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<td>293s</td>
<td>352m, 338s, 282m, 182m, 167m</td>
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<tr>
<td>[RuCl₂(PMe₅Ph₃)]</td>
<td>241s</td>
<td>288w, 263w, 177m</td>
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</table>
ethanol or dichloromethane prolonged reflux of [RuCl₅(PPPh₃)₄] with PEtPh₂ gave lemon-yellow [Ru₂Cl₃(PEtPh₂)₆]Cl, (VI). Comparison of the far-i.r. spectra of these compounds showed that the green compound no use in verifying this statement, confirmation was obtained from 3¹P n.m.r. studies. Thus, when the green complex was dissolved in degassed CDC₁₃ at ca. 225 K the 3¹P n.m.r. spectrum consisted of two strong signals at

![Figure 3](image-url)

Figure 3 ³¹P n.m.r. spectra of [RuCl₅(PEtPh₂)₃] (ca. 0.1M) in CH₂Cl₂-(CD₃)₂CO at (a) 195, (b) 213, (c) 233, (d) 253, (e) 273, (f) 293, (g) 303, and (h) recooled to 213 K

contained no traces of (VI) (see Table) and that the position of ν(RuCl) was similar to that found for [RuCl₅(PPPh₃)₃], consistent with a structure of type (I). Although the ¹H n.m.r. spectrum of this compound was of 30.4 and 73.3 p.p.m. (relative intensity 2:1) which in CH₂Cl₂-(CD₃)₂CO 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 PEtPh₂. Thus, by analogy with the PPh₃ studies, this indicates that the green compound has the same structure in solution as [RuCl₂(PPh₃)₃] and that there is very little dissociation of the type shown in either equation (2) or (3) at this temperature and concentration (ca. 0.1M).

However, when [RuCl₂(PEtPh₂)₃] was first dissolved at room temperature and then cooled for examination, the observed ³¹P n.m.r. spectra were more complicated. Thus, at 195 K in CH₂Cl₂—(CD₃)₂CO, in addition to the peaks at 29.4 and 73.7 p.p.m. ([RuCl₂(PPh₃)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 PEtPh₂), 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 [RuCl₂(PEtPh₂)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 AB₂ pattern [Figure 3(d)] (A 33.7, B 31.5 p.p.m.; δ(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 [RuCl₂(PPh₃)₃] resonances [cf. [RuCl₂(PPh₃)₃]], all the other resonances being slightly decreased in intensity, and the AB₂ resonance pattern began to broaden [Figure 3(e)]. At 293 K the resonance at 43.0 p.p.m. had sharpened considerably and the AB₂ 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 PEtPh₂ 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(d)] the spectrum was similar to that observed earlier at this temperature [Figure 3(b)] except for the following differences: (i) the resonances due to [RuCl₂(PPh₃)₃] and free PEtPh₂ were much weaker on recooling; 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 ³¹P n.m.r. spectra with temperature were observed for [RuCl₂(PEtPh₂)₃] in C₆H₆—CH₂Cl₂ 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 CH₂Cl₂—(CD₃)₂CO and which is absent in benzene, all the other resonances arise from non-ionic species.

The ³¹P n.m.r. spectrum of [Ru₂Cl₃(PPh₃)₅]Cl, (VI), (made by refluxing RuCl₂3OH₂ and excess of PPh₃ in aqueous ethanol) in CDC₂ 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 [RuCl₂(PEtPh₂)₃] was dissolved in CH₂Cl₂ 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. ([RuCl₂(PPh₃)₃] is initially completely insoluble in light petroleum (b.p. 60—80 °C).) Removal of solvent then gave an orange-brown solid whose ³¹P n.m.r. spectrum at 260 K in C₆D₆—hexane consisted of a sharp singlet at 50.4 p.p.m. and an AB₂ pattern of resonances between 33 and 36 p.p.m. (relative intensity 2 : 3). This AB₂ 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 [Ru₂Cl₃(PEtPh₂)₃], (VII), and further support for this formulation comes from molecular-weight measurements in C₆H₆ far-i.r. studies which show both terminal and bridging ν(RuCl) vibrations [cf. ([Ph₅P]₂YRuCl₃RuCl(PPh₃)₂)] (Y = CO
or CS), Table), and the similarity of this data to those for \([\text{RuCl}_4(\text{PEtPh}_3)_6]\) (see later).

Furthermore, when \([\text{RuCl}_4(\text{PEtPh}_3)_6]\) was heated under reflux with excess of \(\text{PETPh}_2\) in ethanol for 3 h a yellow conducting solution was formed which gave a yellow solid on solvent removal. The \(^{31}P\) n.m.r. spectrum of this material [which analysed closely for \(\text{RuCl}_2(\text{PETPh}_2)_2\)] in CDC\(_3\) at 220 K consisted of an AB\(_2\) pattern on which was superimposed a sharp strong singlet at 33.1 p.p.m. \([\text{RuCl}_2(\text{PETPh}_3)_6]\) (Figure 4). However, the AB\(_2\) pattern had a different set of parameters from \([\text{RuCl}_2(\text{PETPh}_3)_6]\), namely A 31.0, B 34.1 p.p.m., \(8(\text{AB})\) 128.6, \(J(\text{AB})\) 63.4 Hz. Similarly, reaction of \([\text{RuCl}_2(\text{PETPh}_3)_6]\) with excess of \(\text{PETPh}_2\) in refluxing ethanol for short periods gave a yellow solid with the same \(^{31}P\) n.m.r. spectrum in CDC\(_3\) 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. \([\text{RuCl}_2(\text{PETPh}_3)_6]\), a weak peak at 43.1 p.p.m. \([\text{RuCl}_2(\text{PETPh}_3)_6]\), weak peaks at 48.5 and 32.1 p.p.m. \([\text{RuCl}_2(\text{PETPh}_3)_6]\), and a very weak AB\(_2\) pattern compared to that observed at 210 K. Thus the species (VIII) giving rise to this AB\(_2\) pattern is only stabilised at low temperature or in the presence of excess of PETPh\(_2\). On raising the temperature in the absence of free PETPh\(_2\) it rearranges to form \([\text{RuCl}_2(\text{PETPh}_3)_6]\), \([\text{RuCl}_2(\text{PETPh}_3)_6]\), \([\text{RuCl}_2(\text{PETPh}_3)_6]\]-Cl, and free PETPh\(_2\).

A complete rationalisation of all these experimental observations is provided by the rearrangement mechanism shown in the Scheme. Thus, it is proposed for \(L = \text{PETPh}_2\) that the dissociative path (i) is of minor importance since only a small amount of dissociation product (II) (resonance at 47 p.p.m.) is observed under all experimental conditions. However, associative processes are very important here and we suggest that ready dimerisation of \([\text{RuCl}_2(\text{PETPh}_3)_6]\), (I), occurs in solution to give the double halide-bridged dimer, (VIII) [step (ii)]. Related double halide-bridged dimers \([\text{RuCl}_2(Y)(\text{PETPh}_3)_3]\) \((Y = \text{CS} 29\) or CO 29) have been characterised. However, (VIII) is very unstable both to phosphine loss with formation of the triple halide-bridged \([\text{Ru}_2\text{Cl}_6(\text{PETPh}_3)_6]\), (VII) [step (iii)], or halide loss with formation of \([\text{Ru}_2\text{Cl}_6(\text{PETPh}_3)_6]\), (VI) [step (iv)]. Also at higher temperatures solvent cleavage of (VIII) occurs to regenerate (I) [step (v)]. In fact, close examination of Figure 3(c) shows extra signals (marked with asterisks) in addition to those from (VII) and (I) which can be attributed to \([\text{RuCl}_2(\text{PETPh}_3)_6]\). Precedents for intramolecular rearrangements of this type are provided by the rearrangement of the related \([\text{RuCl}_2(\text{CS})(\text{PETPh}_3)_5]\) to \([\text{RuCl}_2(\text{CS})(\text{PETPh}_3)_5]\) 29 and of \([\{(\tau-C_5\text{Me}_5)\text{RhCl}_2\}]\) to \([\{(\tau-C_5\text{Me}_5)\text{RhCl}_2\}]\). Thus step (iv) is favoured in polar solvents particularly in the presence of free PETPh\(_2\). In non-polar solvents step (iii) is dominant and no ionic dimer is formed. However, in more polar solvents, after formation of (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 \([\text{RuCl}_2(\text{PETPh}_3)_6]\). Precedents for intramolecular rearrangements of this type are provided by the rearrangement of the related \([\text{RuCl}_2(\text{CS})(\text{PETPh}_3)_5]\) to \([\text{RuCl}_2(\text{CS})(\text{PETPh}_3)_5]\) 29 and of \([\{(\tau-C_5\text{Me}_5)\text{RhCl}_2\}]\) to \([\{(\tau-C_5\text{Me}_5)\text{RhCl}_2\}]\). Thus step (iv) is favoured in polar solvents particularly in the presence of free PETPh\(_2\). In non-polar solvents step (iii) is dominant and no ionic dimer is formed. However, in more polar solvents, after formation of (VII) and (VIII).
free PEtPh₄, slow displacement of the terminal halide group by PEtPh₄ 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 AB₂ 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 PEtPh₄ and this is readily demonstrated by addition of excess of PEtPh₄. The low-temperature broadening which is also reversible is attributed to viscosity effects.

(c) L = PEt₄Ph.—When [RuCl₃(PPh₃)₄] was heated under reflux with excess of PEt₄Ph 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 impossible to distinguish on this evidence alone between [RuCl₃(PEt₂Ph)₅](solvent) and [RuCl₃(PEt₄Ph)₃(solvent)], the far-i.r. spectrum was very similar to that found for [RuCl₃(PEt₂Ph)₅] and [RuCl₃(Y)(PPh₃)₄] (Y = CO or CS) (Table), the compound was dimeric in benzene, and the ³¹P n.m.r. spectra in either CH₂Cl₂—(CDCl₃)₂CO or CDCl₃ from 210 to 310 K consisted of a sharp singlet at 44.3 p.p.m. and an AB₂ pattern of signals at higher field [A 39.1, B 35.4 p.p.m.; ³J(AB) 84.2, ³J(AB) 29.0 Hz] (relative intensity 2 : 3) (Figure 5). However, conclusive proof that this compound was a sample of [(PhEt₂P)₃RuCl₂RuCl₂(PEt₂Ph)₄] came from comparing its ³¹P n.m.r. and far-i.r. spectra with a genuine sample prepared by pyrolysis of [Ru₂Cl₆(PEt₄Ph)₄]Cl in n-propyl propanol at 120 °C.

Attempts to isolate a green solid from this reaction were unsuccessful. Also, when [RuCl₃(PEt₄Ph)₃] was heated under reflux in benzene with excess of PEt₄Ph 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 [Ru₂Cl₆(PEt₂Ph)₅] and free PEt₂Ph signals) which can be attributed to the presence of some [RuCl₃(PEt₂Ph)₅]. (I). When [Ru₂Cl₆(PEt₄Ph)₃] was heated under reflux in ethanol with excess of PEt₄Ph yellow [RuCl₃(PEt₂Ph)₅]Cl (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(PPh₃)₄] with excess of PEt₄Ph was only briefly examined. Again, the analytical data did not unequivocally distinguish between the formulations [RuBr₃(PEt₂Ph)₅] and [RuBr₃(PEt₄Ph)₃(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 = PCl₂Ph₄.—Reaction of [RuCl₃(PPh₃)₄] with excess of PCl₂Ph₄ in refluxing hexane for 3 h gave a nonconducting 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 145.7 p.p.m. and an AB₂ pattern at higher field [A 134.5, B 126.1 p.p.m.; ³J(AB) 341.0, ³J(AB) 34 Hz] confirming the formulation

Thus these reaction products are consistent with the Scheme.

(e) L = PMe₄Ph.—Reaction of [RuCl₃(PPh₃)₄] with excess of PMe₄Ph in refluxing light petroleum (b.p. 60—80 °C) for 3 h gave a crystalline yellow precipitate which analysed closely for [RuCl₃(PMMe₄Ph)₄]. This compound can also be prepared by reaction of mer-[RuCl₃(PMMe₄Ph)₃] with excess of PMe₄Ph in hexane. Although this compound is quite stable in the solid state, it rapidly rearranges in solvents such as CH₂Cl₂ to give [RuCl₃(PMMe₄Ph)₄]Cl. This process can be monitored by the steady increase in conductivity of a CH₂Cl₂ solution with time. After ca. 3 h at 300 K removal of CH₂Cl₂ gave a quantitative yield of [RuCl₃(PMMe₄Ph)₄]Cl. 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

![Figure 5](image-url)
CDCl$_3$ from 210 to 270 K showed two 1:2:1 triplets at 15.8 and -6.5 p.p.m. $[\text{J(PP) } 30.0 \text{ Hz}]$ [Figure 6(a)] consistent with the cis configuration (IX) $[\text{cf. cis-}[\text{RuH}_2\text{Cl_2(PMe}_2\text{Ph)}_4]]$. 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 $[\text{RuCl}_2\text{(PMe}_2\text{Ph)}_3]$, $[\text{RuCl}_2\text{(PMe}_2\text{Ph)}_3\text{Cl}_2]$, $[\text{RuCl}_2\text{(PMe}_2\text{Ph)}_3\text{Cl}]$, or even free PMe$_2$Ph. However, the absence of the latter is due to fast intermolecular exchange at temperatures above 270 K between PMe$_2$Ph and the ionic dimer as was readily shown by adding free PMe$_2$Ph to $[\text{RuCl}_2\text{(PMe}_2\text{Ph)}_3\text{Cl}]$ in CDCl$_3$ solution. The failure to observe any of the other intermediates in this instance. The known high affinity of PMe$_2$Ph for Ru$^{11}$ (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 CDCl$_3$ at 260 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 $[\text{RuH}_2\text{(PMe}_2\text{Ph)}_3]$.34 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 $[\text{RuCl}_2\text{(PMe}_2\text{Ph)}_3\text{Cl}]$. At 250 K the $^{13}$C proton-noise-decoupled n.m.r. spectrum of (IX) in CDCl$_3$ 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. $[\text{J(PP)} 15 \text{ Hz}]$, two triplets for the quaternary carbon atoms of the phenyl rings $[140 \text{ p.p.m.}, \text{J(PP) 17 Hz}]$, 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 $\text{RuCl}_3\cdot 3\text{OH}_2$ and Pr$_3$ 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-co-ordinate Ru$^{11}$ (4d$^9$) compounds containing a triple halide bridge. Only when bulky tertiary phosphines such as PPh$_3$ or P(C$_6$H$_4$Me-3)$_3$ 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 °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 R1C IR 720 far-i.r. spectrometer using pressed Polyethylene discs. $^1$H N.m.r.


![Figure 6](image-url)
spectra were obtained on a Varian Associates HA 100 spectrometer equipped with variable-temperature attachment and 1H and 13C 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% H3PO4 respectively. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

The compounds [Ru2X4(PPh3)6] and [Ru2X4(PPh3)6] (X = Cl or Br) were prepared as described earlier 3 and their 31P 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 phosphine oxides and other oxidation products for the duration of the spectroscopic studies. Pure samples of the ionic dimers [Ru2Cl4L2]Cl (L = PPh3PET2, PET2Ph, or PMe2Ph) were obtained by literature methods.6,7

Dichloro(ethylidiphosphino)diruthenium(II), (I).—The compound [RuCl2(PPh3)4] (1.0 g) was heated under reflux in degassed hexane (30 cm3) with ethylidiphosphine (0.40 cm3) under nitrogen for 18 h. The resulting green crystalline precipitate was filtered off, washed thoroughly with light petroleum (b.p. 60—80 °C) to remove any free phosphine, and dried in vacuo at 40 °C (0.59 g, 88%). m.p. 142 °C (decomp.) (Found: C, 62.0; H, 5.7; Cl, 9.0.

Calculated for C42H45Cl2P3Ru: C, 61.9; H, 5.5; Cl, 8.7%.

Dibromo(ethylidiphosphino)diruthenium(II), (I), was also prepared using [RuBr2(PPh3)4] (0.40 g) and PPh3PET2 (0.40 cm3) (0.22 g, 80%), m.p. 156—158 °C (Found: C, 55.4; H, 5.1.

Calculated for C42H45Br2P3Ru: C, 55.8; H, 5.0%.

def-Tri-μ-chloro-μ-chloro-bis-chloro(ethylidiphosphino)diruthenium(II), (VII).—The compound [RuCl2(PPh3)3] (I) was dissolved in dichloromethane at room temperature to give a green solution and then solvent removed in vacuo 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.p. 118—122 °C (decomp.) (Found: C, 59.1, 59.2; H, 5.4, 5.6%; M in C6H6 1132. Calc. for C42H45Cl2P3Ru: C, 59.4; H, 5.3%; M 1414.

Reaction of [RuCl2(PPh3)3] with PPh3 in Ethanol.—The compound [RuCl2(PPh3)3] (0.14 g), was heated under reflux in degassed ethanol (50 cm3) with PPh3 (0.10 cm3) under nitrogen for 8 h. The solution was filtered to remove excess of green starting material and then solvent removed in vacuo. Addition of light petroleum (b.p. 60—80 °C) to the resulting oil gave a yellow solid which analysed closely for [RuCl2(PPh3)3] (Found: C, 60.6; H, 5.7. Calc. for [RuCl2(PPh3)3]: C, 61.9; H, 5.5%.

31P n.m.r. studies indicated this material to be a mixture of [RuCl2(PPh3)4]Cl, (VI), and [(RuCl2(PPh3)3]Cl, (VII).—def-Tri-μ-chloro-μ-chloro-bis-chloro(ethylidiphosphino)diruthenium(II), (VII).—(a) The compound [RuCl2(PPh3)3] (0.40 g) in degassed light petroleum (b.p. 60—80 °C) (50 cm3) was heated under reflux with diethylphenylphosphine (0.35 cm3) 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 PPh3 (0.11 g, 58%), m.p. 129—132 °C (Found: C, 53.5, 52.4, 61.9; H, 6.7, 6.8, 6.8; Cl, 10.5% ; M (in C6H6) 1115. Calc. for C62H62Cl2P3Ru: C, 51.1; H, 6.4; Cl, 12.1%; M 1174. The variable analytical figures are ascribed to differing amounts of solvent crystallisation (cf. the preparation of [RuCl2(PPh3)3] from [RuCl2(PPh3)3]Cl and n-propyl propionate).31

(b) The same compound was made directly by heating [RuCl2(PPh3)4] (0.40 g) under reflux in light petroleum (b.p. 60—80 °C) with PPh3PET2 (0.85 cm3) for 36 h when orange crystals were precipitated.

def-Tri-μ-chloro-μ-chloro-bis-chloro-μ-bis(diethylphenylphosphino)diruthenium(II), (VII).—The compound [RuCl2(PPh3)4] (0.40 g) in degassed hexane (50 cm3) was treated with chlorodiphenylphosphine (0.40 cm3) 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.p. 191—193 °C (Found: C, 51.2; H, 3.7; Cl, 21.2.

Calculated for C42H38Cl2P3Ru: C, 49.8; H, 3.5; Cl, 22.0%.

Dichlorotetrakis(dimethylphenylphosphino)diruthenium(II), (IX).—(a) The compound [RuCl2(PPh3)4] (0.40 g) in degassed light petroleum (b.p. 60—80 °C) (70 cm3) was heated under reflux with PMe2Ph (0.30 cm3) 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.p. 105—170 °C (Found: C, 53.1; H, 5.6; Cl, 9.7.

Calculated for C42H45Cl2P3Ru: C, 53.9; H, 6.1; Cl, 8.8%.

(b) The compound mer-[RuCl2(PMe2Ph)] (0.10 g) was heated under reflux in hexane (50 cm3) with excess of PMe2Ph (0.04 cm3) 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 [RuCl2(PMe2Ph)]Cl.*

Dibromotetrakis(dimethylphenylphosphino)diruthenium(II), (IX), was also prepared using [RuBr2(PPh3)4] (0.20 g) and PMe2Ph (0.13 cm3) as a yellow solid (0.055 g, 41%), m.p. 144—160 °C (decomp.) (Found: C, 47.6; H, 5.6.

Calculated for C42H38Br2P3Ru: C, 47.2; H, 5.4%.

We thank Johnson, Matthey Ltd. for loans of ruthenium trichloride, the S.R.C. for the award of a research studentship (to P. W. A.), and Messrs. J. Savage and S. G. D. Henderson for experimental assistance.

[4/2670 Received, 23rd December, 1974]

* We thank Dr. L. Ruiz-Ramirez for this preparation.
Cationic and Neutral Complexes of Ruthenium-\(\text{II}\) and \(-\text{III}\) containing Tertiary Phosphines or Arsines and Nitrogen-donor Ligands

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In contrast to the reaction of \([\text{RuX}3(\text{EPh}3)_2(\text{HOMe})]\) (X = Cl or Br; E = P or As) with N-N (N-N = 2,2'-bipyridyl or 1,10-phenanthroline) in CH\(_2\)Cl\(_2\) which gives \([\text{RuX}3(\text{EPh}3)(\text{N-N})]\), the reaction in methanol gives \([\text{RuX}(\text{EPh}3)_3(\text{N-N})_2]\) (X = Cl or Br; E = P). For E = As these cations are only formed if \([\text{RuCl}3(\text{AsPh}3)(\text{N-N})]\) and N-N in methanol are reacted in the presence of Na[BPh\(_4\)]. However, reaction of \([\text{RuCl}3(\text{PPh}3)_2(\text{bipy})]\) and Na[BPh\(_4\)] in methanol gives both \([\text{RuCl}2(\text{PPh}3)(\text{bipy})]\) and \([\text{RuCl}(\text{PPh}3)(\text{bipy})]\), whereas \([\text{RuCl}(\text{PPh}3)(\text{bipy})]\) and PhCN give \([\text{RuCl}(\text{PPh}3)(\text{NCPh})(\text{bipy})]\). Reaction of \(\text{mer-[RuCl}_3(\text{PMe}_2\text{Ph})_3]\) and excess of bipy in methanol followed by recrystallisation from acetone-light petroleum gives \([\text{RuCl}(\text{PMe}_2\text{Ph})_3(\text{bipy})]\) and \([\text{RuCl}(\text{PMe}_2\text{Ph})(\text{bipy})(\text{OCMe}_2)]\) Cl, whereas in CH\(_2\)Cl\(_2\), \([\text{RuCl}_2(\text{PMe}_2\text{Ph})(\text{bipy})]\) and a small amount of \([\text{Hbipy}][\text{RuCl}_2(\text{PMe}_2\text{Ph})(\text{bipy})]\) is formed. With phen the product from CH\(_2\)Cl\(_2\)-hexane is \([\text{RuCl}_2(\text{PMe}_2\text{Ph})(\text{phen})]\), but from methanol, followed by recrystallisation from CH\(_2\)Cl\(_2\)-light petroleum, the main product is \([\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{phen})(\text{CH}_2\text{Cl}_2)]\) Cl together with small amounts of \([\text{Hphen}][\text{RuCl}_2(\text{PMe}_2\text{Ph})(\text{phen})]\) Cl. With 3,4,7,8-tetramethyl-1,10-phenanthroline (Me\(_4\text{phen}\)), reaction with \([\text{RuCl}_3(\text{PMe}_2\text{Ph})_3]\) in methanol gives \([\text{RuCl}(\text{PMe}_2\text{Ph})(\text{Me}_4\text{phen})]\) which on recrystallisation from CH\(_2\)Cl\(_2\)-pentane gives \([\text{RuCl}_2(\text{PMe}_2\text{Ph})(\text{Me}_4\text{phen})(\text{CH}_2\text{Cl}_2)]\) Cl. In contrast, reaction with 2,9-dimethyl-1,10-phenanthroline (Me\(_2\text{phen}\)) gives \([\text{RuCl}_2(\text{Me}_2\text{phen})(\text{Me}_4\text{phen})]\) Cl and \([\text{RuCl}_2(\text{PMe}_2\text{Ph})(\text{Me}_2\text{phen})]\) Cl. All the complexes have been characterised by elemental analysis, \(^1\text{H}\) and \(^{31}\text{P}\) 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\(\text{III}\) complexes containing tertiary phosphines and arsines have been reported elsewhere. However, as reported briefly earlier, when some of these reactions are carried out in more polar solvents such as methanol, \([\text{RuX}(\text{EPh}3)(\text{N-N})]\) forms.
In CH$_2$Cl$_2$, 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 X$^1$ (trans to N–N) and then X$^2$ (or X$^3$) is subsequently displaced to give (I).* The displacement of halide

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* Although no direct experimental evidence is available, we suggest that all complexes (I) have an cis configuration by analogy with earlier studies on [MCl$_x$(N–N)$_2$]Cl (M = Co, Cr, or Rh) which only exhibit cis-octaahedral geometry.  

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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 AsP$_3$ group and the remaining halide ligand by N–N to give [Ru(N–N)$_3$]X$_2$ (II) [step (iv)]. In addition, small amounts of [RuCl(OH)$_2$(N–N)$_2$]Cl$_2$H$_2$O, (III), are produced, presumably by displacement from (I) of the AsP$_3$ group by water [step (v)]. Reactions (iv) and (v) do not occur under these conditions when E = P, presumably because PPh$_3$ is a stronger nucleophile than AsP$_3$. However, the synthesis of [RuCl(AsP$_3$)(bipy)$_3$][BPh$_4$] by reaction of [RuCl$_3$(AsP$_3$)(bipy)] with excess of N–N in MeOH

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Na[BPh₄] in methanol confirms that (I) is initially formed even for E = As [step (iii)].

When [RuCl₃(PPh₃)(O₂NMe)]• 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 Ru⁺⁺⁺ cation [RuCl₃(PPh₃)(bipy)][BPh₄], (IV), and the other product is [RuCl₂(PPh₃)(bipy)]²[BPh₄], (I). Therefore, in methanol, preferential replacement of halide ion rather than PPh₃ occurs and the resulting Ru⁺⁺⁺ cation (IV) can be precipitated by [BPh₄]⁻ ion before substantial reduction to the Ru⁺⁺⁺ 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)(NCPPh)(bipy)]Cl₂H₂O (ref. 1.78 B.M. by Evans' method). The i.r. spectrum contained a weak band at 2222 cm⁻¹ [ν(CN)] suggesting that bonding occurs through the nitrogen. Examination of the far-i.r. spectrum revealed two bands at 320 and 300 cm⁻¹ [ν(RuCl)] consistent with configuration (Va). However, recrystallisation from CHCl₃-pentane gave a product with a single band at 334 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 Bidentate 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)₃(bipy)(OH₂)], and is conducting in CHCl₃. 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 ¹³P 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 7.73 (301 K) whose position was temperature and concentration dependent, indicating the presence of hydrogen-bonded water molecules (cf. [PtCl(phen)(PEt₃)₂][BF₄] in CDCl₃ (methyl region) at 301 K).

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)₃(bipy)][BPh₄]·2H₂O; (Vib) seems even more unlikely but cannot be completely ruled out on the present evidence (cf. [PtCl(phen)(PEt₃)₂][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 three other ligands are so arranged that the phosphorus atom do not lie on a plane of symmetry of the molecule.

Figure 1 ¹H n.m.r. spectrum of [RuCl₃(PMe₂Ph)₃(bipy)][Cl₂H₂O] in CDCl₃ (methyl region) at 301 K.

**In ref. 2, it was shown that [RuCl₃(PPh₃)(O₂NMe)] undergoes the same reactions as [RuCl₃(PPh₃)(HOMe)] providing the entering ligand is a stronger nucleophile than MeNO₂.

† 1 B.M. = 9.27 × 10⁻¹⁴ A m³, 1M = 1 mol dm⁻³.

‡ On the basis of C, H, and N analyses alone this complex was initially considered to be a geometrical isomer of (VIa).
to the $[\text{Hbipy}]^+$ ion.\textsuperscript{12} In hexane-$\text{CH}_2\text{Cl}_2$ (10 : 1 ratio by volume) only $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{bipy})]$ was isolated.

From earlier studies,\textsuperscript{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 $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{phen})]\text{Cl}$ but analysed for $[\text{Hphen}][\text{RuCl}_2(\text{PMe}_2\text{Ph})(\text{phen})]\text{H}_2\text{O}$. This complex is conducting in methanol and showed extra i.r. bands in the region 1 500—1 600 cm\textsuperscript{-1} characteristic of $[\text{Hphen}]^+$ ion.\textsuperscript{12} The main product, which was separated from the orange solid by recrystallisation from $\text{CH}_2\text{Cl}_2$—light petroleum, was the expected dark red $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{phen})](\text{CH}_2\text{Cl}_2)\text{Cl}$, (VIIIA) ($^1\text{H}$ and $^{31}\text{P}$ n.m.r. evidence). Although no evidence was found in this reaction for formation of $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{phen})]\text{Cl}$, addition of a large excess of $\text{PMe}_2\text{Ph}$ to a red $\text{CDCl}_3$ solution of (VIIIA) ($N=N = \text{phen}, S = \text{CH}_2\text{Cl}_2$) rapidly gave an orange solution with a $^1\text{H}$ n.m.r. pattern very similar to that observed for the $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{bipy})]^+$ cation. The main reason for the instability of the ($\text{PMe}_2\text{Ph})_3$ complex here is probably steric. In hexane-$\text{CH}_2\text{Cl}_2$ (10 : 1 v/v) reaction of $A'$ with excess of phen gave neutral $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2(\text{phen})]$, (IX).

In view of these differences in behaviour of bipy and phen, the reaction with $A'$ was extended to some methyl-substituted 1,10-phenanthrolines. Reaction between 3,4,7,8-tetramethyl-1,10-phenanthroline ($\text{Me}_4\text{phen}$) and $A'$ in methanol gave a red solution which after concentration and addition of $\text{CH}_2\text{Cl}_2$—pentane gave orange-red $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{Me}_4\text{phen})]\text{Cl}$. This was confirmed by its proton-noise decoupled $^{31}\text{P}$ n.m.r. spectrum which showed the expected triplet and doublet pattern (relative intensity 1 : 2). However, recrystallisation from $\text{CH}_2\text{Cl}_2$—pentane gave a dark red conducting solid whose $^{31}\text{P}$ n.m.r. spectrum consisted of two doublets of equal intensity. Its $^1\text{H}$ n.m.r. spectrum in $\text{CDCl}_3$ (Figure 2) consisted of two overlapping doublets centred at $\tau = 7.47$ and 7.51 (Me of $\text{Me}_4\text{phen}$), two doublets at $\tau = 7.74$ and 8.00, a 'triplet' at $\tau = 8.64$ (Me of $\text{PMe}_2\text{Ph}$), and a singlet at $\tau = 4.76$ ($\text{CH}_2\text{Cl}_2$). However, decoupling experiments revealed that the 'triplet' is in fact two overlapping doublets and thus the complex is formulated as $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{Me}_4\text{phen})](\text{CH}_2\text{Cl}_2)\text{Cl}$, (VIIIA).

In contrast, the reaction of $A'$ with excess of 2,9-dimethyl-1,10-phenanthroline ($\text{Me}_2\text{phen}$) in methanol gave a dark yellow solution which after concentration and addition of $\text{CH}_2\text{Cl}_2$—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 PMe2Ph ligands. The complex analysed for [RuCl₂(Me2phen)]₂ is strongly

![Figure 1](image)

**Figure 1** ¹H N.m.r. spectrum of [RuCl₂(PMe₂Ph)₃(Ph₂P)] in CDCl₃ (methyl region) at 301 K

conducting in methanol [λ (1 × 10⁻³ m)] 150 S cm⁻² mol⁻¹] suggesting the formulation [Ru₂Cl₂(Ph₂P)]Cl₂ (X) [cf. [Ru₂Cl₂(N-N)₃(Ph₂P)]Cl₂]. The yellow complex was identical in analysis, i.r., and ¹H n.m.r. to the well known [Ru₂Cl₂(PMe₂Ph)]Cl₂.

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 (PMe₂Ph)₃ complex (Via), phen and Me₂phen only give this complex with difficulty and the sterically encumbered Me₂phen gives no complexes containing itself and PMe₂Ph 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 cells. 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% H₃PO₄]. 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.

The complexes [RuCl₂(PPh₃)(bipy)]Cl₂H₂O, [RuCl₂(PPh₃)(bipy)][Y (Y = PF₆ or BF₄)], [RuCl₂(PPh₃)(phen)]Cl₂ (Y = Cl or PF₆), [RuCl₂(AsPh₃)(bipy)]BF₄, [Ru₂Cl₂(PPh₃)₄ (N-N)₃]X₃ (X = Cl or Br; N-N = bipy or phen), [Ru(bipy)₃Cl₂]₄H₂O, and [RuCl₂(OH₂)(bipy)]Cl₂H₂O were prepared as described in ref. 2.

(2,2'-Bipyridyl)dichlorobis(triphenylphosphine) ruthenium-(III) Tetraphenylborate.—The complex [RuCl₂(PMe₂Ph)₃(O₃NMe)] (0.10 g) was heated under reflux under nitrogen in methanol (100 cm³) with an excess of sodium tetraphenylborate (0.10 g) and 2,2'-bipyridyl (0.04 g) for ca. 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, 71.0; H, 5.3; N, 3.4. Calc. for C₃₅H₃₀Cl₃N₃OPRu: C, 69.7; H, 5.0; N, 3.1). The resulting red solution was filtered and the orange complex bis(2,2'-bipyridyl)-chloro(triphenylphosphine) ruthenium(III) tetraphenylborate which precipitated was washed with light petroleum (b.p. 100—120°C) and methanol (20%), m.p. 230°C (Found: C, 75.0; H, 5.1; N, 5.5. Calc. for C₂₃H₂₃BCl₃N₃OPRu: C, 72.8; H, 4.9; N, 5.4%).

(2,2'-Bipyridyl)dichlorophenyl cyano(triphenylphosphine) ruthenium(III) 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 C₃₅H₃₀Cl₃N₃OPRu: C, 56.5; H, 4.0; N, 5.7%). ¹H (6.0 × 10⁻³ m) in CDCl₃ = 8.2 S cm⁻² mol⁻¹; ν(RuCl) at 320 and 300 cm⁻¹. Recrystallisation from CH₂Cl₂-pentane gave an orange isomer, m.p. 168°C [v(RuCl) at 334 cm⁻¹].

(2,2'-Bipyridyl)dichlorotris(dimethylphosphine) ruthenium(III) Chloride Dihydrate.—The complex [RuCl₂(PMe₂Ph)₃ (0.30 g)] 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.l.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 C₂₃H₂₃Cl₃N₃OPRu: C, 52.4; H, 5.8; Cl, 9.1; N, 3.6%). A (1 × 10⁻³ m) in CH₂Cl₂ = 16.5 S cm⁻² mol⁻¹; ν in (CDCl₃) (301 K) (Figure 1) 8.97 (s) and 8.81 (s) [J(PP') = 6.5], 8.18 (d) [J(PP') = 7.5 Hz] (PMe₂Ph), 7.73 (s) (H₂O); and —4 (PMe₂Ph and bipy); ³¹P n.m.r., δ in (CDCl₃) (301 K) 6.88 (t) and 0.38 p.p.m. (d) [relative intensity 1:2, J(PP') = 32.8 Hz].

The concentration of the red filtrate gave a red solid, (acetone) (2,2'-bipyridyl)dichlorobis(dimethylphosphine) ruthenium(III) chloride (30%), m.p. 115°C (decomp.) (Found: C, 51.8; H, 5.5; Cl, 8.1; N, 4.0. Calc. for C₂₃H₂₃Cl₃N₃OPRu: C, 52.6; H, 5.4; Cl, 10.7; N, 4.2%). A (1 × 10⁻³ m) in CH₂Cl₂ = 20.0 S cm⁻² mol⁻¹; τ in (CDCl₃) (301 K) 8.71, 8.58, 8.01, 7.82 (doublets) [J(PP') = 8.5 Hz] (PMe₂Ph), 7.89 (s) (acetone), and 0—4 (PMe₂Ph and bipy); δ in (CDCl₃) (301 K) 27.20 and 15.14 p.p.m. (doublets) [relative intensity 1:1].

phenanthroline)ruthenium(u) chloride, 46.1; (2,2'-bipyridyl)dichloro(dimethylphenylphosphine)-ruthenium(II) Tetraphenylborate Dihydrate.—The complex 
[RuCl(PMe2Ph)3(bipy)]Cl2H2O (0.10 g) was dissolved in methanol (10 cm3) and a three-fold excess of Na[BPh4] (0.12 g) added. After shaking for 4 h 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, 65.8; H, 5.9; N, 2.7. Calc. for 
C80H72Cl6N6P12Ru: C, 56.6; H, 6.1; N, 2.7%). Λ (4 x 103) in CH3Cl = 40.0 S cm2 mol−1; τ (in CDC13) (301 K) 9.03 and 8.84 (triplets) [J(PH) + J(PP)’] 6.5. 8.25 (d) [J(PH) 7.5 Hz] [PMe2Ph], 7.70 (s) (H2O), and 0–5 (PMe2Ph, [BPh4]–, and bipy)

(2,2'-bipyridyl)dichloro(dimethylphenylphosphine)-ruthenium(II).—The complex [RuCl3(PMe2Ph)3] (0.20 g) was heated under reflux in hexane–dichloromethane (100: 
10 cm3) under nitrogen with an excess of phen for ca. 12 h. The resulting dark red solid was collected and washed with light petroleum (b.p. 100–120 °C) (70%), m.p. 100 °C (decomp.) (Found: C, 53.6; H, 4.6; N, 4.7. Calc. for 
C60H60Cl6N6P2Ru: C, 53.8; H, 4.8; N, 4.5%).

Chlororuthenium(II) (3,4,7,8-tetramethyl-
1,10-phenanthroline)ruthenium(II) Chloride.—The complex [RuCl3(PMe2Ph)3] (0.20 g) was heated under reflux in methanol (150 cm3) under nitrogen with an excess of Me2phen (0.08 g) for ca. 10 h. The resulting red solution containing a mixture of two compounds (i.e. evidence) was concentrated to dryness and CH2Cl2-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 (80%), m.p. 190–200 °C (decomp.) (Found: C, 57.2; H, 5.8; N, 3.2. Calc. for 
C60H60Cl6N6P2Ru: C, 58.2; H, 5.9; N, 3.4%). Λ (1 x 103) in CH3Cl = 18.0 S cm2 mol−1; δ (in CDC13) (301 K) 9.01 (s) and 1.09 p.p.m. (d) (relative intensity 1: 2, [J(PP) 32.5 Hz. Recrystallisation of this complex from CH2Cl2-pentane gave red crystals of chloro-
(dichloromethane)bis(dimethylphenylphosphine)(3,4,7,8-tetramethyl-1,10-phenanthroline)ruthenium(II) chloride, m.p. 200–
205 °C (decomp.) (Found: C, 51.6; H, 5.2; N, 3.6. Calc. for 
C60H60Cl6N6P2Ru: C, 61.5; H, 5.2; N, 3.6%). Λ (1 x 103) in CH3Cl = 16.5 S cm2 mol−1; τ (in CDC13) (301 K) (Figure 2) 8.64 (‘t’), 8.00, 7.74 (doublets) [J(PP) 8.5 Hz] [PMe2Ph], 7.47, 7.51 (doublets) (Me of Me2phen), and 4.76 (s) (CH3Cl).

μ-Dichlororuthenium(bis(2,9-dimethyl-1,10-phenanthroline)-
ruthenium(II) Dichloride.—The complex [RuCl3(PMe2Ph)3] (0.20 g) was heated under reflux in methanol (120 cm3) under nitrogen with an excess of Me2phen (0.08 g) for ca. 12 h. The resulting dark yellow solution was concentrated to dryness and CH2Cl2-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 
C60H60Cl6N6P2Ru: C, 56.5; H, 4.1; Cl, 12.1; N, 9.4%), Λ (1 x 103) in MeOH = 150 S cm2 mol−1. Concentration of the filtrate gave yellow crystals of μ-di-
chlororuthenium(bis(dimethylphenylphosphine)ruthenium(II) chloride, m.p. 120 °C (Found: C, 46.1; H, 5.5; Cl, 12.1. Calc. for 
C60H60Cl6N6P2Ru: C, 49.4; H, 5.6; Cl, 12.2%).

We thank Johnson, Matthey Ltd. for generous loans of ruthenium trichloride, the National A. University of Mexico for the award of a fellowship (to L. R. R.), and Dr. A. S. F. Boyd for obtaining the 31P n.m.r. spectra.

[4]2683 Received, 11th December, 1974]
[η⁶-C₆H₆Ru(OH)₃Ru(η⁶-C₆H₆)]Cl 3H₂O (III), is deposited as a crystalline yellow solid. Likewise, with [η⁶-C₆Me₃H₃RuCl₂]₂ and NaOH, [η⁶-C₆Me₃H₃Ru(OH)₃Ru(η⁶-C₆Me₃H₃)]Cl 3H₂O 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[η⁶-C₆H₆RuCl₃] (IV), although it is always difficult to obtain this complex free of CsCl. This product, which is the first reported anionic ruthenium arene complex, is closely related to M[RuCl₃COC₇H₈] (V) (M = Cs, Ph₃(PhCH₂)P; C₇H₈ = bicyclo[2.2.1]-hepta-2,5-diene(norbornadiene)) formed by reaction of [RuCl₂CO(C₇H₈)]₂ with MCl/HCl [4]. However, although V is a good precursor for synthesis of a range of anionic complexes of type Ph₃(PhCH₂)P[RuCl₃COL₂] (L = AsPh₃, C₅H₅N, Me₂SO etc.) [5], attempts to synthesise the unknown fac-[RuCl₃L₃] by reaction of IV with an excess of L gave only the neutral [η⁶-C₆H₆RuCl₂L] compounds.

Acknowledgement

We thank Johnson—Matthey Ltd for loans of ruthenium trichloride and the SRC (DRR) for a research studentship.

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.\textsuperscript{1,2}
Rearrangement Reactions of Some Ruthenium(II) Carbonyl and Thiocarbonyl Triphenylphosphine Complexes

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Reprinted from

JOURNAL OF THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1976
Ruthenium Complexes containing Group 5B Donor Ligands. Part 3.1,2
Rearrangement Reactions of Some Ruthenium(ii) Carboxyl and Thiocarboxyl Triphenylphosphine Complexes

By Peter W. Armit, Wilma J. Sime, and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of [RuCl₂(PPh₃)₃] with [Ru(CO)Cl₂(PPh₃)(dmf)](PPh₃) in acetonitrile (1:1 molar ratio) (dmf = NN-dimethylformamide) gives a high yield of [RuCl₂(PPh₃)(CO)(PPh₃)] = 2Me₂CO, supporting the mechanism proposed earlier for formation of the analogous thiacarbonyl complex. Extensions of this type of coupling reaction to form [RuCl₂(PPh₃)₂BrRuBrCl₂(CO)(PPh₃)] = 2Me₂CO and [RuCl₂(PPh₃)(CO)(PPh₃)] = 2Me₂CO are also described. Recrystallization of [RuCl₂(CO)₃(PPh₃)] from MeOH—CH₂Cl₂ gives [RuCl₂(CO)₂(HMe)(PPh₃)] (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 [RuCl₂(PPh₃)Cl₂(CO)(PPh₃)] = 5. The same isomeric mixture, together with [RuCl₂(CO)Cl₂(PPh₃)] is also formed by reaction of PPh₃ with [RuCl₂(CH₃P)] = [Ru(C₂H₅)Cl₂(CO)(PPh₃)] = 2(1:1 molar ratio). Treatment of (5) with Na[BPh₃] and PPh₃ in CH₂Cl₂ gives a high yield of [RuCl₂(PPh₃)₂BrRuBrCl₂(CO)(PPh₃)] = 6. This cation is also formed, together with (5), by prolonged shaking (4) in ethanol, whereas treatment of (4) with [AsPh₃]Cl—HCl in acetonitrile gives [AsPh₃][RuCl₂(CO)(PPh₃)] = (PPh₃) = Me₂CO = 7. Related complexes are described, starting from [Ru(C₂H₅)₃Cl](PPh₃)]. Finally, this information is used to suggest detailed rearrangement mechanisms in the [RuCl₂(PPh₃)] = 8, [PPh₃(CH₂PPh)] = [Ru(C₂H₅)(CO)(PPh₃)] = 2Me₂CO, and the closely related [RuX₂(PPh₃)] = [RuX₂(PPh₃)] = X = Cl or Br; n = 3 or 4) systems.

In an earlier paper1 we examined the reaction of [RuCl₂(PPh₃)] with carbon disulphide and showed that the three products [RuCl₂Cl₂(PPh₃)] = 1, [RuCl₂(PPh₃)Cl(PPh₃)] (2), and [RuCl₂(PPh₃)₂Cl(PPh₃)] are obtained. The structure of (3) was confirmed by X-ray structural analysis.3 In ref. 1 we indulged in some speculations as to the mechanism of formation of (3), and a scheme was proposed which involved coupling of an intermediate ‘[Ru(C₂H₅)₃Cl] = 4’ [possibly formed by elimination of PPh₃] from (2) with [RuCl₂(PPh₃)]. A competing reaction mechanism was ‘[RuCl₂Cl₂(PPh₃)]’ to give (1). Because of our inability to isolate the ‘[Ru(C₂H₅)₃Cl] = 4’ intermediate (but see later), it was impossible to prove this mechanism definitively. However, related reactions involving carbonyl(triphenylphosphine)ruthenium(ii) complexes have now been studied in some detail4 and some are reported in this paper, together with further studies on thiacarbonyl complexes of Ru[II].

RESULTS

Carbonyl Complexes.—It is well established that reaction of [RuCl₂(PPh₃)] with CO in acetonitrile or benzene gives [Ru(CO)Cl₂(PPh₃)] the isomer formed depending on the reaction conditions.8 However, James et al. have shown that if this carbonylation reaction is performed in more basic solvents such as NN-dimethylformamide (dmf) then the complex [Ru(CO)Cl₂(dmf)](PPh₃) can be isolated. When this was heated under reflux in acetonitrile with [RuCl₂(PPh₃)] a related reaction is the formation of [RuCl₂(PPh₃)₂BrRuBrCl₂(CO)(PPh₃)] from [RuCl₂(PPh₃)] and PPh₃ (2:1 molar ratio) which, presumably, involves initial formation of an intermediate such as ‘[RuCl₂(PPh₃)₂(PF₃)]’ followed by coupling with unchanged [RuCl₂(PPh₃)]. Similarly, coupling of species such as ‘[RuCl₂(PPh₃)] and [RuCl₂(PPh₃)] could be invoked to explain the formation of [RuCl₂Cl₂RuCl₂Cl₂(PPh₃)] from [RuCl₂(PPh₃)] and N₂ in a reverse-osmosis cell.9


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 suggesting a mixture of geometrical isomers which we have been unable to separate by chromatography.

The behaviour of \([\text{Ru(CO)Cl}_2(PPh_3)_2]\) in solution in the absence of \([\text{RuCl}_2(PPh_3)_2]\) is also of some interest. Thus, recrystallisation of this product from MeOH—CHCl_3 under mild conditions was claimed to give the five-coordinate \([\text{Ru(CO)Cl}_2(PPh_3)_2]\) but our recent reinvestigation \(^{18}\) of this product indicates that it should be formulated as the six-coordinate \([\text{Ru(CO)Cl}_2(\text{HOMe})(PPh_3)_2]\) at 1,940 cm\(^{-1}\) (CHCl_3). On the evidence of far-i.r. spectra \([\nu(\text{RuCl})]\) at ca. 330 cm\(^{-1}\) and \(^{31}\text{P}\) n.m.r. spectra at 303 K in CDCI_3 (singlet at ca. 34 p.p.m.), both these solvates are considered to have configuration (4) with trans-chlorides and trans-phosphines.

When, however, \([\text{Ru(CO)Cl}_2(\text{HOMe})(PPh_3)_2]\) was gently heated under reflux in dichloromethane-light petroleum (b.p. 60—80 °C) for several hours, removal of the CHCl_3 of three singlets between 53 and 55 p.p.m. and a complex series of peaks between 36 and 43 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 \([\text{[RuCl}_3]\text{Cl(Cl)}\text{RuCl}_2\text{Ru}([\text{PPh}_3]_2)]\) for which it analyses quite closely. As shown in Figure 1, a small amount of unchanged \([\text{Ru(CO)Cl}_4(\text{HOMe})(\text{PPh}_3)_2]\) invariably contaminates the sample.

Three geometrical isomers are possible for (5) and the \(^{31}\text{P}\) 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 \(\delta_{AB}\). Thus, two of the \(\delta_{AB}\) 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 \(\delta_{AB}\) 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 \(^{31}\text{P}/(\text{PP})\) values (ca. 25 Hz) are consistent with cis-phosphines bound to Ru\(^{14}\). Support for this interpretation comes from the very recent synthesis by similar methods of the related \([\text{[PPh}_3]\text{Cl(Cl)}\text{RuCl}_2\text{Ru}([\text{PPh}_3]_2)][\text{PPh}_3]\), where a combination of \(^{31}\text{P}\) and \(^{19}\text{F}\) n.m.r. spectroscopy provides unequivocal evidence for this formulation.

We have repeated this preparation and shown by \(^{31}\text{P}\) n.m.r. spectroscopy that the same isomeric mixture as above is formed. Also, Head and Nixon \(^{7}\) briefly mentioned the formation of (5) from reaction of \([\text{Ru(CO)Cl}_2]([\text{H}_3]\text{PPh}_3])\) and hydrogen chloride. We have repeated this preparation and shown by \(^{31}\text{P}\) n.m.r. spectroscopy that the same isomeric mixture as above is formed. Also, Head and Nixon \(^{7}\) reported the synthesis of (8) from \([\text{Ru(CO)Cl}_2(PPh_3)_2]\) and hydrogen chloride but no spectral details were given.

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**Table 1**

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Assignment of isomeric forms of ([\text{[PPh}_3]\text{Cl(Cl)}\text{RuCl}_2\text{Ru}([\text{PPh}_3]_2)]) to (^{31}\text{P}) n.m.r. resonances</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(^{31}\text{P}) n.m.r. (CDCI_3 at 213 K), (\delta_p) p.p.m.</td>
</tr>
<tr>
<td>(5a)</td>
<td>(\text{Singlet position} \quad \text{AB Position} )</td>
</tr>
<tr>
<td></td>
<td>54.7</td>
</tr>
<tr>
<td></td>
<td>40.8 (\langle\text{AB} 64.0 \text{ Hz}\rangle)</td>
</tr>
<tr>
<td>(5b)</td>
<td>53.6</td>
</tr>
<tr>
<td></td>
<td>39.6 (\langle\text{AB} 160.9 \text{ Hz}\rangle)</td>
</tr>
<tr>
<td>(5c)</td>
<td>53.2</td>
</tr>
<tr>
<td></td>
<td>38.6 (\langle\text{AB} 155.7 \text{ Hz}\rangle)</td>
</tr>
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</table>

† Very recently, McCleverty et al. \(^{11}\) briefly mentioned the formation of (5) from reaction of \([\text{Ru(CO)Cl}_2]([\text{H}_3]\text{PPh}_3])\) and hydrogen chloride. We have repeated this preparation and shown by \(^{31}\text{P}\) n.m.r. spectroscopy that the same isomeric mixture as above is formed. Also, Head and Nixon \(^{7}\) reported the synthesis of (8) from \([\text{Ru(CO)Cl}_2(PPh_3)_2]\) and hydrogen chloride but no spectral details were given.

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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. $\left[\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2\right]_2$ (1), $^1$ 31.3 p.p.m.) there is a substantial amount of the $\left[\text{Ru}_{2}(\text{CS})\text{Cl}_4(\text{PPh}_3)_3\right]_2$ isomer mixture present.$^1$ In fact, an estimate based on relative n.m.r. peak areas suggests 67% double bridging and 33% triple bridging and this is consistent with the analytical data quoted in ref. 10 (see Experimental section).

When $\left[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2\right]_2$ 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 $\nu$(CO) bands at 1976 and 1923 cm$^{-1}$, and the $^{31}$P n.m.r. spectrum at 243 K in CDCl$_3$ showed the products to be mixtures containing both $\text{Ru}$(CO)$_2$Cl$_2$(PPh$_3$)$_2$ [S = MeOH or Me$_2$CO (or EtOH)] and $\text{Ru}$(CO)$_2$Cl$_4$(PPh$_3$)$_2$ (5) isomers. However, in addition, another AB quartet on relative n.m.r. peak areas of $\left[\text{Ru}$(CO)$_2$Cl$_2$(PPh$_3$)$_2\right]_2$ (1). The additional AB quartet was more intense than the signals from the $\left[\text{Ru}$(CO)$_2$Cl$_4$(PPh$_3$)$_2\right]_2$ (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 consisted of unchanged $\left[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2\right]_2$ and the intensity of the additional AB quartet in the $^{31}$P n.m.r. spectrum was smaller than those signals arising from the $\left[\text{Ru}$(CO)$_2$Cl$_4$(PPh$_3$)$_2\right]_2$ isomers.

When (5) was mixed with PPh$_3$ and Na[BPh$_4$] and shaken in either CH$_2$Cl$_2$, Me$_2$CO, or EtOH for 60 h, a pale yellow solid was isolated which analyses quite closely for $\left[\text{Ph}_3\text{P}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2\right]_2$ [BPh$_4$] (6) [31.3 p.p.m. (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. [$^1$/PP 27.1, $\delta_{AB}$ 113.3 Hz] (cf. for $\left[\text{Ph}_3\text{P}(\text{CS})\text{Cl}RuCl_3Ru(CO)(\text{PPh}_3)_2\right]_2$ (1), the two phosphate groups cis to CO appear at 49.3 p.p.m. with $^1$/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 at terminal $\nu$(RuCl). Thus, this evidence clearly indicates that the cationic dimer (6) is formed both directly from

![Figure 1](image1.png)

**Figure 1** Phosphorus-$^{31}$ n.m.r. spectrum in CDCl$_3$ at 213 K of the product from reaction of $\left[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2\right]_2$ and dichloromethane-light petroleum (b.p. 60–80 °C) reveals that in addition to the doubly-bridged isomers (strong singlets at 17.2 and 25.5 p.p.m. cf. $\left[\text{Ru}$(CS)$_2$Cl$_4$(PPh$_3$)$_2\right]_2$ (1), $^1$ 31.3 p.p.m.) there is a substantial amount of the $\left[\text{Ru}_2$(CS)$_4$(PPh$_3$)$_3\right]_2$ isomer mixture present.$^1$ In fact, an estimate based on relative n.m.r. peak areas suggests 67% double bridging and 33% triple bridging and this is consistent with the analytical data quoted in ref. 10 (see Experimental section).

When $\left[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2\right]_2$ 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 $\nu$(CO) bands at 1976 and 1923 cm$^{-1}$, and the $^{31}$P n.m.r. spectrum at 243 K in CDCl$_3$ showed the products to be mixtures containing both $\text{Ru}$(CO)$_2$Cl$_2$(PPh$_3$)$_2$ [S = MeOH or Me$_2$CO (or EtOH)] and $\text{Ru}$(CO)$_2$Cl$_4$(PPh$_3$)$_2$ (5) isomers. However, in addition, another AB quartet on relative n.m.r. peak areas of $\left[\text{Ru}$(CO)$_2$Cl$_2$(PPh$_3$)$_2\right]_2$ (1). The additional AB quartet was more intense than the signals from the $\left[\text{Ru}$(CO)$_2$Cl$_4$(PPh$_3$)$_2\right]_2$ (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 consisted of unchanged $\left[\text{Ru}(\text{CO})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2\right]_2$ and the intensity of the additional AB quartet in the $^{31}$P n.m.r. spectrum was smaller than those signals arising from the $\left[\text{Ru}$(CO)$_2$Cl$_4$(PPh$_3$)$_2\right]_2$ isomers.

When (5) was mixed with PPh$_3$ and Na[BPh$_4$] and shaken in either CH$_2$Cl$_2$, Me$_2$CO, or EtOH for 60 h, a pale yellow solid was isolated which analyses quite closely for $\left[\text{Ph}_3\text{P}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2\right]_2$ [BPh$_4$] (6) [31.3 p.p.m. (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. [$^1$/PP 27.1, $\delta_{AB}$ 113.3 Hz] (cf. for $\left[\text{Ph}_3\text{P}(\text{CS})\text{Cl}RuCl_3Ru(CO)(\text{PPh}_3)_2\right]_2$ (1), the two phosphate groups cis to CO appear at 49.3 p.p.m. with $^1$/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 at terminal $\nu$(RuCl). Thus, this evidence clearly indicates that the cationic dimer (6) is formed both directly from

![Figure 2](image2.png)

**Figure 2** Phosphorus-$^{31}$ n.m.r. spectrum in CDCl$_3$ at 303 K of the product from reaction of $\left[\text{PPh}_3(\text{CH}_2\text{Ph})_2\right]_2$ [Ru($\text{C}_2\text{H}_4$)Cl$_2$]$_2$ (1) and 2 PPh$_3$ rearrangement of $\left[\text{Ru}$(CO)$_2$Cl$_2$(HOMe)(PPh$_3$)$_2\right]_2$ in polar solvents and by reaction of $\left[\text{Ru}$_2$(\text{CO})$_2$Cl$_4$(PPh$_3$)$_2\right]_2$ with Na[BPh$_4$] in the presence of PPh$_3$.

$^1$ 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.
Finally, when \([\text{Ru}(\text{CO})_2\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2]\) (4) was treated with \([\text{AsPh}_3\text{Cl}_2\text{HCl}]\) in \(\text{Me}_2\text{CO}\) the anionic \([\text{AsPh}_3\text{Cl}_2\text{Ru}(\text{CO})_2\text{Cl}_2(\text{PPh}_3)_2\text{Me}_2\text{CO}]\) (7) \([\nu(\text{CO}) = 1918 \text{ cm}^{-1}\) (Nujol)] can be isolated. Like the corresponding \([\text{M}[\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]]\) \((\text{M} = \text{AsPh}_3^+, \text{PPh}_3(\text{CH}_2\text{PPh}_3)^+, \text{or} \text{NEt}_4^+)\) formed by cleavage of \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) with MCl–HCl, \(^1\) (7) is too insoluble for \(^{31}\text{P}\) n.m.r. studies. However, the far-i.r. spectrum of (7) contained a strong peak at 320 cm\(^{-1}\) indicative of a trans-RuCl\(_2\) group (cf. 320 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 \([\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})(\text{PPh}_3)_2]\) and \([\text{RuCl}_2(\text{PPh}_3)_2]\) to give a high yield of \([\text{Ru}(\text{CO})\text{Cl}_2(\text{PPh}_3)_2]\) strongly supports the proposed mechanism suggested in ref. 1 for the formation of the analogous CS complex. Although the existence of the intermediate ‘\([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\)’ could not be verified directly in the \([\text{RuCl}_2(\text{PPh}_3)_2]\)–CS\(_2\) reaction, we found that reaction of \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) with refluxing dmf gave \([\text{Ru}(\text{CS})\text{Cl}_2(\text{dmf})(\text{PPh}_3)_2]\) \([\nu(\text{CS}) = 1275 \text{ cm}^{-1}\) (Nujol)], whose \(^{31}\text{P}\) n.m.r. spectrum at 303 K in CDC\(_2\) \((\text{singlet} \text{ at 30.2 p.p.m.})\) and far-i.r. spectrum \([\nu(\text{RuCl}) = 325 \text{ cm}^{-1}\)] indicates that configuration (4) is the most likely. Reaction of \([\text{Ru}(\text{CS})\text{Cl}_2(\text{dmf})(\text{PPh}_3)_2]\) and \([\text{RuCl}_2(\text{PPh}_3)_2]\) in refluxing Me\(_2\text{CO}\) \((1:1 \mu\text{olar ratio})\) then gave \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) \((3)\) \([\nu(\text{CS}) = 1284 \text{ cm}^{-1}\) (Nujol)] as the only product, which directly verifies the mechanism suggested earlier.

For completion, the behaviour of \([\text{Ru}(\text{CS})\text{Cl}_2(\text{dmf})(\text{PPh}_3)_2]\) in solution in the absence of \([\text{RuCl}_2(\text{PPh}_3)_2]\) was also briefly investigated. Recrystallisation from hot CH\(_2\text{Cl}_2\)–MeOH gave \([\text{Ru}(\text{CS})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2]\), whose far-i.r. and \(^{31}\text{P}\) n.m.r. spectra indicate configuration (4) as the most likely. This complex, on treatment with hot dichloromethane–light petroleum \((b.p. 60–80 ^\circ\text{C})\), gave a yellow crystalline solid which analyses closely for \([\text{Ph}_2\text{P}]\text{Cl}(\text{SC})\text{RuCl}_2\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2\text{Me}_2\text{CO}]\) (7).

A small amount of this complex \((\text{Me}_2\text{CO} \text{solvent})\) has been prepared previously by shaking \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) in degassed Me\(_2\text{CO}\) for several days. Unlike the analogous CO complex, the \(^{31}\text{P}\) 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. \((\text{relative intensity} 1 : 2)\) and weaker peaks, also of relative intensity \(1 : 2,\) at 50.3 and 35.6 p.p.m. \((\text{cf. ref. 1}).\) However, at 213 K, the \(^{31}\text{P}\) n.m.r. spectrum was better resolved and a tentative assignment of the isomers to the various resonances is given in the Experimental section.

A good indication, however, that an isomeric mixture of \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) complexes has been produced was obtained by its reaction with Na[\text{PPh}_3] and \text{PPh}_3 in CH\(_2\text{Cl}_2\) which gave a high yield of \([\text{Ph}_2\text{P}]\text{(SC)RuCl}_2(\text{CS})\text{Cl}_2(\text{PPh}_3)_2][\text{BPh}_4]\) (6). The \(^{31}\text{P}\) n.m.r. spectrum in CDC\(_2\) at 213 K consisted of a sharp quartet centred at 37.5 p.p.m. \([\gamma(\text{P}) 27.0, \delta_{\text{AB}} 88.6 \text{ Hz}.\) A small amount of this cation, together with the \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) isomeric mixture, was also formed when \([\text{Ru}(\text{CS})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2]\) was shaken in EtOH with an equimolar amount of \text{PPh}_3 for several hours.

**DISCUSSION**

A summary of the preparative methods for the various dimeric complexes of Ru\(^{11}\) 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 \([\text{RuYCl}_2(\text{HOMe})(\text{PPh}_3)_2]\), \(^{31}\text{P}\) 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 \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) isomeric mixture, accompanied by concomitant loss of one \text{PPh}_3 group. In more polar solvents this dimerisation step is accompanied by concomitant Cl\(^-\) displacement giving some \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\text{Cl}\).

However, in the \([\text{RuCl}_2(\text{PPh}_3)_2]\)–CS\(_2\) reaction, where very little \([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) is formed, it seems very reasonable to infer that the ‘\([\text{Ru}(\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\)’ intermediate will initially have cis-\text{PPh}_3 groups. Support for this statement comes from the X-ray structure...
of [RuCl₂(PPh₃)₂]^{+} 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 [RuCl₂(PPh₃)₂]**, shown by **P n.m.r. studies to contain cis-PPh₃ groups. Therefore, a likely structure for the five-co-ordinate intermediate in the [RuCl₂(PPh₃)₂]-CS₂ reaction is [8], formed by elimination of PPh₃S from either [Ru(γ-SCS)Cl(PPh₃)₂]Cl and/or [RuCl₆(PPh₃)₃(SCS)] (see Scheme 1*).

It is then proposed that [8] will undergo three competing reactions, namely: (i) coupling with unchanged [RuCl₂(PPh₃)₂]** or [RuCl₂(PPh₃)₃(SCS)] to give [Ru₂(CS)₂Cl₄(PPh₃)₃]** (3); (ii) self-dimerisation without phosphine loss to generate the six-co-ordinate ([Ru(CS)Cl₂(PPh₃)₂] (1); and (iii) isomerisation to form a complex such as (4) (probably solvated) with the sterically more stable trans-Ru(PPh₃)₂ arrangement. Isomer (4) can then dimerise with concomitant phosphine loss to give some [Ru₂(CS)₂Cl₄(PPh₃)₃] (5) [step (iv)] or dimerise with concomitant chloride-ion displacement to give [Ru₂(CS)₃Cl₃(PPh₃)₄]Cl (6) [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-bipyrimal structures to conform to both the theoretical predictions of Pearson,** Burdett,** and Ross and Hoffmann** for 6 complexes and the available X-ray data** for various five-co-ordinate 6 complexes.

A similar mechanism (Scheme 2) can be proposed to explain the products from the [PPh₃(CH₃Ph)][Ru(CH₃)₃(CO)Cl₃]-2PPh₃ reaction. As discussed fully in ref. 10, it is reasonable to postulate that an intermediate containing an γ-C₇H₈ group is first formed and this then reacts further with PPh₃ to give [Ru(CO)Cl₃(PPh₃)₃]** of structure (9). Analogous complexes [PPh₃(CH₃Ph)][Ru(CO)Cl₃L₂] of this stereochemistry have been characterised for L = AsPh₃, SMe₂, 2,2'-bipyridyl, etc. However, for (9) the combination of the high

\[
\text{Scheme 1} \quad (a) \text{CS}₂; \quad (b) -\text{PPh₃S}; \quad (c) \text{isomerisation}; \quad (d) [\text{RuCl₂(PPh₃)}]; \quad (e) \text{dimerisation}; \quad (f) \text{dmf, heat}; \quad (g) \text{dimerisation} \quad (\text{-PPh₃}); \quad (h) \text{PPh₃,Na[BPh₃]}; \quad (i) \text{dimerisation} \quad (\text{--CP}) \quad (j) \text{dimerisation} \quad (\text{--Cl}^{-})
\]
either of the \([\text{Ru}CO\text{Cl}_2\text{(PPh}_3)_2]\) isomers by generating \([\text{Ru}_2\text{CO}\text{Cl}_3\text{(PPh}_3)_2]\).

The reason why five-co-ordinate complexes (or six-co-ordinate solvates) with trans-PPh\(_3\) groups dimerise to form triple-chloride-bridged complexes with concomitant PPh\(_3\) loss whereas those with cis-PPh\(_3\) groups form double-chloride-bridged dimers without PPh\(_3\) loss 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.* The driving force for all these rearrangements is presumably the direct dimerisation (or cis-PMe\(_2\)Ph groups) 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\(^2\) to obtain evidence for the proposed \([\text{RuCl}_2\text{L}_3\text{]}\) intermediate (except for \(L = \text{PETPPh}_3\)). In fact, further studies reveal that the product giving rise to the \(^{31}\text{P}\) n.m.r. \(\text{AB}_2\) pattern (Figure 4, ref. 2) is not neutral \([\text{RuCl}_2\text{PETPPh}_3\text{]}\) but a cationic complex of probable formula \([\text{RuCl}(\text{HOEt})_2\text{(PETPPh}_3)\text{Cl}]\) or \([\text{RuCl}(\text{HOEt})\text{(PETPPh}_3)_2\text{Cl}_2]\). The disappearance of this \(^{31}\text{P}\) n.m.r.

\[
\begin{align*}
\text{(a)} & \quad \text{PPh}_3; \\
\text{(b)} & \quad \text{C}_2\text{H}_4; \\
\text{(c)} & \quad \text{Cl}^-; \\
\text{(d)} & \quad \text{dimerisation}; \\
\text{(e)} & \quad \text{isomerisation}; \\
\text{(f)} & \quad \text{dimerisation (\text{-PPh}_3)}
\end{align*}
\]

Scheme 2

\[
\begin{array}{c}
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\text{[RuCOCl}(\text{PPh}_3)_2]^- \\
\end{array}
\]

Scheme 3

\[
\begin{align*}
2[\text{RuX}_2\text{L}_4] & \rightarrow 2[\text{RuX}_2\text{L}_3] \\
2[\text{RuX}_2\text{L}_4] & \rightarrow 2[\text{RuX}_2\text{L}_3]
\end{align*}
\]

high stability of six-co-ordinate ruthenium(n) \((4d^8)\) 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 \([\text{RuX}_2\text{L}_n]\) \((L = \text{PR}_3; \text{X} = \text{Cl} \text{ or Br}; \text{n} = 3 \text{ or } 4)\) complexes is incorrect. Thus, instead of dimerisation to a double-halide-bridged complex \([\text{[RuX}_2\text{L}_3]}\) followed by intramolecular displacement by halide ion of either \(L\) to give \([\text{RuX}_2\text{L}_2}\text{Cl}\text{]}\) or \(X^-\) to give \([\text{RuX}_2\text{L}_2}\text{X}\text{]}\) (see Scheme, ref. 2), it is now suggested (Scheme 3) that direct dimerisation of \([\text{RuX}_2\text{L}_3]\) to form either \([\text{RuX}_2\text{L}_3}\text{X}\text{]}\) or \([\text{RuX}_2\text{L}_3}\text{Cl}\text{]}\) occurs accompanied by concomitant loss of either \(L\) or \(X^-\) groups respectively. The amount of each product formed depends on the relative strengths

* Note added in proof. Additional experimental evidence for this suggestion is the isolation of \([\text{[RuCOCl}(\text{PETPPh}_3)_2]}\), from a solution thought to contain \([\text{RuCOCl}(\text{PETPPh}_3)_2]\) with cis-PMe\(_2\)Ph groups (C. F. J. Barnard, A. Daniels, J. Jeffery, and R. J. Mawby, J.C.S. Dalton, 1976, 959).
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 457 and 235 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the 150—400 cm⁻¹ region on a Beckman RlC 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% H₃PO₄. Conductivity measurements were made on a Portland Electronics model 31 conductivity bridge. Melting points were determined with a Köffler hot-stage microscope and are uncorrected.

Ruthenium(III) trichloride trihydrate (Johnson, Matthey Ltd), carbon monoxide (Air products), triphenylphosphine (B.D.H.), sodium tetrachloroethylene (B.D.H.), and carbon disulphide (Fisons) were obtained as indicated. The complexes [RuX₂(PPh₃)₃]⁰ [RuX₂(CO)(dmf)(PPh₃)] [X = Cl or Br], [PPh₃(CH₂Ph)][Ru(C₂H₅)(CO)Cl₂] and [Ru(CsCl)(PPh₃)]⁰ were prepared as described elsewhere.

(a) Carbonyl Complexes. - Tri-µ-chloro-a-carbonyl-g-chloro-tetrakis(triphenylphosphine)diruthenium(II) - acetone (1/2). The complexes [RuCl₂(PPh₃)₃] (0.12 g) and [Ru(CO)(Cl)₂(dmffPPh₃)] (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 crystals of product were filtered off and washed with diethyl ether. Further crystals of the complex were obtained by evaporation of the filtrate to ca. 10 cm³ (0.13 g, 69%), m.p. 170—171 °C (decomp.); v(CO) at 1 951 cm⁻¹, v(CO) (acetone) at 1 710 cm⁻¹ (Nujol) [Found: C, 61.7; H, 4.7; Cl, 4.4%. Calc. for C₁₁H₁₂O₃Cl₂Ru₂: C, 61.6; H, 4.8; Cl, 4.5%].

(b) Complexes of Carbonyl Chloride. - Di-µ-chloro-a-carbonyl-g-chloro-tetrakis(triphenylphosphine)diruthenium(II) - acetone (1/1). The complex [RuBr₂(PPh₃)₃] (0.12 g) and [Ru(CO)(Cl)₂(dmffPPh₃)] (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 was filtered off and washed with diethyl ether (0.10 g, 56%), m.p. 150—160 °C (decomp.); v(CO) at 1 962 cm⁻¹, v(CO) (acetone) at 1 710 cm⁻¹ (Nujol) [Found: C, 59.0; H, 4.4; Br, 10.0; Cl, 4.6%. Calc. for C₁₄H₁₅Br₂ClO₄P₂Ru₂: C, 58.2; H, 4.2; Br, 10.2; Cl, 4.5%]; far-i.r. spectrum 3175s, 304v, 289s, 278vs, 260m, 250w, 244w, 236m, 228m, and 180bwr cm⁻¹.

Carbonyldichloro(methanol)bis(triphenylphosphine)ruthenium(II). The complex [Ru(CO)₂(Cl)₃(PPh₃)]⁰ [PPh₃ n.m.r. (CDCl₃ at 308 K) 33.9] (p.p.m.; v(RuCl) at 330 cm⁻¹] 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 C₁₁H₁₂O₃Cl₂Ru₂: C, 60.5; H, 4.5; Cl, 9.4%).

The reaction of [Ru₂(CO)₂Cl₄(PPh₃)₃] with H₃P0₄ (1/1) to give further crystals of the product which were filtered off and washed with MeOH and dried in vacuo at 40 °C (Found: C, 60.4; H, 4.3; Cl, 9.0. Calc. for C₁₁H₁₂O₃Cl₂Ru₂: C, 60.4; H, 4.3; Cl, 9.0%).

Tri-µ-chloro-carbonyl-trichlorobis(triphenylphosphine)ruthenium(II). The complex [Ru(CO)₂(HOMe)(PPh₃)] (0.13 g) and [PPh₃] 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)₂Cl₃(HOMe)(PPh₃)] (see Figure 1).

Reaction of [Rh(C₅H₅)₂] with [Ru₂(CO)₂Cl₄(PPh₃)₃] and PPh₃. The complex (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 [PPh₃(CH₂Ph)₃]Cl. The remaining solution was treated with pentane to give a pale orange solid [v(CO) at 2 029m, 1 993s, and 1 960 cm⁻¹ (Nujol)] 109.3 n.m.r. (CDCl₃ at 303 K) as shown in Figure 2 (Found: C, 59.8; H, 4.2. Calc. for mixture of [Ru₂(CO)₂Cl₄(PPh₃)₃] and [PPh₃]Cl) (OC)RuCl₂Ru(PPh₃)] (67:33; C, 59.8; H, 4.0%).

Tri-µ-chloro-bis(carbonyl)bis(triphenylphosphine) ruthenium(II) tetrachloroethylene. The [PPh₃]ClRCuCl₂RuCO(PPh₃)] isomeric mixture (0.12 g). The [Ru₂(CO)₂Cl₃(PPh₃)] (0.034 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 (ν(CO) at 1 976 cm⁻¹ (Nujol)] (Found: C, 66.7; H, 4.9. Calc. for C₁₁H₁₂Cl₄O₃Ru₂: C, 67.9; H, 4.6%). PPh₃ n.m.r. in CDCl₃ at 213 K, 40.8 (q); ν(P₃P) 27.1, δ(P₃P) 113.3 Hz; [Δ(1 × 10⁻⁴ mol dm⁻³) in CH₂Cl₂ = 30 S cm⁻² mol⁻¹]. The complex [Ru₂(CO)₂Cl₃(PPh₃)]Cl was also formed by shaking [Ru₂(CO)₂Cl₃(HOMe)(PPh₃)] in either Me₂CO or EtOH for 3 h (PPh₃ n.m.r. evidence) or without free PPh₃ present. In these reactions, the [Ru₂(CO)₂Cl₃(PPh₃)]Cl isomeric mixture and trace amounts of [Ru₂(CO)₂Cl₃(PPh₃)] were also found.

Tetraphenylarsenic carbonyl(trichlorobis(triphénylphosphine)ruthenium(II) - acetone (1/1). The complex [Ru₂(CO)₂Cl₃(HOME)(PPh₃)] (0.10 g) was suspended in degassed Me₂CO (80 cm³) and treated with a two-fold excess of AsPh₄Cl·CHCl₃ together with PPh₃ (ca. 0.01 g). The mixture was heated for 4 h when orange-yellow crystals of the product precipitated. They were filtered off, washed with water, MeOH, and diethyl ether, and dried in vacuo at 40 °C (13.1 g, 70%), m.p. 155—168 °C (ν(CO) at 1 918 cm⁻¹; ν(CO) (acetone) at 1 710 cm⁻¹ (Nujol)] (Found: C, 64.1; H, 4.7; Cl, 9.0. Calc. for C₁₁H₁₂As₂Cl₃O₃Ru₂: C, 64.0; H, 4.7; Cl, 8.9%). [Δ(1 × 10⁻⁴ mol dm⁻³) in CH₂Cl₂ = 45 S cm⁻² mol⁻¹].
(b) Thiocarbonyl Complexes.—Dicarbonyl(NN-dimethylformamide)thiocarbonyl bis(triphenylphosphine)ruthenium(n). The complex \([\text{Ru}(_2\text{CS})\text{Cl}_2(\text{PPh}_3)_2]\) (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 [v(CS) at 1275 cm\(^{-1}\), v(CO) (dmf) at 1660 cm\(^{-1}\), v(RuCl) at 325 cm\(^{-1}\) (Nujol)] (Found: C, 57.5; H, 4.5; N, 1.7%). Calc. for \(\text{C}_{40}\text{H}_{37}\text{Cl}_2\text{NOP}_2\text{Ru}_2\text{S}_2\): C, 57.8; H, 4.6; N, 1.7%. 31P n.m.r. (CDC\(_3\) at 303 K) 30.2 (s) p.p.m.

Tri-chloro-a-chloro-g-thiocarbonyl-tetra-kis(triphenylphosphine)ruthenium(n). The complexes \([\text{RuCl}_2(\text{PPh}_3)_3]\) (0.19 g) and \([\text{RuCl}_2(\text{dmf})(\text{PPh}_3)_2]\) (0.16 g) were heated under reflux for 4 h in degassed Me\(_2\text{CO}\) (30 cm\(^3\)) under an atmosphere of nitrogen. On cooling the solution, the red solid was deposited together with some unchanged \([\text{RuCl}_2(\text{dmf})(\text{PPh}_3)_2]\). Proof of the formation of (3) was obtained from the 31P n.m.r. spectrum of the products in CDC\(_3\) at 298 K (see ref. 2).

Dicarbonyl(methanol)thiocarbonylbis(triphenylphosphine)ruthenium(n). The complex \([\text{RuCl}_2(\text{dmf})(\text{PPh}_3)_2]\) was recrystallised from hot CH\(_2\text{Cl}_2\)-MeOH to give yellow crystals which were washed with MeOH, m.p. 182—184 °C (Found: C, 57.8; H, 4.5). Calc. for \(\text{C}_{40}\text{H}_{37}\text{Cl}_2\text{OP}_2\text{Ru}_2\text{S}: C, 59.3; H, 4.4\%\); i.r. spectrum (Nujol) 3460 and 1030 cm\(^{-1}\) (co-ordinated MeOH), v(CS) at 1280 cm\(^{-1}\), v(RuCl) at 332 cm\(^{-1}\); 31P n.m.r. (CDC\(_3\) at 303 K) 30.7 (s) p.p.m.

Tri-chloro-a-chloro-g-dithiocarbonyl-tris(triphenylphosphine)ruthenium(n)—dicarbonylmethane (2/1). The complex \([\text{Ru}(_2\text{CS})\text{Cl}_2(\text{HOMe})(\text{PPh}_3)_2]\) was dissolved in CH\(_2\text{Cl}_2\) and light petroleum (b.p. 60—80 °C) was added. The yellow solution was placed on a water-bath and the CH\(_2\text{Cl}_2\) allowed to evaporate off slowly over a period of 24 h to give yellow crystals which were filtered off and washed with diethyl ether, m.p. 264 °C [v(CS) at 1300 br cm\(^{-1}\) (Nujol)] (Found: C, 53.8; H, 3.6%). 31P n.m.r. (in CDC\(_3\) at 213 K): isomers (5a) 49.7 (s) and 37.0 (q) p.p.m. (\(J_{\text{AB}}\) 26.0; \(\delta_{\text{AB}}\) 15.0 Hz), isomers (5b) and (5c) 51.8 (s) and 35.8 (q) p.p.m. (\(J_{\text{AB}}\) 26.0; \(\delta_{\text{AB}}\) 71.4 Hz) and a very weak singlet at 50.9 p.p.m. and weak resonances between 36 and 38 p.p.m.

Tri-chloro-bis[thiocarbonylbis(triphenylphosphine)ruthenium(n)] tetraphenylborate. The \([\text{Ru}_2\text{Cl}_2(\text{PPh}_3)_3]\) isomeric mixture (0.08 g), Na[BPh\(_4\)] (0.022 g), and PPh\(_3\) (0.018 g) were shaken in degassed CH\(_2\text{Cl}_2\) (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 [v(CS) at 1290 cm\(^{-1}\) (Nujol)] (Found: C, 66.5; H, 4.6. Calc. for \(\text{C}_{66}\text{H}_{58}\text{BCl}_2\text{Ru}_2\text{S}_2\): C, 66.7; H, 4.5%); 31P n.m.r. (in CDC\(_3\) at 213 K) 37.5 (q) p.p.m., \(J(\text{P}_1\text{P}_2)\) 27.0; \(\delta(\text{P}_1\text{P}_2)\) 89.8 Hz \((S = 1 \times 10^{-3} \text{ mol dm}^{-3})\) in CH\(_2\text{Cl}_2 = 32 \text{ S cm}^2 \text{ mol}^{-1}\).

We thank Johnson, Matthey Ltd for generous loans of ruthenium(III) trichloride, the S.R.C. for the award of research studentships (to P. W. A. and W. J. S.), and Dr. A. S. F. Boyd for obtaining the 31P n.m.r. spectra.
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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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

Reaction of [RuCl₂CO(C₇H₈)]₂ with acetonitrile gives [RuCl₂CO(MeCN)C₇H₈] (1a), 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 [RuCl₂CO(L)C₇H₈] (L = acrylonitrile and cyclopropyl cyanide) have also been synthesised.

Although the carbonyl diene complexes [RuX₅CO(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 1966,1 surprisingly little work on the reactions of these compounds has been published. Thus, Robinson and Wilkinson1 showed that with pyridine, bridge splitting and diene displacement occur giving [RuCl₂CO(C₅H₅N)₂], whereas with quinoline (quin) trans-[RuCl₂(CO)₂(quin)] is formed. More recently, cleavage of the halide bridges with halide ion to give the [RuX₅CO(C₇H₈)]⁻ anion has been achieved2 and there has been a detailed study of the reactions of [Ph₂(PhCH₂)P] [RuCl₂(CO)(C₇H₈)] with various Lewis bases.3

In contrast, the chemistry of the related [RuX₅Cl]⁻ compounds has been extensively investigated.4 Very recently, Ashworth and Singleton4 reported that the cationic [RuCl₂(C₇H₈)₂(MeCN)₃][PF₆] complexes can be readily synthesised by heating under reflux [RuCl₂(C₇H₈)₂] with acetonitrile, followed by precipitation with [NH₄][PF₆]. In an attempt to prepare the analogous cation [RuCl₂(C₇H₈)₂(MeCN)₃](PF₆) we have examined the reaction of [RuCl₂CO(C₇H₈)]₁ with excess of acetonitrile. However, the main product from this reaction was a crystalline orange compound with analysis corresponding closely to [RuCl₂CO(MeCN)C₇H₈] (1). 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 (1) was undertaken both to verify the formulation and to ascertain the detailed geometry.

RESULTS

Crystal Data.—C₇H₈Cl₂NORu, 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 = 1.777, Z = 4, D₀ = 1.795 g cm⁻³. Cu-Kα radiation, λ = 1.5418 Å; μ(Cu-Kα) = 138.1 cm⁻¹. Space group P2₁/c.

Intensity data were derived from multiple-packs of Weissenburg films by use of an SAAB Mark II automatic film scanner.Layers h0—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.6

From the Patterson function, the ruthenium atom could be placed near 0,0,0, where it contributes significantly only to reflections k = 2n, h + l = 2n. The rest of the structure was found by the DIRDIF procedure,4 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 = XᵢᵢYᵢ, where X = sinθ/0.54 for sinθ < 0.54 (otherwise X = 1) and Y = 37/|F₀| for |F₀| > 37 (otherwise Y = 1.0). Latterly, 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 21843 (4 pp., 1 microfiche).*

DISCUSSION

Bond lengths and angles for (1) are given in Table 2, and a view of the molecule in the Figure. They show unequivocally that the product is (1a). The co-ordination of the ruthenium is essentially octahedral, with the CO and MeCN ligands trans. The greatest deviation

is shown by the N(1)–Ru–C(1) angle (167°). The cyclo-
odiene ligand is in the normal tub conformation, and the carbonyl is approximately and the acetonitrile ligand is accurately collinear with the ruthenium atom.

### Table 1

<table>
<thead>
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<th>Atom</th>
<th>10^4x</th>
<th>10^4y</th>
<th>10^4z</th>
<th>10^4U/Å²</th>
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<td>2510(1)</td>
<td>256(2)</td>
<td>-51(1)</td>
<td>*</td>
</tr>
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<td>Cl(1)</td>
<td>1610(3)</td>
<td>361(10)</td>
<td>1403(14)</td>
<td>*</td>
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<td>535(9)</td>
<td>507(4)</td>
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<td>-813(13)</td>
<td>31</td>
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<td>-3293(40)</td>
<td>1480(23)</td>
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* Anisotropic parameters (Å² × 10⁴). The temperature factor is of form exp [(2π/λ)²U/Å²] for (a), (b), (c), (d)

The deviation of the N–Ru–Cl(1) angle from 180° may be associated with the inclination of the acetonitrile group away from the cyclo-octadiene, shown by the mean N–Ru–Cl and N–Ru–X angles (96.5 and 85.3°). Even so, the contact distances N···Cl(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 2.97 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 [Ph₄(PPh₃)]₂[RuCl₄(C₆H₄)] with various Lewis bases also gave [RuCl₄CO-

![Projection of a single molecule of (I)](image)

### Table 2

**Bond lengths (Å) and bond angles (°) in (I).** X(1) and X(2) represent midpoints of the C(4)–C(6) and C(8)–C(9) bonds respectively.

<table>
<thead>
<tr>
<th>(a) Distances</th>
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<tr>
<td>Ru–Cl(1)</td>
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<td>Ru–X(2)</td>
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<td>C(1)–O</td>
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<table>
<thead>
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<th>(b) Angles</th>
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<td>Cl(1)–Cl(10)</td>
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<tr>
<td>Cl(1)–Cl(11)</td>
</tr>
</tbody>
</table>

### Scheme 1

Bridge cleavage reactions of the various possible isomers of [RuCl₄CO(C₆H₄)]²:-

![Scheme 1](image)
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(C₈H₁₂)]₄ (assuming n = 2, as in ref. 1) 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(C₈H₁₂)]₄ (an insoluble powder), an X-ray structural analysis of its reaction product with acetonitrile strongly suggests that the starting material

\[
\begin{align*}
\text{[RuCl₂CO(C₈H₁₂)]}_₄ \quad &\text{Scheme 2 An alternative mechanism for the formation of [RuCl₂CO(C₈H₁₂)]₄ (Ia)} \\
\end{align*}
\]

has configuration (IIIa) and that the CO group has a stronger trans-labilising effect than does cyclo-octa-1,5-diene.

This conclusion is, of course, based on the reasonable assumption that (I; b—d) are not initially formed and then undergo isomerisation to give (Ia) as the final product. We have also discounted the alternative mechanism (Scheme 2) which involves initial attack on a Ru–C bond to generate an \( \gamma^2 \)-C₈H₁₂ complex followed by bridge cleavage by the diene to produce [RuCl₂CO-(MeCN)C₈H₁₂] (Ia). If this mechanism were correct, 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 inability of MeCN to displace the diene group in [Ph₂(PhCH₂)P][RuCl₂CO(C₇H₈)] also supports this conclusion.

Finally, reaction of [RuCl₂CO(C₇H₈)] with acrylonitrile and cyclopropyl nitrile (L) gives the related [RuCl₂(CO)L(C₈H₁₂)] 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 292 and 457 grating spectrometers for Nujol and hexachlorobutadiene mulls on caesium iodide plates. M.p.s. were determined with a Koffler hot-stage microscope. Standard crystallographic calculations used the X-Ray ’72 program system.*

\[
\begin{align*}
\text{Acetonitrilecarbonyldichloro(cyclo-octa-1,5-diene) ruthenium(II).} &\quad [\text{RuCl₂CO(C₈H₁₂)]₄ \text{ was heated under reflux under nitrogen in acetonitrile for ca. 4 h. The resulting yellow solution was then filtered and concentrated to produce yellow-orange crystals (60%), m.p. 180 °C (decomp.) (Found: C, 37.8; H, 4.4; Cl, 20.2; N, 4.0. C₃H₆Cl₂NORu requires C, 37.8; H, 4.3; Cl, 20.3; N, 4.0%). I.r. spectrum: v(CN) 2 305, v(CO) 1 988, and v(C=C) 1 355 cm}^{-1} &\text{; combination of symmetric CH₃ deformation and C–C stretching vibrations at 2 340 cm}^{-1}. \\
\text{Cyclopropyl nitrile carbonyldichloro(cyclo-octa-1,5-diene) ruthenium(II).} &\quad \text{This was prepared similarly as a yellow crystalline solid, m.p. 150 °C (decomp.) (Found: C, 39.2; H, 4.3; N, 4.4. C₃H₆Cl₂NORu requires C, 39.9; H, 4.2; N, 3.9%). I.r. spectrum: v(CN) 2 158, v(CO) 2 015, and v(C=C) 1 333 cm}^{-1}. \\
\text{Carbonyldichloro(cyclo-octa-1,5-diene) cyclopropyl nitrile ruthenium(II).} &\quad \text{This was prepared similarly as an orange solid, m.p. 190 °C (decomp.) (Found: C, 41.4; H, 4.5; N, 3.8. C₃H₆Cl₂NORu requires C, 41.6; H, 4.5; N, 3.7%). I.r. spectrum: v(CN) 2 388, v(CO) 2 018, and v(C=C) 1 335 cm}^{-1}. \\
\end{align*}
\]

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. R.).

* It is assumed that (III) contains trans CO groups since only one vCO is observed in the i.r. spectrum (see ref. 1).  
*’ X-Ray’ program system, Technical Report TR 192, Computer Science Center, University of Maryland, version of June 1972.
Ruthenium Complexes containing Group 5B Donor Ligands. Part 4. Synthesis, Crystal and Molecular Structure of def-Tri-μ-chloro-h-diphenylphosphinito-bgi-tris(diphenylphosphinous acid)-ac-bis(methyl diphenylphosphinite)diruthenium(II)

Ruthenium Complexes containing Group 5B Donor Ligands. Part 4.†
Synthesis, Crystal and Molecular Structure of def-Tri-μ-chloro-h-diphenylphosphino-bgo-tris(diphenylphosphinous acid)-ac-bis(methyl(diphenylphosphinite)diruthenium(II))


Pyrolysis of solutions containing [(P(OMe)Ph3)3RuCl2Ru(P(OMe)Ph3)3]Cl for 12 h at 120 °C gives yellow crystals (1) shown by X-ray diffraction analysis to be [(P(OMe)Ph3)3RuCl2Ru(P(OMe)Ph3)3]Cl,6. The crystals are monoclinic, space group P21/c with a = 13.19, b = 21.98, c = 24.98 Å, β = 109.40°, and contain one molecule per asymmetric unit. The structure was solved using 1 534 film data, and refined to R 0.11.

Related pyrolysis reactions give the compounds [(P(OEt)Ph3)3[P(OH)Ph3]2RuCl2Ru(P(OH)Ph3)3] (2) and [(P(OEt)Ph3)3[P(OH)Ph3]2RuBr2Ru(P(OH)Ph3)3(PHO)] (3).

In recent years, a number of ruthenium(II) complexes containing tertiary phosphinites P(OR)2R1 and phosphonites P(OR)2R1 have been synthesised. These include compounds such as [RuH2(P(OEt)Ph)3]2,2 [RuCl2(P(OMe)2Ph)3] (R = Me, Et),3 [RuH(RP(OR)Ph)3]X (R = Me, Et; X = [PF6]−; 4 R = Me, X = [BPh3]−; 5,6), [Ru(P(OMe)Ph2)3][PH2]6 and [L2RuX2RuL2][BPh4] (L = P(OMe)Ph, P(OH)Ph, X = Cl; L = P(OEt)Ph2, P(OH)Ph2; X = Cl, Br).6

However, unlike the related tertiary phosphines, no neutral dimeric or anionic complexes of type [L2RuX2RuL2] or [L2RuX2RuL2][L2RuX2RuL2] (L = P(OR)R1 or P(OR)2R1) are known † and therefore, the aim of this present work was an attempt to synthesise such compounds.

RESULTS

Several years ago, Prince and Raspin§ demonstrated that the pyrolysis products of [(PET2Ph3)2RuCl2Ru(PET2PH3)]Cl were dependent upon the solvent media and the temperature of pyrolysis. Thus, in propyl propionate at 60 or 120 °C or methyl acetate at 120 °C, [(PET2Ph3)2RuCl2RuPET2Ph3] was formed ‡ whereas in methyl acetate at 60 °C, [Ru2Cl6(PET2Ph)6][RuCl6-(PET2Ph)6] § was produced.

Thus, by analogy with that work, the yellow solution obtained from the reaction of [(RuCl6(C2H5)3)] and P(OMe)Ph2 in methanol, which contains [(P(OMe)Ph3)3RuCl2Ru(P(OMe)Ph3)]6 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 (400–2000 cm−1) was very similar to

† The diamagnetic complexes [RuCl4(L)] [(RuCl4(L)] [L = P(OEt)3, P(OH)Ph3, P(OH)Ph2] have been synthesised by direct reaction of RuCl with L.5 However, as written, these contain paramagnetic ruthenium(III) anions and therefore, it is more likely that they should be reformulated as [RuCl4(L)] or even [RuCl4(L)] complexes.

‡ For details see Notices to Authors No. 7, in J.C.S. Dalton, 1976, Index issue (items less than 18 pp. are supplied as full-size copies).


‖ W. J. Sime and T. A. Stephenson, unpublished work.

[(P(OMe)Ph3)3RuCl2Ru(P(OMe)Ph3)]Cl, 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 (4000–400 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 Ph2POH and Ph2PO− groups †† in addition to P(OMe)Ph3. The same compound was obtained if the pyrolysis reaction was carried out at 60 °C. Although a full elemental analysis of (1) was obtained, 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).‡‡ 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 [(P(OMe)Ph3)3RuCl2Ru(P(OMe)Ph3)] (1) contains two methyl diphenylphosphinite groups and four other oxyphosphorus ligands. The diamagnetism of the compound and the long Ru···Ru distance (3.425 Å), which indicate no direct metal–metal interaction, suggests a ruthenium(II) complex. One half of the dimer contains the 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 Ph2PO− group and two Ph2POH 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\textsuperscript{13-16} [Figures 2 (ref. 15) and 3 (ref. 16)]. Pyrolysis of the yellow solution obtained from the reaction of $\{\text{RuCl}_2(C\text{H}_4)_3\}_2$ and P(OEt)Ph$_2$ in ethanol also gave an insoluble, crystalline yellow solid (2) whose infrared spectrum contained all the additional features found for (1) [plus bands characteristic of P(OEt)Ph$_2$].

\[ a = 26.01, \ b = 43.79, \ c = 24.56 \text{ Å}, \text{space group} \ F\bar{d}d \text{ (No. 70)}. \]

Photographs indicate a substantially disordered structure, and the calculated density $\left(1.50 \text{ g cm}^{-3}\right)$ indicates


half a molecule per asymmetric unit \((D_e = 1.50 \text{ g cm}^{-3}\)
for \(Z = 16\)), suggesting that the molecules are disordered,
about a two-fold axis or centre of symmetry.

Furthermore, if the yellow solution containing the
\([P(OEt)\text{Ph}_2]_3\text{RuCl}_3\text{Ru}[P(OH)\text{Ph}_2]_2]^{+}\) cation is treated

**Table 2**
Selected bond lengths in (1). Estimated standard deviations are: Ru-Cl, 0.015; Ru-P, 0.018; P-O, 0.05; P-C, 0.07; and O-C, 0.09 Å

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<th>Bond</th>
<th>Length (Å)</th>
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<td>Ru(1)-Cl(1)</td>
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<td>O(5)-O(6)</td>
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**Table 3**
(a) Selected bond angles in (1). Estimated standard deviations are 0.5° for all angles given

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(b) Mean values of chemically distinct angles in (1)

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<tr>
<td>P-O-C</td>
<td>128.2</td>
<td>2</td>
<td>5</td>
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</table>

with an excess of lithium bromide before pyrolysis, the
resulting yellow, crystalline solid (3) analyses very well
for \([P(OEt)\text{Ph}_2]_2[P(OH)\text{Ph}_2]_2\text{Br}_2\text{Ru}[P(OH)\text{Ph}_2]_2]^{+}\).

As expected, \([P(OR)\text{Ph}_2]_3\text{RuCl}_3\text{Ru}[P(OR)\text{Ph}_2]_2]^{+}\)

\([\text{BPh}_4]\) (\(R = \text{Me or Et}\)) was recovered unchanged after
pyrolysis. However, for \([P(OEt)\text{Ph}_2]_3\text{RuCl}_3\text{Ru}[P-
(OEt)\text{Ph}_2]_2]X (X = [\text{SCN}]^{-}, [\text{CN}]^{-}, \text{or} [\text{SPMe}_2]^{-}\),
pyrolysis gave yellow solids whose infrared spectra are
identical with (2). This suggests that the first step is
nucleophilic attack of [X]- on a co-ordinated alkoxyl-
group to give a Ph$_3$PO$^-$ group and RX. This is
presumably followed by stepwise hydrolysis of some of the
P(OR)Ph$_2$ groups, the partially hydrolysed product then
precipitating out because of its insolubility. Attempts
to make (1), (2), or (3) undergo further reactions or to
synthesize the corresponding phosphinite complexes
have proved unsuccessful to date.

**EXPERIMENTAL**

Microanalyses were by B.M.A.C. and the University of
Edinburgh Chemistry Department. I.r. spectra were
recorded in the region 4000—200 cm⁻¹ on 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 Kofler hot-stage microscope and are uncorrected. Standard crystallographic calculations were performed at the Edinburgh Regional Computing Centre.

Crystal Data.—C₃₄H₄₆Cl₂O₈P₈Ru₂. M = 1549, yellow monoclinic plates, α = 13.19(1), β = 21.98(2), c = 24.98(2) Å, β = 109.4(1)°, U = 6 831 Å³, Dₐ = 1.45 g cm⁻³, Z = 4, Dₐ = 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 k0—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/ [(Fo)² 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.

del-Tri-µ-chloro-h-diphenylphosphinato-bgl-tris(diphenylphosphinonic acid)-ac-bis(methyl diphenylphosphinonic)diruthenium(η) * (1).—{[RuCl₃(C₆H₅)₄]}¹⁹ (0.22 g) was refluxed with an excess of P(OMe)₃Ph₃ (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 C₃₄H₄₆Cl₂O₈P₈Ru₂: C, 57.4; H, 4.5. Cl, 6.9; P, 12.0; Ru, 13.0%).

del-Tri-µ-chloro-h-diphenylphosphinato-bgl-tris(diphenylphosphinonic acid)-ac-bis(methyl diphenylphosphinonic)diruthenium(η) (2).—(a) Prepared as for (1) by reaction of [{RuCl₃(C₆H₅)₄}]²⁺ and P(OMe)₃Ph₃ 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 C₃₄H₄₆Cl₂O₈P₈Ru₂: C, 57.9; H, 4.6; Cl, 6.7; P, 11.8%). (b) [{RuCl₃(PPh₃)}₃] (0.20 g) and PClPh₂ (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 C₃₄H₄₆Cl₂O₈P₈Ru₂: C, 57.9; H, 4.6%)

We thank John Matthee 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.

[6/1399 Received, 16th July, 1976]
SYNTHESES AND REARRANGEMENT REACTIONS OF [RuCl₂L₃ or 4]

COMPLEXES (L=P(OR)₃, P(OR)₂Ph, P(OR)Ph₂)

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Summary:— Reaction of [RuCl₂(PPh₃)₃] with excess L in hexane gives either [RuCl₂L₄] (L=P(OMe)₃, P(OMe)₂Ph) or [RuCl₂L₃] (L=P(OMe)Ph₂), P(OEt)Ph₂ which rearrange in polar solvents to the ionic complexes [L₃RuCl₃RuL]Cl (L=P(OMe)₂Ph, P(OMe)Ph₂, P(OEt)Ph₂) and [Ru₃Cl₅L₉]Cl (L=P(OEt)Ph₂, P(OMe)Ph₂).

Recently, we have shown that the monomeric tertiary phosphine complexes [RuCl₂(PR₃)₃ or 4], made by exchange of [RuCl₂(PPh₃)₄] with PR₃ 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 [RuCl₂(PPh₃)₃](I) with tertiary phosphites, phosphonites and phosphinites.

Thus, if (I) is refluxed with excess P(OMe)₃ or P(OMe)₂Ph in hexane, yellow crystals [RuCl₂L₄] are formed. Far ir studies suggest a cis/trans mixture for both compounds in the solid state but in solution, ³¹P 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 [RuCl₂(P(OMe)₂Ph)₄] in CH₂Cl₂ gives [(P(OMe)₂Ph)₃RuCl₃Ru(P(OMe)₂Ph)₃]Cl⁺ isolated as its BPh₄⁻ salt. However, this does not occur for the P(OMe)₃ complex. Reaction of (I) and excess P(OMe)₂Ph in methanol gives the
[Ru(P(OMe)2Ph)6]2+ cation which can also be isolated as a BPh4 salt.

In contrast, reaction of (I) with excess P(OR)Ph2 (R=Me,Et) in hexane gives orange solids of stoichiometry [RuCl2(P(OR)Ph)3], shown to be monomeric by molecular weight measurements in benzene. Variable temperature, proton decoupled 31P nmr studies indicate rapid intramolecular exchange of P(OR)Ph2 groups at temperatures >160K (single resonance observed) but at lower temperatures, more signals are found eg. for [RuCl2(P(Or)Ph)3] in (CD3)2CO/C6H5CH3 at ca 140K, two resonances at 141.1 (broadened doublet) and 167.3ppm (broadened triplet) of relative intensity 2:1 are observed (cf the limiting 31P nmr spectra of [RuCl2L3] (L=PPh3, PEP2Ph) [1]) which is consistent with the square pyramidal geometry expected for a five coordinate d6 complex [4].

Unlike [RuCl2L4] (L=P(OMe)3, P(OMe)2Ph), [RuCl2(P(OR)Ph)3] rapidly rearrange in polar solvents to give ionic complexes. For R=Me, the main product is [(P(OMe)Ph)3RuCl3Ru(P{OMe})3]Cl which is consistent with the mechanism shown in the Scheme. However, for R=Et, the main rearrangement product based on 31P nmr, conductivity and analytical data is the trimeric cation [Ru3Cl3(P(Or)Ph)9]Cl for which the cyclic structure (II) is tentatively proposed. 31P nmr studies indicate that

\[2[RuCl2(PR_3)_4] + 2PR_3 \rightarrow 2[RuCl2(PR_3)_3] \rightarrow \begin{array}{c} \text{PR}_3 \end{array} \]

\[(PR_3 = \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PETPh}_2, \text{PET}_2\text{Ph}, \text{PClPh}_2)\]
small amounts of $[\text{Ru}_3\text{Cl}_5\text{(P(OMe)Ph}_2\text{)}_9]\text{Cl}$ and $[(\text{P(OEt)Ph}_2)_3\text{RuCl}_3\text{Ru(P(OEt)Ph}_2\text{)}_3]\text{Cl}^+$ respectively are also formed.

Reaction between (I) and excess P(OMe)Ph$_2$ in methanol gives an immediate red solution from which the $[\text{RuCl(P(OMe)Ph}_2\text{)}_4\text{MeOH}]^+$ cation can be isolated by addition of NaBPh$_4$. With (I) and excess P(OEt)Ph$_2$ in ethanol, however, a red dimeric cation $[(\text{RuCl(P(OEt)Ph}_2\text{)}_4)_2]$ (BPh$_4$)$_2$ is isolated. On further refluxing the red solutions turned yellow and $[(\text{P(OMe)Ph}_2)_3\text{RuCl}_3\text{Ru(P(OMe)Ph}_2\text{)}_3]\text{Cl}$ and $[\text{Ru}_3\text{Cl}_5\text{(P(OEt)Ph}_2\text{)}_9]\text{Cl}$ respectively are formed. Therefore, a possible rationalisation of the formation of (II) is by facile coupling of $[(\text{RuCl(P(OEt)Ph}_2\text{)}_4)_2]$ and some unreacted $[\text{RuCl}_2(\text{P(OEt)Ph}_2)_3]$ accompanied by displacement of P(OEt)Ph$_2$. In contrast, rapid dimersation of $[\text{RuCl}_2(\text{P(OMe)Ph}_2)_3]$ to form the stable $[(\text{P(OMe)Ph}_2)_3\text{RuCl}_3\text{Ru(P(OMe)Ph}_2\text{)}_3]\text{Cl}$ appears to be the preferred reaction.

Finally, no evidence has been found here for the formation of neutral dimers $[\text{L}_3\text{RuCl}_3\text{RuClL}_2]$ 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 $[(\text{P(OR)Ph}_2)_3\text{RuCl}_3\text{Ru(OR)Ph}_2\text{)}_3]\text{Cl}$ at 120°C gives $[(\text{P(OR)Ph}_2)_2\text{P(OR)Ph}_2\text{)}_2\text{RuCl}_3\text{Ru(P(OR)Ph}_2\text{)}_2(\text{Ph}_2\text{PO})](\text{R=Me,Et})$ with no cleavage of Ru-P bonds [5]. (cf the formation of $[(\text{PET}_2\text{Ph})_3\text{RuCl}_3\text{RuCl(PET}_2\text{Ph)}_2]$ by pyrolysis of $[(\text{PET}_2\text{Ph})_3\text{RuCl}_3\text{Ru(PET}_2\text{Ph)}_3]\text{Cl}$[6]).

These compounds have also been synthesised by reaction of $[\text{Ru}_2\text{C}_7\text{H}_8\text{]}^n$ with excess L in ethanol or methanol [3].
Further studies on these rearrangements and of reactions of the products are in progress.

ACKNOWLEDGEMENT

We thank Johnson-Matthey Ltd for loans of ruthenium trichloride, the SRC for the award of a research studentship (WJS) and Dr. A.S.F. Boyd for obtaining the $^{31}$P nmr spectra.

REFERENCES

Preparation, X-Ray Crystal Structure Analysis, and Reactions of a Novel, Hydroxo-Bridged, Tetranuclear, π-Arene Ruthenium(II) Quadrivalent Cation 

\[ \left[ \left( \eta^1-\text{C}_6\text{H}_6 \right) \text{Ru(OH)} \right] \left( \text{SO}_4 \right)_2 \cdot 12\text{H}_2\text{O} \]

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Reprinted from

Journal of The Chemical Society
Chemical Communications
1977

The Chemical Society, Burlington House, London W1V 0BN
Preparation, X-Ray Crystal Structure Analysis, and Reactions of a Novel, Hydroxo-Bridged, Tetranuclear, $\pi$-Arene Ruthenium(II) Quadrivalent Cation $\left\{\left(\eta^4-C_6H_6\right)Ru(OH)\right\}_4^+\left(\text{SO}_4\right)_2\cdot12\text{H}_2\text{O}$

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Summary

Reaction of $\left\{\left(\eta^4-C_6H_6\right)RuCl_2\right\}_2$ 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.

Recently,\(^1\) we reported that the reaction of $\left\{\left(\eta^4-C_6H_6\right)RuCl_2\right\}_2$ with an excess of aqueous sodium hydroxide gave the yellow triple hydroxy-bridged cation $\left[\left(\eta^4-C_6H_6\right)Ru(OH)_3-Ru(\eta^4-C_6H_6)\right]Cl\cdot3\text{H}_2\text{O}$ (I). The same compound is also formed using excess of aqueous sodium carbonate.

We now find that if $\left\{\left(\eta^4-C_6H_6\right)RuCl_2\right\}_2$ is treated with less sodium carbonate $\left[[\text{Ru}^{II+}]_2\left[\text{CO}_3\right]^-\right]$ 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 tetrameric complex (II) containing both $\pi$-bonded benzene groups and hydroxo bridges.

Crystal data: $C_24H_{52}O_{24}Ru_4S_2$, $M = 1192$, cubic, $a = 12.36-\mu A$, $V = 1889 \mu^3$, $Z = 2$, $D_m = 2.10$, $D_o = 2.14$ g cm$^{-3}$, space group $Pn3m$ (no. 224). From precession photographs (Mo-$K\alpha$ radiation) 204 independent intensities were obtained using a Saab Mark II film scanner linked to a PDP-15 computer. The structure was solved by Patterson and difference Fourier syntheses and has been refined to $R = 0.11$ 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.\(^1\)

\(\text{Figure. Structure of } \left\{\left(\eta^4-C_6H_6\right)Ru(OH)\right\}_4^+\)

\(^1\) 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 \([\{(\text{tj}6-\text{C}_6\text{H}_6)\text{Ru(OH)}\}\text{H}_2\text{O}]^{2+}\) and sulphate anions. The cations have crystallographic \(4 \emph{3m} (T_d)\) 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 76-3 and 102-2° respectively. The arrangement

\[
\begin{align*}
\text{[ArRu(OH)Cl]_2}^+ & \rightarrow \text{[ArRu(OH)Cl]}_2^2+ \\
\text{[ArRu(OH)_2(OH)]^+} & \rightarrow \text{[ArRu(OH)_2(OH)]}^+ \\
\text{[ArRu(OH)_2(OH)]}^+ & \rightarrow \text{[ArRu(OH)_2(OH)]}^+ \\
\text{[ArRu(OH)Cl]}_2^+ & \rightarrow \text{[ArRu(OH)Cl]}_2^2+ \\
\text{[ArRu(OH)_2(OH)]^+} & \rightarrow \text{[ArRu(OH)_2(OH)]}^+ \\
\text{[ArRu(OH)_2(OH)]}^+ & \rightarrow \text{[ArRu(OH)_2(OH)]}^+ \\
\text{[ArRu(OH)_2(OH)]^+} & \rightarrow \text{[ArRu(OH)_2(OH)]}^+ \\
\text{[ArLRu(OH)_2(OH)RuL]}^2+ & \rightarrow \text{[ArRuBr_2]}^2+ \\
\text{[ArLRu(OH)_2(OH)RuL]}^2+ & \rightarrow \text{[ArRuBr_2]}^2+ \\
\text{[ArLRu(OH)_2(OH)RuL]}^2+ & \rightarrow \text{[ArRuBr_2]}^2+
\end{align*}
\]

Scheme. i, H_2O; ii, AgNO_3 or AgBF_4; iii, Na_2CO_3 (1:1 molar ratio); iv, excess of Na_2CO_3 or NaOH; v, dimerisation; vi, excess of Na_2SO_4; vii, aqueous NaOH; viii, aqueous LiBr (1:2 molar ratio); then NH_4PF_6; ix, excess of aqueous LiBr; x, L = pyridine or \(\gamma\)-picoline, then NH_4PF_6

of ruthenium and oxygen atoms may thus be described as a substantially distorted cube in which the Ru---Ru and O---O diagonals are 3-29 and 2-62 Å, respectively (see Figure) (cf. [Me_2Pt(OH)_4]). 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 \(\overline{3m} (D_{3d})\) 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 \(\{\frac{3}{4}; \frac{1}{4}; \frac{1}{4}\}\) in the cell, and are each linked to four others by contacts of benzene rings (3-9 Å) and to a further four by hydrogen bonds to sulphate ions from the OH groups \(\text{O}---\text{O}\) \(\text{ca.} 2-6\ Å\). 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 \(\{\frac{1}{4}; \frac{1}{4}; \frac{1}{4}\}; \text{etc.}\) 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\(^{2}\) it was suggested that in aqueous solution \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{RuCl}_2\}_2\] gave a mixture of \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{RuCl(OH)}\}_2\] and \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{Ru(OH)}^2\}]^+\) and therefore, in basic solution, successive deprotonation of the latter should give \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{Ru(OH)}(\text{OH})_2\}]^+\) and \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{Ru(OH)(OH)}\}_2\text{H}_2\text{O}\}]\) respectively with the dilydroxo speciesfavoured in strongly basic solutions. Because of the bridging propensity of hydroxo groups and the desire of ruthenium(ii) to exhibit six-co-ordination,\(^{4}\) it seems reasonable that \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{Ru(OH)}(\text{OH})_2\}]^+\) will tend to dimerise with concomitant elimination of water to form (I) and similarly, \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{Ru(OH)}(\text{OH})_2\}]^+\) will tetrimerise 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 \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{RuCl}_2\}_2\] with either aqueous AgNO_3 or AgBF_4 \(\text{(which produces the} \{(\text{tij}6-\text{C}_6\text{H}_6)\text{Ru(OH)}(\text{OH})_2\}]^+\) \(\text{cation})\) followed by addition of Na_2CO_3 (1:1 molar ratio) and excess of Na_2SO_4 gives (II) in much higher yields \(\text{(ca.} 60\%)\).

Finally, preliminary work \(\text{(see Scheme)}\) shows that (II) undergoes some interesting reactions. For example, with hydroxide ion, (I) is formed whereas addition of LiBr (1:2 molar ratio) gives the mixed triple bridged \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{Ru(OH)(OH)}\}_2\text{BrRu(}\text{tij}6-\text{C}_6\text{H}_6\}]^+\) cation; with excess of Br- the insoluble \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{RuBr}_2\}]^3\) is precipitated. In contrast, with neutral Lewis bases, \(\text{e.g.} \gamma\)-pyridine or \(\gamma\)-picoline (I) the double hydroxo bridged cations \([\{(\text{tij}6-\text{C}_6\text{H}_6)\text{L}Ru(\text{OH})_2\text{RuL(}\text{tij}6-\text{C}_6\text{H}_6\}]^2\) \(\text{can be isolated.}\)

We thank the S.R.C. for financial support to C.L.J. and D.R.R. and Johnson-Matthey Ltd. for generous loans of hydrated ruthenium trichloride.

\(\text{(Received, 15th December 1976; Com. 1365.)}\)

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\(^{1}\) D. R. Robertson and T. A. Stephenson, \emph{J. Organometallic Chem.}, 1976, 116, 229.


Preliminary Communication

Some \( \eta^5 \)-Cyclohexadienyl Complexes of Ruthenium.

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(Received October 11th, 1977)

Summary:— The compounds \([\eta^5C_6H_6Y]Ru(PR_3)(N-N)PF_6\) \((Y^- = H^-, \text{CN}^-, \text{OH}^-; PR_3 = \text{PMe}_2\text{Ph}, \text{PMePh}_2; N-N = \text{1,10-phenanthroline, 2,2'-bi-pyridyl})\), \([\eta^5C_6Me_3C_6H_14]Ru(\text{PMe}_2\text{Ph})\text{phen}][PF_6] \text{and}[\eta^5C_6H_7Ru\eta^5C_5H_5]\) 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 \( \eta^5 \)-cyclohexadienyl complexes were obtained.

Thus, if \([\{\eta^6\text{-arene}]\text{RuCl}_2\}_{2} \text{(arene} = \text{C}_6\text{H}_6, \text{C}_6\text{Me}_3\text{H}_3\})\) is stirred in methanol with excess 1,10-phenanthroline or 2,2'-bi-
pyridyl (N-N) for ca 1 hour, and then NH₂PF₆ 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)Ir(η₃-PR₃)(N-N)](PF₆)₂ 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-C₅H₆Y)Ru(PR₃)(N-N)]PF₆ were readily isolated. Similarly, [(η₆-C₆H₆Me₃)Ru(PMe₂Ph)(phen)]PF₆ reacted with NaBH₄ to give [(η₅-C₅Me₃H₄)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)₃]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 \( \eta^5 \)-cyclohexadienyl compounds were initially formed.

For the mixed sandwich compound \( [\eta^6-C_6H_{15} Ru^5 C_5H_5]Cl \), however, (made by reaction of \( [\eta^6-C_6H_{15} RuCl]_2 \) with \( TiCl_5 \)\([3]\)) small amounts of the neutral \( \eta^5 \)-cyclohexadienyl complex \( [\eta^5-C_6H_{15} Ru^5 C_5H_5] \) could be isolated from the reaction mixture obtained on addition of \( NaBH_4 \).

\( ^1H \) nmr studies also indicated the formation of some \( [(\eta^5-C_6H_{OMe})Ru^5 C_5H_5] \) on addition of NaOMe, but with NaOH and KCN, nmr studies suggested that ring displacement reactions were more important.

Finally, preliminary studies on the reaction of the triple hydroxide bridged compound \( [C_6H_{15} Ru(OH)_3 RuC_5H_5]BPh_4 \)\([4]\) with \( NaBH_4 \) indicated that two hydride ions may have added to one benzene ring to produce a 1,3 cyclohexadiene ruthenium compound. Similar double hydride ion additions have been observed for the \( [\eta^6-C_6H_{15} Ru^{2+}]_2 \) cation forming \( [\eta^6-C_6H_{15} Ru^5 C_5H_5] \)\([5]\) and in the reaction of \( [\eta^6-C_6H_{15} RuCl]_2 \) with \( NaBH_4 \) in \( d^6-(CH_3)_2SO \), 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.

ACKNOWLEDGEMENT

We thank Johnson-Matthey Ltd. for loans of ruthenium and rhodium trichloride, the SRC for a research studentship (DRR) and Messrs. K. Torbet and D.A. Tanner for experimental assistance.

REFERENCES


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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Reprinted from
JOURNAL
OF
THE CHEMICAL SOCIETY
DALTON TRANSACTIONS
1978
Ruthenium Complexes containing Group 5B Donor Ligands. Part 5.1
Synthesis and Crystal and Molecular Structure of Acetone(carbonyl)-
chloro(trichlorostannio)bis(triphenylphosphine)ruthenium(n)-Acetone
(1/1)
By Robert O. Gould,* Crystallography Laboratory, University of Nijmegen, Toernooiveld, Nijmegen, The Nether¬
lands
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The lemon-yellow crystals (1) obtained by reaction of the red 'carbonyl-containing' ruthenium solution with
SnCl₂ and PPh₃ in acetone have been shown to be [RuCl(SnCl₃)(CO)(PPh₃)₂(OCMe₂)]-Me-iCO and not
[Ru₂Cl₃(SnCl₃)-
(CO)₂(PPh₃)₃(OCMe₂)₂] (3) as previously suggested. The crystals are monoclinic, space group P2₁/c with a =
11.950(3), b = 14.988(3), c = 24.916(2) Å, and β = 92.51(1)°. The structure has been solved with 3 601 dif-
fractometer data and refined to R 0.037. It is, however, possible to obtain (3) by warming (1) in benzene, but it readily loses SnCl₂ to give some [(Ph₃P)(OC)CRuCl₃Ru(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·H₂O' 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.

O:\n
synthesised in our laboratory are \([(\text{RuCl}_2\text{Y(PPh}_3)_2]\), \([(\text{Ph}_3\text{P})_2\text{ClRuCl}_3\text{RuCl}_3\text{RuY(PPh}_3)_2]\) \(2\text{Me}_2\text{CO}\), \([(\text{Ph}_3\text{P})_2\text{YClRuCl}_3\text{RuY(PPh}_3)_2]\) \(2\text{Me}_2\text{CO}\), and \([(\text{Ph}_3\text{P})_2\text{YRuCl}_3\text{RuY(PPh}_3)_2]\) \(2\text{Me}_2\text{CO}\) \((Y = \text{CO or CS})\).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 \(\text{C}_6\text{D}_6\) 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 \(^{119}\text{Sn}\) satellites [\(\text{P}(\text{Sn})\text{250 Hz}\) 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 \(\text{C}_6(m)\) symmetry; the maximum deviation of the atoms \(\text{Ru, Sn, Cl}(1), \text{Cl}(2), \text{O}(1), \text{C}(1), \text{O}(2), \text{C}(39), \text{C}(40), \text{C}(41)\) from their best plane is 0.02 Å. Within this plane the short Ru–C(1) bond is reflected in the large Sn–Ru–C(1) and Cl(1)–Ru–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 Sn–Cl(2) bond is significantly shorter than the two out-of-plane bonds, and the distortion from \(\text{C}_6(3m)\) 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 defined by the Ru–P and P–C bonds are 39° for the rings beginning with C(3) and C(27), 42° for those at C(15) and 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 Cl(1)···C(16) and Cl(1)···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.$^3$ Also the $\nu$(CO) and $^{31}$P n.m.r. values of (1) are similar to those of the related $[\text{RuCl}_4(\text{CO})(\text{HOMe})]$-$\text{(PPh}_3)_2$ (2) [1 940 cm$^{-1}$ (CH$_2$Cl$_2$) and 37.0 p.p.m. (CDCl$_3$ at 303 K) respectively].$^4$ The two i.r. bands at 1 661 and 1 701 cm$^{-1}$ correspond to the carbonyl-stretching frequencies of co-ordinated and solvate acetone respectively (cf. $[\text{RuCl}_4(\text{PPh}_3)_2(\text{OCMe}_2)]$, $\nu$(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

| Bond lengths (Å) for (1). Quantities related by the pseudo-symmetry are printed on the same line |

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#### Table 3

| Angles (°) for (1). Quantities related by the pseudo-symmetry are printed on the same line |

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<td>C-C(phenyl)</td>
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<td>1.412 (max)</td>
</tr>
<tr>
<td></td>
<td>1.392 (mean)</td>
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Although (1) is not a dimer, the complex $[(\text{Ph}_3\text{P})\text{(OC)}(\text{Cl}_2\text{Sn})\text{RuCl}_2\text{Ru}(\text{CO})(\text{PPh}_3)_2]$ (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) (cf. the formation of $[(\text{Ph}_3\text{P})\text{(OC)}\text{ClRuCl}_2\text{Ru}(\text{CO})(\text{PPh}_3)_2]$ by heating $[\text{RuCl}_2(\text{CO})(\text{HOMe})(\text{PPh}_3)_2]$ in dichloromethane–light petroleum (b.p. 60–80 °C)$. A closely related complex to (3), $[(\text{OC})_2(\text{Sn})\text{RuCl}_2\text{Ru}(\text{CO})]$, was obtained by reaction of $[\text{RuCl}_3(\text{OCMe}_2)]$ with SnCl$_2$.

Unfortunately, (3) is not very stable in solution, readily eliminating a molecule of SnCl$_2$ to give some $[(\text{Ph}_3\text{P})\text{(OC)}\text{ClRuCl}_2\text{Ru}(\text{CO})(\text{PPh}_3)_2]$ ($^{31}$P n.m.r. evidence). Originally,$^2$ the pale yellow solid obtained either by heating (1) in benzene or refluxing a mixture of the 'red solution', PPh$_3$, and SnCl$_2$ was assigned the formulation $[\text{RuCl}_4(\text{SnCl}_3)(\text{OC})]_2(\text{PPh}_3)_2$ 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)Cl3Sn]RuCl3Ru[CO]((PPh3)2] and [(Ph3P)(OC)Cl3RuCl3Ru[CO]((PPh3)2]. 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 benzyl). Infrared 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. Phosphorus-31 n.m.r. spectra were obtained on a Varian Associates XL100 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.

**Acetone (carbonyl)chloro(trichlorostannato)bis(triphenylphosphine)ruthenium(II)—Acetone (1/1) (1) —**This was prepared as described in ref. 2 (Found: C, 49.9; H, 4.1; Cl, 14.7; O, 4.6; Sn, 7.9. Calc. for C16H38Cl2O2P2RuSn: C, 50.1; H, 4.1; Cl, 13.8; O, 4.7; 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 RuCl3vH2O) (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 1957 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. (17) (J/F(PSn) 250 Hz).

ag-Dicarbonyl-tri-u-chloro-b-trichlorostannio(triphenylphosphine)diruthenium(II) (3).—Complex (1) was dissolved in warm benzene. After 2 h the solution was reduced in volume and a pale yellow powder precipitated with light petroleum (b.p. 60—80 °C) (Found: C, 47.2; H, 3.3%; M (CHCl3) 1090. Calc. for C16H38Cl2O2P2Ru2Sn: C, 48.8; H, 3.3%; M 1376 [ν(CO) at 1975br cm⁻¹; ν(SnCl) at 320 cm⁻¹]: 31P n.m.r. spectrum in CDCl3 at 303 K: main resonances 53.2 (s) * and 41.4 (q) p.p.m. (JAB 25.9, 8AB 66.1 Hz) corresponding to [(Ph3P)(OC)Cl3RuCl3Ru[CO]((PPh3)2] (see ref. 4) but weaker resonances at 49.9(t).

* In ref. 4, Table 1, a singlet at 54.7 and a quartet at 40.8 p.p.m. were assigned to isomer (5a) but this shows that, in fact, the singlet at 53.2 p.p.m. [originally assigned to isomer (5b) or (5c)] arises from (5a).

† For details see Notices to Authors No. 7, J.C.S. Dalton, 1977, Index issue.

When (1) was heated in benzene, or the 'red solution', SnCl4 and PPh3 in acetone were heated under reflux, a pale yellow solid was deposited (see ref. 2) (Found: C, 53.2; H, 3.4; Cl, 13.7. Calc. for a mixture of 48% [(Ph3P)(OC)Cl3RuCl3Ru[CO]((PPh3)2] and 52% [(Ph3P)(OC)Cl3RuCl3Ru[CO]((PPh3)2]: C, 52.9; H, 3.5; Cl, 13.7%).

Crystal Data for (1).—C16H38Cl2O2P2RuSn, M = 1303, yellow monoclinic prisms, a = 11.950(3), b = 14.988(3), c = 24.916(2) Å, β = 92.51(1)°, U = 4468 Å³, Dm = 1.528, Z = 4, D = 1.534 g cm⁻³, space group P2₁/c (no. 14), Mo-Kα radiation, λ = 0.71069 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 θ ca. 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 F > 3σ(F) 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 partially refined before the unexpected second acetone 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 Fq > 120, where w = 120/Fq. In the last cycle no shift was greater than 0.3σ and wΔF was uniformly spread over ranges of sinθ and Fq. 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.† 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.
DIAMMINE(η⁶-BENZENE)CHLORORUTHENIUM(II)HEXAFLUOROPHOSPHATE
(3/1) AMMONIUM HEXAFLUOROPHOSPHATE, [C₆H₆RuCl(NH₃)₂]₃(PF₆)₃·NH₄PF₆.

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

\[ \left( \eta^6\text{C}_6\text{H}_6 \right) \text{RuCl}_3 \text{Ru}(\eta^6\text{C}_6\text{H}_6) \] PF₆

by the method of Bennett and Smith (1974) in order to compare it with the product isolated
by the reaction of \[ \left( \eta^6\text{C}_6\text{H}_6 \text{RuCl}_2 \right) \text{RuCl}_3 \] and NH₄PF₆ 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) = 0.71073 Å, \( \mu(\text{MoKα}) = 16.0 \text{ cm}^{-1} \),
hexagonal, \( a = 15.9(1) \text{Å}, c = 9.09(1) \text{Å}, U = 1993 \text{Å}^3 \), \( D_m = 2.27 \),
\( D_c = 2.24 \text{ gcm}^{-3} \), \( Z = 2 \), \( F(000) = 1312 \), space group P6₃/m.

Intensity data, structure determination and refinement.
Intensity data were collected on precession photographs using
zirconium-filtered molybdenum radiation. From layers \( h,k \ 0 \rightarrow 3 \)
Table 1
Final positional and thermal parameters and their standard deviations (in parentheses).

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Table 2

Bond distances (Å) and bond angles (°) with standard deviations

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<td>92.6(6)°</td>
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<td>N(1)-Ru-C(2)</td>
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<tr>
<td>Ru-C(1)</td>
<td>2.174(20) Å</td>
<td>N(1)-Ru-C(3)</td>
<td>94.7(6)°</td>
</tr>
<tr>
<td>Ru-C(2)</td>
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<td>N(1)-Ru-C(1)'</td>
<td>157.8(7)°</td>
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<tr>
<td>Ru-C(3)</td>
<td>2.188(20) Å</td>
<td>N(1)-Ru-C(2)'</td>
<td>155.7(6)°</td>
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<tr>
<td>Cl-Ru-N(1)</td>
<td>83.7(5)°</td>
<td>N(1)-Ru-C(3)'</td>
<td>119.1(6)°</td>
</tr>
<tr>
<td>Cl-Ru-C(1)</td>
<td>117.8(5)°</td>
<td>N(1)-Ru-N(1)'</td>
<td>84.0(5)°</td>
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<td>Cl-Ru-C(2)</td>
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<tr>
<td>Cl-Ru-C(3)</td>
<td>156.9(4)°</td>
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</tbody>
</table>

Atoms marked with primes are related to those in the list by the symmetry operation x, -y, z. All distances and angles within the benzene are within three standard deviations of 1.39 Å and 120°.

Anions

| | | | |
| P(1)-F(1) | 1.569(19) Å | P(2)-F(5) | 1.572(38) Å |
| P(1)-F(2) | 1.602(18) Å | P(2)-F(6) | 1.545(50) |
| P(1)-F(3) | 1.573(12)   |           |            |
| P(1)-F(4) | 1.568(13)   |           |            |

All angles within the anions are within three standard deviations of 90 or 180°.

and Θ = 25°. Of these, 738 data had T > 3σ(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 P63 and P63/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 $\bar{3}$ ($S_6$) and $\bar{6}$ ($C_{3h}$) symmetry respectively. An unsuccessful attempt was made to refine the structure in the non-centric space group $P6_3/m$ 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 $W = XY$ 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 $b^*$

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°,
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 $x$, $y$, $\frac{1}{2}$ and $x$, $y$, $\frac{3}{4}$ are shown.
while each of these atoms makes angles with the carbon atoms of the ring of 93°, 119° and 157°. 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 Å) and between atoms of type N(1) and F(1)(3.14 Å). The disorder of the ammonium ions is hardly surprising, as each N(2) is simultaneously 3.01 Å from six atoms of type F(2) and 3.06 Å from six atoms of type F(4). In either orientation of the second PF$_6^-$ ion, each F(5) is 3.14 Å 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


Received: 18 August 1977
Synthesis and Crystal and Molecular Structure of Benzyltriphenylphosphonium Bicyclo[2.2.1]hepta-2,5-diene-carbonyltrichlororuthenate(II) and Benzyltriphenylphosphonium Carboxylpentachlororuthenate(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 [[Ru(CO)Cl2(C7Hg)]2] with an excess of Ph3PCH2Cl and HCl in degassed acetone gives the orange complex [Ph3PCH2Cl]2[Ru(CO)Cl5] (1) and a red solution from which [Ph3PCH2Cl]2[Ru(CO)Cl4]2.CH2Cl2 Cl (2) may be isolated by work-up with dichloromethane. Strong e.s.r. signals indicate that (2) is a ruthenium(III) compound. After removal of (2), further precipitation gave a mixture of products containing [Ru(CO)Cl5]−, [Ru(H2O)(CO)Cl4]2−, and cis-[Ru(CO)2Cl4]2−, indicated by i.r. evidence (cf. the work of Colton and Farthing).

Table 1 Crystal Data

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<th>Compound:</th>
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<td>C24H24Cl2O8Ru</td>
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<td>Pbcn</td>
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<tr>
<td>b/Å</td>
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<tr>
<td>c/Å</td>
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<td>Dm/g cm−3</td>
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<td>1183</td>
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<tr>
<td>Z</td>
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<td>4</td>
</tr>
<tr>
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<td>No. of observations</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 MoKα 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.

Figure 1 Perspective views of the anions of (1) and (2), showing the numbering scheme

Paper: E/055/78
Received (as a submission to JCS Dalton) on 23rd January 1978; transferred by the authors to J. Chem. Research on 11th April 1978.

The anion of (1) is essentially octahedral, with facial Cl ligands, as suggested by its 1H (ref. 1) and 13C (ref. 2) spectra. The anion of (2) is disordered on a site of 2 (C2) symmetry such that the carbonyl group appears to be superimposed on Cl(3). This disorder is, however, not so extensive as that reported for Cs2[Ru(CO)Cl4].

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(1)–C(6) bonds, respectively; primed atoms are related to unprimed by the symmetry operation −x, y, z−x

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<th>(2)</th>
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<td>C(1)–O–Cl(36)</td>
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</table>

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:


Synthesis, Crystal and Molecular Structure of Benzylitriphenyolphosphonium Bicyclic 2.2.1.1.7-hepta-2,5-dienecarbonyl dichlororuthenate(II) and Benzylitriphenyolphosphonium carbonylpentachlororuthenate(III) - dichloromethane (1/2).


Chemistry Department, University of Edinburgh, Edinburgh EH9 3JJ and Crystallography Laboratory, The Catholic University, Nijmegen, The Netherlands.

Reaction of \( \{[\text{RuCl}_2\text{CO(C}_7\text{H}_8)]_2 \} \) with \( \text{Ph}_3(\text{PhCH}_2)\text{PCl/HCl} \) in acetone gave \( \text{Ph}_3(\text{PhCH}_2)\text{P} [\text{RuCl}_3\text{CO(C}_7\text{H}_8)] \) shown to have an octahedral anion with a facial arrangement of chloride ligands. Crystals are monoclinic, space group \( \text{P}2_1/\text{c} \) with \( a = 12.471(5), b = 18.176(2), c = 14.181(4) \), \( \beta = 109.84(4)^\circ \), and contain one formula per asymmetric unit. Work up of the filtrate gave a small amount of the paramagnetic red solid \( \text{Ph}_3(\text{PhCH}_2)\text{P} [\text{Ru}(\text{CO})\text{Cl}_3]. 2\text{CH}_2\text{Cl}_2 \) Crystals are orthorhombic, space group \( \text{Pbcn} \) with \( a = 13.913(10), b = 18.401(9), c = 20.965(9) \), and contain one-half formula per asymmetric unit. The structures were solved with 2359 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 \( \{[\text{RuCl}_2\text{CO(C}_7\text{H}_8)]_2 \} \) with an excess of \( \text{Ph}_3(\text{PhCH}_2)\text{PCl/HCl} \) on degassed

acetone for several days gave the orange complex \( \text{Ph}_3\text{PhCH}_2\text{P}^-\left[\text{RuCl}_3\text{CO(C}_7\text{H}_8\right]_1 \). 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 \( \left(\text{Ph}_3\text{PhCH}_2\text{P}\right)_2\left[\text{Ru(CO)Cl}_5\right]_2\text{CH}_2\text{Cl}_2 \).

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

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<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>space group</th>
<th>( a / \AA )</th>
<th>( b / \AA )</th>
<th>( c / \AA )</th>
<th>( \beta / ^\circ )</th>
<th>( Dm/\mu g \ cm^{-3} )</th>
<th>( De/\mu g \ cm^{-3} )</th>
<th>( M )</th>
<th>( Z )</th>
<th>( \mu (Mo-K_{\alpha})/\text{cm}^{-1} )</th>
<th>No. of observations</th>
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<td>1</td>
<td>( C_{33} H_{30} Cl_{13} O )</td>
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<tr>
<td>2</td>
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\( \theta \) about 15°. For 2, crystals were badly formed, and the number of observations represents only 40% of reflections actually measured \( \theta \leq 20^\circ \), while for 1, 75% of the measured intensities \( \theta \leq 22^\circ \) were significant at the 3\( \sigma \) 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 \((C-H = 1.1\,\text{\AA}},\) 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 1 was \( W = 56/F_0^2 \) for \( F_0 > 56 \) and 1.0 otherwise. For 2, a scheme of the form \( W = 1/(c_F + 0.001|F_0|) \) was used, where \( c_F \) is based on counting statistics. At convergence, \( R \) was 0.045 for 1, and 0.083 for 2.

Fractional co-ordinates for 1 and 2 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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**Solvent**

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| Cl(4)   | 3850(7)    | 1641(5)    | 1953(4)    |
| Cl(5)   | 3583(6)    | 2085(5)    | 2603(5)    |

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Distances and angles in the complex anions. The symbols 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, 1/2 - z.
TABLE 4

Summary of subsidiary distances and angles. Mean ± values are based on the e.s.d.'s from least squares, ± (mean) values are from the spread of the n chemically equivalent values. Distances are given in Å and angles in degrees.

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DISCUSSION

As expected, the anion in \( \mathbf{1} \) is essentially octahedral, with the chloride ligands facial. The geometry of the norbornadiene ligand is similar to that in trans-\( \text{[Ru(} \text{C}_8\text{H}_6\text{NH}_{2})\text{Cl}_2\text{]}^2^- \) where \( \text{Ru-X} = 2.065 \text{Å} \), \( \text{X-Ru-X} = 70.0^\circ \), and the angle corresponding to \( \text{Cl(3)-Ru-C(1)} \) is 156.5°. An example with chloride ions trans to double bonds is given by cis-\( \text{[Ru(} \text{C}_8\text{H}_{12})\text{(MeCN)}\text{Cl}]^4^- \) with the cyclooctadiene ligand allowing a much larger \( \text{X-Ru-X} \) 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 \( \text{(NH}_4)_3[\text{RuCl}_6] \) 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 \( \text{(NH}_4)_2[\text{Ru(CO)}\text{Cl}_5] \) (\( \text{CO} \) 2059 cm\(^{-1}\) ) was isolated. It was suggested that it was formed by reaction of the intermediate \( \text{[Ru(H}_2\text{O})\text{Cl}_5]}^2^- \) anion with carbon monoxide. Later Colton and Farthing\(^6\) and Cleare and Griffith\(^7\) showed that the \( \text{[Ru(CO)}\text{Cl}_5]^2^- \) 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 \( \text{[Ru(H}_2\text{O})(\text{CO})\text{Cl}_4]}^2^- \), then orange \( \text{[Ru(CO)}\text{Cl}_4]^1^2^- \) and finally pale yellow \( \text{[Ru(CO)}\text{Cl}_3]^- \) anions.

Likewise, in this work, although the first precipitate \( 2 \) (after removal of compound \( 1 \)) had a single \( \nu_{\text{CO}} \) band in its ir spectrum at 1991 cm\(^{-1} \) (cf \( \text{Cs}_2 \text{Ru}(\text{CO})\text{Cl}_5 \) \( \nu_{\text{CO}} \) 2038 cm\(^{-1}) \). Further precipitation gave a product with several bands in the \( \nu_{\text{CO}} \) region at 2016, 1994, and 1950-1930s (broad). By comparison with the values cited in reference 6, this would indicate that this is a mixture containing the \( [\text{RuCOCl}]^{2-} \), \( [\text{RuH}_2\text{O}(\text{CO})\text{Cl}]^{2-} \) and cis-\( [\text{Ru}(\text{CO})_2\text{Cl}]^{2-} \) anions.

The crystal structure of a compound containing the \( [\text{Ru}(\text{CO})\text{Cl}]^{2-} \) anion does not seem to have been previously reported. A preliminary study of \( \text{Cs}_2\text{Ru}(\text{CO})\text{Cl}_5 \) \(^8\) showed that the anion was required to have \( \overline{3}m \) symmetry, indicating complete disorder of the CO group over six sites. In \( 2 \), the crystallographic \( 2 (C_2) \) 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\(^\circ\), and Cl-O of 0.56\(^\circ\), considerably less than the resolution of the data. The Ru-Cl(1) (trans to Cl) bond length is similar to that (2.333\(^\circ\)) in \( \text{Cs}_2\text{RuCl}_5\text{H}_2\text{O} \) \(^9\) where the crystallographic twofold 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 conc. HCl in the presence of excess chloride ion. This is evident from the fact that reaction of \( [\text{RuCl}_2\text{CO(diene)}]_2 \) (dienen \( = \text{C}_7\text{H}_8 \), \( \text{C}_8\text{H}_{12} \)) with excess Ph\(_3\)PhCH\(_2\)PCl/HCl in acetone under reflux gave much higher


yields of \((\text{Ph}_3\text{P})_2\left[\text{Ru}(\text{CO})\text{Cl}_5\right]\) 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 \(\text{MCl/HC1}\) is the formation of \(\text{Ph}_4\text{As}^+\left[\text{RuCl}_4\left(\text{PPh}_3\right)_2\right]\left(\text{Me}_2\text{CO}\right)_2\) by reaction of \(\left[\text{RuCl}_2^+\left(\text{PPh}_3\right)_3\text{Cl}^+\right]\) with excess \(\text{Ph}_4\text{AsCl/HC1}\) in acetone. Although the detailed mechanism of this oxidation process is unknown, it is possible that Ru(IV) hydrido intermediates may be involved.

Finally, Berch and Davison\(^{11}\) have shown that the red solution (made by passing \(\text{CO}\) through an ethanolic solution of \(\text{RuCl}_3\cdot3\text{H}_2\text{O}\) for several hours) contains some of the chlorocarbonyl anions of ruthenium(II) and (III) discussed in refs. 6 and 7. Furthermore, they present evidence that the \(\left[\text{RuCl}_2\text{CO}\left(\text{diene}\right)\right]^2-\) compounds are only formed from reaction of diene with the ruthenium(III) chlorocarbonyl anion \(\left[\text{Ru}(\text{CO})\text{Cl}_3\right]^2-\). 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 \(\text{MCl/HC1}\) is applicable.

\[
\begin{align*}
\text{III} & \quad \text{Ru(CO)Cl}_3^2- \quad \text{EtO}H \\
& \quad \text{HCl/C1} \quad \text{MC1/HC1} \\
& \quad \text{II} \quad \left[\text{RuCl}_2\text{CO(C}_7\text{H}_8\right)]_2 \\
& \quad \text{MC1/HC1} \\
\end{align*}
\]

As noted previously, however, the product obtained is very sensitive to the cation used since reaction of \(\left[\text{RuCl}_2\text{CO(C}_7\text{H}_8\right)]_2\) and \(\text{Ph}_4\text{AsCl/HC1}\) in acetone under reflux gave \((\text{Ph}_4\text{As})_2\left[\text{Ru}(\text{CO})\text{Cl}_4\right]_2\). Presumably, \(\left[\text{Ru}(\text{CO})\text{Cl}_5\right]^2-\) is initially formed and then, as in refs. 6 and 7 undergoes reduction with the additional \(\text{CO}\) group being abstracted from the solvent.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000-250 cm\(^{-1}\) on a Perkin Elmer 357 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.

Benzylitriphenylphosphoniumcarbonylpentachlororuthenate(III)-dichloromethane(1/2).

A suspension of the complex \([\text{RuCl}_2\text{CO(C}_7\text{H}_8)\] \(2\) (1.0g) was shaken in degassed acetone (100 cm\(^3\)) under nitrogen for 5 days with an excess of benzylitriphenylphosphonium chloride (2.8g) and concentrated hydrochloric acid (1.0 cm\(^3\)). The resulting orange Ph\(_3\)PhCH\(_2\)P\[RuCl\(_3\)CO(C\(_7\)H\(_8\))] \(1\) was filtered off and purified as described elsewhere. Concentration of the remaining dark red solution under vacuo gave more of the anion \(1\). After filtering off this product, the solution was further concentrated and then a mixture of dichloromethane - light petroleum (bp 110 - 120\(^\circ\)C) was added to precipitate the red crystalline solid (2) mp = 230\(^\circ\)C (but at 120-125\(^\circ\)C, loss of solvent occurs) \(\text{Found: C, 53.6; H, 4.1, Cl, 18.7 P, 6.7. Calc. for C}_{53}\text{H}_{48}\text{Cl}_{9}\text{OPRu: C, 53.8; H, 4.1, Cl, 27.0 P, 5.2%}\). However Calc. for \((\text{Ph}_3\text{PhCH}_2\text{P})_2[\text{RuCl}_5\text{CO}], \text{Cl}, 17.5; \text{P, 6.1%}\) with \(v_{\text{CO}} 1994 \text{ cm}^{-1}; v_{\text{RuCl}} 320 \text{ cm}^{-1}\) (nujol)]\(1\(0.001 \text{ mol dm}^{-3}\) in \text{CH}_2\text{Cl}_2\) = 26.08 cm\(^2\) mol\(^{-1}\).

On leaving the solution to stand, more reddish-brown solid was precipitated. The ir spectrum (nujol mull) showed several carbonyl bands at 1950, 1941 and 1950 - 1930 cm\(^{-1}\) attributed to \(2\) 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 Ph₃PCH₂PCl (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%) νCO 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 $l$, $10/F_o$, $10 F_c$. 
Table 6. Structure factors for (2).

Columns are $l, 10/F_\sigma/, 10/F_G/.$
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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All values are $10^3 U$ in $\text{Å}^2$.

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B. Isotropic temperature factors.

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ELECTROCHEMICAL STUDIES ON TRIPLE-BRIDGED DI-RUTHENIUM(II) COMPOUNDS

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Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)
Received February 20th, 1978

Summary

Voltammetric studies on [(PR₃)₂ClRuᴵᴵCl₃RuᴵᴵY(PR₃)₂] (PR₃ = PPh₃ or tol₃, Y = CO or CS) show a reversible one-electron oxidation to form [(PR₃)₂ClRuᴵᴵᴵCl₃Ruᴵᴵ₃Y(PR₃)₂]⁺ whereas the corresponding oxidation of dialkenium(II) mono-cations [(PR₃)₃RuCl₃Ru(PR₃)₃]⁺ (PR₃ = P(OMe)Ph₂ or Me₂Ph), [(C₆H₆)RuCl₃Ru(C₆H₆)]⁺ and [(C₆H₃R₃)Ru(OH)₃Ru(C₆H₃R₃)]⁺ (R = H or Me) is more difficult and also irreversible. For the (RuCl₃Ru)ₓ⁺ system, the redox series x = 1, 2, 3 is established.

Chatt and Hayter characterised the first triple chloro bridged ruthenium(II) dimers, [Ru₂Cl₃(PR₃)₆]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 i-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 $[\text{Ru}_2\text{Cl}_5(\text{P-n-Bu}_3)_4]$ [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 arsenic systems the common $\text{RuCl}_3\text{Ru}$ 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.

$$\text{(RuCl}_3\text{Ru})^+ \rightleftharpoons (\text{RuCl}_3\text{Ru})^{2+} \rightleftharpoons (\text{RuCl}_3\text{Ru})^{3+} \quad (1)$$

Cyclic voltammetry (CV) and linear alternating current voltammetry (acV) of I and II in $\text{CH}_2\text{Cl}_2/0.5 \ M \ \text{n-Bu}_4\text{NCIO}_4$ 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 $[\text{Ru}_2\text{Cl}_4(\text{PR}_3)_4]^+$ salts by chemical oxidation of I and II using $\text{I}_2$ 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 $\text{CH}_2\text{Cl}_2$ 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-Bu4NCIO4/CH2Cl2.](image)
In contrast to I and II, [Ru₂Cl₃(PR₃)₆]BPh₄ complexes (PR₃ = P(OMe)Ph₂ or PMe₂Ph [9, 10]) in CH₂Cl₂ each undergo an irreversible oxidation (with no CV return wave); an additional reversible one-electron wave of similar CV height is observed at more positive potentials. Evidently the initially formed dication 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-Bu₄NClO₄. 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 [Ru₂Cl₃(H₂O)₆]²⁺ and [Ru₂Cl₃(NH₃)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 Ptol₁ by the less electron-donating PPh₃ 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(PR₃)₂RuClenti takes place to generate a true mixed-valence Ru²⁺⁺⁺⁺ complex rather than an extensively delocalised Ru²⁺⁺ radical. However, X-ray studies on the analogous but symmetrically ligated [Ru₂Cl₃(PBu₃)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 [(NH₃)₄Ru₂(µ-pyrazine)Ru(NH₃)₄]⁺⁺ which have been extensively discussed as models for intramolecular electron-transfer theory [19].

### Table 1

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<td>CH₂Cl₂, As/AgI</td>
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<tr>
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r = reversible wave, E_1/2(CV) = E_p(acV), ΔE_pp(CV) ~ 60 mV; i = irreversible wave, E_1/2(CV) measured at 85% I_p (anodic scan). bSCN⁻ salt gives identical results.
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 \([\text{Ru}_2\text{Cl}_3(\text{CO})(\text{PPh}_3)_4]\) and \([\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]^+\)). 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 \([\text{Ru}_2\text{Cl}_3\text{L}_6]^+\) and \([\text{Ru}_2\text{Cl}_4\text{L}_5]^+\), where L represents any soft neutral ligand, probably represent stable limits; \([\text{Ru}_2\text{Cl}_3\text{L}_6]^2+\) species are only formed at more positive potentials and decompose rapidly, as evidenced by our electrochemical studies. Clearly, complexes of stoichiometry \([\text{Ru}_2\text{Cl}_3\text{L}_4]\) 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 \((\text{RuCl}_3\text{Ru})^+\) complexes the Ru–Ru distance might indeed contract upon oxidation (from ca. 3.4 Å \([16,17]\)), since \([\text{Ru}_2\text{Cl}_5(\text{P-n-Bu}_3\text{L})_4]\) has an internuclear separation of 3.12 Å \([13]\), and in diamagnetic \([\text{Ru}_2(\text{S}_2\text{CNMe}_2)_5]^+\) the relatively unconstrained ruthenium(III)—ruthenium(III) bond length is 2.79 Å \([18]\). However \([\text{Ru}_2\text{Cl}_3(\text{AsPh}_3)_6]\) is paramagnetic \((\mu_{\text{eff}} (293 \text{ K}) 1.95\text{ per Ru})\). 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* SYNTHESSES
AND REARRANGEMENT REACTIONS OF VARIOUS \([\text{RuCl}_2\text{L}_3\text{or}_4]\) COMPLEXES \([\text{L} = \text{P(OMe)}_3, \text{P(OMe)}_2\text{Ph}, \text{P(OR)}\text{Ph}_(R = \text{Me, Et})]\)

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Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

Summary

Reaction of \([\text{RuCl}_2(\text{PPh})_3]\) with an excess of \(\text{L}\) in hexane gives either \([\text{RuCl}_2\text{L}^4] \quad (\text{L} = \text{P(OMe)}_3, \text{P(OMe)}_2\text{Ph})\) or \([\text{RuCl}_2\text{L}^3] \quad (\text{L} = \text{P(OMe)}\text{Ph}, \text{P(OEt)}\text{Ph})\). In polar solvents, \([\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]\) and \([\text{RuCl}_2(\text{P(OMe)}\text{Ph})_3]\) rearrange to the ionic dimers \([\text{RuCl}_2(\text{P(OMe)}\text{Ph})_6]\text{Cl}\) whereas \([\text{RuCl}_2(\text{P(OEt)}\text{Ph})_3]\) converts to the ionic trimer \([\text{Ru}_3\text{Cl}_6(\text{P(OEt)}\text{Ph})_9]\text{Cl}\). Reaction of \([\text{RuCl}_2(\text{PPh})_3]\) with excess of \(\text{P(OR)}\text{Ph}\) in alcohols first generates the red \([\text{RuCl}(\text{P(OMe)}\text{Ph})_4]^+\) and \([\text{Ru}_2\text{Cl}_2(\text{P(OEt)}\text{Ph})_8]^2+\) cations respectively which can be isolated as their \(\text{BPh}_4\) salts, and later, the yellow \([\text{Ru}_3\text{Cl}_6(\text{P(OMe)}\text{Ph})_6]^+\) and \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph})_9]^+\) cations are formed. These various rearrangement processes have been extensively studied by variable temperature \(^{31}\text{P} - ^1\text{H}\) nmr spectroscopy and an overall mechanism of rearrangement for the various \([\text{RuCl}_2\text{L}_3\text{and}_4]\) 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 \([\text{RuCl}_2(\text{P(OMe)}_3)_4]\) was deposited. The far ir spectrum (400-200 cm\(^{-1}\)), containing a strong band at 340 cm\(^{-1}\) assigned to \(v(\text{RuCl})\) from trans chloride groups, [5] and bands at 306 and 295 cm\(^{-1}\) ascribed to \(v(\text{RuCl})\) 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 CDC\(_3\) at both 213 and 298K consisted of a singlet at \(\delta129.4\) ppm and the \(^1\text{H}\) nmr spectrum in CDC\(_3\) at 301K showed a symmetrical quintet centred at 3.84\& (cf similar resonance patterns for trans-[\(\text{Rh}\{\text{P(OMe)}_3\}_4\text{X}Y\}]^+\) 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 CDC\(_3\) at 213K contained a singlet at \(\delta150.5\) ppm (trans isomer) and two triplets at 166.6 and 149.4 ppm \((^2\text{J}^{\text{pp}} 44.0\text{ Hz})(\text{cis isomer})\). On warming to 298K the triplets disappeared and did not reappear
when the solution was recooled. Therefore, as for [RuCl\(_2\)(P\(_3\)O\(_3\)Me\(_3\))\(_4\)], an irreversible cis to trans isomerisation process takes place in solution.

In contrast, reaction of [RuCl\(_2\)(PPh\(_3\))\(_3\)] with an excess of P(OR)Ph\(_2\) (R = Me, Et) in hexane produced orange-brown crystals analysing closely for [RuCl\(_2\)(P(OR)Ph\(_2\))\(_3\)]. The far ir spectra contained a strong band at 337 cm\(^{-1}\) (R = Me), 328 cm\(^{-1}\) (R = 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 \(^{31}\)P-{\(^1\)H} nmr spectra in C\(_6\)D\(_6\) at 298K showed a sharp singlet at 149.5 ppm (R = Me), 144.7 ppm (R = 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 P(OR)Ph\(_2\) ligands renders them equivalent on the nmr timescale, (cf the \(^{31}\)P-{\(^1\)H} nmr spectra of [RuCl\(_2\)(PR\(_3\))\(_3\)] (PR\(_3\) = PPh\(_3\), [2,7] P(p-tolyl)\(_3\) [8]) at ambient temperatures). In support of the latter conclusion, the \(^{31}\)P-{\(^1\)H} nmr spectrum of [RuCl\(_2\)(P)OEt\(_2\)Ph\(_3\)] in (CD\(_3\))\(_2\)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" [RuCl\(_2\)(P(OEt)Ph\(_2\))\(_3\)] structure (IIb). The observed averaged position (146.5 ppm at 193K in (CD\(_3\))\(_2\)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 \([\text{RuCl}_2(\text{P(OEt)Pb})_3]_2\) is much more facile than the corresponding process for \([\text{RuCl}_2(\text{PPh})_3]_2\) (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 \([\text{RuCl}_2(\text{P(OEt)Pb})_3]_2\) are much closer to each other than are the PPh groups in \([\text{RuCl}_2(\text{PPh})_3]_2\). The ligand P(OEt)Pb is less bulky than either P(OEt)Pb or PPh and consequently, the \(^{31}\text{P-}^1\text{H} nmr spectrum of \([\text{RuCl}_2(\text{P(OEt)Pb})_2]_2\) at 140K in \((\text{CD}_3)_2\text{CO}/\text{toluene}\) only contained a broad resonance at 147.0 ppm.

b) Rearrangement of monomeric species in polar solvents

The compound \([\text{RuCl}_2(\text{P(OMe)}_3)_4]_2\) appeared stable in polar solvents, being recovered unchanged both after refluxing in methanol for 6 hours or irradiating with ultraviolet light. The compound \([\text{RuCl}_2(\text{P(OMe)}_2\text{Pb})_4]_2\) 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 then precipitated a pale yellow solid whose \(^{31}\text{P-}^1\text{H} nmr spectrum in CDC\_3 at 298K contained a singlet at 168.7 ppm and also an AB pattern (ν\text{A} 159.6 ppm; ν\text{B} 170.4 ppm; J\text{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 \([\text{RuCl}_2(\text{P(OMe)}_2\text{Pb})_6]_2\text{BPh}_4\), prepared earlier [10] by reaction of \([\text{RuCl}_2(\text{C}_7\text{H}_8)]_n\) with \(\text{P(OMe)}_2\text{Ph}\) in methanol. The AB pattern must arise from an intermediate ionic product containing three phosphinite groups per ruthenium. Possibilities include \([\text{RuCl}(\text{P(OMe)}_2\text{Pb})(\text{Solv})]_2\text{BPh}_4\) or \(\{\text{RuCl}(\text{P(OMe)}_2\text{Pb})_3\text{Solv}\}_2\)\(_2\text{BPh}_4\)\(_2\) 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 \([\text{Ru}_2\text{Cl}_3(\text{PETPh}_2)_6]\)Cl[3].

In contrast, dissolving \([\text{RuCl}_2(\text{POMe})\text{Ph}_2)_3]\) 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\(\mu\)mho (specific conductivity) for a \(10^{-3}\) dm\(^{-3}\) mol. solution after ca 4 hours, which indicated the formation of a 1:1 electrolyte. The addition of \(\text{NaBPh}_4\) then precipitated \([\text{Ru}_2\text{Cl}_3(\text{POMe})\text{Ph}_2)_6]\)BPh\(_4\), synthesised earlier by reaction of \([\{\text{RuCl}_2(\text{C}_7\text{H}_8)\}_n]\) and \(\text{POMe}\) in methanol [10]. This rearrangement reaction has also been studied by \(^{31}\text{P} - ^1\text{H}\) nmr spectroscopy. Thus at 183K in \((\text{CD}_3)_2\text{CO}/\text{CH}_2\text{Cl}_2\), the spectrum consisted of a broad signal at 144 ppm \(([\text{RuCl}_2(\text{POMe})\text{Ph}_2)_3])\) and a sharp singlet at 139.4 ppm due to the rearranged product \([\text{Ru}_2\text{Cl}_3(\text{POMe})\text{Ph}_2)_6]\)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 \([\text{RuCl}_2(\text{POMe})\text{Ph}_2)]\) 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 $[\text{RuCl}_2(\text{P(OEt} \overline{\text{Ph}}_2)]$ was dissolved in CH$_2$Cl$_2$, the initial bright yellow solution also became progressively paler, the conductivity of a $10^{-3}$ dm$^{-3}$ mol. solution increasing to a maximum of 30$\mu$mho over a period of ca 24 hours. Again, the rearrangement has been studied by $^{31}$P–{$^1$H} nmr spectroscopy and, although much slower, followed a similar pattern to that of $[\text{RuCl}_2(\text{P(OMe} \overline{\text{Ph}}_2)]$, 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, $[\text{Ru}_2\text{Cl}_3(\text{P(OEt} \overline{\text{Ph}}_2)_6]$Cl, since the $^{31}$P–{$^1$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 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 $^{31}$P–{$^1$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 $[\text{Ru}_2\text{Cl}_3(\text{P(OEt} \overline{\text{Ph}}_2)_6][\text{RuCl}_3(\text{P(OEt} \overline{\text{Ph}}_2)_3]$. 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 $^{31}$P–{$^1$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 \( \{\text{RuCl}_2(\text{C}_7\text{H}_8)\}_n \) with 
\( \text{P(OEt)}\text{Ph}_2 \) was earlier reported to give on addition of \( \text{NaBPh}_4 \), the ionic dimer \( \{\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_2\}_6 \text{BPh}_4 \) (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 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 \( \{\{\text{RuCl}_2(\text{C}_7\text{H}_8)\}_n\} / \text{P(OMe)}\text{Ph}_2 \) reaction was a singlet at all temperatures, indicating the formation of the \( \{\text{RuCl}_3(\text{P(OMe)}\text{Ph}_2)_6\}^+ \) 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.\(^\dagger\) 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 CDCl\(_3\) and the close similarity of the ethyl region of the \( ^{13}\text{C}-\{^1\text{H}\} \) nmr spectra of (A) in CDCl\(_3\) and \( \{\text{RuCl}_2(\text{P(OEt)}\text{Ph}_2)_3\} \) in C\(_6\)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 CH\(_2\)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 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

\(^\dagger\)For \( \{\text{Ni}(\eta-\text{C}_5\text{H}_5)\{\text{P(OEt)}_3\}_2\{\text{PO(OEt)}_2\}_2\} \), 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 ca 62 ppm [11].
of [Ru$_2$Cl$_3$(P(OMe)Ph)$_2$)$_6$]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 [Ru$_3$Cl$_5$(P(OEt)Ph)$_2$)$_9]^+$ [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(OEt)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(OEt)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 (Ia), 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$_3$·xH$_2$O" in methanol with MeCS$_2$NEt$_2$ gave a minute quantity of golden-brown crystals, shown by X-ray analysis to be [Ru$_3$(SC$_2$NEt$_2$)$_4$(CO)$_3$Cl$_2$] (IV) [12]. Trinuclear iron...
compounds of stoichiometry \([\text{Fe}_3(\text{CO})_6\text{I}_5(\text{SR})_2]\) 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 \(^{31}\text{P}-\{^1\text{H}\}\) nmr spectrum of (A) would have consisted of an AB\(_2\) pattern arising from atoms \(P_2, P_1, P_3\) superimposed on an ABC pattern of twice the intensity arising from atoms \(P_4, P_5, P_6\) and \(P_7, P_8, P_9\). 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 \(P_1\) and \(P_3\) in the supposed AB\(_2\) set. Thus, the expected \(^{31}\text{P}-\{^1\text{H}\}\) 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 \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph}_2)_9]X (X = \text{Cl}^-, \text{BPh}_4^-, \text{PF}_6^-)\) 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 \([\text{Ru}_3\text{Cl}_5-(\text{P(OMe)}\text{Ph}_2)_9]\text{Cl}\).

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][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]\text{BPh}_4^-, \text{but addition of NaBPh}_4^+ \text{to the initial red solution gave a red solid which analysed closely for } [\text{RuCl}(\text{P(OMe)}\text{Ph}_2)_4]^- \text{BPh}_4 (VI). The mull ir 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, $^{31}$P-{H} nmr spectra were studied in (CD$_3$)$_2$CO over a range
of temperatures. (Fig. 3). At 173K (Fig. 3a), several resonances were observed viz a singlet at 139.1 ppm due to the presence of some 

$$[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}\text{Ph})_2]_6\text{BPh}_4$$

in the sample, a singlet at 110.9 ppm due to free P(OMe)Ph, 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 P(OMe)Ph 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 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 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 P atoms in intensity ratio 1:1:2 respectively and belong to a single species which is most probably 

$$[\text{RuCl}(\text{P(OMe)}\text{Ph})_2]_4^+.$$ Structures consistent with two magnetically equivalent and two non-equivalent 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 $^{31}$P-{¹H} nmr spectra in a related complex at low temperature [15]. Thus, for cis- [FeH₂(P(OMe)₂Ph)₄](VII), the $^{31}$P-{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 $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_4]^+$ at 193K can best be explained by invoking the dynamic equilibrium shown in equation (1). Loss of the solvent molecule

\[
\begin{array}{c}
\text{Cl} \quad \text{(Solv)} \\
\text{P(OMe)Ph$_2$} \\
\text{Ru} \\
\text{P(OMe)Ph$_2$} \\
\end{array} \rightleftharpoons
\begin{array}{c}
\text{Cl} \\
\text{P(OMe)Ph$_2$} \\
\text{Ru} \\
\text{P(OMe)Ph$_2$} \\
\end{array}
\]

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)$_2$ 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 $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_3(\text{Solv})]^+$. Furthermore, the addition of excess P(OMe)$_2$ inhibited the formation of

\[
\begin{array}{c}
[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_4(\text{Solv})]^+ \\
\end{array} \rightleftharpoons
\begin{array}{c}
[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_3(\text{Solv})]^+ + \text{P(OMe)Ph$_2$}
\end{array}
\]

(2)

$[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}_2\text{Ph})_6]^+$ in CH$_2$Cl$_2$ whereas the addition of Cl$^-$ to an acetone solution of $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_4]^+$ 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 $[\text{Ru}_2\text{Cl}_3(\text{P(OMe)}_2\text{Ph})_6]^+$ BPh$_4$ and free P(OMe)$_2$ had disappeared. Finally conductivity measurements on an acetone solution of $[\text{RuCl}(\text{P(OMe)}_2\text{Ph})_4]^+$ 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)₂]⁺ appeared in the spectrum at
However, addition of excess $\text{P(OEt)Ph}_2$ inhibited rearrangement to $[\text{Ru}_3\text{Cl}_5(\text{P(OEt)Ph}_2)_9]\text{BPh}_4$ in CH$_2$Cl$_2$, whereas addition of Cl$^-$ to an acetone solution of $[\text{Ru}_2\text{Cl}_2(\text{P(OEt)Ph}_2)_8](\text{BPh}_4)_2$ caused a colour change from red to yellow but the rearrangement process was slower than for $[\text{RuCl}(\text{P(OMe)Ph}_2)_4]\text{BPh}_4$.

d) **Mechanism of rearrangement of $[\text{RuCl}_2\text{L}_{3\text{or4}}]_{\text{species}}$**

It is of interest to conclude this paper by briefly examining possible mechanisms of rearrangement for the various $[\text{RuCl}_2\text{L}_{3\text{or4}}]$ compounds discussed above, particularly with reference to the mechanism proposed earlier [3] (Scheme 1) to rationalise the behaviour of various $[\text{RuCl}_2(\text{PR}_3)_{3\text{or4}}]$ compounds in solution.

First, no evidence has been found in this work for the formation of the neutral dimers $[\text{Ru}_2\text{Cl}_4\text{L}_5]$ $[\text{L} = \text{P(OMe)}_3, \text{P(OMe)}_2\text{Ph}, \text{P(OR)}_2\text{Ph} (\text{R} = \text{Me}, \text{Et})]$ 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 $[\text{RuCl}_2(\text{PMePh}_2)_4][16]$ and $[\text{RuCl}_2(\text{PEtPh}_2)_3][2]$, dissolving $[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]$ in non-polar solvents does not give any $[\text{Ru}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_5]$ 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 $[\text{Ru}_2\text{Cl}_3(\text{P(OMe)Ph}_2)_6]\text{Cl}$ were pyrolysed at 120$^\circ$C for 12 hours since a similar reaction with $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ gave $[\text{Ru}_2\text{Cl}_4(\text{PEt}_2\text{Ph})_5][18]$. However, X-ray structural analysis showed the product to be the unusual neutral dimer $[(\text{P(OMe)Ph}_2)_2(\text{P(OH)Ph}_2)\text{RuCl}_3\text{Ru(POH)}_2\text{(PPh}_2\text{O})_2]$ in which O-R bond rupture rather than Ru-P bond cleavage had occurred [19]. Similarly, pyrolysis of solutions containing the $[\text{Ru}_3\text{Cl}_5(\text{P(OEt)Ph}_2)_9]^+$ cation gave $[\text{Ru}_2\text{Cl}_4(\text{PR}_3)_3]$ but even at 400K, $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ was recovered unchanged, [16], again demonstrating the strength of the Ru-PMe$_2$Ph bonds.
As for \([\text{RuCl}_2(\text{PR}_3)_{3\text{ord}}]\), both [\text{RuCl}_2(\text{POMe}_2\text{Ph})_4] and [\text{RuCl}_2(\text{POMe}_2\text{Ph})_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 \([\text{RuCl}(\text{POMe}_2\text{Ph})_3(\text{solv})]\)^+ (or \([\{\text{RuCl}(\text{POMe}_2\text{Ph})_3(\text{solv})\}_2]\)^2+) strongly suggests that the mechanism of formation of \([\text{Ru}_2\text{Cl}_3(\text{POMe}_2\text{Ph})_6]\)\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 \([\text{RuCl}(\text{PETPh}_2)_{3}\text{(solv)}]\)^+ (or \([\{\text{RuCl}(\text{PETPh}_2)_{3}\text{(solv)}\}_2]\)^2+) has been observed in the formation of \([\text{Ru}_2\text{Cl}_3(\text{PETPh}_2)\text{Cl}]\) from \([\text{RuCl}_2(\text{PETPh}_2)_{3}]\) \([\text{3]}\).

However, with \([\text{RuCl}_2(\text{POMe}_2\text{Ph})_3]\) in polar solvents, the major rearrangement product is the ionic trimer \([\text{Ru}_3\text{Cl}_5(\text{POMe}_2\text{Ph})_9]\)\text{Cl} (III b). A rationalisation of all these results is obtained by postulating the formation of a labile, double-bridged cationic intermediate \([\text{L}_3\text{ClRuCl}_2\text{Ru(solv)}-\text{L}_3]\)^+ by coupling of \([\text{RuCl}_2\text{L}_3]\) and \([\text{RuCl}_3(\text{solv})]\)^2+. 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 \([\text{L}_3\text{Ru(OH)}_3\text{RuL}_3]\)^+ \((L = \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{POMe}_2\text{Ph})_2\) have recently been postulated by Ashworth et al \([\text{20]}\) and such species are probably key intermediates in the mechanism of formation of other triple-bridged cations.™

*Note that in ref \([\text{19]}\), on the basis of analytical and \(^1\text{H}\) nmr data, we and others \([\text{10]}\) assumed that the product from the reaction of \([\{\text{RuCl}_2(\text{C}_7\text{H}_8\text{N})\}_3]\) and \(\text{P(OEt)}\text{Ph}_2\) in ethanol was \([\text{Ru}_2\text{Cl}_3(\text{P(OEt)}\text{Ph})_6]\)\text{Cl} but \(^{31}\text{P}-\text{\(^1\text{H}\)}\) nmr studies now show it to be \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)}\text{Ph})_9]\)\text{Cl}.

™For example, a similar mechanism to that shown in Scheme 3, which involves the double bridged, cationic intermediate \([(\text{arene})\text{XRuX}_2\text{Ru(solv)}\text{arene}]^+\) can be proposed to explain the formation of the triple bridged ionic cations \([\text{areneRuX}_3\text{Ruarene}]^+\) \((X = \text{Cl}, \text{OH}, \text{OR})\) \([\text{21]}\).
Finally, the observations that addition of excess P(OR)Ph₂ (R = Me, Et) to CH₂Cl₂ solutions of [RuCl(P(O)Me)Ph₂]₄BPh₄ (VI) and [Ru₂Cl₂(P(O)Et)Ph₂]₈-(BPh₄)₂ (VIII) respectively inhibited the formation of [Ru₂Cl₃(P(O)Me)Ph₂]₆-BPh₄ and [Ru₃Cl₅(P(O)Et)Ph₂]₉BPh₄, 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 \( \frac{1}{C} \) (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 \( \Lambda_0 \). A subsequent plot of \( \Lambda_0 - \frac{1}{C} \) 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, methyldiphenylphosphinitene, ethyldiphenylphosphinitene (Maybridge); sodium tetraphenylborate (BDH); ammonium hexafluorophosphate (Alfa). \([\text{RuCl}_2(\text{PPh}_3)_3]\) 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(medium).

Proposed \(\nu(\text{RuCl})\) bands underlined.

Dichlorotetrakis(trimethylphosphine)ruthenium(II):- The compound \([\text{RuCl}_2(\text{PPh}_3)_3]\) (0.20g) was refluxed with \(\text{P(OMe)}_3\) (0.40 cm\(^3\)) in hexane (20 cm\(^3\)) for one hour. The solution was cooled and the yellow crystals obtained were filtered off and recrystallized from \(\text{CH}_2\text{Cl}_2/\text{hexane}\) (yield 0.63g 45%) m.p. 145-147°C

[Found: C, 21.6; H, 5.4%; Calc. for \(\text{C}_{12}\text{H}_{36}\text{Cl}_0\text{O}_4\text{P}_4\text{Ru}: C, 21.6; H, 5.4\%\)]

Far ir spectrum:- 340st, 306st, 295st, 284m, 274m, 260w, 250w, 210st, \(\text{^1H nmr (CDCl}_3\text{ at 301K) 3.84 ppm (q) ^31P-\{^1H\} nmr (CDCl}_3\text{ at 298K) 129.4(s) ppm.}\)

Dichlorotetrakis(dimethylphenylphosphonite)ruthenium(II):- The compound \([\text{RuCl}_2(\text{PPh}_3)_3]\) (0.20g) was refluxed with \(\text{P(OMe)}_2\text{Ph}\) (0.40 cm\(^3\)) in hexane (20 cm\(^3\)) for 3 hours to give yellow crystals which were filtered off and recrystallized from \(\text{CH}_2\text{Cl}_2/\text{hexane}\) (0.125g 75%) m.p. 158-160°C

[Found: C, 45.0; H, 5.2%; Calc. for \(\text{C}_{32}\text{H}_{44}\text{Cl}_2\text{O}_4\text{P}_4\text{Ru}: C, 45.0; H, 5.2\%\)]

Far ir spectrum

324st, 308m, 291st, 257sh, 214st; \(\text{^1H nmr (CDCl}_3\text{ at 301K) 3.45 (q), 7.20 (mt) ppm ^31P-\{^1H\} nmr (CDCl}_3\text{ at 213K) 150.5(s), 166.6(t), 1494(t) ^2J}\))

\(\text{pp 44.0 Hz}\)
Dichlorotris(methyldiphenylphosphinite)ruthenium(II): - The compound
\[ \text{[RuCl}_2(\text{PPh}_3)_3] \] (0.20g) was refluxed with P(OMe)Ph \(_2\) (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\(_{33}\)H\(_{66}\) 834. Calc. for C\(_{39}\)H\(_{39}\)Cl\(_3\)O\(_3\)P\(_6\)Ru: C, 57.0; H, 4.7;
Cl, 8.7% M.820 ]

far ir spectrum 337st, 290st,

1\(_H\)nmr (C\(_D\)\(_6\) at 301K) 2.90(pt)

6.90-7.70(mt) ppm

P-{\(\text{H}\)}nmr (C\(_D\)\(_6\) at 298K) 149.5(s) ppm;

(toluene/(CD\(_3\))\(_2\)CO at ca 140K) 147.0(br) ppm.

Dichlorotris(ethyldiphenylphosphinite)ruthenium(II) was similarly prepared
from \[ \text{[RuCl}_2(\text{PPh}_3)_3] \] and P(0Et)Ph\(_2\) (0.160g, 66%)
m.p. 155-157\(^\circ\)C [Found: C, 58.1; H, 5.2; Cl, 8.1%, M(C\(_{33}\)H\(_{66}\) 925. Calc. for C\(_{42}\)H\(_{45}\)Cl\(_3\)O\(_3\)P\(_6\)Ru:

C, 58.3, H, 5.2, Cl, 8.2% M.862 ]

far ir spectrum 328st, 298w, 286st, 272m,

253m, 234m, 214m; \(\text{1H}\)nmr (C\(_D\)\(_6\) at 301K) 0.78(t), 3.40(br) \[3J_{\text{HH}} 7.0 \text{Hz}\],

6.90-7.70 (mt) ppm. \(\text{31P-}{\(\text{1H}\)}\)nmr (C\(_D\)\(_6\) at 298K) 144.7 (s) ppm (toluene/(CD\(_3\))\(_2\)-

CO at ca 140K) 141.1 (br), 167.3 (br) ppm \(\text{13C-}{\(\text{1H}\)}\)nmr (C\(_D\)\(_6\) at 318K) singlets
at 134.3 and 54.8 ppm.

[Hexakis(dimethylphenylphosphonite)ruthenium(II)]tetraphenylborate:- The compound
\[ \text{[RuCl}_2(\text{PPh}_3)_3] \] (0.20g) was refluxed with 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\(_4\)O\(_8\)P\(_{12}\)Ru: C, 65.5; H, 6.0%]

[Chlorotetrakis(methyldiphenylphosphinite)ruthenium(II)]tetraphenylborate:-
The compound \[ \text{[RuCl}_2(\text{PPh}_3)_3] \] (0.20g) was refluxed with P(OMe)Ph\(_2\) (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}BClO_{4}P_{4}Ru:- C, 69.1; H, 5.4; Cl, 2.7%] Conductivity in (CH_{3})_{2}CO at 303K. Slope of \( \frac{\Delta \varepsilon}{\Delta C} \) vs C plot = 140 (for [Ru_{2}Cl_{3}(P(OMe)Ph_{2})]_{4}BPh, slope = 155; for [Ru(nC_{6}H_{4}-(NH_{3})_{3})(PF_{6})_{2}], slope = 350) far IR spectrum 290st, 275sh; {^{1}H} NMR ((CD_{3})_{2}CO at 301K) 3.15 (pt), 6.80-7.20 (mt) ppm. {^{31}P} NMR ((CD_{3})_{2}CO at 173K) 123 (mt), 140 (mt), 157 (mt) ppm. (see Fig. 3a)

{Di-\( \mu \)-chlorobis(tetrakis(ethylidiphenylphosphinite)ruthenium(II)) tetraphenylborate} was prepared similarly by reaction of [RuCl_{2}(PPh_{3})_{3}] with excess P(OEt)Ph_{2} in ethanol, m.p. 91-93°C [Found: C, 68.6; H, 5.8; Cl, 2.6% Calc. for C_{160}H_{160}B_{28}Cl_{8}O_{8}P_{4}Ru_{4}: C, 69.8; H, 5.8; Cl, 2.6%]. Conductivity in (CH_{3})_{2}CO at 303K. Slope of \( \frac{\Delta \varepsilon}{\Delta C} \) vs C plot = 175. Far IR spectrum 270st (br); {^{1}H} NMR ((CD_{3})_{2}CO at 301K) 1.25 (t), 3.40 (br) [J_{HH} 7.0 Hz], 6.80 - 7.20 (mt) ppm. {^{31}P}{^{-1}H} NMR ((CD_{3})_{2}CO at 173K) 119.0 (t), 148.1 (t) ppm (J_{pp} 32.5 Hz) (see Fig. 5a)

{Tri-\( \mu \)-chlorohexakis(methylidiphenylphosphinite)diruthenium(II) tetraphenylborate}:- The compound [RuCl_{2}(PPh_{3})_{3}(0.20g) was refluxed with P(OMe)Ph_{2} (0.20 cm^{3}) in methanol (20 cm^{3}) for 3 hours to give a yellow solution. Addition of NaBPh_{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_{4} to a solution of [RuCl_{2}(P(OMe)-Ph_{2})_{3}] dissolved in methanol. [Found: C, 63.6; H, 5.1% M(CHCl_{3}) 1003. Calc. for C_{102}H_{98}B_{10}Cl_{6}O_{8}P_{4}Ru:- C, 63.6; H, 5.1% M(for 1:1 electrolyte) 962.] Conductivity in (CH_{3})_{2}CO at 303K. Slope of \( \frac{\Delta \varepsilon}{\Delta C} \) vs C plot = 155. Far IR spectrum 228w. {^{1}H} NMR (CDCl_{3} at 301K) 2.95 (pt) 6.90-7.10 (mt) ppm. {^{31}P}{^{-1}H} NMR (CDCl_{3} at 298K) 138.6 (s) ppm {^{13}C}{^{-1}H} NMR (CDCl_{3} at 318K) singlets at 136.5, 125.4, 121.3 (Ph); 133.7, 129.8, 127.0 (BPh^+), 55.2 (Me) ppm.
Tri-μ-chlorohexakis(dimethylphenylphosphonite)diruthenium(II) tetraphenylborate:– The compound [RuCl₂(P₂OMe₂Ph)₄](0.20g) was refluxed in methanol (30 cm³) for 3 hours to give a yellow solution. Addition of NaBPh₄ 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%.

Calc. for C₇₂H₂₆₂B₅Cl₉O₇P₉Ru:– C, 52.4; H, 5.2%]

³¹P-{¹H} nmr (CDCl₃ at 301K) 3.45(q), 7.00–7.20(mt) ppm.

P-®H nmr (CDCl₃ at 298K) 168.7 (s) ppm.

o{1,2; 1,3-μ-chloro,-2,3-di-μ-chloro, 1, chloro-cyclo[tris(ethyldiphenylphosphinite)ruthenium(II)]] tetraphenylborate:– The compound [RuCl₂(PPh₃)₃](0.20g) was refluxed with P(OEt)Ph₂ (0.20 cm³) in ethanol (20 cm³) for 4 hours to give a pale yellow solution. Addition of NaBPh₄(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(CHCl₃) 1350 Calc. for C₁₅₀H₁₅₅BCl₉O₇P₉Ru:– C, 62.7; H, 5.2; Cl, 6.3; P, 9.7%M (1:1 electrolyte), 1435. Conductivity in (CD₃)CO at 303K. Slope of

\[ \Delta \text{ vs } C \] plot = 140. far ir spectrum 314m, 288sh, 272sh, 260s(br), 256sh, 242sh ¹H nmr (CDCl₃ at 301K) 1.18(t) 2.96(br) [³JHH 7.0 Hz], 7.00 – 7.30(mt) ppm ³¹P–¹H nmr (CDCl₃ at 213K) 135(mt) ppm (see Fig. 2) ¹³C–¹H nmr (CDCl₃ at 318K) singlets at 136.5, 125.5, 121.4(Ph); 133.9, 129.8, 126.8 (BPh₄⁻); 64.5 (CH₂); 16.0 (CH₃) ppm.

The corresponding [Ru₃Cl₅(P(OEt)Ph₂)₉]PF₆ was obtained by addition of NH₄PF₆ to the pale yellow solution. [Found: C, 54.2; H, 5.0% Calc. for C₁₂₆H₁₅₅C₁₅₅B₅Cl₉O₇P₉Ru:– C, 56.1; H, 5.1%]

Acknowledgements

We thank Johnson Matthey Ltd. for loans of ruthenium trichloride, the S.R.C. for financial support (W.J.S.), Dr. A.S.F. Boyd and Mr. J.R.A. Millar for running ³¹P and ¹H nmr spectra respectively and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.
References


Fig. 1. $^{31}$P-{$^1$H} nmr spectrum of the rearrangement products of
\[\text{[RuCl}_2(\text{P(OMe)Ph}_2)_3]\] in (CD$_3$)$_2$CO/CH$_2$Cl$_2$ at 213K.

Fig. 2. $^{31}$P-{$^1$H} nmr spectrum of the ionic rearrangement product of
\[\text{[RuCl}_2(\text{P(OEt)Ph}_2)_3]\] in CDCl$_3$ at 213K.

Fig. 3. $^{31}$P-{$^1$H} nmr spectra of \[\text{[RuCl(\text{P(OMe)Ph}_2)BPh}_4\] in (CD$_3$)$_2$CO at
a) 173K b) 193K c) 213K d) 333K.

Fig. 4. $^{31}$P-{$^1$H} nmr spectra of cis-\[\text{FeH}_2(\text{P(OMe)}_2\_4\] in 50\% CH$_2$Cl$_2$-50\%
CHFCl at various temperatures (reproduced from ref [15])

Fig. 5. $^{31}$P-{$^1$H} nmr spectra of \[\text{[Ru}_2\text{Cl}_2(\text{P(OEt})\_2\_8\] (BPh)$_2$ in (CD$_3$)$_2$CO
at a) 173K b) 213K c) 298K.
173K

chemical shift (p.p.m.)

110.9
122.3
124.4
1391
140.0
1570
Fig 3b

3c

Fig 3d

333K
$2[RuCl_2(PR_3)_4] + 2PR_3 \rightarrow 2[RuCl_2(PR_3)_3] \rightleftharpoons \begin{array}{c}
\begin{array}{c}
\text{R}
\text{P}
\text{Cl}
\text{Cl}
\text{PR}_3
\end{array}
\end{array}$

$\text{(PR}_3 = \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PETPh}_2, \text{PET}_2\text{Ph}, \text{PClPh}_2)$

\text{SCHEME 1}
Scheme 2
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,N'-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(dmft-
{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(dmft-
(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)₄(P(p-tolyl)₃)₄] and
[[RuCl₂(CS)]ₚ(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 \([\text{RuCl}_2(\text{PPh}_3)_3]\) with \(\text{CS}_2\) gave the triple chloride bridged complex \([\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_4]\), together with smaller amounts of \([\text{Ru}(\text{CS})_2\text{Cl}(\text{PPh}_3)_3]\), \([\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2]_2\), and \([\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_3]_2\) (various isomers). Later, the compounds \([\text{Ru}_2(Y)\text{Cl}_4(\text{PPh}_3)_4]\) were synthesised in high yield by means of an intermolecular coupling reaction of \([\text{RuCl}_2(\text{PPh}_3)_3]\) and \([\text{Ru}(Y)\text{Cl}_2(\text{dmf})(\text{PPh}_3)_2]\) \((Y = \text{CO, CS}).[3]\)

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 \([\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PR}_3)_2(\text{PR}_3')_2]\).

Results and Discussion

a) Tri-p-tolylphosphine complexes:

Reaction of "\(\text{RuCl}_3\text{H}_2\text{O}\)" with an excess of \(\text{P}(\text{p-tolyl})_3\) in methanol, reported to give \([\text{RuCl}_2(\text{P}(\text{p-tolyl})_3)_4]\) [4], repeatedly produced dark purple crystals of \([\text{RuCl}_2(\text{P}(\text{p-tolyl})_3)_3]\) \((I)\). The \(^{31}\text{P}-(1\text{H})\) nmr spectrum of \((I)\) in \(\text{CH}_2\text{Cl}_2/(\text{CD}_3)_2\text{CO}\) at 190K consisted of a doublet at 6 25.1 ppm and a triplet at 74.3 ppm \((J_{\text{pp}} 28.0\text{Hz})\) (relative intensity 2:1) plus a weak singlet at 28.8 ppm due to \((\text{p-tolyl})_3\text{PO}.\) 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),

\(^{4}\)The reason for this is probably the high pH of the commercial "\(\text{RuCl}_3\cdot\text{H}_2\text{O}\)" 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 \([\text{Ru}(\eta^2-\text{CS}_2)\text{Cl}(\text{Pp-tolyl})_3]\) 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 \([\{\text{RuCl}_2(\text{CS})\{\text{P}(\text{p-tolyl})_3]\}_2]\). 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 \(\delta\) 29.5 ppm together with weaker singlets at 28.5 ppm \([\{\text{p-tolyl}\}_3\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 \(\delta\) 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 N,N-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, [Ru$_2$(CO)Cl$_4$(P(p-tolyl)$_3$)$_4$] whose $^{31}\text{P}-\{^1\text{H}\}$ nmr spectrum in CDCl$_3$ at 298 K contained the expected two AB quartets at δ 47.6 and 38.8 ppm. As for [Ru(CO)Cl$_2$(dmf)(PPh$_3$)$_2$] [3], recrystallisation of compound (II) from methanol gave [Ru(CO)Cl$_2$(MeOH){(Pp-tolyl)$_2$}]$_2$, 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 [Ru$_2$(CO)$_2$Cl$_4$(P(p-tolyl)$_3$)$_3$] (see experimental section and ref [3]).

An attempt to synthesise the mixed tertiary phosphine complex [(PPh$_3$)$_2$ClRuCl$_3$RuCO(P(p-tolyl)$_3$)$_2$] by reaction of [RuCl$_2$(PPh$_3$)$_3$] with [Ru(CO)Cl$_2$(dmf){P(p-tolyl)$_3$}]$_2$ 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 [RuCl$_2$(PPh$_3$)$_3$] occurs and this can then displace P(p-tolyl)$_3$ from the initially formed product [(PPh$_3$)$_2$ClRuCl$_3$RuCO{P(p-tolyl)$_3$}]$_2$ to give, in addition, the compounds [(PPh$_3$)$_2$ClRuCl$_3$Ru(CO){P(p-tolyl)$_3$}]$_n$(PPh$_3$)$_{2-n}$ (n = 0,1).

However, this side reaction does not occur in the reaction between [RuCl$_2$(P(p-tolyl)$_3$)$_3$] and [Ru(CO)Cl$_2$(dmf)(PPh$_3$)$_2$] since an orange solid which analysed for [Ru$_2$(CO)$_2$Cl$_4$(PPh$_3$)$_2$(P(p-tolyl)$_3$)$_3$]$_2$ and whose $^{31}\text{P}-\{^1\text{H}\}$ nmr spectrum in CDCl$_3$ at 298 K contained only two AB patterns at δ 48.0 and 40.2 ppm was obtained.
Finally, the attempted coupling reactions of \([\text{RuCOCl}_2(\text{dmf})(\text{PR}_3)_2]\) (\(\text{PR}_3 = \text{PPPh}_3, \text{P(p-tolyl)}_3\)) with other \([\text{RuCl}_2\text{L}_3]\) (\(\text{L} = \text{P(OMe)Ph}_2, \text{P(OEt)Ph}_2\)) were completely unsuccessful. This is not surprising since earlier studies [1] have shown that these tertiary phosphinite complexes contain very strong \(\text{Ru-P}\) bonds and hence the formation of \([\text{P(OR)Ph}_2)_2\text{ClRuCl}_3\text{Ru(CO)}(\text{PR}_3)_2]\) 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 \([\text{Ru}_2\text{Cl}_3\text{(P(OMe)Ph}_2)_6]\text{Cl}\) or \([\text{Ru}_3\text{Cl}_5(\text{P(OEt)Ph}_2)_9]\text{Cl}\) (i.e. the rearrangement products of \([\text{RuCl}_2(\text{P(OR)Ph}_2)_3]\) 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 \(\text{PETPh}_2\) in hexane [5a]) was shaken in \(\text{CS}_2\) for one hour, a red-pink solid was produced which analysed closely for the expected "\([\text{Ru}(\eta^2-\text{CS}_2)\text{Cl(PEtPh}_2)_3]\)Cl.CS_2". The ir spectrum contained a strong band at 1515 cm\(^{-1}\) which as for \([\text{Ru}(\eta^2-\text{CS}_2)\text{Cl(PPh}_3)_3]\text{ClCS}_2\) [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 "\([\text{Ru}(\eta^2-\text{CS}_2)\text{Cl(PEtPh}_2)_3]\text{Cl}\)" (III) whose ir spectrum no longer contained the band at 1515 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 \(\text{CDCl}_3\) at 298 K consisted of an AMX pattern \([\nu_A 41.1 \text{ ppm}, \nu_M, 34.0 \text{ ppm}; \nu_X 9.2 \text{ ppm}; J_{AM} 28.9 \text{ Hz}, J_{AX} 3.7 \text{ Hz}, J_{MX} 9.2 \text{ Hz}]\) 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 \([\text{RuCl}_2(\text{S}_2\text{CPETPh}_2)^-\text{(PEtPh}_2)^-] \) containing the \( \text{Ph}_2\text{EtP}^+\text{-CS}_2^- \) zwitterion ligand. The related compound "\([\text{Ir}(\text{n}^2\text{CS}_2)(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4" \) has recently been shown to be \([\text{Ir}(\text{S}_2\text{CPh}_3)(\text{CO})(\text{PPh}_3)_2]\text{BPh}_4 \) by X-ray analysis and these authors then suggested that "\([\text{Ru}(\text{n}^2\text{CS}_2)\text{Cl}(\text{PPh}_3)_3]\text{Cl}" \) 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.

\[
\begin{align*}
\text{Ph}_2\text{EtP} & \quad \text{Ru} \\
\text{Cl} & \quad \text{S} \\
\text{A} & \quad \text{X} \\
\text{PEtPh}_2 & \quad \text{PEtPh}_2 \\
\end{align*}
\]

(III)

\[
\begin{align*}
\text{Ph}_2\text{EtP} & \quad \text{Ru} \\
\text{A} & \quad \text{X} \\
\text{S} & \quad \text{S} \\
\text{E} & \quad \text{PEtPh}_2 \\
\text{Cl} & \quad \text{Cl} \\
\text{MeOH} & \quad \text{Cl} \\
\end{align*}
\]

(IV)

\( ^+ \)
The peaks at 1115 and 995 cm\(^{-1} \) in the ir spectrum of (III) can probably be attributed to the \( \nu_{\text{CS}_2\text{(asym)}} \) stretching vibrational mode of the \( \text{PEtPh}_2^+\text{-CS}_2^- \) ligand [7].
Dissolving [RuCl₂(S₂CPEtPh₂)(PETPh₂)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 NaBPh₄ to the purple solution gave a purple solid which analysed quite well for [RuCl(MeOH)(S₂CPEtPh₂)(PETPh₂)₂]BPh₄ (IV). The ³¹P-{¹H} nmr spectrum of (IV) in CDCl₃ at 298 K, which showed an AMX pattern [νₐ 44.6 ppm, νₓ 29.0 ppm, νₓ, 16.4 ppm; JₓM 28.0 Hz, Jₓx 3.5 Hz JₓM 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 [RuCl₂(S₂CPEtPh₂)(PETPh₂)₂]CS₂ was also formed on refluxing [RuCl₂(PETPh₂)₃] in CS₂ 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 (νₜₜ) whilst its ³¹P-{¹H} nmr spectrum at 298 K in CDCl₃ consisted predominantly of a singlet at δ 49.2 ppm and an AB pattern centred at 36.8 ppm, attributed to one isomer of the triple bridged dimer [Ru₂Cl₄(CS)₂(PETPh₂)₃] (see earlier). The spectrum also contained a weak resonance at 43.4 ppm (singlet) due to some unreacted [RuCl₂(PETPh₂)₃] (see ref [5a]) and other weak singlets at 48.4 and 37.8 which might arise from the presence of some [([RuCl₂(CS)(PETPh₂)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 \([\text{Ru(Cl}_2]\text{(dmf)}(\text{PETPh}_2)_2]\) (II) whose ir and \(^{31}\text{P}-\{^1\text{H}\}\) spectra indicated that the compound had the same structure as \([\text{Ru(Cl}_2]\text{(dmf)}(\text{PR}_3)_2]\) (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 \([\text{Ru(Cl}_2]\text{(dmf)}(\text{PETPh}_2)_2]\) and \([\text{Ru(Cl}_2]\text{(MeOH)}(\text{PETPh}_2)_2]\), 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 \([\text{Ru(Cl}_2]\text{(dmf)}(\text{PETPh}_2)_2]\) 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 \(\text{w, 1970s br, 1928 m cm}^{-1}\)) 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 (\(J_{\text{AB}}\) 26.6 Hz; \(\delta_{\text{AB}}\) 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 \(J_{\text{PP}}\) 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-{$^1$H} 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-{$^1$H} 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-{$^1$H} 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$_2$}$_2$-(PETPh$_2$)$_2$]$_2$. 
During the formation of \([\text{Ru}_2(\text{CO})_2\text{Cl}_4(\text{PR}_3)_3]\) from \("\text{Ru}(\text{CO})\text{Cl}_2(\text{PR}_3)_2"\), free tertiary phosphine will be liberated. In the case of \(\text{PPh}_3\), this was observed in the \(^{31}\text{P}-\{\text{H}\}\) nmr spectrum as either free \(\text{PPh}_3\) (-6 ppm) and/or \(\text{Ph}_3\text{PO}\) (29 ppm). However, in reactions of \([\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})(\text{PETPh}_2)_2]\), no free \(\text{PETPh}_2\) (-15.5 ppm) or \(\text{Ph}_2\text{EtPO}\) (35 ppm) was observed. Instead, \([\text{Ru}(\text{CO})\text{Cl}_2(\text{PETPh}_2)_3]\) (doublet and triplet at 18.9 and 35.3 ppm respectively) was formed, probably by direct reaction of \([\text{Ru}(\text{CO})\text{Cl}_2\text{dmf}(\text{PETPh}_2)_2]\) with \(\text{PETPh}_2\).

Finally, an attempt to prepare \([\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PETPh}_2)_4]\) by reaction of \([\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})(\text{PETPh}_2)_2]\) and \([\text{RuCl}_2(\text{PETPh}_2)_3]\) in acetone (1:1 molar ratios) produced a bright orange solid \(\nu_{\text{CO}} 1960 \text{ br})\). However, the \(^{31}\text{P}-\{\text{H}\}\) nmr spectrum of this material in \(\text{CDCl}_3\) at 213 K consisted of peaks corresponding to \([\text{Ru}(\text{CO})\text{Cl}_2(\text{PETPh}_2)_3]\), \([\text{Ru}_2\text{Cl}_4(\text{PETPh}_2)_5]\) (see ref [5a]) together with two \(\text{AB}\) resonances centred at 48.5 ppm \((J_{\text{AB}} 40.1 \text{ Hz}), \delta_{\text{AB}} 191.3 \text{ Hz}\) and 39.4 ppm \((J_{\text{AB}} 26.2 \text{ Hz}; \delta_{\text{AB}} 139.5 \text{ Hz}\) \) attributed to the triple bridged \([\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PETPh}_2)_4]\).

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% \(\text{H}_3\text{PO}_4\).
Melting points were determined with a Köfer 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 \([\text{RuCl}_2(\text{PR}_3)_3]\) (\(\text{PR}_3 = \text{PPh}_3[9]\text{PEtPh}_2 \ [5a]\)) and \([\text{Ru} (\text{CO}) \text{Cl}_2 \text{dmf} (\text{PPh}_3)_2] \ [10]\) were prepared as described earlier. All reactions were carried out in degassed solvents and, except for carbonylation reactions, under a nitrogen atmosphere. \(s(\text{singlet}); \ d(\text{doublet}), \ t(\text{triplet}), \ q(\text{quartet}), \ br(\text{broad})\).

Tri(p-tolylphosphine) Complexes

Dichlorotris(tri-p-tolylphosphine)ruthenium(II):- The compound \("\text{RuCl}_3\text{H}_2\text{O}\"\) (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\(_{63}H_{63}Cl_2P_3Ru\): C, 69.7; H, 5.8%] \(v(\text{RuCl})\) 320 cm\(^{-1}\). \(^{31}\text{P}-{\text{H}}\) nmr [CH\(_2\text{Cl}_2/\text{(CD}_3\text{)}_2\text{CO at 190 K}\) 74.3 (t), 25.1 (d) ppm (\(^2J_{PP} \ 28.0 \text{ Hz})\); at 298 K, 39.9 (s) ppm.
Carbonyldi(chloro)(N,N-dimethylformamide)bis(tri-p-tolylphosphine)ruthenium(II):—

Carbon monoxide was bubbled through a suspension of \( [\text{RuCl}_2\{\text{P}(\text{p-tolyl})_3\}^3] \) (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°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; \( \nu \text{(RuCl)} \) 340 cm\(^{-1}\). 

\[ ^{31}\text{P}-{^1\text{H}}\text{nmr} \ [\text{CDCl}_3 \text{ at } 298 \text{ K}] \] 32.3 (s) ppm.

Tri-\( \mu \)-chloro-a-carbonyl-g-chlorotetrakis(tri-p-tolylphosphine)-diruthenium(II):—

The compounds \( [\text{RuCl}_2\{\text{P}(\text{p-tolyl})_3\}^3] \) (0.10g) and \( [\text{Ru(CO)}\text{Cl}_2(\text{dmf})\{\text{P}(\text{p-tolyl})_3\}^2] \) (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°C [Found: C, 63.1; H, 5.3% Calc for \( \text{C}_{85}\text{H}_{84}\text{Cl}_4\text{O}_4\text{P}_4\text{Ru}_2^- \): C 64.2, H, 5.3%]. \( \nu \text{CO} \) 1975 cm\(^{-1}\). 

\[ ^{31}\text{P}-{^1\text{H}}\text{nmr} \ [\text{CDCl}_3 \text{ at } 298 \text{ K}] \] 47.6 (q) and 38.8 (q) ppm \( [J(\text{P}^1\text{P}^2) \text{ 38.8, } J(\text{P}^3\text{P}^4) \text{ 25.1; } \delta(\text{P}^1\text{P}^2) \text{ 73.0; } \delta(\text{P}^3\text{P}^4) \text{ 97.5 Hz}] \).

Tri-\( \mu \)-chloro-a-carbonyl-g-chloro-bc-bis(triphenylphosphine)-hisp(tri-p-tolylphosphine)-diruthenium (II) was obtained similarly from \( [\text{RuCl}_2\{\text{P}(\text{p-tolyl})_3\}^3] \) and \( [\text{Ru(CO)}\text{Cl}_2(\text{dmf})(\text{PPh}_3)_2] \) [Found: C, 67.5; H, 5.1% Calc for \( \text{C}_{79}\text{H}_{72}\text{Cl}_4\text{O}_4\text{P}_4\text{Ru}_2^- \): C 67.6; H, 5.1%]. \( \nu \text{CO} \) 1975 cm\(^{-1}\). 

\[ ^{31}\text{P}-{^1\text{H}}\text{nmr} \ [\text{CDCl}_3 \text{ at } 298 \text{ K}] \] 48.0 (q) and 40.2 (q) ppm \( [J(\text{P}^1\text{P}^2) \text{ 34.2, } J(\text{P}^3\text{P}^4) \text{ 25.1; } \delta(\text{P}^1\text{P}^2) \text{ 83.2, } \delta(\text{P}^3\text{P}^4) \text{ 99.1 Hz}] \).
Tri-ν-chloro-ag-aicarbonyl-b-chloro-tris(tri-p-tolylphosphine)
diruthenium (II):--

The complex \([\text{Ru(CO)}\text{Cl}_2(\text{MeOH})\text{P(p-tolyl)}_3]\), prepared by recrystallisation of \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})\text{P(p-tolyl)}_3]\) from methanol was shaken in \(\text{CH}_2\text{Cl}_2\) 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. \(\nu_{\text{CO}}\) 1960 cm\(^{-1}\). \(^{31}\text{P}-\{^1\text{H}\}\text{nmr}\) (CDCl\(_3\) at 298K) - 3 isomers

a) 50.5 (s), 41.5 (q) ppm [\(\delta(PP)\) 25.5; \(\delta(PP)\) 24.3 Hz]
b) 51.3 (s), 40.0 (q) ppm [\(\delta(PP)\) 24.9; \(\delta(PP)\) 133.6 Hz]
c) 52.2 (s), 38.9 (q) ppm [\(\delta(PP)\) 26.1; \(\delta(PP)\) 170.2 Hz].

Di-ν-chlorobis[chloro(thiocarbonyl)bis(tri-p-tolylphosphine)]

ruthenium(II)):-- The complex \([\text{RuCl}_2(\text{P(p-tolyl)}_3)]\) (0.25g) was refluxed in \(\text{CS}_2\) (15 cm\(^3\)) for 5 min to give a red solution which was cooled, filtered and reduced in volume (to ca. 5 cm\(^3\)). 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 \(\text{C}_{86}\text{H}_{84}\text{Cl}_4\text{P}_4\text{Ru}_2\text{S}_2\): C, 62.6; H, 5.1%] \(\nu_{\text{CS}}\) 1290 cm\(^{-1}\). \(^{31}\text{P}-\{^1\text{H}\}\text{nmr}\) (CDCl\(_3\) at 298K) 29.5 (s), 42.5 (s) ppm. The remaining solution on standing for 6h deposited tri-ν-chloro-a-chloro-g-(thiocarbonyl)tetrakis-(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 \(\text{C}_{85}\text{H}_{84}\text{Cl}_4\text{P}_4\text{Ru}_2\text{S}\): C, 63.6; H, 5.3%] \(\nu_{\text{CS}}\) 1292 cm\(^{-1}\) \(^{31}\text{P}-\{^1\text{H}\}\text{nmr}\) (CDCl\(_3\) at 298 K) 47.6 (q) and 34.6 (q) ppm [\(\delta(P^1P^2)\) 37.9, \(\delta(P^3P^4)\) 25.1; \(\delta(P^1P^2)\) 80.9, \(\delta(P^3P^4)\) 74.9 Hz].
Ethylidiphenylphosphine Complexes

[Dichlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS^-ruthenium(II)]_ carbondisulphide:-- Shaking the compound [RuCl_2(PPh_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°C [Found: C, 55.1; H, 4.7% Calc for C_{44}H_{45}Cl_{2}P_{3}RuS_4: C, 54.6; H, 4.6%] v(CS_2) 1515 cm^{-1}; v(PhOEt-CSO) 1115, 995 cm^{-1}. Dissolving this solid in CH_2Cl_2 and reprecipitating with light petroleum (bp 60-80°C) gave dichlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS^-ruthenium(II) [Found: C, 57.1; H, 5.0% Calc for C_{43}H_{45}Cl_{2}P_{3}RuS_2: C, 57.9; H, 5.0%] v(PhOEt-CSO) asym 1115, 995 cm^{-1} 31P-{^1H} nmr [CDCl_3 at 298 K] AMX pattern, v_A 41.1; v_M 34.0; v_X 9.2 ppm [J_AM 28.9, J_AX 3.7, J_MX 9.2 Hz]. A small amount of the above complex was also produced, together with an orange solution, on refluxing [RuCl_2(PPh_2)3] in CS_2 for 3h. On standing for 2 days, or alternatively, by addition of light petroleum (bp 60-80°C) to the orange solution, an orange solid was precipitated, consisting mainly of tri-u-chloro(chloro)bis(thiocarbonyl)tris(ethyldiphenylphosphine)diruthenium(II) v_CS 1295 cm^{-1}. 31P-{^1H} nmr [CDCl_3 at 298 K] 49.2 (s) and 36.8 (q) ppm [J(PP) 35.7, δ(PP) 84.1 Hz].

Chlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS^--(methanol)ruthenium(II)tetraphenylborate:-- The complex [RuCl_2(S_2CPPh_2)(PPh_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°C [Found: C, 66.3; H, 5.4% Calc for C_{68}H_{69}BClO_3P_3RuS_2: C 67.7; H, 5.7%] v(PhOEt-CS_2) asym 1115, 980 (br), 850 (br) cm^{-1} 31P-{^1H} nmr [CDCl_3 at 298 K] AMX pattern.
15.

\[ v_A \approx 44.6; \ v_M \approx 29.0; \ v_X \approx 16.3 \text{ ppm} \]  \[ J_{AM} \approx 28.0; \ J_{AX} \approx 3.5; \]

\[ J_{MX} \approx 11.3 \text{ Hz}. \]

Carbonyldi(chloro)(N,N-dimethylformamide)bis(ethyldiphenylphosphine)ruthenium(II):– The compound \([\text{RuCl}_2(\text{PEt}_2\text{Ph})_3]\)
(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 \text{in vacuo} at 40° C; (Yield ca. 80% m.p. 167° (decomp) [Found: C, 54.6; H, 5.3; Cl, 10.2; N, 2.1%] Calc for \(\text{C}_{32}\text{H}_{37}\text{Cl}_{2}\text{NO}_{2}\text{P}_{2}\text{Ru}:\ C, 54.8; \ H, 5.3; \ Cl, 10.1; N, 2.0\%\) \(\nu_{\text{CO}}\) 1928; \(\nu_{\text{CO}}(\text{dmf})\) 1641, \(\nu(\text{RuCl})\) 327 cm\(^{-1}\) \(^{31}\text{P}-\{^1\text{H}\}\text{nmr} \)
[CDC\(_3\) at 213 K] 32.8 (s) ppm; at 308K, 31.5 (s) ppm.

Reaction of \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})(\text{PEt}_2\text{Ph})_2]\) in methylene chloride solution:– \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})(\text{PEt}_2\text{Ph})_2]\) was shaken in CH\(_2\text{Cl}_2\) for 10 hours. Light petroleum (bp 60-80° 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 \(^{31}\text{P}-\{^1\text{H}\}\text{nmr}\) spectrum of this mixture (Fig. 1) has been discussed.

Reaction of \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})(\text{PEt}_2\text{Ph})_2]\) in benzene solution:– \([\text{Ru(CO)}\text{Cl}_2(\text{dmf})(\text{PEt}_2\text{Ph})_2]\) was shaken in benzene for 24 hours. The solvent was then removed under \text{vacuo} to give an orange oil which was dissolved in CH\(_2\text{Cl}_2\) (ca. 2.0 cm\(^3\)). Light petroleum (bp 60-80° C) was then added slowly to give a yellow-orange solid which was filtered and washed with pentane. The \(^{31}\text{P}-\{^1\text{H}\}\text{nmr}\) spectrum of this mixture (Fig. 2) has been discussed.
Reaction of $[\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})(\text{PETPh}_2)_2]$ with $[\text{RuCl}_2(\text{PETPh}_2)_3]$:

The compounds $[\text{Ru}(\text{CO})\text{Cl}_2(\text{dmf})(\text{PETPh}_2)_2]$ (0.07 g) and $[\text{RuCl}_2(\text{PETPh}_2)_3]$ (0.08 g) (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 $^31\text{P}-{^1}\text{H}$nmr spectrum showed the material to be a mixture of compounds (see earlier).

Acknowledgements

We thank Johnson-Matthey Ltd for loans of ruthenium trichloride trihydrate, the SRC for support (P.W.A.; W.J.S.) and Dr. A.S.F. Boyd for obtaining the $^31\text{P}$ nmr spectra.

References


Fig. 1  $^{31}P-{^1H}$ nmr spectra in CDCl$_3$ of the product obtained on shaking [Ru(CO)Cl$_2$(dmf)(PETPh$_2$)$_2$] in CH$_2$Cl$_2$ a) at 213K b) 308K

Fig. 2  $^{31}P-{^1H}$ nmr spectrum in CDCl$_3$ at 213 K of product obtained on shaking [Ru(CO)Cl$_2$(dmf)(PETPh$_2$)$_2$] in C$_6$H$_6$. 
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Ruthenium Complexes containing Group 5B Donor Ligands Part 8 1 Reaction of \([\text{Ru}_2(Y)\text{Cl}_4(\text{PPh}_3)_4]\) \((Y = \text{CO,CS})\) and \([\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}_2]\) with various \(L\) \([L = P(\text{OR})\text{Ph}_2, (R = \text{Me,Et}), P(\text{OMe})_2\text{Ph}]\) and of \([\text{RuCl}_2L_3\text{ or } 4]\) with Carbon Monoxide.

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Reaction of \([\text{Ru}_2Y\text{Cl}_4(\text{PPh}_3)_4]\) \((Y = \text{CO,CS})\) with excess of \(L\) in benzene leads to facile bridge cleavage and ligand exchange to give mixtures of \([\text{RuYCl}_2L_3]\) and \([\text{RuCl}_2L_3\text{ or } 4]\) \([L = P(\text{OR})\text{Ph}_2, (R = \text{Me,Et}), P(\text{OMe})_2\text{Ph}]\). These monosubstituted carbonyl and thiocarbonyl compounds can also be synthesised by carbonylation of \([\text{RuCl}_2L_3\text{ or } 4]\) and reaction of \([\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}_2]\) with excess of \(L\) respectively.

In alcohols, \([\text{RuYCl}_2(P(\text{OR})\text{Ph}_2)_3]\) rearrange to \([\text{Ru}(Y)\text{Cl}(P(\text{OMe})\text{Ph}_2)_3]^+\) and \([\{\text{Ru}(Y)\text{Cl}(P(\text{OMe})\text{Ph}_2)_3\}_2]^2+\) respectively, whereas \([\text{Ru}(Y)\text{Cl}_2(P(\text{OMe})_2\text{Ph})_3]\) is recovered unchanged. Structures are assigned to these compounds mainly on the basis of \(^{1}H\) and \(^{31}P-{^{1}H}\) nmr studies.

In previous papers, successful high yield syntheses of the triple chloride bridged complexes \([\text{Ru}_2(Y)\text{Cl}_4(\text{PR}_3)_4]\), \((Y = \text{CO,CS}; \text{PR}_3 = \text{PPh}_3, \text{P(tolyl)}_3)\); which involved either direct reaction of \([\text{RuCl}_2(\text{PR}_3)_3]\) with \(\text{CS}_2\) or intermolecular coupling of \([\text{Ru}(Y)\text{Cl}_2(\text{dmf})(\text{PR}_3)_2]\) with \([\text{RuCl}_2(\text{PR}_3)_3]\) (1:1 mol ratio) have been reported. 1-3 Using the latter method, a pure sample of the mixed tertiary phosphine complex \([\{P(tolyl)_3\}_2\text{ClRuCl}_3\text{Ru}(\text{CO})(\text{PPh}_3)_2]\) was also obtained by reaction of
\[ \text{[RuCl}_2\text{P(p-tolyl)}_3\text{]} \text{ with [Ru(CO)Cl}_2\text{(dmf)}\text{(PPh}_3\text{)}_2\text{]} \] and an isomeric mixture of \[ \text{[Ru}_2\text{(CO)}\text{Br}_2\text{Cl}_2\text{(PPh}_3\text{)}_4\text{]} \text{ compounds has been generated.} \]

However, attempts to extend this method to the synthesis of other tertiary phosphine, phosphinite or phosphonite complexes of type \[ \text{[Ru}_2\text{(Y)Cl}_4\text{L}_4\text{]} \text{ have not been very successful}. \] Thus, for example, although \[ ^{31}\text{P}_{-\text{1H}} \text{nmr studys did indicate that some [Ru}_2\text{(CO)}\text{Cl}_4\text{(PEtPh}_2\text{)}_4\text{] was formed in the reaction of [RuCl}_2\text{(PEtPh}_2\text{)}_3\text{] with [Ru(CO)Cl}_2\text{(dmf)}\text{(PEtPh}_2\text{)}_2\text{], substantial amounts of other rearrangement products such as [Ru(CO)Cl}_2\text{(PEtPh}_2\text{)}_3\text{] and [Ru}_2\text{Cl}_4\text{(PEtPh}_2\text{)}_5\text{] were also obtained and separation of these proved impossible.} \]

In this paper, the results of our attempts to prepare the compounds \[ \text{[Ru}_2\text{(Y)Cl}_4\text{L}_4\text{]} \text{ [L = P(OR)Ph}_2\text{, (R = Me,Et), P(OMe)}_2\text{Ph]} \text{ by direct exchange of L with [Ru}_2\text{(Y)Cl}_4\text{(PPh}_3\text{)}_4\text{] are described, together with a study of the reactions of various [RuCl}_2\text{L}_3\text{ or 4} \text{] compounds with carbon monoxide and of [RuCl}_2\text{(CS)}\text{(PPh}_3\text{)}_2\text{]} \text{ with various L}. \]

**Results and Discussion**

Reaction of \[ \text{[Ru}_2\text{(CO)}\text{Cl}_4\text{(PPh}_3\text{)}_4\text{]} \text{ with an excess of P(OMe)Ph}_2 \text{ in benzene under reflux produced after lh., a bright yellow solution, which on addition of light petroleum (bp 60-80°C), yielded a yellow solid (A). The }^{31}\text{P}_{-\text{1H}} \text{nmr spectrum of (A) at 298 K in C}_6\text{D}_6 \text{ contained a singlet at 149.86 (due to [RuCl}_2\text{(P(OMe)Ph}_2\text{)}_3\text{]}_4\text{) and a doublet and triplet at 114.9 and 138.56 respectively (J}_\text{pp} = 29.6 \text{ Hz) from [Ru(CO)Cl}_2\text{(P(OMe)Ph}_2\text{)}_3\text{]} \text{ (see below). The ir spectrum of (A) contained a band at 1972 cm}^{-1} \text{ (y}_{\text{CO}} \text{). Clearly, in addition to ligand exchange, facile bridge cleavage has also occurred as shown in the equation. The reaction was repeated using a 1:4 molar ratio of [Ru}_2\text{(CO)}\text{Cl}_4\text{(PPh}_3\text{)}_4\text{] to P(OMe)Ph}_2 \text{ which gave the same products, together with much unreacted starting material, thus indicating that the first step in this reaction is that of bridge cleavage.} \]
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 $[\text{Ru}(\text{CO})\text{Cl}_2(\text{P(OMe)}\text{Ph}_2)_3]$ 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 $\nu$(RuCl) vibrations from a chloride trans to CO and a chloride trans to phosphorus respectively. The $^31$P-$^1$H nmr spectrum exhibited an identical doublet and triplet pattern to that found for (A) whilst the $^1$H nmr spectrum at 301K in C$_6$D$_6$ consisted of a triplet and doublet at 3.19 and 2.846 respectively of intensity ratio 2:1. These results are consistent with structure (1), (Y = CO) containing cis chloride groups and two magnetically equivalent and one non-equivalent P(OMe)Ph$_2$ groups.

Likewise, although reaction of $[\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4]$ with an excess of P(OMe)Ph$_2$ produced an inseparable mixture of $[\text{RuCl}_2(\text{P(OMe)}\text{Ph}_2)_3]$ and $[\text{Ru}(\text{CO})\text{Cl}_2(\text{P(OMe)}\text{Ph}_2)_3]$, 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 $^31$P-$^1$H, $^1$H nmr spectra (Tables 1 and 2 respectively) and IR spectrum ($\nu_{\text{CO}}$ 1980 cm$^{-1}$; $\nu$(RuCl) 302, 279 cm$^{-1}$) were also consistent with structure (1). This compound had been previously synthesised by reaction of $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ with P(OMe)Ph$_2$ in ethanol, although in other instances, only mixtures of $[\text{Ru}(\text{CO})\text{Cl}_2\text{L}_3]$ and $[\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2]$ (L = P(OMe)Ph$_2$, P(OMe)$_2$Ph) were produced by this route. Reaction of $[\text{Ru}_2(\text{CO})\text{Cl}_4(\text{PPh}_3)_4]$ with excess P(OMe)$_2$Ph also gave a mixture of $[\text{RuCl}_2(\text{P(OMe)}_2\text{Ph})_4]$ and $[\text{Ru}(\text{CO})\text{Cl}_2(\text{P(OMe)}_2\text{Ph})_3]$. However, in this case, neither of the compounds readily rearrange in polar solvents and, therefore, recrystallisation from CH$_2$Cl$_2$/methanol produced initially white crystals of $[\text{Ru}(\text{CO})\text{Cl}_2(\text{P(OMe)}_2\text{Ph})_3]$ 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 \([\text{Ru(CO)}_2\text{Cl}_2\text{L}_2]\) \([\text{L} = \text{P(OR)}\text{Ph}_2, \text{P(OR)}_2\text{Ph} (\text{R} = \text{Me, Et})]\) have, in fact, been previously prepared by addition of excess \(\text{L}\) to carbonylated solutions of "\(\text{RuCl}_3\text{H}_2\text{O}\)" in 2-methoxyethanol. As for \([\text{Ru}_2\text{(CO)}_4(\text{PPh}_3)_4]\), reactions of \([\text{Ru}_2\text{Cl}_4(\text{CS})(\text{PPh}_3)_4]\) with \(\text{P(OR)}\text{Ph}_2\) gave an inseparable mixture of \([\text{RuCl}_2(\text{CS})(\text{P(OR)}\text{Ph}_2)_3]\) and \([\text{RuCl}_2(\text{P(OR)}\text{Ph}_2)_3]\) \((\text{R} = \text{Me, Et})\).

However, \([\text{RuCl}_2(\text{CS})(\text{P(OR)}\text{Ph}_2)_3]\) could be obtained in pure state by reaction of the double chloride bridged complex \([\{\text{RuCl}_2(\text{CS})(\text{PPh}_3)_2\}_2]\) with \(\text{P(OR)}\text{Ph}_2\). For \([\text{RuCl}_2(\text{CS})(\text{P(OMe)}\text{Ph}_2)_3]\), the \(31\text{P}-\{^1\text{H}\}\) nmr spectrum at 298 K in \(\text{CD}_6\) 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 \(\text{cm}^{-1}\) \((\nu_{\text{CS}})\), 315 and 286 \(\text{cm}^{-1}\) \((\nu\text{RuCl})\). The \(^1\text{H}\) nmr spectrum in \(\text{CDCl}_3\) 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 \([\text{RuCl}_2(\text{CS})(\text{P(OMe)}\text{Ph}_2)_3]\) 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 \(\text{CH}_2\text{Cl}_2/\text{methanol}\) to give white crystals of \([\text{RuCl}_2(\text{CS})(\text{P(OMe)}_2\text{Ph})_3]\), shown by ir and nmr spectroscopy to have structure (1).

As mentioned earlier, difficulties arose when trying to separate mixtures of \([\text{Ru}(Y)\text{Cl}_2(\text{P(OR)}\text{Ph}_2)_3]\) and \([\text{RuCl}_2(\text{P(OR)}\text{Ph}_2)_3]\) because of the facile rearrangement reactions of both species in polar solvents (see ref. 4 for a detailed discussion of the rearrangement reactions of \([\text{RuCl}_2(\text{P(OR)}\text{Ph}_2)_3]\) compounds). Thus, dissolving \([\text{Ru}(Y)\text{Cl}_2(\text{P(OMe)}\text{Ph}_2)_3]\)
(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(OEt)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.⁸
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 \( \delta \) 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 \( \delta \). These results strongly indicated that the resonance at 120.0 \( \delta \) was due to the monomeric cation \([\text{Ru}\,(\text{CO})\,\text{Cl}(\text{P} \{\text{OE}t\,\text{Ph}_2\})_3]^+\) which increased in concentration as the temperature was raised and the dimer dissociated. Indeed, conductivity measurements at 298 K in \( \text{CH}_2\text{Cl}_2 \) 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 \( \text{CS} \) 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 \( \text{IR} \) 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}(\text{Y})\,\text{Cl}_2(\text{PR}_3)_2\},\text{Y} = \text{CO}; \text{PR}_3 = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{Y} = \text{CS}; \text{PR}_3 = \text{PPh}_3, \text{P(p-tolyl)}\] have been synthesised.

It should be noted that this behaviour of \([\{\text{Ru}\,(\text{CO})\,\text{Cl}(\text{P} \{\text{OE}t\,\text{Ph}_2\})_3\},\text{Y} = \text{CO}; \text{PR}_3 = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{Y} = \text{CS}; \text{PR}_3 = \text{PPh}_3, \text{P(p-tolyl)}\] in solution is analogous to that found for \([\{\text{Ru}\,\text{Cl}(\text{P} \{\text{OE}t\,\text{Ph}_2\})_4\},\text{Y} = \text{CO}; \text{PR}_3 = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{Y} = \text{CS}; \text{PR}_3 = \text{PPh}_3, \text{P(p-tolyl)}\]. This tendency of the \( \text{P} \{\text{OE}t\} \text{Ph}_2 \) complexes to form dimeric species, compared to the corresponding \( \text{P}(\text{OMe})\text{Ph}_2 \) complexes, which appear

* The possibility of frozen-out monomeric structures at this temperature (due to the bulkier \( \text{P} \{\text{OE}t\} \text{Ph}_2 \) groups) seems unlikely in view of the fact that the \( ^{31}\text{P} \{-^1\text{H}\} \) nmr spectrum of \([\text{Ru}\,\text{Cl}_2(\text{P} \{\text{OE}t\} \text{Ph}_2)_3]\) 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 $P(OMe)Ph_2$ compounds would be expected to dimerise preferentially.

This tendency of $[Ru(Y)Cl_2(P(OR)Ph_2)_3]$ 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, $[MX_2(dppp)_2]$ ($M = Ru, Os; X = Cl,Br$; dppp = $Ph_2P(CH_2)_3PPh_2$) compounds were shown to lose a halide ion in boiling alcohol to give the five coordinate cations $[MX(dppp)_2]^+$, isolated as $PF_6^-$ or $BPh_4^-$ salts. Steric effects were clearly important here since the corresponding compounds with smaller diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1,2$) showed no tendency to lose halide ion. Similarly when $[Ru(Y)Cl_2(P(OMe)_2Ph)_3]$ 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 $4000-250 \text{ cm}^{-1}$ on Perkin Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the region $400-200 \text{ cm}^{-1}$ 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 $^{31}P$ 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 $85\% H_3PO_4$. Conductivity measurements were made at 298 K using a model 310 Portland Electronics conductivity bridge. As described earlier, $^4$ plots of $\Lambda_o-\Lambda \ vs \ C^2$ 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)R₂ (R = Me, Et), P(OMe)₂ Ph [Maybridge]. Sodium tetraphenylborate (BDH). [Ru₂(Y)Cl₄(PPh₃)₄] (Y = CO, CS), [{RuCl₂(CS)(PPh₃)₂}₄]²⁻, [RuCl₂L₃] [L = P(OR)R₂ (R = Me, Et)₄], and [RuCl₂(P(OMe)₂ Ph)₄]⁴⁻ were prepared as described earlier. ³¹P-¹H and ¹H 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 ν(RuCl) vibrational bands are underlined.

Carbonyl(dichloro)tris(methylidiphenylphosphinite)ruthenium(II): Carbon monoxide gas was bubbled through a solution of [RuCl₂(P(OMe)₂ Ph)₃] in benzene for 1 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; νCO 1972 cm⁻¹; far ir spectrum 312, 286, 275, 233 cm⁻¹. A similar method was used to prepare carbonyl(dichloro)tris(ethyldiphenylphosphinite) ruthenium(II) from [RuCl₂(P(OEt)₂ Ph)₃] as a white solid; m.p. 203-205°C; νCO 1980 (strong), 1935 (weak) cm⁻¹; far ir spectrum 302, 279, 260, 238 cm⁻¹.

Carbonyl(dichloro)tris(dimethylphenylphosphonite)ruthenium(II): The complex [Ru₂(CO)Cl₄(PPh₃)₄] (0.20 g) was refluxed with excess of P(OMe)₂ Ph (0.40 cm³) 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 CH₂Cl₂/MeOH produced colourless crystals of the complex;
The remaining yellow solution deposited after several days yellow crystals of [RuCl₂(P(OMe)₂Ph)₄].

Similarly, dichloro(thiocarbonyl)tris(dimethylphenylphosphonite) ruthenium(II) was prepared as colourless crystals from [Ru₂Cl₄(CS)(PPh₃)₄]; m.p. 149-151°C; ν₁₃₀₅ cm⁻¹; ν(RuCl) 312, 274 cm⁻¹.

Dichloro(thiocarbonyl)tris(methylidiphenylphosphinite)ruthenium(II): The complex [RuCl₂(CS)(PPh₂)₂]₀ (0.20 g) was refluxed with P(OMe)Ph₂ (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; ν₁₂₇₅ cm⁻¹; far ir spectrum 315, 286, 272, 233 cm⁻¹.

Similarly, dichloro(thiocarbonyl)tris(ethyldiphenylphosphinite)ruthenium(II) was prepared as a yellow solid; ν₁₂₉₅ cm⁻¹; far ir spectrum 305, 280, 265 cm⁻¹.

Carbonyl(chloro)tris(methylidiphenylphosphinite)ruthenium(II) tetraphenyloborate: The complex [Ru(CO)Cl₂(P(OMe)Ph₂)₃]₀ (0.20 g) was dissolved in methanol (15 ml) containing NaBPh₄ (0.20 g). After 24 h, white crystals of the complex were deposited; m.p. 193-195°C; ν₁₈₇₅ cm⁻¹; ν(RuCl) 303 cm⁻¹. Conductivity at 298 K in CH₂Cl₂: slope of Λₒ-Λ vs C⁻ = 148 (for [Ru₂Cl₃(P(OMe)Ph₂)₆]BPh₄, slope = 165). In the same way, chloro(thiocarbonyl)tris(methylidiphenylphosphinite)ruthenium(II) tetraphenylborate was prepared as white crystals; m.p. 174-176°C; ν₁₂₈₅ cm⁻¹; ν(RuCl) 301 cm⁻¹; conductivity at 298 K in CH₂Cl₂: slope of Λₒ-Λ vs C⁻ = 156.

(Bis)[carbonyl(chloro)tris(ethyldiphenylphosphinite)ruthenium(II)]tetraphenylborate: The complex [RuCl₂(CO)(P{Ot}Ph₂)₃]₀ (0.20 g) was dissolved in ethanol (15 ml) containing NaBPh₄ (0.20 g). Over a period of 3 days white crystals of the complex were deposited; m.p. 198-200°C;
\( \nu_{CO} \) 1960 cm\(^{-1}\); far ir spectrum 270, 282, 263, 256 cm\(^{-1}\). Conductivity in CH\(_2\)Cl\(_2\) at 298 K slope of \( A^{-1} \) vs \( C^2 \) = 198. Likewise, [RuCl\(_2\)(CS)(P\{OEt\}Ph\(_2\))\(_3\)] dissolved in ethanol containing NaBPh\(_4\) produced bis[chloro(thiocarbonyl)tris(ethyldiphenylphosphinite)ruthenium(II)]tetraphenylborate: m.p. 112-114\(^\circ\)C; \( \nu_{CS} \) 1285 cm\(^{-1}\); \( \nu(\text{RuCl}) \) 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 \( ^{31}\text{P} \) and \( ^{1}\text{H} \) nmr spectra respectively.

References


\[ \text{L} = \text{P(OMe)}_2\text{Ph}_2, \text{P(OEt)}_2\text{Ph}_2, \text{P(OMe)}_2\text{Ph} \]
\[ \text{Y} = \text{CO}, \text{CS} \]
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s, singlet; d, doublet; t, triplet.

¹ Multiplet ranging over values stated.
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(d) - doublet  
(t) - triplet

\( N = |\text{J(} \text{PH} \text{)} + \text{J(} \text{PH} \text{)}| \)

<sup>a</sup> Multiplet between stated values. <sup>b</sup> Broad resonance
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$^{31}\text{P-}^{1}\text{H}$ nmr spectrum of $\{\text{Ru(CO)Cl(P(\text{OEt})\text{Ph}_2)\}_{2}\}_{2}$ (BPh$_4$)$_2$ in CDCl$_3$ at 213 K
Cationic, Neutral and Anionic Complexes of Ruthenium(II) containing \( \eta^6 \)-Arene Ligands.

D.R. Robertson, T.A. Stephenson* and (in part) T. Arthur, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

Summary

Reaction of \([\{\text{Ru}(C_6H_5)Cl_2\}_2]\) with an excess of CsCl/HCl in ethanol gives the first anionic arene complex of ruthenium Cs[\(\text{Ru}(C_6H_5)Cl_3\)](II) although in aqueous solution this readily loses a chloride ion to give \([\text{Ru}(C_6H_5)Cl_2(H_2O)]\) and reactions with various Lewis bases give the compounds \([\text{Ru}(C_6H_5)Cl_2L]\) (\(L = C_5H_5N, \text{Me}_2\text{SO}, \text{PR}_3\) etc). Reaction of \([\{\text{Ru}(C_6H_5)Cl_2\}_2]\) with \(\text{NH}_4\text{PF}_6\) in methanol gives high yields of the triple chloride bridged complex \([\text{Ru}_2(C_6H_5)_2Cl_3\text{PF}_6](\text{III})\) 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 \([\text{Ru}(C_6H_5)ClL\text{PF}_6]\) (\(L = C_5H_5N, \text{Et}_2\text{S}, \text{AsPh}_3, \text{PR}_3\) etc).
Introduction

In recent years, some reactions of the unusual $\eta^6$-arene complexes $[\text{Ru}(\text{arene})X_2]_2$ (arene = $\text{C}_6\text{H}_6$, $\text{C}_6\text{H}_5\text{OMe}$, $\text{p-}$ and $\text{m-}$ $\text{C}_6\text{H}_4\text{Me}_2$, $\text{C}_6\text{H}_5\text{Me}$, $1,3,5-$ $\text{C}_6\text{H}_3\text{Me}_3$, $\text{p-}$ $\text{MeC}_6\text{H}_4\text{CHMe}_2$; $X = \text{Cl}$ or $\text{Br}$) 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 $[\text{Ru}(\text{arene})X_2L]$ ($L = \text{PR}_3$, $\text{P(OR)}_3$, $\text{AsR}_3$, $\text{C}_5\text{H}_5\text{N}$ 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 $[\text{C}_6\text{H}_3\text{RuCl}_3\text{RuC}_6\text{H}_6]^+$ 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$[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_3]$

As reported earlier [9], reaction of the compound $[\{\text{Ru(CO)}\text{Cl}_2- (\text{C}_7\text{H}_8)\}_2]$ ($\text{C}_7\text{H}_8$ = bicyclo [2.2.1] hepta-2,5-diene) with $\text{MeCl/MeCl} (M = \text{Ph}_3-(\text{PhCH}_2)\text{P}^+$, $\text{Cs}^+$) in degassed acetone gave a high yield of the first anionic diene complex of ruthenium $\text{M}[\text{Ru(CO)}\text{Cl}_3(\text{C}_7\text{H}_8)]$. An attempt has now been made to synthesise the first anionic $\eta^6$-arene ruthenium complex using a similar preparative route. Thus, shaking $[\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2] (\text{I})$ with a mixture of excess CsCl and concentrated HCl in ethanol for several days gave an orange powder analysing closely for Cs$[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_3] (\text{II})$ although it was always difficult to obtain this complex completely free of CsCl. The mull i.r. spectrum of (II) indicated the presence of coordinated benzene and contained a broad band at 280 cm$^{-1}$ assigned to terminal $\nu(\text{RuCl})$ stretching vibration(s). Since compound (II) possesses $C_{3v}$ symmetry, two $\nu(\text{RuCl})$ 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 $v$(RuCl) bands. Unfortunately, attempts to make the corresponding $[\text{Ru}(\text{C}_6\text{H}_5\text{X})_3]^{-}\ (X = \text{Br}^-, \text{I}^-)$ anions, either by reaction of $[\{\text{Ru}(\text{C}_6\text{H}_5\text{X})_2\}_2]$ or $\text{Cs}[\text{Ru}(\text{C}_6\text{H}_5\text{Cl})_3]$ with $X^-$ were unsuccessful, only $[\{\text{Ru}(\text{C}_6\text{H}_5\text{X})_2\}_2]$ being recovered from the reaction mixture in each case.

As expected, $\text{Cs}[\text{Ru}(\text{C}_6\text{H}_5\text{Cl})_3]$ was more soluble in water than $[\{\text{Ru}(\text{C}_6\text{H}_5\text{Cl})_2\}_2]$ and an aqueous solution of (II) was highly conducting (e.g., for a $10^{-3}$ mol dm$^{-3}$ solution, $\sqrt{\mu} = 374$ S cm$^2$ 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 $\text{Cs}[\text{Ru}(\text{C}_6\text{H}_5\text{Cl})_3]$ in $\text{D}_2\text{O}$ consisted of a single $^6\text{C}_6\text{H}_6$ resonance at 6.40$\delta$ whereas that of $[\{\text{Ru}(\text{C}_6\text{H}_5\text{Cl})_2\}_2]$ in $\text{D}_2\text{O}$ showed two coordinated benzene resonances at 6.39(vs) and 6.50(w)$\delta$ which previous workers have assigned to either the aqua complexes $[\text{Ru}(\text{C}_6\text{H}_5\text{Cl}(\text{D}_2\text{O}))_2]^+$ and $[\text{Ru}(\text{C}_6\text{H}_5)(\text{D}_2\text{O})_3]^{2+}$ respectively or to a combination of one of these cations and the neutral complex $[\text{Ru}(\text{C}_6\text{H}_5\text{Cl}_2\text{D}_2\text{O})][1]$. It is therefore

* Zelonka and Baird [1] quoted the resonance positions for $[\{\text{Ru}(\text{C}_6\text{H}_5\text{Cl})_2\}_2]$ in $\text{D}_2\text{O}$ 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 coordinated $^6\text{C}_6\text{H}_6$ resonance in the $^1$H nmr spectrum of $[\text{Ru}(\text{C}_6\text{H}_5\text{Cl}_2(\text{PMe}_2\text{Ph}))$ when run in $\text{CDCl}_6$ 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 $^6\text{C}_6\text{H}_6$ resonances of $[\{\text{Ru}(\text{C}_6\text{H}_5\text{Cl})_2\}_2]$ in $\text{D}_2\text{O}$ 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 6.40δ 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(C₆H₆)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 η-C₆H₆ resonance, and furthermore, slow precipitation of [{Ru(C₆H₆)Cl₂}] also occurred.

Earlier, Ph₃(PhCH₂)₂P[Ru(CO)Cl₃(C₇H₅)] 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 displacement of diene [10]. Attempts, however, to synthesise the unknown fac-[Cl₃L₃]⁻ anions by reaction of Cs[Ru(C₆H₆)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(C₆H₆)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 η-C₆H₆ resonances at 5.65 and 5.90δ. The latter was assigned to the d⁶-Me₂SO complex [Ru(C₆H₆)Cl₂(d⁶-Me₂SO)], (reported in ref [1] to have an η-C₆H₆ ¹H nmr resonance at 5.93δ) and this was verified by synthesising [Ru(C₆H₆)Cl₂(Me₂SO)], either by refluxing [Ru(C₆H₆)Cl₂(C₅H₅N)] or Cs[Ru(C₆H₆)Cl₃] with excess Me₂SO in methanol. In contrast, prolonged refluxing of (II) in neat pyridine gave a mixture of [Ru(C₆H₆)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⁺](I) 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 (IIa). In our hands, however, this reaction produced only low variable yields (ca. 12%) of (IIa) plus, on one
occasion, a further product (see experimental section) shown by X-ray analysis [14] to be \([\text{Ru(NH}_3]_2(\text{C}_6\text{H}_6)\text{Cl}]_3(\text{PF}_6)_3\text{NH}_4\text{PF}_6\). Since the \([\text{Ru}_2(\text{C}_6\text{H}_6)\text{Cl}]_3^+\) cation is isoelectronic with \([\text{Rh}_2\text{Cl}_3(\text{C}_5\text{Me}_5)]^+\), 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 \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2\) in methanol at ambient temperature with a slight excess of NH$_4$PF for 24h gave, in high yield, (>90%) a dark orange-yellow solid which analysed quite well for \([\text{Ru}_2(\text{C}_6\text{H}_6)\text{Cl}_3]\text{PF}_6\) (IIIb). No apparent reaction occurred in the absence of NH$_4$PF or if methanol was replaced by acetone.

The mull 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], \(\gamma(\text{RuCl})\) 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, \(\sqrt{\nu_m} = 82$ S cm$^2$ mol$^{-1}$) and this was supported by \(\sqrt{\nu_o - \nu_c} \propto C^\delta\) 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 $^2$MeNO$_2$ at ambient temperature both showed a single sharp resonance for the $^6$-C$_3$H$_6$ groups at 5.90$\delta$ 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 $^6$Me$_2$SO, more than one $^6$-C$_3$H$_6$ resonance was observed. Thus, the $^1$H nmr spectrum of (IIIA or b) in D$_2$O contained two $^6$-C$_3$H$_6$ resonances at 6.35 and 6.48$\delta$ of comparable $^+\text{Interestingly in ref [3], only a single resonance for (IIIA) in D}_2\text{O at 6.04$\delta$ 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 $\{\text{Ru}({C}_6{H}_6)\text{Cl}_2\}_2$ dissolved in $D_2O$ [6.39 and 6.50 δ – see section a)] indicating facile bridge cleavage has occurred as shown in the equation.

$$\begin{align*}
\text{Solvent} & \quad \text{Solvent} + \\
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\text{Ru} & \quad \text{Ru} \\
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}$$

In $d^6$-Me$_2$SO, three singlets were observed in the $^1H$ nmr spectrum of (IIIb) at 5.95 (vs), 6.15 (w) and 6.50 (s) which corresponded closely to the quoted positions of the $\eta^6$-C$_6$H$_6$ resonances for the species $\text{Ru-}({C}_6{H}_6)\text{Cl}_2(d^6-\text{Me}_2\text{SO})$ (5.93 δ), $\text{Ru}({C}_6{H}_6)\text{Cl}(d^6-\text{Me}_2\text{SO})_2$ (6.12 δ) and $\text{Ru}({C}_6{H}_6)(d^6-\text{Me}_2\text{SO})_3^{2+}$ (6.47 δ) [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 $[\text{Ru}_2\text{Cl}_3L_6]$ $^+$ cations, ($L = \text{PR}_3$, $\text{P(OR)}\text{Ph}_2$, $\text{P(OR)}_2\text{Ph}$), the most likely mechanism of formation of $[\text{Ru}_2({C}_6{H}_6)\text{Cl}_3]^{2+}$ is by intermolecular coupling of the weakly solvated monomers $[\text{Ru}({C}_6{H}_6)\text{Cl}_2(\text{solvant})]$ and $[\text{Ru}({C}_6{H}_6)\text{Cl}(\text{solvant})_2]^{2+}$, the monomers being formed by reaction of $[\{\text{Ru}({C}_6{H}_6)\text{Cl}_2\}_2]$ 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 ethyldiphenylphosphinite complexes [17], via the cationic, double chloride bridged solvated intermediate $\{({C}_6{H}_6)\text{-ClRuCl}_3\text{Ru(solvent)}_2({C}_6{H}_6)\}^{2+}$ which then rearranges readily to (III) (Scheme).

*Unfortunately, the solubility of $[\{\text{Ru}({C}_6{H}_6)\text{Cl}_2\}_2]$ in methanol is too low to obtain $^1H$ nmr evidence for the formation of methanolate monomers although, of course, there is no doubt that analogous monomeric species are readily formed in $D_2O$ 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$_3$L$_{3}$]$^+$ (L = C$_6$H$_5$N, Me$_2$SO, RCN etc) via displacement of 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$_6$H$_5$N)$_2$]PF$_6$. Concentration of the remaining filtrate gave the non-conducting orange-solid trans-[RuCl$_2$(C$_6$H$_5$N)$_4$]. Attempts to retain the chloride bridges but induce replacement of 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$_6$H$_5$N)$_2$]PF$_6$ and trans-[RuCl$_2$(C$_6$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 \(
\text{cis-[RuCl}_2(\text{PMe}_2\text{Ph})_4]\), 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 \([\text{Ru}_2\text{Cl}_3L_6]^+\), 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 \([\text{Ru}(\text{Y})\text{Cl}_2(\text{P(OR)Ph})_2]^{-}\) and \([\text{RuCl}_2(\text{P(OR)Ph})_3]^{-}\) [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 RIIC 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 ¹³C-{¹H} nmr spectra on a Varian XL100 spectrometer operating at 25.2 MHz (¹³C chemical shifts quoted in ppm to high frequency of SiMe₄). Conductivity measurements were made at 298K using a model 310 Portland Electronics conductivity bridge. As described earlier [17] plots of \( \nu_o - \nu_c \) vs \( C^+ \) gave a straight line whose slope is a function of the ionic charges [20]. Melting points were determined with a Kőfler 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.); methyldiphenylphosphine and dimethylphenylphosphine (Maybridge): nitromethane, pyridine, acetonitrile and mesitylene (Fisons); dimethylsulphoxide (Hopkins and Williams); triphenylstibine (Kodak). \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]\) and \([\{\text{Ru}(\text{C}_6\text{H}_3\text{Me})\text{Cl}_2\}_2]\) were prepared as described earlier [1,3] from "RuCl₃·H₂O", 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 \([\{\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2\}_2]\) 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 \([\text{Ru}(\text{C}_6\text{H}_5\text{Cl}_3)]_{2}\) (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\(^\circ\)C (decomp) (Yield 0.31g, 95%) v(RuCl) 280 (broad) cm\(^{-1}\).

Benzene(dichloro)pyridine ruthenium(II): The compound Cs[\text{Ru}(\text{C}_6\text{H}_5\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 resultant yellow solution and addition of diethyl ether gave an orange solid mp. 245\(^\circ\)C (decomp) (0.07g, 86%) v(RuCl) 280 cm\(^{-1}\).

Benzene(dichloro)triphenylphosphine ruthenium(II): The compound Cs[\text{Ru}(\text{C}_6\text{H}_5\text{Cl})] (0.10g; 0.23 mmol) was shaken with excess of \(P\text{Ph}_3\) (0.10g; 0.40 mmol) in methanol for ca 3h to give a dark red crystalline solid mp. 182\(^\circ\)C (0.11g, 91%) v(RuCl) 295, 280 cm\(^{-1}\).

Benzene(dichloro)methylidiphenylphosphine ruthenium(II): mp. 197\(^\circ\)C (0.09g, 82%) v(RuCl) 290, 270 cm\(^{-1}\); benzene(dichloro)dimethylphenylphosphine-ruthenium(II) mp. 175\(^\circ\)C (0.07g; 78%) v(RuCl) 290, 275 cm\(^{-1}\); benzene-(dichloro)triphenylstibine ruthenium(II) mp. 220-222\(^\circ\)C v(RuCl) 290, 269 cm\(^{-1}\) and benzene(dichloro)dimethylsulphoxide ruthenium(II) mp. 211\(^\circ\)C v(RuCl) 291, 272 cm\(^{-1}\) were similarly prepared.
cis-dichlorotetrakis(dimethylphenylphosphine)ruthenium(II): The compound 
Cs[Ru(C₆H₆)Cl₃] (0.10g; 0.23 mmol) was refluxed in methanol with excess 
PMe₂Ph (0.50 cm³) for 6h. The resulting yellow solution on standing 
gave a yellow, crystalline solid mp. 126°C (0.13g; 82%) ν(RuCl) 288, 
241 cm⁻¹.

Tri-μ-chlorobis[(benzene)ruthenium(II)]hexafluorophosphate:-- Method A: 
The complex [{Ru(C₆H₆)Cl₂₂} (0.20g; 0.40 mmol) was heated under reflux 
with water (10 cm³) for 2h. The orange solution was filtered and treated 
with a saturated aqueous solution of NH₄PF₆. 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 [{Ru(NH)₃}₂(C₆H₆)Cl₃(PF₆)₃·NH₄PF₆ 
(νRuCl 285 cm⁻¹; ν(NH) 3180, 3250, 3320, 3370 cm⁻¹; δ(NH) 1615, 1630 cm⁻¹; 
ν(Ru-N) 421, 440, 455 cm⁻¹). Unfortunately, subsequent attempts to 
prepare this latter compound were unsuccessful.

Method B: The complex [{Ru(C₆H₆)Cl₂₂} (0.20g; 0.40 mmol) was stirred in 
methanol (25 cm³) with excess of NH₄PF₆ (0.16g; 1.00 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%) ν(RuCl) 264, 276 cm⁻¹. 
Conductivity in MeNO₂ at 298K. Slope of ν₀ - νc vs C¹/² plot = 207; 
for [{Ru₂Cl₃(PMe₂Ph)]PF₆, slope = 190. ¹³C-{¹H}nmr in d₃-MeNO₂ at 303K. 
82.0 ppm (singlet). The compound is insoluble in CHCl₃, CH₂Cl₂, benzene 
and very sparingly soluble in acetone.

Benzene(chloro)bis(pyridine)ruthenium(II)hexafluorophosphate: The complex 
[Ru₂(C₆H₆)Cl₃]PF₆ (0.09g; 0.14 mmol) was refluxed in ethanol (30 cm³) 
with pyridine (0.40 cm³) for ca 6h. The yellow solution on standing for 
24h gave a yellow crystalline solid mp. 227-229°C (0.05g; 66%) ν(RuCl)
Concentration of the filtrate from this reaction gave an orange solid trans-dichlorotetrakis(pyridine)ruthenium(II) mp. 255°C (decomp) (0.03g; 24%) ν(RuCl) 338 cm⁻¹.

Benzenedichloro(diethylsulphide)ruthenium(II): The complex [Ru₂(C₆H₅)₂Cl₃]PF₆ (0.10g; 0.16 mmol) was refluxed in ethanol (30 cm³) with Et₂S-(0.20 cm³) 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) ν(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, ν(RuCl) 290 cm⁻¹.

Benzenechlorobis(triphenylphosphine)ruthenium(II)hexafluorophosphate: The complex [Ru₂(C₆H₅)₂Cl₃]PF₆ (0.20g; 0.32 mmol) was shaken in methanol (20 cm³) with excess of PPh₃ (0.20g; 0.80 mmol). The red precipitate was filtered off from the yellow solution, recrystallised from CH₂Cl₂/hexane and identified as [Ru(C₆H₅)Cl₂(PPh₃)]. Addition of diethyl ether and hexane to the yellow filtrate gave the yellow crystalline product mp. 172°C (0.11g, 41%), ν(RuCl) 290 cm⁻¹. Similar reactions gave the yellow solids benzenechlorobis(triphenylarsine)ruthenium(II)hexafluorophosphate mp. 142°C, ν(RuCl) 310 cm⁻¹; benzenechlorobis(methyldiphenylphosphine)ruthenium(II)hexafluorophosphate mp. 158°C ν(RuCl) 292 cm⁻¹ and benzenechlorobis(dimethylphenylphosphine)ruthenium(II)hexafluorophosphate mp. 209-211°C, ν(RuCl) 298 cm⁻¹.

Tri-μ-chlorobis[tris(dimethylphenylphosphine)ruthenium(II)]hexafluorophosphate: The compound [Ru₂(C₆H₅)₂Cl₃]PF₆ (0.20g; 0.32 mmol) was refluxed in methanol (20 cm³) with excess of PMe₂Ph (1 cm³) 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 $\ce{C6}$-Areneruthenium(II) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found %</th>
<th>Calculated %</th>
<th>$\sqrt{\nu_m}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>$\text{Cs[Ru(C}_6\text{H}_5\text{)Cl}_3]$</td>
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<td>1.4</td>
<td>-</td>
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<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}_2(\text{C}_5\text{H}_5\text{N})\right]$</td>
<td>40.4</td>
<td>3.3</td>
<td>4.6</td>
</tr>
<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}_2(\text{PPh}_3)\right]$</td>
<td>56.6</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}_2(\text{PMePh}_2)\right]$</td>
<td>49.9</td>
<td>4.1</td>
<td>-</td>
</tr>
<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}_2(\text{Me}_2\text{SO})\right]$</td>
<td>28.8</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>$\left[\text{RuCl}_2(\text{PMe}_2\text{Ph})_4\right]$</td>
<td>52.4</td>
<td>6.1</td>
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<tr>
<td>$\left[\text{Ru}_2(\text{C}_6\text{H}_6\text{)Cl}_3\right]^{PF}_6$</td>
<td>23.8</td>
<td>1.9</td>
<td>16.2</td>
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<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}(\text{C}_5\text{H}_5\text{N})\right]^{PF}_6$</td>
<td>37.0</td>
<td>3.0</td>
<td>5.3</td>
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<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}_2(\text{Et}_2\text{S})\right]$</td>
<td>34.9</td>
<td>4.6</td>
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<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}_2(\text{Et}_2\text{S})_2\right]^{PF}_6$</td>
<td>31.5</td>
<td>4.6</td>
<td>-</td>
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<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}(\text{PPh}_3)_2\right]^{PF}_6$</td>
<td>56.7</td>
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<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}(\text{AsPh}_3)_2\right]^{PF}_6$</td>
<td>51.6</td>
<td>3.7</td>
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<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}(\text{PMePh}_2)_2\right]^{PF}_6$</td>
<td>41.3</td>
<td>4.4</td>
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<tr>
<td>$\left[\text{Ru(C}_6\text{H}_6\text{)Cl}(\text{PMePh}_2)_2\right]^{PF}_6$</td>
<td>50.5</td>
<td>4.8</td>
<td>-</td>
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<tr>
<td>$\left[\text{RuCl}_2(\text{PMe}_2\text{Ph})_2\right]^{PF}_6$</td>
<td>44.9</td>
<td>5.1</td>
<td>-</td>
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<tr>
<td>$\left[\text{Ru(NH}_3)_2(\text{C}_6\text{H}_6\text{)Cl}]_3^{PF}_6\right.$</td>
<td>16.3</td>
<td>2.9</td>
<td>7.1</td>
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</table>

$^a$Equivalent conductivities ($S \text{ cm}^2 \text{ mol}^{-1}$) measured in nitromethane (unless stated) at $10^{-3} \text{ mol dm}^{-3}$ concentration $^b$ measured in $\text{H}_2\text{O}$ $^c$ measured in $\text{CH}_2\text{Cl}_2$ - rearranges to $[\text{RuCl}_3(\text{PMe}_2\text{Ph})]^{PF}_6$. 
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$^6\text{C}_6\text{H}_6$</th>
<th>other resonances</th>
</tr>
</thead>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2]^2_2$</td>
<td>$D_2^b$</td>
<td>6.39$^c$; 6.50$^c$</td>
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<tr>
<td>Cs$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_3]$</td>
<td>$D_2^b$</td>
<td>6.40$^c$</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{C}_5\text{H}_5\text{N})]$</td>
<td>$d^6\text{-Me}_2\text{SO}$</td>
<td>5.65, 5.90$^d$</td>
<td>7.30, 8.80(pyridine)</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{Me}_2\text{SO})]$</td>
<td>CDC1$_3$</td>
<td>5.90</td>
<td>ca 2.70(br) (Me$_2$SO)</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{PPh}_3)]$</td>
<td>CDC1$_3$</td>
<td>5.40</td>
<td>7.50 (PPh$_3$)</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{PMePh}_2)]$</td>
<td>CDC1$_3$</td>
<td>5.40</td>
<td>7.65(Ph); 1.95(d)($^2J_{\text{PH}}$ 12.0Hz) (Me)</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{PMe}_2\text{Ph})]$</td>
<td>CDC1$_3$</td>
<td>5.95</td>
<td>8.03(Ph); 2.48(d)($^2J_{\text{PH}}$ 12.0Hz) (Me)</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{SbPh}_3)]$</td>
<td>CDC1$_3$</td>
<td>5.68</td>
<td>7.40-7.70(SbPh$_3$)</td>
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<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{AsPh}_3)]$</td>
<td>CDC1$_3$</td>
<td>5.50</td>
<td>7.40-7.60(AsPh$_3$)</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}_2(\text{Et}_2\text{S})]$</td>
<td>CDC1$_3$</td>
<td>5.70</td>
<td>2.90(q); 1.35(t) (Et$_2$S)</td>
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<tr>
<td>$[\text{Ru}_2(\text{C}_6\text{H}_6\text{)}\text{Cl}_2]^3_6\text{PF}_6$</td>
<td>$d^3\text{-MeNO}_2$</td>
<td>5.90</td>
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<tr>
<td></td>
<td>$D_2^b$</td>
<td>6.35$^c$, 6.48$^c$</td>
<td></td>
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<tr>
<td></td>
<td>$d^6\text{-Me}_2\text{SO}$</td>
<td>5.95$^c$, 6.15$^c$, 6.50$^c$</td>
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<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}(\text{C}_5\text{H}_5\text{N})]^2_2\text{PF}_6$</td>
<td>$d^6\text{-Me}_2\text{CO}$</td>
<td>6.16</td>
<td>7.45, 8.00, 8.85(pyridine)</td>
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<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}(\text{Et}_2\text{S})]^2_2\text{PF}_6$</td>
<td>CDC1$_3$</td>
<td>5.95</td>
<td>3.00(q); 1.45(t) (Et$_2$S)</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}(\text{PPh}_3)_2]^2_2\text{PF}_6$</td>
<td>CDC1$_3$</td>
<td>5.52</td>
<td>7.30(PPh$_3$)</td>
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<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}(\text{PMePh}_2)_2]^2_2\text{PF}_6$</td>
<td>CDC1$_3$</td>
<td>5.75</td>
<td>7.20-7.60(Ph); 1.60(t) (Me)</td>
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<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}(\text{PMe}_2\text{Ph})_2]^2_2\text{PF}_6$</td>
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<td>7.50(Ph); 1.64(t); 2.12(t)(Me)</td>
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<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}(\text{AsPh}_3)_2]^2_2\text{PF}_6$</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 $[\text{Ru(C}_6\text{H}_6\text{)}\text{Cl}(d^6\text{-Me}_2\text{SO})]$
CI

/ Ru

\ /

CI CI

(II)

solvent

Ru

solvent

Cl

Cl

(III)

PF₆

solvent

PF₆

SCHEME
Some reactions of the $[\text{(η-C}_6\text{H}_5\text{)}\text{Ru(OH)}_3\text{Ru(η-C}_6\text{H}_5\text{)}]^{+}$ cation

D.R. Robertson and T.A. Stephenson
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

Summary:— Reaction of $[\text{(η-C}_6\text{H}_5\text{)}\text{Ru(OH)}_3\text{Ru(η-C}_6\text{H}_5\text{)}]B\text{PH}_4$ (I) with aqueous solutions of $\text{NH}_4\text{PF}_6$ gives $[\text{Ru(NH}_3\text{)}_3\text{C}_6\text{H}_6\text{]}(\text{PF}_6)_2$ (II) whereas refluxing (I) in ROH ($R = \text{Me,Et}$) produced the triple alkoxy-bridged cations $[\text{(η-C}_6\text{H}_5\text{)}\text{Ru(OR)}_3\text{Ru(η-C}_6\text{H}_5\text{)}]B\text{PH}_4$ (III); in contrast, no reaction between (I) and various tertiary phosphines was observed.

Recently, we reported that reaction of $[[\text{Ru(C}_6\text{H}_5\text{)}\text{Cl}_2]_2$ with an excess of either aqueous sodium hydroxide or carbonate gave the triple hydroxy-bridged cation $[(\text{C}_6\text{H}_6\text{)}\text{Ru(OH)}_3\text{Ru(C}_6\text{H}_5\text{)}] \text{Cl.3H}_2\text{O}$ [1,2]. However, although $[\text{Ru}_2(\text{C}_6\text{H}_5\text{)}_2(\text{OH})_3]B\text{PH}_4$ (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$_4$PF$_6$ gave, after several days, a yellow nitrogen-containing solid (ca 40% yield). On the basis of elemental analysis, conductivity measurements in nitromethane, i.r. and $^1\text{H}$ nmr spectral studies, this is best formulated as the trisamine dication $[\text{Ru(NH}_3\text{)}_3\text{C}_6\text{H}_6\text{]}(\text{PF}_6)_2$ (II). A related complex to (II), namely, $[\text{Ru(NH}_3\text{)}_2(\text{C}_6\text{H}_5\text{)}\text{Cl}]_3(\text{PF}_6)_4$ NH PF$_6$ has been obtained in small yield from the reaction of $[[\text{Ru(C}_6\text{H}_5\text{)}\text{Cl}_2]_2$ with hot water, followed by addition of NH$_4$PF$_6$ [3]. Presumably, (II) is formed from the reaction of $[\text{Ru}_2(\text{C}_6\text{H}_5\text{)}_2(\text{OH})_3]^{+}$ with ammonium ion which can act as a weak acid, protonating the OH$^-$ bridges to form the trisqua intermediate $[\text{Ru(H}_2\text{O})_3(\text{C}_6\text{H}_5\text{)}]^{2+}$, which could then undergo replacement of water by ammonia groups (cf the related reactions of $[\text{Ru}_2(\text{OH})_3(\text{PMe}_2\text{Ph})]^{+}$ with acids in various solvents (S) which gave $[\text{RuS}_3(\text{PMe}_2\text{Ph})_3]^{2+}$ 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 cm$^{-1}$ (νOH) but a strong band at 1050 cm$^{-1}$ indicates the presence of -OME groups (cf Ti(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 7.30δ, a $^6$C$_6$H$_6$ peak at 5.48δ and a singlet at 4.42δ (assigned to -OME protons) in the intensity ratio 20:12:9 respectively, (III) is formulated as the triple methoxide bridged complex [((C$_6$H$_6$)Ru(OMe)$_3$Ru(C$_6$H$_6$))BPh$_4^-$]. This formulation is supported by elemental analyses and detailed conductivity measurements in nitromethane indicating a 1:1 electrolyte. Similarly, [Ru$_2$(C$_6$H$_6$)$_2$2(OEt)$_3$]BPh$_4^-$ was obtained by refluxing (I) in ethanol. Again, the mechanism of formation presumably involves protonation of the OH$^-$ bridges by the weak acid ROH to form the [Ru(H$_2$O)$_3$(C$_6$H$_6$)$_2$]$^{2+}$ cation which could then react rapidly with OR$^-$ to give monomeric alkoxide compounds such as [Ru(H$_2$O)(C$_6$H$_6$)OR]$^+$ and [Ru(H$_2$O)(C$_6$H$_6$)(OR)$_2$]$.^+$ As discussed elsewhere for the analogous [Ru$_2$(C$_6$H$_6$)$_2$Cl$_3$]$^+$ [6] and [Ru$_2$Cl$_3$(PR$_3$)$_6$]$^+$ [7] cations, facile intermolecular coupling reactions of these solvated monomers would then give the [Ru$_2$(C$_6$H$_6$)$_2$(OR)$_3$]$^+$ cations.

These alkoxide cations could also be synthesised by reaction of [{Ru(C$_6$H$_6$)Cl$_2$}]$_2$ with freshly prepared NaOEt (R = Me, Et) in alcoholic solvents, and, unlike the corresponding [Ru$_2$(C$_6$H$_6$)$_2$(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 [Ru$_2$(C$_6$H$_6$)$_2$Cl$_3$]$^+$ cation undergoes facile bridge cleavage reactions with a variety of Lewis bases to give monomeric compounds of type [Ru(C$_6$H$_6$)$_2$Cl$_2$]PF$_6$ or [Ru(C$_6$H$_6$)$_2$Cl$_2$L] and/or [RuCl$_2$L$_4$] (L = 5$_5$N, 5$_6$S, (CH$_3$)$_2$SO, PR$_3$ etc) [1,6], [Ru$_2$(C$_6$H$_6$)$_2$(OH)$_3$]BPh$_4^-$ does not react with excess of tertiary phosphines in acetone, even under
reflux conditions for prolonged periods, \((\text{cf} \{\text{Pt(OH)}(\text{PR}_3)_2\}_2\text{BF}_4\}_2\) also does not react with more \text{PR}_3 [8]), the only product isolated being 

\[\text{[Ru}_2(\text{C}_2\text{H}_4)_2(\text{OH})_3\text{BF}_4(\text{CH}_3)_2\text{CO}}.\]

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


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 benzenesulphonate and diphenylphosphinate are reported.

Monocarboxylates of Molybdenum(II).—The compounds of stoichiometry Mo(O·COR)$_2$ (where R = Me, Et, Pr$_n$, Pr'$_t$, C$_6$H$_{11}$, C$_7$H$_{15}$, C$_3$F$_7$, C$_6$H$_5$, m-C$_6$H$_4$Me, C$_6$H$_4$OH, and C$_6$H$_4$F) have been prepared; the acetate$^1$ and benzoate$^2$ have been briefly described previously. Hexacarbonylmolybdenum was heated, either alone or in diethyleneglycol 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 perfluorobutylate 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 ebullioscopic methods. The salicylate is also dimeric in cold acetone (osmometric method). Conductivity measurements on solutions of the perfluorobutylate in acetone and nitrobenzene and of aryl carboxylates in acetone show that the solutions are non-conducting, e.g., for the perfluorobutylate in acetone $\Lambda_{0001}$ = 4.6 ohm$^{-1}$ cm.$^2$ mole$^{-1}$.

Secondly, a single-crystal X-ray-diffraction study of molybdenum(II) acetate$^3$ 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).

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

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3. Lawton and Mason, personal communication.
Molybdenum(II) 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 insolvability 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 perfluorobutyrate 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 perfluorobutyrate 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\(^\circ\), a brown material being obtained. The dark brown product from the reaction at ca. 250\(^\circ\) analyses sufficiently as molybdenum dichloride (ca. 98\% MoCl\(_4\)), 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

<table>
<thead>
<tr>
<th>Table 1. Infrared spectra (carboxylate bands) (in cm(^{-1})) of molybdenum(II) monocarboxylates.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Acetate</td>
</tr>
<tr>
<td>n-Butyrate</td>
</tr>
<tr>
<td>Isobutyrate</td>
</tr>
<tr>
<td>Cyclohexane carboxylate</td>
</tr>
<tr>
<td>Perfluorobutyrate</td>
</tr>
<tr>
<td>Benzoate*</td>
</tr>
<tr>
<td>Fluorobenzoate</td>
</tr>
<tr>
<td>Salicylate</td>
</tr>
<tr>
<td>m-Toluate</td>
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</tbody>
</table>

- All as yellow needles. † In mulls on Grubb-Parsons Spectromaster grating instrument; values to ±0.5 cm. † † In benzene, 1600 cm\(^{-1}\) (sharp).

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 Mo(O-COME)\(_2\)py, and have an infrared spectrum showing strong carboxylate bands at 1410 and 1500 cm\(^{-1}\), as well as characteristic pyridine bands.\(^8\) 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(\(\text{V}\)) 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(\(\text{V}\)).**—The interaction of hexacarbonylmolybdenum with dicarboxylic acids under strictly anhydrous conditions gives green powders of composition Mo(O-CO\(\text{CH}_3\))\(_n\)(CO-O), where \(n = 3\) or \(4\), while, in the presence of small amounts of water, green hydrates, Mo(O-CO\(\text{CH}_3\))\(_n\)(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 sulfoxide 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 3300m and ca. 1650w 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 Perkin-Elmer model 21 and 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 perfluorobutrate, an excess of acid, together with a small amount of its anhydride where available, and hexacarbonylmolybdenum (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, p-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 perfluorobutrate was recrystallised from hot toluene. For the octanoate, the diglyme was removed in vacuo and the residue thoroughly extracted with ether and dried.

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Analyses of molybdenum(II) carboxylates and related compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Found (%)</th>
<th>Required (%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Acetate</td>
<td>C(_2)H(_4)MoO(_4)</td>
<td>22-6</td>
<td>2-9</td>
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<tr>
<td>Propionate</td>
<td>C(_2)H(_5)MoO(_4)</td>
<td>29-6</td>
<td>4-1</td>
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<tr>
<td>(\alpha)-Butyrate</td>
<td>C(_2)H(_5)MoO(_4)</td>
<td>35-7</td>
<td>5-2</td>
</tr>
<tr>
<td>Isobutyrate</td>
<td>C(_3)H(_5)MoO(_4)</td>
<td>35-7</td>
<td>5-2</td>
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<tr>
<td>Cyclohexane carboxylate</td>
<td>C(_8)H(_14)MoO(_4)</td>
<td>48-1</td>
<td>6-5</td>
</tr>
<tr>
<td>Octanolate</td>
<td>C(_9)H(_16)MoO(_4)</td>
<td>48-1</td>
<td>6-5</td>
</tr>
<tr>
<td>Perfluorobutyrate</td>
<td>C(_8)F(_14)MoO(_4)</td>
<td>18-9</td>
<td>-</td>
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<tr>
<td>Fluorobenzoate</td>
<td>C(_8)H(_16)MoO(_4)</td>
<td>45-1</td>
<td>2-3</td>
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<tr>
<td>Salicylate</td>
<td>C(_8)H(_16)MoO(_4)</td>
<td>46-0</td>
<td>3-4</td>
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<tr>
<td>(\mu)-Toluolate</td>
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<td>3-9</td>
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<tr>
<td>Benzenesulphonate</td>
<td>C(_8)H(_16)MoO(_4)S(_2)</td>
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<tr>
<td>Diphenylphosphinate</td>
<td>C(_8)H(_16)MoO(_4)F(_2)</td>
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<td>4-0</td>
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<td>Succinate</td>
<td>C(_8)H(_16)MoO(_4)</td>
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<tr>
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<td>C(_8)H(_16)MoO(_4)</td>
<td>20-8</td>
<td>2-6</td>
</tr>
<tr>
<td>Adipate</td>
<td>C(_2)H(_12)MoO(_4)</td>
<td>29-0</td>
<td>3-7</td>
</tr>
<tr>
<td>Adipate hydrate</td>
<td>C(_2)H(_12)MoO(_4)</td>
<td>29-0</td>
<td>3-7</td>
</tr>
<tr>
<td>Glutarate hydrate</td>
<td>C(_2)H(_12)MoO(_4)</td>
<td>25-4</td>
<td>2-2</td>
</tr>
</tbody>
</table>

* Found: F, 10-3. C\(_{14}\)H\(_4\)F\(_2\)MoO\(_4\) 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 ebullioscopy 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 hexacarbonyl molybdenum. 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 diphenylphosphinate, 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 benzenesulphonlic 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 acetate, m. p. 130—140° (decomp.) (Found: C, 37-2; H, 3-8; N, 4-6; Mo, 34-3. C\(_8\)H\(_{11}\)NMoo4 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\(_{18}\)H\(_{18}\)NMoo4 requires C, 54-6; H, 3-6; N, 3-4; Mo, 23-0%) were prepared.

(2) A warmed solution of the acetate (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\(_9\)H\(_{10}\)NMoo4 requires C, 25-1; H, 2-1; N, 5-8; Mo, 40-2%).

We thank the Climax Molybdenum Company for gifts of hexacarbonyl molybdenum.

Inorganic Chemistry Research Laboratories, Imperial College of Science and Technology, London S.W.7. [Received, November 30th, 1963.]

Table 2.
Carboxylates of Palladium, Platinum and Ruthenium

By Sheila M. Morehouse, A. R. Powell, J. P. Heffer, T. A. Stephenson and G. Wilkinson

Inorganic Chemistry Research Laboratories, Imperial College of Science and Technology, London, S.W.7 and John and Co. Ltd., Wembley

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,¹ 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 are trimeric (Mechrolab Osmometer), whereas oscopically in benzene they are monomeric at 37° molecular weights with intermediates are obtained.

It seems reasonable to assume that the has its normal square planar co-ordination and trimer-monomer system is one involving ligand and chelate groups for the former, and other 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-(OCOCH₃)₂(C₅H₅N)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-CH₃ (Kuhn-Roth), 17·46; M, 950 ± 2 (acetone and chloroform 37°, Mechrolab Osmometer). Required for [Pt(OCOCH₃)₂]₃: O, 20·43; C-CH₃, 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 [Ru₂(OCOCH₃)₄]Cl and the cation, [Ru₂(OCOCH₃)₄OH]⁺; the former thus appears to have both Ru²⁺ and Ru³⁺ 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 carboxyl-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

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(III) 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°.

- The interaction of the carboxylates with various amines, triphenylphosphine and triphenylarsine gives complexes of the type trans-[Pd(OCOR)]_2 with unidentate carboxylate groups.

- Diacetatopalladium(II) was obtained by the reduction of an acetic acid solution of hexahydroxyplatinate(IV) with formic acid. It is trimeric, not isomorphous with [Pd(OCOR)]_2, and does not undergo cleavage reactions with donor ligands.

Studies on rhodium(II) carboxylates 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°, osmometric determinations show they are trimeric, whereas ebullioscopically in benzene (80°) 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° (osmometer) and remains trimeric when its molecular weight is measured ebullioscopically in both benzene (80°) and chlorobenzene (132°), while the two fluoro-carboxylates are both monomeric in ethyl acetate at 37°.

The absorption spectrum of the acetate in benzene or toluene solution (280–1000 μ) shows a single broad charge-transfer band (ε ~1000) at 394 μ, although a stronger band below 280 μ is indicated. Solid-state reflectance spectra of the acetate (750–1000 μ) showed weak peaks at 730, 820, and 910 μ whilst the propionate had peaks at 760, 823, and 920 μ; since these bands were not observed in solutions (0.1M) a value of ε <1 is indicated. The longest wavelength d–d band in PtCl_2 that is assigned to a singlet–triplet transition occurs at 565 μ, 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 μ 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 acetylcetone or with salicylaldehyde to give well-known compounds of the type PdL₂ and with bisacetylcetone-ethylenedi-imine and bissalicylaldehyde-ethylendieni-imine to produce the completely substituted Pd(enbisacac) and Pd(enbissal). 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>Δ(ω₂ - ω₁)</th>
<th>Δω₂ (adduct)</th>
<th>Δω₁ (carb)</th>
<th>Δω₁ (adduct)</th>
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<tbody>
<tr>
<td>[Pd(OCOPh)₂]</td>
<td>1567</td>
<td>1404</td>
<td>163</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>[Pd(OCOPh)₂(Ph₃P)₂]</td>
<td>1623</td>
<td>1319</td>
<td>304</td>
<td>56</td>
<td>83</td>
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<tr>
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<td>50</td>
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<td>—</td>
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<td>[Pd(OCCF₃)₂]</td>
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<td>1456</td>
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<td>—</td>
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<td>1427</td>
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<tr>
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<tr>
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<td>1372</td>
<td>—</td>
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<td>1359</td>
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<td>[Pd(OCCMe)₂(py)₂]</td>
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<td>1372</td>
<td>—</td>
<td>—</td>
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<td>—</td>
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<tr>
<td>[Pd(OCCMe)₂(bipy)]</td>
<td>1600</td>
<td>1427</td>
<td>173</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Among bands in the ω₁ region is the CH₃ rock (ca. 1350). Band obscured by absorption due to Et₃N, 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 diethylamine complex indicated a trans-configuration, and the other complexes are presumably also trans with the exception of the 2,2'-bipyridyl complex [Pd(OCCMe)₂bipy] 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 (C₂F₅ 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 carboxylates. 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 \(\rightarrow\) 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 sulphoxide yielded brown oils. Washing with diethyl ether produced the yellow-brown powder [Pd(OCOF_3)_2(Me_2SO)]_2 (the acetate complex could not be solidified). Dissolution of these oils in aqueous acidified tetraphenylarsenium chloride solution gave the salt of the anion [PdCl_3(Me_2SO)]^- (latter). The infrared spectra contained a strong band at 1148 cm\(^{-1}\) (former) and 1124 cm\(^{-1}\) (latter) assigned to the S=O stretching mode \((i.e.,\ S\text{-bonded})\). Palladium chloride shaken with aqueous dimethyl sulphoxide followed by acidified tetraphenylarsenium chloride produced the anion, further shaking of the original solution giving orange crystals of [PdCl_3(Me_2SO)]_2 (prepared by Cotton et al.\text{4}). Precipitation of the anion is inhibited in alkaline solution, suggesting that the hydroxy-compound is an intermediate. No precipitation occurred with tetaethyl(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_2(Et_2NH)_2]\text{3} was prepared from the acetate complex and potassium or tetramethyammonium bromide. The compound is a non-electrolyte in nitromethane, and precipitation is again inhibited in alkaline solution.

\text{Infrared Spectra.—} Previous work \text{5a} has shown that, since the acetate ion possesses low symmetry \((C_\infty)\), 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 et al.\text{5a} have shown that for a series of \(\alpha\)-amino-acid complexes, bonded through only one oxygen, the antisymmetric COO^- stretching frequency \((\omega_2)\) \textit{increased} and the symmetric COO^- stretching frequency \((\omega_1)\) \textit{decreased} as the M-O bond became stronger. Similar trends were also found in edta complexes,\text{5c} 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 et al.\text{5a} 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, \textit{e.g.}, for sodium acetate \text{6a} 164 cm\(^{-1}\).

However, infrared spectra (Table 1) show that, with one exception (the diethylamine acetate complex), in their adducts of the type [Pd(OCOR)_2(L)_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) \(\omega_2\) \textit{increases} and \(\omega_1\) \textit{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),\text{6a,6b} and in the cleavage of bridged carboxylic systems such as rhodium carbonyl acetate and phthalate with pyridine and triphenylphosphine.\text{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 carboxyl carboxylate adducts also contain several.

In the compound Pd(OCOMe)_2(Et_2NH)_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 tetrahydride, 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 ± 0·02 and 1·31 ± 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, the decrease in \(\omega_2\) 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 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solid state (bridging)</th>
<th>Dissolved state (CCl4 — monodentate)</th>
<th>Difference (\omega_2) (soln.) — (\omega_1) (soln.)</th>
<th>Difference (\omega_2) (soln.) — (\omega_1) (soln.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethyltin acetate</td>
<td>1572</td>
<td>1412</td>
<td>1655</td>
<td>1302</td>
</tr>
<tr>
<td>Tributyltin acetate</td>
<td>1572</td>
<td>1410</td>
<td>1645</td>
<td>1300</td>
</tr>
<tr>
<td>Tributyltin acetate</td>
<td>1570</td>
<td>1408</td>
<td>1630</td>
<td>1304</td>
</tr>
<tr>
<td>Trimethyltin laurate</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 \(\omega_2\).

**Diacacetoplatinum**(II).—Diacacetoplatinum(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 trimeric in acetone, or chloroform at 37° (osmometer), and trimeric ebullioscopically in benzene (80°) and chlorobenzene (132°). However, X-ray powder photographs of platinum and palladium acetates show that the compounds are not isomorphic, 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{OCH}_3]_6\text{(Et}_2\text{NH})_4\]. The absorption spectrum of the acetate in benzene solution (deep red) shows two charge-transfer bands at 319 mp (\(\varepsilon = 2000\)) and 542 mp (\(\varepsilon = 1940\)). However, the solid-state reflectance spectrum (350—1000 mp) is completely different, showing a weak band at 925 mp, a broad band 567 mp and indications of another charge-transfer band at 350 mp (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 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 diacacetoplatinum.

**Rhodium Carboxylates.**—The original Russian findings on rhodium(II) acetate hydrate have been confirmed as in recently published work.\(^9\) 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 265 mhos and is acidic (cf. copper acetate hydrate which also ionises in aqueous solution\textsuperscript{11}) suggesting the equilibrium

\[
[Rh_2(OOCCH_3)_4(H_2O)_2]^{2+} \rightleftharpoons [Rh_2(OOCCH_3)_4(OH)_2]^{2+} + 2H^+
\]

Proton magnetic resonance spectra showed the compounds to be diamagnetic; this indicates that despite the formal bivalence of the rhodium, the d\textsuperscript{7} configuration is absent.

Infrared spectra showed strong bands corresponding to \(\nu_2\) and \(\nu_1\): rhodium formate hydrate 1587 (\(\nu_2\)), 1430 (\(\nu_1\)), \(\Delta\nu 157 \text{ cm}^{-1}\); rhodium propionate hydrate 1570 (\(\nu_2\)), 1420 (\(\nu_1\)), \(\Delta\nu 150 \text{ cm}^{-1}\).

**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 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>14-8</td>
<td>14-4</td>
</tr>
<tr>
<td>Pd(C\textsubscript{2}F\textsubscript{4}CO\textsubscript{2})\textsubscript{2}</td>
<td>16-9</td>
<td>18-6</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py\textsubscript{2}</td>
<td>43-3</td>
<td>48-8</td>
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<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py\textsubscript{2}</td>
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<td>58-8</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})quin</td>
<td>54-2</td>
<td>54-8</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}pyr\textsubscript{2}</td>
<td>39-2</td>
<td>38-9</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}NET\textsubscript{2} \textsubscript{2}</td>
<td>6-6</td>
<td>6-6</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py</td>
<td>7-3</td>
<td>7-3</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py</td>
<td>8-8</td>
<td>8-8</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py</td>
<td>13-3</td>
<td>13-3</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py</td>
<td>19-0</td>
<td>19-0</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py</td>
<td>22-9</td>
<td>22-9</td>
</tr>
<tr>
<td>Pd(MeCO\textsubscript{2})\textsubscript{2}py</td>
<td>26-0</td>
<td>26-0</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 Pd(NO₃)₂·OAc. 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 palladium 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 PdI₆³⁺, but is insoluble in aqueous solutions of sodium chloride, nitrite, and acetate. It is soluble with decomposition in aqueous hydrochloric acid to give PdCl₄²⁻.

X-Ray data are given in Table 4.

| Table 4 |

| X-Ray values for palladium and platinum acetates |

<table>
<thead>
<tr>
<th>d (spacing)</th>
<th>Intensity</th>
<th>d (spacing)</th>
<th>Intensity</th>
<th>d (spacing)</th>
<th>Intensity</th>
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<tr>
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<td>s</td>
<td>3.261</td>
<td>0.0040</td>
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<tr>
<td>7.099</td>
<td>0.018943</td>
<td>vs</td>
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<td>0.1131</td>
<td>w</td>
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<tr>
<td>6.521</td>
<td>0.023516</td>
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<td>2.880</td>
<td>0.1198</td>
<td>w</td>
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<tr>
<td>5.864</td>
<td>0.029061</td>
<td>s</td>
<td>2.826</td>
<td>0.1252</td>
<td>vw</td>
</tr>
<tr>
<td>5.546</td>
<td>0.032512</td>
<td>m</td>
<td>2.756</td>
<td>0.1317</td>
<td>m</td>
</tr>
<tr>
<td>4.902</td>
<td>0.040615</td>
<td>m</td>
<td>2.615</td>
<td>0.1482</td>
<td>m</td>
</tr>
<tr>
<td>4.794</td>
<td>0.043511</td>
<td>w</td>
<td>2.574</td>
<td>0.1509</td>
<td>m</td>
</tr>
<tr>
<td>4.503</td>
<td>0.046317</td>
<td>w</td>
<td>2.482</td>
<td>0.1650</td>
<td>m</td>
</tr>
<tr>
<td>4.318</td>
<td>0.055859</td>
<td>w</td>
<td>2.389</td>
<td>0.1732</td>
<td>m</td>
</tr>
<tr>
<td>3.715</td>
<td>0.0725</td>
<td>m</td>
<td>2.316</td>
<td>0.1884</td>
<td>s</td>
</tr>
<tr>
<td>3.598</td>
<td>0.0772</td>
<td>s</td>
<td>2.206</td>
<td>0.2035</td>
<td>vw</td>
</tr>
</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 diacetato-palladium (0·3 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[(pentfluoroacetoxy) propionate]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].

**Diacetatobispyridinepalladium(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'-bipyridylpalladium(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.

Dibenzoato(bispyridine)palladium(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.

Diacetatobisisoquinolinepalladium(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 dipeptide 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.

Diacetobis(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.

Diacetobis(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 lemon-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°.

Ditrifluoroacetatobis(triphenylarsine)palladium(II).—The ditrifluoroacetate-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.

Dipentafluoropropionatobis(triphenylarsine)palladium(II).—Prepared in the same way as the corresponding trifluoroacetate-complex. It formed bright yellow crystals, m. p. 204–205°.

Ditrifluoroacetato(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 bis(pentafluoropropionato)-complex gave a similar complex, m. p. 180° (decomp.).

Ditrifluoroacetatobis(dimethyl sulfoxide)palladium(II).—Dimethyl sulfoxide was added drop-wise 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.).

_Tetraphenylarsonium Trichloro(dimethyl sulphoxide)palladate(II)._—Diacetatopalladium(II) in
benzene was shaken for several hours with excess of dimethyl sulphoxide. 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 tetraphenyl-
arsonium chloride. The lemon-yellow crystalline salt, m. p. 190° (decomp.) was washed with
water, dried in a desiccator, and finally rewashed with ether (Found: C, 46-0; H, 4-0; Cl, 16-1;
O, 2-5; S, 4-6. C₈H₂₆Cl₂O₉PdS requires C, 46-3; H, 3-3; Cl, 15-8; O, 2-4; S, 4-7%). The salt
is a 1:1 electrolyte in nitromethane.

Infrared spectrum: 1471w, 1433s, 1389w, 1333vw, 1309vw, 1176vw, 1124s (S, O, S-bonded),
1078m, 1020m, 995m, 965w, 930(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 sulphoxide and water for several minutes, filtering the mixture, and then adding a
concentrated aqueous solution of acidified tetraphenylarsonium chloride. When the original
solution was shaken for ca. 30 min., orange crystals of [PdCl₂(OSMe₂)₂] were obtained; they
were washed with water and ether and dried; they had m. p. 190° (decomp.) (Found: Cl, 21-3;
Calc. for C₈H₂₆Cl₂O₉PdS: Cl, 21-2%). The infrared spectrum is identical with that previously
reported.¹²

_Dibromobis(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
rewashed with ether; it had m. p. 180° (decomp.) (Found: C, 23-9; H, 5-2; Br, 38-5; N, 6-7.
Calc. for C₁₂H₂₂Br₂N₂Pd: C, 23-2; H, 5-3; Br, 38-7; N, 6-8%). The compound is a non-
electrolyte in warm nitromethane.

_Diacetatoplatinum._—Sodium hexahydroxyplatinate, Na₃Pt(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 solution
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 ultra-
marine 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=CH₂ (Kuhn Roth), 17-5%;
M (osmometer) at 37° acetone and chloroform, 950 ± 2; (ebullioscopically) in benzene, 937;
chlorobenzene, 888. C₁₂H₁₂O₂Pt requires O, 20-4; Pt, 62-3; C=CH₂, 17-3%; M, 940 (trimmer)).

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°C.

The trifluoroacetato rhodium(II) complex was prepared by the action of trifluoroacetic acid on the hydroxyl oxide followed by extraction of the reaction mixture with dichloromethane. The blue-green product was recrystallised from benzene.

**Diacetopipridierhodium(II).** Pyridine was added dropwise to a cold, methanolic solution of the trifluoroacetato-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°C (decomp.) (Found: C, 36.4; H, 3.7; N, 4.8; O, 21.6. Calc. for C_{11}H_{11}NO_{4}Rh: C, 36.0; H, 3.7; N, 4.7; O, 21.3%).

**Dipropionatepyridinerhodium(II) and diformato(pyridinerhodium(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%). C_{11}H_{13}NO_{4}Rh 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 C_{2}H_{2}NO_{4}Rh: C, 31.0; H, 2.6; N, 5.2%) m.p. 145°C (decomp.). This compound was first prepared by Chernyaev et al. who assigned it the composition [PyHRh(HOCO)].

**Diacetotriphenylphosphine 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. C_{24}H_{24}O_{4}PRh requires C, 54.6; H, 4.6%).

**Dipropionato(triphenylphosphine)rhodium(II).** This complex was similarly prepared and was recrystallised from cyclohexane (Found: C, 56.4; H, 4.9; O, 12.3%; M (ebullioscopic in benzene), 992. C_{24}H_{24}O_{4}PRh requires C, 56.4; H, 4.9; O, 12.5%; M, 1023 [dimer].

**Diformatotriphenylphosphine rhodium(II).** This complex was similarly prepared from the diformato-complex; it was recrystallised from chloroform and petroleum giving orange crystals, m.p. 165°C (decomp.) (Found: C, 52.8; H, 4.6. C_{24}H_{17}O_{4}PRh requires C, 52.6; H, 3.8%).

**Dipropionatopiperidinerhodium(II).** This was prepared by the dropwise addition of piperidine to a cold, methanolic solution of dipropionatorhodium(II). It was recrystallised from petroleum, forming dark red crystals, m.p. 115°C (Found: C, 40.0; H, 6.1; N, 4.3. C_{11}H_{17}NO_{4}Rh requires C, 39.5; H, 6.3; N, 4.2%).

**Dipropionatosquinolinierhodium(II).** Isoquinoline in diethyl ether was added to a cold, methanolic solution of dipropionatorhodium(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. C_{11}H_{17}NO_{4}Rh requires C, 47.6; H, 4.5; N, 3.7; O, 16.9%).

**Di(trifluoroacetato)pyridierhodium(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. C_{8}H_{5}F_{4}NO_{4}Rh requires C, 26.4; H, 1.2%).

We thank the Hercules Powder Company for financial assistance (T. A. S., S. M. M.).

**Inorganic Chemistry Research Laboratories, Imperial College of Science and Technology, London S.W.7.**

**Johnson, Matthey and Co. Ltd., Wembley.**

[Received, November 18th, 1964.]

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1. Preliminary Note: *Chem. and Ind.*, 1964, 544.


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 [Ru₂(OCOR)₄Cl], (R = Me, Et, "Pr), where the ruthenium atoms have formal oxidation states of II and III. 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 the binuclear complex [Ru₂(OCOMe)₃OH(H₂O)]₂, which on hydrolysis yielded [Ru₂(OCOMe)₇(OH)₄(H₂O)₂] and [Ru₂(OCOMe)(OH)₆(H₂O)₂]. Other products from the same reaction were [Ru(OCOMe)₂OH]₂ and [Ru₂(OCOMe)₆OH]; with formic acid, the basic trinuclear complex, [Ru₃(OCOH)₉(OH)₂]HCO₂·5H₂O, 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 obtained [Ru₃(OCOMe)₆(OH)₂]OCOMe·7H₂O analogous to the trinuclear basic complexes of chromium and iron (III). The chlorides of the latter have recently been reformulated [M₃(OCOMe)₆O(H₂O)₃]Cl·xH₂O,(⁴) (M = Fe, Cr); hence the ruthenium complex is probably

[Ru₃(OCOMe)₆O(H₂O)₃]OCOMe·5H₂O.

Interaction of this complex with pyridine followed by the addition of chloroplatinic acid in dilute hydrochloric acid gave [Ru₃(OCOMe)₆(py)₃Cl][PtCl₆]·7H₂O(?).

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 Ru₂(OCOR)₄Cl. 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). 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: Chemy Ind. 544 (1964).
(2) A. W. 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 \([\text{Ru}_2(\text{OCOR})_4(\text{OH})\text{H}_2\text{O}][\text{BPh}_4]\), \((\text{R} = \text{Me}, \text{Et})\). 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 \([\text{Ru}_2(\text{OCOR})_4]^+\), 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 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\text{K})</th>
<th>(10^9\chi_M) (corr) (cgs)</th>
<th>(\mu_{\text{eff}}) B.M.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}_2(\text{OCOMe})_4]\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})_4]\text{Cl})</td>
<td>NMR (MeOH)</td>
<td>294</td>
<td>3596</td>
<td>2·92</td>
</tr>
<tr>
<td>([\text{Ru}_2(\text{OCOPr})_4]\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})_4(\text{OH})\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})_4(\text{OH})\text{H}_2\text{O}][\text{BPh}_4])</td>
<td>Gouy (PhNO),</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 \([\text{Ru}_2(\text{OCOR})_4]\text{OCl}\), this could accommodate the magnetic moment (i.e. 3 unpaired electrons from oxidation states III and IV, \(d^4\), giving \(\sim 4\) 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 \(\text{Ru}=\text{O}\) or \(\text{Ru}=\text{O}\) 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. Cu(HCO$_2$)$_2$·4H$_2$O[6]). 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)$_4$Cl]**

<table>
<thead>
<tr>
<th>T°K</th>
<th>$10^6 \chi_M$ (corr), (cgs)</th>
<th>$1 / \chi_M$ (corr)</th>
<th>$\mu_{\text{eff}}$ B.M.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3446</td>
<td>291.2</td>
<td>2.88</td>
</tr>
<tr>
<td>273</td>
<td>3752</td>
<td>266.8</td>
<td>2.87</td>
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<tr>
<td>255</td>
<td>4000</td>
<td>250.0</td>
<td>2.87</td>
</tr>
<tr>
<td>228</td>
<td>4416</td>
<td>227.1</td>
<td>2.85</td>
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<tr>
<td>208</td>
<td>4824</td>
<td>207.7</td>
<td>2.84</td>
</tr>
<tr>
<td>191.5</td>
<td>5224</td>
<td>191.7</td>
<td>2.84</td>
</tr>
<tr>
<td>166.5</td>
<td>5854</td>
<td>171.0</td>
<td>2.80</td>
</tr>
<tr>
<td>143.5</td>
<td>6633</td>
<td>150.9</td>
<td>2.77</td>
</tr>
<tr>
<td>105.7</td>
<td>8578</td>
<td>116.8</td>
<td>2.71</td>
</tr>
</tbody>
</table>

* Per Ru atom.

In the solid state, the structure of Ru$_2$(OCOR)$_4$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 Ru$_2$(OCOR)$_4$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 –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 –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 –CH$_3$ deformation (1350 cm$^{-1}$) and OCO deformation ($\sim 690$ cm$^{-1}$) frequencies are readily assigned.

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 (n-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 [Ru(OCOR)₂py₂], and less soluble yellow solids [Ru(OCOR)₂py₄] (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 ω₂ – ω₁ suggests symmetrical co-ordination. Similar complexes of iron (II) have been prepared by the action of pyridine on anhydrous ferrous acetate. The tetrakis(pyridine) complex is converted to the bispyridine 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 [Ru(OCOME)₂H₂O]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 [Ru₂(OCOME)₄₋₅(H₂O)]₁₋₂. 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 (ω₂) and 1418 (ω₁) 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 reflushed 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 (ω₂) and 1389, 1309 cm⁻¹ (ω₁), indicative of both symmetrical and unsymmetrical acetate groupings. The analysis corresponds to [Ru₂(OCOMe)₄] (cf. the mixed ferrous-ferric complex [Fe₂(OCOMe)₅]) 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 anyride present failed.

In order to eliminate complications due to chloride, hydrous ruthenium oxide was reflushed 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)₁₅]. Similarly, with propionic acid–propionic anhydride, a material very close in analysis to [Ru₂(OEt₄)₃(H₂O)] 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)₉OH·(H₂O)] (practically the only combination of ruthenium, acetate and water which MOND did not find). 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, Miilheim. M.p.s were determined with a Koler hot-stage microscope and are uncorrected. Infra-red spectra were taken in Nujel 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,[10] 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 ohm 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 “RuCl₃·3H₂O” (1 g) was gently reflushed 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 tetra-acetatodiruthenium (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. C₆H₁₃ClO₄Ru₂ requires C, 20.2; H, 2.5; Cl, 7.50; O, 26.9 per cent; M (for 1:1 electrolyte), 238]; λ, 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)₂H₂O]₄ [Found: C, 19.9; H, 4.1; O, 33.3; M, (methanol)] 460. C₆H₁₂O₄Ru requires C, 20.2; H, 3.4; O, 33.6 per cent; M, (dimer), 476]. It also contained ~3 per cent chlorine and carbonyl-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. [Ru₄(OCOMe)₄(H₂O)$_{1.6}$] requires C, 21.8; H, 3.3; O, 33.9 per cent].

Refluxing the green solution in oxygen for several days still gave a product with analyses close to [Ru(OCOMe)₂H₂O]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, 33.3 per cent]. Finally, (~6 days) an insoluble greenish-black powder was deposited [Found: C, 24.4; H, 3.3. C₁₆H₁₉O₁₆Ru₂ 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 carboxy-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 [Ru₄(OCOMe)$_{4.8}$(H₂O)$_{1.4}$].

**Tetrapropionatodiruthenium (II, III) chloride**

As for the acetate, using the trichloride (1 g), propionic 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. C₁₆H₁₉O₄Cl₂Ru₂ requires C, 27.1; H, 3.8; Cl, 6.7; O, 24.1 per cent; M (for 1:1 electrolyte), 265]; λ (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 —C₆H₄O₆ 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 carboxy-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(OEOEt)$_{4.8}$(H₂O)$_{1.4}$] requires C, 29.0; H, 4.5; O, 30.0 per cent].

**Tetra-n-butytratodiruthenium (II, III) chloride**

As for above, using the trichloride (1 g), n-butyric acid (35 ml) and n-butyric anhydride (10 ml). No attempt was made to remove impurities after ~1 hr since the complex is soluble in hot n-butyric 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. C₁₆H₁₉O₄Cl₂Ru₂ requires C, 32.8; H, 4.9; Cl, 6.0; O, 21.8 per cent; M, (for 1:1 electrolyte), 294]; λ (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. C₁₉H₁₉BO₄Ru 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. C₁₉H₁₉BO₄Ru 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(OCOR)](OH)₅(BPh₄) 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 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-tetrakis(pyridineruthenium (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. C₁₄H₁₂N₄O₄Ru 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; C₁₄H₁₂N₄O₄Ru requires N, 9-9; 11-3 per cent]. The acetate 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 dicarboxylatobis(pyridineruthenium (II) complexes. For the acetate, m.p. > 240° (decomp.) [Found: 6-9; O, 16-5; M (methanol), 388. C₁₄H₁₂N₄O₄Ru requires N, 7-4; O, 16-9 per cent, M, 378]. For the propionate, m.p. > 260° (decomp.), [Found: N, 7-3; C₁₄H₁₂N₄O₄Ru 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)₂py₄ is probably due to the fact that the solution turned green during the measurements.

Infra-red spectra (ω₁, ω₂ cm⁻¹): [Ru(OCOMe)₂py₄], 1585, 1319; [Ru(OCOEt)₂py₄], 1587, 1348; [Ru(OCOMe)₂py₄], 1577, 1538, 1410; [Ru(OCOEt)₂py₄], 1575, 1538, 1408.

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 trichloride.
Acetato complexes of palladium(II)

(Received 10 March 1967)

We have reported\(^1\) the preparation of palladium(II) carboxylates and a number of monomeric adducts of the type [Pd(OCOR\(_2\)]\(_2\)L\(_2\)] (R = Me, Et, CF\(_3\); L = Ph\(_3\)P, py), the latter being obtained by the action of the ligand L in large excess (>1:4 mole ratio) on [Pd(OCOR\(_2\)]\(_3\)]. By using ratios of only 1:2 we have now prepared complexes of the type [Pd(OCOCH\(_3\)]\(_2\)L\(_2\)] (L = Ph2As, Ph3P). These dimeric complexes may be assigned a structure in which there are both bridged and unidentate carboxylate groups. Corresponding halogeno complexes of the type [PdCl\(_2\)L\(_2\)] of amines, phosphines or sulphides are well known\(^2\) and are usually isolated in the trans form although the thio-bridged complex [Pd(PPr\(_3\)]\(_2\)(SeEt)\(_2\)]Cl\(_2\) can be isolated in the cis form. The only other carboxylate complexes of similar structure are the acetone adducts\(^3\) of palladium trifluoroacetate and perfluoropropionate, [Pd(OCOF\(_2\)]\(_2\)Me\(_2\)CO\(_2\)]. The new complexes are insufficiently soluble in benzene to allow the dipole moments to be determined, so that we cannot determine whether the cis or trans forms are the most stable. The i.r. data in Table 1 confirm the presence of both bridging and unidentate groups; the position of the carboxylate bands has been discussed previously\(^4\) in some detail.

![Table 1](image)

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 [Pd(OCOCH\(_3\)]\(_2\)PPh\(_3\)] reacts readily with additional triphenylphosphine, the bridge cleaving to give trans-[Pd(OCOCH\(_3\)]\(_2\)(PPh\(_3\)]\(_2\)]; similarly the triphenyl arsine complex can be cleaved with pyridine to give Pd(OCOCH\(_3\)]\(_2\)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)-µ-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\(^\circ\)); yield essentially quantitative,
m.p., 140–141°. (Found: C, 54·0; H, 4·5; O, 13·3%; M(CHCl₃), 914. C₂₂H₂₁O₄Pd 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 triphenylarsine 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. C₂₂H₂₁AsO₄Pd 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.

Acknowledgement—We thank Johnson, Matthey Ltd. for the loan of palladium acetate.

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A BASIC ACETATO COMPLEX OF TUNGSTEN

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(Received 11 April 1969)

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 [WCl(OC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2})(OC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}H)] (2) and [WB\textsubscript{2}(OH)(OC\textsubscript{6}H\textsubscript{4}CO\textsubscript{2}H)(Et\textsubscript{2}O)] (3) have been reported; benzoic, palmitic acid etc give 4:1 adducts with WCl\textsubscript{4} (4) and 6:1 adducts with WCl\textsubscript{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 Mo(CO)\textsubscript{6} which rapidly deposits yellow crystals of [Mo(OCCCH\textsubscript{3})\textsubscript{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°(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 W = O groups respectively (7a).
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 \([\text{W}_3\text{(OCOC}_3\text{)}_8\text{O(OH)}\text{H}_2\text{O}]\)
requiring C, 17.9; H, 2.5; W, 51.2; O, 28.4% Mwt, 1075; for II and III
\([\text{W}_3\text{(OCOC}_3\text{)}_8\text{O(OH)}\text{C}_3\text{OH}]\) requiring C, 18.7; H, 2.6; W, 50.6; O, 28.1%
Mwt 1088. The empirical formulae \([\text{W}(\text{OCOC}_3\text{)}_2]\) requiring C, 15.9; H, 2.0;
W, 61.0; O, 21.1% or \([\text{W}(\text{OCOC}_3\text{)}_3]\) 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%; \([\text{W}_3\text{(OCOC}_3\text{)}_8\text{O(OH)}\text{C}_3\text{OH}]\) requires 11.1%.

c) Conductivity measurements show the freshly prepared complex to be a
non-electrolyte in ethanol, slightly ionized in methanol \(\Lambda_{0.001M} = 22 \text{ cm}^2\)
ohm⁻¹mole⁻¹) and a 1:1 electrolyte in water \(\Lambda_{0.001M} = 123 \text{ cm}^2\) ohm⁻¹mole⁻¹).
Treatment of a concentrated aqueous solution with AsPh₄ClHCl 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 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 ± 0.2.

e) The compound is diamagnetic suggesting either direct metal-metal interaction as in K₃[W₂Cl₉] (7b) or possibly the presence of a trigonally coordinated oxide ion as in [Cr₃(OOCCH₃)₆O(H₂O)₃]Cl₅H₂O (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 -OH stretching vibration. The latter could conceivably arise from either hydroxy and/or solvent groups in the complex.

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TABLE 1

(1) Retention of the bands associated with symmetrically coordinated acetato groups;

(2) Oxidation state determinations (oxidation to 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 ± 0.2.

(3) The compound is diamagnetic suggesting either direct metal-metal interaction as in K₃[W₂Cl₉] (7b) or possibly the presence of a trigonally coordinated oxide ion as in [Cr₃(OOCCH₃)₆O(H₂O)₃]Cl₅H₂O (9).

(4) 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 -OH stretching vibration. The latter could conceivably arise from either hydroxy and/or solvent groups in the complex.

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(5) 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 \([\text{Cr}_3(\text{OCOCH}_3)_6\text{O(H}_2\text{O})_3]^+\) cation with pyridine etc giving \([\text{Cr}_3(\text{OCOCH}_3)_6(\text{py})_3]^+\) (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.

![Possible Structural Types for Basic Tungsten Acetate](image)

**FIG. 1**

Possible structural types for basic tungsten acetate \((S = \text{H}_2\text{O,CH}_3\text{OH})\)

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.

**Acknowledgement**

We thank Professor G. Wilkinson for helpful discussions, Ethyl Corporation and Climax Molybdenum Company for gifts of tungsten hexacarbonyl
and the School of Chemistry, University of Newcastle upon Tyne for a
vacation studentship (DW).

References

1. For detailed references see C. OLDHAM in Progress in Inorganic Chemistry
   Volume 10, p.223, Interscience, New York (1968); T. A. STEPHENSON,


   (1964) and references therein.

7. See R. V. PARISH in Advances in Inorganic and Radiochemistry Volume 9,
   (a) p.318; (b) p.331; Academic Press, New York (1966).


10. For references and discussion see T. A. STEPHENSON, S. M. MOREHOUSE,
    29, 2122 (1967).
Five- and Six-co-ordinate Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II)

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JOURNAL OF THE CHEMICAL SOCIETY

SECTION A
Inorganic, Physical, and Theoretical Chemistry

1970
Five- and Six-co-ordinate Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato) palladium(II)

By T. A. Stephenson*† and B. D. Faithful, Department of Inorganic Chemistry, University of Newcastle upon Tyne, NE1 7RU

The interaction of Pd(S₂PPh₂)₂ with tertiary phosphines to give both 1:1 (for PPh₃, PEtPh₂, PMe₂Ph, and PEt₃) and 1:2 (for PMe₂Ph and PEt₃) 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' polydentate ligands such as P(o-C₆H₄PPh₂)₃ 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(diarsine)₂I₂], 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 ion on complexes such as [Pd(phen)]₂⁺ and PdX₄²⁻ (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.⁶ The previously unknown compound Pd(S₂PPh₂)₂ is readily obtained as diamagnetic red crystals by treatment of a benzene solution of palladium(II) acetate with a slight excess of diphenylphosphinodithioic acid [Ph₃P(S)SH]. The complex is insufficiently soluble for molecular-weight measurements but mass spectral data at 180° show the highest peak to be at m/e 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 Ph₃PS₂⁻ group are present. Comparison with the i.r. spectrum of Cs(S₂PPh₂)₄.8H₂O (Figure 1b) and earlier work,⁸ indicating C₃e symmetry for the ligand suggests that

![Figure 1](https://example.com/figure1)

\[ \text{Figure 1. Mull i.r. spectrum (800—450 cm}^{-1}\text{) of} \]
\[ (a) \text{Pd(S}_2\text{PPh}_2)_2 \text{and (b) Cs(S}_2\text{PPh}_2)_4\cdot8\text{H}_2\text{O} \]

the asymmetric (ν₁) and symmetric (ν₂) Ph₃PS₂⁻ stretching frequencies can be assigned at 600 and 485 cm⁻¹ respectively with Δ(= ν₁ — ν₂), 115 cm⁻¹. For the caesium salt, the

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¹ For detailed references see Annual Reports, 1967, 64, 310; 1968, 65, 336; E. L. Muetterties and K. A. Schunn, Quart. Rev., 1966, 20, 245.


assignments are $v_1$, 654 cm.$^{-1}$; $v_2$, 488 cm.$^{-1}$; $\Delta$, 166 cm.$^{-1}$. As for co-ordination of other ligands of $C_5v$ symmetry (e.g. acetate *) the smaller value of $\Delta$ compared to the ionic salt supports symmetrically co-ordinated $\text{PPh}_2\text{PS}_2^-$ groups.

The i.r. spectrum of (B) as a mull is complex (Figure 2a). However, by comparison with $\text{trans-PdCl}_2[\text{PPh}_3]$ (Figure 2b) and $[\text{Pd(S}_2\text{PPh}_2)_2[\text{PET}_3]]$ (Figure 5a), $v_1$ and $v_2$ can be assigned at 642 and 538 cm.$^{-1}$ respectively with $\Delta$, 102 cm.$^{-1}$. Although the region is not shown in the figures, there are clearly no additional bands which can be assigned to $v_4$ below 450 cm.$^{-1}$. The small value of $\Delta$ and the fact that both $v_1$ and $v_2$ shift in the same direction as compared with (A), is strong support for simple addition of $\text{PPh}_3$ to form a five-co-ordinate adduct, rather than cleavage of a palladium-sulphur bond to form a four-co-ordinate complex such as (I). If the latter occurred, an increase in $v_1$ and a decrease in $v_2$ with an overall increase in $\Delta$ should be observed. This is illustrated in the analogous carboxylate complex $\text{Pd(OCOCF}_3)_2$ with $v_1$, 1572; $v_2$, 1456; $\Delta$, 116 cm.$^{-1}$; reaction with excess of triphenylarsine produces

\[\text{S—P(:S)Ph}_2\text{S—P(:S)Ph}_2\]

cleavage of the Pd–O bonds to give trans-[Pd(OCOCF₃)_2]\(\text{AsPh}_3\)] with unidentate carboxylate co-ordination (\(v_\text{L} = 1684\); \(v_\text{p} = 1393\); \(\Delta = 291\) cm\(^{-1}\)).

Examination of the i.r. spectrum of (B) dissolved in benzene, dichloromethane (600—450 cm\(^{-1}\)), and particularly carbon disulphide where solvent absorptions do not interfere (600—450 cm\(^{-1}\)) (Figure 3a) shows that the structure of the complex has changed. In particular, the three bands at 498, 486, and 478 cm\(^{-1}\) are replaced by a broad singlet at 490 cm\(^{-1}\) whilst the region 750—660 cm\(^{-1}\) is simplified. The relative intensities of the two bands at 524 and 538 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 mull 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 15 min. without Nujol and then a Nujol mull 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 CS₂) and the relative intensities of the triplet at 605, 612, and 621 cm\(^{-1}\). Furthermore, if this mull is left in the i.r. machine and the spectrum is run in the 750—660 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 490 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

**Figure 4** Mull i.r. spectrum of (C) (600—660 cm\(^{-1}\)): (i) immediately, (ii) 1 min., (iii) 2–5 min., (iv) 4–5 min., (v) 6–5 min., (vi) 9–5 min., etc.

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)₃-Cl] and other \(\pi\)-bonded \(\pi\) 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—1000 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.

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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-co-ordinate 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(S\(_2\)PPh\(_2\))\(_2\).**—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(S\(_2\)PPh\(_2\))\(_2\)(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 57° give a value of 760:725 required for monomer. Mass-spectral studies show only triethylphosphine and its fragmentation pattern. The mul 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 mud at 402, 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 (1500—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(S\(_2\)PPh\(_2\))\(_2\)(PET\(_3\))]\. A Nujol mull (Figure 6a) shows \(v_1\), 650 cm.\(^{-1}\); \(v_2\), 600 cm.\(^{-1}\); \(\Delta\), 90 cm.\(^{-1}\). For reasons discussed earlier, this is strong support for the formation of a six-co-ordinate 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 PS\(_2\) 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(S\(_2\)PPh\(_2\))\(_2\)] and triethylphosphine.

Although the 1:2 complex is quite air-stable, in solution (PhH, CS\(_2\)) 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 triethylphosphine. 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 dimethylidiphenylphosphine 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(S2PPh2)2(PMePh2)]; the Mull i.r. spectrum (Figure 7a) is analogous to that of the triethylphosphine complex with $v_1$, 650 cm.$^{-1}$; $v_2$, 559 cm.$^{-1}$, $\Delta$, 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.$^{-1}$. Removal of the solvent gives the 1 : 1 complex with $v_1$, 645 cm.$^{-1}$; $v_2$, 540 cm.$^{-1}$; $\Delta$, 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(S2PPPh2)2(PEtPh2)]. From a Nujol mull, the following assignments can be made, $v_1$, 646 cm.$^{-1}$; $v_2$, 539 cm.$^{-1}$; $\Delta$, 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 triphenyl arsine, pyridine, and azo-bipyridyl have been completely unsuccessful. Also, treatment of either trans-[PdCl2(AsPh3)] or trans-[Pd(OAc)2(AsPh3)] with a slight excess of diphenylphosphinodithioic acid has produced only Pd(S2PPh2). Addition of an excess of triphenylphosphine 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 triphenylphosphine.

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 dithiobenzoates, but no details are given.

In a recent paper by Fackler and his co-workers, it is reported that both Pd(S2PPh2) and Pd(S2POEt)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(S2CO)(PMePh2)] and [Pd(S2POEt)(PMePh2)] respectively. Such cleavage reactions are, of course, impossible in Pd(S2PPh2) 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.
**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 [Pd(S₂PPh₂)₂(PR₃)], 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 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 [Pd(S₂PPh₂)₂(PR₃)]](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 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. The large size of the ligands and the ability of both the tertiary phosphine and the diphenylphosphinidithioato 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.

* By approximate, it is meant structures resembling idealised TBP more than SP (or vice versa).
† Using framework molecular models, 1 inch = 1 Å with Pd–P: 2.3–2.3 Å (2.34 (avg) Å in [PdL₂(FMe₂PPh)₂]; Pd–S: 2.2–2.4 Å (calculated from covalent radii, 2.14 Å; ca. 2.4 Å in [Ru(S₂CNEt₂)₂]⁺; P–C: 1.80 Å and remainder from X-ray analysis of [Ni(S₂PPh₂)₂].

C: Possible 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 [Pd(S₂PPh₂)₂(PPh₃)] 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 phosphine 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 PR₃ molecule (PEt₃ or PMe₃Ph) to form either cis- [(V) (VI)] or trans- (VII) complexes, but it is impossible to predict from these models which will be sterically more stable. With PEt₃PMe₃ and PPh₃ 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 [Pt(S₂P(OEt)₂)₂(PMe₃Ph)]. 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 → 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

14 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. I.r. 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 MS 9 mass spectrometer.

**Materials.**—Palladium(ii) chloride (Johnson Matthey); triphenylphosphine, triphenylarsine, dimethylphenylphosphine (B.D.H.); triethylphosphine (B. Newton Main). Ethyldiphenylphosphine was prepared from chlorodiphenylphosphine and ethyl Grignard. Palladium(u)—The complex (0.10 g.) was recrystallised from hot benzene, and the solution immediately turned to a pale yellow light precipitate (Found: C, 72.3; H, 6.0; S, 14.8; Pd, 5.1). Palladium(u) acetate (0.50 g.) was dissolved in benzene (45 ml.); the solution was cooled and then added slowly to a stirred solution of diphenylphosphinothioic acid (2.80 g.) in benzene (35 ml.). The yellow-brown acetate solution immediately turned deep cherry-red and after 10 min. red crystals of the complex were deposited; these were recrystallised from hot benzene, washed with diethyl ether, and dried in vacuum (3–20 g., 90%), m.p. 332–333°. Bis(diphenylphosphinothioato)palladium(ii).—The complex (0.10 g.) was dissolved in benzene (10 ml.) and an excess of triphenylphosphine (ca. 10 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 diethyl ether and dried in vacuum at 40° for several hours (0.19 g., 83%), m.p. 114–115° (Found: C, 44.1; H, 6.2; P, 14.8; Pd, 5.1; P, 10.9; S, 21.1%). The compound is only soluble in hot benzene and dichloromethane.

Bis(diphenylphosphinothioato)(triphenylphosphine)palladium(ii).—The complex (0.10 g.) 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 vacuum at 40° for several hours (0.12 g., 84%), m.p. 188–189° (Found: C, 58.1; H, 4.3; P, 11.2; S, 13; Pd, 12.9%. C₃₆H₆₀P₄Pd₂S₄ requires C, 58.1; H, 4.0; P, 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)₂(PPh₃)₂] with an excess of diphenylphosphinothioic acid. The 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 0.058 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-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 = 16.06 Å giving γ = 1998 Å. (1:42) indicated that z = 2. This gave M = 584, compared with the calculated monomeric value of 867.

Bis(diphenylphosphinothioato)(triphenylphosphine)palladium(ii).—The complex Pd₃(PPh₃)₄ (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 vacuum at 40° for several hours (0.20 g., 85%), m.p. 138° (Found: C, 50.5; H, 5.1; P, 12.9; Pd, 15.2; S, 18.6. C₃₆H₆₀P₄Pd₂S₄ requires C, 49.8; H, 4.8; P, 12.9; P, 14.8; S, 17.7%).

Osmometric molecular weight in benzene: for 0.0544 g. of compound found, 706; monomer requires 723.

Bis(diphenylphosphinothioato)bis(triphenylphosphine)palladium(ii).—The complex Pd₃(S₂PPh₂)₄ (0.20 g.) was suspended in benzene (6 ml.) and a slight excess of triethylphosphine (ca. 0.01 g.) 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 diethyl ether and dried in vacuum 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. C₃₆H₆₀P₄Pd₂S₄ 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(diphenylphosphinothioato)bis(dimethylphosphino)-
phosphine)palladium(ii).—As for the triethylphosphine complex, Pd₃(S₂PPh₂)₄ (0.20 g.), and methylidyldiphenylphosphine (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 vacuum (0.15 g., 55%), m.p. 62—65° (Found: C, 54.6; H, 5.2. C₁₉H₁₄P₂Pd₂S₄ 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. C₁₉H₁₄P₂Pd₂S₄ requires C, 51.7; H, 4.2%).

Bis(diphenylphosphinothioato)ethyldiphenylphosphine-
palladium(ii).—As for the other complexes, Pd₃(S₂PPh₂)₄ (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%; C_{38}H_{35}P_3PdS_4 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 triphenyl phosphite.

With (A) and an excess of triphenylarsine, pyridine or 2,2'-bipyridyl, reaction at room temperature or under reflux in benzene produced no evidence for any adduct formation. When trans-[Pd(OAc)_4(AsPh_3)_2] or trans-[PdCl_2(AsPh_3)_2] in benzene was treated with an excess of diphenylphosphinodithioic acid, red crystals of (A) were rapidly deposited.

We thank Johnson Matthey Ltd., for a loan of palladium-(II) chloride.

[9/1639 Received, September 25th, 1969]
Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II).
A Correction

By (Miss) J. M. C. Alison and T. A. Stephenson*

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Reprinted from

Chemical Communications 1970

The Chemical Society, Burlington House, London W1V OBN
Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II).
A Correction

By (Miss) J. M. C. Alison and T. A. Stephenson*

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Summary The 1:1 and 1:2 tertiary phosphine adducts of
Pd(S_2PPh_2)_2, originally formulated as five- and six-co-ordinate complexes, respectively, are probably both
four-co-ordinate.

Recently evidence was reported for 1:1 and 1:2 tertiary phosphine adducts of Pd(S_2PPh_2)_2 which were tentatively formulated as five- and six-co-ordinate complexes, respectively. Further work on these and the isomorphous platinum(II) complexes has now indicated that this formulation is incorrect and that the “six-co-ordinate” complexes are in fact four-co-ordinate.

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 disulfide. 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 electrolyte in this solvent.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
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<tbody>
<tr>
<td>Equivalent conductivities (25°C) of some 1:1 and 1:2 complexes in CH_2Cl_2</td>
</tr>
<tr>
<td><strong>Multiplier</strong></td>
</tr>
<tr>
<td><strong>A</strong> (plus excess of PR_3)</td>
</tr>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>BuNCIO_3</td>
</tr>
<tr>
<td>Pd(S_2PPh_2)_2(PMMe_3)</td>
</tr>
<tr>
<td>Pd(S_2PPh_2)_2(PMePh_2)</td>
</tr>
<tr>
<td>Pd(S_2PPh_2)_2(PMePh_2)</td>
</tr>
<tr>
<td>Pt(S_2PPh_2)_2(PPh_3)</td>
</tr>
<tr>
<td>Pt(S_2PPh_2)_2(PPh_3)</td>
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<tr>
<td>Pt(S_2PPh_2)_2(PMePh_2)</td>
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<tr>
<td>Pt(S_2PPh_2)_2(PMePh_2)</td>
</tr>
</tbody>
</table>

In conductivity consistent with the formation of 1:1 electrolytes (Table 1).

(c) H n.m.r. data on 1:2 platinum(II) complexes of MePh_2P and Me_2PhP in deuteriochloroform (Table 2) indicate a six-arrangement of tertiary phosphine groups (no virtual coupling).

(d) An X-ray structural analysis on [Pd(S_2PPh_2)_2(PPh_3)] is sufficiently advanced to verify the authenticity of structure (I). The mull 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 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-co-ordinate structure postulated earlier for the latter.1 No direct evidence is yet available to support (II) (a crystal structure of [Pd(S_2PPh_2)(PPh_3)] is in progress) but an analogous structure has been postulated by Tebbe and Muetterties for 1:1 tertiary phosphine complexes of palladium(II) difluorodithiophosphate on the basis of i.r. and 19F n.m.r. evidence.

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Value</th>
<th>Multiplicity and J value (Hz)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(S_2PPh_2)_2(PPh_3)]</td>
<td>8-27</td>
<td>three doublets J(P-H) 12-6</td>
</tr>
<tr>
<td>[Pd(S_2PPh_2)_2(PPh_3)]</td>
<td>7-99</td>
<td>three doublets J(P-H) 13-2</td>
</tr>
<tr>
<td>[Pd(S_2PPh_2)_2(PPh_3)]</td>
<td>7-67</td>
<td>three doublets J(P-H) 11-3</td>
</tr>
<tr>
<td>[Pd(S_2PPh_2)_2(PPh_3)]</td>
<td>7-37</td>
<td>three doublets J(P-H) 9-3</td>
</tr>
</tbody>
</table>

* ± 0-01. b J(P-H) ± 0-2 Hz; J(P-H) ± 0-5 Hz.

If (II) is correct, the best explanation for the “isomers” of [Pd(S_2PPh_2)_2(PPh_3)] is probably different orientations of the unidentate diphenylphosphinodithioato-group with respect to the bulky triphenylphosphine ligand.

Finally, preliminary studies on tertiary phosphine complexes of platinum(II) dithiocarbamates 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.

(Received, June 22nd, 1970; Com. 984.)

3 C. A. Beever and A. Fraser, to be published.
Metal Complexes of Sulphur Ligands. Part II.\(^1,2\) Reaction of Bis(diphenylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group Vb 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(S\(_2\)PPh\(_2\))\(_2\) with tertiary phosphines (PPh\(_3\), PMePh\(_2\), PMe\(_2\)Ph) gives crystalline 1:1 and 1:2 adducts. With triphenylarson 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 suggests all these 1:2 adducts have a four-co-ordinate ionic structure and this is confirmed by an X-ray analysis of [Pd(S\(_2\)PPh\(_2\))(PEt\(_3\))\(_2\)]S\(_2\)PPh\(_2\). An X-ray analysis on [Pd(S\(_2\)PPh\(_2\))\(_2\)(PPh\(_3\))] suggests a four-co-ordinate monomeric structure for the 1:1 compounds with uni- and bi-dentate co-ordination of dithiocarb ligands. Finally, an empirical i.r. method for distinguishing unidentate, bidentate, and ionic modes of co-ordination of the diphenylphosphinodithioato-group to platinum and palladium is discussed.

Recently, one of us reported\(^3\) that the compound Pd(S\(_2\)PPh\(_2\))\(_2\) reacted with tertiary phosphines to give both 1:1 and 1:2 adducts. On the basis of i.r. studies, interpreted by analogy with earlier studies on 1:1 and 1:2 Lewis base adducts with palladium carboxylates,\(^3\) these dithioco complexes 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) dithioco complexes M(S-S)\(_2\) [M = Pd or Pt; (S-S)\(_2\) = RCS\(_2\), ROC\(_2\), Et\(_2\)NCS\(_2\), and (EtO)\(_2\)PS\(_2\)] with methylphenylphosphine, in which 1:1 adducts were characterised and formulated as five-co-ordinate compounds on the basis of \(^1\)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 dithiobenzoates, 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 phosphate adducts of Pd(S\(_2\)PPh\(_2\))\(_2\) 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 Vb atoms with the isomorphous Pt(S\(_2\)PPh\(_2\))\(_2\) are presented. These lend support to the conclusions drawn from the palladium study. Analogous structures have also recently been postulated by Tebbe and Muetterties\(^5\) for tertiary phosphate complexes of palladium(II) difluorodithiophosphate on the basis of i.r. and \(^{19}\)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) dithiocarb 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.
precipitation with light petroleum or by removal of solvent under reduced pressure. Molecular weight measurements in chloroform show them to be monomeric. The \( ^1H \) n.m.r. spectra of \([Pt(S_2PPh_2)PPh_3] (PR_3 = PMePh_2 or PMe_2Ph)\) (Table 1) in carbon disulphide or deuteriochloroform consist, 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 methylidiphosphinophosphine adducts of other platinum dihydroxides are given in Table 1. The close similarity of these

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>( ^1H ) n.m.r. data [methyl region (phos)] for some platinum and palladium tertiary phosphine complexes at 301 K</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
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<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
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<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
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<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PMePh_3])</td>
</tr>
</tbody>
</table>

* 0-01. Multiplicity: three doublets except where stated otherwise. \( J(P-H) \pm 0.2 \) Hz; \( J(P-H) \pm 0.5 \) Hz. From J. P. Fackler, jun., W. C. Seidel, and J. A. Fetchin, *J. Amer. Chem. Soc.*, 1968, 90, 2707. * One doublet.

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
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<tbody>
<tr>
<td>Compounds</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
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<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
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<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
</tr>
<tr>
<td>([Pt(S_2PPh_2)PPh_3])</td>
</tr>
</tbody>
</table>

With triphenylarsine, a similar phenomenon is observed to that found with \( \text{Pd}(S_2PPh_2)_2 \). Precipitation of the triphenylarsine complex at room temperature gives a bright yellow crystalline solid. However, precipitation at low temperature (ca. 200 K) gives a pale yellow powder. The mull i.r. spectra and m.p.s of these compounds are different but the solution i.r. spectra (benzene or carbon disulphide) are identical. Both compounds analyse for \([Pt(S_2PPh_2)_2PPh_3]\) and unlike the palladium system, the low temperature form does not change to the bright yellow form in the solid phase. However, this change does occur when the former is dissolved in benzene and reprecipitated at room temperature. Clearly, these observations are consistent with the presence of isomers but speculation on the structure of these isomers is deferred until the section on i.r. studies.

Reaction of \( Pt(S_2PPh_2) \) with an excess of triphenylarsine and triphenylstibine in benzene also gives the 1 : 1 adducts \([Pt(S_2PPh_2)PPh_3] (L = As or Sb)\), although attempts to obtain a different low temperature form have been unsuccessful. In contrast to the phosphine complexes, which are stable in benzene, carbon disulphide, and dichloromethane (non-conducting in the latter, see Table 2), the arsine complex, in solution, slowly reverts to \( Pt(S_2PPh_2) \) and triphenylarsine whereas, in the absence of an excess of triphenylstibine, the stibine complex immediately dissociates in solution. Reaction of \( Pt(S_2PPh_2) \) 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 \( \text{Pd}(S_2PPh_2) \) and triphenylarsine, triphenylstibine, or pyridine. With \( \text{Ni}(S_2PPh_2) \), an excess of pyridine readily gives the green, crystalline 1 : 2 adduct \([Ni(S_2PPh_2)][C_5H_4N]_2\). 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 diphenylphosphinodithiaoato-groups.

If, however, a suspension of \( Pt(S_2PPh_2) \) 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 \([Pt(S_2PPh_2)(PR_3)] (PR_3 = PPh_3, PMePh_2, or PMe_2Ph)\). This is to be contrasted with the behaviour of \( \text{Pd}(S_2PPh_2) \), which forms 1 : 2 adducts in benzene solution with \( PET_3, PMePh_2, \) and \( PMe_2Ph \) but not with \( PETH_3 \) 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 null 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 \([Pt(S_2PPh_2)(PMePh_2)][C_5H_4N]_2\) 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 \([Pt(S_2PPh_2)(AsPPh_3)]_2(S_2PPh_2) \) in benzene solution, addition of an excess of triphenylarsine to a dichloromethane solution of \([Pt(S_2PPh_2)(S_2PPh_2)]_2(AsPPh_3) \) produces a lightening of colour and an appreciable increase in conductivity (Table 2). The

maximum value of \( \Lambda_{0.001M} \) 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 \( ^1H \) n.m.r. data for [Pt(S\(_2\)PPPh\(_2\))(PR\(_3\))\(_2\)]S\(_2\)PPPh\(_2\) (PR\(_3\) = PMe\(_2\)Ph or PMePh\(_2\)) (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 (PET\(_2\), PMe\(_2\)Ph, and PMePh\(_2\)) 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 PETPh\(_2\) in benzene solution,\(^2\) 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\(^2\) 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 \( \text{(II)} \). Confirmation of the authenticity of structure \( \text{(II)} \) has now been established by means of a two-dimensional X-ray diffraction study on [Pd(S\(_2\)PPPh\(_2\))\(_2\)](PET\(_3\))\(_2\)S\(_2\)PPPh\(_2\). The reformulation of the 1:2 compounds as the ionic species \( \text{(II)} \) and their ready interconversion with the 1:1 complexes casts doubt on the validity of the five-co-ordinate structure postulated earlier\(^2\) for the latter. An X-ray structural analysis of [Pd(S\(_2\)PPPh\(_2\))(PET\(_3\))\(_2\)]S\(_2\)PPPh\(_2\) is now sufficiently advanced\(^10\) to verify the unusual structure \( \text{(I)} \) containing four-co-ordinate palladium and bidentate and unidentate diphenylphosphinodithioato-groups. The Figure shows the square-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.

**Table 2**

Equivalent conductivities (298 K) of some platinum and palladium 1:1 and 1:2 complexes

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Compound</th>
<th>Conc. (10(^{-4}) M)</th>
<th>( \Lambda^a + ) excess of PPPh(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>Ph(_2)AsCl, HCl</td>
<td>9-8</td>
<td>55-3</td>
</tr>
<tr>
<td></td>
<td>Bu(_2)NCl</td>
<td>10-1</td>
<td>22-7</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PPh(_3))]</td>
<td>3-1</td>
<td>32-1</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PMe(_3)Ph(_2))]</td>
<td>8-6</td>
<td>1-2</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PMe(_3)Ph(_2))]</td>
<td>2-3</td>
<td>32-3</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(AsPh(_3))]</td>
<td>12-1</td>
<td>6-3</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PMePh(_2))]</td>
<td>8-5</td>
<td>2-1</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PEtPh(_2))]</td>
<td>2-6</td>
<td>2-3</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>8-0</td>
<td>50-2</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>12-0</td>
<td>3-3</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>9-2</td>
<td>33-6</td>
</tr>
<tr>
<td></td>
<td>[Pt(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>8-5</td>
<td>41-9</td>
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<tr>
<td></td>
<td><a href="S(_2)PPPPh(_2)">Pt(diphos)</a></td>
<td>1-7</td>
<td>21-7</td>
</tr>
<tr>
<td></td>
<td><a href="PPh(_3)">Pt(diphos)</a></td>
<td>3-1</td>
<td>12-1</td>
</tr>
<tr>
<td></td>
<td><a href="BPh(_3)">Pt(diphos)</a></td>
<td>8-5</td>
<td>6-4</td>
</tr>
<tr>
<td></td>
<td>[Pd(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>15-7</td>
<td>1-8</td>
</tr>
<tr>
<td></td>
<td>[Pd(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>13-7</td>
<td>2-6</td>
</tr>
<tr>
<td></td>
<td>[Pd(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>10-0</td>
<td>1-5</td>
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<tr>
<td></td>
<td>[Pd(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>2-5</td>
<td>31-6</td>
</tr>
<tr>
<td></td>
<td>[Pd(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>12-0</td>
<td>24-4</td>
</tr>
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<td>[Pd(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>5-5</td>
<td>16-8</td>
</tr>
<tr>
<td></td>
<td>[Pd(S(_2)PPPPh(_2))(PETPh(_2))]</td>
<td>8-3</td>
<td>25-0</td>
</tr>
<tr>
<td></td>
<td>[Ni(S(_2)PPPPh(_2))(C(_2)H(_4))N(_2)]</td>
<td>17-8</td>
<td>1-7</td>
</tr>
<tr>
<td>CH(_2)NO(_3)</td>
<td><a href="S(_2)PPPPh(_2)">Pt(diphos)</a></td>
<td>1-4</td>
<td>66-6</td>
</tr>
<tr>
<td></td>
<td><a href="S(_2)PPPPh(_2)">Pd(diphos)</a></td>
<td>2-6</td>
<td>74-7</td>
</tr>
<tr>
<td></td>
<td>[Pd(PMePh(_2))]S(_2)PPPh(_2)</td>
<td>4-8</td>
<td>42-0</td>
</tr>
<tr>
<td></td>
<td>[Pd(PMePh(_2))]S(_2)PPPh(_2)</td>
<td>11-7</td>
<td>8-3</td>
</tr>
</tbody>
</table>

* In S cm\(^2\) mol\(^{-1}\).  * Addition of excess AsPh\(_3\).

Infrared Spectra.—In an earlier paper,\(^2\) the mode of bonding of the diphenylphosphinodithioato-ligand to palladium was inferred from the position and separation of the asymmetric (\( v_4 \)) and symmetric (\( v_2 \)) PS\(_3^-\) stretching frequencies. At the time, it was considered that this approach was valid and completely analogous to the situation found in carboxylate complexes.\(^3,11\) However, such an approach is now considered unsuitable in view of the fact that, in the Ph\(_2\)PS\(_3^-\) group,\(^11\) for references and discussion see K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* 1st ed. New York and London, 1969.
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 \(\nu_{PS_2}\) 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 \(\nu_{PS_2}\) 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

**Table 3**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Uni-Identate *</th>
<th>Bidentate *</th>
<th>Ionic *</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="S(_2)PPh(_2)">Pt(Pd)</a>(PMe(_2)Ph) [S(_2)PPh(_2)]</td>
<td>645, 539</td>
<td>603, 571</td>
<td></td>
</tr>
<tr>
<td>[Pt(S(_2)PPh(_2)][AsPPh(_3)]</td>
<td>645, 539</td>
<td>603, 571</td>
<td></td>
</tr>
<tr>
<td>[Pt(S(_2)PPh(_2)][SbPPh(_3)]</td>
<td>645, 539</td>
<td>603, 572</td>
<td></td>
</tr>
<tr>
<td>[Pt(S(_2)PPh(_2)][PPh(_3)] [bright yellow]</td>
<td>648, 540</td>
<td>603, 570</td>
<td></td>
</tr>
<tr>
<td>[Pt(S(_2)PPh(_2)][PPh(_3)] [pale yellow]</td>
<td>645, 539</td>
<td>603, 573</td>
<td>650, 560</td>
</tr>
<tr>
<td>[Pt(Pd)](S(_2)PPh(_2)][PPh(_3)]</td>
<td>605, 573</td>
<td>650, 562</td>
<td></td>
</tr>
<tr>
<td>[Pt(Pd)](S(_2)PPh(_2)][PMe(_2)Ph]S(_2)PPh(_2)</td>
<td>605, 573</td>
<td>655, 562</td>
<td></td>
</tr>
<tr>
<td>[Pt(Pd)](S(_2)PPh(_2)][PMe(_2)Ph]PPh(_3)</td>
<td>605, 573</td>
<td>656, 562</td>
<td></td>
</tr>
<tr>
<td>[Pt(Pd)](S(_2)PPh(_2)][PMe(_2)Ph]BPh(_4)</td>
<td>605, 573</td>
<td>660, 563</td>
<td></td>
</tr>
<tr>
<td><a href="diphos">Pt(Pd)</a>(_2)][S(_2)PPh(_2)]</td>
<td>603, 573</td>
<td>650, 563</td>
<td></td>
</tr>
</tbody>
</table>

\* Cf. Ph\(_2\)PS\(_2\)H 638 and 540 cm\(^{-1}\). \* Cf. Pt(S\(_2\)PPh\(_2\)][S\(_2\)PPh\(_2\)] 601 and 567 cm\(^{-1}\). \* Cf. Cs(S\(_2\)PPh\(_2\)] 654 and 562 cm\(^{-1}\).

that the usefulness of these characteristic bands for structure determination might be illustrated. A convincing test of the validity of these assignments is provided by the syntheses of \([Pt(S_2PPh_2)(PMe_2Ph)_2]_X (X^- = Cl^- or BPh_4^-)\), where the i.r. spectra contain 'bidentate' but not 'ionic' bands (Table 3).

The product from reaction of \(M(S_2PPh_2)_2 (M = Pt or Pd)\) with excess 1,2-bis(diphenylphosphino)ethane (Ph\(_2\)PCH\(_2\)CH\(_2\)PPh\(_2\) = diphos) provides an excellent example of the use of these characteristic bands in determining structural details. The white products analysed for \([M(S_2PPh_2)(diphos)_2]_2\) and the i.r. spectra (Table 3) contain only 'ionic' bands, suggesting the compounds should be formulated as \([M(diphos)_2]_2\)(S\(_2\)PPh\(_2\)]\(_2\) or \([S_2PPh_2]_2\)(diphos)\(_2\). This is confirmed by conductivity measurements (Table 2) and by synthesis of \([Pt(diphos)_2]_2\)-(BPh\(_4\))\(_2\) with consequent disappearance of the 'ionic' bands. Similarly, the solution i.r. spectrum of Pt-

\[\text{S}_2\text{PPh}_2\] and excess pyridine 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 \([M(S_2PPh_2)_2PPh_4] (M = Pd or Pt)\) 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 \([M(S_2PPh_2)_2PPh_4]\) 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-co-ordinate 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_2PPh_2)_2\](C\(_6\)H\(_5\)N\(_2\))\(_2\) 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 date, 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 diphenylphosphinodithioate complexes and for following the structural interconversions which are a feature of the dithioacid complexes so far considered.

**EXPERIMENTAL**

Microanalyses were by the Analytical Laboratory, Edinburgh University, and by A. Bernhardt, West Germany.
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 AEI MS20 spectrometer. M.p.s were determined with a Koffer hot-stage microscope and are uncorrected.

**Materials.—**Palladium(II) chloride and potassium tetra-chloroplatinate(II) (Johnson-Matthey); triphenylphosphine and dimethyldiphenylphosphine (B.D.H.), triphenylarsine (Emanuel), triphenylstibine (Koch-Light), triethylphosphine (B. Newton Main); ethyldiphenylphosphine and methyltriphenylphosphine were prepared by the Grignard method. Diphenylphosphinodithioic acid and its caesium salt were prepared as described previously.

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**Platinum Compounds**

**Bis(diphenylphosphinodithioato)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 diphenylphosphinodithioic 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 (2-6 g, 84%). m.p. 298—300° (Found: C, 41.9; H, 2.9; P, 8.8; S, 20.2). 

A second method of preparation is by reaction of platinum(II) acetate and excess diphenylphosphinodithioic acid in warm 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; 

**Bis(diphenylphosphinodithioato)(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 filtration 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, 9.9%). m.p. 122° (Found: C, 53.0; H, 3.8; P, 9.7; S, 15.5). 

**Bis(diphenylphosphinodithioato)bis(triphenylphosphine)platinum(II).—**b. *Pale yellow form.* A solution of the above product

---

* Another method of synthesis (from H₃PtCl and Ph₃P(S)H) is also available: A. Muller, V. V. Krishna Rao, and G. Klinsiek, *Chem. Ber.*, 1971, 104, 1892.
** Palladium Compounds**

\[ \text{Pd}([S_2PPh_2]_2) \], \[ \text{Pd}([S_2PPh]_2PR_3) \] (PR = PPh_3, PMePh, PEtPh_2, and PEt), and \[ \text{Pd}([S_2PPh]_2PR_3)_2 \] (PR = PMePh or PEt) were prepared as described previously.\(^2\)

\[ \text{Bis(diphenylphosphinophosphate)}\text{palladium(II)} \]

**X-Ray Structural Data**

(a) \[ \text{[Pd}([S_2PPh]_2)\text{PPh}_3] \] prepared as in reference 2 gave well-formed triclinic needles from a nitromethane–ether mixture.

\[ \text{Crystal Data.} \quad \text{C}_{32}\text{H}_{35}\text{P} \text{, PdS}_4 \text{, M = 867, } a = 9.02, b = 18.65, c = 22.13 \text{ Å, } \alpha = 90.5, \beta = 90.4, \gamma = 92.5^\circ, \]

\[ D_m = 1.43, D_R = 1.45 \text{ g cm}^{-3}, Z = 4, \text{ space group } \overline{\text{B}1}. \]

816 Independent reflections were obtained from precession data (Cu-K\text{a} radiation), giving about two-thirds of the reciprocal lattice out to a resolution of 1.5 Å. The positions of the palladium, sulphur, and phosphorus atoms were obtained by Patterson and Fourier syntheses, and the phenyl rings, which are only partially resolved, have been idealised and included in further refinement to give the heavy atom framework shown in the Figure. Further data is being collected to refine the structure fully.

(b) The following preliminary report has been provided by Dr. C. A. Beever and Mr. A. Fraser of the University of Edinburgh.

'A crystal of \[ \text{[Pd}([S_2PPh]_2)\text{PEtPh}_2]\text{PPh}_3 \] prepared as in reference 2 was mounted about its needle axis and X-ray photographs taken by the Weissenberg method. From these photographs, the following cell statistics were calculated: \( a = 33.42; b = 8.74; c = 32.02 \text{ Å; } \beta = 121.2^\circ, U = 7400 \text{ Å}^3, Z = 8, \text{ space group } \text{C2/c.} \) 208 hkl Reflections were measured visually and a structure with a four-coordinate palladium atom refined in two dimensions to an \( R \) factor of 0.20. All attempts to refine the structure on the basis of a six-co-ordinate palladium atom were unsuccessful.'
Nickel Compounds

Bis(diphenylphosphinodithioato)nickel(II) was prepared as described elsewhere;\(^1\) \(\nu_{\text{max}}\) (Nujol) 740s, 709s, 685s, 619w, 601w, 573s, 485m, 463w, 454w, 342m.

Bis(diphenylphosphinodithioato)bis(pyridine)nickel(II).—\(\text{Ni(S}_2\text{PPh}_2\text{)}_2\) 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 \(\text{C}_{24}\text{H}_{22}\text{N}_2\text{NiP}_2\text{S}_4\): 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, 386s, 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.).

NOVEL CARBONYLATION PRODUCTS OF RUTHENIUM(II)

DITHIOACID COMPLEXES

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(Received 20 June 1972)

Dialkyl(aryl)phosphinodithioato complexes of ruthenium of type

\[
[\text{Ru}(S_2PR_2)_2L_2]^{-} (I) \quad (R = \text{Me, Et, Ph}; \ L = \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph, P(OPh)}_3
\]

can be prepared by reaction of \([\text{RuCl}_2 \text{ or } 3 \text{L} \text{ or } 4]^{1,2,3}\) with the sodium salt of the appropriate dithioacid. Unlike \([\text{Ru}(S_2\text{CNR}_2)_2L_2]^{-} (R = \text{Me, Et}; \ L = \text{PPh}_3(4), \text{PMe}_2\text{Ph})\), 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 \([\text{Ru}(S_2\text{PR}_2)_2(\text{PR}^\prime_3)^{-} (\text{P(OPh)}_3)]\) and carbonylation under mild conditions to give phosphine carbonyls.
For \( L = \text{PMe}_2\text{Ph} \), carbonylation (1 atm.) of \( I \) in refluxing ethanolic solution leads to two products \([\text{Ru(S}_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})\text{CO}]\) (II) and \([\text{Ru(S}_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})_2\text{CO}]\) (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°) 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 \([\text{Ru(S}_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})\text{CO}]\).

Low temperature carbonylation of \([\text{Ru(S}_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})_2]\) gives a third complex, also of formula \([\text{Ru(S}_2\text{PR}_2)_2(\text{PMe}_2\text{Ph})_2\text{CO}]\) 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 \( L = \text{PMePh}_2, \text{PPh}_3 \) etc., carbonylation of I, even under very mild conditions, gives only
TABLE

Variable Temperature $^1H$ n.m.r. Spectra of some Ruthenium Dithio Compounds in CDCl$_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
<th>$\tau$ Value (S$_2$PMe$_2$)$_2$</th>
<th>$\tau$ Value (Me$_2$ phosphine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$</td>
<td>28</td>
<td>8.33$^c$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-20$^b$</td>
<td>8.33$^d$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-60</td>
<td>7.69$^c$ 8.85$^c$</td>
<td>-</td>
</tr>
<tr>
<td>Ru(S$_2$PMe$_2$)$_2$(PMePh$_2$)$_2$</td>
<td>60</td>
<td>8.39$^c$</td>
<td>8.00$^e$</td>
</tr>
<tr>
<td>0$^b$</td>
<td>8.39$^d$</td>
<td>8.04</td>
<td></td>
</tr>
<tr>
<td>-60</td>
<td>7.84$^c$ 8.75$^c$</td>
<td>8.04$^e$</td>
<td></td>
</tr>
<tr>
<td>Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$</td>
<td>65</td>
<td>8.01$^c$</td>
<td>8.38$^e$</td>
</tr>
<tr>
<td>28$^b$</td>
<td>8.01$^d$</td>
<td>8.38$^d$</td>
<td></td>
</tr>
<tr>
<td>-40</td>
<td>7.69$^c$ 8.14$^c$</td>
<td>8.30$^e$ 8.45$^e$</td>
<td></td>
</tr>
<tr>
<td>Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$</td>
<td>60$^b$</td>
<td>8.17$^d$</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>7.94$^c$ 8.33$^c$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)CO</td>
<td>55</td>
<td>7.84$^c$,7.97$^c$,8.06$^c$,8.40$^c$</td>
<td>8.07$^f$</td>
</tr>
<tr>
<td>-10$^b$</td>
<td>7.83$^c$,7.96$^c$,8.04$^c$,8.37$^c$</td>
<td>8.07$^g$</td>
<td></td>
</tr>
<tr>
<td>-30</td>
<td>7.81$^c$,7.95$^c$,8.03$^c$,8.35$^c$</td>
<td>8.06$^f$ 8.09$^f$</td>
<td></td>
</tr>
<tr>
<td>Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO</td>
<td>28</td>
<td>8.11$^c$ 8.91$^c$</td>
<td>7.86$^h$ 7.89$^h$</td>
</tr>
</tbody>
</table>

- $^a J_{PH} = 12.5$ Hz
- $^b$ coalescence temperature
- $^c$ Doublet, $J_{PH} = 10.0$ Hz
- $^d$ Doublet
- $^e$ Second order spectrum (7) with $J_{PH} + J_{PH'} = 8.5$ Hz
- $^f$ Broad hump
- $^g$ Broadened doublet
- $^h$ 1:2:1 triplet with virtual coupling constant $\tau = 3.5$ Hz.

$[Ru(S_2P_2)_2LCO]$, 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.

References

5. B. Loev and M.M. Goodman, Chem. and Ind., 2026 (1967).
Metal Complexes of Sulphur Ligands. Part III.1 Reaction of Platinum(II) 
$NN'$-Dialkyldithiocarbamates, $O$-Ethyl Dithiocarbonate (Xanthate), and 
$OO'$-Diethyl Dithiophosphate with Tertiary Phosphines

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Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY
DALTON TRANSACTIONS
1973
Metal Complexes of Sulphur Ligands. Part III. Reaction of Platinum(ii) N,N-Dialkylthiocarbamates, O-Ethyl Dithiocarbonate (Xanthate), and O,O'-Diethyl Dithiophosphate 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)₂ compounds [M = Pt, Pd; (S-S)⁻ = S₂CNR₂ (R = Me, Et), S₂COR (R = Et, PhCH₂), −S₂P(OEt)₂, and −S₂PR₃ (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(S-S)] 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)⁻ = S₂COR, S₂P(OEt)₂, nucleophilic attack can also occur on a co-ordinated alkoxy group to give the novel compounds [[R₃P]₂MS₂CO] (I) and [[R₃P]₂MS₂P(O)OEt] (II) respectively.

For [M(S-S)(PR₃)₂(S-S)] compounds containing S₂CNR₂, the presence of excess PR₃ catalyses the reaction between dithiocarbamate ion and dichloromethane, giving CH₃(S₂CNR₂)₂ and [M(S₂CNR₂)(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)₂ (1:1 molar ratio) [M = Pt, Pd; (S-S)⁻ = S₂CNMe₂, S₂COR, −S₂P(OEt)₂, and −S₂PR₃] 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 methylidiphenylphosphine was added to platinum(ii) compounds of ring-substituted dithiobenzoates³ but no further details were given. It was also stated³ that 'diethylthiocarbamate complexes of palladium(ii) and platinum(ii) react only slowly (hours) with excess methylidiphenylphosphine 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 dithiophosphate adducts, further reaction occurred to give the novel complexes [(R₃P)₂(MS₂CO)] (I) and [(R₃P)₂PdS₂P(O)OEt] (II) respectively, for which no convincing mechanism of formation was suggested.

Other studies, however, on tertiary phosphine complexes of M(S₂PR₃)₂ [M = Pd, Pt; R = Ph,¹ Et,¹ Me⁵] and Pd(S₂PF₂)₂⁶ 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(S₂PPh₂)₂PPh₃]⁷ and [Pd(S₂PPh₂)₆- (PE₄Et₂)₃S₂PPh₆]⁸.

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(S₂CNMe₂)₂PR₃].—Rection of Pt(S₂CNEt₂)₂ with either PPh₃ or PMePh₃ (1:1)

molar ratio) in carbon disulphide gives deep lemon-yellow solutions immediately from which crystalline yellow solids of stoichiometry \([\text{Pt(S}_2\text{CNMe}_2)_2\text{PR}_3']\) 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 \(\text{H}\) n.m.r. at 301 K is identical to that reported earlier by Fackler et al.\(^5\) (Table 1). In a further note,\(^3\) these authors state that the p.m.r. behaviour of methylidiphenylphosphinebis-(NN-diethyldithiocarbamate)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 \(\text{H}\) n.m.r. spectra exhibited by \([\text{Pt(S}_2\text{P(OEt)}_2)_2\text{PMePh}_3]_\text{2}\), \([\text{Pt(S}_2\text{PMe}_2)_2\text{PR}_3'](2)\) (\(\text{PR}_3' = \text{PPh}_3, \text{PMePh}_2, \text{etc.}\)) and the variable-temperature \(\text{F}\) n.m.r. spectrum of \([\text{Pd(S}_2\text{PF}_2)_2\text{P(PPh}_3)_2]_\text{2}\).\(^6\) 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 reaction 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 \((S-S)=\text{S}_2\text{CNR}_2\), the observed temperature dependence is not due to restricted rotation about the C-N bond as found, for example, in dithiocarbamate esters.\(^10\) A full line-shape analysis for all compounds of type \([\text{M(S-S)}_2(\text{ER}_3')]_2\) (\(\text{E} = \text{P}, \text{As}, \text{Sb}\)) is in progress to ascertain accurate rate data and will be published later.

The observation of magnetically inequivalent alkyl groups at low temperature for \([\text{Pt(S}_2\text{CNMe}_2)_2\text{PR}_3']\) is inconsistent with the square pyramidal structure (V) 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 \([\text{M(S-S)}_2(\text{ER}_3')]_2\) 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

\* 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.


<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>T/K</th>
<th>Dithio-ligand</th>
<th>CH₂(P'Ph)</th>
<th>Others</th>
<th>fCH₂</th>
<th>fCH₂&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph₂(PhCH₂)₂PS₂CNEt₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>CH₄*</td>
<td>8-86(2)</td>
<td>Ph, 2-0-3(0)</td>
<td>14-0</td>
<td></td>
</tr>
<tr>
<td>Pt(S₂CNEt₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>8-70(2)</td>
<td>6-40(2)</td>
<td>Ph, 2-2-3(0)</td>
<td>10-0</td>
<td>35-0</td>
</tr>
<tr>
<td>Pt(S₂CNEt₂)₂PPh₃</td>
<td>CDCl₃</td>
<td>301</td>
<td>8-89(12)</td>
<td>6-41(8)</td>
<td>Ph, 2-2-3(0)</td>
<td>10-0</td>
<td>35-0</td>
</tr>
<tr>
<td>Pt(S₂CNEt₂)₂(PMePh₂)₂</td>
<td>CDCl₃</td>
<td>301</td>
<td>8-89(12)</td>
<td>6-41(8)</td>
<td>Ph, 2-2-3(0)</td>
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<td>35-0</td>
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<td>6-34(2)</td>
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<tr>
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<td>CDCl₃</td>
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<td>6-53(2)</td>
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<td>Pt(S₂CNMe₂)₂(PPh₃)₂Cl₂H₂O</td>
<td>CDCl₃</td>
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<td>8-80(6)</td>
<td>6-53(2)</td>
<td>Ph, 2-0(0)</td>
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<td>8-80(6)</td>
<td>6-53(2)</td>
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<td>Pt{S₂(OEt₂)₂AsPh₃}</td>
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<td>CH₂(S₂CNEt₂)₂</td>
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<td>8-76(6)</td>
<td>6-30(2)</td>
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<td>301</td>
<td>8-70(12)</td>
<td>5-90(6)</td>
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<td>CDCl₃</td>
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<td>8-70(12)</td>
<td>5-90(6)</td>
<td>Ph, 2-0(0)</td>
<td>9-0</td>
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<td>Pt₂(S₂P(OEt₂)₂)₂PPh₄</td>
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<td>301</td>
<td>8-70(12)</td>
<td>5-90(6)</td>
<td>Ph, 2-0(0)</td>
<td>9-0</td>
<td>34-0</td>
</tr>
</tbody>
</table>

* Singlet; ** doublet; "l" broad.
* Triplet unless otherwise stated. ** Quartet unless otherwise stated. * Phenyl resonance; complex multiplet. ± ±0-5 Hz. ±0-5 Hz.

Table 1

1H N.m.r. data for various sulphur compounds

\( \tau \) Value*,

\( f_{CH₂} \) and \( f_{CH₂"} \)
sufficiently slow for the 'frozen-out' n.m.r. spectrum to be observed.*

It should be noted that for (S-S) = S,CN,R₂, 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 R¹ and R², R³ and R⁴ are magnetically inequivalent and three resonances of intensity ratio 1:1:2 are theoretically expected, whereas only two resonances are observed.

<table>
<thead>
<tr>
<th>Table 2</th>
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<tr>
<td>Free-energy of activation and coalescence temperature (Tₑ/K) obtained from ¹H n.m.r. spectra for various sulphur compounds</td>
</tr>
<tr>
<td>Compound</td>
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<tr>
<td>----------</td>
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<tr>
<td>Pt(S₂P(ΟEt₂)₂)PMe₃</td>
</tr>
<tr>
<td>Pt(S₂PMe₂PMe₃)</td>
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<td>Pt(S₂NCNEt₂)PMe₂Ph</td>
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<td>Pt(S₂NCNEt₂)₂PMe₂Ph₂ &amp; S₂CNEt₂</td>
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<tr>
<td>Pt(S₂NCNEt₂)₂PMe₂Ph₂ &amp; S₂CNEt₂</td>
</tr>
</tbody>
</table>

*+ - 1 K. ^ 1:0.0 mol⁻¹. * Measured on CH₃ triplets. | Measured on CH₄ quartets. *Cf. EJCSNMEt₂ΔG*ₑ/K 63.8 kJ mol⁻¹. *Cf. Me₂CSNMEt₂ΔG*ₑ/K 69.8 kJ mol⁻¹.

However, the atoms (S and P) inducing the magnetic inequivalence in R³ and R⁴ are well removed (six bonds) from these groups, so that the separation between the R³ and R⁴ 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 [Ni(S₂CN,R₂)Cl(PR₃)] and [Ni(S₂CN,R₂)Cl₂] (VII) (one R resonance at 213 K) and even in compounds such as Me²NCOS(SiH₃) 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.

As a similar conclusion has recently been reached by Powell and Chan¹⁶ for these compounds on the basis of detailed variable-temperature ¹H n.m.r. studies on the related complexes [α-allyl Pt(PMe₂Ph)(X-Y)] [X-Y = S,CNMe₂, S,COME]. In addition Davis et al.¹⁰ invoke a similar mechanism for interconversion processes in molybdenum dialkyldithiocarbamates.

As pointed out by a referee, we have assumed that the essential feature of the solid-state structure (viz. the unidentate-bidentate co-ordination) is retained in solution, but this assumption is strongly supported by both the characteristic chemical shifts of the two CH₂ 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 [Pt(S₂NCNEt₂)₂PMe₂Ph₂] by J. M. C. Alston 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 five-coordinate trigonal bipyramidal structure to explain the low-temperature ¹H n.m.r. data, there is a substantial amount of evidence which supports the interpretation given in equation (1). This is as follows. (i) There is a very close similarity of chemical shifts and coupling constants (for the methyl phosphine ¹H n.m.r. resonance at 301 K) for all the dithiocarbamates [Pt(S₂S₂)(PMe₂Ph₂)]¹.²,³,⁷ which is indicative of a similar structure and the X-ray analysis of [Pd(S₂PPh₂)₃PMe₂Ph₂] seven (isomorphous with the corresponding platinum complex) shows this to be of type (III). Furthermore, for [Pt(S₂NCNEt₂)₂PMe₂Ph₂], the position of the low-field CH₂ quartet (3-617) is intermediate between those found for ionic [Pt(S₂NCNEt₂)₂PMe₂Ph₂] and bidentate [6-40 Pt(S₂NCNEt₂)₂ diethyldithiocarbamate groups, suggesting that it probably arises from a unidentate group.

(ii) For the S₂PPh₃ compounds reported earlier,¹ both room- and low-temperature isomeric forms of [M(S₂PPh₃)₂PMe₂Ph₂] (M = Pt, Pd) can be isolated. However, the characteristic i.r. bands of 'bidentate' and 'unidentate' dithiophosphane co-ordination¹ remain unchanged which suggests that a structure of type (III) persists at all temperatures.

(iii) Reaction of either Pt(S-S)₂ or Pt(S-S)₂PR₃ with an excess of tertiary phosphine gives ionic species containing the [Pt(S-S)(PR₃)]²⁺ 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-coordinate 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 Pt(S₂NCNEt₂) in acetone is treated with an excess of PMe₂Ph₂, a pale yellow solution is formed from which pale yellow crystals are rapidly deposited. This compound has an analysis consistent with the formula [Pt(S₂NCNEt₂)-(PMe₂Ph₂)]S₂CNEt₂; the ionic formulation is confirmed by the presence of additional i.r. bands corresponding to those found in Na₃S₂CNEt₂3H₂O (but not in co-ordinated dithiocarbamate groups) and the ready synthesis of [Pt(S₂NCNEt₂)(PMe₂Ph₂)]S₂CNEt₂. As noted earlier¹ for the ionic PR₃ complexes of Pt(S₂PPh₃)₂, this complex also readily dissociates to [Pt(S₂NCNEt₂)(PMe₂Ph₂)] in the presence of nonpolar solvents. In this instance, the increased nucleophilicity of S₂CNEt₂ compared to S₂PPh₃ enhances this tendency. Thus, although the
ionic complex is insoluble in benzene, a yellow solution slowly forms with time and \([\text{Pt(S}_2\text{CNET}_{2})_2\text{PMePh}_2]\) is isolated. Even in diethyl ether, a suspension of the ionic complex turns deep yellow (24 h) and the neutral compound is recovered.

The \(^1H\) 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 \(-S_2\text{CNET}_2\) to PMePh\(_2\) protons is correct for \([\text{Pt(S}_2\text{CNET}_{2})_2\text{PMePh}_2]_2\text{S}_2\text{CNET}_2\), the equilibrium lies well to the right-hand side of equation (2). This is evident since the position of the CH\(_2\) quartet \((\tau 6\,26)\)

\[
[\text{Pt(S}_2\text{CNR}_2]_2\text{PMePh}_2 \rightleftharpoons [\text{Pt(S}_2\text{CNR}_2]_2\text{PMePh}_2 + \text{PMePh}_2 \quad (2)
\]

is identical to that found for \([\text{Pt(S}_2\text{CNET}_{2})_2\text{PMePh}_2]\) 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. for \([\text{Pt(S}_2\text{CNET}_{2})_2\text{PMePh}_2]\), a triplet 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 \(^1H\) 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 \(\tau 6\,37\) (bidentate) and 5-77 (ionic) (separation 60 Hz). In addition, the methyl resonance sharpens such that at 213 K, a strong doublet, centred at \(\tau 8\,09\) with weak \(^195\)Pt satellites is observed [cf. \([\text{Pt(S}_2\text{PPh}_2]_2\text{PMePh}_2]_2\text{S}_2\text{PPh}_2\)].

Thus, down to ca. 265 K, the \(^1H\) n.m.r. changes signify a shift to the left-hand side of equation (2). A similar observation was made earlier \(^{16}\) for \([\text{Pd(S}_2\text{PPh}_2]_2\text{PEt}_3\text{PPh}_2]_2\text{S}_2\text{PPh}_2\) where the intensity of the 540 cm\(^{-1}\) i.r. 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 \(^1H\) n.m.r. data. This gives \(K_{213\,K \times 33 \,mol^{-1}}\), \(\Delta H_{265\,K \times 60 \,kJ \,mol^{-1}}\), \(\Delta S_{191 \,J \,K^{-1} \,mol^{-1}}\). Below 265 K, the \(^1H\) n.m.r. changes are interpreted as a slowing down of the exchange between ionic and bidentate dithiocarbamate groups such that at 213 K, the spectrum corresponds to that expected for a 'frozen-out' ionic structure of type (IV) [cf. \([\text{Pd(S}_2\text{PF}_2]_2\text{PF}_2]_2\text{S}_2\text{PF}_2\)]. The absence at 213 K of a quartet at \(\tau 6\,17\) shows that the equilibrium lies completely to the left-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 bidentate groups can be obtained (Table 2).

Similarly, reaction of \([\text{Pt(S}_2\text{CNR}_2]_2\text{PPh}_2]\) and an excess of \(\text{PPh}_2\) in acetonitrile gives a crystalline sample of [Pt-\(\text{S}_2\text{CNR}_2]_2\text{S}_2\text{CNR}_2].\text{Detailed} \(^1H\) n.m.r. studies in CDCl\(_3\) show the same phenomenon as above, namely, a methyl \(\text{CNR}_2\) resonance \((\tau 6\,71)\) at 301 K, corresponding to \([\text{Pt(S}_2\text{CNR}_2]_2\text{S}_2\text{CNR}_2]\) and when the temperature is lowered, the growth of a peak at \(\tau 6\,53\) (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 \(K_{230\,K} \times 22 \,mol^{-1}\), \(\Delta H_{265\,K} \times 69 \,kJ \,mol^{-1}\), \(\Delta S_{218 \,JK^{-1} \,mol^{-1}}\) and, from the coalescence temperature, an estimate of the activation energy for ionic-bidentate ligand exchange can be obtained (Table 2). All attempts to synthesise \([\text{Pt(S}_2\text{CNET}_{2}]_2\text{PPPh}_2]_2\text{S}_2\text{CNET}_{2}\) have been unsuccessful, the only product isolated being \([\text{Pt(S}_2\text{CNET}_{2}]_2\text{PPPh}_2]\) [cf. the \(\text{Pd(S}_2\text{PF}_2]_2\text{PPPh}_2\)] system].\(^{1,16}\)

If the reactions between \([\text{Pt(S}_2\text{CNET}_{2}]_2\) 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 \(\text{PMPh}_2 \approx \text{PMcPh}_2 \approx \text{PPh}_2\). This phenomenon is accompanied by a steady rise in conductivity, the value finally corresponding to that expected for a 1 : 1 electrolyte. Concentration of the solution and addition of diethyl ether gives white microcrystalline solids (A).

The \(^1\)H n.m.r. of these compounds are similar to those expected for \([\text{Pt(S}_2\text{CNR}_2]_2\text{PR}_3]_2\text{S}_2\text{CNR}_2\) (with averaging of ionic and bidentate dithiocarbamate groups) (Table 1).

except that integration of all these compounds shows that there are insufficient dithiocarbamate protons for this formulation. In fact, the $^1$H n.m.r. spectra are consistent with the formulation $[\text{Pt}(\text{S}_2\text{C} \text{NEt}_2)(\text{PR}_3)_2]\text{X}$ (where X is an anion not containing protons), except for the presence of an additional weak resonance in the region $\sim 6$–$8$. 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 dithiocarbamate 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 $\text{Pt}(\text{S}_2\text{C} \text{NEt}_2)_2$ and an excess of PR$_3$ in dichloromethane are the compounds $[\text{Pt}(\text{S}_2\text{C} \text{NET}_2)(\text{PR}_3)_2]\text{Cl}_2\text{H}_2\text{O}$ (A); we have amassed considerable evidence to support this rather surprising conclusion.

The solid (A) reacts with NaBPh$_4$ or NH$_4$PF$_6$ in acetone–methanol solution to give the compounds $[\text{Pt}(\text{S}_2\text{C} \text{NEt}_2)(\text{PR}_3)_2]\text{Y}$ ($Y = \text{BPh}_4^-$, PF$_6^-$) which have been fully characterised by $^1$H n.m.r., analyses, and conductivity measurements (Tables 1, 4, and 3 respectively). An interesting feature of the $^1$H n.m.r. of these compounds is the upfield shift (ca. 0–2 p.p.m.) of both $\text{S}_2\text{C} \text{NEt}_2$ and PR$_3$ resonances in the BPh$_4^-$, compared to the PF$_6^-$ and Cl$^-$ compounds. Similar observations have been made for the $[\text{Pt}(\text{S}_2\text{P} \text{O}_2 \text{Et})_2(\text{PR}_3)_2]\text{Y}$ series and we suggest that this is a consequence of a ring-current effect in the BPh$_4^-$ 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.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 $[\text{Co}(\text{CO})_2\text{PPPh}_3(\text{H}_2\text{O})\text{Cl}]$ ($\sim 7$–$4$). 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 $^1$H 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 organothio-compound, shown by elemental analysis, mass, and $^1$H n.m.r. spectroscopy to be CH$_2$$(\text{S}_2\text{C} \text{NEt}_2)_2$ (B). This compound has been recently prepared in high yield by refluxing sodium diethyl-dithiocarbamate with anhydrous dichloromethane. 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$_2$3H$_2$O, CH$_2$Cl$_2$ (solvent grade), and any tertiary phosphate for 12 h. The reason why the addition of PR$_3$ facilitates the formation of (B) is not at present clear. The $^1$H n.m.r. spectrum of (B) is of interest that in that at room temperature there are two CH$_2$ quartets. At a higher temperature these coalesce and the estimated free energy of activation for the barrier to free rotation about the C–N bond compares favourably with the value obtained earlier for EtS$\text{CNEt}_2$ (Table 2). Rather surprisingly, this temperature dependence of (B) was not noted in the original preparation.

The mechanism of formation of (A) is most likely via prior formation of $[\text{Pt}(\text{S}_2\text{C} \text{NEt}_2)(\text{PMePh}_2)_2]\text{S}_2\text{C} \text{NEt}_2$. Support for this hypothesis comes from a study of the behaviour of $[\text{Pt}(\text{S}_2\text{C} \text{NET}_2)(\text{PMePh}_2)_2]\text{S}_2\text{C} \text{NET}_2$ in CH$_2$Cl$_2$. The initial deep yellow solution, containing a mixture of 1:2, 1:1 compounds, and free PMePh$_2$, 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 $[\text{Pt}(\text{S}_2\text{C} \text{NET}_2)(\text{PMePh}_2)_2]\text{CHCl}_3$ and the ethereal filtrate contains CH$_2$$(\text{S}_2\text{C} \text{NET}_2)_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 $[\text{Pt}(\text{S}_2\text{C} \text{NET}_2)(\text{PMePh}_2)_2]\text{S}_2\text{C} \text{NET}_2$ in ethanol-free CHCl$_3$ and CCl$_4$ (see earlier), where only nucleophilic attack of $\text{S}_2\text{C} \text{NET}_2$ on the platinum ion occurs. At this juncture, it is not obvious (to us) why ethanol has such a profound effect on the course of the reaction.

\* We thank Dr. M. Barber and Mr. P. Swift of A.E.I. Scientific Apparatus Ltd. for these measurements.

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| Table 3 | Equivalent conductivities (298 K) in CH$_2$Cl$_2$ of some platinum dithio-compounds containing tertiary phosphines |
|---|---|---|
| Compound | Conc. $(10^{-2} \Omega^{-1} cm^{-1})$ | $\Lambda^*$ |
| $\text{Ph}_3\text{AsCl, HCl}$ | 9.5 | 55.3 |
| $\text{Bu}_3\text{SCl}$ | 10.1 | 22.7 |
| $[\text{Pt}(\text{S}_2\text{C} \text{NEt}_2)_2]$ | 3.1 | 32.1 |
| $[\text{Pt}(\text{S}_2\text{CNEt}_2)_2]$ | 9.2 | 3.0 |
| $[\text{Pt}(\text{S}_2\text{CNET}_2)_2]$ | 9.4 | 27.0 |
| $[\text{Pt}(\text{S}_2\text{CNEt}_2)_2]$ | 10.5 | 0.7 |
| $[\text{Pt}(\text{S}_2\text{CNEt}_2)_2]$ | 17.5 | 4.3 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{Cl}_2\text{H}_2\text{O}$ | 12.5 | 34.2 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{BPPh}_4$ | 7.0 | 40.9 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{Cl}_2\text{H}_2\text{O}$ | 11.2 | 36.6 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{BPPh}_4$ | 2.4 | 50.1 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{Cl}_2\text{H}_2\text{O}$ | 14.7 | 38.6 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{BPPh}_4$ | 8.8 | 43.8 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{BPPh}_4$ | 6.4 | 39.4 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{Cl}_2\text{H}_2\text{O}$ | 7.9 | 57.5 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{BPPh}_4$ | 5.9 | 42.7 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]\text{BPPh}_4$ | 9.4 | 27.7 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]$ | 10.2 | 21.6 |
| $[\text{Pt}(\text{SCNEt}_2)(\text{PPPh}_3)_2]+$ excess PF$_6^-$ | 10.0 | 31.0 |

* In $\Omega^{-1} cm^{-2} mol^{-1}$.}
Finally, prolonged reaction of Pt(S2CNMe2)2 and an excess of PR3 in CH2Cl2 followed by precipitation with diethyl ether gives a mixture of [Pt(S2CNMe2)(PR3)2]Cl2H2O and CH2(S2CNMe2)2. The latter, which can be extracted with benzene, is best prepared by shaking a mixture of NaS2CNMe2, 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.\(^{1,2}\)

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 \(S_2P(OEt)_2\) parallel those reported earlier for the PMePh2 derivative\(^3\) (Tables 1 and 2). For [Pt(S2COEt2)2PPh3] in CS2, coalescence of the CH3 triplet occurs at 188 K, 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^-) = S_2COEt, S_2COCH2Ph, S_2P(OEt)_2\] with an excess of PR3 is of considerable interest. Fackler and Seidel\(^4\) have studied the former in some detail and have convincingly demonstrated that the final products are the novel compounds [(R3P)2S2CO] (I) and [(R3P)2PdS2P(O)Et] (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 work\(^5,6\) for the reaction of platinum and palladium dithiocarbamidoxides 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 ion 1:2 complex, followed by nucleophilic attack of the xanthate anion on the alkoxy-group of the co-ordinated xanthate to give the neutral dithiocarboxylate complex and a xanthate ester. A similar scheme involving the ionic intermediate [M(S2P(OEt)2)2(PR3)2]...
(S2P(OEt)3) would explain the formation of [(R"P)2MS2-P(0)(OEt)]. This mechanism accounts for all the experimental observations made by Fackler and Seidel. For example, the observation that platinum compounds undergo the rearrangements 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 benzylcarbocation 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)3 and an excess of PPh3 in CH2Cl2, immediate colouration, 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 (I) (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 [(PPPh3)Pt(S2CO)]. This clearly demonstrates that both nucleophilic attack of S2COEt on a platinum-phosphorus bond and on a co-ordinated alkyl 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 NaBP3 to an acetone-methanol solution of Pt(S2COEt)3 and an excess of PPh3 (within 30 s of mixing) gives a precipitate of [Pt(S2COEt)2PPh3]BP3, 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)3)2 with an excess of PPh3 in CH2Cl2 produces rapid colouration 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 [PPPh3(Pt-S2P(OEt)3)] together, in the latter case, with some [Pt(S2P(OEt)3)2PPh3]. However, it is possible to isolate and characterise [Pt(S2P(OEt)3)2PPh3]BP3 (Tables 1, 3, and 4) by addition of an excess of NaBP3 to an acetone-methanol mixture of the same reactants. It should be noted that for xanthate and dithiophosphate, there is no evidence here, or elsewhere, for side-reactions with chlorinated solvents.

Conclusion.—Reaction of platinum (and palladium) dithioacetyl 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) = S2PR3 (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 S2PR3 on the metal. Similar processes occur for S2P(OEt)2, S2CNR2, and S2CNPh2, but, in addition, competing nucleophilic attacks on a co-ordinated alkyl 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 earlier2,3 the very recent brief mention of 'essentially planar PPh3-P co-ordination for Pt(S2PPh2)2[PtS2CO] with the dangling sulphur atom 3.5-8 Å from the platinum(II) ion'19 (cf. in Pd(S2PPh3)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. 1H 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 Köfler hot-stage microscope and are uncorrected.

Materials.—Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine, sodium diethylthiocarbamate (B.D.H.); sodium dimethylthiocarbamate (Ralph Emanuel). The other tertiary phosphines were prepared by standard literature methods.

**NN-Dialkylidithiocarbamate Complexes.** — Bis(NN-di¬
methylidithiocarbamate)platinum(II). Potassium tetrachloro-
platinatet(II) in a minimum volume of hot water was mixed
with an ethanolic solution of an excess of sodium NN di-
methylidithiocarbamate and shaken for 24 h. The yellow
product was washed with water and ethanol and air dried,
m.p. 305—308° (Found: C, 16-8; H, 2-9; N, 6-3. Calc. for
C_12H_12N_2PtS_4; C, 16-6; H, 2-8; N, 6-4%). Bis(NN-di-
ethyldithiocarbamate)platinum(II) **m.p. 245—250°C** was
prepared in the same way using K_2PtCl_4 and Na_2S_2CNEt-
_2H_2O.

Bis(NN-dimethylidithiocarbamate) palladium(II). **** Palladium(II) acetate was dissolved in benzene-dichloro-
methane and shaken for several hours with an ethanolic
solution containing an excess of Na_2S_2CNEt_2H_2O. The
yellow precipitate of the product was filtered off, washed with
water and ethanol, and air-dried (Found: C, 20-3; H, 3-3; N, 7-5.
Calc. for C_9H_14N_2PdS_4; C, 20-8; H, 3-5; N, 8-1%).

Bis(NN-diethylidithiocarbamate)triphenylphosphineplati-
num(II). Bis(NN-diethylidithiocarbamate)platinum(II) was
suspended in carbon disulphide and treated with triphenyl
phosphate (< 1: 1 molar ratio). An orange-yellow solution
was immediately formed, together with unchanged Pt-
(S_2CNEt_2)Cl; the latter was removed by filtration. Partial
removal of the solvent followed by cooling (200 K) gave
the yellow crystalline product; this was washed with
diethyl ether and dried in vacuo. Bis(NN-diethylidithio-
carbamate)methylidiphosphineplatinum(II) was pre-
pared in the same way, using a deficiency of PMePh_2 under
nitrogen. Preparation of the PMePh_2 compound was
complicated by the side-reaction between the phosphine
and CS_2. These products are soluble in chloroform, dichloro-
methane, carbon disulphide, and benzene; and insoluble in
ethanol, acetone, and dimethyl sulphoxide.

**NN-Diethylidithiocarbamatebis(methylidiphosphinephos-
phine)platinum(II).** NN-Diethylidithiocarbamate, Pt(S_2C-
NEt_2)Cl (90-90 mmol) in acetonitrile (5 ml) was treated with an excess of methylidiphosphine (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-
Diethylidithiocarbamate)bis(methylidiphosphinephosphine)
platinum(II) NN-diethylidithiocarbamate was made by the same
method. These compounds are very unstable, readily
rearranging to form [Pt(S_2CNMe_2)(PMePh_2)] and free
PMePh_2 on prolonged exposure to benzene, diethyl ether,
or acetone. Attempts to make the corresponding triphenyl-
phosphine and dimethylidiphosphine ionous species were
unsuccessful. The former gave only [Pt(S_2CNMe_2)Cl]_2
and the latter an intractable oil.

**NN-Diethylidithiocarbamatebis(methylidiphosphinephos-
phine)platinum(II) chloride monohydrate.** Method (A).
Pt(S_2CNMe_2)Cl in dichloromethane (dried over MgSO_4)
was treated with a three-fold excess of PMePh_2 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(S_2CNMe_2)(PMePh_2)]Cl 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 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 methylidihydro-
bis(NN-diethylidithiocarbamate), m.p. 70—71°C [Found: C, 42-6; H, 7-1; N, 9-0%]. Another method of preparation is to shake a mixture of
Na_2S_2CNEt_2H_2O, dichlormethane (not scrupulously dried),
and a tertiary phosphine (PPh_3, PMePh_2, or PMePh_3) for
24 h. Solvent removal and trituration of the resulting oil
with light petroleum (b.p. 60—80°C) gave the product
colourless (b.p. and mass 19 and 1H n.m.r. spectroscopy.
The same compound was also formed (but in lower
yield) when the reaction was carried out in the absence of
PPh_3. Complexes [Pt(S_2CNMe_2)(PPh_3)(CH_2Cl_2)]_2
(PK_3—PPh_3, PMePh_2) were also made by the procedure
outlined in method (A), together with some CH_2(S_2CNMe_2).

**NN-Diethylidithiocarbamatebis(methylidiphosphinephos-
phine)platinum(II) chloride monohydrate.** Method A. The
method used was exactly as for the preparation of
[Pt-(S_2CNMe_2)(PMePh_2)]Cl,2H_2O, using a suspension of Pt-
(S_2CNMe_2)Cl, in dichloromethane and a three-fold excess of
PMePh_2. Precipitation with either diethyl ether or light
petroleum (b.p. 60—80°C) gave a mixture of [Pt(S_2CNMe_2)Cl]
(PMMePh_2)Cl,2H_2O and CH_2(S_2CNMe_2). The latter
was also 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,
methylidihydrobis(NN-diethylidithiocarbamate) was isolated
(m.p. 93—98°C) [Found: C, 33-7; H, 5-3; N, 10-9; CH_2(S_2CNMe_2)
requires C, 33-1; H, 5-1; N, 11-0%]. The compound was
also made by shaking a mixture of Na_2S_2CNEt_2, CH_2Cl_2,
and tertiary phosphine (PPh_3, PMePh_2, or PMePh_3); mass
yield (254 [CH_2(S_2CNMe_2)]. 166 [Me_2NCS_2CH_2S]), and 88
(Me_2CS_2S) [ref. 18].

In the absence of tertiary phosphine, only tetramethyl-
thiuriam disulphide (Found: C, 31-3; H, 5-2; N, 11-9. Calc.
for C_9H_14N_2S_4; C, 30-0; H, 5-0; N, 11-7%) and Na_2S_2CNEt_2
were detected.

Method (B). From [Pt(S_2CNMe_2)(PMePh_2)]Cl,2S_2CNMe_2
dissolved in CH_2Cl_2, the deep yellow solution slowly be-
coming colourless. Precipitation with diethyl ether and
evacuation of CH_2(S_2CNMe_2) with benzene gave the white
product.

[Pt(S_2CNMe_2)(PPh_3)Cl]_2CH_2Cl_2 (PK_3—PPh_3, PMePh_2)
and [Pd(S_2CNMe_2)(PMePh_2)]Cl,2H_2O were also made by the procedure outlined in method (A), together
with some CH_2(S_2CNMe_2).

**NN-Diethylidithiocarbamatebis(methylidiphosphinephos-
phine)platinum(II) tetrathiydroporphorane.** [Pt(S_2C-
NEt_2)(PMePh_2)]Cl,2H_2O was dissolved in methanol and treated
with a concentrated acetonitrile solution of NaBP_4. 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 reac-
bion between [Pt(S_2CNMe_2)(PMePh_2)]Cl,2S_2CNMe_2 and
NaBP_4 in ethanol.

Similarly, the complexes [Pt(S_2CNMe_2)(PPh_3)Cl]_2BP_4
[Pt(S_2CNMe_2)(PPh_3)Cl]_2BP_4 (R = Me, Et; PK_3—PPh_3, PMePh_2, PPh_2)
were prepared from [Pt(S_2CNMe_2)(PPh_3)Cl]_2BP_4 and an excess of NaBP_4.

**NN-Diethylidithiocarbamatebis(methylidiphosphinephos-
phine)platinum(II) hexafluorophosphorane.** [Pt(S_2C-
NEt_2)(PMePh_2)]_2BP_4.

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Cl$_2$H$_2$O 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(S$_2$CNMe$_2$)(PMePh$_3$)$_2$]PF$_6$ and [Pt(S$_2$CNMe$_2$)(PPh$_3$)$_4$]PF$_6$ were also prepared by this method.

**O.O’-Diethyl Dithiophosphate Complexes.**—Bis(O.O’-diethyl dithiophosphate)platinum(II) was prepared as described earlier (mp 124°C) [26] (Found: C, 17-2; H, 3-5. Calc. for C$_8$H$_20$O$_4$P$_2$: C, 49-2; H, 3-3%).

Bis(O.O’-diethyl dithiophosphate)(triphenylphosphine)platinum(II). Pt[S$_2$P(OEt)$_2$]$_2$ was shaken with triphenylphosphine (1:1 molar ratio) in dichloromethane to give a 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(S$_2$P(OEt)$_2$)(PPh$_3$)$_2$AsPh$_3$] was prepared in situ by reaction of Pt(S$_2$P(OEt)$_2$)$_2$ and an excess of AsPh$_3$ in CDC$_3$. O.Ethyl dithiophosphatobis(triphenylphosphine)platinum(II). Pt[S$_2$P(OEt)$_2$]$_2$ and PPh$_3$ (ca. 1:3 molar ratios) were refluxed in CHCl$_3$ for ca. 3 h during which time the initial yellow solution slowly became colourless. Removal of solvent and addition of diethyl ether gave a white product. Reaction of Pt(S$_2$P(OEt)$_2$)$_2$ and an excess of PPh$_3$ in CH$_2$Cl$_2$ rapidly gave a colourless conducting solution, presumably containing the ionic [Pt(S$_2$P(OEt)$_2$)(PPh$_3$)$_2$S$_2$P(OEt)$_2$] 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 [PPh$_3$]Pt(S$_2$P(OEt)$_2$).

**O.O’-Diethyl dithiocarbamatebis(triphenylphosphine)platinum(II) tetraphenylborate.** Pt(S$_2$COEt)$_2$ was treated with an excess of PPh$_3$ in a minimum volume of acetone, followed by addition of an aqueous solution of NaBPh$_4$. The white precipitate was well washed with water and diethyl ether and dried in vacuo (40°C). O.Ethyl Dithiocarbonate Complexes.—Bis(O-ethyl dithiocarbonate)triphenylphosphineplatinum(II). Pt[S$_2$COEt]$_2$ and PPh$_3$ (1:1 molar ratio) were shaken in a minimum volume of CHCl$_3$ 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 diethyl ether and dried in vacuo (40°C). The same product (contaminated with a small amount of [Pt(S$_2$CO)-PPh$_3$]$_2$) was also obtained by reaction of Pt(S$_2$COEt)$_2$ with an excess of PPh$_3$ in CHCl$_3$ followed by immediate addition of an excess of light petroleum (b.p. 40–60°C).

(Dithiocarbonate)bis(triphenylphosphine)platinum(II)–chloroform. Pt(S$_2$COEt)$_2$ was shaken with an excess of PPh$_3$ 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 product, which was non-conducting when redissolved in CH$_2$Cl$_2$ (mp 256°C) (Found: C, 49-2; H, 3-3%). Calc. for C$_{38}$H$_{31}$Cl$_3$OP$_2$PtS$_2$: C, 49-1; H, 3-3%.)

O.Ethyl dithiocarbamatebis(triphenylphosphine)platinum(II) tetrachloroplatinate. Pt(S$_2$COEt)$_2$ was treated with an excess of PPh$_3$ in a minimum volume of acetone, followed immediately by addition of an aqueous solution of NaBPh$_4$. The resulting white precipitate was well washed with water and diethyl ether 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 $^1$H n.m.r. spectra.

[21443 Received, 21st June, 1972]

**References**

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. \([\text{MoO(S}_2\text{P(OEt)}_2]_2\), \([\text{Mo}_2\text{O}_3(\text{S}_2\text{COEt})_4] \) and \([\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2] \) (1). Only a few examples of low-valent dithioacid molybdenum compounds are known, e.g. \([\text{Mo(NO)}_2(\text{S}_2\text{CNR}_2)_2] \) (2), \([\text{Mo(CO)}_n(\text{S}_2\text{CNR}_2)_2] \) (n = 2, 3) (3) and \([\text{Mo(CO)}_2(\text{PPh}_3)(\text{S}_2\text{CNR}_2)_2] \) (4). A versatile method of synthesis of low-valent, binuclear molybdenum halides e.g. \(\text{Mo}_2\text{Cl}_4\)\(^{4-}\), \(\text{Mo}_2\text{Cl}_8\)\(^{3-}\) 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-ethyldithiocarbonate:- Treatment of molybdenum (II) acetate (6) with potassium ethylxanthate in degassed methanol leads to the precipitation of a red crystalline solid analysing closely for \([\text{Mo(S}_2\text{COEt})_2]_2\) (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
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b From F. W. Moore and M. L. Larson, Inorg. Chem. 6 998 (1967)
c Nujol mulls.
d KBr discs

e Band energy maximum (10³ cm⁻¹)

f Maximum molar extinction coefficients (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.

b) Monothiobenzoate:- Reaction of molybdenum (II) acetate with ammonium monothiobenzoate in degassed methanol gives a red precipitate of [Mo(SOCPh)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. Packler 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 2.12 Å).
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 (\( \nu_{CO} \) 1465 cm\(^{-1}\); \( \nu_{CS} \) 960 cm\(^{-1}\)) which is consistent with either of the structures shown below (cf. the structure of \([Ni(PhCOS)_2]_2EtOH\) (10) with \( \nu_{CO} \) 1508 cm\(^{-1}\); \( \nu_{CS} \) 958 cm\(^{-1}\) (9)).

\[
\begin{array}{c}
\text{Mo} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\quad \text{or} \quad
\begin{array}{c}
\text{Mo} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

(c) \(N,N^1\)-Dialkylthiocarbamates:— Reaction of molybdenum (II) acetate in a degassed minimum volume of methanol with excess \(NaS_2CNR_2\) (R = Et, \(^1\)Pr) gives immediate crystalline green precipitates which analyse closely for \([Mo(S_2CNR_2)_2]_n\) (D). Unfortunately, it was impossible to obtain molecular weights because of the very rapid oxidation to purple \([MoO_3(S_2CNR_2)_4]\). 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 \([Mo(S_2CNR_2)_2]_n\) (E) are obtained but these have a more complicated \(^1\)H n.m.r. spectra than compounds D. In fact, \(^1\)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 Mo₂(OCOCH₃)₄ and excess NH₄S₂PPh₂ in ethanol, incomplete substitution of acetate occurs giving a very insoluble orange precipitate of composition [Mo(OCOCH₃)(S₂PPh₂)]ₙ (F). However, if [Mo₂(OCOCH₃)₄] is reacted with diphenylphosphinodithioic acid in benzene or F is treated with HS₂PPh₂ in benzene, a very insoluble green compound of formula [Mo(S₂PPh₂)₂]ₙ is formed. Neither of these compounds appear to exhibit νMo = O or νMo-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(dialkyl-phosphinodithioato)-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

Reprinted from
JOURNAL
OF
THE CHEMICAL SOCIETY
DALTON TRANSACTIONS
1973
Metal Complexes of Sulphur Ligands. Part IV. 1 Reaction of Bis(dialkylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group VB Atoms

By David F. Steele and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of the complexes [Pt(S2PR2)2]R (R = Me or Et) with tertiary phosphines gives four co-ordinate complexes [Pt(S2PR2)2(PR3)] and [Pt(S2PR2)(PR3)2]S2PR2. Variable-temperature 1H 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 [Pt(S–S)2ER3] [(S–S) = –S2CNEt2, –S2P(OEt)2, or –S2PMe2; E = P or As] suggests a concerted mechanism in which both bond-breaking and bond-making steps are important. For the complex [Pd(S2PMe2)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 NaBPh4 or NaPF6 to solutions containing the ionic species provides a general method of synthesising the complexes [M(S2PR2)(PR3)2]X (M = Pt or Pd; R = Me or Ph; X = BPh4− or PF6−). For M = Pt and X = BPh4−, these complexes readily react with Ph4AsX (Y = Cl, Br, or I) giving Ph4AsBPh4 and (Pt(S2PMe2)(PR3)2)Y. However, for the complexes [Pd(S2PMe2)(PR3)2]BPh4 (R = Me or Ph) dissolution in CH3CN–EtOH:CH3CN–EtOH (Y = Cl or Br), or in acetone containing added halide ion produces rapid rearrangement to give [Pd(S2PR2)2Y(PPh3)]. This rearrangement does not occur for X = PF6− and a tentative mechanism involving a labile π- or σ-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 [M(S–S)2] [M = Pt or Pd; (S–S) = –S2PPh2, –S2CNR2, –S2COR, or –S2P(OEt)2] with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate adducts [M(S–S)2PR3] and [M(S–S)(PR3)2](S–S) with unidentate–bidentate and bidentate–ionic dithio-ligand coordination respectively. Similar results were briefly reported by Tebbe and Muetterties 3 for the complex [Pd(S2PF2)2]. It has also been demonstrated that the ionic complexes readily reverted to [M(S–S)2PR3] when dissolved in non-polar solvents via nucleophilic attack by (S–S)− on the metal.1,2 Furthermore, variable-temperature 1H n.m.r. studies on the platinum 1:1 adducts of the dithiocarbamato- and ditiophosphato-complexes indicated rapid interchange of the uni- and bi-dentate 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 [M(S2PPh2)2ER3] complexes 3 since phenyl groups are not amenable to such 1H 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 R, we have carried out a study of the reactions of the complexes [M(S2PR2)2] (M = Pt or Pd; R = Me or Et) with ligands containing Group VB atoms and the results are reported below.


RESULTS AND DISCUSSION

Complexes of Stoichiometry \([\text{M(S}_2\text{PR}_2)_2\text{ER}_3']\).—Reaction of the complex \([\text{Pt(S}_2\text{PMe}_3)_2\text{PPh}_3]\) with tertiary phosphines (1:1 molar ratio) in benzene or chloroform gave immediate yellow solutions from which complexes of stoichiometry \([\text{Pt(S}_2\text{PMe}_3)_2\text{PR}_3']\) were readily isolated by concentration and precipitation with pentane. These complexes are diamagnetic (sharp \(^1\text{H} \text{n.m.r. signals}) and non-conducting in dichloromethane. For the complex \([\text{Pt(S}_2\text{PMe}_3)_2\text{PMe}_2\text{Ph}]\), however, coalescence was registered by concentration and precipitation with pentane. These complexes are diamagnetic (sharp \(^1\text{H} \text{n.m.r. signals}) and non-conducting in dichloromethane. For the complex \([\text{Pt(S}_2\text{PMe}_3)_2\text{PMe}_2\text{Ph}]\), however, coalescence was registered by concentration and precipitation with pentane. These complexes are diamagnetic (sharp \(^1\text{H} \text{n.m.r. signals}) and non-conducting in dichloromethane.

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 283 K has already been quoted in Table 2 (ref. 1) for the complex \([\text{Pt(S}_2\text{PMe}_3)_2\text{PPh}_3]\), a full line–shape analysis has now been performed on the complexes \([\text{Pt(S}_2\text{PMe}_3)_2\text{ER}_3']\) (ER\(_3') = \text{PPh}_3, \text{PMe}_3\text{C}_6\text{F}_5, \text{or AsPh}_3\) as well as \([\text{Pt(S}_2\text{CNET}_3)_2\text{PPh}_3]\) and \([\text{Pt(S}_2\text{P(OEt)}_2)_2\text{PPh}_3]\)

### Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>(\tau) Value (^b)</th>
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</thead>
<tbody>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PPh}_3])</td>
<td>CHCl(_3)</td>
<td>7.99</td>
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<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PMe}_2\text{Ph}])</td>
<td>CHCl(_3)</td>
<td>7.99</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PMe}_2\text{Ph}])</td>
<td>CCl(_4)</td>
<td>7.99</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PMe}_2\text{Ph}])</td>
<td>CCl(_4)</td>
<td>7.99</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PR}_3'])</td>
<td>CHCl(_3)</td>
<td>7.99</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PR}_3'])</td>
<td>CCl(_4)</td>
<td>7.99</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PR}_3'])</td>
<td>CCl(_4)</td>
<td>7.99</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_3)_2\text{PR}_3'])</td>
<td>CCl(_4)</td>
<td>7.99</td>
</tr>
</tbody>
</table>

\(^a\) At 291 K unless otherwise stated. \(^b\) All doublets with \(J\) \text{PH} 12.0 Hz. \(^c\) Triplet of doublets (platinum), \(J\) \text{PH} 38.0, \(J\) \text{RE} 11.8 Hz; doublet (palladium) \(J\) \text{PH} 11.0 Hz. \(^d\) Phenyl resonance; complex multiplet. \(^e\) Numbers in parentheses indicate normalised integrated intensities. \(^f\) Measured at 223 K. \(^g\) Resonances too close to integrate separately. \(^h\) Two resonances of total intensity \([\text{i}]. \(^i\) From the complex \([\text{Pt(S}_2\text{PMe}_3)_2\text{PPh}_3]\) \([\text{S}_2\text{PMe}_3\text{C}_6\text{F}_5]\) with rapid bidentate–ionic exchange. \(^j\) From the complex \([\text{Pt(S}_2\text{PMe}_3)_2\text{PPh}_3]\) \([\text{S}_2\text{PMe}_3\text{C}_6\text{F}_5]\) with rapid unidentate–bidentate exchange. \(^k\) Since \(^1\text{H} \text{n.m.r. type spectrum, the coupling constant is } [J\text{PH} + J\text{PH}] = 9.5 \text{ Hz.}

[\text{Pt(S}_2\text{PMe}_3)_2\text{PPh}_3]\), 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 \([\text{Pt(S}_2\text{PMe}_3)_2\text{AsPh}_3]\). However, with \text{PMe}_3\text{C}_6\text{F}_5\text{ or AsEt}_3\text{ (for } M = \text{Pt})\) the products are too soluble to be satisfactorily isolated and, although treatment with ammonia and pyridine indicated some reaction in solution, attempts 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. \([\text{Pt(S}_2\text{PMe}_3)_2\text{PPh}_3]\)].

Like the analogous complexes \([\text{M(S}_2\text{S}_2)\text{ER}_3']\), these 1:1 adducts apparently undergo a rapid intramolecular rearrangement reaction, since, at ambient temperatures, all the complexes exhibited a single doublet for the dimethylphosphinothioate methyl protons (with \(J\text{PH} \approx 13.0 \text{ Hz.}\) 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 \([\text{Pt(S}_2\text{PMe}_3)_2\text{PR}_3']\) (PR\(_3') = \text{PMe}_3\text{Ph}_3\text{ or PMe}_3\text{Ph}_2\) 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

\* Whilst this work was in progress, complete characterisation of the complexes \([\text{M(S}_2\text{PR}_2)_2]\) (M = Ni, Pd, or Pt; R = Me, Ph, F, CF\(_3\), or OEt) was reported (R. G. Cavell, W. Byers, E. D. Day, and P. M. Watkins, Inorg. Chem., 1972, 11, 1988), 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.  

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 [Pt(S2P(OEt)2)2(PPh3)], activation parameters obtained in CH3Cl2 and CH2Cl2-CS2 (1 : 1) were very similar, indicating the absence of a solvent-assisted bond-rupture mechanism. However, examination of the data for (S-S) = S2PMe2 reveals that the rate of rearrangement is dependent on the ligand ER3'. The relative rates are in the order PMe2Ph ~ PMePh2 ≫ PPh2C6F5 ~ PPh3 > AsPh3, clearly indicating that cleavage of the metal-sulphur bond trans to ER3' is an important factor in the rate-determining step. However, another important observation is that, although for ER3' = PPh3 free energies of activation for complexes with different dithio-ligands are quite similar (54—57 kJ mol⁻¹), the enthalpies of activation for the ~S2CNEt2 and ~S2P(OEt)2 complexes (29 and 33 kJ mol⁻¹ respectively) are much lower than that for the ~S2PMe2 complex (54 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 ΔSₚ 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 ~S2CNEt2 > ~S2P(OEt)2 > ~S2PR3, then the lower enthalpy values for the stronger nucleophiles suggest that the bondbreaking 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 entropy values [a dissociative mechanism would give rise to a positive entropy term] and the tendency for rearrangement. This clearly indicates the lower nucleophilicity of ~S2PMe2 compared to ~S2CNR2 (cf. ref. 1). For the PPh3 complex, variable-temperature ¹H n.m.r. studies (in CH3Cl2) showed the same phenomenon as observed earlier ¹ for [Pt(S2CNR2)(PMePh2)].S2CNR2, i.e. stabilisation of the ionic species at lower temperature (Table 1). However, in this instance, the complexity of the spectrum prevented attempts to estimate the equilibrium constant for this process from the ¹H n.m.r. data.

Reaction of the complex [Pd(S2PMe2)] with an excess of PR3' in methanol also gave some ionic products (conductivity evidence) but, on attempted isolation, these rapidly reverted to the 1:1 complexes. This is to be compared with the successful isolation of the pure ionic ~S2PPh3 palladium complexes ² (except for PPh3 and P(PPh3)2], a fact which may reflect the stronger nucleophilicity of ~S2PMe2 compared to ~S2PPh3. For PR3' = PPh3, reaction either in very concentrated methanol solution or with a large excess of phosphine led to precipitation of the complex [Pd(PPh3)3], a reaction not observed with [Pd(S2PMe2)] and PPh3 or with [Pt(S2PMe2)] and any phosphine.


Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>k_{act} (298)</th>
<th>ΔH_{vis}</th>
<th>ΔS_{vis}</th>
<th>ΔG_{vis}</th>
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<tr>
<td>[Pt(S2PMe2)2]PPh3</td>
<td>CH3Cl2</td>
<td>1 114</td>
<td>57-8 ± 1</td>
<td>55-3 ± 1</td>
<td>-19 ± 4</td>
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<tr>
<td>[Pt(S2PMe2)2]PPh3</td>
<td>CH3Cl2</td>
<td>1 008</td>
<td>55-3 ± 1</td>
<td>54-8 ± 1</td>
<td>-4 ± 3</td>
</tr>
<tr>
<td>[Pt(S2PMe2)2]PPh3</td>
<td>CH2Cl2-CS2</td>
<td>1 518</td>
<td>46-0 ± 3</td>
<td>43-5 ± 3</td>
<td>-38 ± 11</td>
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<tr>
<td>[Pt(S2PMe2)2]PPh3</td>
<td>CH3Cl2</td>
<td>1 620</td>
<td>31-5 ± 3</td>
<td>29-2 ± 3</td>
<td>-94 ± 10</td>
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<tr>
<td>[Pt(S2PMe2)2]PPh3</td>
<td>CH3Cl2</td>
<td>1 220</td>
<td>34-0 ± 3</td>
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<tr>
<td>[Pt(S2PMe2)2]PPh3</td>
<td>CH3Cl2</td>
<td>2 008</td>
<td>31-3 ± 3</td>
<td>32-6 ± 3</td>
<td>-72 ± 36</td>
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</table>

entrapment. This reveals that the strength of the bond varies in accordance with the size of the ligand.
However, when the reaction of the complexes [M(S2PMe2)2] and an excess of PR3 (ca. 1: 3 molar ratio) in dilute methanol solution was followed by immediate addition of either sodium tetraphenylborate or hexafluorophosphate, precipitation of the ionic complexes [M(S2PMe2)(PR3)2]X (X = BF4 or PF6) occurred. A similar reaction between the complex [Pd(S2PPh3)3] and PPh4 also resulted in formation of the previously unisolable [Pd(S2PPh3)(PPh3)]+ 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 S2PMe2 and PR3 protons were shifted by ca. 0.2–0.4 ppm 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(S2CNR3)(PF6)]2−X (X = BF4 or PF6) series).1 Reaction of the platinum triphenylphosphine tetraphenylborate complexes with Ph4AsY (Y = Cl, Br, or I) in chloroform led to immediate precipitation of the very insoluble Ph4AsBF4 and the isolation of [Pt(S2PMe2)(PPh3)]BF4 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)(PPh3)]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)(Cl)]PPh3. The corresponding bromo-complexes were isolated if the BPh4− salts were dissolved in CHBr3 or CH2Br2 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 reactions1 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)(PPh3)]PF6 was dissolved in halogenated solvents or in acetone with an excess of halide present, the species was recovered unchanged. The rearrangement is also confined to the PPh4 complexes, since we found no evidence of rearrangement for [Pd(S2PMe2)(PMePh2)]BPh4 when dissolved in chloroform. For the ionic platinum phosphine complexes, irrespective of the nature of the counter-anion, no rearrangement occurred, even after heating under reflux in chloroform-ethanol for 3 days. The arsine complex [Pt(S2PMe2)(AsPh3)]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) complexes4 coupled with the lower stability of these ionic palladium(II) species, as established in earlier studies.1,2 Earlier work3 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 phosphites7 and for formation of metal-phenyl σ-bonds via fission of a boron-carbon bond.8 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 (Ia) or (IIb) followed by displacement by a stronger nucleophile such as halide ion. At present, insufficient evidence is available to distinguish between these two possibilities.

I.r. Studies.—In earlier work with diphenylphosphinodithioates,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>
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<th>Complex</th>
<th>Unidentate</th>
<th>Bidentate</th>
<th>Ionic</th>
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<tr>
<td>[Pt(S2PMe3)]</td>
<td>572w</td>
<td>565w</td>
<td>570w</td>
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<td>598s</td>
<td>570w</td>
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<tr>
<td>[Pt(S2PMe3)(PMePh2)]</td>
<td>578s</td>
<td>570w</td>
<td>570w</td>
</tr>
<tr>
<td>[Pt(S2PMe3)(PPh3)]</td>
<td>612m, 560w</td>
<td>610s</td>
<td>560w</td>
</tr>
<tr>
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<td>572w</td>
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<td>[Pt(S2PMe3)(PMePh2)]</td>
<td>575w</td>
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<tr>
<td>[Pt(S2PMe3)(PPh3)]</td>
<td>570w</td>
<td>570w</td>
<td>570w</td>
</tr>
</tbody>
</table>

1 Ionic region masked by BPh4− vibrations at 605s, 612m, and 625w cm−1.* PF6− Vibrations at 612mv and 560vs cm−1.

Characteristic bands (650–560 cm−1) for determining the mode of co-ordination of the dimethylphosphinodithioato-group to palladium(II) and platinum(II) ions.

These diagnostic band positions were then used to infer the types of bonding in other \( \text{S}_2 \text{PMe}_2 \) 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, \(^2\) 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 \( \text{PS}_2 \) 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 co-ordination mode with those found earlier for \( \text{S}_2 \text{PPh}_2 \) complexes \(^4\) suggests that this is the higher-energy band. A band at 505 cm\(^{-1} \) in the complex \([\text{Pt(S}_2\text{PMe}_2)_2\text{PPh}_3]\) 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 225 grating spectrometer using Nujol mulls on caesium iodide plates. \(^3\) 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 a Varian Mat 500 mass spectrometer and conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Koffer hot-stage microscope and are uncorrected.

**Materials**—Potassium tetrachloroplatinat(II) and palladium(II) chloride (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine (B.D.H.); triphenylarsine (Ralph Emanuel). Triphenylphosphine and triphenylarsine were recrystallised from ethanol before use. Methyldiphenylphosphine was made by the Grignard method from chlorodiphenylphosphine. Sodium dimethyl- and diethyl-phosphine-dithioates were made by standard methods. \(^8\) Triethylarsine and pentafluorophenyl(diényl)phosphine were kindly supplied by Dr. D. I. Nichols. Operations involving free tertiary phosphines (other than PPh\(_3\)) were carried out under an atmosphere of nitrogen.

**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. \(^9\) 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-

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### 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>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_2)_2\text{PPh}_3])</td>
<td>211–214</td>
<td>37.0</td>
<td>37.4</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_2)_2\text{PMe}_2])</td>
<td>156–158</td>
<td>32.9</td>
<td>34.9</td>
</tr>
<tr>
<td>([\text{Pt(S}_2\text{PMe}_2)_2\text{PPh}_3])</td>
<td>226–228</td>
<td>56.9</td>
<td>57.9</td>
</tr>
</tbody>
</table>

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- In \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \); measured in \( \text{CHCl}_3 \) (10\(^+\mbox{m}\)) at 298 K.
- Experimental molecular weight (acetone).
- Calc. molecular weight.
- A band.
- \( \text{S}_2 \text{PMe}_2 \) complex.
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 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. The final activation parameters, obtained by the usual methods, are shown in Table 2 along with assessed error limits.

Bis(dimethylphosphinodithioato)platinum(ii).—Potassium tetrachloroplannardium(ii) (5-00 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 recrystallised from chloroform (Yield 4.25 g, 80%). (Found: C, 10-7; H, 2-6. Calc. for C_{n}H_{m}P_{n}S_{4} P: C, 10-8; H, 9-7%). The same complex was prepared independently by Cavell et al. and the i.r., e.r. and mass spectra are thoroughly discussed in their paper.

Bis(dimethylphosphinodithioato)(triphenylphosphine)platinum(ii).—The complex [Pt(S_{2}PMe_{2})_{2}] was suspended in benzene or chloroform and treated with a 1:1 mole 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 recrystallised from chloroform–pentane. In a similar manner, bis(dimethylphosphinodithioato)(methylidiphenylphosphine)platinum(ii), bis(dimethylphosphinodithioato)(triphenylphosphine)platinum(ii), and bis(dimethylphosphinodithioato)(pentfluorophenyl(diphenyl)phosphine)platinum(ii) were prepared.

Bis(dimethylphosphinodithioato)(triphenylarsine)platinum(ii).—A suspension of [Pt(S_{2}PPh_{2})_{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 off, washed with light petroleum, and air-dried. The products 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) was prepared as for the complex [Pt(S_{2}PMe_{2})_{2}], using K_{2}CO_{3} and Na_{2}S_{2}P_{2}Et_{2}·2H_{2}O (Found: C, 19-4; H, 4-1. Calc. for C_{n}H_{m}P_{n}S_{4} P: C, 19-3; H, 4-0%). H N.m.r. spectrum: δ 8-60 (CH_{2}, doublet of quartets, J_{3,6,9}, 7-0 Hz; J_{6,9,11}, 9-0 Hz) and 8-61 (CH_{2}, doublet of triplets, J_{3,6,9}, 21-0 Hz). I.r. spectrum (650–500 cm\(^{-1}\)): 560,sh, 570s, and 500m cm\(^{-1}\).

Bis(dimethylphosphinodithioato)(triphenylphosphine)platinum(ii) was prepared as for the complex [Pt(S_{2}PMe_{2})_{2}], using K_{2}CO_{3} and Na_{2}S_{2}P_{2}Et_{2}·2H_{2}O (Found: C, 19-4; H, 4-1. Calc. for C_{n}H_{m}P_{n}S_{4} P: C, 19-3; H, 4-0%). H N.m.r. spectrum: δ 8-60 (CH_{2}, doublet of quartets, J_{3,6,9}, 7-0 Hz; J_{6,9,11}, 9-0 Hz) and 8-61 (CH_{2}, doublet of triplets, J_{3,6,9}, 21-0 Hz). I.r. spectrum (650–500 cm\(^{-1}\)): 560,sh, 570s, and 500m cm\(^{-1}\).


innum(ii) was prepared as for the complex [Pt(S_{2}PMe_{2})_{2}]PPh_{3}.
1 H N.m.r. spectrum (301 K): δ 2-60 (phenyl multiplet); 8-06 (CH_{2}, J_{p,CH}, 11-0 Hz); and 8-82 (CH_{2}, J_{p,CH}, 7-0 Hz, J_{p,CH}, 21-0 Hz). On warming, some broadening of the –CH_{2} and –CH_{3} resonances at 293 K occurred indicating still rapid unidentate–bidentate exchange at this temperature. I.r. spectrum (650–500 cm\(^{-1}\)): 590s and 572w,sh cm\(^{-1}\).

Bis(dimethylphosphinodithioato)palladium(ii).—Method (A). Palladium(ii) acetate was dissolved in benzene–acetic acid and heated under reflux for 2 h with a slight excess of sodium dimethylphosphinodithioato dihydrate in methanol. On cooling, the dark-red-brown crystalline product was filtered off and washed with water, methanol, and diethyl ether (Found: C, 13-9; H, 3-4. Calc. for C_{n}H_{m}P_{n}S_{4}: C, 13-5; H, 3-4%).

Method (B). Palladium(ii) chloride was suspended in acetic acid and heated under reflux for 3 h with an excess of Na_{2}S_{2}P_{2}Et_{2}·2H_{2}O. The resulting orange-red solution was filtered hot 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)palladium(ii).—A suspension of the complex [Pt(S_{2}PMe_{2})Cl] in benzene was treated with an excess of triphenylphosphine (ca. 1: 2 mole ratio). On warming gently, a dark red solution was obtained which, on addition of pentane, precipitated the orange-yellow product which was recrystallised from chloroform. A similar method was used to make the complexes [Pt(S_{2}PMe_{2})ClPPh_{3}] and [Pt(S_{2}PMe_{2})PPh_{4}].

(Dimethylphosphinodithioato)bis(triphenylphosphine)palladium(ii) (Found: C, 19-4; H, 4-1. Calc. for C_{n}H_{m}P_{n}S_{4}: C, 19-3; H, 4-0%). H N.m.r. spectrum: δ 8-60 (CH_{2}, doublet of quartets, J_{3,6,9}, 7-0 Hz; J_{6,9,11}, 9-0 Hz) and 8-61 (CH_{2}, doublet of triplets, J_{3,6,9}, 21-0 Hz). I.r. spectrum (650–500 cm\(^{-1}\)): 560,sh, 570s, and 500m cm\(^{-1}\).

solution using a large excess of triphenylphosphine gave instead a yellow crystalline precipitate of tetrakis(triphenylphosphine)palladium(0), m.p. 103—105 °C (lit., 100—105 °C) (Found: C, 75.7; H, 5.1. Calc. for C_{72}H_{60}P_4Pd: C, 75.1; H, 5.2%).

(Dimethylphosphinodithioato)bis(triphenylphosphine)-platinum(II) Chloride.—The complex [Pt(S_2PMe_2)(PPh_3)_2]BPh_4 (0.2 g) was dissolved in chloroform (10 cm^3) and treated with Ph_4AsCl, HCl (0.07 g) (1: 1 mole ratio) in chloroform (5 cm^3). The mixture was stirred for 10 min, the precipitate of Ph_4AsBPh_4 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(S_2PMe_2)(PPh_3)_2]Y (Y = Br^- or I^-) were made in similar manner.

Chloro(dimethylphosphinodithioato)triphenylphosphine-palladium(II).—The complex [Pd(S_2PMe_2)(PPh_3)_2]BPh_4 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). 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 CHBr_3 or CH_2Br_2 plus ethanol (ca. 2%) as solvent, the reaction taking ca. 30 min for completion. The complex [Pd(S_2PPh_2)(Cl)(PPh_3)] was similarly prepared from [Pd(S_2PPh_2)(PPh_3)_2]BPh_4 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 \( \textit{NN} \)-Dialkylthiocarbamato-complexes of Ruthenium(II)

By David J. Cole-Hamilton and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ
Metal Complexes of Sulphur Ligands. Part V.1,2 Dialkyl-, Diaryl-phosphinothioato-and \( \text{NN} \)-Dialkylthiocarbamato-complexes of Ruthenium(II)

By David J. Cole-Hamilton and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Complexes of general formula \([\text{Ru}(\text{S-S})_{2}L_{2}]\) \([\text{S-S}]^{-} = \text{S}_{3}\text{PR}_{2} \) \((\text{R} = \text{Me, Et, Ph}), \text{S}_{3}\text{CNR}_{3} \) \(\text{R} = \text{Me, Et}), \text{S}_{3}\text{COEt}, \) and \(\text{S}_{3}\text{P}((\text{OEt})_{2})\) with ligands containing Group \(\text{Vb}\) donor atoms \((\text{L})\) have been synthesised by the reaction of various ruthenium(II) and (III) tertiary phosphine and phosphite complexes with \(\text{Na}(\text{S-S})\). For \(\text{S-S}^{-} = \text{S}_{3}\text{PR}_{2}\) these compounds are readily carbonylated to give the monocarbonyls \([\text{Ru}(\text{S-S})_{2}L\text{(CO)}]\). However, the dicarboxyls can be synthesised directly, from ruthenium carbonyl halides and \(\text{NaS}_{3}\text{PR}_{2}\). Although the corresponding dithiocarbamates are resistant to carbonylation, all these compounds undergo ligand exchange reactions with ligands of greater basicity \((\text{L'})\) to give either \([\text{Ru}(\text{S-S})_{2}L']\) and/or \([\text{Ru}(\text{S-S})_{2}L''\text{CO}]\). All these compounds have been thoroughly examined by i.r., mass, and 

1H n.m.r. spectroscopy and the latter indicates a cis-configuration. Most of these compounds also show temperature variable 1H n.m.r. spectra, attributable to facile interconversion of optical enantiomers (for the \(\text{S}_{3}\text{PR}_{2}\) compounds), restricted rotation about the \(-\text{CN}\) bond (for the \(\text{S}_{3}\text{CNR}_{3}\) compounds), and, in some cases, hindered rotation about the ruthenium-phosphorus bonds.

Finally, for \([\text{Ru}(\text{S-S})_{2}L\text{(PMePh}_{2})_{2}]\) carbonylation gives, in addition to \([\text{Ru}(\text{S-S})_{2}L\text{(PMePh}_{2})_{2}\text{CO}]\), two isomers of formula \([\text{Ru}(\text{S}_{3}\text{P}_{2}L')_{2}\text{(PMePh}_{2})_{2}\text{CO}]\). The structures of these compounds have been established by 1H, 31P 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 \([\text{M(S-S)}_{2}]\) compounds \([\text{M} = \text{Pt, Pd}; \text{(S-S)}^{-} = \text{S}_{3}\text{PR}_{2} \) \((\text{R} = \text{Me, Et, Ph}), \text{S}_{3}\text{CNR}_{3} \) \(\text{R} = \text{Me, Et}), \text{S}_{3}\text{COEt}, \) and \(\text{S}_{3}\text{P}((\text{OEt})_{2})\) with ligands containing Group \(\text{Vb}\) donor atoms \((\text{L})\) 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 \([\text{M(S-S)}_{2}L]\) and \([\text{M(S-S)L}_{2}]\) (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 dithio-ligand, 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 dithiocacids 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.

3 (a) D. J. Cole-Hamilton and T. A. Stephenson, to be published.
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 dithioacid ligands has been confined to relatively few papers and most of these have been concerned with complexes containing NN-dialkyl-dithiocarbamato-groups. Thus, complexes such as [Ru(S$_2$CNRR')$_2$] (R = Me, Et, Ph), 8 [Ru(S$_2$CNCH$_2$)$_2$(CO)$_2$]$_6$, 9 [Ru(S$_2$CNR$_2$)$_2$(CO)$_2$] (R = Me, PhCH$_3$)$_2$, 8 [Ru(S$_2$CNRR')$_2$(CO)$_2$] (R = Me, PhCH$_3$)$_2$, 8 [Ru(S$_2$CNRR')$_2$(PF$_3$)$_2$] (R = Me, Et, Ph)$_2$, 9 [Ru(S$_2$CNEt)$_2$(Me$_2$SO)$_2$], 10 [Ru(S$_2$CNRR')$_2$(S$_2$CF$_3$)$_2$] (R = R' = Me, Et; R = Me, R' = Ph) 11 and [Ru(NO$_3$)-(S$_2$CNRR')$_2$] (R = Me, Et) 12 have been reported but the last is the only example to date of a ruthenium compound containing a danging dithioacid group. Related 1,2-dithiole complexes of ruthenium of type [Ru(S$_2$C$_x$(CF$_y$)$_z$)(CO)$_n$(ER$_3$)$_m$]$_n$ (n = 1; 0; E = P, As) have also been recently reported. 13

In contrast, apart from brief references to the synthesis of [Ru(S$_2$Pr$_3$)$_3$] (R = Et, 14 Ph), 15 no investigation of ruthenium dialkyl (or diaryl)phosphinodithioato species has been made.

By analogy with our earlier palladium and platinum studies, 13 our first attempts to synthesise a range of ruthenium dithioacid compounds were made either by reacting tertiary phosphines directly with [Ru(S$_2$Pr$_3$)$_3$] or by refluxing an ethanolic solution of RuCl$_3$·H$_2$O, Na$_3$S$_2$Pr$_2$, and PMe$_3$Ph. In both cases, the main product was [Ru(S$_2$Pr$_3$)$_3$], which provides an effective demonstration of the substitutial inertness of the ruthenium(II) (25) coordination sphere in this instance. Therefore, we tried another method, which has been successfully used to prepare other metal dithioacid complexes; namely, direct reaction between metal halogeno-complexes and an alkali metal salt of the appropriate dithioacid.

\[ \text{H}_2\text{RuCl}_2\text{Fe(CO)}_3\text{Cl} + \text{NaS}_2\text{CMeMe}_2 \rightarrow (\text{H}_2\text{RuCl}_2\text{Fe(CO)}_3\text{CMeMe}_2 + \text{NaCl}) \]

Thus, when [RuCl$_3$(PF$_3$)$_3$]$_2$ and [RuCl$_3$(PET$_3$)$_3$]$_2$, 16 [RuCl$_3$(PET$_3$)$_3$]$_2$, 18a [RuCl$_3$(PMe$_3$Ph)$_3$]$_2$, 19

- Shorter reaction times with stoichiometric amounts of Na$_3$S$_2$Pr$_2$ give paramagnetic species which have not been completely characterised to date.

or mer-[RuCl$_3$(PMe$_3$Ph)$_3$]$_2$ 20 are gently refluxed in ethanol with an excess of Na$_3$S$_2$Pr$_2$ (R = Me, Et, Ph) for ca. two hours orange solutions are formed. On cooling these solutions and after filtering off any precipitate of sodium chloride red or orange crystals of composition [Ru(S$_2$Pr$_3$)$_2$L$_2$] (A = L = tertiary phosphine) are deposited in high yield.* Similar products are formed using acetone or methanol as solvent, except for [RuCl$_3$(PMe$_3$Ph)$_3$]Cl in methanol when a red solid, believed to be of composition [Ru$_6$Cl$_6$(PMe$_3$Ph)$_6$(S$_2$Pr$_3$)$_3$] is also precipitated. Similar compounds can be obtained by pyrolysis of [RuCl$_3$(PPh)$_3$]$_2$_S$_2$Pr$_3$Cl (cf. the pyrolysis of [RuCl$_3$(PET$_3$)$_3$]Cl giving [RuCl$_3$(PET$_3$)$_3$]$_2$) and these will be discussed in more detail in a later publication. In this instance, the dimer is readily separated from [Ru(S$_2$Pr$_3$)$_2$(PMe$_3$Ph)$_3$] by the technique of dry column chromatography. 22 For [RuCl$_3$(PPh)$_3$]$_2$ and Na$_3$S$_2$PPh$_2$, [Ru(S$_2$PPh$_2$)$_2$(PPh)$_3$]$_2$ 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(S$_2$PPh$_2$)$_2$(PPh)$_3$]$_2$ and [Ru(S$_2$PPh$_2$)$_2$(PPh)$_3$]$_2$ is probably formed. (Cf. the formation of mono- and bis-carbonyldithiocarbamato-ruthenium complexes 8 and [RuCl$_3$(PPh)$_3$]$_2$ (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(S$_2$PPh$_2$)$_2$(PPh)$_3$]$_2$ 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 osmetry and by an X-ray analysis 40 on [Ru(S$_2$PET$_3$)$_2$(PMe$_3$Ph)$_3$]$_2$. The compounds are non-electrolytes and diamagnetic (by Evans' method), 20 and exhibit sharp $^1$H n.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 ...
addition of an excess of tertiary phosphine, is also dependent on the nature of L, a qualitative order being PPPh₃ > PMePh₂ > PMe₃Ph. The solvent medium is also important, since studies indicate that increasing the percentage of CDCl₃ in CDCl₃-CD₂Cl₂ mixtures increases the rate of oxidation.

In the reaction of [RuCl₄(P(OPh)₃)]₂⁺ with an excess of Na₅S₂P₂R₂, 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 ethynyl 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 1 |
|---|---|---|---|
| Complex | Colour | M.p. (°C) | Found % | Required % |
| cis-[Ru(S₂PMe₂)₂(PPh₃)₄] | Red | 103-105 | 64:2 4:7 | 64:1 4:5 |
| cis-[Ru(S₂PMe₂)₂(PMe₂Ph₂)₄] | Orange | 116-118 | 50:1 4:4 | 60:1 4:6 |
| cis-[Ru(S₂PMe₂)₂(PMe₂Ph₃)₄] | Orange | 247-248 | 54:7 4:7 | 64:7 4:8 |
| cis-[Ru(S₂PMe₂)₂(PMePh₂)₄] | Orange | 279-280(d) | 47:8 5:0 | 47:9 5:1 |
| cis-[Ru(S₂PMe₂)₂(PMePh₃)₄] | Orange | 212(d) | 38:3 5:2 | 38:3 5:4 |
| cis-[Ru(S₂PMe₂)₂(PMePh₃)₄] | Orange | 158 | 48:7 5:6 | 49:3 5:4 |
| cis-[Ru(S₂PMe₂)₂(PMePh₃)₄] | Red | 156-157 | 42:7 6:1 | 42:7 6:1 |
| cis-[Ru(S₂PMe₂)₂(PMePh₃)₄] | Red | 124-125 | 56:3 5:3 | 56:7 5:4 |
| cis-[Ru(S₂PMe₂)₂(PMePh₃)₄] | Red | 168-169 | 38:1 4:8 | 38:3 4:9 |
| cis-[Ru(S₂PMe₂)₂(PPh₃)₄] | Orange | 204-206 | 42:8 5:5 | 42:8 5:5 |
| cis-[Ru(S₂CNCMe₂)₂(PPh₃)₄] | Orange | 199-200 | 54:2 4:7 | 54:2 4:4 |
| cis-[Ru(S₂CNCMe₂)₂(PPh₃)₄] | Orange | 198-199 | 53:0 4:6 | 52:0 4:6 |
| cis-[Ru(S₂CNCMe₂)₂(PPh₃)₄] | Orange | 123-125 | 43:3 4:3 | 720* 4:2 |
| cis-[Ru(S₂CNCMe₂)₂(PPh₃)₄] | Orange | 161-163 | 37:3 4:4 | 37:3 4:3 |
| cis-[Ru(S₂CNCMe₂)₂(PPh₃)₄] | Yellow | 34-44 | 30:2 4:6 | 30:2 4:5 |
| cis-[Ru(S₂CNCMe₂)₂(PPh₃)₄] | Yellow | 103-104 | 40:0 3:9 | 40:1 3:9 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 117-119 | 19:3 4:4 | 19:1 4:2 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 104-106 | 40:8 4:3 | 40:9 3:9 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 95-115(d) | 59:3 4:7 | 54:5 4:7 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 134-135(d) | 38:2 5:2 | 38:6 5:2 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 102-108(d) | 37:4 5:1 | 38:6 5:2 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 89-90 | 47:8 3:2 | 47:6 3:1 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 159-160 | 17:9 3:0 | 17:7 2:9 |
| cis-[Ru(S₂CNCMe₂)₂(PMe₂Ph₂)₄] | Yellow | 239-231 | 24:5 3:1 | 24:8 3:0 |

* Molecular weight measured osmotically at 37° in benzene. * Molecular weight from parent ion peak (¹⁹Ru isotope) in mass spectrum. * Sublimes at 160 °C. * Configuration C. * Configuration D. * Sublimes at 170 °C.

in refluxing ethanol for one hour, reaction with an excess of Na₅S₂P₂Me₂ gives a sample of [Ru(S₂PMe₂)₂(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)₂(P(OPh)₃)]₂⁺ together with a peak at m/e 780 (¹⁹Ru isotope) which can only arise from the species [Ru(S₂PMe₂)₂(P(OPh)₃)]₂⁺ since there is no way of obtaining a fragment of this mass number by degradation of [Ru(S₂PMe₂)₂(POPh)₃]₂⁺. Consistent with this interpretation, the ¹H n.m.r. spectrum of the resultant oil shows peaks attributable to [Ru(S₂PMe₂)₂(P(OPh)₃)]₂⁺, together with a number of other tertiary phosphite compounds (see Experimental section). However, if the reaction between [RuCl₄(P(OPh)₃)]₂⁺ and excess Na₅S₂P₂Me₂ is carried out in refluxing methanol, even for comparatively short reaction times, a pure sample of [Ru(S₂PMe₂)₂(POPh)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 phosphine complexes.

Muettiettes et al.²⁵ have reported that triphenyl phosphite, when co-ordinated to ruthenium, does not

appear to undergo transesterification by alcohols, whereas such reactions readily occur with the free ligands. Therefore, at first sight, the transesterification of the tertiary phosphite groups in [Ru(S₂PMe₂)₂(P(OPh)₃)] appears surprising. However, since the starting material has four phosphites per ruthenium and the product only two, then two must be released during the reaction, presumably as free tertiary phosphite. This free triphenylphosphite may then be transesterified giving, in the case where methanol is solvent, trimethylphosphite. The trimethylphosphite, forming a stronger nucleophile than its triphenyl analogue, can then replace the co-ordinated P(OPh)₃ groups to give [Ru(S₂PMe₂)(POME)₃]. This conclusion is supported by the observation that [Ru(S₂PMe₂)(P(OPh)₃)] may be recovered unaltered after refluxing in degassed methanol for 24 h. Presumably the ease of formation of the POME₃ complex, compared with the P(OEt)₃ complex, is a reflection of the greater nucleophilicity of the methoxide compared to the ethoxide ion.

Finally, reaction of mer-[RuCl₂(PMe₂Ph)₃] with an excess of Na₂S₂CNMe₂ gives [Ru₂(S₂CNMe₂)₂(PMe₂Ph)₃], analogous to the triphenylphosphine complex reported elsewhere.  

Reactions of [Ru(S-S)₂L₂] Complexes.—All the compounds of type (A) readily react with carbon monoxide under very mild conditions to give the monocarbonyl species [Ru(S₂PR₂)₂L₂(CO)] (B). For L = PPh₃, AsPh₃, R = Me, the same compounds are also formed by prolonged interaction of cis-[RuCl₂(CO)L₂] with Na₂S₂PMe₂. In contrast, in agreement with earlier work, attempted carbonylation of the corresponding [Ru(S₂CNMe₂)₂(PR')₂] compounds (PR'₃ = PMe₂Ph, PPh₃), even under pressure, gives only unchanged starting material. Furthermore, attempts to displace the remaining L group from [Ru(S₂PR₂)₂L₂(CO)] to give [Ru(S₂PR₂)₂(CO)₂] have also proved unsuccessful. However, the dicarbonyl complexes [Ru(S₂PR₂)₂(CO)₃] (R = Me, Ph) have been synthesised from Cs₂[RuCl₄(CO)₂] and Na₂S₂PMe₂ and from [Ru₂(CO)₄] and Ph₂P(SH)₂ combinations respectively. Similarly, reaction of [Ru₂(CO)₄] with tetramethylthiuram disulphide gives the previously characterised [Ru₂(S₂CNMe₂)₂(CO)₃]. A small amount of this product is also formed by prolonged reaction of cis-[RuCl₂(CO)₄(PPh₃)] with Na₂S₂CNMe₂. Although [Ru₂(S₂CNMe₂)₂(CO)₃] does not react with PR₃, the corresponding [Ru(S₂PR₂)₂(CO)₃] are readily converted to [Ru(S₂PR₂)(PR₃)₂(CO)]. Thus, it appears that the products [Ru(S₂PR₂)(L)(CO)] are thermodynamically very stable, being readily formed from [Ru(S₂PMe₂)₂L₂] or [Ru(S₂PR₂)(CO)₃], whereas with (S-S) = S₂CNMe₂ no evidence has been found for the mixed species. For L = PMe₂Ph, reaction of [Ru(S₂PR₂)(PMe₂Ph)₂] and carbon monoxide gives, in addition to [Ru(S₂PR₂)(PMe₂Ph)CO], two other complexes which both analyse for [Ru(S₂PR₂)(PMe₂Ph)₂CO]. 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(S₂S)₂L₂] compounds undergo ligand exchange reactions with other phosphorus ligands of greater basicity. Thus, for [Ru(S₂PR₂)(L₂)], where L = PPh₃ or PMe₂Ph, reaction with PMe₂Ph(L') gives [Ru(S₂PR₂)L(L')]; similarly, both L groups are displaced by L' when L = PPh₃, L' = PMe₂Ph and also with [Ru(S₂CNMe₂)(PPh₃)] and an excess of PMe₂Ph, [Ru(S₂CNMe₂)(PMe₂Ph)] is exclusively formed. These results can be readily rationalised on the basis that the compounds [Ru(S-S)₂L₂] are both sterically and electronically favoured compared with the mixed ligand complexes [Ru(S-S)₂L]'. However, when the phosphine complexes are treated with P(OEt)₃, steric effects become more important. Thus, [Ru(S₂PR₂)(PMe₂Ph)₂] and P(OEt)₃, give only the mixed ligand complex [Ru(S₂PR₂)(PMe₂Ph)(P(OEt)₃)] whereas with [Ru(S-S)₂(PMe₂Ph)₂] and P(OEt)₃, both [Ru(S-S)₂(PMe₂Ph)(P(OEt)₃)] and [Ru(S-S)₂(P(OEt)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(OEt)₃ which will favour the bis-phosphine complex and the greater sterically crowding in the bis-phosphine complex compared to the mixed phosphine-phosphite species.

Spectroscopic Properties of Dithioacid Complexes.—(a) Infrared Spectra. The i.r. spectra of all the complexes reported are rather complicated, showing absorptions due to the tertiary phosphine or phosphite groups, as well as the phosphorodithioate ligands. However, a recent paper from this laboratory indicates that for platinum and palladium(ii) diphenylphosphinodithioate complexes there appears to be an empirical i.r. method of distinguishing between bidentate, ion, and unidentate co-ordination of the S₂PPh₂ group. Thus, bidentate co-ordination is characterised by two bands at 603,570 cm⁻¹ (ionic), 650,660 cm⁻¹; and unidentate, 645,540 cm⁻¹. Similarly, platinum and palladium(ii) dimethylphosphinodithioate complexes 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(S₂PR₂)(CO)₃] or [Ru(S₂PR₂)](complex) and carbon monoxide gives, in addition to [Ru(S₂PR₂)(PMe₂Ph)CO], etc.
The dimethyl and thus shows successive ion peaks of the parent ~$S_2PR_2$~ co-ordination. For the compounds [Ru($S_2PR_2$)$_2$(PMe$_2$Ph)$_2$CO], in addition to the 'bidentate' bands, there are absorptions at 645, 540 cm$^{-1}$ ($S_2PPh_2$) and ca. 600 cm$^{-1}$ ($S_2PFMe_2$), indicative of unidentate co-ordination although 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($S_2PR_2$)$_2$L]$^{2+}$ are observed. For the [Ru($S_2PR_2$)$_2$(PMe$_2$Ph$_2$)CO] compounds, exactly the same parent ion and fragmentation pattern is observed as for [RU($S_2PR_2$)$_2$(PMe$_2$Ph)$_2$] due to ready loss of a $PMe_2Ph$ group. The phosphate complexes containing a carbonyl group give more complicated mass spectra.

**Table 2**

Infrared spectra of various ruthenium dithioacetyl complexes (shoulders in italics)

<table>
<thead>
<tr>
<th>Complex</th>
<th><del>$S_2PR_2$</del> bands (cm$^{-1}$)</th>
<th><del>$S_2PR_2$</del> bands (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PPh$_3$)$_2$]</td>
<td>583</td>
<td>1933 (1945) *</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(P{OMe}$_3$)$_2$]</td>
<td>587</td>
<td>589</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>579</td>
<td>589</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>608, 572, 568</td>
<td>1929 (1948) *</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>609, 570</td>
<td>1939, 1929, (1940) *</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>611, 573</td>
<td>1961, 1944, 1967 *</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>615, 573</td>
<td>1934</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>615, 573</td>
<td>1930</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>615, 573</td>
<td>1955, 1938</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>615, 573</td>
<td>1945, 1958, 1970</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>615, 573</td>
<td>(2042, 1967) *</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>608, 565</td>
<td>(2030, 1960) *</td>
</tr>
<tr>
<td>cis-[Ru($S_2PMe_2$)$_2$(PMe$_2$Ph)$_2$]</td>
<td>608, 565</td>
<td>612, 560</td>
</tr>
</tbody>
</table>

*a* Measured in CHCl$_3$ solution.  
*b* Configuration C.  
*c* Configuration D.  
* Measured in CDCl$_3$ 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 ~$S_2PR_2$~ co-ordination in platinum metal complexes.

(b) **Mass spectra.** The complexes of formula [Ru($S_2PR_2$)$_2$($S_2PR_2$)$_2$] 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-phosphate 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($S_2PMe_2$)$_2$(P{OMe}$_3$)$_2$]~$^+$~ (Table 3) which shows successive loss of methyl groups and oxygen atoms from the phosphate groups.

The carbonyl-containing compounds [Ru($S_2PR_2$)$_2$($S_2PR_2$)$_2$L($CO$)] and [Ru($S_2PR_2$)$_2$($S_2PR_2$)$_2$PMe$_2$Ph$_2$]~$^+$~CO are also more volatile than their bis-phosphate parent compounds and thus give reasonable mass spectra. For L = ~$^+$~ Because of the complexity of the ~$^+$~H n.m.r. spectra of the ~$S_2PR_2$~ compounds, the n.m.r. studies have been confined to the dimethyl (and diphenyl) phosphinodithioato-complexes.

(c) **H N.m.r. spectra.** *(i) Complexes of formula [Ru($S_2PR_2$)$_2$L$_2$].** For L = PMe$_2$Ph or PMe$_2$Ph, the room temperature resonance arising from the methyl groups on the phosphines (a H$_n$PP'H$_n$ second-order type
spectrum \( n = 3 \) or 6 \(^{28}\) consists of a sharp doublet with a broad hump situated between the doublet \(^{*}\) (see Figure 1b). Comparison with other similar ruthenium tertiary phosphine complexes is of interest. Thus, for trans-[RuCl\(_2\)(PM\(_2\)Ph)]\(_3\), the \(^1H\) n.m.r. spectrum consists of a 'virtually' coupled 1,2,1 triplet from the trans phosphines and a doublet arising from the cis-phosphine, due to the fact that in this compound \(J(PP)(\text{trans})\) is very large and \(J(PP)(\text{cis})\) is effectively zero. \(^{29}\) However, in some complexes, where the cis-phosphines are in equivalent chemical environments best explanation for these observations is that the complex has a 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 trans phosphines of cis-[RuCl\(_2\)(CO)(PM\(_2\)Ph)]\(_3\). \(^{29}\) If \((A; L = \text{PM}\_2\text{Ph})\) had a trans-configuration, then the two methyl groups on the one PM\(_2\)Ph ligand would be in identical chemical environments, giving rise to one resonance, irrespective of the rate of rotation about the ruthenium-phosphorus bond. For \(L = \text{PMe}\_3\text{Ph}\), the similarity of the shape of the pseudo-triplet to that for \(L = \text{PM}\_2\text{Ph}\), and for \(L = \text{POMe}\_3\), the close similarity of the observed second-order spectrum with that obtained for cis-[PtX\(_2\)(POMe)]\(_3\) \(^{31}\) is further evidence for cis-stereochemistry in these compounds.

However, full confirmation of cis stereochemistry for all these tertiary phosphine and phosphite complexes comes from an examination of the low temperature \(^1H\) n.m.r. spectra of the methyl groups of the \(\text{S}_2\text{PM}\_2\text{Ph}\) ligands. For cis-[Ru(S\(_2\)PM\(_2\)Ph)]\(_2\)L\(_3\)], two types of inequivalent dithioacid methyl groups (c and d in Figure 2) are present, which should give two signals, each split into a doublet by the \(^{31P}\) nuclei, whereas for trans stereochemistry only one doublet should be observed. Experimentally, the low temperature \(^1H\) n.m.r. spectra of all bis-phosphine and -phosphite compounds consists of two doublets, indicative of cis stereochemistry.

---

**Table 4**

<table>
<thead>
<tr>
<th>Mass no. of (^{102}\text{Ru}) peak</th>
<th>Probable ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>640</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>650 (metastable)</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>690</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>730</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>770</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>810</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>850</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>890</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>930</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>970</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>1010</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
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<tr>
<td>1050</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>1090</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
<tr>
<td>1130</td>
<td>([\text{Ru(S}_2\text{PMe}_2\text{O)}_2\text{P(Ph)}_3\text{CO}]^+)</td>
</tr>
</tbody>
</table>

\(^*\) All peaks show the characteristic ruthenium isotopic pattern.

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**Figure 1** Variable temperature \(^1H\) n.m.r. spectrum of [Ru(S\(_2\)PMe\(_2\)Me\(_2\)PMe\(_2\)Ph)]\(_2\) in CDCl\(_3\): (a) 338 K; (b) 301 K; (c) 253 K

---

also possess than on influenced possible explanation of this is that makes them resonant at even higher fields. Similar effects have been observed in the compounds \(M(S-S\)–\(PR_2)_2\) where the \(R\) and \(R^*\) resonances are shifted \(\tau\) to 0.2–0.4 upfield with respect to their positions in the corresponding \(PF_2^-\) and \(Cl^-\) salts. Also in recent studies on the interaction of benzene with arsenic, antimony, and bismuth dithiocarbamates. For \(L = P(OPh)_{3}\), the higher field doublet resonates at \(\tau\) 8.35. This is lower than that in the \(PPh_3\) complex, presumably because the phenyl groups are further away from the \(\text{syn methyl groups, producing less efficient shielding.}

(ii) Complexes of formula \([Ru(S_2PR_2)_2L(CO)]\) and \([Ru(S_2PR_2)_2L\]'. 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 \(\text{H}^\text{n.m.r.}, an observation consistent with either \(\text{cis or trans stereochemistry. However, for \(L = PMe}_2\) the chemical shifts of the methyl groups 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 \(\tau\) 8.08 (\(L = \text{P(O}Me)_3\)) to \(\tau\) 8.94 (\(L = \text{PPh}_3\)) (Table 5).

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 \(\tau\) 8.08 (\(L = \text{P(O}Me)_3\)) to \(\tau\) 8.94 (\(L = \text{PPh}_3\)) (Table 5). A possible explanation of this is that the lower field doublet arises from the methyl groups \(\text{anti to the phosphorus ligands (d in Figure 2)} and the higher field doublet from the methyl groups \(\text{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 \(\text{syn methyls, making them resonant at even higher fields. Similar effects have been observed in the compounds \([M(S-S\)–\(PR_2)_2]\) where the \(R\) and \(R^*\) resonances are shifted \(\tau\) to 0.2–0.4 upfield with respect to their positions in the corresponding \(PF_2^-\) and \(Cl^-\) salts. Also in recent studies on the interaction of benzene with arsenic, antimony, and bismuth dithiocarbamates. For \(L = P(OPh)_{3}\), the higher field doublet resonates at \(\tau\) 8.35. This is lower than that in the \(PPh_3\) complex, presumably because the phenyl groups are further away from the \(\text{syn methyl groups, producing less efficient shielding.}

(ii) Complexes of formula \([Ru(S_2PR_2)_2L(CO)]\) and \([Ru(S_2PR_2)_2L\]'. 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 \(\text{H}^\text{n.m.r.}, an observation consistent with either \(\text{cis or trans stereochemistry. However, for \(L = PMe}_2\)
<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Dithioligand (Me groups)</th>
<th>$\tau$ Value</th>
<th>$T_c/K$</th>
<th>Me(phosphorus ligand) $\tau$ Value</th>
<th>$T_c/K$</th>
<th>Phenyl groups $\tau$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Me2}$)$<em>2$(P$</em>{Ph2}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>215</td>
<td>7.73 (12.0), 8.94 (12.0)</td>
<td>256</td>
<td>2.4—3.1</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Me2}$)$<em>2$(PMe$</em>{Ph2}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>329</td>
<td>8.28 (12.5)</td>
<td>278</td>
<td>8.05 *(8-9.0)</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Me2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CDCl$_3$</td>
<td>213</td>
<td>8.63 (12-5)</td>
<td>298</td>
<td>8.43 *(9-0.0)</td>
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<td>cis-[Ru(S$<em>2$P$</em>{Me2}$)$_2$(S$<em>2$P$</em>{Ph2}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>232</td>
<td>9.14 (12-0)</td>
<td>278</td>
<td>8.27—8.30</td>
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<td>cis-[Ru(S$<em>2$P$</em>{Me2}$)$<em>2$(P$</em>{OPh}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>257</td>
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<td>330</td>
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<td>9.35 (12-5)</td>
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<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CDCl$_3$</td>
<td>243</td>
<td>9.08 (12-5)</td>
<td>273</td>
<td>8.41 (8-0.0)</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{OPh}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>9.08 (12-5)</td>
<td>278</td>
<td>8.49 *(8-0.0)</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CH$_2$Cl$_2$</td>
<td>253</td>
<td>&gt;300</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<td></td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{OPh}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>298</td>
<td>7.96 (13-0), 8.63 (13-0),</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8.63 (13-0), 8.62 (13-0),</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{OPh}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8.63 (13-0), 8.62 (13-0),</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CDCl$_3$</td>
<td>243</td>
<td>8.70 (13-0), 9.04 (13-0),</td>
<td>&gt;330</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{OPh}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8.70 (13-0), 8.62 (13-0),</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CDCl$_3$</td>
<td>257</td>
<td>8.80 (13-0), 8.80 (13-0),</td>
<td>&gt;330</td>
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<td>CDCl$_3$</td>
<td>301</td>
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<td>&gt;330</td>
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<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CDCl$_3$</td>
<td>257</td>
<td>8.80 (13-0), 8.80 (13-0),</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<td>CDCl$_3$</td>
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<td>&gt;330</td>
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<td>CDCl$_3$</td>
<td>257</td>
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<td>&gt;330</td>
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<tr>
<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{OPh}$)$_2$]</td>
<td>CDCl$_3$</td>
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<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
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<td>&gt;330</td>
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<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{Me2}Ph$)$_2$]</td>
<td>CDCl$_3$</td>
<td>257</td>
<td>8.80 (13-0), 8.80 (13-0),</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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<td>cis-[Ru(S$<em>2$P$</em>{Ph2}$)$<em>2$(P$</em>{OPh}$)$_2$]</td>
<td>CDCl$_3$</td>
<td>301</td>
<td>8.80 (13-0), 8.80 (13-0),</td>
<td>&gt;330</td>
<td>8.19 *(10-0)</td>
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Note: All values are given in °C unless specified otherwise.
For \([\text{Ru(S}_{2}\text{PMe}_{2})_{2}(\text{POMe}_{3})\text{CO}])\) the two higher field doublets are superimposed (Table 5). These two resonances presumably arise from the methyl groups \(\text{syn} \) to the phosphine and \(\text{syn} \) to the phosphite ligands (e and f respectively—Figure 3a). In this instance, although the \(\text{PMe}_{3}\text{Ph} \) group has fewer phenyl rings than \(\text{P(OPh)}_{3} \), those on the phosphate 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-\(\text{PMe}_{2}\text{Ph} \) and bis-\(\text{P(OPh)}_{3} \) complexes are fairly close, being \(\tau \) 8.14 and 8.35 respectively.

For \([\text{Ru(S}_{2}\text{PMe}_{2})_{2}(\text{POMe}_{3})\text{CO}])\), 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-\(\text{P(OMe)}_{3} \) 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-ligands of the \(\text{cis-}[\text{Ru(S}_{2}\text{PMe}_{2})_{2}L_{2}(\text{CO})]\) and \(\text{cis-}[\text{Ru(S}_{2}\text{PMe}_{2})_{2}(\text{CO})_{2}]\) complexes, are temperature invariant up to ca. 330 K (although measurements on \(\text{cis-}[\text{Ru(S}_{2}\text{PMe}_{2})_{2}(\text{PPh})_{2}(\text{CO})]\) at higher temperatures in chlorobenzene indicate similar behaviour to that described below for \([\text{Ru-S}_{2}\text{PMe}_{2})_{2}(\text{PPh})_{2}(\text{P(OPh)}_{3}])\). However, those of the \([\text{Ru(S}_{2}\text{PMe}_{2})_{2}L'_{2}]\) compounds show marked changes at lower temperatures. For example, on warming \([\text{Ru(S}_{2}\text{PMe}_{2})_{2}(\text{PPh})_{2}(\text{P(OPh)}_{3}])\), the four methyl doublets present at low temperature (Figure 4a) begin to broaden, the inner two coalescing at ca. 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](https://example.com/figure4.png)

**Figure 4**: Variable temperature \(^1\text{H} \) n.m.r. spectrum of \([\text{Ru(S}_{2}\text{PMe}_{2})_{2}(\text{PPh})_{2}(\text{P(OPh)}_{3}])\): (a) 233 K in \(\text{CH}_{2}\text{Cl}_{2} \); (b) 283 K in \(\text{CH}_{2}\text{Cl}_{2} \); (c) 310 K in \(\text{CH}_{2}\text{Cl}_{2} \); (d) 383 K in \(\text{CH}_{2}\text{Cl}_{2} \).
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 40 481 983 Hz collapses the doublets labelled e and g whereas irradiation at 40 482 100 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(S₂CNMe₂)₂L₂]. It was reported earlier⁹ that the ¹H n.m.r. spectrum of [Ru(S₂CNMe₂)₂(PPh₃)₂]₃⁺ shows S₂CNMe₂ methyl resonances at 7-7 18 and 7-7 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 acetone), we have obtained a crystalline yellow solid, analysing for [Ru(S₂CNMe₂)₂(PPh₃)₂]MeCO, whose n.m.r. spectrum contains two methyl resonances of the same intensity at 7-7 06 and 7-7 25; there is also a peak at 7-7 86 (acetone). This spectrum is consistent with a cis-configuration. Similarly, for [Ru(S₂CNMe₂)₂(PMe₂Ph)₂], prepared from mer-[RuCl₃(PMe₂Ph)₂], the low temperature ¹H n.m.r. spectrum consists of two pseudo-triplets (PMe₂Ph groups) and two singlets (S₂CNMe₂ 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 again 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(S₂CNMe₂)₂(PPh₃)₂(P(OFPh)₃)₂] 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(S₂CNMe₂)₂(PPh₃)₂] with an excess of PMe₂Ph in ethanol gives two products which both analyse for [Ru(S₂CNMe₂)₂(PMę₂Ph)₂]. The ¹H 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. Hoffmann, J. Chem. Phys., 1965, 88, 2892) confirm that exchange only occurs between groups h, e and g, f respectively.

**Mechanism of Carbonylation of cis-[Ru(S₂PRS)₂(PMe₂Ph)₂].—When cis-[Ru(S₂PRS)₂(PMe₂Ph)₂] (A) (R = Me, Ph) is carbonylated in refluxing ethanol or acetone for a prolonged period, a mixture of cis-[Ru(S₂PRS)₂(PMe₂Ph)CO] (B) and [Ru(S₂PRS)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 B 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(S₂PRS)₂(PMe₂Ph)CO] (D) may be isolated if the carbonylation 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 ¹H n.m.r. (since all the compounds have different spectra) or by observing the change in ν(CO) position since for R = Ph: ν(CO)(D) = 1984; ν(CO)(B) = 1948; ν(CO)(C) = 1946 cm⁻¹ (all measured in CDCl₃). Measurement of the rate of loss of the carbonyl band intensity for D gives a rate constant for this rearrangement reaction of 1.7 × 10⁻⁴ s⁻¹ at 323 K (t₁/₂ = 65 min) and also confirms that the process is first order with respect to D.

Thus, these observations are consistent with the carbonylation 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) retains its usual six-coordinate stereochemistry,† and we therefore have unidentate and bidentate S₂PR₂ groups,‡ there are four possible isomers for compounds of formula [Ru(S₂PRS)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(NO)(S₂CSMe₂)].†³

‡ This is suggested by the i.r. spectra of C and D (see earlier) (cf. [Ru(NO)(S₂CSMe₂)₂]¹⁵)

room temperature $^1$H n.m.r. spectrum of C consists of two doublets (from the $\text{S}_2\text{PMe}_2$ groups) and a 1,3,3,1 quartet for the $\text{PMe}_2\text{Ph}$ groups \textit{i.e.} two overlapping

\[\begin{align*}
\text{(A)} & \quad \text{[Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)$_2$]} + \text{CO} \rightarrow \text{[Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)$_2$CO]} \\
\text{(B)} & \quad \text{[Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)CO]} + \text{PMe$_2$Ph} \rightarrow \text{[Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)$_2$CO]}
\end{align*}\]

\[\text{(C)}
\]

**Figure 5** Possible isomeric forms for $\text{[Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)$_2$CO]}$ assuming bidentate and unidentate $\text{S}_2\text{PR}_2$ co-ordination

1,2,1 \text{ 'virtually-coupled' triplets as is seen for } R = \text{Ph} \text{ (Table 5). At higher temperatures, these collapse to a single triplet although a detailed observation of this process is obscured (for } R = \text{Me} \text{) by the increased tendency to rearrange to compound B at these higher temperatures. In contrast, the two } \text{S}_2\text{PMe}_2 \text{ 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) \textit{i.e.} trans $\text{PMe}_2\text{Ph}$ groups with slow exchange of uni/bidentate $\text{S}_2\text{PR}_2$ 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 dithio-acid ligand.*}

The $^1$H n.m.r. spectrum of D \textit{(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 $^{31}$P n.m.r. spectrum of the complex (Figure 7). The decoupling studies (see Figure 6) also indicate that the 14 line $^1$H n.m.r. spectrum is comprised of 8 doublets (with four of the doublets partially superimposed). \textit{NB: The irradiation frequencies given in Figure 6 are different from the frequencies of the phosphorus nuclei obtained from the Fourier transform spectrum (Figure 7) because the former are obtained from the HA 100 spectrometer (with Schlumberger FS80 frequency synthesiser attachment) whereas the

\[\begin{align*}
\text{(D)} & \quad \text{[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO]} \\
\text{(E)} & \quad \text{[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$]} \\
\text{(F)} & \quad \text{[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$]} \\
\text{(G)} & \quad \text{[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$]}
\end{align*}\]

\[\text{Figure 5} \quad \text{Possible isomeric forms for } [\text{Ru(S$_2$PR$_2$)$_2$(PMe$_2$Ph)$_2$CO]} \text{ assuming bidentate and unidentate } \text{S}_2\text{PR}_2 \text{ co-ordination}\]

\[\text{Figure 6} \quad ^1\text{H N.m.r. spectrum of } [\text{Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO]} \text{ (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.)}

\[\text{Figure 7} \quad ^{31}\text{P N.m.r. spectrum of } [\text{Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO]} \text{ (D) [Ph region] at 114 355 170 Hz; the 8 doublets of Figure 6 all split into two triplets; the } ^1\text{H n.m.r. spectrum then shows that each } \text{S}_2\text{PR}_2 \text{ group is attached to a different phosphorus of a different dithio-acid ligand.}

\[\begin{align*}
\text{Figure 6} & \quad ^1\text{H N.m.r. spectrum of } [\text{Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO]} \text{ (D) [methyl region] at 273 K; irradiating at 40 482 120 Hz decouples 1 and 1'; at 40 480 770 Hz decouples 2 and 2'; at 40 478 777 Hz decouples 3 and 3'; and at 40 477 700 Hz decouples 4 and 4' (note Assignments of 2 and 2', 3 and 3', 4 and 4' are arbitrary.)}
\end{align*}\]

\[\begin{align*}
\text{Figure 7} & \quad ^{31}\text{P N.m.r. spectrum of } [\text{Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$CO]} \text{ (D) [Ph region] at 114 355 170 Hz; the 8 doublets of Figure 6 all split into two triplets; the } ^1\text{H n.m.r. spectrum then shows that each } \text{S}_2\text{PR}_2 \text{ group is attached to a different phosphorus of a different dithio-acid ligand.}
\end{align*}\]

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* A recent note (S. D. Robinson and M. F. Uttley, Chem. Comm., 1972, 1047) reports the synthesis of the analogous $[\text{Ru(OMe)}_2(\text{PPh}_3)_2\text{CO}]$ compound with uni/bidentate acetato-groups but the detailed stereochemistry is not given. \textit{Added in proof:} In the full paper (J.C.S. Dalton, 1973, 1012) the analogous carboxylato-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 equivalent 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 dithioacid ligands. However, addition of methyl iodide to a dichloromethane solution of D produces an immediate increase in conductivity. A similar increase is observed for [Pt(S2PMe2)2(PMe2Ph)] (where un/bidentate co-ordination is well established) and compound C, but with [Pt(S2PMe2)2] and [Ru(S2PMe2)2PMe2Ph] there is no change. This conductivity increase is attributed to the formation of the complex [Ru(S2PMe2)(Me2PMe2)(PMe2Ph)2CO] by methylation of the unco-ordinated sulphur atom. Furthermore, the 1H n.m.r. spectrum of the conducting solution is not significantly different from that of D, except for extra signals at 3 6-96 (SMe group) and 3 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 PMe2Ph groups equivalent) fit the 1H and 31P n.m.r. data. However, (II) and (III) are both possible structures since in both cases hindered rotation about the ruthenium-phosphorus bond 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 S2PMe2 ligand, the two Me groups will always remain inequivalent. However, (III) would be expected to have a ν(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 S2PR2 ligand whereas (II) should have a higher ν(CO) since the CO group is trans to a stronger π-acceptor ligand and hence back donation into the π* orbitals of the CO group will be reduced. This 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 31P n.m.r. spectrum (Figure 7)]. Assuming structure (II) is more feasible than (III), then these phosphorus atoms can be assigned as follows: P1 and P2 belong to the S2PMe2 groups and P3 and P4 to the PMe2Ph groups. This assignment is based on the chemical shift positions of the 31P nuclei compared to those in [Ru(S2PMe2)(CO)2] and [Ru(S2PMe2)2(PMe2Ph)] (see Figure 7) together with the fact that the lower field methyl doublets (which correspond to the S2PMe2 methyl resonances) are decoupled by irradiating at frequencies corresponding to phosphorus atoms P1 and P2. In [Ru(S2PMe2)2(PMe2Ph)CO], the separation between the methyl dithioacid group syn to PMe2Ph 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 P1 (44 Hz). In contrast, those attached to P2 (2 and 2') are only separated by 6 Hz. We therefore assign P1 to the phosphorus atom of the bidentate S2PMe2 group and P2 to the unidentate S2PMe2 group. Finally, since P3 couples to P1 whereas P4 does not (Figure 7) it seems likely that P3 is more nearly trans to P1 than is P4 and therefore P3 and P4 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 PMe2Ph group. This is consistent with the bond lengths found in cis-[Ru(S2PPh2)2(PMe2Ph)]6, where the Ru-S bonds trans to the PMe2Ph 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 PMe2Ph situated trans to each other, together with the favourable energy change associated with the conversion of unidentate to bidentate S2PMe2 co-ordination, results in the expulsion of a PMe2Ph group and the formation of B. Finally, the high affinity of PMe2Ph for ruthenium(II) is demonstrated by its attack on the Ru-S bond trans to PMe2Ph to give C. As was inferred earlier for the ligand exchange reactions of [Ru(S2PR2)2L2] 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(S2PR2)2(PMe2Ph)CO] to give cis-[Ru(S2PR2)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(S₅PMe₂Ph)₂(CO)]₂ reacts with an excess of PMe₂Ph, even in the presence of CO, to give cis-[Ru(S₅PMe₂Ph)(PMe₂Ph)]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 phosphites) and nucleophilicities (tertiary phosphines) towards ruthenium(II) of these other ligands compared to PMe₂Ph, although, doubtless, a similar mechanism of carboxylation is applicable. It is also reasonable to postulate a similar mechanistic scheme for formation of the mixed ligand species [Ru(S₅PR₃)₂(LL)] although, again, no intermediates of type D (or C) have been observed.

Finally, the unsuccessful attempts to carboxylate the cis-[Ru(S₅CNR₂)₂(LL)] complexes are probably due to the stronger nucleophilicity of S₅CNR₂ compared to S₅PR₂ (see reference 1), preventing formation of a compound of type D.

**EXPERIMENTAL**

Microanalyses were by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Molecular weights were determined on a Perkin-Elmer–Hitachi 115 osmometer at 37°C. 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. ¹H N.m.r. spectra and solution magnetic moments (Evans’ method) were obtained on a Varian Associates HA 100 spectrometer and ¹¹P n.m.r. spectra on a Varian XL 100 spectrometer operating in the Pulse and Fourier Transform mode at 40–60 MHz. Heteronuclear 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 Kofler hot-stage microscope and are uncorrected.

**Materials.**—Ruthenium trichloride trihydrate (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine; triphenyl phosphite (B.D.H.); methyldiphenylphosphine (Strem); PPh₃ was made by a standard literature method; carbon monoxide (Air products); Na₅S₅CNMe₂, 2H₂O (Ralph Emanuel). Sodium diethy1- and dimethylphenylphosphinodithioates were prepared as described earlier and ammonium diphosphinodithioate from Ph₃P₂S₃H and ammonia in benzene. Operations involving free tertiary phosphines and phosphites (with the exception of P[OPPh₃]₂ and P[OPh₃]) 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)bis(diphenylphos-

*The one possible exception is with [Ru(S₅PMe₂Ph)₂(PMe₂Ph)]₂ where carboxylation gives a transient species with w(CO) 1907 cm⁻¹ (type D) but unfortunately this could not be separated from starting material.
Starting materials & Volume of EtOH & Reaction time & Yield & Product  
| mer-[RuCl₂(PMe₃)₄] | 50 ml | 4 h | 0.14 g & (66%) | cis-[Ru(S₂PMe₂)₂(PMe₃Ph)₂] |
| NH₃S₂PPh₂ (0.05 g) & 20 ml | 1 h | 0.05 g & (60%) | cis-[Ru(S₂PMe₂)₂(PMe₃Ph)₂] |
| [RuCl₃(PMe₃Ph)₃]Cl (0.08 g) & 70 ml | 3 h | 0.70 g & (100%) | cis-[Ru(S₂PMe₂)₂(PMe₃Ph)₂] |
| mer-[RuCl₂(PMe₃Ph)₃] (0.05 g) & 70 ml | 15 min | 0.70 g & (100%) | cis-[Ru(S₂PMe₂)₂(PMe₃Ph)₂] |
| [RuCl₃(PPh₃)₂] (0.80 g) & 20 ml | 1h | 0.25 g & (48%) | cis-[Ru(S₂PMe₂)₂(PPh₃)] |
| mer-[RuCl₂(PPh₃)₃] (0.50 g) & 25 ml | 3 h | 0.39 g & (71%) | cis-[Ru(S₂PMe₂)₂(PPh₃)] |

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(S₂PMe₂)₂(PPh₃)] (0.10 g) and PMe₃Ph (0.03 ml) were refluxed in acetonitrile 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; 76%).

Reaction of [RuCl₂(PPh₃)₃] (0.60 g) with NaS₂PMe₂ (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 976, [Ru(S₂PMe₂)₂(PPh₃)₂] +; 928, [Ru(S₂PMe₂)₂(PPh₃)₂(PMe₃Ph)] +; 790, [Ru(S₂PMe₂)₂(PPh₃)₂(OEt)₂] +; etc. 1H N.M.R. spectrum (225 K): [Ru(S₂PMe₂)₂(PPh₃)₂(OEt)₂] +; 7.89 (12.5); 8.20 (12.5) [S₂PMe₂]; 5.80; 8.97 (6.0) [Et groups]; [Ru(S₂PMe₂)₂(PPh₃)(OEt)₂] +; 7.91, 8.13 (S₂PMe₂); 5.93; 8.80 (6.0) [Et groups] intensity ratio 6:1 (Found: C, 42.9; H, 4.9. Cis-[Ru(S₂PMe₂)₂(PPh₃)₂(PMe₃Ph)] requires C, 43.9; H, 4.8. Cis-[Ru(S₂PMe₂)₂(PPh₃)(OEt)₂] requires C, 37.0; H, 5.4. For 6:1 ratio, calculated analysis is C, 42.9; H, 4.9%).

Reactions of [RuCl₂(PPh₃)₃] (0.60 g) with NaS₂PMe₂ in refluxing ethanol for 24 h gives, on solvent removal, an oil with mass spectral peaks m/e 928, [Ru(S₂PMe₂)₂(PPh₃)₂] +; 790, [Ru(S₂PMe₂)₂(PMe₃Ph)₂] +; 732, [Ru(S₂PMe₂)₂(PMe₃Ph)₂(OEt)₂] +; 684, [Ru(S₂PMe₂)₂(PMe₃Ph)₂(PMe₃Ph)] +; etc. cis-Bis(dimethylphosphinodithioato)bis(trimethylarsine)ruthenium(II): [RuCl₂(PPh₃)₃] (0.50 g) and NaS₂PMe₂ (0.30 g) were refluxed in methanol (30 ml) for 3 h. The resultant yellow solution was filtered hot, and, after concentration, allowed to slowly crystallise at 273 K for 10 days. The orange crystals so formed were filtered and washed with water, methanol, and n-pentane (0.06 g; 28%). On further solvent removal from the filtrate, an oily white solid was deposited which on recrystallisation was identified as phenol (by its 1H N.M.R. spectrum). The ruthenium complex readily decomposed on air exposure to give a black solid.

cis-Bis(dimethylphosphinodithioato)(triphenylphosphine)(triphenylphosphine)ruthenium(II). — cis-[Ru(S₂PMe₂)₂(PPh₃)₂] (0.08 g) and P(OEt)₃ (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, 0.05 g, 35%). The yellow filtrate was allowed to crystallise overnight to give a sample of cis-[Ru(S₂PMe₂)₂(PPh₃)₂] (0.04 g, 45%).

cis-Bis(dimethylphosphinodithioato)(dimethylphenylphosphine)(triphenylphosphine)ruthenium(II). — cis-[Ru(S₂PMe₂)₂(PMe₃Ph)₂] (0.20 g) was refluxed with P(OEt)₃ (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(dimethylphosphinodithioato)(dimethylphenylphosphine)(triphenylphosphine)ruthenium(II). — cis-[Ru(S₂PMe₂)₂(PMe₃Ph)₂] (0.08 g) and P(OEt)₃ (0.05 ml) were refluxed 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(dimethylphosphinodithioato)carbonyl(triphenylphosphine)ruthenium(II). — (a) cis-[Ru(S₂PMe₂)₂(PPh₃)₂] (0.10 g) and PPh₃ (0.40 g) were carbonylated in refluxing ethanol for two hours. The resultant solution was evaporated to dryness and the residue recrystallised from CH₂Cl₂-light petroleum (b.p. 60–80°) to give orange crystals of the complex (0.05 g, 41%).

(b) cis-[Ru(S₂PMe₂)₃] (0.02 g) and PPh₃ (0.04 g) were refluxed in ethanol (25 ml) for two hours. Removal of solvent gave an orange oil which was redissolved in diethyl ether and after leaving at 273 K for 12 h, orange crystals of the product were deposited (0.05 g, 92%).

cis-[RuCl₂(PPh₃)₃] (0.13 g) and NaS₂PMe₂ (0.26 g) were refluxed in acetonitrile (20 ml) for 6 h. The resultant solution was filtered, evaporated to dryness, and then 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 yellow solution was evaporated to dryness and the residue recrystallised from CH₂Cl₂-n-pentane to give orange crystals of the complex (0.08 g, 73%).

cis-Bis(dimethylphosphinodithioato)carbonyl(triphenylarsine)ruthenium(II). — cis-[RuCl₂(PPh₃)₃] (0.06 g) and NaS₂PMe₂ (0.09 g) were refluxed in acetonitrile (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 resultant orange oil chromatographed on a dry alumina 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(dimethylphosphinodithioato)carbonyl(methylidiphenylphosphine)ruthenium(II). — cis-[Ru(S₂PMe₂)₂(PMe₃Ph)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-[Ru(S₂PMe₂)₂(PMe₃Ph)₂] (0.01 g) in CH₂Cl₂ for 10 min and recrystallisation from CH₂Cl₂-hexane gave yellow crystals of cis-bis-(dimethylphosphinodithioato)carbonyl(triphenylphosphite)ruthenium(II) (0.01 g, 25%) whereas carbonylation of cis-[Ru(S₂PMe₂)₂(PPh₃)₂] (0.07 g) in refluxing acetone for 4 h gave, after recrystallisation from CH₂Cl₂-n-pentane, yellow crystals of cis-bis(dimethylphosphinodithioato)carbonyl(triphenylphosphite)ruthenium(II) (0.03 g, 60%).
cis-Bis(dimethylphosphinodithioato)carbonyl(dimethylphenylphosphine)ruthenium(ii), (D).—cis-[Ru(S2PPh2)2(Ph2PMe)2](0·20 g) was carbonylated for one minute in cold CH2Cl2. Then, pentane was added and the resulting orange solution evaporation to dryness and the orange solid collected without further purification (0·21 g, 100%).

cis-Bis(dimethylphosphinodithioato)bis(carbonyl) ruthenium(ii).—cis-[RuCl4(CO)2](0·50 g) and NaS2PMe2 (0·50 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(diphenylphosphinodithioato)bis(carbonyl)ruthenium(ii).—[Ru2(CO)4] (0·20 g) and an excess of Ph3P:S:H were refluxed together 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)- ruthenium(ii).—Acetone.—[RuCl2(PPh3)4] (0·26 g) and NaS2-CNMe22H2O (0·15 g) were shaken in acetone (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°.

cis-Bis(dimethylidithiocarbamato)bis(dimethylphenylphosphine)-ruthenium(ii).—mer-[RuCl2(PMe2Ph)4] (0·16 g) and NaS2-CNMe22H2O (0·16 g) were shaken in degassed CH2Cl2 under nitrogen for eight hours. The resulting greenish yellow solution was filtered to remove any precipitated sodium chloride and evaporated to dryness. Chromatography on a dry alumina column with benzene gave an intense yellow band (ca. Rp value 0·6) together with a number of weaker bands of lower Rp value. The yellow band was removed with diethyl ether, giving on removal of solvent the yellow product (0·13 g, 88%).

cis-Bis(dimethylidithiocarbamato)bis(triphenylphosphine)- ruthenium(ii).—cis-[Ru(S2CNMe2)2(PPh3)2](0·20 g) was refluxed with PMe2Ph (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 were filtered off, and 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(S2CNMe2)2(PMe2Ph)2](0·10 g, 71%).

Bis(diphenylphosphinodithioato)carbonylbis(dimethyl-phenylphosphine)ruthenium(i), (C).—cis-[Ru(S2PPh2)2(PMe2Ph)2](0·35 g) was dissolved in CH2Cl2 (30 ml) and carbonylated for 1 h at room temperature. The yellow solution was evaporated to dryness and eluted from a silica column with CH2Cl2. Two yellow bands were found and the first was extracted with CH2Cl2 and the solution evaporated to dryness to give the crystalline product (0·04 g, 13%). The other band was removed with diethyl ether, the solution evaporated to dryness, and the residue recrystallised from CH2Cl2-light petroleum (b.p. 40—60°) to give [Ru(S2PPh2)2(PMe2Ph)2] (10 ml) and carbonylated for 1 h at room temperature. The yellow solution was evaporated to dryness and eluted from a silica column with CH2Cl2. Two yellow bands were found and the first was extracted with CH2Cl2 and the solution evaporated to dryness to give the crystalline product (0·04 g, 14%).

Bis(diphenylphosphinodithioato)carbonylcarbonyl(dimethylphenylphosphine)ruthenium(i).—cis-[Ru(S2PPh2)2(PMe2Ph)2](0·30 g) was carbonylated in refluxing ethanol (40 ml) for two hours to give a yellow solution. Concentration to dryness, followed by chromatography on a dry alumina column with benzene gave two bands. The first was eluted with diethyl ether, evaporated to dryness and the residue recrystallised from benzene-light petroleum (b.p. 100—120°) to give a very small amount of cis-[Ru(S2PPh2)2(PMe2Ph)2] (0·015 g, 14%). The second (more intense) orange band was also eluted with diethyl ether and after evaporation to dryness (in the cold) was recrystallised from benzene-n-pentane to give the required product (0·10 g, 31%).

Bis(diphenylphosphinodithioato)carbonylcarbonyl(dimethylphenylphosphine)ruthenium(i).—cis-[Ru(S2PPh2)2(PMe2Ph)2](0·20 g) was carbonylated for one minute in cold CH2Cl2. 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(dimethylphosphinodithioato)bis(carbonyl) ruthenium(ii).—cis-[RuCl4(CO)2](0·50 g) and NaS2PMe2 (0·50 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(diphenylphosphinodithioato)bis(carbonyl)ruthenium(ii).—[Ru2(CO)4] (0·20 g) and an excess of Ph3P:S:H were refluxed together 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.
moval of solvent and recrystallisation from hexane gave the product (0.001 g, 2%).

We thank Johnson-Matthey Ltd. for generous loans of ruthenium trichloride, the University of Edinburgh for an award (to D. J. C.-H.), Dr. J. A. McCleverty and Dr. D. W. H. Rankin for helpful discussions, Mr. J. Miller for obtaining the variable temperature 1H n.m.r. spectra, and Dr. D. F. Steele and Mr. P. W. Armit for some experimental assistance.

[3/1495 Received, 16th July, 1973]
Metal Complexes of Sulphur Ligands. Part VI.\textsuperscript{1,2} Studies of Facile Optical Isomerism Reactions in Dimethylphosphinodithioato-complexes of Ruthenium(II)

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Reprinted from JOURNAL OF THE CHEMICAL SOCIETY DALTON TRANSACTIONS

1974
Metal Complexes of Sulphur Ligands. Part VI. 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, PMe₂Ph, PMe₃Ph, P(OMe)₃, P(OPh)₃], cis-[Ru(S₂PMe₂)₂(PPh₃)(P(OPh)₃)] and cis-[Ru(S₂PMe₂)₂(PPh₂)(P(OPh)₃)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, PMe₂Ph, P(OPh)₃] 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;³ and relatively few have discussed detailed mechanisms of optical isomerism in complexes of type cis-[M(chelate)₃X₃].²⁶ Furthermore, with the exception of a very recent note on variable temperature ¹H n.m.r. studies of [Ru(S₂CNRR)₃] (R = Me, R₁ = PhCH₂),⁴ this paper represents the only other published work on the facile interconversion of optical isomers in rhenium 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 compounds of 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 S₈PMe₂ 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)₂L(CO)], four methyl doublets are expected although in some instances, two of the doublets are accidentally superimposed. For cis-[Ru(S₂PMe₂)₂(PPh₃)](P(OH)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 methy1 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. Serpone and D. G. Bickley in Progr. Inorg. Chem., 1972, 17 (Part II) (a) pp. 416—500, (b) 500—542.


¹ Part V, D. J. Cole-Hamilton and T. A. Stephenson, preceding paper.
that the rate and the associated activation parameters are dependent on the solvent media in which the measurements are made. For cis-[Ru(S2PMe2)2(PMe2Ph)]2, measurements in C6H6, C6H5Cl, and CDCl3 respectively (Figure 2) show an increasing inversion rate accompanied by a substantial decrease in ΔH* and ΔS* values, particularly on changing from C6H6 to C6H5Cl (or CDCl3). In addition, measuring the inversion rate (by line-shape analysis) at 301 K for CS2-CDCl3 solutions of cis-[Ru(S2PMe2)2(PMe2Ph)]2, in which the CDCl3 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>log₁₀k[298 °C] *</th>
<th>Ea *</th>
<th>ΔH* [kJ mol⁻¹]</th>
<th>ΔS* [kJ mol⁻¹ K⁻¹]</th>
<th>ΔG* [kJ mol⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-[Ru(S2PMe2)2(PPh3)]2</td>
<td>CDCl3</td>
<td>3.53 ± 0.02</td>
<td>49.6 ± 1</td>
<td>47.1 ± 1</td>
<td>-10 ± 3</td>
<td>52.8 ± 0.1</td>
</tr>
<tr>
<td>cis-[Ru(S2PMe2)2(PMe2Ph)]2</td>
<td>CDCl3</td>
<td>2.78 ± 0.02</td>
<td>60.6 ± 2</td>
<td>58.0 ± 2</td>
<td>3 ± 7</td>
<td>571 ± 0.2</td>
</tr>
<tr>
<td>cis-[Ru(S2PMe2)2(PMe2)]2</td>
<td>CDCl3</td>
<td>2.23 ± 0.34</td>
<td>67.8 ± 2</td>
<td>66.9 ± 2</td>
<td>17 ± 13</td>
<td>60.9 ± 2</td>
</tr>
<tr>
<td>cis-[Ru(S2PMe2)2(PPh3)]2</td>
<td>CDCl3</td>
<td>1.61 ± 0.12</td>
<td>62.0 ± 1</td>
<td>59.9 ± 1</td>
<td>-10 ± 4</td>
<td>63.8 ± 0.1</td>
</tr>
<tr>
<td>cis-[Ru(S2PMe2)2(PPh3)]2</td>
<td>CH2Cl2</td>
<td>1.01 ± 0.01</td>
<td>69.7 ± 1</td>
<td>67.9 ± 1</td>
<td>0 ± 4</td>
<td>67.2 ± 0.1</td>
</tr>
<tr>
<td>cis-[Ru(S2PMe2)2(PMe2Ph)]2</td>
<td>CH2Cl2</td>
<td>0.04 ± 0.12</td>
<td>126 ± 4</td>
<td>123 ± 4</td>
<td>170 ± 11</td>
<td>72.7 ± 0.1</td>
</tr>
<tr>
<td>cis-[Ru(S2PMe2)2(PMe2)]2</td>
<td>CH2Cl2</td>
<td>0.61 ± 0.05</td>
<td>47.9 ± 2</td>
<td>47.3 ± 2</td>
<td>-62 ± 15</td>
<td>63.8 ± 0.1</td>
</tr>
<tr>
<td>cis-[Ru(S2PMe2)2(PMe2Ph)]2</td>
<td>CH2Cl2</td>
<td>-1.90 ± 0.08</td>
<td>121 ± 2</td>
<td>119 ± 2</td>
<td>78 ± 0.1</td>
<td>63.8 ± 0.1</td>
</tr>
</tbody>
</table>

* Units of k, s⁻¹. * Units, kJ mol⁻¹. Obtained from analysis of exchange of inner doublets g and f. Obtained from analysis of exchange of outer doublets e and h. For cis-[Ru(S2PMe2)2(CO)]2, no scrambling of methyl groups at 330 K.

| Table 1 Rates and activation parameters obtained by line shape analysis for the inversion process cis-Δ ↔ cis-Γ in some ruthenium(ii) dimethylphosphinodithioate complexes |

Figure 1 Arrhenius plots (log₁₀k vs. 1/T) for various cis-[Ru(S2PMe2)2L2] compounds in CDCl3: □, L = PPh3; ■, L = PMePh2; ○, L = P(OCH3); □, L = PMe2Ph; a, L = P(OMe)3; b, L = PMe2Ph. on CDCl3 concentration (Figure 3). In a given solvent (CDCl3), the inversion rate is also dependent on the group L, the relative order being PPh3 > PMePh2 > P(OMe)3 > PMe2Ph > P(OMe)3 > CO. It is also of interest that the rate of oxidation of cis-[Ru(S2PMe2)2L2] 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(S2PMe2)2(PMe2Ph)]2 (R = Me, Ph) the two pseudo-triplets arising from the PMe2Ph methyl groups at low temperature in CDCl3 are separated by 13 and 8 Hz, and these coalesce at ca. 278 and 273 K respectively. From this data, the free energies of activation for this averaging process are estimated to be 57.4 and 58.6 kJ mol⁻¹ respectively.

\[ \Delta G^* \] obtained from the \( \text{^1} \text{H} \) n.m.r. signals of cis-[Ru(S\text{S}CNMe\text{e})\text{L}]\text{PMe}_2\text{Ph})_2] \) by line shape analysis at 293 K (63.4 kJ mol\(^{-1}\)) indicates that these \( \text{PMe}_2\text{Ph} \) 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-dimethylidithiocarbamate-complexes. — For cis-[Ru(S\text{S}CNMe\text{e})\text{L}]\text{PMe}_2\text{Ph})_2] \( \text{L} = \text{PMe}_2\text{Ph}, \text{PPh}_3, \text{P(OPh)}_3 \), the low temperature \( \text{^1} \text{H} \) n.m.r. spectra consists of two \( \text{^1} \text{H} \) n.m.r. signals which coalesce at higher temperatures.

\[ \Delta G^* \] values for the \( \text{CN} \) bond rotation process is tentatively attributed to substantial differences in the degree of solvation of the \( \text{PPh}_3 \) and \( \text{P(OPh)}_3 \) complexes, which might arise as a consequence of replacing phenyl with phenoxy groups.

Finally for cis-[Ru(S\text{S}CNMe\text{e})\text{L}]\text{PMe}_2\text{Ph})_2] \) the estimated free energy of activation \( \Delta G^* \) for averaging the two pseudo-triplets of the \( \text{PMe}_2\text{Ph} \) methyl groups is 54.0 kJ mol\(^{-1}\) (at \( T = 253 \text{ K} \)) which is again attributed to rapid rotation at higher temperatures about the ruthenium–phosphorus bonds.

### DISCUSSION

Possible Mechanisms of the Inversion Process in Dimethylphosphenodithioato-complexes. — The possible mechanisms for the inversion process in these complexes will now be considered, starting with intramolecular twisting mechanisms.

(i) Bailar (or trigonal) twist.\(^*\) In this mechanism,

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### DISCUSSION

Possible Mechanisms of the Inversion Process in Dimethylphosphenodithioato-complexes. — The possible mechanisms for the inversion process in these complexes will now be considered, starting 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-C₃) whilst keeping the opposite face fixed. In the complexes cis-[Ru(S₂PMe₂)₂LL'], 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 = PPh₃, L' = P(OPh)₃ and the starting configuration arbitrarily chosen is designated cis-Δ 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 anticlockwise) in order to determine if such a process gives the optical isomer and also interchanges only the chemical environments of the methyl groups e, h and g, f respectively. Examination of Figure 5a and Table 3 shows that rotation about the i-C₃(1) axis in a clockwise direction gives the trans isomer whereas an anticlockwise twist gives the cis-Δ isomer. However, the S₂PMe₂ 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-C₃(2) or i-C₃(3) in a clockwise direction is impossible because it leads to a configuration in which a S₂PMe₂ group would have to span 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 cis-[Ru(S₂PMe₂)₂(PPh₃)] and cis-[Ru(S₂PMe₂)₂(P(OPh)₃)CO] (see Part V) show that this is not the case. Finally, rotation about

and not produce of the spectra of the groups and groups g and h are chemically equivalent and, therefore, if this were the inversion mechanism, the $^1H$ n.m.r. spectrum of the compounds cis-[Ru(S₂PMe₂)₂L₂] should be temperature invariant. This is not the case and therefore a mechanism involving a trigonal twist about this axis is also rejected.

(ii) Ráy-Dutt (or rhombic) twist. For cis-[Ru(S₂PMe₂)₂L₂], this inversion mechanism may 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(S₂PMe₂)₂L₂] this does not produce any scrambling of the methyl resonances and so this twisting mechanism can also be discarded.

Final rejection of a trigonal or rhombic twist mechanism comprising rotation about one or several of these axes is based on a consideration of steric effects on the expected trigonal prismatic transition state. If a twisting mechanism is important, the activation energy for the process should be dependent on the size of L, being higher the bulkier the ligand. However, the results given in Table 1 reveal no apparent correlation with the size of L e.g. the bis-[PPh₃] complex has a smaller activation energy than the bis-[PMe₂Ph] complex which is smaller than the bis-[C₆H₆] complex. The large dependence of rate and associated activation parameters on solvent composition is also not compatible with a twist mechanism.

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(S₂PMe₂)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 $^1S₂PMe₂$ groups. This is not the case for a mixture of cis-[Ru(S₂PMe₂)₂(PPh₃)]₂ and cis-[Ru(S₂PMe₂)₂(PMe₂Ph)]₂ in CDCl₃ which shows only the unchanged $^1H$ n.m.r. spectral patterns of the two components. Furthermore, the $^1H$ n.m.r. spectrum of a mixture of cis-[Ru(S₂PMe₂)₂(PMe₂Ph)]₂ and free PMe₂Ph 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(S₂PR₂)₂L₂] and cis-[Ru(S₂PR₂)₂L₂] should give some of the mixed species cis-[Ru(S₂PR₂)₂(S₂PR₂)₅] 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(S₂PR₂)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. Thus, if this mechanism is correct, it must involve cleavage of a ruthenium–sulphur bond which is $trans$ to a phosphorus ligand. This statement can be rationalised on the basis that the larger $trans$ influence of the phosphorus ligands, compared to the $^1S₂PR₂$ groups, should preferentially weaken the ruthenium–sulphur bonds $trans$ to them. This suggestion is supported by the bond lengths found in cis-[Ru(S₂PEt₂)₂(PMe₂Ph)]₅ where the Ru–S bonds $trans$ to the PMe₂Ph groups are ca. 0.2 Å longer than those $trans$ to another sulphur atom.

A possible mechanism of inversion of the compounds cis-[Ru(S₂PMMe₂)₂L₂] which involves two ruthenium–sulphur bond cleavage sub-steps is outlined in Figure 6. It now remains to examine this mechanism to see if it is consistent with the experimental results presented earlier.

First, it is important to note that this overall mechanism not only leads to optical isomerism but also interchanges the chemical environments of methyl groups e.g. and f respectively. Also, the mechanism as written is symmetrical (since cis-$\Delta$ cis-$\Lambda$) and it obeys the Principle of Microscopic Reversibility. Furthermore, the solvent-assisted bond rupture step (I) is consistent with the observed first order dependence on CDCl₃ concentration in CS₂–CDCl₃ solutions.† On changing to a less solvating medium such as benzene, step (I) should be slower and the overall inversion rate should decrease as is observed experimentally (Table 1). Although there is no obvious correlation of rate


† This does not necessarily mean that step (I) 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).†

†† This is consistent with the experimental results presented earlier.


with the size of L, there is a good correlation between rate and the trans influence of L as established independently by \(^1\)H n.m.r. and i.r. studies \(^1\)six. PPh\(_3\) > PMePh\(_2\) > PMe\(_2\)Ph > P(OMe)\(_3\) ∼ 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.

![Proposed solvent-assisted bond rupture mechanism](image)

\[\text{cis-}^\Delta \rightarrow \text{cis-}[\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{LL'}] \rightarrow \text{cis-}[\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{LL'P}](X = \text{CDCl}_3 \text{ or C}_6\text{H}_5\text{Cl}). \] 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-L\(_2\), -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 CDCl\(_3\) (or C\(_6\)H\(_5\)Cl) to C\(_6\)H\(_6\) 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-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{PPPh}_3]\text{CO}\) in C\(_6\)H\(_5\)Cl are \(\Delta H^*\), 119.3 kJ mol\(^{-1}\); \(\Delta S^*\), 119 J K\(^{-1}\) mol\(^{-1}\). In terms of the proposed mechanism, step (1) must involve cleavage of the Ru-S bond trans to PPh\(_3\) (highest trans influence ligand) and step (2), that of the Ru-S bond trans to CO. Furthermore, it is reasonable to expect the rate of step (1) to be comparable to that in cis-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{P} \text{Ph}_3]\text{Co}\). This compound has overall activation parameters of 47.7 kJ mol\(^{-1}\) (\(\Delta H^*\)) and -19.1 J K\(^{-1}\) mol\(^{-1}\) (\(\Delta S^*\)) in CDCl\(_3\). However, since the overall rate constant is considerably higher for the bis-PPh\(_3\) compound compared to the phosphine carbonyl complex, this can only mean that the observed rate and activation parameters for cis-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{P} \text{Ph}_3]\text{Co}\) 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'). These inferred values for \(\Delta H^*\) and \(\Delta S^*\) would be consistent with a dissociative mechanism \(^{14}\) for step (2) in which bond-breaking of the Ru-S bond 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-L\(_2\) compounds in CDCl\(_3\) (or C\(_6\)H\(_5\)Cl) 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 -19.1 J K\(^{-1}\) mol\(^{-1}\) (\(\Delta S^*\)). Thus, it seems reasonable to propose that in solvents such as CDCl\(_3\) and C\(_6\)H\(_5\)Cl, 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 cis-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{P} \text{Ph}_3](\text{P}{\text{OPh}}_3)\text{Co}\), the activation parameters are found to be \(\Delta H^*\), 44.8 kJ mol\(^{-1}\); \(\Delta S^*\), -62 J K\(^{-1}\) mol\(^{-1}\) and again step (1) must involve cleavage of the Ru-S bond trans to PPh\(_3\) and step (2) that of the Ru-S bond trans to P(OPh)\(_3\). In this instance, the overall rates of inversion for the bis-PPh\(_3\) 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 cis-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{P} \text{Me}_2\text{Ph}]{\text{P} \text{Ph}_3}]\) is examined in C\(_6\)H\(_5\) rather than CDCl\(_3\) (or C\(_6\)H\(_5\)Cl) 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 cis-\([\text{Ru}(\text{S}_2\text{PMe}_2)_2\text{P} \text{Ph}_3](\text{P}{\text{OPh}}_3)]\) in C\(_6\)H\(_5\) and C\(_6\)H\(_5\)Cl (two methyl doublets) is consistent with retention of the same overall inversion mechanism.

Finally, the apparent inability of the corresponding cis-[Ru(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>L<sub>2</sub>] compounds to undergo inversion, even at elevated temperatures, is consistent with the stronger nucleophilicity of S<sub>2</sub>CNR<sub>2</sub> compared to S<sub>2</sub>PR<sub>2</sub> 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.  

Kinetic Line Shape Analysis.—<sup>1</sup>H 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. The exchange process was considered for the purpose of computation as consisting of 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 (T<sub>2</sub>) were obtained for each compound by measurement of peak width at half height under slow exchange conditions. The same value of T<sub>2</sub> was used for all line-shape calculations on a given compound because, for L = PMe<sub>2</sub>Ph and P(OMe)<sub>3</sub>, 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 (log<sub>10</sub>£ 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 <sup>1</sup>H n.m.r. spectra, and the Atlas Computer Laboratory for a copy of their Shape Function programme.

[1/196 Received, 16th July, 1973]


Metal Complexes of Sulphur Ligands. Part VII.\textsuperscript{1} Reaction of \textit{mer}-Tri-chlorotris(dimethylphenylphosphine)rhodium(III) with \textit{NN}-Dimethylthiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and \textit{O}-Ethyl Dithiocarbonate (Xanthate) Ligands

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Reprinted from JOURNAL OF THE CHEMICAL SOCIETY DALTON TRANSACTIONS 1974
Metal Complexes of Sulphur Ligands. Part VII. Reaction of mer-Tri-chlorotris(dimethylphenylphosphine)rhodium(III) with NN-Dimethylthio-carbamate, Dimethyl- and Diphenyl-phosphinodithioate, and O-Ethyl Dithiocarbonate (Xanthate) Ligands

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Reactions of the complex mer-[RhCl3(PMe3)3] (I), with excess of (S–S)− ion [(S–S)− = S2CNMe2, S2PMe2, S2PPh2, 1,1′-COEt] have been thoroughly studied. On shaking in methanol for 10 min, the complexes mer-[RhCl3(S–S)(PMe3)3] (II), are formed which contain a unidentate dithio-acid group. Recrystallisation of complexes (IV) from non-polar solvents gives trans-[RhCl3(S–S)(PMe3)3] (II). For (S–S)− = S2PMe2 or S2PPh2 further recrystallisation gives small amounts of cis-cis-cis-isomers (VII). Conversely, for (S–S)− = S2CNMe2 or S2COEt, reaction of complexes (IV) with NaSPh in methanol gives some mer-[RhCl3(S–S)-(PMe3)3S2PPh2]BPh4 (V), 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 filtrate, gives high yields of cis-[Rh(S–S)(PMe3)3]Y (III; (S–S)− = S2CNMe2, S2PMe2 or S2PPh2). Reaction of the complex mer-[RhCl3(PMe3)3] with Na2S2CNMe2,2H2O in ethanol gives both cis- and trans-[Rh(S2CNMe2)3(PMe3)3]Y (III, and (VI) respectively). In contrast, reaction of complex (I) with KSCN gives mer-[RhCl3(S2CO)(S2COEt)(PMe3)3] (X). K[RhCl3(S2CNMe2)(S2COEt)2(PMe3)3] (XII), and trans- and cis-[Rh(S2CO)(S2COEt)(PMe3)3] (XIII) and (XIV) respectively), which can be separated by chromatography. Complexes thus obtained have been characterised by elemental analysis and i.r. and n.m.r. spectroscopy (1H and 31P), and a detailed mechanism for the overall reaction is postulated.

Previous papers in this series have been concerned with an examination of dithio-acid complexes of palladium,8–5 platinum,8–5 and ruthenium,1,4,7, and, in particular, those complexes with ligands containing Group VB donor atoms (I) have been thoroughly studied. 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)2L] 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 isomers via ruthenium-sulphur bond rupture [for (S–S)− = S2PMe2] and rotation about the C≡N 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 rare8 and where, in general, complexes are less labile than those formed with ruthenium.5,9 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,6 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.: [Rh(S2PR3)3] (R = Ph,19 Et,11 or F12; [Rh(S2CNPR3)3] (R = Me,13–14 or Bu,15; [Rh(S2CR3)3] (R = Ph or PhCH3);16 NH[Rh(S2CNPh)3];16 [Rh(S2P(OrEt)3)3]17 [Rh(S2CNPR3)3]PF6 (R = Me15 or Et10); [Rh(S2CNPh3)]PF6;11 [Rh(S2CNPh3)(CO)]PF6;15 [Rh(S2CNMe2)(CO)]PF6;15 [Rh(S2PPh3)]PF6;15 [Rh(S2PMe2)]PF6;13 [Rh(S2CNPh3)(CO)]PF6;18 and [Rh(S2CNPh3)(CO)]PF6.18 The alternative method of preparing these complexes, namely by direct reaction of free ligand with complexes
TABLE 1
Analytical data for some rhodium dithio-acid complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M.p. (°C)</th>
<th>Found (%)</th>
<th>Calc. (%)</th>
<th>Δ (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-[RhCl₂(S₂CO)(PMe₂Ph)₂]</td>
<td>(II) Orange</td>
<td>207—208</td>
<td>39-9 4-9 2-6 12-5</td>
<td>40-0 4-9 2-5 12-5</td>
<td></td>
</tr>
<tr>
<td>cis-[Rh(S₂CNMe₂)(PMe₂Ph)₂]PF₆</td>
<td>(III) Yellow</td>
<td>174—178</td>
<td>58-7 5-7 2-8</td>
<td>59-9 5-8 3-0 64-8 (3-5)</td>
<td></td>
</tr>
<tr>
<td>mer-[RhCl₂(S₂CO)(PMe₂Ph)₂]PF₆</td>
<td>(IV) Orange</td>
<td>189—195</td>
<td>45-4 5-5 1-7</td>
<td>45-8 5-5 2-0 (10-5)</td>
<td></td>
</tr>
</tbody>
</table>

*In 1 cm⁻¹ mol⁻¹; measured in MoNO₃ at 298 K; conc. (10⁻⁴ M) in parentheses. ¹ Mixture of cis- and trans-isomers (H 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>ν(RhCl)</th>
<th>Dithio-acid ligand absorptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>mer-[RhCl₂(PMe₂Ph)₂]</td>
<td>(I) 339, 313, 273</td>
<td>1320 *</td>
</tr>
<tr>
<td>mer-[RhCl₂(S₂CNMe₂)(PMe₂Ph)₂]</td>
<td>(IV) 339, 313, 273</td>
<td>1320 *</td>
</tr>
<tr>
<td>mer-[RhCl₂(S₂CNMe₂)(PMe₂Ph)₂]PF₆</td>
<td>(VII) 339, 313, 273</td>
<td>1320 *</td>
</tr>
<tr>
<td>trans-[RhCl₂(S₂CO)(PMe₂Ph)₂]PF₆</td>
<td>(II) 339, 313, 273</td>
<td>1320 *</td>
</tr>
<tr>
<td>cis-cis-[RhCl₂(S₂CO)(PMe₂Ph)₂]PF₆</td>
<td>(III) 339, 313, 273</td>
<td>1320 *</td>
</tr>
<tr>
<td>trans-[RhCl₂(S₂CO)(PMe₂Ph)₂]PF₆</td>
<td>(XII) 339, 313, 273</td>
<td>1320 *</td>
</tr>
<tr>
<td>cis-[RhCl₂(S₂CO)(PMe₂Ph)₂]PF₆</td>
<td>(XII) 339, 313, 273</td>
<td>1320 *</td>
</tr>
<tr>
<td>K[RhCl₂(S₂CO)(PMe₂Ph)₂]PF₆</td>
<td>(XV) 339, 313, 273</td>
<td>1320 *</td>
</tr>
</tbody>
</table>

* ν(C=O) (S₂CO); ** ν(C=O) (S₂CNMe₂); *** ν(C=S) (S₂CNMe₂); D. Coucouvanis, Progr. Inorg. Chem., 1970, 11, 605 and ref. therein. ¹ Band for unidentate S₂PMe₂ (refs. 5 and 6). ² Band for dithio-acid S₂CO; J. P. Fackler, jun., and W. C. Seidel, Inorg. Chem., 1969, 8, 1631. ³ Higher-energy band positions masked by BPh₄⁻ or PF₆⁻ vibrations.
already containing the dithio-acid ligands, has also been used, but less frequently, e.g., in the preparation of \( [\text{Rh}(S_2\text{PF}_3)(\text{CO})_2L] \) (\( L = \text{PPh}_3, \text{AsPh}_3, \) or \( \text{SbPh}_3 \)) from \( [\text{Rh}(S_2\text{PF}_3)(\text{CO})_2]^2L \).

**In this work, reaction of the complex** \( \text{mer}-[\text{RhCl}_3\text{S}_2\text{CNMe}_2\text{PMe}_2\text{Ph}]_3 \) (I), \( \text{mer}-[\text{RhCl}_3\text{S}_2\text{CNMe}_2\text{S}_2\text{CO}\text{PMe}_2\text{Ph}]_3 \) (II), \( \text{mer}-[\text{RhCl}_3\text{S}_2\text{CNMe}_2\text{PMe}_2\text{Ph}]_3\text{BPh}_4 \) (IV), and \( \text{mer}-[\text{RhCl}_3\text{S}_2\text{CNMe}_2\text{BPh}_4]_3 \) (III), \( \text{mer}-[\text{RhCl}_3\text{S}_2\text{CNMe}_2\text{S}_2\text{CO}\text{PMe}_2\text{Ph}]_3 \) (V) 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 by column chromatography, or, in general, by recrystallisation under solvent vapour.

**Table 3**

<table>
<thead>
<tr>
<th>Complex</th>
<th>( T/K )</th>
<th>( \tau ) Value *</th>
<th>Dithio-ligand</th>
<th>Methyl groups of phosphate</th>
<th>Phenyl groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>mer-[RhCl\text{S}2\text{CO}(\text{PMe}_2\text{Ph})_3] &gt; (X)</td>
<td>301</td>
<td>8-34 (t)</td>
<td>4-3</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>trans-[RhCl\text{S}_2\text{CNMe}_2\text{PMe}_2\text{Ph}]_3 &gt; (II)</td>
<td>301</td>
<td>7-86 (d)</td>
<td>4-100</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>trans-[RhCl\text{S}_2\text{CNMe}_2\text{PMe}_2\text{Ph}]_3 &gt; (II)</td>
<td>301</td>
<td>7-86 (d)</td>
<td>4-100</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>cis-cis-[Rh\text{S}2\text{CO}(\text{S}2\text{CO})\text{PMe}_2\text{Ph}]_2 &gt; (VI)</td>
<td>301</td>
<td>7-82 (d)</td>
<td>10-0</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>cis-[Rh\text{S}2\text{CO}(\text{S}2\text{CO})\text{PMe}_2\text{Ph}]_2 &gt; (VI)</td>
<td>301</td>
<td>7-82 (d)</td>
<td>10-0</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>cis-[Rh\text{S}2\text{CNMe}_2\text{BPh}_4]_3 &gt; (III)</td>
<td>301</td>
<td>7-86 (d)</td>
<td>10-0</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>cis-[Rh\text{S}2\text{CNMe}_2\text{BPh}_4]_3 &gt; (III)</td>
<td>301</td>
<td>7-86 (d)</td>
<td>10-0</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>cis-[Rh\text{S}2\text{CNMe}_2\text{BPh}_4]_3 &gt; (III)</td>
<td>301</td>
<td>7-86 (d)</td>
<td>10-0</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
<tr>
<td>cis-[Rh\text{S}2\text{CNMe}_2\text{BPh}_4]_3 &gt; (III)</td>
<td>301</td>
<td>7-86 (d)</td>
<td>10-0</td>
<td>7-80 (d)</td>
<td>11-0</td>
</tr>
</tbody>
</table>

* \( \tau \) values are in Hz. * Since \( H,\text{PPh}_3 \) type spectrum, coupling constant is \( J_{\text{PH}} \) in Hz. * \( J_{\text{PH}} \) in Hz. * \( J_{\text{CNMe}_2} \) in Hz. * Pseudo-doubblet. * Measured in (CD)_3CO. * 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-Dimethyl-dithiocarbamo-complexes.** — Heating complex (I) under reflux with an excess of NaS_2CNMe_2H_2O in ethanol for 1 h led to formation of two products. These were readily separated, since one of them, \( [\text{RhCl}_3\text{S}_2\text{CNMe}_2\text{BPh}_4]_3 \) (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_4PF_6. The latter salts are strongly conducting in CH_2Cl_2 and analyse for \( [\text{Rh}(\text{S}2\text{CNMe}_2\text{BPh}_4)]_3 \) (III; \( Y = \text{BPh}_4^- \) or \( \text{PF}_6^- \)). Longer 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 \( [\text{RhCl}_3\text{S}_2\text{CNMe}_2\text{BPh}_4]_3 \) (V) formed which, on setting aside in CDCl_3 for 48 h, reverted to (I) and free PMe_2Ph.

Finally, when the complex mer-[RhCl_3(PMe_2Ph)_3] was used instead of (I) long-term reaction in ethanol heated under reflux with excess of NaS_2CNMe_2H_2O, followed by addition of NaBPh_4, gave two ionic complexes, both of formula \( [\text{Rh}(\text{S}_2\text{CNMe}_2\text{BPh}_4)_3]_2 \) (III) and (VI), together with very small amounts of \( [\text{Rh}(\text{S}_2\text{CNMe}_2\text{BPh}_4)]_3 \).**
expected $[\text{Rh}((S_2PPh)_2)(PMe_2Ph)]_2$Y ($\text{Y} = \text{BPh}_4^-$ or $\text{PF}_6^-$). In addition, very small amounts of an ethanol-insoluble complex formed for $[\text{RhCl}((S_2PPh)_2)(PMe_2Ph)]_2$, (VII), were obtained. However, when the reaction was carried out using NaS$_2$PMe$_2$·2H$_2$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 $^1$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 $[\text{RhCl}(PPh)_3]$). The complex $[\text{Rh}((S_2PMe_2)(PMe_2Ph))_2]$BPh$_4$, (III), was, however, prepared as a yellow microcrystalline solid either by excluding oxygen completely from the reaction in ethanol or by reaction of fae- $[\text{RhCl}((PMe_2Ph)]_2$ with excess of NaS$_2$PMe$_2$·2H$_2$O in acetone, followed by addition of NaBPh$_4$. The compound is, in fact, stable both in the solid state and in solution; however, a red solution is rapidly formed when the complex is dissolved in ethanol or methanol in the presence of excess of NaS$_2$PMe$_2$·2H$_2$O and air.

Short-term reactions between complex (I) and NaS$_2$PMe$_2$·2H$_2$O or NH$_4$S$_2$PPh$_2$ also differed slightly from one another. The dimethylphosphinodithioatoion behaved like the $NN$-dimethylthiocarbamato-ion, giving, after shaking for 10 min in methanol, orange $[\text{RhCl}(S_2PMe)_2(PMe_2Ph)]_2$, (IV), which, on recrystallisation from deuteriochloroform-hexane, gave $[\text{RhCl}((S_2PMe)_2(PMe_2Ph)]_2$, (II). Recrystallisation of the latter from 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 NH$_4$S$_2$PPh$_2$ in ethanol for 10 min gave only $[\text{RhCl}(S_2PPh)(PMe_2Ph)]_2$, (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 $[\text{RhCl}(S_2PMe)_2(PMe_2Ph)]_2$BPh$_4$, by reaction between $[\text{RhCl}(S_2PMe)_2(PMe_2Ph)]_2$, (IV), NaBPh$_4$, and PMe$_2$Ph in methanol yielded only $[\text{RhCl}(PMe_2Ph)]_2$BPh$_4$, (VIII), or, if oxygen was excluded, a mixture of $[\text{RhCl}(S_2PMe)_2]$BPh$_4$, (IX) and $[\text{RhCl}(S_2PMe)(PMe_2Ph)]_2$, (II). Compound (VIII) was also formed as the sole product from reaction of $[\text{Rh}(S_2PMe_2)]_2$, PMe$_2$Ph, and NaBPh$_4$.

O-Ethyl Dithiocarbonate (Xanthate) and Dithiocarbonate Complexes.—The reaction of K$_2$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)].

\[
\text{R}'_3\text{P} = \begin{array}{c}
\text{O} \\
\text{S}_2\text{COR} \\
\text{R}'_3\text{P}
\end{array} \\
\text{S}_2\text{COR} + \text{RS}_2\text{COP} \quad \text{(I)}
\]

Thus, when complex (I) was heated under reflux in ethanol with excess of K$_2$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 $[\text{RhCl}((S_2CO)(PMe_2Ph)]_2$, (X), $K[\text{RhCl}(S_2CO)(PMe_2Ph)]_2$, (XI), and two isomers of $[\text{Rh}(S_2CO)(PMe_2Ph)]_2$, (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 $[\text{RhCl}((S_2CO)(PMe_2Ph)]_2$, (II), was isolated.

As for (S–S)$^\pm = \text{S}_2\text{CNMe}_2$, shaking complex (I) and K$_2$COEt in methanol for 10 min gave the dark orange $[\text{RhCl}((S_2CO)(PMe_2Ph)]_2$, (IV), which yielded (II) on recrystallisation from hot methanol or chloroform–hexane. This interconversion was also affected by heating (IV) to its melting point ($120-123^\circ$ C), whereupon PMe$_2$Ph was evolved and the orange residue consisted largely of compound (II).

Finally, when complex (IV) (S–S)$^\pm = \text{S}_2\text{COEt}$ was shaken in ethanol with excess of NaBPh$_4$ for several weeks, a small amount of $[\text{RhCl}((S_2CO)(PMe_2Ph)]_2$, (BPh$_4$, (V), was deposited. The latter complex was also prepared in high yield by reaction of (I) and K$_2$COEt (1:1 molar ratio) in methanol heated under reflux for 60 min, followed by addition of NaBPh$_4$. 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 ν(RhCl) stretching vibrations for complex (I) and Brookes and Shaw 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 $trans$ to a PMe$_2$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 ν(RhCl) region was similar to that of (I) (Table 2) except that the lowest band had disappeared, indicating that the chloride ion $trans$ to phosphine has been replaced. This
Compounds shown in broken square brackets were not isolated.
is in agreement with the larger trans-labelling 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) = S₂PMe₂ the absorption at 601 cm⁻¹, 5.6 and for (S-S) = S₂CNMe₂ the position of ν(CN) below 1 470 cm⁻¹, both suggest that the sulphur ligands are co-ordinated through only one sulphur atom. Since there was little change in the ν(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 ν(RhCl) region or between the ν(PS) region for complexes (II) and (VII), although other parts of their i.r. spectra and their ¹H 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 ν(RhCl) bands and, hence, little spectrochemical 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 ¹H 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 dithio-ligands 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]²⁻].

In fact, ¹H n.m.r. spectra of the complexes [V; (S-S) = S₂CNMe₂] and (X) did show two triplets arising from the trans-phosphine groups, indicating that there is no plane of symmetry passing through these phosphines and hence (V) is assigned the structure shown in the Scheme. Further evidence that complex [V; S-S] = S₂CNMe₂ 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 S-CN 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, ⁹JₚRh value when compared to | ⁹JₚRh + ⁹JₚRh |.²⁸ Even at this temperature. Complex (X) is most probably formed from [V; (S-S) = S₂COEt] by attack of a previously displaced chloride ion on the co-ordinated O-ethyl dithiocarbamato-group.

Complexes (II) showed only one dithioligand resonance in each case, together with one H₂P=P′H₄ pseudo-doublet * which arises from the PMe₂Ph groups. Since ⁹JₚRh 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) = S₂CNMe₂ or S₂PMe₂ 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 ¹H n.m.r. spectra of the complex [VII; (S-S) = S₂PMe₂] 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 should 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(EP₃)₂] (E = P or As) where recrystallisation of trans-[RuCl₂(CO)₂(EP₃)₂] gives the more stable cis-cis-cis-isomer.²⁹

The ¹H n.m.r. spectrum of complex (XI) consisted of broad peaks in the phenyl region, together with a single sharp triplet at ³8.22. This can only occur if the phosphine groups are mutually trans ('virtually coupled' triplet with large ⁹JₚRh).²⁸ A possible mode of formation of this rather unusual complex is by attack of potassium chloride, formed from reaction of (I) and K₃COEt 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.

¹H 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 \([\text{Ru}(S_{2}\text{PMe}_2)\text{Ph})]_2\text{CO}\). For complex (XIII), the proton-noise-decoupled \(^{31}\text{P}\) 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 \(^{103}\text{Rh}\) n.m.r. spectrum of complex (XIII) was also measured by decoupling the proton spectrum. Each peak arising from a methyl group in the \(^{1}\text{H}\) n.m.r. spectrum was rather broad (2–3 Hz) due to \(^{103}\text{Rh}-^{1}\text{H}\) 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) \([S-S]^-=\text{S}_{2}\text{CNMe}_2, Y=\text{BPh}_4^-\) or \(\text{PF}_6^-\); \([S-S]^-=\text{S}_2\text{PMe}_2, Y=\text{BPh}_4^-\) all had low-temperature \(^1\text{H}\) 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 \(^1\text{H}\) n.m.r. spectrum of the complex \([\text{Rh}(S_{2}\text{PMe}_2)\text{Ph})_2\text{BPh}_4^-\) 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:\([\text{Ru}(S_{2}\text{PMe}_2)\text{Ph})_2\text{BPh}_4^-\) complex, the inversion process cis\(\text{cis}-\Delta \leftrightarrow \text{cis}\)-\(\Delta\) is very slow on the n.m.r. time scale. The complexes cis-\([\text{Rh}(S_{2}\text{CNMe}_2)\text{Ph})_2\text{BPh}_4^-\) (\(Y=\text{BPh}_4^-\) or \(\text{PF}_6^-\)) both gave rise to a single doublet in the proton-noise-decoupled \(^{31}\text{P}\) n.m.r. spectrum due to coupling with the \(^{103}\text{Rh}\) nucleus and this coupling was found to be temperature invariant in each case. In contrast, the \(^1\text{H}\) n.m.r. spectrum of the \(\text{PF}_6^-\) salt showed marked variations with temperature giving only a singlet for the \(\text{S}_{2}\text{CNMe}_2\) 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 singlet 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\(^{30}\) indicates that the complex cis-\([\text{Os}(S_{2}\text{CNMe}_2)_2(\text{PMMe}_2\text{Ph})_2]\) shows similar variable-temperature \(^1\text{H}\) 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 \(^1\text{H}\) 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.\(^6\)

* In this instance there is probably only one preferred rotamer, since further cooling does not give rise to the additional signals which would be expected if, when no rotation is possible, the phosphine group has more than one preferred configuration.
It is important to note that exchange of the environments 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-phosphine 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; L = PMe2Ph] and Na5C2NMe2·2H2O are, as expected, geometrical isomers of [Rh-(S,C2NMe2)2(PMe2Ph)2]Y. Thus, 1H n.m.r. spectra of complexes (VI; Y = BPh4 or PF6) consisted of one S,C2NMe2 resonance and a 'virtually coupled' triplet phosphine methyl resonance, whereas (III), which could not be satisfactorily separated from the trans-isomer, had two S,C2NMe2 resonances and one pseudo-doublet phosphine resonance in each case. The fact that the trans-isomer is formed more readily when the phosphine is PMe2Ph rather than PMe2PhCH3 can presumably be attributed to the greater steric size of PMe2Ph. It should be noted at this point that the analogous complex [Rh(S,C2NMe2)2(PPh2)2]BF4 has been assigned a trans-stereocchemistry 18 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 mer-[RhCl3(PMe2Ph)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 factor, rather than any large intrinsic differences in lability of the co-ordination spheres of rhodium(III) and ruthenium(II), which accounts for the difference in behaviour. It is very probable that reactions of the dithio-acid ligands with mer-[RuCl3(PMe2Ph)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 407 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. 1H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer and 31P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform mode at 40·5 MHz (31P chemical shifts are given in p.p.m. to high frequency of 85% H3PO4). 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 Kofler hot-stage microscope and are uncorrected.

Rhodium trichloride trihydrate (Johnson, Matthey Ltd), dimethylphenylphosphine (B.D.H.), methylphenylphosphine (Strem), Na5C2NMe2,2H2O (Ralph Emanuel), and K3COEt (B.D.H.) were obtained as indicated. Sodium dimethylphosphinodithioate was prepared as described earlier 21 and ammonium diphenylphosphinodithioate from Ph3P=HS2O 22 and ammonia in benzene. The complexes mer-[RhCl3(PMe2Ph)3], (I), fac-[RhCl3(PMe2Ph)3], and mer-[RhCl3(PPh2)3] were synthesised by published methods. 21

Preparations.—trans-Dichloro(NN-dimethylthiodicarbamato)bis(dimethylphenylphosphine)rhodium(III), (II) and cis-bis(NN-dimethylthiodicarbamato)bis(dimethylphenylphosphine)rhodium(III) tetraphenylborate, (III). (II) (0·25 g) and excess of Na5C2NMe2,2H2O (0·25 g) were heated under reflux in ethanol (20 cm³) for 60 min and the resulting orange solution was cooled and filtered. The residue was well washed with water 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 NaBPh4, in ethanol, and the resulting yellow precipitate filtered off, washed with water, ethanol, and pentane, and then recrystallised from dichloromethane–ethanol to give complex (III) (0·20 g, 51%). 31P N.m.r. spectrum of (III) in CDCl3: 4·5 p.p.m. (doublet, JPP 112 Hz). When complex (I) and Na5C2NMe2,2H2O were heated under reflux in ethanol for 16 h, only (III) (0·35 g, 92%) was isolated on addition of NaBPh4.

cis-Bis(NN-dimethylthiodicarbamato)bis(dimethylphenylphosphine)rhodium(III) hexafluorophosphate, (III), was similarly prepared except that excess of NH4PF6 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. These were filtered off, and washed with water, ethanol, and pentane and then recrystallised from dichloromethane–ethanol to give complex (III) (0·50 g, 98%). 31P N.m.r. spectrum in CDCl3: 4·37 (doublet) (JPP 114); -147·2 p.p.m. (heptet, JPP 727 Hz). cis- and trans-Bis(NN-dimethylthiodicarbamato)bis(methylphenylphosphine)rhodium(III) tetraphenylborate, (III) and (VI). These complexes were prepared as above, by heating under reflux of cis-[RhCl3(PMe2Ph)3] (0·20 g) and excess of Na5C2NMe2,2H2O (0·15 g) in ethanol (20 cm³) for 16 h. Addition of NaBPh4 then gave an immediate yellow precipitate consisting of a mixture of the cis- and trans-isomers (III) and (VI) (1H 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-[Rh(S2CMe2)4(PMe2Ph)3]PF6,


(III) and (VI), were prepared from mer-[RhCl₂(PMe₂Ph)₃] and Na₅S₆CNMe₂(H₂O) followed by addition of excess of NH₃PF₆. 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-dimethylcyclohexanoo)tris(dimethylphenylphosphine)rhodium(III), (IV). A suspension of the complex (I) (0-25 g) was shaken with excess of Na₅S₆CNMe₂(H₂O) (0-20 g) in methanol (25 cm³) for 10 min. The resulting orange solid (IV) was filtered off and washed with water, methanol, and pentane (0-25 g, 88%). Recrystallisation from dichloromethane-hexane gave trans-[RhCl₂(S₆CNMe₂)(PMe₂Ph)₃] (II).

mer-Chloro NN-dimethylcyclohexanoo)tris(dimethylphenylphosphine)rhodium(III) tetraphenylborate, (V). The complex mer-[RhCl₂(S₆CNMe₂)(PMe₂Ph)₃] (0-23 g), Na₅B₆PH₄ (0-36 g), and PMe₂Ph (0-20 cm³) were shaken in methanol for 24 h under a nitrogen atmosphere. The resulting mixture of orange and yellow solids was treated with hot ethanol 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 treated with Na₅B₆PH₄ to give (III) (0-30 g) and Na₅S₆PMe₂,2H₂O (0-20 g) added. The resulting yellow solution filtered hot on an order to remove potassium chloride. It was then evaporated to dryness and the yellow oil dissolved in CH₂Cl₂. Excess of K₅COEt was filtered off and the solution allowed to stand whereupon yellow needle-shaped crystals of potassium dichlorobis(dimethylphenylphosphine)(diisothiocarbamate)(II) were obtained by recrystallisation from dichloromethane-water.

The yellow oil was dissolved in CH₂Cl₂ (25 cm³) for 2 days. The orange crystals were filtered from the red-brown solution and washed with water, methanol, and pentane (0-22 g, 80%). Recrystallisation of complex (II) from toluene gave mainly (II) together with small quantities of cis-cis-cis-[RhCl₂(S₆PMe₂)(PMe₂Ph)₃] (VII).

Reactions.—mer-[RhCl₂(S₆CNMe₂)(PMe₂Ph)₃] (IV), with Na₅B₆PH₄ and PMe₂Ph. Complex (IV) (0-22 g), Na₅B₆PH₄ (0-32 g), and PMe₂Ph (0-10 cm³) were shaken in degassed methanol for 10 min. The resulting red solution of Na₅B₆PH₄ was filtered off and the filtrate was treated with Na₅B₆PH₄ to give an immediate orange precipitate (III), which was recrystallised from dichloromethane-methanol to remove any NH₃PF₆ (0-46 g, 80%). The complex cis-[Rha(S₆PMe₂)(PMe₂Ph)₃]PF₆ (III), was similarly prepared except that the orange ethanolic solution was treated with excess of NH₃PF₆ and the complex separated slowly as large yellow crystals (0-40 g, 80%). The PF₆⁻ salt was also obtained in a pure state by dissolving the PF₆⁻ salt in methanol and adding excess of Na₅B₆PH₄.

trans-Dichlorobis(dimethylphenylphosphine)(diphenylphosphinothioato)rhodium(III), (II). Complex (I) (0-20 g) and NH₃S₆PPh₃ (0-20 g) were shaken in methanol (25 cm³) for 10 min. Excess of starting material was filtered off and, after 3 days, large crystals of the complex were formed in the filtrate. These were filtered and washed with diethyl ether and pentane (yield 0-11 g, 50%). Recrystallisation from ethanol gave a mixture of mainly (II) and small amounts of the cis-cis-cis-isomer (VII) (i.e. evidence).

cis-Bis(dimethylphenylphosphine)bis(dimethylphenylphosphinodithioato)rhodium(III) tetraphenylborate, (III). Complex (I) (0-30 g) and Na₅S₆PMe₂,2H₂O (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 Na₅B₆PH₄ (0-20 g) added. The resulting yellow solid was filtered off under a nitrogen atmosphere and washed with water, ethanol, and pentane (yield 0-30 g, 61%). Omission of nitrogen from the reaction gave a red solution from which a red solid was precipitated by addition of excess of Na₅B₆PH₄. 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-[RhCl₂(PMe₂Ph)₃] (0-07 g) and excess of Na₅S₆PMe₂,2H₂O (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 Na₅S₆PMe₂,2H₂O, again evaporating to dryness, dissolving in methanol, and adding excess of Na₅B₆PH₄, complex (III) was obtained as yellow microcrystals.

mer-Dichlorobis(dimethylphenylphosphine)(dimethylphosphinodithioato)rhodium(III), (IV). This complex was prepared by shaking (I) (0-40 g) and Na₅S₆PMe₂,2H₂O (0-24 g) in methanol (40 cm³) for 10 min (0-41 g, 90%). Recrystallisation from deuteroethanol-hexane gave trans-dichlorobis(dimethylphenylphosphine)(dimethylphosphinodithioato)rhodium(III), (II). This complex was also obtained by shaking (I) (0-30 g) and Na₅S₆PMe₂,2H₂O (0-30 g) in ethanol (20 cm³) for 2 days. The orange crystals were filtered from the red-brown solution and washed with water, methanol, and pentane (0-22 g, 80%). Recrystallisation of complex (II) from toluene gave mainly (II) together with small quantities of cis-cis-cis-[RhCl₂(S₆PMe₂)(PMe₂Ph)₃] (VII).

Reactions.—mer-[RhCl₂(S₆CNMe₂)(PMe₂Ph)₃] (IV), with Na₅B₆PH₄ and PMe₂Ph. Complex (IV) (0-32 g), Na₅B₆PH₄ (0-32 g), and PMe₂Ph (0-10 cm³) were shaken in degassed methanol for 10 min. The resulting red solution of Na₅B₆PH₄ was filtered off and the filtrate was treated with Na₅B₆PH₄ to give an immediate orange precipitate (III), which was recrystallised from dichloromethane-methanol to remove any NH₃PF₆ (0-36 g, 80%). The complex cis-[Rh₂(S₆PMe₂)(PMe₂Ph)₃]PF₆ (III), was similarly prepared except that the orange ethanolic solution was treated with excess of NH₃PF₆ and the complex separated slowly as large yellow crystals (0-40 g, 80%). The PF₆⁻ salt was also obtained in a pure state by dissolving the PF₆⁻ salt in methanol and adding excess of Na₅B₆PH₄.

trans-Dichlorobis(dimethylphenylphosphine)(diphenylphosphinodithioato)rhodium(III), (II). Complex (I) (0-20 g) and NH₃S₆S₂PPh₂ (0-20 g) were shaken in methanol (25 cm³) for 10 min. Excess of starting material was filtered off and, after 3 days, large crystals of the complex were formed in the filtrate. These were filtered and washed with diethyl ether and pentane (yield 0-11 g, 50%). Recrystallisation from ethanol gave a mixture of mainly (II) and small amounts of the cis-cis-cis-isomer (VII) (i.e. evidence).

cis-Bis(dimethylphenylphosphine)bis(dimethylphosphinodithioato)rhodium(III) tetraphenylborate, (III). Complex (I) (0-30 g) and Na₅S₆PMe₂,2H₂O (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 Na₅B₆PH₄ (0-20 g) added. The resulting yellow solid was filtered off under a nitrogen atmosphere and washed with water, ethanol, and pentane (yield 0-30 g, 61%). Omission of nitrogen from the reaction gave a red solution from which a red solid was precipitated by addition of excess of Na₅B₆PH₄. 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-[RhCl₂(PMe₂Ph)₃] (0-07 g) and excess of Na₅S₆PMe₂,2H₂O (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 Na₅S₆PMe₂,2H₂O, again evaporating to dryness, dissolving in methanol, and adding excess of Na₅B₆PH₄, complex (III) was obtained as yellow microcrystals.
The first yellow band gave trans-bis(dimethylphenylphosphine)(dithiocarbonato)(O-ethyl dithiocarbonato)rhodium(iii) (XII) (0.05 g, 17.5%). The orange band gave mer-chlorotris(dimethylphenylphosphine)(dithiocarbonato)rhodium(iii) (X) (0.05 g, 16%), and the second yellow band yielded cis-bis(dimethylphenylphosphine)(dithiocarbonato)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); $J_{P_{\text{Rh}-1}}$, 118, $J_{P_{\text{Rh}-2}}$, 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$_2$CO$_2$Et (0.08 g, 1:1 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$_2$CO$_2$Et (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-dichlorobis(dimethylphenylphosphine)(O-ethyl dithiocarbonato)rhodium(iii) (II) (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$_2$CO$_2$Et gave (XIII).

When complex (I) (0.30 g) and K$_2$CO$_2$Et (0.30 g) were shaken in methanol (25 cm$^3$) for 10 min the orange complex mer-dichlorotris(dimethylphenylphosphine)(O-ethyl dithiocarbonato)rhodium(iii) (IV) (0.30 g, 88%) was deposited. Recrystallisation of this complex from methanol (or chloroform-hexane) gave trans-(RhCl$_2$(S$_2$CO$_2$Et)(PMe$_2$Ph)$_2$) (II). Finally, when the complex mer-(RhCl$_2$(S$_2$CO$_2$Et)(PMe$_2$Ph)$_2$) (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-ethyl dithiocarbonato)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$_2$CO$_2$Et (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, 86%).

We thank Johnson, Matthey Ltd. for loans of rhodium trichloride, the University of Edinburgh for an award (to D. J. C.-H.), and Dr. A. S. F. Boyd and Mr. J. Miller for obtaining the $^{31}$P and $^1$H n.m.r. spectra respectively.

[4/209 Received, 4th February, 1974]
REACTIONS OF PLATINUM (II) AND PALLADIUM (II) XANTHATES WITH XANTHATE IONS

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(Received 30 April 1974)

It is now well established that when reaction occurs between $[\text{Ni}(\text{S-S})]_2$ \((\text{S-S} = \text{S}_2\text{CNR}_2, \text{S}_2\text{COR}, \text{S}_2\text{P(OR)}_2, \text{S}_2\text{PR}_2 \text{etc})\) and most nitrogen or phosphorus donor ligands \((\text{L})\), either five co-ordinate $[\text{Ni}(\text{S-S})_2\text{L}]$ and/or six co-ordinate $[\text{Ni}(\text{S-S})_2\text{L}_2]$ 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 $\text{Me}_3\text{PhNCl}$ gives the dark green complex $\text{Me}_3\text{PhN}[\text{Ni}(\text{S}_2\text{COEt})_3]$ which was assigned a six co-ordinate octahedral structure on the basis of electronic spectral evidence (2).

In contrast, the reaction of the isomorphous $[\text{M}(\text{S-S})]_2$ complexes \((\text{M}=\text{Pd, Pt})\) with tertiary phosphines occurs by stepwise cleavage of metal-sulphur bonds to generate the four co-ordinate compounds $[\text{M}(\text{S-S})_2\text{PR}_3']$ and $[\text{M}(\text{S-S})(\text{PR}_3')_2]$ (S-S) which exhibit unidentate/bidentate and bidentate/ionic modes of bonding of the dithioacid 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 \(\text{Ph}_4\text{As[Pt(S}_2\text{COEt})_3]\) (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 \(\text{Ph}_4\text{As[Pt(S}_2\text{CO}^\text{I} \text{Pr})_3]\) (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 \(\text{CDCl}_3\) which consists of two sharp methyl triplets at \(T=8.55\) and \(T=8.72\) of relative intensity 1:2. Two overlapping methylene quartets centred at \(T=5.57\) are also observed. Similarly for (II) at 223K, two sharp doublets were observed for the methyl protons at \(T=8.53\) and \(T=8.71\) also of relative intensity 1:2. The \(^{19}\text{F}\) n.m.r. spectrum of a related compound \(\text{n-}(\text{C}_3\text{H}_7)_4\text{N[Pt(S}_2\text{PF}_2)_3]\) 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 \(\text{S}_2\text{PF}_2\) 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 \([\text{cf.}[\text{M}(\text{S-S})_2\text{PR}']_3\text{ complexes (3)}]\). 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**

**Analytical Data for some Platinum and Palladium Xanthates**

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (t/°)</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>(\lambda^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{COEt})_3])</td>
<td>112</td>
<td>41.9</td>
<td>3.8</td>
<td>20.2</td>
<td>42.1</td>
<td>3.7</td>
<td>20.2</td>
<td>59.5</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO}^i\text{Pr})_3])</td>
<td>117-119</td>
<td>43.9</td>
<td>4.2</td>
<td>19.3</td>
<td>44.8</td>
<td>4.3</td>
<td>19.5</td>
<td>51.0</td>
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<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>
<td>15.9</td>
<td>42.5</td>
<td>3.2</td>
<td>16.2</td>
<td>57.5</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})(\text{S}_2\text{CO}^i\text{Pr})])</td>
<td>122-124</td>
<td>42.8</td>
<td>3.2</td>
<td>15.7</td>
<td>43.2</td>
<td>3.3</td>
<td>15.9</td>
<td>43.4</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pd}(\text{S}_2\text{CO})(\text{S}_2\text{COEt})])</td>
<td>155</td>
<td>47.5</td>
<td>3.6</td>
<td>18.3</td>
<td>47.9</td>
<td>3.6</td>
<td>18.5</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Ph}_4\text{As}[\text{Pt}(\text{S}_2\text{CO})(\text{S}_2\text{COME})])</td>
<td>136-138</td>
<td>41.5</td>
<td>3.1</td>
<td>16.6</td>
<td>41.7</td>
<td>3.0</td>
<td>16.5</td>
<td>54.2</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>
<td>11.4</td>
<td>52.4</td>
<td>3.5</td>
<td>11.2</td>
<td>137.6</td>
</tr>
</tbody>
</table>

* Equivalents conductivity \((\text{Scm}^2\text{mol}^{-1})\) 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 \([\text{Pt}(\text{S}_2\text{CO})(\text{PMePh}_2)_2]\) \((1696(s), 1681(sh), 1615(s) \text{ cm}^{-1}\) \((6)\) 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).

\[
\text{viz. } \left( R_3P \right)_2 \overset{S\rightleftharpoons\text{C-O-R}}{M} \overset{S\rightleftharpoons\text{C-O-R}}{S_2\text{COR}} \rightarrow \left( R_3P \right)_2 \overset{\text{C=O}}{M} + \text{RS}_2\text{COR}
\]

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 PPh$_3$ which gave [PPh$_3$]$_2$Pt(S$_2$CO)] (cf. the reaction of [Pt(S$_2$CS)$_2$]$_{2}^{2-}$ with PMePh$_2$ giving [(PMePh$_2$)$_2$Pt(S$_2$CS)] (8)). The same compound is obtained from the reaction between Ph$_4$As[Pt(S$_2$CO)(S$_2$COEt)] and PPh$_3$.

**SCHEME**

For [Pt(S$_2$COMe)$_2$] and KS$_2$COMe, (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 Ph$_4$As[Pt(S$_2$CO)(S$_2$COMe)] were deposited.

Work is now in progress on attempts to synthesise the related species [M(S-S)$_3$]$^-$ (S-S = $^{3-}$S$_2$CNR$_2$, $^{3-}$S$_2$P(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.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

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JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1975
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

The tris(chelate) complexes \[ \text{[Ru(S}_2\text{PMe}_2)_2(diene)] \] \{diene = bicyclo[2.2.1]hepta-2,5-diene (nbd) or cyclo-octa-1,5-diene (cot)\} have been synthesised by the reaction of \{[RuCl}_2(diene)]_2\} with Na[S_2PMe_2]·2H_2O in either ethanol or N,N-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 = Ph_2P[CH_2]_2PPh_2 (dppe), Ph_2PCH_2PPh_2 (dppm), C_6H_4(AsMe_2)_2 (pdma)\}. For L—L = pdma, \text{trans-[Ru(S}_2\text{PMe}_2)_2(pdma)]} is also formed. Unlike the corresponding cis-\[ \text{[Ru(S}_2\text{PMe}_2)_2L_2] \] \{L = PR_3 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 paper we proposed that the temperature-variable \(^1\)H n.m.r. spectra of complexes of the type cis-


\[ \text{[Ru(S}_2\text{PMe}_2)_2I}_2] \] \{I = PPh_3, PMePh_2, PMe_2Ph, P(OMe)_3 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-[Ru(S₂PMe₂)₂(L)L'] [L = PPh₃; L' = P[OPPh₃] or CO] in solvating media (CDCl₃ or PhCl) the mechanism of these inversion processes involves initial S₂2 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 [Me₂PS₂] group with concomitant loss of solvent to form the optical isomer [Scheme 1(a)]. In a non-solvating media (C₆H₆) 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 uni- and bi-dentate sulphur ligands occurs via a dissociative mechanism irrespective of the solvent. We have now synthesised some tris(chelate) complexes [Ru(S₂PMe₂)₂(L-L)] [L-L = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, nbd), cyclo-octa-1,5-diene (cot), Ph₃P(CH₂)₂PPh₂ (dppe), Ph₂PCH₂PPh₂ (dpdm), or C₆H₄(AsMe₂)₂ (pdma)] and examined their variable-temperature ¹H 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 [[RuCl₂(diene)]₃] (diene = nbd or cot) and Na[S₂CNMe₂] in hot NN-dimethylformamide has recently been shown to produce [Ru(S₂CNMe₂)₂(diene)] in high yield.¹ We have found that [Ru(S₂PMe₂)₂(diene)] may be prepared in analogous fashion using Na[S₂PMe₂]·2H₂O and furthermore that the diene moiety is labile, being readily replaced by CO or PPh₃ to give the known cis-[Ru(S₂PMe₂)₂(L)] complexes ² (L = CO or PPh₃). Reaction of [Ru(S₂PMe₂)₂(diene)] in ethanol with chelating ligands also causes exchange producing [Ru(S₂PMe₂)₂(L-L)] [L-L = Ph₂P(CH₂)₂PPh₂ (dppe), Ph₂PCH₂PPh₂ (dpdm), or C₆H₄(AsMe₂)₂ (pdma)], although when excess of pdma was used a complex of formula [Ru(S₂PMe₂)₂(pdma)]₂ was formed. This complex may also be isolated in low yield by prolonged reaction of trans-RuCl₂(L-L)₂ and Na[S₂PMe₂] heated under reflux in ethanol.

**Spectroscopic Properties of [Ru(S₂PMe₂)₂(L-L)].**—

**I.r. spectra.** The i.r. spectra of the complexes [Ru(S₂PMe₂)₂(L-L)] all showed absorptions arising from the chelating L-L ligands and from the [Me₂PS₂]⁻ groups. The bidentate nature of the latter is indicated in every case by the position of v(PS) between 580 and 590 cm⁻¹.⁴,⁵ However for [Ru(S₂PMe₂)₂(pdma)]₂ the only peak in the region 500—700 cm⁻¹ was a sharp absorption at 600 cm⁻¹ with a shoulder at 585 cm⁻¹ which suggests that both [Me₂PS₂]⁻ groups are probably bound through only one sulphur atom.⁴,³ This observation is supported by ¹H n.m.r. data (see below).

**¹H 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 = cot 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 ¹H n.m.r. signals arising from the expected H₃PPh₂ 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 = nbd, signals are assigned as arising from four olefinic protons.

(± 6·15), two methylene protons (± 8·70), and two bridge-head protons (± 5·90). For L-L = pdma, a poorly-resolved AA'BB' type spectrum arising from the phenylene protons was observed, centred at ± 2·40, whilst the methyl groups of pdma gave rise to two sharp singlets at ± 8·24 and 8·60. For L-L = dppm, apart from the phenyl resonances, a sharp triplet at ± 5·03 was seen, which arises from splitting of the methylene protons’ resonance by the two chemically equivalent 3P nuclei.

As for [Ru(S₂PMe₂)₂(L₂)], the methyl groups on the [Me₂PS₂]⁻ ligands gave rise to two doublets for all [Ru(S₂PMe₂)₂(L-L)] at low temperatures; however, in contrast to the behaviour of [Ru(S₂PMe₂)₂L₂] [L = PR₃ or P(O)R₃], these resonances remained sharp on warming to 373 K in PhCl. Above this temperature for L-L = diene the signals began to broaden but, since the b.p. of PhCl is 403 K, the condition of fast exchange of the [Me₂PS₂]⁻ methyl groups is never reached.

Finally, [Ru(S₂PMe₂)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 ± 8·02, and a sharp doublet from the methyl groups of the [Me₂PS₂]⁻ ligands (± 8·46). This spectrum was temperature invariant (233–333 K) and this is best explained if the two [Me₂PS₂]⁻ ligands are both unidentate 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 series² we proposed that complexes [Ru(S₂PMe₂)₂(L-L)] invert by the solvent-assisted bond-rupture 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(S₂PMe₂)₂(L-L)]. Thus for [Ru(S₂PMe₂)₂(dppm)] the very low rate constant and the high positive values found for ΔH and ΔS² (Table 2) could be explained either by sub-step (i) or (iii) in the mechanism shown in Scheme (1a) being slow and rate determining.² That is either the chelating ligands have low trans influences, thus making step (ii) slow (as was proposed for cis-[Ru(S₂PMe₂)₂(PPh₃)CO] and cis-[Ru(S₂PMe₂)₂(η-C₆H₅)₂]² or they prevent the solvent from entering the co-ordination sphere for steric reasons, thus making step (i) dissociative slow (as is found for cis-[Ru(S₂PMe₂)₂(PMe₂Ph)₂] in a non-co-ordinating medium such as benzene).²

The literature available on the trans influences of these ligands is somewhat erratic since, although dimes all appear to have low trans influences, dpe 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.⁶ Hence, at least for [Ru(S₂PMe₂)₂(pdma)], the observed low rate of inversion is incompatible with the known high trans influence of this ligand, which suggests that either the steric constraint proposed above or a different inversion mechanism to that given in Scheme 1(a) is responsible.

On further consideration there are a number of other possible microscopic paths for this inversion mechanism [Scheme 1(b)]. These are all consistent with the experimental data in Part VI apart from the last which causes exchange between the wrong pairs of methyl groups and hence does not explain the temperature-variable H n.m.r. spectra of cis-[Ru(S₂PMe₂)₂(PPh₃)] [P(OMe)₃]. It is to be noted that whereas the mechanism shown in Scheme 1(a) involves attack of the solvent molecule (Y) in a position close to the Ru-S bond to be broken so that the solvent simply takes the place of the dissociating sulphur atom in the co-ordination sphere, those in 1(b) involve a pentagonal-bipyramidal intermediate in which the.

---

**Table 1**

<table>
<thead>
<tr>
<th>Complex</th>
<th>[Me₂PS₂]⁻ (Me group)</th>
<th>L-L</th>
<th>Phenyl or phenoxy group</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(S₂PMe₂)₂(phen)]</td>
<td>7·78 (12·5), 7·80 (13·0)</td>
<td>5·90, 6·18, 8·70</td>
<td></td>
</tr>
<tr>
<td>[Ru(S₂PMe₂)₂(cot)]</td>
<td>8·20 (13·0), 8·25 (12·6)</td>
<td>6·35, 7·80</td>
<td></td>
</tr>
<tr>
<td>[Ru(S₂PMe₂)₂(dpe)]</td>
<td>7·90 (13·0), 9·25 (13·0)</td>
<td>d</td>
<td>2·0—3·0</td>
</tr>
<tr>
<td>[Ru(S₂PMe₂)₂(dppm)]</td>
<td>8·25 (13·0), 8·28 (12·5)</td>
<td>6·20 (12·0), 8·24 (s), 8·60 (s)</td>
<td>2·1—2·8</td>
</tr>
<tr>
<td>[Ru(S₂PMe₂)₂(pdma)]</td>
<td>8·75 (13·0), 8·25 (12·6)</td>
<td>8·02 (s)</td>
<td>2·1—2·6</td>
</tr>
</tbody>
</table>

s = Singlet, t = triplet.

*± 0·01. Doublet: j(PH) in parentheses (± 0·2 Hz).

---

**Table 2**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>Log₁₀(k/s⁻¹)</th>
<th>E₁</th>
<th>ΔH₁</th>
<th>ΔS₁</th>
<th>ΔG₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(S₂PMe₂)₂(dppm)]</td>
<td>PhCl</td>
<td>3·0 ± 0·30</td>
<td>7·1</td>
<td>7·1</td>
<td>7·1</td>
<td>7·1</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₂(PPh₃)CO]</td>
<td>PhCl</td>
<td>1·90 ± 0·08</td>
<td>6·9</td>
<td>6·9</td>
<td>6·9</td>
<td>6·9</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₂(PMe₂Ph)₂]</td>
<td>PhCl</td>
<td>1·01 ± 0·01</td>
<td>6·7</td>
<td>6·7</td>
<td>6·7</td>
<td>6·7</td>
</tr>
<tr>
<td>cis-[Ru(S₂PMe₂)₂(PMe₂Ph)₂]</td>
<td>C₂H₅</td>
<td>0·04 ± 0·12</td>
<td>10·0</td>
<td>10·0</td>
<td>10·0</td>
<td>10·0</td>
</tr>
</tbody>
</table>

* See ref. 2.

---

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

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(L)L'] in solvating media (CDCl₃ or PhCl) is that shown in Scheme 2(a), whereas in a non-solvating medium and for [Ru(S₂PMe₂)₂(L-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,‡ 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 dppe 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.

Scheme 2 Postulated mechanisms of inversion for cis-[Ru(S₂PMe₂)₂(L)L']: (a) in a polar solvent; (b) in a non-polar solvent

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 width at half height under slow-exchange conditions. Life-times obtained by this fitting procedure were then used to construct an Arrenius plot (log₁₀T₂ 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 Kölffler 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(diphenylphosphinomethyl)ethane (dpmm), 1,2-bis(diphenylphosphino)ethane (dppe), sodium dimethylphosphinodithioate, 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(dimethylphosphinodithioato)ruthenium(ii).—(a) The complex [(RuCl₂(nbd))₂]⁹ (0-20 g) and Na[S₂PMe₂]•2H₂O ⁹ (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 \([\text{RuCl}_2(\text{nbd})]_2\) (0-28 g) was added to a hot solution of \(\text{Na}[\text{S}_2\text{PMe}_2]-2\text{H}_2\text{O}\) (0-29 g) in \(\text{NN}-\text{dimethylformamide (8 cm}^3\). After cooling and addition remove excess of \(\text{trans-[RuCl}_2(\text{dppe})]_2\) and \(\text{NaCl}\) and, on cooling, the complex precipitated as orange crystals (0-06 g, 39%).

\[
\text{[1,2-Bis(diphenylphosphino)methane]bis(dimethylphosphino-}
\]

\[
\text{dithioato)ruthenium(II).—The complex [Ru(S}_2\text{PMe}_2^-}
\]

\[
\text{(nbd)] (0-05 g) and dppm (0-10 g) were shaken in ethanol}
\]

\[
\text{of water, the brown solid was filtered off and recrystallised from}
\]

\[
\text{aqueous acetone as orange crystals (0-17 g, 41%).}
\]

(Cyclo-octa-1,5-diene)bis(dimethylphosphinodithioato)ruthenium(II) was similarly prepared from \(\text{[RuCl}_2(\text{cot})]_n\) (0-28 g) and \(\text{Na}[\text{S}_2\text{PMe}_2]-2\text{H}_2\text{O}\) (0-29 g) as orange crystals.

\[
\text{[1,2-Bis(diphenylphosphino)ethane]bis(dimethylphosphino-}
\]

\[
\text{dithioato)ruthenium(II).—(a) The complex [Ru(S}_2\text{PMe}_2^-}
\]

\[
\text{(nbd)] (0-11 g) was heated under reflux with dppe (0-10 g) in}
\]

\[
\text{acetone for 24 h. Cooling and concentrating the solution}
\]

\[
\text{then afforded the complex as orange crystals which were}
\]

\[
\text{recrystallised from CH}_2\text{Cl}_2-\text{n-hexane (0-10 g, 58%).}
\]

(b) The complex \(\text{trans-[RuCl}_2(\text{dppe})]_2\) (0-20 g) and \(\text{Na}[\text{S}_2\text{PMe}_2^-]-2\text{H}_2\text{O}\) (0-20 g) were heated under reflux in ethanol (25 cm³) for 24 h. The solution was filtered hot to (20 cm³) for 5 h. The orange crystals were filtered off and washed with water, ethanol, and n-pentane (0-13 g, 80%).

\[
\text{trans-Bis(dimethylphosphinodithioato)bis(o-phenylenebis-}
\]

\[
\text{(dimethylarsine)}\text{ruthenium(II).—The complex [Ru(S}_2\text{PMe}_2^-}
\]

\[
\text{(nbd)] (0-05 g) and pdma (0-2 cm³) were heated under re-
\]

\[
\text{flux in ethanol (10 cm³) for 10 min. The pink crystals were}
\]

\[
\text{filtered off and washed with water, ethanol, and n-pentane}
\]

\[
\text{(0-085 g, 97%). Recrystallisation from boiling toluene gave}
\]

\[
\text{orange crystals of the product in 100% yield.}
\]

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.

\[
\text{[4/2339 Received, 8th November, 1974]}
\]
Preliminary communication

REACTION OF PALLADIUM DIENE AND 2-PHENYL AZO-PHENYL COMPLEXES WITH SOME SULPHUR-CONTAINING NUCLEOPHILES

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(Received December 10th, 1975)

Summary

The syntheses of \([\text{PdX}(S-S)]_2\) \([X = \text{Cl, Br; } (S-S)^- = \text{~S}_2\text{CNR}_2, ~\text{~S}_2\text{COR}]\) via \([\text{C}_8\text{H}_{12}\text{PdCl}_2]\) or \([\text{PhN}_2\text{C}_6\text{H}_4\text{Pd(OOCOCH}_3)]_2\) 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 \([\text{dienePdCl}_2]\) complexes with various nucleophiles containing oxygen or nitrogen donor atoms (e.g. \(\text{~OR, ~OCOR, NH}_2\text{R etc.}\) show that, usually, attack on one of the coordinated double bonds occurs to give substituted alketyl complexes [1].

We now report that the reaction between \([\text{C}_8\text{H}_{12}\text{PdCl}_2]\) \((\text{C}_8\text{H}_{12} = 1,5\text{-cyclooctadiene})\) and S-containing nucleophiles such as \(N,N'\text{-dialkyl- and } O\text{-alkyl-dithiocarbamate anions } (S-S^-) \) \((1:1 \text{ molar ratios})\) 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 \([\text{PdCl}(\text{S}_2\text{CNR}_2)L]\) (II) \((L = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{C}_5\text{H}_5\text{N, CO etc.})\). For \(L = \text{tertiary phosphine}, \) these complexes can also be synthesised by reaction of \([\text{PdCl}_2(PR_3)]_2\) with either \(\text{Me}_2\text{SnCl(S}_2\text{CNR}_2)\) [3] or \(\text{Na(S-S)} (\text{(S-S)}^- = \text{~S}_2\text{CNR}_2 \text{[3,4], ~S}_2\text{COR [4], ~S}_2\text{ PR}_2 \text{[4]}\) but, with weaker Lewis

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**With the exception of \(\text{CF}_3\text{S}^- \) [2], this appears to be the first reported reaction between anionic sulphur-containing nucleophiles and \([\text{dienePdCl}_2]\) compounds.
bases in the coordination sphere, only $[\text{Pd}(S—S)_2]$ are formed by this route. Reaction of II with AgBF$_4$ in tetrahydrofuran, followed by addition of another Lewis base ($L'$) and NaBPh$_4$ readily gives the mixed ligand complexes $[\text{Pd}(S_2CNR_2)LL']$ BPh$_4$ (III) (e.g. $L = \text{PPh}_3$, $L' = \text{AsPh}_3$, $C_5H_5N$ etc). Similarly, reaction of I with Ph$_3$PhCH$_2$PCl/HCl gives the anionic Ph$_3$PhCH$_2$P$[\text{PdCl}_2(S_2$-$CNR_2)]$ (IV). The related $[\text{Pd}(S_2COR)_3]$~ has been described elsewhere [5].

\begin{align*}
\text{SCHEME 1. (i) } & L = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{C}_5\text{H}_5\text{N}, \text{CO} \text{ etc.}; \ (ii) \ L = \text{PPh}_3; \ L' = \text{AsPh}_3, \text{C}_5\text{H}_5\text{N} \text{ etc.}; \ (iii) \ M = \text{Ph}_3\text{PHCH}_2\text{P}^+; \ (iv) \ X = \text{Br}, \Gamma, '\text{SPh}; \ (v) \ L = \text{PPh}_3, X = '\text{SPh}; \ L = \text{PPh}_3, X = \text{Br}; \ (vi) \ (S—S)' = '\text{S}_2\text{PMer}'; \ '\text{S}_2\text{COEt}$.\end{align*}
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\(_2\)CN(R\(_2\))\(_2\)])\(_2\) (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\(_2\)CN(R\(_2\))) (1:2 molar ratio) (eq. 2).

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\(_3\) is reported to give [Pd(S-t-Bu)(S-S)PMePh\(_3\)]\(_n\), originally formulated from \(^1\)H NMR studies as five coordinate dimers [8]*.

However, we have found that reaction of [Pd(SPh)(S\(_2\)CNEt\(_2\))]\(_2\) with PPh\(_3\) gives the red, crystalline monomeric [Pd(SPh)(S\(_2\)CNEt\(_2\))PPh\(_3\)] (VI).

Finally, preliminary studies indicate that reaction of [PdCl(S\(_2\)CN(R\(_2\))]\(_2\) with other dithioacid anions gives the mixed [Pd(S\(_2\)CN(R\(_2\)))(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 $[\eta^6$-C₆H₆RuCl₂]₂ AND $[\eta^5$-C₅Me₅RhCl₂]₂ WITH SOME SULPHUR-CONTAINING NUCLEOPHILES

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(Received December 27th, 1975)

Summary

The dithioacid ligand complexes $[\eta^6$-C₆H₆Ru(S₂PR₂)₂], $[\eta^5$-C₅Me₅Rh(S-S)]₂, [(S-S)- = S₂PR₂, S₂CNR₂, S₂COR], $[\eta^5$-C₅Me₅RhCl(S₂CNR₂)] and $[\eta^5$-C₅Me₅RhCl(S₂PMe₂)(S₂CNMe₂)] have been synthesised by reaction of $[\eta^6$-C₆H₆RuCl₂]₂ and $[\eta^5$-C₅Me₅RhCl₂]₂ respectively with Na(S-S).

In recent papers, the synthesis of the complexes cis-[Ru(S-S)₂ diene] [(S-S)- = S₂CNR₂ [1,2], S₂PR₂ [2]; diene = 1,5-C₈H₁₂, C₇H₈] by reaction of [RuCl₂ (diene)]ₙ with Na(S-S) have been described. In this note, we wish to report the results of the related reactions between $[\eta^6$-C₆H₆RuCl₂]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 Ph₂P(CH₂)ₙPPh₂ (n = 1, 4) giving $[\eta^6$-C₆H₆RuCl₂(Ph₂PCH₂PPh₂)] and $([\eta^6$-C₆H₆RuCl₂]₂ {Ph₂P(CH₂)₄PPh₂}) with mono- and bi-dentate coordination respectively [3].
Reaction of I with NaS$_2$PR$_2$ in water (1:2 molar ratio) gives monomeric complexes of formula $[\eta^6$-C$_6$H$_6$Ru(S$_2$PR$_2$)$_2]$ (R = Me, Ph, OMe, OEt). $^1$H and $^{31}$P NMR studies reveal that these compounds are best formulated with mono- and bi-dentate ligands [structure (II)], e.g. for -S$_2$PMe$_2$, the $^1$H NMR spectrum at 303 K consists of three doublets of relative intensity (2; 1; 1) (2$\ J$(PH) 12.0 Hz) in addition to a singlet at δ 5.88 ppm ($\eta^6$-C$_6$H$_6$). However, although they are stereochemically rigid at room temperature, ready decomposition in solution as indicated by the appearance of free benzene ($^1$H and $^{13}$C NMR) and -S$_2$PR$_2$ ($^{31}$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.

Therefore, since I does not give a very wide range of arene complexes containing dithioacid ligands, we have investigated similar reactions with the isoelectronic $[\eta^5$-C$_5$Me$_5$RhCl$_2$]$_2$ (III) [5]. Thus; III reacts with -S$_2$PR$_2$ (1:1 mole ratio) (R = Me, Ph) to give $[\eta^5$-C$_5$Me$_5$Rh(S$_2$PR$_2$)$_2]$ (IV). Unlike I, however, III reacts with the stronger nucleophiles -S$_2$CNR$_2$ and -S$_2$COR, without loss of the π-bonded ring, to give the analogous $[\eta^5$-C$_5$Me$_5$Rh-(S–S)$_2$] (IV). NMR studies at ambient temperature confirm the presence of inequivalent dithioacid ligands in all these compounds and variable temperature studies at higher temperatures reveal that interconversion of mono- and bi-dentate dithioacid ligands occurs. A detailed kinetic line-shape analysis of this process is now in progress. Reaction of III with NaS$_2$CNMe$_2$ (1:1 mole ratio) gives $[\eta^5$-C$_5$Me$_5$RhCl(S$_2$CNMe$_2$)]*, from which the mixed dithioacid complex $[\eta^5$-C$_5$Me$_5$Rh(S$_2$PMe$_2$)(S$_2$CNMe$_2$)]* can be synthesised. NMR studies show the latter to have bidentate -S$_2$CNMe$_2$ and unidentate -S$_2$PMe$_2$ 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 \([M(S-S)\text{L}]\) compounds \((M=\text{Pd, Pt}; S-S=\text{S}_2\text{PR}_2, \text{S}_2\text{COR} \text{and } \text{S}_2\text{P(OR)}_2)\). In particular, a study of the various rearrangement reactions exhibited by the products \([M(S-S)\text{L}]\) and \([M(S-S)\text{L}]\text{Y} \,(Y=\text{S-}, \text{BPh}_4^-, \text{Cl}^-, \text{PF}_6^-)\) has been described (1). One reaction was the conversion of \([\text{Pd}(\text{S}_2\text{PR}_2)\text{BPh}_4^-] (R=\text{Me, Ph})\) to \([\text{Pd}(\text{S}_2\text{PR}_2)\text{BPh}_3]\) when dissolved in either \(\text{CH}_2\text{X}_2\) or \(\text{CHX}_3\) \((X=\text{Cl, Br})\)(1). Unfortunately, this particular rearrangement appears to be confined to compounds containing a combination of \(\text{Pd}, \text{PPh}_3, \text{S}_2\text{PR}_2\) and \(\text{BPh}_4^-\) and thus does not provide a general method of synthesising the series \([\text{MX}(\text{S-S})\text{PR}_3]\).

Although \([\text{NiX}(\text{S-S})\text{PR}_3]\) \((\text{S-S}=\text{S}_2\text{CNR}_2, \text{S}_2\text{COR})\) compounds have recently been reported, \([\text{PdX}(\text{S}_2\text{PR}_2)\text{BPh}_3]\) 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

\([\text{NiX}(\text{S}_2\text{CNR}_2)\text{PR}_3]\) \((2, 3)\), reaction of \(\text{PdCl}_2\) \((\text{or K}_2\text{PtCl}_4), \text{PR}_3\) and \(\text{NaS}_2\text{CNR}_2\text{H}_2\text{O} \,(\text{or NaS}_2\text{PR}_2)\) gave only \([\text{M}(\text{S-S})]\). Similarly, although reactions of \([\text{Pd}(\text{S}_2\text{PR}_2)\text{BPh}_4^-] \) with excess \(\text{AgX} \,(X=\text{Cl, Br, I, SCN})\) in acetone readily gave \([\text{PdX}(\text{S}_2\text{PR}_2)\text{PR}_3]\), the corresponding exchange reactions with \([\text{Pt}(\text{S-S})\text{PR}_3]\) \((\text{S-S}=\text{S}_2\text{PR}_2, \text{S}_2\text{CNR}_2)\) were very inefficient and produced only low yields of the required product (especially for \(\text{S-S}=\text{S}_2\text{CNR}_2\)).
### TABLE 1

Analytical Data for some Platinum (II) and Palladium (II) Dithioacid Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found °/o</th>
<th>Required °/o</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[PtCl(S₂CNEt₂)PMePh₂]</td>
<td>37.2 4.1 2.3 Cl, 6.0</td>
<td>37.4 4.0 2.4 Cl, 6.1</td>
</tr>
<tr>
<td>[PtCl(S₂CNEt₂)PMe₂Ph]</td>
<td>29.4 4.0 2.9</td>
<td>61a 516b</td>
</tr>
<tr>
<td>[Pt(S₂CNEt₂)(S₂PMe₂)PMePh₂]</td>
<td>36.0 4.5 2.2</td>
<td>-</td>
</tr>
<tr>
<td>[PdCl(S₂CNEt₂)PMe₂Ph]</td>
<td>36.4 5.0 3.3 Cl, 8.2</td>
<td>445a 428b</td>
</tr>
<tr>
<td>[PdBr(S₂CNEt₂)PMe₂Ph]</td>
<td>33.2 4.3 2.9</td>
<td>533a 473b</td>
</tr>
<tr>
<td>[PdI(S₂CNEt₂)PMe₂Ph]</td>
<td>30.3 4.1 2.7</td>
<td>1.24.8</td>
</tr>
<tr>
<td>[PdCl(S₂COEt)PMe₂Ph]</td>
<td>33.0 4.0</td>
<td>-</td>
</tr>
<tr>
<td>[PdCl(S₂CPH₂)PMe₂Ph]</td>
<td>26.7 5.8</td>
<td>-</td>
</tr>
<tr>
<td>[PdI(S₂CNEt₂)(PMe₂Ph)PPh₃]</td>
<td>24.3 3.5</td>
<td>-</td>
</tr>
<tr>
<td>[PdI(S₂CNEt₂)(PMe₂Ph)C₅H₅N]</td>
<td>67.8 6.0 1.3</td>
<td>-</td>
</tr>
</tbody>
</table>

* Molecular weight measured osmotically at 37° in chloroform

b Molecular weight from parent ion peak (196Pd or 195Pt isotope) in mass spectrum

### TABLE 2

Hnmr Data in CDCl₃ at 301K for some Platinum (II) and Palladium (II) Dithioacid Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>CH₃b</th>
<th>CH₂b</th>
<th>Methyl groups of phosphinec</th>
<th>Phenyl groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[PtCl(S₂CNEt₂)PMePh₂]</td>
<td>1.26(t), 1.19(t)</td>
<td>3.64(q), 3.47(q)</td>
<td>2.16(t, d)d</td>
<td>7.32-7.82(m)</td>
</tr>
<tr>
<td>[PtCl(S₂CNEt₂)PMe₂Ph]</td>
<td>1.28(t), 1.25(t)</td>
<td>3.66(q), 3.55(q)</td>
<td>1.83(t, d)n</td>
<td>7.32-7.86(m)</td>
</tr>
<tr>
<td>[Pt(S₂CNEt₂)(S₂PMe₂)PMePh₂]</td>
<td>1.29(t), 1.21(t)</td>
<td>3.68(q), 3.50(q)</td>
<td>2.29(t, d)h</td>
<td>7.32-7.80(m)</td>
</tr>
<tr>
<td>[PdCl(S₂CNEt₂)PMe₂Ph]</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>[PdI(S₂CNEt₂)PMe₂Ph]</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(S₂PMe₂)PMe₂Ph]</td>
<td>2.00(d)f</td>
<td>-</td>
<td>1.77(d)</td>
<td>7.32-7.80(m)</td>
</tr>
</tbody>
</table>

d=doublet; t=triplet; q=quartet; m=multiplet

---

a 5.0, 5.1 JCH₃CH₃, 7.0Hz c 2JPH₁, 1.0Hz d 3JPH₁, 34.0Hz e 3JPH₁, 35.5Hz f 3JPH₁, 35.0Hz g 4JPH₁, 5.0Hz h 4JPH₁, 5.0Hz i 5JPH₁, 36.0Hz j 5JPH₁, 36.0Hz
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$_2$Ph; M=Pt; X=Cl; PR$_3$ = PMe$_2$Ph, PMePh$_2$) with various alkali metal dithio acid salts ($^{\text{S}_2PR_2}$, $^{\text{S}_2\text{CNR}_2}$, $^{\text{S}_2\text{COR}}$) in 1:2 molar ratio in acetone (Pd) or acetone/CH$_2$Cl$_2$ (Pt) provides an excellent general method of synthesising a wide range of these compounds$^\dagger$. 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).

![Structure (I)](image)

Full confirmation of structure (I) is obtained from the $^1$H nmr spectra of the diethyl dithiocarbamate derivatives which show two magnetically inequivalent ethyl groups at ambient temperature. As expected for a structure of this type, the $^{\text{S}_2\text{PMe}_2}$ 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

![Structure (II)](image)

![Structure (III)](image)

$^\dagger$ Very recently, N Sonoda and T Tanaka, Inorg Chim Acta 12 261 (1975) have independently reported the synthesis of the related $[\text{PdCl(XYCNR}_2)\text{PR}_3]$ (R=Me, Et; PR$_3$ = PMe$_2$Ph, PPh$_3$, PMe$_2$Ph; X=S, Y=Se) by reaction of $[\text{PdCl}_2(\text{PR}_3)]_2$ with Me$_2$SnCl(XYCNR$_2$). $[\text{PdCl}(^{\text{S}_2\text{CNR}_2})\text{PR}_3]$ (R=Me, Et; PR$_3$ = PPh$_3$, PMePh$_2$) are also briefly described.
[Pt(S₂CNEt₂)₂PMePh₂] (5) and [Pt(S₂PMe₂)₂PMePh₂] (1), this compound is stereochemically rigid even at 330K. As expected, reaction of [PtCl(S₂PMe₂)PMePh₂] with NaS₂CNEt₂·3H₂O gives Pt(S₂CNEt₂)⁺, indicating the greater nucleophilicity of S₂CNEt₂ compared to S₂PMe₂. 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)PMe₂Ph] with AgBF₄ in tetrahydrofuran produces a white precipitate of AgCl and a yellow solution thought to contain the solvated cation [Pd(THF)(S₂CNEt₂)PMe₂Ph]⁺. Addition of various ligands (L) to this solution followed by treatment with NaBPh₄ readily gives the mixed ligand complexes [Pd(S₂CNEt₂)(PMe₂Ph)L] BPh₄ (III) (L=PPh₃, 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(NN-diethylidiselenocarbamato)-selenium(II)


Reprinted from JOURNAL OF THE CHEMICAL SOCIETY DALTON TRANSACTIONS 1976
Crystal and Molecular Structure of Bis(NW-diethyldiselenocarbamato)-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(NW-diethyldiselenocarbamoyl)diselenide (I), an aqueous solution of sodium diethyldiselenocarbamate was allowed to react with atmospheric oxygen.1 Two products were obtained by fractional crystallisation of the resulting orange solid from ethanol–chloroform: bis(NW-diethyldiselenocarbamato)selenium(II) (II), and bis(NW-diethyldiseleno-1 P. Barnard and D. T. Woodbridge, J. Chem. Soc., 1961, 2922.
carbamoyl)selenium(n) (III). The crystal structure of (II) is reported here.

\[
\text{Et}_2\text{N}C(\text{Se})\text{Se}C(\text{Se})\text{NEt}_2 \quad \text{Et}_2\text{N}C(\text{Se})\text{Se}C(\text{Se})\text{Se}\text{C(Se)}\text{NEt}_2
\]

(III) (IV)

**EXPERIMENTAL**

*Crystal Data.* — C₁₀H₂₀N₂Se₅, M = 563, orange monoclinic needles, \(a = 6.707(5), b = 9.978(6), c = 25.41(1) \text{ Å}, \beta = 90.75(5)^\circ, U = 1\text{700}\text{ Å}^3, D_m = 2.17, Z = 4, D_o = 2.20 \text{ g cm}^{-3}.

Space group \(P2_1/n\) (non-standard setting of \(P2_1/c\), No. 14).

Cu-K\(\alpha\) radiation, \(\lambda = 1.5418 \text{ Å}; \mu_{(\text{Cu-K\(\alpha\)})} = 144 \text{ cm}^{-1}.

Structure Determination. — Data for layers 0–5\(\kappa\)l were collected on multi-film packs, by the equi-inclination Weissenberg method. The crystal chosen was approximately cylindrical, elongated along \(\langle 100 \rangle\) with a mean cross-sectional area of 0.06 mm². 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, 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 \(W = X, Y, Z\), where \(X = \sin\beta/0.22\) for \(\sin\beta < 0.22\) and 1.0 otherwise, and \(Y = 150|F_o|/|F_o| > 150\) 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).

All standard crystallographic calculations were done by use of the 'X-Ray '72' program system 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 \(C_i\) \((m)\) symmetry; excluding terminal methyl groups, they are planar with \(C_{2g}\) symmetry, the maximum deviation from the plane being 0.4 Å \((C(7))\).

The corresponding bis(\(\text{NN-diethyldithiocarbamato-}\)selenium(n)) (IV) has been reported. Its molecular structure is very similar: mean Se–Se distances in (IV)

**Figure 1** Projection of a molecule of (II) on its best plane

**Figure 2** Projection of a molecule of (II) on its best plane

2.32 and 2.76 Å, while in (II) the mean Se–Se distances are 2.46 and 2.82 Å. As would be expected,

2. 'X-Ray '72' program system, Technical Report TR 192, Computer Science Center, University of Maryland, version of June 1972.

the difference between the two bonds in the SeSe$_4$ system is much less than that in the SeS$_4$ 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 $P2_12_12_1$. 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).  

Brondmo et al. 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(diethylidiselenophosphinato)tellurium(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 establishd for the sulphur analogues where, for example, the Ni-S bonds in bis(diethyl-dithiocarbamato)nickel(II) (2.202 Å)$^7$ are significantly shorter than those in bis(dimethyldithiophosphinato)-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.

Metal Complexes of Sulphur Ligands. Part 10. Reaction of mer-Trichlorotris(dimethylphenylphosphine)osmium(III) with Dimethylidithiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and O-Ethyl Dithiocarbonate Ligands

By David J. Cole-Hamilton and T. Anthony Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

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JOURNAL
OF
THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1976
Metal Complexes of Sulphur Ligands. Part 10. Reaction of mer-Trichlororos(trimethylphenylphosphine)osmium(III) with Dimethylthiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and O-Ethyl Dithiocarbonate Ligands

By David J. Cole-Hamilton and T. Anthony Stephenson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reactions of the complex mer-[OsCl₃(PMe₂Ph)₃] (1) with excess of S₂⁻ ion (S₂⁻ = S₂CNMe₂⁻, S₂PMe₂⁻, or S₂COEt) have been thoroughly studied. For [S₂CNMe₂⁻], refluxing in methanol for 90 min gives a high yield of cis-[Os(PMe₂Ph)₃(S₂CNMe₂)₂] (2), whereas shaking in methanol gives mer-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (3). Reaction of (3) with Na[S₂CNMe₂]·2H₂O in refluxing ethanol gives (2) together with small amounts of fac-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (6) and fac-[Os(OC₂H₅)₃(PMe₂Ph)₂(S₂CNMe₂)] (7). Similarly, for S₂⁻ = S₂PMe₂⁻ or S₂PPPh₃⁻, reaction with (1) in refluxing ethanol gives cis-[Os(PMe₂Ph)₃(S₂PR₂)₂] (R = Me (7) or Ph (8)). However, shaking in methanol gives paramagnetic mer-[OsCl₄(PMe₂Ph)₃(S₂PR₂)₂] [R = Me (9) or Ph (10)]. Recrystallisation of (9) from boiling benzene gives trans-[OsCl₄(PMe₂Ph)₃(S₂PR₂)₂] (11), whereas prolonged standing in cold benzene gives a purple oil containing the cation [OsCl₄(PMe₂Ph)₃(S₂PR₂)]⁺ (12) together with (1) and brown crystalline mer-[OsCl₄(PMe₂Ph)₃(S₂PR₂)] (13). Carbonylation of (7) in refluxing ethanol in the presence of sulphur gives cis-[Os(CO)(PMe₂Ph)₃(S₂PR₂)] (14) together with a brown oil containing PMe₃PhS and a complex of probable formula [Os(CO)(PMe₂Ph)(S₂PR₂)] (15). In the presence of PMe₃Ph, carbonylation of (7) gives [Os(CO)(PMe₂Ph)(S₂PR₂)] (16) whereas in cold CH₂Cl₂-C₆H₄ a different isomeric form of [Os(CO)(PMe₂Ph)(S₂PR₂)] (17) is produced. In contrast, reaction of (1) with K[S₂COEt] under all conditions gives only mer-[OsCl₄(PMe₂Ph)₃(S₂COEt)] (18). The complexes have been characterised by elemental analyses and mass, i.r., and n.m.r. spectroscopy (¹H and ³¹P), and detailed mechanisms for the overall reaction and the carbonylation of (7) are postulated.

In Part 7 of this series the investigation of the reactions of mer-[RhCl₃(PMe₂Ph)₃] with dithiocarbamate ligands gave considerable insight into the possible nature of some of the paramagnetic intermediates which might be formed in the preparation of cis-[Ru(PMe₂Ph)₂(S₂PR₂)] (R = Me or Ph) from mer-[RuCl₂(PMe₂Ph)₃]. However, because of the stability of rhodium(III) complexes with respect to reduction to Rh(II), no information could be gleaned about the step at which reduction to Ru(II) occurs or the nature of any ruthenium(II) intermediates. It was therefore felt, since osmium has stable oxidation states of both II and III and is also less labile than ruthenium in both of these oxidation states, that an investigation of the reactions of mer-[OsCl₃(PMe₂Ph)₃] with dithiocarbamate ligands might shed some extra light on the mechanism of formation of cis-[Ru(PMe₂Ph)₂(S₂PR₂)], from mer-[RuCl₄(PMe₂Ph)₃].

With the exception of a very recent paper on osmium dialkylidithiocarbamates and O-alkyl dithiocarbonates, very little work has been published on osmium...
complexes containing dithioacid ligands. Earlier examples include the synthesis of [Os(S2CNMe2)2] from the reaction of [NH4]2[OsCl6] with Na[SHCN].6 A brief mention of [OsCl(bipy)(S2CN \( \text{CH}_2\text{CN} \)] (bipy = 2,2'-bipyridyl) from the interaction of [OsCl(bipy)2] and K[SN(CN)2].6

Analytical data for the new complexes are given in Table 1 and spectroscopic properties in Tables 2–4.

**Dimethyl dithiocarbamato-complexes.**—When complex (1) was heated under reflux with excess of Na[SHCN], 2H2O in ethanol for 90 min, a yellow complex of composition [Os(PMe2Ph)2(S2CNMe2)] (2) was isolated in 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 Sg[SCNMe2]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 [OsCl2(PMe2Ph)3]9 was isolated and this was

**Table 1**

Analytical data for some osmium dithioacid 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>mer-[OsCl2(PMe2Ph)3(S2PMe2)] (9)</td>
<td>Purple</td>
<td>140–142</td>
<td>C 39.8</td>
<td>H 4.9</td>
</tr>
<tr>
<td>mer-[OsCl2(PMe2Ph)3(S2PPh2)] (10)</td>
<td>Purple</td>
<td>104–105</td>
<td>C 46.6</td>
<td>H 4.6</td>
</tr>
<tr>
<td>trans-[OsCl2(PMe2Ph)3(S2PMe2)] (11)</td>
<td>Red</td>
<td>207–210</td>
<td>C 32.6</td>
<td>H 4.3</td>
</tr>
<tr>
<td>mer-[OsCl2(PMe2Ph)3(S2PMe2)] (13)</td>
<td>Brown</td>
<td>198–200</td>
<td>C 39.9</td>
<td>H 4.7</td>
</tr>
<tr>
<td>fac-[OsCl2(PMe2Ph)3(S2CNMe2)] (3)</td>
<td>Yellow</td>
<td>140–150</td>
<td>C 42.6</td>
<td>H 5.3</td>
</tr>
<tr>
<td>fac-[OsCl2(PMe2Ph)3(S2CNMe2)] (5)</td>
<td>Yellow</td>
<td>172–174</td>
<td>C 42.4</td>
<td>H 5.2</td>
</tr>
<tr>
<td>fac-[OsCl2(PMe2Ph)3(S2CNMe2)] (6)</td>
<td>Yellow</td>
<td>206–210</td>
<td>C 41.5</td>
<td>H 5.2</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)3(S2PMe2)] (7)</td>
<td>Orange</td>
<td>123–125</td>
<td>C 42.5</td>
<td>H 5.2</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)3(S2PPh2)] (2)</td>
<td>Orange</td>
<td>189–190</td>
<td>C 33.5</td>
<td>H 4.9</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PMe2)2] (18)</td>
<td>Orange</td>
<td>238</td>
<td>C 40.5</td>
<td>H 4.5</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PPh2)2] (8)</td>
<td>Orange</td>
<td>122–127</td>
<td>C 37.5</td>
<td>H 4.9</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PMe2)(S2COEt)] (1)</td>
<td>Yellow</td>
<td>155–158</td>
<td>C 34.0</td>
<td>H 4.7</td>
</tr>
</tbody>
</table>

* Obtained in CH2Cl2 at 301 K by Evans' method. 1 B.M. \( \approx 9.27 \times 10^{-24} \) A m². 2 Decomposition.

**Table 2**

I.r. spectra (cm\(^{-1}\)) of various osmium dithioacid complexes as nulls

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu(\text{OsCl}) )</th>
<th>Dithioacid ligand absorptions</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>mer-[OsCl2(PMe2Ph)3(S2PMe2)] (9)</td>
<td>350 m, 312 s, 270 m</td>
<td>600 vš</td>
<td>1040 vš</td>
</tr>
<tr>
<td>mer-[OsCl2(PMe2Ph)3(S2PPh2)] (10)</td>
<td>350 w, 318 m</td>
<td>645 s, 540 s</td>
<td>425 s</td>
</tr>
<tr>
<td>trans-[OsCl2(PMe2Ph)3(S2PMe2)] (11)</td>
<td>360 s, br</td>
<td>628 m</td>
<td>580 m</td>
</tr>
<tr>
<td>mer-[OsCl2(PMe2Ph)3(S2CNMe2)] (3)</td>
<td>340 w</td>
<td>1 510 m</td>
<td>1050 m</td>
</tr>
<tr>
<td>fac-[OsCl2(PMe2Ph)3(S2CNMe2)] (5)</td>
<td>350 w</td>
<td>1 510 m</td>
<td>1050 m</td>
</tr>
<tr>
<td>fac-[OsCl2(PMe2Ph)3(S2CNMe2)] (6)</td>
<td>350 w</td>
<td>1 515 m</td>
<td>1045 m</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PMe2)2] (18)</td>
<td>350 w</td>
<td>1 520 m</td>
<td>1045 m</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PPh2)2] (8)</td>
<td>350 w</td>
<td>585 m</td>
<td>1045 m</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PPh2)2] (12)</td>
<td>680 w, 571 vs</td>
<td>5101 vš, br</td>
<td>200 vs</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PPh2)2] (14)</td>
<td>580 w</td>
<td>1 610 m, br</td>
<td>2 160 m</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PPh2)2] (16)</td>
<td>580 w</td>
<td>1 610 m, br</td>
<td>2 160 m</td>
</tr>
<tr>
<td>cis-[OsCl2(PMe2Ph)(S2PPh2)2] (17)</td>
<td>580 w</td>
<td>1 610 m, br</td>
<td>2 160 m</td>
</tr>
</tbody>
</table>

† Band(s) for undentate [S,PR2]−.
‡ Bands for bidentate [S,PR2]− (refs. as in a). 4 s(CN) [bidentate [S,NCNMe2]−]

**RESULTS AND DISCUSSION**

It is reported that mer-[OsCl2(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.8 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-[OsCl2(PMe2Ph)3] (1) with various dithioacid anions are described below.

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6 R. A. Bozis, University Microfilms, 72-14-064 (Chem. Abs., 1972, 72, 108887y).
oxidised quantitatively to mer-[OsCl₂(PMe₂Ph)₃] and PMe₂PhO on standing in CDCl₃ [cf. the reaction of 

Table 3

<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>Dithio-ligand</th>
<th>Phosphine Me groups</th>
<th>Phenol</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>mer-[OsCl₂(PMe₂Ph)₃(PMe₂Ph)] (13)</td>
<td>301</td>
<td>1.53 (d) (14.5)</td>
<td>2.0 (t) (8.0), 1.82 (t) (8.5), 1.36 (d) (10.5)</td>
<td>7.9—7.0</td>
<td></td>
</tr>
<tr>
<td>mer-[OsCl₂(PMe₂Ph)₃(S₂CNMe₂)] (3)</td>
<td>301</td>
<td>3.08</td>
<td>1.80 (s), 1.66 (s), 1.34 (d)</td>
<td>7.6—6.6</td>
<td></td>
</tr>
<tr>
<td>fac-[OsCl₂(PMe₂Ph)₃(S₂CNMe₂)] (5)</td>
<td>301</td>
<td>2.90 (s)</td>
<td>7.0</td>
<td>7.8—6.8</td>
<td></td>
</tr>
<tr>
<td>fac-[OsCl₂(PMe₂Ph)₃(S₂COEt)] (6)</td>
<td>301</td>
<td>2.76 (s)</td>
<td>1.99 (q) (7.0), 1.96 (d) (7.0), 1.35 (d) (8.0)</td>
<td>7.8—6.7</td>
<td></td>
</tr>
<tr>
<td>mer-[OsCl₂(PMe₂Ph)₃(SCOEt)] (18)</td>
<td>301</td>
<td>4.30 (q) (7.0), 1.43 (t) (7.0)</td>
<td>1.96 (q) (7.0)</td>
<td>7.6—6.6</td>
<td></td>
</tr>
<tr>
<td>mer-[OsBr₂(PMe₂Ph)₃(S₂COEt)] (19)</td>
<td>301</td>
<td>4.20 (q) / 1.39 (t) (7.0)</td>
<td>1.60 (d) (8.0)</td>
<td>7.6—6.6</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂CNMe₂)] (7)</td>
<td>273</td>
<td>2.10 (d) (12.5)</td>
<td>1.71 (q) (8.5), 1.64 (q) (8.5)</td>
<td>7.3—6.7</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (8)</td>
<td>333</td>
<td>1.39</td>
<td>1.67 (q) (8.5)</td>
<td>7.3—6.7</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (9)</td>
<td>301</td>
<td>3.25 (s), 3.18 (s)</td>
<td>1.62 (q) (8.0), 1.54 (q) (8.0)</td>
<td>7.3—6.9</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (10)</td>
<td>313</td>
<td>3.16 (s)</td>
<td>1.60 (q) (8.5), 1.55 (q) (8.5)</td>
<td>7.3—6.9</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (11)</td>
<td>253</td>
<td>2.15 (d) (12.5), 1.96 (d) (12.5)</td>
<td>2.04 (d) (9.5), 2.02 (d) (9.5)</td>
<td>7.7—6.3</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (12)</td>
<td>333</td>
<td>2.09 (d) (13.0)</td>
<td>1.97 (d) (9.5)</td>
<td>7.7—6.3</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (13)</td>
<td>333</td>
<td>1.89 (d) (12.5)</td>
<td>2.09 (d) (11.0)</td>
<td>8.1—7.9</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (14)</td>
<td>301</td>
<td>1.44 (d) (12.5)</td>
<td>2.12 (d) (12.5)</td>
<td>8.1—7.9</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (15)</td>
<td>301</td>
<td>1.91 (d) (12.0)</td>
<td>2.21 (q) (7.0)</td>
<td>7.8—7.2</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (16)</td>
<td>301</td>
<td>1.00 (d) (12.0)</td>
<td>1.78 (d) (9.5), 1.74 (d) (9.5)</td>
<td>7.6—6.8</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (17)</td>
<td>253</td>
<td>2.02 (d) (12.0)</td>
<td>1.62 (d) (9.5)</td>
<td>7.6—6.8</td>
<td></td>
</tr>
<tr>
<td>cis-[Os(PMe₂Ph)₂(S₂COEt)] (18)</td>
<td>253</td>
<td>2.01 (d) (12.6), 1.46 (d) (12.0)</td>
<td>2.09 (d) (11.0)</td>
<td>8.1—7.9</td>
<td></td>
</tr>
</tbody>
</table>

Attempts to prepare complexes of formula [Os(PMe₂Ph)₂(S₂CNMe₂)] by shaking (3) with Na₂S₂CNMe₂·2H₂O in 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 Na₂S₂CNMe₂·2H₂O and the fifth was an orange compound of higher Kᵣ 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 Kᵣ value: [Os(PMe₂Ph)₂(S₂CNMe₂)] [S₂COEt] (2), (1), [OsCl₂(PMe₂Ph)₃(S₂CNMe₂)] (1) [but with different spectral properties from (3)], [Os(OEt)₂(PMe₂Ph)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 Na₂S₂CNMe₂·2H₂O does give rise to the formation of (2), the yield of (2) (50%) is not as high as from the reaction of mer-[OsCl₂(PMe₂Ph)₃] (1) with Na₂S₂CNMe₂·2H₂O (80%). Thus, although (3)

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. 

**Diphonyl- and Dimethyl-phosphinothiolato-complexes.**—As for dithiocarbamate, reactions of (1) with excess of Na[S2PMe2]2·2H2O or [NH4][S2PPh2] in refluxing ethanol led to the formation of orange solutions from which crystalline complexes of formula [Os(PMe2Ph)3(S2PMe2)]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(PMe2Ph)4(S2PMe2)]3,13 broadening of the previously sharp 1H 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 PMe2PhS. During one of the preparations of (7), a pale yellow solid was also isolated. This is the well known [OsCl2(PMe2Ph)3]Cl which is formed when (1) is heated under reflux in aqueous ethanol.8

As with mer-[RhCl2(PMe2Ph)3],2 shaking (1) with excess of Na[S2PMe2]2·2H2O in methanol produced a complex of formula [OsCl2(PMe2Ph)3(S2PMe2)] (9). In this case, the complex is purple and a reaction time of 90 min (cf. 10 min for Rh4) was required for complete conversion. The analogous complex [OsCl2(PMe2Ph)3(S2PPh2)] (10) was also prepared by reaction of (1) in CH2Cl2 with a methanolic solution of Na[S2PPh2], followed by evaporation of the CH2Cl2 and collection of the methanol-insoluble product. Since (10) is more difficult to prepare than (9) and less amenable to 1H 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-[RhCl2(PMe2Ph)3(S2PMe2)] on recrystallisation of mer-[RhCl2(PMe2Ph)3(S2PMe2)]3 but when the solution was warmed and allowed to stand quantitative conversion

into red mer-[OsCl2(PMe2Ph)3] occurred, whilst prolonged reaction of (9) with PMe2Ph in cold CHCl3 produced a yellow solution from which [OsCl2(PMe2Ph)3]Cl was isolated. Recrystallisation of (9) from boiling benzene in air gave a red complex of formula [OsCl2(PMe2Ph)3(S2PMe2)] (11) together with some PMe2PhO, 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 [OsCl2(PMe2Ph)3(S2PMe2)]+ (12), a brown crystalline solid of formula [OsCl2(PMe2Ph)3(S2PMe2)] (13), and mer-[OsCl2(PMe2Ph)3] (1). Longer reaction times in cold benzene (4 weeks) produced only (13) and (1). Finally, shaking (9) in acetone 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(PMe2Ph)2(S2PMe2)]8 [Os(PMe2Ph)2(S2PMe2)] (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)(PMe2Ph)(S2PMe2)] (14) together with a brown oil which contained (i.r. and n.m.r. evidence) both PMe2PhS and a complex with two cis-CO, of probable formula [Os(CO)2(PMe2Ph)2(S2PMe2)] (15). When the carbynolation reaction was carried out in the presence of excess of PMe2Ph, a yellow crystalline complex of formula [Os(CO)(PMe2Ph)2(S2PMe2)] was exclusively formed. Finally, reaction of (7) with CO in cold CH2Cl2-C6H6 gave another yellow complex, probably also of formula [Os(CO)(PMe2Ph)2(S2PMe2)], which rapidly becomes green on air exposure and whose structure will be discussed later.

**O-ethyl Dithiocarbonate-complexes.**—The reaction of (1) with K[S2COEt] is rather different from those with the other dithiocarbionato anions 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 [OsCl2(PMe2Ph)2(S2COEt)] (16). Attempts to persuade this complex to react further with either K[S2COEt] or Na[S2CNMe2]·2H2O were abortive yielding only unchanged starting materials in both cases. An attempt to prepare the complex [Os(PMe2Ph)2(S2COEt)2] by reaction of mer-[OsBr2(PMe2Ph)3] with K[S2COEt] was also fruitless since, although no solid product could be isolated, a 1H n.m.r. spectrum of the resulting orange oil indicated that [OsBr2(PMe2Ph)2(S2COEt)] (19) was the only identifiable product.

**Spectroscopic Properties of the Dithiocarbonato-complexes.**—I.r. spectra. Like mer-[RhCl2(PMe2Ph)3],2 mer-[OsCl2(PMe2Ph)3] has three i.r.-active ν[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 trans to the highest trans-influence ligand (PMe2Ph). Then, the two absorptions at 350 and 312 cm−1 are assigned as arising predominantly from the symmetric (νs) and asymmetric (νas) Cl-Os-Cl stretching vibrations. Although the exact assignment of these two absorption frequencies to νs and νas is not possible, since in a molecule of this size mixing with other vibrations of the same symmetry will occur,14 this region may be used as a 'fingerprint' in assigning stereochemistry to related molecules.

Analysis of the ν[OsCl] region of [OsCl2(PMe2Ph)3(S2PMe2)] (R = Me or Ph) (Table 2) indicates that in both cases the chloride ion trans to phosphine has been removed, as expected in view of the greater trans influence of PMe2Ph compared to chloride. This fact, coupled with the observations that absorptions in the v(PS)

region indicate that only unidentate \([S_2PR_3]^-\) groups are present and that \([\text{RhCl(PMe}_2\text{Ph)}_3(S_2\text{PMe}_2)]\) has a meridional configuration,\(^3\) leads to the conclusion that complexes (9) and (10) have the structure shown in Scheme 1. The complex \([\text{OsCl}_2(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)]\) (11) has a strong absorption at 300 cm\(^{-1}\) indicative of a trans-\text{OsCl}_2 arrangement.

![Scheme 1](image)

Scheme 1: Proposed mechanism for the reaction of \(\text{mer-[OsCl}_3(\text{PMe}_2\text{Ph})_3]\) (1) with \(S^-S^-\) (complexes shown in broken square brackets were not isolated). (i) \(-\text{Cl}^-\); (ii) \(-\text{PMe}_2\text{Ph}^-\); (iii) \(+e^+\); (iv) \(S^-S^-\)
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 dithioacid absorptions 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 1 030 cm⁻¹ in [Os(OC)(PMe₂Ph₂)(S₂CNMe₂)₆] (6) is in the region expected for an ethoxy-group directly bound to a metal (1 000—1 100 cm⁻¹).12

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 [Os(CO)(PMe₂Ph₂)(S₂PMe₂)₆] (16 and 17) as well as [Os(CO)(PMe₂Ph₂)(S₂PMe₂)₂] (15) probably contain both uni- and bi-dentate [S₂PMe₂]⁻ groups and that (15) 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 PMe₂Ph (cf. [Ru(CO)(PMe₂Ph₂)(S₂PMe₂)₂] (D) in ref. 3). Finally, the absence of a peak at 600 cm⁻¹ in the i.r. spectrum of [Os(CO)(PMe₂Ph₂)(S₂PMe₂)] indicates that this complex probably does not contain unidentate [S₂PMe₂]⁻ groups.

Mass spectra. The mass spectra of [Os(CO)(PMe₂Ph₂)(S₂PMe₂)₂] (14) and [Os(CO)(PMe₂Ph₂)(S₂PMe₂)] (16) were identical since (16) readily loses PMe₂Ph at high temperatures to form (14). Their mass spectra showed well defined, intense, osmium isotope patterns which correspond to [Os(CO)(PMe₂Ph₂)(S₂PMe₂)₂]⁺ (608), [Os(CO)(PMe₂Ph₂)(S₂PMe₂)]⁺ (580), [Os(S₂PMe₂)₂]⁺ (442), and [Os(PMe₂Ph₂)(S₂PMe₂)₂]²⁺ (290), as well as several weaker patterns corresponding to loss of methyl groups and large metastable-ion signals at m/e 560 and 347 which correspond to loss of CO from [Os(CO)(PMe₂Ph₂)(S₂PMe₂)]⁺ and of PMe₂Ph from [Os(PMe₂Ph₂)(S₂PMe₂)]²⁺ respectively.

The mass spectrum of [OsCl(PMe₂Ph₂)(S₂CNMe₂)] (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(PMe₂Ph₂)(S₂CNMe₂)] (2) and [OsCl(PMe₂Ph₂)(S₂CNMe₂)] (9). 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(PMe₂Ph₂)(S₂CNMe₂)] (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-[OsCl₄(PMe₂Ph₂)(S₂PR₂)] [(R = Me (9) or Ph (10))] and of trans-[OsCl₄(PMe₂Ph₂)(S₂PMe₂)] (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 ¹³ (see Table 1) lie well within the range expected for one unpaired electron and are consistent with the formulation of these complexes as containing Os⁺⁺. However, the structures of (9), (10), and (11) as indicated by their i.r. spectra are consistent with those of the analogous diamagnetic rhodium(III) complexes ¹⁴ as well as with their modes of preparation, which involve replacement of the most labile chloride ion in (1) by a unidentate [S–S]⁻ ligand [(9) and (10)] followed by chelation of this dithioacid 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(PMe₂Ph₂)(S₂PR₂)] (X = Cl, S–S = S₂PMe₂⁻ (13) or SOCl⁻ (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 [S₂PMe₂]⁻ 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(PMe₂Ph₂)(S₂CNMe₂)] (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 to X is unique, giving rise to a single methyl doublet.

The ¹H.n.m.r. spectrum of [OsCl(PMe₂Ph₂)(S₂CNMe₂)] (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

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 \( \text{fac} \) isomer. Irradiation in the \( ^{31} \text{P} \) resonance region produced sharpening of the slightly broad singlets at \( \delta \ 1.80 \) and 1.66 p.p.m. which indicates that these are separate resonances with some \( \text{P}-\text{H} \) 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 \( ^{1} \text{H} \) 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 \( ^{1} \text{H} \) n.m.r. spectra of \([\text{Os}(\text{PMe}_{2}\text{Ph})_{3}(S-S)_2] \ (7), \ \text{S}_{2}\text{PPh}_2^- \ (8)\), or \([\text{S}_{2}\text{CNMe}_2^- \ (2)\) are all consistent with \( \text{cis} \) stereochemistry, although the non-equivalence of the methyl groups of (8) was not seen even at 213 K. As for \( \text{cis} \)-[Ru(\text{PMe}_{2}\text{Ph})_{3}(\text{S}_{2}\text{PMe}_2)_{2}]\), the two doublets arising from the \( \text{S}_{2}\text{PMe}_2^- \) groups of (7) broadened and coalesced on warming, but in this case the coalescence temperature was \( \text{ca.} \ 328 \) K and the fast-exchange limit was not reached in \( \text{CDCl}_3 \). 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) and rates together with related activation parameters for the inversion in \( \text{CDCl}_3 \) and \( \text{C}_6\text{H}_6 \) are given in Table 5. Since there is negligible difference in \( \Delta H^\dagger \) for the inversion on changing the solvent from \( \text{CDCl}_3 \) to \( \text{C}_6\text{H}_6 \), it is unlikely that the doublets from the phosphine methyl groups gradually moved together without broadening. This behaviour is similar to that found for \( \text{cis} \)-[Ru(\text{PMe}_{2}\text{Ph})_{3}(\text{S}_{2}\text{CNMe}_2)_{2}] \text{\ }^{1,15} \) and \( \text{cis} \)-[Rh(\text{PMe}_{2}\text{Ph})_{2}(\text{S}_{2}\text{CNMe}_2)_{2}] \text{\ }^{\text{[BPPh}_{3}]_{1}^{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 \( \text{C}-\text{N} \) bonds of the \( \text{S}_{2}\text{CNMe}_2^- \) ligands and coincidental equivalence of the signals from different rotamers at higher temperatures.

The low-temperature \( ^{1} \text{H} \) n.m.r. spectrum of \([\text{Os}(\text{CO})\text{(PMe}_{2}\text{Ph})(\text{S}_{2}\text{PMe}_2)_{2}] \ (14) \) consisted of six doublets arising from the six inequivalent methyl groups in the molecule indicating \( \text{cis} \) 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 dithioacid doublets (b and b') move together until at \( \text{ca.} \ 283 \) 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 shieldings effects on the two methyl groups at different temperatures.†

The presence of a triplet from the methyl groups of the phosphanes and doublets from the \( \text{S}_{2}\text{PMe}_2^- \) methyl groups in the \( ^{1} \text{H} \) n.m.r. spectrum of \([\text{Os}(\text{CO})(\text{PMe}_{2}\text{Ph})(\text{S}_{2}\text{PMe}_2)_{2}] \) (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 \([\text{Ru}(\text{CO})(\text{PMe}_{2}\text{Ph})(\text{S}_{2}\text{PMe}_2)_{2}] \) complex C, Figure 8 in ref 3) the \( ^{1} \text{H} \) 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 \( \text{PMe}_2\text{Ph} \) to give \( \text{cis} \)-[Ru(\text{CO})(\text{PMe}_{2}\text{Ph})(\text{S}_{2}\text{PMe}_2)_{2}] \text{\ }^{3} \) (16) may be kept in solution at \( 323 \) K for several hours or may be recovered unchanged on recrystallisation from \( \text{CH}_2\text{Cl}_2-C_6\text{H}_{14} \). This is presumably a reflection of the greater inertness of \( \text{Os}^{1} \) compared to \( \text{Ru}^{11} \).

<table>
<thead>
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<th>Table 5</th>
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<td>Rates and activation parameters for the inversion process ( \text{cis} ) ( \Delta \rightarrow \text{cis} ) ( \Delta ) for ([\text{Os}(\text{PMe}<em>{2}\text{Ph})(\text{S}</em>{2}\text{PMe}<em>2)</em>{2}] )</td>
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<tr>
<td>Solvent</td>
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<td>( \text{CDCl}_3 )</td>
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<td>( \text{C}_6\text{H}_6 )</td>
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* A weak e.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 complex itself. The nature of this impurity is unclear although the presence of \([\text{OsCl}(\text{PMe}_{2}\text{Ph})(\text{S}_{2}\text{CNMe}_2)_{2}] \) in the mass spectrum of (3) (Table 3) could indicate that \([\text{OsCl}(\text{PMe}_{2}\text{Ph})(\text{S}_{2}\text{CNMe}_2)_{2}] \) is the impurity, but this could also be formed in the mass spectrometer.

† Since the four-membered rings in \( \text{cis} \)-[Ru(\text{PMe}_{2}\text{Ph})(\text{S}_{2}\text{PMe}_2)_{2}] \) are not planar in the solid state, it may be that this is also the case at low temperature for \( \text{cis} \)-[Os(\text{CO})(\text{PMe}_{2}\text{Ph})(\text{S}_{2}\text{PMe}_2)_{2}] \) in solution, and that on warming fast 'inversion' of these rings occurs which fortuitously causes equal shielding effects of the two methyl groups on one \( \text{S}_{2}\text{PMe}_2^- \) ligand at \( 283 \) K.

The other isomer of \([\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\) (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 8 1.74 p.p.m., which has twice the intensity of the other doublets, is composed of two accidentally degenerate resonances from methyl groups 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 of \([\text{Ru(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\) (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 \(\text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\) in the presence of sulphur 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 \([\text{S}_2\text{PMe}_2]^+\) 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.

\[\text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\]

\[\text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\]

Finally, \(^{31}\text{P}\) decoupling studies on the \(^1\text{H}\) n.m.r. spectrum of the brown oil obtained from carbonylation of \(\text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\) in the presence of sulphur 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 \([\text{S}_2\text{PMe}_2]^+\) 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.

\[\text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\]

\[\text{cis-}[\text{Os(CO)}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]\]
unidentate [S₂PMe₂]⁻ 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-[OsCl₃
(PMe₂Ph)₃] into cis-[Os(PMe₂Ph)₂(S−S)₂].—Since the only complex obtainable from the reaction of (1) with K[S₂COEt] is mer-[OsCl₂(PMe₂Ph)₃(S₂COEt)] it is clear that this complex does not react with K[S₂COEt] and that the chloride ion in this complex is inert. This indicates that the sulphur atom of the [S₂COEt]⁻ moiety has a low trans effect and is not able to labilise 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)(OH₂)₃(S–S)] [S–S' = S₂CNR₂, S₂COR, or S₂PR₂⁻] with Lewis bases 19 has shown that the trans effects of these dithioacid ligands are low but of comparable magnitude. Thus, since mer-[OsCl₂(PMe₂Ph)₃
(S₂CNMe₂)] (3) reacts with [S−S']⁻ to give cis-[Os(PMe₂
Ph)₂(S₂CNMe₂)(S−S')⁻] [S−S' = S₂CNMe₂⁻] (2) this mechanism of these reactions cannot involve direct displacement of chloride ion by [S−S']⁻. However, since fac-[OsCl₂(PMe₂Ph)₃
(S₂CNMe₂)] (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 [S−S']⁻ since in the fac isomer the chloride ion is trans to the high trans-effect ligand, PMe₆. The formation of fac-[Os(OEt)₂(PMe₂Ph)₃
(S₂CNMe₂)] (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 Na[S₂CNMe₂]·2H₂O 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 isonic osmium(III) intermediates with the reduction to Os¹¹ occurring as the last step (see Scheme 1).

Since mer-[OsCl₂(PMe₂Ph)₃](S₂PMe₂)] (13) is only formed on prolonged standing of mer-[OsCl₂(PMe₂Ph)₃](S₂PMe₂)] (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(PMe₂
Ph)₂(S₂PMe₂)] (7) from (1) in refluxing ethanol does not involve (13) as an intermediate but rather goes by the path which involves osmium(III) cations. Then, the purple ionic oil probably contains [OsCl₂(PMe₂Ph)₃(S₂PMe₂)] (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 [S₂PMe₂]⁻ and give mer-[OsCl₂(PMe₂Ph)₃] (1).

It still remains to explain why neither of the paths shown in Scheme 1 is open to the reaction of (1) with K[S₂COEt] in refluxing ethanol. The latter is thought to be excluded because the strongly reducing nature of [S₂COEt]⁻ causes reduction to Os¹¹ before [OsCl₂(PMe₂
Ph)₃(S₂COEt)] can react with more [S₂COEt]⁻. Since it is well documented that the ease with which isomerisations of complexes occur is dependent on the substituents in the molecule,20 we propose that mer-[OsCl₂(PMe₂Ph)₃(S₂COEt)] (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 prepared by the University of Edinburgh Chemistry Department. i.r. spectra were recorded in the 250—4 000 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 Porthill Electronics 310 conductivity bridge. Hydrogen-1 n.m.r. spectra and solution magnetic moments (Evans' method) 21 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 40.50 MHz. 31P chemical shifts are given in p.p.m. to high frequency of 86% H₂PO₄. Kinetic line-shape analysis on cis-[Os(PMe₂Ph)₂(S₂PMe₂)] 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 Schlumberger FS20 frequency synthesiser. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Materials.—Ammonium hexachloro-osmate(IV) (Johnson, Matthey Ltd), carbon mono-oxide (Air Products), dimethylphenylphosphine (B.D.H.), Na[S₂CNMe₂]·2H₂O (Ralph Emanuel), and K[S₂COEt] (B.D.H.) were obtained as indicated. Sodium dimethylphenylphosphinodithioate, and sodium and ammonium dimethylphosphinodithioate were prepared as described earlier. 3 All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere unless otherwise stated.

Preparations.—mer-Trichloroiridium(dimethylphosphine)osmium(III).—The salt [NH₄]₂[OsCl₆] (2.0 g) and PMe₆ (3 cm³) were heated under reflux in 2-methoxy-ethanol (50 cm³) containing concentrated HCl (5 cm³) for 16 h. The resulting red solution was filtered hot to remove [NH₄]Cl and allowed to crystallise. The red crystals were collected and washed with water, ethanol, and n-pentane (3.0 g, 93%).

mer-Trichloroiridium(dimethylphosphine)osmium(III). The complex mer-[OsCl₂(PMe₂Ph)₂] (0.35 g) and LiBr (2.0 g) were heated under reflux in ethanol (20 cm³) 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-Dichloroiridium(dimethylphosphine)(diphenylphosphinodithioato)osmium(III).—The complex mer-[OsCl₂(PMe₂Ph)₂] (0.15 g) in CH₂Cl₂ (15 cm³) and Na[S₂PPh₂] (0.20 g) in methanol (10 cm³) 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-Dichlorodimethylphenylphosphine(dimethylphosphinodithioato)osmium(III) (9). Complex (1) (0.30 g) and Na[S$_2$PMe$_2$]$_2$H$_2$O (0.30 g) were soaked in methanol (25 cm$^3$) 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$_2$Cl$_2$-C$_6$H$_4$$_2$ gave red crystals of (1).

cis-(Dimethylthiocarbamato)bis(dimethylphenylphosphinodithioato)osmium(III) (11). The complex cis-[OsCl$_2$(PMe$_2$Ph)$_3$($S_2$PMe$_2$)$_2$] (9) (0.10 g) was dissolved in benzene (5 cm$^3$) and allowed to stand in air for 2 weeks. Addition of n-hexane to the solution then precipitated a purple oil (12) from which the brown solution was decanted and allowed to crystallise slowly. The complex precipitated in low yield as brown needles and after filtration the filtrate deposited red crystals of (1). When the reaction was allowed to proceed for 4 weeks, no purple oil was formed but approximately equal molar ratios of (13) and (1). The purple oil (12) may also be prepared by allowing mer-[OsCl$_2$(PMe$_2$Ph)$_3$($S_2$PMe$_2$)$_2$] (9) to stand in acetone in the presence of air for several days; (12) and (1) were then the sole products.

cis-Bis(dimethylphenylphosphine)(dimethylphosphinodithioato)osmium(III) (7). Complex (1) (0.60 g) and Na[S$_2$PMe$_2$]$_2$H$_2$O (0.50 g) were heated under reflux in ethanol (25 cm$^3$) 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 [OsCl$_2$(PMe$_2$Ph)$_3$]Cl. Similarly prepared were cis-bis(dimethylphenylphosphine)-bis(diphenylphosphinodithioato)osmium(III) (8) from (1) (0.16 g) and [NH$_4$][S$_2$PPh$_2$] (0.20 g) as orange crystals (0.10 g; 50%) and cis-bis(dimethylthiocarbamato)bis(dimethylphenylphosphinodithioato)osmium(III) (2) from (1) (0.10 g) and Na[S$_2$NCNMe$_2$]$_2$H$_2$O (0.10 g) in ethanol (10 cm$^3$) 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$_2$(PMe$_2$Ph)$_3$][S$_2$CNEt$_2$] (3) (0.028 g) with Na[S$_2$NCNMe$_2$]$_2$H$_2$O (0.02 g) in refluxing ethanol (5 cm$^3$) 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 $R_f$ values and colours to those obtained from the reaction of (1) with Na[S$_2$NCNMe$_2$]$_2$H$_2$O. Thus, the total yield of (2) was ca. 50%.

cis-(Dimethylthiocarbamato)bis(dimethylphenylphosphino)phosphine(O-ethyl dithiocarbonate)osmium(II) (14). The complex cis-[Os(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$] (7) (0.10 g) was heated under reflux in ethanol (15 cm$^3$) for 60 min. The resulting orange oil could not be recrystallised. The complex precipitated in low yield as brown needles and after filtration the filtrate deposited red crystals of (1). When the reaction was allowed to proceed for 4 weeks, no purple oil was formed but approximately equal molar ratios of (13) and (1). The purple oil (12) may also be prepared by allowing mer-[OsCl$_2$(PMe$_2$Ph)$_3$($S_2$PMe$_2$)$_2$] (9) to stand in acetone in the presence of air for several days; (12) and (1) were then the sole products.

cis-Carbonyl(dimethylphenylphosphino)phosphine(bis(dimethylphosphinodithioato)osmium(II) (14). The complex cis-[Os(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$] (7) (0.10 g) and sulphur (0.01 g) were heated under reflux in ethanol (15 cm$^3$), 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$_2$Cl$_2$-C$_6$H$_4$ to give a brown oil which contained (15), (14), and PMe$_2$Ph$_3$S. The yellow supernatant was decanted and allowed to crystallise to give the product as yellow crystals (0.04 g, 47%).

Carbonyl(dimethylphenylphosphino)phosphine(bis(dimethylphosphinodithioato)osmium(II) (17). The complex cis-[Os(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$] (7) (0.10 g) and PMe$_2$Ph$_3$ (0.20 cm$^3$) were carbonylated in refluxing ethanol (15 cm$^3$) for 30 min. On cooling, the resulting yellow solution gave yellow crystals of the product (0.07 g, 67%).

Carbonyl(dimethylphenylphosphino)phosphine(bis(dimethylphosphinodithioato)osmium(II) (11). The complex cis-[Os(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$] (7) (0.05 g) was carbonylated in CH$_2$Cl$_2$-C$_6$H$_4$$_2$ (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(vi), the University of Edinburgh for an award (to D. J. C.-H), and Dr. A. S. F. Boyd and Mr. J. R. A. Millar for obtaining the $^{1}H$ and $^{13}C$ n.m.r. spectra respectively.
Metal Complexes of Sulphur Ligands. Part 11.¹ 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

Reprinted from
JOURNAL
OF
THE CHEMICAL SOCIETY
DALTON TRANSACTIONS
1977
Metal Complexes of Sulphur Ligands. Part 11.1 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

Reaction of the complexes [Pt(S₂CO₄)₂] with K[S₂COR] (R = Et or Pr) followed by addition of [AsPh₄]Cl generates [AsPh₄][Pt(S₂COR)₂]. Variable-temperature ¹H n.m.r. studies indicate rapid unidentate–bidentate exchange at ambient temperature. Attempted recrystallisation from CH₂Cl₂ or CDCl₃ results in an intramolecular rearrangement to give [AsPh₄][Pt(S₂CO)(S₂COR)]. Reaction of [Pd(S₂COEt)₂] with K[S₂CO] and [AsPh₄]Cl gives [AsPh₄][Pd(S₂CO)(S₂COEt)] as the main product. Reaction of [Pt(S₂COR)₂] with K[S₂COR] (R = Me, or CH₃Ph) and [AsPh₄]Cl generates [AsPh₄][Pt(S₂CO)(S₂COMe)] or [AsPh₄][Pt(S₂CO)₂], both of which give [Pt(S₂CO)[L]] on addition of various Lewis bases L (L = PMe₂Ph, PMe₂Ph, or PMe₂CH₂Ph). The salt [AsPh₄][Pt(S₂COR)₂] is shown by X-ray diffraction analysis to have square-planar stereochemistry with one a- and two uni-dentate [S₂COEt]⁻ groups. The crystals are monoclinic, space group P2₁/c with a = 9.95, b = 14.26, c = 25.82 Å, β = 99.3°.

It is now well established that when reaction occurs between [Ni(S₂S₄)] (S₂S₄ = [S₄CNR₄]⁻, [S₄COR]⁻, [S₄P(OR)₄]⁻, [S₄PR₃]⁻, etc.) and most nitrogen- or phosphorus-donor ligands (L) either five-co-ordinate [NiL(S₂S₄)] and/or six-co-ordinate [NiL₂(S₂S₄)] adducts are formed, depending on the nature of the ligand used. Furthermore, it has been shown that reaction of NiCl₂·6H₂O, NaN₂CO₄Et, and [PMMe₃Ph]Cl gives the dark green complex [PMMe₃Ph][Ni(N₂CO₄Et)] which was assigned a six-co-ordinate octahedral structure on the basis of electronic-spectral evidence and preliminary X-ray studies. In contrast, some of the earlier papers in this series have shown that the reaction of the isomorphous [M(S₂S₄)] complexes (M = Pd or Pt) with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate the four-co-ordinate square-planar complexes [M(PR₃)₂(S₂S₄)] and [M(PR₃)](P₃S₄)[S₂S₄] which exhibit unidentate–bidentate and bidentate–ionic modes of bonding of the dithiocarbamate groups respectively.

In this paper, we report the full results of reactions between various platinum(II) and palladium(II) dithiocarbonates with dithiocarbonate ions 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 [Pt(S₂CO₄)₂] with excess of [AsPh₄] and [S₂COEt] 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 [AsPh₄][Pt(S₂CO₄)₂] (I). This complex could also be prepared by treating [Pt(S₂COEt)₂] with excess of A. D'Addario, Ph.D. Thesis, 1970, University Microfilms, Ann Arbor, Michigan.


K[S_CoEt] in acetone followed by addition of methanolic [AsPh]_2[CHCl]. An X-ray structural analysis of (I) (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 unidentate dithiocarbonate groups (cf. [Au(S_CNEnt)_2])?. The complex [AsPh]_2[Pt(S_COPr)_2] (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) $^1$H n.m.r. spectrum of (I) in again this change was reversible. Hence, these observations are indicative of a facile intramolecular unidentate-bidentate scrambling process at higher temperatures, similar to that already proposed to explain the temperature-dependent n.m.r. changes of the neutral [M(PR$_3$)(S-S$_2$)$_2$] complexes. Unfortunately, because of decomposition and irreversible rearrangement processes 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 [AsPh]_2[Pt(S_CoEt)_2] (1). 5-33H$_{35}$.

As$_2$PtS$_6$, M = 942, yellow monoclinic needles, a = 9.95(1), b = 14.26(1), c = 25.82(1) Å, $\beta = 99.3(2)^\circ$, $U = 3 615$ Å$^3$, $D_m = 1.70$, $Z = 4$, $D_e = 1.73$ g cm$^{-3}$.

**Table 1**

| Fractional co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^4$/Å$^2$) for (1). Mean standard deviations for atomic positions are: Pt, 0.003; As, 0.007; S, 0.02; O, 0.05; C, 0.08; ring centres, 0.03 Å |
|---|---|---|---|---|---|
| Atom | x | y | z | U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{12}$ | U$_{13}$ | U$_{23}$ |
| Pt(1) | 3.048 | 1.106 | 0.592 | * | 3.77 | 3.77 | 4.06 | 91 |
| As(1) | -0.09 | 1.019 | 3.452 | * | 1.36 | 1.36 | 1.36 | 31 |
| S(1) | 5.677 | 1.312 | 0.656 | 59 | 1.16 | 1.16 | 1.16 | 1.16 | 109 |
| S(2) | 1.465 | 0.957 | 1.168 | 76 | 1.16 | 1.16 | 1.16 | 1.16 | 85 |
| S(3) | 3.358 | 4.894 | 0.599 | 111 | 1.16 | 1.16 | 1.16 | 1.16 | 93 |
| S(4) | 3.225 | 2.762 | 1.068 | 66 | 1.16 | 1.16 | 1.16 | 1.16 | 71 |
| S(5) | 3.491 | -3.262 | 0.991 | 63 | 1.16 | 1.16 | 1.16 | 1.16 | 89 |
| S(6) | -1.20 | -1.163 | 1.718 | 113 | 1.16 | 1.16 | 1.16 | 1.16 | 77 |
| O(1) | 2.446 | -0.201 | 1.799 | 96 | 1.16 | 1.16 | 1.16 | 1.16 | 75 |
| O(2) | 3.285 | 4.911 | 2.255 | 103 | 1.16 | 1.16 | 1.16 | 1.16 | 79 |
| O(3) | 6.703 | -3.566 | 0.644 | 64 | 1.16 | 1.16 | 1.16 | 1.16 | 71 |
| C(1) | -1.795 | 0.983 | 3.018 | 47 | 1.16 | 1.16 | 1.16 | 1.16 | 103 |
| C(2) | -1.959 | 1.210 | 2.484 | 63 | 1.16 | 1.16 | 1.16 | 1.16 | 123 |
| C(3) | -2.228 | 1.696 | 2.167 | 58 | 1.16 | 1.16 | 1.16 | 1.16 | 97 |
| C(4) | -3.353 | 7.545 | 2.384 | 40 | 1.16 | 1.16 | 1.16 | 1.16 | 144 |
| C(5) | -5.217 | 5.227 | 2.917 | 67 | 1.16 | 1.16 | 1.16 | 1.16 | 240 |
| C(6) | -2.901 | 6.411 | 3.235 | 108 | 1.16 | 1.16 | 1.16 | 1.16 | 166 |
| C(7) | -4.422 | 1.557 | 4.087 | 26 | 1.16 | 1.16 | 1.16 | 1.16 | 89 |
| C(8) | 2.44 | 1.164 | 4.558 | 65 | 1.16 | 1.16 | 1.16 | 1.16 | 71 |
| C(9) | 4.1 | 1.551 | 5.038 | 66 | 1.16 | 1.16 | 1.16 | 1.16 | 68 |
| C(10) | -8.47 | 2.310 | 5.046 | 32 | 1.16 | 1.16 | 1.16 | 1.16 | 71 |
| C(11) | -1.533 | 2.882 | 4.576 | 81 | 1.16 | 1.16 | 1.16 | 1.16 | 40 |

| * Anisotropic thermal parameters |
|---|---|---|---|---|---|---|---|---|
| Atom | U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{12}$ | U$_{13}$ | U$_{23}$ |
| Pt(1) | 58 | 163 | 37 | 8 | 3 | 3 |
| As(1) | 57 | 117 | 35 | 0 | 6 | 6 |

CDCl$_3$ which consisted of two sharp methyl triplets at $\delta$ 1.45 and 1.28 p.p.m. of relative intensity 1:2. Two overlapping methylene quartets centred at $\delta$ 4.43 p.p.m. were also observed. Similarly, for (2) at 223 K, two sharp doublets were observed for the methyl protons at $\delta$ 1.47 and 1.29 p.p.m. of relative intensity 1:2; in addition to a weak multiplet at $\delta$ 4.50 p.p.m. from the methine protons. The $^{19}$F n.m.r. spectrum of a related complex [NPr$_3$][Pd(S$_2$PF$_2$)$_2$] 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 [S$_2$PF$_2$]$^-$ groups respectively.

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(S$_2$PF$_2$)$_2$]$^-$ ion, the $^{19}$F n.m.r. spectrum at ambient temperature consisted of a single broad doublet and Space group $P2_1/c$, No. 14; Cu-K$_{\alpha}$ radiation, $\lambda = 1.5418$ Å, $\mu$(Cu-K$_{\alpha}$) = 119 cm$^{-1}$.

**Structure determination.** Considerable difficulty was experienced in choosing a suitable crystal. Layers 006 were eventually collected by the equi-inclination Weissenberg method using multiple film packs. Intensities were estimated photometrically, using a Saab rotating-drum film scanner, and 1 292 independent data were taken as significant above background. No absorption 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. Idealised phenyl rings, with C-C 1.40 Å, were fitted to regions.

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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 [Et4N][Cd(S2COEt)3]9 and [Et4N][Te(S2COEt)3]10 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

![Perspective view of the anion of (1)](image)

**Scheme 1** Proposed intramolecular mechanism for conversion of $[M(S_2COR)_3]^{-}$ into $[M(S_2CO)(S_2COR)]^{-}$

| Bond lengths ($\AA$) and angles (°) for the platinum co-ordination in (1) |
|-----------------|-----------------|-----------------|
| 0. Bond lengths  |                  |                  |
| Pt(1)–S(1)      | 2.327(17)        | Pt(1)–S(5)      | 2.293(27)        |
| Pt(1)–S(2)      | 2.318(10)        | Pt(1)–S(6)      | 4.85(3)          |
| Pt(1)–S(3)      | 4.97(3)          | Pt(1)–O(1)      | 3.34(6)          |
| Pt(1)–S(4)      | 2.294(32)        | Pt(1)–O(2)      | 3.28(6)          |

**Table 2**

| Bond lengths (Å) and angles (°) for the platinum co-ordination in (1) |
|-----------------|-----------------|-----------------|
| 0. Bond lengths  |                  |                  |
| Pt(1)–S(1)      | 2.327(17)        | Pt(1)–S(5)      | 2.293(27)        |
| Pt(1)–S(2)      | 2.318(10)        | Pt(1)–S(6)      | 4.85(3)          |
| Pt(1)–S(3)      | 4.97(3)          | Pt(1)–O(1)      | 3.34(6)          |
| Pt(1)–S(4)      | 2.294(32)        | Pt(1)–O(2)      | 3.28(6)          |

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contain unidentate dithiocarbonate groups. Other recent possible examples are [M(PPh3)(S2COEt)2] (M = Pd or Pt), [Pd([L=3,2-dithiocarbamate]PMMe2Ph)(S2COEt)],12 and [RhCl([PMe2Ph]2)(S2COEt)].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 678m, 1 600s, and 1 576m cm⁻¹. These values are reasonably close to the characteristic frequencies reported for the dithiocarbonate ion in [Pt(PMePh2)2-

(S2CO)] (1) and [Pt(S2CO)(S2COEt)] (1) at 1 700s and 1 608s cm⁻¹.1,14 and trans-

[Rh(PMePh2)(S2CO)(S2COEt)] (1) at 1 670br and 1 668s cm⁻¹.1,15 and analytical data confirm that (3) is [AsPh4][Pt(S2CO)(S2COEt)]. A similar complex [AsPh4]-

[Pt(S2CO)(S2COEt)] (4) was formed from (2) either by recrystallisation from CH2Cl2 or CHCl3 or by leaving

methanol–diethyl ether or acetone solutions of (2) to stand for 24 h.

Reaction of [Pt(S2COEt)2] with excess of K[S2COEt] in acetone followed by filtration into a methanolic solution of [AsPh4]Cl·HCl gave a bright orange-yellow precipitate with an i.r. spectrum almost identical to that of (3) and the formulation [AsPh4][Pd(S2CO)(S2COEt)] 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 [Pd(S2COEt)2]- anion rearranges very rapidly to [Pd(S2CO)(S2COEt)] 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

As expected, this intramolecular rearrangement is inhibited in more solvating solvents since increasing solvation of the unidentate dithiocarbonate groups will decrease the nucleophilicity of the free sulphur atoms. The alternative intermolecular mechanism shown in Scheme 2 is considered unlikely because if true some rearranged product would be expected to form immediately on reaction of [Pt(S2CO)2] with K[S2CO].

Attempts to extend the range of [Pt(S2CO)2] ions were unsuccessful. For O-benzyl dithiocarbonate, the

only complex which could be isolated at all molar ratios of [Pt(S2COCH2Ph)2] to K[S2COCH2Ph] (from 1:1 to 1:5) was [AsPh4][Pt(S2CO)2] (5). The i.r. spectrum of this yellow crystalline solid showed no bands between 1 200 and 1 300 cm⁻¹ (dithiocarbonate) but strong absorptions at 1 690(s), 1 670m, 1 590s, and 1 574s cm⁻¹ indicative of dithiocarbonato-ligands. Confirmation of this formulation was obtained from the high conductivity value of (5) in nitromethane, characteristic of a 1:2 electrolyte,15 and the reactions of (5) with various Lewis bases L (L = PPh3, PMe3Ph, or PMe2Ph, PC6H5PhPh) which readily gave [PtL2(S2CO)] [cf. the reaction of (Pt(S2CS)2]- with PMe3Ph giving [Pt-

(PMe3Ph)2(S2CS)]].16 The same complexes were obtained

References


Scheme 2 Alternative intermolecular mechanism for conversion of [M(S2COR)3]- into [M(S2CO][S2COR)]-
from the reactions of [AsPh₄][Pt(S₂CO)(S₂COET)] and excess of L. For [Pt(S₂COME)₂] and K[S₂COME] (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 [AsPh₄][Pt(S₂CO)(S₂COME)] were deposited. Presumably, the inability to isolate the [Pt(S₂COCH₂Ph)₂]⁺ and [Pt(S₂COME)⁻] anions is a reflection of the great stability of the benzylidenejcarbomion generated in the transition state in the mechanism shown in Scheme 1 and of the high nucleophilicity of the S₂COME⁻ group. The final step in formation of (5) is probably intermolecular attack of S₂COR⁻ on the co-ordinated alkoxy-group in [Pt(S₂CO)(S₂COR)].

Finally, reactions of [Pt(S=S)₂] (S=S = [S₂PMe₂]⁻, [S₂PPPh₂]⁻, or [S₂CNET₂]⁻) with Na[S=S] under similar conditions gave only starting materials and, unlike the recent synthesis of [NBu₄]Zn(S₂CNPr₂)₂(NBu↓) (R = Me or Et) by reaction of [Zn(S₂CNET₂)] and [NBu↓](S₂CNET₂),¹⁷ no reaction was observed between [Pd(S₂CNET₂)] and [NBu↓](S₂CNET₂) or [Pt(S₂CNET₂)₂] and [NBu↓](S₂CNET₂).

**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 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 Portland 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 600 spectrophotometer using unmatched silica cells. Melting points were determined with a Kölfer hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride [Johnson Matthey Ltd.], [AsPh₄]CH₂HCl (Koch Light Ltd.), PPh₃, and K[S₂COET] (B.D.H.) were used as obtained. The salts K[S₂COR] (R = Me, Pr¹, or CH₂Ph) were synthesised as described in ref. 2α and (M[S₂COR]₂) (M = Pd or Pt) as described earlier.¹⁸ Operations were carried out under nitrogen and in degassed solvents.

**Tetrakis(10-ethyl dithiocarbonato)palladate(II)** (1).—An excess of K[S₂COET] (0.50 g) was added to [Pt(S₂COET)₂] (0.20 g) in acetic acid (10 cm³) and the resulting yellow solution was gently warmed and then immediately filtered into a methanolic solution (20 cm³) of [AsPh₄]CH₂HCl (0.25 g). On cooling, yellow needles of the product formed which were filtered off, washed with water, methanol, benzene, and diethyl ether, m.p. 112 °C (Found: C, 41.9; H, 3.8; S, 20.2). Calc. for [Pt(S₂COET)₂][AsPh₄]CH₂HCl: C, 42.1; H, 3.7; S, 20.4%. A (1 × 10⁻³ mol dm⁻³) in MeNO₂ = 59.5 S cm² mol⁻¹, v(C≡O) (S₂COET⁻) at 1280s and 1210s cm⁻¹ (mull), 1260 cm⁻¹ (in CH₂Cl₂). **Tetrakisharmonium tris(10-ethyl dithiocarbonato)palladate(II)** (2) was similarly prepared from K[S₂COET] and [Pt(S₂COET)₂], m.p. 117—119 °C (Found: C, 43.9; H, 4.2; S, 19.3%. Calc. for [Pt(S₂CO)(S₂COET)] and [K(S₂COET)₂]: C, 43.9; H, 4.2; S, 19.5%. A (1 × 10⁻³ mol dm⁻³) in MeNO₂ = 51.0 S cm² mol⁻¹, v(C≡O) (S₂COET⁻) at 1280s and 1210s cm⁻¹ (mull), 1260 cm⁻¹ (in CH₂Cl₂). The tetrakisharmonium tris(10-ethyl dithiocarbonato)palladate(II) was prepared in like manner using methanol instead of acetone. The very small amount of buff product was characterised by i.r. spectroscopy.

**Tetrakersanion (Dithiocarbonato)(O-ethyl dithiocarbonato)palladate(II)** (3).—This complex was formed as orange-yellow crystals by the recrystallisation of [AsPh₄][Pt(S₂COET)₂] from CH₂Cl₂ or CHCl₃ by leaving methanol—diethyl ether or acetone solutions of [AsPh₄][Pt(S₂COET)₂] to stand for 24 h. m.p. 141 °C (Found: C, 42.5; H, 3.1; S, 15.9. Calc. for [Pt(S₂CO)(S₂COET)₂]: C, 42.5; H, 3.2; S, 16.3%). A (1 × 10⁻³ mol dm⁻³) in MeNO₂ = 57.5 S cm² mol⁻¹, v(C≡O) (S₂COET⁻) at 1250s cm⁻¹ (mull), v(C≡O) (S₂COET⁻) at 1678s, 1600s, and 1575s cm⁻¹ (mull). **Tetrakisharmonium (dithiocarbonato)(O-isopropyl dithiocarbonato)palladate(II)** (4) was similarly prepared from [AsPh₄][Pt(S₂COET)₂], m.p. 122—124 °C (Found: C, 42.8; H, 3.2; S, 15.7. Calc. for [Pt(S₂CO)(S₂COET)₂]: C, 42.3; H, 3.3; S, 15.9%. A (1 × 10⁻³ mol dm⁻³) in MeNO₂ = 43.4 S cm² mol⁻¹, v(C≡O) (S₂COET⁻) at 1270s and 1210s cm⁻¹, v(C≡O) (S₂COET⁻) at 1680s, 1600s, and 1575s cm⁻¹ (mull). **Tetrakisharmonium (Dithiocarbonato)(O-methyl dithiocarbonato)palladate(II)** (5).—The complex [Pt(S₂COME)₂] and K[S₂COME] (1:1 or 1:2 molar ratio) were dissolved in acetone and the resulting yellow solution was filtered into a methanolic solution of [AsPh₄]CH₂HCl. Potassium chloride was then filtered off and the filtrate evaporated almost to dryness to produce orange crystals of the product which were filtered off and washed with water, methanol, and diethyl ether, m.p. 136—138 °C (Found: C, 41.5; H, 3.1; S, 16.6. Calc. for [Pt(S₂COET)₃]: C, 41.6; H, S, 3.2; Pt, 16.5%). A (1 × 10⁻³ mol dm⁻³) in MeNO₂ = 137.6 S cm² mol⁻¹, v(C≡O) (S₂COET⁻) at 1690s, 1670m, 1590s, and 1574s cm⁻¹ (mull). The same product was obtained from the reaction of [Pt(S₂COME)₂] and a five-fold excess of K[S₂COME].

**Tetrakisharmonium (O-ethyl dithiocarbonato)palladate(II)** (6).—This complex was prepared from [Pt(S₂COET)₂], K[S₂COET], and [AsPh₄]CH₂HCl using the same method as used for [AsPh₄][Pt(S₂COET)₂]. The product precipitated as orange-yellow crystals which were washed and dried as before, m.p. 155 °C (Found: C, 47.8, H, 3.6, S, 18.3. Calc. for [Pt(S₂COET)₃]: C, 47.9, H, S, 18.3%. A (1 × 10⁻³ mol dm⁻³) in MeNO₂ = 1250s cm⁻¹, v(C≡O) (S₂COET⁻) at 1678s, 1600s, and 1575s cm⁻¹ (mull). **Dichalcobaltato(triphenylphosphine)platinate(II).**—The salt [AsPh₄][Pt(S₂CO₃)] and excess of PPh₃ were heated under reflux in dichloromethane for 3 h to give a pale yellow

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 C37H30OP2PtS2: C, 54.8; H, 3.7%). v(C=O) (S2CO̊̊̊) at 1 690m and 1 615s cm⁻¹ (null). The same product was obtained from the reaction of [AsPh₄][Pt(S₂CO)₂] and Ph₃PC₂H₄PF₆, m.p. 262—265 °C (Found: C, 47.2; H, 3.5. Calc. for C27H21OP2PtS2: C, 47.3; H, 3.5%). v(C=O) (S₂CO̊̊̊) at 1 690s and 1 620s cm⁻¹ (null).

Crystallographic calculations were made 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., 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.

[6/1465 Received, 27th July, 1976]

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

Reprinted from JOURNAL OF THE CHEMICAL SOCIETY DALTON TRANSACTIONS 1977
Metal Complexes of Sulphur Ligands. Part 12.  

SYNTHESIS, CHARACTERISATION, AND REACTIONS OF PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF TYPE [MX(PR')3(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 EH3 3JF

Reaction of [Pd(PR')3(S2PPh2)2] (PR' = PPh3 or PMe2Ph) with excess of AgX in acetone (X = Cl, Br, I, or SCN) leads to facile replacement of the unidentate [S2PPh2]– group by X– to give [PdX(PR')3(S2PPh2)]. Similar reactions with [Pt(PR')3(S–S)2] (S–S = [S2PPh2]– or [S2CNEt2]–) are not very efficient and a better general method of synthesising [MX(PR')3(S–S)] complexes (M = Pd or Pt; X = Cl, Br, or I; S–S = [S2PMe2]–, [S2CNPr'2]–, [S2CNPR2]–, or [S2COEt]–) is by reaction of equimolar amounts of ([MX(PR')3]2) and alkali-metal dithioacid salts. The complexes [MX(PR')3(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.

RESULTS AND DISCUSSION

In contrast to the method of preparation of [NiX(PR')3(S2CNPh2)] reaction of PdCl2 (or K2[PtCl4]) PR'3 and Na[S2CNPh2]·2H2O (or Na[S2PR3]·2H2O) gave only [M(S–S)2]. However, reactions of [Pd(PR')3(S2PR2)] with excess of AgX (X = Cl, Br, I, or SCN) in acetone readily gave high yields of the required [PdX(PR')3(S2PR2)] by replacement of the unidentate [S2PR2]– group by X– under mild conditions. Unfortunately, this method cannot be used to prepare the analogous [PdX(PR')3(S2CNPh2)] because of the inability to isolate the corresponding [PdX(PR')3(S2CNPh2)] complexes. Furthermore, the corresponding exchange reactions with [Pt(PR')3(S–S)2] (S–S = [S2PR2]– or [S2CNPh2]–) were very inefficient and produced only low yields of the required products [PtX(PR')3(S–S)] (especially for S–S = [S2CNPh2]–) even on prolonged refluxing. Presumably, this is a reflection of the high lability of Pd–S complexes of this type, and also some reactions of these complexes.

In previous papers in this series ² the results of the reactions of various tertiary phosphines, arsines, and stibines (L) with the square-planar [M(S–S)L2] complexes {M = Pd or Pt; S–S = [S2PR2]–, [S2COR]–, [S2CNR2]–, or [S2P(OR)2]–} have been reported. In particular, a study of the various rearrangement reactions exhibited by the products [M(S–S)L2] and [M(S–S)L2]Y (Y = BPh4–, Cl–, or PF6–) has been described. One reaction was the conversion of [Pd(PPh3)[S2PR2]][BPh4] (R = Me or Ph) into [PdX(PPh3)[S2PR2]] when dissolved in either CH2X2 or CHX2 (X = Cl or Br). ² Unfortunately, this particular rearrangement was confined to complexes containing a combination of Pd, PPh3, [S2PR2]–, and [BPh4]– and thus does not provide a general method of synthesising the series [MX(PR')3(S–S)] (X = halide). Although [NiX(PR')3(S–S)] (S–S = [S2CNPh2]– (refs. 3–5) or [S2COR]– (ref. 6)) complexes have recently been reported, [PdX(PPh3)[S2PR2]] 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)

5 J. P. Packler, jun., personal communication.
compared to Pt–S bonds and the fact that dithiocarbamatates form stronger bonds to platinum than phosphino-
odthioates.²

However, an excellent general method of synthesising a wide range of these complexes is by careful reaction of the well known halide-bridged dimers \( [(\text{MX}_2\text{PR}_3)_2] \) 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 dithiocarbido co-ordination (see Experimental section). However, full confirmation of structure (1) was obtained from the \(^1\text{H} \) n.m.r. spectra of the dialkylidithiocarbamato-derivatives which showed two magnetically inequivalent alkyl groups at ambient

### Table 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (%)</th>
<th>Calc. (%)</th>
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<tbody>
<tr>
<td>([\text{Pt}([\text{PPh}_3]){\text{SCN}}(\text{S}_2\text{PPh}_2)])</td>
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<td>([\text{Pt}([\text{PPh}_3]){\text{SCN}}(\text{S}_2\text{PPh}_2)])</td>
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<td>4.0</td>
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<td>50.0</td>
<td>5.0</td>
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<td>39.2</td>
<td>5.0</td>
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<td>([\text{Pt}([\text{PPh}_3]){\text{SCN}}(\text{S}_2\text{PPh}_2)])</td>
<td>29.7</td>
<td>4.2</td>
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<td>([\text{Pt}([\text{PPh}_3]){\text{SCN}}(\text{S}_2\text{PPh}_2)])</td>
<td>26.7</td>
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<td>5.0</td>
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<td>4.1</td>
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<td>5.5</td>
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<td>([\text{Pt}([\text{PPh}_3]){\text{SCN}}(\text{S}_2\text{PPh}_2)])</td>
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<td>4.0</td>
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<td>29.4</td>
<td>4.0</td>
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<td>60.0</td>
<td>4.5</td>
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</table>

* Molecular weight measured osmotically at 37 °C in acetone. \(b\) From parent ion peak \(^{195}\text{Pt}\) or \(^{197}\text{Pt}\) isotope in mass spectrum. \(c\) Cl, 8.2 (Calc.: 8.3%). \(d\) Measured osmotically at 37 °C in chloroform. \(e\) I, 24.8 (Calc.: 24.5%). \(f\) Cl, 6.0 (Calc.: 6.1%).

### Table 2

<table>
<thead>
<tr>
<th>Complex</th>
<th>CH₄ (b)</th>
<th>CH₄ (b)</th>
<th>Me of phosphine (c)</th>
<th>Ph</th>
</tr>
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<td>([\text{Pt}([\text{PPh}_3])\text{Me}_2\text{S}_2\text{PMe}_3])</td>
<td>1.45 (t)</td>
<td>1.75 (t)</td>
<td>1.22 (t)</td>
<td>1.95 (d)</td>
</tr>
<tr>
<td>([\text{Pt}([\text{PPh}_3])\text{Me}_2\text{S}_2\text{PMe}_3])</td>
<td>1.45 (t)</td>
<td>1.75 (t)</td>
<td>1.22 (t)</td>
<td>1.95 (d)</td>
</tr>
<tr>
<td>([\text{Pt}([\text{PPh}_3])\text{Me}_2\text{S}_2\text{PMe}_3])</td>
<td>1.45 (t)</td>
<td>1.75 (t)</td>
<td>1.22 (t)</td>
<td>1.95 (d)</td>
</tr>
<tr>
<td>([\text{Pt}([\text{PPh}_3])\text{Me}_2\text{S}_2\text{PMe}_3])</td>
<td>1.45 (t)</td>
<td>1.75 (t)</td>
<td>1.22 (t)</td>
<td>1.95 (d)</td>
</tr>
<tr>
<td>([\text{Pt}([\text{PPh}_3])\text{Me}_2\text{S}_2\text{PMe}_3])</td>
<td>1.45 (t)</td>
<td>1.75 (t)</td>
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<td>1.95 (d)</td>
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<tr>
<td>([\text{Pt}([\text{PPh}_3])\text{Me}_2\text{S}_2\text{PMe}_3])</td>
<td>1.45 (t)</td>
<td>1.75 (t)</td>
<td>1.22 (t)</td>
<td>1.95 (d)</td>
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<tr>
<td>([\text{Pt}([\text{PPh}_3])\text{Me}_2\text{S}_2\text{PMe}_3])</td>
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<td>1.45 (t)</td>
<td>1.75 (t)</td>
<td>1.22 (t)</td>
<td>1.95 (d)</td>
</tr>
</tbody>
</table>

\(a\) \(b\) \(c\) \(d\) \(e\) \(f\) \(g\) \(h\) \(i\) \(j\) \(k\) \(l\) \(m\) \(n\) \(o\) \(p\) \(q\) \(r\) \(s\) \(t\) \(u\) \(v\) \(w\) \(x\) \(y\) \(z\)
temperature. As expected for a structure of this type, the
[S$_2$PMe$_6$]$^-$ complexes exhibited only one methyl resonance
from the dithioacid group (Table 2). Up to 330 K (the
limit of our studies) the $^1$H n.m.r. spectra of the dithio-
carbamato-complexes were temperature invariant. How-
ever, Fackler$^5$ 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
−CN partial double bond.

The observation of magnetically inequivalent dithio-
carbamato-alkyl groups in complexes (1) at ambient
temperature indicates that our earlier explanation$^9$ of
the apparent magnetic equivalence of R$^3$ and R$^4$ in
[Pt(PR$_3$)$_2$(S$_2$CNR$_2$)$_2$] (2) at low temperature [namely
that the atoms (S and P) inducing the magnetic inequival-
ence 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] is
clearly incorrect. Furthermore, unlike [NiX(PR$_3$)$_2$(S$_2$-
CNR$_2$)] 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 [Pt(PMe$_2$Ph)$_2$(S$_2$CNET$_2$)$_2$] since in the $^1$H
n.m.r. spectrum at 213 and 301 K the PMe$_2$Ph
group exhibited a sharp triplet of doublets centred at

\[ \delta 2.28 \text{ p.p.m. [with } 3J/\text{PtH} = 38.0 \text{ and } 2J/\text{PtH} = 10.0 \text{ Hz]} \]

This is also evident from the $^{31}$P n.m.r. spectra of
[Pt-(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$] (Figure) which show that
$1/J/\text{PtP}$ 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 $2J/\text{PtP}$ $= 254.7 \text{ Hz}$; $S_2$PMe$_2$, $92.1 \text{ p.p.m.}$ and $S_2$PMe$_2$, $105.3 \text{ Hz}$ ($P_3^3$ $571.1$

\[ \text{p.p.m. at 218 K [cf. } [\text{Pt}(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$][PF$_6$]	ext{, }2J/\text{PtP} \]

191.0 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$^3$ and R$^4$ in (2) at
low temperature can only be produced by the fortuitously
similar electronic effects of the PR$_3$ and [S$_2$CNR$_2$]$^-$
groups.

Reaction of excess of Na[S$_2$CNR$_2$].3H$_2$O (R = Et or
Pr) with [MX(PR$_3$)$_2$]$_2$ gave [M(S$_2$CNR$_2$)$_2$].$^6$ whereas
excess of Na[S$_2$PMe$_2$].2H$_2$O gave the well known$^2$
[M(PR$_3$)$_2$S$_2$PMe$_2$]$_2$. The difference in behaviour is
again presumably a reflection of the higher nucleo-
philicity of [S$_2$CNR$_2$] compared to [S$_2$PMe$_2$]. In
contrast, reaction of [MX(PR$_3$)$_2$]$_2$ with silver carboxylates
gives the dimeric [MX(O$_2$CR)(PR$_3$)$_2$] (1 : 2 molar
ratio)$^9$ and [M(O$_2$CR)(PR$_3$)$_2$] (1 : 4 molar ratio)$^10$
respectively.

The complexes [MX(PR$_3$)(S-S)] are useful starting
materials for a number of reactions. For example, reaction of
[PtCl(PMe$_2$Ph)$_2$(S$_2$CNET$_2$)$_2$] with Na[S$_2$PMe$_2$],
2H$_2$O gave the mixed dithio-complex [Pt(PMe$_2$Ph)$_2$
(S$_2$CNET$_2$)$_2$]$_2$. The i.r. spectrum of this complex
had bands at 600 and 1 530 cm$^{-1}$ indicative of unidentate
[S$_2$PMe$_2$]$^-$ (ref. 2) and bidentate [S$_2$CNET$_2$]$^-$
co-ordination$^{11}$ respectively. The $^1$H n.m.r. spectrum (Table 2)
confirmed structure (4) with bidentate [S$_2$CNET$_2$]$^-$ and
undentate [S$_2$PMe$_2$]$^-$ groups. Unlike the corresponding
[Pt(PMe$_2$Ph)$_2$(S$_2$CNET$_2$)$_2$]$^8$ and [Pt(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)$_2$]$^3$
this complex is stereochemically rigid even at 330 K. In
contrast, reaction of [PtCl(PMe$_2$Ph)$_2$(S$_2$PMe$_2$)] with
Na[S$_2$CNET$_2$].3H$_2$O gave [Pt(S$_2$CNET$_2$)$_2$], indicating the
greater nucleophilicity of [S$_2$CNET$_2$]$^-$ compared to
[S$_2$PMe$_2$]$^-$$. Similarly, reaction of [NiCl(PMe$_2$Ph)$_2$(S$_2$NR$_2$)]
and Na[S$_2$CNR$_2$].3H$_2$O (R = Me or Et) gave only
[Ni(S$_2$CNR$_2$)$_2$]$^4$.

Finally, reaction of [PtCl(PMe$_2$Ph)$_2$(S$_2$CNET$_2$)$_2$] with
Ag[BF₄] in tetrahydrofuran (thf) produces a white precipitate of AgCl and a yellow solution which probably contains the solvated cation [Pd(thf)(PMe₂Ph)(S₂CNEt₂)]⁺. Addition of various ligands (L) to this solution followed by treatment with Na[BPh₄] then gave the mixed-ligand cationic complexes [PdL(PMe₂Ph)(S₂CNEt₂)][BPh₄] (L = PPh₃ or P₃S₃N) 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(PPh₃)[Pd(PMe₂Ph)(S₂CNEt₂)][BPh₄] can be synthesised by reaction of [Pt(PPh₃)(PMe₂Ph)]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 Nujol and hexachlorobutadiene mulls on caesium 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 40.5 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 with a Kölff hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson, Matthey Ltd.), triphenylphosphine, sodium diethyldithiocarbamate, and sodium tetrathylborate (B.D.H.), dimethylphenylphosphine and methyl-diphenylphosphine (Maybridge Chemical Company) were obtained as indicated. The compounds Na[S₂PMe₂]₂[BF₄] (12) [PdXₓ(PMe₂Ph)₂] (X = Cl, Br, or I), [PtCl₂(Ph₃P)] (13) [PtCl₂(PPh₃)] (14) [Pd(PPh₃)] (15) [Pd(PPh₃)(PMe₂Ph)], [Pt(PPh₃)(PMe₂Ph)] (16) [Pt(PPh₃)(PMe₂Ph)], and [Pt(PPh₃)(S₂CNEt₂)] (17) were synthesised as described earlier.

Infrared bands diagnostic of bidentate [S₂PPh₂]⁻, [S₂PMe₂]⁻ and [S₂CNR₂]⁻ co-ordination [11,12] are listed for each complex.

**Palladium Complexes.—Diphenylphosphinodithioato(thiocyanato)(triphenylphosphine)palladium(II).** The complex [Pd(PPh₃)[Pd(PMe₂Ph)]₂] (1:6 molar ratio) was shaken together in acetone for 1 h after which the solution was filtered to remove insoluble 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, v(PS₂) at 603 and 572 cm⁻¹, v(CN) at 2 100 cm⁻¹. Similarly, bromo(diphenylphosphinodithioato)(triphenylphosphine)palladium(II), m.p. 211–213°C, v(PS₂) at 600 and 570 cm⁻¹, diphenylphosphinodithioato(ido)(triphenylphosphine)palladium(II), m.p. 602 and 572 cm⁻¹, were prepared from [PdBr₂(PMe₂Ph)] and [Pd(PMe₂Ph)(PPh₃)], m.p. 570 cm⁻¹, and dimethylphenylphosphinodithioato(ido)palladium(II), m.p. 603 and 572 cm⁻¹, were prepared by reaction of [Pd(PR₃)₂(S₂PPh₂)] with the appropriate silver salt.

**Chloro(dimethylphenylphosphine)(dimethylphosphinodithioato)palladium(II).** The salt Na[S₂PMe₂]₂[BF₄] (0.03 g) was added to an acetone solution of [PdCl₂(PMe₂Ph)] (0.10 g) (2:1 molar ratio) and the mixture shaken for ca. 2 h. 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), v(PS₂) at 570 cm⁻¹, v(PdCl) at 340 cm⁻¹. Similarly, bromo(dimethylphenylphosphine)(dimethylphosphinodithioato)palladium(II), v(PS₂) at 570 cm⁻¹, and dimethylphenylphosphinodithioato(ido)palladium(II), m.p. 258–240°C, v(PS₂) at 570 cm⁻¹, were prepared from [PdBr₂(PMe₂Ph)] and [Pd(PMe₂Ph)] respectively.

**Chloro(diethyldithiocarbamato)(dimethylphenylphosphine)-palladium(II).** The complex [PdCl₂(PMe₂Ph)] and Na[S₂CNEt₂]·3H₂O (1:2 molar ratio) were shaken in acetone for ca. 1 h to give a yellow solution 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, v(CN) at 1 530 cm⁻¹, v(PdCl) at 300 cm⁻¹. Similarly, bromo(diethyldithiocarbamato)(dimethylphenylphosphine)palladium(II), m.p. 145–147°C, v(CN) at 1 530 cm⁻¹, were prepared from [PdBr₂(PMe₂Ph)] and [Pd(PMe₂Ph)] respectively, and chloro(di-isopropylidithiocarbamato)(dimethylphenylphosphine)palladium(II), v(CN) at 1 530 cm⁻¹, was obtained from [PdCl₂(PMe₂Ph)] and Na[S₂CNEt₂]·3H₂O. Likewise, reaction of [PdCl₂-PMe₂Ph)] and K(S₂CNEt₂) (1:2 molar ratio) gave chloro(dimethylphenylphosphine)(O-diethylidithiocarbamato)palladium(II), m.p. 148–150°C (decomp.), v(CO) at 1 260 cm⁻¹, v(PdCl) at 300 cm⁻¹.

**Diethyldithiocarbamato(dimethylphenylphosphine)(triphenylphosphine)palladium(II) tetraphenylborate.** The complex [PdCl(PMe₂Ph)(S₂CNEt₂)] (0.04 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, v(CN) at 1 525 cm⁻¹, λ(1 x 10⁻³ mol dm⁻³) in CH₂Cl₂ = 38.0 S cm² mol⁻¹. Diethyldithiocarbamato(dimethylphenylphosphine)pyridinepalladium(II) tetraphenylborate was prepared as above by adding an excess of pyridine to the orange solution of [Pd(thf)(PMe₂Ph)(S₂CNEt₂)][BPh₄] to give a pale yellow solution. Removal of solvent followed by addition of Na[BPh₄] in methanol then gave a yellow precipitate which was washed with water, methanol, and diethyl ether, m.p. 126–128°C, v(CN) at 1 520 cm⁻¹, λ(1 x 10⁻³ mol dm⁻³) in CH₂Cl₂ = 35.0 S cm² mol⁻¹.

Platinum Complexes.—Diphenylphosphinodithioato(thiocyanato)(triphenylphosphine)platinum(II). The complex
\([\text{Pt}(\text{PPh}_3)(\text{S}_2\text{PPh}_2)_2]\) 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 reprecipitated 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 2110 cm⁻¹.

Similarly, bromo(diphenylphosphinodithioato)(triphenylphosphine)platinum(II) was prepared from \([\text{Pt}(\text{PPh}_3)(\text{S}_2\text{PPh}_2)_2]\) and AgBr, ν(PS2) at 600 and 570 cm⁻¹.

Dimethylphosphinodithioato(triphenylarsine)(triphenylphosphine)platinum(II) tetraphenylborate. The complex \([\text{Pt}(\text{PPh}_3)(\text{S}_2\text{PMe}_2)_2]\) 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(diethyldithiocarbamato)(methyldiphenylphosphine)platinum(II). The salt Na[CN(S2CNEt2)]·3H2O (0.045 g) was dissolved in acetone, added to \([\text{PtCl}_2(\text{PMePh}_2)_2]\) (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. Similarily, chloro(diethyldithiocarbamato)(dimethylphenylphosphine)platinum(II) was prepared from \([\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]\) and Na[S2CNEt2]·3H2O, m.p. 163—165 °C, ν(CN) at 1530 cm⁻¹, and chloro(dimethylphosphinodithioato)(methyl(diphenylphosphine)platinum(II) was obtained from \([\text{PtCl}_2(\text{PMePh}_2)_2]\) and Na[S2PMe2]·2H2O, ν(PS2) at 573 cm⁻¹.

Diethyldithiocarbamato(dimethylphosphinodithioato)(methyl-diphenylphosphine)platinum(II). The complex \([\text{PtCl}_2(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNEt}_2)]\) was dissolved in acetone-methanol 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 reprecipitated with light petroleum (b.p. 60—80 °C) to give the pale yellow product, ν(PS2) at 600 and 570 cm⁻¹. Similarly, chloro(diethyldithiocarbamato)(dimethylphosphinodithioato)(methyl-diphenylphosphine)platinum(II) was prepared from \([\text{PtCl}_2(\text{PMe}_2\text{Ph})(\text{S}_2\text{CNEt}_2)]\) and Na[S2PMe2]·2H2O, ν(PS2) at 573 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 31P n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Mecrolab osmometer.

[6/1588 Received, 13th August, 1976]
Metal Complexes of Sulphur Ligands. Part 13.\textsuperscript{1} Reaction of Dichloro-(\(\eta\)-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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JOURNAL
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THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1977
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

Reaction of [Pd(C8H12)Cl2] (C8H12 = cyclo-octa-1,5-diene) with equimolar amounts of various alkali-metal dithioacid salts ([S-S]− = [S2CNEt2]−, [S2COET]−, or [S2PMe2]−) gives the chloride-bridged dimers {[PdCl(S-S)]2} (1). Metathetical reactions of these give the corresponding {[PdX(S-S)]2} (X = Br− or [SPH−]). Cleavage of these complexes with Lewis bases gives [PdCl(S-S)I] (2: L = PPh3, [S-S]− = [S2CNEt2]−, [S2COET]−, or [S2PMe2]−; L = AsPh3, SbPh3, or C8H11N, [S-S]− = [S2CNEt2]−). and with MCl·M′[PdCl(S-S)2] (3; M = [AsPh3]+ or [PPPh3(CH2Ph)+]) are formed. Reaction of (1: [S-S]− = [S2CNEt2]−) with Na[S2PMe2]-2H2O gives [Pd(S2CNEt2)2PPh3] (4a) which partially disproportionates in solution to [Pd(S2CNEt2)2] and [Pd(S2PMe2)2]. Complex (4a) reacts with PPh3 to give [Pd(PPh3)2(S2CNEt2)2(S2PMe2)] (5a) which possesses bidentate [S2CNEt2]− and unidentate [S2PMe2]− groups. In contrast, reaction of [Pt(C8H12)Cl2] and Na[S2CNEt2]-3H2O (1:1 mol ratio) gives {[PtCl(S2CNEt2)]C8H12} (6a) which in turn reacts with PPh3 to give [PdCl(PPh3)(S2CNEt2)[C8H12]]CI·H2O. Reaction of (6a) and Na[S2PMe2]-2H2O gives [Pd(S2CNEt2)2PPh3] (4a) which on treatment with PPh3 gives [Pt(PPh3)2(S2CNEt2)-(S2PMe2)] (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 [M(diene)Cl] complexes (M = Pd or Pt) with various nucleophiles containing oxygen- or nitrogen-donor atoms (e.g. OR, OMe, NRH, etc.) show that, usually, attack on one of the co-ordinated double bonds occurs to give substituted alkynyl complexes.2 In contrast, in the only previously reported reaction of [M(diene)Cl] complexes with sulphur-containing nucleophiles, reaction of [Pt(C8H12)Cl2] with Ag(SCF3)2 gives [Pt(C8H12)(SCF3)2] whereas with [Pd(C8H12)Cl2] the nortricycyl derivatives [Pd2(C8H12SCF3)2Cl] and [Pd(C8H12SCF3)2Cl(SCF3)] are obtained.3

In this paper, we report the full results4 of reactions between [M(C8H12)Cl2] (M = Pd or Pt; C8H12 = cyclo-octa-1,5-diene) and various dithioacid anions 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 Na[S2CNEt2]-3H2O to [Pd(C8H12)Cl2] in methylene chloride (1:1 mol ratio) gave an orange solution from which an orange solid of empirical formula ([PdCl(S2CNEt2)]4) was isolated.5 With excess of Na[S2CNEt2]-3H2O, the well known6 [Pd(S2CNEt2)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).

Scheme: Mechanism of formation of {[PdCl(S-S)]2} (S-S)− = [S2CNEt2]−, [S2COET]−, or [S2PMe2]−. (i) C8H12: (ii) Dimerisation; (iii) excess of [S-S]− came from the far-i.r. spectrum which showed a strong band at 300 cm−1 (bridging v(PdCl)).7 not present in {[PdBr(S2CNEt2)]2} which can be prepared either by reaction of [PdBr2(C8H12)] with Na[S2CNEt2]-3H2O (1:1 mol ratio) or by reaction of {[PdCl(S2CNEt2)]2} with excess of lithium bromide. Similarly, the chloride

bridges in (1) were readily exchanged for [SPh]− by treatment with Na[SPh] to give [{Pd(SPh)2(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)] which can almost certainly be attributed to the high insolubility of [Pd(S2CNMe2)]*.

The analogous [{PdCl(S2COEt)}2] was similarly prepared by reaction of [Pd(C8H12)Cl2] and K2[Sn(S2CNR2)] in methylene chloride. When [{PdCl(S2CNMe2)}2] was isolated, it was red in methylene chloride. Reaction of [Pd(C8H12)Cl2] with equimolar amounts of Na[S2PMe2]·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 [{PdCl(S2PMe2)}2] is initially formed. With excess of Na[S2PMe2]·2H2O, [Pd(S2PMe2)]* was readily isolated. In the Scheme, the probable mechanism of formation of these chloride-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 Pd4.

In common with other halide-bridged dimers, e.g. [{(Rh(CO)5)2}2]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).

![Image](image_url)

TABLE 1

<table>
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<tr>
<th>Complex</th>
<th>CH4</th>
<th>CH4</th>
<th>Other ligand resonances</th>
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<tr>
<td>[{PdCl(S2CNMe2)}2]</td>
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<td>3.69 (q)</td>
<td>7.00—8.00 (m)</td>
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<td>[{PdBr(S2CNMe2)}2]</td>
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<td>4.67 (q)</td>
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<td>3.70 (q)</td>
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<tr>
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<td>7.38—7.80 (m)</td>
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<tr>
<td>[{Pt(Ph3)2(S2CNMe2)}2]</td>
<td>1.11 (t)</td>
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</table>

For these complexes, the n.m.r. spectra were recorded in CDCl3 at 301 K for some palladium(II) and platinum(II) dithioacid complexes.

Reaction of $[\text{Pd}(\text{SPh})\text{C}_{2}\text{NEt}_{2}]_{2}$ with PPh$_3$ gave the red, crystalline, monomeric $[\text{Pd}(\text{PPh})_{3}\text{C}_{2}\text{NEt}_{2}] allege$ whose $^1\text{H}$ n.m.r. spectrum shows the magnetically inequivalent ethyl groups expected for a structure of type (2). Earlier, Andrews et al. synthesized $[\text{M}(\text{SPh})_{2}\text{C}_{2}\text{NEt}_{2}]_{2}$ ($\text{M}$ = Pd or Pt) by reaction of $[\text{M}(\text{SPh})_{2}\text{C}_{2}\text{SPh}]_{2}$ with $\text{NET}_{3}$. Reaction of these complexes with PMePh$_2$ was reported to give $[\text{M}(\text{PMePh})_{2}\text{SPh}]_{2}$ with $\text{NET}_{3}$. However, the $^1\text{H}$ n.m.r. spectrum in CDC$_3$ of the orange-yellow product contained more signals than expected for (4a). Comparison with the $^1\text{H}$ n.m.r. spectra of $[\text{Pd}(\text{SPh})\text{C}_{2}\text{NEt}_{2}]_{2}$ and $[\text{Pd}(\text{SPh})_{2}\text{PMe}]_{2}$ 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 1) were assigned to (4a).

Support for this conclusion came from the observation that mixing equimolar amounts of $[\text{Pd}(\text{SPh})\text{C}_{2}\text{NEt}_{2}]_{2}$ and $[\text{Pd}(\text{SPh})_{2}\text{PMe}]_{2}$ in CDC$_3$ at 301 K gave the same $^1\text{H}$ n.m.r. spectrum. The equilibrium shown in equation (1) was established after ca. 1 h and lies predominantly to the right-hand side.

$$[\text{Pd}(\text{SPh})\text{C}_{2}\text{NEt}_{2}]_{2} + [\text{Pd}(\text{SPh})_{2}\text{PMe}]_{2} \rightleftharpoons 2[\text{Pd}(\text{SPh})\text{C}_{2}\text{NEt}_{2})(\text{SPh})_{2}PMe]_{2} \tag{1}$$

Similarly, Fackler recently showed that mixing $[\text{Ni}(\text{SPh})_{2}\text{C}_{2}\text{NEt}_{2}]_{2}$ and $[\text{Ni}(\text{SPh})_{2}\text{PMe}]_{2}$ in CDC$_3$ produced extra resonances in the $^1\text{H}$ n.m.r. spectrum assigned to the mixed complex $[\text{Ni}(\text{SPh})_{2}\text{C}_{2}\text{NEt}_{2})(\text{SPh})_{2}\text{PMe}]_{2}$. In contrast, the $^1\text{H}$ n.m.r. spectrum of a mixture of $[\text{Pt}(\text{SPh})\text{C}_{2}\text{NEt}_{2}]_{2}$ and $[\text{Pt}(\text{SPh})_{2}\text{PMe}]_{2}$ in CDC$_3$ at 301 K showed no evidence for the formation of $[\text{Pt}(\text{SPh})\text{C}_{2}\text{NEt}_{2})(\text{SPh})_{2}\text{PMe}]_{2}$, which can again be attributed to the decreased lability of Pt-S compared to Pd-S and Ni-S bonds. In accordance with this, $[\text{Pt}(\text{SPh})\text{C}_{2}\text{NEt}_{2})$-$\text{SPh}]_{2}$ (4b) (see later) does not disproporionate 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 1).

Addition of an excess of PPh$_3$ to a suspension of $[\text{Pd}(\text{SPh})\text{C}_{2}\text{NEt}_{2})_{2}$ in benzene produced a yellow solid analysing closely for $[\text{Pd}(\text{PPh})_{3}\text{C}_{2}\text{NEt}_{2})(\text{SPh})_{2}\text{PMe}]_{2}$ (5a). The i.r. spectrum of (5a) was virtually identical with that of $[\text{Pt}(\text{PPh})_{3}\text{C}_{2}\text{NEt}_{2})(\text{SPh})_{2}\text{PMe}]_{2}$ (6b) indicating unidentate $[\text{SPh}]_{2}\text{PMe}]_{2}$ with $\nu(\text{PS})$ at 605 cm$^{-1}$ and bidentate $[\text{SPh}]_{2}\text{PMe}]_{2}$ with $\nu(\text{CN})$ at 1515 cm$^{-1}$ co-ordination. However, although the $^1\text{H}$ n.m.r. spectrum of the platinum complex was completely consistent with structure (5) (Table 1), that of the palladium complex contained small additional resonances superimposed on some of those of (5a). These appear to correspond to

reaction of \([\text{PtMe}(\text{C}_8\text{H}_{12})](\text{HOME})]\)[PF_6] with an equimolar amount of Na[S_2CNEt_2]·3H_2O. This then reacts with PPH_3 and AsPH_3 (1) to give the soluble neutral complexes \([\text{PtMe}(\text{C}_8\text{H}_{12})]_2\) 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 \([\text{PtMe}(\text{C}_8\text{H}_{12})]_2\) with an equimolar amount of Na[S_2CNEt_2]·3H_2O. Similarly, reaction of \([\text{PtCl}(\text{S}_2\text{CNEt}_2)]_2\cdot\text{C}_8\text{H}_{12}\) with PPH_3 (1:1 mol ratio) readily gave \([\text{PtCl}(\text{PPPh}_3)](\text{S}_2\text{CNEt}_2)\) and free \(\text{C}_8\text{H}_{12}\) was also detected supporting our formulation (6a). As expected, the 1H n.m.r. spectrum of the latter complex showed magnetically inequivalent ethyl groups at ambient temperature. With excess of PPH_3 in methylene chloride, \([\text{Pt}(\text{PPPh}_3)(\text{S}_2\text{CNEt}_2)](\text{Cl}·\text{H}_2\text{O})\) was isolated and this was identical in spectroscopic properties to the product obtained earlier by prolonged reaction of \([\text{Pt}(\text{S}_2\text{CNEt}_2)]\) with an excess of PPH_3 in methylene chloride. The related \([\text{Pt}(\text{PE}_{2}\text{Ph}_3)(\text{S}_2\text{CNEt}_2)](\text{Cl}·\text{H}_2\text{O})\) has also been prepared by reaction of \([\text{PtCl}_2(\text{PE}_{2}\text{Ph}_3)]\) with Na[S_2CNEt_2]·3H_2O.†

Hence, unlike reactions of \([\text{M}(\text{diene})\text{Cl}]\) \((\text{M} = \text{Pd} \text{ or Pt})\) with various oxygen- and nitrogen-containing nucleophiles which give the same type of product, their behaviour with \([\text{S}_2\text{CNEt}_2]^-\) is quite different giving \([\text{PtCl}(\text{S}_2\text{CNEt}_2)]\) and \([\text{PtCl}(\text{S}_2\text{CNEt}_2)](\text{C}_8\text{H}_{12})\) respectively.‡ This difference in behaviour is presumably a consequence of the weaker palladium–olefin than platinum–olefin bonds and coupled with the insolubility of complex (6a).

Reaction of (6a) with Na[S_2CNEt_2]·3H_2O gave \([\text{Pt}(\text{S}_2\text{CNEt}_2)]\) and free \(\text{C}_8\text{H}_{12}\). Therefore, (6a) was treated with an equimolar amount of Na[S_2PM_2]·3H_2O in acetone–methylene chloride to give a yellow solid shown by analysis and i.r. and 1H n.m.r. spectroscopy (Table 1) to be \([\text{Pt}(\text{S}_2\text{CNEt}_2)](\text{S}_2\text{PM}_2)\) (4b). Unlike \([\text{Pt}(\text{S}_2\text{CNEt}_2)](\text{S}_2\text{PMe}_2)\) (4a) reported earlier in this paper, there was no evidence for disproportionation into \([\text{Pt}(\text{S}_2\text{CNEt}_2)]\) and \([\text{Pt}(\text{S}_2\text{PMe}_2)]\) when dissolved in solution at 301 K. Reaction of (4b) with PPH_3 in benzene gave the pale yellow solid \([\text{Pt}(\text{PPh}_3)(\text{S}_2\text{CNEt}_2)](\text{S}_2\text{PMe}_2)\) (5b) which, like the analogous \([\text{Pt}(\text{PM}_{2}\text{Ph}_3)(\text{S}_2\text{CNEt}_2)](\text{S}_2\text{PM}_2)\) reported elsewhere, has unidentate \([\text{S}_2\text{PMe}_2]^-\) and bidentate \([\text{S}_2\text{CNEt}_2]^-\) co-ordination (i.r. and 1H n.m.r. evidence) and is stereochemically rigid even at 330 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 benzil. Infrared 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. Hydrogen-I 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 Koffer hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinato(II) and palladium(II) chloride (Johnson, Matthey Ltd.) and PPh_3, Na[S_2CNEt_2]·3H_2O, K[S_2COEt], and AsPH_3·CHCl_3 (B.D.H.) were used as received. The compounds Na[S_2PM_2]·2H_2O, \([\text{Pt}(\text{C}_8\text{H}_{12})\text{Cl}_2]\), and \([\text{Pt}(\text{C}_8\text{H}_{12})\text{Cl}_2]\) were synthesised as described earlier. Analytical data for the new complexes are given in Table 2 together with i.r. bands diagnostic of complexes (6a) and (6b).
the mode of co-ordination of $[S_2CNET_2]^{-}$ (ref. 14) and $[S_2PMe_2]^{-}$ (ref. 9).

Palladium Complexes.—Di-$\mu$-chloro-bis(diethyl dithiocarbamato)palladium(II). The salt Na$_2$[S$_2$CNET$_2$]$\cdot$H$_2$O (0.30 g) in acetone was added to a methylene chloride solution of [Pd(C$_8$H$_8$)$_2$Cl$_2$] (0.36 g) to give a white precipitate (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 to precipitate the orange product which was washed with diethyl ether and dried in air, m.p. 236—237°C, $v$(CN) at 1 535 cm$^{-1}$.

Di-$\mu$-bromo-bis(diethyl dithiocarbamato)palladium(II) was prepared in the same way by reaction of [PdBr$_2$(C$_8$H$_8$)$_2$] and Na$_2$[S$_2$CNET$_2$]$\cdot$H$_2$O (1 : 1 mol ratio), m.p. 210—212°C, $v$(CN) at 1 535 cm$^{-1}$. Alternatively, [PdBr$_2$(C$_8$H$_8$)$_2$]$_2$ was prepared by shaking [PdCl$_2$(C$_8$H$_8$)$_2$]$_2$ with excess of lithium bromide in acetone 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(diethyl dithiocarbamato)palladium(II). Sodium benzenethiolate in acetone was added to a methylene chloride solution of [PdCl$_2$(C$_8$H$_8$)$_2$]$_2$ 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, m.p. 228—230°C, $v$(CN) at 1 510 cm$^{-1}$.

Di-$\mu$-chloro-bis(0-ethyl dithiocarbamato)palladium(II). The salt K$_2$[S$_2$COET] (0.08 g) in acetone was added to a methylene chloride solution of [Pd(C$_8$H$_8$)$_2$Cl$_2$] (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.

Chloro(diethyl dithiocarbamato)(triphenylphosphine)palladium(II). Addition of excess of PP$_3$ to a methylene chloride solution of [PdCl$_2$(S$_2$CNET$_2$)$_2$] 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, $v$(CN) at 1 535 cm$^{-1}$, Chloro(diethyl dithiocarbamato)(triphenylarsine)palladium(II), m.p. 133—135°C, $v$(CN) at 1 535 cm$^{-1}$, chloro(diethyl dithiocarbamato)(triphenylstibine)palladium(II), $v$(CN) at 1 535 cm$^{-1}$, and chloro(diethyl dithiocarbamato)(tripyrindine)palladium(II), m.p. 154—155°C, $v$(CN) at 1 535 cm$^{-1}$, were similarly prepared by reaction of [PdCl$_2$(S$_2$CNET$_2$)$_2$] with AsPh$_3$, SbPh$_3$, and C$_6$H$_5$N respectively.

Table 2

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* Molecular weight measured osmotically at 37°C in chloroform; calculated values are given in parentheses.
Benzyltriph enylphosphonium dichloro(diethyldithiocarb amato)palladate(II). The complex \([\text{PdCl(S}_2\text{CNEt}_2]_2\) \((0.28\) g in acetone was shaken with excess of \([\text{PPh}_3(\text{CH}_2\text{Ph})]\)\(\text{Cl}\) 
\((1.00\) g) and concentrated hydrochloric acid \((1\) cm\(^3\)) for 24 h. The solvent was then removed \(\text{in vacuo}\) and the product was extracted into methylene chloride. Addition of light petroleum \((\text{b.p.}\ 60—80\ ^\circ\text{C})\) 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, \(v(\text{CN})\) at 1522 cm\(^{-1}\). Triphenylarsenium dichloro(diethyldithiocarb amato)palladate(II) was prepared similarly by reaction of \([\text{PdCl(S}_2\text{CNEt}_2]_2\) with excess of \([\text{AsPh}_3]\) \(\cdot\) CHCl in acetone, \(v(\text{CN})\) at 1522 cm\(^{-1}\).

"(Diethyldithiocarb amato)triphenylphosphine)palladium(II)." An excess of \(\text{Na}[\text{S}_2\text{PMe}_2] \cdot 2\text{H}_2\text{O}\) in acetone was added to an acetone solution of \([\text{PdCl(S}_2\text{CNEt}_2]_2\) to give a pale orange solution and a white precipitate \((\text{NaCl})\). 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, \(v(\text{CN})\) at 515 and \(v(\text{PS}_2)\) at 578 cm\(^{-1}\).

"(Diethyldithiocarb amato)(dimethylphenylphosphinodithioato)triphenylphosphine)palladium(II)." Excess of triphenylphosphine was added to a suspension of \([\text{Pd(S}_2\text{CNEt}_2]_2\) \(-\text{S}_2\text{PMe}_2]_2\) in benzene to give a yellow solution.

Platinum Complexes.—trans-\(\mu_1\)-2–7,5–6–8–Cyclo-octa 1,5-diene)-bis[chloro(diethyldithiocarb amato)palladium(II)]. The salt \(\text{Na}[\text{S}_2\text{CNEt}_2] \cdot 3\text{H}_2\text{O}\) \((0.11\) g) in acetone was added to a methylene chloride solution of \([\text{Pt(C}_8\text{H}_12\text{Cl}_2]_2\) \((0.19\) g) to give an immediate white precipitate \((\text{NaCl})\) 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 \(\text{NaCl}\), then with methanol and diethyl ether, and dried in air, m.p. 190—192 °C, \(v(\text{CN})\) at 1550 cm\(^{-1}\).

Chloro(diethyldithiocarb amato)(triphenylphosphine)-platinum(II). Triphenylphosphine \((0.07\) g) was added to a suspension of \([\text{PtCl(S}_2\text{CNEt}_2]_2\) \(-\text{C}_8\text{H}_12]_2\) \((0.11\) g) in methylene chloride to give a pale yellow solution. Removal of some solvent and addition of diethyl ether–pentine 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, \(v(\text{CN})\) at 1550 cm\(^{-1}\).

(Diethyldithiocarb amato)bis(triphenylphosphine)platinum chloride—water \((1/1)\). An excess of \(\text{PPh}_3\) was added to a suspension of \([\text{PtCl(S}_2\text{CNEt}_2]_2\) \(-\text{C}_8\text{H}_12]_2\) 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, \(v(\text{CN})\) at 1550 cm\(^{-1}\).

(Diethyldithiocarb amato)bis(dimethylphenylphosphine)-platinum chloride—water \((1/1)\). Excess of \(\text{Na}[\text{S}_2\text{CNEt}_2] \cdot 3\text{H}_2\text{O}\) in acetone was added to cis-\([\text{PtCl}(\text{PMe}_2\text{Ph})]_2\) in methylene chloride and shaken for 15 min to give a very pale yellow solution and a white precipitate \((\text{NaCl})\). 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 \(17\) by the prolonged interaction of \([\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]_2\) and \(\text{PPh}_3\) in methylene chloride.

(Diethyldithiocarb amato)bis(dimethylphenylphosphinodithioato)(tri phenylphosphine)platinum(II). Excess of \(\text{Na}[\text{S}_2\text{PMe}_2] \cdot 2\text{H}_2\text{O}\) in acetone was added to a suspension of \([\text{PtCl(S}_2\text{CNEt}_2]_2\) \(-\text{C}_8\text{H}_12]_2\) in methylene chloride and stirred for ca. 1 h. The yellow solution was then filtered through Celite to remove \(\text{NaCl}\) and the solvent was removed \(\text{in vacuo}\). The resulting yellow product was extracted into methylene chloride, reprecipitated by addition of pentane and washed with water, methanol, and diethyl ether, m.p. 197—200 °C (decomp.), \(v(\text{CN})\) at 1528 and \(v(\text{PS}_2)\) at 578 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, and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.
Metal Complexes of Sulphur Ligands. Part 14. Reaction of Palladium(II) and Platinum(II) Dithiocarbamate 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

Reprinted from JOURNAL OF THE CHEMICAL SOCIETY DALTON TRANSACTIONS 1977
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-(diphenylphosphinous acid) palladium(II)

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Prolonged reaction of [Pd(S$_2$PMe$_2$)$_2$] with excess PPh$_3$(OR) (R = Me or Et) in either methylene chloride or benzene gives the four-co-ordinate complex [Pd(S$_2$PMe$_2$)(PPh$_3$O){PPh$_3$(OH)}]$_2$ (1a) shown by spectroscopic evidence and X-ray structural analysis to contain the symmetrically hydrogen-bonded PPh$_3$POHOPPh$_3$ ligand. Crystals of (1a) are monoclinic, space group P2$_1$/c, with a = 8.86(1), b = 22.12(2), c = 9.69(1) Å, β = 111.5(2)°.

The acidic hydrogen atom links two equivalent diphenylphosphinite groups with O...O 2.41 Å. Similar complexes [M(S=S)(PPh$_3$O){PPh$_3$(OH)}]$_2$ (M = Pd, S=S = [S$_2$PPh$_2$]$^-$ or [S$_2$CN$_2$]$^-$; M = Pt, S=S = [S$_2$PMe$_2$]$^-$ or [S$_2$CNEt$_2$]$^-$) have been prepared by reaction of [M(S=S)$_2$] with PPh$_3$(OR) or, for M = Pd, by reaction of [PdCl$_2$(PPh$_3$O)PPh$_3$(OH)]$_2$ with the appropriate dithioacid anion (1:2 molar ratio). A careful study of the [Pt(S$_2$CNEt$_2$)-PPh$_2$(OMe)] reaction has resulted in the isolation of the intermediates [Pt(S$_2$CNEt$_2$)(PPh$_3$(OMe)]$_2$ (2; X = [PPh$_3$- or Cl]- and [Pt(S$_2$CNEt$_2$)(PPh$_3$O){PPh$_3$(OMe)}] (3) and a mechanism of formation of [Pt(S$_2$CNEt$_2$)(PPh$_3$(OMe)]$_2$ (1b) involving both nucleophilic attack on a P-OMe bond and subsequent hydrolysis of a P-OMe bond is proposed. In contrast, reaction of [M(S$_2$CO)(PPh$_3$O)]$_2$ with PPh$_3$(OEt) gives [M(S$_2$CO)·PPh$_3$(OEt)]$_2$, although [Pd(S$_2$CO)(PPh$_3$(OEt)]$_2$ (M = Pd or Pt), although [Pd(S$_2$PMe$_2$)(PPh$_3$(OH)]$_2$ can be synthesised from [[PdCl$_2$(PPh$_3$O)PPh$_3$(OH)]$_2$ and K[S$_2$P(OEt)] (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)$_2$L$_2$] complexes (M = Pd or Pt; S=S = [S$_2$PR$_2$]$^-$, [S$_2$CN$_2$]$^-$, [S$_2$COR]$^-$, or [S$_2$P(OR)$_2$]$^-$) have been reported. These studies clearly show that reaction occurs by stepwise cleavage of metal–sulphur bonds to generate the four-co-ordinate square-planar complexes [M(S=S)L$_2$] and [M(S=S)L$_2$][S=S] which exhibit unidentate–bidentate and bidentate–ionic modes of bonding of the dithioacid groups respectively. In addition, for these ion [S$_2$COR]$^-$ and [S$_2$P(OR)$_2$]$^-$ complexes, nucleophilic attack can also occur on a co-ordinated alkoxy-group to give [M(S$_2$CO)L$_2$] and [M(S$_2$P(OEt)L)]$_2$ respectively.

In this paper, we report the results of reactions between various palladium(II) and platinum(II) dithioacid complexes and tertiary phosphinites PPh$_3$(OR) (R = Me or Et) in which, on the basis of earlier work, both hydrolysis of the P–OR group 3 and/or nucleophilic attack on the P–OR group 4 might be expected to play a significant role.

RESULTS AND DISCUSSION

Addition of an excess of PPh$_3$(OMe) to a methylene chloride solution of [Pd(S$_2$PMe$_2$)$_2$] 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 a pale yellow, non-conducting, crystalline precipitate (1a) was obtained. The $^1$H n.m.r. spectrum of this product contained in addition to the phenyl multiplet, a sharp doublet at 8 1.97 p.p.m. (1/2H 12.0 Hz (relative intensity 10:3) assigned to the methyl protons of the [S$_2$PMe$_2$]$^-$ 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 PPh$_3$(OEt) 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(S$_2$CN$_2$)(PR$_3$)$_2$][S$_2$CN$_2$] with CH$_2$Cl$_2$, which gave [M(S$_2$CN$_2$)(PR$_3$)$_2$]Cl and CH$_3$$_2$SNCN$_2$) and suggests that either hydrolysis and/or nucleophilic attack on the P–OR group has occurred.

Complex (1a) analysed closely for [Pd(S$_2$PMe$_2$)(PPh$_3$O)·PPh$_3$(OH)] and is monomeric in chloroform at 37 °C. However, all attempts to observe the $^1$H n.m.r. signal of the acid hydrogen on the co-ordinated diphenylphosphinous acid proved unsuccessful (cf. related studies on [[MX(PPh$_3$O)PPh$_3$(OH)]$_2$] (M = Pt or Pd; X = Cl or Br) 6 although Beaulieu et al. 9 found such a signal at 8 13.43 p.p.m. for [PtH(PMePh$_2$)(PPh$_3$O)PPh$_3$(OH)]). The i.r. spectrum of (1a) shows several bands in the P–O stretching region (850–1 100 cm$^{-1}$). However, the three strong bands at 850, 895, and 944 cm$^{-1}$ are also observed for the starting material [Pd(S$_2$PMe$_2$)$_2$] while that at 1 100 cm$^{-1}$ corresponds to a band usually observed in phenylphosphate complexes 6 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 1 010 cm\(^{-1}\) is assigned to a \(\nu(PO)\) stretching mode. The peak at 582 cm\(^{-1}\) is consistent with bidentate coordination of the \([S\text{PMe}_2]^-\) group.\(^{2}\) The absence of \(\nu(\text{OH})\) in the normal region of the i.r. spectrum (ca. 3 200 cm\(^{-1}\)) is consistent with a symmetrical hydrogen-bonded system of the type first postulated by Dixon and Rattray \(^{6}\) in \([\text{MX(PPh}_3\text{O)}[\text{PPh}_2\text{OH}])_3\], etc., and later confirmed by an X-ray structural analysis on the related \([\text{Pd-SCN)(PPh}_3\text{O)}[\text{PPh}_2\text{OH}])_2\].\(^{8}\)

![Diagram](image)

Further evidence for the validity of this statement is based on the \(^{31}\text{P}\) n.m.r. spectrum (proton decoupled) of (1a) which shows the expected AX\(_2\) pattern with resonances centred at \(84 29\) (\([S\text{PMe}_2]^-\)) and 83.20 p.p.m. (Ph\(_2\text{POH}OPh\)) respectively, and the fact that reaction of \([\text{PdCl(PPh}_3\text{O)}[\text{PPh}_2\text{OH}])_3\] with Na\([S\text{PMe}_2]2\text{H}_2\text{O (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 structural analysis which is reported in detail below. Analogous complexes \([\text{M(S-S)}(\text{PPh}_3\text{O})[\text{PPh}_2\text{OH}])\) \((\text{M} = \text{Pd, S-S} = [\text{S}\text{PMe}_2]^- \text{or [S}_2\text{CNEt}_2]^-; \text{M} = \text{Pt, S-S} = [\text{S}_2\text{PMe}_2]^- \text{or [S}_2\text{CNEt}_2]^-)\) were prepared by prolonged reaction of \([\text{M(S-S)}]_2\) with excess of PPh\(_3\) (OR) in methylene chloride and fully characterised by elemental analyses, and i.r., \(^1\text{H}, \text{and }^{31}\text{P}\) n.m.r. spectroscopy (see Experimental section). The palladium complexes were also synthesised by reaction of \([\text{PdCl(PPh}_3\text{O)}[\text{PPh}_2\text{OH}])_3\] with either \([\text{NH}_4][\text{S}\text{PMe}_2]2\text{H}_2\text{O}\) or \([\text{Na}[\text{S}_2\text{CNEt}_2]3\text{H}_2\text{O (1 : 2 molar ratio)}\)

Crystal Data for (1a).—\(\text{C}_{28}\text{H}_{27}\text{O}_2\text{P}_3\text{PdS}_2\), \(M = 634\), pale yellow monoclinic needles, \(a = 6.86(1)\), \(b = 22.12(2)\), \(c = 9.69(1)\) \(\text{Å}\), \(\beta = 111.6(3)^\circ\), \(\gamma = 136.8\) \(\text{Å}^3\), \(D_m = 1.564 \text{ g cm}^{-3}\). Space group \(P2_1/m\) (No. 13), Cu-K\(_\alpha\) radiation, \(\lambda = 1.5418\) \(\text{Å}\), \(\mu(\text{Cu-K\(_\alpha\)}) = 88.7\) cm\(^{-1}\).

Structure Determination.—Data for layers 0—4 \(kl\) were collected on multilap packs by the equi-inclination Weissenberg method. Intensities were evaluated by the Photocam 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 mm\(^2\). Cylindrical absorption corrections\(^{9}\) 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 \(P2_1/m\) rather than the non-centric \(P2_1\). The phenyl rings were constrained to be planar with all C-C distances \(1.40 \text{ Å}\) and all C-C-C angles \(120^\circ\), 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[|F|]) for [|F|] > 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 \(R = 0.077\). 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>
<thead>
<tr>
<th>Table 1</th>
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<tr>
<td>Fractional co-ordinates and thermal parameters (all (\times 10^4)) for (1a). For the phenyl rings [atoms C(1)—C(6) and C(7)—C(12)] the estimated standard deviation of the ring centres is 0.008 Å</td>
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<tr>
<td>Pd</td>
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<td>P(1)</td>
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<td>P(2)</td>
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* Anisotropic thermal parameters (\(\times 10^4\))

The structure-factor table is deposited as Supplementary Publication No. SUP 22021 (4 pp., 1 microfiche).*

Description of the Structure.—The structure of (1a) is monoclinic with crystallographic \(m(P_2)\) 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 Pd\(_{11}\) 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°


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 diphenylphosphinite 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, 1/2 − y, z. Estimated standard deviations are given only when atoms in the phenyl rings are not involved. | |
| | Intermolecular contacts less than 3.5 Å are listed | |
| Pd—S | 2.403(4) | S—Pd—S' | 82.5(2) |
| Pd—P(1) | 2.204(4) | S—Pd—P(1) | 92.4(1) |
| S—P(2) | 2.000(6) | S—Pd—P(1') | 175.6(3) |
| P(1)—O | 1.546(14) | P(1)—Pd—P(1') | 91.6(2) |
| P(1)—C(1) | 1.800 | Pd—S—P(2) | 84.3(2) |
| P(1)—C(7) | 1.807 | Pd—Pd—O | 114.8(4) |
| P(2)—C(13) | 1.796(22) | Pd—P(1)—C(1) | 114.2 |
| P(3)—C(14) | 1.834(37) | Pd—P(1)—C(7) | 113.8 |
| O···O' | 2.414(20) | O—P(1)—C(1) | 106.1 |
| O···C(11) [1 + x, y, z] | 3.32 | O—P(1)—C(7) | 105.9 |
| O···C(12) [1 + x, y, z] | 3.35 | C(1)—P(1)—C(7) | 102.9 |
| O···C(13) [x, y, z − 1] | 3.45 | S—P(2)—C(13) | 110.1(6) |

* 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(η3-PMe3)2(PMMe3)2].10

Figure 1 Projection of (1a) on to the symmetry plane

Figure 2 Projection of (1a) on to the symmetry plane

slightly distorted from m symmetry; the planes of the two phenyl rings are inclined at 63 and 59° 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)···O(1') distance even shorter; a greater one would bring the rings C(7)—C(12) and C(7')—C(12') closer together. As it is, the separation of C(12) and C(12') is 3.68 Å, and the hydrogen atoms bonded to these will be ca. 2.5 Å apart.

Thus, the interaction of the diphenylphosphinite and diphenylphosphinous acid groups in (1a) is very similar to that in [[Pd(SCN)(PPh2O)][PPh2(OH)]2] where an O···O distance of 2.421 Å and two independent P—O bonds of 1.549 and 1.536 Å were reported.8 This supports the suggestion of Naik et al.8 and other workers that such interactions are normal for complexes of Pt11 and Pd11 containing diphenylphosphinite and diphenylphosphinous acid ligands in cis orientation to each other.

In an attempt to determine the detailed mechanism of formation of these complexes the nature of the products formed during the reaction of [M(S2CNEt2)2] with PPh2(OMe) were carefully examined. Thus, reaction of [M(S2CNEt2)2] with excess of PPh2(OMe) in methanol followed either immediately (Pt) or within 30 min (Pd) by addition of Na[BPh4] gave a precipitate of [M(S2CNEt2)2PPh2(OMe)]2[BPh4] (2). Complexes (2) were characterised by elemental analyses, conductivity measurements in methylene chloride which are indicative of 1:1 electrolytes, 1H n.m.r. spectra which show the presence of a 'pseudo-triplet' * for the methoxy-groups with [3J(PH) + 4J(P'H)] 12.0 Hz † and magnetically equivalent ethyl groups, and 13P n.m.r. spectra which for M = Pt shows the expected 1:4:1 triplet [J(PtP) 3749.0 Hz] indicative of magnetically equivalent phosphorus-bonded PPh2(OMe) groups. These results clearly show that, as in the case of tertiary

† cf. cis-[MCl2(PPh2(OMe))2] (M = Pd or Pt) with [3J(PH) + 4J(P'H)] 12.5 Hz.11

phosphines, the initial rapid increase in conductivity on mixing [M(S-S)] and PPh₂(OR) is due to the formation of [M(S-S)]{PPh₂(OR)}₂[S-S] presumably by stepwise cleavage of metal-sulphur bonds.

However, rather surprisingly, treatment of a methylene chloride solution of (2; M = Pt) with Na[S₂CNEt₂]·3H₂O in acetone led after 3 d only to the recovery of 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 [AsPh₃]Cl·HCl which precipitated the very insoluble [AsPh₃][BPh₃] and left a methylene chloride solution containing [Pt(S₂CNEt₂){PPh₂(OMe)}₂]Cl. 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[S₂CNEt₂]·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 two doublets at δ 3.87 [PPh₂(OMe)], two closely spaced quartets at 3.52 and 3.56, a triplet at 1.23 p.p.m. ([S₂CNEt₂]²⁻), and a multiplet in the aromatic region. The ³¹P n.m.r. spectrum (proton decoupled) in CDCl₃ at 225 K consisted of two doublets at δ 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. Each of the doublets exhibited platinum satellites with J(PtP) 3 264.8 and 4 212.3 Hz respectively, confirming directly bonded phosphorus atoms in each ligand. The i.r. spectrum showed a strong v(PO) stretch at 1 050 cm⁻¹ with v(CN) at 1 530 cm⁻¹ indicative of bidentate [S₂CNEt₂]²⁻ coordination.

All this spectroscopic information together with the analytical data is consistent with the formulation of (3) as [Pt(S₂CNEt₂){PPh₂(OMe)}{PPh₂(OMe)}]. By analogy with the complex [Ni(η-c₅H₅){P(OEt)₃}]; Ω(OEt)₃] which shows two doublets centred at δ 147.5 [P(OEt)₃] and 85.8 p.p.m. [PO(OEt)₃], and the position of the PPh₂(OMe) resonance for [Pt(S₂CNEt₂){PPh₂(OMe)}₂] ([PPh₂(OMe)]δ(94.20 p.p.m.), the resonance at 94.14 p.p.m. is assigned to PPh₂(OMe) and that at 38.89 p.p.m. to [PPh₂O]⁻.

Complex (3) was also isolated by reaction of [Pt(S₂CNEt₂)] and excess of PPh₂(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(S₂CNEt₂){PPh₂(OMe)}₂]·[S₂CNEt₂] readily rearranges to (3) by nucleophilic attack of [S₂CNEt₂]⁻ on a co-ordinated PPh₂(OMe) group.

Related studies of nucleophilic attack on co-ordinated alkoxyporphorus ligands are well documented.

Another portion of the [Pt(S₂CNEt₂){PPh₂(OMe)}₂]Cl solution was treated with an equimolar amount of Na[S₂CNEt₂]·3H₂O together with a few drops of PPh₂(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(S₂CNEt₂){PPh₂(OH)}{PPh₂(OMe)}] (1b). This complex was also formed if a methylene chloride solution of [Pt(S₂CNEt₂){PPh₂(OMe)}{PPh₂(OMe)}] (3) was treated with a small amount of PPh₂(OMe) for a prolonged period, whereas in the absence of free PPh₂(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 PPh₂(OMe) group by free PPh₂(OMe) and subsequent formation of the stable six-membered Pt[PPh₂(OH)]PPh₂ ring structure. Evidence for the generation of some PPh₂(OMe) under these conditions comes from ¹H n.m.r. studies on PPh₂(OMe)–CDCl₃ solutions which show the appearance of methanol and the concomitant disappearance of methoxy-resonances on prolonged standing. Conductivity studies on PPh₂(OMe)–CDCl₃ solutions indicate that PPh₂(OMe) and not ·PPh₂(OMe) 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. Similar displacement reactions of co-ordinated PPh₂(OMe) by free PPh₂(OMe) are also proposed to explain the formation of [Pt(PPh₂O)₃(PPh₂(OH))₂] from [Pt(PPh₂O)₃(OBu)₃] and free PPh₂(OBu) when left in ethanol for 4 d.

When the methylene chloride solution of [Pt(S₂CNEt₂){PPh₂(OMe)}₂]Cl was treated with only a few drops of PPh₂(OMe) and left for several days (1b) was again isolated, whereas in the absence of PPh₂(OMe) some of (3) was produced. However, the rate of decrease in conductivity in both these solutions was much slower compared to those containing [S₂CNEt₂]⁻ ion which is simply a reflection of the greater nucleophilicity of [S₂CNEt₂]⁻ compared to Cl⁻ ion.

A summary of the reactions involved in the formation of [M(S₂CNEt₂)₂{PPh₂(OMe)}{PPh₂(OH)}] 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(S₂PR₂)₂{PPh₂(OH)}{PPh₂(OH)}] from [M(S₂PR₂)₂] and excess of PPh₂(OMe) but attempts to confirm this have not been completely successful.
example, reaction of $[\text{Pd}(\text{S}_2\text{PPPh}_2)_2]$ and $\text{PPPh}_4(\text{OMe})$ in methanol followed by addition of $\text{Na}[\text{BPh}_3]$ gave a pale yellow precipitate but this rapidly turned brown (cf. the analogous $[\text{Pd}(\text{S}_2\text{PPPh}_2)(\text{PPPh}_2)_2][\text{BPh}_3]$ which also rapidly decomposed in the solid state). However, treatment of $[\text{Pd}(\text{S}_2\text{PPPh}_2)_2]$ with $\text{PPPh}_4(\text{OMe})$ in methylene chloride followed by solvent removal after ca. 10 min and addition of diethyl ether gave a yellow non-conducting solid whose $^1\text{H}$ n.m.r. spectrum was consistent with the formulation $[\text{Pd}(\text{S}_2\text{PPPh}_2)(\text{PPPh}_2)_2][\text{BPh}_3]$. $^1\text{H}$ n.m.r. spectrum of $\text{PPPh}_3(\text{OH})$ at 30.00–8.00 p.p.m., (30), $\text{PhH}$ and, therefore, it is highly likely that the mechanism shown in the Scheme also applies to $[\text{S}_2\text{PPPh}_2]^{2-}$ complexes.

Finally, it was of some interest to examine the reaction between palladium(II) and platinum(II) alkyl dithiocarbonates and $\text{PPPh}_4(\text{OR})$ because of the presence of two types of alkoxo group which might undergo nucleophilic attack. Thus, reaction of $[\text{Pd}(\text{S}_2\text{CO})_2][\text{PPPh}_4(\text{OH})]$ in methylene chloride with excess of $\text{PPPh}_4(\text{OEt})$ gave an immediate red conducting solution which slowly turned yellow accom¬panied by a steady decrease in conductivity. Treatment of the latter with diethyl ether–light petroleum (b.p. 60–80 °C) gave a non-conducting yellow solid analysing for $[\text{Pd}(\text{S}_2\text{CO})_2][\text{PPPh}_4(\text{OEt})]_2]$. The i.r. spectrum consisted of bands at 1690s, 1618s, and 1586w cm$^{-1}$ characteristic of $\nu$(CO) in dithiocarbonato-complexes, but no bands between 1200 and 1300 cm$^{-1}$ attributable to $[\text{S}_2\text{CO}]^{-}$ groups. The $^1\text{H}$ n.m.r. spectrum consisted of a triplet at 8.106 (CH$_3$) and a complicated multiplet at 3.79 p.p.m. (CH$_2$) similar to that reported for $[\text{cis-PdCl}_2(\text{PPPh}_4(\text{OEt}))]_2$. The $^31\text{P}$ n.m.r. spectrum (proton decoupled) contained a single resonance at 116.62 p.p.m. An analogous complex was formed by reaction of $[\text{Pt}(\text{S}_2\text{CO})_2][\text{PPPh}_4(\text{OEt})]$ with $\text{PPPh}_4(\text{OEt})$.

Thus, this evidence clearly indicates that nucleophilic attack of the $[\text{S}_2\text{CO}]^{-}$ ion occurred specifically on the co-ordinated $[\text{S}_2\text{CO}]^{-}$ propoxy-group in the $[\text{M}(\text{S}_2\text{CO})_2][\text{PPPh}_4(\text{OEt})_2][\text{S}_2\text{CO}]^{-}$ intermediate and no evidence has been found for further reactions of the [M-

![Scheme](image-url)
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-1 n.m.r. spectra were obtained on a Varian Associates HA-100 and EM360 spectrometers. 31P n.m.r. spectra on a Varian XL100 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% H3PO4). Melting points were determined with a K"oller hot-stage microscope and are uncorrected.

Potassium tetrachloroplatinate(II) and palladium(II) chloride [Johnson, Matthey Ltd., Na2[S2CNEt2]·3H2O, Na[BPh4], and [AsPh3]Cl-HCl (B.D.H.), and PPh3(OEt) and PPh3(OEt) (Maybridge Chemical Company) were obtained as indicated. The compounds Na2[S2PMe2]-2H2O, 21P [NH4][S2PMe2]·20 [K[S2CO3]]·21 [M[S2CNEt2]·22 [M(S2PMe2)] (M = Me3 or Ph3), and [M(S2CO3)]·24 were synthetised as described earlier. Solvents were used as purchased.

Infrared bands diagnostic of [S2PMe2]−21 [S2PMe2]−2 and [S2CNEt2]13 bidentate-co-ordination are listed for each complex and, unless otherwise stated, 1H n.m.r. spectra were recorded in CDCl3 at 301 K and 31P n.m.r. spectra (proton decoupled) in CDCl3 at 90.5 K. Relative intensities are given in parentheses and s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and p = pseudo-triplet.

**Palladium Complexes.**—Dimethylphosphinothioato(di-phenylphosphinidio)(diethylphosphinous acid)palladium(II). Method (A). An excess of [PdCl2(OH)](H2O) or [PdCl2[NH3](H2O)] was added to a methylene chloride solution of [Pd(S2CNEt2)] 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(PO) 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 CHCl3) 550. Calc. for C26H20O2P4S3PdS2·C, 49.2; H, 4.3; P, 14.7; Pd, 16.7; S, 10.1%; M (in CHCl3) 564.3. N.m.r. spectra: 1H, 1.97 (d, 6) 31P/PP 12.0 Hz) ([S2PMe2]) and 7.50—7.90 p.p.m. (m, 20) (Ph), 31P, 83.20 (d, 2) (PPh3OPOHPh3) and 84.29 p.p.m. (p, t) (S2CNEt2) 7.4 Hz) [31P/PP 7.4 Hz).

The complexes were prepared similarly using [Pd(S2CNEt2)] and [Pd(S2CNEt2) respectively. Diphosphinothioato(dimethylphosphinothioato)(dimethylphosphinous acid)palladium(II). m.p. 184—185 °C, v(PS2) at 560 and 750 cm−1, v(PO) at 1 009 cm−1 (Found: C, 56.8; H, 4.3. Calc. for C25H18O2P4S2PdS2·C, 57.0; H, 4.1%). N.m.r. spectra: 1H, 7.20—7.80 p.p.m. (m, Ph), 31P, 78.66 (t, 1) ([S2PMe2]) and 83.46 p.p.m. (m, d, 2) (PPh3OPOHPh3) 31P/PP 6.7 Hz). DN-Dithioldithiocarbamate(diphenylphosphinothioato)(diphenylphosphinous acid)palladium(II), m.p. 218—220 °C, v(CN) at 1 514 cm−1, v(PO) at 1 017 cm−1 (Found: C, 52.7; H, 4.7; N, 2.1. Calc. for C25H18O2P4S2PdS2·C, 53.0; H, 4.7; N, 2.1%). N.m.r. spectra: 1H, 1.20 (t, 6), 3.67 (q, 4) ([S2CNEt2]) 31P/PP 7.0 Hz), and 7.20—7.90 (m, 20) (Ph), 31P, 84.50 p.p.m. (m, 6).

Following the suggestion in ref. 3, we have used the term diphenylphosphinido to describe P-bonded [PPh3(O)]—rather than the previously used diphenylphosphinate.

† 10 is the total relative intensity of the methylene quartet and methoxy pseudo-triplet because the resonances are too close to integrate separately.
[Pt(S₂CNEt₂)₂] and PPh₄(OMe). NN-Diethylthiocarbamato(diphenylphosphinothiophospho)-
diphenylphosphinonic acid)platinum(II), m.p. 242—244 °C, v(CN) at 1 530 cm⁻¹, v(PO) at 1 020 cm⁻¹ (Found: C, 46.9; H, 4.4; N, 1.9%; M (in CHCl₃) 758. Calc. for C₃₉H₃₉O₃N₂P₄S₂: C, 60.3; H, 4.3; N, 1.8%).

An excess of PPh₄(OMe) was added to a methylene chloride solution of '[Pt(S₂CNEt₂)(PPh₄(OMe))₂]Cl' and leaving for several days, by reaction of the same solution with Na[S₂CNEt₂]·3H₂O and PPh₄(OMe) (formed more rapidly), or by reaction of a methylene chloride solution of [Pt(S₂CNEt₂)(PPh₄)₂] with PPh₄(OMe) for 24 h.

(11) Calcd. for C₂₉H₃₀N₂O₂P₂PtS₂: C, 60.3; H, 4.3; N, 1.8%. N.m.r. spectra: ¹H, 1.93 (t,6), 3.50 (q), 3.56 (q,4) ([S₂CNEt₂]²⁻) [²J(HH) 7.0 Hz], and 7.20—7.90 p.p.m. (m,20) (Ph); ³¹P, 51.4 (CsD₂O) 2749.0 Hz.

(11) Calcd. for C₂₉H₃₀N₂O₂P₂PtS₂: C, 60.3; H, 4.3; N, 1.8%. N.m.r. spectra: ¹H, 1.93 (t,6), 3.50 (q), 3.56 (q,4) ([S₂CNEt₂]²⁻) [²J(HH) 7.0 Hz], and 7.20—7.90 p.p.m. (m,20) (Ph); ³¹P, 51.4 (CsD₂O) 2749.0 Hz.

All the standard crystallographic calculations were made at the Edinburgh Regional Computing Centre using the 'X-Ray '74' program.²⁵

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 Mechrolab osmometer.

SYNTHESSES AND CHARACTERISATION OF SOME TRIPHENYLCYANOBORATE COMPLEXES OF RHODIUM(III), RUTHENIUM(II) AND PALLADIUM(II)

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(Received April 4th, 1977)

Summary

The triphenylcyanoborate (N-bonded) complexes \( \eta^5\)-(CsMe\(_5\))Rh(S–S)–NCBPh\(_3\) \( \text{S–S}^– = \text{S}_2\text{PMe}_2, \text{S}_2\text{PPh}_2, \text{S}_2\text{CNMe}_2 \), \( \eta^6\)-(C\(_6\)H\(_6\))Ru(S\(_2\)PPh\(_2\))–NCBPh\(_3\) and \( \text{Pd}(S\(_2\)CNEt\(_2\))(PMe\(_2\)Ph)(NCBPh\(_3\)) \) have been synthesised and characterised by both spectroscopic and X-ray structural methods.

Recently the syntheses of \( \eta^5\)-(CsMe\(_5\))Rh(S–S)L \) (I: \( S^– = \text{S}_2\text{PMe}_2, \text{S}_2\text{PR}_2 \) \( R = \text{Me, Ph} \)) by treatment of \( \eta^5\)-(CsMe\(_5\))RhCl–(S–S) \( \text{Cl}_2 \) 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 \( \eta^5\)-(CsMe\(_5\))Rh(S–S)(MeOH) \( \text{BPh}_4\) which are very useful precursors for generating a range of cations \( \eta^5\)-(CsMe\(_5\))Rh(S–S)L \) BPh\(_4\) (III: \( L = \text{PPh}_3, \text{PMePh}_2, \text{AsPh}_3, \text{C}_5\text{H}_5\text{N}, \text{CO}, \text{etc} \)). However, attempts to synthesise \( \eta^5\)-(CsMe\(_5\))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) S2PMe2; (b) S2PPh2; (c) S2CNMe2). 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 \(\sim\text{NCBPh}_3\) group [2], and all show bands characteristic of bidentate coordination of the dithiocarbamate ligands. The mass spectrum of IVc has a peak at \(m/e 626\) corresponding to \(\left\{\eta^5-(C_5Me_5)Rh(S_2CNMe_2)NCBPh_3\right\}^+\) 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 5.179 (C\(_5\)Me\(_5\)), 3.17 (\(\sim\text{S}_2\text{CNMe}_2\)) and 7.21 ppm (\(\sim\text{NCBPh}_3\)) 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 \(a = 24.013 \pm 0.006\) A, \(b = 9.368 \pm 0.002\) A, \(c = 14.643 \pm 0.001\) A, \(\beta = 106.70 \pm 0.01^\circ\), \(Z = 4\) 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 \(\left\{\eta^5-(C_5Me_5)Rh(S_2PMe_2)NCBPh_3\right\}\) (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>
</thead>
<tbody>
<tr>
<td>Rh—S(1)</td>
<td>2.41(1)</td>
</tr>
<tr>
<td>Rh—S(2)</td>
<td>2.43(1)</td>
</tr>
<tr>
<td>Rh—N</td>
<td>2.00(4)</td>
</tr>
<tr>
<td>Rh—C—Me$_3$</td>
<td>1.81</td>
</tr>
<tr>
<td>N—C</td>
<td>1.16(5)</td>
</tr>
<tr>
<td>C—B</td>
<td>1.58(5)</td>
</tr>
<tr>
<td>S(l)—P</td>
<td>2.01(1)</td>
</tr>
<tr>
<td>S(2)—P</td>
<td>2.01(1)</td>
</tr>
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<tr>
<td>N—C</td>
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<td>C—B</td>
<td>1.58(5)</td>
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<tr>
<td>S(l)—P</td>
<td>2.01(1)</td>
</tr>
<tr>
<td>S(2)—P</td>
<td>2.01(1)</td>
</tr>
<tr>
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<td>168.9(2.8)</td>
</tr>
<tr>
<td>N—C—B</td>
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<td>S(l)—Rh—S(2)</td>
<td>82.0(3)</td>
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<tr>
<td>N—Rh—C$_5$Mes°</td>
<td>123.0</td>
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<tr>
<td>S(l)—Rh—C$_5$Mes°</td>
<td>125.7</td>
</tr>
</tbody>
</table>

Torsion angle about C—N: $-30.0^\circ$

$^a$Distance to the centre of gravity of the pentamethylcyclopentadienyl ring.

(Rh—S$_2$) 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. \{η$^5$-(C$_5$H$_5$)M(PPh$_3$)$_2$NCBPh$_3$ \} (M = Fe, Ru) [3], \{η$^5$-(C$_5$H$_5$)Ru(PPh$_3$)$_2$NCBPh$_3$ \} [3] and \{(PPh$_3$)CuNCBPh$_3$ \}$^-$-CHCl$_3$ [2] and all these compounds have been prepared by means of direct reaction with NaBPh$_3$CN.

In this work, the BPh$_3$CN$^-$ anion is generated in situ, possibly by reaction of hydrogen cyanide with BPh$_4$$. Earlier studies on C$_2$(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 \{η$^6$-(C$_6$H$_6$)Ru(S$_2$PPh$_2$)Cl \} with a methanolic solution of C$_2$(CN)$_4$ and NaBPh$_4$ gives \{η$^6$-(C$_6$H$_6$)Ru(S$_2$PPh$_2$)NCBPh$_3$ \} and \{(Pd(S$_2$CNEt$_2$)(PMe$_2$Ph))(THF)$^+$ \} [5], followed by C$_2$(CN)$_4$ and NaBPh$_4$ in methanol gives \{(Pd(S$_2$CNEt$_2$)(PMe$_2$Ph)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

REACTIONS OF [RuCl₂L₃] \( (L = \text{P(OMe)}\text{Ph}_2, \text{P(OEt)}\text{Ph}_2) \) AND

[RuCl₂L₄] \( (L = \text{P(OMe)}_2\text{Ph}, \text{PMe}_2\text{Ph}, \text{PMePh}_2) \) WITH VARIOUS
DITHIOACID LIGANDS

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(Received 28 March 1977)

Reactions of [RuCl₂L₃] \( (L = \text{PPh}_3, \text{PETPh}_2) \) and \textit{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] \( [S-S =
\text{S}_2\text{PR}_2(R = \text{Me, Et, Ph}), \text{S}_2\text{CNR}_2(R = \text{Me, Et, Ph}), \text{S}_2\text{COMe}] \) containing
bidentate dithioacid groups and, in most instances, \textit{cis} tertiary
phosphine ligands.\(^{(1)}\)

In this preliminary communication, we now report the
reactions of more [RuCl₂L₃] \( [L = \text{P(OMe)}\text{Ph}_2, \text{P(OEt)}\text{Ph}_2(2)] \) and
[RuCl₂L₄][L = \text{P(OMe)}_2\text{Ph} (2), \text{PMe}_2\text{Ph} (3), \text{PMePh}_2 (4)] compounds with
various alkali metal dithioacid salts \( [\text{S}_2\text{PR}_2(R = \text{Me, Ph}), \text{S}_2\text{CNR}_2(R = \text{Me, Et})] \). 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] \( (L = \text{P(OMe)}_2\text{Ph}, \text{PMePh}_2) \)
with all the dithioacid ligands above give compounds of type
\( (I) \) and \textit{no} intermediate products are observed. However, when
[RuCl₂(PMe₂Ph)₄] is shaken with Na₃[\text{S}_2\text{PMe}_2\text{H}_2] in benzene, a
yellow solid analysing for [RuCl(S₂PMe₂)(PMe₂Ph)₃] \( (II) \) is
obtained. The \( ^{31}\text{P}-\text{¹H} \) nmr spectrum of \( (II) \) at 213K in CDC₁₃
consists of an AB₂ pattern \( \text{[A, 20.4, B, 16.1 ppm; \delta(AB)174.2, J(AB)33.0, Hz]} \) due to the three \text{PMe}_2\text{Ph} groups and a singlet at
94.0 ppm due to the \( \text{S}_2\text{PMe}_2 \) ligand. The \( \text{¹H} \) nmr spectrum at
213K in CDC₁₃ consists of two overlapping 'pseudo-doublets'\(^{+}\)

\(^{+}\text{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, \( J(\text{PP}) \) value when
compared to \( |J(\text{PH}) + J(\text{PH}^-)| \).\(^{(6)}\)
at 1.88\(^\circ\) and three doublets at 1.19, 1.60 and 2.17\(^\circ\). This information is consistent with structure (II). Thus the 'pseudo-doublets' arise from the methyl groups of the two PMe\(_2\)Ph ligands trans to S\(_2\)PMe\(_2\) and the doublet at 1.60\(^\circ\) from the other PMe\(_2\)Ph group [cf. fac -\(\{\text{OsCl}(S\_2\text{CNMe}_2)(\text{PMe}_2\text{Ph})_3\}\) (5)]. The other two doublets (which decouple at the same phosphorus frequency) are from the inequivalent methyl groups of the S\(_2\)PMe\(_2\) ligand.

![Diagram](II)

If (II) is dissolved in methanol, a red conducting solution is obtained and addition of NaBPh\(_4\) gives red crystals analysing for \([\text{Ru}(S\_2\text{PMe}_2)(\text{PMe}_2\text{Ph})_3]B\text{Ph}_4\) (III). A band at 580 cm\(^{-1}\) in the infrared spectrum of (III) suggests bidentate coordination of the S\(_2\)PMe\(_2\) group (7) and conductivity studies in dichloromethane indicate a 1:1 electrolyte. The 31P-(\(^1\)H) nmr spectrum of (III) at 213K in CDCl\(_3\) consists of a doublet at 32.4 ppm (PMe\(_2\)Ph) and a quartet at 110.3 ppm (S\(_2\)PMe\(_2\)) \[J(PP') \approx 3.6\text{Hz}\]. The \(^1\)H nmr spectrum at 213K in CDCl\(_3\) also indicates that rapid intramolecular scrambling of the PMe\(_2\)Ph groups is occurring since it consists of a 'pseudo-triplet' \(^*-\) at 1.37\(^\circ\) (PMe\(_2\)Ph) and a doublet at 1.82\(^\circ\) (S\(_2\)PMe\(_2\)). This information is consistent with a monomeric, five coordinate structure and a preliminary X-ray structural analysis (8) on the related \([\text{Ru}(S\_2\text{PPh}_2)(\text{PMe}_2\text{Ph})_3]B\text{Ph}_4\) complex indicates a square pyramidal structure (III).

![Diagram](III)

\(^*\) 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 \(|J(\text{PH}) + J(\text{PH'})|\) value (cf. cis-[Ru(S\(_2\text{PMe}_2)_2(\text{PMe}_2\text{Ph})_2]\) (1))
Prolonged reaction of \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) with \(\text{NaS}_2\text{PMe}_2\cdot 2\text{H}_2\text{O}\) gives the previously reported cis-\([\text{Ru}(\text{SMe}_2\text{Ph})_2(\text{PMe}_2\text{Ph})_2]\) \(1\).

Similar results to those above have been obtained for the reaction of \([\text{RuCl}_2(\text{P(OR)}\text{Ph})_2_3]\) \(\text{R}=\text{Me},\text{Et}\) with \(\text{NaS}_2\text{PR}_2\) \(\text{R}=\text{Me},\text{Ph}\), and a reaction sequence for the formation of complexes cis- \([\text{Ru}(\text{S-S})_2\text{L}_2]\) from \([\text{RuCl}_2\text{L}_3\text{or}_4]\) is outlined in the Scheme.

**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 \(^{31}\text{P}\) 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[(η-
arene)dichlororuthenium] and Bis[dichloro(η-pentamethylcyclopenta-
dienyl)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

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY
DALTON TRANSACTIONS

1978
In previous papers on dithioacid complexes of the rarer platinum metals ruthenium, rhodium, and osmium and on examination of the racemic [(C5H5)2Ru2(CO)6](PF6)2 and various rhodium(ii) tertiary phosphine, phosphinite, phosphonite, and phosphite complexes with dithiocarbamate ligands, and also with the reaction of [(RuCl2(diene))2] which gave the complexes cis-[Ru(diene)(SC2NMe2)] (diene = bicyclo[2.2.1]hept-2-5-diene or cyclo-octa-1,5-diene).

In this paper, we report the full results of reactions of the complexes [(Ru(η-arene)Cl2)] (1; arene = C6H6 or C5H5Me) and [(M(C6Me6)Cl2)] (2; M = Ru or Ir) complexes with some dithiocarbamate anions. Although several reactions of (1) with unidentate Lewis bases have been reported, this is only the second study involving ligands capable of bidentate co-ordination. Earlier reaction of (1) with Ph3PCH2PPh3 (dppe) gave [Ru(η-C6H5)Cl2(dppe)] with the dppe ligand bound in a unidentate fashion whereas with Ph3PCl(2-5-6)PPh3 (dpb) the dimeric [(Ru(η-C6H5)Cl2)(dpb)] with a bridging dpb group was formed. Similarly, with (2; M = Ru), Ph3P(2-5-6)PPh3 (dppe) gave [Ru(η-C6H5)Cl2(dppe)] and [(Ru(η-C6H5)Cl2)(dppe)] with excess 1 1 mol ratios of (2 : dppe) respectively. The complex [Ru(η-C6H5)Cl2(dppe)] then reacted readily with NaH[PF6] in ethanol to give [Ru(η-C6H5)Cl2(dppe)][PF6].

RESULTS AND DISCUSSION

Reaction of (1; arene = C6H6) in aqueous media with an excess of Na[SP2R2] (R = Me, OMe, or OEt) or NaH[SP2P2R2] 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 together with IH and 31P n.m.r. (Tables 1 and 2 respectively) and i.r. studies (see Experimental section) these solids are best formulated as mononuclear [Ru(η-C6H5)2(SP2R2)] (3) with one bi- and one unidentate [1]...
dentate [S₂PR₄]⁻ group. Thus, the positions of ν(PS₃) in the i.r. spectra of the methyl- and phenyl-substituted [S₂PR₄]⁻ complexes were diagnostic of the presence of both bi- and uni-dentate co-ordination (see refs. 13 and 14 respectively). Furthermore, the ¹H n.m.r. spectrum in CDCl₃ at 301 K of [Ru(γ-C₅H₅)(S₂PMe₃)₄] consisted of a singlet at δ 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**

Hydrogen-¹ n.m.r. data for various ruthenium(II) dithioacid complexes at 301 K

<table>
<thead>
<tr>
<th>Complex</th>
<th>Dithio-ligand</th>
<th>²H-Arene</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>2.10 (d) [12.0]</td>
<td>[S₂PR₄]</td>
<td>5.88 (s) [3]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>1.95 (d) [12.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>1.89 (d) [12.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>7.0—8.3 (m) [10]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>3.79 (d) [14.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>3.68 (d) [14.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>4.10 (m) [6], 6.26 (m) [6]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>2.14 (d) [12.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>1.95 (d) [12.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>6.9—8.3 (m) [20]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>7.2—8.2 (m) [5]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>2.02 (d) [12.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>1.32 (d) [12.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>1.05 (d) [12.0]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>7.2—8.2 (m) [25]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>7.2—8.2 (m) [25]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>6.0—7.6 (m) [36]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>7.2—8.2 (m) [10]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>7.2—8.2 (m) [25]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>7.2—8.2 (m) [25]</td>
<td></td>
<td>5.80 (s) [2]</td>
</tr>
</tbody>
</table>

s = Singlet, d = doublet, and m = multiplet.

* In CDCl₃ unless otherwise stated. ① J(¹H) (in Hz) values are given in parentheses. Numbers in square brackets indicate normalised integrated intensities. ② Methyl resonance of C₃H₆Me₃. ③ Pyridine resonance; others masked by phenyl resonances. ④ Intensity includes aromatic resonances from other ligands. ⑤ Methyl resonance of PMe₃. ⑥ In CDCl₃. ⑦ Methyl resonance of P(OMe)₃.

**Table 2**

Phosphorus-³¹ n.m.r. data (proton-noise decoupled) for various ruthenium(II) and rhodium(III) dithioacid complexes in CDCl₃

<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>[S₂PR₄]</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>303</td>
<td>108.6 (s), 62.6 (s)</td>
<td>24.6 (d) (16.5) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>308</td>
<td>85.0 (d) (16.5) ①</td>
<td>123.9 (d) (19.0) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>91.7 (s)</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>85.0 (d) (16.5) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
<tr>
<td>[Ru(γ-C₅H₅)(S₂PMe₃)₄]</td>
<td>298</td>
<td>95.7 (d) (19.0) ①</td>
<td>5.51 (s) ①</td>
</tr>
</tbody>
</table>

* Chemical shifts reported to high frequency of 85% H₃PO₄. ① On standing, an additional peak appears at 54.4 p.p.m. ([S₂PMe₃]⁻).

**P-(¹H) n.m.r. of [PF₃]⁻ ion: multiplet at ca. 144 p.p.m. ② J(¹H) 715 Hz. ③ J(FF) in Hz. ④ J(RhP) in Hz. ⑤ In chlorobenzene-⁴H₂-toluene. ⑥ Overlapping doublet of doublets. ⑦ Doublet of doublets. ⑧ J(RhP) in Hz.
\[ ^{31} \text{P n.m.r. spectra of the } [S_2\text{PMe}_2]^- \text{ and } [S_2\text{PPh}_2]^- \text{ complexes at } 303 \text{ K each showed two resonances consistent with structure (3).} \]

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

\[ \text{Table 3} \]

Hydrogen-1 n.m.r. data for various rhodium(III) and iridium(III) dithioacid complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>( T/K )</th>
<th>Dithio-ligand</th>
<th>( \tau_{CMe_2} )</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}(\tau-CMe_2)(S_2\text{PMe}_2)]_2 )</td>
<td>343</td>
<td>( 0.69(\text{d}) ) [3]</td>
<td>( 1.69 ) (s) [6]</td>
<td>( 0.70—7.5 \text{ m} [35] )</td>
</tr>
<tr>
<td>301</td>
<td>( 1.8(\text{d}) ) [4]</td>
<td>( 1.54 ) (s) [16]</td>
<td>7.0—7.5 (m) [35]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-CMe_2)(S_2\text{PPh}_2)]_2 )</td>
<td>301</td>
<td>( 0.70(\text{d}) ) [4]</td>
<td>( 1.69 ) (s) [6]</td>
<td>( 0.70—7.5 \text{ m} [35] )</td>
</tr>
<tr>
<td>301</td>
<td>( 2.04(\text{d}) ) [4]</td>
<td>( 1.54 ) (s) [16]</td>
<td>7.0—7.5 (m) [35]</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}(\tau-CMe_2)(PMe_2\text{Ph})(S_2\text{CNMe}_2)]_2 )</td>
<td>301</td>
<td>( 0.69(\text{d}) ) [3]</td>
<td>( 1.69 ) (s) [6]</td>
<td>( 0.70—7.5 \text{ m} [35] )</td>
</tr>
<tr>
<td>301</td>
<td>( 2.04(\text{d}) ) [4]</td>
<td>( 1.54 ) (s) [16]</td>
<td>7.0—7.5 (m) [35]</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{unii- and bi-dentate } [S_2\text{PR}_2]^- \text{ groups was observed} \]

(cf.12 [Pt(PR\text{2})_2(S_2\text{PR}_2)\text{]. However, on leaving as a solid in air (for R = Me) or in solution (all R) for several days some decomposition occurred as indicated by the appearance of free benzene in the \(^1\text{H} \text{n.m.r. spectra and of} \ [S_2\text{PR}_2]^- \text{ ion in the} \ ^{31}\text{P n.m.r. spectra. Decom-} \]

complexes \([\text{Ru}(\tau-C_6\text{H}_5)(S-S)]_2 \text{ (S-S} = [S_2\text{COR}]^- \text{ or} \ [S_2\text{CNR}_2]^- \text{)} \) 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(S₂CNMe₂)₂]₃, [Ru₂(S₂CNMe₂)Cl]₁₅ etc. were formed.

In an attempt to retain the arene ring, the methyl-substituted arene dimer [(Ru(γ-C₆H₅Me)₂)Cl]₂ was treated with Na[S₂CNMe₂] and K[S₂COR] but again ring displacement accompanied chloride-ion substitution in each case. However, with the less nucleophilic [S₂PR₂]⁻ (R = Me or Ph), [Ru(γ-C₆H₅Me)](S₂PR₂)₂] were isolated and characterised as above (Tables 1 and 2). For R = Me, the complex is more stable than [Ru(γ-C₆H₅)₂-(S₂PMe₂)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 γ-bonded benzene ruthenium(II)–sulphur complexes, it was decided to investigate the reactions of the isoelectronic [(Rh(γ-C₆H₅Me)₂)Cl]₂ (2) with these ligands because earlier studies had indicated the inertness of the Rh-C₆Me₅ bond towards a range of nucleophiles. Thus (2) was dissolved in either water or methyl cyanide and treated with an excess of [S-S]⁻ ion ([S-S]⁻ = [S₂PMé₂]⁻, [S₂PPh₂]⁻, [S₂CNMe₂]⁻, [S₂CNEt₂]⁻, [S₂COMe]⁻, or [S₂COEt]⁻) to give either orange-red solutions which could be extracted with diethyl 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 [Rh(γ-C₆Me₅)(S₂PMé₂)₂] in CDCl₃ consisted of a singlet at δ 1.71 p.p.m. (from the C₆Me₅ ring) and a rather complicated multiplet between 1.8 and 2.3 p.p.m. On cooling, this multiplet was resolved into three

\[
\begin{array}{c}
\text{(4a)} \quad R = \text{Me or Ph} \\
\text{(4b)} \quad R = \text{Me or Et} \\
\text{(4c)}
\end{array}
\]

\[\text{[Rh(γ-C₆Me₅)(S-S)₂] (4)}\] containing one bi- and one uni-dentate [S-S]⁻ group. As expected, these complexes were much more stable thermally than the isoelectronic [Ru(arene)(S₂PR₂)₂] and showed little sign of decomposition on leaving in solution for prolonged periods.

Thus, at ambient temperature, the ¹H n.m.r. spectrum of [Rh(γ-C₆Me₅)(S₂PMé₂)₂] in CDCl₃ consists of a singlet at δ 1.71 p.p.m. (from the C₆Me₅ ring) and a rather complicated multiplet between 1.8 and 2.3 p.p.m. On cooling, this multiplet was resolved into three.

**Table 4**

Carbon-13 n.m.r. spectrum (proton-noise decoupled) for [Rh(γ-C₆Me₅)(S₂CNMe₂)₂] in CDCl₃ at 318 K

<table>
<thead>
<tr>
<th>δ ¹³C p.p.m.</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>220.7 (d)</td>
<td>[J(CH) 120.5 Hz] S₂CNMe₂ (bidentate)</td>
</tr>
<tr>
<td>209.0 (s)</td>
<td>S₂CNMe₂ (unidentate)</td>
</tr>
<tr>
<td>96.0 (d)</td>
<td>[J(CH) 7.3 Hz] C₂Me</td>
</tr>
<tr>
<td>46.8 (s)</td>
<td>S₂CNMe₂ (unidentate)</td>
</tr>
<tr>
<td>38.4 (s)</td>
<td>S₂CNMe₂ (bidentate)</td>
</tr>
<tr>
<td>9.3 (s)</td>
<td>C₂Me</td>
</tr>
</tbody>
</table>

* A small amount of tris(pentane-2,4-dionato)chromium was added.

Chemical shifts to high frequency of SiMe₃. Assigned to bi-rather than uni-dentate [S₂CNEt₂]⁻ because of larger [J(CH)] (see text), and also [Rh(γ-C₆Me₅)(NCBPPh₂)₂-(S₂CNMe₂)] with bidentate [S₂CNMe₂]⁻ resonance at 206.2 p.p.m. [J(CH)] 4.0 Hz. * cf. [Rh(γ-C₆Me₅)(NCBPPh₂)₂-(S₂CNMe₂)] with bidentate [S₂CNMe₂]⁻ resonance at 36.9 p.p.m.


doublets of relative intensity 2:1:1 at 2.11, 1.93, and 1.90 p.p.m. respectively [J(CH)] 12.5 Hz as expected for structure (4a; R = Me). On warming the solution, the doublets broadened and coalesced at 335 K giving a single doublet centred at 2.02 p.p.m. [J(CH)] 12.5 Hz (Table 3). This phenomenon, which is concentration independent and reversible with temperature, suggested that rapid intramolecular scrambling of dithioacid

\[\text{\footnotesize{15 See A. R. Hendrickson, J. M. Hope, and R. L. Martin, J.C.S. Dalton, 1976, 2032 and refs. therein for better methods of preparation of these complexes.}}\]
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 CDC\textsubscript{6} (because of their large separation (1 474 Hz) and the low boiling point of CDC\textsubscript{6}), use of chlorobenzene as solvent produced a single \textsuperscript{31}P n.m.r. resonance, indicative of fast uni- and bi-dentate \textsuperscript{[S\textsubscript{2}PMe\textsubscript{2}]} exchange at 405 K.

For \([\text{Rh}(\gamma\text{-C\textsubscript{6}Me\textsubscript{5}})(\text{S\textsubscript{2}CNMe\textsubscript{2}})\text{]}\), the \textsuperscript{1}H n.m.r. spectrum in CDC\textsubscript{6} at \(\leq 301\) K consisted of two singlets of equal intensity at \(\approx 3.58\) and 3.15 p.p.m. (from \([\text{S\textsubscript{2}CNMe\textsubscript{2}}]^{-}\)) in addition to the singlet at 1.73 p.p.m. from the \textsubscript{C\textsubscript{6}Me\textsubscript{5}} ring. Here the two methyl groups on the bidentate \textsuperscript{[S\textsubscript{2}PMe\textsubscript{2}]} group will be magnetically equivalent as shown in structure (4b; \(R = Me\)) assuming rapid rotation of the unidentate \textsuperscript{[S\textsubscript{2}CNMe\textsubscript{2}]} group about the Rh-S and/or C-S bonds. The \textsuperscript{13}C n.m.r. spectrum of this complex in CDC\textsubscript{6} at 318 K was also consistent with the proposed structure (4b) (see Table 4). Note that unequivocal assignment of the signals of the methyl groups arising from bi- and uni-dentate \textsuperscript{[S\textsubscript{2}CNMe\textsubscript{2}]} ligands in this spectrum was possible by comparison with the \textsuperscript{13}C n.m.r. spectrum of \([\text{Rh}(\gamma\text{-C\textsubscript{5}Me\textsubscript{5}})(\text{NCBPh\textsubscript{3}})\text{]}(\text{S\textsubscript{2}CNMe\textsubscript{2}})]\) (see later) which contained only a bidentate \textsuperscript{[S\textsubscript{2}CNMe\textsubscript{2}]} resonance at 36.9 p.p.m.

On increasing the temperature, broadening of the two methyl singlets in the \textsuperscript{1}H n.m.r. spectrum occurred followed by coalescence and the appearance of a singlet situated midway between the original signals (see Table 3). A full line-shape analysis on this data gave the rate constants and associated activation parameters for the kinetic process shown in equation (1) (Table 5). Similarly, the \textsuperscript{1}H n.m.r. spectrum of \([\text{Rh}(\gamma\text{-C\textsubscript{5}Me\textsubscript{5}})(\text{S\textsubscript{2}COEt})\text{]}\) in CDC\textsubscript{6} at 301 K consisted of two quartets (\(CH_{3}\)) and two triplets (\(CH_{2}\)) as expected for structure (4c; \(R = Et\)). At higher temperatures, coalescence and averaging of these signals was observed and the results of a line-shape analysis on the methylene resonances are given in Table 5. For \([\text{Rh}(\gamma\text{-C\textsubscript{5}Me\textsubscript{5}})(\text{S\textsubscript{2}COMe\textsubscript{2}})]\), although two methyl singlets were observed in the \textsuperscript{1}H n.m.r. spectrum at 301 K, decomposition occurred before coalescence of these signals was observed (<345 K).

\begin{table}[h]
\centering
\caption{Rates and activation parameters obtained by line-shape analysis for some rhodium(\textit{III}) and iridium(\textit{III}) dithioacid complexes in PhCl}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Complex & \(\ln(k_{\text{mel}}/s^{-1})\) & \(E^{\dagger}\) & \(\Delta H_{\text{act}}^{\ddagger}\) & \(\Delta S_{\text{act}}^{\ddagger}\) & \(\Delta G_{\text{act}}^{\ddagger}\) \\
\hline
\([\text{Rh}(\gamma\text{-C\textsubscript{5}Me\textsubscript{5}})(\text{S\textsubscript{2}CNMe\textsubscript{2}})]\) & -0.74 & 86.3 \pm 6 & 83.8 \pm 6 & 20.5 \pm 43 & 74.7 \pm 7 \textsuperscript{a} \\
\([\text{Rh}(\gamma\text{-C\textsubscript{5}Me\textsubscript{5}})(\text{S\textsubscript{2}COEt})\text{]}\) & -1.65 & 88.1 \pm 3 & 85.6 \pm 3 & 28.8 \pm 30 & 77.0 \pm 3 \textsuperscript{b} \\
\([\text{Ir}(\gamma\text{-C\textsubscript{5}Me\textsubscript{5}})(\text{S\textsubscript{2}CNMe\textsubscript{2}})]\) & -4.69 & 95.1 \pm 4 & 92.6 \pm 4 & 27.5 \pm 23 & 84.4 \pm 3 \textsuperscript{c} \\
\hline
\end{tabular}
\textsuperscript{a} \(\Delta G_{\text{act}}^{\ddagger} = 72.0 \pm 3 \text{ kJ mol}^{-1}\) \((T = 390 \text{ K})\). \textsuperscript{b} Obtained from monitoring methylene resonances. \textsuperscript{c} \(\Delta G_{\text{act}}^{\ddagger} = 75.2 \pm 3 \text{ kJ mol}^{-1}\) \((T = 361 \text{ K for methylene resonances})\). \textsuperscript{d} \(T > 402 \text{ K}\).
\end{table}

Interestingly, for \([\text{Rh}(\gamma\text{-C\textsubscript{5}Me\textsubscript{5}})(\text{S\textsubscript{2}CNMe\textsubscript{2}})]\), the \textsuperscript{1}H n.m.r. spectrum in CDC\textsubscript{6} at 253 K for the methylene region consisted of an overlapping doublet of quartets centred at \(\approx 3.47\) p.p.m. and a multiplet centred at 3.66 p.p.m. which was readily analysed as arising from an ABM\textsubscript{2} 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 8(AB) first decreased and then broadening occurred. In chlorobenzene, at \(>350\) K, coalescence of these resonances occurred to give a broad averaged resonance at 3.77 p.p.m.

This behaviour can be rationalised on the basis of a 'frozen-out' structure (4b; \(R = Et\)) in solution at lower temperature with the two protons of each CH\textsubscript{3} group in the bidentate \textsuperscript{[S\textsubscript{2}CNMe\textsubscript{2}]} ligand forming a diastereotopic pair, thus producing an ABM\textsubscript{2} spin system for these ethyl groups. Similar patterns have been observed elsewhere.\textsuperscript{16} The methylene protons of the unidentate \textsuperscript{[S\textsubscript{2}CNMe\textsubscript{2}]} ligands should also produce diastereotopic pairs and hence an ABM\textsubscript{3} spin system for the ethyl groups. However, in this instance, the difference in chemical environment was probably so slight because of ready rotation about the Rh-S and/or C-S bonds that the outer lines of the ABM\textsubscript{3} pattern were too weak to be observed. Increasing the temperature then led to both rapid rotation about the –CN bonds and uni- and bi-dentate exchange which produced equivalence of all the methylene protons on the n.m.r. time scale.

Although the error limits for the kinetic line-shape

\textsuperscript{16} See, for example, R. J. Cross, T. H. Green, and R. Keat, J.C.S. Dalton, 1976, 1150.
data given in Table 5 are rather large, especially for the $\Delta S^i$ values, comparisons with kinetic data obtained for the related $[\text{Pt}(S-S)L]$ complexes $^{13}$ are of interest. In the latter, the negative $\Delta S^i$ values and the dependence of rate on both dithioacid ligand and L group were interpreted in terms of an associative intramolecular mechanism. In this instance, the positive $\Delta S^i$ values indicate an essentially dissociative intramolecular process which is consistent with other kinetic studies on rhodium(III) complexes. $^{17}$

For completion, the analogous $[\text{Ir}((\eta-C_5\text{Me}_5))(S_2\text{CNMe}_2)_2]$ was synthesised from $[[\text{Ir}((\eta-C_5\text{Me}_5)\text{Cl})_2]$ $^{14}$ and an excess of Na$_2$S$_2$CNMe$_2$). A line-shape analysis performed on the $^3$H n.m.r. spectra of this complex gave the kinetic parameters shown in Table 5. Again, an essentially dissociatively controlled, intramolecular, exchange process was suggested (positive $\Delta S^i$ value) and the considerably larger $\Delta G^i + T_\text{c}$ 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 $\Delta G^i+T_\text{c}$ and $\Delta G^i$ ($T_\text{c} =$ coalescence temperature) for these complexes provided a good internal check on the validity of this line-shape data.

![Diagram](image)

(5) $S-S^2 = [S_2\text{CNMe}_2]^-$, [S$_2$PMe$_2]^-$, or [S$_2$PPh$_2]^-$

If (2: $M = \text{Rh}$) was treated with either Na$_2$S$_2$PMe$_2$-2H$_2$O, Na$_2$S$_2$PPh$_2$-2H$_2$O, or NaH$_4$S$_2$PPh$_2$ in a 1:2 mol ratio, then the monomeric complexes $[\text{Rh}((\eta-C_5\text{Me}_5)\text{Cl}(S-S))$ (5) were formed. Similarly, reaction of (1: arene $= C_6\text{H}_6$) with Na$_2$S$_2$PPh$_2$ (1:2 mol ratio) in methanol gave $[\text{Ru}((\eta-C_5\text{Me}_5)\text{Cl}(S_2\text{PPh}_2))]$, although with Na$_2$S$_2$PMe$_2$-2H$_2$O only $[\text{Ru}((\eta-C_5\text{Me}_5)(S_2\text{PMe}_2))]$ could be isolated. Attempts to make $[\text{Rh}((\eta-C_5\text{Me}_5)\text{Cl}(S_2\text{COR}))$ were also unsuccessful due to the formation of inseparable mixtures whose i.r. spectra indicated the formation of some dithiocarbamate $[S_2\text{CO}]^-$ as well as alkyl dithiocarbonate complexes.

The above complexes have been fully characterised by analytical data, i.r. $[\nu(\text{PS}_2)$ and $\nu(\text{CN})$ positions], and $^1$H and $^{31}$P n.m.r. studies (Tables 2-4). For example, the $^{31}$P n.m.r. spectrum of $[\text{Rh}((\eta-C_5\text{Me}_5)\text{Cl}(S_2\text{PMe}_2))]$ in C$_2$D$_2$ at 298 K contained a doublet at $87.6$ p.p.m. $[^3J(\text{RhP}) 10.8$ Hz] (cf. $[\text{Rh}((\eta-C_5\text{Me}_5)\text{Cl}(S_2\text{PMe}_2))]$ whose $^{31}$P n.m.r. spectrum at 233 K had two doublets at $99.9$ $[^3J(\text{RhP}) 10.1$] and $57.5$ p.p.m. $[^3J(\text{RhP}) 3.6$ Hz]). This clearly showed that the higher-frequency resonances were due to bidentate $[S_2\text{PMe}_2]^-$ groups and that these could also be differentiated from unidentate $[S_2\text{PMe}_2]^-$ groups by virtue of their larger $^2J(\text{RhP})$ coupling constants. Similarly, for $[\text{Pt}(\text{PM}_{2}\text{PH}_2)]$, it was found that at 218 K the $^{31}$P n.m.r. signal of the bidentate $[\text{SP}_{2}\text{PH}_2]$ group was a triplet at $87.8$ p.p.m. $[^3J(\text{PtP}) 276.8$ Hz] and the unidentate $[\text{SP}_{2}\text{PH}_2]$ group gave a triplet at $57.1$ p.p.m. $[^3J(\text{PtP}) 105.3$ Hz]. Further examples include $[\text{Ru}((\eta-C_5\text{H}_8)\text{Cl}(S_2\text{PPh}_2))$ $^{31}$P n.m.r. at 298 K showed a singlet at 91.7 p.p.m. compared to $[\text{Ru}((\eta-C_5\text{H}_8)(S_2\text{PPh}_2))]$ (singlets at 85.9 and 68.9 p.p.m.) and $[\text{Pt}(\text{P}_{2}\text{Ph}_2)]$ $^{31}$P n.m.r. spectrum had a triplet at 92.1 p.p.m. $[^3J(\text{PtP}) 254.7$ Hz] from the bidentate $[\text{SP}_{2}\text{PH}_2]$-group. Thus, $^{31}$P n.m.r. chemical shifts and coupling constants (where appropriate) in these $[S_2\text{PR}_2]$ complexes are, like $\nu(\text{PS}_2)$ values, $^{13,14}$ diagnostic of the type(s) of co-ordination present.

The complexes $[\text{Rh}((\eta-C_5\text{Me}_5)\text{Cl}(S-S))$ (5) were useful starting materials for synthesising a variety of complexes. Thus, reaction of (6: $S-S^2 = [S_2\text{CNMe}_2]^-$) in methanol with an excess of either LiBr, NaI, or K(SCN) led to replacement of the chloride group to give $[\text{Rh}((\eta-C_5\text{Me}_5)\text{X}(S_2\text{CNMe}_2))]$ $[X = \text{Br}^-, \text{I}^-, \text{or SCN}^-]$, whereas reaction with Na$_2$S$_2$PMe$_2$-2H$_2$O (1:1 mol ratio) in methyl cyanide gave the mixed dithiocacid complex $[\text{Rh}((\eta-C_5\text{Me}_5)(S_2\text{CNMe}_2)(S_2\text{PMe}_2))]$ (6). The i.r. spectrum of this complex had bands at 1524 and 600 cm$^{-1}$ indicative of bidentate $[S_2\text{CNMe}_2]^-$ (ref. 19) and unidentate $[S_2\text{PMe}_2]$-co-ordination $^{13}$ like the analogous $[\text{Pt}(\text{PR}_3)(\text{S}_{2}\text{CNMe}_2)(\text{S}_{2}\text{PMe}_2)]$ (PR$_3$ = PMe$_2$) $^{18}$ or PPh$_3$ $^{20}$. $^3$H n.m.r. studies showed that (6) was stereochemically rigid at elevated temperatures, a fact attributed to the low nucelophility of $[S_2\text{PMe}_2]$- compared to $[S_2\text{CNMe}_2]^-$ similarly. Reaction of (5: $S-S^2 = [S_2\text{CNMe}_2]^-$) with Na$_4$S$_2$PPh$_2$ and

K[S$_2$COMe] (1:1 mol ratio) gave $[\text{Rh}((\eta-C_5\text{Me}_5)(S_2\text{CNMe}_2)(S_2\text{PPh}_2))]$ and $[\text{Rh}((\eta-C_5\text{Me}_5)(S_2\text{CNMe}_2)(S_2\text{COMe})]$ respectively. Again, i.r. studies on $[\text{Rh}((\eta-C_5\text{Me}_5)(S_2\text{CNMe}_2)(S_2\text{PPh}_2))]$ clearly indicated unidentate $[S_2\text{PPh}_2]$- $\nu(\text{PS}_2)$ at 646 and 535 cm$^{-1}$ $^{14}$ and bidentate $[S_2\text{CNMe}_2]^-$ $\nu(\text{CN})$ at 1520 cm$^{-1}$ $^{19}$ co-ordination. For $[\text{Rh}((\eta-C_5\text{Me}_5)(S_2\text{CNMe}_2)(S_2\text{COMe})]$ 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(η-C₅Me₃)Cl(S₂CNMe₂)] (3.20) and [Rh(η-C₅Me₃)- (S₂CNMe₂)(S₂PMe₃)] (3.21 p.p.m.), also supported bidentate [S₂CNMe₂]²⁻ co-ordination.

If [Rh(η-C₅Me₃)(S₂CNMe₂)] was dissolved in methanol a conducting solution was obtained and addition of Na[BPh₄] precipitated solvated [Rh(η-C₅Me₃)(HOMe)-(S₂CNMe₂)][BPh₄]. The latter was then used as a precursor for synthesising a range of cationic complexes of the type [Rh(η-C₅Me₃)(S₂CNMe₂)L][BPh₄] (L = PPh₃, PMePh₂, CO, AsPh₃, or C₆H₅N). Similarly, reaction of [Rh(η-C₅Me₃)Cl(S₂PPh₂)] and [Ru(η-C₅H₅)(S₂PPh₂)] in alcoholic media with excess of L followed by addition of [NH₄][PF₆] gave the analogous [Rh(η-C₅Me₃)(S₂PPh₂)L][PF₆] (L = PPh₃, PMePh₂ or P(OMe)₃, SbPh₃, or C₆H₅N) respectively. Alternatively, this type of complex could be prepared by shaking either [Ru(arene)-Cl₂(arene)] (arene = C₅H₅ or C₆H₅Me)¹¹, Na[S₂PMe₃]-2H₂O (or [NH₄][S₂PPh₂]) (1 : 1 mol ratio), and excess of Na[BPh₄] in ethanol to give [Rh(η-C₅Me₃)(PPh₃)(S₂CNMe₂)][BPh₄].

All these complexes, which are 1 : 1 electrolytes in methylene chloride, have been fully characterised by elemental analyses, and i.r. (which showed bidentate dithioacid 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(η-C₅Me₃)(PPh₃)] in CDCl₃ at 298 K consisted of an overlapping doublet of doublets at 8 103.3 p.p.m. (bidentate [S₂PMe₃]⁻ resonance) due to the fortuitously similar values of ¹J(RhP) 9.2 and ³J(PP) 9.7 Hz, and a doublet of doublets at 35.9 p.p.m. (PPh₃) with ¹J(RhP) 144.8 and ³J(PP) 9.7 Hz.

Attempts to make related cationic complexes by reaction of [5; S-S⁻ = [S₂CNMe₂]⁻], a large anion, and potentially bidentate ligands such as 2,2'-bipyridyl, 1,10-phenanthroline, and cyclo-oct-1,5-diene were unsuccessful. However, treatment of [5; S-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 dimeric [[[(Rh(η-C₅Me₃)(S₂CNMe₂))₂(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,¹² 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 C₅Me₃ groups. Furthermore, the small doublet splitting of 3.0 Hz of the latter resonance, arising from coupling of a phosphorus ligand to the C₅Me₃ 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(η-C₅Me₃)(S₂PPh₂)]₂(dppe)]). Likewise (5; S-S⁻ = [S₂CNMe₂]⁻) reacted with excess of dppe and Na[BPh₄] in methanol to give [[Rh(η-C₅Me₃)(S₂CNMe₂)]₂(dppe)] and [Rh(η-C₅Me₃)(S₂PMe₂)] dppe, and Na[BPh₄] gave [[Rh(η-C₅Me₃)(S₂PPh₂)]₂(dppe)][BPh₄].

In view of the above studies, a surprising reaction occurred when (5; S-S⁻ = [S₂PMe₃]⁻, [S₂PPh₂]⁻, or [S₂CNMe₂]⁻) were treated with C₅(CN)₄ in methanol, cyanotriphenylborate anion was based on spectroscopic data. Thus, the i.r. spectra of all complexes (8) contained a CN stretching band at ca. 2180 cm⁻¹, indicative of cyanide rather than isocyanide co-ordination of the [BPh₄(CN)]⁻ group and all showed bands characteristic of bidentate co-ordination of the dithioacid ligands. The mass spectrum of (8; S-S⁻ = [S₂CNMe₂]⁻) had a peak at 381 m/z, corresponding to the empirical formula [Rh(η-C₅Me₃)(S₂CNMe₂)]₂.

peak at m/e 626 corresponding to [Rh(=C\textsubscript{Ph})\textsubscript{2}N\textsubscript{Me\textsubscript{2}}]\textsuperscript{+} together with a fragmentation pattern consistent with this formulation. Furthermore, the \textsuperscript{1}H n.m.r. spectrum of (8; S=S' = [S\textsubscript{2}PMe\textsubscript{2}]\textsuperscript{2-}) in CDCl\textsubscript{3} at 303 K had the expected three signals at 1.79 (s) (CMe\textsubscript{3}), 3.17 (s) ([S\textsubscript{2}CMe\textsubscript{3}]\textsuperscript{2-}), and 7.0-7.5 (m) p.p.m. ([PhBCN]) of relative intensity 5: 2: 5.

However, unequivocal proof of the solid-state structure of (8; S=S' = [S\textsubscript{2}PMe\textsubscript{2}]\textsuperscript{2-}) came from a preliminary X-ray structural analysis\textsuperscript{22} 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\textsubscript{Ph})\textsubscript{2}N\textsubscript{Me\textsubscript{2}}] (M = Fe or Ru),\textsuperscript{23} [Ru(=C\textsubscript{Ph})\textsubscript{2}NC\textsubscript{Ph} \textsubscript{3}N\textsubscript{Me\textsubscript{2}}] \textsubscript{2+} and [Cu(NC\textsubscript{Ph} \textsubscript{3}N\textsubscript{Me\textsubscript{2}})\textsubscript{2}CH\textsubscript{2}Cl\textsubscript{2}] and all these were prepared by means of direct reaction with Na[BPh\textsubscript{4}(CN)].\textsuperscript{24} Here, the [BPh\textsubscript{4}(CN)]\textsuperscript{-} anion was generated in situ, possibly by reaction of hydrogen cyanide with [BPh\textsubscript{4}]\textsuperscript{+}, since earlier studies on C\textsubscript{2}CN\textsubscript{4} have shown that HCN was readily released on its reaction with alkoxide ions in the presence of certain catalysts.\textsuperscript{25}

However, it should be noted that this rather unusual reaction is not confined to rhodium. Thus, reaction of [Ru(=C\textsubscript{Ph})\textsubscript{2}Cl(f expose complexes to co operation with Na[BPh\textsubscript{4}(CN)].\textsuperscript{26} For details, see M. C. Cornock, D. R. Robertson, T. A. Stephenson, C. L. Jones, G. H. W. Milburn, and L. Sawyer, J. Organometallic Chem., 1977, 135, C50.

Ruthenium Complexes.—(\textsuperscript{-}Benzene)bis(dimethylphosphinothiolato)ruthenium(\textit{ii}). The complex \{[Ru(=C\textsubscript{Ph})\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{2+} (0.20 g, 0.4 mmol) was dissolved in water with gentle warming. Excess of Na[S\textsubscript{2}PMe\textsubscript{2}]\textsubscript{2}H\textsubscript{2}O (0.55 g, 3 mmol) was then added to the orange solution, producing an immediate colour change to deep red. Extraction with diethyl ether, followed by separation and drying over anhydrous sodium sulphate gave a red other solution. Concentration of this solution gave a dark red crystalline precipitate, m.p. 140 °C (decomp.), v(PS\textsubscript{2}) at 608(0) and 584(b) cm\textsuperscript{-1}. (\textsuperscript{-}Benzene)bis(OO'\textsuperscript{-}diethyl dithiophosphate)ruthenium(\textit{ii}) was similarly prepared as a dark red crystalline solid, m.p. 110 °C (decomp.), from [Ru(=C\textsubscript{Ph})\textsubscript{2}Cl\textsubscript{2}] and Na[S\textsubscript{2}P(O)Me\textsubscript{2}].

An additional preparation gave an oil on concentration of the

\[\Delta G_{\text{T}} = 19.06 T_{\text{c}}(10.319 + \log T_{\text{c}})^2 \]

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-

\[\Delta G_{\text{T}} = \frac{R T_{\text{c}}}{\lambda_{\text{T}}} = \text{rate constant at temperature } T_{\text{c}} (= \pi \lambda_{\text{T}}^2) \text{ where } \pi_{\text{T}} = \text{separation of peaks in the absence of exchange.}

Analytical, molecular weight, and conductivity data are given in Supplementary Publication No. SUP 22220, and \textsuperscript{1}H n.m.r. data for ruthenium, and selected rhodium and iridium complexes in Tables 1 and 3,\textsuperscript{13} and \textsuperscript{12} H n.m.r. data in Table 2. Infrared bands diagnostic of the mode of coordination of [S\textsubscript{2}PMe\textsubscript{2}]\textsuperscript{2-} (ref. 13) and [S\textsubscript{2}PMe\textsubscript{2}]\textsuperscript{2-} ligands\textsuperscript{14} are listed for the various complexes (b = bidentate, u = unbidentate, i = ionic). Finally, all the reactions under reflux were carried out in degassed solvents under an atmosphere of nitrogen.
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.).

6. Benzene)bis(diphenylphosphinodithioato)ruthenium(II).
The product from reaction of [(Ru(η-C5H5)Cl2)]11 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. 175 °C, v(PS2) at 643 and 548 (u) and 610 and 575 (b) cm−1.

Bis(dimethylphosphinodithioato)(η-methylene) ruthenium(II), red, m.p. 145 °C (decomp.), v(PS2) at 601 (u) and 585 (b) cm−1, and bis(diphenylphosphinodithioato)(η-methylene)- ruthenium(II), orange-red, m.p. 186 °C, v(PS2) at 647 and 541 (u), and 604 and 580 (b) cm−1, were prepared as above using [(Ru(η-C5H5)Cl2)]11 and an excess of Na[S2PMe2].

6. Benzene)chloro(diphenylphosphinodithioato)ruthenium(II). The complex [(Ru(η-C5H5)Cl2)]11 (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(PS2) at 608 and 587 (b) cm−1.

6. Benzene)dimethylphosphinodithioato)pyridinoruthenium(II) tetracyanoborate. The complex [(Ru(η-C5H5)Cl2)(NC3H5)]11 (0.066 g, 0.2 mmol), Na[S2PPh2] (0.07 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 cm3. 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(PS2) at 652 (b) cm−1.

Similarly prepared were (diphenylphosphinodithioato)- (η-mesitylene)pyridinoruthenium(II) tetracyanoborate from [Ru(η-C5H5)Me2Cl2(NC3H5)]11 [NH4][S2PPh2] and Na[BPh4] as a yellow solid, m.p. 199 °C (decomp.), v(PS2) at 604 and 580 (b) cm−1 and (diphenylphosphinodithioato)(η-mesitylene)- pyridinoruthenium(II) tetracyanoborate, v(PS2) at 652 (b) cm−1, from [Ru(η-C5H5)Me2Cl2(NC3H5)]11, Na[S2PMe2]2H2O, and Na[BPh4].

6. Benzene)dimethylphosphinodithioato)(triptychophosphate)ruthenium(II) hexafluorophosphate. The complex [Ru(η-C5H5)Cl(S2PPh2)][PF6] (0.09 g, 0.2 mmol) was shaken in ethanol with excess of triphenylphosphate (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(PS2) at 605 and 580 (b) cm−1. The following yellow solutions were prepared similarly: [Ru(η-C5H5)- (PMethyl)][(S2PPh2)][PF6], m.p. 129 °C, v(PS2) at 602 and 580 (b) cm−1; [Ru(η-C5H5)(POMe3)][S2PPh2][PF6], m.p. 190 °C, v(PS2) at 603 and 580 (b) cm−1; [Ru(η-C5H5)(S2PPh2)(SPh3)][PF6], m.p. 211 °C, v(PS2) at 600 and 577 (b) cm−1; and [Ru(η-C5H5)(NHC6H5)][S2PPh2][PF6], m.p. 202 °C, v(PS2) at 605 and 580 (b) cm−1.

6. Benzene)cyano(triphenylborato)(diphenylphosphinodithioato)ruthenium(II). The complex [Ru(η-C5H5)Cl (S2PPh2)] (0.09 g, 0.2 mmol) dissolved in methanol on addition of tetracyanomethane (0.13 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(PS2) at 602 and 580 (b) cm−1.

Rhodium Complexes.—Bis(dimethylphosphinodithioato)(η-pentamethylcyclopentadieny) rhodium(III). The complex [(Rh(η-C5Me5)Cl2)]11 (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(PS2) at 600 (u) and 588 (b) cm−1. Bis(diphenylphosphinodithioato)(η-pentamethylcyclopentadieny) rhodium(III), m.p. 214 °C, v(PS2) at 648 and 539 (u), and 603 and 575 (b) cm−1, was similarly prepared from [(Rh(η-C5Me5)Cl2)]11 (0.12 g) and [NH4][S2PPh2] (0.42 g).

Bis(dimethylthio carbamato)(η-pentamethylcyclopentadieny) rhodium(III). The complex [(Rh(η-C5Me5)Cl2)]11 (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(diethyl dicarboxamato)(η-pentamethylcyclopentadieny) rhodium(III), m.p. 223 °C, was similarly prepared from [(Rh(η-C5Me5)- Cl2)]11 (0.12 g) and Na[S2CNMe2]2H2O (0.33 g).

Rhodium Complexes.—Bis(dimethylphosphinodithioato)(η-pentamethylcyclopentadieny) rhodium(III). The complex [(Rh(η-C5Me5)Cl2)]11 (0.12 g, 0.2 mmol) was dissolved in water (20 cm3). Addition of excess of K[S2CNMe2] (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 acetone—water. Bis(O-ethyl dithiocarbamato)(η-pentamethylcyclopentadieny)rhodium(III), m.p. 120 °C, was similarly prepared from [(Rh(η-C5Me5)Cl2)]11 (0.12 g) and excess of K[SCOEt] (0.26 g).

Chloro(dimethylthiocarbamato)(η-pentamethylcyclopentadieny) rhodium(III). The complex [(Rh(η-C5Me5)Cl2)]11 (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(RhCl) at 270 cm−1. Chloro(dimethylphosphinodithioato)(η-pentamethylcyclopentadieny)rhodium(III), v(PS2) at 588 (b) cm−1 and v(RhCl) at 283 (cm−1), and chloro(dimethylphosphinodithioato)(η-pentamethylcyclopentadieny)rhodium(III), m.p. 247 °C, v(PS2) at 603 and 574 (b) cm−1, v(RhCl) 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(dimethylthiocarbamato)(η-pentamethylcyclopentadieny) rhodium(III). The complex [(Rh(η-C5Me5)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 [(Rh(η-C5Me5)Cl(S2CNMe2)]2, m.p. 247 °C, and [(Rh(η-C5Me5)- (SCN)][S2CNMe2], m.p. 161 °C, v(CN) at 2065 cm−1, were similarly prepared from [(Rh(η-C5Me5)Cl(S2CNMe2)] and NaI or K[SCN] respectively.
(Dimethylthiocarbamato)(dimeylphosphino)dithiocarboxylato)(\(\eta\)-pentamethylcyclopentadienyl)rhodium(III). The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) (0.13 g, 0.4 mmol) and Na\(\text{[PMePh}_3]\) \(2\text{H}_2\text{O}\) (0.074 g, 0.4 mmol) (1:1 mol ratio) were stirred in methylv cyanide for 3 h. The solution was filtered to remove NaCl, concentrated to dryness, and the residue recrystallized from methylene chloride-pentane, m.p. 157 °C, v(\(\text{PS}_2\)) at 600 (cm\(^{-1}\)). Similarly, \((\text{dimethylthiocarbamato})(\text{diphenylphosphino})\) dithiocarbamato)(\(\eta\)-pentamethylcyclopentadienyl)rhodium(III), m.p. 224 °C, v(\(\text{PS}_2\)) at 666 and 536 (cm\(^{-1}\)), and \((\text{dimethylthiocarbamato})(\text{O-methyl dihydrocarbonato})(\eta\)-pentamethylcyclopentadienyl)rhodium(III), m.p. 181 °C, were prepared from \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) and \([\text{NH}_4][\text{PPh}_3]\) or [K(\text{S,COME})] respectively.

\((\text{Dimethylthiocarbamato})(\text{methanol})(\eta\)-pentamethylcyclopentadienyl)rhodium(III) tetracyanoborate. The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) (0.10 g, 0.25 mmol) was dissolved in methanol (10 cm\(^3\)) and treated with tetracyanoethylene (0.13 g, 1.0 mmol). The resulting yellow solution was stirred for 3 h. After filtration off NaCl, the filtrate was concentrated to dryness and the residue extracted with ethyl ether, m.p. 205 °C. The analogous \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{PPh}_3)]\) (0.11 g, 0.2 mmol) was shaken in ethanolic solution of Na\(\text{[S,CNMe}_2]\) \(2\text{H}_2\text{O}\) (0.09 g, 0.5 mmol) and Na\(\text{[PPh}_3]\) (0.17 g, 0.5 mmol) for 24 h. The reacting orange solid was filtered off and washed thoroughly with warm water, ethanol, and diethyl ether, m.p. 205 °C. The analogous \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{PPh}_3)]\) (0.12 g, 0.2 mmol) was dissolved in methanol (10 cm\(^3\)) and excess of \(\text{PMePh}_3\) (0.13 g, 0.6 mmol) added. The solution became orange-yellow on gentle warming and addition of Na\(\text{[PPh}_3]\) gave an orange crystalline product on cooling. Similar methods were used to prepare the analogous \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{PPh}_3)]\) \(2\text{H}_2\text{O}\), \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{NCBPh}_3)]\), and \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{NCBPh}_3)]\) \(2\text{H}_2\text{O}\), m.p. 97 °C, and \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,COME})]\) \(2\text{H}_2\text{O}\). m.p. 192 °C.

Carbonyl(dimethylthiocarbamato)(\(\eta\)-pentamethylcyclopentadienyl)rhodium(ii) tetracyanoborate. The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) (0.10 g, 0.25 mmol) was dissolved in methanol (50 cm\(^3\)) and carbon monoxide bubbled through the solution for 4 h. Addition of Na\(\text{[PPh}_3]\) to the resulting yellow solution gave a crystalline yellow solid, m.p. 183 °C, v(\(\text{CO}\)) at 2.070 cm\(^{-1}\).

\((\text{Diphenylphosphino)dithiocarboxylato})(\text{methyldiphenylphosphino})(\eta\)-pentamethylcyclopentadienyl)rhodium(III) hexafluoroporphosphate. The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) (0.10 g, 0.2 mmol) was dissolved in methanol (15 cm\(^3\)). On addition of several drops of \(\text{PMePh}_3\), the solution became yellow and addition of excess of \(\text{NH}_3\) \(\text{[PF}_3]\) then gave an orange-yellow crystalline solid, v(\(\text{PS}_2\)) at 603 and 577(b) cm\(^{-1}\). \((\text{Diphenylphosphino)dithiocarboxylato})(\eta\)-pentamethylcyclopentadienyl)(triphenylphosphine)rhodium(III) hexafluoroporphosphate was similarly prepared, m.p. 214 °C, v(\(\text{PS}_2\)) at 608 and 572(b) cm\(^{-1}\).

\mu-\text{[1,2-Bis(diphenylphosphino)ethane]}-\text{bis(dimethylthiocarbamato)}(\eta\)-pentamethylcyclopentadienyl)rhodium(III) bis(tetracyanoborate). The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) (0.08 g) was dissolved in methanol. Addition of excess of \(\text{Ph}_3\text{PCH}_2\text{C}_6\text{H}_4\text{PPh}_3\) (0.15 g) accompanied by gentle warming gave a yellow solution from which a yellow solid was precipitated on addition of Na\(\text{[BPh}_4]\), m.p. 217 °C. The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) \(2\text{H}_2\text{O}\), m.p. 200 °C, was similarly prepared.

\(\mu\)-\text{[1,2-Bis(diphenylphosphino)ethane]}-\text{bis(dimethylphosphino)dithiocarboxylato})(\eta\)-pentamethylcyclopentadienyl)rhodium(III) bis(tetracyanoborate), v(\(\text{PS}_2\)) at 603 and 574(b) cm\(^{-1}\), was also prepared as above from \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) dppe, and Na\(\text{[BPh}_4]\).

\((\text{Dimethylphosphino)dithiocarboxylato})(\text{methylphosphino)diphosphino})(\eta\)-pentamethylcyclopentadienyl)rhodium(III) dimethylphosphino)dithiocarbamate. The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,CNMe}_2)]\) was dissolved in benzene and several drops of \(\text{PMePh}_3\) were added to give a yellow solution which, on standing, deposited a yellow crystalline solid, m.p. 226 °C, v(\(\text{PS}_2\)) at 610(i) and 575(b) cm\(^{-1}\).

\((\text{Cyano} \text{triphenylborato})(\text{dimethylthiocarbamato})(\text{methyldiphenylphosphino})(\text{triphenylphosphino})(\eta\)-pentamethylcyclopentadienyl)rhodium(III). The complex \([\text{Rh}(\eta-C_5\text{Me}_5)\text{Cl}(\text{S,PMe}_3)]\) \(2\text{H}_2\text{O}\), m.p. 197 °C. 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 \(\text{N}_{19}^\text{F}\) n.m.r. spectra, Mr. J. R. A. Millar for the \(\text{H}\) and \(\text{C}\) n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Mechrolab oscilomter.

[7/1180 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 Monothiobenzoates, and the Crystal and Molecular Structure of (4-Amino-2-imino-4-methylpentane)bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(n)

By Robert O. Gould,* T. Anthony Stephenson,* and Mary A. Thomson, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of [RuCl₂(PPh₃)₃] with an excess of Na[SO₂C₆H₄] or [NH₄][SO₂C₆H₄] in either acetone or methanol and mer-[RuCl₂(PMe₂Ph)₃] with Na[SO₂C₆H₄] in acetone gives six-co-ordinate [Ru(SO₂C₆H₄)₂(PR₃)₂] [PR₃ = PPh₃ (1) or PMe₂Ph (2)] shown by i.r. and ¹H and ³¹P 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 [Ru(SO₂C₆H₄)₂(PR₃)₂L₂] [PR₃ = PPh₃, L = CO or NH₃ (3a); PR₃ = PMe₂Ph, L = CO, NH₃, or NH₂Et (3b)] shown by spectroscopic methods to have trans-S-bonded [SO₂C₆H₄]⁻ groups with trans-PPh₃, trans-L (3a), and cis-PMe₂Ph, cis-L (3b) groups respectively. In contrast, reaction of mer-[RuCl₂(PMe₂Ph)₃] with excess of [NH₄]₂[SO₂C₆H₄] in acetone gives a nitrogen-containing product (4) shown by X-ray analysis to be [Ru(SO₂C₆H₄)₂{HNC(Me)CH₂CMe₂NH₂}(PMe₂Ph)₂]. The crystals are orthorhombic, space group Pna₂₁ with a = 23.899(2), b = 11.163(1), and c = 13.889(3) Å. 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 dithioacid ligands was reported to give the six-co-ordinate [Ru(S-S)₂(PR₃)₂] (S-S⁻ = [S₂PR₃]⁻ or [S₂CNCR₂]⁻). Detailed variable-temperature ¹H 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-[RuCl₆(PMe₂Ph)₃] and [RuCl₄(PPh₃)₂] with sodium and ammonium monothiobenzoates 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)₂] was heated under reflux with an excess of Na[SOCPH] or [NH₄][SOCPH] in either acetone or methanol solvent an orange-yellow non-conducting solid of composition [Ru(SOCPH)₄(PPh₃)₂]

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 monothio-benzoate ligand. Earlier, Savant et al.⁵ assigned these vibrations in Na[SOCPH] 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 monothio-benzoate 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 [SOCPH]⁻ 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} n.m.r. spectrum (singlet at 8 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 and amine region) consists of a single broad resonance at 8 1.42 p.p.m. and a much sharper singlet at 8 1.06 p.p.m. By comparison with earlier studies,²,⁶ these patterns are indicative of the presence of two isomers containing cis- and trans-PMe₂Ph groups respectively. Furthermore, phosphorus-³¹ n.m.r. 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 8 39.0 p.p.m. and a very weak signal at 4.6 p.p.m.

<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>Methyl of phosphine</th>
<th>Other ligand resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(SOCPH)₄(PMe₂Ph)₂]</td>
<td>300</td>
<td>1.42(pt), 1.57(t)</td>
<td>7.00—8.00(m) ²</td>
</tr>
<tr>
<td>[Ru(SOCPH)₄(NH₄)[PMe₂Ph]₂]</td>
<td>260</td>
<td>1.32(pt), 1.46(pt), 1.57(t)</td>
<td>7.00—8.00(m) ²</td>
</tr>
<tr>
<td>[Ru(SOCPH)₄(PMe₂Ph)(CO)₂]</td>
<td>300</td>
<td>1.75(pt)</td>
<td>7.00—8.00(m) ²</td>
</tr>
<tr>
<td>[Ru(SOCPH)₄(NH₄)[PMe₂Ph]₂]</td>
<td>250</td>
<td>1.60(pt)</td>
<td>7.00—8.00(m) ²</td>
</tr>
<tr>
<td>[Ru(SOCPH)₄(NH₄)[HNC(Me)CH₂CMe₂NH₄][PMe₂Ph]₂]</td>
<td>300</td>
<td>1.43(d), 1.86(d)</td>
<td>7.00—8.00(m) ²</td>
</tr>
<tr>
<td>250</td>
<td>1.63(d), 1.20(d)</td>
<td>1.06(s), 1.58(s), 2.31(s), 1.35(t)</td>
<td>8.98(br) ²</td>
</tr>
</tbody>
</table>

* 8 = Singlet, d = doublet, t = triplet, pt = pseudo-triplet, and m = multiplet. ² Phenyl resonances. ³ Overlapping doublet of doublets. ⁴ Gem-Methyl, imine-C-methyl, and methylene protons from HNC(Me)CH₂CMe₂NH₄ ligand. ⁵ NH₄ protons.

The reddish brown product [Ru(SOCPH)₄(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.

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 8 1.32 and 1.46 p.p.m. This behaviour, which is concentration-independent and

| Table 1 |
| Mull i.r. spectra of various monothio-benzoate complexes of ruthenium(II) |

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(CO) (cm⁻¹)</th>
<th>ν(CS) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na[SOCPH]</td>
<td>1500</td>
<td>960</td>
</tr>
<tr>
<td>[Ru(SOCPH)₄(PPh₃)]</td>
<td>1500</td>
<td>965</td>
</tr>
<tr>
<td>[Ru(SOCPH)₄(NH₄)(PPh₃)]</td>
<td>1550</td>
<td>935</td>
</tr>
<tr>
<td>[Ru(SOCPH)₂(PPh₃)]</td>
<td>1550</td>
<td>935</td>
</tr>
<tr>
<td>[Ru(SOCPH)₂(PMe₂Ph)]</td>
<td>1470</td>
<td>965</td>
</tr>
<tr>
<td>[Ru(SOCPH)₂(PMe₂Ph)₂]</td>
<td>1470</td>
<td>965</td>
</tr>
<tr>
<td>[Ru(SOCPH)₂(NH₂Et)₂]</td>
<td>1570</td>
<td>945</td>
</tr>
<tr>
<td>[Ru(SOCPH)₂(NM₂Ph)]</td>
<td>1570</td>
<td>945</td>
</tr>
<tr>
<td>[Ru(SOCPH)₂(HNC(Me)CH₂CMe₂NH₄)₂]</td>
<td>1325</td>
<td>935</td>
</tr>
</tbody>
</table>

† Low values of ν(CO) attributed to intramolecular hydrogen bonding between carbonyl groups and the amine group (see text).
reversible with temperature, is analogous to that observed earlier for $[M(S_{2}PMe_{4})_{2}](PMe_{2}Ph)_{2}$ (M = Ru$^{2+}$ or Os$^{7}$) and is likewise attributed to rapid interconversion on the n.m.r. time scale of two optical isomers of (2) [see equation (1)]. As expected for an isomer containing \( trans \)-PMe$_{2}$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 \([Ru(SOCPh)_{2}L_{2}(PR_{3})_{2}](L = CO; PR_{3} = PPh_{3}(3a)\) or PMe$_{2}$Ph (3b)]. The Nujol i.r. spectra of both of these complexes revealed that an increase in the \( \nu(CO) \) (SOCPh) and a decrease in the \( \nu(CS) \) band positions, compared to those of (1) and (2), had occurred (Table 1) indicative of unidentate co-ordination of the [SOCPh]$^{-}$ groups through sulphur in both cases. However, the i.r. spectrum of (3a) contained only a single terminal \( \nu(CO) \) absorption band at \( 1950 \) cm$^{-1}$ whereas those of (3b) had two \( \nu(CO) \) bands at \( 2025 \) and \( 2005 \) cm$^{-1}$ suggesting \( trans \) and \( cis \) carboxyl-group arrangements respectively.

The $^1H$ n.m.r. spectrum of (3b; \( L = CO \)) in CDCl$_{3}$ (methyl region) at \( 240-300 \) K exhibited a single 'pseudo-triplet' pattern at \( \delta 1.60 \) p.p.m. and the $^{31}P$-$^{1H}$ n.m.r. spectrum at \( 303 \) K contained a singlet at \( -10.8 \) p.p.m. This large change in $^{31}P$ n.m.r. chemical shift on going from (2) to (3b) suggests that substitution of the carbonyl groups occurs \( trans \) to the PMe$_{2}$Ph groups. Therefore, this n.m.r. and i.r. evidence indicates that complex (3b; \( L = CO \)) has a structure containing \( cis \)-carbonyls, \( cis \)-PMe$_{2}$Ph, and \( trans \)-S-bonded [SOCPh]$^{-}$ groups. This is consistent with the 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 $^{31}P$-$^{1H}$ n.m.r. spectrum of complex (3a; \( L = CO \)) consists of a singlet at \( \delta 42.8 \) p.p.m. The relatively small change in $^{31}P$ n.m.r. chemical shifts on going from (1) to (3a) (\( L = CO \)) together with the i.r. data given above is consistent with a structure containing \( trans \)-carbonyls, \( trans \)-PPh$_{3}$, and \( trans \)-S-bonded [SOCPh]$^{-}$ groups. In support of this conclusion, the reaction of all-\( trans \)-[RuCl$_{4}$(CO)$_{2}$PPh$_{3}$]$_{2}$ and [NH$_{4}$][SOCPh] in acetone under reflux also gave a high yield of complex (3a; \( L = CO \)).

Therefore, this evidence strongly suggests that complex (1) has a structure with \( trans \)-PPh$_{3}$ groups (cf. the minor isomer of [Ru(SOCPh)$_{3}$(PMe$_{2}$Ph)$_{2}$]). Presumably, the larger size of the PPh$_{3}$ groups facilitating formation of trans rather than cis isomers, allied with the high \( trans \) effect of PMe$_{2}$Ph groups favouring a cis rather than a \( trans \) 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 [Ru(SOCPh)$_{3}$(NH$_{3}$)$_{2}$(PPh$_{3}$)$_{2}$]. Again, i.r. studies indicate the presence of unidentate S-bonded [SOCPh]$^{-}$ groups (Table 1) and the $^{31}P$-$^{1H}$ n.m.r. spectrum shows a singlet at $\delta 46.3$ p.p.m. consistent with structure (3a; \( L = NH_{3} \)). In contrast, reaction of complex (2) with ammonia yields a product \textit{in situ} whose $^1H$ n.m.r. spectrum in CDCl$_{3}$ exhibits a 'pseudo-triplet' at $\delta 1.75$ p.p.m. and whose $^{31}P$-$^{1H}$ 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 NH$_{2}$Et, complex (2) gave the yellow-brown solid [Ru(SOCPh)$_{3}$(NH$_{2}$Et)$_{2}$(PMe$_{2}$Ph)$_{2}$] whose $^1H$ and $^{31}P$ n.m.r. spectra were also consistent with structure (3b; \( L = NH_{2}Et \)). Thus, the low sensitivity of the $^{31}P$ n.m.r. resonance signals to a change in Lewis base for the PPh$_{3}$ compared to the PMe$_{2}$Ph complexes adds further support to the structural assignments made above.

Unlike the reactions of [RuCl$_{4}$(PPh$_{3}$)$_{2}$] with either [NH$_{4}$][SOCPh] or Na[SOCPh] in methanol or acetone which yielded the same product (1), the reaction of mer-[RuCl$_{3}$(PMe$_{2}$Ph)$_{2}$] with [NH$_{4}$][SOCPh] in acetone, either

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 v(CO) (1,530 cm⁻¹) and a decrease in that for
v(CS) (935 cm⁻¹), compared to the values for complex
(2), which again suggests the presence of unidentate
S-bonded [SOPh]⁻ groups. The mass spectrum of (4),
like that of (2), shows a strong peak at m/e 652 [¹⁰⁹Ru
isotope] corresponding to [Ru(SOPh)₃(PMe₂Ph)₂]⁺ and
the same fragmentation pattern for m/e values >100
which correspond to loss and subsequent breakdown of
[SOPh]⁻ 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(PP) 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
generally inequivalent methyl groups. The three
singlet resonances show no significant variation with
temperature. The ³¹P-¹H n.m.r. spectrum at 308 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 mag¬
netically 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 × 0.1 × 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).—C₃₅H₄₈N₂O₂P₃Ru₂, M = 765,
reddish brown prismatic crystals, a = 23.899(2), b =
11.163(1), c = 13.889(3) Å, U = 3,705 Å³, D₃ₐ = 1.34,
Z = 4, D = 1.37 g cm⁻³, F(000) = 1,502, space group
Pna₂₁ (no. 33), 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 h80→6. Cell dimensions were determined by the
a₁—a₂ splitting method applied to 23 zero-layer
reflections with θ ≥ 75°. All the films were scanned by
the S.R.C. Microdensitometer Service and, after merging,
2,249 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 co-
ordinates and an arbitrary z, is pseudo-centric, and some
difficulty was experienced in choosing suitable S and P
coodinates 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 = XY with X = (sin θ)/0.3 for sin θ < 0.3 and 1.0
otherwise, and Y = 35/[F₀] for |F₀| > 35 and 1.0 other¬
wise. Ruthenium, S, and P atoms were given aniso-
tropic 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 pa¬
rameters, and important interatomic distances and angles
deposited as Supplementary Publication No. SUP
22243 (13 pp.).

The structure. A view of the complex molecule is
given in the Figure. The complex shows only slight

![Figure A perspective view of (4)](image)

deviations from ideal octahedral angles about the
ruthenium atom. In the imino-amino-ligand the imine
C(32)—N(1) bond [1.333(26) Å] is a significant 0.15 Å
shorter than the amine C(31)—N(1) 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)CH₂CMe₂NH₂)₂][NO₃]₂, made
by reaction of Cu(NO₃)₂ and ammonia in acetone, X-ray
analysis showed C—NH 1.30, C—NH₂ 1.51, Cu—NH
1.98, and Cu—NH₂ 2.01 Å.

An interesting feature of the structure is the orienta¬
tion of the [SOPh]⁻ ligands, which brings the carbonyl
oxygens within hydrogen-bonding distances (2.870 and
2.851 Å) of the amine nitrogen. In one case this results
in the Ru atom being non-coplanar with the SOCPh
group: Ru—S(1)—C(9)—O(1) 149°. Such hydrogen bonding
presumably lends stability to the molecule and may

* For details see Notices to Authors No. 7, J.C.S. Dalton, 1977.
Index issue.

† See P. R. Hoffman and K. G. Caulton, J. Amer. Chem. Soc.,
1975, 97, 4221 and refs. therein.

explain the unexpectedly low value of the v(CO) wave-number (1.530 cm$^{-1}$) in the i.r. spectrum of (4) and also in that of [Ru(SOCPh)$_2$(NH$_2$Et)$_2$(PMe$_2$Ph)$_2$] (Table 1).

### Table 3

Atomic positional parameters ($\times$ 10$^4$) for (4) with estimated standard deviations in parentheses

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Similarly in the i.r. spectra of both [Ni(O$_2$CMe)$_2$]$_2$4H$_2$O$^{11}$ and [Pd(O$_2$CMe)$_2$(NH$_2$Et)$_2$]$^{12}$, the low value of v$_{asym}$(CO) is attributed to intramolecular hydrogen bonding between the unco-ordinated oxygens of the carboxylate groups and water or amine groups respectively.

The three singlets in the $^1$H n.m.r. spectrum are assigned to gem-methyl groups (8 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.$^{13}$) the related signals in [Ni([HNC(Me)]CH$_2$CMe$_2$NH$_2$)$_2$][BF$_4$]$^{14}$. 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 $^1$H 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

![Scheme 1](image)

**Scheme 1** Fragmentation pattern of the 4-amino-2-imino-4-methylpentane molecule

The reaction 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

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earlier, [Ru(SOCPH)4(NH3)6(PMe2Ph)6] 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)4(PMe2Ph)6] (2) followed by reaction with ammonia to give the diammine species. Since reaction of [Ru(SOCPH)4(PMe2Ph)6] with either [NH3][PF6] or [NH3][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 PMe2Ph 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 3.

This is similar to a mechanism proposed elsewhere 15 to explain the formation of ruthenium imine complexes from reaction of ruthenium ammine and various organocarbonyl-containing compounds. An added attraction of the mechanism shown in this Scheme is that diammine groups are essential for formation of the imine amino chelating ligand and therefore this provides a good rationale for the inability to form the corresponding species starting from either [RuCl2(PPh3)2] or [RuCl2(SOCPH)2(NH3)2] (3a).

However, attempts to condense acetone (or mesity oxide) with [Ru(SOCPH)4(NH3)6(PMe2Ph)6] or ethyl methyl ketone with [Ru(SOCPH)4(NH3)6(PMe2Ph)6] were also unsuccessful suggesting that steric constraints are another important consideration.

The diammine bis(triphénylphosphine) ruthenium(II) complex is of interest as a model for the ammine complex of ruthenium in the amine-hydrocarbon catalyst. The structure of the diammine complex was determined by single-crystal X-ray diffraction. The crystal structure is shown in Figure 1. The complex is a dimer of two monomeric units, with each monomer containing a five-coordinate ruthenium atom. The five-coordinate geometry around the ruthenium atom is completed by two nitrogen atoms from the diammine ligand, one phosphorus atom from each of the two triphenylphosphine ligands, and one carbon atom from the acetone molecule.

![Scheme 2 Possible mechanism of formation of [Ru(SOCPH)4(NH3)6(PMe2Ph)6](4).](image)

Experimental

Microanalyses were performed by the Department of Physical Chemistry. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the range 250—4 000 cm⁻¹ on a Perkin—Elmer 557 grating spectrometer using Nujol and hexane as KBr. The n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe, and proton-noise-decoupled 31P n.m.r. spectra on a Varian XL 100 spectrometer in the range 10—160 MHz (1H) and 0—160 MHz (31P). The chemical shifts quoted in p.p.m. to high frequency of 85% H3PO4. Mass spectra were obtained on an A.E.I. MS90 spectrometer. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Crystallographic calculations were made using the X-RAY 72 system 18 as implemented at the Edinburgh Regional Computing Centre.

Bis[monothiobenzoato]bis(triphénylphosphine)ruthenium(II) complex was prepared by reaction of [RuCl2(PPh3)2] with [RuCl2(SOCPH)2]. 15

**Scheme 2** Possible mechanism of formation of [Ru(SOCPH)4(NH3)6(PMe2Ph)6](4). (i) [SOCPH]: (ii) NH3; (iii) [RuCl2(PPh3)2] + [RuCl2(SOCPH)2] + [NH3][PF6] + [NH3][SOCPH] + CH3COCH3 → [Ru(SOCPH)4(NH3)6(PMe2Ph)6](4)


ruthenium(n).—The complex \([\text{Ru}^{14+}\text{SOSCPh}_2\text{(PPPh}_2)_2] \) (0.10 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 \(^{31}P\) n.m.r. studies using a sample prepared in CDC\(\text{3} \) (see Discussion section). Attempts at isolation were unsuccessful. \(^{31}P\) n.m.r. spectrum in CDC\(\text{3} \) at 303 K: \(\delta\) 29.3 (s) p.p.m.

Diacarbonyl(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(n).—The complex \([\text{Ru}^{14+}\text{SOSCPh}_2\text{(PPPh}_2)_2] \) (0.10 g) was dissolved in chloroform (10 cm³) and ammonia 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. 155—155 °C (Found: C, 53.8; H, 4.6. Calc. for \(\text{C}_{46}\text{H}_{44}\text{N}_2\text{O}_4\text{P}_2\text{RuS}_2: C, 54.2; H, 4.5\%\). \(^{31}P\) n.m.r. spectrum in CDC\(\text{3} \) at 303 K: \(\delta\) 10.8 (s) p.p.m.

Bis(dimethylphenylphosphine)bis(ethylamine)bis(monothiobenzoato)ruthenium(n).—The complex \([\text{Ru}^{14+}\text{SOSCPh}_2\text{PM}_{\text{EPh}}_2] \) (0.10 g) was dissolved in chloroform (20 cm³) with ethylamine (0.50 cm³, 79% 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, 64.0; H, 6.0; N, 3.7. Calc. for \(\text{C}_{48}\text{H}_{50}\text{N}_2\text{O}_4\text{P}_2\text{RuS}_2: C, 55.1; H, 6.2; N, 3.8\%\). \(^{31}P\) n.m.r. spectrum in CDC\(\text{3} \) at 303 K: \(\delta\) 22.3 (s) p.p.m.

(4-Amino-2-azima-4-methylpentane)bis(dimethylphenylphosphine)bis(monothiobenzoato)ruthenium(n).—Method (a). The compounds mer-[\text{RuCl}_2\text{PM}_{\text{EPh}}_2] \) (0.30 g) and \([\text{NH}_3]\text{SOSCPh} \) (0.05 g) were heated in the minimum volume of acetonitrile (20 cm³), and the solution was filtered and left to stand 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 acetonitrile (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(CHC\(\text{3}\)Cl) 724. Calc. for \(\text{C}_{48}\text{H}_{50}\text{N}_2\text{O}_4\text{P}_2\text{RuS}_2: C, 56.5; H, 6.0; N, 3.7%. M 765). Method (b). The complex \([\text{Ru}^{14+}\text{SOSCPh}_2\text{PM}_{\text{EPh}}_2] \) (0.10 g) in chloroform (10 cm³) was treated with ammonia gas to give the diaminine complex in situ (see earlier). Acetonitrile (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, \([\text{Ru}^{14+}\text{SOSCPh}_2\text{PM}_{\text{EPh}}_2] \) (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. \(^{31}P\) n.m.r. spectrum in CDC\(\text{3} \) at 303 K: \(\delta\) 19.9 (q) p.p.m. \([\text{PP}]\) 32.9 Hz, \([\text{PP}]\) 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 \(^{31}P\) n.m.r. spectra, and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.

[7/1559 Received, 19th September, 1977]
Metal Complexes of Sulphur Ligands Part 171 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 monothiobenzoic 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 \(\text{Na}_2\text{PtCl}_4\) and \(\text{Na}[\text{PhCOS}]\) in ethanolic or aqueous media. All these materials, however, react with an excess of various Lewis bases \(L\) or \(L-L\) \([L = \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{AsPh}_3, \text{SbPh}_3, \text{C}_6\text{H}_5\text{N}; L-L = 2,2'\text{-bipyridyl}, \text{Ph}_2\text{P(CH}_2\text{)}_x\text{PPh}_2 (x = 1, 2)]\) 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 \([\text{Pd(MeCO)}_2]_2(\text{PR}_3)_2\) 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 \([\text{M(PhCOS)}_nL]\) or \([\text{M(PhCOS)L}_2][\text{PhCOS}]\) respectively.
The reaction of \( [\text{M}(\text{S-S})_2] \) compounds (\( \text{M} = \text{Pd, Pt}; \text{S-S} = \text{S}_2\text{PR}_2, \text{S}_2\text{P(OR)}_2, \text{S}_2\text{CNR}_2, \text{S}_2\text{COR} \)) 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 \( [\text{Pd}(\text{RCO}_2)_2]_n \) with various Lewis bases has also been published.\(^4,5\) In this paper, we now report on the reactions of \( [\text{M}(\text{PhCOS})_2]_n \) compounds (\( \text{M} = \text{Pd, Pt} \)) 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 \( [\text{Pd}(\text{MeCO}_2)]_3 \)\(^7\) and \( [\text{Pd}(\text{PhCOS})_2]_3 \)\(^8\) are trimeric in the solid state, (although of quite different molecular structure),\(^\dagger\) and ebullioscopic

\(^\dagger\)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 [Pd(PhCO₂)₂]₃ indicate a trimer, it seems reasonable to expect that [Pd(PhCOS)]₂ would also possess at least a trimeric structure in the solid state.

As discussed elsewhere, the most useful method for establishing the mode of bonding of the mono thiobenzoate group is infrared spectroscopy. Thus, Savant et al. showed that in Na[PhCOS], v_{CO} 1500, v_{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 v_{CO} and v_{CS} are expected to remain almost unaffected eg for [Ru(PhCOS)(PPh₃)₂] v_{CO} 1500, v_{CS} 965 cm⁻¹. However, as the interaction with the metal through sulphur increases and that through oxygen decreases, it is expected that v_{CO} will increase and v_{CS} will decrease in energy. Thus, for [Pd(PhCOS)]₂ 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.¹²

Without X-ray structural information, the exact structure of this mono thiobenzoate 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 [Pd(PhCOS)]₂ is similar to that of [Hg(PhCOS)]₂ (v_{CO} 1630, v_{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 [Pd(OSCNR₂)]₂ compounds.¹¹

For [Pt(PhCOS)]₂, 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 v_{CO} and v_{CS} vibrations respectively of PhCOS⁻ groups and again suggest

¹²For PhCOSH, v_{CO} = 1690 cm⁻¹ but the absence of a band at 2560 cm⁻¹ (v_{SH}) shows that no free mono thiobenzoic 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 \(\text{Me}_2\text{CS}_2\) produced several structural variations of \([\text{Pd(MeCS}_2)_2]_n\) 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 \([\text{Ni(PhCOS)}_2]_n\) \(\text{EtOH}\), \((\nu_{\text{CO}} 1508; \nu_{\text{CS}} 958 \text{ cm}\(^{-1}\))\(^{15}\) the platinum compound with ir bands

\(^*\text{Platinum(II) acetate has a tetrameric structure containing strong metal-metal interactions}^{12}\) whereas platinum(II) dithiocumate has a dimeric structure with strong metal-metal bonds.\(^{13}\) The ir spectrum of \([\text{Pt(PhCS}_2)_2]_2\) indicates that it has a similar dimeric structure.\(^{13}\)
at 1530 and 950 cm$^{-1}$ may also have a dimeric structure with bridging PhCOS$^-\text{groups.}$

Although complete characterisation of these $[\text{M(PhCOS)}_2]_n$ 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 $[\text{M(PhCOS)}_2L_2]$ ($\text{M} = \text{Pd, Pt}$; $\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{AsPh}_3, \text{SbPh}_3, \text{C}_5\text{H}_5\text{N}$). The ir spectra of all these compounds show $\nu_{\text{CO}}$ bands between 1550 - 1600 cm$^{-1}$ and $\nu_{\text{CS}}$ bands between 900 - 940 cm$^{-1}$ (Table 1) indicative of strong M-S and weak M-O interactions. (cf $[\text{Ru(CO)}_2(\text{PMe}_2\text{Ph})_2(\text{PhCOS})_2]$ $\nu_{\text{CO}}(\text{PhCOS})$ 1600, 1570; $\nu_{\text{CS}}$ 945 cm$^{-1}$, which has S-bonded PhCOS$^-\text{groups}$). 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).

\[
\begin{align*}
\text{(1)} \\
\text{(2)}
\end{align*}
\]

Examination of the $^{31}\text{P}$ and $^1\text{H}$ nmr spectra of the compounds $[\text{M(PhCOS)}_2L_2]$ ($\text{L} = \text{PMe}_2\text{Ph, PMePh}_2$) has enabled the isomeric form to be established.

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$^\dagger$In fact Oro et al.\textsuperscript{16} reported that reaction of $\text{PdCl}_2$ with $\text{Na[PhCOS]}$ in water gave $[\text{Pd(PhCOS)}_2]^\dagger_2$ ($\nu_{\text{CO}}$ 1530 cm$^{-1}$) which was dimeric in benzene. In our hands, however, reaction of $\text{Na}_2\text{PdCl}_4$ and $\text{Na[PhCOS]}$ 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$^{-1}$.

$^\ddagger$[Pd(PhCOS)$_2$($\text{C}_5\text{H}_5\text{N}$)$_2$] has been briefly reported elsewhere\textsuperscript{16} although the $\nu_{\text{CO}}$ band was assigned to a peak at 1700 cm$^{-1}$ which was not found in the ir spectrum of our sample.
Thus, the \(^{31}\text{P}-^{1}\text{H}\) nmr spectra in each instance, showed either a singlet (Pd) or a 1,4,1 triplet (Pt) (\(J_{\text{PtP}} \cong 2600\) Hz) indicative of a single isomer with directly bonded PR\(_3\) groups. The \(^1\text{H}\) 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 \(^1\text{H}\) nmr studies for \([\text{Pd(pyrm)}_2(\text{PMe}_2\text{Ph})_2]\) (pyrm = N-pyrrolidin-1-ylmonothiocarbamate).\(^{18}\)

Earlier,\(^4\) the analogous \([\text{Pd(MeCO})_2(\text{Et}_2\text{NH})_2]\) 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 \(^1\text{H}\) nmr spectra of \([\text{Pd(MeCO})_2(\text{PR})_2]\) (PR = PMe\(_2\)Ph, PMePh\(_2\)) made by reaction of \([\text{Pd(MeCO})_2]^2\) with excess PR\(_3\), both show a "pseudo-doublet"* pattern for the methyl resonance indicative of the cis-configuration (4). The \(^{31}\text{P}-^{1}\text{H}\) nmr spectrum of \([\text{Pd(MeCO})_2(\text{PMe}_2\text{Ph})_2]\) showed a singlet at 5.35 consistent with only one isomer in solution. For \([\text{Pt(CF}_3\text{CO})_2(\text{PMe}_2\text{Ph})_2]\), however, made by reaction of \([\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]\) with \([\text{Ag(CF}_3\text{CO})]\), the \(^1\text{H}\) nmr spectrum showed a "virtually-coupled" triplet pattern indicating the trans structure (3).\(^{19}\)

\[ \text{(3)} \]

\[ \text{(4)} \]

The compound \([\text{Pd(MeCO})_2\text{bipy}]\) (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 \(J_{\text{pp}}\) value when compared to \(|J_{\text{PH}} + J_{\text{PH'}}|\).
meric, non-conducting compounds $[M(\text{PhCOS})_2(L-L)]$ ($M = \text{Pd}, \text{Pt}$; $L-L = \text{bipy}, \text{P}_2\text{P}(\text{CH}_2\text{PPh}_2), \text{Ph}_2\text{P}(\text{CH}_2\text{PPh}_2)$) which must have the cis-configuration (1).

An interesting feature here is the big difference between the positions of the $^{31}\text{P}$ nmr resonances in $[\text{M(PhCOS)}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ (37.35 $^{[\text{Pd}]}$, 49.15 $^{[\text{Pt}]})$ and $[\text{M(PhCOS)}_2(\text{Ph}_2\text{P}(\text{CH}_2\text{PPh}_2))]$ (57.05 $^{[\text{Pd}]}, 45.85^{[\text{Pt}]}$). This big difference between $^{31}\text{P}$ nmr chemical shifts in 4 and 5 membered phosphorus ring compounds has been found elsewhere but an acceptable explanation has not yet been suggested.

Comparison of the platinum-phosphorus coupling constants in the various compounds indicates that the trans-influence of the PhCOS$^-$ group is slightly lower than that of PMe$_2\text{Ph}$ or PMePh$_2$, but considerably greater than chloride. Thus, trans-$[\text{Pt(PhCOS)}_2(\text{PMe}_2\text{Ph})_2]$ and trans-$[\text{Pt(PhCOS)}_2(\text{PMePh}_2)_2]$ have $^{1}{J}_{\text{PtP}}$ values of 2546 and 2655 Hz respectively compared to 2761 and 3018 Hz in cis-$[\text{Pt(PhCOS)}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]$ and cis-$[\text{Pt(PhCOS)}_2(\text{Ph}_2\text{P}(\text{CH}_2\text{PPh}_2))]$ respectively. The compounds cis-$[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$ and cis-$[\text{PtCl}_2(\text{PMePh}_2)_2]$ have $^{1}{J}_{\text{PtP}}$ values of 3549 and 3616 Hz respectively.

In contrast to the reaction of $[\text{Pd(MeCO}_2)_2]_3$ with stoichiometric amounts of Eph$_3$ ($E = \text{P, As}$) which gave the dimeric compounds $[\text{Pd(MeCO}_2)_2\text{Eph}_3]_2$ (5) and of $[\text{M(S-S})_2\text{PR}_3]$ with PR$_3$ which gave the monomeric compounds $[\text{M(S-S})_2\text{PR}_3]_2$ (6), attempts to obtain the analogous $[\text{M(PhCOS)}_2\text{L}]_n$ have been unsuccessful. Thus, reaction of $[\text{M(PhCOS)}_2]_2$ with stoichiometric amounts of L only led to the isolation of $[\text{M(PhCOS)}_2\text{L}]_2$ and unreacted $[\text{M(PhCOS)}_2]_2$. Furthermore, monitoring the reaction between $[\text{Pd(PhCOS)}_2]_n$

**This structure (6) has now been established by X-ray analyses for $[\text{Pd(S}_2\text{PPh}_2)_2\text{PPh}_3]^{22}_{25}$, $[\text{Pt(S}_2\text{C}_6\text{H}_5\text{C}_3\text{H}_7\text{PMePh}_2]^{24}$, $[\text{Pt(S}_2\text{CNEt}_2)_2\text{PPh}_3]^{23,25}$, $[\text{Pt(S}_2\text{POEt}_2)_2\text{PPh}_3]^{25}$ and $[\text{Pt(S}_2\text{COEt}_2)_2\text{PPh}_3]^{25}$.
and small amounts of PMePh₂ in benzene confirmed that only the bisphosphine complex was generated in spectroscopically detectable amounts.

For [Pd(MeCO₂)₂₄₇₃]₂, only one methyl resonance is observed in the ¹H 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 ¹H nmr spectra have been observed elsewhere for [Pd(RCO₂)₂PMe₂Ph]₂ (5), [made by reaction of [PdCl₂(PMe₂Ph)]₂ with [Ag(RCO₂)] (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 [Pd(MeCO₂)₂PR₃]₂ (PR₃ = PMe₂Ph, PMePh₂) by reaction of [Pd(MeCO₂)₂]₃ with stoichiometric amounts of PR₃ were unsuccessful, giving inseparable mixtures of the dimers and [Pd(MeCO₂)₂(PR₃)₂]. Furthermore, unlike [Pd(MeCO₂)₂(PPh₃)₂] which rearranged to [Pd(MeCO₂)₂-PPh₃]₂ when left in benzene for 12 hours, [Pd(MeCO₂)₂(PR₃)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 [PdX₂L₂] to [PdX₂L] which takes place far more readily for X = I⁻ than for X = 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 \([M(PhCOS)_2]\). Thus reaction of \([M(PhCOS)_2]\) 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\(_2\)PtCl\(_4\) with PR\(_3\) in water which gives initially \([M(PR\(_3\))_4]-[MCl\(_4\)]\) and then rearranges to \([MCl\(_2(PR\(_3\))_2)]\), the ionic species here are probably \([Pd(PR\(_3\))_4][Pd(MeCO\_2)_4]\).

Finally, contrary to earlier reports,\(^2\) there is some very recent evidence for the formation of neutral 1:2 dithioacid compounds \([M(S-S)]\). Thus, Fackler\(^2\) has shown by X-ray analysis that the reaction product from \([Pt(S_2CN\(^-\)Bu\(_2\))_2]\) treated with excess PMe\(_2\)Ph in acetone/diethylether is the neutral monomer \([Pt(S_2CN\(^-\)Bu\(_2\))_2(PMe\(_2\)Ph)_2]\) (8) with trans monodentate bonded \(-S_2CN\(^-\)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
work-up.†

Thus, reaction of $[ \text{M}(\text{S}_2\text{PR}_2)_2 ]$ 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 $[ \text{Pd}(\text{S}_2\text{PPh}_2)(\text{PEt}_3)_2](\text{S}_2\text{PPh}_2)_2$ together with the observation of identical mull and solution ir spectra.$^{22,32}$

A reexamination of the ir spectra of the dithiocarbanate compounds prepared as reported in Ref. 28 also confirms that these are genuine ionic species $[ \text{Pt}(\text{S}_2\text{CNR}_2)(\text{PMePh})_2]$, $\text{S}_2\text{CNR}_2$, and not neutral $[ \text{Pt}(\text{S}_2\text{CNR}_2)_2(\text{PMePh})_2]$ which rapidly rearrange to the ionic species in solution.$^{1\ddagger}$

However, reaction of $[ \text{M}(\text{S}_2\text{PR}_2)_2 ]$ 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 $\text{S}_2\text{PPh}_2$ coordination$^{22}$ but no bands at 560 or 570 cm$^{-1}$ characteristic of ionic or bidentate $\text{S}_2\text{PPh}_2$ ligands.$^{22}$ These products are very unstable, readily rearranging in solution to give the ionic $[ \text{M}(\text{S}_2\text{PPh}_2)(\text{PR}_3)_2]\text{S}_2\text{PPh}_2$ compounds.

Conclusion: Although the reaction of $[ \text{Pd}(\text{MeCO})_2)_3$ with various Lewis bases (L) gives both the 1:1 and 1:2 adducts $[ \text{Pd}(\text{MeCO})_2L]$ and $[ \text{Pd}(\text{MeCO})_2L_2]$ and likewise, with $[ \text{M}(\text{S}-\text{S})_2]$, reaction with tertiary phosphines gives $[ \text{M}(\text{S}-\text{S})_2\text{PR}_3]$, $[ \text{M}(\text{S}-\text{S})(\text{PR}_3)_2]$, $\text{S}_2\text{S}$ or $[ \text{M}(\text{S}-\text{S})(\text{PR}_3)_2]$, reaction of $[ \text{M}(\text{PhCO})_2\text{L}_n]$ with a variety of Lewis bases gives only the neutral $[ \text{M}(\text{PhCO})_2\text{L}_2]$ or $[ \text{M}(\text{PhCO})_2(\text{L-L})]$.

†Similarly with $[ \text{Ni}(\text{S}-\text{S})_2]$ where it is well established that the five and six coordinate adducts $[ \text{Ni}(\text{S}-\text{S})_2\text{L}]$ and $[ \text{Ni}(\text{S}-\text{S})_2\text{L}_2]$ respectively are readily formed with a range of nitrogen donor ligands, $^{22}$ very recent work has shown that reaction of $[ \text{Ni}(\text{S}-\text{COR})_2]$, $[ \text{Ni}(\text{S}-\text{COR})_2]_2$, $[ \text{Ni}(\text{S}-\text{COR})_2]_2$ containing unidentate xanthate groups.$^{30}$ Also, reaction of $[ \text{Ni}(\text{S}-\text{P}[\text{OMe}]_2)_2]$ with $\text{Ph}_2\text{PC}_2\text{HAsPh}_2$ gives $[ \text{Ni}(\text{S}-\text{P}[\text{OMe}]_2)(\text{Ph}_2\text{PC}_2\text{HAsPh}_2)_2]$, probably via the ionic intermediate $[ \text{Ni}(\text{S}-\text{P}[\text{OMe}]_2)(\text{Ph}_2\text{PC}_2\text{HAsPh}_2)_2]$, $\text{S}_2\text{P}[\text{OMe}]_2$.$^{31}$

††Thus, $\nu_{\text{CN}}$ in the ir spectra (mull and KBr disc) of these compounds and of $[ \text{Pt}(\text{S}_2\text{CNR}_2)(\text{PMePh})_2]$ occurs at ca 1560 cm$^{-1}$ (bidentate $\text{S}_2\text{CNR}_2$ coordination)$^{34}$ whereas in $[ \text{Pt}(\text{S}_2\text{CNR}_2^1\text{Bu}_2)_2(\text{PMePh})_2]$, $\nu_{\text{CN}} = 1465$ cm$^{-1}$ (unidentate $\text{S}_2\text{CNR}_2$ 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 40.5MHz \((^{31}\text{P}\text{ chemical shifts quoted in ppm to high frequency of } 85\% \text{ H}_3\text{PO}_4\)). 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, methyldiphenylphosphine (Maybridge Chemical Company) were obtained as indicated. \(\text{Na[PhCOS]}\), \(\text{Ph}_2\text{PCH}_2\text{PPh}_2\), \(\text{Ph}_2\text{P-CH}_2\text{PPh}_2\), \(36\text{[Pd(OCOMe)}_2\text{]}_2\), \(4\text{[Pd(OCOMe)}_2\text{AsPh}_3\text{]}\), \(5\text{[Pt(S}_2\text{CNR}_2\text{-} \text{PMePh}_2\text{)}_2\text{]}\) \((\text{Y = S}_2\text{CNR}_2\text{, Cl}^-, \text{BPh}_4^-, \text{PF}_6^-)\) were prepared as described earlier. Analytical data and characteristic IR bands for various monothiobenzoate compounds are given in Table 1 and \(^1\text{H}\) and \(^{31}\text{P}\) 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 (0.90gd⁻¹) 1504 (2.08gd⁻¹), 1672 (4.08gd⁻¹) Calc. for C₁₄H₁₀O₂Pd₂S; C,44.2; H,2.6%; M 380 (monomer)] Ir spectrum(nujol mull):- 1670vs (ν_CO), 875vs (ν_CS).

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 C₁₄H₁₀O₂Pt₂S₂; C,35.8; H,2.1%] Ir spectrum(nujol mull):- 1660s, 1595s, 1570-1520vs (broad)cm⁻¹ (ν_CO); 920s, 880s (ν_CS).

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)]₂EtOH] C,37.3; H,3.1%] Ir spectrum (nujol mull) 1660w, 1590vs, 1570-1520vs (broad)cm⁻¹ (ν_CO); 950-920vs (broad), 880w cm⁻¹ (ν_CS).

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 ($\nu_{CO}$); 950vs, 920w ($\nu_{CS}$).

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) ($\nu_{CO}$); 950-920 vs (broad); 880w cm$^{-1}$ ($\nu_{CS}$).

Qualitative analysis showed that none of these platinum monothiobenzoate complexes contained any chlorine.

General method of preparation of $[\text{M(PhCOS)}_{2}(\text{L-L})]_{2}$ and $[\text{M(PhCOS)}_{2}(\text{L-L})]_{2}$ compounds:- The compounds $[\text{M(PhCOS)}_{2}]_{n}$ (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 $\text{L} = \text{SbPh}_{3}$ 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 $\text{C}_{20}\text{H}_{28}\text{O}_{4}\text{P}$: - C, 48.0; H, 5.6%] IR spectrum (mull) v asym ($\text{CO}^-$) 1590, vsym 1330 cm$^{-1}$. 
cis-Bis(acetato)bis(methyl(diphenylphosphine)palladium(II) was similarly prepared from [Pd(OCOMe)]_3 and an excess of PMePh_2 [Found; C, 57.5; H, 5.1%. Calc for C_{30}H_{32}O_4P_2Pd: C, 57.7, H, 5.1%.] IR spectrum (mull) v asym (CO^-) 1580; vsym 1315 cm^-1.

We thank Johnson Matthey Ltd. for loans of palladium(II) chloride and potassium tetrachloroplatinate(II), the SRC for financial support (JAG, MCC), Professor J.P. Fackler Jr., for furnishing results prior to publication, Dr. A.S.F. Boyd for obtaining the ^31P nmr spectra and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.
References


25. J.P. Fackler Jr., personal communication.


## TABLE 1

Analytical Data and some Characteristic IR Bands (nujol mull) for some Palladium(II) and Platinum(II) Monothiobenzoate Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>m.p. (°C)</th>
<th>Found %</th>
<th>Required %</th>
<th>ν&lt;sub&gt;CO&lt;/sub&gt; cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>ν&lt;sub&gt;CS&lt;/sub&gt; cm&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>yellow</td>
<td>215-220</td>
<td>67.3 4.7 - -</td>
<td>66.3 4.4 - -</td>
<td>1595s,1570s</td>
<td>910vs</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(PMePh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>yellow</td>
<td>190-192</td>
<td>61.6 4.7 - -</td>
<td>61.5 4.6 - -</td>
<td>1590s,1565s</td>
<td>930sh,915vs</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;Ph)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>yellow</td>
<td>168</td>
<td>54.1 5.3 - -</td>
<td>54.8 4.9 - -</td>
<td>1595s,1560s</td>
<td>610vs&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>pale brown</td>
<td>173-174</td>
<td>56.5 3.9 - 1045</td>
<td>56.8 3.9 - 1077</td>
<td>1590s,1560s</td>
<td>925sh,910vs</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(SbPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>yellow</td>
<td>175</td>
<td>52.3 3.7 - 1160</td>
<td>52.3 3.6 - 1171</td>
<td>1600(s),1570(s)</td>
<td>910vs</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;N)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>pale brown</td>
<td>129</td>
<td>53.5 3.9 5.6 -</td>
<td>53.5 3.7 5.3 -</td>
<td>1590s,1565s</td>
<td>935m,912s</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(bipy)</td>
<td>yellow</td>
<td>280(decomp)</td>
<td>54.8 3.5 5.0 -</td>
<td>53.7 3.4 5.2 -</td>
<td>1600vs,1570m</td>
<td>930s,910vs</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(Ph&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;PPh&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>brown</td>
<td>194-196</td>
<td>61.4 4.3 - -</td>
<td>61.3 4.2 - -</td>
<td>1595vs,1560s</td>
<td>930s,910vs</td>
</tr>
<tr>
<td>Pd(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(Ph&lt;sub&gt;2&lt;/sub&gt;PCl&lt;sub&gt;2&lt;/sub&gt;PPh&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>pale brown</td>
<td>231</td>
<td>61.9 4.4 - -</td>
<td>61.7 4.1 - -</td>
<td>1590s,1560s</td>
<td>925sh,911vs</td>
</tr>
<tr>
<td>Pt(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>yellow</td>
<td>263-264</td>
<td>59.4 4.2 - -</td>
<td>59.4 4.0 - -</td>
<td>1600s,1575s</td>
<td>915vs</td>
</tr>
<tr>
<td>Pt(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(PMePh&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>pale yellow</td>
<td>160-164</td>
<td>55.0 4.1 - -</td>
<td>55.2 4.1 - -</td>
<td>1593s,1570s</td>
<td>930s,910vs</td>
</tr>
<tr>
<td>Pt(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(PMe&lt;sub&gt;2&lt;/sub&gt;Ph&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>pale yellow</td>
<td>203</td>
<td>48.2 4.5 - -</td>
<td>48.3 4.3 - -</td>
<td>1600s,1570m</td>
<td>910vs&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Pt(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(AsPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>pale brown</td>
<td>250-252</td>
<td>53.0 3.7 - -</td>
<td>52.5 3.6 - -</td>
<td>1590s,1570s</td>
<td>925sh,905vs</td>
</tr>
<tr>
<td>Pt(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(bipy)</td>
<td>pale brown</td>
<td>&gt;300</td>
<td>45.3 2.9 4.0 -</td>
<td>46.1 2.9 4.5 -</td>
<td>1595s,1565s</td>
<td>935sh,920vs</td>
</tr>
<tr>
<td>Pt(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(Ph&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;PPh&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>pale brown</td>
<td>148-155</td>
<td>50.7 3.6 - 929</td>
<td>49.9 3.4 - 937</td>
<td>1595s,1570s</td>
<td>925sh,910vs</td>
</tr>
<tr>
<td>Pt(PhCOS)&lt;sub&gt;2&lt;/sub&gt;(Ph&lt;sub&gt;2&lt;/sub&gt;P(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;PPh&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>yellow</td>
<td>228</td>
<td>55.0 4.0 - 895</td>
<td>55.4 3.9 - 866</td>
<td>1590s,1565s</td>
<td>910vs</td>
</tr>
</tbody>
</table>

<sup>a</sup> Molecular weight measured osmometrically at 37°C in chloroform

<sup>b</sup> Partially masked by strong PMe<sub>2</sub>Ph vibration at 900 cm<sup>-1</sup>.
TABLE 2

$^1$H and $^{31}$P-$^1$H nmr data in CDCl$_3$ for various palladium(II) and platinum(II) complexes at 300K

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^1$H nmr $^a$</th>
<th>$^{31}$P nmr $^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Pd(PhCOS)}_2(\text{PMePh}_2)_2]$</td>
<td>2.14(t)$^c$</td>
<td>7.0-8.2(m) 12.3(s)</td>
</tr>
<tr>
<td>$[\text{Pd(PhCOS)}_2(\text{PMe}_2\text{Ph})_2]$</td>
<td>1.79(t)$^c$</td>
<td>7.0-7.8(m) -2.6(s)</td>
</tr>
<tr>
<td>$[\text{Pd(PhCOS)}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$</td>
<td>4.10(t)$^d$</td>
<td>7.0-8.0(m) -37.3(s)</td>
</tr>
<tr>
<td>$[\text{Pd(PhCOS)}_2(\text{Ph}_2\text{P}(\text{Ph}_2)_2\text{PPh}_2)_2]$</td>
<td>2.33(m)$^e$</td>
<td>7.0-8.2(m) 57.0(s)</td>
</tr>
<tr>
<td>$[\text{Pd(MeCO}_2)_2(\text{PMe}_2\text{Ph})_2]$</td>
<td>2.00(s)</td>
<td>1.42(pd)$^f$</td>
</tr>
<tr>
<td>$[\text{Pd(MeCO}_2)_2(\text{PMePh}_2)_2]$</td>
<td>1.64(s)</td>
<td>1.68(pd)$^f$</td>
</tr>
<tr>
<td>$[\text{Pd(MeCO}_2)_2(\text{PPh}_3)_2]$</td>
<td>0.85(s)</td>
<td>7.0-7.8(m) 14.8(s)</td>
</tr>
<tr>
<td>$[\text{Pd(MeCO}_2)_2\text{AsPh}_3]$</td>
<td>1.44(s), 1.47(s), 1.41(s)$^g$</td>
<td>7.0-8.0(m)</td>
</tr>
<tr>
<td>$[\text{Pd(MeCO}_2)_2\text{PPh}_3]$</td>
<td>1.42(s)</td>
<td>7.0-8.0(m) 19.7(s)</td>
</tr>
<tr>
<td>$[\text{Pt(PhCOS)}_2(\text{PMePh}_2)_2]$</td>
<td>2.23(t.t.$^c$)$^h$</td>
<td>7.0-7.9(m) 8.2(t)$^i$12655.3</td>
</tr>
<tr>
<td>$[\text{Pt(PhCOS)}_2(\text{PMe}_2\text{Ph})_2]$</td>
<td>1.86(t.t.$^c$)$^h$</td>
<td>7.0-8.0(m) -6.2(t)$^i$12546.0</td>
</tr>
<tr>
<td>$[\text{Pt(PhCOS)}_2(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$</td>
<td>4.43$^j$</td>
<td>7.0-8.0(m) -49.1(t)$^i$12761.0</td>
</tr>
<tr>
<td>$[\text{Pt(PhCOS)}_2(\text{Ph}_2\text{P}(\text{Ph}_2)_2\text{PPh}_2)_2]$</td>
<td>2.18(m)$^e$</td>
<td>7.0-8.0(m) 45.8(t)$^i$13017.0</td>
</tr>
</tbody>
</table>

s = singlet, pd = pseudo doublet, t = triplet, m = multiplet

$^a \pm 0.01 \quad ^b \pm 0.05 \quad ^c |2J_{PH} + 4J_{PH}| = 7.0\text{Hz} \quad ^d \text{CH}_2 \text{resonance} \quad ^e 2J_{PH} 10.0\text{Hz}$

$^f \text{CH}_2 \text{resonance} \quad ^g |2J_{PH} + 4J_{PH}| = 11.0\text{Hz} \quad ^h \text{At 223K} \quad ^i 2J_{PH} 28.0\text{Hz} \quad ^j 1.4.1 \text{triplet}$

$^j \text{Too insoluble to determine splitting pattern}$
Metal Complexes of Sulphur Ligands Part 18

Reaction of $[\text{RuCl}_2 \text{L}_3]$ and $[\text{RuCl}_2 \text{L}^4]$ (L = PR$_3$, P(OR)Ph$_2$, P(OR)$_2$Ph) with various Dithioacid Ligands.

By Wilma J. Sime and T. Anthony Stephenson*, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ.

Reaction of the compounds $[\text{RuCl}_2 \text{L}_4]$ (L = P(OMe)$_2$Ph, PMePh$_2$) and $[\text{RuCl}_2 \text{P}^2 \text{EtPh}_2]$ with various alkali metal dithioacid salts gives, under all conditions, the complexes $[\text{Ru}(S-S)_2 \text{L}_2]$

$[S-S^\ominus = S_2 \text{PR}_1^1 (R^1 = \text{Me, Ph}), -S_2 \text{COMe}, -S_2 \text{CNR}^1 (R = \text{Me, Et})]$. In contrast the products of reaction of cis-$[\text{RuCl}_2 \text{PMe}_2]^4$ and $[\text{RuCl}_2 \text{P}^2 \text{OR} \text{Ph}_2]$ with these dithioacid anions are very sensitive to reaction conditions. For example, shaking with Na[S$_2$PR$_2^1$] in benzene gives the yellow complexes $[\text{RuCl}(S_2 \text{PR}_2^1) \text{L}_3]$ which readily rearrange to the red five coordinate cations $[\text{Ru}(S_2 \text{PR}_2^1) \text{L}_3]^+$ in alcoholic media. In contrast, shaking with K[S$_2$COMe] gives the six coordinate $[\text{Ru}(S_2 \text{COMe})_2 \text{L}_3]$ (with mono-/bidentate $-S_2 \text{COMe}$ coordination), which on heating, rearrange irreversibly to $[\text{Ru}(S_2 \text{COMe})_2 \text{L}_2]$. Reaction of $[\text{RuCl}_2 \text{PMe}_2]^4$ with Na[S$_2$CNR$_2^1$]xH$_2$O for very short periods in ethanol gives the $[\text{Ru}(S_2 \text{CNR}_2^1)(\text{PMe}_2 \text{Ph})]^+$ cation whereas in benzene, $[\text{Ru}(S_2 \text{CNR}_2^1)_2(\text{PMe}_2 \text{Ph})_3]$ are formed. All these compounds have been fully characterised by elemental analyses, $^1$H and $^{31}$P-$^1$H nmr spectroscopy and a general mechanism for the formation of $[\text{Ru}(S-S)_2 \text{L}_2]$ 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 \([\text{Ru}(\text{S-S})\text{L}_2]\) \((\text{S-S} = \text{S}_2\text{PR}^1(\text{R}^1 = \text{Me, Et, Ph}), \text{S}_2\text{CNR}^1(\text{R} = \text{Me, Et, Ph}), \text{S}_2\text{COME})\) containing bidentate dithioacid groups and, in most instances, cis tertiary phosphine ligands.

In this paper, we now report the reactions of more \([\text{RuCl}_2 \text{L}_3]\) \((\text{L} = \text{P(OMe)Ph}_2, \text{P(PEt)Ph}_2)\) and \([\text{RuCl}_2 \text{L}_4]\) \((\text{L} = \text{P(OMe)Ph}, \text{PMe}_2\text{Ph})\) compounds with various alkali metal dithioacid salts \([\text{S}_2\text{PR}^1(\text{R}^1 = \text{Me, Ph}), \text{S}_2\text{COME}, \text{S}_2\text{CNR}^1(\text{R} = \text{Me, Et})]\). Again the final products were \([\text{Ru}(\text{S-S})\text{L}_2]\) 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 \([\text{Ru}(\text{S-S})\text{L}_2]\) has been proposed.

**Results and Discussion**

a) Diphenyl- and dimethylphosphinodithioate complexes:– Prolonged reflux of \([\text{RuCl}_2(\text{P(OR})\text{Ph})_3]\) (R = Me, Et) with an excess of \(\text{Na}[\text{S}_2\text{PMe}_2]\)-2H2O in alcohol produced a brown solution from which, for R = Me, no solid could be isolated, but where for R = Et a small amount of red-brown crystals analysing for \([\text{Ru}(\text{S}_2\text{PMe}_2)(\text{P(0Et)Ph})_2]\) (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, and the \(^{31}\text{P}\) nmr spectrum in CDCl\(_3\) at 303K (Table 2) consisted of two triplets at 140.76 and 86.70\(\delta\) 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\(\delta\) due to the methyl groups of \(-\text{S}_2\text{PMe}_2\) and resonances at 3.30 and 1.20\(\delta\) from P(0Et)Ph. Unfortunately, at lower temperatures, the spectrum became very broad and
thus, the isomeric form could not be determined. Similarly, prolonged reaction of cis-[RuCl₂(PMe₂Ph)₄] with Na[S₂PMe₂]₂·H₂O produced yellow crystals, shown by ³¹P and ¹H nmr spectroscopy to be identical to those obtained from mer-[RuCl₃(PMe₂Ph)₃] viz cis-[Ru(S₂PMe₂)₂(PMe₂Ph)₂]²⁺.

However, shaking [RuCl₂(PMe₂Ph)₄] or [RuCl₂(P(OR)Ph₂)₃] in methanol (R = Me) or ethanol (R = Et) with NaS₂PR²⁻ (R²⁻ = Me, Ph) for a short time produced red, conducting solutions, which on addition of NaBPh₄ precipitated red solids analysing closely for [Ru(S₂PPh₂)L₃]BPh₄. The ir spectra contained bands at ca 580 cm⁻¹ consistent with bidentate S₂PR²⁻ 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 CHCl₃ on [Ru(S₂PMe₂)(PMe₂Ph)₃]BPh₄ (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 [Ru(S₂PPh₂)(PMe₂Ph)₃]BPh₄.¹⁰⁻ The cation has a distorted square pyramidal geometry as found (and predicted) for several other five coordinate ruthenium(II) complexes.¹¹

The ³¹P-¹H nmr spectrum of [Ru(S₂PMe₂)(PMe₂Ph)₃]BPh₄ in CDCl₃ at 298K consisted of a doublet at 32.36 ppm (‼_pp \( J = 3.6 \) Hz) due to the PMe₂Ph groups which, because of facile intramolecular scrambling, are rendered equivalent and thus equally coupled to the S₂PMe₂ group, and a quartet at 110.31 ppm due to the S₂PMe₂ group coupled equally to the three PMe₂Ph groups. Similarly, the ¹H nmr spectrum at 301K consisted of a doublet (‼_PH = 13 Hz) due to the S₂PMe₂ methyl groups (equivalent because of facile PMe₂Ph 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 \([J(\text{PH})+J(\text{PH})] \) value (cf cis-[Ru(S₂PMe₂)₂(PMe₂Ph)₂]²⁺)
the PMe₂ Ph methyl groups. Neither the 31P or 1H nmr spectra changed on cooling to 213K indicating that intramolecular scrambling was still rapid at these temperatures.

If [RuCl₂(P{OR|Ph})₃] or [RuCl₂(PMe₂ Ph)] were shaken with Na[S₂PMé₂]₂H₂O in benzene, however, yellow non-conducting solids analysing for [RuCl(S₂PMé₂)L₃] were obtained. These were fairly stable in CHCl₃ or CH₂Cl₂ but in methanol or ethanol, red solutions containing the [Ru(S₂PMé₂)L₃]⁺ cations were formed immediately. The 31P-(¹H) nmr spectrum of [RuCl(S₂PMé₂)(PMe₂ Ph)] at 213K in CDCl₃ consisted of an unsymmetrical quartet centred at 93.906 (S₂PMé₂ group) and an AB₂ pattern (νA 20.38; νB 16.06; ²JAB 33.0 Hz)(PMe₂ Ph groups). At 298K, the AB₂ pattern broadened and a singlet appeared at 21.26 corresponding to [Ru₂Cl₃(PMe₂ Ph)]Cl, formed presumably by the slow decomposition of [RuCl(S₂PMé₂)(PMe₂ Ph)] in chlorinated solvents.

The ¹H nmr spectrum at 233K in CDCl₃ contained two doublets at 1.19 and 2.17 which both collapsed at the same 3¹P nmr frequency (viz 95.56⁺) indicating that they arise from the methyl groups of S₂PMé₂. There was also a doublet at 1.60 (decoupling ³¹P nmr frequency = 19.56) and a broad resonance at 1.88 due to the PMe₂ Ph groups. At 298K, only a broad resonance at 1.70 was observed, indicating that, on the one hand, all the PMe₂ Ph groups and, on the other, the methyls of S₂PMé₂ had become equivalent.

- The irradiation frequencies are different from the frequencies of the ³¹P 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 $^2$S$_2$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$^\text{OMe}$ 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$_2^1$)$_2$- (P$^\text{OMe}$ Ph)$_2$]. The $^1$H nmr spectrum at 301K of [Ru(S$_2$PMe$_2^2$)$_2$(P$^\text{OMe}$ Ph)$_2^2$] 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 $^3$P nmr frequency) at 3.42 and 3.58$\delta$ and two doublets (also decoupling at the same $^3$P nmr frequency) at 1.71 and 2.12$\delta$. This low temperature spectrum is consistent with a $^\text{cis}$-configuration and the mechanism of interconversion of optical isomers which occurred at higher temperatures is probably identical to that established earlier for other $^\text{cis}$-[Ru(S$_2$PMe$_2$)$_2$L$_2$] complexes.\textsuperscript{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 $|J_{pp} + J_{ph}|$.\textsuperscript{12}
b) O-methylidithiocarbonate complexes

Shaking [RuCl₂(P{OR}Ph₂)₃] (R = Me, Et) or [RuCl₂(PMe₂Ph)₄] with excess K[S₂COME] in methanol produced yellow, non-conducting solids analyzing for [Ru(S₂COME)₂L₃]. The IR spectra contained several bands in the region 1000-1200 cm⁻¹ indicating the presence of coordinated S₂COME groups and the ³¹P-¹H) nmr spectrum at 298K (for L = PMe₂Ph) consisted of an AB₂ pattern, confirming the presence of three PMe₂Ph groups. The ¹H nmr spectrum of this compound in CDCl₃ at 301K contained two resonances at 3.92 and 3.655 (S₂COME) 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 (PMe₂Ph groups), (Table 3). The doublet could be assigned to a PMe₂Ph group trans to the monodentate dithioacid ligand and the "pseudo-triplet" to the two cis PMe₂Ph groups, each trans to a sulphur of the bidentate ligand.

If [Ru(S₂COME)₂(P{OME}_{2}Ph₂)₃] was heated under reflux in the presence of K[S₂COME], orange-yellow crystals of [Ru(S₂COME)₂(P{OME}_{2}Ph₂)₂] were produced. The ³¹P-¹H) nmr spectrum in CDCl₃ at 298K consisted of a singlet at 146.516 while the ¹H nmr contained a singlet at 3.716 (S₂COME) and a "pseudo-triplet" at 3.226 (PMe₂Ph) suggesting a cis configuration.

An intractable yellow oil was obtained from the reaction between [RuCl₂(P{OME}_{2}Ph₂)₄] and excess K[S₂COME] but shaking [RuCl₂(PMe₂Ph₂)₄] and [RuCl₂(PEtPh₂)₃] with excess of K[S₂COME] in alcohol produced [Ru(S₂COME)₂L₂]. For [Ru(S₂COME)₂(PMe₂Ph₂)₂], the ³¹P and ¹H nmr spectra at both 218 and 298K were consistent with a cis-configuration. However, for [Ru(S₂COME)₂(PEtPh₂)₂], the ³¹P-¹H) nmr spectrum at 218K in CDCl₃ consisted of two singlets of equal intensity, at 50.32 and 44.316. As the temperature was raised, the singlet at 44.316 increased.
\(^1\)H nmr spectrum of \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_4]\)BPh\(_4\) in CDCl\(_3\) at 301K contained a singlet at 2.37\(\delta\), "pseudo-triplet" at 1.76\(\delta\) and triplet at 1.27\(\delta\) in the intensity ratio 1:2:2, assigned to the \(S\text{CNMe}_2\) \(^-\) the cis phosphines (\(P_A\) and \(P_B\)) and the trans phosphines (\(P_C\) and \(P_D\)) respectively.

The reaction between \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) and Na\([S\text{CNMe}_2]_2\)\(\text{H}_2\text{O}\) in benzene, however, produced a bright yellow non-conducting solid analysing for \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_3]\). The \(^{31}\text{P}^{-1}\text{H}\) nmr spectrum in CDCl\(_3\) at 298K exhibited an AB\(_2\) pattern (\(\nu_A = 14.19; \nu_B = 11.48\delta; \ J_{AB} = 29.5\) Hz) and the \(^1\)H nmr spectrum under the same conditions contained two singlets at 3.49 and 2.90\(\delta\) (assigned to mono- and bidentate \(S\text{CNMe}_2\) groups respectively), two overlapping "pseudo-doublets" at 1.96\(\delta\) arising from the two phosphine groups trans to bidentate \(S\text{CNMe}_2\) and a doublet at 1.07\(\delta\) from the phosphine ligand trans to the unidentate group.

This compound was also precipitated as yellow crystals on prolonged reaction of \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_4]\) with Na\([S\text{CNMe}_2]_2\)\(\text{H}_2\text{O}\) in methanol. The reaction presumably does not give \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_2]\) because of the insolubility of \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_3]\) in methanol.

When \([\text{RuCl}_2(\text{PMe}_2\text{Ph})_3]\) was shaken with an excess of Na\([S\text{CNMe}]_2\)\(\text{H}_2\text{O}\) (\(R^1 = \text{Me, Et}\)) in ethanol, \(\text{cis-}[\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_2]\) (isomer confirmed by \(^{31}\text{P}\) and \(^1\)H nmr evidence) was the major product, together with a small amount of the \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_3]^+\) cation which was trapped out by addition of NaBPh\(_4\). In benzene, the major product was \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_1^-\text{Ph}_2)\text{Ph}_3]\) shown by \(^{31}\text{P}\) nmr spectroscopy to partially convert to \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMe}_2\text{Ph})_2]\) in solution.

As for the other dithioacid ligands, treatment of \([\text{RuCl}_2L_4]\) (\(L = \text{PMePh}_2, \text{P(OMe)}_2\text{Ph}\)) and \([\text{RuCl}_2(\text{PETPh}_2)_3]\) with Na\([S\text{CNR}]_2\)\(\text{H}_2\text{O}\) under all conditions gave only \([\text{Ru}(S\text{CNR}_2)_2L_2]\). All the \(^{31}\text{P}^{-1}\text{H}\) nmr spectra, (except \([\text{Ru}(S\text{CNMe}_2)_2(\text{PMePh}_2)_2]\) which was too insoluble for either \(^{31}\text{P}\) or \(^1\)H nmr studies), consisted of a singlet except those of \([\text{Ru}(S\text{CNMe}_2)_2(\text{PETPh}_2)_2]\) which contained
two singlets, the higher frequency signals decreasing in intensity as the temperature was raised from 213 to 298K. This suggested, as for \( [\text{Ru(S}_2\text{COMe)}_2(\text{PETPh})_2] \), an irreversible isomerisation, which was shown for \( [\text{Ru(S}_2\text{CNMe)}_2(\text{PETPh})_2] \) to be from the trans to the cis isomer by means of the relative intensities of the three \( {^7}\text{S}_2\text{CNMe}_2 \) methyl resonances in the \( {^1}\text{H} \) nmr spectrum at 301K, two of which are of equal intensity and much more intense than the third.

The \( {^1}\text{H} \) nmr spectra of the remaining complexes were all consistent with a cis stereochemistry. (See Table 3).

\[ \text{d) Proposed mechanism of formation of } [\text{Ru(S-S)}_2\text{L}_2] \text{ from } [\text{RuCl}_2\text{L}_3 \text{ or } 4] \]

In view of the above results, in which several intermediates produced in the formation of \( [\text{Ru(S-S)}_2\text{L}_2] \) have been isolated, a reaction scheme for the formation of \( [\text{Ru(S-S)}_2\text{L}_2] \text{ from } [\text{RuCl}_2\text{L}_3 \text{ and } 4] \) can now be proposed, (Scheme 2).

Thus for \( [\text{RuCl}_2\text{L}_3] \text{ (II)} \) 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 (IV) is stable in benzene when \( (\text{S-S})^{-} = {^7}\text{S}_2\text{PR}_2 \) but in alcohol, it loses chloride ion and converts to the cation (V) which can then react with more \( \text{Na}[{^7}\text{S}_2\text{PR}_2] \) to give (VI). However, (IV) is not stable in benzene in the presence of stronger nucleophiles such as \( ^{-}\text{S}_2\text{COMe} \) and \( ^{-}\text{S}_2\text{CNR}_2 \), which replace the chloride ion to produce (VI), although in polar solvents, for \( (\text{S-S})^{-} = {^7}\text{S}_2\text{CNR}_2 \) 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 \( [\text{RuCl}_2\text{L}_4] \text{ (I)} \) the reaction with \( \text{Na}[{^7}\text{S}_2\text{PR}_2] \) 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 \(\text{Na}[\text{S}_2\text{CNR}^1_2]\times\text{H}_2\text{O}\) in alcohol produced the cationic species (VIII) containing four L groups, which is probably formed by the rapid attack of the more nucleophilic \(\text{S}_2\text{CNR}^1_2\) ligand on \([\text{RuCl}_2\text{L}_4]\), which occurs prior to loss of L. Subsequent loss of L and reaction with \(\text{S}_2\text{CNR}^1_2\) 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 \(\text{K}[\text{S}_2\text{COMe}]\) 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 \([\text{RuCl}_2(\text{P(OR)Ph}_2)_3]\) \((\text{R} = \text{Me, Et})\) with dithioacid ligands, as opposed to the corresponding reactions of \([\text{RuCl}_2\text{L}_4]\) \((\text{L} = \text{PMePh}_2, \text{P(OMe)}_2\text{Ph} )\) and \([\text{RuCl}_2(\text{PEtPh}_2)_3]\), which yield only \([\text{Ru(S-S)}\text{L}_2]\), 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 \([\text{Ru(S-S)}\text{L}_2]\) (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% $H_3PO_4$. 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 $\lambda$ (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 $\lambda_0$. A subsequent plot of $\lambda_0 - \lambda$ vs $C^{\frac{3}{2}}$ gave a straight line whose slope is a function of the ionic charges.$^{14}$ 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); $NaS_2CNR_{2}H_2O$ ($R = Me, Et; Ralph Emanuel$) $Na[S_2PMe_2]_2H_2O$,$^{15}$ $Na[S_2PPh_2]^{15}$ and $K[S_2COMe]^{16}$ were prepared by standard literature methods. The various $[RuCl_2L_3]$ or $4]$ complexes were prepared as described elsewhere.$^{3-7}$

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 [RuCl$_2$(PMe$_2$Ph)$_4$] (0.20 g) and Na[S$_2$PMe$_2$]-2H$_2$O (0.20 g) were shaken in benzene (20 ml) for 1 h. The resulting yellow solution was filtered to remove any unreacted Na[S$_2$PMe$_2$]-2H$_2$O 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:

v$_{PS_2}$ 600 cm$^{-1}$.

Chloro(dimethylphosphinodithioato)tris(methylidiphenylphosphinite)-ruthenium(II): The compounds [RuCl$_2$(P(OMe)Ph)$_3$] (0.20 g) and Na[S$_2$PMe$_2$]-2H$_2$O (0.20 g) were shaken in benzene (20 ml) for 1 h, 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; v$_{PS_2}$ 595 cm$^{-1}$.

Similarly, chloro(dimethylphosphinodithioato)tris(ethyldiphenylphosphinite)ruthenium(II) was prepared from [RuCl$_2$(P(0Et)Ph)$_3$] m.p. 116-118°C; v$_{PS_2}$ 595 cm$^{-1}$.

(Dimethylphosphinodithioato)tris(dimethylphenylphosphine)-ruthenium(II)tetraphenylborate: The compounds [RuCl$_2$(PMe$_2$Ph)$_4$] (0.20 g) and Na[S$_2$PMe$_2$]-2H$_2$O (0.20 g) were shaken in methanol (20 ml) for 5 m to give a red solution. After filtering to remove any unreacted Na[S$_2$PMe$_2$]-2H$_2$O, a solution of NaBPh$_4$ (0.20 g) in methanol (5 ml) was added and the red crystals formed were filtered off and washed with water and diethyl ether m.p. 149-151°C; v$_{PS_2}$, 580 cm$^{-1}$. Conductivity in acetone; slope of $\lambda_m$-1 vs C$^\frac{1}{2}$ plot = 192 (For [Ru$_2$Cl$_3$(P(OMe)Ph)$_2$]BPh$_4$, slope = 155; for [Ru($\eta$-C$_6$H$_5$)(NH)$_3$]$_2$(PF$_6$)$_2$, slope = 350). Similarly, reaction with Na[S$_2$PPh$_2$] produced red crystals of (diphenylphosphinodithioato)tris-
(dimethylphenylphosphine)ruthenium(II)tetraphenylborate m.p. 160-162°C; \( \nu_{PS_2} \), 570 cm\(^{-1}\).

(Dimethylphosphinodithioato)tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate m.p. 184-186°C; \( \nu_{PS_2} \), 580 cm\(^{-1}\); conductivity in acetone, slope = 215 and diphenylphosphinodithioato-tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate m.p. 150-152°C; \( \nu_{PS_2} \), 570 cm\(^{-1}\) were prepared as red-brown and orange-brown solids respectively by shaking \( [\text{RuCl}_2(P(\text{OMe})\text{Ph})_3] \) with Na\([\text{S}_2\text{PR}_2]\) in methanol for 5m., followed by addition of NaBPh\(_4\) in methanol to the resulting red solutions. Similarly, (dimethylphosphinodithioato)tris(ethyldiphenylphosphinite)ruthenium(II)tetraphenylborate m.p. 116-118°C; \( \nu_{PS_2} \), 580 cm\(^{-1}\) and diphenylphosphinodithioato-tris(ethyldiphenylphosphinite)ruthenium(II)tetraphenylborate m.p. 174-176°C; \( \nu_{PS_2} \), 570 cm\(^{-1}\) were prepared as red-brown and orange-brown solids respectively.

Bis(dimethylphosphinodithioato)bis(ethyldiphenylphosphinite)ruthenium(II):- The compounds \( [\text{RuCl}_2(P(\text{OEt})\text{Ph})_3] \) (0.20g) and Na\([\text{S}_2\text{PMe}_2]\)\(2\text{H}_2\text{O}\) (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 \( [\text{RuCl}_2(P(\text{OMe})\text{Ph})_4] \) (0.20g) and Na\([\text{S}_2\text{PMe}_2]\)\(2\text{H}_2\text{O}\) (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 \( [\text{RuCl}_2(P(\text{OMe})\text{Ph})_4] \) with Na\([\text{S}_2\text{PPh}_2]\).
O-methyldithiocarbonate complexes

Bis(O-methyldithiocarbonato)tris(dimethylphenylphosphine)ruthenium(II): The compounds [RuCl₂(PMe₂Ph)₄] (0.20 g) and K₂S₂COMe (0.20 g) were shaken in methanol (30 ml.) for 2 h. 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(O-methyldithiocarbonato)tris(dimethylphenylphosphinite)ruthenium(II), m.p. 111-113°C and bis-(O-methyldithiocarbonato)tris(methylhexylphosphinite)ruthenium(II) m.p. 106-108°C were prepared similarly from [RuCl₂(P(OR)₂Ph)₃] (R = Me, Et) respectively. Bis(O-methyldithiocarbonato)bis(dimethyldiphenylphosphinite)ruthenium(II):- The compound [Ru(S₂COMe)₂(P(OMe)Ph₂)₃] (0.20 g) was refluxed in CH₂Cl₂ (20 ml.) containing K[S₂COMe] (0.05 g) for 1 h. to give an orange-yellow solution. Methanol (10 ml.) 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(O-methyldithiocarbonato)bis(methyldiphenylphosphinite)ruthenium(II):- The compounds [RuCl₂(PMe₃Ph)₄] (0.20 g) and K[S₂COMe] (0.20 g) were shaken in methanol for 12 h. The bright yellow solid obtained was filtered off and washed with water and diethyl ether m.p. 163-165°C. The complex bis(O-methyldithiocarbonato)bis(ethyldiphenylphosphinite)ruthenium(II) was prepared similarly as a yellow solid from [RuCl₂(PEt₃Ph)₃] m.p. 147-149°C.

N,N dialkyldithiocarbamate complexes

(Dimethyldithiocarbamate)tetrakis(dimethylphenylphosphine)ruthenium(II)-tetraphenylborate: The compounds [RuCl₂(PMe₂Ph)₄] (0.20 g) and Na[S₂CNMe₂]₂H₂O (0.20 g) were shaken in methanol for 5 h. After filtering, NaB₄P₄ (0.20 g) was added, the white precipitate filtered off and washed with methanol and diethyl ether m.p. 154-155°C; ν 1525 cm⁻¹;
conductivity in CH$_2$Cl$_2$, slope of $\frac{1}{V} - \frac{1}{V_0}$ vs. $C^2$ plot = 185. Similarly, (diethylthiocarbamato)tetrakis(dimethylphenylphosphine)ruthenium(II)-tetraphenylborate, $\nu_{CN}$ 1492 cm$^{-1}$, was prepared using Na[S$_2$CNEt$_2$]$_3$H$_2$O.

Bis(dimethylthiocarbamato)tris(dimethylphenylphosphine)ruthenium(II)-
The compounds [RuCl$_2$($^{13}$POMe$_2$Ph)$_4$] (0.20g) and Na[S$_2$CNMe$_2$]$_2$H$_2$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; $\nu_{CN}$ 1510 cm$^{-1}$. Bis(dimethylthiocarbamato)tris(methylidiphenylphosphinite)ruthenium(II), was prepared similarly from [RuCl$_2$($^{13}$POMe$_2$Ph)$_3$] m.p. 95-97°C; $\nu_{CN}$ 1500 cm$^{-1}$ (broad).

(Dimethylthiocarbamato)tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate:- The compounds [RuCl$_2$($^{13}$POMe$_2$Ph)$_3$] (0.20g) and Na[S$_2$CNMe$_2$]$_2$H$_2$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 CH$_2$Cl$_2$/MeOH gave yellow crystals of [Ru$_2$Cl$_3$($^{13}$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; $\nu_{CN}$ 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; $\nu_{CN}$ 1510 cm$^{-1}$. Similarly, reaction with Na[S$_2$CNEt$_2$]$_3$H$_2$O gave (diethylthiocarbamato)tris(methylidiphenylphosphinite)ruthenium(II)tetraphenylborate as red crystals, $\nu_{CN}$ 1480 cm$^{-1}$ and bis(diethylthiocarbamato)-
bis(methylidiphenylphosphinite)ruthenium(II) as yellow crystals m.p. 170-172°C; $\nu_{CN}$ 1482 cm$^{-1}$.

Bis(dimethylthiocarbamato)bis(dimethylphenylphosphonite)ruthenium-
(II):- The compounds [RuCl$_2$($^{13}$POMe$_2$Ph)$_4$] (0.20g) and Na[S$_2$CNMe$_2$]$_2$H$_2$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; $\nu_{CN}$ 1520 cm$^{-1}$. Reaction with Na[S$_2$CNEt$_2$]$_3$H$_2$O yielded
yellow crystals of bis(diethylidithiocarbamato)bis(dimethylphenylphosphonite)ruthenium(II) m.p. 125-127°C; $\nu_{\text{CN}}$ 1482 cm$^{-1}$. The complexes bis(dimethylidithiocarbamato)bis(methylidiphosphine)ruthenium(II) m.p. 229-231°C; $\nu_{\text{CN}}$ 1515 cm$^{-1}$; bis(diethylidithiocarbamato)bis(methylidiphosphine)ruthenium(II), m.p. 84-86°C; $\nu_{\text{CN}}$ 1485 cm$^{-1}$; bis(dimethylidithiocarbamato)bis(ethylidiphosphine)ruthenium(II) m.p. 133-135°C; $\nu_{\text{CN}}$ 1515 cm$^{-1}$ and bis(diethylidithiocarbamato)bis(ethylidiphosphine)ruthenium(II) m.p. 152-154°C; $\nu_{\text{CN}}$ 1480 cm$^{-1}$ were all obtained as yellow solids by shaking $[\text{RuCl}_2(\text{PMePh}_3)_2]_2$ (0.20g) and $[\text{RuCl}_2(\text{PETPPh}_3)_2$] (0.20g) respectively with $\text{Na}[\text{S}_2\text{CNEt}_2]_2\text{H}_2\text{O}$ (0.20g) and $\text{Na}[\text{S}_2\text{CNEt}_2]_3\text{H}_2\text{O}$ (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 $^{31}\text{P}$ and $^1\text{H}$ 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.


### Analytical data for some ruthenium(II) dithioacid complexes

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<td>[Ru(S₂PMe₂)(P(OEt)Ph₂)₃]BPh₄</td>
<td>35.5 4.8</td>
<td>688 34.7 4.9</td>
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<tr>
<td>[Ru(S₂PPh₂)(P(OEt)Ph₂)₃]BPh₄</td>
<td>51.0 4.6</td>
<td>51.1 4.5</td>
</tr>
<tr>
<td>[Ru(S₂COMe₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>52.5 4.9</td>
<td>53.4 4.7</td>
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<tr>
<td>[Ru(S₂COMe₂)(P(OMe)Ph₂)₃]BPh₄</td>
<td>53.9 5.1</td>
<td>54.9 5.1</td>
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<tr>
<td>[Ru(S₂COMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>45.6 5.3</td>
<td>726 46.0 5.3</td>
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<tr>
<td>[Ru(S₂COMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>50.5 4.5</td>
<td>50.4 4.5</td>
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<tr>
<td>[Ru(S₂COMe₂)(PETPh₂)₂]</td>
<td>51.4 4.8</td>
<td>51.6 4.8</td>
</tr>
<tr>
<td>[Ru(S₂COMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>49.1 4.3</td>
<td>48.4 4.3</td>
</tr>
<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>65.3 6.3 1.4 612 64.2 6.2 1.5 546</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>66.0 6.5 1.3</td>
<td>65.3 6.6 1.2</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
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<td>54.7 5.2 2.8</td>
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<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
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<td>66.6 5.4 1.2</td>
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<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
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<td>67.0 5.6 1.2</td>
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<td>49.8 4.9 3.6</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
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<td>52.1 5.5 3.4</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
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<td>37.7 4.8 4.0</td>
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<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>42.0 5.5 3.7</td>
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<td>51.8 5.1 3.8</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>52.9 5.5 3.3</td>
<td>54.2 5.7 3.5</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>53.3 5.3 3.4</td>
<td>53.1 5.4 3.6</td>
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<tr>
<td>[Ru(S₂CNMe₂)(PMe₂Ph)₃]BPh₄</td>
<td>57.1 5.9 3.2</td>
<td>55.3 6.0 3.4</td>
</tr>
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*a* Measured osmometrically at 37°C in CHCl₃

*b* Half actual molecular weight since 1:1 electrolyte
### TABLE 2

Phosphorus – 31 nmr data (proton-noise decoupled) for some ruthenium dithioacid complexes in CDCl$_3$

<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>$\delta_{SP}^a$</th>
<th>Other resonances $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<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; $^2J</em>{AB}$ 33.0Hz)</td>
</tr>
<tr>
<td>[RuCl($S_2$PMe$_2$)(POMe$_2$Ph)$_3$]</td>
<td>298</td>
<td>96.65$^d$</td>
<td>139.67$^d$</td>
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<tr>
<td>[RuCl($S_2$PMe$_2$)(POEt$_2$Ph)$_3$]</td>
<td>298</td>
<td>109.38$^d$</td>
<td>140.42$^d$</td>
</tr>
<tr>
<td>[Ru($S_2$PMe$_2$)(PMe$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>110.31(q)</td>
<td>32.36(d) ($^3J_{PP}$ = 3.6Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$PPh$_2$)(PMe$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>104.26$^d$</td>
<td>32.29$^d$</td>
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<tr>
<td>[Ru($S_2$PMe$_2$)(POMe$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>111.58(q)</td>
<td>144.85(d) ($^3J_{PP}$ = 4.4Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$PPh$_2$)(POMe$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>103.96$^d$</td>
<td>144.98$^d$</td>
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<tr>
<td>[Ru($S_2$PMe$_2$)(POEt$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>109.90(q)</td>
<td>141.53(d) ($^3J_{PP}$ = 4.7Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$PPh$_2$)(POEt$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>102.52(q)</td>
<td>141.39(d) ($^3J_{PP}$ = 4.8Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$PMe$_2$)(POEt$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>303</td>
<td>86.70(t)</td>
<td>140.76(t) ($^3J_{PP}$ = 6.0Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$PMe$_2$)(POEt$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>88.53(t)</td>
<td>170.54(t) ($^3J_{PP}$ = 6.8Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$PPh$_2$)(POEt$_2$Ph)$_3$]$^3$BPh$_4$</td>
<td>298</td>
<td>89.47(t)</td>
<td>170.97(t) ($^3J_{PP}$ = 6.3Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$COMe)$_2$)(PMe$_2$Ph)$_3$]</td>
<td>298</td>
<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 7.62; $\nu_B$ 10.61; $^2J</em>{AB}$ 30.3Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$COMe)$_2$)(POMe$_2$Ph)$_3$]</td>
<td>298</td>
<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 136.70; $\nu_B$, 138.89; $^2J</em>{AB}$ 35.0 Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$COMe)$_2$)(POEt$_2$Ph)$_3$]</td>
<td>298</td>
<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 132.64; $\nu_B$, 135.06; $^2J</em>{AB}$ 34.8 Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$COMe)$_2$)(POEt$_2$Ph)$_3$]</td>
<td>298</td>
<td>-</td>
<td>146.51(s)</td>
</tr>
<tr>
<td>[Ru($S_2$COMe)$_2$)(PMePh)$_2$]</td>
<td>218</td>
<td>-</td>
<td>30.89(s)</td>
</tr>
<tr>
<td>[Ru($S_2$COMe)$_2$)(PET$_2$Ph)$_2$]</td>
<td>218</td>
<td>-</td>
<td>50.32(s)$^e$, 44.31(s)$^f$</td>
</tr>
<tr>
<td>[Ru($S_2$CNMe)$_2$)(PMe$_2$Ph)$_4$]$^3$BPh$_4$</td>
<td>298</td>
<td>-</td>
<td>6.02(t), -3.68(t) ($^2J_{PP}$ = 27.0Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$CNMe)$_2$)(PMe$_2$Ph)$_4$]$^3$BPh$_4$</td>
<td>298</td>
<td>-</td>
<td>5.12(t), -3.32(t) ($^2J_{PP}$ = 28.0Hz)</td>
</tr>
<tr>
<td>[Ru($S_2$CNMe)$_2$)(PMe$_2$Ph)$_3$]</td>
<td>298</td>
<td>-</td>
<td>AB$<em>2$ pattern; ($\nu_A$, 14.19; $\nu_B$, 11.48; $^2J</em>{AB}$ 29.5Hz)</td>
</tr>
<tr>
<td>Complex</td>
<td>T/K</td>
<td>$\delta^a$/ppm</td>
<td>Other resonances$^b$</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>-----</td>
<td>----------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNMe}_2\text{)}_2(\text{POMe})\text{Ph}_2\text{)}_2]$</td>
<td>218</td>
<td>-</td>
<td>143.80$^d$</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNMe}_2\text{)}_2(\text{POMe})\text{Ph}_2\text{)}_3]\text{BPh}_4$</td>
<td>218</td>
<td>-</td>
<td>145.47(s)</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNEt}_2\text{)}_2(\text{POMe})\text{Ph}_2\text{)}_3]\text{BPh}_4$</td>
<td>218</td>
<td>-</td>
<td>145.54(s)</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNMe}_2\text{)}_2(\text{POMe})\text{Ph}_2\text{)}_2]$</td>
<td>298</td>
<td>-</td>
<td>147.57(s)</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNEt}_2\text{)}_2(\text{POMe})\text{Ph}_2\text{)}_2]$</td>
<td>298</td>
<td>-</td>
<td>148.37(s)</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNEt}_2\text{)}_2(\text{PMe})\text{Ph}_2\text{)}_2]$</td>
<td>298</td>
<td>-</td>
<td>31.40(s)</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNEt}_2\text{)}_2(\text{PETPh}_2\text{)}_2]$</td>
<td>218</td>
<td>-</td>
<td>54.42(s)$^e$, 45.76(s)$^f$</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNEt}_2\text{)}_2(\text{PETPh}_2\text{)}_2]$</td>
<td>218</td>
<td>-</td>
<td>54.11(s)$^e$, 45.82(s)$^f$</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNMe}_2\text{)}_2(\text{POMe})\text{Ph}_2\text{)}_2]$</td>
<td>298</td>
<td>-</td>
<td>176.15(s)</td>
</tr>
<tr>
<td>$[\text{Ru(S}_2\text{CNEt}_2\text{)}_2(\text{POMe})\text{Ph}_2\text{)}_2]$</td>
<td>298</td>
<td>-</td>
<td>176.64(s)</td>
</tr>
</tbody>
</table>

(s) - singlet;  (d) - doublet;  (t) - triplet;  (q) - quartet

$^a$ Chemical shifts reported to high frequency of 85% H$_3$PO$_4$.

$^b$ Resonances from tertiary phosphine, phosphonite or phosphonite ligands.

$^c$ Multiplet resembling unsymmetrical quartet.

$^d$ Broad.  $^e$ Decreases in intensity as temperature raised.

$^f$ Increases in intensity as temperature raised.
<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>Dithioligand</th>
<th>Other resonances</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{RuCl(S}_2\text{PMe}_2')(\text{PMe}_2\text{Ph})_3])</td>
<td>233</td>
<td>2.17(d), 1.19(d) (^2J_{\text{PH}}) 12.5Hz</td>
<td>1.60(d) (^2J_{\text{PH}}) 8.0Hz</td>
</tr>
<tr>
<td>([\text{RuCl(S}_2\text{PMe}_2')(\text{P[OMe]Ph}_2)_3])</td>
<td>301</td>
<td>1.36(d) (^2J_{\text{PH}}) 12.0Hz</td>
<td>1.88 (^a) 7.28-7.36(m) (^b)</td>
</tr>
<tr>
<td>([\text{RuCl(S}_2\text{PMe}_2')(\text{P[OEt]Ph}_2)_3])</td>
<td>301</td>
<td>1.52(d) (^2J_{\text{PH}}) 12.0Hz</td>
<td>3.20 (^a); 7.10-7.60(m) (^b)</td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{PMe}_2')(\text{PMe}_2\text{Ph})_3]) BPh₄</td>
<td>301</td>
<td>1.82(d) (^2J_{\text{PH}}) 13.0Hz</td>
<td>1.37(pt) (N=8.0\text{Hz}) (^b) 6.96-7.50(m) (^b)</td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{PMe}_2')(\text{P[OMe]Ph}_2)_3]) BPh₄</td>
<td>301</td>
<td>1.44(d) (^2J_{\text{PH}}) 12.5Hz</td>
<td>3.12(pt) (N=11.5\text{Hz}) (^b) 6.98-7.50(m) (^b)</td>
</tr>
<tr>
<td>([\text{Ru(S}_2\text{PMe}_2')(\text{P[OEt]Ph}_2)_3]) BPh₄</td>
<td>301</td>
<td>1.36(d) (^2J_{\text{PH}}) 13.0Hz</td>
<td>1.19(t), 3.40 (^a) 6.94-7.50(m) (^b)</td>
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<td>([\text{Ru(S}_2\text{PMe}_2')(\text{P[OEt]Ph}_2)_2])</td>
<td>301</td>
<td>1.43(d) (^2J_{\text{PH}}) 12.0Hz</td>
<td>1.20(t) (^3J_{\text{HH}}) 7.0Hz</td>
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<tr>
<td>([\text{Ru(S}_2\text{PMe}_2')(\text{P[OMe]Ph}_2)_2])</td>
<td>213</td>
<td>1.71(d), 2.12(d) (^2J_{\text{PH}}) 13.0Hz</td>
<td>3.42(pt), 3.58(pt) (N=12.0\text{Hz}) 7.36-7.70(m) (^b)</td>
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<td>([\text{Ru(S}_2\text{COMe}_2')(\text{PMe}_2\text{Ph})_3])</td>
<td>301</td>
<td>3.65(s), 3.92(s)</td>
<td>1.83(pt) (N=8.0\text{Hz})</td>
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<td></td>
<td>1.19(d) (^2J_{\text{PH}}) 7.5Hz</td>
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<td>7.30-7.60(m) (^b)</td>
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<tr>
<td>Complex</td>
<td>T/K</td>
<td>Dithioligand</td>
<td>δ±0.01ppm</td>
</tr>
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<tr>
<td>[Ru(S_{2}COMe)<em>{2}(P{OMe}Ph</em>{2})_{3}]</td>
<td>301</td>
<td>3.33(s),3.46(s)</td>
<td>3.22(pt)(N=11.0Hz)</td>
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<td>3.10(d)(J_{PH} 10.5Hz)</td>
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<td>7.00-7.60(m)</td>
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<tr>
<td>[Ru(S_{2}COMe)<em>{2}(P{OEt}Ph</em>{2})_{3}]</td>
<td>301</td>
<td>2.96(s),3.33(s)</td>
<td>3.00-3.40(m)</td>
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<td>1.26(m)</td>
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<td>[Ru(S_{2}COMe)<em>{2}(P{OMe}Ph</em>{2})_{2}]</td>
<td>301</td>
<td>3.71</td>
<td>3.22(pt)(N=11.0Hz)</td>
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<td>7.10-7.40(m)</td>
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<tr>
<td>[Ru(S_{2}COMe)<em>{2}(PMePh</em>{2})_{2}]</td>
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<td>3.81(s)</td>
<td>1.88(pt)(N=7.5Hz)</td>
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<td>7.18(m)</td>
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<td>[Ru(S_{2}COMe)<em>{2}(PEtPh</em>{2})_{2}]</td>
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<td>3.72(s),3.85(s)</td>
<td>2.30, 0.60(m)</td>
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<td>7.18(m)</td>
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<td>[Ru(S_{2}CNMe_{2})(PMe_{2}Ph)<em>{4}]BPh</em>{4}</td>
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<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)</td>
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<td>[Ru(S_{2}CNMe_{2})(PMe_{2}Ph)<em>{4}]BPh</em>{4}</td>
<td>301</td>
<td>2.90(q),0.82(t)(^{3}J_{HH} 7.0Hz)</td>
<td>1.72(pt)(N=6.5Hz)</td>
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<td>1.27(t)(N=5.0Hz)</td>
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<td>6.98-7.44(m)</td>
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<td>[Ru(S_{2}CNMe_{2})(PMe_{2}Ph)_{3}]</td>
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<td>2.90(s),3.49(s)</td>
<td>1.96, 1.07(d)(^{2}J_{PH} 8.0Hz)</td>
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<td>7.31(m)</td>
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<tr>
<td>[Ru(S_{2}CNMe_{2})(P{OMe}Ph_{2})_{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></td>
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<td>7.20-7.60(m)</td>
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</tbody>
</table>
TABLE 3  (continued)

<table>
<thead>
<tr>
<th>Complex</th>
<th>T/K</th>
<th>( \delta \pm 0.01 )ppm</th>
<th>Other resonances</th>
</tr>
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<tbody>
<tr>
<td>([ Ru(S_2CNEt_2)^2(POMePh_2)_2 ] )</td>
<td>301</td>
<td>3.44( q ); 3.60( q )</td>
<td>3.22( pt )( N=11.0 )Hz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.06( t ); 1.09( t )</td>
<td>7.20-7.60( m )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^3)( J_{HH} )7.0Hz</td>
<td></td>
</tr>
<tr>
<td>([ Ru(S_2CNEt_2)(PMPh_2)_2 ] )</td>
<td>301</td>
<td>3.57( ^e ) 1.07( t )( ^3)( J_{HH} )7.0Hz</td>
<td>1.78( pt )( N=4.0 )Hz</td>
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<tr>
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<td>7.10-7.40( m )^b</td>
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<td>([ Ru(S_2CNMe_2)(PETPh_2)_2 ] )</td>
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<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>([ Ru(S_2CNET_2)(PETPh_2)_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>1.11^i</td>
<td>7.00-7.40( m )^b</td>
</tr>
<tr>
<td>([ Ru(S_2CNMe_2)(POMePh_2)_2 ] )</td>
<td>301</td>
<td>2.91( s ); 3.04( s )</td>
<td>3.48( t ), 3.61( t )( N=7.5 )Hz</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

\( N = |J(\text{PH}) + J(\text{PH})|^1 | \)

\( ^a \) Broad resonance  \( ^b \) Phenyl group resonances  \( ^c \) Overlapping quartets  \( ^d \) Contains at least one triplet

\( ^e \) ABM\(_3\) 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 1.186 are observed.
1. Possible rearrangements of \([\text{RuCl}_2(\text{S}_2\text{PMe}_2)\text{L}_3]\) at 298K

2. Mechanism of formation of \([\text{Ru}(\text{S-S})_2\text{L}_2]\) from \([\text{RuCl}_2\text{L}_4]\) and \([\text{RuCl}_2\text{L}_3]\).

(*cis isomer for \(\text{L} = \text{PMe}_2\text{Ph};\) trans isomer for \(\text{L} = \text{P(OMe)}_2\text{Ph}\))
Scheme 1
Scheme 2