SYNTHETIC, STRUCTURAL AND SPECTROSCOPIC STUDIES ON SOME PLATINUM GROUP METAL COMPLEXES

by

EWAN B. McASLAN

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Declaration

I declare that, except where otherwise stated, the work presented in this thesis was conducted by myself from October 1982 until September 1985. It has not been submitted, in whole or in part, for any other degree.

Certain of the results reported in Chapter 2 have already been published.

Acknowledgements

I am indebted to my supervisor, the late Dr. T.A. Stephenson for his boundless enthusiasm and encouragement throughout this work. I am also grateful to the Science and Engineering Research Council for financial assistance and to Johnson Matthey plc for loans of precious metals.

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I would also like to thank Dr. G.A. Heath and Dr. M. Schröder for their advice following the untimely death of Dr. T.A. Stephenson.

Finally, I am deeply indebted to Mrs. Christian Ranken for typing this thesis.

ABSTRACT

Chapter 1: A brief survey of the chemistry of some tertiary phosphine complexes of rhodium, iridium and ruthenium.

Chapter 2: A study of the products obtained by the reaction of $RhCl_3.3H_2O$ with various ratios of PEt_2Ph is reported. Alternative high yield routes to the species $[Rh_2Cl_6(PR_3)_3]$ (PR_3 = PMe_2Ph, PEt_2Ph and $PPr^n{}_2Ph$) are described. The synthesis and characterisation of the compounds $[Rh_2Cl_5(PR_3)_4]$-BPh_4 are presented and possible mechanisms of formation are discussed. The isolation and characterisation, by physical and chemical methods together with an X-ray crystal structural analysis, of solvated monomer mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$ are reported. The variable temperature $^{31}P-\{^1H\}$ n.m.r. spectra of the various species are discussed. A scheme linking the various complexes is presented.

Chapter 3: Attempts to prepare iridium analogues of the species discussed in chapter 2 are described. Instead of the desired products mer-$[IrI_3(PMe_2Ph)_2$-$(NH_3)]$ was formed. The synthesis and characterisation by physical and chemical methods are reported together with an X-ray crystal structural analysis.

Chapter 4: A brief survey of the various preparations used in the synthesis of complexes containing the $[(R_2PO)_2H]^-$ and $[(R_2PO)_3H_2]^-$ ligands is given.

Chapter 5: The alternative routes resulting in the synthesis and characterisation of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ are described. The synthesis and characterisation of the five-coordinated species $[Rh(L_2)\{(Ph_2PO)_3Na(OH_2)_x\}]$ $(x = 1,2)$ prepared by the reaction of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ with various bidentate ligands L_2 $[L_2-(S_2CNMe_2)^-$, $(S_2CNEt_2)^-$ $(S(O)CPh)^-$, $(O_2CPh)^-$ and $(O_2C-C_6H_4-4-CH_3)^-]$ are reported. The X-ray crystal structures of $[RhCl\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$ and $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu-OH_2)\}]_2.4CHCl_3$ are presented.

Chapter 6: The reaction of *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ with hydrolysed Ph_2PCl in $MeOH/H_2O$ (7:1, v/v) is reinvestigated. Prolonged reaction generates *trans*-$[RuCl_2(Ph_2PH)_4]$ via $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ and possible mechanisms of formation are discussed. The X-ray crystal structure of *trans*-$[RuCl_2(Ph_2PH)_4].2CHCl_3$ is presented.

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Chapter 1

Some Tertiary Phosphine Halo-Complexes Of Rhodium, Ruthenium and Iridium

1.1 Introduction

Since Chapters 2 and 3 are concerned with the synthesis and subsequent reactions of rhodium(III) and iridium(III) halo-complexes containing tertiary phosphines, it is of interest to discuss the earlier work carried out in these areas. In order to place the understanding of the above systems in perspective, a brief survey of the chemistry of the related ruthenium species is included.

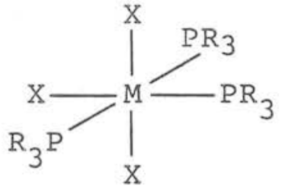
Tertiary phosphine complexes of the transition metals have received a good deal of attention, especially in recent years, and have been discussed in several books and reviews on coordination chemistry[1,2,3,4].

1.2 Rhodium

1.2.1 Mononuclear species

The preparation of rhodium(III) halide complexes containing tertiary phosphines was first reported by Chatt *et al*. in 1964 [5]. They found that rhodium(III) halides generally formed complexes of stoichiometry $[RhX_3(PR_3)_3]$ although sometimes binuclear $[Rh_2X_6(PR_3)_n]$ (n=3,4) and cationic *trans*-$[RhX_2(PR_3)_4]^+$ (X = halogen, R = alkyl or aryl group) could be isolated.

Complexes of the type $[MX_3(PR_3)_3]$ (M = metal) can exist as one of two possible isomers. In the meridional form (1) two of the phosphines are *trans* to each other, while in the facial isomer (2) all of them are cis. The mer-isomer is therefore sterically preferred.



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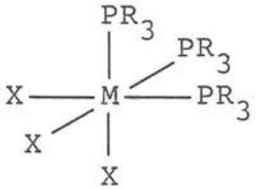

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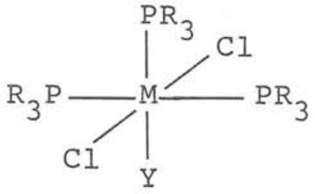
Chatt et al. obtained the mononuclear complexes mer-$[RhCl_3(PR_3)_3]$ (R_3 = Et_3, $Pr^n{}_3$, $Bu^n{}_3$, Me_2Ph, Et_2Ph) by the addition of PR_3 (3 mol.) to a hot alcoholic solution of $RhCl_3.3H_2O$. These orange compounds were assigned a meridional configuration on the basis of dipole moment studies and this was subsequently confirmed by ^1H n.m.r.[6], i.r., Raman[6,7,8,9], ^{31}P n.m.r.[10,11] spectroscopy (see Section 1.2.2) and finally by crystallographic studies[12]. For mer-$[RhCl_3(PEt_2Ph)_3]$ the latter indicates that the rhodium atom is in a distorted octahedral environment with the bond lengths consistent with a trans-influence for phosphorus greater than chloride[12].

Brookes and Shaw showed that the chloride trans to phosphine in mer-$[RhCl_3(PMe_2Ph)_3]$ is more labile to displacement by nucleophilic reagents than the other two, since this complex, when treated with the appropriate alkali-metal salt in hot acetone or ethanol for a few minutes, readily gives species of the type $[RhCl_2Y(PMe_2Ph)_3]$ (3) (Y = Br, I, NCO, NCS, N_3 or NO_2).

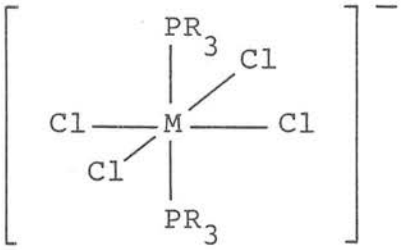


(3)

They also found that under more vigorous conditions (e.g. several hours at reflux temperatures), further substitution occurs generating complexes of the type mer-[$RhY_3(PMe_2Ph)_3$][6].

The fac-[$RhCl_3(PR_3)_3$] complexes are less well known and Intille noted that they have been prepared only with the smaller tertiary phosphines[13]. On a number of occasions they have been obtained as by-products in the preparation of the meridional forms[5,6,7] and their formation is favoured by more polar solvents. Photochemical irradiation of the mer-isomer is often the best method available to prepare the facial isomer in reasonable yield[14,15] and a wide range of fac-[$RhX_3(PR_3)_3$] complexes (X = usually Cl; R_3 = Me_3[13,14,16], Et_3, Me_2Ph[13,14], Et_2Ph[14,15], $Pr^n{}_2Ph$, $Bu^n{}_2Ph$ [14]) have now been synthesised photochemically. Their configurations have been established by i.r., Raman[7,8,9] and ^{31}P n.m.r.[14] spectroscopy.

In addition to the neutral complexes [$RhCl_3(PR_3)_3$] some charged mononuclear rhodium(III) species have also been prepared. For example, Brookes and Shaw isolated the compound [$PHMe_2Ph$][$RhCl_4(PMe_2Ph)_2$], (4), in very low yield (2-3%) from the reaction mixture used to prepare mer- and fac-$[RhCl_3(PMe_3Ph)_3]$[6].



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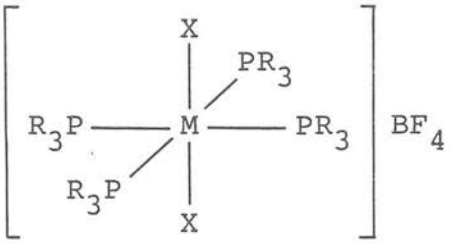
Alternative high yield routes were reported by Stephenson who prepared the orange compound $[Ph_4As][RhCl_4(PPh_3)_2]$ from reaction of $[RhCl(PPh_3)_3]$ or $[RhCl(CO)(PPh_3)_2]$ with an excess of $[Ph_4AsCl.HCl]$ in acetone. It was also established that as for the ruthenium analogues, treatment of the $[RhCl_4(PPh_3)_2]^-$ anion with neat PMe_2Ph gives the $[RhCl_4(PMe_2Ph)_2]^-$ anion. Facile exchange of chloride with X^- (X = Br, SCN) also occurs in solution, but unlike the corresponding ruthenium complexes, $[RhX_4(PR_3)_2]^-$ does not undergo solvolysis in nitromethane, methylcyanide etc, to generate neutral $[RhX_3(PR_3)_2S]$ compounds[17].

Finally, a high yield route to the mononuclear cationic complexes trans-$[RhX_2(PMe_3)_4]BF_4$, (5), is by reaction of mer-$[RhCl_3(PMe_3)_3]$ with one mole equivalent of $[Ag(PMe_3).NO_3]$ in dichloromethane followed by treatment with $H[BF_4]$[16].



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1.2.2 Spectroscopic studies

The synthesis of these various rhodium(III) complexes was parallelled by the application of several important spectroscopic studies to determine their structure. For example, detailed vibrational spectra of <u>mer</u>- and <u>fac</u>-$[RhX_3(PMe_3)_3]$ and the <u>trans</u>-$[RhX_2(PMe_3)_4]^+$ cation were recorded and assigned over the range 800-50 cm^{-1}. In this study Goggin and Knight used trimethylphosphine which, being a much simpler ligand than those used in previous vibrational studies[6,8,9], enabled unambiguous assignment of the ν(Rh-X) stretching frequencies to be made[16].

In the earlier work on these rhodium(III) complexes, methods of structural determination were limited to dipole moment studies and in some cases ^1H n.m.r. spectroscopy where the phenomenon of "virtual coupling" proved helpful[18]. In free dimethylphenylphosphine the ^1H n.m.r. resonance of the methyl protons is a symmetrical doublet due to spin-spin interaction with the phosphorus nuclei (^{31}P, spin ½, 100%

abundance). However, Jenkins and Shaw observed that when two molecules of this phosphine were present in a complex in trans-positions to one another, the methyl resonance is usually a very well defined and narrow 1:2:1 triplet. This is an example of "virtual coupling" and arises as a consequence of the strong coupling between phosphorus atoms in trans positions.

With phosphorus ligands in mutually cis-positions, the ^1H n.m.r. resonance of the methyl protons is usually a simple doublet because of the weak coupling of the two phosphorus nuclei.

Hence the ^1H n.m.r. resonance pattern for the complexes mer-$[MX_3(PMe_2Ph)_3]$ is a 1:2:1 triplet and a symmetrical doublet of relative intensity 2:1 which indicates two phosphines to be in mutual trans-positions, the other being cis[18].

With the availability of more powerful spectrometers, detailed ^1H n.m.r. spectra for the mer- and fac-$[RhX_3(PMe_3)_3]$ (X = Cl, Br) have been recorded and the spectra discussed in terms of $[AX_9]_2BY_9$ (mer) and $[AX_9]$ (fac) spin systems[19].

The advent of $^{31}P\{^1H\}$ n.m.r. spectroscopy and its subsequent use to study complexes of several different transition metals with phosphorus donor ligands had shown the technique to be very helpful in stereochemical assignment. This was possible from the observed patterns which arose due to the $^2J_{P-P}$ couplings. Preliminary studies indicated that ^{31}P n.m.r. spectroscopy was an especially powerful technique for the rhodium-phosphine systems[10], since like ^{31}P, ^{103}Rh (100% abundance) has nuclear spin $I=\frac{1}{2}$ thus giving rise to $^{103}Rh-^{31}P$ couplings which give additional structural information.

However, it was not until random-noise decoupling of the aryl and alkyl hydrogens in the phosphines was possible that well defined spectra were obtained and the usefulness of the $^1J_{Rh-P}$ couplings fully realised[11,14,20].

Inspection of the coupling constant data indicates that the coupling constants are larger for complexes of Rh(I) than for those of Rh(III). Moreover, for compounds of both oxidation states the rhodium-phosphorus coupling is always larger for a phosphorus _trans_ to a halogen than for mutually _trans_ phosphorus atoms. It is also apparent that $^1J_{Rh-P}$ values for the facial complexes are similar to the $^1J_{Rh-P}$ values for the phosphorus atom _trans_ to chlorine in the meridional isomer, and quite different from the $^1J_{Rh-P}$ coupling constants observed for the mutually _trans_ phosphorus atoms. Table 1.1 lists typical values for $^1J_{Rh-P}$ coupling constants observed for these compounds[11].

1.2.3 Binuclear species

In addition to the several types of mononuclear species isolated, the binuclear complexes $[Rh_2Cl_6(PR_3)_n]$ [n = 3, $R_3 = Et_3$; n = 4, $R_3 = Et_3$, $Pr^n{}_3$, $Bu^n{}_3$, $(n\text{-pentyl})_3$] were also prepared by Chatt _et al_. These stable chloro-bridged binuclear compounds were formed when limiting amounts of phosphine ligand were present[5].

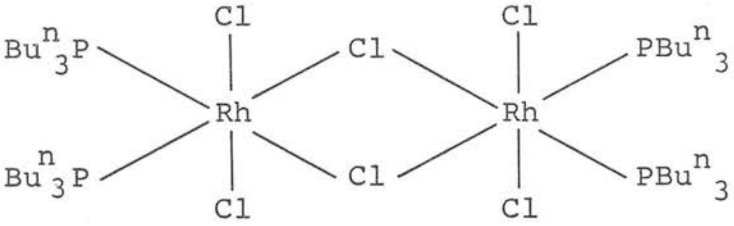
The reaction of $RhCl_3.3H_2O$ with PEt_3 (in 2:3 molar ratio) gives the binuclear complex $[Rh_2Cl_6(PEt_3)_3]$ which was presumed to have three chlorine atoms bridging two octahedrally co-ordinated rhodium atoms. Although the dipole moment of the compound was very high, it was not possible to determine unequivocally its configuration since several isomers of formula $[Rh_2Cl_6(PEt_3)_3]$ having large dipole moments are possible.

The same authors found that on treating $RhCl_3.3H_2O$ in ethanol with PEt_3 (in 1:2 molar ratio), another type of binuclear species $[Rh_2Cl_6(PEt_3)_4]$ was readily obtained. An alternative route to this compound was by the reaction of mer-$[RhCl_3(PEt_3)_3]$ with $RhCl_3.3H_2O$ (2:1 molar ratio) in hot ethanol.

Treatment of the chloro-complex $[Rh_2Cl_6(PBu^n{}_3)_4]$ with LiBr gave the corresponding bromo-analogue but attempts to prepare the iodo-complex gave mixtures. These binuclear species were considered to have two bridging halogen atoms such that each rhodium centre was octahedrally coordinated. Again it was not possible to determine unequivocally the configurations of the complexes on the basis of their dipole moments.

The double chloro-bridged complexes were found to react rapidly with free tertiary phosphine to give the mononuclear species $[RhCl_3(PR_3)_3]$ but attempts to prepare the mixed compounds $[RhCl_3(C_5H_5N)(PR_3)_2]$ by treating the double bridged compounds with pyridine (2 mol.) gave only inseparable mixtures[5].

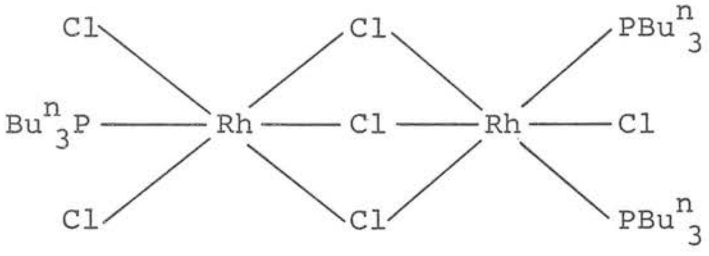
Since the original work, there have been several re-investigations and several different structures proposed for the double bridged compounds. Thus, Brown and Green proposed configuration (6) for the complex $[Rh_2Cl_6(PBu^n{}_3)_4]$ on the basis of their $^{31}P-\{^1H\}$ n.m.r. data which showed a single doublet with a $^{1}J_{Rh-P}$ coupling constant of 115Hz[11]. This data suggested that all the phosphines were equivalent and all trans to chlorine. However they noted that their proposed configuration (6), was inconsistent with the measured high dipole moment[5,11].



(6)

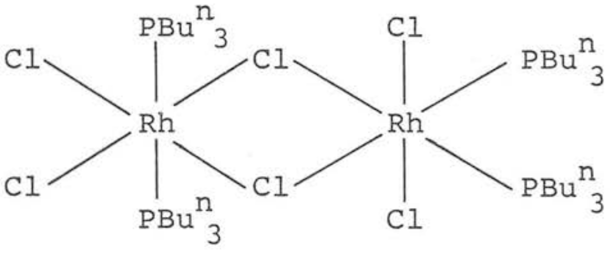
Allen and Gabuji[21] reported that Chatt's method of preparation of $[Rh_2Cl_6(PBu^n_3)_4]$[5] gave a mixture from which it was possible to separate the compounds mer-$[RhCl_3(PBu^n_3)_3]$, $[Rh_2Cl_6(PBu^n_3)_3]$ and $[Rh_2Cl_6(PBu^n_3)_4]$. The $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Rh_2Cl_6(PBu^n_3)_3]$ contained two doublets of intensity ratio 2:1 and with $^{1}J_{Rh-P}$ coupling constants of 117.7Hz and 115.2Hz respectively. This data suggested two equivalent phosphines attached to one rhodium atom and one phosphine on the other rhodium centre with all three phosphines trans to chlorine. On the basis of this evidence, configuration (7) was proposed for the complexes $[Rh_2Cl_6(PR_3)_3]$.

Examination of the $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Rh_2Cl_6(PBu^n_3)_4]$ also revealed two doublets but in this case they were of equal intensity with $^{1}J_{Rh-P}$ coupling constants



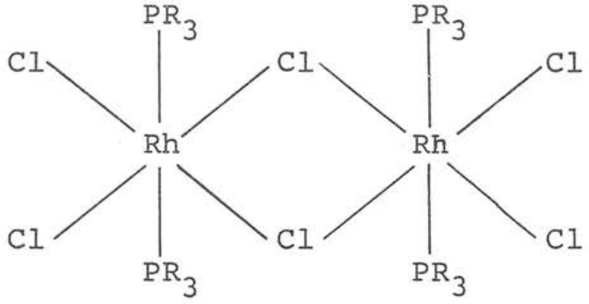
(7)

of 115.5Hz and 79.7Hz. This suggested two equivalent mutually <u>trans</u> phosphines bound to one rhodium atom and another two equivalent phosphines on the other rhodium both <u>trans</u> to chlorine. Thus configuration (8) was proposed for the double bridged species.



(8)

An alternative route to the binuclear compounds $[Rh_2X_6(PR_3)_4]$ was reported by Intille, namely slow crystallisation from solutions of <u>mer</u>-$[RhX_3(PR_3)_3]$ (R_3 = Me_3, Et_3, $Pr^n{}_3$, Me_2Ph, Cy_3) which had been exposed to air. It was suggested that loss of one phosphine, perhaps by oxidation to the phosphine oxide, leaves a coordinatively unsaturated $RhX_3(PR_3)_2$ moiety and hence facile dimerisation via bridging chlorines is encouraged. In this case the ^1H n.m.r. spectra of the trimethyl and dimethylphenyl derivatives suggested a mutually trans arrangement of all the phosphine ligands as shown in configuration (9)[13].



(9)

Brookes and Shaw briefly reported that the compound $[Rh(CO)Cl_3(PPr^n_3)_2]$ when irradiated in benzene solution lost CO and gave the binuclear bridged complex $[Rh_2Cl_6(PPr^n_3)_4]$ but no structural details were given[15].

The confusion concerning the structure of these binuclear compounds, especially the double bridged species, was largely dissipated following the examination of the X-ray crystal structures of the PBu^n_3 derivatives. Hence the X-ray crystal structure determination of $[Rh_2Cl_6(PBu^n_3)_3]$ showed the molecule to have a confacial bioctahedral structure with three chloride bridges, each of which is trans to one phosphine and one terminal chloride. There are two phosphines attached to one rhodium atom and one phosphine bound to the other. The arrangement of tertiary phosphine and terminal chlorine is consistent with the labilising effect of the phosphine groups, since each bridging chlorine is trans to only one phosphine. This structure (see Fig.1.1) is consistent with the solution ^{31}P n.m.r. data[21] from which configuration (7) was proposed[22].

In the case of the compound $[Rh_2Cl_6(PBu^n{}_3)_4]$ the two rhodium centres, each with octahedral coordination, lie on a two-fold axis. The two phosphines bound to one rhodium atom are <u>cis</u> to each other and <u>trans</u> to bridging chlorines, while the two phosphines on the other rhodium centre are <u>trans</u> to each other. This structure (see Fig.1.2) is in accord with the large dipole moment[5] and with the solution $^{31}P-\{^1H\}$ n.m.r. data[21] from which configuration (8) was proposed[23].

In both structures[22,23] the average values for the different types of Rh-Cl and Rh-P bond lengths are comparable to those from related compounds and are in agreement with a <u>trans</u>-influence for phosphine ligands greater than that for chloride.

Fig.1.1: X-ray crystal structure of $[(PBu^n_3)_2ClRhCl_3RhCl_2(PBu^n_3)]$ (bond lengths ±0.01Å)

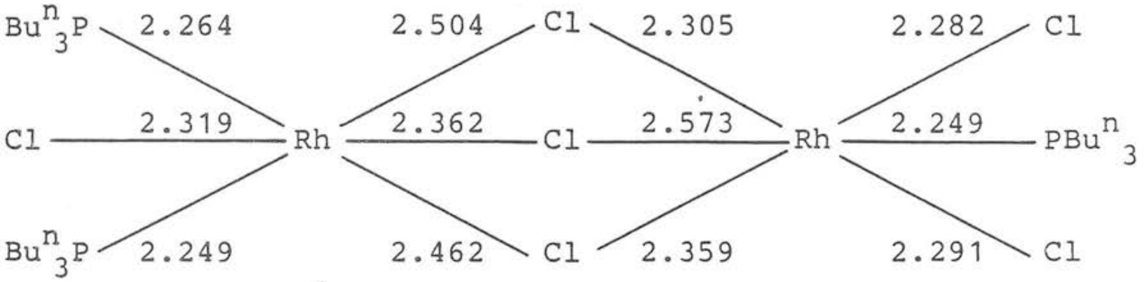
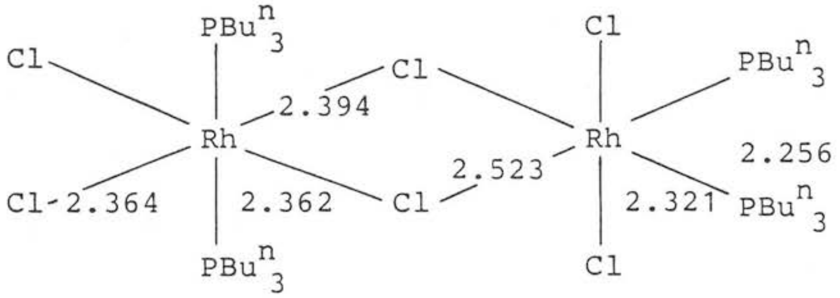


Fig.1.2: X-ray crystal structure of $[(PBu^n_3)_2Cl_2RhCl_2RhCl_2(PBu^n_3)_2]$ (bond length ±0.015Å)



1.3 Ruthenium

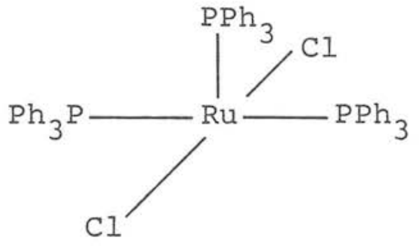
1.3.1 Mononuclear species

Ruthenium(II)

The reaction of a six-fold excess of PPh_3 with "$RuCl_3.3H_2O$" in MeOH[24,25], EtOH or iso-propanol[26] for several hours under refluxing conditions gives the red-brown complex $[RuCl_2(PPh_3)_3]$ whereas prolonged shaking at ambient temperature, forms $[RuCl_2(PPh_3)_4]$[24]. However, $^{31}P\{^1H\}$ n.m.r. studies[27,28] show that this is best formulated as $[RuCl_2(PPh_3)_3.PPh_3]$ with one PPh_3 group trapped in the lattice.

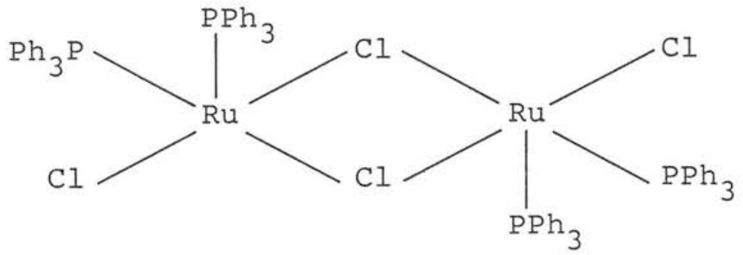
Prolonged reaction at room temperature in methanol using a 1:2 molar ratio of Ru to PPh_3 is found to yield the green ruthenium(III) complex $[RuCl_3(PPh_3)_2(MeOH)]$[24]. However these reactants in iso-butanol or cyclohexanol generate black polymeric $[RuCl_2(PPh_3)_2]_n$[26]. The polymeric compound can also be obtained either by heating $[RuCl_2(PPh_3)_3]$ under reflux in methylethylketone[29] or from the reduction of $[RuCl_3(PPh_3)_2(MeOH)]$ with hydrogen[30,31]. Other authors report that solvents such as 2-methoxyethanol and benzylalcohol take part in the reaction producing $[RuHCl(CO)(PPh_3)_3]$[26,32] and $[RuCl_2(CO)(PPh_3)_3]$[26] respectively.

Alternative routes to the complex $[RuCl_2(PPh_3)_3]$ include the treatment of $[RuH_2(N_2)(PPh_3)_3]$ (or $[RuH_2(PPh_3)_4]$) with HCl[33] and the reaction of $Cs[Ru(\eta-C_6H_6)Cl_3]$[34] (or the reduced "ruthenium blue" solution[35]) with PPh_3. The X-ray crystal structure determined by La Placa and Ibers confirmed that $[RuCl_2(PPh_3)_3]$ is five coordinate with a distorted square pyramidal geometry (10) with one of the phenyl ortho hydrogens blocking the sixth coordination site[36].



(10)

Initial osmometric molecular weight studies in acetone on $[RuCl_2(PPh_3)_n]$ (n = 3,4)[24] and spectrophotometric measurements in deoxygenated benzene supported these conclusions[37]. However, later investigations using variable temperature $^{31}P-\{^1H\}$ n.m.r. spectroscopy revealed that the dissociation product $[RuCl_2(PPh_3)_2]_n$ is, in non-polar media, the five coordinate dimer (11)[27,28] rather than the four coordinate monomer originally proposed[24].



(11)

Therefore equation [2] rather than equation [1] is a better representation of the species present in non-polar media[27,28].

$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2] + PPh_3$ ..... [1]

$2[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl_2(PPh_3)_2]_2 + 2PPh_3$ ..... [2]

In more polar media, conductometric[24], spectrophotometric[37] and ^{31}P-{^1H} n.m.r. spectroscopic studies[28] reveal the presence of an alternative dissociation pathway for [$RuCl_2(PPh_3)_3$], namely loss of Cl^- to produce the Ru(II) cations (see Eqns [3] and [4]) although very recent unpublished work by Nekleva indicates that the triple chloro-bridged binuclear species [Ru_2Cl_4(DMA)$(PPh_3)_4$] (DMA = dimethylacetamide) is present[38].

$$[RuCl_2(PPh_3)_3] \rightleftharpoons [RuCl(PPh_3)_3]^+ + Cl^- \quad ..... [3]$$

$$[RuCl(PPh_3)_3]Cl \rightleftharpoons [RuCl(PPh_3)_2]Cl + PPh_3 \quad ..... [4]$$

The synthesis of pure [$RuBr_2(PPh_3)_3$] by reaction of methanolic "$RuCl_3.xH_2O$"/LiBr solutions with PPh_3 was also claimed[24] but subsequent ^{31}P-{^1H} n.m.r. studies have shown the product to be a mixture of [$RuCl_xBr_{2-x}(PPh_3)_3$] (x = 0-2)[27]. However pure [$RuBr_2(PPh_3)_3$] was successfully prepared by Lindsay from the reaction of [$Ph_3(PhCH_2)P]_3[Ru_2Br_9$] with PPh_3 in methanol and the bromo-analogue was shown to have very similar properties to [$RuCl_2(PPh_3)_3$][39].

Most phosphorus-donor ligands react with "$RuCl_3.xH_2O$" in aqueous ethanol or 2-methoxyethanol to give the triple chloro-bridged compounds [$Ru_2Cl_3(PR_3)_6$]Cl which do not generally react with an excess of PR_3 to give the complexes [$RuCl_2(PR_3)_4$]. A better route to these monomeric species is by the reaction of PR_3 with [$RuCl_2(PPh_3)_{3\text{ or }4}$], usually in non-polar media to minimise the formation of ionic species. This method affords both [$RuCl_2(PR_3)_3$][R_3 = $EtPh_2$ [28], $MePh_2$, $(MeCH_2CH(Ph)CH_2)Ph_2$ [40], Me(Ph)$(PhCH_2)$[41], etc] and

$[RuCl_2(PR_3)_4]$ [R_3= Me, Ph (<u>cis</u>[28], <u>trans</u>[42]), Et_3, $MePh_2$ [42], Me_3 [43,44], $(MeCH_2CH(Ph)CH_2)Ph_2$ [40]].

Many of these monomeric complexes undergo facile rearrangement in solution to form various bi- and sometimes tri-nuclear species.

Ruthenium (III)

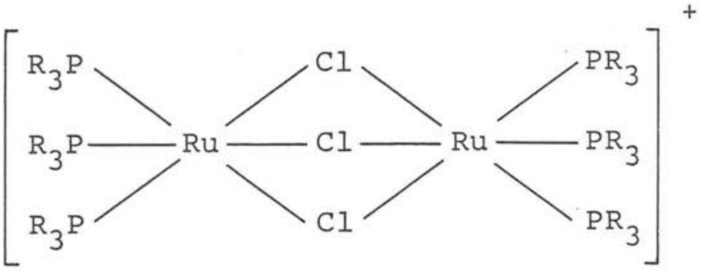
An extensive series of paramagnetic Ru(III) complexes $[RuCl_3(PR_3)_3]$ (R_3 = Me_2Ph, Et_2Ph, $Bu^n{}_2Ph$, PPh_3) can be synthesised from "$RuCl_3.xH_2O$", conc.HCl and PR_3 in ethanol by using much shorter reaction times than those required to yield $[Ru_2Cl_3(PR_3)_6]Cl$ or $[RuCl_2(PR_3)_4]$[45,46,47]. These complexes were assigned a meridional configuration (1) on the basis of i.r. and e.s.r. studies[8,48,49]. Chatt <u>et</u> <u>al</u>. successfully prepared the bromo-analogues by refluxing the chloro-species $[RuCl_3(PR_3)_3]$ with a solution containing an excess of LiBr[47].

Stephenson and Wilkinson isolated green crystals of the solvated complex $[RuCl_3(PPh_3)_2(MeOH)]$ by shaking PPh_3 and "$RuCl_3.xH_2O$" (2:1 molar ratio) in an excess of methanol for several days. By using ethanol as the solvent they were able to prepare the analogous species $[RuCl_3(PPh_3)_2(EtOH)]$. However, from the solution in cold acetone, brown crystals of $[RuCl_3(PPh_3)_2(Me_2CO)]$ are quickly deposited, demonstrating the lability of the alcohol ligand[24]. This lability makes the complex an excellent precursor for the synthesis of a wide range of low-spin Ru(III) compounds containing O-, N- or S-donor ligands[24,50,51,52].

1.3.2 Binuclear species

Ru_2 (II,II)

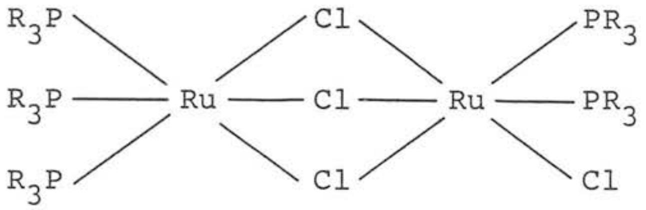
Compounds of the type $[(PR_3)_3RuCl_3Ru(PR_3)_3]Y$ (R_3 = Me_2Ph, Et_2Ph, $MePh_2$, $EtPh_2$; Y = Cl^-, ClO_4^-, SCN^-, BPh_4^-) were first prepared by Chatt and Hayter by reaction of "$RuCl_3.xH_2O$" with PR_3 in aqueous methanol or ethanol[53]. A wider range of these cations are now available from a variety of routes involving reaction of "$RuCl_3.xH_2O$", $[RuCl_2(nbd)]_n$, $[RuCl_2(PPh_3)_n]$, Ru-arenes or the reduced "ruthenium blue" solution with PR_3 in polar media[28,34,35,46,54,55,56]. The confacial bioctahedral geometry (12) has been verified by X-ray structural analyses for PR_3 = PEt_2Ph (Y = <u>mer</u>-$[RuCl_3(PEt_2Ph)_3]^-$)[57], PMe_2Ph (Y = PF_6^-) [58] and PMe_3 (Y = BF_4^-) [59].



(12)

The related cations $[(PR_3)_3RuX_3Ru(PR_3)_3]^+$ (X = OH^-, R_3 = Me_2Ph, $MePh_2$; X = F^-, I^-, R_3 = Me_2Ph, $MePh_2$) were synthesised by Singleton <u>et al</u>. from the reaction of $[RuH(NH_2NMe_2)_3(cod)]^+$ with PR_3 in acetone followed by addition of HX [60]. Treatment of these hydroxo-complexes with HX in $MeNO_2$ provides a high yield route to the pure $[Ru_2X_3(PR_3)_6]^+$ cations (R_3 = Me_2Ph; X = Cl^-, Br^-, I^-)[39]. The iodo- and bromo-derivatives were previously claimed to have been generated from $[Ru_2Cl_3(PR_3)_6]^+$ and NaI or from "$RuCl_3.xH_2O$", LiBr and PR_3 respectively[56] but recent $^{31}P-\{^1H\}$ n.m.r. evidence indicates that these are a mixture of $[Ru_2Cl_nX_{3-n}(PR_3)_6]^+$ cations[39].

Raspin et al reported that pyrolysis of $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in methylacetate or n-propylpropionate gives $[Ru_2Cl_3(PEt_2Ph)_6][RuCl_3(PEt_2Ph)_3]$ and/or the neutral binuclear complex $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ (13) (X-ray analyses available)[57,61,62].

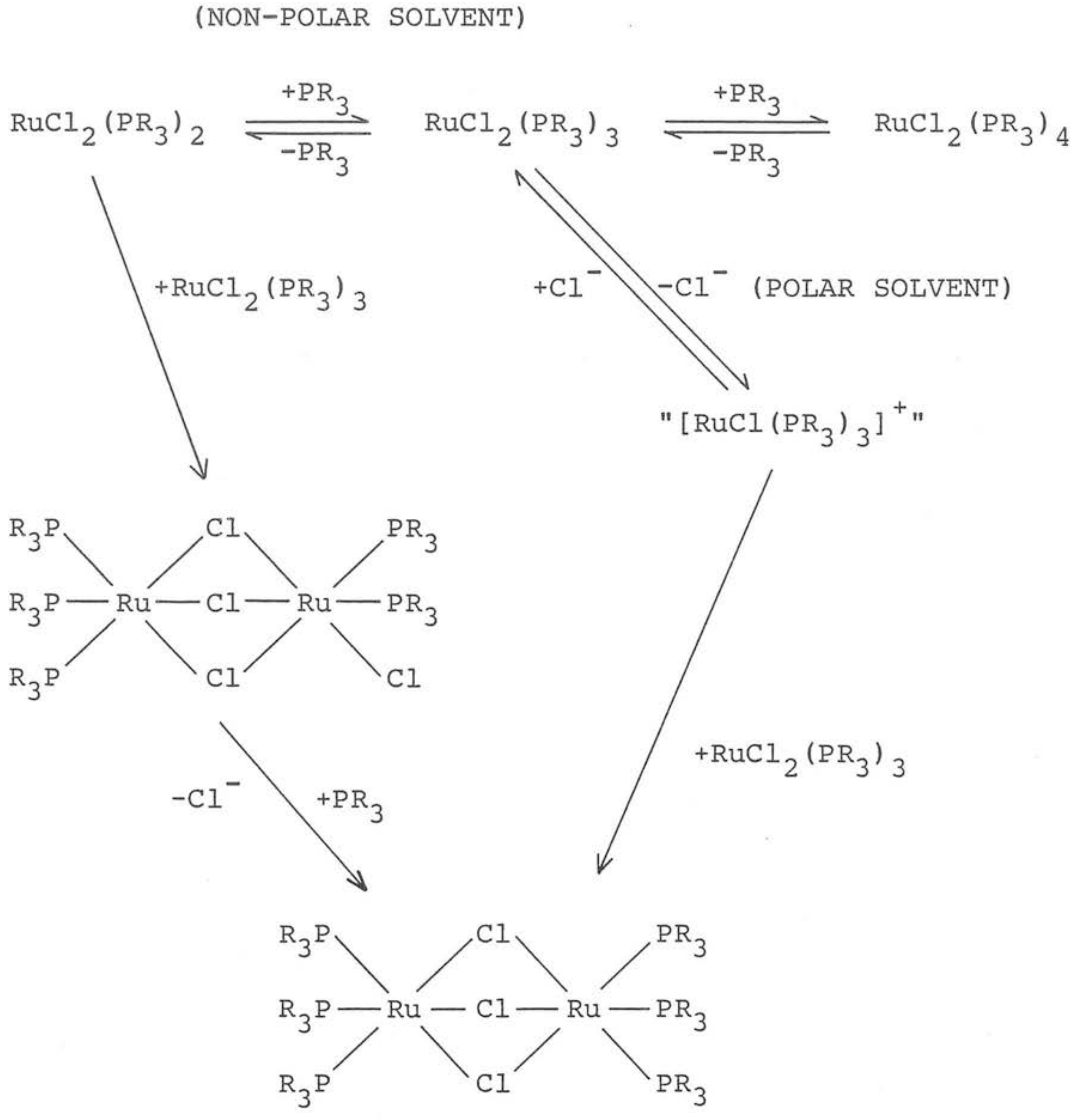


(13)

An alternative route to the latter, devised by Stephenson et al., is by reaction of $[RuCl_2(PPh_3)_3]$ with PR_3 in non-polar solvents such as hexane or petroleum ether. Monomeric $[RuCl_2(PR_3)_{3\ or\ 4}]$ are first produced and in solution these rearrange to $[Ru_2Cl_4(PR_3)_5]$ and/or $[Ru_2Cl_3(PR_3)_6]Cl$ depending on the nature of PR_3 and of the solvent (Scheme 1.1). High yields of $[Ru_2Cl_4(PR_3)_5]$ (R_3 = Et_2Ph, $EtPh_2$) can be prepared by this intermolecular coupling method[28].

A compound of empirical formula $[RuCl(PMe_3)_4]Cl$ was isolated by Wilkinson et al from trans-$[RuCl_2(PMe_3)_4]$ left in benzene for several weeks. However its $^{31}P-\{^1H\}$ n.m.r. spectrum which consists of an A_2X_2 pattern at ambient temperature strongly suggests the complex is the double chloro-

Scheme 1.1 - Transformations of $[RuCl_2(PR_3)_4]$ (PR_3 = tertiary phosphine)

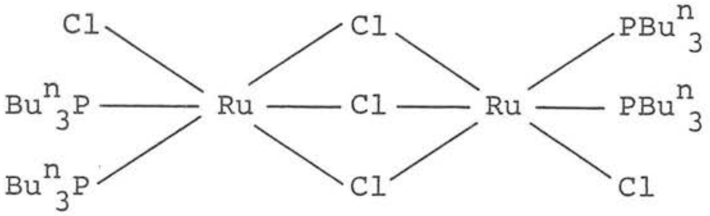


(N.B.: In solution vacant sixth coordination positions are probably occupied by solvent molecules).

bridged dication $[RuCl(PMe_3)_4]_2Cl_2$ [43].

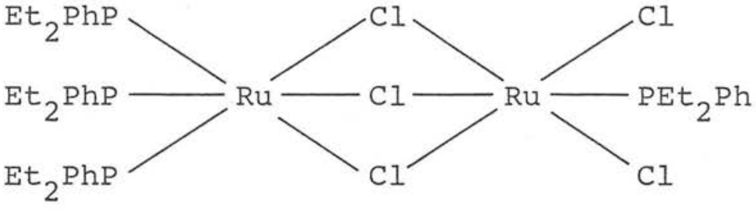
Ru_2(II,III)

In 1967, Nicholson reported the first formally mixed valence Ru_2(II,III) complexes $[Ru_2Cl_5(PR_3)_4]$ (R_3 = $Bu^n{}_3$, $(pent)^n{}_3$) which were synthesised by the prolonged interaction of excess PR_3 on "$RuCl_3.xH_2O$" in ethanol[63]. The "symmetric" structure (14) of these species was subsequently confirmed by X-ray analysis for the PBu^n, derivative[64].



(14)

However, Stephenson et al showed that the compound $[Ru_2Cl_5(PEt_2Ph)_4]$ displayed the asymmetrical structure (15).



(15)

Evidence for this formulation was obtained from e.s.r., magnetic and electrochemical studies and is supported by the single crystal X-ray structure determination of $[(PEt_2Ph)_3RuCl_3RuCl_2(PEt_2Ph)]$ (15)[65]. Since $[(PEt_2Ph)_3RuCl_3RuCl_2(PEt_2Ph)]$ was obtained by aerial oxidation of $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ in hydrochloric acid/ nitromethane, the exclusive formation of configuration (15) is indicative of selective oxidation of the "harder" $RuCl(PEt_2Ph)_2$ end of the Ru_2(II,II) binuclear compound, accompanied by substitution by further chloride.

Other mixed valence triple halo-bridged Ru_2(II,III) complexes such as $[Ru_2Cl_3(PEt_2Ph)_6]^{2+}$ and $[Ru_2Cl_4(PEt_2Ph)_5]^+$ can be generated electrochemically from stable Ru(II,II) or Ru_2(III,III) compounds and characterised by _in situ_ spectroscopic measurements. An examination of the intervalence charge transfer bands in the optical spectra of these complexes reveals that the degree of metal-metal interaction decreases as the molecular asymmetry increases. Bulk electrogeneration, followed by _in situ_ characterisation of Ru_2(II,II) anions such as $[(PEt_2Ph)Cl_2RuCl_3Ru(PEt_2Ph)_3]^-$ is also possible[39,66]

Ru_2(III,III)

Electrogeneration and _in situ_ spectroscopic characterisation of triply bridged binuclear Ru_2(III,III) cations such as $[Ru_2Cl_5(PEt_2Ph)_4]^+$, $[Ru_2Cl_4(PEt_2Ph)_5]^{2+}$ and $[Ru_2Cl_3(PEt_2Ph)_6]^{3+}$ has been accomplished but with very few exceptions these electrogenerated species readily decompose if the temperature rises above 260K and therefore no attempts were made to isolate them from solution[66].

1.4 Iridium

1.4.1 Mononuclear species

Most of the early investigations into iridium(III) halide complexes containing tertiary phosphines employed haloiridic acid $[IrX_6]^{2-}$ as the starting material. Being an iridium(IV) species it was necessary to carry out a reduction before the desired reaction could proceed. However, the use of iridium(III) trichloride, which has become commercially available in recent years, is more convenient since no reduction is required.

Chloroiridic acid was reduced to an iridium(III) chloro-complex with boiling ethanol in the presence of hydrochloric acid and then tertiary phosphine added. Chatt et al reported that when PEt_3 was added, prolonged boiling led to a mixture of three mononuclear compounds namely, mer- and fac-$[IrCl_3(PEt_3)_3]$ and also the anionic species $[IrCl_4(PEt_3)_2]^-$ isolated as its $[PHEt_3]^+$ salt[67].

The same authors found that the yellow mer-$[IrCl_3(PEt_3)_3]$ was best prepared in 2-methoxyethanol since this resulted in both a high yield and a much shorter reaction time. The compounds mer-$[IrCl_3(PR_3)_3]$ have been prepared with a wide variety of tertiary phosphines using this latter method (R_3 = Et_3, $Pr^n{}_3$, Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$, $Bu^n{}_2Ph$, $MePh_2$, $(p\text{-}MeC_6H_4)Et_2$, 2-phenylisophinodoline)[67,68,69].

In alcohols, the use of $[IrBr_6]^{2-}$ produces hydrido-species on treatment with phosphines although Jenkins and Shaw reported that mer-$[IrBr_3(PEt_2Ph)_3]$ could be prepared from $[IrBr_6]^{2-}$ in methylethylketone[68].

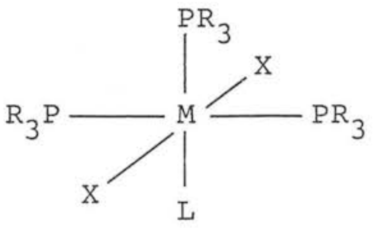
The related tri-iodo complexes mer-$[IrI_3(PR_3)_3]$ (R_3 = Et_3, Me_2Ph, Et_2Ph) are prepared from the trichloro-compound by prolonged treatment with NaI, again using a ketonic solvent to prevent the formation of iridium-hydride species[68].

The yellow compounds originally obtained by Chatt et al were assigned the meridional configuration (1) on the basis of dipole moment studies[67] and this was subsequently confirmed by several spectroscopic techniques such as i.r.[8,9,16,68] and Raman[9,16] spectroscopy. The positions of the iridium-chlorine stretching frequencies can be divided into three groups depending on the _trans_ ligand, 320-303 cm^{-1} (_trans_-chlorine), 278-262 cm^{-1} (_trans_-tertiary phosphine or -tertiary arsine) and 249-246 cm^{-1} (_trans_-hydrogen). The assignment of the iridium-chlorine stretching bands was confirmed by substitution of the chloride by another ligand. In cases where identification of iridium-chlorine stretches was inconclusive ^{1}H n.m.r. spectroscopy was often able to confirm the stereochemistry[8,18,19,70,71]. This was possible due to the"virtual coupling" phenomenon (see Section 1.2.2) but was restricted to complexes with methylphosphines. Since ^{31}P n.m.r. spectroscopy provides unequivocal stereochemical proof between the facial and meridional isomers for any phosphine complex, if sufficiently soluble, many of the iridium complexes have been examined by this spectroscopic technique[14,20,72].

The difference in lability of a halogen _trans_ to phosphine compared with _trans_ to another halogen was demonstrated by several reactions and has been exploited to generate some interesting mixed halogen species.

Thus, when _mer_-$[IrCl_3(PEt_2Ph)_3]$ was treated with a hot ethanolic solution of KOH (1 mol.), Jenkins and Shaw found that the chlorine atom _trans_ to the phosphorus was replaced by hydrogen to give the yellow hydrido-complex $[IrHCl_2(PEt_2Ph)_3]$. Configuration (3) (Y=H) was assigned on the basis of a low dipole moment and also on the ^{1}H n.m.r. pattern of the hydride ligand. On treating this yellow hydride with nitric acid in the presence of NaI, hydrogen was evolved and the monoiodo-species $[IrICl_2(PEt_2Ph)_3]$ (3) obtained. Similarly, the complexes $[IrYCl_2(PMe_2Ph)_3]$ (3), (Y=I or CN) were generated by treating the corresponding trichloro-complex with NaI (excess) or NaCN (1 mol.). The same authors were able to extend the series of compounds by the interaction of $[IrHBr_2(PEt_2Ph)_3]$ (3) with hydrochloric acid to yield the corresponding dibromochloro-compound $[IrClBr_2(PEt_2Ph)_3]$ (3)[68].

Shaw and Slade found that the chloride ligand *trans* to the phosphorus group was not sufficiently labile to be displaced by carbon monoxide or pyridine. However, they reported that if the chloride ligand in the *trans*-position to phosphorus in *mer*-$[IrCl_3(PMe_3Ph)_3]$ was first replaced by nitrate, then the nitrate ligand could be rapidly and completely displaced by a neutral ligand, L, to generate the cationic species $[IrLCl_2(PMe_2Ph)_3]^+$ (16, L=CO, py, NH_3, β-picoline, γ-picoline) while displacement with an anion gave the neutral compounds $[IrYCl_2(PMe_2Ph)_3]$ (3; $Y=N_3$, NO_2, OMe, Br, I, CN)[70].



(16)

The facial isomer of the complexes $[IrX_3(PR_3)_3]$ were generally prepared in low yield as by-products of the synthesis of the meridional forms. They were found to be less soluble and have a paler colour than their meridional counterpart.

On standing in solution it was noted that mer-$[IrCl_3(PR_3)_3]$ isomerised slowly to the facial form and from this observation a high yield synthesis of fac-$[IrX_3(PR_3)_3]$ (X=Cl, Br, I; $R_3=Me_3$, Et_3, $Bu^n{}_3$, $Pr^n{}_2Ph$, $Bu^n{}_2Ph$) by irradiation of the corresponding meridional compound in benzene solution was developed[11]. An investigation by Shaw et al indicated that neither the nature of the solvent (benzene, chloroform, acetone) or the concentration of the iridium complex had a significant effect on the rate of isomerisation and the detailed mechanism by which this change occurs is unclear.

These authors also found that the chloride ligands of fac-$[IrCl_3(PEt_3)_3]$ were replaced in stepwise fashion by iodide by treatment with one or two equivalents or an excess of sodium iodide[73].

As with the analagous rhodium system previously discussed (see Section 1.2.1) mononuclear iridium(III) anionic and cationic species have been isolated.

Goggin and Knight prepared the cations $[IrX_2(PMe_3)_4]^+$ (X=Cl, Br) by treating mer-$[IrX_3(PMe_3)_3]$ with one equivalent of $[Ag(PMe_3).NO_3]$ in dichloromethane[16], and their i.r.[16] and ^1H n.m.r.[19] spectra indicate a trans configuration (5).

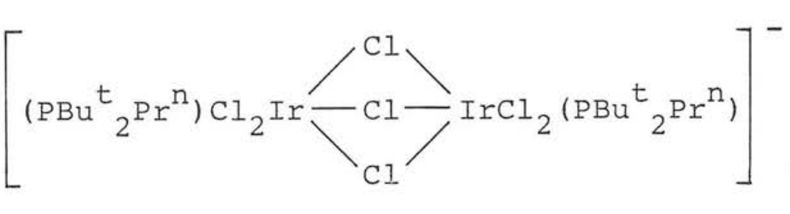
The iridium(III) anions $[IrCl_4(PR_3)_2]^-$ ($R_3=Me_3$[16], Et_3, Et_2Ph [67], Me_2Ph [68]) were originally isolated as by-products of the preparation of the meridional complexes $[IrCl_3(PR_3)_3]$ from chloroiridic acid. However, Chatt et al successfully prepared the compound $[PPr^n{}_3H][IrCl_4(PPr^n{}_3)_2]$ from $IrCl_3.3H_2O$ with concentrated HCl and $PPr^n{}_3$ (4 mol.) in ethanol[9]. These complexes were also assigned a trans configuration (4) on the basis of their i.r. [9,16,68] and Raman[9,10] spectra.

1.4.2 Binuclear species

Binuclear iridium complexes which contain hydride and/or carbonyl ligands are numerous and well characterised. However, examples of binuclear compounds containing only tertiary phosphine and halide ligands are extremely rare.

The chloro-bridged complex $[Ir_2Cl_6(PEt_3)_4]$ was prepared by Chatt *et al* from the reaction of chloroiridic acid with 2-methoxyethanol followed by addition of PEt_3 (2 mol.) and heating under reflux for 50 minutes. The molecular weight, measured ebullioscopically in chloroform, and the formation of a non-conducting solution in nitromethane, favour the binuclear bridged structure for this complex. Unfortunately the compound was too insoluble in non-polar solvents such as benzene for its dipole moment to be determined[67].

On heating a solution of chloroiridic acid in *iso*-propanol for a few minutes it becomes green corresponding to reduction of Ir(IV) to Ir(III). Shaw *et al* reported that treatment of this solution with 2-3 molar equivalents of $PBu^t_2Pr^n$ followed by refluxing for 17 hours gave orange crystals on cooling. The product was formulated as $[PBu^t_2Pr^nH][Ir_2Cl_7(PBu^t_2Pr^n)_2]$ (17) on the basis of conductivity, i.r., ^1H n.m.r. and ^{31}P n.m.r. evidence[74].

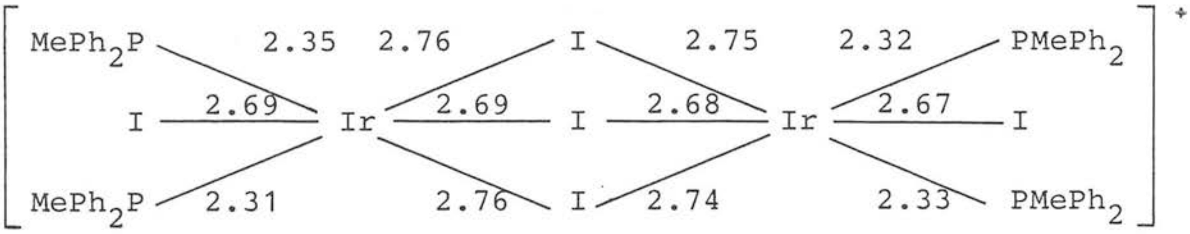


(17)

During studies on oxidative addition reactions of the cations $[IrL_4]^+$ (L = neutral donor ligand) with the halogens

X_2 (X=Cl, Br, I), Nolte et al[75] found that when L =$P(OMe)Ph_2$ and $PMePh_2$, the addition reactions were usually accompanied by the loss of one or two molecules of L from the coordination sphere. This ligand loss was enhanced on going from Cl to Br to I and only with I_2 were complexes of stoichiometry $[IrI_4L_2]$ (L=$P(OMe)Ph_2$, $PMePh_2$) isolated. An X-ray structural determination of the compound of stoichiometry $[IrI_4(PMePh_2)_2]$ was undertaken and revealed the product to be the salt $[Ir_2I_5(PMePh_2)_4]I_3$. The triple iodo-bridged cation was shown to have the "symmetrical" configuration (18), (Fig.1.3).

Fig.1.3 - X-ray crystal structure of $[(PMePh_2)_2IIrI_3IrI(PMePh_2)_2]I_3$ (bond lengths ±0.01Å)



(18)

Table 1.1 - Typical observed values for ${}^{1}J_{Rh-P}$ coupling constants

Type of Complex	Oxidation State	Coupling Constant (Hz) P *trans* to X	 P *trans* to P
$RhX(PR_3)_3$	Rh(I)	180-190	140-150
$RhX_3(PR_3)_3$	Rh(III)	110-120	80-90

Chapter 2

Synthesis and Interconversion Reactions of Some Rhodium(III) Chloride Tertiary Phosphine Complexes

2.1 Introduction

Rhodium(III) halide tertiary phosphine compounds were first isolated some 20 years ago. Since then both the spectroscopic and chemical properties of the various monomeric rhodium(III) species have been extensively investigated (see Section 1.2.1).

However, the binuclear rhodium(III) complexes $[Rh_2Cl_6(PR_3)_n]$ (n=3,4) have not received much attention and, as a result, little is known about either their mode of formation or possible interconversion reactions [c.f. studies on related chloro-bridged diruthenium(II) species (see Section 1.3.2)].

This chapter describes our reinvestigation of the preparation of these materials and the use, in particular, of variable temperature $^{31}P-\{^1H\}$ n.m.r. spectroscopy to examine both the isolated products and the species present in the mother liquor.

2.2 A reinvestigation of previous reactions

The preparation of the complexes mer-$[RhCl_3(PR_3)_3]^5$ was successfully repeated by means of the reaction of $RhCl_3.3H_2O$ with PR_3 1:3.5 molar ratio; $R_3=Me_2Ph$, Et_2Ph, $Pr^n{}_2Ph$, $EtPh_2$), in refluxing ethanol. The orange products which were obtained in high yield gave good $^{31}P-\{^1H\}$ n.m.r. spectra (see Table 2.1).

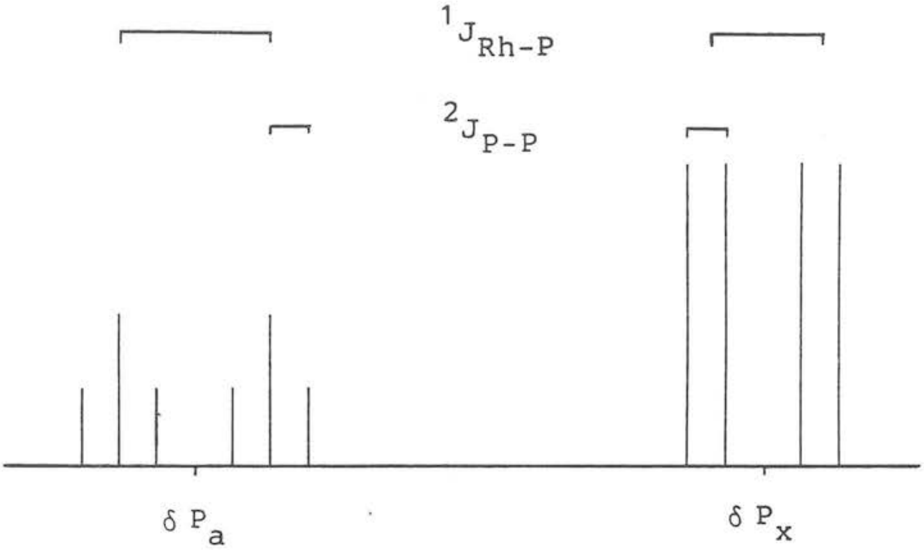
The use of this technique to aid structural assignment is well illustrated by considering the $^{31}P-\{^1H\}$ n.m.r. spectrum of the meridional isomer. There are two types of phosphorus atom in the meridional compound: a pair which are mutually trans and one which is trans to a chlorine. The simple spectrum (ignoring $^2J_{P-P}$ coupling) should show a pair of doublets with an intensity ratio of 2:1. The doublet of intensity 2, representing the mutually trans phosphorus atoms, should have a $^1J_{Rh-P}$ coupling constant of 80-90Hz while the less intense doublet would be expected to have a $^1J_{Rh-P}$ coupling constant of 110-120Hz, since the phosphorus concerned is trans to chlorine. If the cis ^{31}P-^{31}P couplings are then considered, each line of the stronger resonance should be split into a doublet by the single phosphorus atom while its resonance should be split into a triplet by the equivalent pair of phosphorus atoms (Fig.2.1).

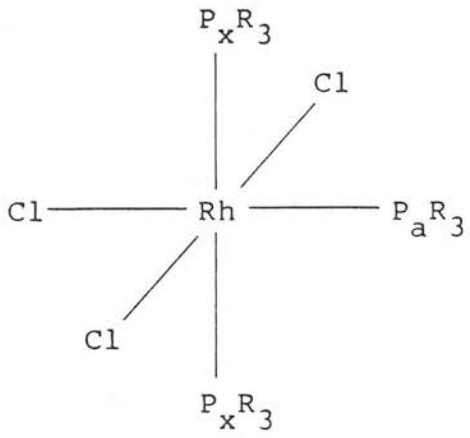
The binuclear triple chloro-bridged complex $[Rh_2Cl_6(PEt_2Ph)_3]$ was obtained in high yield by the method reported by Chatt et al.[5] which involved refluxing an ethanolic solution of $RhCl_3.3H_2O$ and PEt_2Ph (1:1.5 molar ratio). This compound, which was isolated as a brown powder, showed the expected ^{31}P-$\{^1H\}$ n.m.r. spectrum containing two doublets, centred at δ=49.2 ($^1J_{Rh-P}$=114.8Hz) and δ=37.5 p.p.m. ($^1J_{Rh-P}$=117.2Hz), of intensity ratio 1:2 which is consistent with configuration (7)[21,22]

Treatment of the mother liquor from this reaction with $Na[BPh_4]$ then gave a small amount of the new cationic complex $[(PEt_2Ph)_2ClRhCl_3RhCl(PEt_2Ph)_2]BPh_4$ (see Section 2.4 for a detailed discussion of this species).

However, our attempts to isolate the double chloro-bridged species $[Rh_2Cl_6(PR_3)_4]$ (R_3=Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$, $EtPh_2$) by the variety of routes discussed in Section 1.2.3 have proved fruitless. In our hands the reaction of $RhCl_3.3H_2O$ with

Fig.2.1 - The expected $^{31}P-\{^{1}H\}$ n.m.r. spectrum of mer-$[RhCl_3(PR_3)_3]$



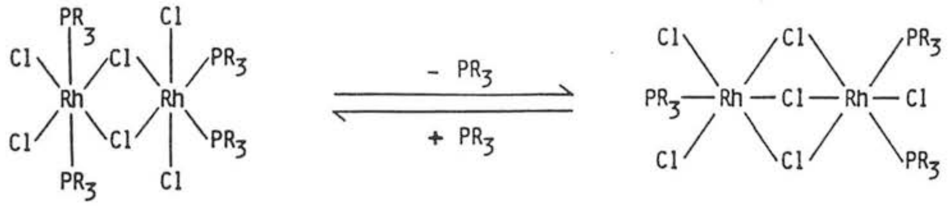


PEt_2Ph (1:2 molar ratio) in refluxing aqueous ethanol gave a precipitate of $[Rh_2Cl_6(PEt_2Ph)_3]$, with the complex $[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$ being obtained from the subsequent mother liquor on treatment with $Na[BPh_4]$. Similarly the interaction of $RhCl_3.3H_2O$ with mer-$[RhCl_3(PR_3)_3]$ (1:2 molar ratio), also in refluxing aqueous ethanol, yielded $[Rh_2Cl_6(PR_3)_3]$ (R_3=Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$, $EtPh_2$) and $[Rh_2Cl_5(PR_3)_4]BPh_4$ (R_3=Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$). The slow crystallisation from solutions of mer-$[RhCl_3(PR_3)_3]$ (R_3=Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) exposed to air also proved unsuccessful with the meridional complex being recovered.

Therefore, an in situ generation of the elusive double bridged complex was attempted at low temperature using $^{31}P-\{^1H\}$ n.m.r. spectroscopy to monitor the progress of the reaction. The triple bridged compound $[Rh_2Cl_6(PEt_2Ph)_3]$ was dissolved in $CDCl_3$, the solution cooled to 223K and treated with PEt_2Ph (1:4-5 molar ratio). The $^{31}P-\{^1H\}$ n.m.r. signal due to the triple bridged species disappeared and two new doublets were observed. These new doublets, of equal intensity, with centres at δ=34.3 p.p.m. ($^1J_{Rh-P}$=114.8Hz) and δ=8.7 p.p.m. ($^1J_{Rh-P}$=80.6Hz) indicated the compound contains two different pairs of tertiary phosphine, one pair trans to chlorine ($^1J_{Rh-P}$=114.8Hz) with the other pair being mutually trans ($^1J_{Rh-P}$=80.6Hz). This spectrum is consistent with the generation of the double chloro-bridged complex $[(PEt_2Ph)_2Cl_2Rh(\mu-Cl)_2RhCl_2(PEt_2Ph)_2]$ with configuration (8) (cf the crystal structure determination of $[Rh_2Cl_6(PBu^n{}_3)_4]$[23]). In the presence of an excess of PEt_2Ph this complex is then replaced by mer-$[RhCl_3(PEt_2Ph)_3]$ presumably as a result of facile bridge cleavage. Finally, at ambient temperature, in the presence of an excess of PEt_2Ph, only the meridional compound was observed (Fig.2.2).

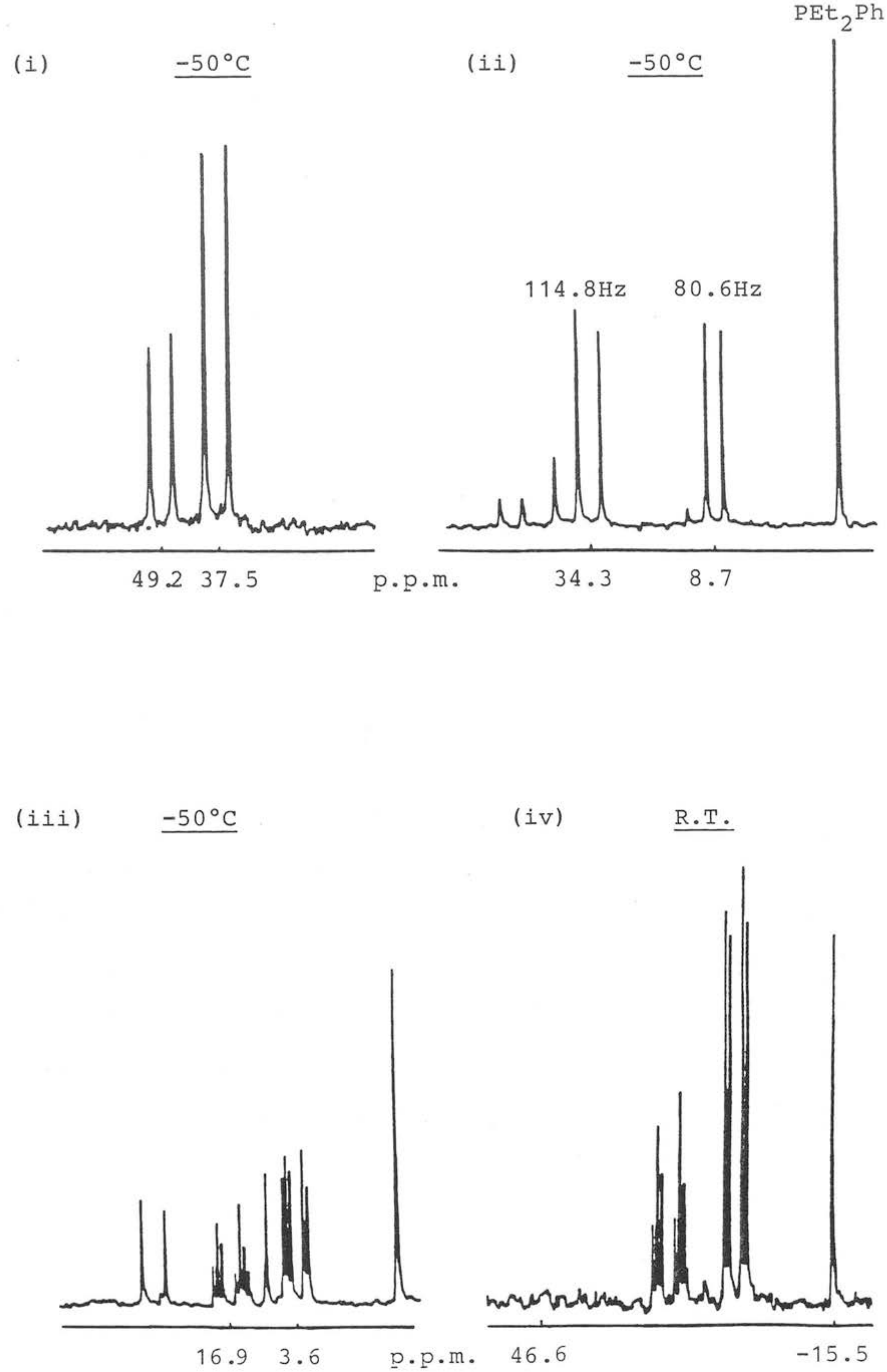
Having established spectral evidence for the formation of the complex $[Rh_2Cl_6(PEt_2Ph)_4]$ an attempt to isolate the species was made by treatment of a chloroform solution of $[Rh_2Cl_6(PEt_2Ph)_3]$ with one molar equivalent of PEt_2Ph at ambient temperature. However the resulting yellow powder obtained after reduction of volume and work-up with petroleum ether (b.p. 40-60°C) contained only unreacted starting material and the meridional complex. The product obtained from the repetition of this reaction in the more polar solvent ethanol was shown to contain a mixture of $[Rh_2Cl_6(PEt_2Ph)_3]$, mer-$[RhCl_3(PEt_2Ph)_3]$ and $[Rh_2Cl_5(PEt_2Ph)_4]Cl$.

Therefore it must be concluded that although the double bridged complex $[Rh_2Cl_6(PEt_2Ph)_4]$ can be generated, ($^{31}P-\{^1H\}$ n.m.r. evidence), it is not isolable with this particular phosphine. In non-polar media the double bridged species prefers to eliminate one molecule of PEt_2Ph and thereby regenerate the triple bridged $[Rh_2Cl_6(PEt_2Ph)_3]$ (Eqn.[5]), while the presence of an excess of phosphine results in complete bridge cleavage to give mer-$[RhCl_3(PEt_2Ph)_3]$.

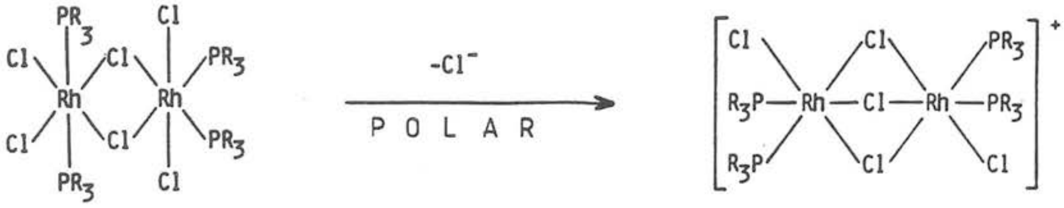


$PR_3 = PEt_2Ph$ ...... [5]

Fig.2.2 - The $^{31}P-\{^{1}H\}$ n.m.r. spectra of the reaction of $[Rh_2Cl_6(PEt_2Ph)_3]$ with PEt_2Ph



Alternatively, in more polar media, the double bridged compound eliminates a chloride ion to form the cation $[Rh_2Cl_5(PEt_2Ph)_4]^+$ (see Eqn.[6], Scheme 2.1 and Section 2.6 for a more detailed discussion).

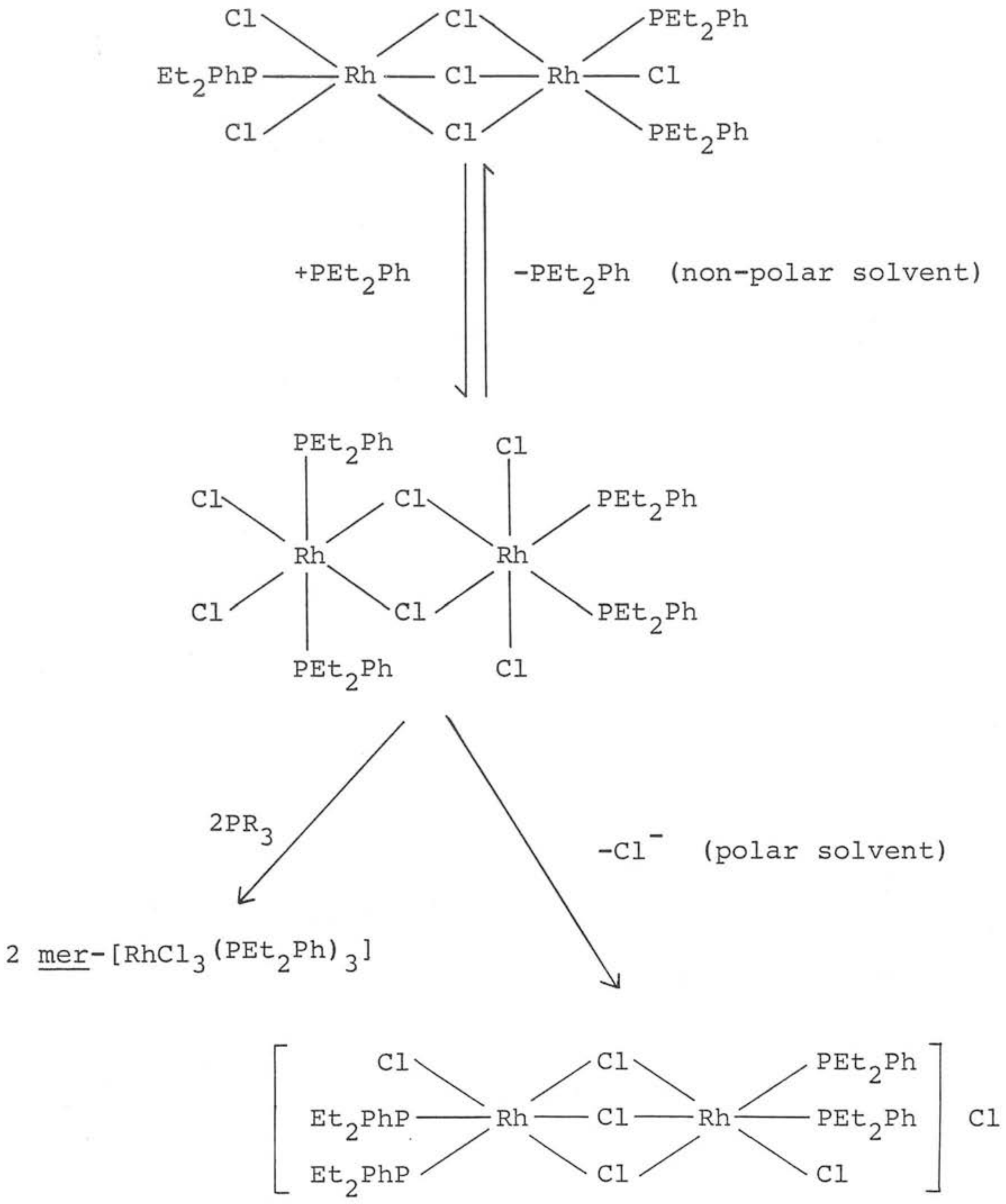


PR_3 = PEt_2Ph ...... [6]

Presumably the formation of the more stable triple chloro-bridge is the main driving force for these facile rearrangement reactions.

The majority of the reactions discussed in this Section so far have led to the isolation of more than one species. The type and yield of the complexes obtained from any particular reaction appeared to be independent of the starting materials and route involved. However, the products obtained did seem to be closely related to the overall rhodium:phosphine ratio for the reaction in question. Hence a study of the reaction between various ratios of $RhCl_3.3H_2O$ and PEt_2Ph in hot ethanol was undertaken, (Table 2.2), and this indicates that at 1:4 molar ratios, only <u>mer</u>-$[RhCl_3(PEt_2Ph)_3]$ is isolated. However, at 1:3 molar ratios the <u>mer</u>-monomer is precipitated with $[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$ being obtained from the mother

Scheme 2.1 - Possible routes of formation and interconversion of $[Rh_2Cl_6(PEt_2Ph)_4]$



liquor on treatment with Na[BPh$_4$]. At 1:2 molar ratios some [Rh$_2$Cl$_6$(PEt$_2$Ph)$_3$] is precipitated with the cationic [Rh$_2$Cl$_5$(PEt$_2$Ph)$_4$]$^+$ being once again trapped out with [BPh$_4$]$^-$. This study shows that the ratio of rhodium:phosphine in the compounds generated closely matches the experimental quantities which were employed. It should also be noted that the double bridged [Rh$_2$Cl$_6$(PEt$_2$Ph)$_4$] was not successfully isolated from these reactions.

2.3 An alternative high yield route to [Rh$_2$Cl$_6$(PR$_3$)$_3$] complexes and their variable temperature ^{31}P-{^{1}H} n.m.r. spectra

i) Alternative routes

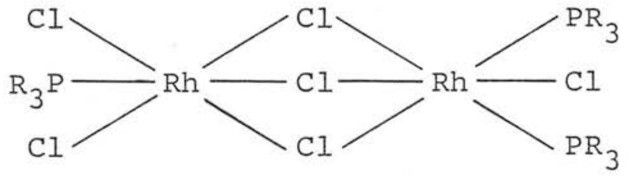
Chatt et al first reported the synthesis of the compound [Rh$_2$Cl$_6$(PEt$_3$)$_3$] by the reaction of RhCl$_3$.3H$_2$O with PEt$_3$ (2:3 molar ratio)[5]. Our study of the products isolated from the reaction of RhCl$_3$.3H$_2$O with various ratios of PEt$_2$Ph shows that the PEt$_2$Ph analogue was obtained in highest yield when a 2:3 molar ratio of rhodium:phosphine was used. This is not unexpected since the molecule itself has a rhodium:phosphine ratio of 2:3 and we have observed the occurrence of bridge cleavage in the presence of additional phosphine. Thus treatment of [Rh$_2$Cl$_6$(PEt$_2$Ph)$_3$] with PEt$_2$Ph gave mixtures of mer-[RhCl$_3$(PEt$_2$Ph)$_3$], [Rh$_2$Cl$_6$(PEt$_2$Ph)$_3$] and [Rh$_2$Cl$_5$(PEt$_2$Ph)$_4$]Cl, depending upon the polarity of the solvent used, whereas, in the presence of an excess of PEt$_2$Ph, only the meridional complex was obtained via the double chloro-bridged intermediate [Rh$_2$Cl$_6$(PEt$_2$Ph)$_4$] (see Section 2.2 for ^{31}P-{^{1}H} n.m.r. evidence).

In the previous section, it was noted that in the majority of the reactions discussed, e.g. the interaction of $RhCl_3.3H_2O$ with $\underline{mer}\text{-}[RhCl_3(PEt_2Ph)_3]$ (1:2 molar ratio) or PEt_2Ph (various ratios), it was the rhodium:phosphine ratio of the starting materials, rather than the nature of the reagents themselves, which appeared to govern the composition of the final products.

Thus we have found that another high yield route to the complexes $[Rh_2Cl_6(PR_3)_3]$ (R_3=Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$, $EtPh_2$) is by the reaction of equimolar quantities of $RhCl_3.3H_2O$ and $\underline{mer}\text{-}[RhCl_3(PR_3)_3]$ (giving a rhodium:phosphine ratio of 2:3) in refluxing ethanol. Treatment of the mother liquor with $Na[BPh_4]$ then gave small amounts of the cationic complex $[Rh_2Cl_5(PR_3)_4]BPh_4$ (R_3=Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) (Eqn.[7]).

$$RhCl_3.3H_2O + \underline{mer}\text{-}[RhCl_3(PR_3)_3] \xrightarrow[\substack{EtOH \\ \Delta}]{1:1m.r.} [Rh_2Cl_6(PR_3)_3] + [Rh_2Cl_5(PR_3)_4]BPh_4 \qquad ......\ [7]$$

The $^{31}P\{^1H\}$n.m.r. spectra of the complexes $[Rh_2Cl_6(PR_3)_3]$ obtained by this route have shown them to have the same structure (7) that was observed from the direct reaction between $RhCl_3.3H_2O$ and phosphine (2:3 molar ratio).



(7)

In this configuration the phosphines, two on one rhodium and one on the other, are arranged such that all three bridging chlorines are trans to only one phosphine ligand. Since the starting materials used in our new route were $RhCl_3.3H_2O$ and the meridional complex, it is interesting to note that transfer of a phosphine group from one rhodium to the other has occurred during the formation of these triple chloro-bridged species. One possible mechanism of formation could involve initial combination of $RhCl_3.3H_2O$ and mer-$[RhCl_3(PR_3)_3]$, with elimination of water molecules, to generate some form of chloro-bridged intermediate. Intermolecular transfer of PR_3 could then be followed by the completion of the triple chloro-bridge. However, this mechanism is unable to account for the presence in solution of either the solvated monomer mer-$[RhCl_3(PR_3)_2(H_2O)]$ or the cation $[Rh_2Cl_5(PR_3)_4]^+$ (see Section 2.5 for $^{31}P-\{^1H\}$ n.m.r. evidence). The high yield of $[Rh_2Cl_6(PR_3)_3]$ as a single isomer from the various reactions, together with the observation of the solvated monomer strongly suggests that, as in the analogous ruthenium system[76], intermolecular coupling of species such as mer-$[RhCl_3(PR_3)_2(H_2O)]$ and $[RhCl_3(PR_3)(H_2O)_2]$ is involved in its formation.

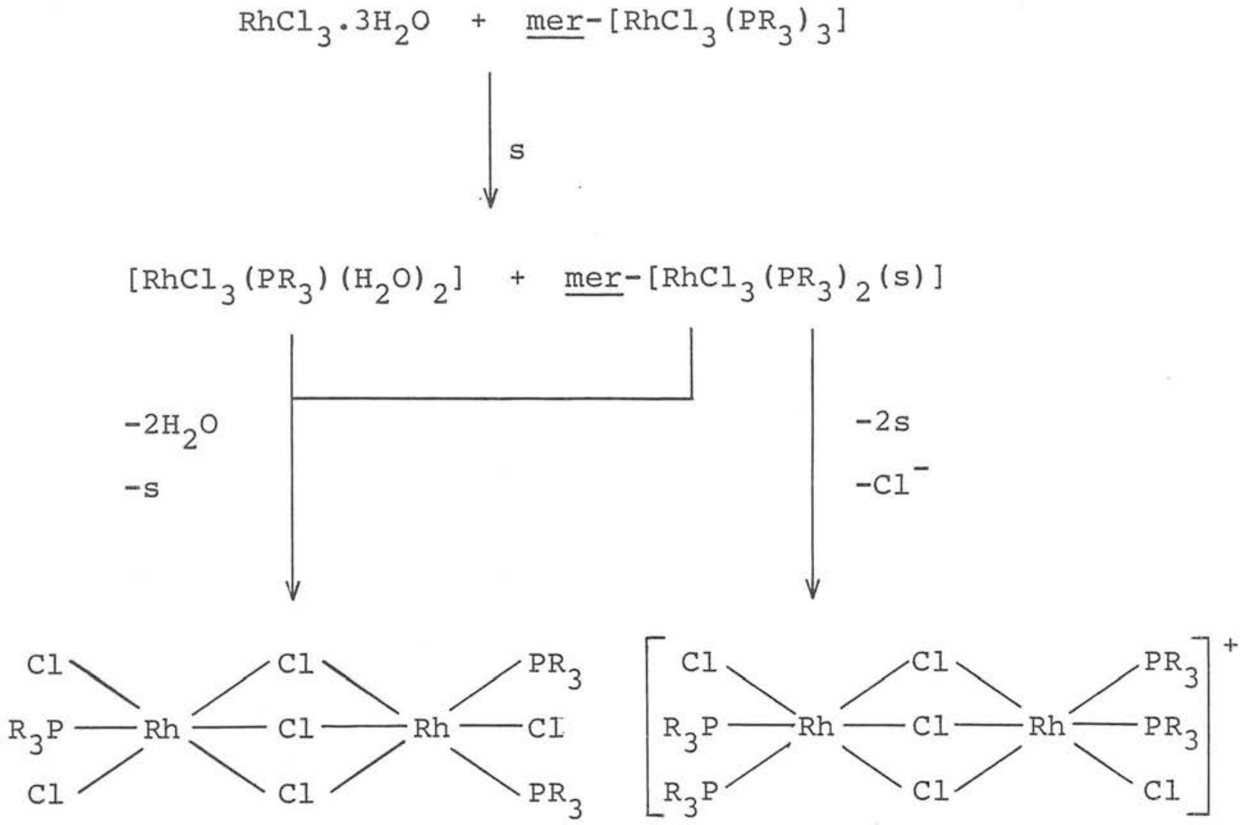
Since there is no evidence for the dissociation of phosphine from the meridional complexes on the n.m.r. time-scale, it appears that the presence of $RhCl_3.3H_2O$ is essential for the formation of the solvated monomer in this reaction. Therefore we propose that in solution $RhCl_3.3H_2O$ abstracts a phosphine ligand from the meridional complex thereby generating the solvated monomers $[RhCl_3(PR_3)(H_2O)_2]$ and mer-[$RhCl_3(PR_3)_2(s)$] (s = solvent molecule). The neutral triple chloro-bridged [$Rh_2Cl_6(PR_3)_3$] is then readily generated by the intermolecular coupling of these two solvated monomers (Scheme 2.2). The formation of the cation $[Rh_2Cl_5(PR_3)_4]^+$, which is isolated in low yield as its $[BPh_4]^-$ salt,can also be explained by the presence of the solvated monomer [$RhCl_3(PR_3)_2(s)$]. Dimerisation of this species, which again would involve elimination of solvent, followed by completion of the triple chloro-bridge and elimination of a chloride ion would result in the formation of the cation $[Rh_2Cl_5(PR_3)_4]^+$ (see Section 2.6 for detailed discussion).

ii) Variable temperature $^{31}P-\{^1H\}$ n.m.r. spectral studies

In dilute $CDCl_3$ solution, the $^{31}P-\{^1H\}$ n.m.r. spectrum of the complexes [$Rh_2Cl_6(PR_3)_3$] (R_3=Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) at 223K is the same as that observed at ambient temperature; i.e. two doublets of intensity ratio 1:2 with $^1J_{Rh-P}$ coupling constants consistent with the phosphines being trans to chloride (Fig.2.2).

However, unlike [$Rh_2Cl_6(PMe_2Ph)_3$], the complexes [$Rh_2Cl_6(PEt_2Ph)_3$] and [$Rh_2Cl_6(PPr^n{}_2Ph)_3$] are sufficiently soluble, due to their longer alkyl chains, to give extremely concentrated $CDCl_3$solutions. Examination of these concentrated solutions by $^{31}P-\{^1H\}$ n.m.r. spectroscopy shows the growth of another pattern, accompanied by a slight broadening of the original resonances, as the temperature is lowered [Fig.2.3(i)-(iii)]. This new pattern also contains two doublets of intensity ratio 1:2 with $^1J_{Rh-P}$ coupling constants consistent with phosphine trans to chloride only. If the solution under examination is suitably concentrated the species

Scheme 2.2 - Possible mechanism of formation of $[Rh_2Cl_6(PR_3)_3]$



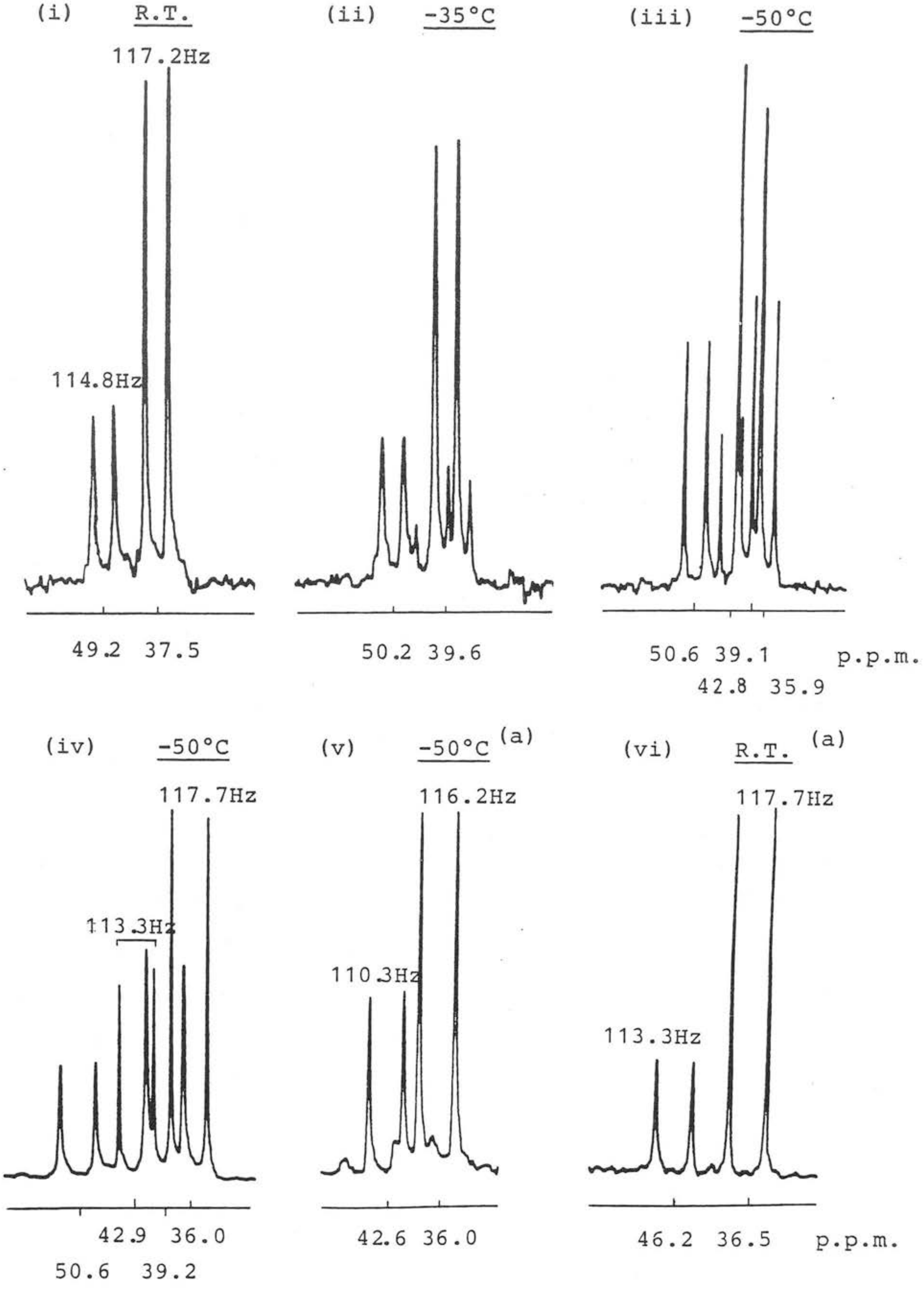
represented by this new pattern can become the dominant one [Fig.2.3(iv)].

This behaviour, which is dependent upon both concentration and temperature, is readily reversible. The concentration dependence suggests that this is an intermolecular interaction, thus ruling out a simple intramolecular triple to double chloro-bridge interconversion. There is no evidence for phosphine dissociation since rhodium-phosphorus coupling is retained and no free phosphine signal is observed. However, addition of chloride ion in the form of either $[AsPh_4]Cl$ or LiCl results in a reduction in intensity of the unknown species. This could indicate that either its formation involves the loss of chloride ion or that the unknown species exists in equilibrium with $[Rh_2Cl_6(PR_3)_3]$, the position of which is altered by the addition of Cl^- to the system. Alternatively it may be that the species contains weak linkages which are readily cleaved in the presence of an excess of chloride ion. Interestingly addition of methanol or ethanol to the $CDCl_3$ solution results in a spectacular effect with the signal representing $[Rh_2Cl_6(PR_3)_3]$ being virtually lost [Fig.2.3(v)]. Unfortunately we were unable to determine whether the function of these solvents is merely to increase the polarity of the solution, thereby facilitating chloride loss, or whether the solvent becomes coordinated, since the low temperature ^1H n.m.r. spectra obtained were extremely broad and ill-defined.

On rewarming to room temperature, coalescence is observed in the $^{31}P-\{^1H\}$ n.m.r. spectra and at room temperature the original spectrum of $[Rh_2Cl_6(PR_3)_3]$ is regained although solvent shifted to higher frequency [Fig.2.3(vi)].

In conclusion the nature of the species formed in

Fig.2.3 - The variable temperature $^{31}P-\{^1H\}$ n.m.r. spectra of $[Rh_2Cl_6(PEt_2Ph)_3]$, (in $CDCl_3$)



a) EtOH added

concentrated $CDCl_3$ solution is still a mystery. We tentatively suggest that it could be some form of polymeric structure containing weak linkages, possibly single chloro-bridges, the formation of which might require the loss of chloride to create a vacant coordination site for the bridge to form. However, the role of the added alcohols may be the key to solving this mystery and further investigation is required to determine the role of the alcohol and whether or not chloride ion is lost.

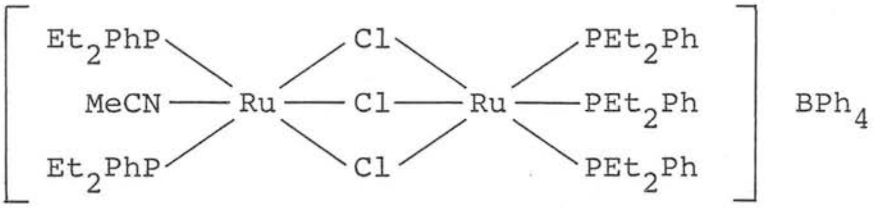
2.4 Synthesis and characterisation of $[Rh_2Cl_5(PR_3)_4]BPh_4$

It was noted in Section 2.2 that the new triple chloro-bridged cations $[(PR_3)_2ClRh(\mu\text{-}Cl)_3RhCl(PR_3)_2]^+$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) could be isolated as their $[BPh_4]^-$ salts from the mother liquors obtained, after the filtration of precipitated <u>mer</u>-$[RhCl_3(PR_3)_3]$ or $[Rh_2Cl_6(PR_3)_3]$, from reactions with an overall rhodium:phosphine molar ratio of 1:1.5-3.5. Thus the cations were obtained from a variety of routes namely; the interaction of $RhCl_3.3H_2O$ with either PEt_2Ph (1:1.5-3.5 molar ratio) or 2 molar equivalents of <u>mer</u>-$[RhCl_3(PR_3)_3]$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) and finally from the attempted partial bridge cleavage of $[Rh_2Cl_6(PEt_2Ph)_3]$ using an equimolar amount of PEt_2Ph in a polar medium. Not surprisingly the compounds $[Rh_2Cl_5(PR_3)_4]BPh_4$ are isolated in highest yield from those reactions having a rhodium:phosphine ratio in the region 1:2-2.5.

The use of metal ions such as Ag^+, Na^+ and Tl^+ to provide a convenient method for the abstraction of coordinated chloride from transition metal complexes is becoming increasingly more widespread. In suitable solvents the abstracted chloride is generally precipitated in the form of the metal chloride salt which is then easily removed by filtration. This simple method readily lends itself to the replacement of bound chloride by many types of ligand, both neutral and anionic, and to the synthesis of a wide variety of species.

This method was employed by Stephenson et al who reported that extended treatment of an isomeric mixture of $[Ru_2Cl_4Y_2(PPh_3)_3]$ with equimolar quantities of $Na[BPh_4]$ and PPh_3, in polar solvents, gave the complex $[Ru_2Cl_3Y_2(PPh_3)_4]BPh_4$ (Y = CO, CS) with the elimination of chloride[77].

Subsequently, Lindsay prepared the highly conducting green compound $[Ru_2Cl_3(PEt_2Ph)_5(MeCN)]BPh_4$ (19) by prolonged shaking of a CH_2Cl_2 solution of $[Ru_2Cl_4(PEt_2Ph)_5]$ with MeCN and $Na[BPh_4]$ (1:1:1 molar ratio).

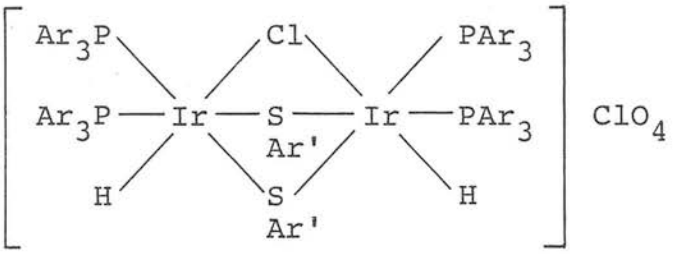


(19)

The mechanism of formation of (19) is not known; however, two possibilities include cleavage to monomers followed by recombination or direct substitution of the terminal chloride in the binuclear unit. The high yield of the reaction with no apparent side-products was interpreted to be indicative of the latter process[78].

Brown et al found that the reaction of $[IrCl(C_2H_4)_2(PPh_3)_2]$ with $Ag[BF_4]$ in ethylene-saturated CH_2Cl_2 gave the species $[Ir(C_2H_4)_3(PPh_3)_2]BF_4$ which, although isolable as a white needle-like crystal, could not be stored without slow decomposition occurring even at 243K under ethene[79].

The dimeric iridium(III) hydride complexes $[IrHCl(SAr')(PAr_3)_2]_2$ (Ar = $4\text{-}CH_3C_6H_4$ or C_6H_5, Ar' = $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$, $4\text{-}FC_6H_4$ or C_6H_5) were shown by Kelly and Senoff to react with $Ag[ClO_4]$ in refluxing acetone to form the complexes $[(PAr_3)_2HIr(SAr')_2ClIrH(PAr_3)_2]ClO_4.xMe_2CO$, (x = 0-3), (20).

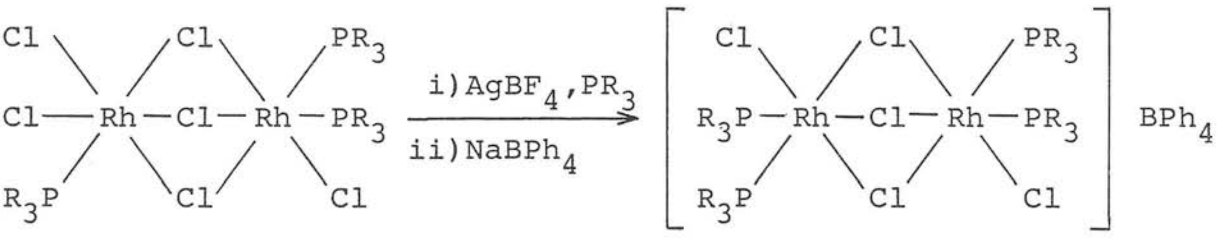


(20)

One of the iridium-chlorine bonds is cleaved by Ag^+ and the double arenethiolato-bridged cation formed then rearranges to form the more stable triple bridged complex, as confirmed by X-ray structural analysis[80].

Recently, Easton et al have described a simple, high yield method of incorporating ligands such as N_2, alkenes, alkynes etc into the terminal positions of $[L_{3-x}Cl_xRuCl_3RuCl_yL_{3-y}]$ by displacement of terminal chlorine using $M[BF_4]$ (M = Ag, Na or Tl). For example, reaction of $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ in CH_2Cl_2 with equimolar amounts of $Tl[BF_4]$ in the presence of an excess of L at ambient temperature and pressure, (L = N_2, C_2H_4, PhC≡CH, $MeO_2CC{\equiv}CCO_2Me$, MeCN, $MeNO_2$, PEt_2Ph), produces the cationic complexes $[(PEt_2Ph)_3RuCl_3RuL(PEt_2Ph)_2]BF_4$ in almost quantitative yield[81].

We have found that the cations $[Rh_2Cl_5(PR_3)_4]^+$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) can also be prepared in high yield by the reaction of $[Rh_2Cl_6(PR_3)_3]$ with equimolar quantities of $Ag[BF_4]$ and PR_3 in refluxing ethanol followed by addition of $[BPh_4]^-$ (Eqn.[8]). This formulation is confirmed by microanalyses, infrared studies [ν(RhCl), 357-310, 260-242 (bridge) cm^{-1}] and from conductance measurements in dichloromethane (see Experimental Section).



(21)

...... [8]

Note that treatment of $[Rh_2Cl_6(PEt_2Ph)_3]$ with PEt_2Ph alone gives mixtures of <u>mer</u>-$[RhCl_3(PEt_2Ph)_3]$, $[Rh_2Cl_6(PEt_2Ph)_3]$ and $[Rh_2Cl_5(PEt_2Ph)_4]Cl$ depending upon the polarity of the solvent used, whereas, in the presence of an excess of PEt_2Ph, only the meridional complex is obtained <u>via</u> $[Rh_2Cl_6(PEt_2Ph)_4]$ (see Section 2.2).

Configuration (21) indicates that, in these cations, the phosphorus atoms on a given rhodium atom should be magnetically inequivalent because they are eclipsed by a PR_3

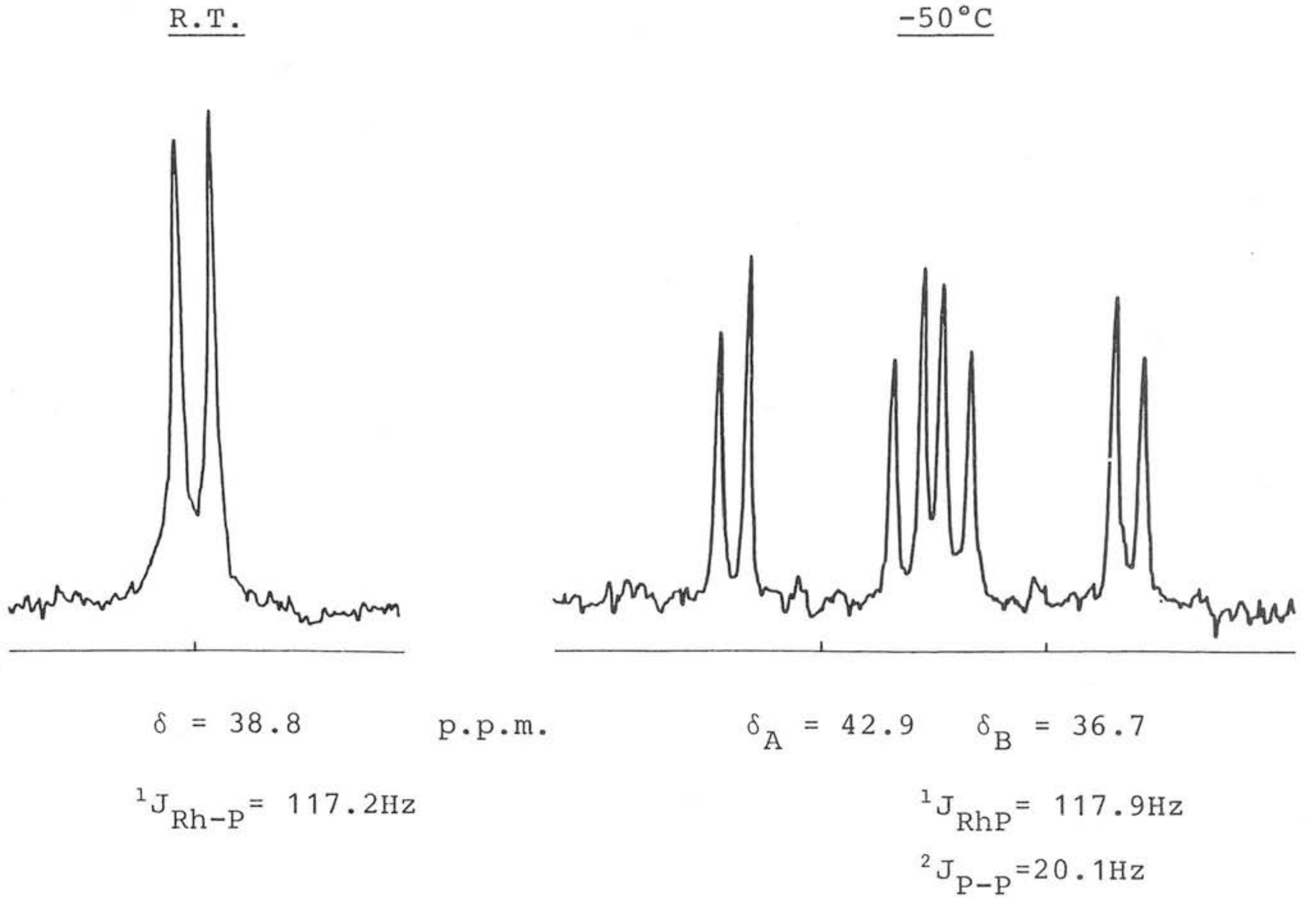
and Cl group respectively.

The $^{31}P-\{^1H\}$ n.m.r. spectra of these cations consist of a broad doublet at ambient temperature but on cooling to 223K the ABX pattern (Fig.2.4) expected for structure (21) is observed [e.g. for $PR_3 = PEt_2Ph$, $^{31}P-\{^1H\}$ n.m.r. in $CDCl_3$ at 298K $\delta = 38.8$ p.p.m., $^1J_{Rh-P} = 117.2Hz$ (broad doublet); at 223K, ABX, $\delta_A = 42.9$ p.p.m., $^1J_{Rh-P_A} = 117.9Hz$, $\delta_B = 36.7$ p.p.m., $^1J_{Rh-P_B} = 116.5Hz$, $^2J_{P_A-P_B} = 20.1Hz$ (see Table 2.1)]. These changes in spectra are concentration independent, reversible with temperature, and occur with retention of rhodium-phosphine coupling.

While this magnetic inequivalence accounts for the observed low temperature $^{31}P-\{^1H\}$ n.m.r. spectrum, an explanation is required for the spectrum at ambient temperature where the two phosphine ligands are magnetically equivalent. Since rhodium-phosphorus coupling is retained throughout, the equilibration process cannot involve the breaking and making of rhodium-phosphorus bonds.

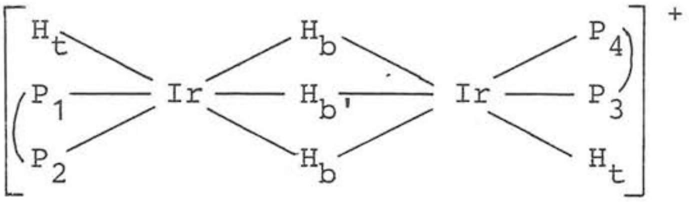
In configuration (21) one of the bridging chlorines is trans to two phosphine groups while the other bridging chlorines are trans to one phosphine and one terminal chlorine. Therefore it was initially considered that the observed fluxionality was due to rapid interconversion at ambient temperature between the triple and solvated double bridged species (see Scheme 2.3), resulting in the phosphine groups becoming magnetically equivalent. The partial bridge cleavage, required by this process, could be enhanced by one of the bridging chlorines being subject to the trans effect of two phosphine groups. At low temperature this process

Fig.2.4. Variable temperature $^{31}P-(^{1}H)$ n.m.r. spectra of $[Rh_2Cl_5(PEt_2Ph)_4]^{+}$ (a)



is slow and the groups remain magnetically inequivalent.

However similar variable temperature $^{31}P-\{^{1}H\}$ n.m.r. spectral behaviour are found for the $[Rh_2Cl_5\{(PPh_2O)_2H\}_2]^-$ anion[82] and the $[Ir_2H_5L_4]^+$ cations (L_2 = $2PPh_3$ [83], $Ph_2P(CH_2)_3PPh_2$ [84]). An examination of the iridium cation $[Ir_2H_5(Ph_2P(CH_2)_3PPh_2)_2]^+$, (22), using variable temperature ^{1}H n.m.r. spectroscopy revealed that although the bridging hydrides H_b and $H_{b'}$ were observed to undergo rapid interchange, bridge and terminal hydrides did not show any sign of exchange on the n.m.r. timescale.

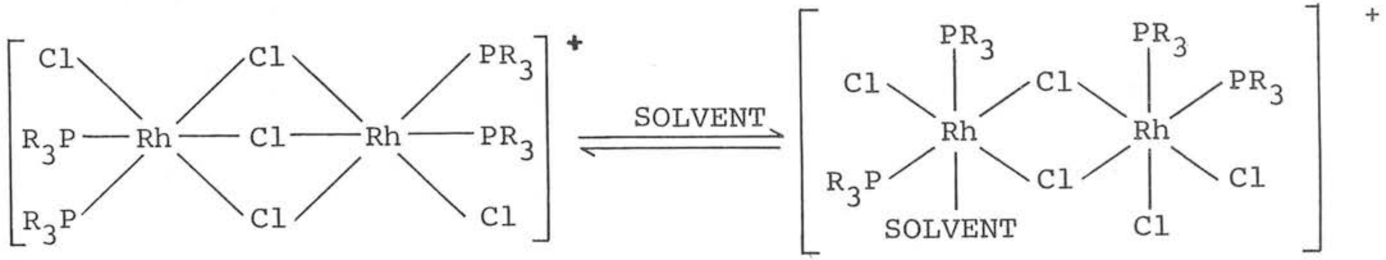


(22)

Rotation of one end of the molecule with respect to the other around the three-fold axis, rather than facile terminal/bridge ligand interchange <u>via</u> double and/or single bridged intermediates, is proposed to explain the temperature dependent n.m.r. spectra of these hydrides[84],

The insensitivity of the scrambling process in the cationic complexes $[Rh_2Cl_5(PR_3)_4]^+$ to change in solvent is consistent with a rotation rather than a cleavage pathway being responsible for the averaging of the phosphorus environments at ambient temperature.

Scheme 2.3 - Possible process to account for the magnetic equivalence of the phosphine groups in the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the cations $[Rh_2Cl_5(PR_3)_4]^+$ at ambient temperature



2.5 Isolation and characterisation of the solvated monomer mer-$[RhCl_3(PR_3)_2(H_2O)]$

The use of a capillary lock containing a deuterated solvent has enabled us to examine the $^{31}P-\{^1H\}$ n.m.r. spectra of non-deuterated reaction solutions. Studies of this type were conducted in the hope that we might observe the intermediates involved in the formation of the various complexes mer-$[RhCl_3(PR_3)_3]$, $[Rh_2Cl_6(PR_3)_3]$ and $[Rh_2Cl_5(PR_3)_4]^+$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$).

$^{31}P-\{^1H\}$ n.m.r. spectroscopy reveals that, after filtration of mer-$[RhCl_3(PR_3)_3]$ (or $[Rh_2Cl_6(PR_3)_3]$), the mother liquors of the various reactions from which the compounds $[Rh_2Cl_5(PR_3)_4]BPh_4$ were isolated, contain two major species. Both of these show broad doublets at ambient temperature and ABX patterns at low temperature (Fig.2.5) with the higher frequency pattern corresponding to the triple chloro-bridged cation $[Rh_2Cl_5(PR_3)_4]^+$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$).

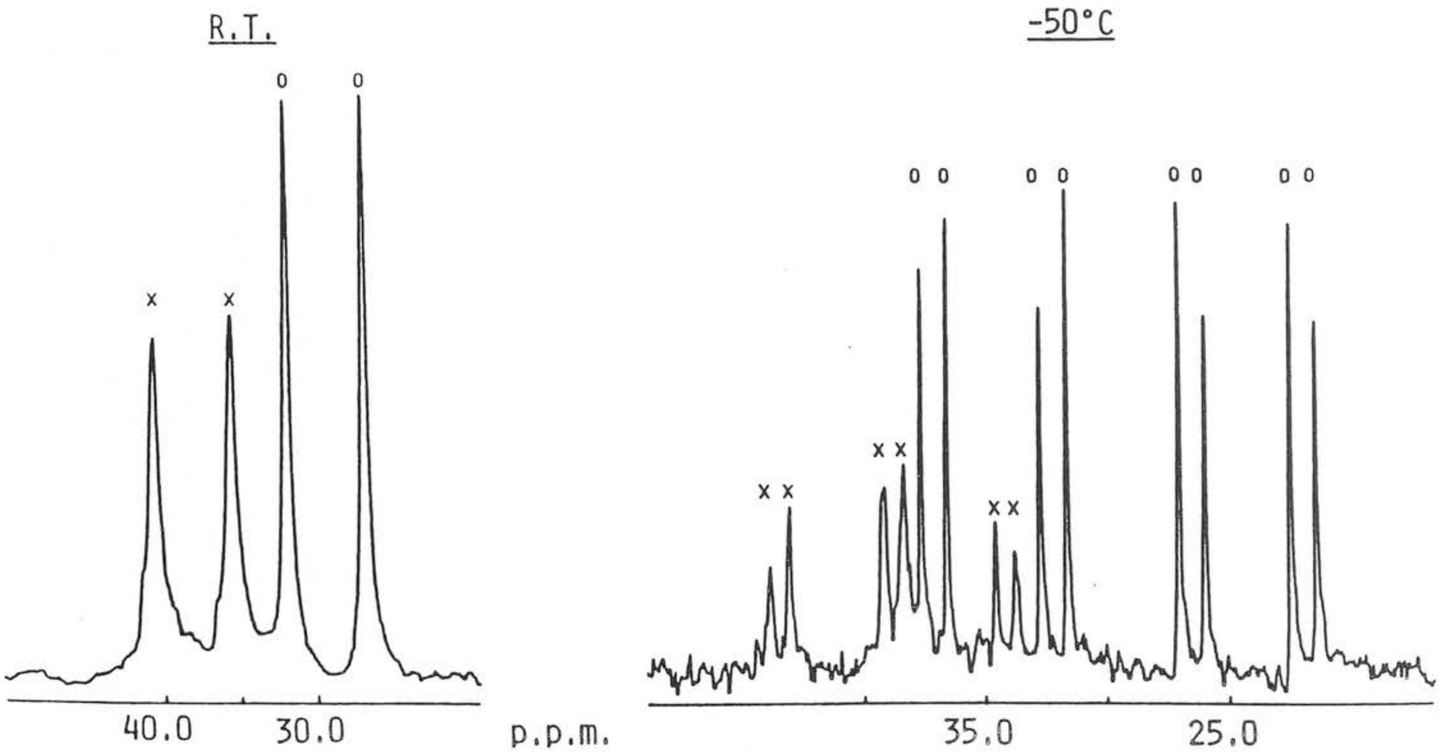
Initially, the other ABX pattern was thought to be due to another isomer of a neutral double chloro-bridged complex with the fluxionality also arising from rotation of one end of the molecule with respect to the other. These compounds were successfully isolated as yellow powders for PR_3 = PMe_2Ph, PEt_2Ph , (the $Pr^n{}_2Ph$ complex was found to be too soluble). However, the i.r. spectra of these powders indicate the presence of solvent [ν(OH), ca.1640 cm^{-1}]. Furthermore, an X-ray structural analysis (see section 2.5.2) of this species isolated as crystals from the mother liquor of the $RhCl_3.3H_2O$/mer-$[RhCl_3(PEt_2Ph)_3]$ (1:2 molar ratio) reaction in the absence of added $[BPh_4]^-$ shows it to be the

Fig.2.5. Variable temperature $^{31}P-\{^1H\}$ n.m.r. spectra of the mother liquor obtained from the various reactions:-

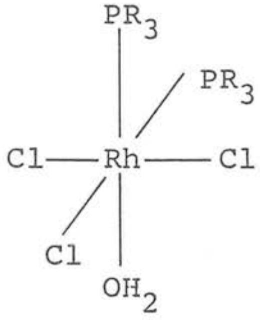
(a) $[Rh_2Cl_6(PR_3)_3]$ + $AgBF_4$ + PR_3 (1:1:1 m.r.)

(b) $RhCl_3.3H_2O$ + mer -$[RhCl_3(PR_3)_3]$ (1:1-2 m.r.)

(c) $RhCl_3.3H_2O$ + PR_3 (1:1.5-3.5 m.r.)



aquated monomer mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$ (23).



(23)

The presence of magnetically inequivalent PR_3 groups in (23) is responsible for the ABX at low temperature (eg for PR_3 = PEt_2Ph . $^{31}P-\{^1H\}$ n.m.r. in $CDCl_3$ at 298K δ = 32.1 p.p.m., $^1J_{Rh-P}$= 117.7Hz (broad doublet); at 223K, ABX δ_A = 36.4 p.p.m., $^1J_{Rh-P_A}$ = 120.6Hz, δ_B = 28.8 p.p.m. $^1J_{Rh-P_B}$ = 114.7Hz, $^2J_{P_A-P_B}$ = 25.0Hz). Facile dissociation of the water ligand on raising the temperature presumably generates a five coordinate intermediate in which rapid intramolecular exchange of PR_3 groups can occur [cf $[RuCl_2(PPh_3)_3]$ and related species (see section 1.3.1)].

Although the structure was not that of the long-sought-after double chloro-bridged complex, the aquated monomer is a useful species to have isolated since it is proposed to be involved in the formation of the triple chloro-bridged compounds $[Rh_2Cl_6(PR_3)_3]$ (see section 2.3) and $[Rh_2Cl_5(PR_3)_4]^+$ (see section 2.6). Furthermore, treatment of mer-$[RhCl_3(PR_3)_2(H_2O)]$ (R_3 = Me_2Ph, Et_2Ph) in $CDCl_3$ with Me_2Ph or PEt_2Ph respectively gave the corresponding meridional complex at ambient temperature ($^{31}P-\{^1H\}$ n.m.r. evidence).

In an attempt to obtain spectral evidence for the existence of the other postulated solvated monomer, namely, $[RhCl_3(PR_3)(H_2O)_2]$ an in situ low temperature generation of mer-$[RhCl_3(PEt_2Ph)_3]$ from $RhCl_3.3H_2O$ and PEt_2Ph was conducted in d^6-acetone at 213K. Using ${}^{31}P-\{{}^1H\}$ n.m.r. spectroscopy it was hoped to be able to observe the sequence shown in equation [9].

$$\begin{tikzcd}
 & RhCl_3.3H_2O \arrow[r, "PEt_2Ph"] & {[RhCl_3(PEt_2Ph)(H_2O)_2]} \arrow[d, "PEt_2Ph"'] \\
\text{mer-}[RhCl_3(PEt_2Ph)_3] & & \text{mer-}[RhCl_3(PEt_2Ph)_2(H_2O)] \arrow[ll, "PEt_2Ph"']
\end{tikzcd}$$

..... [9]

Unfortunately this was not successful since, even at the temperature in the presence of a slight excess of PEt_2Ph, the meridional complex was formed too rapidly to even observe the known $[RhCl_3(PEt_2Ph)_2(H_2O)]$. Further lowering of the temperature was not possible due to the low solubility of the reagents.

2.5.2 The X-ray crystal structure of mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$ 0.5 EtOH

Details of the solution of the structure are given in the experimental section. The final atomic positions are given in Table 2.3, selected bond distances in Table 2.4 and selected bond angles in Table 2.5.

There are two crystallographically independent aquated monomers, in one of which one of the phosphine methyl groups is disordered over two positions. Otherwise there are no significant differences in bond lengths and angles between the two monomers.

The coordination about the rhodium atom is a distorted octahedron and, in keeping with the high trans influence of phosphine ligands compared to chloride, the average Rh-Cl bond length is 2.447(14)Å when trans to a phosphine group and 2.342(9)Å when trans to a chloride. Similar effects are observed in the meridional isomer of $[RhCl_3(PEt_2Ph)_3]$ which has corresponding bond lengths of 2.429(3)Å and 2.362(3)Å.[12]

There were no interpretable intermolecular contacts between the badly disordered ethanol solvent molecule and the aquated monomer.

The molecular structure of both aquated monomers is shown in Figure 2.6, an ORTEP diagram of molecule 2 in Figure 2.7 and a cell packing diagram in Figure 2.8.*

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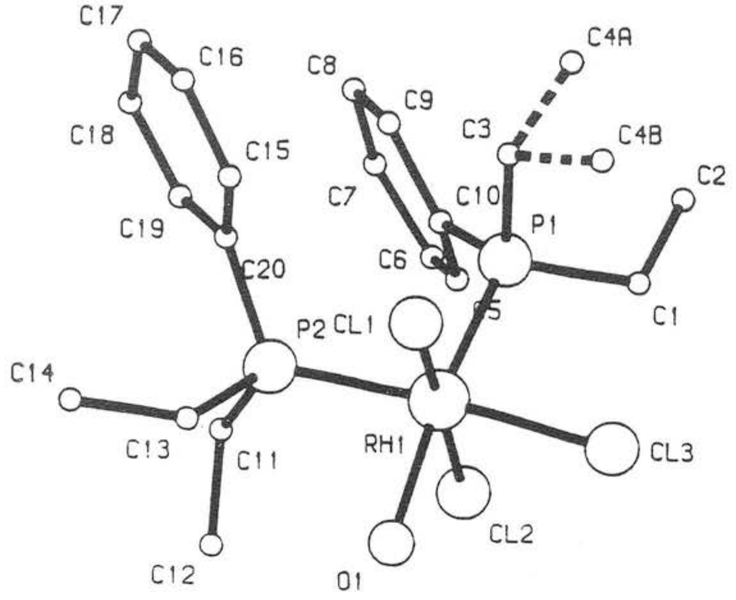
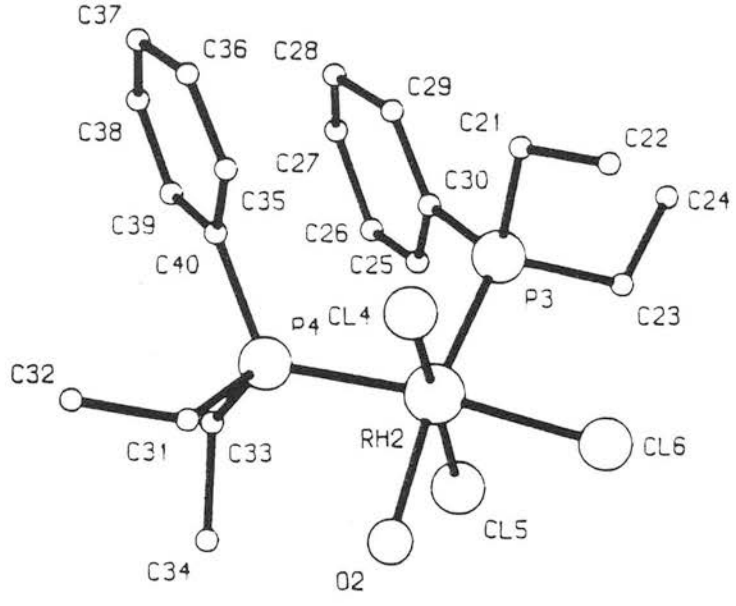
* For clarity the disordered ethanol molecule is represented by the three most suitable positions.

Fig.2.6. The structure of the aquated monomer mer-[RhCl$_3$(PEt$_2$Ph)$_2$(H$_2$O)]



Molecule 1



Molecule 2

Fig.2.7 An ORTEP diagram of molecule 2 of mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$

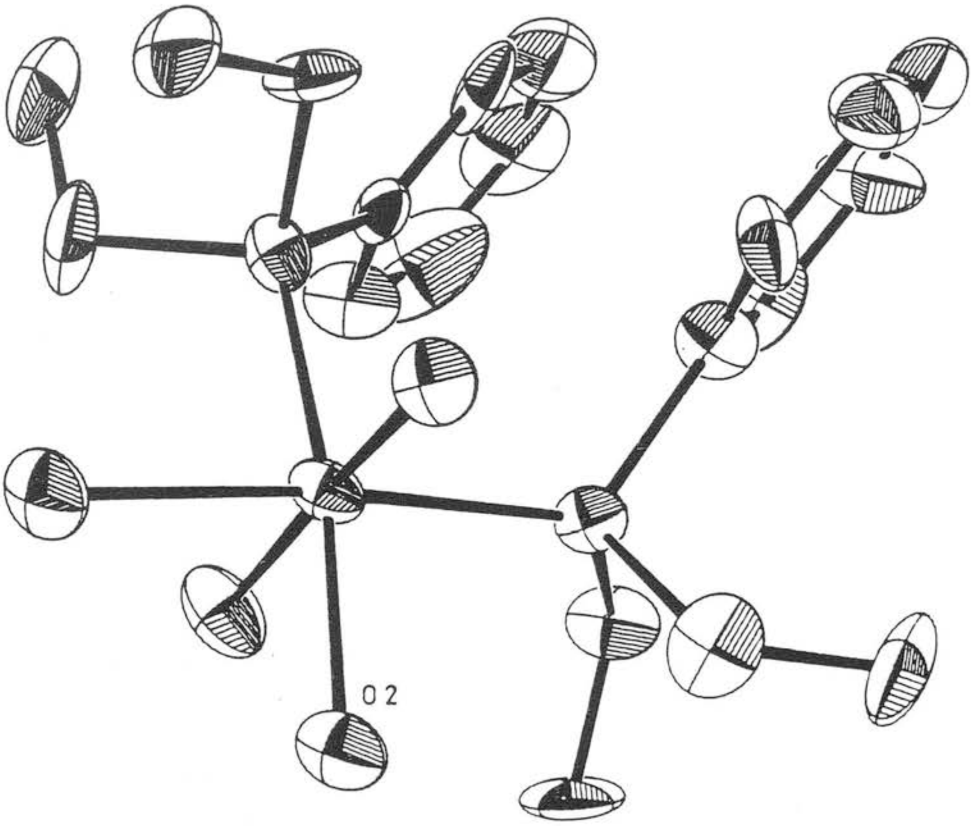
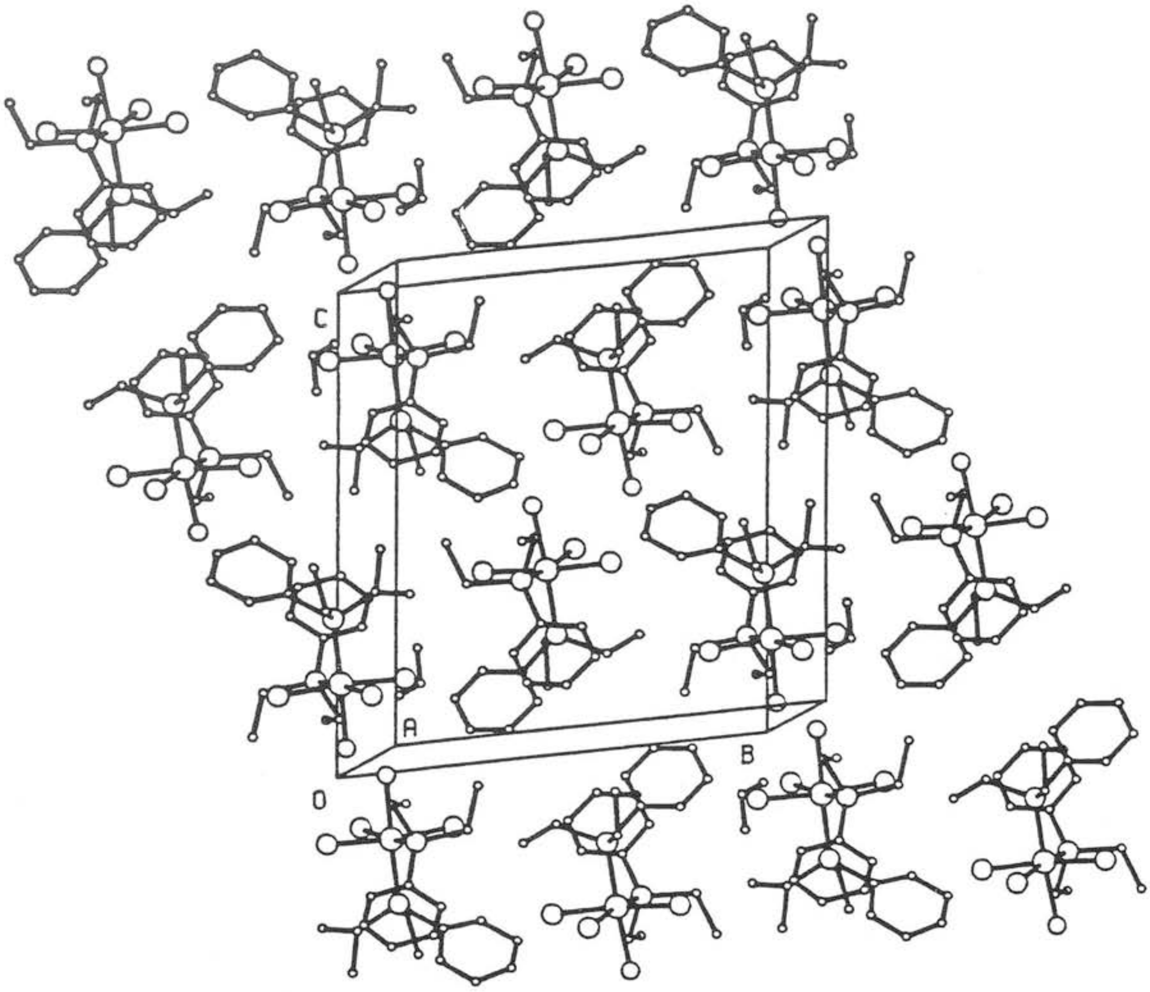


Fig.2.8 A crystal packing diagram for mer-$[RhCl_3(PEt_2Ph)_2(H_2O)].0.5\ C_2H_6O$



2.6 Proposed mechanisms of formation of the triple chloro-bridged cations $[Rh_2Cl_5(PR_3)_4]^+$

The triple chloro-bridged cationic complexes $[Rh_2Cl_5(PR_3)_4]^+$ have been isolated from the mother liquors of a variety of different reactions. These include the treatment of $RhCl_3 \cdot 3H_2O$ with either PEt_2Ph (1:1.5-3.5 molar ratio) or mer-$[RhCl_3(PR_3)_3]$ (1:1-2 molar ratio), and also from the interaction of equimolar amounts of $[Rh_2Cl_6(PR_3)_3]$, $Ag[BF_4]$ and PR_3 (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$). With such a variety of synthetic routes available, and having characterised the aquated monomeric intermediate $[RhCl_3(PR_3)_2(H_2O)]$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$), it is appropriate at this point to speculate on the mechanism of formation of these cationic complexes.

The $^{31}P-\{^1H\}$ n.m.r. spectra of the various mother liquors, after precipitation of mer-$[RhCl_3(PR_3)_3]$ or $[Rh_2Cl_6(PR_3)_3]$, indicate that there are two major species present in solution, namely, the cation $[Rh_2Cl_5(PR_3)_4]^+$ and the aquated monomer $[RhCl_3(PR_3)_2(H_2O)]$ generally in similar amounts (see section 2.5). Addition of $Na[BPh_4]$ to these ethanolic solutions then results in precipitation of the compound $[Rh_2Cl_5(PR_3)_4]BPh_4$ in high yield. The mother liquor obtained after filtration of the $[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$ precipitate was also examined by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. This confirmed that the cationic species had been removed from solution and furthermore that little or no solvated monomer remained in this mother liquor. This strongly suggested that the solvated monomer had further reacted to form more $[Rh_2Cl_5(PEt_2Ph)_4]^+$ as this cation was removed from the solution by precipitation as its $[BPh_4]^-$ salt.

This led us to speculate whether the solvated monomer would behave similarly if the salt of the cationic complex remained in the system and was not precipitated from solution. Therefore a mixture of $[Rh_2Cl_5(PEt_2Ph)_4]Cl$ and $[RhCl_3(PEt_2Ph)_2(H_2O)]$ were dissolved in $CDCl_3$ and treated with an excess of $Na[BPh_4]$ whereupon no precipitation was observed. However, the $^{31}P-\{^1H\}$ n.m.r. spectrum obtained following the treatment indicates loss of the signal due to the solvated monomer with only that of the cation being observed. Interestingly, treatment of a similar mixture with $[AsPh_4]Cl$ resulted in the opposite effect with the $^{31}P-\{^1H\}$ n.m.r. spectrum containing only the signal due to the solvated monomer. These observations were readily verified by taking $[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$ and $[RhCl_3(PEt_2Ph)_2(H_2O)]$ separately in $CDCl_3$ and treating them with an excess of $[AsPh_4]Cl$ and $Na[BPh_4]$ respectively. $^{31}P-\{^1H\}$ n.m.r. spectroscopy indicated that in both these in situ reactions conversion to the other species had occurred. It would appear that in solution the two species exist in facile equilibrium, the position of which can be altered readily by the addition ($[AsPh_4]Cl$) or removal ($Na[BPh_4]$) of chloride (Eqn.[10]).

$$[Rh_2Cl_5(PEt_2Ph)_4]^+ \underset{NaBPh_4}{\overset{AsPh_4Cl}{\rightleftharpoons}} 2[RhCl_3(PEt_2Ph)_2(s)] \quad \ldots \quad [10]$$

Therefore we propose that one of the possible mechanisms of formation of the triple chloro-bridged cations involves the dimerisation of two solvated monomers. In the process of the dimerisation the two solvent molecules would be displaced and a double chloro-bridged species, $[Rh_2Cl_6(PR_3)_4]$, generated. Subsequent attack at the other rhodium centre by one of the non-bridging chlorides could result in the displacement of chloride, but more importantly, the consequence of which would be the formation of the triple chloro-bridged cation (Fig.2.9).

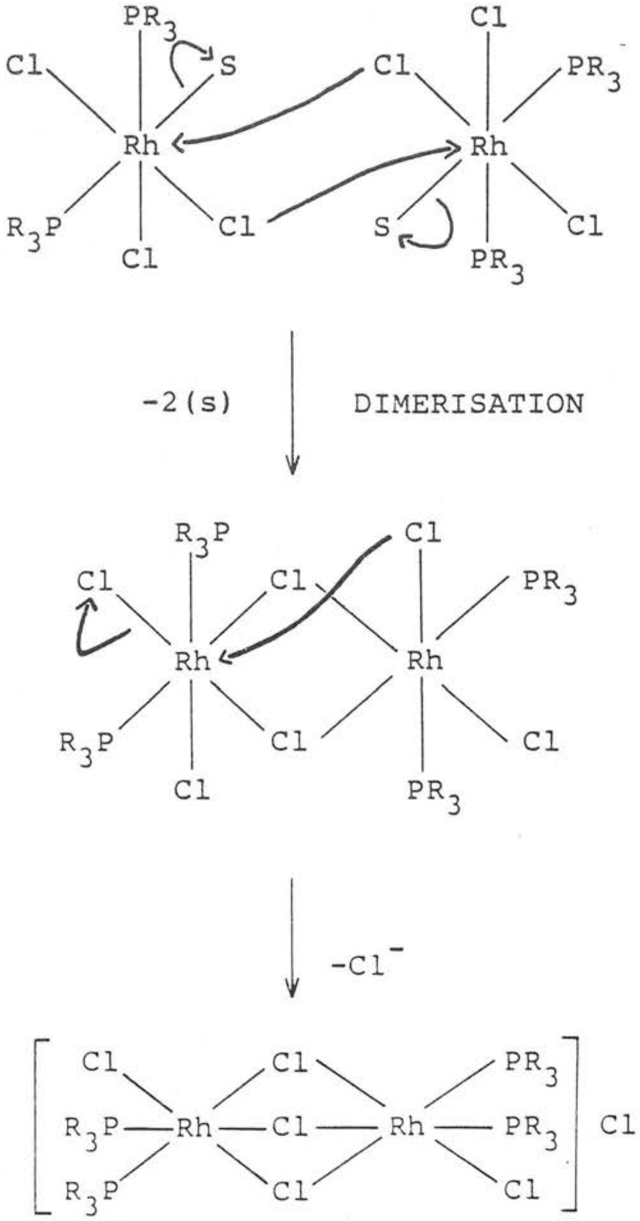
In previous sections we found that high yields of the cations $[Rh_2Cl_5(PR_3)_4]^+$ were obtained from three different routes, all of which had rhodium:phosphine ratios of 1:2. The high yield obtained from the reaction of $RhCl_3.3H_2O$ with 2 molar equivalents of PR_3 can be understood in terms of the formation of the aquated monomer $[RhCl_3(PR_3)_2(H_2O)]$. In this case this could readily be achieved by the stepwise displacement of two waters from the $RhCl_3.3H_2O$ by coordination of two phosphine molecules. With only a rhodium:added phosphine ratio of 1:2 the stepwise displacement cannot proceed further and halts at this stage (Eqn.[11]).

$$RhCl_3.3H_2O \xrightarrow{PR_3} [RhCl_3(PR_3)(H_2O)_2] \xrightarrow{PR_3} [RhCl_3(PR_3)_2(H_2O)] \qquad ..... [11]$$

Similarly, the redistribution of phosphine between $RhCl_3.3H_2O$ and two molecules of <u>mer</u>-$[RhCl_3(PR_3)_3]$ in ethanol could lead to the formation of three molecules of $[RhCl_3(PR_3)_2(s)]$ ($S = H_2O$ or EtOH), which could then react as above to form the triple chloro-bridged cations.

The interaction of equimolar quantities of $[Rh_2Cl_6(PR_3)_3]$,

Fig.2.9 - Possible mechanism of formation of $[Rh_2Cl_5(PR_3)_4]^+$ from dimerisation of the solvated monomer *mer*-$[RhCl_3(PR_3)_2(s)]$

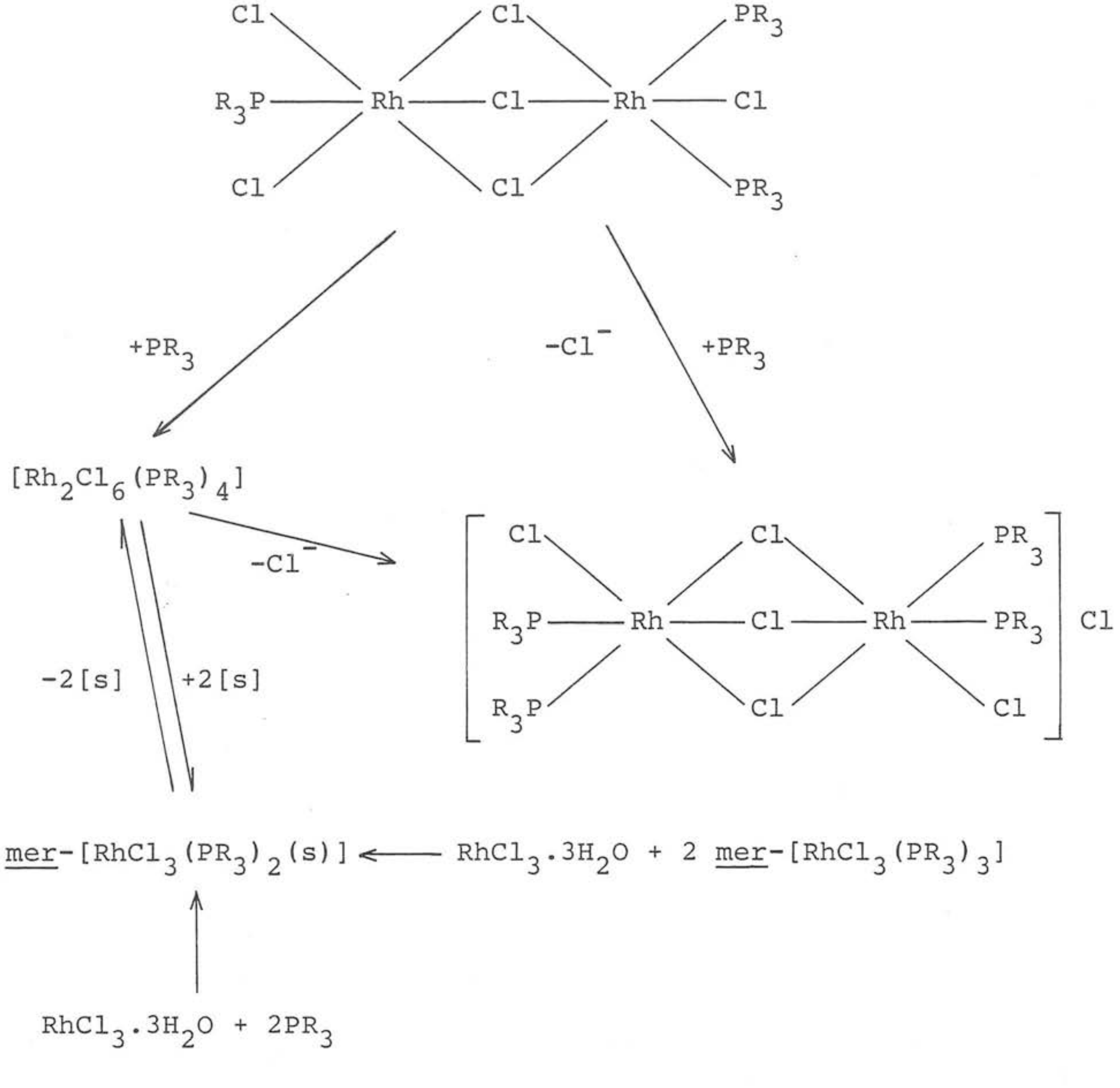


$Ag[BF_4]$ and PR_3 clearly requires a different route to that of the above dimerisation since the triple chloro-bridge is already intact. The role of the Ag^+ ion is believed to be that of terminal chloride extraction. Incorporation of the free phosphine into the vacant coordination site would result in the formation of the triple bridged cation (Scheme 2.4).

However, there are other processes which could operate concurrently. The interaction of the free phosphine with $[Rh_2Cl_6(PR_3)_3]$, prior to that of Ag^+, would generate a double chloro-bridged intermediate $[Rh_2Cl_6(PR_3)_4]$. We have been unable to isolate the intermediate (also see section 2.2) which suggests that the species is not particularly stable. It would appear that such compounds prefer to either eliminate a ligand such as chloride, thereby forming the triple chloro-bridged cation, or undergo complete bridge cleavage. In the presence of an excess of phosphine the monomeric meridional complexes are formed; however, cleavage of the double chloro-bridge by molecules of a coordinating solvent could result in the generation of the solvated monomer $[RhCl_3(PR_3)_2(s)]$. Our studies using $^{31}P-\{^1H\}$ n.m.r. spectroscopy have shown that, not only is the solvated monomer present in solution but also that it exists in equilibrium with the triple chloro-bridged cations $[Rh_2Cl_5(PR_3)_4]^+$ presumably via the double bridged intermediate. In this system the loss of chloride would, almost certainly, be aided by the presence of the Ag^+ ions (see scheme 2.4) .

Although we have not observed the double bridged intermediate in these reactions, the presence of the solvated monomer is strong evidence for the occurrence of this intermediate species.

Scheme 2.4 - Proposed routes of formation to $[Rh_2Cl_5(PR_3)_4]^+$



2.7 The variable temperature $^{31}P-\{^{1}H\}$ n.m.r. spectra of mer-$[RhCl_3(PR_3)_3]$

The expected $^{31}P-\{^{1}H\}$ n.m.r. spectra for the meridional complexes $[RhCl_3(PR_3)_3]$ is an AMX_2 pattern. As discussed in section 2.2, this consists of a doublet of triplets and a doublet of doublets with an intensity ratio of 1:2. However, while conducting a low temperature in situ generation of mer-$[RhCl_3(PPr^n{}_2Ph)_3]$, it was found that the complex exhibits marked temperature dependent behaviour.

The $^{31}P-\{^{1}H\}$ n.m.r. spectra obtained for the above compound on the Jeol FX60Q (24.2MHz) instrument did indeed show the expected at ambient temperature. However, on lowering the temperature each doublet first broadens and then sharpens slightly at 223K to reveal two broad triplets [see Fig.2.10(i)-(v)]. The doublet of triplets arising from the cis phosphine is unchanged and remain sharp throughout indicating that only the mutually trans phosphines are affected. The process was found to be reversible with temperature and since the same spectrum is obtained in very dilute solution [Fig.2.1(vi)] it is also concentration independent indicating it arises from an intramolecular effect. Furthermore since no free phosphine signal is observed and rhodium-phosphorus coupling is retained throughout, it is clear that dissociation of phosphine is not involved. It is also likely that loss of chloride ion has no great part to play either, since the process is found to be solvent independent occurring in either $CDCl_3$ or d^6-acetone with the addition of ethanol having no effect in both cases.

We believe that the intramolecular process responsible for this temperature dependent phenomenon is a conformational

Fig.2.10 The variable temperature $^{31}P-\{^{1}H\}$ n.m.r. spectra of mer-$[RhCl_3(PPr^n{}_2Ph)_3]$, (in $CDCl_3$)

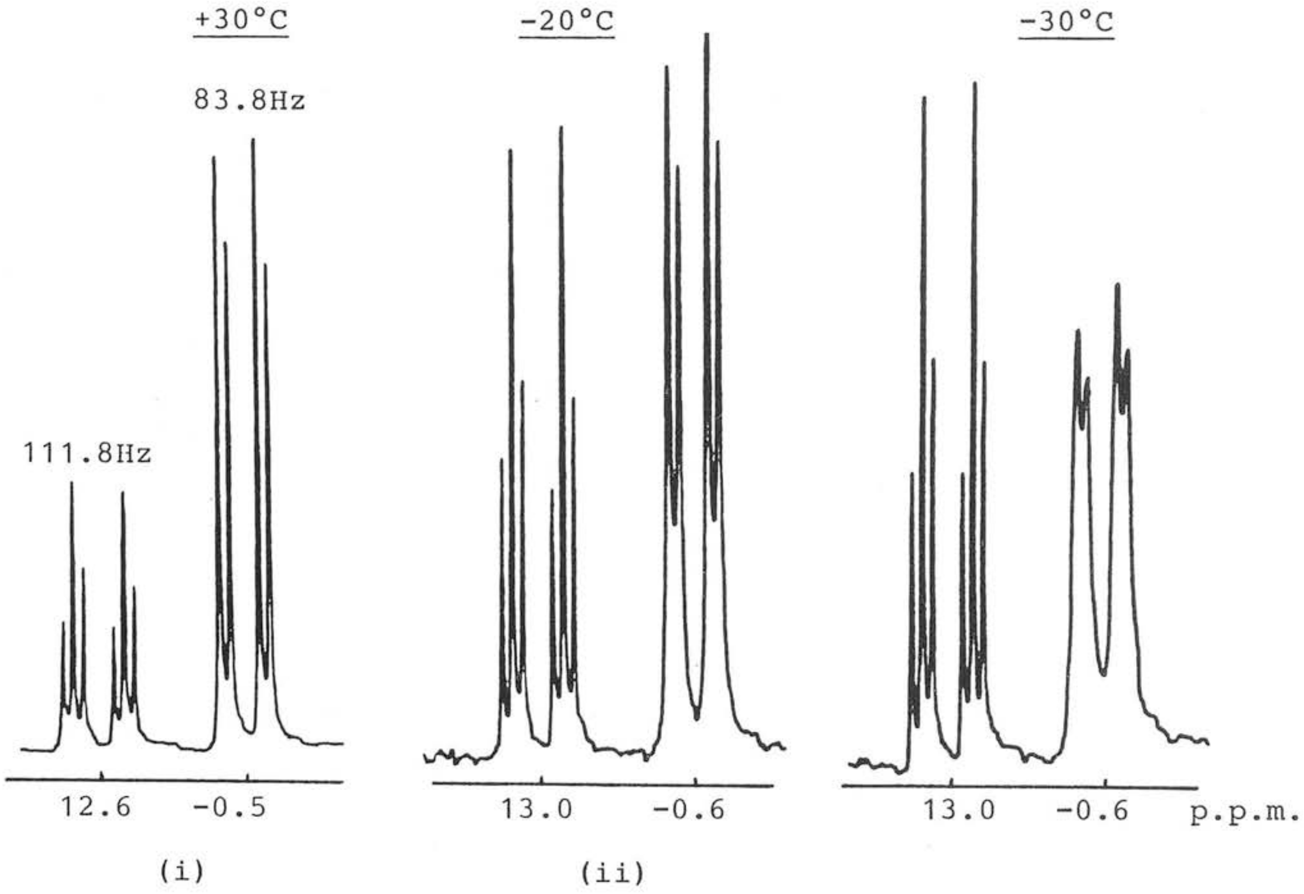
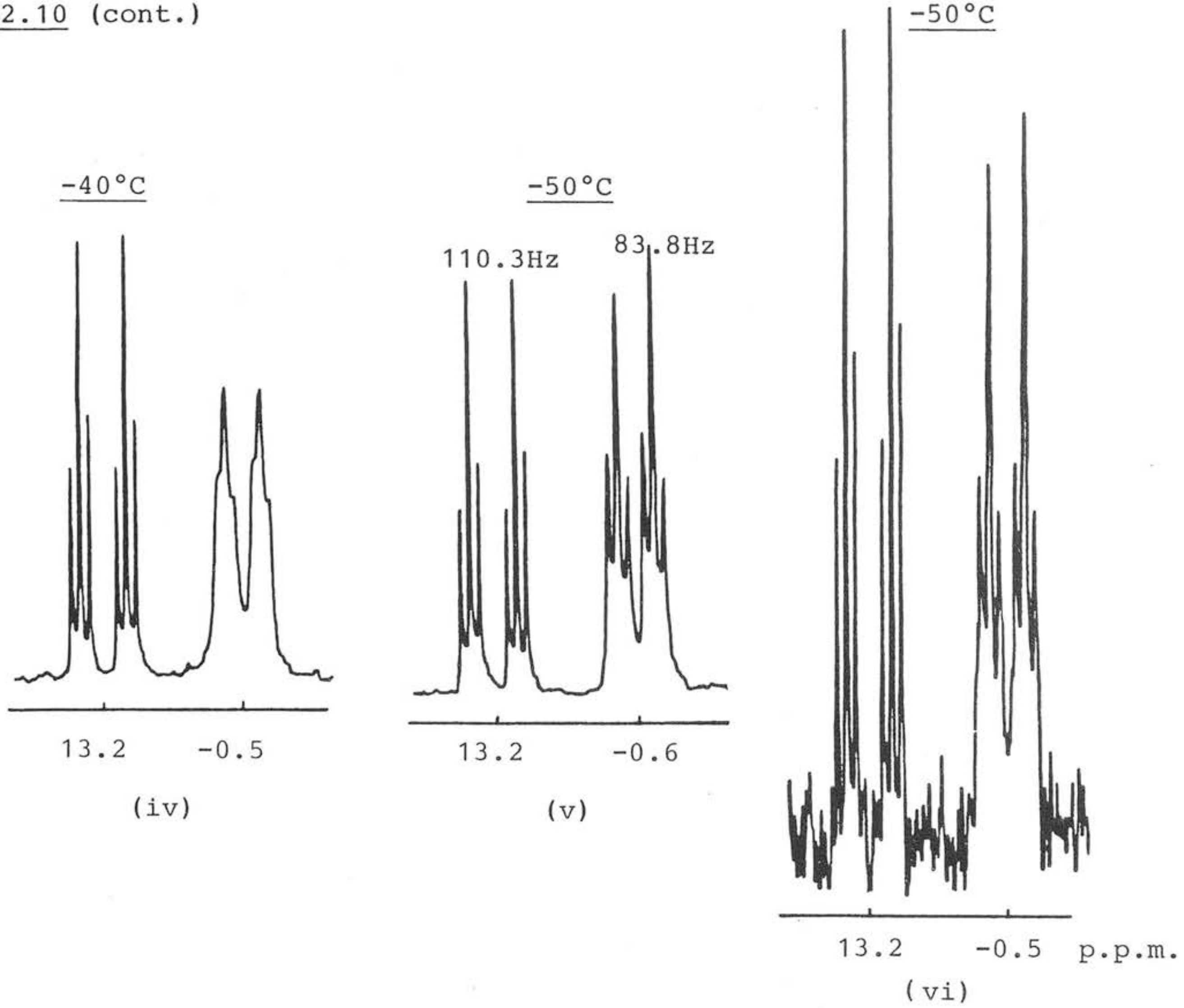


Fig.2.10 (cont.)



effect arising from restricted rotation about the rhodium-phosphorus bond. This rotation is hindered as a result of the steric interaction between mutually cis bulky phosphine groups. At low temperature the change in pattern observed indicates that the two trans phosphorus atoms have become magnetically inequivalent and now couple to each other, in addition to the rhodium and cis phosphine as before.

Two bond trans $^{31}P-^{31}P$ coupling constants tend to be of the order of several hundred hertz and in this case, the $^{2}J_{P-Ptrans}$ coupling constant of 497.3Hz is several times greater than the chemical shift difference ($\Delta\nu$) of 159.3Hz for the two trans phosphines. The calculated value for the ratio $J/\Delta\nu$ of 3.12 indicates that the low temperature $^{31}P-\{^{1}H\}$ n.m.r. pattern obtained at 24.2MHz (FX60Q) for the trans phosphines is far removed from the first order case which requires $J/\Delta\nu < 1/6$. Hence we would expect to obtain a second order AB pattern for the two trans phosphines each line of which would be split into a doublet due to coupling to the rhodium and into a further doublet as a result of coupling to the cis phosphine. Figure 2.11 (not to scale) shows the type of 16 line pattern expected which, unfortunately, does not match the observed doublet of broad triplets. However, as the ratio of $^{J}AB/\Delta\nu$ increases from the AX case, so the relative intensities of the inner transitions increase with respect to the outer transitions and as the ratio is increased without limit, the quartet approaches a singlet. The outer peaks are reduced to vanishingly small satellites and the AB spectrum is reduced in effect to an A_2 spectrum. This is demonstrated in Figure 2.12 which shows the calculated

Fig.2.11 Predicted low temperature $^{31}P-\{^{1}H\}$ n.m.r. pattern for trans phosphines in mer-$RhCl_3(PPr^n{}_2Ph)_3$

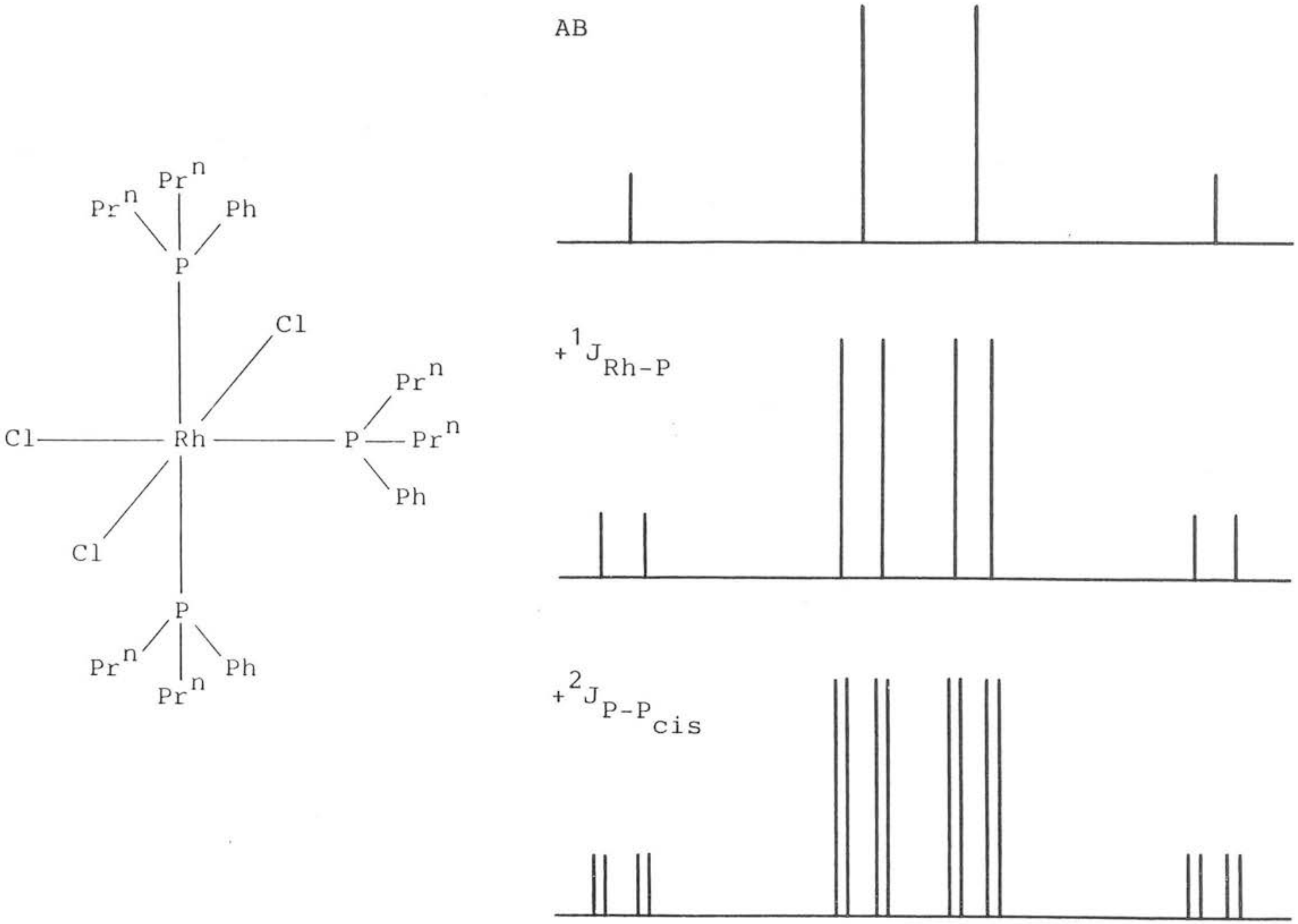
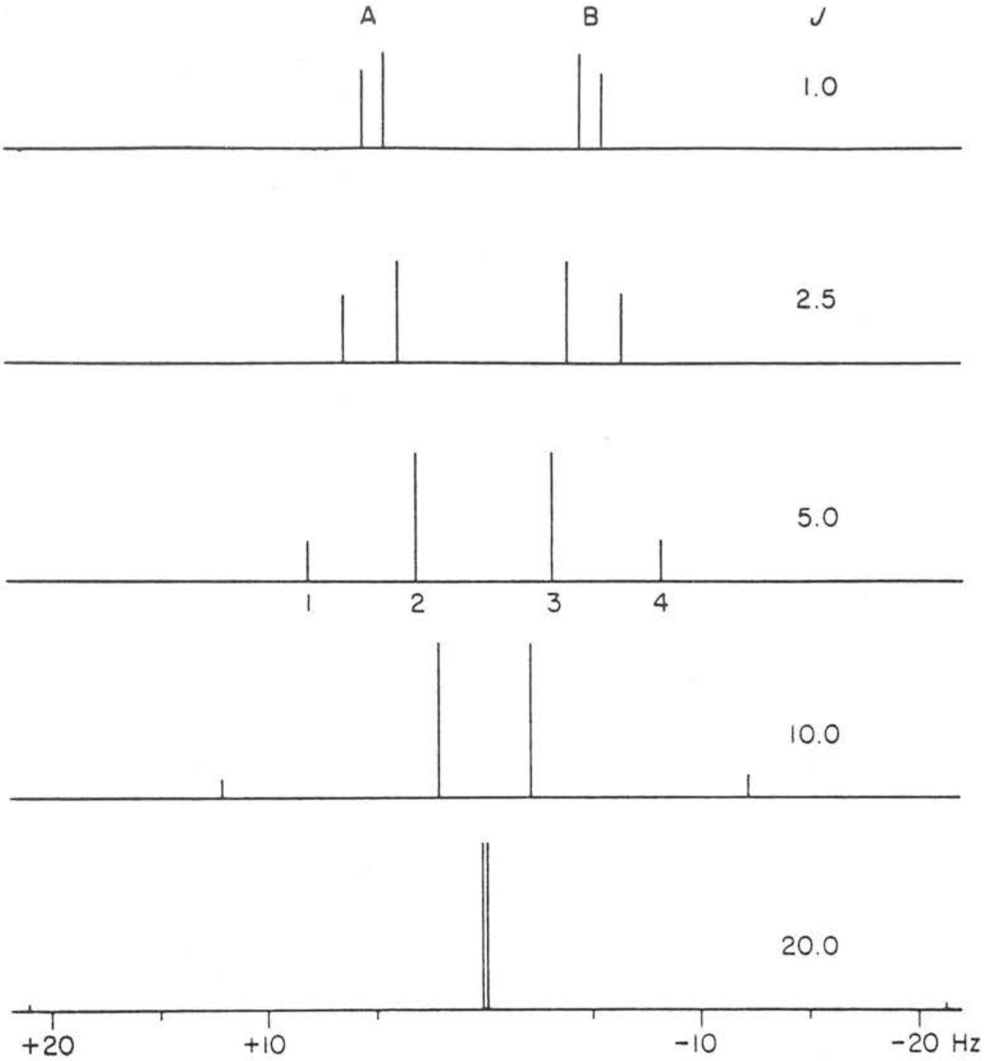


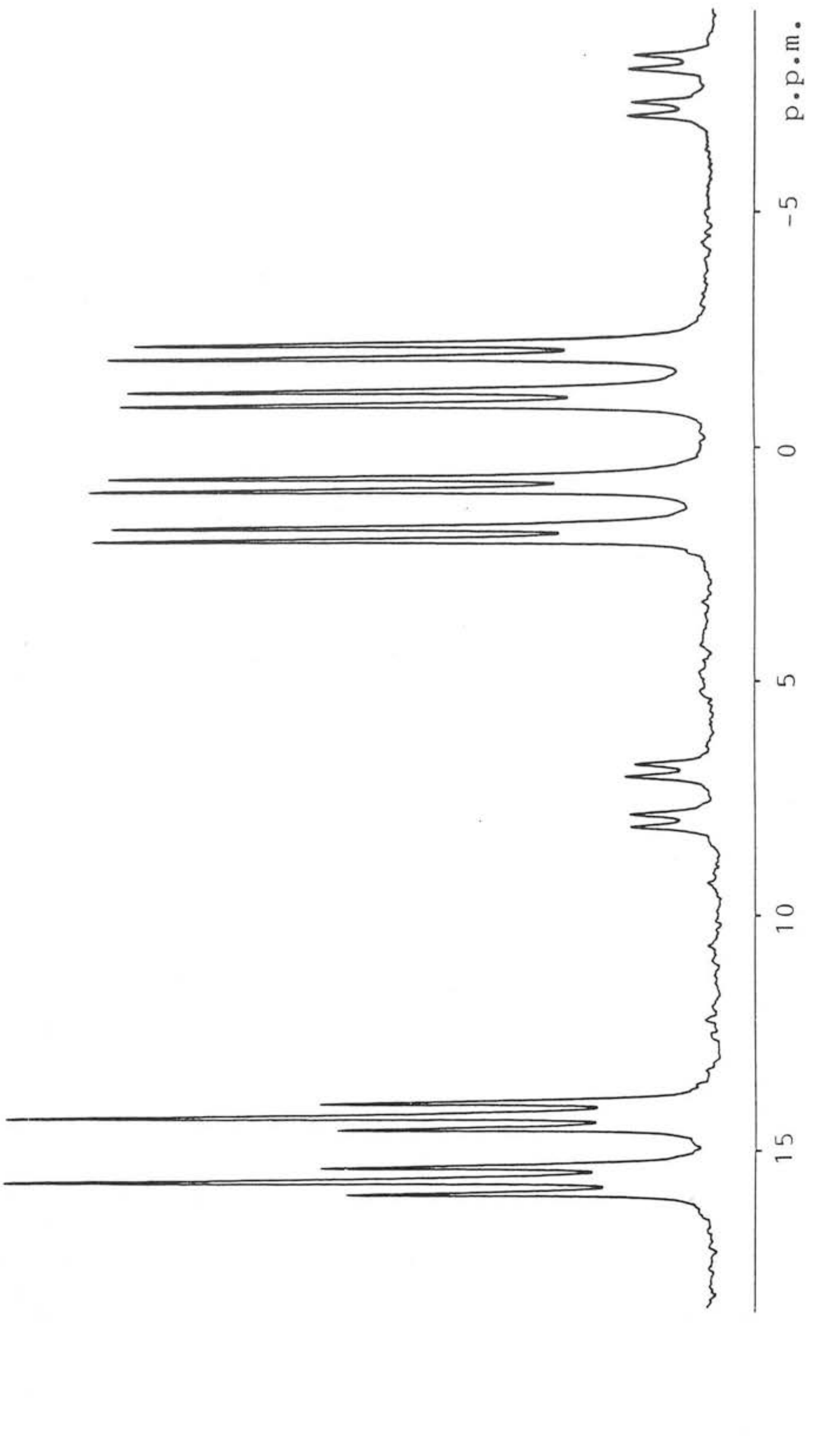
Fig.2.12 Calculated AB spectra for different values of J_{AB} with ν_A 5.0Hz; ν_B -5.0Hz



AB spectra for various values of J_{AB} for a given value of $\Delta\nu$ of 10Hz[85,86]. In view of this we believed that our predicted pattern was indeed correct with the spectra obtained on the 24.2MHz spectrometer being sufficiently second order that the outer lines were not observed and the inner lines so close that they overlapped to such an extent that they appeared as two broad triplets. Because the spin-spin coupling interaction is independent of the applied magnetic field whereas the chemical shift sepatation (in Hz) is proportional to it, in general any n.m.r. spectrum becomes simpler (more first order), on going to higher applied fields. We therefore obtained the low temperature $^{31}P-\{^{1}H\}$ n.m.r. spectrum of the <u>mer</u>-$[RhCl_3(PPr^n{}_2Ph)_3]$ using the Brücker WP200SY spectrometer (81.0MHz). Despite still being markedly second order, it was sufficiently less so to reveal the outer lines, separate the inner lines and reveal the pattern predicted for the mutually <u>trans</u> phosphines (Fig.2.13). In this spectrum the $^{2}J_{P-Ptrans}$ coupling constant of 497.3Hz is unchanged whereas the chemical shift difference between the two <u>trans</u> phosphines is now some 533.5Hz giving $^{J}AB/\Delta\nu$ a value of 0.93. It is also worth noting that the resonance due to the <u>cis</u> phosphine has remained as a doublet of triplets indicating that although they are now magnetically inequivalent, the two <u>trans</u> phosphines couple equally to the <u>cis</u> phosphine.

In order to explain this temperature dependent behaviour, we have to consider the rate of rotation around the rhodium-phosphorus bond. On lowering the temperature the lines broaden as the rotation becomes slower relative to the n.m.r. timescale and two unstructured resonances are observed for

Fig.2.13 The $^{31}P-\{^{1}H\}$ n.m.r. spectrum of mer-$[RhCl_3(PPr^n{}_2Ph)_3]$ at -50°C in $CDCl_3$ obtained using the WP200SY spectrometer



the trans phosphines. As the temperature falls further the rotation becomes slower than the chemical shift difference (in Hz) of the two trans phosphines which are now magnetically inequivalent. The lines once more become sharp and structure is observed in keeping with the preferred conformer's spin system (ABMX). It is most probably the arrangement of the alkyl and aryl groups on the cis phosphine which result in the trans phosphines becoming magnetically inequivalent.

One would expect that a reduction in the steric bulk of the phosphine would result in a lowering of the energy barrier to rotation. The $^{31}P-\{^{1}H\}$ n.m.r. spectra of other meridional complexes containing phosphines with smaller alkyl chains were examined at low temperature using the FX60Q spectrometer. The mer-$[RhCl_3(PEt_2Ph)_3]$ showed similar temperature dependent behaviour but a lower temperature was required before this effect was observed. At 223K the resonances had not sharpened much and were considerably broader and less well defined than with the $PPr^n{}_2Ph$ ligand. Not unexpectedly the complexes mer-$[RhCl_3(PR_3)_3]$ (R_3 = Me_2Ph, Me_3) containing the smaller phosphines did not show any temperature dependent behaviour which indicated free rotation about the rhodium-phosphorus bond relative to the n.m.r. timescale.

2.8 Miscellaneous Reactions

Having successfully prepared the cationic complex $[Rh_2Cl_5(PR_3)_4]^+$ from $[Rh_2Cl_6(PR_3)_3]$ it was hoped to be able to extend the series by synthesising the dication $[Rh_2Cl_4(PR_3)_5]^{2+}$. The attempted reaction of the cation

$[Rh_2Cl_5(PEt_2Ph)_4]^+$ with equimolar quantities of $Ag[BF_4]$ and PEt_2Ph failed to generate the desired species yielding, instead, a mixture of both binuclear and mononuclear species. The treatment of $[Rh_2Cl_6(PEt_2Ph)_3]$ with 2 molar equivalents of $Ag[BF_4]$ and PEt_2Ph similarly resulted only in the isolation of a mixture of complexes.

An alternative approach by which we sought to extend the series, in both directions, was through the interaction of the triple chloro-bridged trianion $[Rh_2Cl_9]^{3-}$ with various ratios of $Ag[BF_4]$ and PEt_2Ph under refluxing conditions. It was hoped that it would be possible to remove selectively a number of terminal chlorides, insert phosphine in their place, and generate a wider range of compounds. The reaction of 1:1:1 and 1:2:2 molar ratios of the reagents failed to yield any product. The interaction of a 1:3:3 molar ratio was more promising in that a mixture of species, of which $[Rh_2Cl_6(PEt_2Ph)_3]$ was the major component, was obtained. On increasing the ratio of 1:4:4 the reaction was found to be somewhat cleaner than the previous ones resulting in the compound $[Rh_2Cl_6(PEt_2Ph)_3]$ being isolated in low yield (32%). Furthermore, $^{31}P-\{^1H\}$ n.m.r. spectral evidence indicated that the cation $[Rh_2Cl_5(PEt_2Ph)_4]^+$ was present in the mother liquor. Finally a 1:6:6 molar ratio gave <u>mer</u>-$[RhCl_3(PEt_2Ph)_3]$ presumably as a result of facile bridge cleavage of any $[Rh_2Cl_6(PEt_2Ph)_3]$ that was formed. Once more $^{31}P-\{^1H\}$ spectral evidence was obtained for the presence of the cationic complex in the mother liquor. The absence of the solvated monomer in the last two cases is probably due to the removal of free chloride ion from solution (see section 2.6) in the form of precipitated AgCl.

In an attempt to synthesise mixed species of the type $[(PR_3)_2ClRhCl_3RhCl(PR_3)(PR'_3)]^+$ (R_3 = Et_2Ph, R' = Ph_3, Me_2Ph; R = $EtPh_2$, R' = Ph_3, Et_2Ph) equimolar quantities of $[Rh_2Cl_6(PR_3)_3]$, $Ag[BF_4]$ and PR'_3 were refluxed in ethanol. When triphenylphosphine was used no reaction was observed other than the production of known binuclear and mononuclear species resulting from the cannibilisation of the starting material due to the removal of Cl^- by the Ag^+. However in the other cases reaction did occur but only inseparable mixtures (including mixed phosphine species) were obtained. Similarly the reaction of $[Rh_2Cl_6(PEt_2Ph)_3]$ with $Ag[BF_4]$ and $AsPh_3$ gave an inseparable mixture containing both known PEt_2Ph complexes and unknown species.

It has been shown that the complexes $[Rh_2Cl_6(PR_3)_3]$ were successfully prepared in high yield by the interaction of the corresponding meridional compound with one molar equivalent of $RhCl_3.3H_2O$. It was hoped to be able to develop this into a more general route by which the interaction of various mononuclear species with an equimolar quantity of $RhCl_3.3H_2O$ would lead to a wide variety of triple chloro-bridged compounds. For example, in an attempt to prepare $[(PR_3)Cl_2RhCl_3RhCl(CO)(PR_3)]$ the complex $[RhCl(CO)(PR_3)_2]$ (R_3 = Ph_3, Et_2Ph) was treated with an equimolar amount of $RhCl_3.3H_2O$ in refluxing ethanol. Unfortunately no reaction was observed and only the starting materials were recovered.

2.9 Conclusions

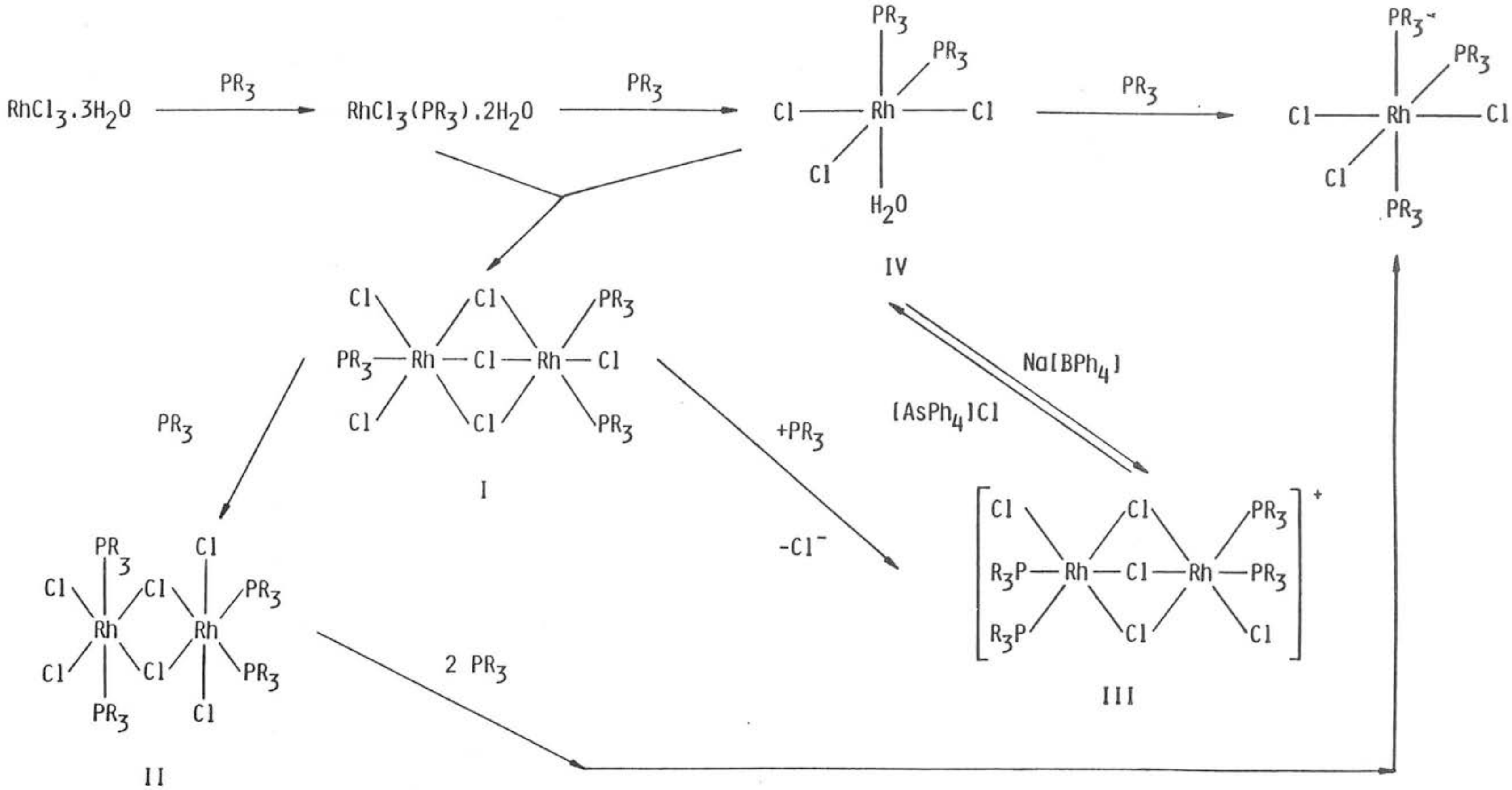
As can be seen from the work reported in chapters 1 and 2, it is, possible to synthesise a variety of both mono- and binuclear tertiary phosphine complexes of rhodium(III). The nature of the species obtained appears to be very dependent upon the relative amounts of rhodium and phosphine used. A comparison of our work with the original studies discussed in chapter 1 would seem to suggest that in some cases the type of compound isolated is also dependent upon the type of phosphine used. One of the major disappointments of our study was our inability to isolate a double chloro-bridged compound. These were first reported by Chatt *et al.*[5] using trialkylphosphines. The majority of our work was conducted with dialkylphenylphosphines and our attempts to prepare this type of complex resulted in the isolation of the triple chloro-bridged cation $[Rh_2Cl_5(PR_3)_4]^+$ and the subsequent discovery of its coexistence with the solvated monomer $[RhCl_3(PR_3)_2(H_2O)]$. Interestingly, preliminary studies using ethyldiphenyl-phosphine have resulted in neither the double nor the triple chloro-bridged tetrabisphosphine complexes being isolated. Further studies are required before this difference in behaviour can be attributed to either an electronic or a steric effect, if indeed, differentiation between the two is possible.

In the course of our studies we have been able to synthesise the cationic $[Rh_2Cl_5(PR_3)_4]^+$ in high yield by a variety of routes. Furthermore, the isolation of the solvated monomer has enabled us to postulate possible mechanisms of formation for the various species involved.

This understanding made it possible for us to develop an alternative high yield synthesis of the triple chloro-bridged $[Rh_2Cl_6(PR_3)_3]$. These reactions together with the in situ generations studied by $^{31}P-\{^1H\}$ n.m.r. spectroscopy have revealed that the various complexes in this system can be readily interconverted. These routes are shown in scheme 2.5.

Ready access to variable temperature $^{31}P-\{^1H\}$ n.m.r. spectroscopy has been crucial to this study. In this respect one of the most useful aids has been the use of a capillary lock. This has enabled us to study reaction solutions, mother liquors and also the behaviour of some of the species in non-deuterated solvents. Its use is largely responsible for the discovery of what turned out to be the solvated monomer $[RhCl_3(PEt_2Ph)_2(H_2O)]$ without which, our understanding of this system would not be nearly as great. However, it should be noted that our understanding is not yet complete. Whilst examining some of the reaction solutions and mother liquors we have occasionally observed the occurrence of other doublets in the $^{31}P-\{^1H\}$ n.m.r. spectra indicating the presence of small amounts of other species but neither their isolation nor characterisation have been possible.

Scheme 2.5 Possible mechanism of formation and interconversion of the various species



2.10 Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000-200 cm^{-1} region on Perkin Elmer 557 and 598 spectrometers as Nujol mulls on caesium iodide plates. Hydrogen-1-n.m.r. spectra were recorded on a Brücker WP80SY spectrometer. Phosphorus-31 n.m.r. (proton noise decoupled) were recorded on Jeol FX60Q (24.2MHz) and Brücker WP200SY (81.0MHz) spectrometers (^{31}P n.m.r. chemical shifts are reported in p.p.m. to high frequency of 85% H_3PO_4). Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298K. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Rhodium trichloride trihydrate was supplied by Johnson Matthey P.L.C. and all other starting materials were obtained from normal commercial suppliers and used as supplied.

The compounds mer-$[RhCl_3(PR_3)_3]$[5] (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$, $EtPh_2$), $[Rh_2Cl_6(PEt_2Ph)_3]$[5], $[RhCl(CO)(PR_3)_2]$[87] (R_3 = Ph_3, Et_2Ph), $[NBu^n{}_4]_3[Rh_2Cl_9]$[88] were prepared by published procedures. All reactions were carried out under dry nitrogen although the isolated complexes were air stable. ^{31}P-$\{^1H\}$ n.m.r. data for the new complexes are given in Table 2.1.

Crystal Structure Determination of mer-[$RhCl_3(PEt_2Ph)_2(H_2O)$]. 0.5EtOH

Crystals suitable for X-ray analysis were obtained from the ethanolic mother liquor of the reaction of $RhCl_3.3H_2O$ with mer-[$RhCl_3(PEt_2Ph)_3$] (1:2 molar ratio). A yellow crystal of dimension 0.4x0.2x0.05 mm (plate) was chosen and precession photographs indicated a triclinic space group. Accurate cell dimensions were obtained by least squares refinement of 20 reflections on an Enraf-Nonius CAD-4 diffractometer with monochromated Mo-K_α radiation.

Crystal Data: $C_{20}H_{32}Cl_3O_2P_2Rh.\ 0.5C_2H_6O$, M = 582.8, $\underline{a}$ = 11.108(3), $\underline{b}$ = 14.483(4), $\underline{c}$ = 16.321(5)Å, α = 83.38(2), β = 84.38(2), γ = 79.21(2)°, V = 2554.2Å^3, D_c = 1.515g cm^{-3}, Dm = 1.495 g cm^{-3} (by flotation), Z = 4, F(000) = 1196, μ(Mo-K_α) = 11.11 cm^{-1}, λ(Mo-K_α) = 0.71069Å. The space group is $P\bar{1}$.

Intensity data were collected by an ω-2θ scan for θ out to 22°. A standard reflection was monitored regularly throughout data collection but no decay was observed. Intensities were measured for 6216 independent reflections of which 2653 had $I>3\sigma(I)$. No absorption correction was applied.

Structure Solution and Refinement

The refinement was based on the 2653 reflections with $I>3\sigma(I)$. The structure was solved by conventional Patterson and difference Fourier techniques. The two rhodium atoms were located from a Patterson map using SHELX-84[89]. Subsequent difference Fourier syntheses revealed all non-hydrogen atoms in the molecules. The structure refinement was carried out using SHELX[90].

The structure consists of two crystallographically unrelated aquated monomers. One of these molecules was found to contain a methyl group which was disordered over two positions and in the refinement each of these was given a fixed site occupancy of 0.5. Some disorder was apparent in the phenyl ring of the phosphine containing the disordered methyl group. Smooth convergence of this partially disordered structure was facilitated using a constrained least squares refinement in which all phenyl groups were input as idealised planar rings with C-C bond lengths of 1.395Å. All other C-C bonds were constrained to 1.54Å with a weight of 0.02. Constraints were also placed on the P(1)-C(10), (1.83±0.01Å), and P(2)-C(13), (1.81±0.02Å) bonds.

The solvent molecule was identified as ethanol from the ^{1}H n.m.r. spectrum of the crystals in $CDCl_3$ which showed a quartet [δ = 3.7 p.p.m., $^3J_{H-H}$ = 7.0Hz (quartet)] but the associated triplet was hidden under the phosphine resonances. The position of the ethanol in the crystal was found to be severely disordered. Best refinement occurred by modelling the electron density in the area of the solvent ethanol as carbon atoms with half occupancy of four independent sites. These carbons were refined isotropically.

The disordered methyl carbon and all the phenyl carbon atoms in molecule 1 were also refined isotropically. The remaining atoms in molecule 1 and all of those in molecule 2 were refined anisotropically. No hydrogen atoms were included in the refinement. A weighting scheme of the form W^{-1} =

$\sigma^2(F)+0.005|F|^2$ was applied and the final R factor, based on 414 adjustable parameters was R=0.072, R_w=0.097 for the 2653 observed data. The maximum shift/esd at this stage was 0.70 and a final difference Fourier map showed two peaks each of about 1.5 $\varepsilon\text{Å}^{-3}$ both of which occurred near the rhodium atom.

The atomic scattering factor for Rh was taken from reference (91).

Final fractional coordinates are given in Table 2.3, selected bond distances in Table 2.4 and selected bond angles in Table 2.5. The structure of the aquated monomers is shown in Figure 2.6, an ORTEP plot of molecule 2 in Figure 2.7 and a cell packing diagram in Figure 2.8.

Mononuclear Compounds

mer-Trichlorotris(dimethylphenylphosphine)rhodium(III): mer-$RhCl_3(PMe_2Ph)_3$

i) The compound $RhCl_3.3H_2O$ (0.50 g) was heated under reflux in aqueous ethanol (50 cm^3) with PEt_2Ph (0.92 g; 1:3.5 molar ratio) for 10-15 mins. On cooling, the product was obtained as an orange powder which was filtered off, washed with ethanol, diethylether and dried in vacuo at 60°C, m.p.216-218°C (decomp), (yield 0.94 g, 79.4%). (Found, C, 46.3; H, 5.4. Calc. for $C_{24}H_{33}Cl_3P_3Rh$:- C, 46.2; H, 5.3%).

I.r. spectrum (nujol mull); ν(RhCl), 341 m, 312 w, 270 w cm^{-1}.

mer-Trichlorotris(diethylphenylphosphine)rhodium(III): mer-$RhCl_3(PEt_2Ph)_3$

i) Method as for (i) above using $RhCl_3 \cdot 3H_2O$ (0.20 g) and PEt_2Ph (0.43 g, 1:3.5 molar ratio). The product was isolated as orange microcrystals, m.p. 172-174°C (decomp), (0.33 g, 61.2%). (Found, C, 51.0; H, 6.4. Calc. for $C_{30}H_{45}Cl_3P_3Rh$:- C, 50.9; H, 6.4%). I.r. spectrum (nujol mull); ν(RhCl), 338 w, 318w, 271w cm^{-1}.

mer-Trichlorotris(di-n-propylphenylphosphine)rhodium(III): mer-$RhCl_3(PPr^n{}_2Ph)_3$

Method as for (i) above using $RhCl_3.3H_2O$ (0.60 g) and $PPr^n{}_2Ph$ (1.52 g, 1:3.5 molar ratio). The product was obtained as orange microcrystals, m.p. 175-178°C (decomp), (1.42 g, 78.7%). (Found: C, 54.3; H, 7.1. Calc. for $C_{36}H_{57}Cl_3P_3Rh$:- C, 54.6; H, 7.3%). I.r. spectrum (nujol mull); ν(RhCl), 337 m, 265 w cm^{-1}.

mer-Trichlorotris(ethyldiphenylphosphine)rhodium(III): mer-$RhCl_3(PEtPh_2)_3$

Method as for (i) above using $RhCl_3.3H_2O$ (0.5 g) and $PEtPh_2$ (1.42 g, 1:3.5 molar ratio). The product was isolated as a yellow powder, m.p. 129-132°C (decomp), (1.42 g, 87.8%). (Found, C, 60.4; H, 5.6. Calc. for $C_{42}H_{45}Cl_3P_3Rh$:- C, 59.2; H, 5.3%). I.r. spectrum (nujol mull); ν(RhCl), 297w, 269m cm^{-1}.

mer-Aquatrichlorobis(dimethylphenylphosphine)rhodium(III): mer-$RhCl_3(PMe_2Ph)_2(H_2O)$

(i) The compounds $RhCl_3.3H_2O$ (0.10 g) and mer-[$RhCl_3(PMe_2Ph)_3$] (0.47 g, 1:2 molar ratio) were heated under reflux in aqueous ethanol for 10 mins. After filtering, the mother liquor was left to stand in air for several days. The product was obtained as a yellow powder which was filtered off, washed with chloroform, ethanol and dried *in vacuo* at 60°C, m.p. 220-223°C (decomp). (0.10 g, 17.4%). (Found, C, 38.5; H, 4.9. Calc. for $C_{16}H_{24}Cl_3OP_2Rh$:- C, 38.2; H, 4.8%). I.r. spectrum (nujol mull), ν(RhCl), 337m, 310w; ν(OH), 1640s br cm^{-1}.

mer-Aquatrichlorobis(diethylphenylphosphine)rhodium(III): mer-$RhCl_3(PEt_2Ph)_2(H_2O)$

(i) Method as for (i) above using $RhCl_3.3H_2O$ (0.10 g) and mer-[$RhCl_3(PEt_2Ph)_3$] (0.54 g, 1:2 molar ratio). The product was isolated as an orange powder, m.p. 194-195°C (decomp), (0.09 g, 14.6%). (Found, C, 42.7; H, 5.2. Calc. for $C_{20}H_{32}Cl_3OP_2Rh$:- C, 42.9; H, 5.8%). I.r. spectrum (nujol mull), ν(RhCl), 341m, 318m; ν(OH), 1635s br cm^{-1}.

Binuclear Compounds

Tri-μ-chlorotrichlorotris(dimethylphenylphosphine)dirhodium (III): $Rh_2Cl_6(PMe_2Ph)_3$

(i) The compounds mer-[$RhCl_3(PMe_2Ph)_3$] (0.47 g) and $RhCl_3.3H_2O$ (0.10 g, 1:1 molar ratio) were added to aqueous ethanol (40 cm^3) and the mixture heated under reflux for *ca* 15 mins.

The resulting suspension was reduced in volume to ca 20 cm^3 and the product filtered off as brown microcrystals which were then washed with ethanol, diethylether and dried *in vacuo* at 60°C, m.p. 157-159°C (decomp.). (0.42 g, 71.7%). (Found, C, 34.8; H, 4.2. Calc. for $C_{24}H_{33}Cl_6P_3Rh_2$:- C, 34.7; H, 4.0%). I.r. spectrum (nujol mull): ν(RhCl), 340m, 321m sh, 250w, 240w cm^{-1}. Treatment of the resulting mother liquor with a slight excess of $Na[BPh_4]$ (0.04 g) gave the compound Tri-μ-chlorodichlorotetrakis(dimethylphenylphosphine)dirhodium(III) tetraphenylborate as a yellow powder. This was filtered off, washed with ethanol and dried *in vacuo* at 60°C (0.10 g, 10.5%).

Tri-μ-chlorotrichlorotris(diethylphenylphosphine)dirhodium(III): $Rh_2Cl_6(PEt_2Ph)_3$

(i) Method as for (i) above using *mer*-$[RhCl_3(PEt_2Ph)_3]$ (0.54 g) and $RhCl_3.3H_2O$ (0.10 g, 1:1 molar ratio) from which the product was isolated as brown microcrystals. m.p. 139-142°C (decomp). (0.44 g, 63.2%). (Found, C, 39.5; H, 5.2. Calc. for $C_{30}H_{45}Cl_6P_3Rh_2$:- C, 39.3; H, 4.9%). I.r. spectrum (nujol mull); ν(RhCl), 341m, 318m, 250w, 239w cm^{-1}. Treatment of the resulting mother liquor with a slight excess of $Na[BPh_4]$ (0.05 g) gave the compound Tri-μ-chlorodichlorotetrakis-(diethylphenylphosphine)dirhodium(III) tetraphenylborate as a yellow powder (0.16 g, 15.4%).

(ii) The compounds $RhCl_3.3H_2O$ (0.30 g) and PEt_2Ph (0.36 g, 1:1.5 molar ratio) were refluxed in aqueous ethanol (50 cm^3) for 1 hr. On cooling the product separated as a brown powder which was filtered off, washed with ethanol, diethylether and dried in vacuo at 60°C (0.46 g, 88.1%). Reduction in volume of the resulting mother liquor to ca 20 cm^3 followed by treatment with a slight excess of $Na[BPh_4]$ (0.02 g) gave the compound Tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)dirhodium(III) tetraphenylborate as a yellow powder. This was filtered off, washed with ethanol and dried in vacuo (0.05 g, 6.4%).

Tri-μ-chlorotrichlorotris(di-n-propylphenylphosphine)dirhodium(III): $Rh_2Cl_6(PPr^n{}_2Ph)_3$

(i) Method as for (i) above using mer-$[RhCl_3(PPr^n{}_2Ph)_3]$ (0.59 g) and $RhCl_3.3H_2O$ (0.20 g, 1:1 molar ratio) from which the product was isolated as brown microcrystals, m.p. 118-121°C (decomp). (0.30 g, 19.9%). (Found, C, 43.0; H, 5.5. Calc. for $C_{36}H_{57}Cl_6P_3Rh_2$:- C, 43.2; H, 5.7%). I.r. spectrum (nujol mull); ν(RhCl), 340 m, 252w cm^{-1}. Treatment of the resulting mother liquor with a slight excess of $Na[BPh_4]$ (0.02 g) gave the compound Tri-μ-chlorodichlorotetrakis(di-n-propylphenylphosphine)dirhodium(III) tetraphenylborate as a yellow powder (0.05 g, 4.5%).

Tri-μ-chlorotrichlorotris(ethyldiphenylphosphine)dirhodium(III): $Rh_2Cl_6(PEtPh_2)_3$

(i) Method as for (i) above using mer-$[RhCl_3(PEtPh_2)_3]$ (0.65 g) and $RhCl_3.3H_2O$ (0.20 g, 1:1 molar ratio) from which the product was isolated as a brown powder, (0.53 g, 65.8%). (Found, C, 47.4; H, 4.3. Calc. for $C_{42}H_{45}Cl_6P_3Rh_2$:- C, 47.5; H, 4.3%). I.r. spectrum (nujol mull); ν(RhCl), 337 m, 251w

cm^{-1}. Treatment of the mother liquor with Na[BPh_4] did not yield any cationic complex.

Tri-μ-chlorodichlorotetrakis(dimethylphenylphosphine)dirhodium(III) tetraphenylborate: $[Rh_2Cl_5(PMe_2Ph)_4]BPh_4$

(i) Equimolar quantities of $[Rh_2Cl_6(PMe_2Ph)_3]$ (0.50 g), Ag[BF_4] (0.12 g) and PMe_2Ph (0.09 g) were heated under reflux in degassed aqueous ethanol (40 cm^3) for 1 hr and filtered hot through celite to remove the AgCl formed. The resulting orange mother liquor was reduced in volume to *ca* 15 cm^3 then treated with a slight excess of Na[BPh_4] (0.18 g). The product was obtained as a yellow powder which was filtered off, washed with ethanol and dried *in vacuo* at 60°C, m.p. 188-190°C (decomp). (0.62 g, 82.3%). (Found, C, 53.4; H, 5.2. Calc. for $C_{56}H_{64}BCl_5P_4Rh_2$:- C, 53.6; H, 5.1%). I.r. spectrum (nujol mull); ν(RhCl), 335m, 325m sh, 260w, 242m. [$\Lambda(1 \times 10^{-3}M)$ in CH_2Cl_2 = 44 $\Omega^{-1}cm^2mol^{-1}$].

(ii) The compounds *mer*-$[RhCl_3(PMe_2Ph)_3]$ (0.47 g) and $RhCl_3.3H_2O$ (0.10 g, 2:1 molar ratio) were added to aqueous ethanol (50 cm^3) and the mixture heated under reflux for 30 min. The resulting orange solution was reduced in volume to *ca* 20 cm^3 and, after cooling, filtered to remove the brown compound Tri-μ-chlorotrichlorotris(dimethylphenylphosphine)dirhodium(III), (0.07 g, 14.8%). Treatment of the resulting mother liquor with a slight excess of Na[BPh_4] (0.15 g) gave the product as a yellow powder which was filtered off, washed with ethanol and dried *in vacuo* at 60°C (0.46 g, 64.4%).

The compound can also be isolated as a byproduct, in low yield, following the addition of Na[BPh_4] to the mother liquor from the following reaction.

(iii) *mer*-$[RhCl_3(PMe_2Ph)_3]$ and $RhCl_3.3H_2O$ (1:1 molar ratio), (yield 10.5%).

Tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)dirhodium(III) tetraphenylborate: $[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$

(i) Method as for (i) above using $[Rh_2Cl_6(PEt_2Ph)_3]$ (0.30 g), $Ag[BF_4]$ (0.07 g) and PEt_2Ph (0.06 g) from which the product was obtained as a yellow powder, m.p. 164-165°C (decomp), (0.30 g, 67.1%). (Found, C, 56.0; H, 5.9. Calc. for $C_{64}H_{80}BCl_5P_4Rh_2$:- C, 56.2; H, 5.9%). *I.r. spectrum (nujol mull)*; ν(RhCl), 350m, 320m, 250m, 244m cm^{-1}. [Λ ($1x10^{-3}M$) in CH_2Cl_2 = 46 $\Omega^{-1}cm^2mol^{-1}$].

(ii) Method as for (ii) above using *mer*-$[RhCl_3(PEt_2Ph)_3]$ (0.54 g) and $RhCl_3.3H_2O$ (0.10 g, 2:1 molar ratio) from which the product was obtained as a yellow powder, (0.44 g, 56.5%), after filtration to remove the brown compound *Tri-μ-chlorotrichloro(diethylphenylphosphine)dirhodium(III)* (0.10 g, 191.%).

(iii) $RhCl_3.3H_2O$ (0.20 g) and PEt_2Ph (0.24 g, 1:2 molar ratio) were refluxed in aqueous ethanol (20-25 cm^3) for 1 hr. The resulting suspension was reduced in volume to *ca* 10 cm^3 whereupon the brown powder *Tri-μ-chlorotrichlorotris(diethylphenylphosphine)dirhodium(III)*, (0.04 g, 11.5%), was removed by filtration. Treatment of the resulting orange solution with a slight excess of $Na[BPh_4]$ (0.11 g) gave the compound as a yellow powder which was filtered off, washed with ethanol and dried *in vacuo* at 60°C. (0.38 g, 73.2%).

(iv) Method as for (iii) using $RhCl_3.3H_2O$ (0.20 g) and PEt_2Ph (0.31 g, 1:2.5 molar ratio) from which the compound was isolated as a yellow powder, (0.39 g, 75.1%), after filtration to remove the yellow mer-trichlorotris(diethylphenylphosphine)rhodium(III), (0.03 g, 5.6%).

The compound can also be isolated in lower yield by treatment of the ethanolic mother liquor from the following reactions with $Na[BPh_4]$.

(v) $RhCl_3.3H_2O$ and mer-$[RhCl_3(PEt_2Ph)_3]$ (1:1 molar ratio) - 15.4%.

(vi) $RhCl_3.3H_2O$ and PEt_2Ph (1:1.5 molar ratio) - 6.4%.

(vii) $RhCl_3.3H_2O$ and PEt_2Ph (1:3 molar ratio) - 57.8%.

(viii) $RhCl_3.3H_2O$ and PEt_2Ph (1:3.5 molar ratio) - 9.6%.

Tri-μ-chlorodichlorotetrakis(di-n-propylphenylphosphine)-dirhodium(III) tetraphenylborate: $[Rh_2Cl_5(PPr^n{}_2Ph)_4]BPh_4$

(i) Method as for (i) above using $[Rh_2Cl_6(PPr^n{}_2Ph)_3]$(0.31 g), $Ag[BF_4]$ (0.06 g) and $PPr^n{}_2Ph$ (0.06 g) from which the product was obtained as a yellow powder, m.p. 98-102°C (decomp), (0.29 g, 63.3%). (Found, C, 59.4; H, 6.8. Calc. for $C_{72}H_{96}BCl_5P_4Rh_2$:- C, 58.5; H, 6.5%). I.r. spectrum (nujol mull); ν(RhCl), 357m, 310w, 260m, 251w. [$\Lambda(1\times10^{-3}M)$ in CH_2Cl_2 = 49 $\Omega^{-1}cm^2mol^{-1}$].

(ii) Method as for (ii) above using mer-$[RhCl_3(PPr^n{}_2Ph)_3]$ (0.24 g) and $RhCl_3.3H_2O$ (0.04 g, 2:1 molar ratio) from which the product was obtained as a yellow powder (0.23 g, 68.2%), after filtration to remove the brown compound Tri-μ-chlorotrichlorotris(di-n-propylphenylphosphine)dirhodium(III), (0.03 g, 13.2%).

Reaction of mer-$[RhCl_3(PR_3)_3]$ with $RhCl_3.3H_2O$ (2:1 molar ratio)

a) $PR_3 = PMe_2Ph$

(i) The compounds mer-$[RhCl_3(PMe_2Ph)_3]$ (0.47 g) and $RhCl_3.3H_2O$ (0.10 g) were added to aqueous ethanol (50 cm^3) and the mixture heated under reflux for 30 min. The resulting orange solution was reduced in volume to ca 20 cm^3 and, after cooling, the complex Tri-μ-chlorotrichlorotris(dimethylphenylphosphine)dirhodium(III) separated as an orange-brown powder. This was filtered off, washed with ethanol, diethylether and dried in vacuo at 60°C, (0.07 g, 14.8%). Treatment of the resulting mother liquor with a slight excess of $Na[BPh_4]$ (0.15 g) gave the compound Tri-μ-chlorotrichlorotetrakis-(dimethylphenylphosphine)dirhodium(III) tetraphenylborate as a yellow powder which was filtered off, washed with ethanol and dried in vacuo at 60°C (0.46 g, 64.4%).

b) $PR_3 = PEt_2Ph$

(i) Method as for a(i) above using mer-$[RhCl_3(PEt_2Ph)_3]$ (0.54 g) and $RhCl_3.3H_2O$ (0.1 g) from which Tri-μ-chlorotrichlorotris(diethylphenylphosphine)dirhodium(III), (0.10 g, 19.1%) and Tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)dirhodium(III) tetraphenylborate (0.44 g, 56.5%) were isolated as an orange-brown powder and a yellow powder respectively.

c) $PR_3 = PPr^n{}_2Ph$

(i) Method as for a(i) above using mer-$[RhCl_3(PPr^n{}_2Ph)_3]$ (0.24 g) and $RhCl_3.3H_2O$ (0.04 g) from which Tri-μ-chlorotrichlorotris(di-n-propylphenylphosphine)dirhodium(III) (0.03 g, 13.2%) and Tri-μ-chlorodichlorotetrakis(di-n-propylphenylphosphine)dirhodium(III) tetraphenylborate (0.20 g, 59.3%) were isolated as an orange-brown powder and a yellow powder respectively.

d) $PR_3 = PEtPh_2$

(i) Method as for a(i) above using mer-[$RhCl_3(PEtPh_2)_3$] (0.52 g) and $RhCl_3.3H_2O$ (0.08 g) from which Tri-μ-chlorotrichlorotris(ethyldiphenylphosphine)dirhodium(III) (0.30 g, 46.5%) was isolated as an orange-brown powder. Treatment of the resulting mother liquor with Na[BPh_4] failed to yield any cationic complex.

Interaction of $Rh_2Cl_6(PEt_2Ph)_3$ with PEt_2Ph

(i) [$Rh_2Cl_6(PEt_2Ph)_3$] (0.22 g) and PEt_2Ph (0.04 g, 1:1 molar ratio) were added to chloroform (20 cm^3) and the solution shaken at ambient temperature overnight. The solution was then reduced to a very small volume and then worked-up with petroleum ether (b.p.40-60°C) to yield a yellow powder. This was shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to contain an inseparable mixture of mer-Trichlorotris(diethylphenylphosphine)rhodium(III) and Tri-μ-chlorotrichlorotris(diethylphenylphosphine)dirhodium(III).

(ii) [$Rh_2Cl_6(PEt_2Ph)_3$] (0.22 g) and PEt_2Ph (0.04 g, 1:1 molar ratio) were added to aqueous ethanol (20 cm^3) and the suspension shaken at ambient temperature for 2 days. The reaction mixture was reduced to a small volume and a yellow powder filtered off. This was shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to contain an inseparable mixture of mer-trichlorotris(diethylphenylphosphine)rhodium(III), tri-μ-chlorotrichlorotris(diethylphenylphosphine)dirhodium(III) and tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)-dirhodium(III) chloride.

(iii) $[Rh_2Cl_6[PEt_2Ph)_3]$ (0.30 g) and an excess of PEt_2Ph (0.22 g, 1:4 molar ratio) were refluxed in aqueous ethanol (50 cm^3) for 30 min. On cooling mer-trichlorotris(diethylphenylphosphine)rhodium(III) separated as orange microcrystals which were filtered off, washed with ethanol, diethylether and dried in vacuo at 60°C (0.41 g, 88.6%).

Reaction of $RhCl_3.3H_2O$ with PEt_2Ph (Various Rh:PEt_2Ph Ratios)

(a) 1:1 Molar ratio

$RhCl_3.3H_2O$ (0.20 g) and PEt_2Ph (0.12 g) were refluxed in aqueous ethanol (20-25 cm^3) for 1 hr. The resulting suspension was reduced in volume to ca 10 cm^3 and, after cooling, the complex Tri-μ-chlorotrichlorotris(diethylphenylphosphine)-dirhodium(III) filtered off as a brown powder which was then washed with ethanol, diethylether and dried in vacuo at 60°C (0.16 g, 45.9%). Treatment of the resulting mother liquor with $Na[BPh_4]$ failed to yield any cationic complex.

(b) 1:1.5 Molar ratio

$RhCl_3.3H_2O$ (0.30 g) and PEt_2Ph (0.36 g) were refluxed in aqueous ethanol (20-25 cm^3) for 1 hr. The resulting suspension was reduced in volume to ca 10 cm^3 and, after cooling, the complex Tri-μ-chlorotrichlorotris(diethylphenylphosphine)dirhodium(III) filtered off as a brown powder which was then washed with ethanol, diethylether and dried in vacuo at 60°C (0.46 g, 88.1%). Treatment of the resulting mother liquor with a slight excess of Na[BPh_4] (0.02 g) gave the compound Tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)-dirhodium(III) tetraphenylborate as a yellow powder. This was filtered off, washed with ethanol and dried *in vacuo* at 60°C (0.05 g, 6.4%).

(c) 1:2 Molar ratio

Method as (b) above using $RhCl_3.3H_2O$ (0.20 g) and PEt_2Ph (0.24 g) from which Tri-μ-chlorotris(diethylphenylphosphine)dirhodium(III), (0.04 g, 11.5%) and Tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)dirhodium(III) tetraphenylborate, (0.38 g, 73.2%) were isolated as brown and yellow powders respectively.

(d) 1:2.5 Molar ratio

Method as (b) above using $RhCl_3.3H_2O$ (0.20 g) and PEt_2Ph (0.31 g) from which *mer*-Trichlorotris(diethylphenylphosphine)-rhodium(III), (0.03 g, 5.6%) and Tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)dirhodium(III) tetraphenylborate, (0.39 g, 75.1%), were isolated as orange microcrystals and a yellow powder respectively.

(e) 1:3 Molar ratio

Method as (b) above using $RhCl_3.3H_2O$ (0.20 g) and PEt_2Ph (0.37 g) from which *mer*-trichlorotris(diethylphenylphosphine)-rhodium(III), (0.12 g, 22.3%), and Tri-μ-chlorodichlorotetrakis(diethylphenylphosphine)dirhodium(III) tetraphenylborate, (0.30 g, 57.8%), were isolated as orange microcrystals and a yellow powder respectively.

(f) 1:3.5 Molar ratio

Method as (b) above using $RhCl_3.3H_2O$ (0.2 g) and PEt_2Ph (0.43 g) from which mer-Trichlorotris(diethylphenylphosphine)rhodium(III), (0.36 g, 67.0%), and Tri-μ-chloro-dichlorotetrakis(diethylphenylphosphine)dirhodium(III) tetraphenylborate, (0.05 g, 9.6%), were isolated as orange microcrystals and a yellow powder respectively.

(g) 1:4 Molar ratio

Method as (b) above using $RhCl_3.3H_2O$ (0.2 g) and PEt_2Ph (0.48 g) from which mer-Trichlorotris(diethylphenylphosphine)-rhodium(III), (0.41 g, 76.3%) was isolated as orange microcrystals. Treatment of the mother liquor with $Na[BPh_4]$ failed to yield any of the cationic complex.

Reactions involving the $[Rh_2Cl_9]^{3-}$ anion

(i) $[NBu^n{}_4]_3[Rh_2Cl_9]$ (0.30 g), $Ag[BF_4]$ (0.18 g) and PEt_2Ph (0.16 g, 1:4:4 molar ratio) were refluxed in aqueous ethanol for 90 minutes. The suspension was then filtered hot through celite to remove AgCl. The celite was washed with dichloromethane and the washings added to the mother liquor. This was then reduced in volume whereupon Tri-μ-chlorotrichlorotris(diethylphenylphosphine)dirhodium(III) was isolated as a brown powder (0.07 g, 31.9%).

(ii) Method as for (i) above using $[NBu^n{}_4]_3[Rh_2Cl_9]$ (0.30 g), $Ag[BF_4]$ (0.27 g) and PEt_2Ph (0.24 g, 1:6:6 molar ratio) from which mer-Trichlorotris(diethylphenylphosphine)rhodium(III) was obtained as a yellow powder (0.26 g, 76.7%).

TABLE 2.1 - $^{31}P-\{^1H\}$ n.m.r. spectral data of the rhodium complexes discussed in chapter 2

	conditions	pattern	δ(p.p.m.)	$^1J_{Rh-P}$(Hz)	$^2J_{P-P}$(Hz)	intensity ratio
mer-[$RhCl_3(PMe_3)_3$]	a	d x t	7.5	113.3	28.5	1
		d x d	-8.1	84.1		2
mer-[$RhCl_3(PMe_2Ph)_3$]	a	d x t	4.7	112.3	25.5	1
		d x d	-5.6	85.4		2
mer-[$RhCl_3(PEt_2Ph)_3$]	a	d x t	17.3	112.4	22.0	1
		d x d	4.2	83.0		2
mer-[$RhCl_3(PPr^n_2Ph)_3$]	a	d x t	12.6	111.3	22.8	1
		d x d	-0.4	84.0		2
	b	d x t	14.8	110.2	22.8	1
		ABMX	δ_A 3.1	83.9	22.7 (cis)	2
			δ_B -3.4	83.9	497.3 (trans)	
mer-[$RhCl_3(PEtPh_2)_3$]	a	d x t	20.5	114.7	22.8	1
		d x d	9.0	84.3		2

Table 2.1 (cont.)

	conditions	pattern	δ(p.p.m.)	$^1J_{Rh-P}$(Hz)	$^2J_{P-P}$(Hz)	intensity ratio
$[RhCl_3(PMe_2Ph)_2(H_2O)]$	a	d(br)	16.7	114.8		
	c	ABX	δ_A 24.2	117.3	29.6	
			δ_B 18.6	111.5		
$[RhCl_3(PEt_2Ph)_2(H_2O)]$	a	d(br)	32.1	117.7		
	d	ABX	δ_A 36.4	120.6	25.0	
			δ_B 28.8	114.7		
	e	d(br)	29.7	117.2		
	f	ABX	δ_A 34.7	122.1	26.9	
			δ_B 24.3	114.7		
$[RhCl_3(PPr^n{}_2Ph)(H_2O)]$	e	d(br)	24.0	118.2		
	f	ABX	δ_A 28.5	121.6	26.9	
			δ_B 18.6	113.8		

Table 2.1 (cont.)

	conditions	pattern	δ(p.p.m.)	$^1J_{Rh-P}$(Hz)	$^2J_{P-P}$(Hz)	intensity ratio
$[Rh_2Cl_6(PMe_2Ph)_3]$	a	d	33.6	112.8		1
		d	21.7	117.2		2
$[Rh_2Cl_6(PEt_2Ph)_3]$	a	d	49.2	114.8		1
		d	37.5	117.2		2
$[Rh_2Cl_6(PPr^n{}_2Ph)_3]$	a	d	42.8	114.3		1
		d	31.1	118.2		2
$[Rh_2Cl_6(PEtPh_2)_3]$	a	d	46.4	117.2		1
		d	34.3	119.6		2
$[Rh_2Cl_5(PMe_2Ph)_4]BPh_4$	a	d(br)	23.4	116.0		
	d	ABX	δ_A 26.9	117.2	24.7	
			δ_B 23.2	115.2		

Table 2.1 (cont.)

	conditions	pattern		δ (p.p.m.)	$^1J_{Rh-P}$ (Hz)	$^2J_{P-P}$ (Hz)	intensity ratio
$[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$	a	d(br)		38.8	119.6		
	d	ABX	δ_A	42.9	117.9	20.1	
			δ_B	36.7	116.5		
$[Rh_2Cl_5(PPr^n{}_2Ph)_4]BPh_4$	a	d(br)		32.6	116.7		
	d	ABX	δ_A	33.9	118.0	20.3	
			δ_B	28.3	115.4		

a) $CDCl_3$, RT

b) CD_2Cl_2, 183K

c) $CDCl_3$/EtOH, 223K

d) $CDCl_3$, 223K

e) EtOH/d^6-acetone capillary lock, RT

f) EtOH/d^6-acetone capillary lock, 223K

TABLE 2.2 - Percentage of products isolated from the reaction of $RhCl_3.3H_2O$ with various ratios of PEt_2Ph [(a)]

Rh : PEt_2Ph	1:1	2:3	1:2	2:5	1:3	2:7	1:4
$[Rh_2Cl_6(PEt_2Ph)_3]$	46	88	11	0	0	0	0
$[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$	0	6	73	75	58	10	0
mer-$[RhCl_3(PEt_2Ph)_3]$	0	0	0	6	22	67	76

(a) Reaction in refluxing ethanol for 1 hour.

Table 2.3 - Fractional Coordinates for

mer-[$RhCl_3(PEt_2Ph)_2(H_2O)$]. 0.5 EtOH

Fractional coordinates with standard deviation ( )

Atom	x	y	z
Rh(1)	0.04442(18)	0.12134(13)	0.85790(11)
P(1)	-0.0006(6)	0.1466(5)	0.7235(4)
P(2)	0.2422(6)	0.1518(4)	0.8363(4)
Cl(1)	0.1278(6)	-0.0402(4)	0.8565(4)
Cl(2)	-0.0444(6)	0.2785(4)	0.8743(4)
Cl(3)	-0.1575(6)	0.0773(4)	0.8993(4)
O(1)	0.0641(15)	0.1061(11)	0.9916(9)
C(1)	-0.1651(23)	0.1855(20)	0.7183(15)
C(2)	-0.2076(24)	0.2224(21)	0.6308(14)
C(3)	0.048(4)	0.0406(24)	0.6724(19)
C(4A)	-0.004(7)	0.028(6)	0.590(3)
C(4B)	-0.047(7)	-0.025(6)	0.698(5)
C(5)	-0.0019(16)	0.3321(10)	0.6738(10)
C(6)	0.0257(16)	0.4119(10)	0.6245(10)
C(7)	0.1162(16)	0.4021(10)	0.5590(10)
C(8)	0.1791(16)	0.3126(10)	0.5427(10)
C(9)	0.1516(16)	0.2328(10)	0.5920(10)
C(10)	0.0611(16)	0.2426(10)	0.6575(10)
C(11)	0.2549(23)	0.2721(16)	0.8472(13)
C(12)	0.2310(23)	0.2968(17)	0.9387(13)
C(13)	0.3360(17)	0.0804(17)	0.9148(12)
C(14)	0.4710(21)	0.0981(20)	0.9051(17)
C(15)	0.3682(14)	0.0274(9)	0.7282(8)
C(16)	0.4498(14)	0.0011(9)	0.6608(8)
C(17)	0.4980(14)	0.0698(9)	0.6074(8)
C(18)	0.4646(14)	0.1648(9)	0.6212(8)
C(19)	0.3830(14)	0.1911(9)	0.6885(8)
C(20)	0.3348(14)	0.1224(9)	0.7420(8)
Rh(2)	0.52520(17)	0.41422(13)	0.35379(11)
P(3)	0.4727(5)	0.4437(4)	0.2221(4)
P(4)	0.7199(5)	0.3303(4)	0.3271(3)
Cl(4)	0.6132(5)	0.5498(4)	0.3515(4)
Cl(5)	0.4348(6)	0.2798(4)	0.3697(4)
Cl(6)	0.3288(6)	0.5051(4)	0.4020(4)
O(2)	0.5508(14)	0.3793(11)	0.4884(9)
C(21)	0.5012(22)	0.5574(14)	0.1703(13)
C(22)	0.4122(23)	0.6423(17)	0.2047(16)
C(23)	0.3073(21)	0.4469(23)	0.2153(15)
C(24)	0.2701(3)	0.459(3)	0.1253(16)
C(25)	0.5114(16)	0.2675(11)	0.1614(10)
C(26)	0.5577(16)	0.2024(11)	0.1044(10)
C(27)	0.6330(16)	0.2277(11)	0,0351(10)
C(28)	0.6620(16)	0.3182(11)	0.0228(10)
C(29)	0.6157(16)	0.3834(11)	0.0798(10)
C(30)	0.5404(16)	0.3580(11)	0.1490(10)

Table 2.3 (cont.)

Atom	x	y	z
C(31)	0.8184(20)	0.3508(17)	0.4070(15)
C(32)	0.9534(19)	0.3012(19)	0.3952(19)
C(33)	0.7375(24)	0.2033(15)	0.3338(12)
C(34)	0.712(3)	0.1563(18)	0.4242(13)
C(35)	0.8433(14)	0.4512(9)	0.2157(9)
C(36)	0.9171(14)	0.4729(9)	0.1446(9)
C(37)	0.9569(14)	0.4059(9)	0.0883(9)
C(38)	0.9230(14)	0.3171(9)	0.1033(9)
C(39)	0.8492(14)	0.2954(9)	0.1744(9)
C(40)	0.8093(14)	0.8624(9)	0.2307(9)

Ethanol solvent molecule

Atom	x	y	z
C(41)	0.220(19)	0.145(15)	0.220(13)
C(42)	0.301(9)	0.091(8)	0.148(7)
C(44)	0.3151(14)	0.085(10)	0.223(10)
C(45)	0.231(13)	0.169(11)	0.159(10)

Table 2.4 - Selected bond lengths for mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$

Bond lengths (Å) with standard deviations ( )

Molecule 1		Molecule 2	
Rh(1) - P(1)	2.271(6)	Rh(2) - P(3)	2.254(6)
Rh(1) - P(2)	2.306(6)	Rh(2) - P(4)	2.302(6)
Rh(1) -Cl(1)	2.351(6)	Rh(2) -Cl(4)	2.347(6)
Rh(1) -Cl(2)	2.339(6)	Rh(2) -Cl(5)	2.330(7)
Rh(1) -Cl(3)	2.457(7)	Rh(2) -Cl(6)	2.437(6)
Rh(1) - O(1)	2.196(16)	Rh(2) - O(2)	2.231(15)
P(1) - C(1)	1.82(3)	P(3) -C(21)	1.830(23)
P(1) - C(3)	1.80(4)	P(3) -C(23)	1.84(3)
P(1) -C(10)	1.851	P(3) -C(30)	1.828(18)
P(2) -C(11)	1.804(24)	P(4) -C(31)	1.865(25)
P(2) -C(13)	1.830	P(4) -C(33)	1.804(23)
P(2) -C(20)	1.813(15)	P(4) -C(40)	1.839(16)
C(1) - C(2)	1.55	C(21) -C(22)	1.55
C(3) -C(4A)	1.55	C(23) -C(24)	1.55
C(3) -C(4B)	1.55	C(25) -C(26)	1.395(23)
C(5) - C(6)	1.395(23)	C(25) -C(30)	1.395(23)
C(5) -C(10)	1.395(23)	C(31) -C(32)	1.54
C(11) -C(12)	1.56	C(33) -C(34)	1.56
C(13) -C(14)	1.56	C(35) -C(36)	1.395(21)
C(15) -C(16)	1.395(20)	C(35) -C(40)	1.395(21)
C(15) -C(20)	1.395(20)		

Table 2.5 - Selected bond angles for mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$

Bond angles (°) with standard deviation ( )

Molecule 1		Molecule 2	
P(1) -Rh(1) - P(2)	96.99(23)	P(3) -Rh(2) - P(4)	97.63(22)
P(1) -Rh(1) -Cl(1)	96.39(23)	P(3) -Rh(2) -Cl(4)	95.22(22)
P(1) -Rh(1) -Cl(2)	88.99(23)	P(3) -Rh(2) -Cl(5)	89.77(23)
P(1) -Rh(1) -Cl(3)	90.50(23)	P(3) -Rh(2) -Cl(6)	90.53(22)
P(1) -Rh(1) - O(1)	172.8(4)	P(3) -Rh(2) - O(2)	171.8(4)
P(2) -Rh(1) -Cl(1)	88.10(22)	P(4) -Rh(2) -Cl(4)	88.18(21)
P(2) -Rh(1) -Cl(2)	94.14(22)	P(4) -Rh(2) -Cl(5)	93.41(23)
P(2) -Rh(1) -Cl(3)	172.05(23)	P(4) -Rh(2) -Cl(6)	171.53(23)
P(2) -Rh(1) - O(1)	88.6(4)	P(4) -Rh(2) - O(2)	88.0(4)
Cl(1) -Rh(1) -Cl(2)	173.88(23)	Cl(4) -Rh(2) -Cl(5)	174.52(23)
Cl(1) -Rh(1) -Cl(3)	88.42(22)	Cl(4) -Rh(2) -Cl(6)	88.83(21)
Cl(1) -Rh(1) - O(1)	88.4(4)	Cl(4) -Rh(2) - O(2)	90.8(4)
Cl(2) -Rh(1) -Cl(3)	88.64(22)	Cl(5) -Rh(2) -Cl(6)	88.87(23)
Cl(2) -Rh(1) - O(1)	86.0(4)	Cl(5) -Rh(2) - O(2)	84.0(4)
Cl(3) -Rh(1) - O(1)	84.2(4)	Cl(6) -Rh(2) - O(2)	84.1(4)
Rh(1) - P(1) - C(1)	109.5(9)	Rh(2) - P(3) -C(21)	114.5(7)
Rh(1) - P(1) - C(3)	110.9(12)	Rh(2) - P(3) -C(23)	112.0(9)
Rh(1) - P(1) -C(10)	117.7(6)	Rh(2) - P(3) -C(30)	118.2(6)
C(1) - P(1) - C(3)	109.5(15)	C(21) - P(3) -C(23)	104.6(11)
C(1) - P(1) -C(10)	101.6(10)	C(21) - P(3) -C(30)	104.6(9)
C(3) - P(1) -C(10)	107.1(13)	C(23) - P(3) -C(30)	101.3(10)
Rh(1) - P(2) -C(11)	114.4(8)	Rh(2) - P(4) -C(31)	108.2(8)
Rh(1) - P(2) -C(13)	109.2(7)	Rh(2) - P(4) -C(33)	117.5(8)
Rh(1) - P(2) -C(20)	120.1(5)	Rh(2) - P(4) -C(40)	119.0(5)
C(11) - P(2) -C(13)	104.8(10)	C(31) - P(4) -C(33)	103.6(11)
C(11) - P(2) -C(20)	105.4(9)	C(31) - P(4) -C(40)	101.8(9)
C(13) - P(2) -C(20)	101.3(9)	C(33) - P(4) -C(40)	104.6(9)
P(1) - C(1) - C(2)	115.5(18)	P(3) -C(21) -C(22)	112.6(16)
P(1) - C(3) -C(4A)	121.6(36)	P(3) -C(23) -C(24)	113.2(20)
P(1) - C(3) -C(4B)	108.5(36)	P(4) -C(31) -C(32)	114.0(17)
P(2) -C(11) -C(12)	112.9(16)	P(4) -C(33) -C(34)	112.6(16)
P(2) -C(13) -C(14)	112.4(16)		

Chapter 3

Synthesis and Characterisation of the Complex mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$

3.1 Introduction

Like their rhodium counterparts, there has been considerable interest in the spectroscopic and chemical properties of the mononuclear iridium(III) halide tertiary phosphine species (see chapter 1, section 1.4.1). To date, however, there have been few reports of binuclear iridium(III) compounds containing only tertiary phosphine and halide ligands, although complexes which also contain hydride or carbonyl ligands are well known.

Following our studies of the binuclear rhodium complexes, described in chapter 2, it was envisaged that analogous synthetic routes could be employed to prepare the related iridium complexes and these studies form the subject of this chapter.

3.2 Results and discussion

The only binuclear iridium(III) complex described in section 1.4.2 which has been unequivocally characterised by X-ray analysis is the triple iodo-bridged cation $[(PMePh_2)_2IIrI_3IrI(PMePh_2)_2]^+$ [75]. Interestingly, the configuration of this binuclear iridium cation (Fig.1.3) differs from that established for the analogous dirhodium chloro-cations $[Rh_2Cl_5(PR_3)_4]^+$, (21), (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) which are discussed in section 2.4. Although both complexes have two phosphines attached to each metal centre, the two configurations differ in the arrangement of the phosphines with respect to the bridging halogen atoms and to the ligands on the other metal centre which they eclipse.

In the case of the dirhodium cation, configuration (21), one bridging chlorine is trans to two phosphines, with the other two bridging chlorines trans to one phosphine and one terminal chloride ligand. Furthermore, the phosphines on a given rhodium centre are magnetically inequivalent because they are eclipsed by a phosphine and chloride group respectively. However, the binuclear iridium cation has two bridging iodines which are trans to two phosphines with the other bridging iodine trans to two terminal iodines. In this case both phosphorus atoms on a given iridium are eclipsed by tertiary phosphine and are consequently magnetically equivalent. On the basis of this structure, the $^{31}P-\{^{1}H\}$ n.m.r. spectrum of this binuclear iridium cation would be expected to show a singlet and not to exhibit temperature dependent behaviour.

The structural differences observed between these binuclear rhodium and iridium cations led to the thought that use of a different phosphine ligand might produce a binuclear iridium cation with configuration (21). It was also of interest to determine whether the triple iodo-bridge could be cleaved with an excess of iodide ion to generate the solvated monomer $[IrI_3(PR_3)_2(s)]$ (s = solvent molecule) corresponding to the mer-$[RhCl_3(PR_3)_2(H_2O)]$ found in the analagous rhodium system.

Since the complexes $[Rh_2Cl_5(PR_3)_4]^+$, which exhibit configuration (21), were prepared with dialkylphenylphosphines it was hoped that the complex $[Ir_2I_5(PMe_2Ph)_4]^+$, if successfully generated from the treatment of $[Ir(PMe_2Ph)_4]^+$ with I_2, would crystallise in configuration (21) and not as for the known $[Ir_2I_5(PMePh_2)_4]^+$ cation.

The iridium(I) cations $[Ir(PR_3)_4]X$ [PR_3 = PMe_2Ph, $PMePh_2$, $P(OMe)_2Ph$, $P(OMe)Ph_2$, $P(OEt)Ph_2$; X = BPh_4, PF_6 or ClO_4] were first prepared by Haines and Singleton by the reaction of $[IrCl(COD)]_2$ (COD = cycloocta-1,5-diene) with eight molar equivalents of the PR_3 ligand in refluxing ethanol followed by treatment with an excess of X^-. However, the authors also stressed that the preparation of $[Ir(PMe_2Ph)_4]BPh_4$ must be performed under strict anaerobic conditions to prevent the formation of the dioxygen adduct. Indeed, the salt $[Ir(PMe_2Ph)_4]BPh_4$ was found to absorb oxygen slowly in the solid state and rapidly in solution to give the dioxygen product $[Ir(O_2)(PMe_2Ph)_4]BPh_4$ [92]. Similarly in this work, spectral analysis of the product obtained by this route, using the $[PF_6]^-$ counter anion, indicated the presence of the dioxygen adduct. Thus the $^{31}P-\{^1H\}$ n.m.r. spectrum of the product in $CDCl_3$ showed a singlet at δ = -35.9 p.p.m. and an A_2X_2 pattern (δ_A = -99.8 p.p.m., δ_B = -112.5 p.p.m., $^2J_{P-P}$= 19.5Hz) corresponding to the $[Ir(PMe_2Ph)_4]^+$ cation and the dioxygen adduct respectively. Confirmation that the impurity was in fact the dioxygen adduct was obtained from the infrared spectrum which showed a ν(O-O) vibration at 841 cm^{-1}.

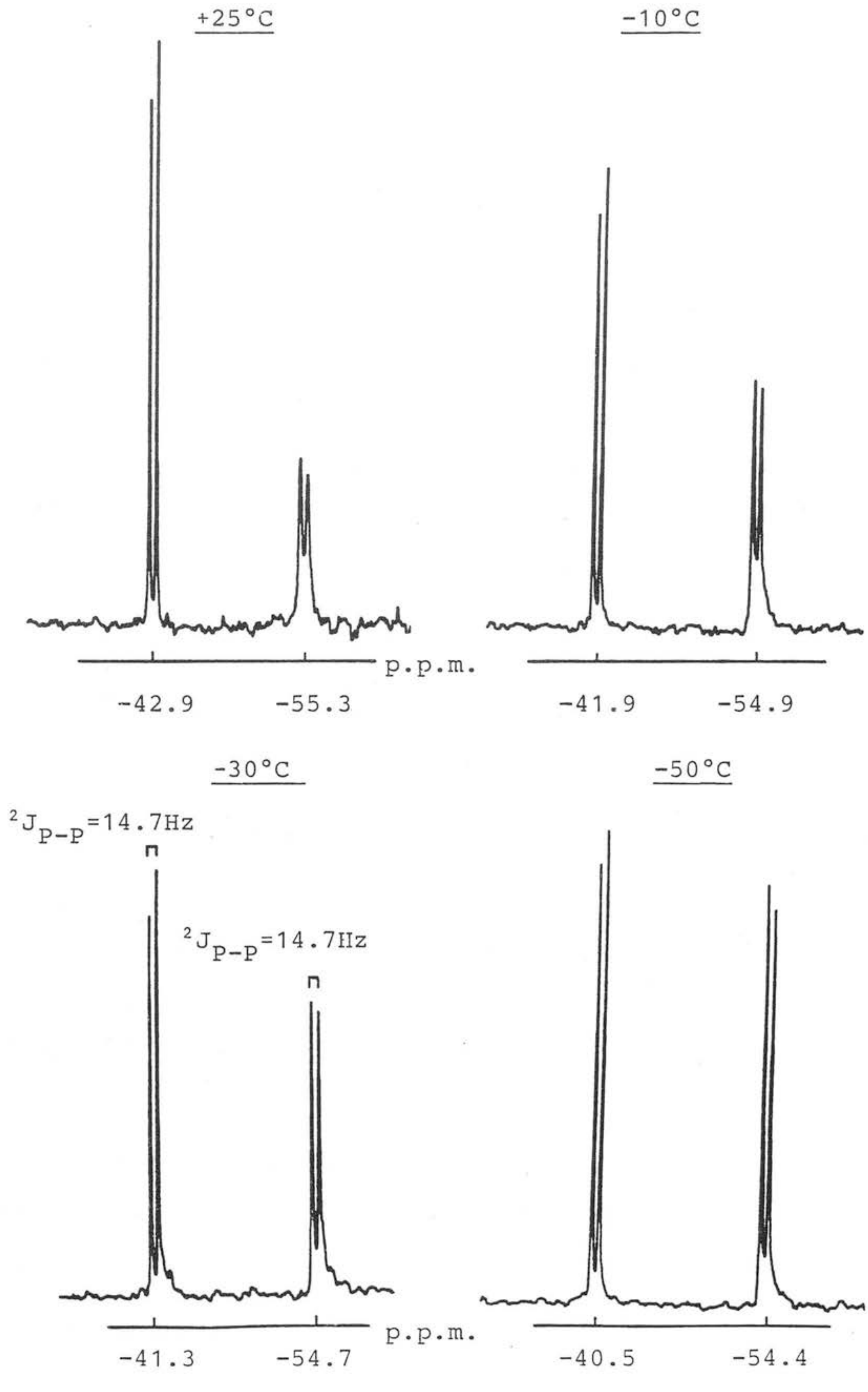
As a result of this marked susceptibility to dioxygen, the preparation of the binuclear iridium species was attempted as a "one-pot" synthesis conducted under an atmosphere of dinitrogen. In order to generate the iridium(I) cationic salt, an ethanolic solution containing a large amount of $NH_4[PF_6]$ was degassed and, following the addition of

$[IrCl(COD)]_2$ and PMe_2Ph (1:8 molar ratio) respectively, this was then heated under reflux for 15 minutes. On cooling, a biege powder, presumed to be $[Ir(PMe_2Ph)_4]PF_6$, was deposited. A large excess of I_2 was then added to the suspension and further refluxing, for several hours, resulted in the precipitation of an orange powder. Soxhlet extraction of this product with chloroform resulted in a deep orange solution which deposited orange-red crystals on slow evaporation in air.

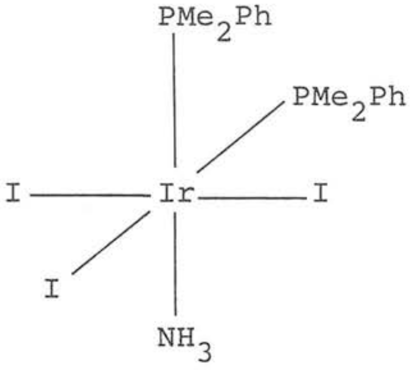
The $^{31}P-\{^1H\}$ n.m.r. spectra exhibited by these crystals in solution were found to be temperature dependent. Thus, at ambient temperature in $CDCl_3$ the spectrum obtained contains two doublets, the one at higher frequency (δ = -42.9 p.p.m. $^2J_{P-P}$=14.7Hz) being sharp whereas the other doublet (δ = -55.3 p.p.m., $^2J_{P-P}$=14.7Hz) is much broader. On cooling, the higher frequency resonance remains unchanged; however, the lower frequency signal is observed to sharpen considerably such that at 223K it appears to be as sharp and as intense as the unchanged resonance (see Fig.3.1). Furthermore, the low frequency signal broadened slightly on elevating the temperature to 343K.

If the structure was as shown in (21), the cation $[Ir_2I_5(PMe_2Ph)_4]^+$ could give rise to an AX pattern in the $^{31}P-\{^1H\}$ n.m.r. spectrum. However, the unusual temperature dependence, which is observed for only one of the doublets, could not be readily explained by this structure. After further investigation it became apparent that the crystals were not that of the desired binuclear iridium cation since they were found to be non-conducting in nitromethane and their

Fig.3.1 The Variable temperature $^{31}P-\{^{1}H\}$ n.m.r. spectra of mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$, (in $CDCl_3$)



elemental analysis indicated the presence of nitrogen. The composition and structure of the species was subsequently revealed by X-ray analysis to be <u>mer</u>-$[IrI_3(PMe_2Ph)_2(NH_3)]$, (24).



(24)

The presence of magnetically inequivalent PMe_2Ph groups in (24) is responsible for the AX pattern with the sharp, higher frequency resonance assigned to the phosphine <u>trans</u> to iodine and the broad, lower frequency signal arising from the phosphine <u>trans</u> to the ammine group. The broadening observed at ambient temperature in the latter doublet is attributed to interaction between the spin-½ ^{31}P nucleus and the quadrupolar (I=1) ^{14}N nucleus. On the basis of spin-coupling considerations, both lines of the latter doublet would be expected to be split into three lines of equal intensity, with the splitting due to the scalar coupling constant $^2J_{NP}$. The intensities of the three lines should be equal because each spin state m_I (^{14}N) = +1,0 and -1, is equally probable. In the above spectra (Fig.3.1), this splitting is not observed because of the rapid spin-lattice

(T_{1N}) relaxation times of the ^{14}N nucleus. As the sample is cooled, this ^{14}N relaxation process becomes more efficient and this increased rate of relaxation of the ^{14}N nucleus thereby broadens the lines. When the exchange rate (i.e. T_{1N}^{-1}) becomes comparable in magnitude to $^2J_{NP}$, the triplet lines begin to merge, and a single line is observed when $T_{1N}^{-1} > {}^2J_{NP}$. The width of this resonance line decreases as T_{1N}^{-1} increases still further. At this stage of the process, the ^{14}N nucleus has become self-decoupled from the ^{31}P nuclei and the expected AX pattern is observed in the $^{31}P-\{^1H\}$ n.m.r. spectrum [Fig.3.1(iv)].

It is interesting to note the similarities between the complex mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$, (24), and the aquated monomer mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$, (21). Both structures possess two mutually trans halogen atoms, a phosphine trans to a halogen and a phosphine trans to a neutral donor ligand (NH_3 or H_2O). Reaction of the aquated monomer mer-$[RhCl_3(PR_3)_2(H_2O)]$ ($R_3 = Me_2Ph, Et_2Ph$), in $CDCl_3$, with PMe_2Ph or PEt_2Ph respectively was found to generate the corresponding meridional trisphosphine complex at ambient temperature (see section 2.5). Similarly, gentle warming of a $CDCl_3$ solution of the analogous mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$ in the presence of an excess of PMe_2Ph was found to give the meridional compound $[IrI_3(PMe_2Ph)_3]$ (in situ $^{31}P-\{^1H\}$ n.m.r. evidence).

To date, our attempts to prepare the ammine complex by treating previously isolated samples of $[Ir(PMe_2Ph)_4]PF_6$ and its dioxygen adduct contaminent with $NH_4[PF_6]$ and I_2 under refluxing conditions have proved fruitless. Therefore the mechanism of formation of the ammine complex is not known although presumably deprotonation of $[NH_4]^+$, presumably by traces of $[EtO]^-$ anion, and oxidation of Ir^{I} to Ir^{III} by iodine are important steps.

3.2.2 The X-ray crystal structure of *mer*-$[IrI_3(PMe_2Ph)_2(NH_3)]$

Details of the method solution of this structure are given in the experimental section. The final atomic positions are presented in Table 3.1 and selected bond distances and angles in Table 3.2.

The coordination about the iridium atom is octahedral. The high *trans* influence of phosphine ligands compared with halide is reflected in the iridium-iodine bond lengths. When *trans* to phosphine the Ir-I bond length is 2.741(1)Å whereas the average length is 2.674(10)Å for the mutually *trans* iodine atoms. Similar effects are observed in the cation $[Ir_2I_5(PMe_2Ph)_4]^+$ 75 which shows corresponding bond lengths of 2.75(1)Å and 2.68(1)Å.

The molecular structure of the complex is shown in Figure 3.2, an ORTEP diagram of the molecule in Figure 3.3 and a cell packing diagram in Figure 3.4.

Fig.3.2 The structure of mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$

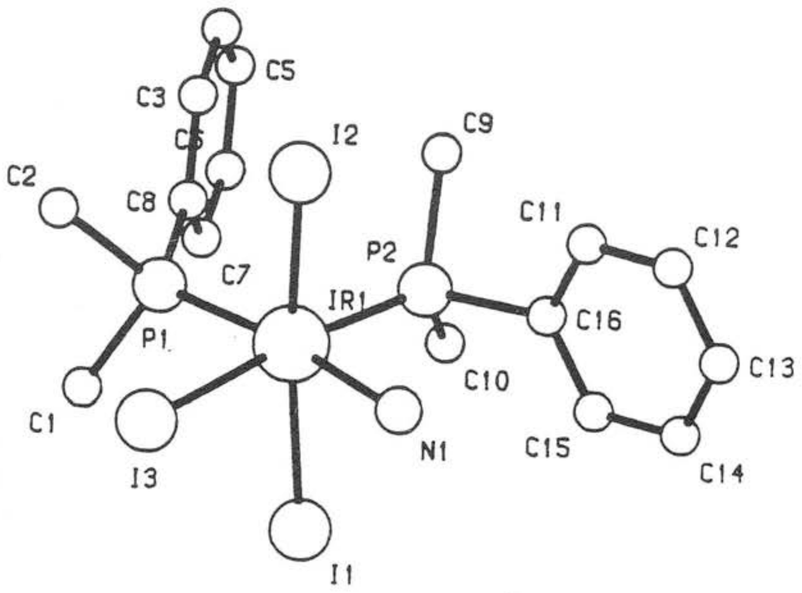


Fig.3.3 An ORTEP diagram of mer-[IrI$_3$(PMe$_2$Ph)$_2$(NH$_3$)]

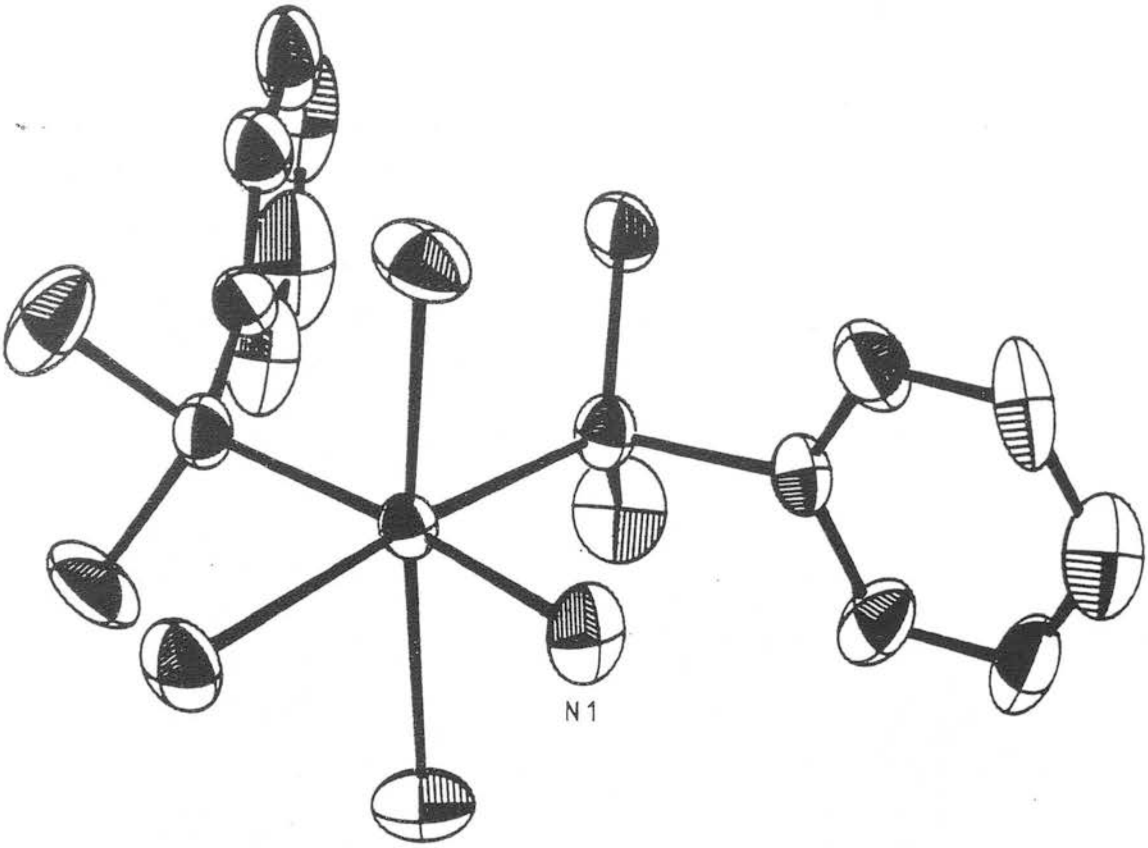
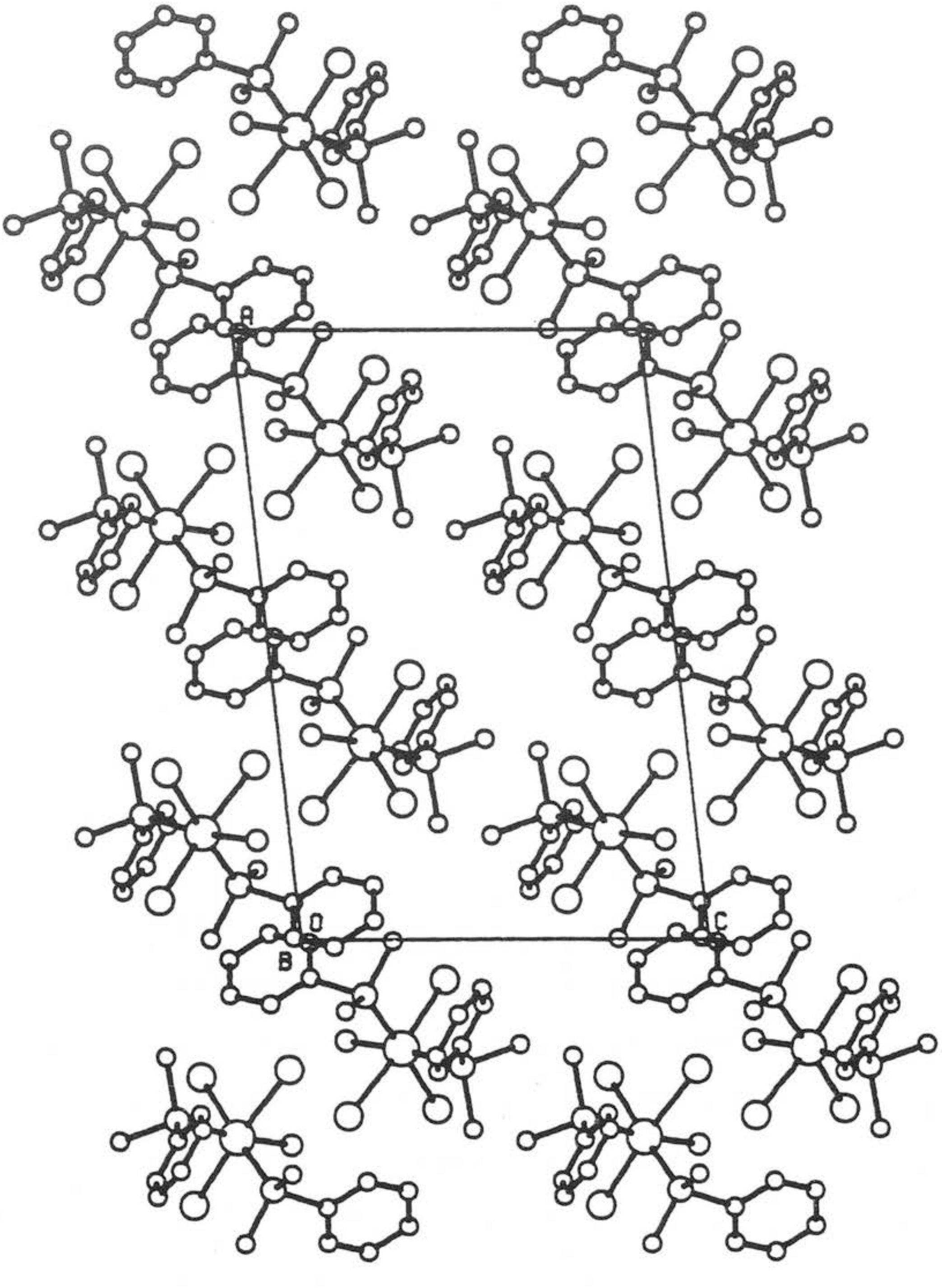


Fig.3.4 A crystal packing diagram of mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$



3.3 Further attempts to synthesise binuclear iridium(III) complexes

It was hoped that it would be possible to prepare analogous binuclear iridium(III) compounds by employing similar routes to those used to prepare successfully the binuclear rhodium compounds described in chapter 2.

However reaction of $IrCl_3.3H_2O$ with 2 molar equivalents of PEt_2Ph under refluxing conditions in either ethanol or 2-methoxyethanol resulted only in the formation of mer-$[IrCl_3(PEt_2Ph)_3]$. In agreement with previous studies[67] it was found that 2-methoxyethanol gave the higher yield (58% compared to 32% for ethanol) in much shorter reaction time. Presumably mer-$[IrCl_3(PEt_2Ph)_3]$ is formed by sequential displacement of H_2O by PEt_2Ph, although examination of the reaction solution by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy revealed that there were no other phosphine containing species present. This suggests that the formation of the iridium analogue of the aquated monomer mer-$[RhCl_3(PEt_2Ph)_2(H_2O)]$ is not favoured with respect to mer-$[IrCl_3(PMe_2Ph)_3]$. Reaction of $IrCl_3.3H_2O$ with equimolar quantities of mer-$[IrCl_3(PR_3)_3]$ (R_3 = Me_2Ph, Et_2Ph) confirms this conclusion, since, even after prolonged refluxing in 2-methoxyethanol, no reaction was observed and only starting materials were recovered. The $IrCl_3.3H_2O$ appears to be unable to abstract a phosphine group from the mer-$[IrCl_3(PR_3)_3]$ to generate the solvated monomers $[IrCl_3(PR_3)(H_2O)_2]$ and $[IrCl_3(PR_3)_2(s)]$, (s = solvent), which it was hoped would then couple, with the elimination of solvent molecules, to give the binuclear species

$[Ir_2Cl_6(PR_3)_3]$.

Under more forcing conditions i.e. in iso-butylalcohol under reflux, reaction was observed. However, the product was shown by infrared and ^{31}P n.m.r. spectroscopy to be a mixture of inseparable iridium-hydride species since the infrared spectrum contained sharp bands at 2220 and 2253 cm^{-1} corresponding to $\nu(Ir\text{-}H)$ stretches, and the proton coupled ^{31}P n.m.r. spectrum showed $^2J_{PH}$ couplings of 102.7 and 96.3Hz (trans) and 12.3, 10.9 and 10.2Hz (cis). This product mixture was not investigated further.

In an attempt to eliminate the hydride species, and yet maintain the more forcing conditions, equimolar quantities of $IrCl_3.3H_2O$ and mer-$[IrCl_3(PEt_2Ph)_3]$ were heated in 1-methylnaphthalene. Since the starting materials were not particularly soluble in the reaction medium, it was not surprising that no reaction was observed and only starting materials recovered.

In contrast to $RhCl_3.3H_2O$ which abstracts a phosphine from the complexes mer-$[RhCl_3(PR_3)_3]$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$ and $EtPh_2$) to form the binuclear compounds $[Rh_2Cl_6(PR_3)_3]$ (see section 2.3), $IrCl_3.3H_2O$ would appear to be unable to do likewise with mer-$[IrCl_3(PEt_2Ph)_3]$. Despite refluxing in both ethanol and 2-methoxyethanol, $RhCl_3.3H_2O$ was also found to be unable to abstract a phosphine from $[IrCl_3(PEt_2Ph)_3]$ and therefore the solvated monomer $[RhCl_3(PEt_2Ph)(H_2O)_2]$ and $[IrCl_3(PEt_2Ph)_2(s)]$ (s = solvent molecule) and ultimately the mixed metal binuclear species $[(PEt_2Ph)Cl_2RhCl_3IrCl(PEt_2Ph)_2]$ were not generated.

Finally, rather surprisingly, attempted reaction of $IrCl_3.3H_2O$ with an equimolar quantity of mer-$[RhCl_3(PEt_2Ph)_3]$ in both ethanol and 2-methoxyethanol under reflux also proved to be unsuccessful since only starting materials were recovered.

3.4 Conclusions

Attempts to synthesise the di-iridium and mixed metal rhodium-iridium binuclear triple chloro-bridged tertiary phosphine complexes analagous to the dirhodium species described in Chapter 2 have been unsuccessful. The possible method of preparation involving coupling of the appropriate solvated monomers failed probably because of the extreme inertness of the phosphine to iridium bond.

However, the isolation of the complex mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$ is encouraging. Although the NH_3 group could be displaced by PMe_2Ph, more forcing conditions were required compared with the solvated monomers mer-$[RhCl_3(PR_3)_2(H_2O)]$ (R_3 = Me_2Ph, Et_2Ph). Synthesis of a similar complex with the ammonia ligand replaced by a more labile group could lead to the type of species required for the formation of binuclear iridium halogen bridged compounds.

3.5 Experimental

Microanalysis, infrared and n.m.r. spectra, melting point and conductivity measurements were obtained as in Chapter 2, Section 2.10.

Materials

As in Chapter 2 together with $IrCl_3.3H_2O$ (from Johnson Matthey P.L.C.).

The compounds $[IrCl(COD)]_2$[93] and mer-$[IrCl_3(PR_3)_3]$ (R_3 = Me_2Ph, Et_2Ph)[67] were synthesised by literature methods.

Crystal structure determination of mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$

Crystals suitable for X-ray analysis were obtained by the evaporation in air of a chloroform solution of the complex. An orange red crystal (0.30x0.20x0.13 mm) was chosen and accurate cell dimensions were obtained by least squares refinement of 21 reflections measured on an Enraf-Nonius CAD4 diffractometer with monochromatised Mo-K_α radiation.

Crystal Data: $C_{16}H_{25}I_3IrNP_2$, M = 582.8.
$\underline{a}$ = 17.940(4), $\underline{b}$ = 11.062(5), $\underline{c}$ = 11.743(2) Å,
β = 96.63(2)°, V = 2314.9 $Å^3$, D_c = 2.485 g cm^{-3}, Z = 4,
F(000) = 1576, μ(Mo-K_α) = 98.44 cm^{-1}, λ(Mo-K_α) = 0.71069 Å.
The space group is $P2_1/c$.

Intensity data were collected by an ω-2θ scan for θ out to 22°. Intensities were measured for 2830 independent reflections of which 2173 had I>2.50(I). No crystal decay was observed and an empirical absorption correction was applied[94].

Structure solution and refinement

The refinement was based on the 2173 reflections with $I > 2.5\sigma(I)$. The structure was solved by conventional Patterson and difference Fourier techniques. The iridium and the three iodine atoms were located from a Patterson map using SHELX-84 [89]. Subsequent difference Fourier syntheses revealed all non-hydrogen atoms in the molecule. The structure refinement was carried out using SHELX[90]. All the atoms were refined anisotropically and the phenyl rings of the phosphines were constrained to be idealised planar hexagons. No hydrogen atoms were included in the refinement. A weighting scheme of the form $w^{-1}=\sigma^2(F)+0.0005|F|^2$ was applied and the final R factor, based on 184 adjustable parameters was R = 0.031, R_w = 0.042 for the 2173 observed data. The maximum shift/esd at this stage was 0.20 and a final difference Fourier map showed two peaks, each of about $1\varepsilon\mathrm{\AA}^{-3}$, which occurred in the region of the iridium and one of the iodine atoms.

The atomic scattering factor for Ir and I were taken from reference (91).

Final fractional coordinates are given in Table 3.1 and selected bond distances and angles in Table 3.2. The structure of the complex is shown in Figure 3.2, an ORTEP diagram of the molecule in Figure 3.3 and a cell packing diagram in Figure 3.4.

<u>mer</u>-Amminetri-iodobis(dimethylphenylphosphine)iridium(III)

The salt $NH_4[PF_6]$ (0.40 g) was dissolved in aqueous ethanol (50 cm^3). After degassing, the solution was treated with $[IrCl(COD)]_2$ (0.30 g) and PMe_2Ph (0.6 cm^3, 1:8 molar ratio) and the mixture heated under reflux for 15 min. On cooling, a beige precipitate separated whereupon I_2 (1.13 g, 1:20 molar ratio) was added to the suspension and this was then refluxed for a further four hours. Following cooling to ambient temperature, an orange powder was filtered off and then soxhlet extraction with chloroform. On prolonged standing in air the resulting solution deposited orange-red crystals which were filtered off and dried in vacuo at 60°C. m.p. 211-214°C (decomp). (Yield 0.65 g, 86.4%). (Found, C, 22.1; H, 3.0; N, 1.6. Calc. for $C_{16}H_{25}NI_3IrP_2$: C, 21.9; H, 3.0; N, 1.7%). $^{31}P-\{^1H\}$ n.m.r. spectrum ($CDCl_3$, 298K); d. δ = -42.9 p.p.m., br.d. δ = -55.3 p.p.m. $^2J_{P-P}$= 14.7Hz. Non-conducting in nitromethane.

Table 3.1 - Fractional coordinates for

mer-[$IrI_3(PMe_2Ph)_2(NH_3)$]

	Fractional coordinates with standard deviation ( )		
Atom	*x*	*y*	*z*
Ir(1)	0.32281(2)	0.24873(2)	0.21407(3)
I(1)	0.43382(5)	0.36861(8)	0.33920(8)
I(2)	0.21229(5)	0.16160(8)	0.06603(7)
I(3)	0.22403(5)	0.41347(7)	0.28556(7)
P(1)	0.29356(19)	0.1248(3)	0.35785(25)
P(2)	0.40842(17)	0.1264(3)	0.13909(24)
N(1)	0.3351(6)	0.3842(8)	0.0855(8)
C(1)	0.3277(11)	0.1813(13)	0.5033(11)
C(2)	0.1938(8)	0.0969(12)	0.3672(15)
C(3)	0.2856(5)	-0.1188(8)	0.2967(7)
C(4)	0.3102(5)	-0.2385(8)	0.2984(7)
C(5)	0.3765(5)	-0.2710(8)	0.3654(7)
C(6)	0.4181(5)	-0.1838(8)	0.4307(7)
C(7)	0.3935(5)	-0.0642(8)	0.4291(7)
C(8)	0.3273(5)	-0.0316(8)	0.3621(7)
C(9)	0.3832(9)	-0.0248(10)	0.0866(12)
C(10)	0.4975(7)	0.0932(12)	0.2264(12)
C(11)	0.3947(4)	0.1763(7)	-0.0957(6)
C(12)	0.4102(4)	0.2401(7)	-0.1928(6)
C(13)	0.4681(4)	0.3249(7)	-0.1846(6)
C(14)	0.5106(4)	0.3459(7)	-0.0793(6)
C(15)	0.4952(4)	0.2821(7)	0.0178(6)
C(16)	0.4372(4)	0.1973(7)	0.0096(6)

Table 3.2 - Selected bond lengths and angles for mer-$[IrI_3(PMe_2Ph)_2(NH_3)]$

a) Bond lengths (Å) with standard deviation ( )

Ir(1) - I(1)	2.6851(10)	P(1) - C(1)	1.856(16)
Ir(1) - I(2)	2.6624(9)	P(1) - C(2)	1.832(16)
Ir(1) - I(3)	2.7408(9)	P(1) - C(8)	1.832(9)
Ir(1) - P(1)	2.282(3)	P(2) - C(9)	1.821(14)
Ir(1) - P(2)	2.298(3)	P(2) - C(10)	1.834(14)
Ir(1) - N(1)	2.156(10)	P(2) - C(16)	1.837(8)

b) Bond angles (°) with standard deviation ( )

I(1) - Ir(1) - I(2)	170.32(3)	Ir(1) - P(1) - C(1)	113.5(5)
I(1) - Ir(1) - I(3)	88.21(3)	Ir(1) - P(1) - C(2)	117.1(5)
I(1) - Ir(1) - P(1)	96.37(8)	Ir(1) - P(1) - C(8)	118.9(3)
I(1) - Ir(1) - P(2)	90.84(8)	C(1) - P(1) - C(2)	102.9(7)
I(1) - Ir(1) - N(1)	84.9(3)	C(1) - P(1) - C(8)	102.8(6)
I(2) - Ir(1) - I(3)	88.96(3)	C(2) - P(1) - C(8)	99.3(6)
I(2) - Ir(1) - P(1)	92.76(8)	Ir(1) - P(2) - C(9)	121.3(5)
I(2) - Ir(1) - P(2)	90.95(8)	Ir(1) - P(2) - C(10)	118.8(4)
I(2) - Ir(1) - N(1)	85.6(3)	Ir(1) - P(2) - C(16)	109.3(3)
I(3) - Ir(1) - P(1)	87.74(8)	C(9) - P(2) - C(10)	99.9(6)
I(3) - Ir(1) - P(2)	173.59(8)	C(9) - P(2) - C(16)	101.2(5)
I(3) - Ir(1) - N(1)	82.8(3)	C(10) - P(2) - C(16)	103.8(5)
P(1) - Ir(1) - P(2)	98.67(11)		
P(1) - Ir(1) - N(1)	170.4(3)		
P(2) - Ir(1) - N(1)	90.8(3)		

Chapter 4

Some Metal Complexes Containing Secondary Phosphinito Ligands

4.1 Introduction

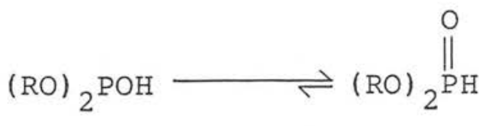
As the second part of the thesis is primarily concerned with the synthesis, characterisation and reactions of phosphinous acid, R_2POH, and secondary phosphinito, $[R_2PO]^-$, complexes of rhodium, it is of relevance in this introductory chapter to discuss briefly some of the earlier work carried out in this area. Some studies on the related secondary phosphito, $[(RO)_2PO]^-$, complexes are also discussed. This area of coordination chemistry has attracted quite a lot of attention in the last fifteen years and as such has been the subject of reviews by Roundhill *et al.*[95] and Walther[96].

4.2 Some metal complexes containing secondary phosphinito ligands

Substituted phosphinous acids, R_2POH, and secondary phosphites, $(RO)_2POH$, are known for a wide variety of substituent groups R[97,98]. The compounds exist in two tautomeric forms, one of which is tetracoordinate about a pentavalent phosphorus while the other contains a tricoordinated trivalent phosphorus atom (Eqns. [11] and [12]).

$$R_2POH \rightleftharpoons R_2\overset{\overset{O}{\|}}{P}H$$

...... [11]



$$(RO)_2POH \rightleftharpoons (RO)_2\overset{\overset{O}{\|}}{P}H$$

...... [12]

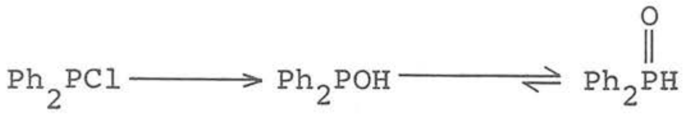
In recent years, the chemistry of secondary phosphine chalcogenides, particularly their coordination chemistry, has attracted increasing interest, one reason being the manifold reactivity of these ambivalent species.

For phosphinous acids with R=Me,Ph these equilibria lie predominantly to the right hand side[99], although there is chemical evidence for the presence of a small amount of the P(III) form (see later). With electronegative substituents on the phosphorus atom the equilibrium is shifted to the left such that $(C_6F_5)_2POH$ exists as a mixture of both tautomers[100] while $(CF_3)_2POH$ exists almost entirely as the P(III) hydroxy phosphine form[101].

These parent compounds are weak acids and thus treating them with strong base will yield the corresponding conjugate base $[R_2PO]^-$.

The diversity of these species as ligands arises mainly from two factors. Firstly, the tri-coordinate tautomeric form of the acid structurally resembles a tertiary phosphine, and hence can coordinate to a metal ion in the well known manner of such ligands. Secondly deprotonation yields a uninegatively charged ion which resembles the ambidentate thiocyanate ion in being able to coordinate through two separate ends of the ligand.

Although for R=Me,Ph the P(III) form is spectroscopically undetectable in the free ligand, it can be stabilised by complexation. This can arise as the reactivity of a bond of a coordinated phosphine is frequently different from that same bond in the uncoordinated phosphine (ie Eqns [13] and [14]).



$$Ph_2PCl \longrightarrow Ph_2POH \rightleftharpoons Ph_2\overset{\overset{O}{\|}}{P}H$$ ....[13]

$$\underline{cis}\text{-}[PtCl_2(PR_3)(Ph_2PCl)] \xrightarrow{H^+/H_2O} \underline{cis}\text{-}[PtCl_2(PR_3)(Ph_2POH)]$$ ..[14]

Chatt and Heaton successfully exploited the hydrolysis of monochlorophosphine complexes of the type <u>cis</u>-$[PtX_2(PR^1_3)$-$(Ph_2OCl)]$ (X = Cl, Br, I, R and R^1 = alkyl or phenyl group) to prepare a series of Ph_2POH compounds, an example of which is shown in equation [14][102].

However, the hydrolysis of phosphorus-halide bonds has long been a source of preparation of phosphorus-hydroxy and -alkoxy linkages. Schutzenberger and Fontaine showed in 1872 that if platinum metal was reacted with phosphorus pentachloride then the species formed, $[PtCl_2(PCl_3)]_n$ and $[PtCl_2(PCl_3)_2]$, reacted with H_2O to form $[PtCl_2(P(OH)_3)]_n$ (later studies showed that n=2) and $[PtCl_2(P(OH)_3)_2]$ respectively[103]. Some six decades later, in 1936, Davis and Ehrlich prepared $[CuCl(PCl_3)_2]$ which reacted with MeOH to yield $[CuCl(P(OMe)_3)_2]$ [104].

The hydrolysis of chlorophosphine complexes became increasingly used as a synthetic route to the formation of compounds containing the less stable hydroxy tautomer R_2POH. In Austin's thesis the hydrolysis reactions of platinum and palladium complexes of Ph_2PCl and $PhPCl_2$ with H_2O were described (Eqns [15] and [16]).

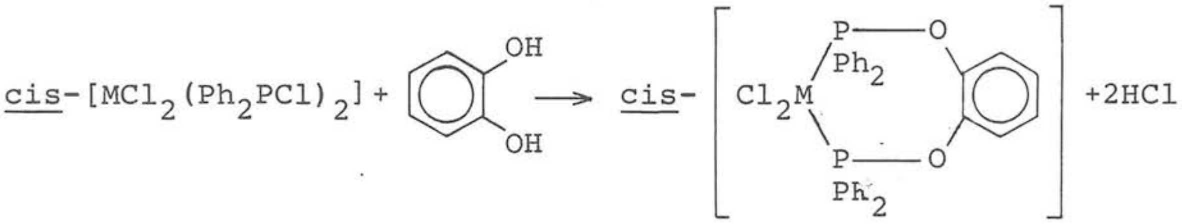
$$\underline{cis}\text{-}[MCl_2(Ph_2PCl)_2]+H_2O \rightarrow \underline{cis}\text{-}[MCl_2(Ph_2POH)_2]+HCl$$ ...[15]

$$\underline{cis}\text{-}[MCl_2(PhPCl_2)_2]+H_2O \rightarrow \underline{cis}\text{-}[MCl_2(PhP(OH)Cl)_2+HCl$$ ..[16]

The same author also showed that these species react with other hydroxylic reagents to give closely related compounds (Eqns [17], [18] and [19])[105].

$$\underline{cis}\text{-}[MCl_2(Ph_2PCl)_2] + 2HOCH_2CH_2OH \longrightarrow \underline{cis}\text{-}[MCl_2(Ph_2POCH_2CH_2OH)_2] + 2HCl \quad \ldots [17]$$

$$\underline{cis}\text{-}[MCl_2(PhPCl_2)_2] + 4HOCH_2CH_2OH \longrightarrow \underline{cis}\text{-}[MCl_2(PhP(OCH_2CH_2OH)_2)_2] + 4HCl \quad \ldots\ldots [18]$$



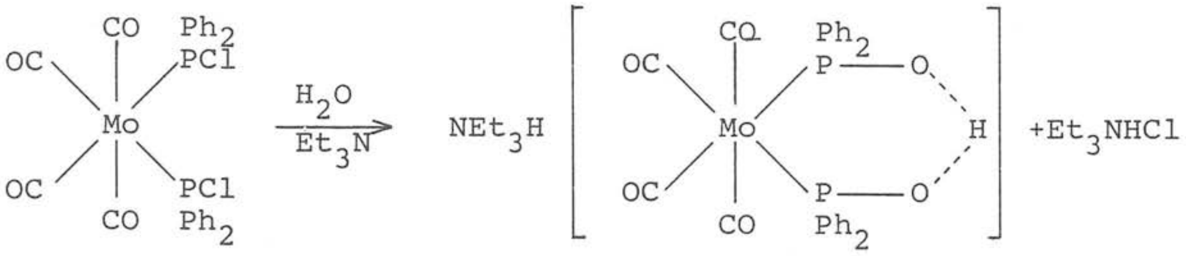
..... [19]

However, one of the most systematic studies on the hydrolysis of chlorophosphine complexes to give hydroxy species has been carried out in recent years on complexes of molybdenum by Kraihanzel and co-workers. In 1972 Kraihanzel and Bartish reported that, like the platinum species, molybdenum chlorophosphine complexes $[Mo(CO)_5(R_2PCl)]$, (R = Me,Ph), hydrolysed to give the phosphinous acid species $[Mo(CO)_5(R_2POH)]$[106].

The same authors were later able to show that the molybdenum chlorophosphine complexes react with other nucleophiles to give a variety of related species $[Mo(CO)_5(R_2PX)]$ (X = OMe, OEt, SEt, NH_2, NHMe, NMe_2) (Eqn.[20])[107].

$$[Mo(CO)_5(R_2PCl)] \xrightarrow{HX} [Mo(CO)_5(R_2PX)] + HCl \quad \ldots\ldots [20]$$

Kraihanzel and Gray extended the hydrolysis reactions further in 1978 when, using a *cis*-bischlorophosphine complex they obtained a compound $[NEt_3H][Mo(CO)_4\{(Ph_2PO)_2H\}]$ (25) which has both a phosphinous acid and phosphinito ligand in the same molecule (Eqn.[21])[108].



(25) ...... [21]

This *cis* arrangement allows strong hydrogen bonding between the two phosphorus ligands and the formulated product is one containing a symmetrically hydrogen-bonded moiety. Confirmation that this species is the thermodynamically favourable one was demonstrated by Wong and Bradley who found it was the product of the hydrolysis of both *cis*- and *trans*-$[Mo(CO)_4(Ph_2PCl)_2]$[109].

This *trans* to *cis* isomerisation step is somewhat unexpected at first sight since in $[Mo(CO)_4(PR_3)_2]$ complexes, there is found to be a slight preference for the *trans* isomer[110]. However, this preference must have been overcome by the favourable proton bridging interaction that is available only in the *cis* form of the $[Mo(CO)_4\{(Ph_2PO)_2H\}]^-$ anion.

Complexes containing the symmetrically hydrogen-bonded ligand $[R_2POHOPR_2]^-$ have in fact been known for over ten years and are found whenever a phosphinous acid and a phosphinito ligand occur *cis* to each other. Although there are now a variety of synthetic routes to these compounds, $[Mo(CO)_4\{(Ph_2PO)_2H\}]^-$ was the first example where hydrolysis of coordinated chlorophosphines was the method employed.

The first report of complexes of this type, with cis phosphite and phosphito ligands, was by Troitskaya et al. who reported the preparation of $[Pt\{((EtO)_2PO)_2H\}_2]$ from $[Pt(P(OEt)_3)_4][PtCl_4]$. This reaction was thought to proceed by hydrolysis of either coordinated or free triethylphosphite[111]. The same author later prepared similar compounds with various other alkyl substituents (R=Me, Pr^n, Bu^n) and from palladium metal[112].

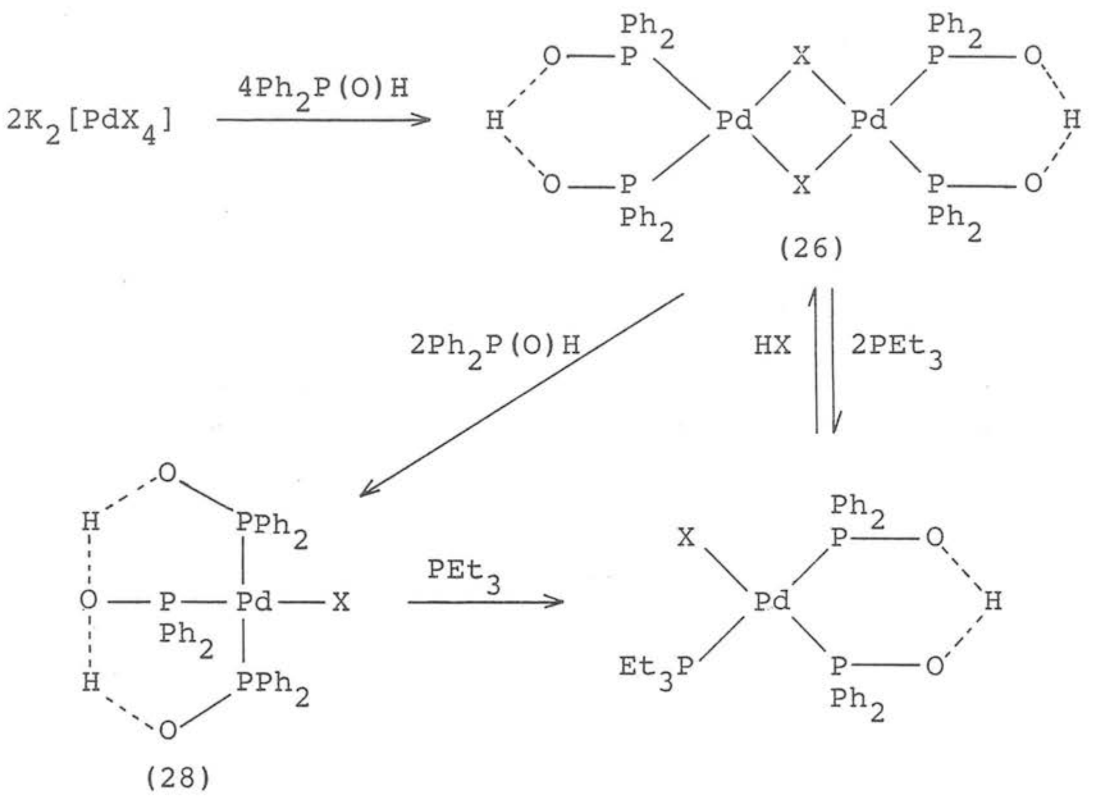
A variety of complexes containing cis phosphinous acid and phosphinito ligands linked by strong intramolecular hydrogen bonding were reported by Dixon and Rattray following the isolation and subsequent reactions of the product obtained from the interaction of $K_2[MX_4]$ (M = Pd, Pt; X = Cl, Br) with diphenylphosphine oxide.

Thus, the reaction of diphenylphosphine oxide with the $[PdCl_4]^{2-}$ ion gave the double chloro-bridged species $[Pd(\mu\text{-}Cl)\{(Ph_2PO)_2H\}]_2$ (26), (scheme 4.1).

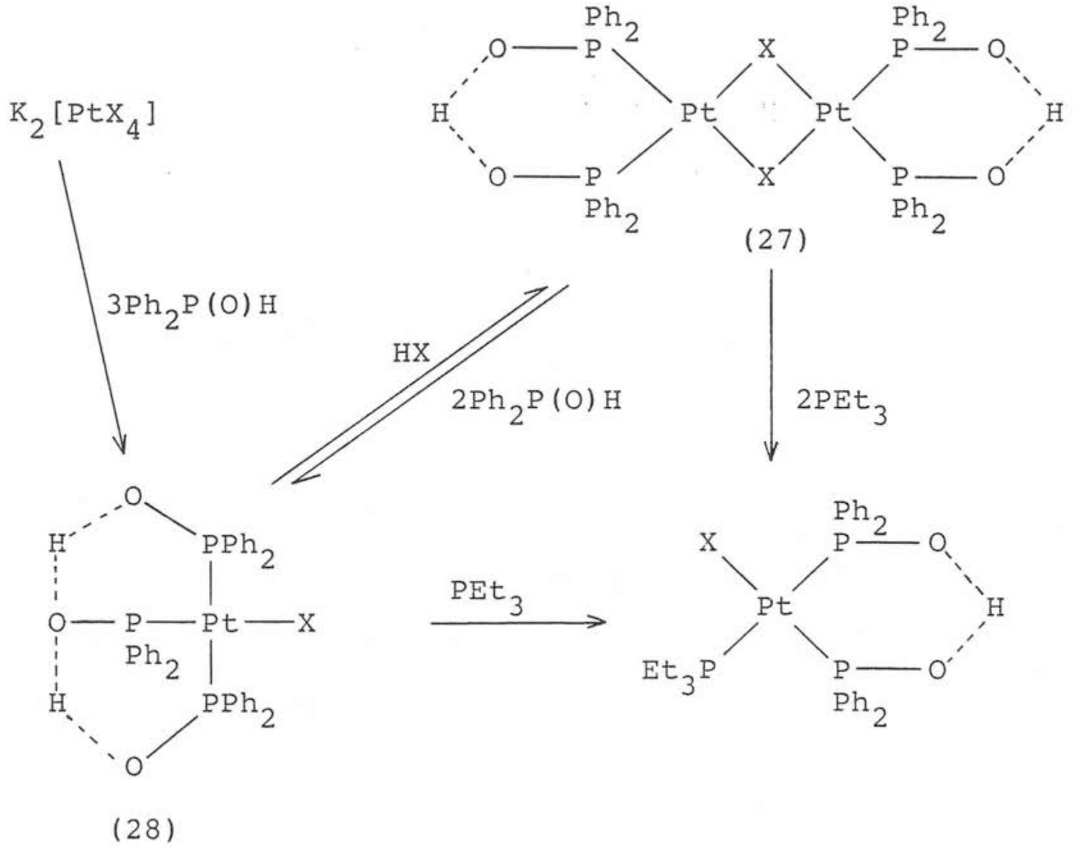
In contrast to the palladium complex, the $[PtCl_4]^{2-}$ ion reacts with diphenylphosphine oxide to give the monomer $[PtCl\{(Ph_2PO)_3H_2\}]$ (see later); however subsequent treatment of this species with HCl yields the corresponding $[Pt(\mu\text{-}Cl)\{(Ph_2PO)_2H\}]_2$ (27), (scheme 4.2).

Furthermore, reaction of these double halo-bridged species with equimolar quantities of PEt_3 and $Ph_2P(O)H$ resulted in bridge cleavage and the formation of the compounds cis-$[MX(PEt_3)\{(Ph_2PO)_2H\}]$ and $[MX\{(Ph_2PO)_3H_2\}]$ (M = Pd, Pt; X = Cl, Br) respectively (schemes 4.1 and 4.2). On the basis

Scheme 4.1 - Reactions of palladium complexes (X = Cl, Br)

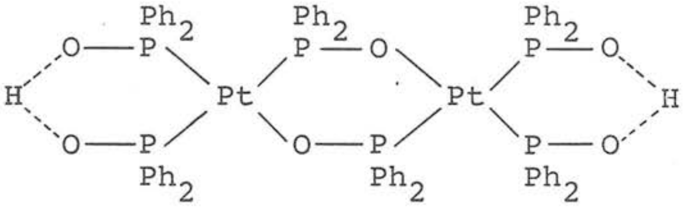


Scheme 4.2 - Reactions of platinum complexes (X = Cl, Br)



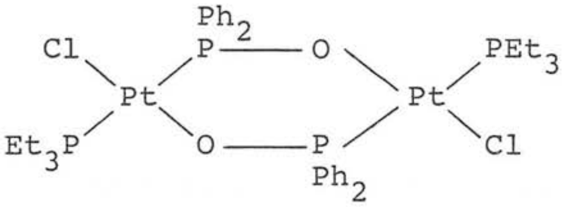
of i.r. spectral data, the $[MX\{(Ph_2PO)_3H_2\}]$ complexes were assigned a configuration (28) in which the hydrogen-bonding has been extended to form a tridentate ligand.

It is also interesting to note that the phosphinito ligands are capable of bridge formation. Hence treatment of $[PtCl\{(Ph_2PO)_3H_2\}]$ with NaOH gave the phosphinito-bridged species $[Pt(\mu\text{-}OPPh_2)\{(Ph_2PO)_2H\}]_2$, (29)[113].



(29)

Another example of this phosphinito bridging mode had previously been observed by Chatt and Heaton in the complex $[PtCl(\mu\text{-}OPPh_2)(PEt_3)]_2$, (30), which was obtained by treatment of <u>cis</u>-$[PtCl_2(Ph_2POH)(PEt_3)]$ with an equimolar amount of NaOMe [102].



(30)

Other synthetic routes employed to generate complexes containing the $[R_2POHOPR_2]^-$ ligand include the hydrolysis of the acetylenic phosphine species $[MCl_2(Ph_2PC{\equiv}CCF_3)_2]$, (M = Pd, Pt), in aqueous ethanol to form the chloro-bridged dimers

$[M(\mu\text{-}Cl)\{(Ph_2PO)_2H\}]_2$. Using metathetical reactions the analagous bromo and thiocyanato complexes were also prepared[114, 115].

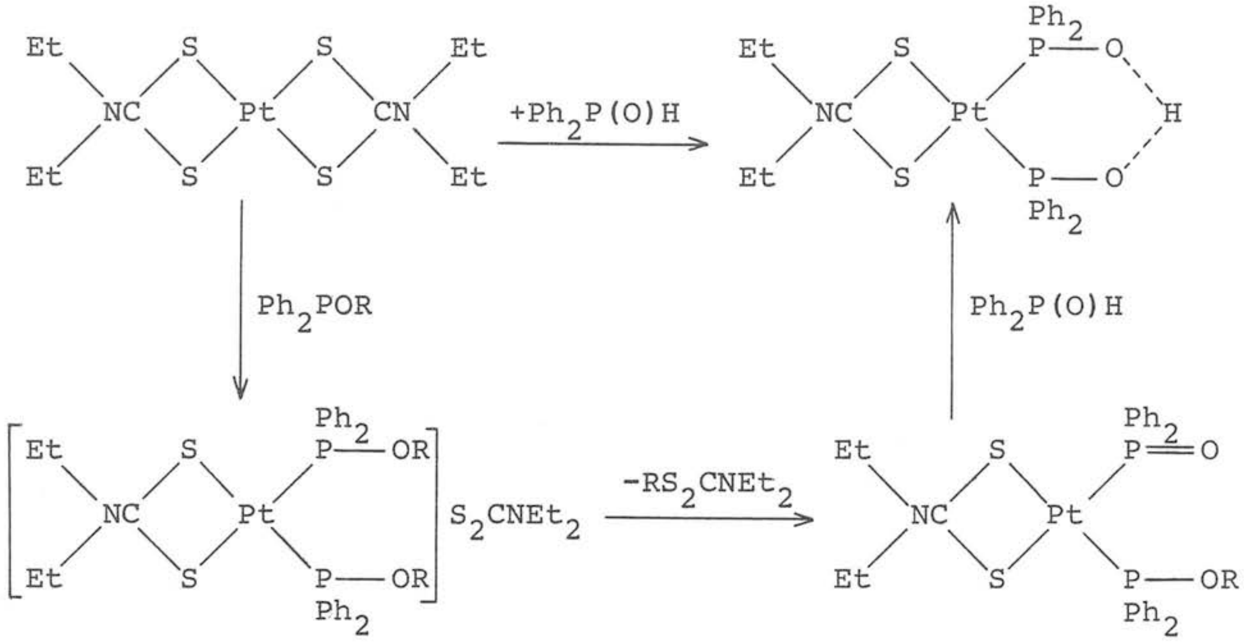
Roundhill and Kong found that the oxygen-alkyl bond in a coordinated phosphinite ligand could also be hydrolysed, following their isolation of the compound $[Pt\{(Ph_2PO)_2H\}_2]$ from solutions of $[Pt(Ph_2POR)_4]$ (R = Me, Bu^n) which had been left standing in air[116].

Some years later, another route, also involving the nucleophilic cleavage of an oxygen-alkyl bond in a coordinated phosphinito ligand, was reported by Stephenson _et al_. In dichloromethane solution, the compound $[Pt(S_2CNEt_2)(Ph_2POMe)_2]$ $[S_2CNEt_2]$ was found to rearrange as a result of nucleophilic attack of the $[S_2CNEt_2]^-$ ion on a coordinated Ph_2POMe group. The $[Pt(S_2CNEt_2)(Ph_2PO)(Ph_2POMe)]$ so formed, was then treated with free $Ph_2P(O)H$ resulting in the displacement of the coordinated Ph_2POMe group and the formation of the complex $[Pt(S_2CNEt_2)\{(Ph_2PO)_2H\}]$ (scheme 4.3)[117].

At present there are some conflicting reports in the literature regarding the symmetric nature of the $[R_2POHOPR_2]^-$ ligand.

If the system were not symmetrical, or the ligands were not mutually _cis_, then i.r. absorptions would be expected for ν(P-OH) at _ca_ 880 cm^{-1}, ν(P=O) at _ca_ 1100 cm^{-1} and ν(PO-H) at _ca_ 3200 cm^{-1} [102]. Dixon and Rattray reported that complexes such as $[PdX\{(Ph_2PO)_2H\}]_2$ which contain the $[R_2POHOPR_2]^-$ ligand show only a single P-O stretching absorption in the range 970-1040 cm^{-1} which is consistent with a ring structure with P-O bonds intermediate between single and double bonds.

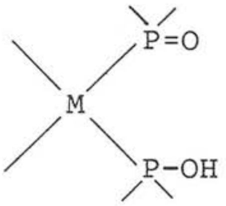
Scheme 4.3 - Proposed mechanism for conversion of $[Pt(S_2CNEt_2)_2]$ into $[Pt(S_2CNEt_2)\{(Ph_2PO)_2H\}]$



Furthermore, there is an absence of PO-H stretching bands in their normal position at ca 3200 cm^{-1}. This is to be expected if strong symmetrical hydrogen bonding is present since the ν(P-OH) band is broadened and shifted to lower frequency by this interaction[113].

The X-ray crystal structure determinations of a wide variety of species which contain the $[R_2POHOPR_2]^-$ ligand have now been reported.

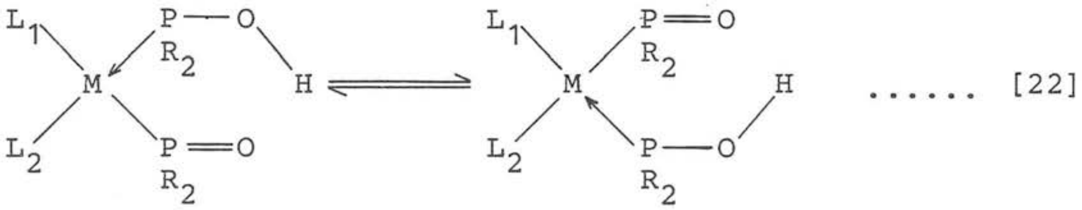
In the structures of the following species, $[Pd(S_2CNMe_2)\{(Ph_2PO)_2H\}]$ [117], $[Pt\{((MeO)_2PO)_2H\}_2]$ [118] and $[Pd(\mu\text{-}SCN)\{(Ph_2PO)_2H\}]_2$ [114] the O···O distances, generally found to be approximately 2.4Å, are short and are less than twice the Van der Waals radius of oxygen (2x1.5Å), which implies the presence of a hydrogen bond. It is generally regarded as definitive evidence for a hydrogen bond if the O···O distance is <2.5Å [119]. Furthermore the P-O distances, which range from 1.527-1.549Å are found within experimental error, to be equal within a given complex thus ruling out the possibility of (31), in which the P=O bond would be expected to be shorter than the P-OH bond.



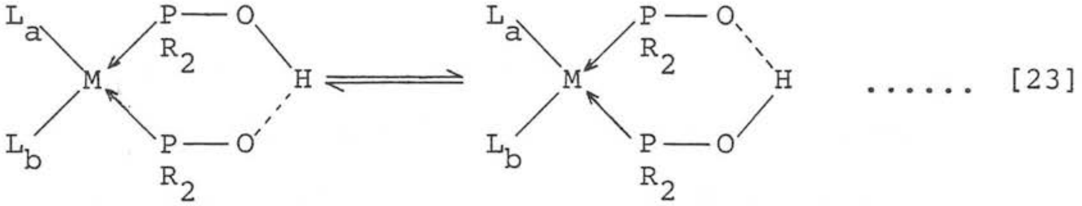
(31)

The X-ray structure determination of the complexes $[RuCl_2(NO)\{((EtO)_2PO)_2H\}]_2$ [120] and $[Ph_4As][Rh_2Cl_5\{(Ph_2PO)_2H\}_2]^-$ [121] have also been reported and once again a close O···O distance of approximately 2.4Å is observed. However, it is found that within the $[R_2POHOPR_2]^-$ ligand one of the P-O distances is significantly shorter than the other, implying a significant asymmetry in the ligand. Furthermore, the physically sensible refinement of the hydroxy hydrogen atoms shows that there are no symmetrical hydrogen bonds in the crystal and also that the asymmetry in the metallocycle cannot be explained by packing arguments alone[120,121].

Sperline and Roundhill suggested that complexes containing the ligand $[R_2POHOPR_2]^-$ can be formally represented by equations [22] and [23], where R is an alkyl, aryl, alkoxy or phenoxy group and L_a, L_b, L_1 and L_2 represent the other ligands coordinated to the metal[122].



...... [22]

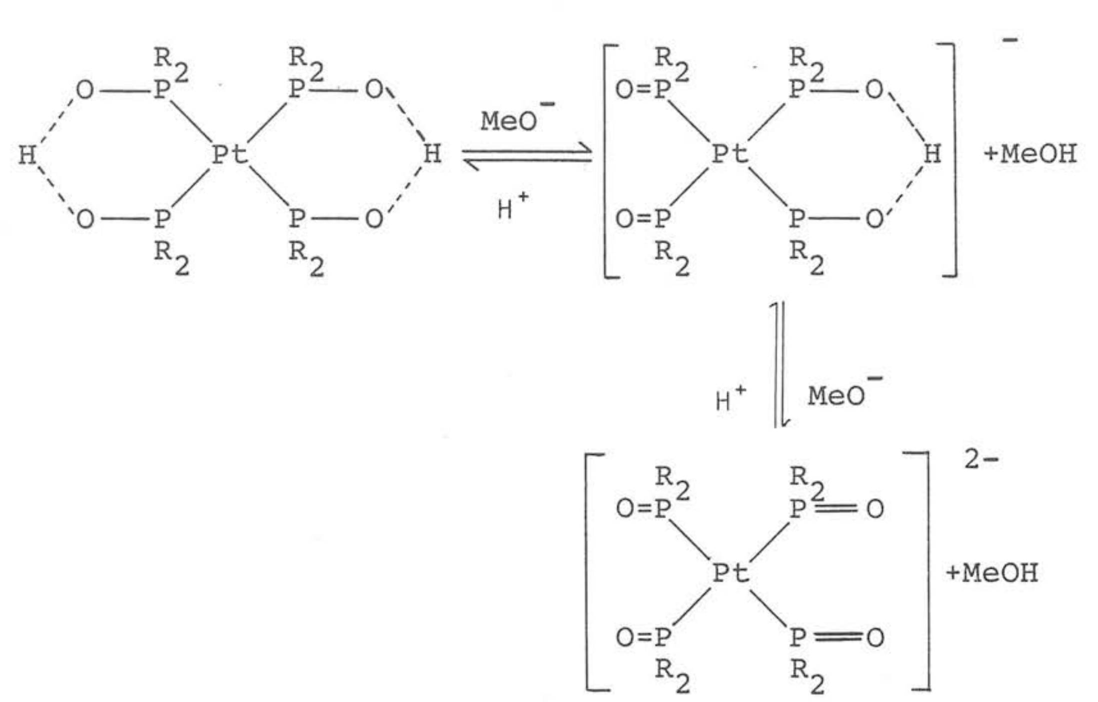


...... [23]

Southern *et al* propose that one possible explanation for the symmetric or asymmetric nature of these ring systems is in the type of metal-phosphorus bonding and hence the phosphorus-oxygen bonding. If the bonding is represented as in equation [23], the two oxygen atoms are equivalent, both being sp^3 hybridised and separated by approximately 2.4Å, and the hydrogen will be symmetrically bonded to both oxygens. On the other hand, when the bonding is represented as in equation [22] with the oxygen atoms still separated by approximately 2.4Å, the non-equivalence of the oxygen atoms, one being sp^2 hybridised and the other sp^3 hybridised, will induce asymmetry in the O···H···O bonding.

Thus for compounds such as $[Pd(S_2PMe_2)\{(Ph_2PO)_2H\}]$ in which the observed P-O bond lengths are equal and are in the range of P-O single bond lengths, (1.53-1.60Å), observed in transition metal-phosphinite and -phosphite complexes, it would appear that the O···H···O system is symmetric. Moreover, in $[RuCl_2(NO)\{((EtO)_2PO)_2H\}]_2$, although the Ru-P bond distances are equivalent, the observed P-O bond lengths are not equal, with one being very much shorter than a P-O single bond distance. Therefore it would appear that the bonding is much nearer that represented by equation [22]; hence it is normal that the O···H···O system is asymmetric[120].

The bridging hydrogen in the $[R_2POHOPR_2]^-$ ligands is acidic and can be readily removed by treatment with base. Using conductometric measurements, Roundhill et al showed that $[Pt\{((MeO)_2PO)_2H\}_2]$ is a dibasic acid by monitoring the sequential removal of the two acidic protons by methoxide ion (Eqn [24])[122,123].

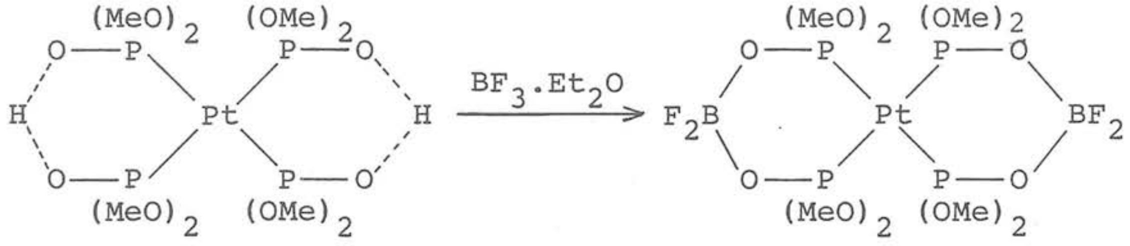


...... [24]

The proton can sometimes be observed by ^{1}H n.m.r. spectroscopy where it occurs as a broad resonance in the region δ=10-15 p.p.m. and can readily be exchanged by treatment with D_2O [108,115,124].

Furthermore, it has been found that the acidic proton can be replaced by a variety of groups such as $[BF_2]^+$, $[SiCl_2]^{2+}$, etc, or by metal ions, which affords a viable synthetic route to mixed metal oligomers with a wide variety of metals in specific sites (see later examples).

Hence, Austin found that the acidic protons in $[Pt\{((MeO)_2PO)_2H\}_2]$ could be replaced by treatment with $BF_3.Et_2O$ (Eqn [25])[105].



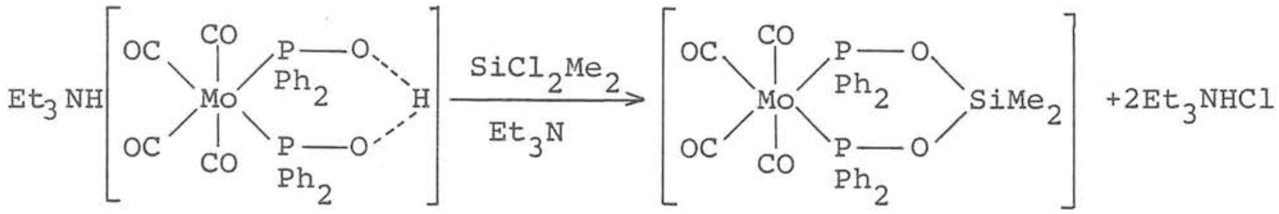
...... [25]

The structure of the resulting BF_2-capped compound $[Pt\{((MeO)_2PO)_2BF_2\}_2]$ was later confirmed by X-ray analysis which showed the six-membered ring to have a chair conformation[125].

Typical vibrations of the $[Ph_2POBF_2OPPh_2]^-$ ligand occur in the i.r. spectrum 1060, 1005 and 890 cm^{-1}, the latter especially being proposed to be of diagnostic value[126].

To date, the majority of work involving species containing $[R_2POHOPR_2]^-$ ligands has been carried out using platinum and palladium. However, attention is turning increasingly towards the development of synthetic routes to phosphinous acid complexes of other transition metals. Furthermore, the tendency for workers in the area to replace the acidic hydrogen by several different types of groups has led to the formation of a wide variety of new species.

For example, having synthesised the compound $[Et_3NH][Mo(CO)_4\{(Ph_2PO)_2H\}]$, Gray and Kraihanzel were then able to generate new complexes containing unusual heterocylic rings by reacting the species with various chlorosilanes (Eqns [26] and [27])[108].



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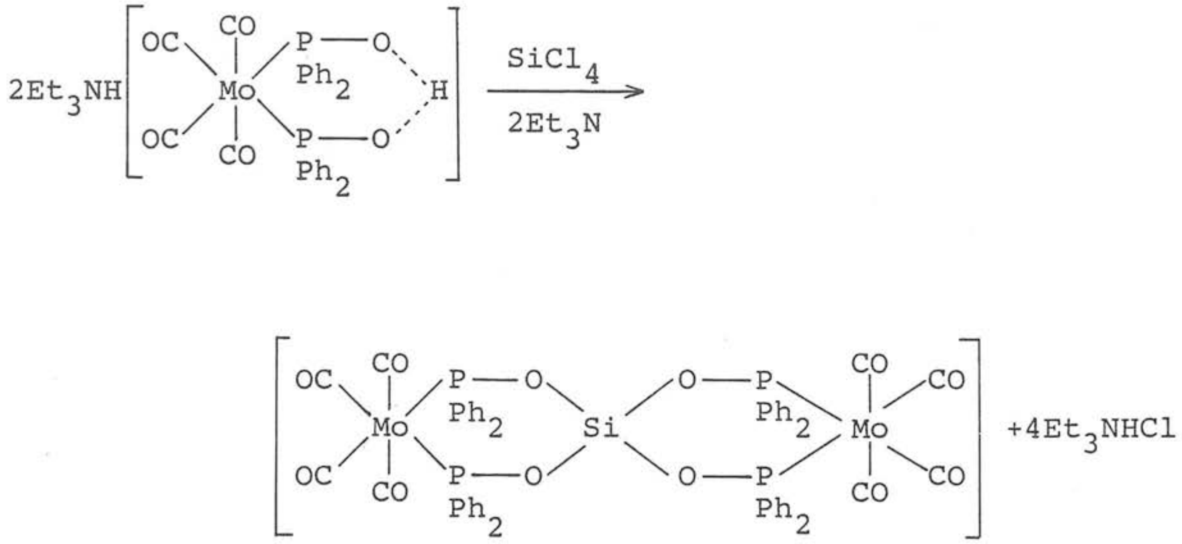
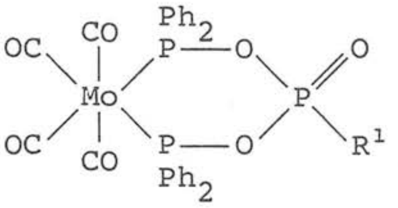


...... [27]

Although the reaction of $[Et_3NH][Mo(CO)_4\{(Ph_2PO)_2H\}]$ with $Cl_2P(O)R^1$ does not yield the desired $Mo(CO)_4\{(Ph_2PO)_2\text{-}P(O)R^1\}]$ complexes they have been successfully prepared recently by treating <u>cis</u>-$[Mo(CO)_4(Ph_2PCl)_2]$ with the appropriate phosphonic acid, $(HO)_2P(O)R^1$ (R = Me, Et, Ph, CH_2Ph, C_6H_4-p-OMe, CH_2Cl, CH_2CH_2Cl) (Eqn [28])[127].

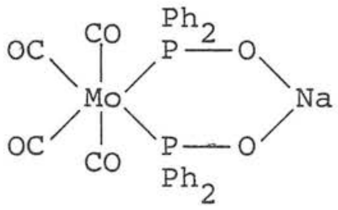
cis-$[Mo(CO)_4(Ph_2PCl)_2]$ + $(HO)_2P(O)R^1$ + Et_3N

$\xrightarrow{THF}$ $2Et_3NHCl$ +



...... [28]

Gray and Kraihanzel also reported that reaction of $[Et_3NH][Mo(CO)_4\{(Ph_2PO)_2H\}]$ with NaOH and $[NEt_4]Cl$ led to substitution of the proton by the Na^+. It is proposed that the sodium ion in the resulting $[Mo(CO)_4\{(Ph_2PO)_2Na\}]^-$ (32) is two-coordinate and occupies a bridging position similar to that of the hydrogen it replaced[108].

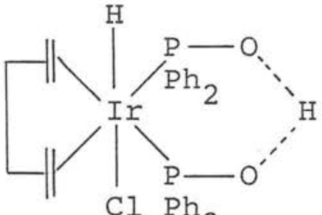


(32)

Similarly Sperline and Roundhill found that the complexes $[PtCl\{((MeO)_2PO)_2H\}L]$ ($L = PEt_3, PPh_3$) were acidic and that the proton could be removed by titration with NaOMe. The resulting anionic compound will bind to Cu(II), Co(II), UO_2(VI) and Th(IV) via the oxygens to give the mixed metal complexes $[\{PtCl((RO)_2PO)_2L\}_nM]$ ($n = 2$, R = Me, $L = PEt_3$, M = Cu, UO_2 and $L = PPh_3$, M = Co; $n = 2$, R = Ph, $L = PEt_3$, M = Cu; $n = 4$, R = Me, $L = PPh_3$, M = Th)[122].

Bennett and Mitchell conducted some studies on iridium species and showed that if $[IrCl(C_8H_{14})_2]_2$ is treated with a secondary phosphite in the presence of PPh_3, then iridium complexes of the type $[IrHCl\{((MeO)_2PO)_2H\}(PPh_3)_2]$ are formed. The use of this route enabled the authors to prepare a series of compounds with different phosphites and Lewis bases[128].

Duncan *et al* carried out further investigations of iridium species using complexes containing 1,5-cyclooctadiene instead of cyclooctene. Treatment of $[IrCl(C_8H_{12})]_2$ with an excess of Ph_2PCl in methanol-water (7:1, v/v) gives the colourless microcrystalline species $[IrHCl(C_8H_{12})\{(Ph_2PO)_2H\}]$ (33)



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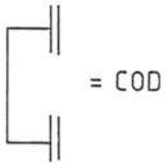
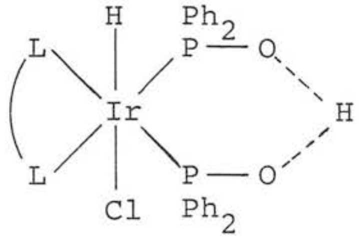


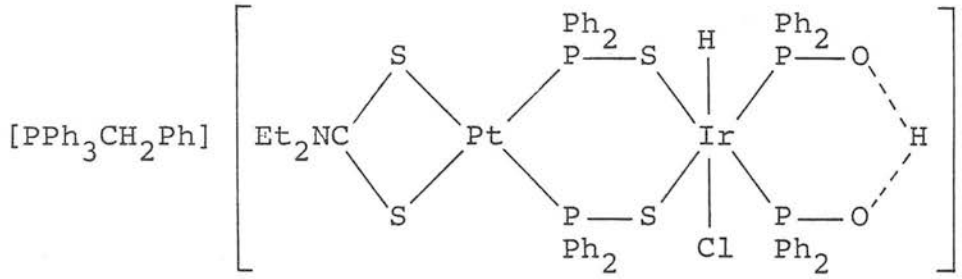
Diene dissociation readily occurs and, in the absence of added ligand, polymeric materials are probably formed. However, in the presence of bidentate ligands the complexes $[IrHCl(L\text{-}L)\{(Ph_2PO)_2H\}]$ (34) (L-L = $Ph_2As(CH_2)_2AsPh$, $PhS(CH_2)_2SPh$ and $Ph_2P(CH_2)_2PPh_2$) are obtained



(34)

Reaction of (34) with $BF_3.Et_2O$, and HBF_4 leads to the respective formation of $[IrHCl(L-L)\{(Ph_2PO)_2BF_2\}]$ and $[IrHCl(L-L)(Ph_2POH)_2]BF_4$ (L-L = $Ph_2As(CH_2)_2AsPh_2$ or $PhS(CH_2)_2SPh_2$). The latter compounds readily lose HF to give the BF_2-capped products.

An important property of these diphenylphosphinito and related complexes is that they can be used to prepare heterobimetallic compounds. Thus, if equimolar quantities of $[IrHCl(C_8H_{12})\{(Ph_2PO)_2H\}]$ and $[PPh_3(CH_2Ph)][Pt(S_2CNEt_2)(PPh_2S)_2]$ are shaken in $CHCl_3$ the heterobimetallic complex $[PPh_3(CH_2Ph)][(Et_2NCS_2)Pt(\mu-PPh_2S)_2IrHCl\{(Ph_2PO)_2H\}]$ (35) is obtained.

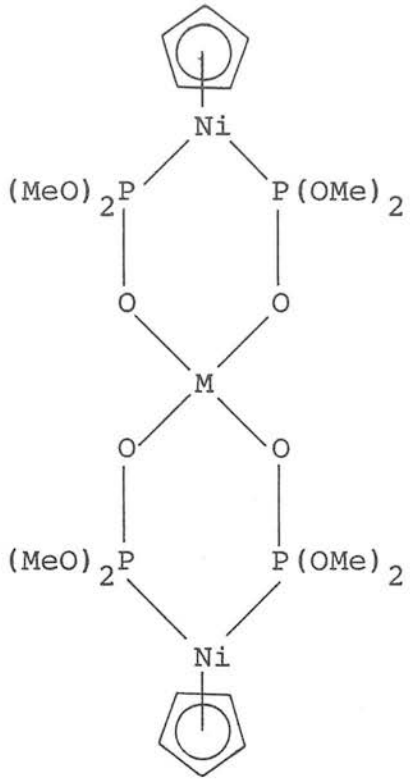


(35)

However, the more usual approach, involving substitution of the hydroxylic hydrogen by a second metal ion, leads to the preparation of heterobimetallic and trimetallic compounds. Hence reaction of $[IrHCl(Ph_2As(CH_2)_2AsPh_2)\{(Ph_2PO)_2H\}]$ with $[VO(acac)_2]$ or $[Co(acac)_2]_4$ (acac = acetylacetonate) results in substitution of this proton by VO_2^{2+} or Co^{2+}. Consequently the species $[IrHCl(Ph_2As(CH_2)_2AsPh_2)(\mu-Ph_2PO)_2M(acac)]$ and $[\{IrHCl(Ph_2As(CH_2)_2AsPh_2)(\mu-Ph_2PO)_2\}_2M]$ (M = VO_2^{2+}, Co^{2+}) have been isolated[129].

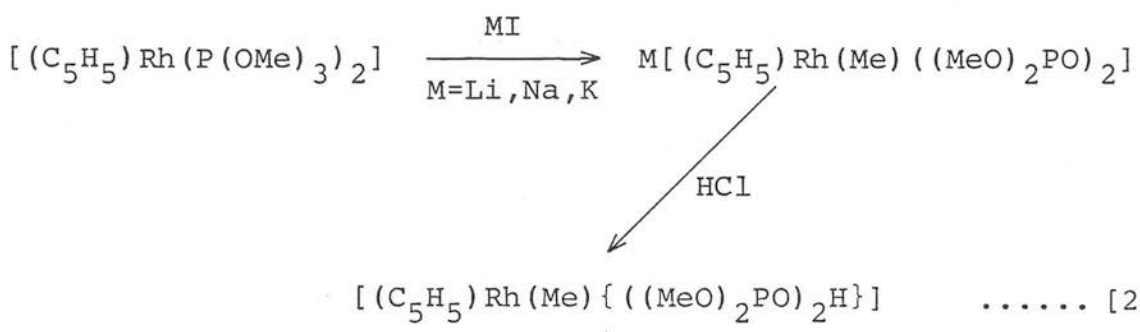
In contrast, related (diene)-rhodium(I) compounds react with various $R_2P(O)H$ ligands, undergoing facile diene displacement to generate quite different species. Furthermore, the nature of the product from the reaction $[RhCl(C_8H_{12})]_2$ with an excess of Ph_2PCl in aqueous methanol depends critically on the water to methanol ratio. At low water:methanol ratios (1:15, v/v) the only products formed are the well known cations $[Rh(Ph_2POMe)_4]^+$ and $[RhHCl(Ph_2POMe)_4]^+$. However, at higher water:methanol ratios (1:7, v/v), short reaction time at ambient temperature, followed by addition of various large cations gave the binuclear triple chloro-bridged anionic complexes $M[Rh_2Cl_5\{(Ph_2PO)_2H\}_2]$, ($M = AsPh_4$, $PPh_3(CH_2Ph)$) (see earlier)[121].

Another line of investigation, largely conducted by Werner and co-workers involves the reaction of various bis(η-cyclopentadienyl) metal complexes with secondary phosphites. It was found that treatment of $[Ni(\eta\text{-}C_5H_5)_2]$ with $(MeO)_2P(O)H$ gives the mononuclear compound $[Ni(\eta\text{-}C_5H_5)\{((MeO)_2PO)_2H\}]$ which in turn yields the BF_2-capped species $[Ni(\eta\text{-}C_5H_5)\{((MeO)_2PO)_2BF_2\}]$ on reaction with HBF_4. The interaction of $[Ni(\eta\text{-}C_5H_5)\{((MeO)_2PO)_2H\}]$ with $CoCl_2$ and $ZnCl_2$ affords the trinuclear complexes $[\{Ni(\eta\text{-}C_5H_5)((MeO)_2PO)_2\}_2M]$ (36, M = Co, Zn)[130].



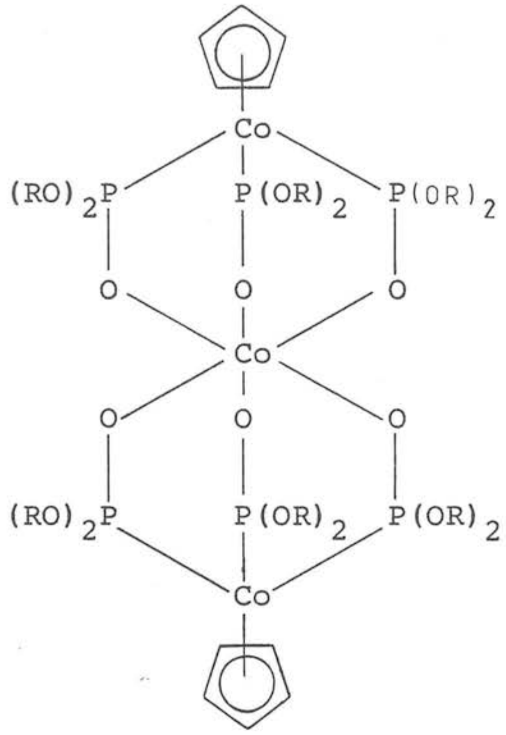
(36)

Studies similar to those conducted on nickel, were carried out with rhodium cyclopentadienyl complexes. These showed that rhodium compounds containing the $[R_2POHOPR_2]^-$ ligand could be formed in a two-stage reaction (Eqn [29])^{131}.



$$[(C_5H_5)Rh(P(OMe)_3)_2] \xrightarrow[M=Li,Na,K]{MI} M[(C_5H_5)Rh(Me)((MeO)_2PO)_2] \xrightarrow{HCl} [(C_5H_5)Rh(Me)\{((MeO)_2PO)_2H\}] \quad ...... [29]$$

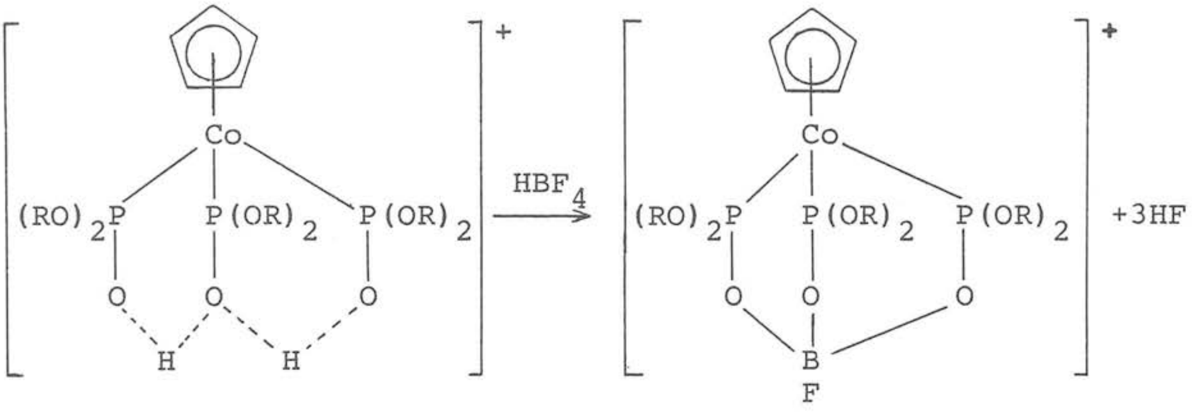
However, unlike the nickel and rhodium work, treatment of $[Co(\eta\text{-}C_5H_5)_2]$ with an excess of $(RO)_2P(O)H$ gave the novel trinuclear cobalt complexes $[Co_3(\eta\text{-}C_5H_5)((RO)_2PO)_6]$ (37) *via* an intermediate species $[Co(\eta\text{-}C_5H_5)(P(OR)_3)_2]$ (R = Me, Et)[132].



(37)

Addition of strong mineral acid to this "triple sandwich" complex results in the formation of the compounds $[Co(\eta\text{-}C_5H_5)\{((RO)_2PO)_3H_2\}]$ (38, R = Me, Et) containing the hydrogen-bonded ligand $[((RO)_2PO)_3H_2]^-$. Furthermore, if the acid employed is HBF_4 then the reaction does not stop at this stage but continues to give the tri-capped species $[Co(\eta\text{-}C_5H_5)\{((RO)_2PO)_3BF\}]$ (39, R = Me, Et) (Eqn [30]).

$[Co_3(\eta\text{-}C_5H_5)_2((RO)_2PO)_6] + H_2SO_4, H_3PO_4, HNO_3$ or $HBF_4 \longrightarrow$

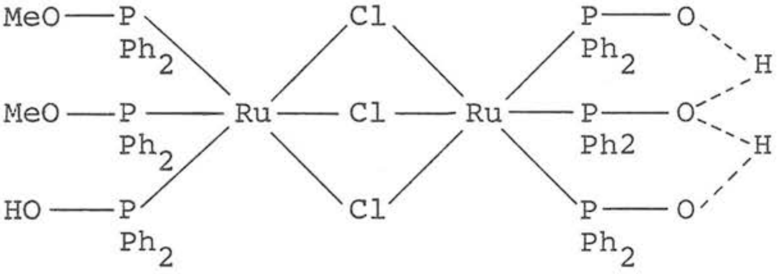


(38) (39) ...... [30]

A single crystal X-ray structure for the complex with R=Et verified the unusual BF cap and shows the tris(diethylphosphito)-fluoroborate anion coordinated to the metal as a tridentate cage-forming ligand[133].

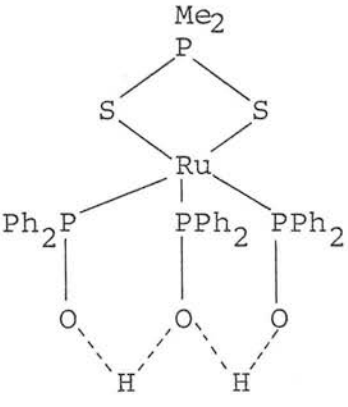
Recent studies by Kläui <u>et al</u> indicate that the anionic half-sandwich complexes $[Co(\eta\text{-}C_5H_5)(R_2PO)_3]^-$ (R = Et, CH_2Ph) can react as tridentate oxygen ligands. Thus reaction with metal ions, M^{n+}, such as Al^{3+}, Ce^{4+}, Pr^{3+}, Eu^{3+} and Fe^{3+} in aqueous solution have yielded the species $[\{Co(\eta\text{-}C_5H_5)(R_2PO)_3\}_2M]^{(n-2)+}$ [134]. Furthermore, reaction of $[Co(\eta\text{-}C_5H_5)((RO)_2PO)_3]^-$ with the metal carbonyl species $[M(CO)_3(CH_3CN)_3]$ (M = Cr, Mo, W) and $[MBr(CO)_5]$ (M = Mn, Re) generated the tricarbonyl derivatives $[Co(\eta\text{-}C_5H_5)((RO)_2PO)_3M(CO)_3]^{n-}$ (n = O, M = Mn, Re, R = Me, Et; n = 1, M = Cr, Mo, W, R = Et)[135,136].

Some ruthenium complexes containing the tridentate hydrogen-bonded ligand have been isolated by Stephenson <u>et al</u>. Thus, in 1969, Prince and Raspin demonstrated that the pyrolysis products of $[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]Cl$ were dependent upon the solvent media and the temperature of pyrolysis[137]. By analogy with that work the yellow solution obtained from the reaction of $[\{RuCl_2(C_7H_8)\}_n]$ and Ph_2POMe in methanol, which contains $[(Ph_2POMe)_3RuCl_3Ru(Ph_2POMe)_3]Cl$ was reduced in volume and then pyrolysed at 120°C for 12 hours. The resulting bright yellow crystalline solid was shown by X-ray analysis to be $[(Ph_2POMe)_2(Ph_2POH)RuCl_3Ru\{(Ph_2PO)_3H_2\}]$ (40)[138].



(40)

The same author later prepared another ruthenium complex containing the same tridentate ligand. The five coordinate species $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ (41) was synthesised by the reaction of <u>cis</u>-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ with a large excess of Ph_2PCl in acetone to which <u>ca</u> 10% water was added to convert the free chlorophosphine to $Ph_2P(O)H$.



(41)

Treatment with $BF_3.Et_2O$ appears to give the BF-capped species $[Ru(S_2PMe_2)\{(Ph_2PO)_3BF\}]$. Furthermore, $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ reacts with carbon monoxide to give the six-coordinate complex $[Ru(S_2PMe_2)(CO)\{(Ph_2PO)_3H_2\}]$[139].

As this brief survey indicates, there is a variety of synthetic routes to the formation of complexes containing phosphinito ligands. To date the majority of species isolated contain the bidentate ligand $[R_2POHOPR_2]^-$. The following chapters describe further studies on rhodium and ruthenium phosphinito complexes in which the hydrogen-bonding has been extended to form the tridentate ligand $[(R_2PO)_3H_2]^-$.

Chapter 5

Synthesis and Reactions of Diphenylphosphinito Complexes of Rhodium(III).

5.1 Introduction

Although the chemistry of transition metal complexes containing phosphinito ligands has attracted increasing interest in recent years, there have been relatively few such phosphinito rhodium species synthesised to date. Duncan et al. recently reported the preparation of the triple chloro-bridged anion $[Rh_2Cl_5\{(Ph_2PO)_2H\}_2]^-$ by displacement of diene from $[RhCl(COD)]_2$[82]. The close resemblance of this species to the compounds $[Rh_2Cl_5(PR_3)_4][BPh_4]$ (R_3 = Me_2Ph, Et_2Ph, $Pr^n{}_2Ph$) described in chapter 2 led us to investigate further the direct reaction of $RhCl_3.3H_2O$ and $Ph_2P(O)H$. It was envisaged that this might lead, not only to the development of a simpler route to $[Rh_2Cl_5\{(Ph_2PO)_2H\}_2]^-$, but also to phosphinito analogues of the complexes $[Rh_2Cl_6(PR_3)_3]$, $[RhCl_3(PR_3)_3]$ and $[RhCl_3(PR_3)_2(H_2O)]$.

In this chapter our attempts to synthesise rhodium complexes containing the bidentate $[(Ph_2PO)_2H]^-$ and tridentate $[(Ph_2PO)_3H_2]^-$ ligands are described.

5.2 Synthesis and characterisation of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$

As discussed in chapter 4, the species $Ph_2P(O)H$ can be readily generated *in situ* by hydrolysis of the phosphorus-chlorine bond in Ph_2PCl. In our hands, treatment of $RhCl_3.3H_2O$ with an excess of $Ph_2P(O)H$ formed by pre-hydrolysis of Ph_2PCl in methanol:water (7:1, v/v), (giving an *in situ* mixture of $Ph_2P(O)H$ and HCl), yielded only the well known rhodium(I) cation $[Rh(Ph_2POMe)_4]^+$, isolated in low yield (*ca*.10%) as its $[BPh_4]^-$ salt. This was somewhat surprising since there was no evidence for the existence of any *free* Ph_2POMe in the phosphine solution used. The ^{31}P n.m.r. spectrum of this hydrolysed solution contains only one resonance (δ = 21.0 p.p.m., $^1J_{P-H}$=483.1Hz (doublet)) which corresponds to $Ph_2P(O)H$ (Eqn. [31]).

$$Ph_2PCl + H_2O \longrightarrow Ph_2P(O)H + HCl \qquad \ldots\ldots\ldots [31]$$

There is no resonance near 111 p.p.m. due to Ph_2POMe. Moreover, the presence of HCl in the solution can be demonstrated by the low pH of the solution. Duncan observed a similar phenomenon following the treatment of $[RhCl(COD)]_2$ with an excess of pre-hydrolysed Ph_2PCl in $MeOH/H_2O$ (15:1, v/v). Further studies indicated that when the chlorophosphine is hydrolysed to give $Ph_2P(O)H$, a very small amount of Ph_2POMe is also formed, although this is such a small amount that it cannot be detected spectroscopically (Eqn.[32]).

$$Ph_2PCl \xrightarrow{H_2O} Ph_2P(O)H + HCl \xrightarrow{MeOH} Ph_2POMe + H_2O$$

..... [32]

This small amount of tertiary phosphinite present reacts, in preference over $Ph_2P(O)H$, to form the $[Rh(Ph_2POMe)_4]^+$ cation. Consistent with greater nucleophilicity of P(III) in Ph_2POMe than P(V) in $Ph_2P(O)H$. As Ph_2POMe is removed from the solution by its reaction with $RhCl_3.3H_2O$, more will be formed to restore the equilibrium which has been set up between the two phosphines (Eqn.[32]). Furthermore, it is known that $Ph_2P(O)H$ exists in equilibrium with a small amount of Ph_2POH and although the latter has never been spectroscopically detected in solution, reactions can occur via this P(III) form (see chapter 4)[140].

Whilst the reaction of $RhCl_3.3H_2O$ with pre-hydrolysed Ph_2PCl in $MeOH/H_2O$ (7:1, v/v) failed to yield any rhodium-phosphinito species, the situation with $Rh(NO_3)_3.2H_2O$ is quite different.

Treatment of $Rh(NO_3)_3.2H_2O$ with pre-hydrolysed Ph_2PCl (1:3 molar ratio) in $MeOH/H_2O$ (7:1, v/v) under refluxing conditions for four hours gave a yellow solution from which a pale yellow powder precipitated. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the product in solution was found to be temperature dependent. At ambient temperature in $CDCl_3$ the spectrum showed a broad doublet (δ = 88.9 p.p.m., $^1J_{Rh-P}$= 124.5Hz); however, on lowering the temperature the resonances were observed to broaden and then sharpen revealing an A_2MX

pattern with resonances at δ_A=91.3 p.p.m., $^1J_{Rh-P}$=131.3Hz, $^2J_{P-P}$=22.0Hz (doublet of doublets) and δ_B=83.1 p.p.m., $^1J_{Rh-P}$=114.8Hz, $^2J_{P-P}$=22.0Hz (doublet of triplets). Furthermore, these changes in spectra are reversible, concentration independent, and occur with retention of the rhodium-phosphine coupling.

The product was found to be non-conducting in nitromethane and elemental analysis indicated the presence of nitrogen. Further support for the presence of nitrate and phosphinito groups is obtained from the infrared spectrum which contains stretching bands at 1519, 1241 cm^{-1}, $\nu(NO_3)$ and 1025, 1001, 970 cm^{-1}, ν(P-O). In addition, the presence of several bands in the 240 cm^{-1} region suggested the complex might also contain a Rh-Cl bond. Unfortunately this spectral evidence, coupled with the elemental analysis and conductivity measurements is not sufficient to unequivocally determine the nature of the compound as various formulations fit the available data. Nevertheless, believing that the rhodium complex contained phosphinito, nitrate and chloride groups an alternative, more convenient route using $RhCl_3.3H_2O$, was devised.

Hence Ph_2PCl was dissolved in a solution of MeOH/H_2O (7:1, v/v) to which conc. HNO_3 (1.0 cm^3) had been added. The solution was then left for a sufficient period of time to allow hydrolysis of the chlorophosphine to occur before $RhCl_3.3H_2O$ (4:1 molar ratio) was added. Pale yellow crystals were isolated from the reaction mixture following shaking at ambient temperature for four months. The $^{31}P-\{^1H\}$ n.m.r. spectrum of these crystals in $CDCl_3$ at 298K contains a broad doublet (δ = 88.9 p.p.m., $^1J_{Rh-P}$=124.5Hz) and a singlet (δ =

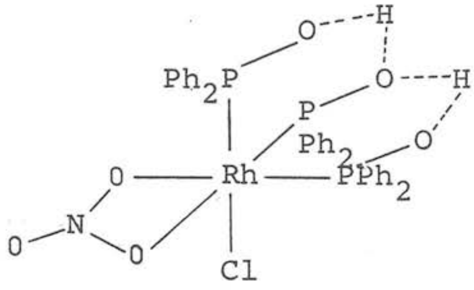
21.8 p.p.m.). The ^{31}P n.m.r. spectrum obtained with proton coupling showed a $^{1}J_{P-H}$ coupling constant of 494.2Hz for the resonance at δ = 21.8 p.p.m. which, therefore, can be assigned to $Ph_2P(O)H$.

Attempts to remove $Ph_2P(O)H$ from the crystals by washing with a variety of solvents were unsuccessful. A possible explanation for this behaviour is that the species contained in the crystals decomposes upon dissolution in the $CDCl_3$, thereby giving rise to both $Ph_2P(O)H$ and the fluxional complex previously obtained by the $Rh(NO_3)_3.2H_2O$ route. Alternatively, both routes might generate the same rhodium species with the crystals also containing $Ph_2P(O)H$ of crystallisation.

On cooling the $CDCl_3$ solution of the crystals to 223K the broad doublet (δ = 88.9 p.p.m., $^{1}J_{Rh-P}$=124.5Hz) was observed to broaden then sharpen revealing the A_2MX pattern [δ_A=91.3 p.p.m., $^{1}J_{Rh-P}$=131.3Hz, $^{2}J_{P-P}$=22.0Hz (doublet of doublets), δ_B=83.1 p.p.m., $^{1}J_{Rh-P}$=114.8Hz, $^{2}J_{P-P}$=22.0Hz (doublet of triplets)] previously shown by the compound obtained using $Rh(NO_3)_3.2H_2O$. Moreover, there was no coalescence observed between the resonances due to the fluxional species and the $Ph_2P(O)H$. This, together with the fact that the Rh-P coupling is retained throughout, indicates that the fluxional behaviour observed at ambient temperature is not a result of exchange between bound and free $Ph_2P(O)H$.

An X-ray crystal structure determination subsequently revealed the composition of the crystals to be $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$. This confirms that the $Ph_2P(O)H$ observed in the ^{31}P n.m.r. spectra of the crystals arises due to $Ph_2P(O)H$ of crystallisation and that both the

$Rh(NO_3)_3.2H_2O$ and $RhCl_3.3H_2O/HNO_3$ routes lead to the formation of the same complex, namely $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ (42).



(42)

It is proposed that the temperature dependent behaviour observed in the $^{31}P-\{^1H\}$ n.m.r. spectra of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ arises from reversible coordinative isomerism of the nitrate group from bidentate to unidentate coordination leading to an averaging of the phosphorus environments. On cooling, this process is inhibited and the A_2MX pattern arises since two phosphorus atoms are trans to an oxygen and the other is trans to a chloride.

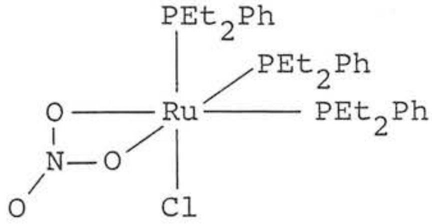
Although the isolation of the crystals of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$ was essential to determining the nature of the product, the crystals could only be obtained in very low yield (ca.10%), even after reaction at room temperature for several months. However, under refluxing conditions for 3-4 hours, the mixture gives a yellow solution from which the $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ precipitated as a pale yellow powder on cooling. Moreover, careful addition of water (ca.5-10 cm^3) to the resulting suspension results in further precipitation of the product. This treatment increases the yield to ca.81% compared with a yield of ca.67% obtained from the original route using $Rh(NO_3)_3.2H_2O$.

$[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ was also obtained in somewhat lower yield (ca.43%) by the reaction, at refluxing temperatures, of $RhCl_3.3H_2O$ and pre-hydrolysed Ph_2PCl (1:4 molar ratio) in a solution of $MeOH/H_2O$ (7:1, v/v) to which $Na[NO_3]$ had been added in place of the conc.HNO_3.

5.2.2 The X-ray crystal structure of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$.

The crystal structure determination was carried out by L. Sawyer at Napier College, Edinburgh.

Details of the solution of the structure are given in the experimental section. The final atomic positions are given in Table 5.1 and selected bond distances and angles in Table 5.2. The rhodium atom is coordinated in an octahedral arrangement. The Rh-O bond lengths of 2.250(7) and 2.205(7)Å indicate that the $[NO_3]^-$ group is not symmetrically bound. Asymmetrically bound NO_3^- has been observed also by Easton in the closely related complex $[RuCl(NO_3)(PEt_2Ph)_3]$ (43) which has Ru-O bond lengths of 2.276(7) and 2.155(7)Å [141].



(43)

In $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$ the O-Rh-O angle is 58.7(3)° similar to that observed by Easton for the O-Ru-O angle of 58.0(3)° in $[RuCl(NO_3)(PEt_2Ph)_3]$. The O-N-O angles are not significantly different from 120° and the nitrate group is essentially flat with the rhodium lying 0.25Å out of the plane on the same side as the chloride.

The rhodium-phosphorus bond lengths observed for the anion $[Rh_2Cl_5\{(Ph_2PO)_2H\}_2]^-$ are of a distance lying between 2.268(4) and 2.272Å [121]. However, in $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$ the rhodium-phosphorus bond lengths are significantly different with distances of Rh-P(1) = 2.310(3)Å, Rh-P(2) = 2.265(3)Å and Rh-P(3) = 2.228(3)Å.These differences may reflect not only the greater trans influence of chloride than nitrate, but also the stereochemical arrangement whereby O(1) and O(2) are closer to each other than to O(3). P(1) is trans to the chloride and would therefore be expected to have a longer rhodium-phosphorus bond length than P(2) and P(3) which are trans to nitrate oxygens. However, the difference between Rh-P(2) and Rh-P(3) distances is less readily explained since both are trans to oxygen with comparable P-Rh-O angles (P(2)-Rh-O(5) = 161.2(2)°, P(3)-Rh-O(7) = 165.4(2)°).

Attempts to locate the three non-phenyl hydrogens yielded only H(3) which refined well and gave an O(3)-H(3) distance of 0.85(12)Å. In addition, the distances H(3)-O(4) = 1.79(12)Å and O(3)-O(4) = 2.601(10)Å strongly suggest that H(3) is asymmetrically hydrogen-bonded to O(4) of the $Ph_2P(O)H$ solvate molecule. The P(4)-O(4) bond length (1.494(7)Å) is significantly shorter than the P-O bond lengths of the coordinated phosphinito groups (1.538(9)Å to 1.571(8)Å), consistent with the P(V) form of $Ph_2P(O)H$ with the hydrogen bound to P(4). Nonetheless, these latter distances are comparable to those observed in the complexes $[Pd(SCN)\{(Ph_2PO)_2H\}]_2$[114], $[Pd(S_2PMe_2)\{(Ph_2PO)_2H\}]$[117], $[Rh_2Cl_5\{(Ph_2PO)_2H\}_2]$[121] and $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2$ (see later) all of which show typical P-O bond lengths of the order of 1.536-1.555Å.

Whereas the O(1)-O(3) = 3.157(10)Å and O(2)-O(3) = 3.204 (10)Å distances are too long to allow hydrogen-bonding between these pairs of oxygens, the O(1)-O(2) distance of 2.400(19)Å strongly suggests that the remaining proton is hydrogen-bonded to the latter pair of oxygens. Furthermore, it is interesting to note that with the P(1)-O(1) and P(2)-O(2) bond lengths found to be 1.564(8) and 1.538(9)Å respectively, this may suggest that the hydrogen-bond between these two oxygens is asymmetric.

The molecular structure is shown in Figure 5.1 and an ORTEP diagram of the molecule together with the $Ph_2P(O)H$ solvate in Figure 5.2.

Fig.5.1 - The structure of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$

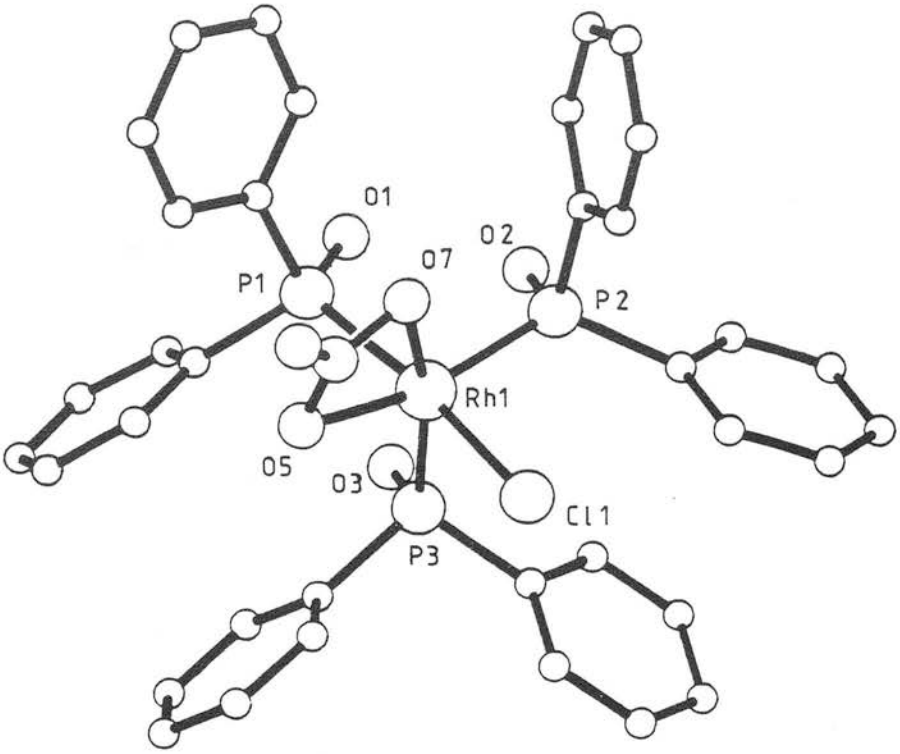
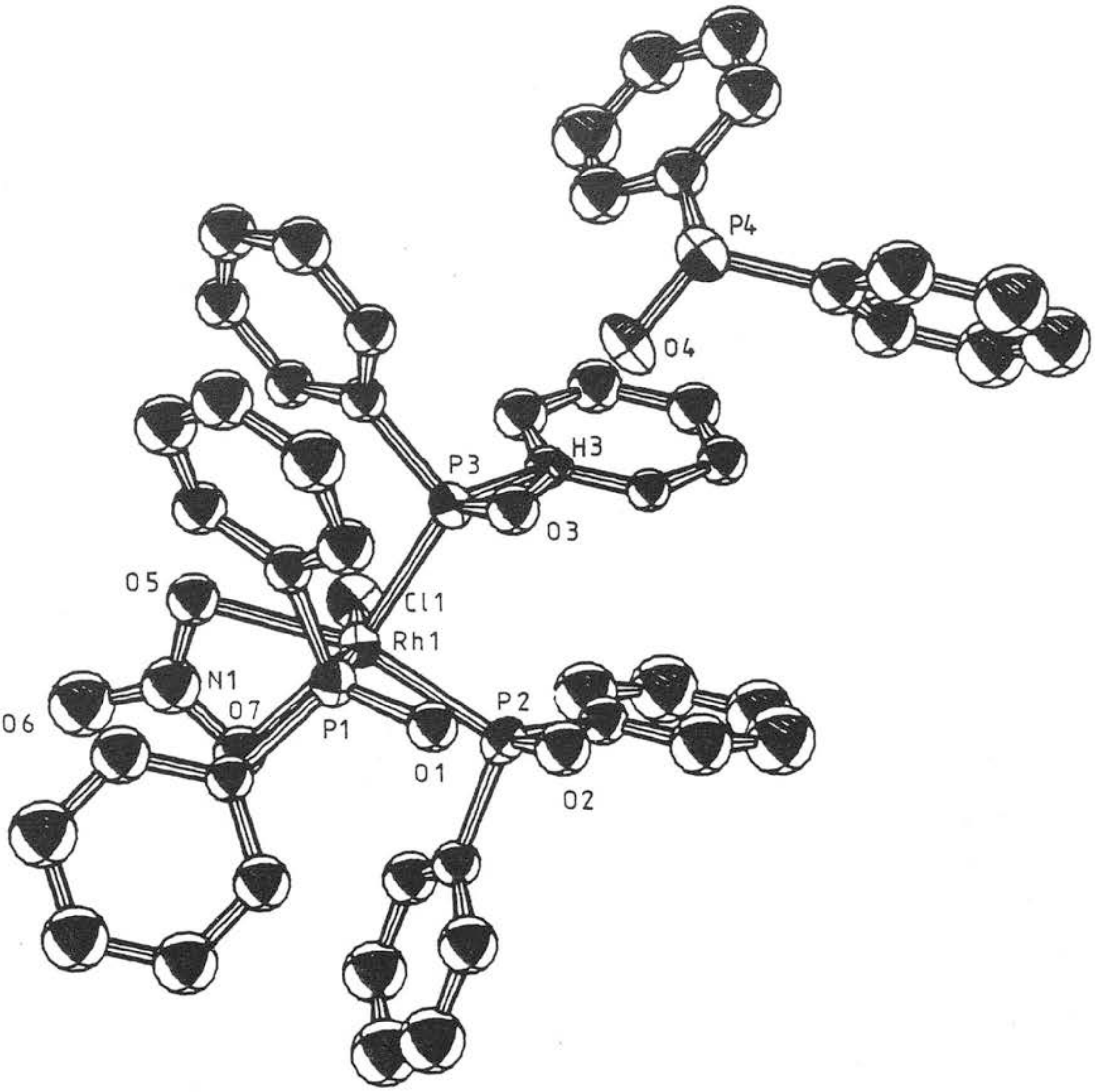


Fig.5.2 - An ORTEP diagram of [RhCl(NO_3){($Ph_2PO)_3H_2$}].$Ph_2P(O)H$



5.3 Reactions of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ involving replacement of the acidic hydrogens

It is well established that the acidic proton in the $[R_2POHOPR_2]^-$ ligand can be readily replaced by a wide selection of groups or metal ions and has led to the synthesis of a variety of mixed-metal oligomers (see chapter 4). Compared with the number of species containing the $[R_2POHOPR_2]^-$ ligand, there have been relatively few reports of complexes containing the tridentate ligand $[(R_2PO)_3H_2]^-$. As a consequence there have been correspondingly few attempts to replace the acidic hydrogens in such groups. However, Robertson and Stephenson reported that treatment of $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ with $BF_3.Et_2O$ generates the BF-capped species $[Ru(S_2PMe_2)\{(Ph_2PO)_3BF\}]$[139]. It was envisaged therefore that a range of derivatives of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ could be synthesised by replacement of the acidic hydrogens.

On treatment with Et_3N, the $^{31}P-\{^1H\}$ n.m.r. spectrum of a $CDCl_3$ solution of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ at ambient temperature changes from a broad doublet at $\delta = 88.9$ p.p.m. ($^1J_{Rh-P}$=124.5Hz) to a broad doublet centred at $\delta = 77.8$ p.p.m. ($^1J_{Rh-P}$=132.4Hz). Further treatment of the resulting solution with the stronger base NaOMe, resulted in the disappearance of the latter resonance and the emergence of two sharp doublets at $\delta = 80.0$ p.p.m. ($^1J_{Rh-P}$=141.2Hz) and at $\delta = 73.1$ p.p.m. ($^1J_{Rh-P}$=144.1Hz) with the former the predominant resonance in a ratio of <u>ca</u>.5:1. This same spectrum is also obtained when NaOMe alone is used but in this case the doublet at $\delta = 77.8$ p.p.m. is not observed.

Attempts to isolate the species generated have proved unsuccessful and clearly their identification is not possible from these preliminary investigations. The isolation of deprotonated forms of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ may prove to be impossible due to reprotonation of the phosphinito moiety. Since the acidic protons were not observed in the ^1H n.m.r. spectrum of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ a conductometric titration may be required to determine whether both protons are removed when treated with a base. In such cases where stronger bases are used, displacement of the nitrate (and possibly the chloride) may be prevalent.

The reaction of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ with $BF_3.Et_2O$ in $CHCl_3$ appeared to be more promising with a white microcrystalline powder being obtained on work-up with petroleum ether (b.p. 40-60°C). The $^{31}P-\{^1H\}$ n.m.r. spectrum of the product in d^6-dmso shows a doublet of broad doublets centred at $\delta = 88.7$ p.p.m. with a $^1J_{Rh-P}$ coupling constant of 122.8Hz and a further coupling of 5.1Hz. The origin of the latter coupling and indeed the nature of the species has yet to be determined. However the product is found to be conducting in nitromethane and elemental analyses indicate that nitrate is no longer present. The ^1H n.m.r. spectrum contains only resonances due to the phenyl groups of the phosphinito groups with no evidence for hydride ligands being found.

Although a preliminary ^{11}B n.m.r. spectrum indicates the presence of $[BF_4]^-$, spectral evidence for $\{(Ph_2PO)_3BF\}^-$, or even $\{(Ph_2PO)_3(BF_2)_2\}^-$, has yet to be found. However, it is interesting to note that the $^{31}P-\{^1H\}$ n.m.r. spectrum of $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ ($\delta = 122.8$ p.p.m. (d), $\delta = 102.4$

p.p.m. (q), ${}^3J_{P-P}$=4.4Hz) is not dramatically changed upon BF-capping. The phosphinito doublet becomes a broad unresolved peak at δ = 126.0 p.p.m. while the $[S_2PMe_2]^-$ quartet found at δ = 103.0 p.p.m. remains sharp and is also shifted only slightly to higher frequency. Furthermore, decoupling experiments carried out on ${}^{11}B$ n.m.r. and ${}^{19}F$ n.m.r. spectra enabled the ${}^3J_{P-F}$ and ${}^1J_{B-F}$ coupling constants to be determined to be 10.6Hz and 11.8Hz respectively[139]. Since the ${}^{31}P-\{{}^1H\}$ n.m.r. spectral resonances of the product obtained by treating $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ with $BF_3.Et_2O$ are broad, remain virtually in the same position and would appear to have a further coupling constant of ca.5Hz, the ${}^{11}B$ n.m.r. and ${}^{19}F$ n.m.r. spectra merit further investigation.

The other intriguing question regards the nature of the group resulting in the loss of the nitrate ligand. There is no evidence for a hydride from the ${}^1H$ n.m.r. spectrum and it may be that a fluorine moiety, such as F^-, BF_3 or even $[BF_4]^-$, has displaced the nitrate, and possibly even the chloride, to generate a species which may be fluxional. Again, ${}^{19}F$ n.m.r. spectroscopy should provide valuable information in this respect.

Although the products from these attempted deprotonation reactions have not been identified fully, it is clear that in each case reaction has occurred and therefore merit further investigation.

In addition to the deprotonation reactions, the ability of various bidentate ligands to displace the nitrate from $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ was also investigated. The results of this study are presented in the following section.

5.4 Reaction of $RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ with bidentate ligands

The nitrate anion shows particularly weak Lewis base properties; it is a poor σ donor and has little if any π-acceptor capacity. In addition the high polarity of $M-ONO_2$ bonds caused by the strong inductive effect of the nitrate anion, facilitates nucleophilic attack on nitrato complexes. For these reasons the nitrate anion is widely regarded as a highly labile ligand of relatively poor co-ordinating power, particularly toward platinum group metals[142,143].

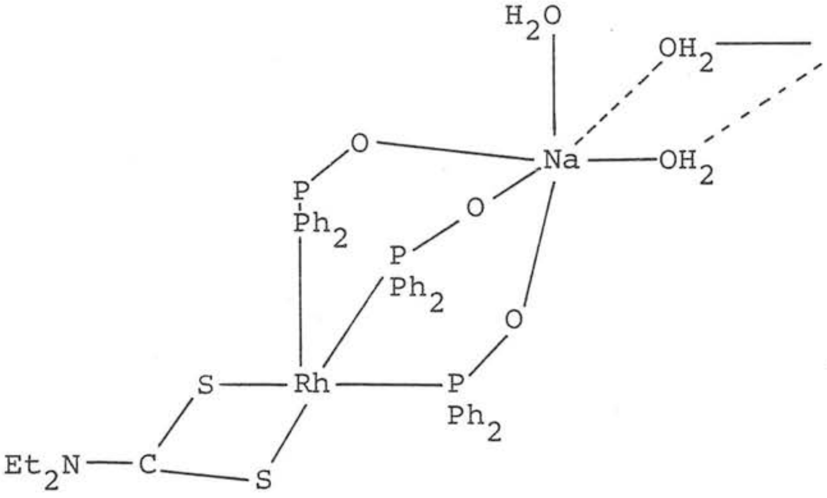
Having prepared the nitrato complexes $[Ru(NO_3)_2(CO)(PPh_3)_2]$ and $[RuH(NO_3)(CO)(PPh_3)_2]$ Critchlow and Robinson reported that treatment of these species with stronger chelating ligands, including acetate, N,N-dimethylcarbamate and thioacetate, could lead to displacement of the nitrate anion. Some of the species subsequently isolated include $[Ru(L-L)_2(CO)(PPh_3)_2]$ ($L-L = O_2CMe_2$, $S(O)CMe_2$, $S_2\ CNMe_2$) and $[RuH(L-L)(CO)(PPh_3)_2]$ ($L-L = O_2CMe_2$, S_2CNMe_2)[144]. This work, together with the observation that the nitrato ligand in $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ is fluxional in solution at ambient temperature suggested that it might be readily displaced. It was envisaged that reaction with a selection of bidentate ligands would result in the synthesis of a variety of species of general type $[RhCl(L-L)\{(Ph_2PO)_3H_2\}]$.

5.4.1 With N,N-dialkyldithiocarbamates

The reaction of [RhCl(NO_3){(Ph_2PO)$_3H_2$}] with NaS_2CNR_2 R = Me, Et; 1:5 molar ratio) in refluxing MeOH/H_2O (1:1, v/v) yields an orange powder irrespective of the dithiocarbamate alkyl group. Both products show a doublet in their $^{31}P-\{^1H\}$ n.m.r. spectra obtained in d^6-acetone at ambient temperature (e.g. for R=Et; δ = 68.5 p.p.m., $^1J_{Rh-P}$=131.8Hz). Interestingly though, on cooling even to 183K, no temperature dependent behaviour is observed. Since neither the expected A_2MX pattern nor any temperature dependent behaviour were observed, a more complex reaction other than the simple replacement of the nitrate ligand by the dithiocarbamate had presumably occurred.

The infrared spectra of the compounds confirmed the presence of the phosphinito and dithiocarbamate ligands with stretching bands in the regions ca.1070 cm^{-1}, ν(P-O) and ca. 1500 cm^{-1}, ν(C-N). Furthermore, the presence of water is indicated by a broad band at ca.1600 cm^{-1}. The ^1H n.m.r. spectra of the compounds show resonances due to water, phosphinito phenyl groups and dithiocarbamate methyl or ethyl groups and indicate a $Ph_2PO:S_2CNR_2$ ratio of 3:1. In the case of R=Et, the phenyl multiplet is centred at δ = 7.1 p.p.m. while the resonances from the ethyl protons of the dithiocarbamate ligand show the expected quartet and triplet patterns which are centred at δ = 3.8 p.p.m. (q) and δ = 1.3 p.p.m. (t), ($^3J_{H-H}$=7.0Hz) respectively. No evidence for a hydride ligand was found. Furthermore, although both compounds give a positive flame test for sodium they are found to be non-conducting in nitromethane.

As in the case of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$, the complex from which they were derived, the nature of the compounds could not be determined unambiguously from the available data. However, following examination by $^{31}P-\{^1H\}$ n.m.r. spectroscopy, a $CDCl_3$ solution of the diethyldithiocarbamate compound deposited a large octahedral crystal on standing for 3 days. Subsequent X-ray analysis revealed the complex to be the unusual five-coordinate rhodium(III) species $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2$ (44). The molecule is dimeric as a result of two asymmetric sodium-water bridges which gives the sodium octahedral geometry (see Fig.5.5).



(44)

Interestingly the dithiocarbamate ligand has not only displaced the nitrate but the chloride as well. The ORTEP diagram (Fig.5.4) indicates that the resulting five-coordinate rhodium(III) species is square pyramidal.

While authors invariably comment on the near energetic equality of the trigonal bipyramid and the square pyramid, an examination of the literature shows that d^6-complexes, when they can be induced to be five-coordinate, are best classified as square pyramidal[145].

In the solid state structure of $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2$ two of the phosphorus atoms are <u>trans</u> to the carbamate sulphurs while the remaining phosphinito has no <u>trans</u> ligand. On the basis of this structure one might expect an A_2MX type pattern in the solution $^{31}P\text{-}\{^1H\}$ n.m.r. spectra. However, the observation of a doublet at all temperatures from ambient to 183K, indicates the molecule is fluxional even though all three phosphinito ligands are bound to the sodium ion. Since the rhodium-phosphorus coupling is retained throughout, the fluxional process does not involve cleavage of the rhodium-phosphorus bonds. A more likely explanation of the temperature dependent behaviour is a pseudorotation similar to the Berry mechanism but with the square pyramid as the ground state and the trigonal bypyramid as the transition state.

5.4.2 <u>X-Ray crystal structure of $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2.4CHCl_3$</u>

Details of the solution of the structure are given in the experimental section. The final atomic positions are given in Table 5.3 and selected bond distances and angles in Table 5.4.

The coordination around the rhodium(III) centre is square pyramidal. The base of the pyramid is formed by the two dithiocarbamate sulphurs together with the phosphorus atoms of the two phosphinito groups which are trans to the sulphurs. The remaining phosphinito ligand forms the apex and has no ligand trans to it. Consequently the Rh(1)-P(2) bond length of 2.219(4)Å is markedly shorter than the Rh(1)-P(1) and Rh(1)-P(3) distances of 2.311(4)Å and 2.293(4)Å respectively. These latter distances are found to be equivalent within the error limits which is not unexpected since both the phosphinito groups concerned are trans to sulphur.

The three phosphinito oxygens form a tripod which is coordinated to the sodium. A similar effect was observed by Gray and Kraihanzel who reported that the reaction of $[Et_3NH][Mo(CO)_4\{(Ph_2PO)_2H\}]$ with NaOH and Et_4NCl led to substitution of the proton by sodium ion. It is proposed that the sodium ion in the resulting $[Me(CO)_4\{(Ph_2PO)_2Na\}]^-$ is two-coordinate and occupies a bridging position similar to that of the proton it displaced[108]. In $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2$ the sodium not only bridges the three phosphinito oxygens but is also bound to the oxygens of three water molecules. However, there are only two water molecules per $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)_2\}]$ moiety but, as a result of a long range interaction, the sodium is coordinated to one water from the other monomer in addition to the two of its own. In turn one of the latter pair of oxygens is also involved in an equivalent long range interaction with the sodium of the other monomer. Thus both sodium ions in the dimer achieve octahedral coordination as a result of the double aquo-bridge, which is markedly asymmetric with sodium-oxygen bond lengths of 2.379(5)Å

(O(4)) and 3.720(8) (O(4')).

The molecular structure of the monomeric unit is shown in Figure 5.3, an ORTEP diagram of the monomeric unit in Figure 5.4, the molecular structure of the dimer in Figure 5.5 and a cell packing diagram in Figure 5.6.

Fig.5.3 - The structure of the monomer

$[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]$

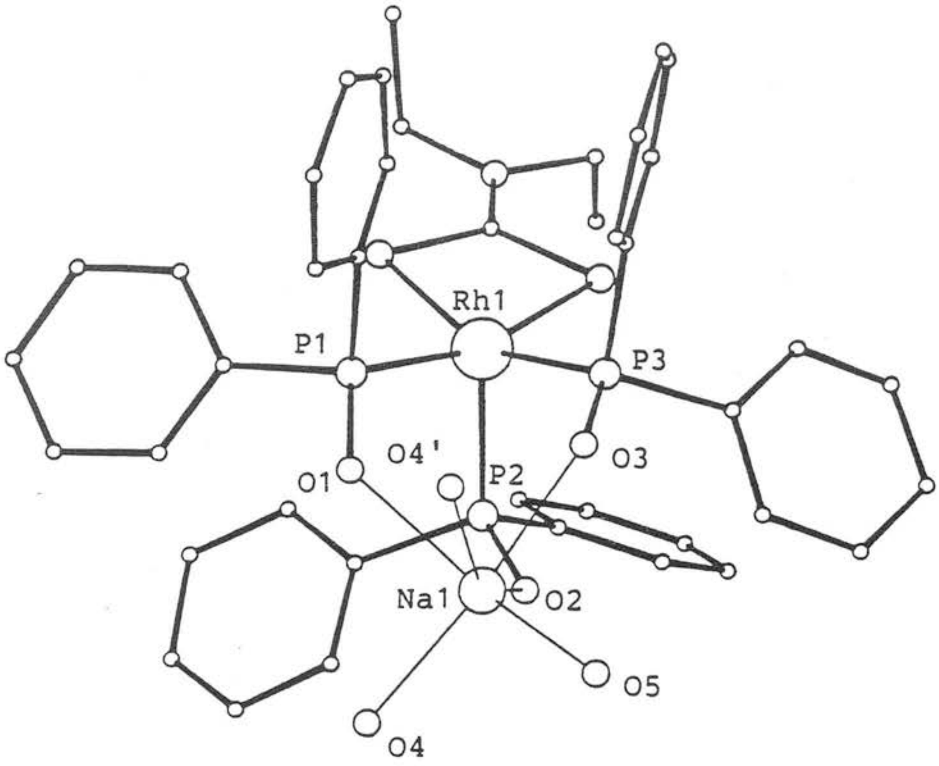


Fig.5.4 - An ORTEP diagram of the monomer

$[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu-OH_2)\}]$

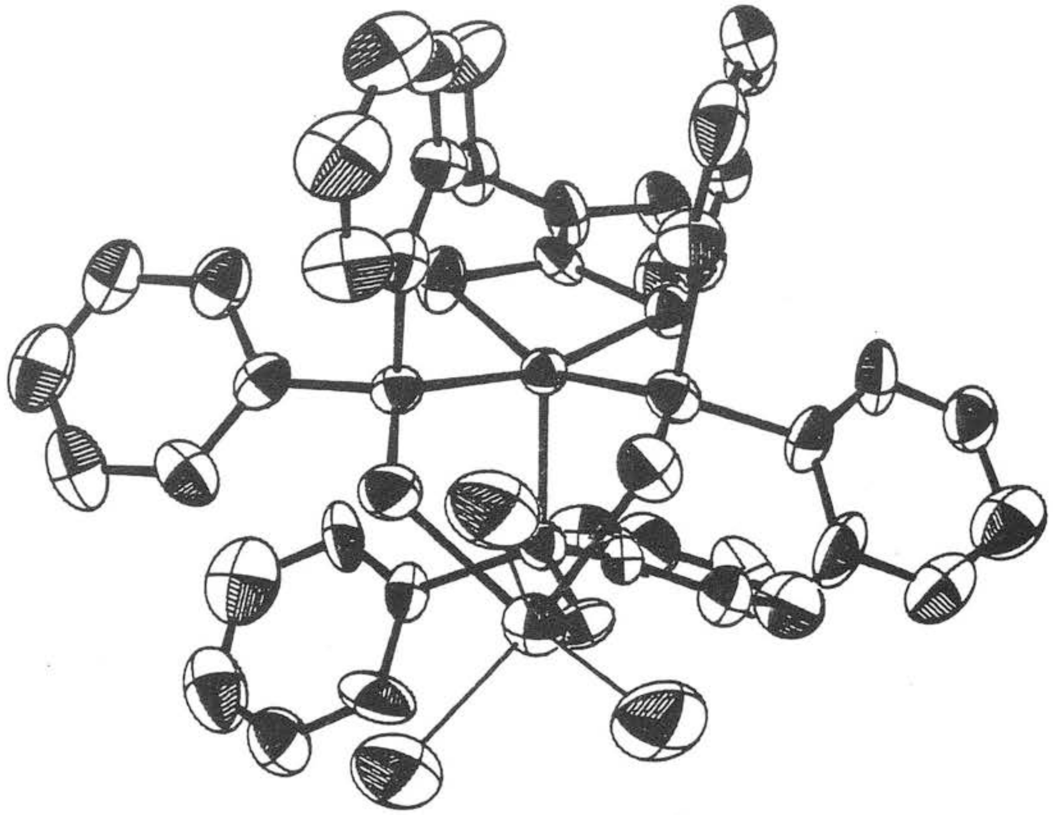


Fig.5.5 - The structure of the dimer

$[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2.4CHCl_3$

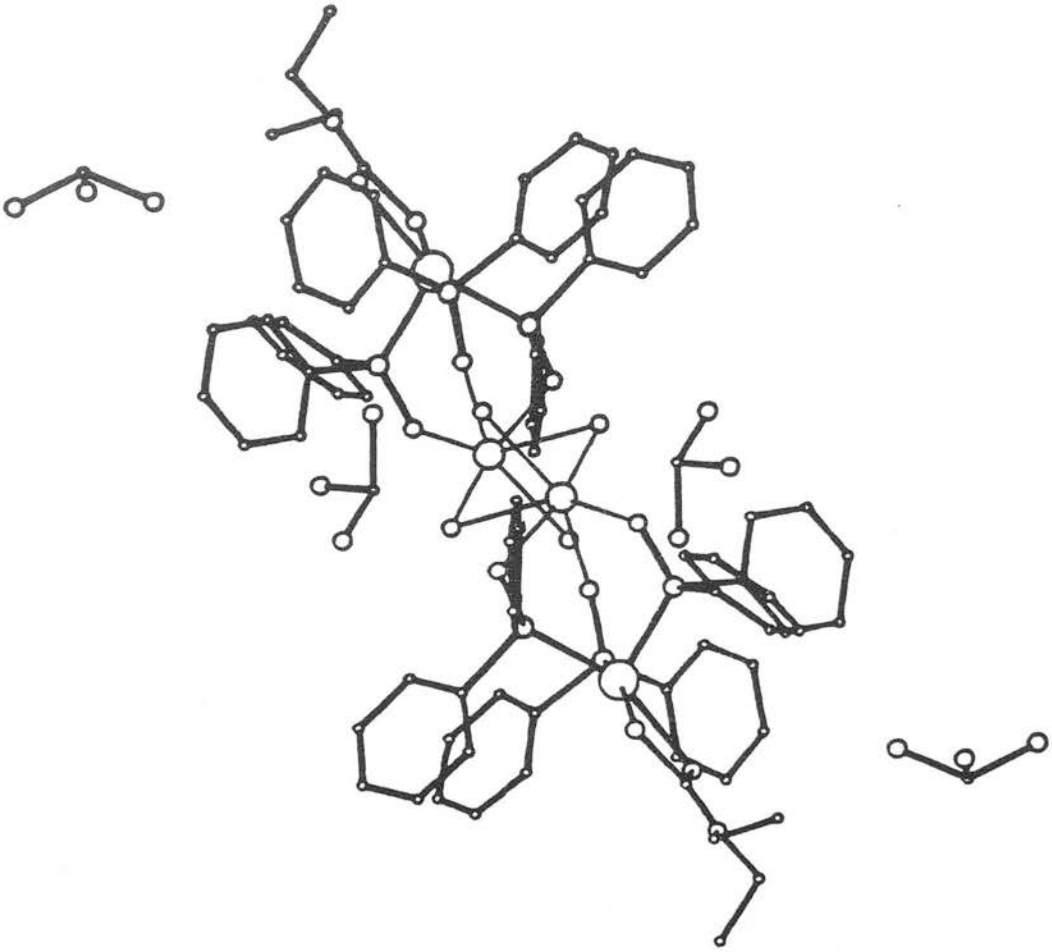
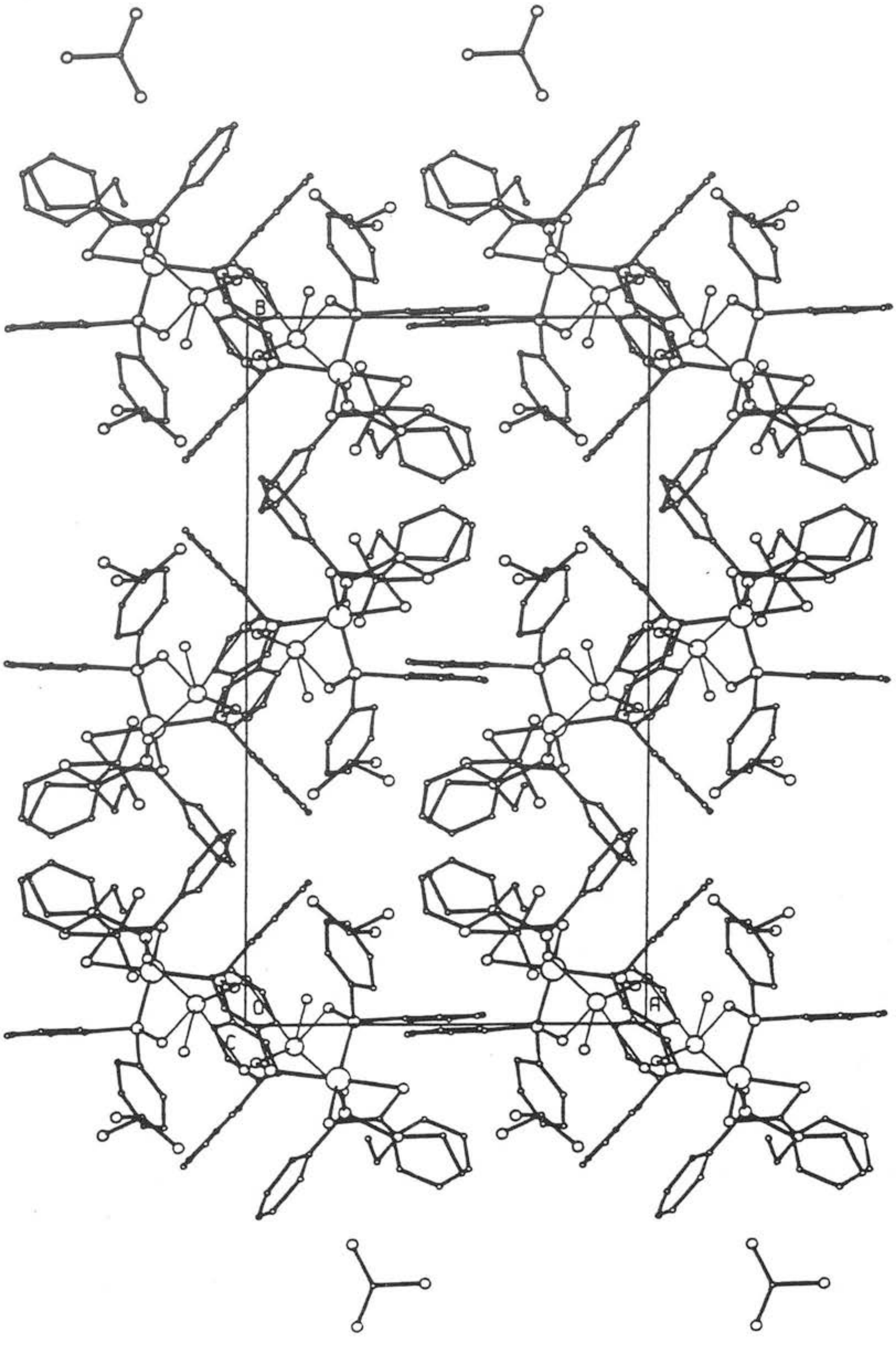


Fig.5.6 - A crystal packing diagram of $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2.4CHCl_3$



5.4.3 With carboxylates

With the characterisation of $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)_2\}]$ revealing five coordinate rhodium(III) it was of interest to determine whether other bidentate ligands would result in the rhodium being coordinated in a similar manner.

Hence $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ and NaO_2CPh (1:5 molar ratio) were refluxed in $MeOH/CHCl_3$ (1:1, v/v). Following the removal of excess benzoate, work up of the resulting filtrate using petroleum ether (b.p. 40-60°C) resulted in a pale yellow powder.

The $^{31}P-\{^1H\}$ n.m.r. spectrum of this compound in d^6-acetone at 298K consists of a broad doublet centred at δ = 69.6 p.p.m. ($^1J_{Rh-P}$=145.6Hz). On cooling to 223K the doublet remains unchanged. Unfortunately further cooling leads to precipitation of the complex from solution with concurrent loss of resolution of the spectrum.

The compound shows infrared stretching vibrations at 1070, 1025, 1000 cm^{-1}, ν(P-O), 1495, 1485 cm^{-1}, $\nu(OCO)_{asym}$, 1438, 1422 cm^{-1}, $\nu(OCO)_{sym}$ indicating the presence of phosphinito and benzoate groups. A broad band at 1615 cm^{-1} also suggested the presence of water.

Unfortunately the resonances due to the phenyl protons of the phosphinito and benzoate groups overlap in the ^1H n.m.r. spectrum and so it was not possible to determine the phosphinito:benzoate ratio. The compound was found to be non-conducting in nitromethane yet gave a positive flame test for sodium.

Interestingly the data obtained for this species closely resembles that obtained for the five-coordinate complex $[Rh(S_2CNR_2)\{(Ph_2PO)_3Na(OH_2)_n\}]$ (R = Me, n=1; R = Et, n=2). This and the elemental analyses for C and H strongly suggest that the product should be formulated as $[Rh(O_2CPh)\{(Ph_2PO)_3Na(OH_2)\}]$.

Further evidence for this formulation is obtained from the analogous reaction of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ with 4-methylbenzoic acid and sodium carbonate (1:5:5 molar ratio) in acetone/H_2O (20 cm^3; 3:1, v/v) also under refluxing conditions.

The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the resulting yellow-brown powder in d^6-acetone at ambient temperature consists of a doublet centred at δ = 67.8 p.p.m. ($^1J_{Rh-P}$=142.7Hz). As with the benzoate species, no change is observed on cooling to 213K with further cooling again resulting in precipitation of the complex.

The infrared spectra show similar bands to those of the benzoate species and indicate the presence of phosphinito, 4-methylbenzoate and water. The product is non-conducting in nitromethane despite giving a positive plane test for sodium.

However, for the 4-methylbenzoate complex additional information regarding the phosphinito:4-methylbenzoate ratio can be obtained from the ^1H n.m.r. spectrum. This shows resonances due to the 4-methylbenzoate protons with an AB pattern centred at δ = 7.8 p.p.m. ($^3J_{H-H}$=8.0Hz) and a singlet at δ = 2.5 p.p.m. with the multiplet due to the phosphinito protons centred at δ = 7.4 p.p.m. Furthermore, the integrals of the peaks indicate a phosphinito:4-methylbenzoate ratio of 3:1 which, together with the elemental analyses for C and H, strongly suggests the product should be formulated as $[Rh(O_2C{-}C_6H_4{-}CH_3)\{(Ph_2PO)_3Na(OH_2)_3\}]$.

Interestingly treatment of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ with either benzoic acid or 4-methylbenzoic acid alone failed to yield any reaction with the starting materials being recovered even after refluxing for prolonged periods of up to 20 hours. However, as found with the 4-methylbenzoate complex discussed previously, inclusion of a base such as NaOMe or in these cases Na_2CO_3 results in the formation of the species $[Rh(O_2CR)\{(Ph_2PO)_3Na(OH_2)_x\}]$ ($R = C_6H_5$, n=1; $R = C_6H_4{-}4{-}CH_3$, n=3). In these cases the amount of sodium carbonate added was equimolar with the carboxylic acid. One possible function of the sodium carbonate or methoxide may be simply that of *in situ* generation of $[RCOO]^-$. However, it is also possible that the presence of the sodium ion aids the loss of chloride from the coordination sphere of the rhodium.

Reaction between $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ and monothiobenzoic acid alone yielded an inseparable mixture of unknown species.

Hence $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ and PhC(O)SH (1:5 molar ratio) were stirred in $MeOH/CHCl_3$ (1:1, v.v) to which NaOMe was added until the solution became basic. Following refluxing, work-up of the resulting solution gave an orange microcrystalline powder. Since the product was not particularly soluble in d^6-acetone the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were obtained in CD_2Cl_2 and show a doublet centred at

δ = 72.8 p.p.m. ($^1J_{Rh-P}$=136.7Hz) at 298K. However, on cooling to 183K no temperature dependent behaviour was observed. Furthermore, addition of acetone to the solution at reduced temperatures also had no effect suggesting that a solvent dependent process was not involved. The infrared spectrum confirmed the presence of phosphinito and monothiobenzoate ligands with stretching frequencies found at 1090, 1080, 1069 cm^{-1}, ν(P-O), 1494, ν(C-O) and 958 cm^{-1}, ν(C-S). A broad band at 1610 cm^{-1} also suggests the presence of water.

Identification of the positions of the C-O and C-S stretching frequencies in the infrared spectra is a most convenient method of determining the mode of bonding of the monothiobenzoate ligand. Earlier Savant et al.[146] assigned bands at 1500 and 960 cm^{-1} in Na S(O)CPh to the ν(C-O) and ν(C-S) stretching vibrations respectively and then, by comparison with these values, elucidated the mode of bonding in a series of metal monothiobenzoate complexes. Thus, for bidentate coordination both ν(C-O) and ν(C-S) remain almost unaffected but, as the interaction through sulphur becomes more important than that through oxygen, ν(C-O) increases and ν(C-S) decreases.

The infrared spectrum of the product isolated from the reaction of PhC(O)SH and NaOMe with $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ shows that the monothiobenzoate ligand is bound in a bidentate manner, thus reinforcing the belief that the complex is also a five coordinate rhodium(III) species.

The ^{1}H n.m.r. spectrum shows resonances due to water and phenyl protons but it was not possible to distinguish between those of the phosphinito or monothiobenzoate groups. As in previous cases, the product was found to give a positive flame test for sodium yet was non-conducting in nitromethane.

The accumulated data together with elemental analyses for C and H indicate that the compound be formulated as $[Rh(S(O)CPh)\{(Ph_2PO)_3Na(OH_2)\}]$.

5.5 Miscellaneous reactions

Robertson and Stephenson recently reported that the five coordinate complex $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ reacts with carbon monoxide under very mild conditions to give the six coordinate $[Ru(CO)(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$. It was also found that prolonged reaction times gave rise to some $[Ru(CO)(S_2PMe_2)\{(Ph_2PO)_2H\}]$[139].

In an attempt to prepare the rhodium analogue of the five coordinate ruthenium species, $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ was treated with NaS_2PMe_2 (1:4 molar ratio) in $MeOH/CHCl_3$. Despite varying both the reaction time and temperature only mixtures of, as yet unknown, species were obtained.

However, having prepared the five coordinate, 16 electron rhodium(III) species $[Rh(L\text{-}L)\{(Ph_2PO)_3Na(OH_2)_x\}]$ with a variety of bidentate anionic ligands (L-L = S_2CNMe_2, x=1; S_2CNEt_2, x=2; S(O)CPh, x=1; O_2CPh, x=1; $O_2C\text{-}C_6H_4\text{-}4\text{-}CH_3$, x=3) it was envisaged that it would be possible to insert a small ligand into the vacant coordination site. Unfortunately, preliminary <u>in situ</u> reactions monitored by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy are not promising. No reaction was observed at 298K between $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)_2\}]$ and CS_2, CO, PhCN, MeCN or C_6H_5N in $CDCl_3$ nor likewise between

$[Rh(S(O)CPh)\{(Ph_2PO)_3Na(OH_2)\}]$ and PhCN or MeCN under similar conditions.

Finally, in view of the synthesis of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ by the interaction of $RhCl_3.3H_2O$, pre-hydrolysed Ph_2PCl in $MeOH/H_2O$ (7:1, v/v) and conc.HNO_3, a similar approach was attempted using acetic and 4-methylbenzoic acids in place of the nitric acid. It was envisaged that this might provide a general route to species of the type $[RhCl(L-L)\{(Ph_2PO)_3H_2\}]$ or $[Rh(L-L)\{(Ph_2PO)_3H_2\}]$ but, unfortunately, in both cases no reaction was observed.

5.6 Experimental

Physical measurements were as for those described in the previous experimental sections 2.10 and 3.5. Boron-11 n.m.r. spectra were obtained on a Brücker WP200SY (64.21MHz) spectrometer. $^{31}P-\{^1H\}$ n.m.r. data for the new complexes are given in Table 5.5.

Materials

As in chapters 2 and 3 together with Ph_2PCl, NaS_2CNMe_2, NaS_2CNEt_2, NaO_2CPh, PhC(O)SH (Aldrich), $CH_3-C_6H_4-p-CO_2H$ (Koch-Light Laboratories Ltd), $PhCO_2H$, $BF_3.Et_2O$, $NaNO_3$ (Fisons), Na_2CO_3 (B.D.H.) were used as supplied. The compound $NaS_2PMe_2.2H_2O$ was prepared as described in the literature[147]. NaOMe was prepared by reaction of sodium metal with methanol and $Rh(NO_3)_3.2H_2O$ was supplied by Dr. T.A. Stephenson.

Crystal Structure Determination of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$.

Crystals suitable for X-ray analysis were isolated from the reaction conducted at ambient temperature involving the pre-hydrolysed Ph_2PCl in $MeOH/H_2O$ (48 cm^3; 7:1, v/v) with conc. HNO_3 (1.0 cm^3). An elongated, pale yellow crystal (0.2 x 0.2 x 0.4 mm) was selected and Weissenberg photographs indicated a triclinic space group. Accurate cell dimensions were obtained by least squares refinement of 18 reflections measured on an Enraf-Nonius CAD-4 diffractometer with monochromatised Mo-K_α radiation.

Crystal Data: $C_{36}H_{32}ClNO_6P_4Rh.C_{12}H_{11}OP$ M = 1008.0
$\underline{a}$ = 8.982(2), $\underline{b}$ = 14.318(3), $\underline{c}$ = 17.960(5)Å,
α = 85.79(2), β = 89.44(2), γ = 80.62(2)°,
$\underline{V}$ = 2275.9$Å^3$ $\underline{D}_c$ = 1.45 g cm^{-3}, $\underline{D}_m$ = 1.44 g cm^{-3} (by flotation), Z = 2, $\underline{F}$ (000) = 1016, μ(Mo-K_α) = 6.07 cm^{-1}, λ(Mo-K_α) = 0.71069Å. The space group is $P\bar{1}$

Intensity data were collected by ω-2θ scans of varying times up to 180 seconds such that, where possible $\underline{I}>3\sigma(\underline{I})$. Three standard reflections, monitored throughout data collection, showed no time-dependent decay. Of the 3525 intensities measured between $2<\theta<20°$, 2265 had $I>3\sigma(I)$.

Structure solution and refinement

The refinement was based on the 2265 reflections with $\underline{I}>3\sigma(\underline{I})$. The structure was solved by conventional Patterson and difference Fourier techniques. A Patterson synthesis revealed the Rh-Rh vector and the remaining non-hydrogen atoms were revealed by difference Fourier summations. The structure refinement was carried out using SHELX76 [90]. Some five cycles of least squares refinement reduced the $\underline{R}$-factor from 0.318 to 0.048. Phenyl rings were refined as rigid groups and during the last two cycles the phenyl hydrogen atoms were added in their calculated positions and allowed to ride on the carbon atoms to which they were attached. Their temperature factors were refined such that one value applied to all hydrogens on the same phenyl ring. The Rh, Cl, P atoms and O(7) were refined anisotropically. Attempts to refine the three protons found only one, attached to O(3). A weighting scheme of the form $W^{-1} = \sigma^2(\underline{F}) + 0.0006(\underline{F})^2$ was applied for a final cycle and the final residuals, based on 123 adjustable parameters, were $\underline{R} = 0.047$, $\underline{R}_w = 0.054$ for the 2265 observed data. The maximum shift/esd in the final cycle was 0.41 and a final difference Fourier map showed no peak above, nor trough below $0.5\varepsilon\text{Å}^{-3}$. No extinction correction was made. All scattering factors were inlaid in the program except those for Rh which were taken from reference (91).

Final fractional coordinates are given in Table 5.1 and selected bond distances and angles in Table 5.2. The molecular structure is shown in Figure 5.1 and an ORTEP diagram of the molecule together with the $Ph_2P(O)H$ solvate in Figure 5.2.

Crystal Structure Determination of $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2.4CHCl_3$.

On standing in air for several days a chloroform solution of $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)_2\}]$ deposited a large orange hexagonal crystal. This was then cut to a size suitable for X-ray analysis. Accurate cell dimensions were obtained by least-squares refinement of 25 reflections measured on an Enraf-Nonius CAD4 diffractometer with monochromatised Mo-K_α radiation.

Crystal Data: $C_{82}H_{88}N_2Na_2O_{10}P_6Rh_2S_4.4CHCl_3$, $M = 2304.9$
$\underline{a} = 14.046(19)$, $\underline{b} = 27.008(8)$, $\underline{c} = 15.986(7)$Å,
$\beta = 108.31(6)°$, $\underline{V} = 5124.6Å^3$, $\underline{D}_c = 1.494$ g cm^{-3},
$\underline{Z} = 2$, $\underline{F}(000) = 2344$, μ(Mo-K_α) = 55.46 cm^{-1},
λ(Mo-K_α) = 0.71069Å. The space group is $\underline{P}2_1/\underline{C}$.

Intensity data were collected by ω-2θ scans. Two standard reflections were monitored regularly throughout the data collection. On the basis of these measurements the data were corrected for isotropic decay with the minimum and maximum drift corrections being 0.870 and 1.123 respectively. The observed decay is probably a result of loss of chloroform of crystallisation from the crystal. Intensities were measured for 5458 independent reflections ($2<\theta<21°$) of which 3273 had $\underline{I}>3\sigma(\underline{I})$. An absorption correction was applied with the minimum and maximum corrections being 0.8 and 1.2 respectively.

Structure Solution and Refinement

The refinement was based on the 3273 reflections with $I > 3\sigma(I)$. The structure was solved by conventional Patterson and difference Fourier techniques. The rhodium atom was located from a Patterson map using SHELX84[89]. Subsequent difference Fourier syntheses revealed all non-hydrogen atoms in the molecule. The structure refinement was carried out using SHELX76[80]. All non-hydrogen atoms were refined anisotropically. The position of one of the chloroform solvate molecules was found to be dissolved such that each chlorine partially occupied two sites. The chlorines in the positions with major (87%) occupancy were refined anisotropically while those of minor (13%) occupancy were refined isotropically. The other chloroform solvate molecule was refined anisotropically. No hydrogen atoms were included in the refinement. Unit weights were applied and the final residuals, based on 327 adjustable parameters was $R = 0.070$, $R_w = 0.078$ for the 3273 observed data. The maximum shift/esd in the final cycle was 0.011 and a final difference Fourier map showed no peak above, nor trough below $1.1 \varepsilon \mathring{A}^{-3}$. All scattering factors were inlaid in the program except those for Rh which were taken from reference (91).

Final fractional coordinates are given in Table 5.3 and selected bond distances and angles in Table 5.4. The molecular structure of the monomeric unit is shown in Figure 5.3, an ORTEP diagram of the monomeric unit in Figure 5.4, the molecular structure of the dimer in Figure 5.5 and a packing diagram in Figure 5.6.

Chloronitrato[bishydrogentris(diphenylphosphinito)] rhodium(III): $RhCl(NO_3)\{(Ph_2PO)_3H_2\}$

i) Ph_2PCl (0.61 g) was dissolved in $MeOH/H_2O$ (24 cm^3; 7:1, v/v) and the solution left to hydrolyse. $Rh(NO_3)_3.2H_2O$ (0.30 g, 4:1 molar ratio) was added and the solution refluxed for 4 hours giving a yellow solution which deposited a pale yellow powder. This was filtered off, washed with water and diethyl ether and dried *in vacuo* at 60°C. m.p. 183-185°C (decomp). (Yield 0.50 g, 66.6%). (Found, C, 53.2; H, 4.0; N, 1.5. Calc. for $C_{36}H_{32}NClO_6P_3Rh$:- C, 53.7; H, 4.0; N, 1.7%). Infrared spectrum (nujol and HCB mulls); ν(P-O), 1025s, 1001s, 970s; $\nu(NO_3)$, 1519s, 1241s; ν(Rh-Cl), 240w cm^{-1}.

ii) Ph_2PCl (1.0 g) was dissolved in $MeOH/H_2O$ (48 cm^3; 7:1, v/v) to which conc. HNO_3 (1.0 cm^3) had been added and the mixture allowed to hydrolyse. $RhCl_3.3H_2O$ (0.3 g, 4:1 molar ratio) was then added and the mixture refluxed gently for 3½ hours. On cooling the resulting suspension was treated with H_2O (*ca*.5-10 cm^3) and the pale yellow powder filtered off, washed with methanol and diethyl ether and dried *in vacuo* at 60°C. m.p. 182-185°C (decomp). (Yield 0.75 g, 81.0%). (Found, C, 53.3; H, 3.9; N, 1.6. Calc. for $C_{36}H_{32}NClO_6P_3Rh$:- C, 53.7; H, 4.0; N, 1.7%). I.r. spectrum (nujol and HCB mulls); ν(P-O), 1027s, 1002s, 968s; $\nu(NO_3)$, 1521s, 1242s; ν(Rh-Cl), 241w cm^{-1}.

iii) Ph_2PCl (1.0 g) was dissolved in $MeOH/H_2O$ (48 cm^3; 7:1, v/v) to which $NaNO_3$ (3.0 g) had been added and the mixture allowed to hydrolyse. $RhCl_3.3H_2O$ (0.30 g, 4:1 molar ratio) was then added and the mixture refluxed gently for 4 hours, cooled then treated with H_2O (ca.5-10 cm^3). The product was then isolated as a pale yellow powder, washed with methanol and diethyl ether and dried *in vacuo* at 60°C. (Yield 0.44 g, 47.5%).

Chloronitrato[hydrogenbis(diphenylphosphinito)](diphenylphosphinous acid)rhodium(III).Diphenylphosphine Oxide Solvate: $[RhCl(NO)_3\{(Ph_2PO)_2H\}(Ph_2POH)].Ph_2P(O)H$

Ph_2PCl (0.75 g) was dissolved in $MeOH/H_2O$ (24 cm^3; 7:1, v/v) to which conc. HNO_3 (1.0 cm^3) had been added and the mixture allowed to hydrolyse. $RhCl_3.3H_2O$ (0.3 g, 3:1 molar ratio) was added and the resulting solution shaken at ambient temperature for 4 months. Pale yellow crystals were then filtered off, washed with methanol and diethyl ether and dried *in vacuo* at 60°C. m.p. 156-160°C (decomp). (Yield 0.08 g, 6.9%). (Found, C, 56.2; H, 4.5; N, 1.2. Calc. for $C_{48}H_{43}NClO_7P_4Rh$:- C, 57.2; H, 4.3; N, 1.4%.

N,N-Dimethyldithiocarbamatotris[μ-diphenylphosphinito-*O*(Na)-*P*(Rh)]rhodium(III) sodium(I). Hydrate: $Rh(S_2CNMe_2)\{(Ph_2PO)_3Na(OH_2)\}$

$[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ (0.30 g) and NaS_2CNMe_2 (0.31 g; 1:5 molar ratio) were added to $MeOH/CHCl_3$ (20 cm^3, 1:1, v/v) and the mixture heated under refluxing conditions for 90 mins. The resulting suspension was cooled in the fridge overnight after which the product was filtered off as orange microcrystals which were then washed with methanol and water and dried in vacuo at 60°C. m.p. 207-209°C (decomp) (0.30 g, 92.9%). (Found, C, 53.9; H, 4.1; N, 1.5. Calc. for $C_{39}H_{38}NNaO_4P_3RhS_2$:- C, 54.0; H, 4.4; N, 1.6%). I.r. spectrum (nujol and HCB mulls); ν(P-O), 1075s, 1060s cm^{-1}; ν(C-N), 1520s cm^{-1}.

N,N-Diethyldithiocarbamatotris[μ-diphenylphosphinito-O(Na)P(Rh)]rhodium(III) sodium(I).Dihydrate: $Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)_2\}$

$[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ (0.30 g) and NaS_2CNEt_2 (0.33 g; 1:5 molar ratio) were refluxed in $MeOH/CHCl_3$ (20 cm^3, 1:1, v/v) for 90 mins. The resulting suspension was placed in the fridge overnight after which the product was filtered off, washed with methanol and water and dried in vacuo at 60°C. m.p. 180-183°C (decomp). (0.30 g, 88.2%). (Found, C, 53.9; H, 4.8; N, 1.5. Calc. for $C_{41}H_{44}NNaO_5P_3RhS_2$:- C, 53.9; H, 4.2; N, 1.5%). I.r. spectrum (nujol and HCB mulls); ν(P-O), 1078s, 1063s cm^{-1}; ν(C-N), 1497s cm^{-1}.

Benzoatotris[μ-diphenylphosphinito-O(Na)P(Rh)rhodium(III) sodium(I). Hydrate: $Rh(O_2CPh)\{(Ph_2PO)_3Na(OH_2)\}$

1) $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ (0.3 g) and NaO_2CPh (0.27 g, 1:5 molar ratio) were refluxed in $MeOH/CHCl_3$ (20 cm^3; 1:1, v/v) for 16 hours. The solution was then reduced in volume to ca.5-10 cm^3 and the excess NaO_2CPh removed by filtration and washed with chloroform. The filtrate and the washings were then combined and the resulting golden yellow solution reduced in volume, almost to dryness. Work-up with P.E. (b.p. 40-60°C) gave the product as a pale yellow powder which was filtered off, washed with water and dried in vacuo at 60°C. m.p. 105-110°C (decomp). (0.27 g, 83.5%). (Found, C, 59.9; H, 4.3. Calc. for $C_{43}H_{37}NaO_6P_3Rh$:- C, 59.5; H, 4.3%). I.r. spectrum (nujol and HCB mulls); ν(P-O), 1070s, 1025s, 1000s cm^{-1}; $\nu(OCO)_{asym}$, 1495w, 1485 cm^{-1}; $\nu(OCO)_{sym}$, 1438s, 1422s cm^{-1}.

2) $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ (0.30 g), $PhCO_2H$ (0.23 g) and $Na_2CO_3.10H_2O$ (0.48 g; 1:5:5 molar ratio) were refluxed in acetone/water (20 cm^3; 3:1, v/v) for 10 hours. The resulting solution was reduced in volume to ca.5 cm^3 and the product obtained as a yellow powder which was filtered off, washed with water and dried in vacuo at 60°C. (0.16 g, 49.5%).

4-Methylbenzoatotris[μ-diphenylphosphinito-O(Na)P(Rh)]-rhodium(III) sodium(I). Hydrate: $Rh(O_2C-C_6H_4-4-CH_3)\{(Ph_2PO)_3Na(OH_2)\}$

$[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ (0.30 g), 4-methylbenzoic acid (0.26 g) and $Na_2CO_3.10H_2O$ (0.54 g; 1:5:5 molar ratio) were refluxed in acetone/water (20 cm^3; 3:1, v/v). The resulting brown solution was reduced in volume to ca.5 cm^3 and the product was filtered off as a yellow-brown powder which was then washed with water and dried in vacuo at 60°C. m.p. 173-175°C (decomp), (0.13 g, 38.0%). (Found, C, 58.4; H, 4.6. Calc. for $C_{44}H_{43}NaO_8P_3Rh$:- C, 57.5; H, 4.6%). I.r. spectrum (nujol and HCB mulls):- ν(P-O), 1092s, 1080s, 1068s cm^{-1}; $\nu(OCO)_{sym}$, 1438m, 1421s cm^{-1}.

Monothiobenzoatotris[μ-diphenylphosphinito-O(Na)P(Rh)]-rhodium(III) sodium(I). Hydrate: $Rh(S(O)CPh)\{(Ph_2PO)_3Na(OH_2)\}$

$[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ (0.30 g) and PhCOSH (0.25 g; 1:5 molar ratio) were stirred in $MeOH/CHCl_3$ (20 cm^3; 1:1, v/v). NaOMe was then added until the solution became basic whereupon it was refluxed for 2 hours. The resulting solution was reduced in volume (almost to dryness) and then redissolved in a solution of $EtOH/CH_2Cl_2$ (ca.10 cm^3; 1:1, v/v). Following cooling in a fridge overnight, a yellow-orange powder was obtained by filtration. Using a soxhlet apparatus this was then extracted with $CHCl_3$ giving an orange solution. Reduction in volume followed by careful addition of ethanol (ca.10 cm^3) yielded the product as an orange microcrystalline powder which was filtered off and dried *in vacuo* at 60°C. m.p. 220-222°C (decomp). (0.13 g, 39.3%). (Found, C, 58.5; H, 4.0. Calc. for $C_{43}H_{37}NaO_5P_3RhS$: C, 58.4; H, 4.2%). *I.r. spectra (nujol and HCB mulls)*; ν(P-O), 1090s, 1080s, 1069s cm^{-1}; ν(C-O), 1494m cm^{-1}; ν(C-S), 948m cm^{-1}.

Table 5.1 - Fractional coordinates for $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$

Fractional coordinates with standard deviations ( ).

Atom	x	y	z
Rh1	-0.05501(11)	0.68378(6)	0.76589(5)
Cl1	-0.26930(36)	0.63595(21)	0.70978(17)
P1	0.14452(37)	0.71188(21)	0.83644(17)
O1	0.24810(78)	0.77786(46)	0.79655(36)
P2	0.05471(38)	0.73288(22)	0.65923(16)
O2	0.15789(86)	0.80654(51)	0.67033(38)
P3	-0.17839(36)	0.82955(20)	0.77940(16)
O3	-0.07350(80)	0.90557(48)	0.78882(36)
H3	0.89848(1375)	0.96543(803)	0.78698(636)
O5	-0.11298(83)	0.59086(52)	0.86480(38)
O7	0.02829(85)	0.52985(47)	0.77538(41)
N1	-0.04512(117)	0.51860(77)	0.83494(58)
O6	-0.04978(98)	0.43775(64)	0.86407(46)
C11	0.26687(79)	0.60216(42)	0.86438(42)
C12	0.23978(79)	0.54323(42)	0.92663(42)
C13	0.34162(79)	0.46080(42)	0.94588(42)
C14	0.47057(79)	0.43732(42)	0.90291(42)
C15	0.49766(79)	0.49625(42)	0.84066(42)
C16	0.39581(79)	0.57867(42)	0.82140(42)
H12	0.13995(79)	0.56141(42)	0.95991(42)
H13	0.32064(79)	0.41517(42)	0.99408(42)
H14	0.54941(79)	0.37350(42)	0.91781(42)
H15	0.59748(79)	0.47807(42)	0.80737(42)
H16	0.41679(79)	0.62429(42)	0.77321(42)
C111	0.08768(83)	0.76460(49)	0.92324(32)
C112	-0.00420(83)	0.72634(49)	0.97629(32)
C113	-0.03609(83)	0.76902(49)	1.04320(32)
C114	0.02391(83)	0.84996(49)	1.05707(32)
C115	0.11581(83)	0.88823(49)	1.00402(32)
C116	0.14769(83)	0.84554(49)	0.93711(32)
H112	-0.05066(83)	0.66367(49)	0.96556(32)
H113	-0.10722(83)	0.73940(49)	1.08427(32)
H114	-0.00077(83)	0.88301(49)	1.10886(32)
H115	0.16226(83)	0.95089(49)	1.01474(32)
H116	0.21884(83)	0.87517(49)	0.89604(32)
C221	0.16896(90)	0.62662(44)	0.63028(38)
C222	0.32543(90)	0.62101(44)	0.62848(38)
C223	0.41606(90)	0.53928(44)	0.60625(38)
C224	0.35024(90)	0.46318(44)	0.58582(38)
C225	0.19379(90)	0.46879(44)	0.58763(38)
C226	0.10314(90)	0.55052(44)	0.60986(38)
H222	0.37638(90)	0.67992(44)	0.64429(38)
H223	0.53720(90)	0.53493(44)	0.60485(38)
H224	0.42042(90)	0.39991(44)	0.56861(38)
H225	0.14283(90)	0.40988(44)	0.57182(38)
H226	-0.01799(90)	0.55487(44)	0.61125(38)

Table 5.1 (cont.)

Atom	x	y	z
C21	-0.05102(94)	0.77833(57)	0.57492(35)
C22	0.01100(94)	0.84679(57)	0.53122(35)
C23	-0.05289(94)	0.88130(57)	0.46213(35)
C24	-0.17879(94)	0.84732(57)	0.43674(35)
C25	-0.24081(94)	0.77885(57)	0.48046(35)
C26	-0.17692(94)	0.74434(57)	0.54955(35)
H22	0.10848(94)	0.87309(57)	0.55087(35)
H23	-0.00486(94)	0.93430(57)	0.42829(35)
H24	-0.22826(94)	0.87404(57)	0.38325(35)
H25	-0.33829(94)	0.75255(57)	0.46080(35)
H26	-0.22494(94)	0.69133(57)	0.58337(35)
C31	-0.29045(75)	0.82663(51)	0.86279(31)
C32	-0,28623(75)	0.89499(51)	0.91381(31)
C33	-0.37231(75)	0.89350(51)	0.97878(31)
C34	-0.46261(75)	0.82364(51)	0.99274(31)
C35	-0.46683(75)	0.75528(51)	0.94172(31)
C36	-0.38075(75)	0.75678(51)	0.87675(31)
H32	-0.21633(75)	0.94907(51)	0.90300(31)
H33	-0.36905(75)	0.94643(51)	1.01828(31)
H34	-0.52925(75)	0.82249(51)	1.04304(31)
H35	-0.53673(75)	0.70120(51)	0.95252(31)
H36	-0.38402(75)	0.70385(51)	0.83723(31)
C331	-0.30612(76)	0.88339(45)	0.70615(32)
C332	-0.45225(76)	0.86306(45)	0.70136(32)
C333	-0.54939(76)	0.90894(45)	0.64516(32)
C334	-0.50041(76)	0.97518(45)	0.59377(32)
C335	-0.35429(76)	0.99551(45)	0.59857(32)
C336	-0.25714(76)	0.94962(45)	0.65476(32)
H332	-0.4916(76)	0.81178(45)	0.74114(32)
H333	-0.66253(76)	0.89320(45)	0.64145(32)
H334	-0.57564(76)	1.01069(45)	0.55027(32)
H335	-0.31637(76)	1.04677(45)	0.55878(32)
H336	-0.14401(76)	0.96536(45)	0.65847(32)

Diphenylphosphine oxide solvate molecule

Atom	x	y	z
P4	-0.31926(40)	0.17059(23)	0.79158(18)
O4	-0.21873(89)	0.07651(50)	0.79982(41)
C41	-0.27395(92)	0.24669(53)	0.71590(41)
C42	-0.31482(92)	0.23319(53)	0.64324(41)
C43	-0.27722(92)	0.29324(53)	0.58385(41)
C44	-0.19878(92)	0.36680(53)	0.59712(41)
C45	-0.15791(92)	0.38030(53)	0.66977(41)
C46	-0.19548(92)	0.32024(53)	0.72916(41)

Table 5.1 (cont.)

Atom	x	y	z
H42	-0.37555(92)	0.17624(53)	0.63297(41)
H43	-0.30887(92)	0.28280(53)	0.52729(41)
H44	-0.16968(92)	0.41330(53)	0.55114(41)
H45	-0.09717(92)	0.43724(53)	0.68004(41)
H46	-0.16385(92)	0.33069(53)	0.78542(41)
C441	-0.51522(92)	0.16471(47)	0.78493(42)
C442	-0.56343(92)	0.07671(47)	0.79137(42)
C443	-0.71601(92)	0.07130(47)	0.78335(42)
C444	-0.82040(92)	0.15390(47)	0.76889(42)
C445	-0.77220(92)	0.24190(47)	0.76245(42)
C446	-0.61961(92)	0.24731(47)	0.77047(42)
H442	-0.48261(92)	0.01276(47)	0.80257(42)
H443	-0.75333(92)	0.00317(47)	0.78833(42)
H444	-0.93854(92)	0.14972(47)	0.76268(42)
H445	-0.85302(92)	0.30585(47)	0.75126(42)
H446	-0.58229(92)	0.31544(47)	0.76549(42)

Table 5.2 - Selected bond lengths and angles for $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}].Ph_2P(O)H$

a) Bond lengths (Å) with standard deviations ( )

Rh(1) - P(1)	2.310(3)	O(1) - O(2)	2.400(10)
Rh(1) - P(2)	2.265(3)	O(1) - O(3)	3.157(10)
Rh(1) - P(3)	2.228(3)	O(2) - O(3)	3.204(10)
Rh(1) - O(5)	2.250(7)	O(4) - O(1)	5.486(10)
Rh(1) - O(7)	2.205(7)	O(4) - O(2)	5.361(11)
N(1) - O(5)	1.266(13)	O(4) - O(3)	2.601(10)
N(1) - O(6)	1.242(14)	O(1) - H(3)	3.780(118)
N(1) - o(7)	1.266(13)	O(2) - H(3)	3.724(118)
P(1) - O(1)	1.564(8)	O(3) - H(3)	0.851(118)
P(2) - O(2)	1.538(9)	O(4) - H(3)	1.791(118)
P(3) - O(3)	1.571(8)		
P(4) - O(4)	1.494(7)		

b) Bond angles (°) with standard deviations ( ).

P(1) - Rh(1) - P(2)	91.3(1)	O(5) - N(1) - O(6)	120.3(1.0)
P(1) - Rh(1) - P(3)	91.2(1)	O(5) - N(1) - O(7)	119.1(1.0)
P(1) - Rh(1) - Cl(1)	170.3(1)	O(6) - N(1) - O(7)	120.5(1.0)
P(1) - Rh(1) - O(5)	86.5(2)	Rh(1) - P(1) - O(1)	115.3(0.3)
P(1) - Rh(1) - O(7)	91.3(2)	Rh(1) - P(2) - O(2)	113.6(0.3)
P(2) - Rh(1) - P(3)	91.6(1)	Rh(1) - P(3) - O(3)	114.3(0.3)
P(2) - Rh(1) - Cl(1)	97.5(1)	P(1) - O(1) - H(3)	85.5(8.0)
P(2) - Rh(1) - O(5)	161.2(2)	P(2) - O(2) - H(3)	98.2(8.0)
P(2) - Rh(1) - O(7)	102.7(2)	P(3) - O(3) - H(3)	126.3(8.0)
P(3) - Rh(1) - Cl(1)	92.5(1)	P(4) - O(4) - H(3)	166.9(8.0)
P(3) - Rh(1) - O(5)	107.2(2)	O(3) - H(3) - O(1)	38.3(8.0)
P(3) - Rh(1) - O(7)	165.4(2)	O(3) - H(3) - O(2)	46.9(8.0)
Cl(1) - Rh(1) - O(5)	83.8(2)	O(3) - H(3) - O(4)	158.4(8.0)
Cl(1) - Rh(1) - O(7)	82.9(2)	O(4) - H(3) - O(1)	158.6(8.0)
O(5) - Rh(1) - O(7)	58.7(3)	O(4) - H(3) - O(2)	150.9(8.0)
		O(1) - H(3) - O(2)	37.3(8.0)

Table 5.3 - Fractional coordinates for

$[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2.4CHCl_3$

Fractional coordinates with standard deviations ( ).

Atom	x	y	z
Rh(1)	0.76733(8)	0.07740(5)	0.17403(7)
S(1)	0.7903(3)	0.13944(17)	0.0640(3)
S(2)	0.6038(3)	0.09070(15)	0.06519(24)
C(37)	0.6643(10)	0.1342(5)	0.0117(9)
N(1)	0.6163(9)	0.1609(5)	-0.0622(8)
C(38)	0.6709(11)	0.1970(7)	-0.1077(10)
C(39)	0.6940(15)	0.1621(9)	-0.1816(13)
C(40)	0.5052(11)	0.1582(7)	-0.1028(10)
C(41)	0.4561(13)	0.2117(8)	-0.0903(13)
P(1)	0.9359(3)	0.06425(15)	0.24668(23)
P(2)	0.7508(3)	0.12521(15)	0.28750(25)
P(3)	0.7287(3)	-0.00347(16)	0.23257(24)
O(1)	0.9723(7)	0.0525(4)	0.3464(6)
O(2)	0.7552(7)	0.0953(4)	0.3703(5)
O(3)	0.7919(7)	-0.0240(4)	0.3209(6)
Na(1)	0.8767(4)	0.03075(24)	0.4378(4)
O(4)	1.0019(10)	0.0631(6)	0.5665(8)
O(5)	0.8468(10)	-0.0372(6)	0.5399(8)
C(1)	1.0535(15)	-0.0253(8)	0.2366(12)
C(2)	1.0847(16)	-0.0684(8)	0.1893(17)
C(3)	1.0349(17)	-0.0789(9)	0.0987(15)
C(4)	0.9594(14)	-0.0464(7)	0.0586(12)
C(5)	0.9228(11)	-0.0030(6)	0.1001(9)
C(6)	0.9690(11)	0.0052(6)	0.1884(10)
C(7)	1.0722(12)	0.1509(7)	0.3023(11)
C(8)	1.1405(14)	0.1912(8)	0.2945(14)
C(9)	1.1531(14)	0.1992(8)	0.2109(16)
C(10)	1.0981(13)	0.1680(8)	0.1371(13)
C(11)	1.0310(12)	0.1270(7)	0.1481(11)
C(12)	1.0150(10)	0.1179(6)	0.2305(10)
C(13)	0.8803(14)	0.1917(7)	0.4126(11)
C(14)	0.9431(15)	0.2375(8)	0.4413(14)
C(15)	0.9665(15)	0.2727(9)	0.3864(18)
C(16)	0.9291(15)	0.2640(8)	0.2896(17)
C(17)	0.8605(11)	0.2187(6)	0,2584(11)
C(18)	0.8389(10)	0.1837(5)	0.3189(10)
C(19)	0.5519(13)	0.1352(8)	0.2721(12)
C(20)	0.4515(13)	0.1601(9)	0.2396(13)
C(21)	0.4391(14)	0.2064(7)	0.1867(14)
C(22)	0.5160(15)	0.2314(8)	0.1643(13)
C(23)	0.6137(13)	0.2064(7)	0.1934(10)
C(24)	0.6286(11)	0.1601(6)	0.2477(10)
C(25)	0.7948(12)	-0.1007(7)	0.1868(12)
C(26)	0.7965(14)	-0.1447(7)	0.1237(16)

Table 5.3 (cont.)

Atom	x	y	z
C(27)	0.7434(15)	-0.1411(8)	0.0346(13)
C(28)	0.6886(12)	-0.0951(7)	0.0031(12)
C(29)	0.6814(12)	-0.0517(6)	0.0613(11)
C(30)	0.7352(12)	-0.0572(6)	0.1528(11)
C(31)	0.5141(12)	-0.0101(7)	0.1584(11)
C(32)	0.4210(13)	-0.0122(7)	0.1680(12)
C(33)	0.4047(17)	-0.0136(8)	0.2520(15)
C(34)	0.4897(17)	-0.0079(8)	0.3264(14)
C(35)	0.5884(14)	-0.0056(7)	0.3207(13)
C(36)	0.5997(11)	-0.0086(7)	0.2343(11)

Chloroform solvent molecules

C(42)	0.740(3)	-0.1291(11)	0.4121(13)
Cl(2)	0.8338(7)	-0.1745(4)	0.4441(6)
Cl(1)	0.6461(8)	-0.1562(4)	0.3207(7)
Cl(3)	0.6772(8)	-0.1298(7)	0.4926(8)
C(43)	0.6772(18)	0.3720(9)	0.0186(15)
Cl(4)	0.7169(10)	0.4307(5)	0.0745(7)
Cl(5)	0.5487(8)	0.3694(6)	0.0083(8)
Cl(6)	0.7333(13)	0.3135(5)	0.0737(9)
Cl(7)	0.805(3)	0.3760(19)	0.105(3)
Cl(8)	0.628(4)	0.3187(20)	0.013(3)
Cl(9)	0.625(5)	0.419(3)	0.056(4)

Table 5.4 - Selected bond lengths and angles for $[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)(\mu\text{-}OH_2)\}]_2.4CHCl_3$

a) Bond lengths (Å) with standard deviations ( ).

Rh(1) - S(1)	2.402(4)	P(2) - O(2)	1.490(10)
Rh(1) - S(2)	2.431(4)	P(2) - C(18)	1.835(15)
Rh(1) - P(1)	2.311(4)	P(2) - C(24)	1.837(16)
Rh(1) - P(2)	2.219(4)	P(3) - O(3)	1.497(11)
Rh(1) - P(3)	2.293(4)	P(3) - C(30)	1.836(17)
S(1) - C(37)	1.710(14)	P(3) - C(36)	1.827(17)
S(2) - C(37)	1.733(14)	Na(1) - O(1)	2.335(11)
P(1) - O(1)	1.540(10)	Na(1) - O(2)	2.308(11)
P(1) - C(6)	1.835(16)	Na(1) - O(3)	2.289(11)
P(1) - C(12)	1.775(15)	Na(1) - O(4)	2.379(15)
		Na(1) - O(5)	2.435(15)
		Na(1) - O(4')	3.720(8)

b) Bond angles (°) with standard deviations ( ).

S(1) - Rh(1) - S(2)	73.11(14)	Rh(1) - P(3) - O(3)	121.2(4)
S(1) - Rh(1) - P(1)	95.73(14)	Rh(1) - P(3) - C(30)	104.0(5)
S(1) - Rh(1) - P(2)	110.49(15)	Rh(1) - P(3) - C(36)	115.2(5)
S(1) - Rh(1) - P(3)	157.97(15)	O(1) -Na(1) - O(2)	92.6(4)
S(2) - Rh(1) - P(1)	165.65(14)	O(1) -Na(1) - O(3)	82.7(4)
S(2) - Rh(1) - P(2)	101.42(14)	O(1) -Na(1) - O(4)	93.0(5)
S(2) - Rh(1) - P(3)	96.35(14)	O(1) -Na(1) - O(5)	145.4(5)
P(1) - Rh(1) - P(2)	90.83(14)	O(2) -Na(1) - O(3)	83.4(4)
P(1) - Rh(1) - S(3)	90.96(14)	O(2) -Na(1) - O(4)	115.1(5)
P(2) - Rh(1) - P(3)	90.31(15)	O(2) -Na(1) - O(5)	120.3(5)
Rh(1) - S(1) - C(37)	87.4(5)	O(3) -Na(1) - O(4)	161.3(5)
Rh(1) - S(2) - C(37)	86.0(5)	O(3) -Na(1) - O(5)	90.4(5)
S(1) - C(37) - S(2)	113.4(8)	O(4) -Na(1) - O(5)	82.9(5)
Rh(1) - P(1) - O(1)	120.1(4)	Na(1) - O(1) - P(1)	128.2(6)
Rh(1) - P(1) - C(6)	103.6(5)	Na(1) - O(2) - P(2)	123.8(6)
Rh(1) - P(1) - C(12)	114.8(5)	Na(1) - O(3) - P(3)	125.7(6)
Rh(1) - P(2) - O(2)	119.4(4)		
Rh(1) - P(2) - C(18)	112.6(5)		
Rh(1) - P(2) - C(24)	106.3(5)		

Table 5.5 - $^{31}P-\{^{1}H\}$ n.m.r. spectral data of the rhodium complexes discussed in chapter 5

	conditions	pattern	δ(p.p.m.)	$^{1}J_{Rh-P}$(Hz)	$^{2}J_{P-P}$(Hz)	Intensity ratio
$[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$	a	d (br)	88.9	124.5		
	b	A_2MX	δ_A 91.3	131.3	22.0	2
			δ_B 83.1	114.8		1
$[Rh(S_2CNMe_2)\{(Ph_2PO)_3Na(OH_2)\}]$	c	d	68.2	130.9		
$[Rh(S_2CNEt_2)\{(Ph_2PO)_3Na(OH_2)_2\}]$	c	d	68.5	131.8		
	d	d	70.4	129.4		
$[Rh(O_2CPh)\{(Ph_2PO)_3Na(OH_2)\}]$	c	d	69.6	145.6		
	e	d	68.3	144.2		
$[Rh(O_2C-C_6H_4-CH_3)\{(Ph_2PO)_3Na(OH_2)_3\}]$	c	d	67.8	142.7		
	f	d	69.2	141.1		
$[Rh(S(O)CPh)\{(Ph_2PO)_3Na(OH_2)\}]$	g	d	72.8	136.7		
	h	d	72.2	138.3		

Table 5.5 (continued)

a) $CDCl_3$, RT

b) $CDCl_3$, 223K

c) d^6-acetone, RT

d) d^6-acetone, 173K

e) d^6-acetone, 223K

f) d^6-acetone, 213K

g) CH_2Cl_2, RT

h) CD_2Cl_2, 183K

Chapter 6

Further Investigation Of The Reaction Of *cis*-[Ru(S_2PMe_2)$_2$(PPh_3)$_2$] With Diphenylphosphine Oxide

6.1 Introduction

The attempts to extend the chemistry of $[RhCl(NO_3)\{(Ph_2PO)_3H_2\}]$ through deprotonation of the tridentate ligand $\{(Ph_2PO)_3H_2\}^-$ by a variety of groups had proved to be somewhat unsatisfactory in that, although reaction was observed, the products obtained had not been fully characterised (see section 5.3).

Robertson and Stephenson had reported the preparation of the BF-capped complex $[Ru(S_2PMe_2)\{(Ph_2PO)_3BF\}]$ by treating $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ with $BF_3.Et_2O$[139]. It was envisaged that an investigation of this reaction might yield information that would be helpful towards the characterisation of the rhodium products. Furthermore, reaction of the $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ moiety with a variety of suitable groups would extend the chemistry of not only the complex itself, but also of the tridentate $\{(Ph_2PO)_3H_2\}^-$ ligand.

6.2 Further investigation of the reaction of *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ with $Ph_2P(O)H$

Robertson and Stephenson prepared $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ by adding *cis*-$[Ru(S_2PMe_2)(PPh_3)_2]$ to a solution of a large excess of Ph_2PCl in a mixture of methanol and water (10:1, v/v). The resulting suspension was then stirred under reflux for two hours and the resulting solution filtered hot and left to stand in a refrigerator for several days whereupon the product was obtained as an orange-red crystalline material in *ca*.37% yield[139]. In our hands, it was found that extended reaction times (6-8 hours) gave rise to a yellow suspension from which a yellow powder was isolated instead of the orange-red $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$.

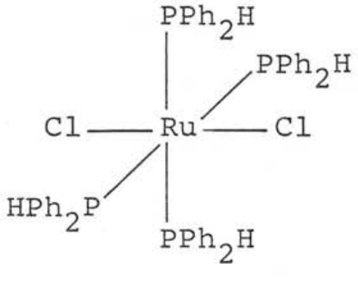
The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the yellow product shows two triplets centred at δ = 39.3 p.p.m. and at δ = 23.9 p.p.m. both with a $^2J_{P-P}$ coupling constant of 29.4Hz. On cooling to 223K no temperature dependent behaviour was observed. However, the proton coupled ^{31}P n.m.r. spectrum at 298K reveals a $^1J_{P-H}$ coupling constant of 296.1Hz on both triplets suggesting that the phosphorus moieties are secondary phosphines. Interestingly the ^{31}P-$\{^1H\}$ n.m.r. spectra contain no resonance corresponding to the $[S_2PMe_2]^-$ group. The absence of this ligand is confirmed by both the infrared spectrum which contains no characteristic stretching bands at *ca*.590 cm^{-1}, $\nu(PS_2)$, and by the ^1H n.m.r. spectrum which contains only signals attributable to phenyl protons.

In addition the infrared spectrum contains bands at

2353, 2340 and 2332 cm^{-1}, ν(P-H) and also in the 320-250 cm^{-1} region indicative of ν(Ru-Cl). The product was also found to be non-conducting in dichloromethane.

On the basis of the available data the product was formulated as the known compound cis-[$RuCl_2(Ph_2PH)_4$]. This conclusion was supported by elemental analyses and is also consistent with retention of a ruthenium(II) oxidation state as evidenced by the sharp n.m.r. resonances. More importantly, the data are also consistent with that previously obtained for cis-[$RuCl_2(Ph_2PH)_4$] prepared by reacting [$Ru_2Cl_3(PMePh_2)_6$]Cl with Ph_2PH in ethanol under refluxing conditions[148] or by treating cis-[$RuH_2(Ph_2PH)_4$] with HCl[149]. The trans isomer has also been synthesised by a route involving the reaction of Ph_2PH with boiling ethanolic $RuCl_3.xH_2O$[150].

Additional confirmation was obtained from a $CHCl_3$ solution of the powder which deposited pale yellow crystals on standing. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the crystals in $CDCl_3$ at 298K shows a singlet at δ = 19.7 p.p.m. attributable to the corresponding trans isomer and indicating that cis-trans isomerisation had occurred in solution while standing. X-Ray analysis of one of the crystals confirmed the structure to be the known complex trans-[$RuCl_2(Ph_2PH)_4$] (45).



(45)

Initially the reaction of cis-[Ru(S_2PMe_2)$_2$(PPh_3)$_2$] with the pre-hydrolysed $Ph_2PCl|MeOH|H_2O$ solution yielded only the cis-[$RuCl_2$(Ph_2PH)$_4$]. However, with more prolonged reaction times (ca.10-12 hours) some trans isomer was also obtained presumably as a result of cis-trans isomerisation.

From the colour changes observed during the reaction of the cis-[Ru(S_2PMe_2)$_2$(PPh_3)$_2$] with the pre-hydrolysed $Ph_2PCl|MeOH|H_2O$ solution, together with the fact that it could be isolated in the course of the reaction, it was suspected that the five coordinate [Ru(S_2PMe_2){(Ph_2PO)$_3H_2$}] is an intermediate through which the cis-[$RuCl_2$(Ph_2PH)$_4$] is formed. Therefore [Ru(S_2PMe_2){(Ph_2PO)$_3H_2$}] was added to a solution of $Ph_2P(O)H$, generated by the in situ hydrolysis of Ph_2PCl, in a mixture of methanol and water (10:1, v/v). Following prolonged refluxing (ca.10-12 hours) a yellow powder was obtained and was shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to contain both the cis and trans isomers of [$RuCl_2$(Ph_2PH)$_4$] in a ratio of ca.4:1.

Furthermore, [Ru(S_2PMe_2) {(Ph_2PO)$_3H_2$}] was dissolved in aqueous methanol and treated with Ph_2PH and conc.HCl. A yellow solution was obtained after refluxing for the much reduced reaction time of one hour. Subsequent work-up with ethanol led to the isolation of a yellow powder which was also found to contain a mixture of both the cis- and trans-[$RuCl_2$(Ph_2PH)$_4$] (ca.6:1 ratio). Interestingly, reaction of [Ru(S_2PMe_2){(Ph_2PO)$_3H_2$}] with Ph_2PH under the same conditions in the absence of HCl gave a complex mixture of unknown products ($^{31}P-\{^1H\}$ n.m.r. evidence). This indicates that protonation and subsequent removal of a coordinated $[S_2PMe_2]^-$ group by the HCl released in the <u>in situ</u> hydrolysis of Ph_2PCl is probably a key step in the formation of the $[RuCl_2(Ph_2PH)_4]$ by this route. A similar conclusion was drawn by Robertson and Stephenson regarding the formation of $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ itself from <u>cis</u>-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ <u>via</u> the intermediate $[Ru(S_2PMe_2)\{(Ph_2PO)_2H\}(PPh_3)]$[139].

The much reduced reaction times observed for $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ with conc.HCl and Ph_2PH suggests, not unexpectedly, that the reaction times observed with the pre-hydrolysed $Ph_2PCl|MeOH|H_2O$ mixtures are governed by the availability of Ph_2PH, the origin of which is a point of interest.

The isolation of a compound with diphenylphosphine ligands from the hydrolysed Ph_2PCl solution might seem surprising at first sight. However, it has been shown that many secondary phosphine oxides decompose when heated above their melting points. The usual decomposition leads to the formation of a dialkylphosphinic acid and a dialkylphosphine by disproportionation (Eqn. [33])[151].

$$2R_2P(O)H \longrightarrow R_2P(O)OH + R_2PH \qquad \ldots\ldots\ldots \quad [33]$$

It is proposed that under the extended refluxing conditions employed, the diphenylphosphine oxide disproportionates in a similar manner after which the phosphine binds to the ruthenium.

To date the original objectives outlined in the introduction have yet to be explored.

6.2.2 The X-ray crystal structure of trans-$[RuCl_2(Ph_2PH)_4].2CHCl_3$

Details of the method of solution of this structure are given in the experimental section. The final atomic positions are presented in Table 6.1 and selected bond distances and angles in Table 6.2.

The geometry around the ruthenium atom, which lies on a centre of inversion, is that of an octahedron with the chlorine atoms necessarily occupying positions trans to each other.

The distances in this structure are all reasonable with the Ru(1)-P(1) (2.3508(8)Å), Ru(1)-P(2) (2.3665(8)Å) and Ru(1)-Cl(1) (2.4317(8)Å) bond lengths in close agreement with the corresponding distances in the analagous complex trans-$[RuCl_2(Me_2PH)_4]$ (2.323(1), 2.331(1) and 2.440(1)Å respectively[150].

An ORTEP diagram of the molecule is shown in Figure 6.1 and a packing diagram in Figure 6.2*.

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* For clarity the chloroform solvate molecules are not shown.

Fig.6.1 - An ORTEP diagram of trans-$[RuCl_2(Ph_2PH)_4]$

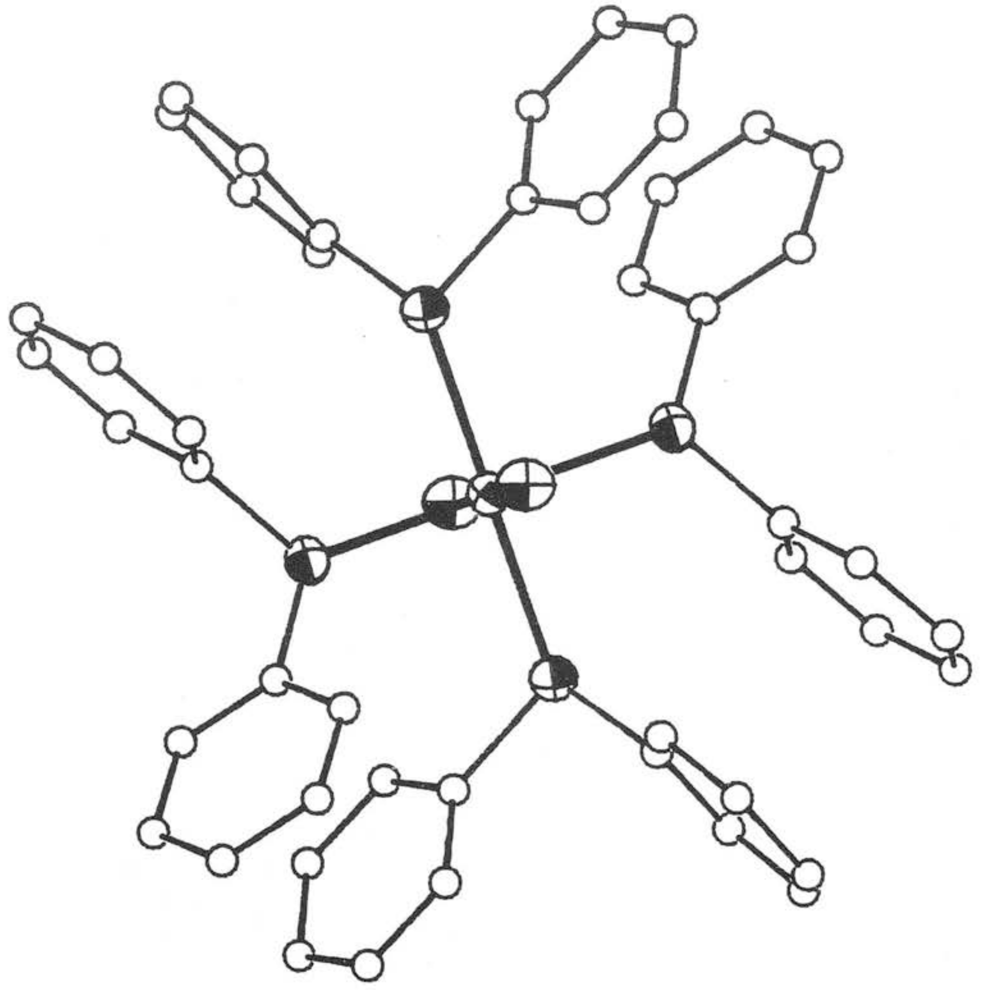
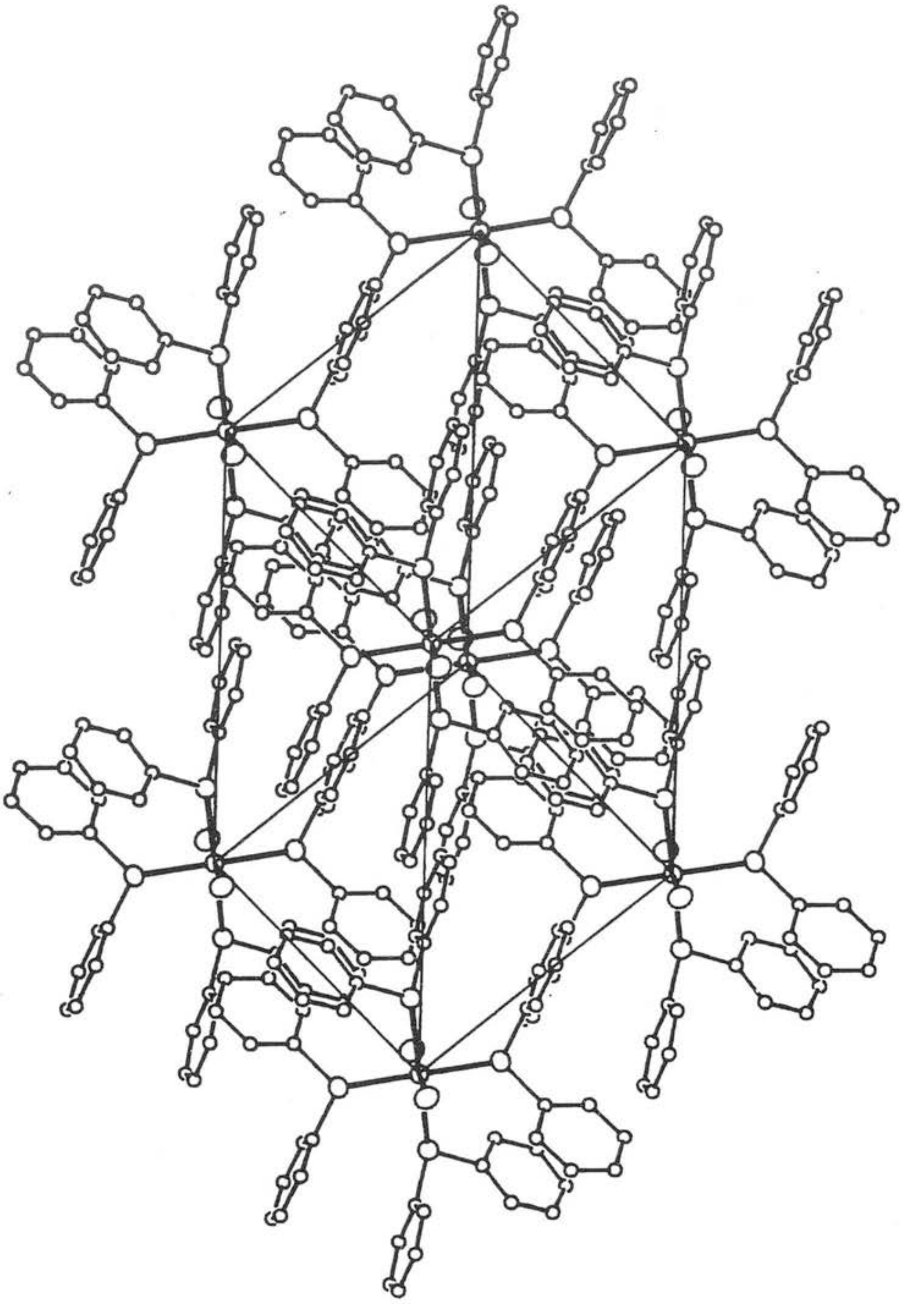


Fig.6.2 - A crystal packing diagram of trans-[$RuCl_2(Ph_2PH)_4$].$2CHCl_3$



6.3 Experimental

Physical measurements were obtained as described in the previous experimental sections 2.10, 3.5 and 5.6.

Materials

As in chapters 2, 3 and 5 together with Ph_2PH (Maybridge). The compound cis-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ was prepared as described in reference (152).

Crystal structure determination of trans-$[RuCl_2(Ph_2PH)_4].2CHCl_3$

Crystals suitable for X-ray analysis were obtained from a chloroform solution of cis-$[RuCl_2(Ph_2PH)_4]$ on standing in air. A pale yellow ingot of dimensions 0.6 x 0.4 x 0.3 mm was chosen and accurate unit cell dimensions were obtained by least-squares refinement of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer with monochromatised M_o-K_α radiation.

Crystal Data: $C_{48}H_{44}Cl_2P_4Ru.2CHCl_3$, $\underline{M} = 1155.7$,
$\underline{a} = 10.4314(11)$, $\underline{b} = 10.5379(28)$, $\underline{c} = 13.2413(8)\text{Å}$,
$\alpha = 70.106(13)$, $\beta = 73.208(7)$, $\gamma = 77.191(13)°$,
$\underline{V} = 1298.0\text{Å}^3$, $\underline{D}_c = 1.460\ \text{g cm}^{-3}$, $\underline{Z} = 1$,
$F(000) = 580$, $\mu = (M_o\text{-}K_\alpha) = 8.65\ \text{cm}^{-1}$,
$\lambda(M_o\text{-}K_\alpha) = 0.71069\text{Å}$. The space group is $\underline{P\bar{1}}$

Intensity data were collected by ω-2θ scans. A standard reflection was monitored regularly throughout the data collection. On the basis of these measurements the data were corrected for isotropic decay with minimum and maximum drift corrections of 0.811 and 1.301 respectively. The observed decay is probably a result of loss of chloroform of crystallisation from the crystal. Intensities were measured for 3386 independent reflections ($2<\theta<22.5°$) of which 3154 had $\underline{I}>\sigma(\underline{I})$. No absorption correction was applied.

Structure solution and refinement

The refinement was based on the 3154 reflections with $\underline{I} > \sigma(\underline{I})$. The structure was solved by conventional Patterson and difference Fourier techniques. The ruthenium atom was located from a Patterson map using SHELX84[89] and was found to lie on a special position, (0,0,0) indicating centrosymmetric coordination. Subsequent difference Fourier syntheses revealed all non-hydrogen atoms in the molecule. The structure refinement was carried out using SHELX76[90]. All non-hydrogen atoms were refined anisotropically. The phenyl rings were constrained to be idealised planar hexagons with C-C and C-H bond lengths of 1.395Å and 1.080Å respectively. The P-H bonds were constrained such that the P(1)-H(31) and P(2)-H(41) bond lengths were 1.34±0.02Å. A weighting scheme of the form $w^{-1} = \sigma^2(\underline{F}) + 0.000179(\underline{F})^2$ was applied and the final residuals based on 244 refined parameters were $\underline{R} = 0.031$, $\underline{R}_w = 0.045$ for the 3154 observed data. The maximum shift/esd in the final cycle was 0.021 and a final difference Fourier map showed no peak above, nor trough below, 1.0εÅ^{-3}. All scattering factors were inlaid in the program except those for Ru which were taken from reference (91).

Final fractional coordinates are given in Table 6.1 and selected bond distances and angles in Table 6.2. The structure of the complex is shown in Figure 6.1 and a cell packing diagram in Figure 6.2.

cis-Dichlorotetrakis(diphenylphosphine)ruthenium(II): cis-$RuCl_2(Ph_2PH)_4$

i) A large excess of Ph_2PCl (2.00 g) was dissolved in $MeOH/H_2O$ (55 cm^3: 10:1, v/v) and the mixture allowed to hydrolyse. cis-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ (0.20 g; 40:1 molar ratio) was then added and the solution refluxed for 6-8 hours. The resulting yellow solution was filtered whereupon the product was obtained as a yellow powder which was then washed with diethyl ether and dried *in vacuo* at 60°C. m.p. 276-281°C (decomp). (Yield 0.18 g, 90.4%). (Found, C, 63.2; H, 5.4. Calc. for $C_{48}H_{44}Cl_2P_4Ru$:- C, 62.9; H, 4.9%). Infrared spectrum (nujol mull); ν(P-H), 2353w, 2340sh, 2332m; ν(Ru-Cl), 301m, 267m cm^{-1}.

Mixtures of cis- and trans-dichlorotetrakis(diphenylphosphine)-ruthenium(II):

cis- and trans-$RuCl_2(Ph_2PH)_4$

1) Ph_2PCl (0.53 g) was dissolved in $MeOH/H_2O$ (55 cm^3; 10:1, v/v) and the mixture allowed to hydrolyse. $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ (0.05 g, 40:1 molar ratio) was added and the solution refluxed for 10-12 hours. The resulting yellow solution was reduced in volume giving a mixture of cis- and trans-$[RuCl_2(Ph_2PH)_4]$ as a yellow powder which was filtered off, washed with diethyl ether and dried *in vacuo* at 60°C, (0.03 g, 53.2%).

2) $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ (0.05 g) was dissolved in

aqueous methanol (50 cm^3), treated with HCl (1.0 cm^3, conc.) and Ph_2PH (0.45 g, 1:40 molar ratio) and the solution refluxed for 1 hour. The resulting yellow solution was reduced in volume and the yellow powder obtained by filtration was then washed with diethyl ether and dried in vacuo at 60°C. Analysis by $^{31}P-\{^1H\}$ n.m.r. spectroscopy revealed the product to be a mixture of both cis- and trans-$[RuCl_2(Ph_2PH)_4]$. (Yield ca.70% and 12% respectively).

Table 6.1 - Fractional coordinates for *trans*-[$RuCl_2(Ph_2PH)_4$].$2CHCl_3$

Fractional coordinates with standard deviations ( ).

Atom	x	y	z
Ru(1)	0.00000(0)	0.00000(0)	0.00000(0)
P(1)	-0.13685(7)	0.20997(7)	-0.00095(7)
P(2)	-0.01471(8)	0.03077(8)	-0.18207(6)
Cl(1)	0.18880(7)	0.12867(8)	-0.09829(6)
H(31)	-0.0701	0.3142	-0.0624
H(41)	0.1078	0.0178	-0.2477
C(1)	-0.1279(3)	0.36237(23)	0.13247(23)
C(2)	-0.1701(3)	0.40346(23)	0.22794(23)
C(3)	-0.2756(3)	0.34772(23)	0.31299(23)
C(4)	-0.3391(3)	0.25088(23)	0.30257(23)
C(5)	-9,2969(3)	0.20979(23)	0.20709(23)
C(6)	-0.1913(3)	0.26554(23)	0.12204(23)
C(7)	-0.33772(23)	0.39820(18)	-0.09041(21)
C(8)	-0.45835(23)	0.43862(18)	-0.12548(21)
C(9)	-0.53340(23)	0.34086(18)	-0.11944(21)
C(10)	-0.48781(23)	0.20267(18)	-0.07833(21)
C(11)	-0.36718(23)	0.16225(18)	-0.04326(21)
C(12)	-0.29213(23)	0.26002(18)	-0.04930(21)
C(13)	-0.20119(22)	-0.14118(24)	-0.15371(15)
C(14)	-0.26011(22)	-0.22012(24)	-0.18903(15)
C(15)	-0.20661(22)	-0.23769(24)	-0.29363(15)
C(16)	-0.09418(22)	-0.17632(24)	-0.36291(15)
C(17)	-0.03526(22)	-0.09738(24)	-0.32759(15)
C(18)	-0.08876(22)	-0.07981(24)	-0.22299(15)
C(19)	-0.18940(19)	0.22025(18)	-0.30712(18)
C(20)	-0.23448(19)	0.34983(18)	-0.36995(18)
C(21)	-0.16407(19)	0.45836(18)	-0.39304(18)
C(22)	-0.04857(19)	0.43732(18)	-0.35329(18)
C(23)	-0.00349(19)	0.30774(18)	-0.29047(18)
C(24)	-0.07391(19)	0.19920(18)	-0.26738(18)
H(1)	-0.0462	0.4055	0.0666
H(2)	-0.1210	0.4784	0.2360
H(3)	-0.3083	0.3795	0.3869
H(4)	-0.4208	0.2077	0.3684
H(5)	-0.3460	0.1348	0.1990
H(7)	-0.2796	0.4739	-0.0951
H(8)	-0.4937	0.5456	-0.1573
H(9)	-0.6268	0.3722	-0.1466
H(10)	-0.5459	0.1270	-0.0737
H(11)	-0.3319	0.0553	-0.0114
H(13)	-0.2426	-0.1276	-0.0727
H(14)	-0.3472	-0.2676	-0.1354
H(15)	-0.2522	-0.2988	-0.3210
H(16)	-0.0528	-0.1899	-0.4439

Table 6.1 (continued)

Atom	x	y	z
H(17)	0.0518	-0.0499	-0.3812
H(19)	-0.2439	0.1362	-0.2893
H(20)	-0.3239	0.3661	-0.4007
H(21)	-0.1990	0.5587	-0.4417
H(22)	0.0059	0.5214	-0.3712
H(23)	0.0859	0.2915	-0.2597

Chloroform solvent molecule

Atom	x	y	z
C(25)	-0.6129(4)	0.1764(4)	-0.3637(3)
Cl(2)	-0.67819(12)	0.13620(13)	-0.45444(10)
Cl(3)	-0.45929(12)	0.07484(13)	-0.34803(13)
Cl(4)	-0.59500(14)	0.34822(12)	-0.40950(14)
H(51)	-0.6830	0.1562	-0.2839

Table 6.2 - Selected bond lengths and angles for *trans*-$[RuCl_2(Ph_2PH)_4].2CHCl_3$

a) Bond lengths (Å) with standard deviations ( ).

Ru(1) - P(1)	2.3505(8)	P(1) - C(12)	1.8172(25)
Ru(1) - P(2)	2.3665(8)	P(2) - H(41)	1.33(3)
Ru(1) - Cl(1)	2.4317(8)	P(2) - C(18)	1.8217(24)
P(1) - H(31)	1.33(3)	P(2) - C(24)	1.8331(23)
P(1) - C(6)	1.812(3)		

b) Bond angles (°) with standard deviations ( ).

P(1) - Ru(1) - P(2)	90.34(3)	C(6) - P(1) - C(12)	100.18(12)
P(1) - Ru(1) - Cl(1)	87.13(3)	Ru(1) - P(2) - H(41)	110.8(15)
P(2) - Ru(1) - Cl(1)	82.00(3)	Ru(1) - P(2) - C(18)	125.27(8)
Ru(1) - P(1) - H(31)	111.8(14)	Ru(1) - P(2) - C(24)	120.29(8)
Ru(1) - P(1) - C(6)	120.73(10)	H(41) - P(2) - C(18)	97.1(15)
Ru(1) - P(1) - C(12)	122.76(8)	H(41) - P(2) - C(24)	96.2(15)
H(31) - P(1) - C(6)	95.2(14)	C(18) - P(2) - C(24)	101.30(11)
H(31) - P(1) - C(12)	101.3(14)		

References

1. C.A. McAuliffe, "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", McMillan, 1973.
2. C.A. McAuliffe and W. Levason, "Phosphine, Arsine and Stibine Complexes of the Transition Elements", Elsevier, 1979.
3. E.A. Seddon and K.R. Seddon, "The Chemistry of Ruthenium", Elsevier, 1984.
4. M. Schröder and T.A. Stephenson, "Ruthenium" in Comprehensive Coordination Chemistry, Pergamon Press.
5. J. Chatt, N.P. Johnson, and B.L. Shaw, J.Chem.Soc., 1964, 2508.
6. P.R. Brookes and B.L. Shaw, J.Chem.Soc.(A), 1967, 1079.
7. M.A. Bennett, R.J.H. Clark, and D.L. Milner, Inorg.Chem., 1967, 6, 1647.
8. J. Chatt, G.J. Leigh, and D.M.P. Mingos, J.Chem.Soc.(A), 1969, 1674.
9. J. Chatt, G.J. Leigh, and D.M.P. Mingos, J.Chem.Soc.(A), 1969, 2972.
10. S.O. Grim and R.A. Ference, Inorg.Nucl.Chem.Lett., 1966, 2, 205.
11. T.H. Brown and P.J. Green, J.Am.Chem.Soc., 1970, 92, 2359.
12. A.C. Skapski and F.A. Stephens, J.Chem.Soc., Dalton Trans., 1973, 1789.
13. G.M. Intille, Inorg.Chem., 1972, 11, 695.
14. S.O. Grim and L.C. Satek, J.Coord.Chem., 1974, 3, 307.

15. P.R. Brookes and B.L. Shaw, *J.Chem.Soc., Chem.Commun.*, 1968, 919.

16. P.L. Goggin and J.R. Knight, *J.Chem.Soc., Dalton Trans.*, 1973, 1489.

17. T.A. Stephenson, *J.Chem.Soc.(A)*, 1970, 889.

18. J.M. Jenkins and B.L. Shaw, *Proc.Chem.Soc.*, 1963, 279.

19. P.L. Goggin, R.J. Goodfellow, J.R. Knight, M.G. Norton and B.F. Taylor, *J.Chem.Soc., Dalton Trans.*, 1973, 2220.

20. B.E. Mann, C. Masters, and B.L. Shaw, *J.Chem.Soc., Dalton Trans.*, 1972, 704.

21. F.H. Allen and K.M. Gabuji, *Inorg.Nucl.Chem.Lett.*, 1971, *7*, 833.

22. J.A. Muir, R. Baretty, and M.M. Muir, *Acta Cryst.*, 1976, *B32*, 315.

23. J.A. Muir, M.M. Muir, and A.J. Rivera, *Acta Cryst.*, 1974, *B30*, 2062.

24. T.A. Stephenson and G. Wilkinson, *J.Inorg.Nucl.Chem.*, 1966, *28*, 945.

25. P.S. Hallman, T.A. Stephenson, and G. Wilkinson, *Inorg.Synth.*, 1970, *12*, 237.

26. R.K. Poddar and U. Agarwala, *Indian J.Chem.*, 1971, *9*, 477.

27. P.R. Hoffmann and K.G. Caulton, *J.Am.Chem.Soc.*, 1975, *97*, 4221.

28. P.W. Armit, A.S.F. Boyd, and T.A. Stephenson, *J.Chem. Soc., Dalton Trans.*, 1975, 1663.

29. J.D. Gilbert and G. Wilkinson, *J.Chem.Soc.(A)*, 1969, 1479.

30. B.R. James, A.D. Rattray, and D.K.W. Wang, *J.Chem.Soc., Chem.Commun.*, 1976, 792.

31. B.R. James, L.D. Markham, A.D. Rattray, and D.K.W. Wang, Inorg.Chim.Acta, 1976, 20, L25.

32. L. Vaska and J.W.Di Luzio, J.Am.Chem.Soc., 1962, 83, 1262.

33. W.H. Knoth, J.Am.Chem.Soc., 1968, 90, 7172.

34. D.R. Robertson, T.A. Stephenson, and T. Arthur, J.Organomet.Chem., 1978, 162, 121.

35. J.D. Gilbert, D. Rose, and G. Wilkinson, J.Chem.Soc.(A), 1970, 2765.

36. S.J. Le Placa and J.A. Ibers, Inorg.Chem., 1965, 4, 778.

37. B.R. James and L.D. Markham, Inorg.Chem., 1974, 13, 97.

38. T.W. Dekleva, Ph.D. Thesis, University of British Columbia, 1983.

39. A.J. Lindsay, Ph.D. Thesis, University of Edinburgh, 1982.

40. B.R. James, D.K.W. Wang, and R.F. Voigt, J.Chem.Soc., Chem.Commun., 1975, 574.

41. K. Ohkuba, I. Terada, and K. Yoshinagu, Chem.Lett., 1977, 1467.

42. S.D. Chappell, D.J. Cole-Hamilton, A.M.R. Galas, and M.B. Hursthouse, J.Chem.Soc., Dalton Trans., 1982, 1867.

43. R.A. Jones, F.M. Real, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse, and K.M.A. Malik, J.Chem.Soc., Dalton Trans., 1980, 511.

44. H. Singer, E. Hademer, U. Oehmichen, and P. Dixneuf, J.Organomet.Chem., 1979, 178, C13.

45. J. Chatt, B.L. Shaw, and A.E. Field, J.Chem.Soc., 1964, 3466 and references therein.

46. K.G. Srinivasamurthy, N.M.N. Gowda, and G.K.N. Reddy, J.Inorg.Nucl.Chem., 1977, 39, 1977.

47. J. Chatt, G.J. Leigh, D.M.P. Mingos, and R.J. Paska, J.Chem.Soc.(A), 1968, 2636 and references therein.

48. J.E. Fergusson and P.F. Heveldt, J.Inorg.Nucl.Chem., 1977, 39, 825.

49. A. Hudson and M.J. Kennedy, J.Chem.Soc.(A), 1969, 1116.

50. L. Ruiz-Ramírez, T.A. Stephenson, and E.S. Switkes, J.Chem.Soc., Dalton Trans., 1973, 1770.

51. J.C. Muscarella and J.R. Crook, J.Chem.Soc., Dalton Trans., 1978, 1152.

52. G. Mercatti and F. Morazzoni, Gazz.Chim.Ital., 1979, 109, 161.

53. J. Chatt and R.G. Hayter, J.Chem.Soc., 1961, 896.

54. R.H. Crabtree and A.J. Pearman, J.Organomet.Chem., 1977, 141, 325.

55. P.G. Douglas and B.L. Shaw, J.Chem.Soc., Dalton Trans., 1973, 2078.

56. J.M. Jenkins, M.S. Lupin and B.L. Shaw, J.Chem.Soc.(A), 1968, 741.

57. K.A. Raspin, J.Chem.Soc.(A), 1969, 461.

58. M. Laing and L. Pope, Acta Cryst., 1976, B32, 1547.

59. J.A. Slater, G. Wilkinson, M. Thornton-Pett, and M.B. Hursthouse, J.Chem.Soc., Dalton Trans., 1984, 1731.

60. T.V. Ashworth, M.J. Nolte, and E. Singleton, J.Chem.Soc., Chem.Commun., 1977, 936.

61. R.H. Prince and K.A. Raspin, J.Chem.Soc.(A), 1969, 612.

62. N.W. Alcock and K.A. Raspin, J.Chem.Soc.(A), 1968, 2108.

63. J.K. Nicholson, Angew.Chem.Int.Ed.Engl., 1967, 6, 264.

64. G. Chioccola, J.J. Daly, and J.K. Nicholson, Angew.Chem.Int.Ed.Engl., 1968, 7, 131.

65. R. Contreras, G.G. Elliot, R.O. Gould, G.A. Heath, A.J. Lindsay, and T.A. Stephenson, *J.Organomet.Chem.*, 1981, *215*, C6.

66. G.A. Heath, A.J. Lindsay, T.A. Stephenson, and D.K. Vattis, *J.Organomet.Chem.*, 1982, *233*, 353 and references therein.

67. J. Chatt, A.E. Field, and B.L. Shaw, *J.Chem.Soc.*, 1963, 3371.

68. J.M. Jenkins and B.L. Shaw, *J.Chem.Soc.*, 1965, 6789.

69. J.W. Collier and F.G. Mann, *J.Chem.Soc.*, 1964, 1815.

70. B.L. Shaw and R.M. Slade, *J.Chem.Soc.(A)*, 1971, 1184.

71. J.M. Jenkins and B.L. Shaw, *J.Chem.Soc.(A)*, 1966, 1407.

72. S.O. Grim and R.A. Ference, *J.Coord.Chem.*, 1973, *2*, 225.

73. P.R. Brookes, C. Masters, and B.L. Shaw, *J.Chem.Soc.(A)*, 1971, 3756.

74. C. Masters, B.L. Shaw, and R.E. Stainbank, *J.Chem.Soc., Dalton Trans.*, 1972, 664.

75. M.J. Nolte, E. Singleton, and E. Van Der Stok, *Acta Cryst.*, 1978, *B34*, 1684.

76. W.J. Sime and T.A. Stephenson, *J.Organomet.Chem.*, 1978, *161*, 245 and references therein.

77. P.W. Armit, W.J. Sime, and T.A. Stephenson, *J.Chem. Soc., Dalton Trans.*, 1976, 2121.

78. A.J. Lindsay, Ph.D.Thesis, University of Edinburgh, 1982.

79. J.M. Brown, R.A. John, and A.R. Lucy, *J.Organomet.Chem.*, 1985, *279*, 245.

80. T.L. Kelly and C.V. Senoff, *Canad.J.Chem.*, 1976, *54*, 1860.

81. T. Easton, G.A. Heath, T.A. Stephenson and M.Bochmann, J.Chem.Soc., Chem.Commun., 1985, 154.

82. J.A.S. Duncan, T.A. Stephenson, M.D. Walkinshaw, D. Hedden, and D.M. Roundhill, Angew.Chem.Int.Ed.Engl., 1982, 21, 452.

83. R.H. Crabtree, H. Felkin, and G.E. Morris, J.Organomet. Chem., 1977, 141, 205.

84. H.H. Wang and L.H. Pignolet, Inorg.Chem., 1980, 19, 1470.

85. R.J. Abrahams and P. Loftus, "Proton and Carbon-13 N.M.R. Spectroscopy", Heyden, 1980.

86. F.A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, 1969.

87. J. Chatt and B.L. Shaw, J.Chem.Soc., 1966, 1437.

88. J.E. Fergusson and R.R. Sherlock, Aust.J.Chem., 1977, 30, 1445.

89. G.M. Sheldrick, SHELX 1984, Programs for Crystal Structure Determination, University of Gottingen.

90. G.M. Sheldrick, SHELX 1976, Program for Crystal Structure Determination, University of Cambridge, England.

91. International Tables for Crystallography, Vol.IV, Kynoch Press.

92. L.M. Haines and E. Singleton, J.Chem.Soc.,Dalton Trans., 1972, 1891.

93. J.L. Herde, J.C. Lambert, and C.V. Senoff, Inorg.Synth., 1974, 15, 18.

94. N. Walker and J. Stuart, Acta Cryst., 1983, A39, 159.

95. D.M. Roundhill, R.P. Sperline, and W.B. Beaulieu, Coord.Chem.Reviews, 1978, 26, 263.

96. B. Walther, Coord.Chem.Reviews, 1984, 60, 67.

97. L.A. Hamilton and P.S. Landis in G.M. Kosolapoff and L. Maier (Eds.), Organic Phosphorus Compounds, Vol.4, Wiley, New York, 1972, p.463.

98. J.G. Verkade and K.J. Coskran in G.M. Kosolapoff and L. Maier (Eds.), Organic Phosphorus Compounds, Vol.2, Wiley, New York, 1972, p.1.

99. L.A. Hamilton and P.S. Landis in G.M. Kosolapoff and L. Maier (Eds.), Organic Phosphorus Compounds, Vol.4, Wiley, New York, 1972, p.485.

100. D.D. Magnelli, G. Tesi, J.N. Lowe, and W.E. McQuiston, Inorg.Chem., 1966, 5, 547.

101. J.E. Griffiths and A.B. Burg, J.Am.Chem.Soc., 1960, 82, 1507.

102. J. Chatt and B.T. Heaton, J.Chem.Soc.(A), 1968, 2745.

103. P. Schutzenberger and R. Fontaine, Bull.Soc.Chim., 1872, 17, 482.

104. T.L. Davis and P. Ehrlich, J.Am.Chem.Soc., 1936, 58, 2151.

105. T.E. Austin, Ph.D.Thesis, University of North Carolina, 1966.

106. C.S. Kraihanzel and C.M. Bartish, J.Am.Chem.Soc., 1972, 94, 3572.

107. C.S. Kraihanzel and C.M. Bartish, J.Organometal.Chem., 1972, 43, 343.

108. G.M. Gray and C.S. Kraihanzel, J.Organometal.Chem., 1978, 146, 23.

109. E.H. Wong and F.C. Bradley, Inorg.Chem., 1981, 20, 2333.

110. D.J. Darensbourg, Inorg.Chem., 1979, 18, 14.

111. A.A. Grinberg and A.D. Troitskaya, *Bull.Acad.Sci. U.R.S.S., Classe Sci.Chim.*, 1944, 178; *Chem.Abstr.*, 1945, *39*, 1604(4).

112. (a) A.D. Troitskaya and T.B. Itskovich, *Trudy Kazan. Khim.Tekhol.Inst.im.S.M.Kirova*, 1954-55, 19-20, 79; *Chem.Abstr.*, 1957, *51*, 11149a.

(b) A.D. Troitskaya and Z.L. Shmakova, *Russ.J.Inorg. Chem.*, 1971, *16*, 590.

(c) See reference 95 and references therein.

113. K.R. Dixon and A.D. Rattray, *Canad.J.Chem.*, 1971, *49*, 3997.

114. D.V. Naik, G.T. Palenick, S.J. Jacobson, and A.J. Carty, *J.Am.Chem.Soc.*, 1974, *96*, 2286.

115. A.J. Carty, S.E. Jacobson, R.T. Simpson, and N.J.Taylor, *J.Am.Chem.Soc.*, 1975, *97*, 7254.

116. P.C. Kong and D.M. Roundhill, *Inorg.Chem.*, 1972, *11*, 749.

117. M.C. Cornock, R.O. Gould, C.L. Jones, and T.A. Stephenson, *J.Chem.Soc.,Dalton Trans.*, 1977, 1307.

118. J.M. Solar, R.D. Rogers, and W.R. Mason, *Inorg.Chem.*, 1984, *23*, 373.

119. D. Hadzi, B.Ord, and A. Novak, *Spectrochem.Acta, Part A,* 1973, *29*, 1745.

120. T.G. Southern, P.H. Dixneuf, J. Le Marouille, and D. Grandjean, *Inorg.Chem.*, 1979, *18*, 2987.

121. J.A.S. Duncan, T.A. Stephenson, M.D. Walkinshaw, D. Hedden, and D.M. Roundhill, *J.Chem.Soc.,Dalton Trans.*, 1984, 801.

122. R.P. Sperline and D.M. Roundhill, Inorg.Chem., 1977, 16, 2612.

123. R.P. Sperline, M.K. Dickson, and D.M. Roundhill, J.Chem.Soc.,Chem.Commun., 1977, 62.

124. W.B. Beaulieu, T.B. Rauchfuss, and D.M. Roundhill, Inorg.Chem., 1975, 14, 1732.

125. D.E. Berry, G.W. Bushnell, and K.R. Dixon, Inorg.Chem., 1982, 21, 957.

126. K.R. Dixon and A.D. Rattray, Inorg.Chem., 1977, 16, 209.

127. G.M. Gray and K.A. Redmill, J.Organomet.Chem., 1985, 280, 105.

128. M.A. Bennett and T.R.B. Mitchell, J.Organomet.Chem., 1974, 70, C30.

129. J.A.S. Duncan, T.A. Stephenson, W.B. Beaulieu, and D.M. Roundhill, J.Chem.Soc.,Dalton Trans., 1983, 1755.

130. H. Werner and T.N. Khai, Angew.Chem.(Int.Edn.), 1977, 16, 324.

131. R. Feser and H. Werner, Z.Anorg.Allg.Chem., 1979, 458, 301.

132. V. Harder, E. Dubler, and H. Werner, J.Organomet.Chem., 1974, 71, 427.

133. W. Klaüi, H. Neukomn, H. Werner, and G. Huttner, Chem.Ber., 1977, 110, 2283.

134. W. Klaüi, W. Eberspach, and R. Schwarz, J.Organomet. Chem., 1983, 252, 347.

135. W. Klaüi, A. Müller, and M. Scotti, J.Organomet.Chem., 1983, 253, 45.

136. W. Klaüi, J. Okuda, M. Scotti, and M. Valderrama, J.Organomet.Chem., 1985, 280, C26.

137. R.H. Prince and K.A. Raspin, J.Inorg.Nuclear Chem., 1969, 31, 695.

138. R.O. Gould, C.L. Jones, W.J. Sime, and T.A. Stephenson, J.Chem.Soc.,Dalton Trans., 1977, 669.

139. I.W. Robertson and T.A. Stephenson, Inorg.Chim.Acta, 1980, 45, L215.

140. J.A.S. Duncan, Ph.D.Thesis, University of Edinburgh, 1983.

141. T. Easton, Ph.D.Thesis, University of Edinburgh, 1986.

142. P.B. Critchlow and S.D. Robinson, Coord.Chem.Rev., 1978, 25, 69.

143. P.B. Critchlow and S.D. Robinson, J.Organomet.Chem., 1976, 114, C46.

144. P.B. Critchlow and S.D. Robinson, Inorg.Chem., 1978, 17, 1902.

145. P.R. Hoffman and K.G. Caulton, J.Am.Chem.Soc., 1975, 97, 4221.

146. V.V. Savant, J. Gopalakrishnan, and C.C. Patel, Inorg.Chem., 1970, 9, 748.

147. R.G. Cavell, W. Byers, and E.D. Day, Inorg.Chem., 1971, 10, 2710.

148. J.R. Sanders, J.Chem.Soc.(A), 1971, 2991.

149. J.R. Sanders, J.Chem.Soc.,Dalton Trans., 1972, 1333.

150. F.A. Cotton, B.A. Frenz, and D.L. Hunter, Inorg.Chim. Acta, 1976, 16, 203.

151. G.M. Kosolapoff and L. Maier, "Organic Phospho Compounds", Vol.4, 486.

152. D.J. Cole-Hamilton and T.A. Stephenson, J.Chem.Soc., Dalton Trans., 1974, 739.

Post-Graduate Courses

Pulse Sequences And Their Applications To N.M.R. Spectroscopy	Dr. G.A. Morris (Manchester University)
Aspects of Structural Chemistry	Dr. C. Glidewell (St. Andrews University)
The Chemistry Of Photographic Processes	Dr. L.A. Williams (formerly of Kodak Ltd)
Electrochemistry In And Out Of Mothballs	Dr. G.A. Heath
Topics In Transition Metal Coordination Chemistry	Dr. M. Schröder
University Of Strathclyde Inorganic Club Conference 1983, 85	
Departmental Inorganic Seminars And Colloquia (3 years).	