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Preliminary Communication

SYNTHESES AND REARRANGEMENT REACTIONS OF [$RuCl_2L_{3\ or\ 4}$] COMPLEXES (L=$P(OR)_3$, $P(OR)_2Ph$, $P(OR)Ph_2$)

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Summary:- Reaction of [$RuCl_2(PPh_3)_3$] with excess L in hexane gives either [$RuCl_2L_4$] (L=$P(OMe)_3$, $P(OMe)_2Ph$) or [$RuCl_2L_3$] (L=$P(OMe)Ph_2$, $P(OEt)Ph_2$) which rearrange in polar solvents to the ionic complexes [$L_3RuCl_3RuL_3$] Cl (L=$P(OMe)_2Ph$, $P(OMe)Ph_2$, $P(OEt)Ph_2$) and [$Ru_3Cl_5L_9$] Cl (L=$P(OEt)Ph_2$, $P(OMe)Ph_2$).

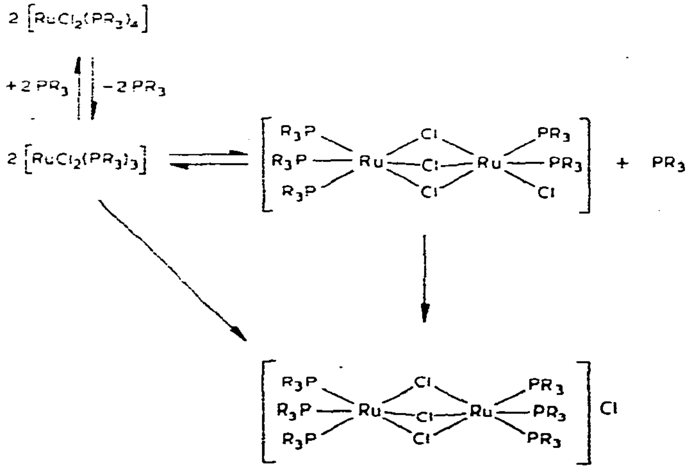
Recently, we have shown that the monomeric tertiary phosphine complexes [$RuCl_2(PR_3)_{3\ or\ 4}$] , made by exchange of [$RuCl_2(PPh_3)_4$] with PR_3 in non-polar solvents [1] undergo facile rearrangement reactions in solution as shown in the Scheme [2]. In an attempt to verify the generality of this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

Thus, if (I) is refluxed with excess $P(OMe)_3$ or $P(OMe)_2Ph$ in hexane, yellow crystals [$RuCl_2L_4$] are formed. Far ir studies suggest a cis/trans mixture for both compounds in the solid state but in solution, ^{31}P nmr spectroscopy indicates that irreversible cis→trans isomerisation readily occurs. Although the cis-isomers are then stable indefinitely at ambient temperature in solution, thermolysis or photolysis of [$RuCl_2(P\{OMe\}_2Ph)_4$] in CH_2Cl_2 gives [$(P\{OMe\}_2Ph)_3RuCl_3Ru(P\{OMe\}_2Ph)_3$] $Cl^{\dagger}$ isolated as its BPh_4^- salt. However, this does not occur for the $P(OMe)_3$ complex. Reaction of (I) and excess $P(OMe)_2Ph$ in methanol gives the

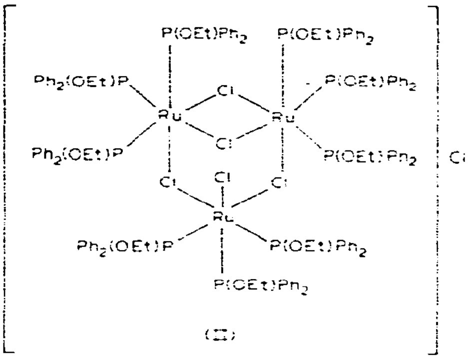
$[Ru(P\{OMe\}_2Ph)_6]^{2+}$ cation[‡] which can also be isolated as a BPh_4^- salt.

In contrast, reaction of (I) with excess $P(OR)Ph_2$ (R=Me,Et) in hexane gives orange solids of stoichiometry $[RuCl_2(P(OR)Ph_2)_3]$, shown to be monomeric by molecular weight measurements in benzene. Variable temperature, proton decoupled ^{31}P nmr studies indicate rapid intramolecular exchange of $P(OR)Ph_2$ groups at temperatures >160K (single resonance observed) but at lower temperatures, more signals are found eg. for $[RuCl_2(P\{OEt\}Ph_2)_3]$ in $(CD_3)_2CO/C_6H_5CH_3$ at ca 140K, two resonances at 141.1 (broadened doublet) and 167.3ppm (broadened triplet) of relative intensity 2:1 are observed (cf the limiting ^{31}P nmr spectra of $[RuCl_2L_3]$ {L=PPh_3,$PEtPh_2$}[1]) which is consistent with the square pyramidal geometry expected for a five coordinate d^6 complex [4] .

Unlike $[RuCl_2L_4]$ (L=$P(OMe)_3$, $P(OMe)_2Ph$), $[RuCl_2(P(OR)Ph_2)_3]$ rapidly rearrange in polar solvents to give ionic complexes. For R=Me, the main product is $[(P\{OMe\}Ph_2)_3RuCl_3Ru(P\{OMe\}Ph_2)_3]$ Cl[‡] which is consistent with the mechanism shown in the Scheme. However, for R=Et, the main rearrangement product based on ^{31}P nmr, conductivity and analytical data is the trimeric cation $[Ru_3Cl_5(P\{OEt\}Ph_2)_9]Cl$ for which the cyclic structure (II) is tentatively proposed. ^{31}P nmr studies indicate that



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



(II)

small amounts of [$Ru_3Cl_5(P\{OMe\}Ph_2)_9$]Cl and [$(P\{OEt\}Ph_2)_3RuCl_3Ru(P\{OEt\}Ph_2)_3$]-Cl† respectively are also formed.

Reaction between (I) and excess $P(OMe)Ph_2$ in methanol gives an immediate red solution from which the [$RuCl(P\{OMe\}Ph_2)_4MeOH$]$^+$ cation can be isolated by addition of $NaBPh_4$. With (I) and excess $P(OEt)Ph_2$ in ethanol, however, a red dimeric cation [$\{RuCl(P\{OEt\}Ph_2)_4\}_2$] $(BPh_4)_2$ is isolated. On further refluxing, the red solutions turned yellow and [$(P\{OMe(Ph_2)_3RuCl_3Ru(P\{OMe\}Ph_2)_3$]Cl and [$Ru_3Cl_5(P\{OEt\}Ph_2)_9$]Cl respectively are formed. Therefore, a possible rationalisation of the formation of (II) is by facile coupling c[$\{RuCl(P\{OEt\}Ph_2)_4\}_2$]$Cl_2$ and some unreacted [$RuCl_2(P\{OEt\}Ph_2)_3$] accompanied by displacement of $P(OEt)Ph_2$. In contrast, rapid dimersation of [$RuCl_2(P\{OMe\}Ph_2)_3$] to form the stable [$(P\{OMe\}Ph_2)_3$-$RuCl_3Ru(P\{OMe\}Ph_2)_3$]Cl appears to be the prefered reaction.

Finally, no evidence has been found here for the formation of neutral dimers [$L_3RuCl_3RuClL_2$] which is indicative of stronger Ru-P bonds in these alkoxy substituted phosphine complexes compared to those containing tertiary phosphines. In support of this, pyrolysis of [$(P\{OR\}Ph_2)_3RuCl_3Ru(P\{OR\}Ph_2)_3$]Cl at 120°C gives [$(P\{OR\}Ph_2)_2(P(OH)Ph_2)$-$RuCl_3Ru(P(OH)Ph_2)_2(Ph_2PO)$] (R=Me,Et) with no cleavage of Ru-P bonds [5] (*cf* the formation of [$(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2$] by pyrolysis of [$(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3$]Cl[6]).

[†] These compounds have also been synthesised by reaction of [$\{RuCl_2C_7H_8\}_n$]

Further studies on these rearrangements and of reactions of the products are in progress.

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