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RUTHENIUM COMPLEXES CONTAINING GROUP 5B DONOR LIGANDS. VI*. SYNTHESES AND REARRANGEMENT REACTIONS OF VARIOUS $[RuCl_2L_{3 or 4}]$ COMPLEXES $[L = P(OMe)_3, P(OMe)_2Ph, P(OR)Ph_2 (R = Me, Et)]$

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Summary

Reaction of $[RuCl_2(PPh_3)_3]$ with an excess of L in hexane gives either $[RuCl_2L_4]$ ($L = P(OMe)_3$, $P(OMe)_2Ph$) or $[RuCl_2L_3]$ ($L = P(OMe)Ph_2$, $P(OEt)Ph_2$). In polar solvents, $[RuCl_2\{P(OMe)_2Ph\}_4]$ and $[RuCl_2(P(OMe)Ph_2)_3]$ rearrange to the ionic dimers $[Ru_2Cl_3L_6]Cl$ whereas $[RuCl_2(P(OEt)Ph_2)_3]$ converts to the ionic trimer $[Ru_3Cl_5(P(OEt)Ph_2)_9]Cl$. Reaction of $[RuCl_2(PPh_3)_3]$ with excess of $P(OR)Ph_2$ in alcohols first generates the red $[RuCl(P\{OMe\}Ph_2)_4]^+$ and $[Ru_2Cl_2(P(OEt)Ph_2)_8]^{2+}$ cations respectively which can be isolated as their BPh_4^- salts, and later, the yellow $[Ru_2Cl_3(P(OMe)Ph_2)_6]^+$ and $[Ru_3Cl_5(P(OEt)Ph_2)_9]^+$ cations are formed. These various rearrangement processes have been extensively studied by variable temperature $^{31}P-\{^1H\}$ nmr spectroscopy and an overall mechanism of rearrangement for the various $[RuCl_2L_{3 and 4}]$ compounds in solution is proposed.

Introduction

Recently, we have shown that the monomeric tertiary phosphine complexes $[RuCl_2(PR_3)_{3 or 4}]$, made by exchange of $[RuCl_2(PPh_3)_4]$ with PR_3 in non-polar solvents [2] undergo facile rearrangement reactions in solution as shown in Scheme 1 [3]. In an attempt to verify the generality of this rearrangement pattern, we now report the full results [4] of studies on exchange reactions of $[RuCl_2(PPh_3)_3]$ (I) with tertiary phosphites, phosphonites and phosphinites.

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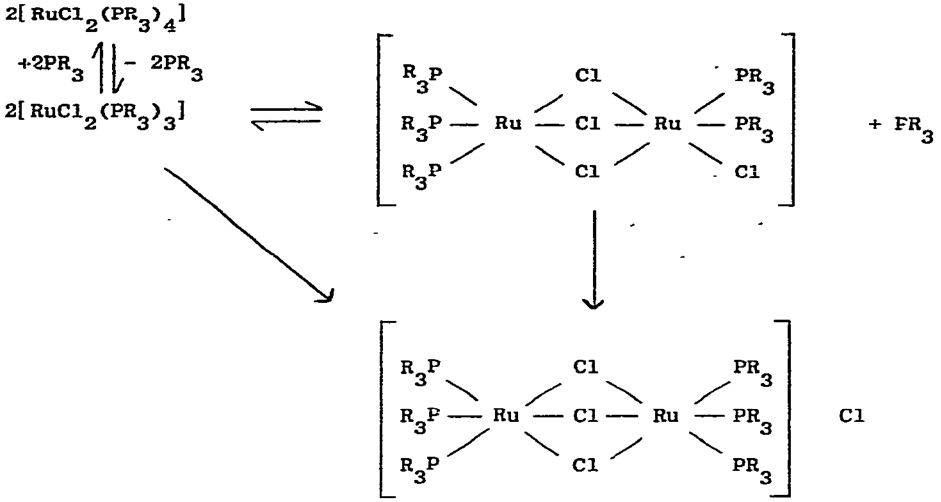
*For Part V, see ref 1.



(PR_3 = $PMePh_2$, PMe_2Ph, $PEtPh_2$, PEt_2Ph, $PClPh_2$)

SCHEME 1

Results and Discussion

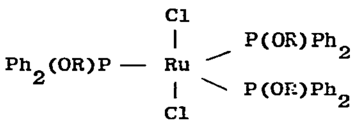
a) Preparation of monomeric neutral complexes

On refluxing compound (I) with an excess of $P(OMe)_3$ in hexane, a yellow crystalline solid analysing for $[RuCl_2\{P(OMe)_3\}_4]$ was deposited. The far ir spectrum (400-200 cm^{-1}), containing a strong band at 340 cm^{-1} assigned to ν(RuCl) from trans chloride groups, [5] and bands at 306 and 295 cm^{-} ascribed to ν(RuCl) vibrations from chloride groups trans to phosphorus [5] indicated a cis/trans isomer mixture in the solid state. However, the $^{31}P-\{^1H\}$ nmr spectra in $CDCl_3$ at both 213 and 298K consisted of a singlet at δ129.4 ppm and the ^1H nmr spectrum in $CDCl_3$ at 301K showed a symmetrical quintet centred at 3.84δ (cf similar resonance patterns for trans-$[Rh\{P(OMe)_3\}_4XY]^+$ cations [$X = Y = Br^-$; $X = H^-$, $Y = Br^-$; $X = Me^-$; $Y = I^-$][6]). Thus, these results indicate that rapid, irreversible rearrangement to the trans isomer occurs in solution.

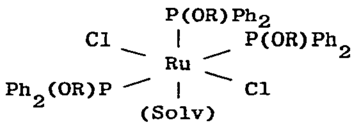
The compound $[RuCl_2(P\{OMe\}_2Ph)_4]$ was also prepared by this method and its far ir spectrum, containing bands at 324, 308 and 291 cm^{-1} again indicated the presence of both cis and trans isomers in the solid state.

The $^{31}P-\{^{1}H\}$ nmr spectrum in $CDCl_3$ at 213K contained a singlet at δ150.5 ppm (trans isomer) and two triplets at 166.6 and 149.4 ppm ($^{2}J_{pp}$ 44.0 Hz)(cis isomer). On warming to 298K the triplets disappeared and did not reappear when the solution was recooled. Therefore, as for $[RuCl_2(P\{OMe\}_3)_4]$, an irreversible cis to trans isomerisation process takes place in solution.

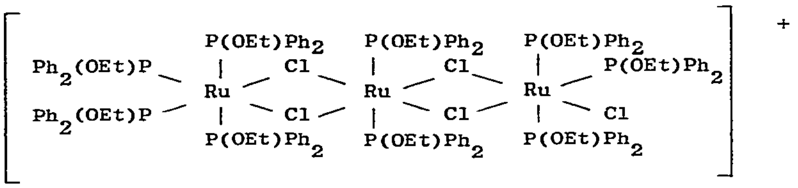
In contrast, reaction of $[RuCl_2(PPh_3)_3]$ with an excess of $P(OR)Ph_2$ (R = Me, Et) in hexane produced orange-brown crystals analysing closely



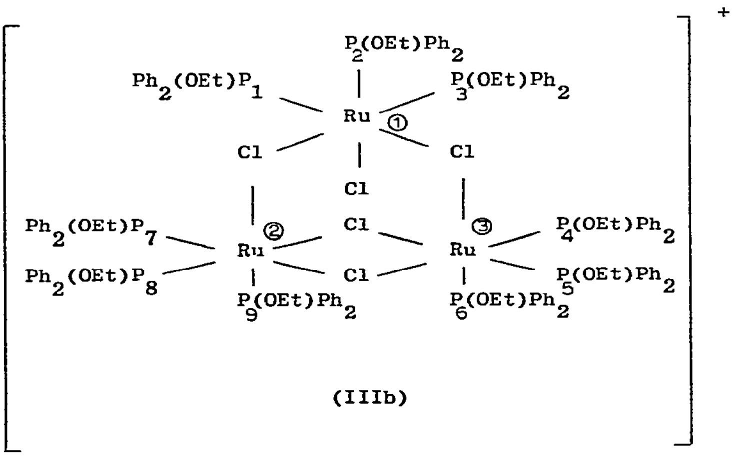
(IIa)



(IIb)



(IIIa)



(IIIb)

for [$RuCl_2(P(OR)Ph_2)_3$]. The far ir spectra contained a strong band at 337 cm^{-1} (R = Me), 328 cm^{-1} (R = Et) indicating the presence of trans chloride groups. The compounds dissolved in many common polar solvents but rapidly rearranged (see below). However, they were soluble and stable in benzene or toluene and osmometric molecular weight-measurements in benzene at 294K indicated that the complexes are monomeric. The $^{31}P-\{^1H\}$ nmr spectra in C_6D_6 at 298K showed a sharp singlet at 149.5 ppm (R = Me), 144.7 ppm (R = Et) indicating that the tertiary phosphinite groups were magnetically equivalent at this temperature. Possibilities to explain this equivalence include a trigonal bipyramidal structure (IIa) or more likely,* a square pyramidal or weakly solvated octahedral structure (IIb) in which facile scrambling of axial and equatorial $P(OR)Ph_2$ ligands renders them equivalent on the nmr timescale,(cf the $^{31}P-\{^1H\}$ nmr spectra of [$RuCl_2(PR_3)_3$] (PR_3 = PPh_3, [2,7] P(p-tolyl)$_3$ [9]) at ambient temperatures). In support of the latter conclusion, the $^{31}P-\{^1H\}$ nmr spectrum of [$RuCl_2(P\}OEt\{Ph_2)_3$] in $(CD_3)_2CO$/toluene at 140K consisted of two broad resonances at 167.3 and 141.1 ppm of relative intensity 1:2 and these nmr changes were concentration independent and reversible with temperature. Thus, although no spin-spin couplings were resolved (probably because of viscosity effects at this temperature), these resonances can be ascribed respectively to the expected triplet and doublet pattern for the "frozen-out" $\{RuCl_2(P(OEt)Ph_2)_3\}$ structure (IIb). The observed averaged position (146.5 ppm at 193K in $(CD_3)_2CO$/toluene) and that calculated on the basis of the low temperature spectrum at 140K (149.8 ppm) provides further support for the correctness of the above interpretation of this nmr data.

This scrambling process producing equivalence of all the phosphinite groups of [$RuCl_2(P(OEt)Ph_2)_3$] is much more facile than the corresponding

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*X-ray structural data shows that most five coordinate d^6 complexes have an essentially square pyramidal structure [7] and this is supported by recent theoretical arguments.[8]

process for [$RuCl_2(PPh_3)_3$] (see refs [2] and [7]) This is attributed to two factors <u>viz</u> the less bulky ligands and the fact that the resonances for the different phosphinite groups of [$RuCl_2(P(OEt)Ph_2)_3$] are much closer to each other than are the PPh_3 groups in [$RuCl_2(PPh_3)_3$]. The ligand $P(OMe)Ph_2$ is less bulky than either $P(OEt)Ph_2$ or PPh_3 and consequently, the $^{31}P-\{^1H\}$ nmr spectrum of [$RuCl_2\{P(OMe)Ph_2\}_3$] at 140K in $(CD_3)_2CO$/toluene only contained a broad resonance at 147.0 ppm.

<u>b) Rearrangement of monomeric species in polar solvents</u>

The compound [$RuCl_2\{P(OMe)_3\}_4$] appeared stable in polar solvents, being recovered unchanged both after refluxing in methanol for 6 hours or irradiating with ultraviolet light. The compound [$RuCl_2\{P(OMe)_2Ph\}_4$] did not rearrange on leaving at room temperature in methanol but after refluxing this solution for one hour, a yellow conducting solution was obtained. Addition of $NaBPh_4$ then precipitated a pale yellow solid whose $^{31}P-\{^1H\}$ nmr spectrum in $CDCl_3$ at 298K contained a singlet at 168.7 ppm and also an AB_2 pattern (ν_A 159.6 ppm; ν_B 170.4 ppm; J_{AB} 58.4 Hz). On refluxing for a further hour the $^{31}P-\{^1H\}$ nmr spectrum of the product showed only the singlet. This corresponds to [$Ru_2Cl_3\{P(OMe)_2Ph\}_6$]BPh_4, prepared earlier [10] by reaction of [$\{RuCl_2(C_7H_8)\}_n$] with $P(OMe)_2Ph$ in methanol. The AB_2 pattern must arise from an intermediate ionic product containing three phosphonite groups per ruthenium. Possibilities include [$RuCl(P\{OMe\}_2Ph)_3(Solv)_2$]$BPh_4$ or [$\{RuCl(P\{OMe\}_2Ph)_3Solv\}_2$]$(BPh_4)_2$ but it was impossible to differentiate further between these formulations because of the inability to separate this intermediate from the ionic dimer. A similar cationic intermediate has been observed on reaction of [$RuCl_2(PEtPh_2)_3$] with $PEtPh_2$ in ethanol for short periods, together with some [$Ru_2Cl_3(PEtPh_2)_6$]Cl[3].

In contrast, dissolving [$RuCl_2(P(OMe)Ph_2)_3$] in CH_2Cl_2 produced initially a bright yellow solution which gradually became paler in colour and also increased in conductivity, reaching a maximum of 29μmho (specific conductivity) for a 10^{-3} dm^{-3} mol. solution after <u>ca</u> 4 hours, which indicated the formation of a 1:1 electrolyte. The addition of $NaBPh_4$ then precipitated $[Ru_2Cl_3(P(OMe)Ph_2)_6]BPh_4$, synthesised earlier by reaction of $[\{RuCl_2(C_7H_8)\}_n]$ and $P(OMe)Ph_2$ in methanol [10]. This rearrangement reaction has also been studied by $^{31}P-\{^1H\}$ nmr spectroscopy. Thus at 183K in $(CD_3)_2CO/CH_2Cl_2$, the spectrum consisted of a broad signal at 144 ppm ($[RuCl_2(P\{OMe\}Ph_2)_3]$) and a sharp singlet at 139.4 ppm due to the rearranged product $[Ru_2Cl_3(P\{OMe\}Ph_2)_6]Cl$. As the temperature was raised, the signal at 144 ppm sharpened and decreased in intensity whilst the signal at 139.4 ppm increased in intensity, such that at 303K, almost all of the monomer had been converted to the ionic dimer. The rearrangement was irreversible since cooling the mixture had no effect on the intensity ratios observed at ambient temperature.

Unlike the $[RuCl_2(P\{OMe\}_2Ph)_4]$ rearrangement process, no intermediate products were observed, but an expansion of the spectrum when the sample was recooled to 213K showed a number of weak peaks at the base of the singlet at 139 ppm (Fig. 1). After the sample was allowed to stand at

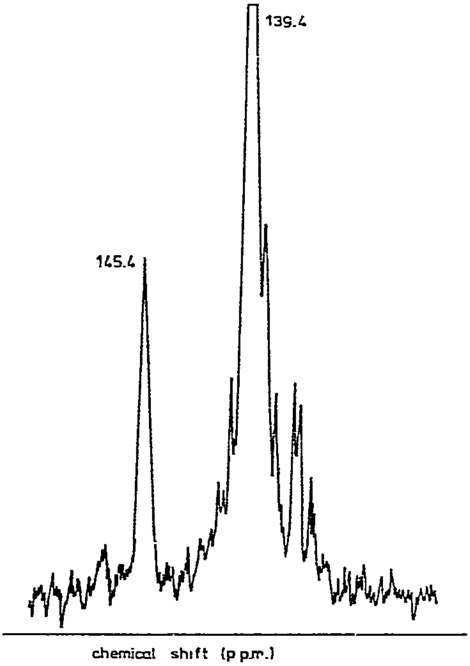

Fig. 1. $^{31}P-\{^1H\}$ nmr spectrum of the rearrangement products of $[RuCl_2(P(OMe)Ph_2)_3]$ in $(CD_3)_2CO/CH_2Cl_2$ at 213K.

room temperature for 48 hours, the spectrum, rerun at 213K, contained no resonance due to the monomer but the weak peaks at the base of the singlet were still present. These are attributed to a small amount of another rearrangement product (see below).

When $[RuCl_2(P\{OEt\}Ph_2)_3]$ was dissolved in CH_2Cl_2, the initial bright yellow solution also became progressively paler, the conductivity of a 10^{-3} dm^{-3} mol. solution increasing to a maximum of 30μmho over a period of ca 24 hours. Again, the rearrangement has been studied by $^{31}P-\{^1H\}$ nmr spectroscopy and, although much slower, followed a similar pattern to that of $[RuCl_2(P\{OMe\}Ph_2)_3]$, namely, irreversible conversion of the monomer to an ionic species. However, there is one very important difference here in that the rearrangement product (A) was not the triple bridged ionic dimer, $[Ru_2Cl_3(P\{OEt\}Ph_2)_6]Cl$, since the $^{31}P-\{^1H\}$ nmr spectrum at 213K in $CDCl_3$ was not a singlet but a complicated multiplet consisting of at least 20 lines. (Fig. 2). Leaving the sample

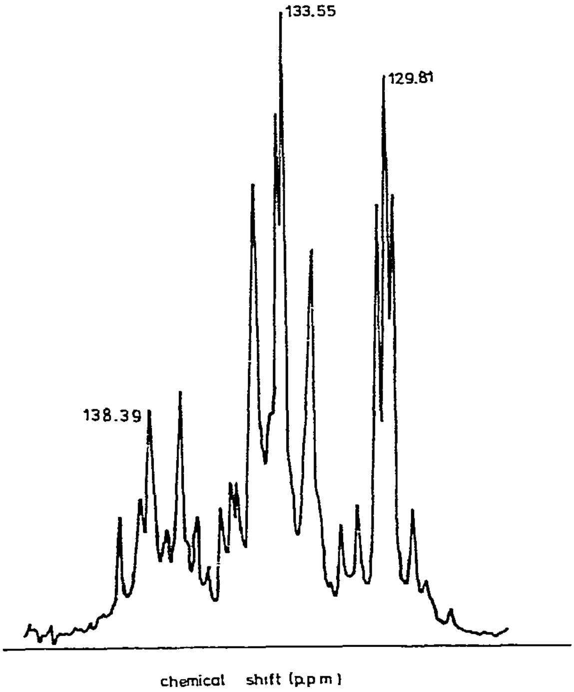

Fig. 2. $^{31}P-\{^1H\}$ nmr spectrum of the ionic rearrangement product of $[RuCl_2(P(OEt)Ph_2)_3]$ in $CDCl_3$ at 213K.

in solution for 3 days and then rerunning the spectrum at 213K showed that all of the monomer had been converted to (A). On warming to 303K, the multiplet collapsed to a broad resonance centred at ca 135 ppm which suggested that rapid intramolecular scrambling of all the $P(OEt)Ph_2$ groups was taking place at this temperature. Subsequent recooling to 213K gave the original sharp multiplet shown in Fig. 2 and this remained unaltered, even after leaving the solution for 12 weeks. The addition of either $NaBPh_4$ or NH_4PF_6 gave a pale yellow solid but addition of $AsPh_4Cl.HCl$ gave no precipitate, implying that the phosphorus containing species present is only cationic in nature. This was verified by running the ^{31}P- $\{^1H\}$ nmr spectrum in $CDCl_3$ at 213K of the BPh_4^- salt which consisted of an identical multiplet to that shown in Fig. 2. Therefore (A) cannot be for example $[Ru_2Cl_3(P\{OEt\}Ph_2)_6][RuCl_3(P\{OEt\}Ph_2)_3]$. Furthermore, samples of (A) with counteranions BPh_4^- or PF_6^-, prepared on several different occasions and run in a variety of different solvents eg $(CD_3)_2CO$, $CDCl_3$, $(CD_3)_2CO/CH_2Cl_2$, all displayed the <u>same</u> ^{31}P- $\{^1H\}$ nmr spectrum at 213K, suggesting that the product is a <u>single</u> species and not a mixture.

It is interesting to note that reaction of $[\{RuCl_2(C_7H_8)\}_n]$ with $P(OEt)Ph_2$ was earlier reported to give on addition of $NaBPh_4$, the ionic dimer $[Ru_2Cl_3(P\{OEt\}Ph_2)_6]BPh_4$ (based on analytical and ^1H nmr data)[10]. On repeating this reaction, we found that the ^{31}P- $\{^1H\}$ nmr spectrum of the product in $CDCl_3$ at 213K was the <u>same</u> as that shown in Fig. 2. In contrast, the ^{31}P- $\{^1H\}$ nmr spectrum of the product from the $[\{RuCl_2(C_7H_8)\}_n]$ $P(OMe)Ph_2$ reaction was a <u>singlet</u> at all temperatures, indicating the formation of the $[Ru_2Cl_3(P(OMe)Ph_2)_6]^+$ cation.

The ir spectrum (4000-400 cm^{-1}) of (A) [BPh_4^- salt] was identical to that of $[RuCl_2(P\{OEt\}Ph_2)_3]$ except for the additional bands due to the anion and, therefore, this suggested that no change in the $P(OEt)Ph_2$ groups has occurred during the rearrangement process. The narrow range of chemical shifts (ca 10 ppm) observed in the ^{31}P- $\{^1H\}$ nmr spectrum of (A) is also consistent with the non-formation of $Ru-P(O)Ph_2$ or $Ru-P(OH)Ph_2$

linkages.[†] Further support for this conclusion is the absence of ethanol or ethyl chloride in the ^1H nmr spectrum or g.l.c. trace of a 3 day old solution of $[RuCl_2(P(OEt)Ph_2)_3]$ in $CDCl_3$ and the close similarity of the ethyl region of the ^{13}C- $\{^1H\}$ nmr spectra of (A) in $CDCl_3$ and $[RuCl_2(P\{OEt\}Ph_2)_3]$ in C_6D_6 (see experimental section).

Since no free $P(OEt)Ph_2$ was observed in the ^{31}P- $\{^1H\}$ nmr spectrum on rearrangement of $[RuCl_2(P(OEt)Ph_2)_3]$ to (A) in various solvents, (A) must still contain an average of three $P(OEt)Ph_2$ groups per Ru atom. Conductivity measurements in both CH_2Cl_2 and acetone were consistent with the presence of the a 1:1 electrolyte (see experimental section). Furthermore, the molecular weight of the BPh_4^- salt in $CHCl_3$ was found to be 1350 and thus, for a 1:1 electrolyte, the actual molecular weight would be 2700. As a check on the validity of this conclusion the molecular weight of $[Ru_2Cl_3(P(OMe)Ph_2)_6]BPh_4$ in $CHCl_3$ was found to be 1003; required for 1:1 electrolyte 962. Support for the high molecular weight of (A) also came from the far ir spectrum of the BPh_4^- salt which contained bands at 314 and *ca* 260 cm^{-1}, indicating the presence of both terminal and bridging chloride groups.

On the basis of all this data, compound (A) is best formulated as containing the trimeric ruthenium(II) cation $[Ru_3Cl_5(P(OEt)Ph_2)_9]^+$ [calculated mol. wt. of BPh_4^- salt = 2870] and analytical data for salts of the various counterions are also reasonably consistent with this formulation. Two possible structures which fit most of these experimental observations are (IIIa) and (IIIb). However, the linear structure (IIIa) can be readily eliminated on the basis that facile intramolecular scrambling of all $P(OEt)Ph_2$ groups in such a structure is impossible. The closed structure (IIIb) containing one terminal chloride group, one double chloride bridge, two single chloride bridges and three $P(OEt)Ph_2$ groups per ruthenium is much more feasible when

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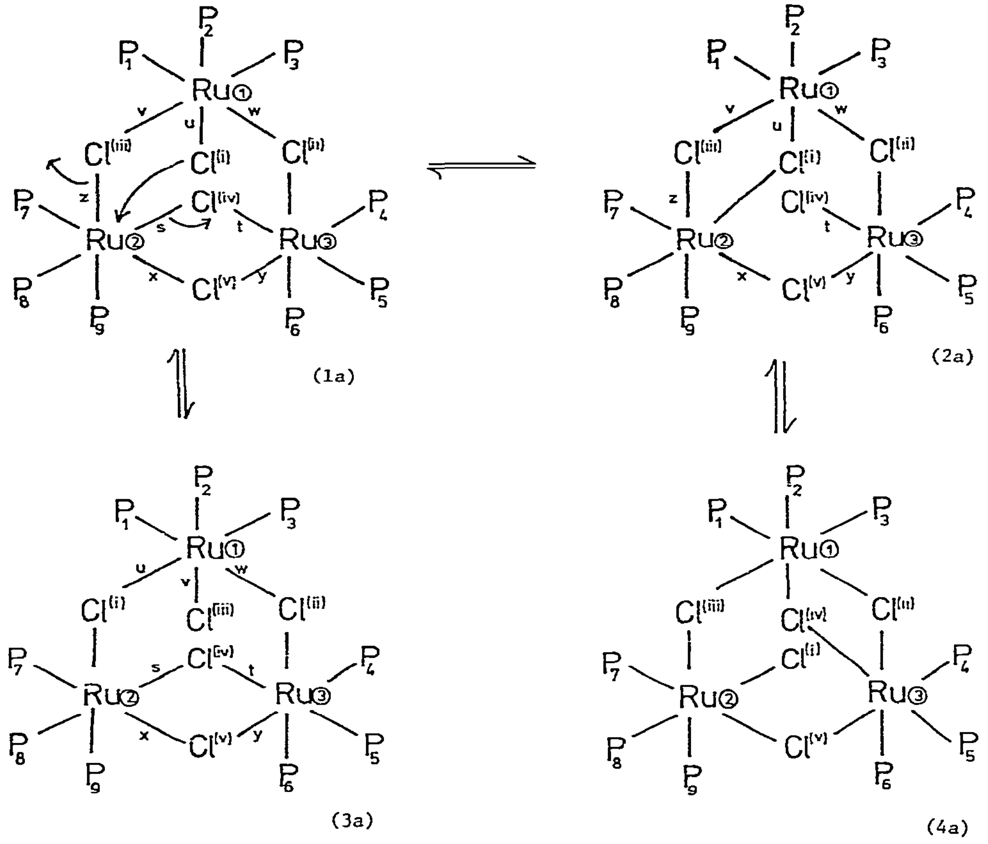
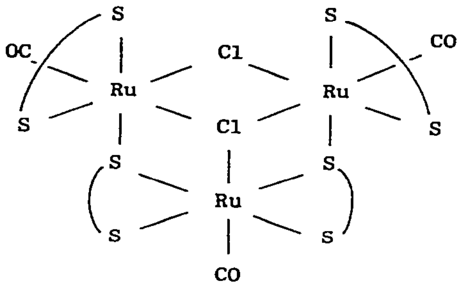
[†] For $[Ni(\eta\text{-}C_5H_5)\{P(OEt)_3\}\{PO(OEt)_2\}]$, the ^{31}P- $\{^1H\}$ nmr spectrum shows two doublets centred at δ147.5 $[P(OEt)_3]$ and 85.8 ppm $[PO(OEt)_2]$, a separation of *ca* 62 ppm [11].



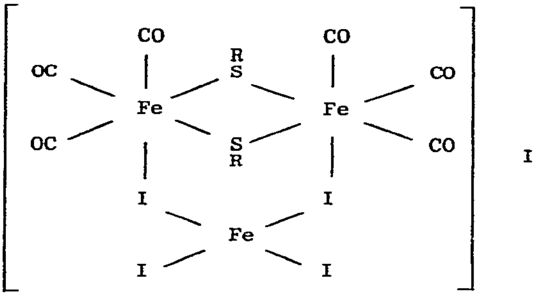
SCHEME 2

trying to explain the fluxional nature of (A) and Scheme 2 indicates how it is possible to rationalise this facile intramolecular scrambling process in terms of a structure such as (IIIb). This, in (1a), terminal chloride (i) positioned on Ru(1) can form a bond with Ru(2) with the subsequent breaking of bond(s), to form (2a) in which the terminal chloride is now on Ru(3) or bond(z) to form (3a) in which the chlorides (i) and (iii) have interconverted. Similarly, (2a) and (4a) can rearrange intramolecularly, and so on, with the result that all the phosphinite groups become equivalent when such rearrangement processes are sufficiently rapid on the nmr time scale.

This is not the first example of a trimeric ruthenium(II) complex. For example, reaction of a carbonylated solution of "$RuCl_3xH_2O$" in methanol with $MeCS_2NEt_2$ gave a minute quantity of golden-brown crystals, shown by



(IV) (S-S$^-$ = $^-$S$_2$CNEt$_2$)



(V)

X-ray analysis to be [$Ru_3(S_2CNEt_2)_4(CO)_3Cl_2$] (IV) [12]. Trinuclear iron compounds of stoichiometry [$Fe_3(CO)_6I_5(SR)_2$] have also been reported [13] and one of the proposed structures (V) for these 1:1 electrolytes is very similar to that of (IIb).

Unfortunately, extensive recrystallisation attempts on (A) have failed to produce crystals suitable for an X-ray analysis and therefore unequivocal evidence for both the composition and detailed structure of (A) is still lacking.

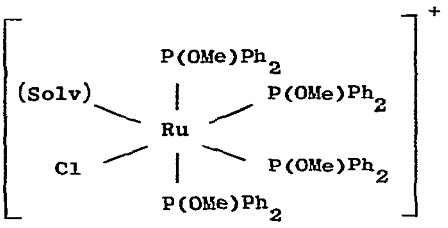
On the basis of structure (IIb), (assuming a regular octahedral geometry around each Ru ion), it might have been expected that the $^{31}P-\{^1H\}$ nmr spectrum of (A) would have consisted of an AB_2 pattern arising from atoms P_2, P_1, P_3 superimposed on an ABC pattern of twice the intensity arising from atoms P_4, P_5, P_6 and P_7, P_8, P_9. Several attempts have been made to fit such a theoretical pattern of lines to the observed pattern shown in Fig. 2, using the computer simulation program LAOCOON, but unfortunately, these attempts were not successful. For several reasons, however, this failure does not necessarily invalidate the correctness of structure (IIIb). First, as stated above, the theoretical nmr pattern was formulated on the basis of a regular octahedral environment around each Ru ion, but it is quite likely that small deviations from regular geometry might occur, sufficient to destroy, for example, the postulated magnetic equivalence of the two ABC sets or the equivalence of atoms P_1 and P_3 in the supposed AB_2 set. Thus, the expected $^{31}P-\{^1H\}$ nmr spectrum of (IIIb) might more realistically be a superposition of three slightly different ABC subsets *ie* 9 coupling constants and 9 chemical shifts would then be required to completely define this spin system. Another difficulty is the quality of the experimental spectrum. Thus, although 20 lines can be counted, the combination of narrow spectral width (*ca* 10 ppm), low temperature (producing some viscosity broadening), and complexity of signals, imply that it is highly likely that many overlapping resonances are present (*NB* a single ABC spin system can generate a maximum of 15 lines). Therefore, in this situation, insufficient unambiguous experimental information is available to completely solve this nmr problem.

Nevertheless, although the structure is not completely proven by nmr spectral analysis, the wide range of chemical and spectroscopic evidence does, in our view, strongly support the formulation of (A) as $[Ru_3Cl_5(P(OEt)Ph_2)_9]X$ ($X = Cl^-$, BPh_4^-, PF_6^-) with structure (IIIb).

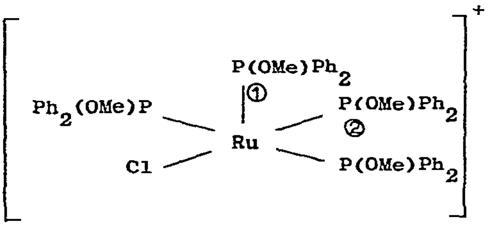
Finally, the weak peaks appearing at the base of the singlet (Fig. 1) correspond very closely to those in Fig. 2 and are therefore considered to arise from the presence of a small amount of $[Ru_3Cl_5(P\{OMe\}Ph_2)_9]Cl$.

c) Reaction of $[RuCl_2(PPh_3)_3]$(I) with L in polar solvents

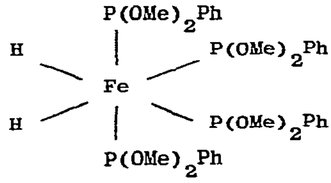
Reaction of compound (I) with excess of L ($L = P(OMe)_3$, $P(OMe)_2Ph$) in methanol produced the previously known [10,14] $[RuL_6]^{2+}$ complexes



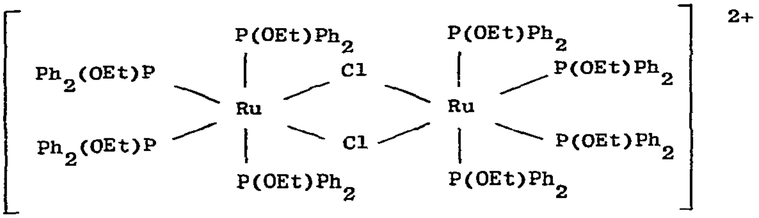
(VIa)



(VIb)



(VII)



(VIII)

readily isolated as BPh_4^- salts. In contrast, refluxing (I) with an excess of $P(OMe)Ph_2$ in methanol for a short time gave a deep red solution which gradually, over a period of two hours, turned yellow in colour. Addition of $NaBPh_4$ to the yellow solution produced $[Ru_2Cl_3(P\{OMe\}Ph_2)_6]BPh_4$, but addition of $NaBPh_4$ to the initial red solution gave a red solid which analysed closely for $[RuCl(P\{OMe\}Ph_2)_4]$-BPh_4 (VI). The mull ir spectrum of (VI), in which there was no evidence of a coordinated solvent molecule, contained, in addition to bands due to $P(OMe)Ph_2$ and BPh_4^-, a band at 290 cm^{-1} attributed to $\nu(RuCl)$ of a

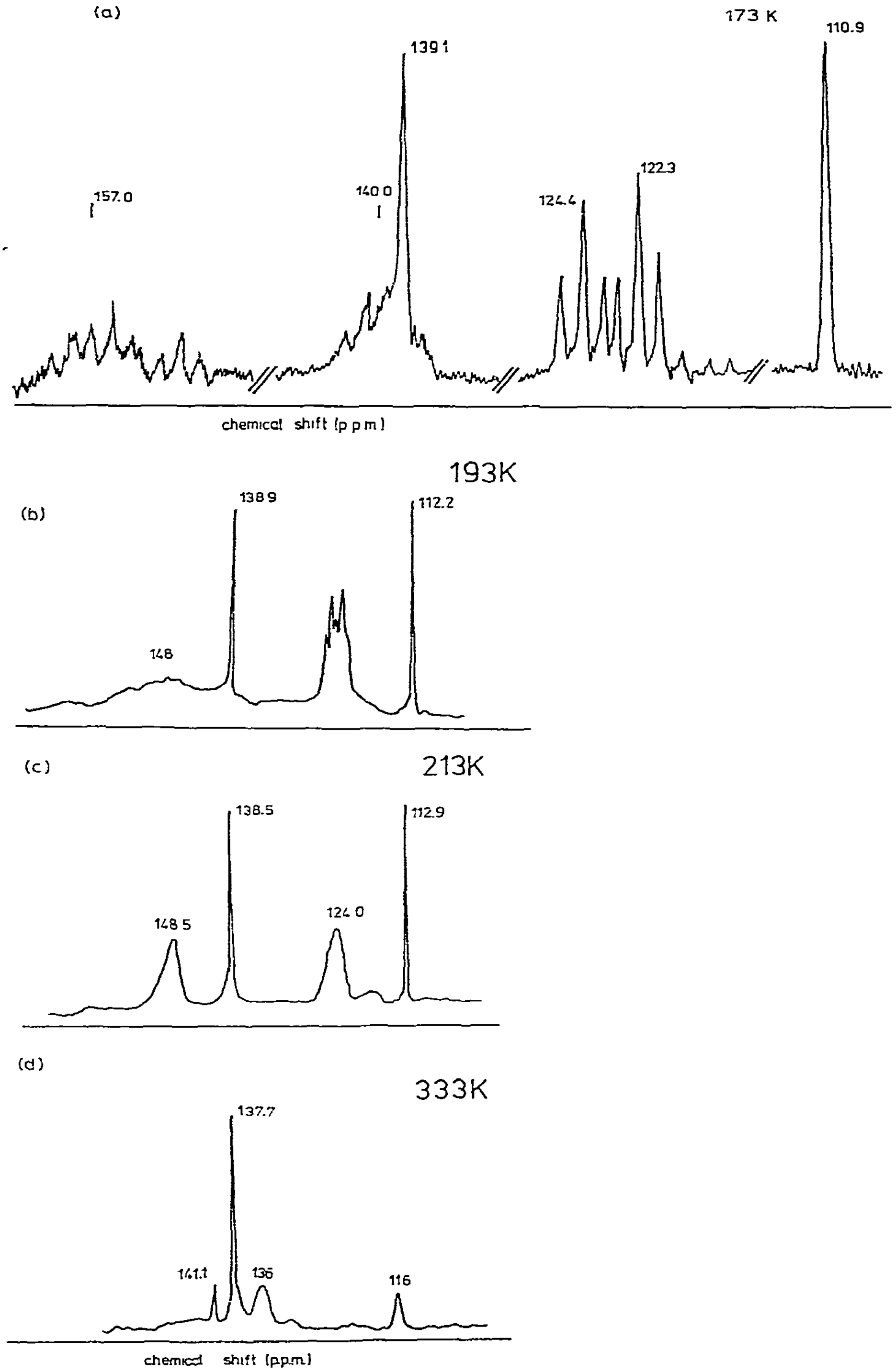


Fig. 3. $^{31}P-\{^{1}H\}$ nmr spectra of $[RuCl(P(OMe)Ph_2)_4]BPh_4$ in $(CD_3)_2CO$ a

a) 173K b) 193K c) 213K d) 333K.

chloride ion trans to phosphorus. This complex slowly rearranged to the ionic dimer in chlorinated solvents but was stable in acetone and therefore, $^{31}P-\{^{1}H\}$ nmr spectra were studied in $(CD_3)_2CO$ over a range of temperatures. (Fig. 3). At 173K (Fig. 3a), several resonances were observed viz a singlet at 139.1 ppm due to the presence of some $[Ru_2Cl_3(P(OMe)Ph_2)_6]BPh_4$ in the sample, a singlet at 110.9 ppm due to free $P(OMe)Ph_2$, two multiplets at 157 and 140 ppm and sharp resonances resembling two triplets centred at 123 ppm. As the temperature was raised, the broad multiplets at 157 and 140 ppm coalesced to a broad hump at 148 ppm which on further warming sharpened up to a peak at 148.5 ppm (Fig. 3b and c). The resonance at 123 ppm also collapsed on warming and at 213K a broad peak at 124.0 ppm was observed (Fig. 3c). At 333K, (Fig. 3d) the peaks at 148.5 and 124.0 ppm disappeared and a broad resonance at 136 ppm appeared. No change in the singlet due to free $P(OMe)Ph_2$ occurred up to 213K but at 333K, it had broadened considerably and shifted to higher frequency.

In the spectrum obtained at 173K (Fig. 3a), it appeared initially that the resonances at 157 and 140 ppm on the one hand and at 123 ppm on the other might arise from two different species. On examining the spectra at higher temperatures, the observed coalescence of the multiplets at 157 and 140 ppm to a resonance at 148 ppm indicates that they arise from the same species and that each peak corresponds to the same number of P atoms in that species. However, as the temperature is further raised the resonances at 148 and 123 ppm then coalesced to a resonance midway between them which implies that they also arise from the same species and correspond to the same number of P atoms. Cooling the solution restores the spectrum to that shown in Fig. 3a. Hence, it appears that the multiplets at 157, 140 and 123 ppm are produced by P atoms in intensity ratio 1;1;2 respectively and belong to a single species which is most probably $[RuCl(P\{OMe\}Ph_2)_4]^+$. Structures consistent with two magnetically equivalent and two non-equivalent P atoms are (VIa) with the sixth position of the octahedral complex in solution occupied by a solvent molecule or (VI b) with no coordinated solvent.

Unfortunately all attempts to reproduce the spectrum at 173K (Fig. 3a) assuming an ABC_2 spin system and using computer simulation techniques have proved unsuccessful since no combination of chemical shift and coupling constant data could simulate the symmetrical pattern centred at 123 ppm.[†] However, a precedent exists in the literature for the occurrence of unexpected $^{31}P-\{^1H\}$ nmr spectra in a related complex at low temperature [15]. Thus, for cis- $[FeH_2(P\{OMe\}_2Ph)_4]$ (VII), the $^{31}P-\{^1H\}$ nmr spectrum at 210K consisted of the expected A_2B_2 pattern (Fig. 4). However, as the temperature was lowered, the triplets broadened but at 187K they sharpened up again to give more complex patterns with the lower frequency resonance sharpening up more rapidly than the one at higher frequency. In fact, at 150K, the shape of the lower frequency resonance is virtually identical to that observed in Fig. 3a.

The explanation offered by Meakin et al [15] is that the bulky $P(OMe)_2Ph$ ligands interact in such a way as to reduce the symmetry of the molecule below that shown in (VII) and that the ligands motions are sufficiently restricted such that the reduction of symmetry is maintained on the nmr time scale at these low temperatures. In support of this interpretation, the solid state structure of $[FeH_2\{P(OEt)_2Ph\}_4]$ differs appreciably from the idealised C_{2v} symmetry shown in (VII) and this distortion is attributed more to interligand interactions than crystal packing effects.

By comparison of the spectra in Fig. 4 with those in Fig. 3, it seems probable that such a situation also occurs for $\{RuCl(P(OMe)Ph_2)_4\}^+$. In the latter case, a frozen-out ABC_2 spectrum was not observed at higher temperatures because of rapid intramolecular scrambling processes and at lower temperatures the equatorial phosphinite groups in (VI a) [and P_1 and P_2 of (VI b)] are in different chemical environments so that two multiplets are observed in contrast to the one for the equatorial phosphonite groups of $[FeH_2(P\{OMe\}_2Ph)_4]$.

[†] The other two multiplets at 157 and 140 ppm are much broader and it is difficult to tell whether or not they match the simulated spectra.

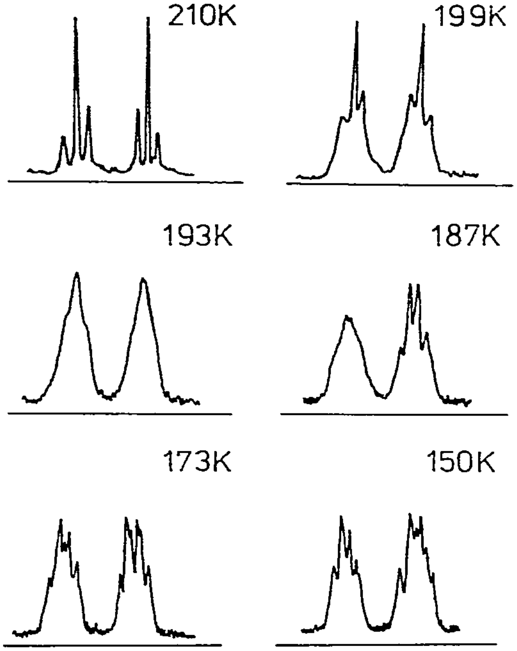
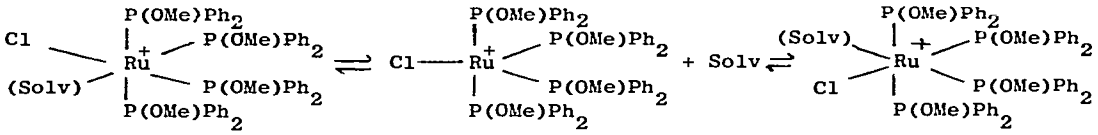


Fig. 4. ^{31}P- {^{1}H} nmr spectra of cis -[$FeH_2\{P(OMe)_2Ph\}_4$] in 50% CH_2Cl_2-50% CHF_2Cl at various temperatures (reproduced from ref [15])

The equivalence of the equatorial tertiary phosphinite groups of [$RuCl(P\{OMe\}Ph_2)_4]^+$ at 193K can best be explained by invoking the dynamic equilibrium shown in equation (1). Loss of the solvent molecule



(1)

occurs to form a 5 coordinate intermediate in which there is no facile overall rearrangement at this low temperature. Recombination of the solvent molecule trans to the other equatorial ligand then causes the two equatorial ligands to become equivalent on the nmr timescale. At higher temperatures further scrambling of axial and equatorial ligands via a pseudorotation process is proposed. Some intermolecular exchange with free $P(OMe)Ph_2$ also starts to occur at higher temperatures suggesting the equilibrium shown in equation

(2) is becoming of some importance and a small additional resonance is observed at 141 ppm (Fig. 3d) which may be due to the cation $[RuCl\{P(OMe)Ph_2\}_3(Solv)_2]^+$. Furthermore, the addition of excess $P(OMe)Ph_2$ inhibited the formation of

$$[RuCl\{P(OMe)Ph_2\}_4(Solv)]^+ \rightleftharpoons [RuCl\{P(OMe)Ph_2\}_3(Solv)_2]^+ + P(OMe)Ph_2 \qquad (2)$$

$[Ru_2Cl_3\{P(OMe)Ph_2\}_6]^+$ in CH_2Cl_2 whereas the addition of Cl^- to an acetone solution of $[RuCl\{P(OMe)Ph_2\}_4]BPh_4$ caused a colour change from red to yellow and rerunning the spectrum at 298K showed that all the resonances except those due to $[Ru_2Cl_3\{P(OMe)Ph_2\}_6]BPh_4$ and free $P(OMe)Ph_2$ had disappeared. Finally conductivity measurements on an acetone solution of $[RuCl(P\{OMe\}Ph_2)_4]BPh_4$ indicated the presence of a 1:1 electrolyte.

The reaction between compound (I) and excess of $P(OEt)Ph_2$ in ethanol, as for $P(OMe)Ph_2$, produced initially a red solution which slowly turned yellow in colour. Addition of $NaBPh_4$ to the yellow solution gave $[Ru_3Cl_5(P(OEt)Ph_2)_9]BPh_4$ and from the red solution a red solid analysing for $[RuCl(P(OEt)Ph_2)_4]BPh_4$ was obtained. However, the $^{31}P-\{^1H\}$ nmr spectra of this compound at various temperatures in $(CD_3)_2CO$ contained several different features from those of $[RuCl(P(OMe)Ph_2)_4]BPh_4$. At 173K (Fig. 5a), the spectrum contained a multiplet centred at 135 ppm due to the presence of some $[Ru_3Cl_5(P(OEt)Ph_2)_9]BPh_4$, a singlet (not shown) at 110.1 ppm due to free $P(OEt)Ph_2$, and two triplets at 148.1 and 119.0 ppm (J_{pp} 29.2 Hz). As the temperature was raised, the triplets broadened (Fig 5b) and at 298K coalesced to a broad peak superimposed on the resonance at 135 ppm due to the trimer (Fig. 5c). The triplets, which reappeared on cooling the solution to 173K must arise from the double chloride bridged dimer $[Ru_2Cl_2(P(OEt)Ph_2)_8](BPh_4)_2$ (VIII) since a monomer would, as in the case of $[RuCl(P(OMe)Ph_2)_4]^+$, be expected to give a more complicated spectrum. The presence of such a dimer in the solid state is suggested by a broad band at 270 cm^{-1} in the far ir spectrum which was not observed for $[RuCl(P(OMe)Ph_2)_4]BPh_4$. However, the collapse and coalescence of the triplets at higher temperatures is not consistent with retention of this dimeric structure in solution,

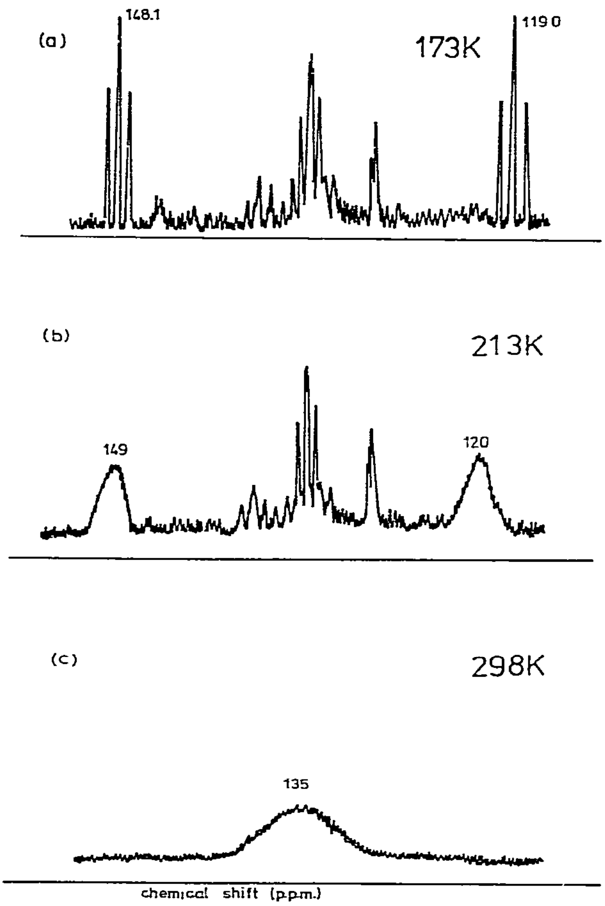


Fig. 5. $^{31}P-\{^{1}H\}$ nmr spectra of $[Ru_2Cl_2(P\{OEt\}Ph_2)_8](BPh_4)_2$ in $(CD_3)_2CO$ at a) 173K b) 213K c) 298K.

and it would suggest that the dimer is cleaved to produce the manomer $[RuCl(P(OEt)Ph_2)_4]^+$ as the temperature is raised (*cf* the $^{31}P-\{^{1}H\}$ nmr spectra of compounds (VII) (Fig. 3) and (VIII) (Fig. 5) at 213K and above). Furthermore, conductivity measurements on (VIII) at 298K in acetone indicated the presence of a 1:1 electrolyte. No evidence for exchange with free $P(OEt)Ph_2$ was observed since the resonance at 110.1 ppm remained sharp at all temperatures and no additional resonance which could be attributed to $[RuCl(P(OEt)Ph_2)_3(Solv)_2]^+$ appeared in the spectrum at

298K. However, addition of excess $P(OEt)Ph_2$ inhibited rearrangement to $[Ru_3Cl_5(P(OEt)Ph_2)_9]BPh_4$ in CH_2Cl_2, whereas addition of Cl^- to an acetone solution of $[Ru_2Cl_2(P(OEt)Ph_2)_8](BPh_4)_2$ caused a colour change from red to yellow but the rearrangement process was slower than for $[RuCl(P(OMe)Ph_2)_4]BPh_4$,

d) Mechanism of rearrangement of $[RuCl_2L_{3or4}]$ species

It is of interest to conclude this paper by briefly examining possible mechanisms of rearrangement for the various $[RuCl_2L_{3or4}]$ compounds discussed above, particularly with reference to the mechanism proposed earlier [3] (Scheme 1) to rationalise the behaviour of various $[RuCl_2(PR_3)_{3or4}]$ compounds in solution.

First, no evidence has been found in this work for the formation of the neutral dimers $[Ru_2Cl_4L_5]$ [L = $P(OMe)_3$, $P(OMe)_2Ph$, $P(OR)Ph_2$ (R = Me, Et)] which can presumably be attributed to the stronger Ru-P bonds found in these alkoxy substituted phosphine complexes compared to those containing most tertiary phosphines. Further support for this conclusion comes from the observation that unlike $[RuCl_2(PMePh_2)_4]$[16] and $[RuCl_2(PEtPh_2)_3]$[2], dissolving $[RuCl_2(PMe_2Ph)_4]$ in non-polar solvents does <u>not</u> give any $[Ru_2Cl_4(PMe_2Ph)_5]$ and this can be attributed to the well-known high affinity of PMe_2Ph for Ru(II) [17].

In an attempt to obtain such compounds, solutions containing $[Ru_2Cl_3(P(OMe)Ph_2)_6]Cl$ were pyrolysed at 120°C for 12 hours since a similar reaction with $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ gave $[Ru_2Cl_4(PEt_2Ph)_5]$[18][†]. However, X-ray structural analysis showed the product to be the unusual neutral dimer $[(P(OMe)Ph_2)_2(P(OH)Ph_2)RuCl_3Ru(P(OH)Ph_2)_2(PPh_2O)]$ in which O-R bond rupture rather than Ru-P bond cleavage had occurred [19]. Similarly, pyrolysis of solutions containing the $[Ru_3Cl_5(P(OEt)Ph_2)_9]^+$ cation gave

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[†] Similarly, pyrolysis of $[Ru_2Cl_3(PR_3)_6]Cl$ (PR_3 = $PMePh_2$, $PEtPh_2$) gives $[Ru_2Cl_4(PR_3)_5]$ but even at 400K, $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ was recovered unchanged [16], again demonstrating the strength of the $Ru\text{-}PMe_2Ph$ bonds.

$[(P(OEt)Ph_2)_2(P(OH)Ph_2)RuCl_3Ru(P(OH)Ph_2)_2(PPh_2O)]$ [19] .*

As for $[RuCl_2(PR_3)_{3or4}]$, both $[RuCl_2(P(OMe)_2Ph)_4]$ and $[RuCl_2(P(OMe)Ph_2)_3]$ rearranged to the ionic dimers $[Ru_2Cl_3L_6]Cl$ when dissolved in polar solvents. The observation of an ionic intermediate $[RuCl(P\{OMe\}_2Ph)_3(solv)_2]^+$ (or $[\{RuCl(P\{OMe\}_2Ph)_3(solv)\}_2]^{2+}$) strongly suggests that the mechanism of formation of $[Ru_2Cl_3(P\{OMe\}_2Ph)_6]Cl$ involves prior dissociation of Cl^- from the neutral monomer followed by coupling of this cation with more of the neutral monomer (see Scheme 3). A similar ionic intermediate $[RuCl(PEtPh_2)_3(solv)_2]^+$ (or $[\{RuCl(PEtPh_2)_3(solv)\}_2]^{2+}$) has been observed in the formation of $[Ru_2Cl_3(PEtPh_2)_6]Cl$ from $[RuCl_2(PEtPh_2)_3]$. [3]

However, with $[RuCl_2(P(OEt)Ph_2)_3]$ in polar solvents, the major rearrangement product is the ionic trimer $[Ru_3Cl_5(P(OEt)Ph_2)_9]Cl$ (III b). A rationalisation of <u>all</u> these results is obtained by postulating the formation of a labile, double-bridged cationic intermediate $[L_3ClRuCl_2Ru(solv)\text{-}L_3]^+$ by coupling of $[RuCl_2L_3]$ and $[RuClL_3(solv)_2]^+$. This can then either rearrange in intramolecular fashion (pathway a) to generate the triple chloride bridged species or combine with another molecule of $[RuCl_2L_3]$ (pathway b) to give the ionic trimer (Scheme 3). The factors which determine the preferred pathway a or b are not understood at present and further work with a wider range of ligands to try and establish these factors is now in progress.

However, it is gratifying that similar double bridged cations $[L_3(OH)\text{-}Ru(OH)_2RuL_3]^+$ which rearrange to $[L_3Ru(OH)_3RuL_3]^+$ (L = PMe_2Ph, $PMePh_2$, $P(OMe)Ph_2$) have recently been postulated by Ashworth <u>et al</u> [20] and such species are probably key intermediates in the mechanism of formation of other triple-bridged cations.+

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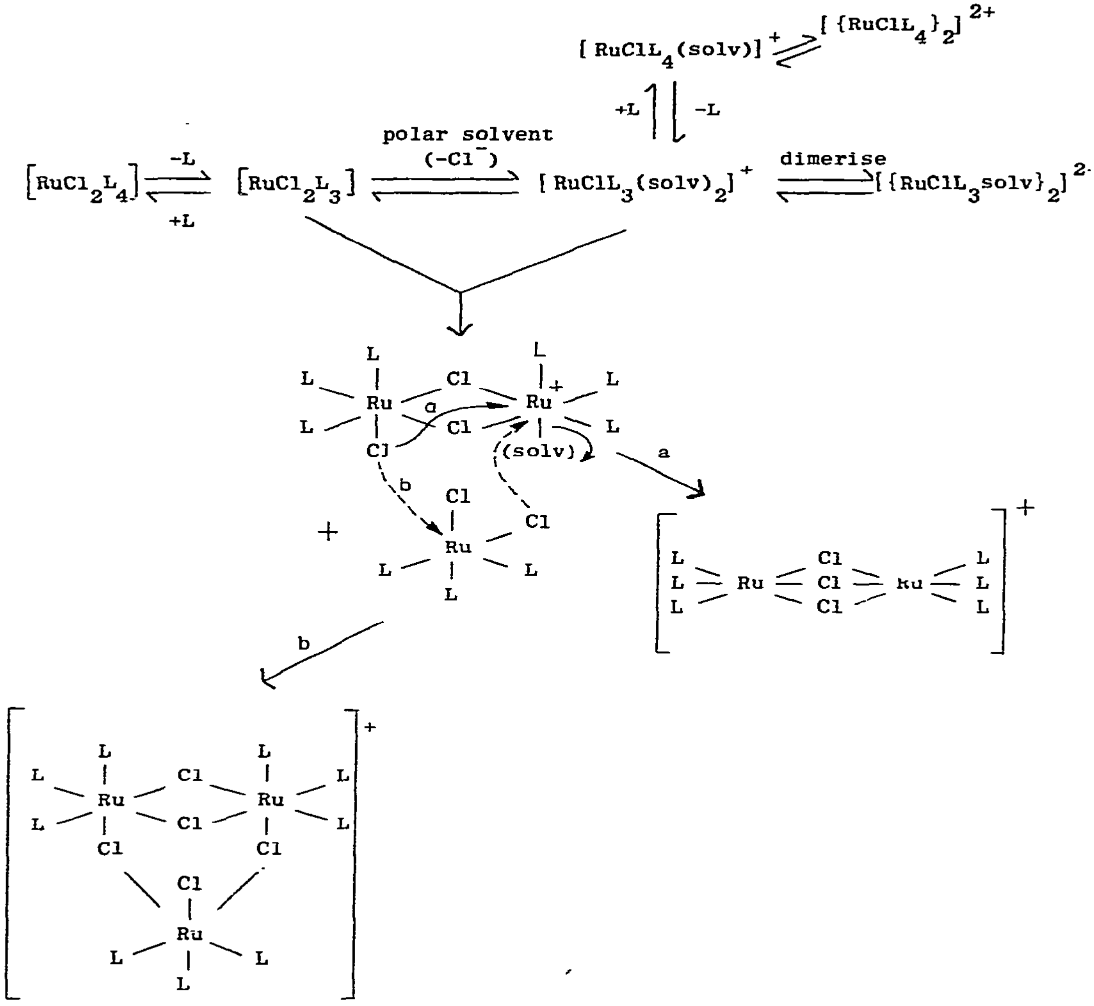
*Note that in ref [19], on the basis of analytical and ^1H nmr data, we and others [10] assumed that the product from the reaction of $[\{RuCl_2(C_7H_8)_n\}]$ and $P(OEt)Ph_2$ in ethanol was $[Ru_2Cl_3(P(OEt)Ph_2)_6]Cl$ but $^{31}P\text{-}\{^1H\}$ nmr studies now show it to be $[Ru_3Cl_5(P(OEt)Ph_2)_9]Cl$.

+For example, a similar mechanism to that shown in Scheme 3, which involves the double bridged, cationic intermediate $[(arene)XRuX_2Ru(solv)arene]^+$ can b proposed to explain the formation of the triple bridged ionic cations $[areneRuX_3Ruarene]^+$ ($X = Cl^-, OH^-, OR^-$) [21]



SCHEME 3

Finally, the observations that addition of excess $\mathrm{P(OR)Ph_2}$ (R = Me,Et) to $\mathrm{CH_2Cl_2}$ solutions of $[\mathrm{RuCl(P\{OMe\}Ph_2)_4}]\mathrm{BPh_4}$ (VI) and $[\mathrm{Ru_2Cl_2(P\{OEt\}Ph_2)_8}]$-$\mathrm{(BPh_4)_2}$ (VIII) respectively inhibited the formation of $[\mathrm{Ru_2Cl_3(P\{OMe\}Ph_2)_6}]$-$\mathrm{BPh_4}$ and $[\mathrm{Ru_3Cl_5(P\{OEt\}Ph_2)_9}]\mathrm{BPh_4}$, whereas addition of $\mathrm{Cl^-}$ to acetone solutions of (VI) and (VIII) accelerated the formation of these species, supports the mechanism shown in Scheme 3.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department, B.M.A.C. and A. Bernhardt, West Germany. Molecular weights were determined on a Mechrolab Vapour Pressure osmometer (model 301A) calibrated with benzil. Infrared spectra were recorded in the region 4000-250 cm^{-1} on Perkin Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the region 400-200 cm^{-1} on a Beckman RIIC IR 720 far ir. spectrometer using pressed Polythene discs. Hydrogen-1 nmr spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable temperature attachment and carbon-13 nmr spectra on a Varian CFT-20 spectrometer operating at 20 MHz (^{13}C chemical shifts are quoted in ppm to high frequency of TMS). Phosphorus-31 nmr spectra were obtained on a Varian Associates XL100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m to high frequency of 85% H_3PO_4. Melting points were determined with a Kôfler hot-stage microscope and are uncorrected.

Conductivity measurements were made at 303K using a model 310 Portland Electronics conductivity bridge. Conductivity vs concentration data were obtained over a range of concentrations (2×10^{-3} to 5×10^{-3} dm^{-3} mol) and a plot of Λ_c(equivalent conductance) against $C^{\frac{1}{2}}$ (concentration in equivalents dm^{-3}) gave a straight line which on extrapolation to $C^{\frac{1}{2}} = 0$ gave Λ_o. A subsequent plot of $\Lambda_o - \Lambda_c$ vs $C^{\frac{1}{2}}$ gave a straight line whose slope is a function of the ionic charges [22]. Thus, the slopes obtained for various samples were compared with those for known 1:1 and 2:1 electrolytes and hence the electrolyte type could be determined.

Materials

Ruthenium trichloride trihydrate (Johnson Matthey); triphenylphosphine (Aldrich); trimethylphosphite (Fisons); dimethylphenylphosphonite, methyldiphenylphosphinite, ethyldiphenylphosphinite (Maybridge); sodium tetraphenylborate (BDH); ammonium hexafluorophosphate (Alfa). $[RuCl_2(PPh_3)_3]$ was prepared as described earlier [23].

All reactions were carried out in degassed solvents under a nitrogen atmosphere. s(singlet); t(triplet); pt(pseudotriplet); q(quintet); mt(multiplet); br(broad); sh(shoulder); st(strong); w(weak); m(medium). Proposed ν(RuCl) bands underlined.

Dichlorotetrakis(trimethylphosphine)ruthenium(II):- The compound [$RuCl_2(PPh_3)_3$] (0.20g) was refluxed with $P(OMe)_3$ (0.40 cm^3) in hexane (20 cm^3) for one hour. The solution was cooled and the yellow crystals obtained were filtered off and recrystallised from CH_2Cl_2/hexane (yield 0.63g 45%) m.p. 145-147°C [Found: C, 21.6; H, 5.4%; Calc. for $C_{12}H_{36}Cl_2O_{12}P_4Ru$: C, 21.6; H, 5.4%] far ir spectrum:- 340st, 306st, 295st, 284m, 274m, 260w, 250w, 210st, ^1H nmr ($CDCl_3$ at 301K) 3.84 ppm (q) ^{31}P-{^1H} nmr ($CDCl_3$ at 298K) 129.4(s) ppm.

Dichlorotetrakis(dimethylphenylphosphonite)ruthenium(II):- The compound [$RuCl_2(PPh_3)_3$] (0.20g) was refluxed with $P(OMe)_2Ph$ (0.40 cm^3) in hexane (20 cm^3) for 3 hours to give yellow crystals which were filtered off and recyrstallised from CH_2Cl_2/hexane (0.125g 75%) m.p. 158-160°C [Found: C, 45.0; H, 5 2%; Calc. for $C_{32}H_{44}Cl_2O_8P_4Ru$:- C, 45.0; H, 5.2%] far ir spectrum 324st, 308m, 291st, 257sh, 214st; ^1H nmr ($CDCl_3$ at 301K) 3.45 (q), 7.20 (mt) ppm ^{31}P-{^1H} nmr ($CDCl_3$ at 213K) 150.5(s), 166.6(t), 149.4(t) [$^2J_{pp}$ 44.0 Hz]

Dichlorotris(methyldiphenylphosphinite)ruthenium(II):- The compound [$RuCl_2(PPh_3)_3$] (0.20g) was refluxed with $P(OMe)Ph_2$ (0.20 cm^3) in hexane (20 cm^3) for 3 hours. The resulting orange-brown solid was filtered off and washed with hexane (0.168g, 95%) m.p. 164-166°C [Found: C, 56.5, H, 4.6, Cl, 8.7%, M(C_6H_6) 834. Calc. for $C_{39}H_{39}Cl_2O_3P_3Ru$:- C, 57.0; H, 4.7; Cl, 8.7% M.820] far ir spectrum 337st, 290st, 280sh. ^1H nmr (C_6D_6 at 301K) 2.90(pt) 6.9-7.70(mt) ppm ^{31}P- {^1H} nmr (C_6D_6 at 298K) 149.5(s) ppm; (toluene/$(CD_3)_2CO$ at ca 140K) 147.0(br) ppm. ^{13}C- {^1H} nmr (C_6D_6 at 318K) singlets at 134.3 and 54.8 ppm.

Dichlorotris(ethyldiphenylphosphinite)ruthenium(II) was similarly prepared from [$RuCl_2(PPh_3)_3$] and $P(OEt)Ph_2$ (0.160g, 66%) m.p. 155-157°C [Found: C, 58.1; H, 5.2; Cl, 8.1%, M(C_6H_6) 925. Calc. for $C_{42}H_{45}Cl_2O_3P_3Ru$:- C, 58.3, H, 5.2, Cl, 8.2% M 862] far ir spectrum 328st, 298w, 286st, 272m, 253m, 234m, 214m; ^1H nmr (C_6D_6 at 301K) 0.78(t), 3.40(br) [$^3J_{HH}$ 7.0 Hz], 6.90-7.70 (mt) ppm. $^{31}P-\{^1H\}$ nmr (C_6D_6 at 298K) 144.7 (s) ppm (toluene/$(CD_3)_2$-CO at ca 140K) 141.1 (br), 167.3 (br) ppm $^{13}C-\{^1H\}$ nmr (C_6D_6 at 318K) singlets at 134.3, 64.5 and 16.1 ppm.

[Hexakis(dimethylphenylphosphonite)ruthenium(II)] tetraphenylborate:- The compound [$RuCl_2(PPh_3)_3$] (0.20g) was refluxed with $P(OMe)_2Ph$ (0.40 cm^3) in methanol (20 cm^3) for 3 hours to give a very pale yellow solution which was cooled and then $NaBPh_4$ (0.25g) added. A white solid precipitated which was filtered off and recrystallised from CH_2Cl_2/MeOH to give colourless crystals of the complex m.p. 209-211°C [Found: C, 65.2; H, 6.0%; Calc. for $C_{96}H_{106}B_2O_{12}P_6Ru$: C, 65.5; H, 6.0%]

[Chlorotetrakis(methyldiphenylphosphinite)ruthenium(II)] tetraphenylborate:- The compound [$RuCl_2(PPh_3)_3$] (0.20g) was refluxed with $P(OMe)Ph_2$ (0.20 cm^3) in methanol (20 cm^3) for 5m to give a deep red solution and the solution then filtered to remove any unreacted starting material. Addition of $NaBPh_4$ (0.25g) gave a red precipitate, recrystallised from $(CH_3)_2CO$/MeOH m.p. 96-98°C [Found: C, 68.3; H, 5.3. Cl, 3.6% Calc. for $C_{76}H_{72}BClO_4P_4Ru$:- C, 69.1; H, 5.4; Cl, 2.7%] Conductivity in $(CH_3)_2CO$ at 303K. Slope of $\Lambda_o - \Lambda_c$ vs $c^{\frac{1}{2}}$ plot = 140 (for [$Ru_2Cl_3(P\{OMe\}Ph_2)_6$]BPh_4, slope = 155; for [$Ru(\eta C_6H_6)$-$(NH_3)_3$] $(PF_6)_2$, slope = 350) far ir spectrum 290st, 275sh; ^1H nmr ($(CD_3)_2CO$ at 301K) 3.15 (pt), 6.80-7.20 (mt) ppm ^{31}P nmr [$(CD_3)_2CO$ at 173K] 123(mt), 140(mt), 157(mt) ppm. (see Fig. 3a)

{Di-μ-chlorobis[tetrakis(ethyldiphenylphosphinite)ruthenium(II)]}tetraphenylborate was prepared similarly by reaction of [$RuCl_2(PPh_3)_3$] with excess $P(OEt)Ph_2$ in ethanol, m.p. 91-93°C [Found: C, 69.6; H, 5.8; Cl, 2.6% Calc. for $C_{160}H_{160}B_2Cl_2O_8P_8Ru_2$: C, 69.8; H, 5.8; Cl, 2.6%]. Conductivity in $(CH_3)_2CO$ at 303K. Slope of $\Lambda_o - \Lambda_c$ vs $c^{\frac{1}{2}}$ plot = 175. Far ir spectrum 270st(br); ^1H nmr [$(CD_3)_2CO$ at 301K)] 1.25(t), 3.40(br) [$^3J_{HH}$ 7.0 Hz], 6.80 - 7.20(mt) ppm. $^{31}P-\{^1H\}$ nmr [$(CD_3)_2CO$ at 173K] 119.0(t), 148.1(t) ppm ($^2J_{PP}$ 32.5 Hz) (see Fig. 5a)

[Tri-μ-chlorohexakis(methyldiphenylphosphinite)diruthenium(II)] tetraphenylborate:- The compound [$RuCl_2(PPh_3)_3$](0.20g) was refluxed with $P(OMe)Ph_2$

(0.20 cm^3) in methanol (20 cm^3) for 3 hours to give a yellow solution. Addition of NaBPh$_4$ (0.20g) then produced a pale yellow solid which was filtered off and recrystallised from CH$_2$Cl$_2$/MeOH m.p. 202-204°C. The same compound was also obtained by adding NaBPh$_4$ to a solution of [RuCl$_2$(P{OMe}-Ph$_2$)$_3$] dissolved in methanol. [Found: C, 63.6; H, 5.1% M(CHCl$_3$) 1003. Calc. for C$_{102}$H$_{98}$BCl$_3$O$_6$P$_6$Ru$_2$:- C, 63.6; H, 5.1% M(for 1:1 electrolyte) 962.] Conductivity in (CH$_3$)$_2$CO at 303K. Slope of $\Lambda_o - \Lambda_c$ vs $c^{\frac{1}{2}}$ plot = 155. far ir spectrum 295st, 260st(br), 228w. ^{1}H nmr (CDCl$_3$ at 301K) 2.95(pt) 6.90-7.10(mt) ppm. ^{31}P-{^{1}H}nmr (CDCl$_3$ at 298K) 138.6(s) ppm ^{13}C-{^{1}H} nmr (CDCl$_3$ at 318K) singlets at 136.5, 125.4, 121.3 (Ph); 133.7, 129.8, 127.0 (BPh$_4^-$), 55.2 (Me) ppm.

[Tri-μ-chlorohexakis(dimethylphenylphosphonite)diruthenium(II)]tetraphenylborate:- The compound [RuCl$_2$(P{OMe}$_2$Ph)$_4$] (0.20g) was refluxed in methanol (30 cm^3) for 3 hours to give a yellow solution. Addition of NaBPh$_4$ then precipitated a very pale yellow solid which was filtered off and washed with methanol; m.p. 186-188°C [Found: C, 52.3; H, 5.3% Calc. for C$_{72}$H$_{86}$BCl$_3$O$_6$P$_6$Ru$_2$:- C, 52.4; H, 5.2%] ^{1}H nmr (CDCl$_3$ at 301K) 3.45(q), 7.00-7.20(mt) ppm. ^{31}P- {^{1}H} nmr (CDCl$_3$ at 298K) 168.7 (s) ppm.

{1,2; 1,3-μ-chloro,-2,3-di-μ-chloro, 1, chloro-cyclo[tris(ethyldiphenylphosphinite)ruthenium(II)]}tetraphenylborate:- The compound [RuCl$_2$(PPh$_3$)$_3$] (0.20g) was refluxed with P(OEt)Ph$_2$ (0.20 cm^3) in ethanol (20 cm^3) for 4hours to give a pale yellow solution. Addition of NaBPh$_4$(0.20g) precipitated the complex as a pale yellow solid which was filtered off and washed with ethanol m.p. 174-176°C [Found: C, 60.1; H, 5.2; Cl, 6.3; P, 8.7%, M(CHCl$_3$) 1350 Calc. for C$_{150}$H$_{155}$BCl$_5$O$_9$P$_9$Ru$_3$:- C, 62.7; H, 5.2; Cl, 6.3; P, 9.7%M (1:1 electrolyte), 1435 . Conductivity in (CD$_3$)$_2$CO at 303K. Slope of $\Lambda_o - \Lambda_c$ vs $c^{\frac{1}{2}}$ plot = 140. far ir spectrum 314m, 288sh, 272sh, 260s(br), 256sh, 242sh ^{1}H nmr (CDCl$_3$ at 301K) 1.18(t) 2.96(br) [$^3J_{HH}$ 7.0 Hz], 7.00 - 7.30(mt) ppm ^{31}P-{^{1}H} nmr (CDCl$_3$ at 213K) 135(mt) ppm (see Fig. 2) ^{13}C- {^{1}H}nmr (CDCl$_3$ at 318K) singlets at 136.5, 125.5, 121.4(Ph); 133.9, 129.8, 126.8 (BPh$_4^-$); 64.5 (CH$_2$); 16.0 (CH$_3$) ppm.

The corresponding [Ru$_3$Cl$_5$(P{OEt}Ph$_2$)$_9$]PF$_6$ was obtained by addition of

NH_4PF_6 to the pale yellow solution. [Found: C,54.2; H, 5.0% Calc. for C_{126}, $H_{135}Cl_5F_6P_{10}Ru_3$:- C, 56.1; H, 5.1%].

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