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RUTHENIUM COMPLEXES CONTAINING GROUP 5B DONOR LIGANDS PART VII*. REARRANGEMENT REACTIONS OF SOME RUTHENIUM (II) COMPLEXES CONTAINING TRIPHENYLPHOSPHINE, TRI-p-TOLYLPHOSPHINE OR ETHYLDIPHENYLPHOSPHINE LIGANDS.

P.W. ARMIT, W.J. SIME, T.A. STEPHENSON*
and(in part) L. SCOTT

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3J

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Summary

As for $[RuCl_2(PPh_3)_3]$, carbonylation of $[RuCl_2(PR_3)_3]$ $[PR_3 = P(p\text{-tolyl})_3, PEtPh_2)$ in N,N^1-dimethylformamide (dmf) gives $[Ru(CO)Cl_2(dmf)(PR_3)_2]$ (II). For $PR_3 = PEtPh_2$, rearrangement of (II) in various solvents gives inseparable mixtures (^{31}P evidence) but for $PR_3 = P(p\text{-tolyl})_3$ $[Ru_2(CO)_2Cl_4\{P(p\text{-tolyl})_3\}_3]$ is obtained. Reaction of $[Ru(CO)Cl_2(dmf)\{P(p\text{-tolyl})_3\}_2]$ with $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ (1:1 mol ratio) gives $[Ru_2(CO)Cl_4\{P(p\text{-tolyl})_3\}_4]$ whereas reaction of $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ with $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ gives $[Ru_2(CO)Cl_4(PPh_3)_2\{P(p\text{-tolyl})_3\}_2]$. Reaction of $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ with CS_2 gives the related $[Ru_2Cl_4(CS)\{P(p\text{-tolyl})_3\}_4]$ and $[\{RuCl_2(CS)\}P(p\text{-tolyl})_3\}_2\}_2]$ whereas $[RuCl_2(PEtPh_2)_3]$ and CS_2 produce $[RuCl_2(S_2CPEtPh_2)(PEtPh_2)_2]CS_2$ and $[Ru_2Cl_4(CS)_2(PEtPh_2)_3]$.

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[*] For Part VI, see ref 1.

Introduction

Earlier, it was shown that reaction of $[RuCl_2(PPh_3)_3]$ with CS_2 gave the triple chloride bridged complex $[Ru_2Cl_4(CS)(PPh_3)_4]$, together with smaller amounts of $[Ru(\eta^2\text{-}CS_2)Cl(PPh_3)_3]Cl$, $[\{RuCl_2(CS)(PPh_3)_2\}_2]$ and $[Ru_2Cl_4(CS)_2(PPh_3)_3]$ (various isomers) [2]. Later, the compounds $[Ru_2(Y)Cl_4(PPh_3)_4]$ were synthesised in high yield by means of an intermolecular coupling reaction of $[RuCl_2(PPh_3)_3]$ and $[Ru(Y)Cl_2(dmf)(PPh_3)_2]$ (Y = CO,CS).[3]

In this paper we now report on our attempts to utilise both these methods to synthesise analogous compounds with other tertiary phosphines such as tri-p-tolylphosphine and ethyldiphenylphosphine and also to synthesise mixed tertiary phosphine complexes $[Ru_2(CO)Cl_4(PR_3)_2(PR_3^1)_2]$.

Results and Discussion

a) Tri-p-tolylphosphine complexes:

Reaction of "$RuCl_33H_2O$" with an excess of $P(p\text{-tolyl})_3$ in methanol, reported to give $[RuCl_2\{P(p\text{-tolyl})_3\}_4]$ [4], repeatedly produced dark purple crystals of $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ (I)†. The $^{31}P\text{-}\{^1H\}$ nmr spectrum of (I) in $CH_2Cl_2/(CD_3)_2CO$ at 190K consisted of a doublet at δ 25.1 ppm and a triplet at 74.3 ppm ($^2J_{pp}$ 28.0Hz) (relative intensity 2:1) plus a weak singlet at 28.8 ppm due to $(p\text{-tolyl})_3PO$. As the temperature was raised the doublet and triplet collapsed and at 298K coalesced to a broad singlet at 39.9 ppm. These nmr changes were concentration independent and reversible with temperature, and, taken in conjunction with the ir spectrum which contained a band at 320 cm^{-1}, (indicative of a trans Cl-Ru-Cl arrangement), suggest a structure analogous to that of $[RuCl_2(PPh_3)_3]$ [5] which

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† The reason for this is probably the high pH of the commercial "$RuCl_3.3H_2O$" used which favours formation of the tris species.

is undergoing rapid intramolecular exchange of P(p-tolyl)$_3$ groups at ambient temperature.

When compound (I) was refluxed in CS_2 for a short time, a red solution was obtained, but in contrast to the analogous reaction of $[RuCl_2(PPh_3)_3]$, no $[Ru(\eta^2\text{-}CS_2)Cl\{(Pp\text{-tolyl})_3\}_3]Cl$ was deposited [6,2]. Addition of light petroleum(b.p. 60-80°C), however, precipitated a pink solid analysing closely for the double chloride bridged complex $[\{RuCl_2(CS)\{P(p\text{-tolyl})_3\}_2\}_2]$. The ir spectrum contained a band at 1290 cm^{-1}(ν_{CS}) and the $^{31}P\text{-}\{^1H\}$ nmr spectrum in $CDCl_3$ at 298K consisted of a strong singlet at δ 29.5 ppm together with weaker singlets at 28.5 ppm [(p-tolyl)$_3$PO] and 42.5 ppm. The peaks at 29.5 and 42.5 ppm are possibly due to different isomeric forms of $[\{RuCl_2(CS)\text{-}\{P(p\text{-tolyl})_3\}_2\}_2]$. The remaining solution on standing for 6 hours deposited an orange solid whose $^{31}P\text{-}\{^1H\}$nmr spectrum in $CDCl_3$ at 298K displayed two AB quartets at δ 47.6 and 34.6 ppm and which analysed for the triple chloride bridged complex $[Ru_2Cl_4(CS)\{P(p\text{-tolyl})_3\}_4]$. ($\nu_{CS}$ 1292 cm^{-1}).

Treatment of $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ with CO in N,N-dimethylformamide (dmf) readily gave $[Ru(CO)Cl_2(dmf)\{P(p\text{-tolyl})_3\}_2]$ (II) whose i.r. spectrum showed ν_{CO} 1935 cm^{-1}, ν_{RuCl} 340 cm^{-1} and a broad band at 1645 cm^{-1} due to coordinated dmf and whose $^{31}P\text{-}\{^1H\}$nmr spectrum at 298 K in $CDCl_3$ contained a singlet at 32.3 ppm. Therefore, $[Ru(CO)Cl_2(dmf)\{P(p\text{-tolyl})_3\}_2]$ has an analogous structure to $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ with trans phosphines and trans chlorides [3].

Reaction of compound (II) with compound (I) (1:1 molar ratio) in ethanol then gave the triple chloride bridged dimer. $[Ru_2(CO)Cl_4\{P(p\text{-tolyl})_3\}_4]$ whose $^{31}P\text{-}\{^1H\}$ nmr spectrum in $CDCl_3$ at 298 K contained the expected two AB quartets at δ 47.6 and 38.8 ppm. As for $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ [3], recrystallisation of compound (II) from methanol gave

$[Ru(CO)Cl_2(MeOH)\{(Pp\text{-}tolyl)_2\}_2]$, and shaking the latter in CH_2Cl_2 for several days produced a yellow brown solid, whose $^{31}P\text{-}\{^1H\}$ nmr spectrum in $CDCl_3$ at 298 K, showed it to contain the three possible geometrical isomers of $[Ru_2(CO)_2Cl_4\{P(p\text{-}tolyl)_3\}_3]$ (see experimental section and ref [3]).

An attempt to synthesise the mixed tertiary phosphine complex $[(PPh_3)_2ClRuCl_3RuCO\{P(p\text{-}tolyl)_3\}_2]$ by reaction of $[RuCl_2(PPh_3)_3]$ with $[Ru(CO)Cl_2(dmf)\{P(p\text{-}tolyl)_3\}_2]$ gave an orange solid but its $^{31}P\text{-}\{^1H\}$ nmr spectrum showed a large number of resonances in the region 46-50 ppm indicating a mixture of products. A possible explanation is that during the coupling process, dissociation of PPh_3 from $[RuCl_2(PPh_3)_3]$ occurs and this can then displace $P(p\text{-}tolyl)_3$ from the initially formed product $[(PPh_3)_2ClRuCl_3Ru(CO)\{P(p\text{-}tolyl)_3\}_2]$ to give, in addition, the compounds $[(PPh_3)_2ClRuCl_3Ru(CO)\{P(p\text{-}tolyl)_3\}_n(PPh_3)_{2-n}]$ $(n = 0,1)$.

However, this side reaction does not occur in the reaction between $[RuCl_2\{P(p\text{-}tolyl)_3\}_3]$ and $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ since an orange solid which analysed for $[Ru_2(CO)Cl_4(PPh_3)_2\{P(p\text{-}tolyl)_3\}_2$ and whose $^{31}P\text{-}\{^1H\}$ nmr spectrum in $CDCl_3$ at 298 K contained only two AB patterns at δ 48.0 and 40.2 ppm was obtained.

Finally, the attempted coupling reactions of $[Ru(CO)Cl_2(dmf)(PR_3)_2]$ $(PR_3 = PPh_3, P(p\text{-}tolyl)_3)$ with other $[RuCl_2L_3]$ $(L = P(OMe)Ph_2, P(OEt)Ph_2)$ were completely unsuccessful. This is not surprising since earlier studies [1] have shown that these tertiary phosphinite complexes contain very strong Ru-P bonds and hence the formation of $[(P(OR)Ph_2)_2ClRuCl_3Ru(CO)(PR_3)_2]$ is completely inhibited. Instead, the reaction products obtained in acetone were unreacted $[RuCOCl_2(dmf)(PR_3)_2]$, $[Ru_2(CO)_2Cl_4(PR_3)_3]$, and either $[Ru_2Cl_3\{P(OMe)Ph_2\}_6]Cl$ or $[Ru_3Cl_5\{P(OEt)Ph_2\}_9]Cl$ (i.e. the rearrangement products of $[RuCl_2(P(OR)Ph_2)_3]$ in polar solvents [1].

b) Ethyldiphenylphosphine complexes:

When green$[RuCl_2(PEtPh_2)_3]$ (prepared by reaction of $[RuCl_2(PPh_3)_4]$ with excess $PEtPh_2$ in hexane [5a]) was shaken in CS_2 for one hour, a red-pink solid was produced which analysed closely for the expected "$[Ru(\eta^2-CS_2)Cl(PEtPh_2)_3]$—$Cl.CS_2$". The ir spectrum contained a strong band at 1515 cm^{-1} which as for $[Ru(\eta^2CS_2)Cl(PPh_3)_3]ClCS_2$[2,6] is associated with a CS_2 solvate. This was proved by dissolving the complex in CH_2Cl_2 and reprecipitating with light petroleum (bp 60-80°C) to give a product analysing for "$[Ru(\eta^2-CS_2)Cl(PEtPh_2)_3]Cl$" (III) whose ir spectrum no longer contained the band at 1515 cm^{-1}. Ir bands at 1115 and 995 cm^{-1} which could be attributed to the η^2-CS_2 group [7] were also present. The $^{31}P-\{^1H\}$ nmr spectrum of (III) in $CDCl_3$ at 298 K consisted of an AMX pattern [ν_A 41.1 ppm, ν_M, 34.0 ppm; ν_X 9.2 ppm; J_{AM} 28.9 Hz, J_{AX} 3.7 Hz J_{MX} 9.2 Hz] indicating that the compound contained three magnetically inequivalent $PEtPh_2$ groups. However, the low values of J_{AX} and J_{MX} together with the fact that compound (III) gave non-conducting solutions in CH_2Cl_2 and acetone strongly suggests that it should be reformulated as $[RuCl_2(S_2CPEtPh_2)$-$(PEtPh_2)_2]$ containing the $Ph_2EtP^+-CS_2^-$ zwitterion ligand.† The related compound "$[Ir(\eta^2CS_2)(CO)(PPh_3)_3]BPh_4$" has recently been shown to be $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]BPh_4$ by X-ray analysis and these authors then suggested that "$[Ru(\eta^2-CS_2)Cl(PPh_3)_3]Cl$" also probably contained a $PPh_3^+-CS_2^-$ ligand [8]. Unfortunately, this PPh_3 complex is too insoluble for ^{31}P nmr studies.

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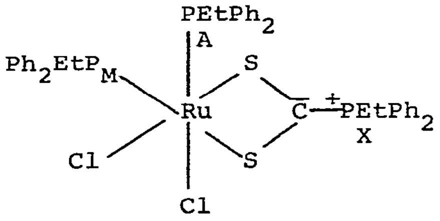
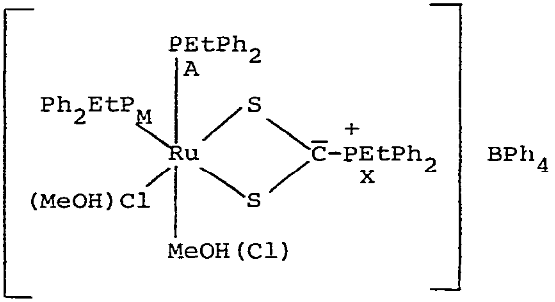
† The peaks at 1115 and 995 cm^{-1} in the ir spectrum of (III) can probably be attributed to the $\nu_{CS_2(asym)}$ stretching vibrational mode of the $PEtPh_2^+-CS_2^-$ ligand [7].



(III)



(IV)

Dissolving $[RuCl_2(S_2CPEtPh_2)(PEtPh_2)_2]$ in methanol produced a conducting purple solution which on standing for several hours gradually turned blue in colour and eventually green, the latter change being most likely due to oxidation to a Ru(III) species. Addition of $NaBPh_4$ to the purple solution gave a purple solid which analysed quite well for $[RuCl(MeOH)(S_2CPEtPh_2)(PEtPh_2)_2]BPh_4$ (IV). The $^{31}P-\{^1H\}$ nmr spectrum of (IV) in $CDCl_3$ at 298 K, which showed an AMX pattern [ν_A 44.6 ppm, ν_M 29.0 ppm, ν_X, 16.4 ppm; J_{AM} 28.0 Hz, J_{AX} 3.5 Hz J_{MX} 11.3 Hz] was consistent with this formulation and either of the structures shown. Unfortunately, no solid could be isolated from the blue solution formed on further rearrangement of (IV).

A small amount of $[RuCl_2(S_2CPEtPh_2)(PEtPh_2)_2]CS_2$ was also formed on refluxing $[RuCl_2(PEtPh_2)_3]$ in CS_2 for several hours. After filtering off this material, an orange solution remained which on standing deposited a non-conducting orange solid. Its ir spectrum contained a strong band at 1295 cm^{-1} (ν_{CS})

whilst its $^{31}P-\{^1H\}$ nmr spectrum at 298 K in $CDCl_3$ consisted predominantly of a singlet at δ 49.2 ppm and an AB pattern centred at 36.8 ppm, attributed to one isomer of the triple bridged dimer $[Ru_2Cl_4(CS)_2(PEtPh_2)_3]$ (see earlier). The spectrum also contained a weak resonance at 43.4 ppm (singlet) due to some unreacted $[RuCl_2(PEtPh_2)_3]$ (see ref [5a]) and other weak singlets at 48.4 and 37.8 which might arise from the presence of some $[\{RuCl_2(CS)(PEtPh_2)_2\}_2]$. The spectrum also contained a small multiplet at 18.0 ppm of unknown origin.

Treatment of $[RuCl_2(PEtPh_2)_3]$ with CO in dmf readily gave $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ (II) whose ir and $^{31}P-\{^1H\}$ spectra indicated that the compound had the same structure as $[Ru(CO)Cl_2(dmf)(PR_3)_2]$ (PR_3 = PPh_3, $P(p\text{-tolyl})_3$). Like these compounds, the coordinated dmf molecule could be replaced by methanol although in this instance, recrystallisation of (II) (PR_3 = $PEtPh_2$) from MeOH or CH_2Cl_2/MeOH always produced mixtures of $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ and $[Ru(CO)Cl_2(MeOH)(PEtPh_2)_2]$, indicating that the dmf group was more strongly complexed than for the PPh_3 and $P(p\text{-tolyl})_3$ compounds.

In less polar solvents such as methylene chloride, (II) (PR_3 = $PEtPh_2$) behaved in a similar manner to its PPh_3 and $P(p\text{-tolyl})_3$ analogues except that the rate of rearrangement was much slower and, that the products could not be isolated in pure form. Identification of the products was therefore based mainly on the $^{31}P-\{^1H\}$ nmr spectra of the resulting mixtures.

Thus when $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ was shaken in CH_2Cl_2 for 10 hours and the solvent then removed under vacuo, a yellow solid (with ν_{CO} 2040 w, 1970s br, 1928 m cm^{-1}) was obtained. The $^{31}P-\{^1H\}$ nmr spectrum of this mixture at 213 K in $CDCl_3$ (Fig. 1a) consisted of a strong singlet at δ 32.6 (dmf solvate), a weak doublet at 18.7 ppm, a weak broad resonance at ca. 35 ppm, an AB pattern centred at 41.2 ppm (J_{AB} 26.6 Hz;

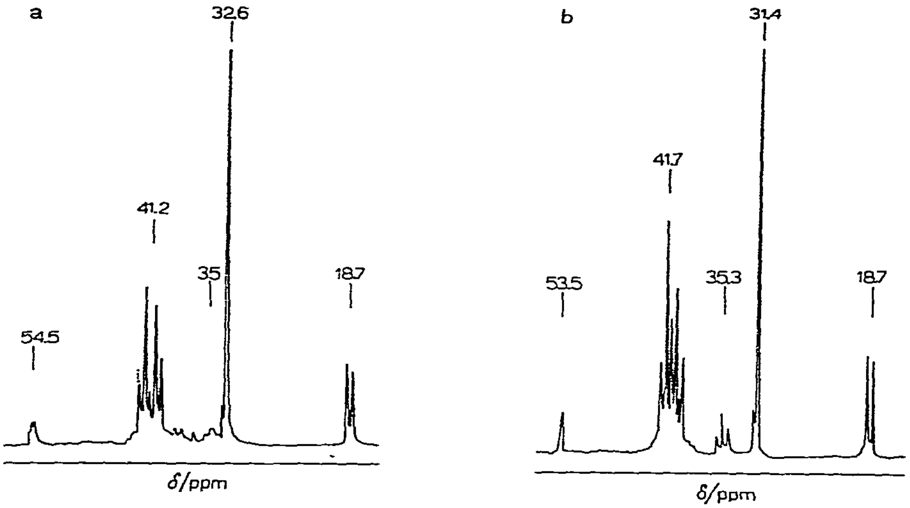


Fig. 1 $^{31}P-\{^{1}H\}$ nmr spectra in $CDCl_3$ of the product obtained on shaking $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ in CH_2Cl_2 a) at 213K b) 308K

δ_{AB} 70.0 Hz) superimposed on some weak resonances and another broad resonance at ca. 54.5 ppm. On raising the temperature to 308 K, the position of the singlet from the unreacted dmf solvate moved to 31.4 ppm (Fig. 1b), the broad resonance at 35.3 ppm sharpened into a triplet (with J_{PP} 25.7 Hz) and the doublet at 18.7 ppm (J_{PP} 25.5 Hz) also sharpened. The AB quartet became more intense as were the additional peaks superimposed upon it (ca. 37-44 ppm) and the resonance at 53.5 ppm became a sharp singlet.

When $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ was shaken in benzene for 24 hours and the solvent removed, the ir spectrum of the yellow-orange product showed a broad band at 1950 cm^{-1}. The $^{31}P-\{^{1}H\}$ nmr spectrum of this material in $CDCl_3$ at 213 K (Fig. 2) showed no evidence for the AB pattern observed in the spectrum of the product obtained from rearrangement in CH_2Cl_2. However, the resonances at ca 37 to 44 ppm were increased in intensity and the previously weak resonance at 53.5 ppm now exhibited three

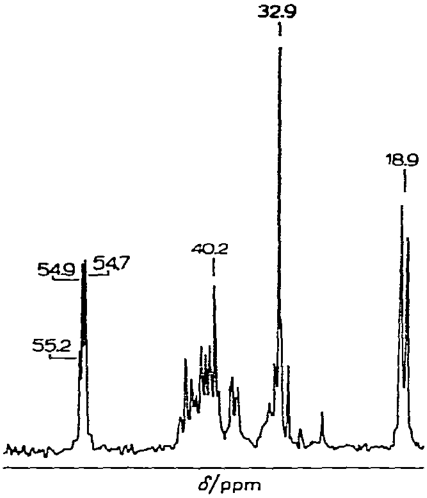


Fig. 2 $^{31}P-\{^{1}H\}$ nmr spectrum in $CDCl_3$ at 213 K of product obtained on shaking [Ru(CO)Cl_2(dmf)($PEtPh_2$)$_2$] in C_6H_6.

singlets at 55.2, 54.9 and 54.7 ppm. The doublet at 18.9 ppm and the broadened triplet at ca 34 ppm were also more intense. A singlet from unreacted dmf solvate appeared at 32.9 ppm and other weak signals were observed at ca. 32, 26 and 20 ppm.

The resonances at 37 to 44 ppm together with the signals at ca. 54 ppm may be assigned to the three possible geometrical isomers of [Ru_2(CO)$_2Cl_4$($PEtPh_2$)$_3$] (cf. ref [3]) which are the major rearrangement products in benzene. The AB quartet observed in the $^{31}P-\{^{1}H\}$ nmr spectrum of the CH_2Cl_2 reaction at 41.2 ppm can be assigned to the ionic species [Ru_2(CO)$_2Cl_3$($PEtPh_2$)$_4$]Cl (cf [Ru_2(CO)$_2Cl_3$(PPh_3)$_4$]Cl whose $^{31}P-\{^{1}H\}$ nmr spectrum showed an AB quartet at 40.6 ppm [3]). The weak singlets at ca. 32, 26 and 20 ppm probably correspond to isomers of the double halide bridged complex [{Ru(CO)Cl_2-($PEtPh_2$)$_2$}$_2$].

During the formation of [Ru_2(CO)$_2Cl_4$(PR_3)$_3$] from "Ru(CO)Cl_2(PR_3)$_2$", free tertiary phosphine will be liberated. In the case of PPh_3, this was observed in the $^{31}P-\{H\}$ nmr spectrum as either free PPh_3(-6 ppm) and/or Ph_3PO(29 ppm). However, in reactions of [Ru(CO)Cl_2(dmf)($PEtPh_2$)$_2$], no free $PEtPh_2$(-15.5 ppm) or Ph_2EtPO (35 ppm) was observed. Instead, [Ru(CO)Cl_2($PEtPh_2$)$_3$] (doublet and triplet at 18.9 and 35.3 ppm respectively) was formed, probably by direct reaction of [Ru(CO)Cl_2dmf($PEtPh_2$)$_2$] with $PEtPh_2$.

Finally, an attempt to prepare [Ru_2(CO)Cl_4($PEtPh_2$)$_4$] by reaction of [Ru(CO)Cl_2(dmf)($PEtPh_2$)$_2$] and [$RuCl_2$($PEtPh_2$)$_3$] in acetone (1:1 molar ratios) produced a bright orange solid (ν_{CO} 1960 br). However, the $^{31}P-\{^1H\}$ nmr spectrum of this material in $CDCl_3$ at 213 K consisted of peaks corresponding to [Ru(CO)Cl_2($PEtPh_2$)$_3$], [Ru_2Cl_4($PEtPh_2$)$_5$] (see ref [5a]) together with two AB resonances centred at 48.5 ppm (J_{AB} 40.1 Hz) δ_{AB} 191.3 Hz) and 39.4 ppm (J_{AB} 26.2 Hz; δ_{AB} 139.5 Hz) attributed to the triple bridged [Ru_2(CO)Cl_4($PEtPh_2$)$_4$]. Unfortunately, attempts to separate these compounds were unsuccessful.

Experimental

Microanalyses were by BMAC and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000-250 cm^{-1}on Perkin Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Phosphorus-31 nmr spectra were obtained on a Varian Associates XL100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m.to high frequency of 85% H_3PO_4. Melting points were determined with a Köfler hot stage microscope and are uncorrected.

Materials

Ruthenium trichloride trihydrate (Johnson Matthey), carbon monoxide (Air products) carbon disulphide (Fisons). Tri-p-tolylphosphine and ethyldiphenylphosphine were prepared by standard literature methods. The compounds [$RuCl_2(PR_3)_3$] (PR_3 = PPh_3[9] $PEtPh_2$ [5a]) and [$Ru(CO)Cl_2dmf(PPh_3)_2$] [10] were prepared as described earlier. All reactions were carried out in degassed solvents and, except for carbonylation reactions, under a nitrogen atmosphere. s(singlet); d(doublet), t(triplet), q(quartet), br(broad).

Tri(p-tolylphosphine)Complexes

Dichlorotris(tri-p-tolylphosphine)ruthenium(II): The compound "$RuCl_33H_2O$" (0.50g) was refluxed with an excess of tri-p-tolylphosphine (2.50g) in methanol (25 cm^3) for 16h. The dark purple crystals obtained were filtered off and washed with diethyl ether (yield 75%) m.p. 138-140°C [Found C 69.7; H, 5.8% Calc for $C_{63}H_{63}Cl_2P_3Ru$:- C, 69.7; H, 5.8%] ν(RuCl) 320 cm^{-1}. $^{31}P-\{^1H\}$ nmr [$CH_2Cl_2/(CD_3)_2CO$ at 190 K] 74.3 (t), 25.1 (d) ppm ($^2J_{PP}$ 28.0 Hz); at 298 K, 39.9 (s) ppm.

Carbonyldi(chloro)(N,N-dimethylformamide)bis(tri-p-tolylphosphine)ruthenium(II):

Carbon monoxide was bubbled through a suspension of [$RuCl_2$-{$P(p\text{-tolyl})_3$}$_3$] (0.40g) in N,N-dimethylformamide (4.0 cm^3) for several minutes to give a yellow solution. Diethylether (5 cm^3) was then added, the solution shaken for one hour and the resulting yellow solid filtered off and dried *in vacuo* (Yield 85%): m.p. 173-175°C. [Found: C, 62.6; H, 5.7; N, 1.6% Calc for $C_{46}H_{49}Cl_2NO_2P_2Ru$:- C, 62.6; H, 5.5; N, 1.6%]. ν_{CO} 1935, ν_{CO}(dmf) 1645; ν(RuCl) 340 cm^{-1}. $^{31}P-\{^1H\}$nmr [$CDCl_3$ at 298 K] 32.3 (s) ppm.

Tri-μ-chloro-a-carbonyl-g-chlorotetrakis(tri-p-tolylphosphine)-diruthenium(II):

The compounds $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ (0.10g) and $[Ru(CO)Cl_2(dmf)\{P(p\text{-tolyl})_3\}_2]$ (0.08g) were refluxed together in ethanol (20 cm^3) for 6 h to give an orange solution. On cooling, an orange *solid* formed which was filtered off and dried in *vacuo* (Yield *ca* 80%); m.p. 155-157°C [Found: C, 63.1; H, 5.3% Calc for $C_{85}H_{84}Cl_4OP_4Ru$ C 64.2, H, 5.3%] ν_{CO} 1975 cm^{-1}. $^{31}P\text{-}\{^1H\}$nmr [$CDCl_3$ at 298 K] 47.6 (q) and 38.8 (q) ppm [J(P^1P^2) 38.8, (JP^3P^4) 25.1; δ(P^1P^2) 73.0; δ(P^3P^4) 97.5 Hz].

Tri-μ-chloro-a-carbonyl-g-chloro-bc-bis(triphenylphosphine)-hi bis(tri-p-tolylphosphine)diruthenium (II) was obtained similarly from $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ and $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ [Found: C, 67.5; H, 5.1% Calc for $C_{79}H_{72}Cl_4OP_4Ru_2$:- C 67.6; H, 5.1%] ν_{CO} 1975 cm^{-1} $^{31}P\text{-}\{^1H\}$ nmr [$CDCl_3$ at 298 K] 48.0 (q) and 40.2 (q) ppm [J(P^1P^2) 34.2, J(P^3P^4) 25.1; δ(P^1P^2) 83.2, δ(P^3P^4) 99.1 Hz].

Tri-μ-chloro-ag-dicarbonyl-b-chloro-tris(tri-p-tolylphosphine) diruthenium (II):

The complex $[Ru(CO)Cl_2(MeOH)\{P(p\text{-tolyl})_3\}_2]$, prepared by recrystallisation of $[Ru(CO)Cl_2(dmf)\{P(p\text{-tolyl})_3\}_2]$ from methanol was shaken in CH_2Cl_2 for 4 days. The resultant solution was reduced in volume and light petroleum (bp 60-80°C) added to precipitate the complex as a yellow brown *solid*. ν_{CO} 1960 cm^{-1}. $^{31}P\text{-}\{^1H\}$nmr ($CDCl_3$ at 298K)-3 isomers a) 50.5 (s), 41.5 (q) ppm [J(PP) 25.5; δ(PP) 24.3 Hz]

b) 51.3 (s), 40.0 (q) ppm [J(PP) 24.9; δ(PP) 133.6 Hz]

c) 52.2 (s), 38.9 (q) ppm [J(PP) 26.1; δ(PP) 170.2 Hz].

Di-μ-chlorobis[chloro(thiocarbonyl)bis(tri-p-tolylphosphine) ruthenium(II)]: The complex $[RuCl_2\{P(p\text{-tolyl})_3\}_3]$ (0.25g) was refluxed in CS_2(15 cm^3) for 5 min to give a red solution which was cooled, filtered and reduced in volume (to *ca.* 5 cm^3). Addition of light petroleum (bp 60-80°C) then precipitated a pink *solid* which was filtered off and dried *in vacuo* (Yield *ca.* 15%) [Found: C, 62.5; H, 5.2% Calc for $C_{86}H_{84}Cl_4P_4Ru_2S_2$:- C, 62.6; H, 5.1%] ν_{CS} 1290 cm^{-1}. *$^{31}P-\{^1H\}$nmr* [CDCl$_3$ at 298K] 29.5 (s), 42.5 (s) ppm. The remaining solution on standing for 6h deposited *tri-μ-chloro-a-chloro-g-(thiocarbonyl)tetrakis-(tri-p-tolylphosphine)diruthenium(II)* as an orange *solid* which was filtered off and dried in *vacuo* (Yield *ca.* 30%); m.p. 160-162°C [Found: C, 64.2; H, 5.4%, Calc for $C_{85}H_{84}Cl_4P_4Ru_2S$:- C, 63.6; H, 5.3%] ν_{CS} 1292 cm^{-1} *$^{31}P-\{^1H\}$nmr* [CDCl$_3$ at 298 K] 47.6 (q) and 34.6 (q) ppm [$J(P^1P^2)$ 37.9, $J(P^3P^4)$ 25.1; $\delta(P^1P^2)$ 80.9, $\delta(P^3P^4)$ 74.9 Hz].

Ethyldiphenylphosphine Complexes

[Dichlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS^1-ruthenium(II)] carbondisulphide: Shaking the compound $[RuCl_2(PEtPh_2)_3]$(0.20g) in carbon disulphide (20 cm^3) for one hour produced a red-pink *solid* which was filtered off (Yield 70%) m.p. 170-172°C [Found: C, 55.1; H, 4.7% Calc for $C_{44}H_{45}Cl_2P_3RuS_4$:- C, 54.6; H, 4.6%] $\nu(CS_2)$ 1515cm^{-1}; $\nu(Ph_2Et\overset{+}{P}-\bar{C}S_2)_{asym}$ 1115, 995 cm^{-1}. Dissolving this solid in CH_2Cl_2 and reprecipitating with light petroleum (bp 60-80°C) gave *dichlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS^1-ruthenium (II)* [Found: C, 57.1; H, 5.0% Calc for $C_{43}H_{45}Cl_2P_3RuS_2$:- C, 57.9; H, 5.0%] $\nu(Ph_2Et\overset{+}{P}-\bar{C}S_2)_{asym}$ 1115, 995 cm^{-1} *$^{31}P-\{^1H\}$ nmr* [CDCl$_3$ at 298 K] AMX pattern, ν_A 41.1; ν_M 34.0; ν_X 9.2 ppm [J_{AM} 28.9, J_{AX} 3.7, J_{MX} 9.2 Hz].

A small amount of the above complex was also produced, together with an orange solution, on refluxing [$RuCl_2(PEtPh_2)_3$] in CS_2 for 3h. On standing for 2 days, or alternatively, by addition of light petroleum (bp 60-80°C) to the orange solution, an orange solid was precipitated, consisting mainly of *tri-μ-chloro(chloro)bis(thiocarbonyl)tris(ethyldiphenylphosphine)diruthenium(II* ν_{CS} 1295 cm^{-1}. *^{31}P-{^{1}H}nmr* [$CDCl_3$ at 298 K] 49.2 (s) and 36.8 (q) ppm [J(PP) 35.7, δ(PP) 84.1 Hz].

Chlorobis(ethyldiphenylphosphine)ethyldiphenylphosphoniodithiocarboxylato-SS^{1}-(methanol)ruthenium(II)tetraphenylborate: The complex [$RuCl_2(S_2CPEtPh_2)(PEtPh_2)_2$] was dissolved in methanol to give a purple solution. Addition of $NaBPh_4$ then precipitated the complex as a purple *solid* which was filtered off, m.p. 120-122°C [Found: C, 66.3; H, 5.4% Calc for $C_{68}H_{69}BClOP_3RuS_2$:- C 67.7; H, 5.7%] $\nu(Ph_2Et\overset{+}{P}-\overset{-}{C}S_2)_{asym}$ 1115, 980 (br), 850 (br) cm^{-1} *^{31}P-{^{1}H}nmr* [$CDCl_3$ at 298 K] AMX pattern ν_A 44.6; ν_M, 29.0; ν_X 16.3 ppm [J_{AM} 28.0; J_{AX} 3.5; J_{MX} 11.3 Hz].

Carbonyldi(chloro)(N,N-dimethylformamide)bis(ethyldiphenylphosphine)ruthenium(II): The compound [$RuCl_2(PEtPh_2)_3$] (0.15g) was suspended in N,N-dimethylformamide (1.5 cm^3) and warmed gently in a very slow stream of carbon monoxide to deposit some yellow crystals. The solution was then cooled in ice, diethyl ether added, the complex filtered off and washed with diethyl ether, pentane and dried in *vacuo* at 40°C;(Yield *ca*.80 m.p. 167° (decomp) [Found: C, 54.6; H, 5.3; Cl, 10.2; N, 2.1% Calc for $C_{32}H_{37}Cl_2NO_2P_2Ru$: C, 54.8; H, 5.3; Cl, 10.1; N, 2.0%] ν_{CO} 1928; ν_{CO}(dmf) 1641, ν(RuCl) 327 cm^{-1} *^{31}P-{^{1}H}nmr* [$CDCl_3$ at 213 K] 32.8 (s) ppm; at 308K, 31.5 (s) ppm.

Reaction of $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ in methylene chloride solution: $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ was shaken in CH_2Cl_2 for 10 hours. Light petroleum (bp 60-80°C) was added to the resulting yellow solution and most of the solvent removed to precipitate a pale yellow powder. This solid was filtered and washed with diethyl ether. The $^{31}P-\{^1H\}$ nmr spectrum of this mixture (Fig. 1) has been discussed.

Reaction of $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ in benzene solution: $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ was shaken in benzene for 24 hours. The solvent was then removed under vacuo to give an orange oil which was dissolved in CH_2Cl_2 (ca. 2.0 cm^3). Light petroleum (bp 60-80°C) was then added slowly to give a yellow-orange solid which was filtered and washed with pentane. The $^{31}P-\{^1H\}$nmr spectrum of this mixture (Fig. 2) has been discussed.

Reaction of $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ with $[RuCl_2(PEtPh_2)_3]$; The compounds $[Ru(CO)Cl_2(dmf)(PEtPh_2)_2]$ (0.07g) and $[RuCl_2(PEtPh_2)_3]$ (0.08g) (1:1 mol ratios) were refluxed in acetone (ca. 30 cm^3) for 5 hours. The solution was cooled and concentrated to ca. 5 cm^3. An excess of light petroleum (bp 60-80°C) was then added and the resulting orange solid filtered. The $^{31}P-\{^1H\}$nmr spectrum showed the material to be a mixture of compounds (see earlier).

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