Some Reactions of Coordinated Ligands in

Platinum Metal Chemistry

By

Iain W. Robertson
To my parents
DECLARATION

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results have already been published.
I am indebted to Dr. T.A. Stephenson for his encouragement and assistance during the length of this work. I am also grateful to the University of Edinburgh for financial assistance and experimental facilities and to Johnson Matthey Ltd. for loans of precious metals.

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Finally, I am indebted to Miss A. Erskine for typing this manuscript.
ABSTRACT

Chapter 1: A brief survey of the chemistry of coordinated arene and halo phosphorus ligands is given.

Chapter 2: The synthesis and characterisation of some \( \eta^6 \)-arene complexes of ruthenium(II) is described. The reaction of these arene complexes containing non-labile ligands with various anionic nucleophiles leads to the formation of \( \eta^5 \)-cyclohexadienyl complexes.

Chapter 3: The preparation and characterisation of several arene cyclopentadienyl complexes of ruthenium(II) and osmium(II) is described. Ruthenocene is prepared but does not react readily with arenes to yield the mixed sandwich complexes. This behaviour is contrasted with that of ferrocene. The arene cyclopentadienyl cations are not found to undergo reaction with nucleophiles to give stable products.

Chapter 4: The synthesis and characterisation of some complexes of ruthenium(II) containing chlorophosphine and tertiary phosphinite ligands is described and some possible mechanisms for their formation are discussed. The complexes are not found to undergo nucleophilic displacement and hydrolysis reactions at phosphorus to give new substituted phosphine complexes.

Chapter 5: The reactions of \( \text{PPh}_2\text{Cl} \) with various ruthenium complexes under solvolysis conditions are described. The stereochemically non-rigid complex \( \text{Ru}(\text{S}_2\text{PMe}_2)\{(\text{PPh}_2\text{O})_3\text{H}_2\} \) was prepared and fully characterised. Its reactions with various \( \text{M(acac)}_n \)
BF$_3$·Et$_2$O and CO were studied. The unusual binuclear complex [Ru$_2$Cl$_2$(μ-P(OMe)$_2$O)(p-MeC$_6$H$_4$CHMe$_2$)$_2$]PF$_6$ was prepared and characterised by its $^1$H n.m.r. spectrum and analytical data. A possible mechanism for its formation is proposed.

Chapter 6: The electrochemical behaviour of several of the new compounds discussed in the previous chapters is described and the results briefly discussed.

Appendix: Some aspects of the $^{31}$P-$^1$H n.m.r. relaxation effects in the spectra of several of the compounds described in Chapters 4 and 5 are discussed.
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CHAPTER 1

Some Reactions of Coordinated Ligands
1.1 Introduction

Since this thesis is concerned with reactions of coordinated arenes (Chapters 2 and 3) and reactions of coordinated phosphine ligands (Chapters 4 and 5), some of the earlier work on these subjects is discussed briefly in this introductory first chapter.

1.2 Reactions of coordinated arenes

The coordination of an arene ring to a transition metal ion can considerably modify its reactivity towards various types of reagent. The most important effect of coordination is on reactivity towards nucleophilic and electrophilic substitution.

Thus, the reaction of an aromatic compound with nucleophiles is greatly enhanced by coordination to a metal ion. This can be explained by the shift of electron density away from the arene, induced by the positive charge on the metal ion. This is supported by the decrease in metal-ligand interaction when electron releasing substituents are present on the arene, as reflected in mass spectral fragmentation studies. This drain of electrons is also shown by the increased acidity of coordinated phenol and benzoic acid, and the decreased basicity of aniline in arene metal tricarbonyl complexes. The metal tricarbonyl unit thus produces a similar effect to the nitro-group in uncoordinated arenes. In these complexes the carbonyl groups act as a sink for the electron density withdrawn from the arene. This effect is demonstrated by the observed
dipole moments of a range of Cr(arene)(CO)₃ complexes which indicate a large charge separation with the carbonyl groups being negative with respect to the arene. Hydrogen-1-n.m.r. studies show that the aromatic proton resonances shift to low frequency on complexation⁵, which also indicates a withdrawal of electrons from the ring. Finally, molecular orbital calculations show a net positive charge on the arene group in the Cr(η-C₆H₆)(CO)₃ complex⁶.

When a nucleophile reacts with a complexed arene, the reaction can follow two possible routes, either resulting in simple addition of the nucleophile to the ring, forming an η⁵-cyclohexadienyl complex, or replacement of a suitable leaving group, forming a substituted arene complex.

The first type of reaction tends to occur with cationic arene complexes in which the overall positive charge on the cation increases the net positive charge on the arene ring. The η⁵-cyclohexadienyl ligand which results from this reaction is stabilised by coordination to a metal centre. A good example of this type of reaction is that of the cation [Fe(η-C₆H₆)(η-C₅H₅)]⁺ with LiAlH₄ (which acts as a source of hydride ion) to give the neutral complex Fe(η⁵-C₆H₇)(η-C₅H₅)⁷. Other nucleophiles such as alkyl anions also add to give Fe(η⁵-C₆H₆R)(η-C₅H₅), and the isoelectronic manganese cation [Mn(η-C₆H₆)(CO)₃]⁺ adds hydride ion to give Mn(η⁵-C₆H₇)(CO)₃ in a similar way⁸.

The second type of reaction, which is equivalent to a nucleophilic aromatic substitution, occurs in the case of
arene metal tricarbonyls in which the arene bears a suitable leaving group such as a chlorine atom. A typical reaction of this type is that of a carbonion $R^-$ with $\text{Cr}(\eta-C_6H_5Cl)(CO)_3$ (1) (equation [1]).

![Proposed Mechanism of Nucleophilic Substitution of Cr(\eta-C_6H_5Cl)(CO)_3](image)

The above reaction has been shown to involve a series of equilibria between intermediates (3)-(6) (Figure 1.1).

![Proposed Mechanism of Nucleophilic Substitution of Cr(\eta-C_6H_5Cl)(CO)_3](image)
Intermediate (6) can then undergo irreversible elimination of chloride ion to give (2). The equilibria between the various intermediates have been demonstrated by quenching reactions of the type shown above with a mild oxidising agent such as iodine which produces mixtures of the arenes derived from the cyclohexadienyl complexes (3)-(5) which are present in the early stages of the reaction. For example, reaction of Cr(n-C_{6}H_{5}Cl)(CO)_{3} with Li[C(CH_{3})_{2}CN] for a short period followed by iodine oxidation gave a mixture of the three arenes (7-9).

![Chemical structures](image)

The intermediates shown in Figure 1.1 are analogous to those postulated for nucleophilic attack on highly activated arenes^{10} e.g. reactions of 1,3,5-trinitrochlorobenzene (equation [2]).
An alternative route for nucleophilic aromatic substitution is that involving an aryne intermediate which occurs when the nucleophile is a strong base and there are no activating groups on the arene (equation [3]).

This mechanism can be eliminated as a possibility for coordinated arenes by studying the products when alkyl substitution is present on the arene, e.g. the reaction of Cr(p-FC₆H₄Me)(CO)₃ with sodium methoxide gave only Cr(p-MeOC₆H₄Me)(CO)₃ and no meta isomer which should be formed by random attack of methoxide on the aryne if it had been generated.

On prolonged reaction between Cr(η-C₆H₅Cl)(CO)₃ and Li[C(CH₃)₂CN], only the substitution product (2) is obtained, in almost quantitative yield. This reaction is thus a convenient method for obtaining alkylated arenes from aryl halides as the arene can be easily coordinated to the metal by reaction with Cr(CO)₆₁¹ and the organic moiety then removed by oxidation of the complex with iodine or cerium(IV) ion¹¹,¹².

The addition of nucleophiles in these reactions is almost exclusively exo i.e. to the face of the arene
Evidence for this stereospecificity is supplied by a combination of spectroscopic and chemical evidence. For example, a recent study of the reactions of the dicationic sandwich cation $[\text{Rh}(\eta^5-\text{C}_5\text{Me}_4\text{Et})(\eta^6-\text{C}_6\text{H}_6)]^{2+}$ demonstrated, both by hydrogen-1- n.m.r. and x-ray structural analysis, that addition to the arene ring was exclusively exo. Thus, the deuterated cation $[\text{Rh}(\eta^5-\text{C}_5\text{Me}_4\text{Et})(\eta^6-\text{C}_6\text{D}_6)]^{2+}$ was treated with hydride ion to obtain the $[\text{Rh}(\eta^5-\text{C}_5\text{Me}_4\text{Et})-(\eta^5-\text{C}_5\text{D}_6\text{H})]^+$ cation. This cation has a proton n.m.r. spectrum which consists of a single line at the position assigned to the exo hydrogen in the non-deuterated cation. This evidence indicates that addition must be stereospecific as non-stereospecific addition would lead to a mixture of two cations, each of which would show a single line in its $^1\text{H}$ n.m.r. spectrum. The hexafluorophosphate salt of the cation shows a strong infra-red spectral band at the low frequency of 2825 cm$^{-1}$. The presence of a band at this frequency has been interpreted as good evidence for the presence of an exo hydrogen. This product slowly loses
hydride ion in solution (accelerated by the presence of protons) to give isotopically pure \([\text{Rh}(\eta^5\text{C}_5\text{Me}_4\text{Et})(\text{C}_6\text{D}_6)](\text{PF}_6)_2\)
(better than 95\% isotopic purity on the basis of \(^1\text{H}\) n.m.r. evidence), and therefore both addition and loss of hydride ion must be stereospecific. Also an x-ray structural study of the product of the reaction (10) between the \([\text{Rh}(\eta^5\text{C}_5\text{Me}_4\text{Et})-(\text{C}_6\text{H}_6)]^{2+}\) and trimethyl phosphite\(^{14}\) shows that the added nucleophile occupies the \textit{exo} position on the cyclohexadienyl ligand.

Another example of this stereospecificity is the complex \(\text{Re}(\eta^5\text{C}_6\text{Me}_6\text{H})(\text{CO})_3\)\(^{15}\) (11) which is obtained by the addition of hydride ion to the cation \([\text{Re}(\eta^5\text{C}_6\text{Me}_6)(\text{CO})_3]^+\). An x-ray diffraction study shows that the methyl group on the ring carbon which has been attacked by the hydride ion is in the \textit{endo} position. As the steric interaction between the metal ion and an \textit{endo} methyl group must be greater than that with an \textit{endo} hydrogen atom there must be a compelling reason for the hydrogen to occupy the \textit{exo} position preferentially. (See later).
As mentioned above, the infra-red spectra of complexes containing an exo hydrogen on the ring have frequently been found to contain a sharp band at around 2800 - 2900 cm\(^{-1}\). This has generally been interpreted as good evidence of the presence of an exo C-H bond. The low frequency of the C-H stretching vibration is often explained by an interaction between the delocalised π-orbitals of the cyclohexadienyl ligand and the σ orbital of the exo C-H bond. The geometry of the system is such that appreciable overlap between these orbitals is then possible. The drain of electron density from the π-system produced by the positive charge on the metal results in a drain from the C-H\(_{exo}\) bond. This produces a weakening of the bond, thus reducing the vibrational frequency. It is interesting to note that it was originally thought that the low frequency position was due to a direct interaction between the metal and the C-H bond leading to an assignment of the stereochemistry of attack as endo rather than exo.

Recently, however, the use of a low frequency C-H stretch in the infra-red spectrum of a complex of a carbocyclic ligand to assign the stereochemistry of addition has been questioned\(^{16}\). Thus, treatment of a cationic arene complex with deuteride ion instead of hydride ion produces a cyclohexadienyl complex with no low frequency C-H stretching band in its infra-red spectrum. However the deuteration will affect both the exo and endo C-H stretches since they are strongly coupled and cannot be considered separately from each other. It is therefore
suggested that the infra-red spectrum is not a reliable indication of \textit{exo} addition. It was shown that a more reliable method of obtaining stereochemical information was the deuterium n.m.r. spectrum. Studies of BD\textsubscript{4}\textsuperscript{-} treatment of the cycloheptatrienyl complex cation \([\text{Mo}(\pi\text{-C}_7\text{H}_7)(\text{CO})_3]^{+}\) showed that the addition was only moderately stereoselective with the \textit{exo}:\textit{endo} addition ratio being roughly 2.5:1 from the hydrogen-2- n.m.r. spectrum since signals due to both D\textsubscript{exo} and D\textsubscript{endo} groups were observed\textsuperscript{16}.

In spite of the above study, however, it appears that addition to coordinated arenes is generally stereospecific in nature. Two possible explanations have been advanced for this behaviour. It may be due either to steric shielding of the \textit{endo} face of the arene by the metal and the other associated ligands or to a distortion of the \(\pi\) orbitals of the arene by the metal which makes the \textit{exo} face more positive than the \textit{endo} face and thus favours \textit{exo} attack. Most probably, a combination of these two factors results in the observed \textit{exo} addition. The steric factor is clearly important since reactions involving groups attached to the ring also show a preference for one stereoisomer over the other, e.g. equation \([5]\textsuperscript{17}].
Mixed ring sandwich complexes bearing arene ligands almost invariably undergo reactions with nucleophiles on the arene rather than on the other carbocyclic ring, e.g. equations [6] - [8].

\[
\begin{align*}
\text{Fe} & + \text{H}^+ \rightarrow \text{Fe} & \text{[6]} \\
\text{Mo} & + \text{H}^- \rightarrow \text{Mo} & \text{[7]} \\
\text{Co} & + \text{H}^- \rightarrow \text{Co} & \text{[8]}
\end{align*}
\]

This preference for nucleophilic attack at an arene ring is rationalised by a set of rules proposed by Green et al.\textsuperscript{21}. These state that addition to a cyclic polyene is preferred for an even number of coordinated carbon atoms, i.e. attack on a \(\eta^6\)-polyene ring is favoured over \(\eta^7\) - or \(\eta^5\) polyene rings.
In an earlier paper, Green had also observed that addition of a nucleophile to a coordinated organic ligand tended to proceed in such a way that the formal oxidation state of the metal is retained, if the original cation is relatively electron rich.

One exception to these general rules, however, is in the reactions of the cation \( \text{[Fe(C}_5\text{H}_5)(\eta^5\text{-C}_6\text{Me}_6)]}^+ \). It undergoes hydride attack as predicted to give \( \text{Fe(\eta}^5\text{-C}_5\text{H}_5\text{-C}_6\text{Me}_6\text{H}) \) but reacts with methyllithium to give \( \text{Fe(\eta}^4\text{-C}_5\text{H}_5\text{Me})(\eta\text{C}_6\text{Me}_6) \). This difference in the site of attack is attributed to steric hindrance because of the methyl groups on the arene ring. Steric effects also operate in other hexamethylbenzene complexes. For example, the hexamethylbenzene manganese tricarbonyl complex often undergoes nucleophilic attack more readily on the carbonyl ligands than on the arene (Figure 1.2).

\[ \text{Figure 1.2} \]

Some Reactions of the \( \text{[Mn(\eta-C}_6\text{Me}_6)(\text{CO})}_3 \)^+ cation with Nucleophile.
The adducts formed by hydride addition can then be treated with hydride abstracting agents to regenerate the original cation (equation [9]).

\[
\begin{align*}
\text{Mn} & \quad + \text{Ph}_3\text{C}[\text{BF}_4] \quad \rightarrow \quad \text{Mn} \quad + \text{Ph}_3\text{CH} \\
\text{OC} \quad \text{CO} \quad \text{CO} & \quad \text{OC} \quad \text{CO} \quad \text{CO}
\end{align*}
\]  

[9]

The triphenylmethyl cation has a strong preference for exo abstraction (presumably steric in origin) but in the case of the hexamethylbenzene complex (12) the endo hydride on the C\textsubscript{5}H\textsubscript{5}Me ring is removed to give the methyl substituted cyclopentadienyl cation (13) (equation [10]).

\[
\begin{align*}
\text{Fe} & \quad + \text{Ph}_3\text{C}[\text{BF}_4] \quad \rightarrow \quad \text{Fe} \quad \text{BF}_4 \quad + \text{Ph}_3\text{CH} \\
\text{Me} & \quad \text{BF}_4 \quad \text{Ph}_3\text{CH}
\end{align*}
\]  

[10]
N-bromosuccinimide has also been used to abstract hydride ion from cyclohexadienyl complexes but it has less stereoselectivity than triphenyl methyl cation \(^{26}\). The triphenyl methyl cation will also remove some other nucleophiles such as cyanide ion (equation [11]) providing they are in the exo position.

\[
\begin{align*}
\text{CN} & \quad \text{H} \\
\text{Mn} & \quad + \text{Ph}_3\text{C}^{[\text{BF}_4]} \rightarrow \begin{bmatrix} \text{Mn}(\text{CO})_3 \end{bmatrix} \text{BF}_4 \\
\text{OC} & \quad \text{CO} \quad \text{CO}
\end{align*}
\]

[11]

Rearrangement of the cyclohexadienyl complex can also take place by migration of the endo hydrogen. For example, reaction of the \([\text{Mn}(\eta^5-\text{C}_6\text{H}_6\text{R})(\text{CO})_3]^+\) cation with alkyllithium produces the complex \(\text{Mn}(\eta^5-\text{C}_6\text{H}_6\text{R})(\text{CO})_3\). Heating this complex to \(130^\circ - 150^\circ\) then causes a rearrangement to occur and hydride abstraction with \(\text{Ph}_3\text{C}^{[\text{BF}_4]}\) can then take place \(^{26}\) (Figure 1.3)
1.3 Effects of substituents on arene ring reactivity

When the coordinated arene is substituted it tends to undergo nucleophilic attack at the unsubstituted positions\(^7\). Thus a complex of mesitylene (1,3,5-trimethylbenzene) will react at the C-H aromatic carbons rather than at the C-CH\(_3\) carbon positions. This is probably due in part to the electron releasing properties of the methyl group and also to the steric effect. The methyl group has, however, no apparent directive effect. A substituent such as methoxy which has a mesomeric as well as an inductive effect will tend to favour attack at a position meta to the substituent\(^28\) since this carries the least partial negative charge (equation [12]).

![Figure 1.3](image)

**Figure 1.3**

Rearrangement of the Mn\(\text{\(n^5\)-C\(_6\)H\(_6\)R})\)(CO)\(_3\) complex
The delocalisation of negative charge to the ortho and para positions will make these positions less susceptible to nucleophilic attack by reducing the partial positive charge caused by coordination. A \(-\text{CO}_2\text{Me}\) substituent\(^{29}\) leads to predominantly ortho hydride attack, whereas the \(-\text{NMe}_2\) group has a similar effect to the methoxy group and this is stronger than the effect of the methyl group. Thus, the cation [\(\text{Mn(}n\text{-}p\text{-MeC}_6\text{H}_4\text{NMe}_2\text{)}(\text{CO})_3\)]\(^{+}\) reacts with LiAlH\(_4\) to give the product (15\(^{30}\)) in which the hydride ion adds to a position meta to the \text{NMe}_2 group (Equation [13]).

\[
\text{MeO-} \xrightarrow{\text{ML}_x} \text{MeO}^+ \xrightarrow{\text{ML}_x} \text{MeO}^+ \quad [12]
\]
However, although these reactions do show some directive effects these are generally much less marked than for electrophilic substitution reactions on an uncoordinated arene. It has been suggested that the metal interferes with the transmission of electronic effects around the ring thus reducing the importance of resonance relative to inductive effects\textsuperscript{31}.

1.4 Other reactions of coordinated arenes

The acidity of the C-H bonds of coordinated arenes is much higher than that of the uncoordinated arene. Thus, Cr(\(\pi\)-C\(_6\)H\(_6\))\(_2\) will undergo H/D exchange when treated with sodium ethoxide in O-deuterated ethanol and the corresponding Cr(I) cation [Cr(\(\pi\)-C\(_6\)H\(_6\))\(_2\)]\(^+\) undergoes isotopic exchange when treated with NaOD in D\(_2\)O \textsuperscript{32}. In contrast the uncoordinated benzene ring does not undergo ring proton exchange even when treated with potassium amide in liquid ammonia.

The only known electrophilic substitution reaction of arene chromium tricarbonyl complexes is the Friedel Crafts acylation reaction undergone by benzene and substituted benzene chromium tricarbonyls to give the corresponding acetyl substituted complexes (equation [14]) \textsuperscript{33}.

\[
\begin{array}{c}
\text{C}_6\text{H}_6\text{Cr} \quad + \quad \text{CH}_3\text{COCl} \\
\begin{array}{c}
\text{OC} \\
\text{CO} \\
\text{CO}
\end{array}
\quad \rightarrow \quad \begin{array}{c}
\text{C}_6\text{H}_6\text{Cr} \\
\begin{array}{c}
\text{OC} \\
\text{CO} \\
\text{CO}
\end{array}
\end{array}
\end{array}
\]

\textsuperscript{33}
However, the complexed arene can undergo easy metallation reactions with alkyllithiums and alkylsodiu.rns although this type of reaction frequently gives multiple metallations and a complex mixture of products. A singly lithiated complex (17) can be obtained by treatment of the binuclear complex \([(CO)_{3}Cr(\text{n-C}_{6}\text{H}_{5}\text{HgC}_{6}\text{H}_{5})\text{Cr(CO)}_{3}]\) (16) with \text{n-bu}tyllithium\textsuperscript{34} (equation [15]).

\[
\begin{align*}
\text{Cr} & \quad \text{Cr} \\
\text{OC} \quad \text{CO} \quad \text{CO} & \quad \text{OC} \quad \text{CO} \quad \text{CO} \\
\text{Hg} & \quad \text{+ 2n-BuLi} \\
\text{(16)} & \quad \downarrow \\
\text{Cr} & \quad \text{Cr} \\
\text{OC} \quad \text{CO} \quad \text{CO} & \quad \text{OC} \quad \text{CO} \quad \text{CO} \\
\text{Li} & \quad \text{Li} \\
\text{(17)} & \quad \rightarrow \\
\text{Cr} & \quad \text{Cr} \\
\text{OC} \quad \text{CO} \quad \text{CO} & \quad \text{OC} \quad \text{CO} \quad \text{CO} \\
\text{PPh}_{2} & \quad \text{PPh}_{2} \\
\text{(18)} & \quad \text{(18)} \\
\text{[15]} & \quad \text{} \\
\end{align*}
\]

Compound (17) can then react with chlorodiphenylphosphine to form the unusual triphenylphosphine complex (18) coordinated through one of the phenyl rings.
The dilithiated complex (19) also reacts with carbon dioxide in a similar way to Grignard reagents to give a carboxylato substituted bis arene complex (20) and with trimethylsilyl chloride to give the trimethylsilyl complex (21), (Figure 1.4).

![Chemical structures of complexes 19, 20, and 21 with reactions](image)

**Figure 1.4**

Some Reactions of Cr(n-C₆H₅Li)₂
Finally reaction with nucleophiles involving substitution at benzylic carbon atoms is accelerated by stabilisation of the intermediate benzylic carbonium ion\textsuperscript{36} by the metal through the interaction of filled metal d-orbitals with the vacant orbital at the cation site (equation [16]).

\[
\begin{align*}
\text{CH}_2\text{Cl} & \quad \text{ML}_x \\
\rightarrow & \quad \left[ \begin{array}{c}
\text{CH}_2 \\
\text{ML}_x \end{array} \right] \\
\downarrow & \\
\text{CH}_2\text{Y} \quad \text{ML}_x
\end{align*}
\]

1.5 Some reactions of coordinated halo phosphine ligands

The reactivity of a bond to a coordinated phosphorus atom is frequently quite different from the same bond in an uncoordinated phosphine, and thus reaction of complexed phosphines can often lead to the formation of ligands which are unstable in the free state.

The earliest report of the preparation and characterisation of a metal complex of a reactive phosphorus ligand was made by Schützenberger and Fontaine in 1872\textsuperscript{37}. They reacted platinum metal with phosphorus pentachloride to obtain the complexes PtCl\textsubscript{2}(PCl\textsubscript{3})\textsubscript{2} and [{PtCl\textsubscript{2}(PCl\textsubscript{3})}\textsubscript{2}] which were found to react with water and ethanol to give
the products $\text{PtCl}_2\{\text{P(OR)}_3\}_2$ and $[\{\text{PtCl}_2\{\text{P(OR)}_3\}_2] (R = \text{H}, \text{Et})$ respectively. Later, in 1909, Strecker and Schurigin described the synthesis and properties of phosphorus trihalide complexes of the group VIII metals prepared by previous workers and also reported some of their own findings. Although they did not fully characterise any of their products, they did note that some reacted with water, amines and alcohols. In 1936, the complex $\text{CuCl}(\text{PCl}_3)_2$ was prepared and found to react with aniline, phenol and aliphatic alcohols. With methanol the complex gave $\text{CuCl}(\text{P(OMe)}_3)_2$. This reaction probably does not involve the coordinated $\text{PCl}_3$ ligand since the parent complex undergoes facile dissociation and the reaction therefore probably occurs between the alcohol and free $\text{PCl}_3$ followed by recombination with the metal ion.

More recently, systematic studies of the reactions of coordinated halophosphines have been carried out. Wilkinson prepared complexes of zerovalent nickel, the stability of which was found to vary considerably. Thus, $\text{Ni(PCl}_3)_4$ was prepared by ligand exchange of $\text{Ni(CO)}_4$ with $\text{PCl}_3$. It was stable towards water over a period of several days, and decomposed only slowly in a basic solution, although ammonia solution produced more rapid decomposition. The complex $\text{Ni(PBr}_3)_4$ was prepared from $\text{Ni(PCl}_3)_4$ and $\text{PBr}_3$ by ligand exchange, and $\text{Ni(PF}_3)_4$ by fluorination of the $\text{PCl}_3$ complex using $\text{SbF}_3$. The relative stability of these complexes towards hydrolysis was $\text{PF}_3 > \text{PCl}_3 > \text{PBr}_3$ with the $\text{PF}_3$ complex being particularly inert. The molecule $\text{PF}_3$ undergoes very
rapid hydrolysis in the free state as do the other phosphorus(III) halides. Other nickel(0) complexes which have been prepared also show decreased reactivity of P-F bonds towards hydrolysis\textsuperscript{42}. In contrast, Chatt and Williams\textsuperscript{43} prepared the complexes PtCl\textsubscript{2}(PF\textsubscript{3})\textsubscript{2} and [{PtCl\textsubscript{2}(PF\textsubscript{3})}\textsubscript{2}], the properties of which could not be studied owing to the ease of hydrolysis of the ligands.

The high stability of the P-F bonds in some complexes is also demonstrated by the reaction of the hydride complexes MH\textsubscript{2}(PF\textsubscript{3})\textsubscript{4} (M = Fe, Ru) with potassium amalgam producing anions with no cleavage of the P-F bonds (equation [17])\textsuperscript{44}.

\[
2\text{K} + \text{MH}_2(\text{PF}_3)_4 \rightarrow \text{K}_2[\text{M}(\text{PF}_3)_4] + \text{H}_2 \quad \ldots \ldots \ldots \text{[17]}
\]

Although Ni(PF\textsubscript{3})\textsubscript{4} and Fe(PF\textsubscript{3})\textsubscript{5} do not undergo hydrolysis in neutral solution, they react readily with $\text{Ba}_2(\text{OH})_2$ solution to give the anions $[\text{Ni}(\text{PF}_3)_3(\text{PF}_2\text{O})]$\textsuperscript{-} and $[\text{Fe}(\text{PF}_3)_4\text{PF}_2\text{O}]$\textsuperscript{-} respectively as their barium salts\textsuperscript{45}. These anions react with alkyl halides to give M(PF\textsubscript{3})\textsubscript{n}(PF\textsubscript{2}OR) (M = Fe, n = 4; M = Ni, n = 3)\textsuperscript{46}. The complex Ni(P(OMe)\textsubscript{3})\textsubscript{4} could be obtained by treatment of Ni(PF\textsubscript{3})\textsubscript{4} with sodium methoxide and Ni(PF\textsubscript{2}OMe)\textsubscript{4} by similar treatment of Ni(PF\textsubscript{2}Cl)\textsubscript{4}\textsuperscript{47a}. Reaction of Ni(PCl\textsubscript{3})\textsubscript{4} with methoxide ion also produced Ni(P(OMe)\textsubscript{3})\textsubscript{4} whereas treatment with pure methanol gave a mixture of products by decomposition of the complex, including (MeO)\textsubscript{2}P(O)H and methyl chloride\textsuperscript{47b}. 
Some studies have also been reported of the hydrolysis of coordinated PPh₂Cl and PMe₂Cl ligands to give complexes of the less stable hydroxy tautomers of the secondary phosphine oxides (R₂P(O)H). Although no trace of the hydroxy tautomers (R₂POH) have been detected directly, their presence has been deduced from some reactions of their metal compounds.

A study reported in Austin's thesis described reactions of platinum and palladium complexes of PPh₂Cl and PPhCl₂ with water and other hydroxylic compounds (e.g. equations [18]-[22]).

\[
\text{cis- PtCl₂(PPh₂Cl)₂} + \text{H₂O} \rightarrow \text{cis-PtCl₂(PPh₂OH)₂} \quad \text{[18]}
\]

\[
\text{cis-PtCl₂(PPh₂Cl)₂} + \text{HOCH₂CH₂OH} \rightarrow \text{cis-PtCl₂(PPh₂OCH₂CH₂OH)₂} \quad \text{[19]}
\]

\[
\text{cis- PdCl₂(PPh₂Cl)₂} + \text{PhOH} \rightarrow \text{cis-PdCl₂(PPh₂OPh)₂} \quad \text{[20]}
\]

\[
\text{cis- PdCl₂(PPhCl₂)₂} + \text{HOCH₂CH₂OH} \rightarrow \text{cis- PdCl₂}\{\text{PPh(OCH₂CH₂OH)₂}\} \quad \text{[21]}
\]

\[
\text{cis- PdCl₂(PPhCl₂)₂} + \text{PhOH} \rightarrow \text{PdCl₂(PPh₂OCH₂CH₂OPh)₂} \quad \text{[22]}
\]

The most studied complexes containing halophosphate ligands are those of the type Mo(CO)₅L (L = PPh₂Cl, PMe₂Cl). These complexes react with many compounds containing acidic protons to replace the chlorine by another group X.
with elimination of HCl. This leads to a range of phosphorus ligands which are unknown in the free state (e.g. equations [23]-[26]).

\[
\text{Mo(CO)}_5(\text{PPh}_2\text{Cl}) + \text{ROH} \rightarrow \text{Mo(CO)}_5(\text{PPh}_2\text{OR}) \quad \text{[23]}
\]

\[
\text{Mo(CO)}_5(\text{PPh}_2\text{Cl}) + \text{RSH} \rightarrow \text{Mo(CO)}_5(\text{PPh}_2\text{SR}) \quad \text{[24]}
\]

\[
\text{Mo(CO)}_5(\text{PPh}_2\text{Cl}) + \text{H}_2\text{S} \xrightarrow{\text{R}_3\text{N}} \text{R}_3\text{NH}[\text{Mo(CO)}_5\text{PPh}_2\text{S}] \quad \text{[25]}
\]

\[
\text{Mo(CO)}_5(\text{PMe}_2\text{Cl}) + \text{H}_2\text{S} \xrightarrow{\text{Et}_3\text{N}} \text{Mo(CO)}_5(\text{PMe}_2\text{SH}) \quad \text{[26]}
\]

In the hydrolysis reactions of \(\text{Mo(CO)}_5(\text{PPh}_2\text{Cl})\) and \(\text{Mo(CO)}_5(\text{PMe}_2\text{Cl})\), in addition to the main products \(\text{Mo(CO)}_5(\text{PR}_2\text{OH})\) (\(\text{R} = \text{Me}, \text{Ph}\)) a side product is obtained which is the ligand bridged dinuclear complex \([\text{(CO)}_5\text{MoPR}_2\text{OPR}_2\text{Mo(CO)}_6]\). This results from a coupling reaction between the starting material and the initial hydrolysis product as has been shown by direct reaction between the two compounds for both \(\text{R} = \text{Me}\) and \(\text{R} = \text{Ph}\) and the isolation in high yield of \([\text{(CO)}_5\text{MoPMe}_2\text{OPPh}_2\text{Mo(CO)}_5]\) from \(\text{Mo(CO)}_5(\text{PMe}_2\text{Cl})\) and \(\text{Mo(CO)}_5(\text{PPh}_2\text{OH})\)\(^{50}\). These diphosphoxane ligands are not stable in the free state as they undergo either rearrangement or disproportionation\(^{51}\). Hydrolysis of the corresponding tungsten halophosphine complexes gave only the diphosphoxane complexes as the final products\(^{52}\). The complex \(\text{Mo(CO)}_5(\text{PPh}_2\text{Cl})\) reacts more rapidly with methanol than does \(\text{Mo(CO)}_5(\text{PMe}_2\text{Cl})\) in spite of the greater steric interaction with the phenyl groups. The hydrolysis product \(\text{Mo(CO)}_5(\text{PPh}_2\text{OH})\) is more acidic than \(\text{Mo(CO)}_5(\text{PMe}_2\text{OH})\).
[(CO)₅WPMe₂NMePMe₂W(CO)₅] is obtained on treatment of the tungsten PMe₂Cl complex with methyleamine followed by alkyllithium and a further mole of W(CO)₅PMe₂Cl (equation [27]).

\[
\begin{align*}
W(CO)₅(PMe₂Cl) + MeNH₂ & \rightarrow W(CO)₅(PMe₂NHMe) \\
& \rightarrow Li[W(CO)₅PMe₂NMeW(CO)₅] \\
W(CO)₅PMe₂Cl & \rightarrow [(CO)₅WPMe₂NMePMe₂W(CO)₅].
\end{align*}
\]

The closely related diphosphine complex [(CO)₅MoPMe₂PMe₂Mo(CO)₅] has been obtained on reaction of Mo(CO)₅(PMe₂Cl) with methyl magnesium bromide in addition to the main product Mo(CO)₅PMe₃ [53]. The stereochemical details of these nucleophilic displacement reactions at phosphorus have been studied and it has been shown that the mechanism involves an S_N² type displacement of chloride [54]. The complexes M(CO)₅(PMe₂Cl) (M = Cr, Mo, W) also react with the carbonyl anions [M¹(CO)₅]⁻ (M¹ = Mn, Re) to give bridged binuclear complexes, (CO)₅MPMe₂M¹(CO)₅ which disproportionate on heating to give M(CO)₆ and [M¹(CO)₄PMe₂]₂ [55].

Further hydrolytic reactions of group V donor ligands containing labile chloride groups have been investigated by Chatt and Heaton [56]. They synthesised the complexes cis-PtX₂(MR₂Cl)(M¹R₃) (M,M¹ = P, As; X = halogen) and on treatment with alkali followed by HX obtained the corresponding hydrolysis products cis-PtX₂(MR₂OH)(M¹R₃) (equation [28]).
More recently, studies have been reported of complexes containing two halophosphine ligands cis to each other. On hydrolysis these frequently yield complexes containing a ligand of the type $[R_2POHOPR_2]^-$ in which two $R_2PO^-$ ligands are linked by a hydrogen bond. For example, the complex cis-Mo(CO)$_4$(PPh$_2$Cl)$_2$ reacts with water and other molecules containing an acidic hydrogen (equations [29]-[31]).

$$\text{Mo(CO)}_4(\text{PPh}_2\text{Cl})_2 + \text{H}_2\text{O} \xrightarrow{\text{Et}_3\text{N}} \text{Et}_3\text{NH}[\text{Mo(CO)}_4((\text{PPh}_2\text{O})_2\text{H})] \ldots [29]$$

$$\text{Mo(CO)}_4(\text{PPh}_2\text{Cl})_2 + \text{NH}_3 \rightarrow \text{Mo(CO)}_4(\text{PPh}_2\text{NH}_2)_2 \ldots [30]$$

$$\text{Mo(CO)}_4(\text{PPh}_2\text{Cl})_2 + \text{RNH}_2 \rightarrow \text{Mo(CO)}_4(\text{PPh}_2\text{NHR})_2 \ldots [31]$$

The analogous PMe$_2$Cl complex also reacts with bifunctional nucleophiles to give chelate complexes (equations [32] and [33]).

$$\text{Mo(CO)}_4(\text{PMe}_2\text{Cl})_2 + \text{CH}_2(\text{NH}_2)_2 \rightarrow \ldots [32]$$

$$\text{Mo(CO)}_4(\text{PMe}_2\text{Cl})_2 + \text{MeNHCH}_2\text{CH}_2\text{NHMe} \rightarrow \ldots [33]$$
Further chelates can then be obtained through reactions of some of the substituted complexes (e.g. equation [34]).

$$\text{Mo(CO)}_4(\text{PPh}_2\text{NH}_2)_2 + \text{BuLi} \rightarrow \text{Mo(CO)}_4(\text{PPh}_2\text{NHLi})_2$$

$$\text{SiMe}_2\text{Cl}_2$$

$$\text{Mo} \quad \text{SiMe}_2$$

$$\text{O} \quad \text{PPh}_2\text{NH}$$

$$\text{O} \quad \text{PPh}_2\text{NH}$$

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

The bridging hydrogen atom of the complexes containing the $[\text{R}_2\text{POHOPR}_2]^-$ ligand can be readily removed by treatment with a base and replaced by other groups. The proton can sometimes be detected as a broad line in the $^1\text{H}$ n.m.r. spectrum of the complexes, resonating in a region ca. $\delta$10-15 ppm. It can be exchanged readily with $\text{D}_2\text{O}$ and in extreme cases, the O-H-O bridge is so acidic that the cation resulting from loss of the proton is the stable species in solution, e.g. $[\text{Pt(PP}_2\text{O)}_4]^2^-$ in which the negative charge is stabilised by the electronegative fluorines attached to the phosphorus atom$^{58}$. In the case of the complex $\text{Pt}[\{\text{P(OMe)}_2\text{O}\}_2\text{H}]_2$ the protons can be removed sequentially by treatment of the complex with methoxide ion, the reaction being monitored by conductivity measurements (equation [35])$^{59}$. 
The proton can also be replaced by treatment of the complexes with BF$_3$, SiMe$_3$Cl, SiMe$_2$Cl$_2$, and various transition metal acetylacetonates (e.g. equations [36] - [40]).

$$\text{MePh}_2\text{PtP} \rightarrow \text{MePh}_2\text{PtPB} + \text{BF}_2 + \text{HF} \quad \ldots \quad [36]$$

$$\text{Et}_3\text{P} \rightarrow \text{Et}_3\text{P} + \text{SiMe}_3 + \text{HCl} \quad \ldots \quad [37]$$

$$\text{Et}_3\text{NH}[\text{Mo(CO)}_4(\text{PPh}_2\text{O})_2\text{H}] + \text{SiCl}_2\text{Me} \rightarrow \quad \ldots \quad [38]$$

$$[\text{Et}_3\text{NH}][\text{Mo(CO)}_4(\text{PPh}_2\text{O})_2\text{H}] + \text{SiCl}_4 \rightarrow \quad \ldots \quad [39]$$

$$\text{Cl} + \text{Co(acac)}_2 \rightarrow \quad \ldots \quad [40]$$
The symmetrical nature of the hydrogen bond in these complexes has been demonstrated in a few cases by X-ray structural studies which show that the O-O separation is very short e.g. in the complex \( \text{Pd}(\text{S}_2\text{PMe}_2)(\text{PPPh}_2\text{O})_2\text{H} \) the O-O distance is 2.41 Å. As this distance is much less than twice the van der Waals radius of oxygen, the existence of a hydrogen bond can be inferred from this data. This is also one of the shortest hydrogen bonded distances known, implying that the hydrogen bond must be highly symmetrical. The P-O distances also support the existence of a hydrogen bond. These are equal within the limits of experimental error, which therefore rules out the alternative structure (22).

(22)

The symmetrical nature of the hydrogen-bonded system is also reflected in the observation that no O-H stretching bands are present in the infrared spectra of these complexes at the normal position of about 3600 cm\(^{-1}\). This is to be expected if strong symmetrical hydrogen bonding is present since the \( \nu_{\text{OH}} \) band is broadened and shifted to lower frequency by this interaction.

An alternative route to complexes containing the ligand \([\text{R}_2\text{POHOPR}_2]^-\) is via reaction of a metal complex with \( \text{R}_2\text{P(O)H} \).
Secondary phosphine oxides frequently react in such a way that the unstable tautomer $R_2P(OH)$ appears to be the species involved, or possibly a hydrogen bonded dimer (23) (equation [41]).

\[
\begin{align*}
\text{HP} & \equiv \text{O} - \text{---} - \text{HOPR}_2 \\
(23)
\end{align*}
\]

\[
\begin{align*}
\text{Pt(PPh}_3)_3 + 2\text{Ph}_2\text{P(OH)} & \rightarrow \text{PtP} - \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_3\text{P} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_2\text{P} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_3\text{P} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Pt} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_2
\end{align*}
\]

The above reaction probably occurs via oxidative addition of the P-H bond to the platinum (0) complex (equation [42])

\[
\begin{align*}
\text{Pt(PPh}_3)_3 + \text{Ph}_2\text{POH} & \rightarrow \text{PtP} - \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_3\text{P} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_2\text{P} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_3\text{P} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Pt} & \equiv \text{P} \equiv \text{O} \equiv \text{HOPPh}_2 \\
\text{Ph}_2
\end{align*}
\]

A further method of preparation is by cleavage of the O-alkyl bond in complexes of tertiary phosphites and phosphinites by nucleophiles. An example of this is the reaction of platinum(II) dialkyl dithiocarbamates with alkyldiphenylphosphinites (equation [43]).
Pyrolysis of cationic complexes containing Por linkages can also give complexes containing related hydrogen-bonded ligands (e.g. equation [44]).

\[
\begin{align*}
\text{Et}_2\text{NC} & \quad \text{Pt} \quad \text{S} \quad \text{S} \quad \text{CNET}_2 + \text{PPh}_2\text{OR} \\
\text{ROH}/\text{H}_2\text{O} \quad \rightarrow \quad \text{Et}_2\text{NC} & \quad \text{Pt} \quad \text{P—OR} \quad \text{S}_2\text{CNET}_2 \quad \rightarrow \quad \text{Et}_2\text{NC} & \quad \text{Pt} \quad \text{P} \quad \text{O} \quad \text{R} \\
\end{align*}
\]

\[\text{exchange with PPh}_2\text{OH from hydrolysis of PPh}_2\text{OR}\]
In complex (24) the hydrogen bonding is extended to form a novel tridentate ligand. Reaction of Co\((n-C_5H_5)_2\) with \((RO)_2P(O)H\) \((R = Me, Et, Ph)\) gives the trinuclear mixed valence complex (25).

This complex is formally derived from the monomeric cation (26) analogous to the binuclear ruthenium complex (24).
The complex Ni(η-C₅H₅)₂ also reacts with (RO)₂P(O)H to give a related hydrogen bonded product (27) and these two cyclopentadienyl complexes, (26) and (27) react with HBF₄ to give the complexes (28) and (29) respectively. The nickel complex (27) reacts with metal salts MCl₂ (M = Co, Zn) to give mixed metal complexes \{Ni(η-C₅H₅)((RO)₂PO)₂\}M.

\[
\begin{align*}
\text{(28)} & \\
\text{(29)}
\end{align*}
\]

If the complex Pt{(PPh₂O)₂H}₂ is treated with a bidentate ligand L₂ (L₂ = Ph₂PCH₂CH₂PPh₂, o-Me₂AsC₆H₄AsMe₂), one [(PPh₂O)₂H]⁻ ligand is displaced to give (30). These complexes will also react with metal ions to give the trinuclear cations (31) (M = Cu, Co, Ni, Zn). Inspection of the electronic spectra of the cobalt(II) complexes which are approximately tetrahedral, shows that the ligand field strength of the platinum containing ligand is similar to that
of the thiocyanate anion. The zinc complex of this ligand (for \( L_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2 \)) has a very complex \( ^{31}\text{P} \) n.m.r. spectrum due to second order effects in the coupling of the \( ^{31}\text{P} \) nuclei with \( ^{195}\text{Pt} \). This results in the platinum-195 satellite portion of the spectrum being unsymmetrically arranged about the centre of the spectrum.

1.6 Reactions of complexes containing some other bonds to phosphorus

(a) Phosphorus-nitrogen bonds

The P-N bond of a coordinated ligand will undergo ready cleavage with hydrogen halides and some examples of such reactions are given below (equations [45]-[49]).

\[
\text{Mo(CO)}_5\{\text{P(NMe}_2\text{)}_3\} + \text{HX(l)} \rightarrow \text{Mo(CO)}_5\text{PX}_3 \quad \ldots \quad [45] \\
\text{Mo(CO)}_5\{\text{P(NMe}_2\text{)}_3\} + \text{HCl/pentane} \rightarrow \text{Mo(CO)}_5\{\text{PCl}_n\text{(NMe}_2\text{)}_3-\text{n}\}. \quad [46] \\
\quad (n = 1, 2, 3) \\
\text{trans-Mo(CO)}_4\{\text{P(NMe}_2\text{)}_3\}_2 + \text{HCl(l)} \rightarrow \text{trans-Mo(CO)}_4\{\text{PCl}_3\}_2 \quad \ldots \quad [47]
\]

\[
\text{Mo(CO)}_5\{\text{P(NMe}_2\text{)}_3\} + \text{HI(l)} \rightarrow \text{Mo(CO)}_5\{\text{PI}_3\} + \text{Mo(CO)}_5-\text{(PI}_2\text{NMe}_2\text{)} \quad \ldots \quad [48]
\]

\[
\text{Mn(}\sim\text{C}_5\text{H}_5\text{)}\text{(CO)}_2\{\text{PPh(NEt}_2\text{)}_2\}_2 + \text{HX} \rightarrow \text{Mn(}\sim\text{C}_5\text{H}_5\text{)}\text{(CO)}_2\text{(PPhX}_2\text{)} + \text{Mn(}\sim\text{C}_5\text{H}_5\text{)}\text{(CO)}_2\text{(PPhXNEt}_2\text{)} \quad \ldots \quad [49]
\]
Stable anions can also be produced from complexes of secondary phosphines by treatment with strong bases. For example, KPH₂ reacts with the molybdenum complex (33) of the cyclic secondary phosphine HPCH₂CH₂ to give the anion (34). This anion and analogous ones can then act as a nucleophile in various reactions (equations [52]-[54]).
The reactivity of HX with the P-N bond was reported to be in the order HI>HBr>HCl. The reaction of \( PR_n(NR_2)_{3-n} \) compounds with hydrogen halides may thus be used to synthesise \( PR_nX_{3-n} \) complexes.

(b) **Phosphorus-sulphur bonds**

In contrast to the extensive work on halophosphine complexes (see section 1.5) few studies involving coordinated phosphorus-sulphur bonds have been reported because of the instability of such linkages. For example, the reaction of \( Ph_2PSPh \) with \( Fe(CO)_5 \) gives the binuclear complex \( [Fe(CO)_3(\mu-Ph_2)(\mu-SPh)Fe(CO)_3] \) (32) rather than the expected \( [Fe(CO)_4Ph_2SPhFe(CO)_4] \).  

![Phosphorus-sulphur bond](image)

(c) **Coordinated phosphorus-hydrogen bonds**

The main reactions of coordinated P-H bonds involve cleavage by a strong base and elimination of HX with a metal halide in the presence of a base to produce binuclear complexes (e.g. equations [50] and [51]).
(d) **Complexes containing phosphorus-group IV ligands**

Complexes containing ligands with a P-$M^1$ bond ($M^1 = \text{Si, Ge, Sn}$) can frequently be employed as useful synthetic starting materials for the preparation of complexes containing phosphorus-phosphorus or phosphorus-arsenic ligands (e.g. equations [55] and [56]) \(^\text{76,77}\).

\[
M(CO)_5E\text{Me}_2\text{SnMe}_3 + E^1\text{Me}_2\text{Cl} \rightarrow M(CO)_5E\text{Me}_2E^1\text{Me}_2 + \text{Me}_3\text{SnCl}
\]

($M = \text{Cr, W}$, $E, E^1 = \text{P, As}$) \([55]\)

\[
W(CO)_5\text{PPh}(\text{SnMe}_3)_2 + 2\text{PMe}_2\text{Cl} \\
\downarrow \text{Ph} \\
W(CO)_5\text{PMe}_2\text{PPMe}_2\text{W}(CO)_5
\]

\([56]\) (35)

Complex (35) is one of the few known derivatives of a \(^1\) triphosphane. A similar reaction between Mo(CO)$_5$[PPh(SnMe$_3$)$_2$] and AsMe$_2$Cl gives a complex of a mixed phosphine-arsenic ligand (36).

![Diagram](36)
1.7 Conclusions

In general, it is difficult to see any definite trends in the reactivity of halophosphine and related ligands on complexation as conflicting results have been obtained from studies on different metals. As described in section 1.5 coordinated PF₃ is highly reactive in platinum(II) complexes but is rather inert in nickel(0) complexes. Whether the coordinated PF₃ in the platinum(II) complexes is more or less reactive than the free PF₃ molecules has not been determined. However, with the exception of these complexes the other halophosphine ligands seem to be less reactive when coordinated than in the free state. The other groups present on the phosphorus may also modify its reactivity e.g. PPh₂Cl complexes tend to undergo solvolysis more readily than those of PMe₂Cl and the hydrolysis products MLₓ(PPh₂OH) tend to be more acidic than the corresponding MLₓ(PMe₂OH), probably because of the electron withdrawing nature of aryl substituents relative to alkyl substituents.

The synthesis and characterisation of new halophosphine and oxyphosphine complexes of ruthenium(II) together with attempts to react the P-Cl bonds are described in Chapters 4 and 5.
CHAPTER 2

Cationic $\eta^6$-Arene and $\eta^5$-Cyclohexadienyl Complexes

of Ruthenium containing Nitrogen and Phosphorus Donor Ligands
2.1 Introduction

Reactions of nucleophiles with cationic complexes containing coordinated arene ligands have been extensively studied\textsuperscript{14,31}, due to both potential synthetic utility in introducing a nucleophilic species into a benzene ring and theoretical interest in cyclohexadienyl species stabilised by complexation to a transition metal cation (see Chapter 1 and references therein for further discussion).

Little work has been published however on nucleophilic addition reactions of areneruthenium(II) complexes. Evidence has been obtained for transient ($\eta^5$-$C_6H_6X$)Ru(II) complexes from hydrogen-1 n.m.r. studies but few complexes have been fully characterised, as the products formed in the reactions were too unstable to be isolated. For example, the complex $\left[\{Ru(\eta-C_6H_6)Cl_2\}_2\right]$ in dimethylsulphoxide solution undergoes attack by cyanide ion to give a short-lived species which is thought, on the basis of its hydrogen-1 n.m.r. spectrum to contain a $\eta^5$-$C_6H_6CN$ ligand\textsuperscript{78}. Also the $[Ru(\eta-C_6H_6)_2]^{2+}$ cation undergoes reaction with hydride ion to give a mixture of species resulting from addition of two hydride ions on the complex\textsuperscript{79}. The two products are $\text{Ru}(\eta^6-C_6H_6)(\eta^4-C_6H_8)$ and $\text{Ru}(\eta^5-C_6H_7)_2$, the relative proportions depending on the solvents used. $[\text{Ru}(\eta-C_6H_6)_2]^{2+}$ also undergoes reaction with phenyllithium to give some $\text{Ru}(\eta^5-C_6H_6C_6H_5)_2$. 
Very recently studies have also been reported on reactions of nucleophiles with arene cyclopentadienyl complexes of rhodium(III) $^{14}$. These complexes react with a variety of nucleophiles to give similar $^7\text{cyclohexadienyl-}$ $^7\text{cyclopentadienyl complexes}$. In this chapter the results of reactions of nucleophiles with various monomeric areneruthenium(II) cations are now discussed.

2.2 Results and Discussion

The compound $\{\text{Ru(}\eta^7\text{-C}_6\text{H}_6\text{)}\text{Cl}_2\}_2$ reacts under very mild conditions in methanol with an excess of 1,10-phenanthroline (phen) or 2,2$^1$ bipyridyl (bipy) to give yellow solutions from which bright yellow solids are obtained on addition of excess NH$_4$PF$_6$. These solids are formulated on the basis of elemental analysis (Table 2.1) as $\text{[Ru(}\eta^7\text{-C}_6\text{H}_6\text{)}\text{Cl(N-N)}\text{]}$-PF$_6$ (37) (N-N = bipy or phen). Solutions of the solids in nitromethane over a range of concentrations indicate that they are 1:1 electrolytes, (e.g. for a $10^{-3}$ mol dm$^{-3}$ solution of $\text{[Ru(}\eta^7\text{-C}_6\text{H}_6\text{)}\text{Cl(phen)}\text{]}$PF$_6$, the molar conductivity $\Lambda_m = 7.15 \text{ S cm}^2\text{mol}^{-1}$ and a graph of $\Lambda_0 - \Lambda_e$ vs $C_e$ gives a straight line of slope 233 which is a characteristic value for a 1:1 electrolyte). The infrared spectra (Nujol mulls) of (37) contain bands which are assigned to skeletal vibrations of the rings of the heterocyclic ligands$^{82}$. The spectra also contain sharp bands at ca. 300 cm$^{-1}$ which are assigned to terminal $\nu$(Ru-Cl) stretching vibrations and at ca. 360 cm$^{-1}$ which are assigned to a $\nu$(Ru-N) stretch.
Strong absorption bands at 835 cm\(^{-1}\) and 560 cm\(^{-1}\) confirm the presence of the PF\(_6^-\) anion.

The presence of a coordinated benzene ring is confirmed by examination of the hydrogen-1 n.m.r. spectrum at 298 K in (CD\(_3\))\(_2\)CO, which shows (in the case where N-N = phen) a sharp singlet resonance at 66.33 ppm. This shows the typical low frequency shift of a coordinated benzene ring from free benzene due to a decrease in \(\pi\)-electron density caused by the positively charged metal centre. The \(^1\)H n.m.r. spectrum also contains resonances in the aromatic and heterocyclic regions (multiplets which are centred at 68.20, 8.85 and 9.95 ppm [N-N = phen]) and the intensity ratio of the benzene:phenanthroline resonances is 6:8 which confirms the formulation as [Ru(\(n\)-C\(_6\)H\(_6\))Cl(phen)]PF\(_6\).

Similar complexes [Ru(\(n\)-arene)Cl(N-N)]PF\(_6\) [arene = mesitylene (1,3,5-C\(_6\)H\(_3\)Me\(_3\)), anisole (C\(_6\)H\(_5\)OCH\(_3\)) and p-cymene (p-MeC\(_6\)H\(_4\)CHMe\(_2\)); N-N = phen; arene = anisole; N-N = bipy] can also be prepared from the appropriate [{Ru(\(n\)-arene)Cl\(_2\)}\(_2\)]\(_3\), by reaction with an excess of phen or bipy under the same conditions and characterised as above (see Tables 2.1 and 2.2).
However, prolonged reaction between \([\{\text{Ru}(\eta-C_6H_6)Cl_2\}_2]\) and an excess of phen under reflux conditions in methanol produces complete displacement of chloride and the coordinated benzene ligand giving an orange solid on addition of \(\text{NH}_4\text{PF}_6\) to the reaction solution. The \(^1\text{H}\) n.m.r. and infrared spectra indicate that only phen and \(\text{PF}_6^-\) groups are present and the compound analyses closely for \([\text{Ru}(\text{phen})_3](\text{PF}_6)_2\). This is supported by conductivity measurements in \(\text{CH}_3\text{NO}_2\) which are characteristic of a 1:2 electrolyte (\(\Lambda_m (10^{-3}\ \text{mol dm}^{-3}) = 161.0\ \text{S cm}^2\text{mol}^{-1}\) \(\text{80}\

These cationic chloro complexes all react readily with the tertiary phosphines \(\text{PMe}_2\text{Ph}, \text{PMePh}_2\) or \(\text{PET}_2\text{Ph}\) with displacement of the remaining chloride ligand to give the dications \([\text{Ru}(\text{arene})(\text{PR}_3)(\text{N-N})]^2+\) which can be isolated by addition of further \(\text{NH}_4\text{PF}_6\) to give the pale yellow hexafluorophosphate salts \(\text{38}\). Analytical and hydrogen-1 n.m.r. data support this formulation and conductivity
measurements (Table 2.1) in CH$_3$NO$_2$ or acetone indicate that the complexes are 1:2 electrolytes in solution e.g. for [Ru(\textit{n-C}_6\textit{H}_6)(\textit{PMe}_2\textit{Ph})(\textit{phen})](PF$_6$)$_2$ in nitromethane $\Lambda_m = 158$ S cm$^2$mol$^{-1}$ and a graph of $\Lambda_o - \Lambda_e$ vs $C_e^2$ gives a straight line of slope 390 which are characteristic values for a 1:2 electrolyte.

In contrast to recent reports involving addition of tertiary phosphines to cyclic organic ligands coordinated to manganese$^{84}$, iron$^{85}$, cobalt$^{14}$, rhodium$^{14}$ and other ruthenium$^{86}$ cations no evidence for ring addition by PR$_3$ has been observed in these studies.

However, these dicaticonomic complexes readily undergo ring addition reactions with various other nucleophiles to give bright orange-yellow to red solutions, e.g. addition of NaBH$_4$ to a solution of [Ru(\textit{n-C}_6\textit{H}_6)(\textit{PMe}_2\textit{Ph})(\textit{phen})](PF$_6$)$_2$ produced an almost instantaneous colour change to deep orange. Addition of water to destroy excess NaBH$_4$ followed by extraction of the product with methylene chloride and concentration of the dried methylene chloride extract gave the product as a bright orange-red solid which was stable in air over prolonged periods. The product analysed well for [Ru(\textit{5-C}_6\textit{H}_7)(\textit{PMe}_2\textit{Ph})(\textit{phen})]PF$_6$ (39) and was shown by conductivity measurements to be a 1:1 electrolyte (Table 2.1).

The hydrogen-1 n.m.r. spectrum of this compound (in CDCl$_3$ at 300 K) contains no coordinated benzene resonance at 86.33 ppm, but four weak multiplets appear at 82.38, 2.80, 4.78 and 5.79 ppm (intensity ratio 2:2:2:1 respectively) (Figure 2.1). This indicates that nucleophilic attack by
Figure 2.1: $^1$H n.m.r. spectrum of [Ru($^5$C$_6$H$_5$)(PMe$_2$Ph)(phen)]PF$_6$ in CDCl$_3$ at 300 K
hydride ion on the coordinated C₆H₆ ligand has occurred giving rise to a n⁵-cyclohexadienyl ligand. Integration of the C₆H₇ protons relative to the 1,10 phenanthroline protons and PMe₂Ph protons also shows that the ligands in the other coordination sites have remained unchanged during the reaction.

The resonances arising from the C₆H₇ ligand were assigned by use of homonuclear decoupling experiments. Thus, irradiation of the resonance at δ2.80 ppm caused the resonance at δ4.78 ppm, which was originally a doublet of doublets, to collapse to a single doublet, whereas irradiation of the resonance at δ2.38 ppm caused no change in the resonance at δ4.78 ppm. The resonance at δ5.79 ppm can be assigned unambiguously from the integration of the spectrum as H₄ (see Figure 2.2 for numbering scheme).

![Figure 2.2 Numbering scheme of -Ru(n⁵C₆H₇) fragment](image)

The proton signal for H₃ would be expected to be a doublet of doublets through couplings to H₂ and H₄ and the decoupling experiment showed that there was a doublet of doublets in the spectrum at δ4.78 ppm which collapsed to one doublet on irradiation of the signal at δ2.80 ppm.
Thus the resonance at $\delta 4.78$ ppm must be due to $H_3$ and the symmetrically related $H_5$, while the resonance at $\delta 2.80$ ppm is due to the pair $H_2$ and $H_6$ with the remaining resonance at $\delta 2.38$ ppm being assigned to $H_1$(exo) and $H_1$(endo).

The spectrum could also be assigned by assuming that the effect of nucleophilic addition on the position of the proton resonance relative to the unperturbed benzene ring position ($\delta 6.33$ ppm) decreases with increasing distance from the site of attack, i.e. $H_4$ is the most "benzene-like" and the two $H_1$ protons are most like aliphatic protons with the others coming in intermediate positions. There is certainly a strong correlation between the positions of the proton resonances and the ring position as determined by the decoupling experiment. i.e. $H_4 \delta 5.79$ ppm; $H_3,5 \delta 4.78$ ppm; $H_2,6 \delta 2.80$ ppm; $H_1$(exo/endo) $\delta 2.38$ ppm.

Although the resonances due to $H_1$(exo) and $H_1$(endo) coincide in the spectrum of this compound, there is no reason why they should as they are not equivalent. In some compounds containing the same ligands the proton signals for the two nuclei are distinct from each other, e.g. a similar assignment of resonances has been made for the compound $[Rh(\eta C_5 Me_4 Et)(\eta C_6 H_7)]PF_6$, i.e. $H_4 \delta 6.45$ and $H_3$ and $H_5 \delta 5.27$, $H_2$ and $H_6 \delta 3.60$, $H_1$(endo) $\delta 2.89$, $H_1$(exo) $\delta 2.57$ ppm. This compound also shows the correlation mentioned above, between resonance position and the distance of the corresponding proton from the site of nucleophilic addition.

The spectrum, however, contains separate resonances for the exo and endo protons of the methylene group.
The $^{13}$C-{${}^1$H} spectrum of $[\text{Ru}(\eta^5\text{C}_6\text{H}_7)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$ (Figure 2.2) also shows the loss of the $\text{C}_6\text{H}_6$ resonance at 693.8 ppm (which appears in the spectrum of $[\text{Ru}(\eta^5\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6)_2$ and the appearance of resonances at 627.5, 32.7, 75.9 and 96.1 ppm. The latter are assigned by analogy with the $^{13}$C-{${}^1$H} spectrum of $[\text{Rh}(\eta^5\text{C}_5\text{Me}_4\text{Et})(\eta^5\text{C}_6\text{H}_7)]\text{PF}_6$ to carbon atoms C(1), C(2,6), C(4) and C(3,5) respectively. In the case of this spectrum there is not such a clear correlation between the resonance position and the position of the corresponding carbon in the ring.

The infrared spectrum of $[\text{Ru}(\eta^5\text{C}_6\text{H}_7)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$ (39) (KBr disc) contains a characteristically low frequency C-H stretching vibration outwith the normal range of frequencies for C-H stretches, at 2820 cm$^{-1}$. This is also found in other ($\eta^5\text{C}_6\text{H}_7$) complexes e.g. $\text{Mn}(\eta^5\text{C}_6\text{H}_7)(\text{CO})_3$ and $[\text{Rh}(\eta^5\text{C}_5\text{Me}_4\text{Et})(\eta^5\text{C}_6\text{H}_7)]\text{PF}_6$, and assigned to the $\nu(\text{C-H}_{\text{exo}})$ stretching vibration, as discussed in Chapter 1, section 1.2. The lowering of the frequency of this vibration is believed to be due to interaction of the C-H$_{\text{exo}}$ $\sigma$-orbital with the delocalised $\pi$-system of the ligand which produces a drain of electron density from the bond, thus weakening it and lowering its stretching frequency.

Reaction of the $[\text{Ru}(\eta^5\text{C}_6\text{H}_6)(\text{PR}_3)(\text{N-N})]\text{PF}_6)_2$ complexes described earlier with various nucleophiles $Y^-$ ($Y^-=\text{OH}^-$, $\text{CN}^-$, $\text{H}^-$) produces the cyclohexadienyl complexes $[\text{Ru}(\eta^5\text{C}_6\text{H}_6\text{Y})(\text{PR}_3\text{N-N})]\text{PF}_6$ which were characterised by elemental analysis, conductivity data, infrared spectra
and hydrogen-1 n.m.r. spectra (Table 2.1 and 2.2). It is probable that stereospecific exo addition occurs for the cases where \( Y^- \) is not hydride ion, since the infrared spectra of the products in which \( Y^- = \text{OH}^- \) or \( \text{CN}^- \) contain no low frequency \( v(C-H) \) band in the region around 2800 cm\(^{-1}\). The possible explanations for the preference for stereospecific exo addition rather than endo or nonstereospecific addition are fully discussed in Chapter 1, section 1.2.

Reactions with other nucleophiles which were known to add to other cationic \( \pi \)-arene complexes were also investigated but with little success, no stable products being isolated. The attempts produced no reaction in many cases or extensive decomposition in others. The possible nucleophiles which were tried were \( \text{CH}_3\text{CO}_2^- \), \( R_2\text{NH} \) (\( R = \text{Et}^1\text{Pr} \)), \( \text{RO}^- \) (\( R = \text{Me}, \text{Et}, \text{tBu} \)), \( \text{PhO}^- \), \( \text{PhS}^- \) and \( R_2\text{NCS}_2^- \).

In those cases where no reaction was observed the nucleophiles were generally those with resonance stabilisation of the anion e.g. \( \text{CH}_3\text{CO}_2^- \), \( \text{PhO}^- \), \( R_2\text{NCS}_2^- \). The delocalisation of the negative charge in these anions possibly results in a lowering of the nucleophilicity relative to a non-stabilised anion. However semiquantitative assignments of nucleophilicity have been made and the phenoxide anion generally has a higher value than the hydroxide ion and the phenylsulphide ion is also highly nucleophilic\(^{87}\). The nucleophiles which give stable adducts however are all relatively small with no great steric requirements and it is possible that steric constraints may adversely affect reactions involving larger nucleophiles such as phenoxide.
The alkoxide anions produced decomposition of the starting material. In the case of these reactions the nucleophilicity of the reagent is greater than that of hydroxide ion which reacts readily to give a stable product. The basicity of the alkoxide ions may be an important factor here, possibly producing proton abstraction from the other coordinated ligands which would probably result in decomposition of the compound. It is also well established that alkoxides can undergo $\beta$-elimination reactions to give relatively unstable metal hydrides.

It is appropriate at this point to speculate on possible reaction pathways. A mechanism involving one step, direct attack of the nucleophile on the ring seems consistent with the postulated stereochemistry of the product which contain no exo hydrogen (except where $Y^- = H^-$) and this therefore indicates that the attack of the nucleophile is from above the ring plane (equation [57]). The reactions are also very fast which tends to support a simple one-step process.
An alternative mechanism is one involving initial attack of the nucleophile on the heterocyclic ligand of the complex. This is suggested by the ease with which some complexes containing 2,2'-bipyridyl or 1,10-phenanthroline ligands undergo reactions with such nucleophiles as OH⁻ or CN⁻ and in some cases nucleophiles as weak as H₂O itself (equation [58])

![Chemical structure](image)

As the complexes studied all contain a bidentate nitrogen ligand of this type the mechanism of the reaction could possibly involve a step in which an intermediate with the nucleophile attached to the heterocyclic ligand is involved, followed by transfer to the arene ring. However, this mechanism would not account for the apparent exclusive formation of the exo isomer. Transfer of a group intramolecularly from the heterocyclic ligand to the arene would necessarily produce the endo isomer preferentially since the group to be transferred must be below the plane of the ring. The available evidence suggests that the endo isomer is not produced in any detectable quantity.
The $\eta^5$-cyclohexadienyl complexes were not found to be susceptible to further nucleophilic attack to give $\eta^4$-1,3- or $\eta^4$-1,4-cyclohexadiene complexes. For example, treatment of the complex $[\text{Ru}(\eta^5\text{C}_6\text{H}_6\text{CN})(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$ with excess KCN in tetrahydrofuran under reflux gave a product which was identical with the starting material in all respects, including infra red spectrum, $^1\text{H}$ n.m.r. spectrum and analytical data.

The lack of reactivity of the $\eta^5$-cyclohexadienyl complexes towards nucleophiles is perhaps not surprising as the $\eta^6$-arene complexes are only affected by a small range of nucleophiles and the $\eta$-arene cations carry a greater positive charge than the $\eta^5$-cyclohexadienyl cations. This factor alone should render these cations less susceptible to attack by negatively charged nucleophiles than the parent arene cations.

Recently a set of rules$^{21}$ have been derived to determine the preferred site of attack of a nucleophile on a complex containing carbocyclic ligands. These rules predict that a carbocyclic ligand which donates an even number of electrons to the complex will undergo nucleophilic attack more readily than a ligand donating an odd number. Thus the conversion of an $\eta^6$-ligand to an $\eta^5$-ligand is predicted to be a more facile reaction than an $\eta^5$ to $\eta^4$ conversion.

In support of this it was found that the complex $[\text{Rh}(\eta^5\text{C}_5\text{Me}_5)(\text{PMe}_2\text{Ph})(\text{phen})](\text{PF}_6)_2$ did not undergo reaction with $\text{BH}_4^-$ ion although it is isoelectronic with the
The reaction of the monocations \([\text{Ru}(\eta\text{-arene})\text{Cl(N-N)})\text{PF}_6\] with similar nucleophiles results in similar colour changes to the reactions with the dications but rapid decomposition then occurs preventing isolation of any clean products. Attempts to follow these reactions by \(^1H\) n.m.r. spectroscopy were also unsuccessful since decomposition was too rapid. The instability of these complexes may be due to competition between reactions involving the addition to the coordinated ring and direct attack on the metal centre via substitution of chloride by \(\text{H}^-, \text{CN}^-\) and \(\text{OH}^-\) and ring displacement reactions. Similarly, the compounds \([\text{Ru}(\eta\text{-C}_6\text{H}_6)\text{ClL}_2]\text{PF}_6\) (\(L = \text{PPh}_3, \text{PMe}_2\text{Ph}, \text{Et}_2\text{S, AsPh}_3\) etc.) decompose on addition of \(\text{NaBH}_4\) although for \(L = \text{PMe}_2\text{Ph}, \) \(^1H\) n.m.r. resonances were observed at 33.38 and 3.95 ppm which might have been due to the formation of some \(\eta^5\text{-C}_6\text{H}_7\) complex but this could not be isolated. The cations of type \([\text{Ru}(\eta\text{-C}_6\text{H}_6)L(S_2\text{PR}_2)]^+\) also decompose on addition of \(\text{NaBH}_4\). An intermediate case in stability is that of the complex \([\text{Rh}(\eta\text{-C}_5\text{Me}_4\text{Et})(\eta^5\text{C}_6\text{H}_7)]\text{PF}_6\) which slowly reverts to the arene complex or decomposes by loss of benzene both in solution and in the solid state. In contrast, the \([\text{Ru}(\eta^5\text{-C}_6\text{H}_7)(\text{PR}_3)(\text{N-N})]^2+\) cations are all stable in solution and in the solid state.
The production of stable $\eta^5$-cyclohexadienyl complexes from the compounds $[\text{Ru}(\eta\text{-arene})(\text{PR}_3)(\text{N-N})](\text{PF}_6)_2$ is probably due to the lack of other suitable sites of attack in the complex, since the Ru-P and Ru-N bonds are inert towards displacement of the ligand (unlike Ru-Cl bonds). It is also probably due to the presence of ligands which can accept electrons from the metal ($2,2'$-bipy and 1,10-phen) through back donation from the metal to the antibonding $\pi^*$ delocalised molecular orbitals of the ligand, thus increasing the positive charge on the metal. The presence of tightly bound ligands thus increases the possibility of attack on the arene while also decreasing the possibility of attack at the metal.

2.3 Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra in the range 4000-250 cm$^{-1}$ were recorded on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates or in KBr discs. Hydrogen-1 n.m.r. spectra were recorded on Varian Associates HA-100 and EM-360 spectrometers and $^{13}$C-$^1$H spectra on a Varian CFT-20 spectrometer operating at 20 MHz. ($^{13}$C chemical shifts quoted in ppm to high frequency of tetramethylsilane). Melting points were determined with a Kofler hot stage microscope and are uncorrected. Conductivity measurements were made at 298 K using a model 310 Portland Electronics conductivity bridge. Conductivity vs. concentration data were obtained over a range
of concentrations and a plot of \( \Lambda_e \) (equivalent conductance) vs. \( C_e^{1/2} \) (concentration in equivalent \( \text{dm}^{-3} \)) gave a straight line whose slope is a function of the ionic charges. Thus the slopes obtained for various samples could be compared with those for known 1:1 and 1:2 electrolytes and hence the electrolyte type could be determined.

**Materials**

Ruthenium trichloride hydrate and ammonium hexachloroosmate(IV) (Johnson Matthey), ammonium hexafluorophosphate (Ralph Emanuel Ltd.), methylidiphenylphosphine, dimethylphenylphosphine, diethylphenylphosphine (Maybridge); 2,2'-bipyridyl, 1,10-phenanthroline, sodium borohydride, potassium cyanide (BDH); a-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) (Eastman Chemicals). Various cyclohexa-1,4-dienes were prepared by Birch reduction of arenes and then \([\{\text{Ru(\( \eta \)-arene)Cl}_{2}\}_2]\) (arene = \( \text{C}_6\text{H}_6 \), \( \text{C}_6\text{H}_3\text{Me}_3 \), \( \text{C}_6\text{H}_5\text{OMe} \), \( \text{p-MeC}_6\text{H}_4\text{CHMe}_2 \)) and \([\{\text{Os(\( \eta \)-arene)Cl}_{2}\}_2]\) were synthesised as described elsewhere. Analytical and conductivity data for the various compounds are given in Table 2.1 and hydrogen-1 n.m.r. data in Table 2.2. All reactions were carried out in degassed solvents, under an atmosphere of nitrogen.

**\( \eta \)-Benzene(chloro)(1,10-phenanthroline)-ruthenium(II) hexafluorophosphate**

The compound \([\{\text{Ru(\( \pi \)-\( \text{C}_6\text{H}_6 \))Cl}_{2}\}_2]\) (0.20 g; 0.40 mmol) was stirred in methanol (25 cm\(^3\)) with an excess of 1,10-phenanthroline (0.18 g; 1.00 mmol) for ca. 1 hour.
The reaction mixture was filtered giving an orange-yellow conducting solution. Addition of excess NH₄PF₆ (0.30 g; 2.00 mmol) to this solution precipitated a bright yellow solid which was filtered off and washed with water, methanol and diethyl ether (yield 0.35 g, 82%) ν(Ru-Cl) 295 cm⁻¹.

If the reactants in this reaction are refluxed for ca. 8 hrs. an orange solution is produced which deposits an orange crystalline solid which was recrystallised from acetone/diethyl ether and identified as tris(1,10-phenanthroline)-ruthenium(II) hexafluorophosphate diethyletherate (Found, C, 45.6; H 3.0; N 7.9, Calc for C₄₀H₃₄F₁₂N₆O₆P₂Ru;
C, 45.3, H 3.2, N 7.9%) (m.p. >290°C (decomp.)) νC=N 1600 cm⁻¹; Λₘ (1 x 10⁻³ mol dm⁻³ in CH₃NO₂) 161.0 S cm²mol⁻¹.

η-Benzene(2,2¹-bipyridyl)chlororuthenium(II) hexafluorophosphate was prepared from [{Ru(η-C₆H₆)Cl₂}₂] (0.20 g; 0.40 mmol), 2,2¹-bipyridyl (0.14 g; 1.00 mmol) and NH₄PF₆ (0.30 g; 2.00 mmol) under similar conditions to those described for the 1,10-phenanthroline complex (0.39 g, 85%) ν(RuCl) 295 cm⁻¹.

Chloro(η-mesitylene)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate ν(RuCl) 295 cm⁻¹, (η-anisole)chloro(1,10-phenanthroline) ruthenium(II) hexafluorophosphate (0.15 g, 35%) ν(RuCl) 300 cm⁻¹, (η-anisole)(2,2¹-bipyridyl)chlororuthenium(II) hexafluorophosphate (0.16 g, 40%), chloro(η-p-cymene)(1,10-phenanthroline) ruthenium(II) hexafluorophosphate (0.40 g, 68%) ν(RuCl) 295 cm⁻¹ and (η-benzene)(2,2¹-bipyridyl)₁chloroosmium(II) hexafluorophosphate (0.10 g, 28%) were similarly prepared.
The complexes $\eta$-benzene(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate; $\eta$-benzene(diethylphenylphosphine)(1,10-phenanthroline)-ruthenium(II) hexafluorophosphate; $\eta$-benzene(2,2'-bipyridyl)-(dimethylphenylphosphine)ruthenium(II)-hexafluorophosphate (60%); $\eta$-mesitylene(dimethylphenylphosphine)-(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (62%) were similarly prepared from the appropriate chloro complex and tertiary phosphate.

$\eta^5$-cyclohexadienyl(dimethylphenylphosphine)(1,10-phenruthiolene)ruthenium(II) hexafluorophosphate. The compound $[\text{Ru}(\eta^5-C_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]PF_6_2$ (0.10 g; 0.13 mmol) was dissolved in methanol (20 cm$^3$). Addition of excess of NaBH$_4$ (0.10 g; 2.60 mmol) gave an immediate deep orange-red colouration and the reaction mixture was stirred for 30 min.
Water (20 cm³) was added to destroy the excess of NaBH₄ and the resultant mixture was extracted with 2 x 50 cm³ portions of methylene chloride. The orange solution containing the product was dried (Na₂SO₄) and concentrated by evaporation of the methylene chloride in vacuo. Addition of light petroleum (b.p. 60-80°C) gave the product as an orange solid (0.04 g, 52%).

\[ \eta^5\text{-Cyclohexadienyl} \text{(methyldiphenylphosphine)} (1,10\text{-phenanthroline}) \text{ ruthenium(II) hexafluorophosphate} \ (60\%); \]
\[ \eta^5\text{-cyclohexadienyl} \text{(diethylphenylphosphine)} (1,10\text{-phenanthroline}) \text{ ruthenium(II) hexafluorophosphate} \ (45\%); \]
\[ \eta^5\text{-cyclohexadienyl} \text{(2,2'\text{bipyridyl})} \text{(methyldiphenylphosphine)ruthenium(II) hexafluorophosphate} \ (70\%) \]
and \[ \eta^5\text{-1,3,5-trimethylcyclohexadienyl} \text{(dimethylphenylphosphine)} (1,10\text{-phenanthroline}) \text{ ruthenium(II) hexafluorophosphate} \]
were similarly prepared from the appropriate \[ \left[ \text{Ru} \left( \eta^5\text{-arene} \text{PR}_3 (\text{N-N}) \right) \left( \text{PF}_6 \right)_2 \right] \] and excess of NaBH₄.

\[ \eta^5\text{-1-hydroxocyclohexadienyl} \text{(dimethylphenylphosphine)} \text{(1,10\text{-phenanthroline})} \text{ ruthenium(II) hexafluorophosphate acetone solvate}. \]
The complex \[ \left[ \text{Ru} \left( \eta^5\text{-C}_6\text{H}_6 \text{(PMe}_2\text{Ph}) \text{(phen)} \right) \left( \text{PF}_6 \right)_2 \right] \] (0.10 g; 0.13 mmol) was stirred in a mixture of acetone (15 cm³) and water (5 cm³) with 1 pellet of NaOH (0.032 g; 0.80 mmol) for 1 hour. The orange solid deposited was filtered off and washed thoroughly with water and diethyl ether (0.05 g, 58%) \( v(\text{CO}) \) (acetone) 1705 cm⁻¹.

\[ \eta^5\text{-1-hydroxocyclohexadienyl} \text{(methyldiphenylphosphine)} \text{(1,10\text{-phenanthroline})} \text{ ruthenium(II) hexafluorophosphate} \]
was similarly prepared starting from \[ \left[ \text{Ru} \left( \eta^5\text{-C}_6\text{H}_6 \text{(PMePh}_2 \text{(phen)} \right) \left( \text{PF}_6 \right)_2 \right] \] and NaOH (yield 70%).
The complex $[\text{Ru}(\pi-\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})](\text{PF}_6)_2$ (0.10 g; 0.13 mmol) was stirred in methanol (10 cm$^3$) with an excess of KCN (0.10 g; 1.50 mmol) for ca. 1 hr. The bright yellow precipitate which had formed was filtered off and washed thoroughly with water and diethylether (yield 0.055 g; 61%). Likewise $\pi^5$-cyanocyclohexadienyl (2,2'-bipyridyl)-(dimethylphenylphosphine)ruthenium(II) hexafluorophosphate (50%) and $\pi^5$-1-cyanocyclohexadienyl (2,2'-bipyridyl)(methyl diphenylphosphine)ruthenium(II) hexafluorophosphate (80%) can be synthesised from the appropriate $[\text{Ru}(\pi\text{C}_6\text{H}_6)\text{PR}_3(\text{bipy})](\text{PF}_6)_2$ and KCN.
TABLE 2.1

Analytical and conductivity data for some $^6$-arene and $^5$-cyclohexadienyl-ruthenium complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.P. ($^\circ$C)</th>
<th>Analysis (Found(calcd.) (%)</th>
<th>$\lambda_m$ a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_5$)Cl(phen)]PF$_6$</td>
<td>222 (decomp)</td>
<td>39.9</td>
<td>2.6</td>
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<tr>
<td></td>
<td></td>
<td>(40.0)</td>
<td>(2.6)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_5$)Cl(bipy)]PF$_6$</td>
<td>275 (decomp)</td>
<td>37.2</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(37.3)</td>
<td>(2.7)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_3$Me$_3$)Cl phen]PF$_6$</td>
<td>260 (decomp)</td>
<td>43.0</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(43.3)</td>
<td>(3.4)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_5$OMe)Cl phen]PF$_6$</td>
<td>190 (decomp)</td>
<td>39.8</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(40.0)</td>
<td>(3.0)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_5$OMe)Cl bipy]PF$_6$</td>
<td>220 (decomp)</td>
<td>37.2</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(37.4)</td>
<td>(2.8)</td>
</tr>
<tr>
<td>[Ru(MeC$_6$H$_4$CHMe$_2$)Cl phen]PF$_6$</td>
<td>154 (decomp)</td>
<td>44.5</td>
<td>3.7</td>
</tr>
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<td></td>
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<td>(44.3)</td>
<td>(3.7)</td>
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<tr>
<td>[Os(C$_6$H$_6$)Cl(bipy)]PF$_6$</td>
<td>247-249</td>
<td>31.0</td>
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<td></td>
<td></td>
<td>(31.8)</td>
<td>(2.6)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_6$)(PMe$_2$Ph)phen] (PF$_6$)$_2$</td>
<td>245-247</td>
<td>39.4</td>
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<td>(39.6)</td>
<td>(3.2)</td>
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<tr>
<td>[Ru(C$_6$H$_6$)(PMe$_2$Ph)phen] (PF$_6$)$_2$</td>
<td>263-265 (decomp)</td>
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<td></td>
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<td>(43.8)</td>
<td>(3.2)</td>
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<tr>
<td>[Ru(C$_6$H$_6$)(PET$_2$Ph)phen] (PF$_6$)$_2$</td>
<td>267 (decomp)</td>
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<tr>
<td>[Ru(C$_6$H$_6$)(PMe$_2$Ph)bipy] (PF$_6$)$_2$</td>
<td>227-229</td>
<td>37.3</td>
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<td>(37.8)</td>
<td>(3.3)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_6$)(PMe$_2$Ph)(bipy)] (PF$_6$)$_2$</td>
<td>255-257 (decomp)</td>
<td>42.3</td>
<td>3.2</td>
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<td>(42.2)</td>
<td>(3.5)</td>
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<tr>
<td>[Ru(C$_6$H$_3$Me$_3$)(PMe$_2$Ph)phen] (PF$_6$)$_2$</td>
<td>232-234</td>
<td>41.9</td>
<td>3.7</td>
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<tr>
<td></td>
<td></td>
<td>(42.0)</td>
<td>(3.7)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_5$OMe)(PMe$_2$Ph)bipy] (PF$_6$)$_2$</td>
<td>221-224 (decomp)</td>
<td>37.6</td>
<td>3.3</td>
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<td></td>
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<td>(37.8)</td>
<td>(3.4)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_5$)(PMe$_2$Ph)phen] PF$_6$</td>
<td>162-165</td>
<td>48.2</td>
<td>4.1</td>
</tr>
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<td></td>
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<td>(48.5)</td>
<td>(4.0)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_5$)(PMe$_2$Ph)phen] PF$_6$</td>
<td>178-179 (decomp)</td>
<td>52.8</td>
<td>4.1</td>
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<tr>
<td></td>
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<td>(52.8)</td>
<td>(4.0)</td>
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<tr>
<td>[Ru(C$_6$H$_6$OH)(PMe$_2$Ph)phen] PF$_6$ (acetone)</td>
<td>168-169</td>
<td>48.4</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(48.5)</td>
<td>(4.4)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_6$CN)(PMe$_2$Ph)phen] PF$_6$</td>
<td>230 (decomp)</td>
<td>48.2</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(48.5)</td>
<td>(3.7)</td>
</tr>
<tr>
<td>[Ru(C$_6$H$_6$OH)(PMe$_2$Ph)phen] PF$_6$ (acetone)</td>
<td>110-113</td>
<td>53.0</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(52.4)</td>
<td>(4.4)</td>
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<tr>
<td>Compound</td>
<td>Temperature Range</td>
<td>Conductivity 1</td>
<td>Conductivity 2</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>-------------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>([\text{Ru}(C_6H_7)(\text{PMePh}_2)bipy]PF_6)</td>
<td>177-180 (decomp)</td>
<td>51.0</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(51.1)</td>
<td>(4.1)</td>
</tr>
<tr>
<td>([\text{Ru}(C_6H_6CN)(\text{PMe}_2\text{Ph})bipy]PF_6)</td>
<td>170 (decomp)</td>
<td>45.6</td>
<td>3.6</td>
</tr>
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<td></td>
<td></td>
<td>(46.6)</td>
<td>(3.9)</td>
</tr>
<tr>
<td>([\text{Ru}(C_6H_6CN)(\text{PMePh}_2)bipy]PF_6)</td>
<td>180-181 (decomp)</td>
<td>50.9</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(51.0)</td>
<td>(3.8)</td>
</tr>
<tr>
<td>([\text{Ru}(C_6H_4Me_3)(\text{PMe}_2\text{Ph})(\text{phen})]PF_6)</td>
<td>198-199</td>
<td>50.7</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(50.8)</td>
<td>(4.7)</td>
</tr>
</tbody>
</table>

^a Molar conductivities at 298 K in CH$_3$NO$_2$

^b Molar conductivities at 298 K in acetone (S cm$^2$mol$^{-1}$), measured at 10$^{-3}$ mol dm$^{-3}$ concentration.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$^1$H n.m.r. (δ, ppm)$^a$</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6\text{Cl})(\text{phen})]\text{PF}_6$</td>
<td>Acetone-$d_6$</td>
<td>6.33s</td>
<td>8.20m, 8.85d, 9.95d$^b$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6\text{Cl})(\text{bipy})]\text{PF}_6$</td>
<td>DMSO-$d_6$</td>
<td>6.22s</td>
<td>7.78m, 8.30m, 8.60s, 9.75</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_3\text{Me}_3\text{Cl})(\text{phen})]\text{PF}_6$</td>
<td>Acetone-$d_6$</td>
<td>2.32sd, 5.68s</td>
<td>8.02m, 8.22s, 8.85d, 9.80m</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>Acetone-$d_6$</td>
<td>6.75s</td>
<td>2.27d(11.0)$^e,f$, 6.30m$^g$, 8.05m, 8.75d, 9.65m$^b$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>Acetone-$d_6$</td>
<td>6.80s</td>
<td>2.70d(12.0)$^e,f$, 7.00m$^g$, 8.05m, 8.85d, 10.0d$^b$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>Acetone-$d_6$</td>
<td>6.72s</td>
<td>1.24d(16.0)$^e,h$, 2.76d$^d$, 6.0-6.5m$^d$; 8.0m, 8.78d, 9.65d$^b$</td>
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<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>Acetone-$d_6$</td>
<td>6.73s</td>
<td>2.30d(11.0)$^e,f$, 7.30m$^g$, 7.85m, 8.25d, 9.62m$^g$</td>
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<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>Acetone-$d_6$</td>
<td>6.80s</td>
<td>2.49d(11.0)$^e,f$, 7.80m$^g$, 8.20m, 8.90d, 9.90d$^b$</td>
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<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>CDC$_2$H$_2$</td>
<td>2.89m$^j$</td>
<td>2.90m, 4.76m$^j$, 5.79m, 1.85d(br) (10.0)$^{e,f}$, 6.0m$^b$, 6.6m, 7.8m, 8.30m$^b$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>CDC$_2$H$_2$</td>
<td>2.12m$^j$</td>
<td>2.72m, 4.18m, 5.84m, 1.60m$^f$, 6.90m$^g$, 6.60m$^b$, 7.80m$^b$, 8.28m$^b$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>CDC$_2$H$_2$</td>
<td>2.95m</td>
<td>3.05m, 4.60m, 5.72m, 1.65s$^k$, 1.88m$^g$, 2.00s$^k$, 6.10m, 6.60m, 7.78m, 8.30d, 8.50m$^b,g$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>CDC$_2$H$_2$</td>
<td>3.18s</td>
<td>3.08m, 5.18m, 6.10t, 2.00d(11.0)$^e,f$, 6.15-6.80m, 7.98m, 8.52d, 8.70m$^b,g$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>CDC$_2$H$_2$</td>
<td>2.10m$^j$</td>
<td>2.55m, 4.60m, 5.78m, 1.58s$^f$, 6.90-7.20m, 7.40m, 7.80m$^c,g$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PPh}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>CDC$_2$H$_2$</td>
<td>ca. 2.40$^j$</td>
<td>2.80m, 4.70m, 5.80m, 1.10m$^h$, 2.40$^j$, 6.30m, 7.70m, 8.30m$^b,g$</td>
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<tr>
<td>$\text{H}_{2}$</td>
<td>CDC$_2$H$_2$</td>
<td>2.70m</td>
<td>2.90m, 4.70m, 5.82m, 1.70s$^f$, 6.50-7.00m, 7.70m, 8.25d, 9.30m$^b,g$</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{C}_6\text{H}_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$</td>
<td>CDC$_2$H$_2$</td>
<td>1.30s$^d$, 1.45s$^d$; other resonances 1.45d(9.0)$^e,f$, 6.70m$^g$, at 1.70, 2.30 and 4.35 which may be due to (endo) resonance.</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Internal reference (CH$_3$)$_4$Si, s(singlet); d(doublet); t(triplet); m(multiplet); br(broad).  
$^b$ Resonances due to 1,10-phenanthroline.  
$^c$ Resonances due to 2,2'-bipyridyl.  
$^d$ Methyl resonances of C$_6$H$_3$Me$_3$.  
$^e$ Numbers in round brackets indicate $^2$J(PIH) in Hz.  
$^f$ PMe$_2$Ph or PMe$_2$H, resonance.  
$^g$ Phenyl resonance from phosphine group.  
$^h$ CH$_3$ resonance.  
$^i$ Methylenic resonance of ethyl group.  
$^j$ $^2$H(1) (exo) probably superimposed on $^2$H(1) (endo) resonance.  
$^k$ Hydroxyl resonance.  
$^l$ Resonance due to solvated acetone.  
$^m$ Masked by methylene resonance of ethyl group.
CHAPTER 3

Synthesis and Reactions of Some \( \eta^6 \)-Arene-\( \eta^5 \)-Cyclopentadienyl Complexes of Ruthenium(II) and Osmium(II)
3.1 Introduction

Although many $\eta^6$-arene-$\eta^5$-cyclopentadienyl complexes of iron and a few other first row transition elements have been studied, there have been very few reports of their second and third row analogues.

The most exhaustively studied complexes are those of iron(II) which can be readily prepared by the method of Nesmeyanov which involves displacement of one cyclopentadienyl ligand from ferrocene and its replacement by an arene ring. These reactions are either carried out in the refluxing neat arene, or, in the case of a solid or very high boiling liquid arene, in a refluxing high boiling solvent such as decalin (decahydronaphthalene). The reactions are promoted by the use of a Lewis acid catalyst ($\text{AlCl}_3$ or $\text{AlBr}_3$) used in conjunction with some aluminium metal.

Before our studies began, however, no related reactions on the other two metallocenes of the iron triad had been reported, and the only analogous complex was $\left[\text{Ru}(\eta^5\text{C}_5\text{H}_5)(\eta^5\text{C}_6\text{H}_6)\right]\text{Cl}$ which had been prepared by a different route. Therefore, some studies on the reactions of $\text{Ru}(\eta^5\text{C}_5\text{H}_5)_2$ with arenes under various conditions were carried out.

3.2 Results and Discussion

Ruthenocene was successfully prepared by the method described by Vitulli et al. (see Section 3.4). This involved the reaction of hydrated ruthenium trichloride with freshly...
cracked cyclopentadiene in ethanol in the presence of finely divided zinc metal. However, reactions between various dienes and "RuCl₃·xH₂O" were found to be highly dependent on the acidity of the material used. Commercial "RuCl₃·xH₂O", when in solution, is highly acidic (due to contamination with hydrochloric acid) and use of the material as received from Johnson-Matthey Ltd. gave non-reproducible results in these reactions. Presumably, this was because of side reactions between the dienes and the acid contaminant. If the commercial "RuCl₃·xH₂O" was dissolved in water, however, and evaporated to dryness on a water bath, and this process repeated several times, it was found that the acid contamination could be readily removed. Material purified in this way then gave clean reactions and reproducible results.

The ruthenocene prepared from the purified "RuCl₃·xH₂O" was characterised by its hydrogen-1 n.m.r. spectrum, elemental analysis and its mass spectrum. This method was found to give good, high purity yields of Ru(η₆C₆H₅)₂ (see Experimental Section 3.4).

However, attempts to prepare η⁶-arene-η⁵-cyclopentadienyl complexes of ruthenium(II) from ruthenocene using the Nesmeyanov ligand exchange method proved unsuccessful. Several arenes and modifications of the published synthetic route for iron were tried but none gave more than a small trace of a [Ru(η-5C₅H₅)(η-arene)]⁺ cation. This failure can probably be attributed to the greater inertness of ruthenocene compared with ferrocene which stems from the greater metal-
cyclopentadienyl ring bond energy for ruthenocene. This will lead to a decrease in the reaction rate which is presumably determined by the rate of metal-ring cleavage. The reactions attempted involved the use of the Nesmeyanov method with the arene itself as the reaction solvent (for benzene and toluene) and for higher boiling and solid arenes (such as mesitylene) the reactions were carried out in decalin. In no cases, however, were significant amounts of product obtained. A further method which was examined was photolysis of a methanolic solution of ruthenocene in the presence of some benzene. This also produced no conducting material.

An alternative route to the \( \eta^6 \)-arene-\( \eta^5 \)-cyclopentadienyl complexes of ruthenium(II) is by the reaction of \([\text{Ru}(\eta\text{-arene})\text{Cl}_2]_2\) with cyclopentadienylthallium(I). To date this has only been used for the preparation of \([\text{Ru}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]\text{Cl}\) although several other \([\text{Ru}(\eta\text{-arene})\text{Cl}_2]_2\) complexes (arene = 1,3,5-C\(_6\)H\(_3\)Me\(_3\), C\(_6\)H\(_5\)OMe, C\(_6\)Me\(_6\) and p-MeC\(_6\)H\(_4\)CHMe\(_2\)) are now known. Therefore this was employed to prepare several new \([\text{Ru}(\eta\text{-C}_5\text{H}_5)(\eta\text{-arene})]^+\) cations, which were fully characterised by their hydrogen-1 (Table 3.1) and \(^{13}\text{C}-^1\text{H}\) (Table 3.2) n.m.r. spectra and by elemental analysis. This method was also used to prepare the first mixed sandwich complex of osmium(II) by reaction of \([\text{Os}(\eta\text{-C}_6\text{H}_6)\text{Cl}_2]_2\) with Tl[C\(_5\)H\(_5\)]. Thus \([\text{Ru}(\eta\text{-C}_5\text{H}_5)(\eta\text{-p-MeC}_6\text{H}_4\text{CHMe}_2)]\text{BPh}_4\) was prepared by the addition of two equivalents of Tl[C\(_5\)H\(_5\)] to one equivalent of \([\text{Ru}(\eta\text{-p-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2]_2\) dissolved in acetonitrile. The solution was stirred under nitrogen at room temperature to give a pale yellow solution and a fine precipitate of
thallium(I) chloride which was removed by filtration through celite. Further "work-up" of the resulting solution gave the required sandwich cation as its tetraphenylborate salt (see Section 3.4). The $^1$H n.m.r. spectrum of this complex in (CD$_3$)$_2$SO at 301 K (Figure 3.1) consists of a singlet at $\delta$6.11 ppm which can be assigned to the aromatic protons of the coordinated p-cymene ring, a singlet at $\delta$5.31 ppm which is assigned to the coordinated cyclopentadienyl ring, a singlet at $\delta$2.22 ppm, attributed to the methyl group directly attached to the aromatic ring and a doublet at $\delta$1.15 ppm ($J = 6.0$ Hz) assigned to the methyl groups of the isopropyl substituent. Note that the resonance due to the aromatic protons rather unexpectedly appears in this spectrum as a singlet, unlike most complexes of this arene which normally show an AB quartet pattern (see previous Chapter, Table 2.2). The difference in chemical shifts of these protons, however, is dependent upon the other ligands present in the complex and may be coincidentally zero in this case.

The cations $[M(\pi\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{H}_6)]^+$ (M = Fe, Ru, Os) show distinct trends in their hydrogen-1 and $^{13}$C-{ $^1$H} spectra. In the $^1$H n.m.r. spectra the benzene resonance shows a shift from $\delta$6.41 ppm in the iron complex to $\delta$6.20 ppm in the ruthenium complex to $\delta$6.14 ppm in the osmium complex, i.e. a shift to lower frequency on descending the triad. Conversely, the $\pi\text{-C}_5\text{H}_5$ resonance shifts from $\delta$5.17 to $\delta$5.43 to $\delta$5.67 ppm down the triad i.e. a high frequency shift.

In the $^{13}$C-{ $^1$H} spectra however both C$_6$H$_6$ and C$_5$H$_5$ resonances
Figure 3.1: $^1$H n.m.r. spectrum of [Ru($\eta$-$C_5H_5$)($\eta$-MeC$_6H_4CHMe$_2$)]BPH$_4$
were shifted to low frequency although to different extents. This resulted in the $^{13}$C n.m.r. resonances coming so close together that they could not be unambiguously assigned to the C$_6$H$_6$ and C$_5$H$_5$ rings. At this juncture no convincing explanation can be advanced for these trends.

Some attempts were made to prepare a substituted cyclopentadienythallium(I) compound by using methylcyclopentadiene but unfortunately the product was so unstable that no reactions could be carried out with it. Furthermore as it is not possible to prepare the complexes [Ru(polyaromatic)Cl$_2$]$_2$ (polyaromatic = naphthalene, anthracene etc.), the mixed ring cations [Ru($\pi$-C$_5$H$_5$)($\pi ^6$polyaromatic)]$^+$ could not be synthesised by this route although complexes of this type are well established for iron$^{92}$.

It should be noted however that, recently, some preliminary communications$^{99,100}$ have been published describing the preparation of several mixed sandwich cations of ruthenium(II) using the route from ruthenocene and the appropriate arene. The yields of the cations were very low, however, (generally less than 10%) and depended critically on which aluminium halide was used as the reaction catalyst. Furthermore, the reaction yields were increased by the addition of water to the reaction mixture. Presumably in the presence of AlCl$_3$ this leads to the generation of HCl and subsequent protonation of the ruthenocene complex would facilitate the loss of a cyclopentadienyl ligand. However, even in the presence of water the quoted reaction yield was less than 10% in most cases. This can be compared with yields of 50-80% from the analogous reactions of ferrocene.
3.3 Some Attempted Reactions of the Arenecyclopentadienyl Ruthenium(II) Complexes

It is well established\textsuperscript{92,101} that the corresponding iron(II) cations are very susceptible to nucleophilic attack on the coordinated arene ring by a range of nucleophiles to give stable substituted cyclohexadienyl complexes. The isoelectronic $[\text{Rh}(\eta-\text{C}_5\text{Me}_4\text{Et})(\eta-\text{C}_6\text{H}_6)]^{2+}$\textsuperscript{14} cation also readily undergoes similar reactions. However the mixed sandwich ruthenium cations were found to give no appreciable quantities of cyclohexadienyl complexes when treated with the same nucleophiles which reacted readily with the cations $[\text{Ru}(\eta-\text{arene})\text{PR}_3(\text{N-N})]^2^+$ (see Chapter 2, section 2.2). Thus suspensions of $[\text{Ru}(\eta-\text{C}_5\text{H}_5)(\eta-\text{C}_6\text{H}_6)]\text{PF}_60.5\text{NH}_4\text{PF}_6$ in various solvents (T.H.F., methanol or dioxane) on treatment with Na[BH\textsubscript{4}], produced only traces of the hoped for neutral product $\text{Ru}(\eta-\text{C}_5\text{H}_5)(\eta^5\text{C}_6\text{H}_7)$. In most attempts either no reaction or extensive decomposition occurred, particularly for nucleophiles other than hydride, such as OH\textsuperscript{-} or CN\textsuperscript{-} ion. For example, treatment of $[\text{Ru}(\eta-\text{C}_5\text{H}_5)(\eta-\text{C}_6\text{H}_5\text{OMe})]\text{BPh}_4$ with Na[BH\textsubscript{4}] in diglyme resulted in the formation of a dark brown non-homogeneous solid. Work up of the reaction solution after filtration produced no traces of any solid material.

This low reactivity of the sandwich complexes towards nucleophiles may be due to the charge on the cation. As it has been shown in the previous chapter that the dicaticionic arene complexes $[\text{Ru}(\text{arene})\text{PR}_3(\text{N-N})](\text{PF}_6)_2$ undergo nucleophilic attack only with a limited range of nucleophiles it is not too unexpected that the monocaticionic sandwich complexes fail to react to any significant extent.
It has been found that the cation \([\text{Fe}(C_6H_3Me_3)_2]^{2+}\)
can undergo addition of either one or two moles of
nucleophile\(^{102,103}\) which implies that the 1:1 adduct must
have some stability towards further attack by the second mole
of nucleophile. As the 1:1 adduct is analogous to the
\([\text{M}(C_5H_5)(C_6H_6)]^+\) cations this also suggests that the lower
reactivity of the singly charged sandwich cations is due
to the lower cationic charge.

It has been shown that the iron cation \([\text{Fe}(C_5H_5)(C_6H_6)]^+\)
reacts with hydroxide, alkoxide and amide ions with displacement
of the benzene ring and formation of ferrocene\(^{104}\). Although
no ruthenocene was detected it is possible that a similar
reaction takes place in the reaction of some nucleophiles
with the ruthenium analogues, e.g. the case of \([\text{Ru}(C_5H_5)(C_6H_5OMe)]^-\)
BPh\(_4\) which decomposes on addition of Na[BH\(_4\)]\(_-\). This may be
via displacement of the arene and formation of unstable hydride
species.

Finally, some preliminary electrochemical studies on
these \([\text{M}(C_5H_5)(\text{arene})]^+\) cations and other related complexes
are discussed in Chapter 6.

### 3.4 Experimental

Microanalyses, infrared and n.m.r. spectra, melting point
measurements and conductivity measurements were obtained
as described in Chapter 2, section 2.3.
Materials

As in Chapter 2 together with thallium(I)cyclopentadienide (prepared from freshly cracked cyclopentadiene (Aldrich), sodium hydroxide and thallium(I) sulphate (BDH) and sodium tetraphenylborate (BDH).

*n*-Benzene-*n*-cyclopentadienylruthenium(II) hexafluorophosphate 0.5 ammonium hexafluorophosphate

\[\text{[Ru}(n\text{-C}_6\text{H}_6)\text{Cl}_2]_2\] (0.30 g; 0.60 mmol) was dissolved in acetonitrile (80 cm$^3$) and Tl[C$_5$H$_5$] (0.32 g; 1.17 mmol) was added. The reaction mixture was stirred under nitrogen for four hours. The precipitated thallium(I)chloride was removed by filtration through celite. The resulting orange solution was evaporated to dryness on the rotary evaporator and the orange brown residue redissolved in a small volume of methanol. Addition of NH$_4$PF$_6$ precipitated a light brown solid (Yield 0.28 g, 60%) m.p. 110-112$^\circ$C. Found C 29.3, H 2.9, N 1.5%. Calc. for C$_{11}$H$_{11}$F$_6$PRu. 0.5 NH$_4$PF$_6$; C 28.0, H 2.8, N1.5%.

*n*-p-methylisopropylbenzene-*n*-cyclopentadienylruthenium(II)-tetraphenylborate

\[\text{[Ru}(n\text{-p-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2]_2\] (0.30 g, 0.49 mmol) was dissolved in acetonitrile (80 cm$^3$) and Tl[C$_5$H$_5$] (0.286 g, 1.06 mmol) was added. The reaction mixture was stirred under nitrogen for two hours. Thallium(I)chloride was removed by filtration through celite and the resulting solution evaporated to dryness. The orange-brown residue was redissolved
in methanol and sodium tetraphenylborate added to produce a pale greyish-brown precipitate which was filtered off, washed with methanol and diethyl ether and dried in vacuo at 56°C (0.51 g; 82%). Found C 75.6, H 6.5%, Calc. for C$_{39}$H$_{39}$BRu. C 75.6, H 6.3%, m.p. 168-169°C (decomp).

\( \eta \)-Anisole-\( \eta \)-cyclopentadienyl ruthenium(II) tetraphenylborate (Yield 0.26 g, 47%). Found C 72.1, H 5.5%.
Calcld. for C$_{36}$H$_{33}$BORu C 74.8, H 5.7%, m.p. 123-125°C;

\( \eta \)-benzene-\( \eta \)-cyclo-pentadienyl osmium(II) tetraphenylborate (Yield 0.12 g, 17%), Found C 63.1, H 4.5%, Calc. for C$_{35}$H$_{31}$BOs; C 64.4, H 4.8%, m.p. 125-126°C and \( \eta \)-hexamethylbenzene-\( \eta \)-cyclopentadienyl-ruthenium(II) chloride (see footnote) were all synthesised from the corresponding \([\{M(\eta\text{-arene})Cl_2\}_2]\) and Ti C$_5$H$_5$.

Preparation of Ruthenocene by the method of Vitulli et al

As mentioned in Section 3.2, the reaction of commercial "RuCl$_3$.xH$_2$O" with dienes did not yield consistent results. This was found to be most probably due to contamination of the material with hydrochloric acid, as aqueous solutions were found to be high acidic (pH 2.1.5). A simple procedure

\[ \text{The analytical data for this compound clearly indicates that it is a mixture containing a considerable amount of thallium(I) chloride which cannot be easily removed due to the low solubility of both compounds. The } ^1\text{H and } ^{13}\text{C n.m.r. however strongly support the formulation } [\text{Ru}(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_6\text{Me}_6)]\text{Cl.} \]
was found which removed much of the acidic contamination. This involved evaporation of an aqueous solution of "RuCl₃·xH₂O" to dryness on a waterbath, this being repeated several times until the pH of a solution had risen to ca. 4. The material which had been treated in this way when used in the preparation of [(Ru(η-C₆H₆)Cl₂)₂] was found to be much more reactive towards the 1,3- or 1,4-cyclohexadienes. For example, when purified "RuCl₃·xH₂O" is used, the product is a bright red precipitate which forms after 5-10 minutes. The unpurified material, by contrast, produces a reddish-brown solid after a period of three to four hours. Reaction times with other dienes e.g. 1-methoxycyclohexa-1,4-diene and α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3 diene) were also greatly reduced from those quoted elsewhere.

As attempts to produce ruthenocene by reaction of unpurified "RuCl₃·xH₂O" had proved unsuccessful, it was decided to try a reaction involving the purified material. Some purified RuCl₃·xH₂O (0.27 g) was dissolved in ethanol (30 cm³) and freshly cracked cyclopentadiene (30 cm³) (obtained by distillation of cyclopentadiene dimer at 40°C) was added to the solution. Several grams of zinc dust was added and the reaction mixture stirred for 45 minutes under nitrogen. The excess zinc was removed by filtration leaving a pale yellow solution which was reduced in volume on the rotary evaporator. A yellowish white solid was precipitated from solution and filtered off. The ¹H n.m.r. spectrum was a sharp singlet at δ4.6 ppm (CDCl₃). The mass spectrum of the complex showed a parent ion peak at m/e 232 with a
ruthenium isotope pattern \( \frac{m}{e} \) calc. for \( C_{10}H_{10}Ru \) (based on \( ^{102}Ru \) = 232) and fragmentation corresponding to loss of one and two cyclopentadienyl rings (at \( \frac{m}{e} 167 \) and \( \frac{m}{e} 102 \)).

Attempted reactions of \([Ru(C_5H_5)(\text{arene})]BPh_4\) with nucleophiles were carried out in an ethereal solvent. For example \([Ru(\eta-C_5H_5)(\eta-\text{anisole})]BPh_4\) was suspended in diglyme \((CH_3OCH_2CH_2OCH_2CH_2OCH_3)\) and Na\([BH_4]\) was added. The mixture was then stirred for 30 minutes under nitrogen yielding a dark-brown non-homogeneous and highly insoluble solid. The remaining solution was treated with water and extracted with pentane but evaporation of the pentane extract yielded no solid material.

Treatment of \([Ru(\eta-C_5H_5)(\text{C}_6\text{H}_6)]Cl\) with NaBH\(_4\) in dimethoxyethane has been shown previously\(^{105}\) to give a low yield (ca. 10\%) of the complex \(Ru(\eta-C_5H_5)(\eta^5-C_6H_7)\) which was characterised by its \(^1H\) n.m.r. spectrum, which showed a similar pattern to the \(\eta^5\)-cyclohexadienyl complexes of Chapter 2. Other nucleophiles, however, did not yield clean products and \(^1H\) n.m.r. studies suggested that decomposition occurs by ring displacement.
### TABLE 3.1

Hydrogen-1 n.m.r. data for some ruthenium(II) and osmium(II) n-arene-n-cyclopentadienyl complexes (all in $d^6$-DMSO at 301 K).

<table>
<thead>
<tr>
<th>Compound</th>
<th>n-arene</th>
<th>$n$-C$_5$H$_5$</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru($n$-$C_5H_5$)($n$-$C_6H_6$)]PF$_6$ 0.5 NH$_4$PF$_6$</td>
<td>6.20(s)</td>
<td>5.43(s)</td>
<td>-</td>
</tr>
<tr>
<td>[Ru($n$-$C_5H_5$)($n$-$C_6H_5$OMe)]BPh$_4$</td>
<td>5.8-6.5 (m,5H)$^a$</td>
<td>5.34(s)</td>
<td>6.5-7.3$^c$</td>
</tr>
<tr>
<td></td>
<td>3.67 (s, 3H)$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru($n$-$C_5H_5$)($n$-$p$-MeC$_6$H$_4$CHMe$_2$)]BPh$_4$</td>
<td>6.11(s, 4H)$^d$</td>
<td>5.31(s)</td>
<td>6.5-7.3$^c$</td>
</tr>
<tr>
<td></td>
<td>2.22 (s, 3H)$^e$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.15 (d, 6H, $^3J_{HH}$ = 6.0Hz)$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru($n$-$C_5H_5$)($n$-$C_6Me_5$)]Cl</td>
<td>2.33(s, 18H)$^g$</td>
<td>5.09(s)</td>
<td>-</td>
</tr>
<tr>
<td>[Os($n$-$C_5H_5$)($n$-$C_6H_6$)]BPh$_4$</td>
<td>6.14(s)</td>
<td>5.67(s)</td>
<td>6.5-7.3$^c$</td>
</tr>
</tbody>
</table>

**Key**

- $^a$ C$_6$H$_5$OMe aromatic protons
- $^b$ C$_6$H$_5$OCH$_3$ protons
- $^c$ BPh$_4^-$ protons
- $^d$ $n$-C$_6H_4^-$ protons
- $^e$ MeC$_6$H$_4^-$
- $^f$ $n$-$C_6H_4CH(CH$_3$)$_2$
- $^g$ C$_6$(CH$_3$)$_6$
**TABLE 3.2**

\(^{13}\text{C-}^{1}\text{H}\) n.m.r. data for some ruthenium(II) and osmium(II) arenecyclopentadienyl complexes in $d^6$-DMSO at 301 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n-arene</th>
<th>n-C\textsubscript{5}H\textsubscript{5}</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru}(\text{η-}C\textsubscript{5}H\textsubscript{5})}\quad(\text{η-C\textsubscript{6}H\textsubscript{6}})]PF\textsubscript{6}\quad\text{0.5 NH}_4PF\textsubscript{6}$</td>
<td>85.8</td>
<td>80.9</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Ru}(\text{η-}C\textsubscript{5}H\textsubscript{5})\quad(\text{η-p-MeC\textsubscript{6}H\textsubscript{4}CHMe\textsubscript{2}})]\text{BPh}_4$</td>
<td>111.7 (A)*</td>
<td>80.3</td>
<td>120-140</td>
</tr>
<tr>
<td></td>
<td>100.7 (B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>86.0 (C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>84.0 (D)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.2 (E)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>23.1 (F)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.6 (G)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ru}(\text{η-}C\textsubscript{5}H\textsubscript{5})\quad(\text{η-C\textsubscript{6}H\textsubscript{5}O\textsubscript{Me}})]\text{BPh}_4$</td>
<td>85.8, 84.1,</td>
<td>79.6</td>
<td>120-140</td>
</tr>
<tr>
<td></td>
<td>82.9, 80.0,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.4\textsuperscript{a}, 57.1\textsuperscript{b}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Ru}(\text{η-}C\textsubscript{5}H\textsubscript{5})\quad(\text{η-C\textsubscript{6}Me\textsubscript{6}})]\text{Cl}$</td>
<td>98.9\textsuperscript{c}</td>
<td>81.6</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>17.3\textsuperscript{d}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[\text{Os}(\text{η-}C\textsubscript{5}H\textsubscript{5})\quad(\text{η-C\textsubscript{6}H\textsubscript{6}})]\text{BPh}_4$</td>
<td>76.1, 76.5\textsuperscript{+}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Labelling of p-cymene ring

\textsuperscript{a} aromatic carbons of $C\textsubscript{6}H\textsubscript{5}O\textsubscript{Me}$

\textsuperscript{b} Me carbon of $C\textsubscript{6}H\textsubscript{5}O\textsubscript{Me}$

\textsuperscript{c} Aromatic carbons of $C\textsubscript{6}Me\textsubscript{6}$

\textsuperscript{d} Me carbons of $C\textsubscript{6}Me\textsubscript{6}$

\textsuperscript{+} Not possible to assign resonances unambiguously as they are so close together and similar in intensity.
CHAPTER 4

Synthesis, Characterisation and Reactions of

Ruthenium(II) Complexes containing

$\mbox{PPh}_n\mbox{Cl}_{3-n} (n=0,1,2)$ and $\mbox{PPh}_2\mbox{OR} (R=\mbox{Me},\mbox{Et},\mbox{nPr})$ Ligands
4.1 Introduction

A few compounds containing the hydrogen-bonded ligands \([R_2POHOPR_2]^−\) (R = Ph, OMe, OEt) and \([R_2POHOP(R_2)HOPR_2]^−\) (R = Ph, Me, Et) have been reported in recent years and some reactions of these compounds have been investigated (see Chapter 1, section 1.5 for discussion and detailed references). The interest in these compounds is due mainly to their possible use as ligands to produce mixed metal compounds in which the metal centres are linked by P-O bridging groups and no direct metal-metal interactions are present. To date, however, the majority of the studies with these ligands has been confined to complexes of palladium(II) and platinum(II). In fact when this work was started, the only ruthenium complex containing this type of hydrogen bonded ligand was the rather unusual \([(P(OMe)Ph_2)_2(P(OH)Ph_2)RuCl_3Ru(P(OMe)Ph_2)Cl\}] \(^{24}\) made by pyrolysis for 12 hours at 120°C of solutions containing \([(P(OMe)Ph_2)_3RuCl_3Ru(P(OMe)Ph_2)Cl\}] Cl \(^{63}\).
More recently, the ruthenium nitrosyl complexes
\[ \{\text{RuCl}_2(\text{NO})\{\text{R(}\text{EtO})\text{PO}\}_2\text{H}\}_2 \] (40) \((R = \text{OEt, Ph})\) have also been
synthesised and the structure verified by X-ray analysis
(for \(R = \text{OEt}\))\(^{106}\).

For the preparation of complexes of platinum and palladium (II) containing these ligands, the most common synthetic route is
the reaction of a potentially hydrolysable phosphorus ligand
(i.e. one containing a P-Cl or P-OR bond) with various
platinum(II) or palladium(II) salts in a solvent which is
not completely anhydrous. For example, \(\text{Pt(S}_2\text{CNEt}_2\text{)}_2\) reacts
with \(\text{PPh}_2\text{OR}\) (\(R = \text{Me, Et}\)) in alcohols to which a small amount
of water has been added to give the compound \(\text{Pt(S}_2\text{CNEt}_2\text{)}(\text{PPh}_2\text{O})\text{H}\)
as the final product\(^{61}\). As discussed earlier (Chapter 1,
section 1.5) various intermediates such as \([\text{Pt(S}_2\text{CNEt}_2\text{)}(\text{PPh}_2\text{OR})_2]\text{-S}_2\text{CNEt}_2\)
and \(\text{Pt(S}_2\text{CNEt}_2\text{)}(\text{PPh}_2\text{OR})(\text{PPh}_2\text{O})\) are observed and a
reaction pathway has been proposed (see equation \([43]\), page \(31\))
which clearly reveals that both nucleophilic attack on a
coordinated P-OR bond and subsequent hydrolysis of a P-OR bond
are essential steps. The same final product \(\text{Pt(S}_2\text{CNEt}_2\text{)}(\text{PPh}_2\text{O})\text{H}\)
is also formed by the reaction of \(\text{Pt(S}_2\text{CNEt}_2\text{)}_2\) with \(\text{PPh}_2\text{Cl}\) in
aqueous methanol or by direct reaction with \(\text{Ph}_2\text{P(O)H}\)\(^{107}\).

Earlier, Chatt and Heaton\(^{56}\), Austin\(^{48}\) and Kraihsanzel
\textbf{et al}\(^{57}\) also showed that platinum(II), palladium(II) and
molybdenum(0) complexes containing coordinated chlorophosphine
ligands underwent facile reactions leading to replacement
of the attached chloride with a range of other nucleophiles
(See Chapter 1, equations \([18]-[26], [28]-[33]\) for examples).
Therefore by analogy with these studies it was hoped to synthesise new complexes of ruthenium(II) containing \([R_2\text{POHOPR}_2]^-\) ligands either by further reaction with water of compounds containing P-Cl or P-OR bonds or by reaction of suitable ruthenium salts with PR$_2$Cl in the presence of water. The synthesis, characterisation and attempted reactions of a range of ruthenium(II) complexes containing PPh$_n$Cl$_{3-n}$ \((n = 0, 1, 2)\) and PPh$_2$OR ligands are discussed in this Chapter and reactions with various PR$_2$Cl reagents under hydrolysis conditions in Chapter 5.

4.2 Synthesis and characterisation of dialkyldithiophosphinate complexes of ruthenium(II) containing PPh$_n$Cl$_{3-n}$ \((n = 0, 1, 2)\) and PPh$_2$OR \((R = \text{Et, } \text{Pr})\) ligands.

Several years ago it was demonstrated that the complexes cis-Ru(S$_2$PR$_2$)$_2$(PPh$_3$)$_2$ \((R = \text{Me, Ph})\) underwent facile ligand exchange reactions with phosphorus-containing ligands \((L')\) of greater Lewis basicity to give cis-Ru(S$_2$PR$_2$)$_2$L'$_2$ \((L' = \text{PMe$_2$Ph, PMePh$_2$})\). This exchange process has now been extended to synthesise other complexes of this type with L' = PPh$_n$Cl$_{3-n}$ \((n = 0, 1, 2)\) and PPh$_2$(OR) with the intention of hydrolysing the coordinated P-Cl or P-OR bonds to produce complexes containing a range of POHOP ligands.

Thus reaction of a suspension of cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ with an excess of L' in dry hexane under reflux gave the neutral complexes Ru(S$_2$PMe$_2$)$_2$L'$_2$. The products were characterised by elemental analysis, osmometric molecular
weight determinations, infrared, $^1H$ n.m.r. (Table 4.1) and $^{31}P-(^1H)$ (Table 4.2) n.m.r. spectroscopy.

The infrared spectra of these compounds were rather complicated showing absorptions due to the PPh$_n$Cl$_3$-n and PPh$_2$OR groups as well as the $^2S_2PMe_2$ ligands. However, as discussed elsewhere, platinum(II)$^{109}$, palladium(II)$^{109}$ and ruthenium(II)$^{108}$ dimethyldithiophosphinate complexes show characteristic i.r. bands at 570-585 cm$^{-1}$ (bidentate), 610 cm$^{-1}$ (ionic) and 600 cm$^{-1}$ (unidentate). As listed in the experimental section (4.8) all these compounds have an infrared absorption at 580-585 cm$^{-1}$ indicating bidentate $^2S_2PMe_2$ coordination.

In all cases, the $^{31}P-(^1H)$ n.m.r. spectra consist of a pair of triplets with $^3J_{PP} = 5-10$ Hz which confirms the formulation of the complexes as Ru($^2S_2PMe_2$)$_2L'_2$. Similarly reaction of Ru($^2S_2PMe_2$)$_2$($PPh_3$)$_2$ with an excess of PPh$_2$H in hexane gave Ru($^2S_2PMe_2$)$_2$(PPh$_2$H)$_2$. The retention of the phosphorus-hydrogen bond was confirmed by running a proton-coupled $^{31}P$ n.m.r. spectrum in which a large coupling of 360 Hz was observed, indicative of a directly bound hydrogen. The $^1H$ n.m.r. spectrum also showed a doublet of separation 360 Hz centred at 66.66 ppm. An interesting general feature of the $^{31}P-(^1H)$ n.m.r. spectra of these compounds, however, was the marked difference in intensity between the dithiophosphinate resonance and that of the phosphine, even though the triplet patterns clearly indicate that the same number of phosphorus nuclei contribute to
each peak. Furthermore, this intensity difference increased along the series \( \text{Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPh}_3\text{)}_2 < \text{Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPh}_2\text{Cl})_2 < \text{Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPhCl}_2\text{)}_2 < \text{Ru(S}_2\text{PMe}_2\text{)}_2\text{(PCl}_3\text{)}_2 \) from a ratio of ca. 3:2 (L' = PPh\(_3\)) (\( \text{S}_2\text{PMe}_2 \) resonance more intense in all cases) to ca. 4:1 (L' = PCl\(_3\)), (see Figure 4.1). It was thought that these intensity variations could have their origin either in spin-lattice relaxation time (\( T_1 \)) differences and/or in different nuclear Overhauser enhancements (NOE) in the separate phosphorus nuclei. In an attempt to ascertain the factors responsible for these intensity variations, together with those in related compounds, a series of \( T_1 \) measurements have been performed and these are tabulated and discussed in the Appendix.

These \( ^{31}\text{P-}{^1}\text{H} \) n.m.r. spectral patterns are consistent with either a cis (41) or a trans (42) configuration. However the \( ^1\text{H} \) n.m.r. spectrum at ambient temperature of all the PPh\(_n\)Cl\(_{3-n}\) complexes (and of the PPh\(_2\)H complex) shows two doublets of equal intensity in the methyl region (e.g. see Figure 4.2, L' = PPh\(_2\)Cl). Since the \( ^{31}\text{P-}{^1}\text{H} \) n.m.r. spectrum shows that each product is a pure, single compound, it is not possible that this is due to an equimolar mixture of cis and trans isomers. Therefore, this evidence clearly indicates that the two methyl groups on each dimethyldithiophosphinate ligand are magnetically and chemically non-equivalent at room temperature and this can only be due to the cis isomer being the exclusive product rather than the trans isomer.
Figure 4.1: $^{31}$P-$^1$H n.m.r. spectra of cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_2$Cl)$_2$ and cis-Ru(S$_2$PMe$_2$)$_2$(PCL$_3$)$_2$
Figure 4.2: $^1$H n.m.r. spectrum (methyl region) of Ru(S$_2$PMe$_2$)$_2$(PPh$_2$Cl)$_2$
The chemical shifts of the methyl resonances of the \( \text{S}_2\text{PMe}_2 \) ligands in these \( \text{cis}-\text{Ru(}S_2\text{PMe}_2)_2\text{L'}_2 \) compounds are of interest in that the position of the higher frequency doublet at ca. \( \delta2.0 \) ppm remains almost unaltered by changing \( \text{L'} \) whereas that of the lower frequency doublet is very sensitive to changes in \( \text{L'} \) varying from \( \delta1.98 \) ppm (\( \text{L'} = \text{PCl}_3 \)) to \( 1.14 \) ppm (\( \text{L'} = \text{PPh}_2\text{H} \)) (Table 4.1). A possible explanation of this is that the higher frequency doublet arises from the methyl groups \textit{anti} to the phosphorus ligands \([A \text{ in structure (41)}]\) and the lower frequency doublet from the methyl groups \textit{syn} to the phosphorus ligands. Then the \textit{syn} methyl groups will be influenced by the ring currents of the phenyl rings (when present) on the phosphine causing them to be more shielded than the \textit{anti} methyl groups which would account for their lower frequency position. Furthermore, increasing the number of phenyl groups on the phosphine will lead to increased shielding of the \textit{syn} methyls and hence explain the increased low frequency shift in the order \( \text{PPh}_2\text{H}(1.14) > \text{PPh}_2\text{Cl}(1.32) > \text{PPhCl}_2(1.70) > \text{PCl}_3(1.98) \).
Similar trends are seen in the $^{31}$P chemical shifts of the $S_2PMe_2$ ligands (Table 4.2) and this can also be attributed to increased shielding effects as the number of phenyl groups on the phosphine increases.

The same effect has been observed earlier in the $^1$H n.m.r. spectra of the complexes cis-Ru($S_2PMe_2$)$_2$(PR$_3$)$_2$ [PR$_3$ = PPh$_3$, PMePh$_2$, PMe$_2$Ph] (e.g. for cis-Ru($S_2PMe_2$)$_2$(PPh$_3$)$_2$, two doublets at 82.27 and 1.06 ppm are observed which can be assigned to the anti and syn methyl groups respectively.

In contrast, the $^1$H n.m.r. spectrum of Ru($S_2PMe_2$)$_2$-(PPh$_2$O"Pr)$_2$ in CDC$_1$$_3$ at 301 K shows only one doublet at 81.90 ppm due to the methyl groups of the $S_2PMe_2$ ligands. At first sight, this might suggest that in this instance trans-Ru($S_2PMe_2$)$_2$(PPh$_2$O"Pr)$_2$ has been formed. However, a more likely explanation is that the expected cis isomer has been produced and this is undergoing facile interconversion of optical enantiomers (equation [59]) at ambient temperature to scramble the two methyl environments A and B.
Earlier\textsuperscript{110}, detailed variable temperature $^1$H n.m.r. studies confirmed this facile scrambling process for other $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2(\text{PR}_3)_2$ complexes ($\text{PR}_3 = \text{PPh}_3, \text{PMePh}_2, \text{P(OPh)}_3$ etc.). Also $\text{Ru(S}_2\text{PMe}_2\text{)}_2(\text{PPh}_2\text{OEt})_2$ made, in very small yield, by reaction of $\text{RuCl}_2(\text{PPh}_2\text{OEt})_3$ with $\text{Na[S}_2\text{PMe}_2\text{]}_2\text{H}_2\text{O}$\textsuperscript{111} also shows only one methyl doublet in its $^1$H n.m.r. spectrum at 301 K. Unfortunately at lower temperature the $^1$H n.m.r. spectra of these $\text{PPh}_2\text{OR}$ complexes become very broad and thus it was impossible to unequivocally assign $\text{cis}$ configurations to them on this spectroscopic evidence although it is highly likely.

Thus, $^{31}$P-$^1$H and $^1$H n.m.r. spectra indicate that all the new complexes $\text{Ru(S}_2\text{PMe}_2\text{)}_2\text{L}_2$ have a $\text{cis}$ configuration and that all (except for $\text{L}' = \text{P(OR)Ph}_2$) are stereochemically rigid at room temperature. Similar stereochemical rigidity at ambient temperature has been observed earlier for compounds such as $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2(\text{PPh}_3)\text{CO}$ and $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2(\text{CO})_2$ although measurements at higher temperatures in chlorobenzene on the former reveal that scrambling of methyl groups does occur\textsuperscript{108,110}. Likewise, the $^1$H n.m.r. spectrum of $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2(\text{PPh}_2\text{Cl})_2$ (which initially shows two doublets in the methyl region) undergoes a broadening and coalescence of these resonances when the spectra is run in chlorobenzene at ca. 100°C and a single broad resonance, at a position midway between the two original doublets is observed at 130°C. It was not possible to obtain the limiting fast exchange spectrum.

\textsuperscript{1} The same compound can be made in high yield by reaction of $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2(\text{PPh}_3)_2$ with $\text{PPh}_2\text{OEt}$ in hexane.
since the solvent boils at 135°C but on cooling the sample to room temperature the original spectrum was obtained indicating that an intramolecular scrambling process had occurred.

As discussed in detail elsewhere\textsuperscript{110,112}, the most likely mechanism of inversion of the compounds \textit{cis}-Ru(S\textsubscript{2}PMe\textsubscript{2})\textsubscript{2}L'\textsubscript{2} which is outlined in Figure 4.3, involves two ruthenium-sulphur bond cleavage sub-steps. In this mechanism the relative \textit{trans} influence of the ligand L' determines the rate at which interconversion of the two enantiomeric forms of the complex will occur. Hence, this suggests that ligands such as PPh\textsubscript{2}OR have \textit{trans} influences comparable with PMe\textsubscript{2}Ph etc. (leading to facile inversion) whereas ligands such as PPh\textsubscript{n}Cl\textsubscript{3-n} and PPh\textsubscript{2}H have low \textit{trans} influences like CO leading to slow inversion rates. From the limited data available on the \textit{trans} influences of these ligands\textsuperscript{113}, this appears to be a reasonable suggestion.

\begin{center}
\textbf{Figure 4.3:} Proposed solvent-assisted bond rupture mechanism for optical isomerisation of \textit{cis}-Ru(S\textsubscript{2}PMe\textsubscript{2})\textsubscript{2}L'\textsubscript{2}
\end{center}
4.3 Possible Mechanisms of Formation of cis-Ru(S₂PMe₂)₂L₂ complexes

The complex cis-Ru(S₂PMe₂)₂(PPh₃)₂ is known to undergo ready dissociation in solution to give the coordinatively unsaturated species Ru(S₂PMe₂)₂PPh₃ \textsuperscript{108}. This suggests a possible mechanism of ligand exchange as shown in Figure 4.4 viz. coordination of L' to give the six-coordinate Ru(S₂PMe₂)₂PPh₃L' followed by loss of PPh₃ and incorporation of another molecule of L'.

\[ \text{Figure 4.4} \]

Possible Ligand exchange pathway for cis-Ru(S₂PMe₂)₂L₂ Formation
However, an alternative pathway (Figure 4.5) is closely related to that proposed for the facile inversion process discussed earlier (Figure 4.3), namely cleavage of ruthenium-sulphur bonds by L'.

![Chemical structure diagram](image)

**Figure 4.5**

**Alternative Ligand Exchange Pathway for cis-Ru(S₂PMe₂)₂L'₂ Formation**

This alternative reaction pathway (Figure 4.5) is suggested by the observation that cis-Ru(S₂CNMe₂)₂(PPh₃)₂ does not undergo exchange reactions with PPh₃Cl₃ groups under the same mild conditions as found with cis-Ru(S₂PMe₂)₂(PPh₃)₂. It should also be noted that whereas cis-Ru(S₂PMe₂)₂(PMe₂Ph)₂ is carbonylated under very mild conditions to give
Ru(S₂PMₑ₂)₂CO(PMₑ₂Ph)₂ (43) there is no reaction between cis-Ru(S₂CNMe₂)₂(PR₃)₂ compounds and CO even at high pressures¹⁰⁸. This lack of reactivity involving Ru-S bond cleavage can be attributed to the well known stronger nucleophilicity of S₂CNR₂ compared with S₂PR₂¹⁰⁹, preventing formation of compounds of the type (43).

4.4 Some attempted reactions of cis-Ru(S₂PMₑ₂)₂L'₂ complexes

As stated earlier, the main purpose of synthesising the complexes cis-Ru(S₂PMₑ₂)₂L'₂ with L' groups containing P-Cl or P-OR bonds was to examine their reactions with nucleophiles in an attempt to generate compounds containing the [R₂POHOPR₂]⁻ and related ligands. Unfortunately these reactions have met with little success to date.

For example, the P-Cl bonds in the complexes cis-Ru(S₂PMₑ₂)₂(PPh₂Cl)₂ and cis-Ru(S₂PMₑ₂)₂(PPhCl₂)₂ were found to be unreactive towards water at room temperature in the presence or absence of bases such as triethylamine, carbonate ion and hydroxide ion. Under reflux conditions extensive product decomposition occurred. This contrasts with the behaviour of the molybdenum(0) complex
cis-Mo(CO)$_4$(PPh$_2$Cl)$_2$, which on treatment with water and Et$_3$N in THF gave Et$_3$NH[Mo(CO)$_4$(PPh$_2$O)$_2$H] (equation [29], Chapter 1)$^{57}$ and also with the cis-MCl$_2$(PPh$_2$Cl)$_2$ (M = Pd, Pt) compounds which react with water to give cis-MCl$_2$(PPh$_2$OH)$_2$. It is clear that, as discussed earlier, (see Chapter 1, section 1.7) the behaviour of coordinated halophosphines towards nucleophiles depends critically on such factors as the metal ion to which they are coordinated and the nature of the other ligands present in the coordination sphere.

It appears that in this instance coordination to a ruthenium(II) centre stabilises the P-Cl bonds considerably with respect to hydrolysis reactions. In retrospect, this is probably not too surprising, since Muetterties et al.$^{114}$ reported several years ago that triphenylphosphite when coordinated to ruthenium(II) does not undergo transesterification with alcohols, whereas such reactions occur readily with the free ligands. Also cis-Ru(S$_2$PMe$_2$)$_2$[P(OPh)$_3$]$^2$ can be recovered unchanged even after refluxing in degassed methanol for 24 hours$^{108}$ and likewise, in this work, reaction of cis-Ru(S$_2$PMe$_2$)$_2$$^-$ (PPh$_3$)$_2$ with PPh$_2$OEt in aqueous ethanol gave, as in hexane, only Ru(S$_2$PMe$_2$)$_2$(PPh$_2$OEt)$_2$.

Attempted hydrolysis of Ru(S$_2$PMe$_2$)$_2$(PPh$_2$OEt)$_2$ under acid conditions was also unsuccessful due to apparent facile oxidation of the complex in the presence of even trace amounts of hydrochloric acid. Thus, addition of a few drops of concentrated hydrochloric acid to a solution of Ru(S$_2$PMe$_2$)$_2$(PPh$_2$OEt)$_2$ in methylene chloride produced a rapid darkening of the initial orange solution and on
solvent removal, a dark red-brown solid could be isolated. Electron spin resonance measurements showed the material to be strongly paramagnetic, indicative of the formation of ruthenium(III) species, but the complexity of the pattern suggested that a mixture of products had been formed. Attempts to obtain a $^{31}\text{P}-{}^{1}\text{H}$ n.m.r. spectrum were unsuccessful.

A similar reaction with cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ and hydrochloric acid in methylene chloride also gave a purple-brown solid which exhibited strong e.s.r. signals (Figure 4.6). Hence, this showed the rapid reaction was almost certainly not due to acid hydrolysis of the P-OR bonds. Analysis figures (C, H) could not be fitted to a single formulation but were intermediate between the values calculated for Ru(S$_2$PMe$_2$)Cl$_2$(PPh$_3$)$_2$ and [Ru(S$_2$PMe$_2$)Cl$_2$PPh$_3$]$n$. Because, clearly, product mixtures were formed and also no evidence for involvement of the PPh$_2$OR ligand was indicated, no further studies were carried out on these reactions. However, in view of the more recent observation that reaction of cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ with PPh$_2$Cl/H$_2$O/MeOH mixtures (which gives rise to Ph$_2$P(O)H and HCl in situ) leads to loss of one $^{}S_2$PMe$_2$ ligand and formation of the unusual complex Ru(S$_2$PMe$_2$)(PPh$_2$O)$_3$H$_2$ as the major product (see Chapter 5), it appears that one of the functions of the acid here may be to remove, via protonation, a coordinated $^{}S_2$PMe$_2$ group. Another role of the acid may be to facilitate aerial oxidation and therefore a more detailed investigation of these reactions might now be of considerable interest.
Figure 4.6: E.s.r. spectrum of the product of the reaction between cis-Ru(S₂PMₑ₂)₂⁻(PPh₂OEt)₂ and HCl in CH₂Cl₂
At this juncture, however, it was decided to discontinue work on the reactions of Ru(S₂PMe₂)₂L₂ complexes and instead to try to synthesise other ruthenium(II) complexes containing P-Cl or P-OR bonds but no sulphur ligands. By this modification it was hoped that such complexes might then be more reactive towards hydrolysis.

4.5 Reactions of [{Ru(η-arene)Cl₂}₂] complexes with PPh₂OR (R = Me, Et) ligands.

Earlier, (Chapter 2), the reactions of [{Ru(η-arene)Cl₂}₂] with bidentate nitrogen donor ligands (N-N) = bipy, phen) in methanol to give the cationic [Ru(η-arene)Cl(N-N)]PF₆ complexes were described. These reactions have now been extended to synthesise the related complexes [Ru(η-arene)L₂Cl]BPh₄ (L' = PPh₂OMe, PPh₂OEt) in the hope that further reactions of the coordinated P-OR bonds might then occur. Such reactions could be facilitated by the presence of the formal positive charge, which might be expected to facilitate nucleophilic attack (cf. Chapter 2).

Thus if [{Ru(η-arene)Cl₂}₂] (arene = C₆Me₃H₃, p-MeC₆H₄CHMe₂) are shaken in methanol with an excess of PPh₂OMe for 24 hours, a conducting yellow solution is slowly formed, from which the yellow solids [Ru(η-arene)(PPh₂OMe)₂Cl]BPh₄ can be precipitated on addition of sodium tetrphenylborate. Similarly, reaction of [{Ru(η-C₆Me₃H₃)Cl₂}₂] with PPh₂OEt in ethanol gave a high yield of [Ru(η-C₆Me₃H₃)(PPh₂OEt)₂Cl]BPh₄. The complexes were characterised by elemental analysis, hydrogen-1 n.m.r. (Table 4.1) and ³¹P-{¹H} n.m.r. (Table 4.2) spectroscopy.
For example, the complex \([\text{Ru}(n-C_6\text{Me}_3\text{H}_3)(\text{PPh}_2\text{OMe})_2\text{Cl}]\text{BPh}_4\)

had a \(^1\text{H}\) n.m.r. spectrum in \(\text{CDCl}_3\) at 301 K (Figure 4.7)

which consists of a pair of sharp singlets at 64.71 and 61.63 ppm

of relative intensity 1:3 which were assigned to the coordinated

mesitylene ring; a complex set of resonances extending from

66.60 to 67.70 ppm assigned to the phenyl groups of the

PPh\(_2\)OMe and BPh\(_4\) groups and a resonance consisting of a

sharp doublet with a broad central peak† centred at 63.17 ppm,

assigned to the -OMe groups of the PPh\(_2\)OMe ligands. This last

assignment could be confirmed by irradiation in the phosphorus

n.m.r. range which caused this resonance to collapse to a

sharp singlet.

\[\text{[Ru(n-C_6\text{Me}_3\text{H}_3)(\text{PPh}_2\text{OMe})_2\text{Cl}]BPh}_4\]

(44)

All the \(^{31}\text{P}\)-{\(^1\text{H}\)} n.m.r. spectra of the \([\text{Ru(arene)}(\text{PPh}_2\text{OR})_2\text{Cl}]\text{BPh}_4\) (44) complexes, show, as expected, singlets in the region

expected for coordinated PPh\(_2\)OR ligands.

An exception to the above behaviour is found in the

reaction of \([\{\text{Ru}(n-C_6\text{H}_6)\text{Cl}_2\}_2]\) with PPh\(_2\)OMe in methanol.

† This is called a "pseudo-triplet" pattern and signifies a

relatively large \(J_{PP}\) coupling constant compared to the

\(|3J_{PH} + 5J_{PH}|\) coupling constant. cf. \(\text{cis-Ru(S}_2\text{COMe)}_2(\text{PPh}_2\text{OMe})_2\)
Figure 4.7: $^1$H n.m.r. spectrum of $[\text{Ru}(\eta\text{-C}_6\text{H}_3\text{Me}_3)(\text{PPh}_2\text{OMe})_2\text{Cl}]\text{BPh}_4$ in $\text{CDCl}_3$ at 301 K
Shaking over a 24 hour period also produces a conducting yellow solution from which a solid can be precipitated on addition of Na[BPh₄]. However, the $^{31}$P-{$^1$H} spectrum of this product consisted of two sharp singlets at δ125.0 and δ137.2 ppm. The resonance at δ137.2 ppm corresponds closely in position to that of the known complex [Ru₂Cl₃(PPh₂OMe)₆]Cl (δ139.4 ppm)¹¹⁵. The other is probably due to the complex [Ru($\eta$-C₆H₆)(PPh₂OMe)₂Cl]BPh₄. This conclusion is supported by the $^1$H n.m.r. spectrum of the mixture (Figure 4.8) which contained a singlet resonance at δ5.06 ppm typical of a coordinated benzene ring. A "pseudotriplet" resonance at δ3.12 ppm (assigned to [Ru($\eta$-C₆H₆)(PPh₂OMe)₂Cl]BPh₄) and a broad featureless resonance at δ2.97 ppm (from [Ru₂Cl₃(PPh₂OMe)₆]BPh₄) were also present, each of which could be collapsed separately by irradiation at one of the two phosphorus frequencies.

This partial displacement of the benzene ring under these mild conditions was rather unexpected as the same reaction with [{Ru($\pi$-p-MeC₆H₄CHMe₂)Cl₂}]₂ gives only the complex [{Ru($\pi$-p-MeC₆H₄CHMe₂)Cl₂}]BPh₄ and it has been generally found that the ease of cleavage of the metal-ring bond follows the sequence p-MeC₆H₄CHMe₂ > C₆H₆ > C₆Me₆, e.g. the complex [{Ru($\pi$-p-MeC₆H₄CHMe₂)Cl₂}]₂ is found to undergo complete arene exchange with C₆Me₆¹¹⁶ while the other [{Ru(arene)Cl₂}]₂ do not undergo a similar exchange. This, of course, suggests that the ring-metal bond is weaker in the case of p-cymene than it is for benzene, which conflicts with the observation of benzene displacement but retention of the p-cymene ring here. No explanation can be offered at present for this surprising observation.
Figure 4.8: $^1$H n.m.r. spectrum of the product mixture from the reaction between $[\{\text{Ru}(\text{n-C}_6\text{H}_5)\text{Cl}_2\}_2]$ and $\text{PPh}_2\text{OMe}$
Finally, unlike the PPh<sub>2</sub>OR ligands, no products could be isolated from reactions of the [(Ru(η-arene)Cl<sub>2</sub>)<sub>2</sub>] compounds with PPh<sub>n</sub>Cl<sub>3-n</sub> in non-polar solvents (although some success was obtained in polar solvents; see Chapter 5).

Unfortunately as for the cis-Ru(S<sub>2</sub>PM<sub>2</sub>)<sub>2</sub>L<sub>2</sub> complexes, attempts to react the coordinated P-OR bonds in these new [Ru(η-arene)(PPh<sub>2</sub>OR)<sub>2</sub>Cl]<sup>+</sup> cations were unsuccessful. It was thought at first that as chloride ion is released in the preparation of the arene complexes, then if the initial solutions containing [Ru(arene)(PPh<sub>2</sub>OR)<sub>2</sub>Cl]Cl were left to stand for a prolonged period, the chloride present in solution would attack the cationic complex to produce a neutral phosphinyl complex with loss of the alkyl group as alkyl chloride (equation [60]). However, monitoring the conductivity of the solutions for a period of several days showed that no decrease occurred and the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectra of the products from the aged solutions confirmed that no changes had occurred.

Since chloride ion did not produce cleavage of the O-R bonds the more nucleophilic bromide and iodide ions were also tried (by addition of tetraalkylammonium halides to the solution) but observation of the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectra of the mixture at intervals indicated that no reaction had taken place. Similarly, adding the strong nucleophile
K[S₂COEt] in methanol to a solution of [Ru(C₆H₃Me₃)(PPh₂OMe)₂Cl]BPh₄ in methylene chloride and leaving for several days produced no reaction. Finally, even refluxing the above compound with LiI in petroleum ether (b.p. 100-120°C) led to recovery of only starting material.

4.6 Miscellaneous Reactions

Previously, it has been reported that reaction of RuCl₂(PPh₃)₃ with PPh₂Cl in refluxing hexane gave high yields of the triple chloride bridged binuclear complex (PPh₂Cl)₃RuCl₃RuCl(PPh₂Cl)₂ (45)¹¹⁷.

\[
\begin{array}{c}
\text{Cl} \quad \text{P} \quad \text{Cl} \\
\text{Cl} \quad \text{Ru} \quad \text{Cl} \\
\text{Cl} \quad \text{Cl} \quad \text{Ru} \quad \text{Cl} \\
\text{P} \quad \text{Cl} \quad \text{P}
\end{array}
\]

(45)

This complex has a characteristic \(^{31}\text{P-\text{H}}\) n.m.r. spectrum which consists of a sharp singlet at \(\delta 145.7\) ppm and a second order AB₂ pattern at lower frequency (A 134.5; B 126.1 ppm, \(\delta_{AB} 341.0\) Hz \(J(AB) 34.0\) Hz) corresponding to the tertiary phosphines attached to each ruthenium atom. When attempts were made to react this complex with water or amines, however, no changes were observed in the \(^{31}\text{P-\text{H}}\) spectra of the products indicating that no reaction had taken place.

Finally, in view of the work of Kraihanzel et al.⁵⁷ on reactions of cis-Mo(CO)₄(PPh₂Cl)₂ with a wide range of nucleophiles, some attempts were made to prepare chloro-
phosphine complexes of ruthenium in its zerovalent state. Thus, Ru(CO)$_3$(PPh$_3$)$_2$ was prepared as described earlier$^{118}$ by reaction of "RuCl$_3$.xH$_2$O" in 2-methoxyethanol with aqueous formaldehyde and an excess of triphenylphosphine. However attempts to synthesise Ru(CO)$_3$(PPh$_2$Cl)$_2$ by reaction of Ru(CO)$_3$(PPh$_3$)$_2$ with an excess of PPh$_2$Cl in hexane gave only unreacted starting material. In tetrahydrofuran, the only product isolated was Ph$_3$PO.

4.7 Conclusions

A number of interesting new complexes of ruthenium(II) containing PPh$_n$Cl$_3$-n and PPh$_2$OR ligands have been synthesised and fully characterised by various physicochemical methods. Unfortunately, attempts to react the coordinated P-Cl or P-CR bonds have proved unsuccessful irrespective of the nature of the other ligands attached to the ruthenium ion and whether the complexes are cationic or neutral. This behaviour is to be contrasted with that established for similar complexes of molybdenum(0), platinum(II) and palladium(II) and at this time, no good reason for this lack of reactivity can be proposed.

4.8 Experimental

Physical measurements were as for those included in the previous experimental sections, 2.3 and 3.4. Phosphorus-31 n.m.r. spectra were obtained on a JEOL FX-60Q spectrometer operating in the pulse and Fourier transform mode at 24.2 MHz. (Chemical shifts are quoted in ppm to high frequency of
85% $H_3PO_4$). Molecular weights were determined in benzene solution on a Perkin Elmer Vapour Pressure Osmometer (Model 115) calibrated with benzil. Electron spin resonance measurements were performed on a Hilger and Watts "Microspin" spectrometer operating at 9.33 GHz and employing 100 kHz magnetic field modulation and phase sensitive detection. The magnetic field was measured by means of a proton resonance meter. As usual all reactions were carried out in degassed solvents under an atmosphere of nitrogen. Hydrogen-1-n.m.r. and phosphorus-31-n.m.r. data for the new complexes are given in Tables 4.1 and 4.2 respectively.

**Materials**

Na[$S_2PMe_2$].2H$_2$O $^{119}$, RuCl$_2$(PPh$_3$)$_3$ $^{120}$, cis-Ru($S_2PMe_2$)$_2$(PPh$_3$)$_2$ $^{108}$, cis-Ru($S_2CNMe_2$)$_2$(PPh$_3$)$_2$ $^{108}$, Ru$_2$Cl$_4$(PPh$_2$Cl)$_5$ $^{117}$, Ru(CO)$_3$(PPh$_3$)$_2$ $^{118}$ and various [{Ru(η-árene)Cl$_2$}]$^{78,83}$ were prepared as described in the appropriate references.

PPh$_2$(O$^\text{nPr}$) was prepared by dropwise addition of PPh$_2$Cl (10 cm$^3$) in hexane (15 cm$^3$) to a cooled solution of propan-1-ol (5 cm$^3$) and pyridine (5 cm$^3$) in hexane (15 cm$^3$). The precipitate of [C$_5$H$_5$NH]Cl was filtered off and the filtrate then used without further purification [$^{31}$P-(1H)]; 6111.5 ppm plus small amount of Ph$_2$$^\text{nPrPO}$ (630.0 ppm] since on attempted purification, rearrangement rapidly occurs to give some Ph$_2$$^\text{nPrO}$. 
**cis-Bis(chlorodiphenylphosphine)bis(dimethyldithiophosphinato)-ruthenium(II)**

The compound cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ (0.20 g, 0.23 mmol) was suspended in dry n-hexane (50 cm$^3$) and PPh$_2$Cl (0.20 cm$^3$, 1.09 mmol) was added. The mixture was stirred under reflux for 3 hours. The reaction mixture was then filtered while hot and on cooling a bright yellow precipitate was deposited from the clear filtrate. This was refiltered, washed with cold hexane and dried in vacuo at 56°C, m.p. 125-128°C (decomp) (yield 0.10 g, 55%).

Found C 40.1, H 3.6, M 717 (benzene) Calc. for C$_{28}$H$_{32}$Cl$_2$P$_4$RuS$_4$ C 42.4, H 4.0%, M 792. \(v(\text{PS}_2)\), 585 cm$^{-1}$.

**cis-Bis(dichlorophenylphosphine)bis(dimethyldithiophosphinato)-ruthenium(II)**

The compound cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ (0.20 g, 0.23 mmol) was suspended in dry n-hexane and PPh$_2$Cl (0.20 cm$^3$, 1.45 mmol) was added. The mixture was stirred under reflux for ca. 1.5 hours. This produced a suspension of a yellow solid which was filtered off and washed with n-hexane, m.p. 210°C (decomp) (0.12 g, 75%). Found C 27.3, H 3.2. Calc. for C$_{16}$H$_{22}$Cl$_4$P$_4$RuS$_4$ C 27.1, H 3.1%. \(v(\text{PS}_2)\) 585 cm$^{-1}$. This compound decomposed quite rapidly in the solid state and thus no molecular weight could be determined.
cis-Bis(dimethylthiophosphinato)bis(trichlorophosphine)-ruthenium(II)

The complex cis-Ru(S₂PMe₂)₂(PPh₃)₂ (0.20 g, 0.23 mmol) was suspended in dry n-hexane (50 cm³) and PCl₃ (0.20 cm³, 2.32 mmol) was added. The mixture was stirred under reflux for one hour. It was then filtered and the filtrate was evaporated almost to dryness, precipitating an orange-yellow solid. This was filtered off and washed with hexane m.p. 120°C (decomp) (0.095 g, 68%). Found C 7.8, H 2.0. Calc. for C₄H₁₂Cl₆P₄RuS₄ C 7.7, H 1.9%. ν(PS₂) 580 cm⁻¹.

The complex cis-Ru(S₂PMe₂)₂(PPh₃)₂ (0.20 g, 0.23 mmol) was suspended in n-hexane (50 cm³) and PPh₂H added (0.20 cm³, 1.18 mmol). The mixture was stirred under reflux for one hour giving an orange-yellow solution. This was filtered and evaporated leaving an orange-yellow oil. This was treated with petroleum ether (b.p. 40-60°C) and an orange solid was produced. m.p. 208-210°C (0.097 g, 57%). Found C 47.0, H 4.9 M(C₆H₆) 679. Calc. for C₂₈H₃₄P₄RuS₄ C 46.5, H 4.7% M 723. ν(PS₂) 585 cm⁻¹, ν(PH) 2250 cm⁻¹.

Bis-(dimethylthiophosphinato)bis(n-propyldiphenylphosphinite)-ruthenium(II)

The complex cis-Ru(S₂PMe₂)₂(PPh₃)₂ (0.20 g, 0.23 mmol) was suspended in dry hexane (40 cm³) and refluxed with 5 cm³ of the hexane solution containing an excess of freshly...
prepared PPh$_2$O$^n$Pr for 3 hours. Filtration gave some residual starting material and an orange solid which was washed with petroleum ether (b.p. 40-60°C) (m.p. 238-240°C) (0.11g, 57%). Found C 48.9, H 5.4. Calc. for C$_{34}$H$_{46}$O$_2$P$_4$RuS$_4$ C 48.6, H 5.5%. $\nu$(PS$_2$) 585 cm$^{-1}$.

Bis-(dimethyl(dithiophosphinato))bis(ethyl(diphenylphosphinite)ruthenium(II) was similarly prepared from cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ (0.20 g, 0.23 mmol) and PPh$_2$OEt (0.20 cm$^3$, 1.00 mmol) in hexane (50 cm$^3$) under reflux for 3 hours. The orange solid which precipitated was then filtered off and washed with hexane, m.p. 230°C. (Found C 46.5, H 5.1. Calc. for C$_{34}$H$_{46}$O$_2$P$_4$RuS$_4$; C 47.3, H 5.2%. $\nu$PS$_2$ 588 cm$^{-1}$.)

The same compound was precipitated out when cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ was refluxed with PPh$_2$OEt (0.20 cm$^3$, 1.00 mmol) in 90% aqueous ethanol (50 cm$^3$) for 30 minutes.

**Attempted hydrolysis reactions on Ru(S$_2$PMe$_2$)$_2$L$_2$ compounds**

The complex cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_2$Cl)$_2$ (0.20 g) was shaken in acetone (60 cm$^3$) containing water (5 cm$^3$) for 66 hours. No increase in conductivity of the solution was noted and on removal of the solvent only starting material was obtained. Similarly shaking either this compound or cis-Ru(S$_2$PMe$_2$)$_2$(PPhCl)$_2$ with Na$_2$CO$_3$ or NaOH or Et$_3$N for 24 hours gave only the starting materials on work-up of the solutions.
If these solutions were refluxed for short periods, insoluble grey-brown materials were isolated on solvent removal indicative of extensive product decomposition.

Treatment of \( \text{cis-Ru}(S_2\text{PMe}_2)_2(P\text{Ph}_3)_2 \) in methylene chloride with a few drops of concentrated hydrochloric acid gave an immediate dark brown solution. Removal of solvent then gave a purple-brown solid. Found C 47.2, H 4.6. Calc. for \( \text{Ru}(S_2\text{PMe}_2)\text{Cl}_2(P\text{Ph}_3)_2 \): C 55.5, H 4.4% and for \( [\text{Ru}(S_2\text{PMe}_2)\text{Cl}_2(P\text{Ph}_3)]_n \); C 42.9, H 3.8%. The e.s.r. spectrum of this material in \( \text{CH}_2\text{Cl}_2 \) at 77 K showed a complex pattern (see Figure 4.6) indicative of a mixture of paramagnetic Ru(III) complexes.

Similarly, reaction of \( \text{Ru}(S_2\text{PMe}_2)_2(P\text{Ph}_2\text{OEt})_2 \) in methylene chloride with concentrated hydrochloric acid gave a dark brown solution which on solvent removal produced a dark red-brown solid which was washed with petroleum ether (b.p. 30-40°C). Found C 43.0, H 4.6. Calc. for \( \text{Ru}(S_2\text{PMe}_2)\text{Cl}_2(P\text{Ph}_2\text{OEt})_2 \); C 47.6, H 4.8% and for \( [\{\text{Ru}(S_2\text{PMe}_2)\text{Cl}_2(P\text{Ph}_2\text{OEt})\}_n \]; C 36.4, H 4.0%. Again the e.s.r. spectrum in \( \text{CH}_2\text{Cl}_2 \) at 77 K showed a complex pattern.

**Chloro(\( \eta \)-mesitylene)bis(methyldiphenylphosphinite)ruthenium(II)-tetraphenyborate**

The complex \( [\{\text{Ru}(\eta\text{-mesitylene})\text{Cl}_2\}_2 \) (0.20 g, 0.34 mmol) was suspended in methanol (25 cm\(^3\)) and methyldiphenylphosphinite (0.40 cm\(^3\), 2.00 mmol) was added. The reaction mixture was shaken for 24 hours and filtered giving a yellow solution which was found to be conducting. Sodium tetraphenyborate
was added to the solution giving a bright yellow precipitate which was filtered off and washed with methanol and diethylether m.p. 153-154°C (Yield 0.51 g, 74%).

Found C 70.0, H 5.8. Calc. for C_{59}H_{58}BClO_2P_2Ru; C 70.2, H 5.8%. Similarly chlorobis(ethyldiphenylphosphinite)-(η-mesitylene)ruthenium(II) tetraphenylborate was prepared by treatment of [{Ru(η-C_6H_3Me_3)Cl_2}]_2 (0.20 g, 0.40 mmol) with an excess of ethyldiphenylphosphinite (0.20 cm^3, 1.00 mmol) in ethanol (25 cm^3) for 24 hours at room temperature followed by addition of Na[BPh_4] to give an orange yellow solid m.p. 175-177°C (0.50 g, 70%).

Chloro-(η-p-cymene)bis(methyldiphenylphosphinite)ruthenium(II) tetraphenylborate

The compound [{Ru(η-p-MeC_6H_4CHMe_2)Cl_2}]_2 (0.20 g, 0.33 mmol) was dissolved in methanol (25 cm^3) and methyldiphenylphosphinite (0.20 cm^3, 1.00 mmol) was added. The solution rapidly turned red and the conductivity of the solution was monitored. When this reached a steady maximum value, sodium tetraphenylborate was added, depositing the product as a yellow solid which was filtered off and washed with methanol and diethyl ether, m.p. 164-166°C (0.47 g, 70%).

Found, C 68.7, H 5.8. Calc. for C_{60}H_{60}BClO_2P_2Ru; C 70.5, H 5.9%.

The compound [{Ru(η-C_6H_6)Cl_2}]_2 (0.20 g, 0.40 mmol) was shaken in methanol (25 cm^3) with an excess of methyldiphenylphosphinite (0.40 cm^3, 2.00 mmol) for 24 hours to give a yellow solid. As discussed earlier (section 4.5) ^31P-(^1H)
and $^1$H n.m.r. studies indicate that a mixture of
$[\text{Ru}_2\text{Cl}_3\text{PPh}_2\text{OMe}]_6\text{BPh}_4$ and $[\text{Ru}(\eta-C_6\text{H}_6)\text{PPh}_2\text{OMe}]_2\text{Cl}\text{BPh}_4$
(in ca. equimolar amounts) had been produced.

**Attempted rearrangement reactions on $[\text{Ru}(\eta\text{-arene})\text{PPh}_2\text{OR}]_2\text{Cl}^+$ cations**

The complex $[\text{Ru}(\eta-C_6\text{H}_3\text{Me}_3)\text{PPh}_2\text{OMe}]_2\text{Cl}\text{BPh}_4$ was
dissolved in a small volume of CH$_2$Cl$_2$ and added to a methanolic
solution of $[\text{Ph}_3\text{(PhCH}_2\text{)}\text{P}]\text{Cl}$. The crystalline precipitate of
$[\text{Ph}_3\text{(PhCH}_2\text{)}\text{P}][\text{BPh}_4]$ was filtered off and the solution containing
$[\text{Ru}(\eta-C_6\text{H}_3\text{Me}_3)\text{PPh}_2\text{OMe}]_2\text{Cl}\text{Cl}$ left for several days. No
change in the conductivity of the solution was observed
and on removal of solvent, $^{31}\text{P}-(^1\text{H})$ n.m.r. studies showed
only a singlet at $\delta$130.0 ppm (corresponding to unchanged
cation). Potassium xanthate was added to some of the solution
and left to stand for several days. Removal of solvent
gave a product whose $^{31}\text{P}-(^1\text{H})$ n.m.r. spectrum was identical
to starting material.

Therefore $[\text{Ru}(\eta-C_6\text{H}_3\text{Me}_3)\text{PPh}_2\text{OMe}]_2\text{Cl}\text{BPh}_4$ (0.10 g)
was dissolved in tetrahydrafuran (50 cm$^3$) and shaken with
$^n\text{Bu}_4\text{NI}$ for several hours. However removal of solvent and
examination of the $^{31}\text{P}-(^1\text{H})$ n.m.r. spectrum indicated that
no reaction had taken place. The same was true using
$^n\text{Bu}_4\text{NBr}$.

Finally $[\text{Ru}(\eta-C_6\text{H}_3\text{Me}_3)\text{PPh}_2\text{OMe}]_2\text{Cl}\text{BPh}_4$ (0.20 g) was
suspended in petroleum ether (b.p. 100-120°C) and LiI (0.10 g)
was added. The suspension was heated up to reflux temperature
at which point, a gummy deposit formed on the side of the flask. This was dissolved in CDCl$_3$ and shown by $^{31}$P-$^1$H n.m.r. spectroscopy to be starting material.

**Attempted Reactions of Ru$_2$Cl$_4$(PPh$_2$Cl)$_5$**

(a) Triethylamine (0.50 cm$^3$) was added to a stirred suspension of Ru$_2$Cl$_4$(PPh$_2$Cl)$_5$ (0.20 g) in aqueous methanol (15 cm$^3$). After one hour at room temperature the suspended solid was filtered off and shown to be identical to starting material by $^{31}$P-$^1$H, $^1$H n.m.r. measurements and analysis. Found C 51.2, H 3.4. Calc. for C$_{60}$H$_{50}$Cl$_9$Ru$_2$: C 49.8, H 3.5%.

Similarly, if the above solution was refluxed for two hours, only starting material was recovered. Found C 50.6, H 3.5%.

(b) A solution of Ru$_2$Cl$_4$(PPh$_2$Cl)$_5$ (0.20 g) and p-toluidine (0.20 g) in tetrahydrofuran (30 ml) was refluxed for four hours. After filtering, the orange solution was evaporated to dryness, the residue redissolved in CHCl$_3$ and precipitated from solution by addition of petroleum ether (b.p. 60-80$^\circ$C). The $^{31}$P-$^1$H n.m.r. spectrum of the product was identical with starting material.

**Attempted Reaction of Ru(CO)$_3$(PPh$_3$)$_2$ with PPh$_2$Cl**

(a) The compound Ru(CO)$_3$(PPh$_3$)$_2$ (0.50 g) was suspended in hexane, PPh$_2$Cl (0.60 cm$^3$) added and the reaction mixture refluxed for 45 hours. The resulting solid
was filtered off, washed with hexane and dried in vacuo at 56°C. The solution i.r. spectrum (in THF; \( \nu_{CO} \) 1900 cm\(^{-1} \)) and \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectrum [(THF/C\(_6\)D\(_6\)) \( \delta \) 55.0 ppm (singlet)] are identical with those of a sample of Ru(CO)\(_3\)(PPh\(_3\))\(_2\) \(^{118}\).

(b) A solution of Ru(CO)\(_3\)(PPh\(_3\))\(_2\) (0.28 g) in tetrahydrofuran (60 cm\(^3\)) was heated under reflux with PPh\(_2\)Cl (1.0 cm\(^{-1}\)). After 20 hours some solution was removed and then diethyl ether added to precipitate a white solid, identified as Ph\(_3\)PO (\( \nu_{PO} \) 1180 cm\(^{-1} \)).
### TABLE 4.1
Hydrogen-1 n.m.r. data for some halophosphine and phosphinite complexes of ruthenium(II)
(in CDCl₃ at 301 K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^3$S₂PMe₂</th>
<th>n-arene</th>
<th>PPh₂Cl₃-n or PPh₂OR</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Ru($^3$S₂PMe₂)$_2$(PPh₂Cl)$_2$</td>
<td>1.32(d), 2.06(d) ($^2$J$_{PH}$ 13.0 Hz)</td>
<td>PH (13.0 Hz)</td>
<td>7.0-7.9(m)</td>
</tr>
<tr>
<td>cis-Ru($^3$S₂PMe₂)$_2$(PPhCl₂)$_2$</td>
<td>1.70(d), 2.03(d) ($^2$J$_{PH}$ 13.0 Hz)</td>
<td>PH (13.0 Hz)</td>
<td>7.0-7.9(m)</td>
</tr>
<tr>
<td>cis-Ru($^3$S₂PMe₂)$_2$(PCl₃)$_2$</td>
<td>1.98(d), 2.13(d) ($^2$J$_{PH}$ 13.8 Hz)</td>
<td>PH (13.0 Hz)</td>
<td>-</td>
</tr>
<tr>
<td>cis-Ru($^3$S₂PMe₂)$_2$(PPh₂H)₂</td>
<td>1.14(d), 2.07(d) ($^2$J$_{PH}$ 13.0 Hz)</td>
<td>PH (13.0 Hz)</td>
<td>6.8-7.7(m)</td>
</tr>
<tr>
<td>cis-Ru($^3$S₂PMe₂)$_2$(PPh₂OEt)$_2$</td>
<td>1.43(d) ($^2$J$_{PH}$ 12.0 Hz)</td>
<td>-</td>
<td>1.20(t) $^3$J$_{HH}$ = 7.0 Hz</td>
</tr>
<tr>
<td>cis-Ru($^3$S₂PMe₂)$_2$(PPh₂OPr)$_2$</td>
<td>1.90(d) ($^2$J$_{PH}$ 13.0 Hz)</td>
<td>-</td>
<td>3.40(br), 1.15(t) $^3$J$_{HH}$ = 6.5 Hz</td>
</tr>
<tr>
<td>[Ru(π-C₆H₃Me₃)(PPh₂OMe)₂Cl]BPh₄</td>
<td>-</td>
<td>-</td>
<td>4.71(s), 1.63(s), 3.17(pt), 7.0-8.0(m)</td>
</tr>
<tr>
<td>[Ru(π-p-cymene)(PPh₂OMe)₂Cl]BPh₄</td>
<td>-</td>
<td>-</td>
<td>5.06 (AA'BB')</td>
</tr>
<tr>
<td>[Ru(π-C₆H₆)(PPh₂OMe)₂Cl]BPh₄</td>
<td>-</td>
<td>-</td>
<td>0.91(d, CH₃ of CHMe₂, J 7.0 Hz)</td>
</tr>
<tr>
<td>[Ru(π-C₆H₃Me₃)(PPh₂OEt)₂Cl]BPh₄</td>
<td>-</td>
<td>-</td>
<td>4.79(s), 1.73(s), 3.50(m), 1.00(t)</td>
</tr>
<tr>
<td>[Ru₂Cl₃(PPh₂OMe)₆]BPh₄</td>
<td>-</td>
<td>-</td>
<td>2.97(m)</td>
</tr>
</tbody>
</table>

- PPh₂Cl₃-n or PPh₂OR
- $^2$J$_{PH}$
- $^3$J$_{HH}$
TABLE 4.2

$^{31}P-^1H$ n.m.r. data for some halophosphate and phosphinite complexes of ruthenium(II) (in CDCl$_3$ at 301 K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^3$PMe$_2$</th>
<th>$^{13}$P$_2$Cl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_2$Cl)$_2$</td>
<td>90.0 (t, $^3$J$_{PP}$ 6.1 Hz)</td>
<td>137.0 (t, $^3$J$_{PP}$ 6.1 Hz)</td>
</tr>
<tr>
<td>cis-Ru(S$_2$PMe$_2$)$_2$(PPhCl$_2$)$_2$</td>
<td>92.1 (t, $^3$J$_{PP}$ 7.3 Hz)</td>
<td>164.9 (t, $^3$J$_{PP}$ 7.3 Hz)</td>
</tr>
<tr>
<td>cis-Ru(S$_2$PMe$_2$)$_2$(PCl$_3$)$_2$</td>
<td>95.3 (t, $^3$J$_{PP}$ 9.8 Hz)</td>
<td>138.0 (t, $^3$J$_{PP}$ 9.8 Hz)</td>
</tr>
<tr>
<td>cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_2$H)$_2$</td>
<td>89.2 (t, $^3$J$_{PP}$ 4.2 Hz)</td>
<td>49.0 (t, $^3$J$_{PP}$ 4.2 Hz)</td>
</tr>
<tr>
<td>cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_2$OEt)$_2$</td>
<td>86.5 (t, $^3$J$_{PP}$ 6.0 Hz)</td>
<td>140.1 (t, $^3$J$_{PP}$ 6.0 Hz)</td>
</tr>
<tr>
<td>cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_2$OEt)$_2$</td>
<td>86.7 (t, $^3$J$_{PP}$ 6.0 Hz)</td>
<td>140.8 (t, $^3$J$_{PP}$ 6.0 Hz)</td>
</tr>
<tr>
<td>[Ru(n-C$_6$H$_5$)(PPh$_2$OEt)$_2$Cl]BPh$_4$</td>
<td>125.0(s)</td>
<td></td>
</tr>
<tr>
<td>[Ru(n-C$_6$H$_5$Me$_3$)(PPh$_2$OEt)$_2$Cl]BPh$_4$</td>
<td>130.3(s)</td>
<td></td>
</tr>
<tr>
<td>[Ru(n-p-cymene)(PPh$_2$OEt)$_2$Cl]BPh$_4$</td>
<td>124.5(s)</td>
<td></td>
</tr>
<tr>
<td>[Ru(n-C$_6$H$_5$Me$_3$)(PPh$_2$OEt)$_2$Cl]BPh$_4$</td>
<td>129.2(s)</td>
<td></td>
</tr>
<tr>
<td>[Ru$_2$Cl$_3$(PPh$_2$OEt)$_6$]BPh$_4$</td>
<td>137.2(s)</td>
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CHAPTER 5

Synthesis, Characterisation and Reactions of some Diphenylphosphinous Acid and Dimethylphosphite Complexes of Ruthenium(II)
5.1 Introduction

Since the reactivity of the P-Cl and P-OR bonds towards hydrolytic cleavage is very low in phosphorus ligands such as PPh$_2$Cl and PPh$_2$OR coordinated to a ruthenium(II) centre, the alternative approach of synthesising [$\text{R}_2\text{POHOPR}_2$]$^-$ complexes by in situ hydrolysis of chlorophosphine ligands prior to reaction with ruthenium compounds was considered.

In an aqueous medium PR$_2$Cl (R = phenyl, alkyl) are rapidly hydrolysed to give R$_2$P(O)H which can in principle exist in equilibrium with their phosphorus(II) tautomeric forms. Although the presence of the R$_2$P(OH) forms has never been shown by direct methods, their existence has been inferred from some of their reactions. In fact, some secondary phosphine oxides exist almost exclusively in the hydroxy form, when there are electronegative substituents attached to the phosphorus atom e.g. (CF$_3$)$_2$P(OH).

As discussed in Chapter 1, section 1.5, various nickel(II), platinum(II) and palladium(II) complexes containing the [$\text{R}_2\text{POHOPR}_2$]$^-$ ligands have been synthesised via reaction of suitable metal complexes with R$_2$P(O)H. In this chapter, the results of related studies with various ruthenium(II) compounds are reported.

5.2 Reaction of prehydrolysed PPh$_2$Cl and of (MeO)$_2$P(O)H with cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$

The exchange reaction between cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ with a large excess of PPh$_2$Cl, under reflux, for several
hours in aqueous acetone (ca. 10:90 v/v) gave a red solution from which a red microcrystalline solid A (which was non-conducting in methylene chloride) was obtained on work-up (ca. 30% yield see section 5.6 for details). Large amounts of a white solid B were also obtained. The $^{1}$H n.m.r. spectrum of B in CDCl$_3$ consisted of a doublet at $\delta$1.10 ppm ($J$ 10.0 Hz) and phenyl resonances in a 3:5 intensity ratio respectively. The $^{31}$P-$^{1}$H n.m.r. spectrum in CDCl$_3$ (301 K) showed a sharp singlet at $\delta$34.8 ppm, whereas a selectively decoupled $^{31}$P n.m.r. spectrum (phenyl protons decoupled) consisted of a septet (separation 12.0 Hz) indicating that two methyl groups are close to the phosphorus atom. Elemental analyses showed a high percentage of carbon and hydrogen and qualitative tests revealed that no sulphur was present. A compound which fits all the above data is the adduct (46) formed by the addition of the P-H bond of Ph$_2$P(O)H across the C=O double bond of the acetone solvent. Confirmation of this conclusion is obtained by producing the same material B by the reaction of PPh$_2$Cl with aqueous acetone alone and comparing it with a genuine sample of Ph$_2$(PO)C(OH)Me$_2$. By carrying out the exchange reaction in aqueous methanol, only the red solid A was obtained (in slightly higher yield). The
$^1$H n.m.r. spectrum of A in CDCl$_3$ at 298 K (Table 5.1) consisted of broad phenyl resonances between $\delta$6.5-8.0 ppm, a sharp doublet centred at $\delta$2.00 ppm (separation 12.0 Hz); and a weak broad resonance at $\delta$8.80 ppm. The relative intensity of these signals was 15:3:1 respectively. Furthermore, on addition of a few drops of D$_2$O to the CDCl$_3$ solution, the weak high frequency resonance at $\delta$8.80 ppm disappeared suggesting it corresponded to hydroxo-type protons (cf. related studies on binuclear hydroxo-bridged complexes such as [Ru$_2$(η-C$_6$H$_6$)$_2$(OH)$_3$]BPh$_4$ in which facile H/D exchange with the deuterated solvent leads to rapid loss of the hydroxo proton resonances$^{122}$.

The $^{31}$P-$^1$H n.m.r. spectrum of A in CDCl$_3$ at 298 K (Figure 5.1) contained two resonances, a quartet at $\delta$102.4 in a region characteristic of a symmetrically bonded $^-$S$_2$PMe$_2$ group (cf. [Ru(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$]BPh$_4$, $[\delta$110.3 ppm (quartet) $^-SPMe$_2$]$^{111}$ and a doublet at $\delta$122.8 ppm. A splitting of 4.4 Hz which is typical for $^3$J$_{PP}$ couplings$^{111}$ was observed on both quartet and doublet patterns. The presence of a bidentate $^-$S$_2$PMe$_2$ group is supported by the characteristic infrared band at 590 cm$^{-1}$ ($\nu_{PS2}$). The combination of this spectral data indicates that A contains one $^-$S$_2$PMe$_2$ ligand coupled to three magnetically equivalent phosphorus ligands and associated with two hydroxo type protons and each have two phenyl groups attached. Elemental analysis and osmometric molecular weight measurements in benzene support this conclusion and suggest a five
Figure 5.1: $^{31}\text{P-}^{1}\text{H} \text{n.m.r. spectrum of } \text{Ru}(\text{S}_2\text{PMe}_2)(\text{PPh}_2\text{O})_3\text{H}_2$
coordinate monomeric formulation, \( \text{Ru}(S_2\text{PMe}_2)(\text{PPh}_2\text{O})_3\text{H}_2 \) (47). This is also consistent with retention of a ruthenium(II) oxidation state as evidenced by the sharp n.m.r. resonances. Related five-coordinate monomers \([\text{Ru}(S_2\text{PR}_2)(\text{PMe}_2\text{Ph})_3]\text{BPh}_4\) (48) (\( R = \text{Me}, \text{Ph} \)) have recently been synthesised by reaction of cis-\( \text{RuCl}_2(\text{PMe}_2\text{Ph})_4 \) with \( \text{Na}[S_2\text{PR}_2] \) (\( R = \text{Me}, \text{Ph} \)) in methanol for a short time, followed by addition of \( \text{Na}[\text{BPh}_4] \) (cf. for \( R = \text{Me} \), \( ^{31}\text{P}-{^1}\text{H} \) n.m.r. spectrum in CDCl\(_3\) from 213-298 K \( \delta 32.4 \text{ ppm} (d) \text{ PMe}_2\text{Ph} ; \delta 110.3(q) \) \( ^{-S_2\text{PMe}_2} \) \( ^{3}J_{\text{PP}} 3.6 \text{ Hz} \)) \(^{111}\). Furthermore, for \( R = \text{Ph} \), X-ray structural analysis has shown the cation to have the distorted square pyramidal geometry (48) in the solid state which conforms to the theoretical predictions for five-coordinate \( d^6 \) complexes \(^{123}\). The \( ^{31}\text{P}-{^1}\text{H} \) n.m.r. spectrum of (48) indicates that this compound is undergoing rapid intramolecular scrambling even at 213 K and similarly, for \( \text{Ru}(S_2\text{PMe}_2)(\text{PPh}_2\text{O})_3\text{H}_2 \), no change in the \( ^{31}\text{P}-{^1}\text{H} \) spectrum was observed on cooling to 213 K.

Compound (47) represents another example of a complex containing the unusual hydrogen-bonded tridentate ligand \([\text{R}_2\text{POHOPR}_2(\text{HO})\text{PR}_2]^- \) (cf. [\( \text{Co}(\eta-C_5\text{H}_5)(\{\text{RO}\}_2\text{PO})_3\text{H}_2 \) BF\(_4\) (25)
If cis-Ru(S₂PMe₂)₂(PPh₃)₂ was reacted with only small amounts of PPh₂Cl in aqueous methanol, a mixture of two compounds was produced. These were inseparable either on various chromatographic columns, (extensive decomposition occurred on both silica and alumina) or by solubility differences in various polar or non-polar solvents. The ³¹P-¹H n.m.r. spectrum of this mixture in CDC₁₃ at 298 K (Figure 5.2) showed that one of the products was compound (47) and the other probably Ru(S₂PMe₂){(PPh₂O)₂H}PPh₃ (49). The ³¹P-¹H n.m.r. spectrum of the latter consisted of a triplet of doublets at δ52.4 ppm with ²Jₚₚ = 37.1 Hz and ³Jₚₚ = 4.4 Hz (PPh₃), a doublet of doublets at δ121.3 ppm, ²Jₚₚ = 37.1 Hz and ³Jₚₚ = 2.9 Hz ([PPh₂OHOPPh₂]⁻), and a broad poorly resolved resonance at δ104.7 ppm (S₂PMe₂). The complexity of the S₂PMe₂ resonance was probably due to the small, similar values of the coupling constants to the PPh₃ phosphorus (4.4 Hz) and to the [PPh₂OHOPPh₂]⁻ ligand (2.9 Hz). Reaction of this mixture with more PPh₂Cl in aqueous methanol converted it completely to Ru(S₂PMe₂){(PPh₂O)₃H₂}, confirming that compound (49) is an intermediate in the formation of complex (47).
Figure 5.2: $^{31}$P-$^{1}$H n.m.r. spectrum of a mixture of Ru(S$_2$PMe$_2$)$_2$-((PPh$_2$O)$_3$H$_2$) and Ru(S$_2$PMe$_2$)((PPh$_2$O)$_2$H)PPh$_3$
However reaction of $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPh}_3\text{)}_2$ with $\text{Ph}_2\text{P(O)}\text{H}$ under the same conditions in the absence of HCl gave a complex mixture of products ($^{31}\text{P-}^{1}\text{H}$ n.m.r. evidence) indicating that protonation and subsequent removal of a coordinated $\text{S}_2\text{PMe}_2$ group by the HCl released in the in situ hydrolysis of $\text{PPh}_2\text{Cl}$ is probably a key step in the formation of compounds (47) and (49). It is interesting that, in the absence of $\text{Ph}_2\text{P(O)}\text{H}$, treatment of $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPh}_3\text{)}_2$ (and other complexes of the same type) with small amounts of concentrated hydrochloric acid appears to produce a mixture of paramagnetic species, indicating that facile oxidation of the compound has taken place (see Chapter 4, section 4.4 for further details).

Based on these experimental observations, a possible rationalisation for the formation of compounds (47) and (49) from the reaction of $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPh}_3\text{)}_2$ with $\text{Ph}_2\text{P(O)}\text{H}$ can be proposed (Figure 5.3) (overleaf).

This involves loss of PPh$_3$ to give Ru($\text{S}_2\text{PMe}_2\text{)}_2$PPh$_3$, protonation of a Ru-S bond with release of HS$_2$PMe$_2$ followed by reaction with $\text{Ph}_2\text{P(O)}\text{H}$ to give compound (49) followed by further reaction with $\text{Ph}_2\text{P(O)}\text{H}$ to give compound (47). In support of the role of HCl in removing a coordinated $\text{S}_2\text{PMe}_2$ ligand, reaction of $\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPh}_3\text{)}_2$ with an excess of $\text{(MeO)}_2\text{P(O)}\text{H}$ resulted in displacement of only one triphenylphosphine ligand to give the product

$\text{cis-Ru(S}_2\text{PMe}_2\text{)}_2\text{(PPh}_3\text{)(P(OH)(OMe)}_2\text{)}$ (50). The formulation (50) is supported by elemental analysis and spectroscopic studies.
Thus, the $^{31}$P-$^1$H n.m.r. spectrum in CDCl$_3$ at 298 K (Figure 5.4) consists of a doublet of triplets at $\delta$54.0 ppm with $^2$J$_{PP} = 48.2$ Hz and $^3$J$_{PP} = 5.5$ Hz (PPh$_3$), a broad resonance at $\delta$91.0 ppm ($^3$S$_2$PMe$_2$) and a further doublet of triplets at $\delta$137.0 ppm with $^2$J$_{PP} = 48.2$ Hz and $^3$J$_{PP} = 7.3$ Hz ($^2$O(OMe)$_2$OH).

For this compound (50) it appears that unlike most of the cis-Ru($S_2$PMe$_2$)$_2$L'$_2$ complexes described in Chapter 4, section 4, facile interconversion of the optical enantiomers must occur at room temperature since the two
Figure 5.4: $^{31}\text{P-}{ }^1\text{H}$ n.m.r. spectrum of cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)(P(OMe)(OH)(OMe)$_2$)
dimethyldithiophosphinate ligands are not equivalent in the static structure and hence their phosphorus nuclei would not be expected to couple identically to those of the other ligands.

\[
\begin{align*}
\text{Me}_2\text{P} & \quad \text{S} & \quad \text{S} & \quad \text{Ru} & \quad \text{P} & \quad \text{PPh}_3 \quad \cdots \quad \text{PMe}_2 \\
\text{S} & \quad \text{Ru} & \quad \text{S} & \quad \text{S} & \quad \text{P} & \quad \text{OH} \\
\text{Me}_2\text{P} & \quad \text{S} & \quad \text{S} & \quad \text{Ru} & \quad \text{P} & \quad \text{Me}_2 \\
\end{align*}
\]

However, as discussed in detail earlier, (Chapter 4, see Figure 4.3), if the complex is undergoing rapid equilibration of the two six-coordinate structures (50a) and (50b) via a five or seven-coordinate solvated intermediate by a ruthenium-sulphur bond cleavage, then the \(\text{S}_2\text{PMe}_2\) ligands will become equivalent on the n.m.r. timescale and hence will couple identically to the other ligands.

This conclusion is supported by the observation that in the room temperature \(^1\text{H}\) n.m.r. spectrum of (50) only one doublet is found for the \(\text{S}_2\text{PMe}_2\) ligand, whereas for \(\text{cis-Ru(S}_2\text{PMe}_2)_2\text{L}_2'\) (\(\text{L}' = \text{PPh}_n\text{Cl}_{3-n} ; \, n = 0, 1, 2\)) two doublets are observed due to the slow exchange reaction between their optical enantiomers at ambient temperature. This facile interconversion of \(\text{cis-Ru(S}_2\text{PMe}_2)_2\text{(PPh}_3\text{)(P(OMe)}_2\text{OH)}\) optical enantiomers can be ascribed to the high trans influence of PPh\(_3\) and/or P(OH)(OME)\(_2\) ligands, cf. the
similar behaviour of cis-Ru(S₂PMe₂)₂L'₂ compounds (L' = PPh₃, PMe₂Ph, PPh₂OR). Finally, if the reaction between cis-Ru(S₂PMe₂)₂(PPh₃)₂ and (MeO)₂P(O)H is repeated in the presence of conc. HCl, ³¹P-{¹H} and ¹H n.m.r. spectroscopy reveals that a complex mixture of products is formed and attempts to separate these compounds or to analyse their spectra were unsuccessful.

5.3 Some reactions of the compound Ru(S₂PMe₂){(PPh₂O)₃H₂} (47)

As described in Chapter 1, section 1.5, the bridging hydrogen atom of complexes containing [R₂POHOPR₂]⁻ ligands can be readily replaced by a variety of reagents cf. equations [36]-[40]. Therefore some preliminary studies have been made on the reactivity of Ru(S₂PMe₂){(PPh₂O)₃H₂} (47) towards reagents such as BF₃·Et₂O and several metal acetylacetonates and the results are reported in this section.

Thus, reaction of compound (47) with BF₃·Et₂O in methylene chloride at room temperature led, on solvent removal, to the isolation of an orange solid. The ³¹P-{¹H} n.m.r. spectrum of this material in CDCl₃ at 298 K shows a sharp quartet at δ103.0 ppm (³J_Pp 4.4 Hz) and a broad unresolved peak at δ126.0 ppm which exhibits no improvement in resolution when the number of pulses accumulated is increased or when the temperature of the sample is lowered to 213 K (Figure 5.5). By analogy with previous work on the reaction of the closely related Co₃(η-C₅H₅)₂⁻{(RO)₂PO}₆⁶⁴ (25) with HBF₄ to give the unusual cationic
Figure 5.5: $^{31}\text{P}-\text{H}$ n.m.r. spectrum of Ru(${S}_2{PMe_2})((\text{PPh}_2\text{O})_3\text{BF}$)
complex \textit{[Co(\(\eta\)-C\(_5\)H\(_5\))\{(RO\)_2PO\}_3BF]}BF\(_4\) (28) a similar product \textit{Ru(S\(_2\)PMe\(_2\)}(PPh\(_2\)O\)_3BF (51) is probably formed although the \textit{\textsuperscript{31}P-(\textsuperscript{1}H\)} n.m.r. spectrum is also consistent with a species such as \textit{Ru(S\(_2\)PMe\(_2\}(PPh\(_2\)O\)_3(BF\(_2\))\(_2\) (52).

\begin{center}
\includegraphics[width=0.5\textwidth]{image1.png}
\end{center}

In fact, the experimental carbon and hydrogen analysis figures (C 47.4, H 4.1\%) are closer to those required for compound (52) (C 49.1, H 3.8\%) than for compound (51) (C 53.0, H 4.2\%). However an examination of the boron-\textit{\textsuperscript{11}}- and fluorine-\textit{\textsuperscript{19}}- n.m.r. spectra revealed small amounts of impurities which would, of course, produce some discrepancies between the observed and
calculated carbon and hydrogen analysis figures. Furthermore, direct boron and fluorine analysis on this sample (found F 2.3, B 1.3%) fit very well for compound (51) (required F 2.2, B 1.3%) but not compound (52) (required F 8.2, B 2.4).†

The broad resonance at δ126.0 ppm in the $^{31}$P-{$^1$H} n.m.r. spectrum is assigned to the ligand [(PPh$_2$O)$_3$BF]. The broadening is attributed to the effect of the quadrupolar $^{11}$B nucleus (I = 3/2) such that the $^{3}$J$_{PP}$ coupling is only observed on the $^{17}$S$_2$PMe$_2$ resonance at δ103.0 ppm. This phosphorus is of course sufficiently far away to be unaffected by the boron-11 quadrupole moment. The $^{19}$F n.m.r. spectrum of compound (51) (the purer sample from the "HPF$_6$" reaction) was also run and consisted of a seven line

† A much purer sample of the same product (as revealed by $^{11}$B, $^{19}$F and $^{31}$P-{$^1$H}) was obtained by reaction of Ru(S$_2$PMe$_2$)$_2${(PPh$_2$O)$_3$H$_2$} with "HPF$_6$" in CH$_2$Cl$_2$. The only explanation for this incredible reaction was that the "HPF$_6$" contained some BF$_3$, possibly from interaction over a prolonged period with the plastic container. This possibility was confirmed by running a $^{11}$B spectrum of "HPF$_6$" in D$_2$O which showed a strong resonance close to that expected for BF$_3$. The analysis figures for this compound (found C 49.1, H 4.1, P 13.8, F 2.2%) were very close to those required for Ru(S$_2$PMe$_2$)(PPh$_2$O)$_3$BF. 0.5 CH$_2$Cl$_2$ (C 51.2, H 4.1, P 13.7, F 2.1%).
pattern with lines of approximate relative intensity 1:4:7:8:7:4:1 centred at δ139.9 ppm (Figure 5.6). On decoupling the boron-11 nucleus, the $^{19}$F n.m.r. signal collapsed to a sharp 1,3,3,1 quartet ($^{3}$J$_{PF}$ 10.6 Hz) (Figure 5.7) which confirms that the fluorine atom is coupled to three magnetically equivalent phosphorus nuclei. Furthermore, examination of the $^{19}$F-$^{31}$P n.m.r. spectrum reveals that the $^{19}$F signal is now a 1:1:1:1 quartet pattern (Figure 5.8) indicating that the fluorine atom is coupled to a single boron nucleus ($^{1}$J$_{BF}$ = 11.8 Hz). Hence it is the close coincidence of the sizes of the two coupling constants $^{3}$J$_{PF}$ and $^{1}$J$_{BF}$ which gives rise to the initially rather puzzling seven line spectrum shown in Figure 5.6 i.e. the superposition of four 1;3;3;1 quartet patterns of equal intensity leads to the observed 1;4;7;8;7;4;1 pattern. A $^{11}$B n.m.r. spectrum was also obtained but the structural information could not be obtained from this due to the breadth of the resonance which concealed any couplings.

The compound Ru(S$_{2}$PMe$_{2}$){(PPh$_{2}$O)$_{2}$H$_{2}$} reacts with VO(acac)$_{2}$ in methylene chloride solution to give on work-up a greenish-brown solid which although it was clearly paramagnetic, giving broad e.s.r. signals, did give a $^{31}$P-$^{1}$H n.m.r. spectrum, although with rather broad lines. The spectrum consisted of a triplet at δ123.4 ppm, a doublet at δ146.3 ppm ($^{2}$J$_{PP}$ 44.0 Hz) and a singlet at δ98.7 ppm. This spectrum can be interpreted as arising from a complex (53) in which only two of the available
Figure 5.6: $^{19}\text{F}$ n.m.r. spectrum of $\text{Ru} \left( \text{S}_2\text{PMe}_2 \right) \left( \text{(PPh}_2\text{O})_3\text{BF} \right)$. $\delta 134.3$
Figure 5.7: $^{19}F-^{11}B$ n.m.r. spectrum of Ru($S_2PMe_2$)((PPh$_2$O)$_3$BF)
Figure 5.8: $^{19}$F-$^{31}$P n.m.r. spectrum of Ru($S_2PMe_2$)((PPh$_2$O)$_3$BF)
oxygen atoms are coordinated to a vanadyl group.

This formulation (53) accounts for the observed \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectrum including the shift of the resonance of the diphenylphosphinito groups coordinated to the vanadium(IV) ion (δ146.3 ppm) which is more than 20 ppm to high frequency of the [(PPh\(_2\)O)\(_3\)H\(_2\)]\(^-\) resonance in compound (47). In contrast the resonance position of the unattached PPh\(_2\)OH ligand (δ123.4 ppm) remains almost unchanged. This large shift difference can probably be attributed to the presence of the paramagnetic VO\(^{2+}\) ion only two bonds removed from the phosphorus atoms of the PPh\(_2\)O\(^-\) groups but four bonds away from the uncoordinated PPh\(_2\)OH groups. Further support comes from the observed phosphorus-phosphorus coupling constant of 44 Hz which is typical of values for cis-phosphine groups attached to ruthenium\(^{124}\). No coupling was observed between the PPh\(_2\)OH or PPh\(_2\)O\(^-\) groups and the \(^-\)S\(_2\)PMe\(_2\) ligand but since this is expected to be of the order of 4-5 Hz (for \(^3\)J\(_{pp}\)) and the natural line widths in the \(^{31}\text{P}-(^1\text{H})\) n.m.r. spectrum of (53) were 10-20 Hz, this is hardly surprising.
The compound Ru\((S_2PMe_2)\{(PPh_2O)_3H_2\}\) also reacts with Co(acac)\(_2\) to give on work-up an orange-yellow product which is strongly paramagnetic as evidenced by its e.s.r. spectrum, and the very broad signals in its \(^{31}\text{P}-\{^1\text{H}\}\) n.m.r. spectrum. The latter consists of two broad resonances at \(\delta 123\) and \(\delta 102\) ppm which can be assigned to the \([PPh_2O]^–\) and \(S_2PMe_2\) ligands respectively. Unlike the vanadyl complex, little shift of these resonances compared to those of compound (47) is observed. Furthermore, the analysis figures are consistent with the six-coordinate cobalt(II) complex (54).

Reactions of Ru\((S_2PMe_2)\{(PPh_2O)_3H_2\}\) with the octahedral acetylacetonates Fe(acac)\(_3\), Ga(acac)\(_3\) or In(acac)\(_3\) (the last two in order to obtain diamagnetic complexes) produced highly insoluble materials which precipitated from solution after short reaction times at room temperature. These materials were insoluble that no information could be obtained on their structures from either n.m.r. spectral studies or molecular weight determinations. Elemental analyses are also not very informative in these cases since the various possible
formulations differ only slightly in their expected elemental analyses, these being determined mainly by the composition of the ligand as it has such a high molecular weight. Nevertheless, it is likely that related complexes to (54) namely $M((\text{OPPh}_2)_3\text{Ru(S}_2\text{PMe}_2))_2$ ($M = \text{Fe, Ga, In}$) have been formed. Further characterisation of these interesting trimetallic complexes are still required as well as extension of the reactions to a wider range of transition metal and main group acetylacetonate and halide salts. X-ray structural analysis would probably be the most useful technique to apply to many of these high molecular weight materials, if it is possible to obtain suitable single crystals.

Finally, as the preferred stereochemistry for $d^6$ complexes is octahedral, the complex $\text{Ru(S}_2\text{PMe}_2)\{(\text{PPh}_2\text{O})_3\text{H}_2\}$ being five-coordinate, might be expected to add a further ligand to give a six-coordinate complex provided there are no steric constraints to prevent addition. The most likely ligand to achieve this is carbon monoxide as its steric requirement is fairly small and its Lewis basicity fairly high. When CO was bubbled through a solution of complex (47) in methylene chloride at ambient temperature, the initial orange red solution was rapidly decolourised to a very pale yellow colour. On working up this solution a yellowish-white solid was obtained. This colour change is consistent with a change in stereochemistry from a five coordinate complex to a six-coordinate complex. However the nature of the product obtained in this reaction appears
to depend critically on the CO pressure in the cylinder used. Thus with a high cylinder pressure of CO, a product is generated which can be shown by $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectroscopy to be a mixture of free $\text{Ph}_2\text{P(OH)}$ and a complex giving rise to a doublet at $\delta 94.8$ ppm and a triplet at $\delta 87.4$ ppm, both with $J_{PP} = 8$ Hz indicative of a three-bond coupling. The infra-red spectrum of this material shows a strong $\nu_{\text{CO}}$ stretching vibration at $1930$ cm$^{-1}$. Although attempts to separate this carbonyl complex from $\text{Ph}_2\text{P(OH)}$ were unsuccessful, the spectroscopic evidence suggests that it is best formulated as (55) containing two trans carbonyl ligands, one $S_2\text{PMe}_2$ ligand and one $[\text{Ph}_2\text{POHOPPh}_2]^{-}$ ligand.

This is presumably formed by displacement of a single $\text{PPh}_2\text{OH}$ ligand by carbon monoxide as well as incorporation of a carbonyl group into the vacant coordination site. Later attempts to repeat this experiment using a lower carbon monoxide pressure gave, however, a product with a completely different $^{31}\text{P}-\{^1\text{H}\}$ n.m.r. spectrum at ambient temperature (Figure 5.9). This showed three sets of resonances centred at $\delta 98.4$ ppm (d.d.d.), $\delta 91.9$ ppm (t.d.) and $\delta 86.2$ ppm (d.d.d.) of relative intensity 2:1:1.
Figure 5.9: $^{31}\text{P-}^{1\text{H}}$ n.m.r. spectrum of $\text{Ru}(\text{S}_2\text{PMe}_2)\text{CO((PPh}_2\text{O})_3\text{H}_2)$
This spectrum is consistent with the formation of the expected stereochemically rigid product Ru(S$_2$PMe$_2$)CO{(PPh$_2$O)$_3$H$_2$} (56).

\[
\begin{align*}
\text{Me}_2\text{P} & \quad \text{Ru} \\
\text{S} & \quad \text{PPh}_2 \\
\text{S} & \quad \text{PPh}_2 \\
\text{PPh}_2 \\
\end{align*}
\]

(56)

In support of this conclusion, the $^1$H n.m.r. spectrum contains two $^1$S$_2$PMe$_2$ doublets of equal intensity centred at $\delta 2.03$ and 1.10 ppm which can be assigned to the methyl groups anti and syn to the axial PPh$_2$OH group respectively. Furthermore the intensity ratio of phenyl to methyl groups indicated one [(PPh$_2$O)$_3$H$_2$]$^-$ ligand to one $^1$S$_2$PMe$_2$ ligand.

5.4 Reactions of prehydrolysed PPh$_2$Cl and of (MeO)$_2$P(O)H with some $\{[\text{Ru}(\eta\text{-arene})\text{Cl}_2]\}_2$ complexes

As attempts to hydrolyse or otherwise cleave the O-R bonds in [$\text{Ru}(\eta\text{-arene})(\text{PPh}_2\text{OR})_2\text{Cl}]\text{BPh}_4$ were unsuccessful (see Chapter 4, section 4. for details), the reaction of $\{[\text{Ru}(\eta\text{-arene})\text{Cl}_2]\}_2$ with prehydrolysed PPh$_2$Cl in aqueous methanol was investigated. It was hoped that this would produce either [$\text{Ru}(\eta\text{-arene})(\text{PPh}_2\text{OH})_2\text{Cl}]\text{Cl}$ or the neutral complex Ru(arene){(PPh$_2$O)$_2$H}Cl. However, when
Treatment of a methanolic solution of
\[
\text{[Ru}(n\text{-p-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2)\text{]}_2
\]
with an excess of dimethylphosphite for a short period of time produced a highly conducting solution which deposited an orange solid on addition of ammonium hexafluorophosphate. The structure of the cation was deduced from its hydrogen-1 n.m.r. spectrum (Figure 5.10) and analytical data for the PF\textsubscript{6}\textsuperscript{-} salt. The hydrogen-1 n.m.r. spectrum consisted of an apparent AA'BB' quartet pattern at \(\delta 5.51\) ppm (aromatic protons of the p-cymene ring), a doublet at \(\delta 3.62\) ppm, \(3J_{PH} = 12.0\) Hz \((P(OMe)_2O^-)\), a pair of singlets at \(\delta 2.23\) and \(\delta 1.98\) ppm (aromatic methyls), a pair of doublets at \(\delta 1.37\) and \(\delta 1.20\) ppm with \(3J_{HH} = 7.0\) Hz \((\text{CHMe}_2)\) and two multiplets centred at \(\delta 2.86\) and \(\delta 2.57\) ppm with \(3J_{HH} = 7.0\) Hz \((-\text{CHMe}_2)\). A heteronuclear decoupling experiment with irradiation in the phosphorus-31 n.m.r. region showed that only the \(\delta 3.62\) ppm doublet collapsed to a singlet. This resonance was thus assigned to the dimethylphosphito group. On closer examination of the spectrum, the AA'BB' pattern was seen to be more complex, probably being two overlapping patterns. The hydrogen-1 n.m.r. evidence thus indicates that the cationic species contains two distinct coordinated aromatic rings. Integration of the spectrum shows that it also contains one dimethylphosphito ligand to two coordinated rings. The analysis
Figure 5.10: $^1$H n.m.r. spectrum of $[\text{Ru}_2\text{Cl}_2(\mu-\text{P(O)}\text{Me})_2\text{O})(\text{p-MeC}_6\text{H}_4\text{CHMe}_2)_2]\text{PF}_6$
[[\text{Ru}(\eta^*\text{C}_6\text{H}_6)\text{Cl}_2]_2$ was shaken with \text{PPh}_2\text{Cl}$ in aqueous methanol, the final product was \text{Ru}(\eta^*\text{C}_6\text{H}_6)\text{Cl}_2(\text{PPh}_2\text{OH})$ (57). In a highly polar solvent such as methanol, the product normally obtained in reactions between \[[\text{Ru}(\eta^*\text{C}_6\text{H}_6)\text{Cl}_2]_2$ and neutral unidentate ligands is a cationic complex \[[\text{Ru}(\eta^*\text{C}_6\text{H}_6)L_2\text{Cl}]^+$(see Chapter 4, section 4.5 for details where $L = \text{PPh}_2\text{OR}$, and ref. 91 for details where $L = \text{pyridine}$). An important factor for the reaction stopping at this stage may be the low solubility of \text{Ru}(\eta^*\text{C}_6\text{H}_6)\text{Cl}_2(\text{PPh}_2\text{OH})$.

The hydrogen-$1$ n.m.r. spectrum of (57) contains resonances for coordinated benzene and phenyl groups. Integration of the spectrum shows that there is one \text{PPh}_2\text{OH}$ group present for one coordinated benzene ring. The P-OH resonance was not observed in the $\text{H}$ n.m.r. spectrum. Elemental analysis reveals that the most likely formulation is \text{Ru}(\eta^*\text{C}_6\text{H}_6)\text{Cl}_2(\text{PPh}_2\text{OH})$, which agrees with the hydrogen-$1$ n.m.r. spectrum. The complex [[\text{Ru}(\eta^*\text{C}_6\text{H}_3\text{Me}_3)\text{Cl}_2]_2$ did not react with \text{Ph}_2\text{P(O)}\text{H}/\text{HCl}$ under these conditions, which may be due to the lower solubility of this complex in methanol.

A further reaction which was attempted was that of [[\text{Ru}(\eta^*\text{arene})\text{Cl}_2]_2$ with (\text{MeO})_2\text{P(O)}\text{H}$, which can also exist in equilibrium with its hydroxy tautomer \text{P(O)}\text{Me}_2(\text{OH})$. In the case of [[\text{Ru}(\eta^*\text{p-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2]_2$, this led to the isolation of a rather unexpected binuclear compound (58).
figures fit well for (58) Found C 33.0, H 4.3%;
Calc. for C_{22}H_{34}Cl_2F_6O_3PRu C 33.2, H 4.3%

This compound fits into the general mechanism which has
been postulated for the generation of triple-bridged
binuclear cations in the [(Ru(η-arene)Cl_2)_2] system,
Equations [61] and [62].

\[
\begin{align*}
\text{[(Ru(arene)Cl_2)_2]} & \xrightarrow{S} \text{Arene RuCl}_2S + \text{Arene RuCl}_2^+ \quad \ldots \quad [61] \\
\text{Arene RuCl}_2S + [\text{Arene RuCl}_2^+] & \longrightarrow [\text{Arene}_2\text{Ru}_2\text{Cl}_3]^+ + 3S \quad [62]
\end{align*}
\]

For the compound (58) the analogous mechanism could
be as shown in Figure 5.11.

\[
\begin{align*}
\text{[(Ru(arene)Cl_2)_2]} & \xrightarrow{S} \text{Arene RuCl}_2S + [\text{Arene RuCl}_2^+] \\
\text{Arene RuCl}_2S & \xrightarrow{\text{(MeO)}_2\text{P(O)H}} \text{Arene RuCl}_2[\text{P(OH)(OMe)}_2] \xrightarrow{S} \\
& [\text{Arene RuCl}(S)[\text{P(OH)(OMe)}_2]^+] \\
\text{[Arene RuCl}_2[S[\text{P(OH)(OMe)}_2]]^+ & + [\text{Arene RuCl}_2^+] \\
\downarrow & \\
[\text{Arene}_2\text{Ru}_2\text{Cl}_2(\mu\text{P(OMe)}_2\text{O})]^+ + 3S + H^+ & \\
\end{align*}
\]

**Figure 5.11**

**Possible Mechanism of Formation of [Ru_2(p-MeC_6H_4CHMe_2)_2]^-**

\[(\text{P(OMe)}_2\text{O})\text{Cl}_2\text{PF}_6^-\]
Other [{Ru(\(n\)-arene)Cl\(_2\)]\(_2\)} complexes apparently did not react with dimethylphosphite. However, [{Ru(\(n\)-p-cymene)Cl\(_2\)]\(_2\)} is the only binuclear arene complex which is freely soluble in methanol, and if the reaction is dependent both on the concentration of the complex and of the P(OH)(OMe)\(_2\) in solution, then reaction will occur much more slowly for the less soluble complexes.

5.5 Conclusions

Some success has been achieved in reacting a few ruthenium(II) complexes with PPh\(_2\)Cl/H\(_2\)O and (MeO)\(_2\)P(O)H, most notably with the isolation of the complex Ru(S\(_2\)PMe\(_2\))\{(PPh\(_2\))\(_3\)H\(_2\)} and the study of some of its reactions with BF\(_3\) and metal acetylacetonates. The complex Ru(S\(_2\)PMe\(_2\))(PPh\(_3\))\{(PPh\(_2\))\(_2\)H\} may also be a useful ligand if it can be isolated as a pure compound. Further studies on these and related compounds are now necessary in order to consolidate and extend this work to other metal complexes.

5.6 Experimental

Physical measurements were as for those described in the previous experimental sections 2.3, 3.4 and 4.8. Fluorine-19 n.m.r. spectra were obtained on a Varian XL-100 spectrometer operating at 94.1 MHz and boron-11 n.m.r. spectra on a Bruker WH-360 spectrometer operating at 115.5 MHz, both in the pulse and Fourier transform mode. All reactions were carried out under an atmosphere of nitrogen.
Hydrogen-1 n.m.r. and phosphorus-31 n.m.r. data for the new complexes are given in Tables 5.1 and 5.2 respectively.

Materials

As in Chapters 2 and 4 together with (MeO)₂P(O)H (Aldrich), BF₃·Et₂O (Aldrich), Co(acac)₂ (Koch-Light), Fe(acac)₃, Ga(acac)₃, In(acac)₃ (Alfa Inorganics) and carbon monoxide (British Oxygen Co.) used as received. VO(acac)₂ was prepared using a standard literature method¹²⁵.

(Dimethyldithiophosphinato)diphenylphosphinito bis(diphenylphosphinous acid) ruthenium(II)

The compound cis-Ru(S₂PMe₂)₂(PPh₃)₂ (0.20 g; 0.23 mmol) was added to a solution of PPh₂Cl (2 cm³, 11.2 mmol) in a mixture of methanol (50 cm³) and water (5 cm³). The resulting suspension was stirred under reflux for two hours. The solution was filtered hot and left to stand in a refrigerator for several days. The resulting orange-red crystalline material was filtered off and washed with diethylether and petroleum ether (b.p. 40–60°C, m.p. 235–237°C (Yield 0.07 g, 37%). Found C 54.6, H 4.6%; M 792 (C₆H₆) Calc. for C₃₈H₃₈O₃P₄RuS₂: C 54.9, H 4.6%; M 831.

When the above reaction is carried out using aqueous acetone rather than aqueous methanol as solvent, the crystalline product which is obtained was shown to be a mixture of the above product and a white crystalline organophosphorus product. This mixture was separable by differential solubility in benzene, the ruthenium complex being freely soluble but the organophosphorus compound
being rather insoluble. As described in Section 5.2, the organophosphorus product was identified as \( \text{Ph}_2\text{P(O)(OH)Me}_2 \) by \(^1\text{H}\) and \(^{31}\text{P}(^1\text{H})\) n.m.r. spectroscopy and also by analytical data; Found: C 69.2, H 6.6%; Calc. for \( \text{C}_{15}\text{H}_{17}\text{O}_2\text{P} \):

\[
\text{C} 69.2, \text{H} 6.5%.
\]

When the first reaction was repeated using a smaller quantity of \( \text{PPh}_2\text{Cl} \) (0.20 cm\(^3\), 1.1 mmol) to 0.20 g of \( \text{cis-Ru(S}_2\text{PMe}_2\text{)}_2(\text{PPh}_3)_2 \), in the same volume of solvent, the product of the reaction was an inseparable mixture of \( \text{Ru(S}_2\text{PMe}_2\text{)}_2(\text{PPh}_2\text{O})_2\text{H}_2 \) and a further complex identified as \( \text{Ru(S}_2\text{PMe}_2\text{)}_2\text{PPh}_3(\text{PPh}_2\text{O})_2\text{H} \) from its \(^{31}\text{P}(^1\text{H})\) n.m.r. spectrum (see Section 5.2 for detailed discussion).

(Dimethyldithiophosphinato) [tris(diphenylphosphinito)-fluoroborato] ruthenium(II)

The complex \( \text{Ru(S}_2\text{PMe}_2\text{)}_2(\text{PPh}_2\text{O})_3\text{H}_2 \) (0.10 g, 0.12 mmol) was dissolved in methylene chloride (25 cm\(^3\)) and boron trifluoride diethyl-etherate (0.05 cm\(^3\), 0.44 mmol) was added. The solution was shaken for 4 hours, filtered and the filtrate evaporated to dryness on a rotary evaporator. The orange residue was redissolved in a small volume of methylene chloride and on addition of 50 cm\(^3\) of petroleum ether (b.p. 40-60°C) the product was precipitated as an orange solid which was filtered off and washed with several portions of petroleum ether and dried in vacuo at 56°C (Yield 0.085 g, 82%). Found; C 49.1, H 4.1, P 13.8, F 2.2% Cal. for \( \text{C}_{39}\text{H}_{36}\text{BFO}_3\text{P}_4\text{RuS}_4\cdot0.5\text{CH}_2\text{Cl}_2 \) C 51.2, H 4.1, P 13.7, H 2.2%.
Bis[(dimethyldithiophosphinato)bis(diphenylphosphinito)-(diphenylphosphinous acid)ruthenium(II)] oxovanadium(IV)

Ru(S$_2$PMe$_2$){(PPh$_2$O)$_3$H$_2$} (0.08 g, 0.096 mmol) dissolved in methylene chloride (10 cm$^3$) and added to a solution of VO(acac)$_2$ (0.012 g, 0.046 mmol) in methylene chloride (10 cm$^3$). The mixture rapidly turned a greenish-brown colour. The solution was left for 30 minutes and then evaporated to dryness. Addition of CH$_2$Cl$_2$ followed by petroleum ether (b.p. 40-60°C) gave the product as a greenish brown solid which was filtered off and washed with petroleum ether (b.p. 40-60°C, m.p. 280-284°C) (Yield 0.06 g, 72%).

Found C 52.6, H 4.4, P 7.5, S 13.1%; Calc. for C$_{76}$H$_{74}$O$_7$P$_8$RuS$_4$V: C 52.8, H 4.3, P 7.5, S 14.3%.

Bis[(dimethyldithiophosphinato)bis(diphenylphosphinito)-(diphenylphosphinous acid)ruthenium(II)] cobalt(II)

The complex Ru(S$_2$PMe$_2$){(PPh$_2$O)$_3$H$_2$} (0.10 g, 0.12 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm$^3$) and added to a solution of Co(acac)$_2$ (0.016 g, 0.06 mmol) in CH$_2$Cl$_2$ (10 cm$^3$). The solution was left to stand for 30 minutes and then evaporated to dryness. The residue was then redissolved in a minimum volume of CH$_2$Cl$_2$ and the product precipitated as a pale orange solid by the addition of petroleum ether (b.p. 40-60°C). The solid was filtered off and washed with petroleum ether m.p. 350°C (Yield 0.08 g, 78%); Found C 48.5, H 4.27%; Calc. for C$_{76}$H$_{74}$CoO$_6$P$_8$RuS$_4$: C 49.8, H 4.21%.

Similar reactions were carried out using Fe(acac)$_3$, Ga(acac)$_3$ and In(acac)$_3$ but these yielded highly insoluble
materials, none of which melted below 350°C which may suggest that these materials are polymeric in nature.

Reactions of Ru(S₂PMe₂){(PPh₂O)₃H₂} with carbon monoxide

(a) Ru(S₂PMe₂){(PPh₂O)₃H₂} (0.095 g, 0.12 mmol) was dissolved in CH₂Cl₂ (50 cm³) and CO bubbled rapidly through the solution. The colour of the solution changed from a deep red to very pale yellow within 30 seconds. The solution was evaporated to dryness yielding a pale yellow solid which was isolated by adding a small volume of CH₂Cl₂ followed by petroleum ether (b.p. 40-60°C). The solid was filtered off and washed with petroleum ether (Yield 0.073 g). This solid was identified by its ⁴¹P-{¹H} n.m.r. spectrum as a mixture of trans-Ru(CO)₂(S₂PMe₂){(PPh₂O)₂H} and diphenylphosphine oxide. The mixture could not be separated into its individual components. Ir spectrum (nujol mull) shows νₐₗₐ₉.CO 1930 cm⁻¹.

(b) Ru(S₂PMe₂){(PPh₂O)₃H₂} (0.1 g, 0.12 mmol) was dissolved in CH₂Cl₂ (25 cm³) and CO bubbled slowly through the solution. As described in section 5.3, the cylinder pressure here was much lower than in reaction (a). As soon as the red colour had been discharged, (after a few minutes), the CO flow was stopped and the solution evaporated to dryness. This yielded a pale yellow solid, which was redissolved in a small volume of CH₂Cl₂ and precipitated by addition of petroleum ether (b.p. 40-60°C). The solid was filtered off and washed with petroleum ether. (Yielded 0.085 g, 84%).
The solid was identified by its $^{31}\text{P}-(^1\text{H})$ n.m.r. spectrum as Ru(CO)(S$_2$PMe$_2$)$_2$(PPh$_2$O$_3$H$_2$) (see Table 5.2). Analysis C 53.9, H 4.6%. Calc. for C$_{39}$H$_{38}$O$_4$P$_4$RuS$_2$. C 54.4, H 4.4% [Ir (nujol mull) shows $\nu$$_{CO}$ 1930 cm$^{-1}$].

Other small molecules such as trimethylphosphite and acetonitrile did not insert into the vacant sixth coordination site on the ruthenium ion, suggesting that this site is rather sterically crowded.

\textbf{Cis-Bis(dimethyldithiophosphinato)(dimethylphosphite)-(triphenylphosphine)ruthenium(II)}

The complex cis-Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$ (0.20 g, 0.23 mmol) was suspended in methanol (25 cm$^3$) and (MeO)$_2$P(O)H (0.07 cm$^3$, 0.76 mmol) was added. The reaction mixture was refluxed for three hours producing a red solution. This was evaporated producing a red oil. A small amount of methanol was added and orange crystals were produced on cooling. The crystalline product was filtered off and washed with petroleum ether (b.p. 40-60°C) m.p. 135°C (decomp.) (Yield 0.04 g, 25%). Analysis; Found C 38.7, H 4.6%, Calc. for C$_{24}$H$_{34}$O$_3$P$_4$RuS$_4$ C 39.8, H 4.7%.

\textbf{$\mu$-Dichloro-$\mu$-dimethylphosphitobis[$\eta$-$p$-methylisopropylbenzene-ruthenium(II)]hexafluorophosphate}

The complex [(Ru($\eta$-$p$-MeC$_6$H$_4$CHMe$_2$)Cl$_2$)$_2$] (0.20 g, 0.33 mmol) was dissolved in methanol (25 cm$^3$) and dimethylphosphite (0.40 cm$^3$, 4.4 mmol) was added. The solution was shaken overnight and was found to be conducting. Addition of NH$_4$PF$_6$ precipitated the product as a microcrystalline solid,
m.p. 173-174°C, Found C 33.0, H 4.3%. Calc. for C\textsubscript{22}H\textsubscript{34}Cl\textsubscript{2}F\textsubscript{6}O\textsubscript{3}P\textsubscript{2}Ru C 33.2, H 4.3%.

\textit{\textsuperscript{\textcopyright}}-benzenedichloro(diphenylphosphinous acid)ruthenium(II)

The complex [{Ru(\textit{n}-C\textsubscript{6}H\textsubscript{6})Cl\textsubscript{2}}\textsubscript{2}] (0.30 g, 0.60 mmol) was suspended in a solution of PPh\textsubscript{3}Cl (1 cm\textsuperscript{3}, 5.6 mmol) in a 95.5 (v/v) mixture of methanol and water (25 cm\textsuperscript{3}) and the suspension shaken for 72 hours. This produced an orange-red crystalline solid which was filtered off and washed with methanol and diethyl ether (Yield 0.29 g, 53%). Found C 47.5, H 3.8%. Calc. for C\textsubscript{18}H\textsubscript{17}Cl\textsubscript{2}ORu C 47.8, H 3.8%.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_2\text{PMe}_2^-$</th>
<th>arene</th>
<th>$\text{PPh}_2\text{OH}$ or $\text{P(OMe)}_2\text{(OH)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ru}(S_2\text{PMe}_2){(\text{PPh}_2\text{O})_3\text{H}_2}$</td>
<td>2.00(d, 12.0 Hz)</td>
<td>6.5-8.0(m) (Ph)</td>
<td>8.80(br) (OH)</td>
</tr>
<tr>
<td>$\text{Ru}(S_2\text{PMe}_2){(\text{PPh}_2\text{O})_3\text{BF}}$</td>
<td>2.00(d, 12.0 Hz)</td>
<td>6.5-8.0(m) (Ph)</td>
<td></td>
</tr>
<tr>
<td>$\text{Ru}([\text{CO}],(S_2\text{PMe}_2){(\text{PPh}_2\text{O})_3\text{H}_2}$</td>
<td>2.03(d, 12.5 Hz)</td>
<td>6.8-8.1(m) (Ph)</td>
<td></td>
</tr>
<tr>
<td>$\text{Ru}(S_2\text{PMe}_2){(\text{PPh}_2\text{O})_3\text{H}_2}$</td>
<td>1.95(d, 12.5 Hz)</td>
<td>3.39(d, 11.6 Hz) (P(OMe)$_2$6H)</td>
<td>7.0-7.8(m) (Ph)</td>
</tr>
<tr>
<td>$\text{Ru}(S_2\text{PMe}_2){(\text{PPh}_2\text{O})_3\text{H}_2}$</td>
<td>1.95(d, 12.5 Hz)</td>
<td>3.39(d, 11.6 Hz) (P(OMe)$_2$6H)</td>
<td>7.0-7.8(m) (Ph)</td>
</tr>
<tr>
<td>$\text{Ru}(\text{n-C}_6\text{H}_6)\text{Cl}_2(\text{PPh}_2\text{OH})$</td>
<td>5.50</td>
<td>6.8-8.0(m) (Ph)</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>( S_2PMe_2 )</td>
<td>( PPPh_2OH ) or ( P(O_{Me})_2(\text{OH}) )</td>
<td>( PPPh_3 )</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------</td>
<td>---------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>( \text{Ru}(S_2PMe_2){[(\text{PPPh}_2\text{O})_3\text{H}]_2 } )</td>
<td>102.4 (q, 4.4 Hz)</td>
<td>122.8 (d, 4.4 Hz)</td>
<td>102.4 (q, 4.4 Hz)</td>
</tr>
<tr>
<td>( \text{Ru}(S_2PMe_2){[(\text{PPPh}_2\text{O})_2\text{H}]PPh_3 )</td>
<td>104.7 (br)</td>
<td>121.3 (dd, (^2J_{PP} = 37.1 ) Hz, (^3J_{PP} = 2.9 ) Hz)</td>
<td>52.4 (td, (^2J_{PP} = 4.4 ) Hz, (^3J_{PP} = 4.4 ) Hz)</td>
</tr>
<tr>
<td>( \text{Ru}(S_2PMe_2){[(\text{PPPh}_2\text{O})_3\text{H}]_2\text{VO} )</td>
<td>98.7 (s)</td>
<td>123.4 (t, 44.0 Hz)</td>
<td>123 (br)</td>
</tr>
<tr>
<td>( \text{[Ru}(S_2PMe_2){[(\text{PPPh}_2\text{O})_3\text{H}]_2\text{Co} )</td>
<td>102 (br)</td>
<td>123 (br)</td>
<td>102 (br)</td>
</tr>
<tr>
<td>( \text{trans-Ru}(\text{CO})_2(S_2PMe_2){[(\text{PPPh}_2\text{O})_2\text{H}] )</td>
<td>87.4 (t, 8.0 Hz)</td>
<td>94.8 (d, 8.0 Hz)</td>
<td>91.0 (br)</td>
</tr>
<tr>
<td>( \text{Ru}(\text{CO})(S_2PMe_2){[(\text{PPPh}_2\text{O})_3\text{H}]_2 )</td>
<td>91.9 (td, 7.3 Hz &amp; 1.7 Hz)</td>
<td>98.4 (ddd, 38.0 Hz, 7.6 Hz and 2.0 Hz)</td>
<td>86.2 (ddd, 38.0 Hz, 34.4 Hz and 1.6 Hz)</td>
</tr>
<tr>
<td>( \text{Ru}(S_2PMe_2)<em>2{P(\text{O}</em>{Me})_2(\text{OH}) )</td>
<td>91.0 (br)</td>
<td>137.0 (dt, ( J = 48.2 ) and 7.3 Hz)</td>
<td>54.0 (dt, ( J = 48.2 ) and 5.5 Hz)</td>
</tr>
<tr>
<td>( \text{Ru}(\text{n-C}_6\text{H}_5)\text{Cl}_2{\text{PPPh}_2\text{OH} )</td>
<td>—</td>
<td>107.4 (s)</td>
<td>—</td>
</tr>
</tbody>
</table>
CHAPTER 6

Preliminary Electrochemical Studies on

Some Ruthenium(II) Complexes
6.1 Polarographic studies

Polarography is an electrochemical technique in which the changes of current, resulting from the electrolysis of the solution under investigation, are followed by altering the applied potential between a dropping mercury or other microelectrode and a reference electrode. By plotting the currents obtained when the applied voltage is gradually increased, a current-voltage curve can be obtained.

Cyclic voltammetry (C.V.) is one of the more modern developments which have been made from classical polarography. This is a multisweep technique in which a stationary working electrode is employed, the potential of which is varied at a finite rate as a linear function of time until the extreme potential is attained. At this point the potential is brought back to its original value at the same rate. This results in current-potential curves similar to those shown in Figure 6.1.
These curves provide four parameters as labelled in Figure 6.1: the current \( i^c_p \) and the potential \( E^c_p \) at the peak of the cathodic response, and the corresponding parameters \( i^a_p \) and \( E^a_p \) for the anodic response. It is from these parameters that mechanistic information from the cyclic voltammetric data can be extracted.

Thus, consider a redox couple, the oxidised form of which is present in a solution containing an excess of supporting electrolyte. This supporting electrolyte acts as the major charge carrier when current flows and so diffusion of the reactant from the bulk solution is the sole means of mass transport. In the course of the cathodic variation in potential, the reduced form of the reactant is produced near the electrode while a depletion of the oxidised form occurs. Given sufficient time, the reduced form will diffuse into the bulk of the solution, but the potential is taken back to its initial value at a rate such that some of the reduced form is still present and can possibly undergo a process of oxidation back to form the couple initially present in solution. If this charge transfer process is much more rapid than the rate of diffusion it is termed "reversible", whereas if it is much slower than the rate of diffusion it is termed "irreversible". Decomposition of the products formed on reduction (or oxidation) may also lead to irreversibility. The process can also be "quasi-reversible" in which case the charge transfer process is governed both by diffusion and charge transfer kinetics. The criteria for reversibility in cyclic voltammetry\(^{126}\) are set out in Table 6.1.
# TABLE 6.1
Criteria for the types of charge transfer processes in cyclic voltammetric studies

<table>
<thead>
<tr>
<th>Type</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reversible</strong></td>
<td>$E_p$ independent of $v$</td>
</tr>
<tr>
<td></td>
<td>$E_p^c - E_p^a = 59/n$ mV at 25°C and independent of $v$</td>
</tr>
<tr>
<td></td>
<td>$i_p/v^{1/2}$ (current function) is independent of $v$</td>
</tr>
<tr>
<td></td>
<td>$i_p^a/i_p^c = 1$ for all $v$</td>
</tr>
<tr>
<td><strong>Quasi-reversible</strong></td>
<td>$E_p$ shifts with $v$</td>
</tr>
<tr>
<td></td>
<td>$E_p^c - E_p^a$ increases as $v$ increases</td>
</tr>
<tr>
<td></td>
<td>$i_p/v^{1/2}$ is independent of $v$</td>
</tr>
<tr>
<td></td>
<td>$i_p^a/i_p^c \neq 1$</td>
</tr>
<tr>
<td><strong>Irreversible</strong></td>
<td>$E_p$ shifts with $v$</td>
</tr>
<tr>
<td></td>
<td>$i_p/v^{1/2}$ is constant with $v$</td>
</tr>
<tr>
<td></td>
<td>There is no current on the reverse scan.</td>
</tr>
</tbody>
</table>

where $v =$ scan rate in volt sec$^{-1}$

$n =$ number of electrons involved in oxidation and reduction process.
The other technique which was used was A.C. polarography. In this experiment a d.c. potential is applied to the electrode and is varied as a function of time, it is assumed, at an infinitesimally slow rate. In addition to the d.c. potential, a potential periodic in time, such as a sine wave, is also applied to the electrode. The potential excursions are very small, typically 10 mV peak-to-peak. In addition to the d.c. current flowing from the applied d.c. potential, an alternating (ac) current flows corresponding to the applied sine wave. The net alternating current is monitored as a function of d.c. potential. This produces a plot of a.c. current vs. d.c. potential (see Figure 6.2).

![Figure 6.2 A.C. polarographic current-potential curves](image)

Two parameters can be obtained from this curve, the peak magnitude of the a.c. current and the d.c. potential at this point, which is related to the standard potential for the redox couple. The shape of the peak is diagnostic
<table>
<thead>
<tr>
<th>Type</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reversible</td>
<td>$E_{\text{max}}$ is independent of $w$ ($w = a, c$ frequency)</td>
</tr>
<tr>
<td></td>
<td>Half-peak width is $90/\pi$ mV at $25^\circ\text{C}$ and</td>
</tr>
<tr>
<td></td>
<td>is independent of $w$</td>
</tr>
<tr>
<td></td>
<td>$I(\omega t) = kw^{1/2}$</td>
</tr>
<tr>
<td>Quasi reversible</td>
<td>$E_{\text{max}}$ shifts with $\omega$</td>
</tr>
<tr>
<td></td>
<td>$I(\omega t)$ is non-linear with $w^{1/2}$</td>
</tr>
<tr>
<td>Irreversible</td>
<td>$E_{\text{max}}$ shifts cathodically</td>
</tr>
<tr>
<td></td>
<td>$I_{\text{max}}$ is independent of $\omega$</td>
</tr>
<tr>
<td></td>
<td>The a.c. response is very small and may not be observable.</td>
</tr>
</tbody>
</table>
of the reversibility of the electrode process. For a completely reversible charge transfer process the a.c. peak is a symmetrical Gaussian curve. Reversibility can be determined experimentally by plotting the current-potential curve in both scan directions and if the process is reversible $I_{\text{max}}$ and $E_{\text{max}}$ are independent of the scan direction and scan rate. The criteria for reversibility for A.C. polarography are set out in Table 6.2\textsuperscript{126}.

6.2 Results and Discussion

It was hoped that some of the ruthenium(II) complexes described in this thesis would undergo facile reversible oxidations to generate new ruthenium(III) complexes or even reduction to low valent species. The one electron oxidation process is well established for ruthenium(II) complexes, often occurring at potentials which are easily accessible by electrochemical (and chemical) means, depending on the nature of the coordinated ligands present\textsuperscript{127}. Soft Lewis bases such as carbon monoxide, tertiary phosphines and polyenes would be expected to favour the lower oxidation state and thus increase the potential at which oxidation occurs. Hard ligands, predominantly halide ions and oxygen and nitrogen donor ligands, would be expected to favour the higher oxidation state and thus lower the oxidation potential of the complex. Therefore some of the complexes described earlier were tested for any electrochemical behaviour, and the results are reported below.
6.2.1 \([\text{Ru}(\eta-C_6H_6)(N-N)(PR_3)](PF_6)_2\) complexes

Two complexes were studied, \([\text{Ru}(\eta-C_6H_6(\text{phen})(\text{PMe}_2\text{Ph})](PF_6)_2\) and \([\text{Ru}(\eta-C_6H_6)(\text{bipy})(\text{PMe}_2\text{Ph})](PF_6)_2\). As expected, these two complexes showed very similar behaviour in CH_2Cl_2 (Table 6.3) consisting of an irreversible reduction at -0.95 V (vs a Ag/AgI reference electrode) and no oxidation step before the solvent oxidation at approximately +1.6 V. Both compounds also showed a small peak in the return scan which was not present if the scan direction was reversed before the reduction potential was reached and this must therefore arise from some process involving the product of the reduction.

6.2.2 \([\text{Ru}(\eta^5-C_6H_5Y)(N-N)(PR_3)]PF_6\) complexes

The two complexes studied were \([\text{Ru}(\eta^5-C_6H_7)(\text{phen})(\text{PMe}_2\text{Ph})]PF_6\) and \([\text{Ru}(\eta^5-C_6H_6OH)(\text{phen})(\text{PMePh}_2)]PF_6\). Both complexes showed irreversible behaviour in both oxidation and reduction directions, the cyclohexadienyl complex with waves at +0.95V and -0.95 V and the hydroxocyclohexadienyl complex at +1.08 V and -1.38 V (Table 6.3).

6.2.3 \([\text{Ru}(\eta-C_5H_5)(\eta-\text{arene})]^+\) cations

These mixed sandwich cations were found to be electro-inactive in the various solvents used (e.g. dimethylformamide, dimethylsulphoxide) towards both oxidation and reduction. This is to be contrasted with the corresponding iron(II) cations which undergo a facile reversible reduction to give the neutral paramagnetic complexes Fe(\(\eta-C_5H_5\))(\(\eta-\text{arene}\)).
In general, the results for these arene and cyclopentadienyl ruthenium(II) complexes are as expected, since the ligands on the metal are of the 'soft' type which tend to stabilise lower oxidation states and destabilise higher ones, therefore the ruthenium(II) → ruthenium(III) oxidation steps should occur at a relatively high potential, if at all. The lack of any observed reduction is more surprising since, as mentioned above the corresponding iron cations undergo a one electron reduction readily on electrochemical reduction.

6.2.4 Ru(S-S)₂L'₂ complexes (S-S = S₂PMe₂, S₂CNR₂; L' = various tertiary phosphines)

A number of the Ru(S-S)₂L'₂ complexes described in Chapter 4 were also examined by cyclic voltammetric and A.C. polarographic techniques. The dimethyldithiophosphinate complexes were found to behave quite differently from the dialkyldithiocarbamate compounds (Table 6.3). Hence the cis-Ru(S₂PMe₂)₂L'₂ (L' = PPh₃, PPh₂Cl, PPh₂H, PPh₂O₃Pr) complexes generally showed a reversible oxidation step in CH₂Cl₂ at a moderate potential (E½ < 0.9 V) with the exception of cis-Ru(S₂PMe₂)₂(PPhCl₂)₂ which was found to undergo an irreversible oxidation at +0.66 V vs. a Ag/AgI reference electrode. No reduction step, reversible or otherwise, was observed in the region from 0 to -1.6 V. The complexes cis-Ru(S₂PMe₂)₂(PPh₂H)₂ and cis-Ru(S₂PMe₂)₂(PPh₂Cl)₂ showed more than one oxidation, although the second oxidation steps were irreversible, as might be expected, as this is formally a ruthenium(III) to ruthenium(IV) transformation.
The Ru(S\(_2\)CNR\(_2\))\(_2\)L'\(_2\) (L' = PPh\(_3\), PMePh\(_2\), PEtPh\(_2\)) complexes all show irreversible behaviour on oxidation and no activity in the reduction range. Thus these dithio ligand complexes show the opposite tendency to that expected from earlier studies on these two types of ligand. Dialkyl-dithio carbamate ligands generally stabilise higher oxidation states than dialkyldithiophosphinates\(^{129}\), but in these complexes it was generally observed that the dimethyldithiophosphinates underwent irreversible oxidation steps whereas for the dialkyldithiocarbamate complexes, oxidations were all irreversible. This indicated that the ruthenium(III) cations [Ru(S\(_2\)CNR\(_2\))\(_2\)L'\(_2\)]\(^+\) were less stable than their S\(_2\)PMe\(_2\) analogues. No satisfactory explanation for this observation can be offered at present. Further studies on a wider range of those complexes and attempts to characterise in situ and also isolate their oxidation products should now be made.

6.3 Experimental

Electrochemical studies were carried out using a Princeton Applied Research (PAR 170) instrument. All solutions were degassed with argon prior to measurements to remove dissolved oxygen. The electrolyte solution was 0.50 M tetrabutyl-ammonium fluoroborate in Analar methylene chloride.
The tetrabutylammonium fluoroborate was prepared from tetrabutylammonium hydroxide solution by neutralisation with HBF$_4$ solution. The crude product was recovered by filtration and recrystallised from Analar methanol to give the pure product. The standard reference electrode used for measurements was a silver-silver iodide electrode.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Oxidation behaviour</th>
<th>Reduction behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru}(\eta^5-\text{C}_6\text{H}_5)\text{(phen)}\text{(PMe}_2\text{Ph})]\text{(PF}_6\text{)}\text{_2}))</td>
<td>None</td>
<td>-0.95(i)</td>
</tr>
<tr>
<td>([\text{Ru}(\eta^5-\text{C}_6\text{H}_5)\text{(phen)}\text{(PMe}_2\text{Ph})]\text{(PF}_6\text{)}\text{_2}))</td>
<td>None</td>
<td>-0.94(i)</td>
</tr>
<tr>
<td>([\text{Ru}(\eta^5-\text{C}_6\text{H}_5)\text{(phen)}\text{(PMe}_2\text{Ph})]\text{(PF}_6\text{)}\text{_2}))</td>
<td>+0.95(i)</td>
<td>-0.95(i)</td>
</tr>
<tr>
<td>([\text{Ru}(\eta^5-\text{C}_6\text{H}_5\text{OH})\text{(phen)}\text{(PMePh}_2\text{)}\text{(PF}_6\text{)}\text{_2}))</td>
<td>+1.08(i)</td>
<td>-1.38(i)</td>
</tr>
<tr>
<td>([\text{cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PFPh}_3\text{)}\text{_2}))</td>
<td>+0.50(r)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPh}_2\text{Cl)})</td>
<td>+0.88(r)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPhCl}_2\text{)}\text{_2}))</td>
<td>+1.15(i)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPh}_2\text{OPr)}\text{_2}))</td>
<td>+0.66(i)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPh}_2\text{H)}\text{_2}))</td>
<td>+0.60(r)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{Ru}(S_2\text{CNMe}_2\text{)}\text{_2}\text{(PPh}_3\text{)}\text{_2}))</td>
<td>+0.58(r)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{Ru}(S_2\text{CNMe}_2\text{)}\text{_2}\text{(PPh}_2\text{Et)}\text{_2}))</td>
<td>+0.98(i)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{Ru}(S_2\text{CNMe}_2\text{)}\text{(PPh}_2\text{Me)}\text{_2}))</td>
<td>+1.28(i)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{Ru}(S_2\text{CNMe}_2\text{)}\text{_2}\text{(PPh}_2\text{Et)}\text{_2}))</td>
<td>+0.44(i)</td>
<td>None</td>
</tr>
<tr>
<td>([\text{Ru}(S_2\text{CNMe}_2\text{)}\text{(PPh}_2\text{Me)}\text{_2}))</td>
<td>+1.20(i)</td>
<td>None</td>
</tr>
</tbody>
</table>

\[
\text{TABLE 6.3 Electrode potentials for various ruthenium(II)}
\]
complexes \( E_2 \) (volts) at \(20^\circ\text{C} \) in \(\text{CH}_2\text{Cl}_2/0.50 \text{ M Bu}_4\text{NBF}_4\text{)}\text{, a,b}

\[
\text{Complex} \quad \text{Oxidation behaviour} \quad \text{Reduction behaviour}
\]
\[
\text{[Ru(\eta^5-\text{C}_6\text{H}_5)\text{(phen)}\text{(PMe}_2\text{Ph})(\text{PF}_6\text{)}\text{_2})]} \quad \text{None} \quad -0.95(i)
\]
\[
\text{[Ru(\eta^5-\text{C}_6\text{H}_5)\text{(bipy)}\text{(PMe}_2\text{Ph})(\text{PF}_6\text{)}\text{_2})]} \quad \text{None} \quad -0.94(i)
\]
\[
\text{[Ru(\eta^5-\text{C}_6\text{H}_5\text{OH})\text{(phen)}\text{(PMePh}_2\text{)}\text{(PF}_6\text{)}\text{_2})]} \quad +0.95(i) \quad -0.95(i)
\]
\[
\text{[Ru(\eta^5-\text{C}_6\text{H}_5\text{OH})\text{(phen)}\text{(PMePh}_2\text{)}\text{(PF}_6\text{)}\text{_2})]} \quad +1.08(i) \quad -1.38(i)
\]
\[
\text{[cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PFPh}_3\text{)}\text{_2})\] \quad +0.50(r) \quad \text{None}
\]
\[
\text{[cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPh}_2\text{Cl)}\) \quad +0.88(r) \quad \text{None}
\]
\[
\text{[cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPhCl}_2\text{)}\text{_2})\] \quad +1.15(i) \quad \text{None}
\]
\[
\text{[cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPh}_2\text{OPr)}\text{_2})\] \quad +0.66(i) \quad \text{None}
\]
\[
\text{[cis-Ru}(S_2\text{PMe}_2\text{)}\text{_2}\text{(PPh}_2\text{H)}\text{_2})\] \quad +0.60(r) \quad \text{None}
\]
\[
\text{[Ru}(S_2\text{CNMe}_2\text{)}\text{_2}\text{(PPh}_3\text{)}\text{_2})\] \quad +0.58(r) \quad \text{None}
\]
\[
\text{[Ru}(S_2\text{CNMe}_2\text{)}\text{_2}\text{(PPh}_2\text{Et)}\text{_2})\] \quad +0.98(i) \quad \text{None}
\]
\[
\text{[Ru}(S_2\text{CNMe}_2\text{)}\text{(PPh}_2\text{Me)}\text{_2})\] \quad +1.28(i) \quad \text{None}
\]
\[
\text{[Ru}(S_2\text{CNMe}_2\text{)}\text{(PPh}_2\text{Et)}\text{_2})\] \quad +0.44(i) \quad \text{None}
\]
\[
\text{[Ru}(S_2\text{CNMe}_2\text{)}\text{(PPh}_2\text{Me)}\text{_2})\] \quad +1.20(i) \quad \text{None}
\]
\[
\text{[Ru}(S_2\text{CNMe}_2\text{)}\text{(PPh}_2\text{Et)}\text{_2})\] \quad +1.20(i) \quad \text{None}
\]
\[
\text{[Ru}(\eta^5-\text{C}_6\text{H}_5)\text{(\eta^5-\text{C}_5\text{H}_5})\text{]}\text{Bu}_{4}\text{)} \quad \text{None}\quad \text{None}
\]
\[
\text{[Ru}(\eta^5-\text{C}_6\text{Me}_6)\text{(\eta^5-\text{C}_5\text{H}_5})\text{]}\text{Cl} \quad \text{None}\quad \text{None}
\]

a vs Ag/AgI reference electrode, at which ferrocene is oxidised at +0.60V.
b \( r = \) reversible, \( i = \) irreversible
APPENDIX

$^{31}\text{P}$ Nuclear Magnetic Resonance Relaxation Time Measurements on Some Ruthenium(II) and Platinum(II) Complexes

Al.1 Introduction

A study of the $^{31}\text{P}-^{1}\text{H}$ spectra of some of the complexes cis- Ru(S$_2$PMe$_2$)$_2$L'$_2$, described in Chapter 4, revealed a considerable difference in the intensities of the resonances due to the dimethyldithiophosphinato ligands and those of the tertiary phosphine ligands. These intensity differences could have their origin either in spin-lattice relaxation time ($T_1$) differences and/or in a different nuclear Overhauser enhancement (NOE) in the different phosphorus nuclei. The latter effect is a consequence of failure to achieve full enhancement on proton decoupling because of different relaxation mechanisms competing with the $^{1}\text{H}-^{31}\text{P}$ dipolar mechanism, upon which the N.O.E. depends. Because of the small amount of published work on the $^{31}\text{P}$ spin-lattice relaxation times in transition metal phosphine complexes$^{130}$, it was decided to carry out a series of $T_1$ measurements to obtain information about the factors influencing line intensities in some complexes of platinum(II) and ruthenium(II) containing diphenylphosphininate and dimethylphosphito ligands.
Al.2 Results and Discussion

The measured $T_1$ data for a series of platinum(II) and ruthenium(II) complexes are shown in Table A.1. For comparison purposes, $T_1$ values for $\text{NH}_4[S_2\text{PPh}_2]$, $\text{Ph}_2\text{P(O)H}$ and $(\text{MeO})_2\text{P(O)H}$ are also given. These data have been measured at 303 K, and the solvent is CDCl$_3$, except where otherwise noted. Both the inversion-recovery and progressive saturation methods were used. The compound $\text{NH}_4[S_2\text{PPh}_2]$ has a long relaxation time of 30.0 seconds, a value comparable with that reported for triphenylphosphine$^{131}$. The compound $\text{Ph}_2\text{P(O)H}$ has a short relaxation time of 2.5 seconds. Such a short time arises because of the dipole-dipole relaxation contribution from the directly bound vicinal hydrogen. The dipole-dipole contribution to $T_1$ is inversely proportional to the sixth power of the phosphorus-hydrogen separation$^{132,133}$ and hence a directly bonded proton will make a dominant contribution to the relaxation. The value found for dimethylphosphite is significantly longer (5.5 seconds) even though there is again a P-H bond in the molecule which should dominate the dipole-dipole relaxation$^{134}$.

Coordination to a metal through phosphorus leads to complexes having no P-H bonds and hence the relaxation time $T_1$ is longer in the platinum(II) and ruthenium(II) complexes. The values of $T_1$ for the diphenylphosphinito or dimethylphosphito ligands in the complexes show little variation. The phosphite $T_1$ values remain longer than the phosphine ones and the $T_1$ value appears to be independent
of molecular geometry. Furthermore, the diphenylphosphinito group in the platinum hydride complex PtH{(PPh₂O)₂H}PMe₂Ph does not appear to have a shortened T₁ due to any dipole-dipole relaxation from the hydride ligand. If a major dipole-dipole relaxation contribution was being made by the hydride ligand, the T₁ values would be expected to be significantly less than that found for the diphenylphosphinito ruthenium complex. The hydride compound does, however, show a concentration dependent ³¹P n.m.r. spectrum, the lines P_a and P_c but not P_b showing reversible broadening at high solute concentrations. This observation can be explained by proposal of a monomer-dimer equilibrium occurring in solutions of the complex. The broadening of certain resonances may be indicative of the particular site of association although the specific alternative cannot be decided on the basis of present data.

Coordination of the phosphinito ligand to a metal at one end and a hydrogen-bonded structure at the other end will likely reduce the contribution of spin-rotation relaxation. Nevertheless, this structure arrangement will create a more rigid framework to lengthen the correlation time T_c. Since T₁ is inversely proportional to T_c, this effect will contribute to the relatively short T₁ values in the diphenylphosphinito and dimethylphosphito ligands in the complexes. This increased correlation time may explain why the T₁ values for the coordinated dimethylphosphito ligand are only slightly longer than that of the free compound with its directly bonded hydrogen atom.
The measured $T_1$ values for a series of complexes $\text{cis-Ru(S}_2\text{PMe}_2)_{2}L'_{2}$ ($L' = \text{PPh}_2H, \text{PPh}_2\text{OEt}, \text{PPhCl}_2, \text{PCl}_3$) are shown in Table A2. The $T_1$ values cover a range of 4-14 seconds for the $\text{S}_2\text{PMe}_2$ ligand and 2-14 seconds for the $L'$ ligands. The $T_1$ value for the ligand $L'$ is shortest for $\text{PPh}_2H$ and then becomes progressively longer as the number of phenyl groups on the phosphorus decreases and hence the number of protons in close proximity for dipole-dipole relaxation. The $T_1$ values for these ruthenium complexes show little shortening from the values in $\text{PtH}(\text{PPh}_2\text{O})_{2}H\text{PPh}_2\text{Me}$ indicating that the quadrupolar relaxation contribution from $^{99}\text{Ru}$ and $^{101}\text{Ru}$ is small. The $T_1$ values for the $\text{S}_2\text{PMe}_2$ ligand shows a trend parallel to that of the $L'$ ligand such that in all four complexes the $T_1$ values for the inequivalent phosphorus nuclei are similar in magnitude. Thus, the differing intensities in the $^{31}\text{P}-\{^{1}\text{H}\}$ spectra of these complexes is not due to differences in the $T_1$ values but is a likely consequence of changes in the nuclear Overhauser enhancement. In fact, preliminary studies reveal that proton-coupled spectra of these compounds show no significant intensity differences for the different phosphorus nuclei.

From Table A2 it is apparent that there is a strong correlation between the chemical shift value ($\delta$) and the $T_1$ value for the $\text{S}_2\text{PMe}_2$ ligand. This correlation implies that there is some communication between the ligands. The change in $T_1$ for the $\text{S}_2\text{PMe}_2$ ligand may be partly due to dipole-dipole coupling with the $L'$ ligand, which is
enhanced when \( L' \) has more phenyl rings. This relationship between \( T_1 \) and \( \delta \) would not necessarily be anticipated for a dipole-dipole mechanism but may be indicative of a contribution from a spin-rotation mechanism where both the chemical shift and relaxation time are related in the tensor\(^{135}\). Alternatively, the relaxation mechanism can be completely dipole-dipole and changes in \( T_1 \) due to differences in correlation times.

### A1.3 Experimental

Dimethyolphosphite was a commercial sample which was purified by distillation. Diphenylphosphinous acid\(^ {136}\) and the platinum complexes\(^ {62,68}\) were prepared by literature methods. The ruthenium compounds were synthesised as described in Chapters 4 and 5. The \( T_1 \) values were measured in \( CDCl_3 \) solvent except for \( NH_4[S_2PPh_2] \) which was measured in \( D_2O \). Measurements were made at 303 K and samples were not degassed. Spectra were recorded on either a Varian XL-100 spectrometer in Edinburgh operating at 40.51 MHz (progressive saturation method) or on a Bruker WH-90 spectrometer at Washington State University, Pullman operating at 36.44 MHz (inversion recovery method).

Relaxation time measurements were made using both the inversion recovery method \((90^\circ-\text{At-t})_n\) or the inversion recovery method \((\text{PD-180}^\circ-t-90^\circ-\text{AT})_n\). Quick estimates of \( T_1 \) values were obtained using the inversion recovery null signal method, whence \( T_1 = \frac{t}{\ln 2} \) where \( t \) is the pulse interval required for a null signal. For each compound measured,
the observed spectral width was chosen to be the narrowest that would encompass all the signals from the compound. For the progressive saturation method, the length for each measurement was 8192 points, the maximum available. This led to a digital resolution varying from 0.08 Hz/point to 1.25 Hz/point (for cis-Ru(S₂PMe₂)(PPh₂OEt)₂). A sensitivity enhancement weighting function was applied to all FID's before transformation, ensuring that sufficient points defined all peaks to be measured. Whenever possible, peak integrals were used. Analysis of the results was done by the classical semi-log linearisation followed by least squares analysis of the straight line obtained. Comparison with the three-parameters non-linear least squares method of Gerhards showed identical trends, with slight numerical differences in $T_1$ values.

For the inversion-recovery method a sweep width of 3012 Hz was used incorporating 4096 data points. An acquisition time/scan of 1.36 seconds was used and recovery times chosen which were a minimum of 5 times the $T_1$ value. Delay times were set and data acquisition performed by the computer $T_1$ program. Analysis of the data from $T_1$ measurements was by least squares fitting of the semi-log plot $\ln(S_\infty - S_t)$ against $t$, whence the slope provides $T_1$ value ($S_\infty =$ equilibrium signal intensity, $S_t =$ signal intensity at time $t$). A minimum of four times $t$ values were used and up to 1000 scans had to be collected to obtain acceptable signal-to-noise in the signals. For each method, values were estimated to be good to ±6%.
Table A.1  $T_1$ values for $^{31}$P nuclei in some platinum(II) and ruthenium(II) and the free ligands for comparison

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_1$ (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ph}_2\text{P}$(O)H</td>
<td>2.5$^1$</td>
</tr>
<tr>
<td>$(\text{MeO})_2\text{P}$(O)H</td>
<td>7.5$^1$</td>
</tr>
<tr>
<td>$(\text{NH}_4)[\text{S}_2\text{PPh}_2]\text{O}^-$</td>
<td>30.0$^{2,3}$</td>
</tr>
<tr>
<td>$\text{MeP}_2\text{RuPb}\text{H}_2\text{Me}$</td>
<td>7.4($^{p^a}$), 6.0($^{p^b}$)$^2$</td>
</tr>
<tr>
<td>$\text{MePh}_2\text{P}^a\text{P}^b\text{Ph}_2\text{Ph}_2$</td>
<td>5.9($^{p^a}$), 6.6($^{p^b}$), 6.7($^{p^c}$)$^1$</td>
</tr>
<tr>
<td>(MeO)$_2\text{PtCl}$</td>
<td>7.0($^{p^a}$), 10.4($^{p^b}$), 10.4($^{p^c}$)$^1$</td>
</tr>
<tr>
<td>(MeO)$_2\text{PtEt}_3\text{P}^a$</td>
<td>10.4</td>
</tr>
</tbody>
</table>

1. Measured by inversion-recovery method on a proton-coupled sample.
3. $\text{D}_2\text{O}$ solvent.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_1$ (sec.)</th>
<th>$\delta$ (ppm from $H_3PO_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-Ru($S_2PMe_2$)$_2$(PPh$_2$H)$_2$</td>
<td>$5.3^2, 2.3^3$</td>
<td>89.3</td>
</tr>
<tr>
<td>cis-Ru($S_2PMe_2$)$_2$(PPh$_2$OEt)$_2$</td>
<td>$3.8^2, 4.3^3$</td>
<td>86.5</td>
</tr>
<tr>
<td>cis-Ru($S_2PMe_2$)$_2$(PCl$_2$Ph)$_2$</td>
<td>$7.2^2, 8.7^3$</td>
<td>92.1</td>
</tr>
<tr>
<td>cis-Ru($S_2PMe_2$)$_2$(PCl$_3$)$_2$</td>
<td>$13.6^2, 14.4^3$</td>
<td>95.5</td>
</tr>
</tbody>
</table>

1. Chemical shift of $S_2PMe_2$ ligands in complex
2. $T_1$ for $S_2PMe_2$ ligands
3. $T_1$ for phosphine ligands.
REFERENCES

   (b) D.A. Brown and R.M. Rawlinson, J.C.S.(A), 1969, 1530.


131. P.S. Pregosin and R.W. Kunz, "$^{31}$P and $^{13}$C n.m.r. of Transition Metal Phosphine Complexes", 1979, p.90, Springer-Verlag, New York.


I attended the following postgraduate lecture courses:

- Cage and Cluster Compounds
- Bioinorganic Chemistry
- Double Resonance NMR
- Industrial Inorganic Chemistry
- Mass Spectrometry
- Chemical Applications of Neutron Scattering
- The Cambridge Crystallographic Database

and Departmental seminars and colloquia.
RUTHENIUM COMPLEXES CONTAINING GROUP VB DONOR LIGANDS

IX. CATIONIC \( \eta^6 \)-ARENÉ AND \( \eta^5 \)-CYCLOHEXADIENYL COMPLEXES OF RUTHENIUM CONTAINING NITROGEN AND PHOSPHORUS DONOR LIGANDS

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Summary

Reaction of the compounds \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{PR}_3(\text{N—N})](\text{PF}_6)_2\) with various nucleophiles (\(Y^-\)) give the stable \(\eta^5\)-cyclohexadienyl complexes \([\text{Ru}(\eta^5-\text{C}_6\text{H}_6Y)\text{-PR}_3(\text{N—N})]\text{PF}_6\) (\(Y^- = \text{H}^-, \text{CN}^-, \text{OH}^-; \text{PR}_3 = \text{PMe}_2\text{Ph}, \text{PMe}_2; \text{N—N} = 1,10 \text{ phenanthroline, 2,2'-bipyridyl}\)) and reaction of \([\text{Ru}(\eta^6-\text{C}_6\text{H}_3\text{Me}_3)(\text{PMe}_2\text{Ph})\text{phen}]\text{-}\text{(PF}_6)_2\) with NaBH\(_4\) gives \([\text{Ru}(\eta^5-\text{C}_6\text{H}_4\text{Me}_3)(\text{PMe}_2\text{Ph})\text{phen}]\text{PF}_6\). In contrast, reaction of these nucleophiles with other areneruthenium(II) cationic complexes such as \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}(\text{N—N})]\text{PF}_6\), \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{Cl}(\text{PMe}_2\text{Ph})_2]\text{PF}_6\) and \([\text{Ru}(\eta^6-\text{C}_6\text{H}_6)\text{PMePh}_2(\text{S}_2\text{PPh}_2)]\text{PF}_6\) leads to facile decomposition.

Introduction

Although reactions of nucleophiles with cationic complexes containing coordinated arenes have been studied extensively [2], very 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 [3]. In this paper, we now report our full studies [4] on the reactions of nucleophiles with various cationic areneruthenium(II) compounds where, in some instances, stable \(\eta^5\)-cyclohexadienyl complexes are obtained.

Results and discussion

On stirring \([\text{RuCl}_2(\eta^6-\text{C}_6\text{H}_6)]_2\) in methanol with an excess of 1,10-phenanthrolène (phen) for ca. 1 h, an orange-yellow solution is formed which

* For part VIII see ref. 1.
TABLE 1
ANALYTICAL AND CONDUCTIVITY DATA FOR SOME $\eta^6$-ARENE AND $\eta^5$-CYCLOHEXA-DIENYL-RUTHENIUM COMPLEXES

<table>
<thead>
<tr>
<th>Compound</th>
<th>M.p. (°C)</th>
<th>Analysis (Found(calcd.)) (%)</th>
<th>$\Lambda_m^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6]\text{Cl(phen)}]\text{PF}_6$</td>
<td>222 (decomp)</td>
<td>39.9 (40.0) 2.6 (2.6) 5.3 (5.2)</td>
<td>71</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6]\text{Cl(bipy)}]\text{PF}_6$</td>
<td>275 (decomp)</td>
<td>37.2 (37.3) 2.7 (2.7) 5.5 (5.4)</td>
<td>88</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_3\text{Me}_3]\text{Cl phen}]\text{PF}_6$</td>
<td>260 (decomp)</td>
<td>43.0 (43.3) 3.4 (3.4) 4.8 (4.8)</td>
<td>65</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_5\text{OMe}\text{Cl phen}]\text{PF}_6$</td>
<td>190 (decomp)</td>
<td>39.8 (40.0) 2.7 (3.0) 5.1 (4.9)</td>
<td>130 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_5\text{OMe}\text{bipy}]\text{PF}_6$</td>
<td>220 (decomp)</td>
<td>37.2 (37.4) 2.8 (2.8) 5.1 (4.9)</td>
<td>128 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(MeC}_6\text{H}_4\text{CHMe}_2\text{Cl phen}]\text{PF}_6$</td>
<td>154 (decomp)</td>
<td>44.5 (44.3) 3.7 (3.7) 4.7 (4.7)</td>
<td>120 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{PMe}_2\text{Ph phen}]\text{(PF}_6)\text{]}_2$</td>
<td>245–247</td>
<td>39.4 (39.6) 3.2 (3.2) 5.3 (3.6)</td>
<td>158</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{PMe}_2\text{Ph phen}]\text{(PF}_6)\text{]}_2$</td>
<td>263–265 (decomp)</td>
<td>43.9 (43.8) 3.2 (3.2) 3.3 (3.3)</td>
<td>140</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{PET}_2\text{Ph phen}]\text{(PF}_6)\text{]}_2$</td>
<td>267 (decomp)</td>
<td>41.4 (41.2) 3.7 (3.6) 3.4 (3.4)</td>
<td>174</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{PMe}_2\text{Ph bipy}]\text{(PF}_6)\text{]}_2$</td>
<td>227–229</td>
<td>37.5 (37.8) 3.3 (3.3) 3.7 (3.7)</td>
<td>215 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{PMe}_2\text{Ph (bipy)) (PF}_6)\text{]}_2$</td>
<td>255–257 (decomp)</td>
<td>42.3 (42.2) 3.2 (3.5) 3.5 (3.4)</td>
<td>220 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_3\text{Me}_3\text{PMe}_2\text{Ph phen}]\text{(PF}_6)\text{]}_2$</td>
<td>232–234</td>
<td>41.9 (42.0) 3.7 (3.7) 3.4 (3.7)</td>
<td>160</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_5\text{OMe} \text{PMe}_2\text{Ph bipy}]\text{(PF}_6)\text{]}_2$</td>
<td>221–224 (decomp)</td>
<td>37.6 (37.8) 3.3 (3.4) 3.7 (3.4)</td>
<td>215 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_7\text{PMe}_2\text{Ph phen}]\text{PF}_6$</td>
<td>162–165</td>
<td>48.2 (48.5) 4.1 (4.0) 4.3 (4.3)</td>
<td>73</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_7\text{PMe}_2\text{Ph bipy}]\text{PF}_6$</td>
<td>178–179 (decomp)</td>
<td>52.8 (52.8) 4.1 (4.0) 4.0 (4.0)</td>
<td>135 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{OH} \text{PMe}_2\text{Ph phen}]\text{PF}_6\text{(acetone)}$</td>
<td>168–169</td>
<td>48.4 (48.5) 4.2 (4.4) 3.9 (3.9)</td>
<td>80</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{CN} \text{PMe}_2\text{Ph phen}]\text{PF}_6$</td>
<td>230 (decomp)</td>
<td>48.2 (48.5) 3.8 (3.7) 6.2 (6.3)</td>
<td>76</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{OH} \text{PMePh}_2\text{Ph phen}]\text{PF}_6\text{(acetone)}$</td>
<td>110–113</td>
<td>53.0 (52.4) 4.3 (4.4) 3.5 (3.6)</td>
<td>128 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_7\text{PMePh}_2\text{bipy}]\text{PF}_6$</td>
<td>177–180 (decomp)</td>
<td>51.0 (51.1) 4.2 (4.1) 4.0 (4.1)</td>
<td>110 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_6\text{CN} \text{PMePh}_2\text{bipy}]\text{PF}_6$</td>
<td>170 (decomp)</td>
<td>45.6 (46.6) 3.6 (3.9) 5.7 (6.5)</td>
<td>130 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_5\text{CN} \text{PMePh}_2\text{bipy}]\text{PF}_6$</td>
<td>180–181 (decomp)</td>
<td>50.9 (51.0) 3.8 (3.8) 5.9 (5.9)</td>
<td>140 $^b$</td>
</tr>
<tr>
<td>$[\text{Ru(C}_6\text{H}_4\text{Me}_3\text{PMe}_2\text{Ph (phen)}\text{PF}_6$</td>
<td>198–199</td>
<td>50.7 (50.8) 4.7 (4.7) 3.9 (4.1)</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Molar conductivities at 298 K in CH$_3$NO$_2$. $^b$ Molar conductivities at 298 K in acetone (S cm$^2$ mol$^{-1}$), measured at $10^{-3}$ mol dm$^{-3}$ concentration.
deposits a bright yellow solid on addition of NH₄PF₆. The analysis figures for
this solid (see Table 1) fit for the formulation [Ru(C₆H₅)Cl(phen)PF₆] and con-
ductivity measurements in nitromethane agree with those expected for a 1/1
electrolyte (for a 10⁻³ mol dm⁻³ solution, the molar conductivity Λₘ = 71 S
cm² mol⁻¹ and a graph of Λ₀ − Λₑ vs. Cₑ¹/₂ gives a straight line of slope 233,
which are characteristic values for 1/1 electrolytes [5,6]). The IR spectrum of
this complex shows bands at 715, 776, 1090, 1135, 1211, 1430, 1520, 1579
and 1600 cm⁻¹ which originate from vibrations associated with the heterocyclic
and aromatic rings of the 1,10-phenanthroline ligand [7]. A band at 295 cm⁻¹
can be assigned to the terminal ν(RuCl) stretching vibration whilst a band at
360 cm⁻¹ may be due to a ν(Ru–N) stretch. The presence of PF₆⁻ is shown by
IR absorptions at 835 and 560 cm⁻¹, with the former absorption obscuring the
band normally found at ca. 800 cm⁻¹ which arises from the coordinated ben-
zeene ring. However, the ¹H NMR spectrum at 298 K in (CD₃)₂CO clearly shows
a singlet at δ 6.33 ppm which lies within the region expected for a coordinated
benzene ring whereas a series of multiplets centred at δ 8.20, 8.85 and 9.95
ppm confirms the presence of 1,10-phenanthroline (Table 2). Finally, the
intensity ratio of these resonances is 6 and 8, respectively, which agrees with
the formulation [Ru(C₆H₆)Cl(phen)]PF₆.

The analogous complexes [Ru(arene)Cl(N—N)]PF₆ (arene = C₆H₃Me₃, C₆H₅-
OMe, p-MeC₆H₄CHMe₂; N—N = phen; arene = C₆H₆, C₆H₅OMe; N—N = 2,2'-
bipyridyl(bipy)) have also been prepared by reaction of [{RuCl₂(arene)}₂ with
an excess of phen or bipy under the same reaction conditions and characterised
as above (see Tables 1 and 2).

However, if [{RuCl₂(C₆H₆)}₂ is refluxed with an excess of phen in metha-
nol for ca. 8 h, loss of coordinated benzene occurs as well as bridge cleavage
and halide replacement. Thus, the ¹H NMR spectrum of the orange solid iso-
lated from this reaction mixture by addition of NH₄PF₆ does not show any
coordinated benzene ring resonances and consists only of signals at δ 7.72, 8.43,
8.75 and 8.85 ppm which can be assigned to 1,10-phenanthroline. Analytical
data suggests the formulation [Ru(phen)₃]PF₆ and this is supported by con-
ductivity measurements in CH₃NO₂ which are characteristic of a 1/2 electrolyte
(Λ(1 X 10⁻³ mol dm⁻³) = 161.0 S cm² mol⁻¹ [5]).

All the cationic complexes [Ru(arene)Cl(N—N)]PF₆ react readily with the
tertiary phosphines PMe₂Ph, PMePh₂ or PEt₂Ph to give the dications
[Ru(arene)PR₃(N—N)]²⁺ which can be isolated as their hexafluorophosphate
salts. Analytical (Table 1) and ¹H NMR (Table 2) data support this formulation
and conductivity measurements (Table 1) confirm the dicationic character of the
complexes, e.g. for [Ru(C₆H₅)(PMe₂Ph)(phen)]PF₆ in CH₃NO₂, Λₘ = 158 S cm² mol⁻¹ and a graph of Λ₀ − Λₑ vs. Cₑ¹/₂ gives a straight line of slope
390, which are characteristic values for 1/2 electrolytes [5,6]. In contrast to
recent reports involving addition of tertiary phosphines to cyclic organic
ligands coordinated to manganese [8], iron [9] cobalt or rhodium [2] cations,
no evidence for ring addition by PR₃ has been observed in these studies.

However, these dicationic complexes [Ru(arene)PR₃(N—N)]PF₆ readily
undergo ring addition reactions with various other nucleophiles to give brightly
coloured, air stable, η⁵-cyclohexadienyl complexes. Thus, addition of NaBH₄ to
a methanolic solution of the pale yellow complex [Ru(C₆H₆)(PMe₂Ph)phen]-

(Continued on p. 314)
# TABLE 2

HYDROGEN-1 NMR DATA FOR SOME $\eta^6$-ARENÉ- AND $\eta^5$-CYCLO HEXADIENYL RUTHENIUM COMPLEXES AT 298 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>$^1$H NMR (δ, ppm) $^a$</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\eta^6$-arené</td>
<td>$\eta^5$-cyclohexadienyl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(1)(endo)</td>
<td>H(2,6)</td>
</tr>
<tr>
<td>[Ru(C₆H₆)Cl(phen)]PF₆</td>
<td>Acetone-d₆</td>
<td>6.33s</td>
<td></td>
</tr>
<tr>
<td>[Ru(C₆H₆)Cl(bipy)]PF₆</td>
<td>DMSO-d₆</td>
<td>6.22s</td>
<td></td>
</tr>
<tr>
<td>[Ru(C₆H₃Me₃)Cl(phen)]PF₆</td>
<td>Acetone-d₆</td>
<td>2.32s, 5.68s $^d$</td>
<td></td>
</tr>
<tr>
<td><a href="PF%E2%82%86">Ru(C₆H₆)(PMe₂Ph)(phen)</a>$_2$</td>
<td>Acetone-d₆</td>
<td>6.75s</td>
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<tr>
<td><a href="PF%E2%82%86">Ru(C₆H₆)(PMePh₂)(phen)</a>$_2$</td>
<td>Acetone-d₆</td>
<td>6.80s</td>
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<tr>
<td><a href="PF%E2%82%86">Ru(C₆H₆)(PET₂Ph)(phen)</a>$_2$</td>
<td>Acetone-d₆</td>
<td>6.72s</td>
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<tr>
<td><a href="PF%E2%82%86">Ru(C₆H₆)(PMe₂Ph)bipy</a>$_2$</td>
<td>Acetone-d₆</td>
<td>6.63s</td>
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<tr>
<td><a href="PF%E2%82%86">Ru(C₆H₆)(PMe₂Ph)bipy</a>$_2$</td>
<td>Acetone-d₆</td>
<td>6.73s</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ ppm values, $^b$ chemical shift, $^c$ coupling constant, $^d$ multiplet, $^e$ singlet, $^f$ doublet, $^g$ triplet, $^h$ quartet.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>δ (CDCl₃)</th>
<th>J (Hz)</th>
<th>δ (acetone)</th>
<th>J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(C₆H₇)(PMe₂Ph)phen]PF₆</td>
<td>CDCl₃</td>
<td>2.38m</td>
<td>2.38m</td>
<td>2.80m</td>
<td>4.78dd</td>
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</tr>
<tr>
<td>[Ru(C₆H₇)(PMe₂Ph)phen]PF₆(acetone)</td>
<td>CDCl₃</td>
<td>2.16m</td>
<td>2.16m</td>
<td>2.72m</td>
<td>4.78br</td>
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<td></td>
</tr>
<tr>
<td>[Ru(C₆H₆OH)(PMe₂Ph)phen]PF₆(acetone)</td>
<td>CDCl₃</td>
<td>2.95m</td>
<td>2.95m</td>
<td>3.05m</td>
<td>4.60dd</td>
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<tr>
<td>[Ru(C₆H₆CN)(PMe₂Ph)phen]PF₆</td>
<td>CDCl₃</td>
<td>3.18m</td>
<td>3.18m</td>
<td>3.80dd</td>
<td>5.18dd</td>
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<tr>
<td>[Ru(C₆H₇)(PMePh₂)bipy]PF₆</td>
<td>CDCl₃</td>
<td>2.10m</td>
<td>2.10m</td>
<td>2.55m</td>
<td>4.60br</td>
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</tr>
<tr>
<td>[Ru(C₆H₆OH)(PMe₂Ph)phen]PF₆</td>
<td>CDCl₃</td>
<td>2.70m</td>
<td>2.70m</td>
<td>2.90br</td>
<td>4.70br</td>
</tr>
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<td></td>
</tr>
<tr>
<td>[Ru(C₆H₆Me₃)(PMe₂Ph)phen]PF₆</td>
<td>CDCl₃</td>
<td>1.30s</td>
<td>1.45s</td>
<td>1.45s</td>
<td>1.45s</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

*Internal reference (CH₃)₄Si, s(singlet); d(doublet); t(triplet); m(multiplet; br(broad).  

*Resonances due to 1,10-phenanthroline.  

*Resonances due to 2,2'-bipyridyl.  

*Methyl resonances of C₆H₃Me₃.  

*Numbers in round brackets indicate 2J(PH) in Hz.  

*Resonance due to solvated acetone.  

-Methine resonance of ethyl group.  

-H(1)(exo) probably superimposed on H(1)(endo) resonance.  

*Hydroxyl resonance.  

*Resonance due to ring H's.
produced an immediate colour change to deep orange. Addition of water to this solution to destroy excess NaBH₄, followed by extraction with methylene chloride or chloroform and concentration of the organic extract leads to the orange product. This analysed well for [Ru(η⁵-C₆H₇)(PMe₂Ph)phen]PF₆ and conductivity measurements confirmed the compound is a 1/1 electrolyte (Table 1). The ¹H NMR spectrum of this material in CDCl₃ is very different from that of the starting material in that the coordinated benzene resonance at δ 6.75 ppm has disappeared completely and is replaced by weaker resonances at δ 2.38, 2.80, 4.78 and 5.79 ppm (relative intensity 2/2/2/1, respectively) which are consistent with the presence of a η⁵-cyclohexadienyl ligand. These resonances are very similar to those observed for the reaction of [Ru(C₆H₆)Cl₂]₂ and KCN in (CD₃)₂SO. The cyclohexadienyl complex resulting presumably from the reaction of Ru(C₆H₆)Cl₂(μ-CD₃)₂SO, [Ru(C₆H₆)Cl-(μ-CD₃)₂SO]⁺ or [Ru(C₆H₆)(μ-CD₃)₂SO]₃²⁺ [10] and CN⁻ has never been isolated but the reactions was followed by ¹H NMR spectroscopy [3]. The gradual growth of resonances at δ 2.88, 3.83, 5.05 and 6.00 ppm was observed and these were assigned to H(2) and H(6); H(1)(endo); H(3) and H(5); H(4), respectively (see Fig. 1). Homonuclear decoupling studies on [Ru(η⁵-C₆H₇)(PMe₂Ph)phen]PF₆, however, clearly show that irradiation of the resonance at δ 2.80 ppm collapses the doublet of doublets at δ 4.78 ppm to a doublet whereas irradiation at 2.30 produces no change in this resonance. Hence, for [Ru(η⁵-C₆H₇)(PMe₂Ph)phen]PF₆, the resonances at δ 2.38, 2.80, 4.78 and 5.79 ppm are assigned to H(1) (exo and endo); H(2) and H(6); H(3) and H(5); H(4), respectively. A similar frequency order has recently been proposed for [Rh(C₅Me₄Et)(η⁵-C₆H₇)]PF₆ [2]. Support for this conclusion comes from the ¹H NMR spectra of other η⁵-C₆H₇ compounds (Table 2) and from the ¹³C-¹H NMR spectra of [Ru(C₆H₆)(PMe₂Ph)phen](PF₆)₂ and [Ru(η⁵-C₆H₇)-(PMe₂Ph)phen]PF₆, since the resonance at 93.8 ppm (η⁶-C₆H₆) in the former is replaced in the latter by resonances at 27.5, 32.7, 75.9 and 96.1 ppm. By analogy with the ¹³C-¹H NMR spectrum of [Rh(C₅Me₄Et)(η⁵-C₆H₇)]PF₆ [2] these can be assigned to carbon atoms C(1), C(2, 5), C(4) and C(3, 5), respectively (Fig. 1). The IR spectrum of [Ru(η⁵-C₆H₇)(PMe₂Ph)phen]PF₆ (KBr disc) shows an absorption band at 2820 cm⁻¹ as observed in other η⁵-C₆H₇ compounds (e.g. Mn(η⁵-C₆H₇)(CO)₃ [11], [Rh(C₅Me₄Et)(η⁵-C₆H₇)]PF₆ [2]) and
this is assigned to the $\nu$(C-H exo) stretching vibration.

Similarly, facile reaction of various [Ru(C$_6$H$_6$)(PR$_3$)(N—N)](PF$_6$)$_2$ with other nucleophiles Y$^-$ (Y$^-$ = H$, OH^-$, CN$^-$) leads to formation and isolation of substituted cyclohexadienyl complexes, [Ru(\eta^2-C$_6$H$_{12}$Y)(PR$_3$)(N—N)]PF$_6$, characterised by elemental analysis, conductivity (Table 1) and $^1$H NMR (Table 2) data. The compound [Ru(C$_6$H$_3$Me$_3$)(PMe$_2$Ph)phen](PF$_6$)$_2$ also reacts with NaBH$_4$ to give [Ru(\eta^5-C$_6$H$_5$Me$_3$)(PMe$_2$Ph)phen]PF$_6$. By analogy with related studies [2], stereospecific exo addition of the nucleophiles to the ring probably occurs since the IR spectra of the substituted cyclohexadienyl complex (i.e. Y $\neq$ H) contain no characteristic $\nu$(C—H exo) stretching vibrations at <2850 cm$^{-1}$. No evidence for further attack by these nucleophiles to give disubstituted cyclohexadiene complexes was observed, even under reflux conditions, and attempts to extend these studies to a wider range of nucleophiles such as CH$_3$CO$_2^-$, i-Pr$_2$NH, t-BuO$^-$ and PhS$^-$ were unsuccessful.

The reaction of the monocations [Ru(arene)Cl(N—N)]PF$_6$ with similar nucleophiles also results in immediate colour changes but rapid decomposition then occurs preventing isolation of any clean products. Attempts to follow these reactions by $^1$H NMR spectroscopy were also unsuccessful since decomposition was too rapid. The instability of these complexes towards nucleophiles compared with the dicaticonic complexes may be due to competition between reactions involving addition to the coordinated six-membered ring and direct attack on the metal centre via substitution of chloride for H$, OH^-$ or CN$^-$ groups and/or ring displacement reactions. Similarly, the compounds [Ru(C$_6$H$_6$)ClL$_2$]PF$_6$ (L = PPh$_3$, PMe$_2$Ph, Et$_2$S, AsPh$_3$ etc) [10] decompose on addition of NaBH$_4$ although for L = PMe$_2$Ph, $^1$H NMR resonances were observed at $\delta$ 3.38 and 3.95 ppm which might be due to the formation of some $\eta^5$-C$_6$H$_5$ complex but this could not be isolated. For cations of type [Ru(C$_6$H$_6$)L(S$_2$PR$_2$)]$^+$ [12] rapid decomposition occurred on addition of NaBH$_4$ although in these complexes the hydride ion probably attacks the $\sigma$S$_2$PR$_2$ ligand in preference to the coordinated benzene ring.

In conclusion, the ability of the [Ru(arene)PR$_3$(N—N)]$^{2+}$ cations to react with certain nucleophiles to produce stable $\eta^2$-cyclohexadienyl complexes can probably be attributed to the presence of strong metal—ligand bonds minimising the possibility of alternative reaction pathways and to the high formal positive charge favouring nucleophilic attack. The presence of such good $\pi$-acceptor ligands as PR$_3$ and phen (or bipy) will also render the coordinated arene more susceptible to nucleophilic attack.

**Experimental**

Microanalyses were by 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 or KBr discs. Hydrogen-1 NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and $^{13}$C—($^1$H) NMR spectra on a Varian CFT-20 spectrometer operating at 20 MHz ($^{13}$C chemical shifts quoted in ppm to high frequency of SiMe$_4$). Melting points were determined with a Köfler hot stage microscope and are uncorrected. Conductivity measure-
ments were made at 298 K using a model 310 Portland Electronics conductivity bridge. Conductivity vs. concentration data were obtained over a range of concentrations ($1 \times 10^{-3}$ to $5 \times 10^{-3}$ dm$^{-3}$ mol) for several of the compounds and a plot of $\Lambda_c$ (equivalent conductance) vs. $C_e^{1/2}$ (concentration in equivalent dm$^{-3}$) gave a straight line whose slope is a function of the ionic charges. Thus, the slopes obtained for various samples were compared with those for known 1/1 and 1/2 electrolytes and hence the electrolyte type could be determined [6].

Materials

Ruthenium trichloride hydrate (Johnson Matthey); cyclohexa-1,3-diene, ammonium hexafluorophosphate (Ralph Emanuel Ltd); methyldiphenylphosphine, dimethylphenylphosphine, diethylphenylphosphine (Maybridge), 2,2'-bipyridyl, 1,10-phenanthroline, sodium borohydride, potassium cyanide (BDH); $\alpha$-phellandrene (5-isopropyl-2-methyl-cyclohexa-1,3-diene) (Eastman Chemicals). Various cyclohexa-1,4-dienes were prepared by the Birch reduction of arenes [13] and then $[\{\text{Ru} (\eta_{\text{arene}})\text{Cl}_2\}_2]$ (arene = C$_6$H$_6$, 1,3,5-C$_6$H$_3$Me$_3$, C$_6$H$_5$OMe, p-MeC$_6$H$_4$CHMe$_2$) were synthesised as described earlier [3,14] from “RuCl$_3 \times$ H$_2$O” and the corresponding cyclohexa-1,4 diene (or if available cyclohexa-1,3-diene). Analytical and conductivity data for the various compounds are given in Table 1 and hydrogen-1 NMR data in Table 2. All reactions were carried out in degassed solvents under an atmosphere of nitrogen.

$\eta^6$-Benzene(chloro)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate. The compound $[\{\text{Ru} (\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ (0.20 g; 0.40 mmol) was stirred in methanol (25 cm$^3$) with an excess of 1,10-phenanthroline (0.18 g; 1.00 mmol) for ca. 1 h. The reaction mixture was filtered, and addition of excess NH$_4$PF$_6$ (0.30 g; 2.00 mmol) to the yellow/orange filtrate precipitated the product as a yellow solid, which was filtered off and washed thoroughly with water, methanol and diethyl ether (yield 0.35 g, 82%) $\nu$(RuCl) 295 cm$^{-1}$.

If the reactants in this reaction are refluxed for ca. 8 h, an orange solution is produced which deposits an orange crystalline solid which was recrystallised from acetone/diethyl ether and identified as tris(1,10-phenanthroline)ruthenium(II) hexafluorophosphate diethyletherate. (Found: C, 45.6; H, 3.0; N, 7.9. C$_{40}$H$_{34}$F$_{12}$N$_6$OP$_2$Ru calcd.: C, 45.3; H, 3.2; N, 7.9%) (m.p. >290$^\circ$C (decomp)), $\nu$(C=N) 1600 cm$^{-1}$; $\Lambda_m (1 \times 10^{-3}$ mol dm$^{-3}$ in CH$_3$NO$_2$) 161.0 S cm$^2$ mol$^{-1}$.

$\eta^6$-Benzene(2,2'-bipyridyl)chlororuthenium(II) hexafluorophosphate (nc) was prepared from $[\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}_2\}_2]$ (0.20 g; 0.40 mmol), 2,2'-bipyridyl (0.14 g; 1.00 mmol) and NH$_4$PF$_6$ (0.30 g; 2.00 mmol) under similar conditions to those described for the 1,10-phenanthroline complex (0.39 g, 85%) $\nu$(RuCl) 295 cm$^{-1}$. Chloro($\eta^6$-mesitylene)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) $\nu$(RuCl) 295 cm$^{-1}$, ($\eta^6$-anisole)chloro(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (0.15 g; 35%) $\nu$(RuCl) 300 cm$^{-1}$, $\eta^6$-anisole(2,2'-bipyridyl)chlororuthenium(II) hexafluorophosphate (nc) (0.16 g; 40%) $\nu$(RuCl) 295 cm$^{-1}$ and chloro(p-cymene)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (0.40 g; 68%) $\nu$(RuCl) 295 cm$^{-1}$ were similarly prepared.
$\eta^6$-Benzene(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate. The complex $[\text{Ru}(\eta^6-C_6H_6)Cl(\text{phen})]\text{PF}_6$ (0.10 g; 0.19 mmol) was suspended in methanol (20 cm$^3$) and PMe$_2$Ph (0.10 cm$^3$) was added. The solution was gently warmed until the yellow starting material had completely dissolved (15 min) and then NH$_4$PF$_6$ (0.18 g; 1.00 mmol) was added. On cooling, a very pale yellow crystalline solid was deposited which was filtered off and washed thoroughly with water, then diethyl ether and air dried. Evaporation of the solvent from the filtrate gave more of the complex which was washed with water to remove excess NH$_4$PF$_6$ and recrystallised from acetone/diethyl ether (yield 0.096 g; 66%).

The complexes $\eta^6$-benzene(methylidiphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc); $\eta^6$-benzene(diethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc); $\eta^6$-benzene(2,2'-bipyridyl)(dimethylphenylphosphine)ruthenium(II) hexafluorophosphate (nc); $\eta^6$-benzene(2,2'-bipyridyl)methylidiphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (60%) $\eta^6$-mesitylene(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc), and $\eta^6$-anisole(2,2'-bipyridyl)(dimethylphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (62%) were prepared similarly from the appropriate chloro complex and tertiary phosphine.

$\eta^5$-Cyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate. The compound $[\text{Ru}(\eta^5-C_6H_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$ (0.10 g; 0.13 mmol) was dissolved in methanol (20 cm$^3$). Addition of an excess of NaBH$_4$ (0.10 g; 2.60 mmol) gave an immediate orange/red colouration, and the reaction mixture was stirred for 30 min. Water (20 cm$^3$) was added to destroy the excess of NaBH$_4$ and the resultant mixture was extracted with 2 X 50 cm$^3$ portions of methylene chloride. The orange solution containing the product was dried (Na$_2$SO$_4$) and concentrated by evaporation of the methylene chloride in vacuo. Addition of light petroleum (b.p. 60—80°C) gave the product as an orange solid (0.04 g; 52%).

$\eta^5$-Cyclohexadienyl(methylidiphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (60%), $\eta^5$-cyclohexadienyl(diethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) (45%), $\eta^5$-cyclohexadienyl(2,2'-bipyridyl)(methylidiphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (70%) and $\eta^5$-1,3,5-trimethylcyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate (nc) were similarly prepared from the appropriate $[\text{Ru}(\eta^5-$arene$(\text{PR}_3)(\text{N—N})]\text{PF}_6$$_2$ and excess of NaBH$_4$.

$\eta^5$-1-Hydroxocyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate acetone solvate. The complex $[\text{Ru}(\eta^5-C_6H_6)(\text{PMe}_2\text{Ph})(\text{phen})]\text{PF}_6$ (0.10 g; 0.13 mmol) was stirred in a mixture of acetone (15 cm$^3$) and water (5 cm$^3$) with 1 pellet of NaOH (0.032 g; 0.80 mmol) for 1 h. The orange solid deposited was filtered off and washed thoroughly with water and diethyl ether (0.05 g; 58%) $\nu$(CO) (acetone) 1705 cm$^{-1}$. $\eta^5$-1-Hydroxocyclohexadienyl(methylidiphenylphosphine)(1,10-phenanthroline)ruthenium(II) (nc) was similarly prepared starting from $[\text{Ru}(\eta^5-C_6H_6)-(\text{PMePh}_2)(\text{phen})]\text{PF}_6$ (0.10 g; 0.13 mmol) and NaOH (70%).
\( \eta^5 \)-1-Cyanocyclohexadienyl(dimethylphenylphosphine)(1,10-phenanthroline)ruthenium(II) hexafluorophosphate. The complex \([\text{Ru(} \eta^5 \text{-C}_6\text{H}_6\text{-}(\text{PMe}_2\text{Ph})\text{phen}) \text{(PF}_6\text{)}\text{]_2}\) (0.10 g; 0.13 mmol) was stirred in methanol (10 cm\(^3\)) with an excess of KCN (0.10 g; 1.50 mmol) for ca. 1 h. The bright yellow precipitate which was filtered off and washed thoroughly with water and diethyl ether (0.055 g; 61%). Likewise, \( \eta^5 \)-1-cyanocyclohexadienyl(2,2'-bipyridyl)(dimethylphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (50\%) and \( \eta^5 \)-1-cyanocyclohexadienyl(2,2'-bipyridyl)(methyldiphenylphosphine)ruthenium(II) hexafluorophosphate (nc) (80\%) can be synthesised from the appropriate \([\text{Ru(} \text{C}_6\text{H}_6\text{)}\text{PR}_3 \text{(bipy)} \text{(PF}_6\text{)}\text{]_2}\) and KCN.

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References

Synthesis and Reactions of Some Diphenylphosphinous Acid Complexes of Ruthenium (II) and Platinum (II) containing Dithioacid Ligands

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In recent years, a number of transition metal compounds containing the hydrogen-bonded \( R_2POHOPR_2 \) ligands (\( R = \text{Ph, OMe, OEt} \)) have been synthesised and some reactions of these complexes reported [1]. To date, however, the majority of these studies have been confined to complexes of palladium (II) and platinum (II). In this preliminary communication, we now wish to report the synthesis of some ruthenium (II) dimethyl-dithiophosphinate compounds which contain diphenylphosphinous acid ligands.* Some reactions of these complexes, together with those of the related \([\text{Pt}(S_2CNR_2)(\text{Ph}_2\text{PO})_2\text{H}] (R = \text{Et, }^{1}\text{Pr})\) [4] are also briefly described.

*The only other reported examples of ruthenium (II) complexes containing these types of ligand are \([\{\text{P(OMe)Ph}_2\}_2\{\text{P(OH)Ph}_2\]-\text{RuCl}_3\text{Ru}\{\text{(Ph}_2\text{PO})_3\text{H}_2\}] [2] and \([\{\text{RuCl}_2(\text{NO})\{\text{R(EO)PO}\}_2\text{H}\}_2 \) (\( R = \text{OEt, Ph} \)) [3].
Several years ago, it was demonstrated that the complexes cis-[Ru(S₂PR₂)(PPh₃)₂] (R = Me, Ph) underwent facile exchange reactions with phosphorus containing ligands (L') of greater Lewis basicity to give cis-[Ru(S₂PR₂)L₂] (L' = PMe₂Ph, PMePh₂) [5]. This exchange process has now been extended to synthesise a wider range of cis-[Ru(S₂PMe₂)L₂] (I) complexes (L' = PClPh₂, PCl₂Ph, PCl₃, P(OEt)Ph₂, P(OMe)Ph₂) with the intention of then hydrolysing the coordinated P-Cl or P-OR bonds to produce complexes containing a range of POHOP ligands (cf related studies on Pt/R₂PCl compounds [6]). High yields of the neutral complexes (I) were obtained by refluxing in dry hexane, a suspension of [Ru(S₂PMe₂)(PPh₃)₂] with an excess of L'. The products were characterised by elemental analyses, molecular weight and IR spectral measurements and ¹H and ³¹P-{¹H} nmr studies confirmed the retention of a cis-configuration. However, unlike cis-[Ru(S₂PMe₂)(PPh₃)₂] which undergoes facile interconversion of optical isomers at ambient temperatures [5], all the products (except for L' = P(OEt)Ph₂) exhibited stereochemical rigidity at this temperature although some scrambling was observed at elevated temperatures. Unfortunately all attempts to date to cleave these various P-X bonds and isolate clean products have met with little success, e.g. attempted acid hydrolysis of cis-[Ru(S₂PMe₂)(P(OEt)Ph₂)₂] under very mild conditions gave paramagnetic ruthenium (III) compounds of unknown composition.

Therefore another approach was investigated, namely reaction of cis-[Ru(S₂PMe₂)(PPh₃)₂] with a large excess of PClPh₂ in acetone to which ca 10% water was added to convert the free chlorophosphine to Ph₂P(O)H. After refluxing for several hours, work-up gave a red, non-conducting crystalline
solid formulated as \([\text{Ru}(S_2\text{PMe}_2)\{\text{Ph}_2\text{PO}\}_3\text{H}_2]\) (II) (Yield ca 30%) together with a large amount of white solid identified as \(\text{Ph}_2\text{P}(\text{O})\text{C(OH)}\text{Me}_2\). The latter arises from reaction of \(\text{Ph}_2\text{P}(\text{O})\text{H}\) with acetone and could be eliminated by carrying out the reaction in aqueous methanol. Evidence for compound (II) is based on elemental analyses and molecular weight determination [Found: C, 54.6; H, 4.6; \(M(\text{in C}_6\text{H}_6 \text{ by osmometry}) 794\) Required: C, 54.9; H, 4.6%; \(M 832\)]; \(^1\text{H} \text{nmr in CDCl}_3 \text{ at 298K;} \delta 2.00 \text{ ppm (d)} ^2J_{\text{PH}} 12.0 \text{ Hz}(\text{S}_2\text{PMe}_2); \delta 6.50-8.00 \text{ ppm (m)} \{\text{Ph}_2\text{PO}_3\text{H}_2\}; \delta 8.80 \text{ ppm (broad)} \{\text{Ph}_2\text{PO}_3\text{H}_2\} \) and \(^{31}\text{P}-(^1\text{H}) \text{nmr in CDCl}_3 \text{ at 213-298K;} \delta 102.4 \text{ ppm (q)} (\text{S}_2\text{PMe}_2); \delta 122.8 \text{ ppm (d)} \{\text{Ph}_2\text{PO}_3\text{H}_2\} ^3J_{\text{PP}} 4.4 \text{ Hz. Related five coordinate monomers [Ru(S}_2\text{PR}_2)(\text{PMe}_2\text{Ph})_3\text{BPh}_4 \text{ (R} = \text{Me,Ph)} \) have recently been synthesised, \([\text{R} = \text{Me}; ^{31}\text{P}-(^1\text{H}) \text{nmr spectrum in CDCl}_3 213-298K; \delta 32.4 \text{ ppm (d)} (\text{PMe}_2\text{Ph}); \delta 110.3 \text{ ppm (q)} (\text{S}_2\text{PMe}_2) ^3J_{\text{PP}} 3.6 \text{ Hz} \) and shown by X-ray analysis (for \(\text{R} = \text{Ph}) \) to have a distorted square pyramidal geometry [7]. Furthermore the existence of the interesting \(\text{R}_2\text{POHOP}(\text{R}_2)\text{OHOPR}_2\) tridentate ligands have recently been verified by X-ray analysis on \([\{\text{P(OMe)}\text{Ph}_2\}_2\{\text{P(OH)}\text{Ph}_2\}\text{RuCl}_3\text{Ru} \{\text{Ph}_2\text{PO}\}_3\text{H}_2\}] \) [2] and by characterisation of \([\text{Co}(\eta\text{C}_5\text{H}_5)\{\{\text{RO}\}_2\text{PO}\}_3\text{H}_2\} \text{ BF}_4 \text{ (R} = \text{Me,Et}) \) [8].

If \([\text{Ru}(S}_2\text{PMe}_2)_2(\text{PPPh}_3)_2]\) was reacted with only small amounts of \(\text{PClPh}_2\) in aqueous methanol, an inseparable mixture of two products was obtained. Spectroscopic analysis showed that one of these was compound (II) and the other probably \([\text{Ru}(S}_2\text{PMe}_2)(\text{PPPh}_3)\{\text{Ph}_2\text{PO}\}_2\text{H}\}] \) (III) \(^{31}\text{P}-(^1\text{H}) \text{nmr in CDCl}_3 \text{ at 298K;} \delta 52.4 \text{ ppm (td)} ^2J_{\text{PP}} 37.1 \text{ Hz,} ^3J_{\text{PP}} 4.4 \text{ Hz} (\text{PPPh}_3); \delta 104.7 \text{ ppm (broad)} (\text{S}_2\text{PMe}_2); 121.3 \text{ ppm (d.d)} (\text{Ph}_2\text{POHOPPh}_2)\)
$^{2}J_{pp}$ 37.1 Hz; $^{3}J_{pp}$ 2.9 Hz. Reaction of this mixture with more Ph$_2$P(O)H then gave (II) alone confirming that compound (III) is an intermediate in the formation of complex (II).

However, reaction of [Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$] with Ph$_2$P(O)H under the same conditions gave a complex mixture of products (31P nmr evidence) indicating that protonation and subsequent removal of a coordinated S$_2$PMe$_2$ group by the HCl released in the in situ hydrolysis of PClPh$_2$ is probably a key step in the formation of compounds (II) and (III). In support of this observation, reaction of [Ru(S$_2$PMe$_2$)$_2$(PPh$_3$)$_2$] with an excess of P(OMe)$_2$(O)H in methanol gave a high yield of cis-[Ru(S$_2$PMe$_2$)$_2$PPh$_3$(P{OMe}$_2$(O)H)] (IV) as the only product [Found: C 38.7; H 4.6; Required C, 39.8; H 4.7%; 31P-{1H} nmr in CDCl$_3$ at 298 K; δ 54.0 ppm (dt) $^{2}J_{pp}$ 48.2 Hz, $^{3}J_{pp}$ 5.5 Hz (PPh$_3$) δ 91.0 ppm (broad) (S$_2$PMe$_2$); δ 137.0 ppm (dt) $^{2}J_{pp}$ 48.2, $^{3}J_{pp}$ 7.3 Hz (P{OMe}$_2$(O)H)].

Some preliminary studies on reactions of compound (II) and the closely related [Pt(S$_2$CNR$_2$)(Ph$_2$PO)$_2$H] (V) (R = Et, 1Pr) have also been made. Thus, reaction of (V) with BF$_3$.Et$_2$O gives [Pt(S$_2$CNR$_2$)(Ph$_2$PO)$_2$BF$_2$] (cf related compounds in ref [1]) whereas with (II), reaction with BF$_3$.Et$_2$O appears to give [Ru(S$_2$PMe$_2$)(Ph$_2$PO)$_3$BF] (VI) (cf [Co(η-C$_5$H$_5$)({RO}$_2$PO)$_3$BF]BF$_4$ [8]). Both compounds react with VO(acac)$_2$ to give VO[(OPPh$_2$)$_2$Pt(S$_2$CNR$_2$)] and VO[(OPPh$_2$)$_2$(HOPPh$_2$)Ru(S$_2$PMe$_2$)]$_2$ respectively whereas with Co(acac)$_2$, preliminary evidence suggests that Co[(OPPh$_2$)$_2$Pt(S$_2$CNR$_2$)]$_2$ and Co[(OPPh$_2$)$_3$Ru(S$_2$PMe$_2$)]$_2$ are produced. Further reactions with a wider range of metal salts are now in progress.
Finally, the five coordinate complex (II) reacts with carbon monoxide under very mild conditions to give the six coordinate \([\text{Ru}(\text{S}_2\text{PMe}_2)\text{CO}\{\text{Ph}_2\text{PO}\}_3\text{H}_2]\) but longer reaction times also give some \([\text{Ru}(\text{S}_2\text{PMe}_2)(\text{CO})_2\{\text{Ph}_2\text{PO}\}_2\text{H}\}]\).

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