Ruthenium Complexes containing Group 5B Donor Ligands. Part 3.[1,2] Rearrangement Reactions of Some Ruthenium(II) Carbonyl and Thiocarbonyl Triphenylphosphine Complexes

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Reaction of $[RuCl_2(PPh_3)_3]$ with $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ in acetone (1:1 molar ratio) (dmf = *NN*-dimethylformamide) gives a high yield of $[(Ph_3P)_2ClRuCl_3Ru(CO)(PPh_3)_2]\cdot 2Me_2CO$, supporting the mechanism proposed earlier for formation of the analogous thiocarbonyl complex. Extensions of this type of coupling reaction to form $[(Ph_3P)_2BrRuBrCl_2Ru(CO)(PPh_3)_2]\cdot Me_2CO$ and $[(Ph_3P)_2ClRuBr_2ClRu(CO)(PPh_3)_2]\cdot Me_2CO$ are also described. Recrystallisation of $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ from $MeOH–CH_2Cl_2$ gives $[Ru(CO)Cl_2(HOMe)(PPh_3)_2]$ (4), and prolonged refluxing of the latter in dichloromethane–light petroleum (b.p. 60—80 °C) produces displacement of a PPh_3 group with formation of an isomeric mixture of $[(Ph_3P)Cl(OC)RuCl_3Ru(CO)(PPh_3)_2]$ (5). The same isomeric mixture, together with $[\{Ru(CO)Cl_2(PPh_3)_2\}_2]$, is also formed by reaction of PPh_3 with $[PPh_3(CH_2Ph)][Ru(C_7H_8)(CO)Cl_3]$ (2 : 1 molar ratio). Treatment of (5) with $Na[BPh_4]$ and PPh_3 in CH_2Cl_2 gives a high yield of $[(Ph_3P)_2(OC)RuCl_3Ru(CO)(PPh_3)_2][BPh_4]$ (6). This cation is also formed, together with (5), by prolonged shaking of (4) in ethanol, whereas treatment of (4) with $[AsPh_4]Cl\cdot HCl$ in acetone gives $[AsPh_4][Ru(CO)Cl_3(PPh_3)_2]\cdot Me_2CO$ (7). Related complexes are described, starting from $[Ru(CS)Cl_2(dmf)(PPh_3)_2]$. Finally, all this information is used to suggest detailed rearrangement mechanisms in the $[RuCl_2(PPh_3)_3]–CS_2$, $[PPh_3(CH_2Ph)][Ru(C_7H_8)(CO)Cl_3]–2PPh_3$, and the closely related $[RuX_2(PR_3)_n]–[Ru_2X_3(PR_3)_6]X$ (X = Cl or Br; n = 3 or 4) systems.

IN an earlier paper[1] we examined the reaction of $[RuCl_2(PPh_3)_3]$ with carbon disulphide and showed that the three products $[\{Ru(CS)Cl_2(PPh_3)_2\}_2]$ (1), $[Ru(\eta^2\text{-}CS_2)Cl(PPh_3)_3]Cl$ (2), and $[(Ph_3P)_2ClRuCl_3Ru(CS)(PPh_3)_2]$ (3) are obtained. The structure of (3) was confirmed by *X*-ray structural analysis.[3] In ref. 1 we indulged in some speculation as to the mechanism of formation of (3), and a scheme was proposed which involved coupling of an intermediate '$[Ru(CS)Cl_2(PPh_3)_2]$' [possibly formed by elimination of PPh_3S from (2)] with $[RuCl_2(PPh_3)_3]$. A competing reaction was dimerisation of '$[Ru(CS)Cl_2(PPh_3)_2]$' to give (1).

Because of our inability to isolate the '$[Ru(CS)Cl_2(PPh_3)_2]$' intermediate (but see later), it was impossible to prove this mechanism definitively. However, related reactions involving carbonyl(triphenylphosphine)ruthenium(II) complexes have now been studied in some detail[4] and these are reported in this paper, together with further studies on thiocarbonyl complexes of Ru^{II}.

RESULTS

Carbonyl Complexes.—It is well established that reaction of $[RuCl_2(PPh_3)_3]$ with CO in acetone or benzene gives $[Ru(CO)_2Cl_2(PPh_3)_2]$, the isomer formed depending on the reaction conditions.[5] However, James *et al.*[6] have shown that if this carbonylation reaction is performed in more basic solvents such as *NN*-dimethylformamide (dmf) the complex $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ can be isolated. When this was heated under reflux in acetone with $[RuCl_2(PPh_3)_3]$ (1 : 1 molar ratio), deep red crystals of $[(Ph_3P)_2ClRuCl_3Ru(CO)(PPh_3)_2]\cdot 2Me_2CO$ [ν(CO) at 1 951 cm^{-1}] were isolated in high yield. Confirmation of this formulation is based on the fact that it is isomorphous with $[(Ph_3P)_2ClRuCl_3Ru(CS)(PPh_3)_2]$ (3), and its ^1H-decoupled ^{31}P n.m.r. spectrum in $CDCl_3$ at 298 K consisted of two AB quartets centred at 48.0 and 40.3 p.p.m. [*cf.* (3) with quartets at 48.3 and 36.1 p.p.m.[1]]. This also confirms our earlier assignments[1] for the CS complex in that the higher-frequency quartet arises from the two PPh_3 groups *cis* to Cl^- and the lower-frequency quartet from the two PPh_3 groups *cis* to CS. The values of $^2J(PP)$ (37.5 and 24.6 Hz respectively) are consistent with those observed elsewhere[7] for *cis*-tertiary phosphines bound to Ru^{II}. The far-infrared spectrum with bands at 319s and 250br cm^{-1}, assigned to terminal and bridging ν(RuCl) respectively, is also compatible with this structure [*cf.* (3), with bands at 318s, 308m(sh), and 260m cm^{-1} (ref. 1)].†

Extension of this type of coupling reaction, to synthesise mixed halide-bridged complexes of Ru^{II}, was also attempted. Thus, reaction of $[RuBr_2(PPh_3)_3]$ and $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ in acetone (1 : 1 molar ratio) gave deep red crystals, which analyse closely for the expected $[(Ph_3P)_2BrRuBrCl_2Ru(CO)(PPh_3)_2]\cdot Me_2CO$ [ν(CO) at 1 952 cm^{-1}]. Similarly, reaction of $[RuCl_2(PPh_3)_3]$ and $[RuBr_2(CO)(dmf)(PPh_3)_2]$[6] produced a red solid, analysing closely for the expected $[(Ph_3P)_2ClRuBr_2ClRu(CO)(PPh_3)_2]\cdot Me_2CO$ [ν(CO) at 1 953 cm^{-1}]. The far-i.r. spectra of the two complexes were very similar, with the latter having a stronger band at 317 cm^{-1} [terminal ν(RuCl)]. However, the ^{31}P n.m.r. spectra in $CDCl_3$ at 303 or 213 K were identical, consisting of two complex patterns of resonances between 46—52 and

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† A related reaction is the formation of $[(Ph_3P)_2ClRuCl_3Ru(PPh_3)_2(PF_3)]$ from $[RuCl_2(PPh_3)_3]$ and PF_3 (2 : 1 molar ratio)[8] which, presumably, involves initial formation of an intermediate such as '$[RuCl_2(PPh_3)_2(PF_3)]$,' followed by coupling with unchanged $[RuCl_2(PPh_3)_3]$. Similarly, coupling of species such as '$[RuCl_2(N_2)(PPh_3)_2]$' and $[RuCl_2(PPh_3)_3]$ could be invoked to explain the formation of $[(Ph_3P)_2ClRuCl_3Ru(N_2)(PPh_3)_2]$ from $[RuCl_2(PPh_3)_4]$ and N_2 in a reverse-osmosis cell.[9]

[1] Part 1, T. A. Stephenson, E. S. Switkes, and P. W. Armit, *J.C.S. Dalton*, 1974, 1134.

[2] Part 2, P. W. Armit, A. S. F. Boyd, and T. A. Stephenson, *J.C.S. Dalton*, 1975, 1663.

[3] A. J. F. Fraser and R. O. Gould, *J.C.S. Dalton*, 1974, 1139.

[4] Some of this work has been reported in a preliminary communication: P. W. Armit and T. A. Stephenson, *J. Organometallic Chem.*, 1974, **73**, C33.

[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[6] B. R. James, L. D. Markham, B. C. Hui, and G. L. Rempel, *J.C.S. Dalton*, 1973, 2247.

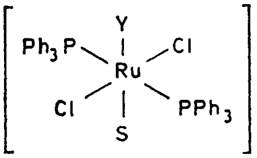
[7] See P. R. Hoffman and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221 and refs. therein.

[8] R. A. Head and J. F. Nixon, *J.C.S. Chem. Comm.*, 1975, 135.

[9] L. W. Gosser, W. H. Knoth, and G. W. Parshall, *J. Amer. Chem. Soc.*, 1973, **95**, 3436.

35—42 p.p.m. Complete analysis of these spectra has, to date, proved impossible but a close examination of both the low- and high-frequency sets of resonances indicates that they consist of a series of overlapping AB quartets suggesting a mixture of geometrical isomers which we have been unable to separate by chromatography.

The behaviour of [Ru(CO)Cl$_2$(dmf)(PPh$_3$)$_2$] in solution in the absence of [RuCl$_2$(PPh$_3$)$_3$] is also of some interest. Thus, recrystallisation of this product from MeOH–CH$_2$Cl$_2$ under mild conditions was claimed to give the five-co-ordinate [Ru(CO)Cl$_2$(PPh$_3$)$_2$],[6] but our recent reinvestigation [10] of this product indicates that it should be reformulated as the six-co-ordinate [Ru(CO)Cl$_2$(HOMe)(PPh$_3$)$_2$] [ν(CO) at 1 940 cm^{-1} (CH$_2$Cl$_2$)]. On the evidence of far-i.r. spectra [ν(RuCl) at *ca.* 330 cm^{-1}] and ^{31}P n.m.r. spectra at 303 K in CDCl$_3$ (singlet at *ca.* 34 p.p.m.), both these solvates are considered to have configuration (4) with *trans*-chlorides and *trans*-phosphines.



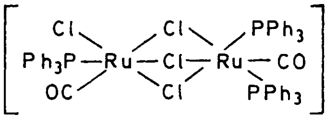
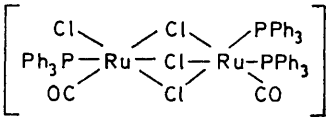
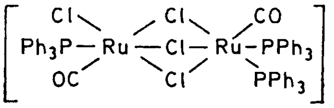
(4) Y=CO or CS
S=dmf or MeOH

When, however, [Ru(CO)Cl$_2$(HOMe)(PPh$_3$)$_2$] was gently heated under reflux in dichloromethane–light petroleum (b.p. 60—80 °C) for several hours, removal of the CH$_2$Cl$_2$ produced a pale orange solid, whose i.r. spectrum contained a broad peak at 1 960 cm^{-1} [ν(CO), in Nujol]. Earlier,[10] we suggested that this complex was a mixture of [{Ru(CO)Cl$_2$(PPh$_3$)$_2$}$_2$] isomers, formed by dimerisation of (4; S = MeOH). However, examination of the ^{31}P n.m.r. spectrum of this material clearly shows that this double-chloride-bridged dimer is not formed to any significant extent. At 213 K in CDCl$_3$ (Figure 1) the ^{31}P n.m.r. spectrum consisted of three singlets between 53 and 55 p.p.m. and a complex series of peaks between 36 and 42 p.p.m. The latter are readily interpreted as three overlapping AB quartets (Table 1) and the product is formulated as the triple-chloride-bridged [(Ph$_3$P)Cl(OC)RuCl$_3$Ru(CO)(PPh$_3$)$_2$] (5), for which it analyses quite closely. As shown in Figure 1, a small amount of unchanged [Ru(CO)Cl$_2$(HOMe)(PPh$_3$)$_2$] invariably contaminates the sample.

Three geometrical isomers are possible for (5) and the ^{31}P n.m.r. spectrum indicates that all three are formed. A tentative assignment of isomers to AB resonances is possible, based on the values of δ_{AB}. Thus, two of the δ_{AB} values are very similar (*ca.* 160 Hz), suggesting these resonances arise from isomers in which one phosphorus atom is eclipsed by a phosphorus atom and the other by a CO or a Cl$^-$ group [isomers (5b) and (5c)]. A further distinction cannot be made on this evidence. The other AB quartet has a much smaller δ_{AB} value (64.0 Hz), indicating that the two phosphorus atoms are probably eclipsed by CO and Cl$^-$ groups respectively [isomer (5a)] (see Table 1).† The unique phosphorus atom in isomers (5b) and (5c) will be eclipsed by another phosphorus atom, and, hence, the chemical shifts should be very similar (53.2 and 53.6 p.p.m.), whereas in (5a) it will be eclipsed by a CO group (54.7 p.p.m.). The relative intensities of the three AB quartets and the three singlets support these assignments. It should also be noted that all the ^2J(PP) values (*ca.* 25 Hz) are consistent with *cis*-phosphines bound to Ru^{II}. Support for this interpretation comes from the very recent synthesis by similar methods of the related [(F$_3$P)(Ph$_3$P)ClRuCl$_3$Ru(PPh$_3$)$_2$(PF$_3$)], where a combination of ^{31}P and ^{19}F n.m.r. spectroscopy provides unequivocal evidence for this formulation and shows that, in this instance, an isomer of type (5b) is the predominant one.[8]

TABLE 1

Assignment of isomeric forms of [(Ph$_3$P)Cl(OC)RuCl$_3$Ru(CO)(PPh$_3$)$_2$] to ^{31}P n.m.r. resonances

			^{31}P n.m.r. (CDCl$_3$ at 213 K), δ/p.p.m.	
Isomer			Singlet position	AB Position
(5a)		∇	54.7	$40.8\begin{pmatrix}\delta_{AB}\ 64.0\ \text{Hz}\\ J_{AB}\ 25.4\ \text{Hz}\end{pmatrix}$
(5b)		O	53.6	$39.6\begin{pmatrix}\delta_{AB}\ 160.9\ \text{Hz}\\ J_{AB}\ 25.3\ \text{Hz}\end{pmatrix}$
(5c)		X	53.2	$38.6\begin{pmatrix}\delta_{AB}\ 155.7\ \text{Hz}\\ J_{AB}\ 25.5\ \text{Hz}\end{pmatrix}$

A reinterpretation of the nature of the products from the reaction of [PPh$_3$(CH$_2$Ph)][Ru(C$_7$H$_8$)(CO)Cl$_3$] and PPh$_3$ (1 : 2 molar ratio) in CH$_2$Cl$_2$ is also appropriate at this junction. Earlier,[10] we formulated the product as a mixture of [{Ru(CO)Cl$_2$(PPh$_3$)$_2$}$_2$] isomers (which could not

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† Very recently, McCleverty *et al.*[11] briefly mentioned the formation of (5) from reaction of [Ru(CO)Cl(H)(PPh$_3$)$_3$] and hydrogen chloride. We have repeated this preparation and shown by ^{31}P n.m.r. spectroscopy that the same isomeric mixture as above is formed. Also, Head and Nixon [8] reported the synthesis of (5) from [Ru(CO)H$_2$(PPh$_3$)$_3$] and hydrogen chloride but no spectral details were given.

[10] L. Ruiz-Ramírez and T. A. Stephenson, *J.C.S. Dalton*, 1974, 1640.

[11] J. A. McCleverty, D. Seddon, and R. N. Whiteley, *J.C.S. Dalton*, 1975, 839.

be separated by chromatography) but a re-examination of the ^{31}P n.m.r. spectrum of this product (Figure 2) clearly shows that in addition to the doubly-bridged isomers (strong singlets at 17.2 and 25.5 p.p.m. *cf.* [$\{Ru(CS)Cl_2(PPh_3)_2\}_2$] (1),[1,*] 31.3 p.p.m.) there is a substantial amount of the [$(Ph_3P)Cl(OC)RuCl_3Ru(CO)(PPh_3)_2$] isomer mixture present.[†] In fact, an estimate based on relative n.m.r. peak areas suggests 67% double bridging and 33% triple bridging and this is consistent with the analytical data quoted in ref. 10 (see Experimental section).

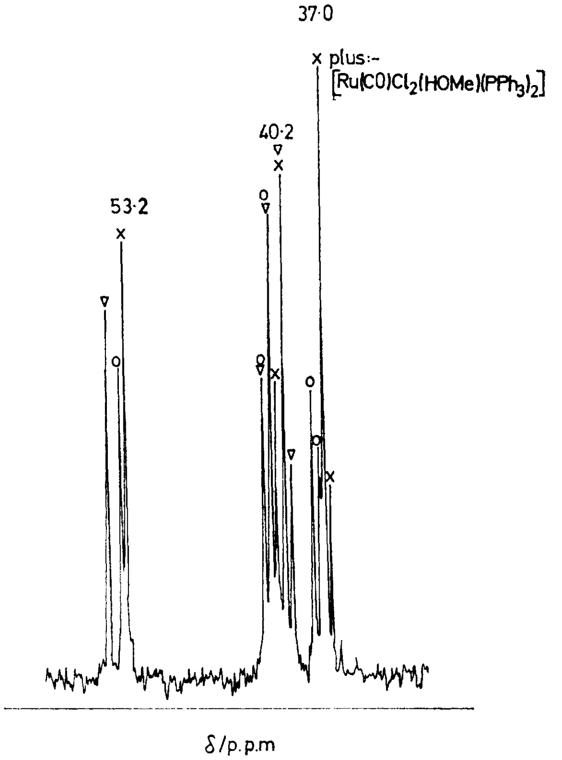


FIGURE 1 Phosphorus-31 n.m.r. spectrum in $CDCl_3$ at 213 K of the product from reaction of [$Ru(CO)Cl_2(HOMe)(PPh_3)_2$], and dichloromethane–light petroleum (b.p. 60—80 °C)

When [$Ru(CO)Cl_2(HOMe)(PPh_3)_2$] was shaken for several hours in more polar solvents, such as Me_2CO or EtOH, with an equimolar amount of PPh_3 a pale yellow solid was precipitated, whose i.r. spectrum (Nujol) contained two ν(CO) bands at 1 978br and 1 928 cm^{-1}. The ^{31}P n.m.r. spectra at 243 K in $CDCl_3$ reveal the products to be mixtures containing both [$Ru(CO)Cl_2(PPh_3)_2S$] [S = MeOH or Me_2CO (or EtOH)] and [$Ru_2(CO)_2Cl_4(PPh_3)_3$] (5) isomers. However, in addition, another AB quartet was observed centred at 40.6 p.p.m. [*J*(PP) 25.6, δ_{AB} 115 Hz] and also weak broad resonances at *ca.* 26 and 18 p.p.m., corresponding to isomers of [$\{Ru(CO)Cl_2(PPh_3)_2\}_2$]. The additional AB quartet was more intense than the signals from the [$Ru_2(CO)_2Cl_4(PPh_3)_3$] (5) isomers, especially in the spectrum of the product from EtOH compared to that from Me_2CO. The same mixture of products was obtained when the reaction was repeated without free PPh_3 present, except that the bulk of the material now consists of unchanged [$Ru(CO)Cl_2(HOMe)(PPh_3)_2$] and the intensity of the additional AB quartet in the ^{31}P n.m.r. spectrum was smaller than those signals arising from the [$Ru_2(CO)_2Cl_4(PPh_3)_3$] isomers.

When (5) was mixed with PPh_3 and Na[BPh_4] and shaken in either CH_2Cl_2, Me_2CO, or EtOH for 50 h, a pale yellow solid was isolated which analyses quite closely for [$(Ph_3P)_2(OC)RuCl_3Ru(CO)(PPh_3)_2$][$BPh_4$] (6) [ν(CO) at 1 976 cm^{-1} (Nujol)]. Support for this formulation is obtained from the ^{31}P n.m.r. spectrum in $CDCl_3$ at 213 K which consisted of an AB quartet centred at 40.8 p.p.m. [*J*(PP) 27.1, δ_{AB} 113.3 Hz] {*cf.* for [$(Ph_3P)_2ClRuCl_3Ru(CO)(PPh_3)_2$], the two phosphine groups *cis* to CO appear at 40.3 p.p.m. with ^2J(PP) 24.6 Hz}. Complex (6) is also a 1 : 1 electrolyte in CH_2Cl_2 and its far-i.r. spectrum showed no band indicative of terminal ν(RuCl). Thus, this evidence clearly indicates that the cationic dimer (6) is formed both directly from rearrangement of [$Ru(CO)Cl_2(HOMe)(PPh_3)_2$] in polar solvents and by reaction of [$Ru_2(CO)_2Cl_4(PPh_3)_3$] with Na[BPh_4] in the presence of PPh_3.

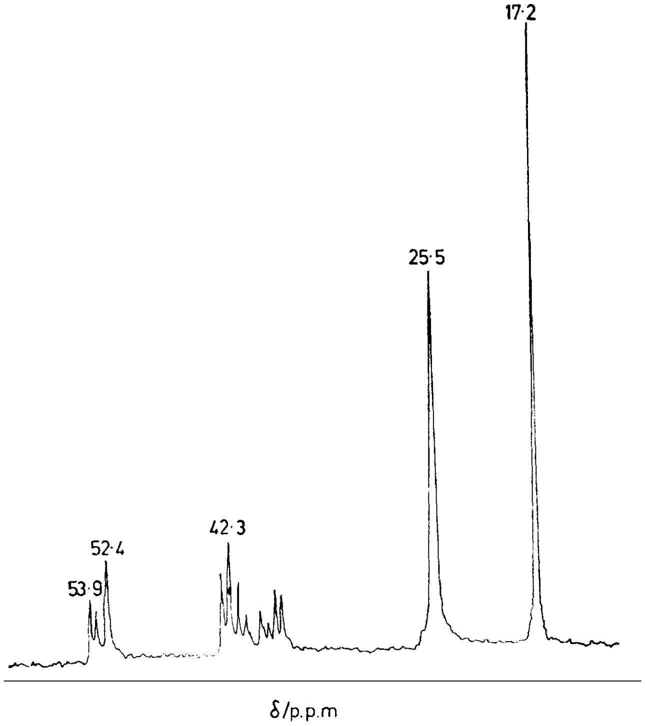
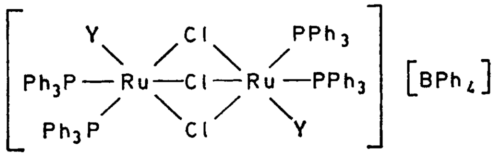


FIGURE 2 Phosphorus-31 n.m.r. spectrum in $CDCl_3$ at 303 K of the product from reaction of [$PPh_3(CH_2Ph)$][$Ru(C_7H_8)(CO)Cl_3$] and 2 PPh_3



(6) Y = CO or CS

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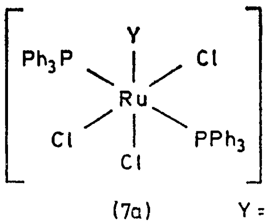
[*] In ref. 1, a ^{31}P n.m.r. singlet at 24.4 p.p.m. (in C_6H_6–C_6D_6) was assigned to an isomer of (1) but subsequent studies have shown this to arise from PPh_3O.

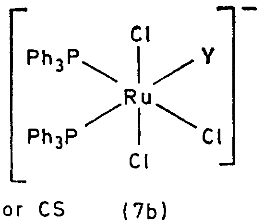
[†] The slight discrepancy between the positions of the resonances from (5) in Figures 1 and 2 is due to the difference in the temperatures at which the spectra were recorded. As the temperature increased, the singlets moved slightly to lower frequency and the quartets to higher frequency, making spectral analysis more difficult.

Finally, when [Ru(CO)Cl_2(HOMe)$(PPh_3)_2$] (4) was treated with [$AsPh_4$]Cl·HCl in Me_2CO the anionic [$AsPh_4$][Ru(CO)$Cl_3(PPh_3)_2$]·Me_2CO (7) [ν(CO) at 1 918 cm^{-1} (Nujol)] can be isolated. Like the corresponding M[Ru(CS)$Cl_3(PPh_3)_2$] [M = $AsPh_4^+$, $PPh_3(CH_2Ph)^+$, or NEt_4^+] formed by cleavage of [{Ru(CS)$Cl_2(PPh_3)_2$}$_2$] with MCl–HCl,[1] (7) is too insoluble for ^{31}P n.m.r. studies. However, the far-i.r. spectrum of (7) contained a strong peak at 320 cm^{-1} indicative of a *trans*-$RuCl_2$ group (*cf.* 320 cm^{-1} for the CS anion [1]), which is consistent with either structure (7a) or (7b). Structure (7a) with *trans*-phosphines is most likely in view of the established stereochemistry of (4) and the postulated instability of (7b) (see ref. 10 and following discussion).



(7a)

Y = CO or CS



(7b)

Thiocarbonyl Complexes.—The success of coupling [Ru(CO)Cl_2(dmf)$(PPh_3)_2$] and [$RuCl_2(PPh_3)_3$] to give a high yield of [Ru_2(CO)$Cl_4(PPh_3)_4$] strongly supports the proposed mechanism suggested in ref. 1 for the formation of the analogous CS complex. Although the existence of the intermediate '[Ru(CS)$Cl_2(PPh_3)_2$]' could not be verified directly in the [$RuCl_2(PPh_3)_3$]–CS_2 reaction, we found that reaction of [{Ru(CS)$Cl_2(PPh_3)_2$}$_2$] with refluxing dmf gave [Ru(CS)Cl_2(dmf)$(PPh_3)_2$] [ν(CS) at 1 275 cm^{-1} (Nujol)], whose ^{31}P n.m.r. spectrum at 303 K in $CDCl_3$ (singlet at 30.2 p.p.m.) and far-i.r. spectrum [ν(RuCl) at 325 cm^{-1}] indicates that configuration (4) is the most likely. Reaction of [Ru(CS)Cl_2(dmf)$(PPh_3)_2$] and [$RuCl_2(PPh_3)_3$] in refluxing Me_2CO (1 : 1 molar ratio) then gave [Ru_2(CS)$Cl_4(PPh_3)_4$] (3) [ν(CS) at 1 284 cm^{-1} (Nujol)] as the only product, which directly verifies the mechanism suggested earlier.

For completion, the behaviour of [Ru(CS)Cl_2(dmf)$(PPh_3)_2$] in solution in the absence of [$RuCl_2(PPh_3)_3$] was also briefly investigated. Recrystallisation from hot CH_2Cl_2–MeOH gave [Ru(CS)Cl_2(HOMe)$(PPh_3)_2$], whose far-i.r. and ^{31}P n.m.r. spectra indicate configuration (4) as the most likely. This complex, on treatment with hot dichloromethane–light petroleum (b.p. 60—80 °C), gave a yellow crystalline solid which analyses closely for [(Ph_3P)Cl(SC)$RuCl_3$Ru(CS)$(PPh_3)_2$]·0.5CH_2Cl_2. A small amount of this complex (Me_2CO solvate) has been prepared previously [1] by shaking [{Ru(CS)$Cl_2(PPh_3)_2$}$_2$] in degassed Me_2CO for several days. Unlike the analogous CO complex, the ^{31}P n.m.r. spectrum at 303 K is not very helpful, consisting of two strong broad peaks at 48.1 and 37.7 p.p.m. (relative intensity 1 : 2) and weaker peaks, also of relative intensity 1 : 2, at 50.3 and 35.6 p.p.m. (*cf.* ref. 1). However, at 213 K, the ^{31}P n.m.r. spectrum was better resolved and a tentative assignment of the isomers to the various resonances is given in the Experimental section.

A good indication, however, that an isomeric mixture of [Ru_2(CS)$Cl_4(PPh_3)_3$] complexes has been produced was obtained by its reaction with Na[BPh_4] and PPh_3 in CH_2Cl_2 which gave a high yield of [$(Ph_3P)_2$(SC)$RuCl_3$Ru(CS)$(PPh_3)_2$][BPh_4] (6). The ^{31}P n.m.r. spectrum in $CDCl_3$ at 213 K consisted of a sharp quartet centred at 37.5 p.p.m. [J(PP) 27.0, δ_{AB} 86.8 Hz]. A small amount of this cation, together with the [Ru_2(CS)$Cl_4(PPh_3)_3$] isomeric mixture, was also formed when [Ru(CS)Cl_2(HOMe)$(PPh_3)_2$] was shaken in EtOH with an equimolar amount of PPh_3 for several hours.

DISCUSSION

A summary of the preparative methods for the various dimeric complexes of Ru^{II} reported in this paper is given in Table 2 and it is of some interest to conclude this paper with a discussion of these various reactions and the different amounts of dimeric complexes they produce.

TABLE 2

Summary of products obtained from rearrangement reactions of various monomeric ruthenium(II) complexes

[$RuYCl_2$(HOMe)$(PPh_3)_2$] $\xrightarrow{(i)-(iii)}$ Mainly [$Ru_2Y_2Cl_4(PPh_3)_3$] isomeric mixture and, for Y = CO, trace amounts of [{$RuYCl_2(PPh_3)_2$}$_2$]

[$RuYCl_2$(HOMe)$(PPh_3)_2$] $\xrightarrow{(iv)}$ Mainly [$RuY_2Cl_2(PPh_3)_3$] isomeric mixture and [$Ru_2Y_2Cl_3(PPh_3)_4$]Cl and, for Y = CO, trace amounts of [{$RuYCl_2(PPh_3)_2$}$_2$]

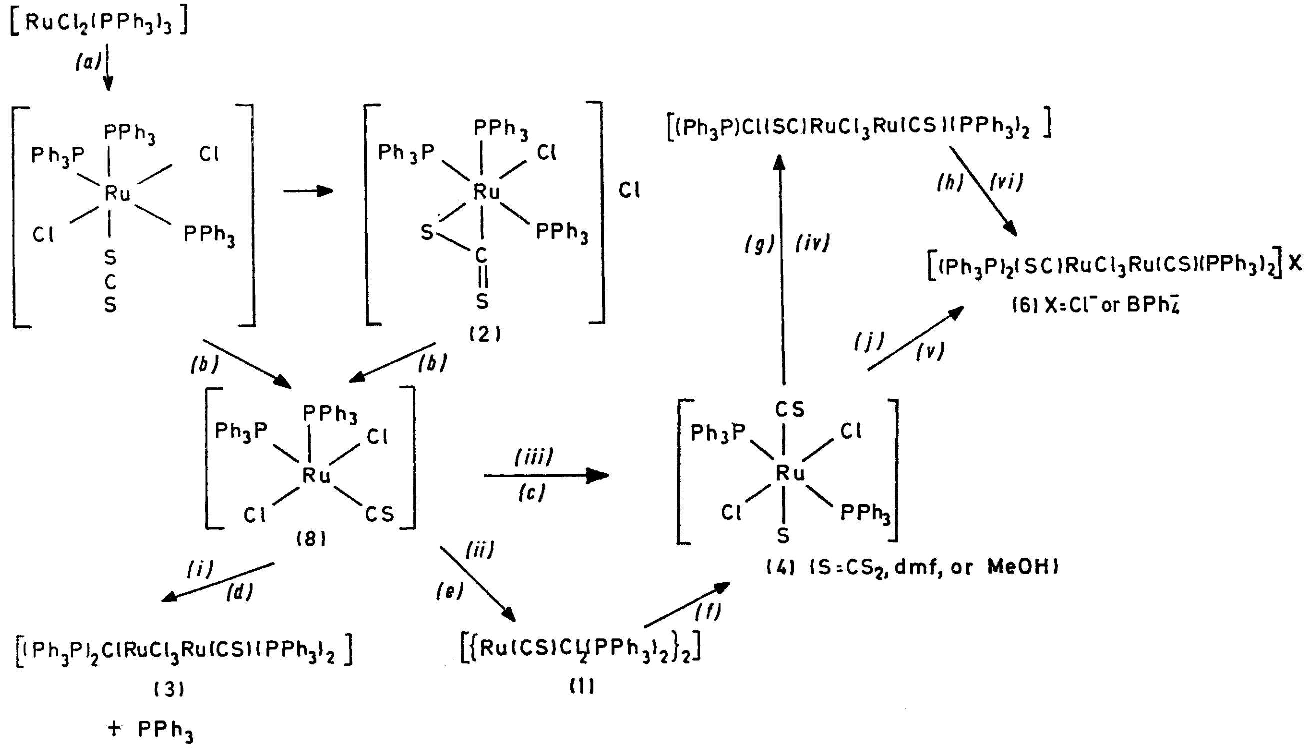
[$RuCl_2(PPh_3)_3$] + CS_2 $\xrightarrow{(iii)}$ [Ru_2(CS)$Cl_4(PPh_3)_4$] (39%), [Ru(η-CS_2)Cl$(PPh_3)_3$]Cl (8%), [{Ru(CS)$Cl_2(PPh_3)_2$}$_2$] (16%), and trace amounts of [$Ru_2(CS)_2Cl_4(PPh_3)_3$] isomeric mixture

[$PPh_3(CH_2Ph)$][Ru(C_7H_8)(CO)Cl_3] + 2PPh_3 $\xrightarrow{(i),\ (iii)}$ [$Ru_2(CO)_2Cl_4(PPh_3)_3$] isomeric mixture (33%) and [{Ru(CO)$Cl_2(PPh_3)_2$}$_2$] (67%)

(*i*) CH_2Cl_2. (*ii*) Light petroleum. (*iii*) Heat. (*iv*) Ethanol or acetone, shake.

We suggest that the mode of dimerisation is very dependent on the stereochemistry of either the starting material or the reactive intermediate. For [$RuYCl_2$(HOMe)$(PPh_3)_2$], ^{31}P n.m.r. and far-i.r. studies unequivocally show structure (4) with *trans*-phosphines and *trans*-chlorides, and here the dimerisation product in solvents of low polarity is almost entirely the [$Ru_2Y_2Cl_4(PPh_3)_3$] isomeric mixture, accompanied by concomitant loss of one PPh_3 group. In more polar solvents this dimerisation step is accompanied by concomitant Cl^- displacement giving some [$Ru_2Y_2Cl_3(PPh_3)_4$]Cl.

However, in the [$RuCl_2(PPh_3)_3$]–CS_2 reaction, where very little [$Ru_2(CS)_2Cl_4(PPh_3)_3$] is formed, it seems very reasonable to infer that the '[Ru(CS)$Cl_2(PPh_3)_2$]' intermediate will initially have *cis*-PPh_3 groups. Support for this statement comes from the *X*-ray structure of $[RuCl_2(PPh_3)_3]$ [12] which shows that the apical Ru–P bond is considerably shorter than the basal Ru–P bonds, together with the structure of its dissociation product $[\{RuCl_2(PPh_3)_2\}_2]$, shown by ^{31}P n.m.r. studies [2,7] to contain *cis*-PPh_3 groups. Therefore, a likely structure for the five-co-ordinate intermediate in the $[RuCl_2(PPh_3)_3]$–CS_2 reaction is (8), formed by elimination of PPh_3S from either $[Ru(\eta^2\text{-}CS_2)Cl(PPh_3)_3]Cl$ and/or $[RuCl_2(PPh_3)_3(SCS)]$ (see Scheme 1 *).



SCHEME 1 (*a*) CS_2; (*b*) $-PPh_3S$; (*c*) isomerisation; (*d*) $[RuCl_2(PPh_3)_3]$; (*e*) dimerisation; (*f*) dmf, heat; (*g*) dimerisation ($-PPh_3$); (*h*) PPh_3,$Na[BPh_4]$; (*j*) dimerisation ($-Cl^-$)

It is then proposed that (8) will undergo three competing reactions, namely: (*i*) coupling with unchanged $[RuCl_2(PPh_3)_3]$ {or $[RuCl_2(PPh_3)_3(SCS)]$} to give $[Ru_2(CS)Cl_4(PPh_3)_4]$ (3); (*ii*) self-dimerisation without phosphine loss to generate the six-co-ordinate $[\{Ru(CS)Cl_2(PPh_3)_2\}_2]$ (1); and (*iii*) isomerisation to form a complex such as (4) (probably solvated) with the sterically more stable *trans*-$Ru(PPh_3)_2$ arrangement. Isomer (4) can then dimerise with concomitant phosphine loss to give some $[Ru_2(CS)_2Cl_4(PPh_3)_3]$ (5) [step (*iv*)] or dimerise with concomitant chloride-ion displacement to give $[Ru_2(CS)_2Cl_3(PPh_3)_4]Cl$ (6) [step (*v*)]. Formation of (6) from (4) is favoured in more polar solvents, particularly in the presence of free PPh_3 which both inhibits formation of (5) and also slowly reacts with (5) to produce some of the ionic dimer [step (*vi*)].

A similar mechanism (Scheme 2) can be proposed to explain the products from the $[PPh_3(CH_2Ph)][Ru(C_7H_8)(CO)Cl_3]$–$2PPh_3$ reaction. As discussed fully in ref. 10, it is reasonable to postulate that an intermediate containing an η^2-C_7H_8 group is first formed and this then reacts further with PPh_3 to give $[Ru(CO)Cl_3(PPh_3)_2]^-$ of structure (9). Analogous complexes $[PPh_3(CH_2Ph)][Ru(CO)Cl_3L_2]$ of this stereochemistry have been characterised for L = $AsPh_3$, SMe_2, 2,2′-bipyridyl, *etc.*[10] However, for (9) the combination of the high *trans* influence of PPh_3, together with the sterically unfavourable *cis* arrangement of these bulky groups (large Tolman ligand cone angles [16]), leads to ready expulsion of a chloride ion to relieve steric crowding and initial formation of a five-co-ordinate complex $[Ru(CO)Cl_2(PPh_3)_2]$ (10) containing *cis*-PPh_3 groups. As for the analogous CS intermediate, this can either dimerise without phosphine loss to form $[\{Ru(CO)Cl_2(PPh_3)_2\}_2]$ or isomerise to a species (11) with *trans*-phosphines which, in turn, dimerises with concomitant PPh_3 loss to form $[Ru_2(CO)_2Cl_4(PPh_3)_3]$. In this instance the proportion of the latter is considerably higher (33%) than in the $[RuCl_2(PPh_3)_3]$–CS_2 reaction, because there is no $[RuCl_2(PPh_3)_3]$ present to remove

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[*] Isomers (8), (10), and (11) are written with essentially square-pyramidal rather than trigonal-bipyramidal structures to conform to both the theoretical predictions of Pearson,[13] Burdett,[14] and Rossi and Hoffmann [15] for d^6 complexes and the available *X*-ray data [7] for various five-co-ordinate d^6 complexes.

[12] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.

[13] R. G. Pearson, *J. Amer. Chem. Soc.*, 1969, **91**, 4947.

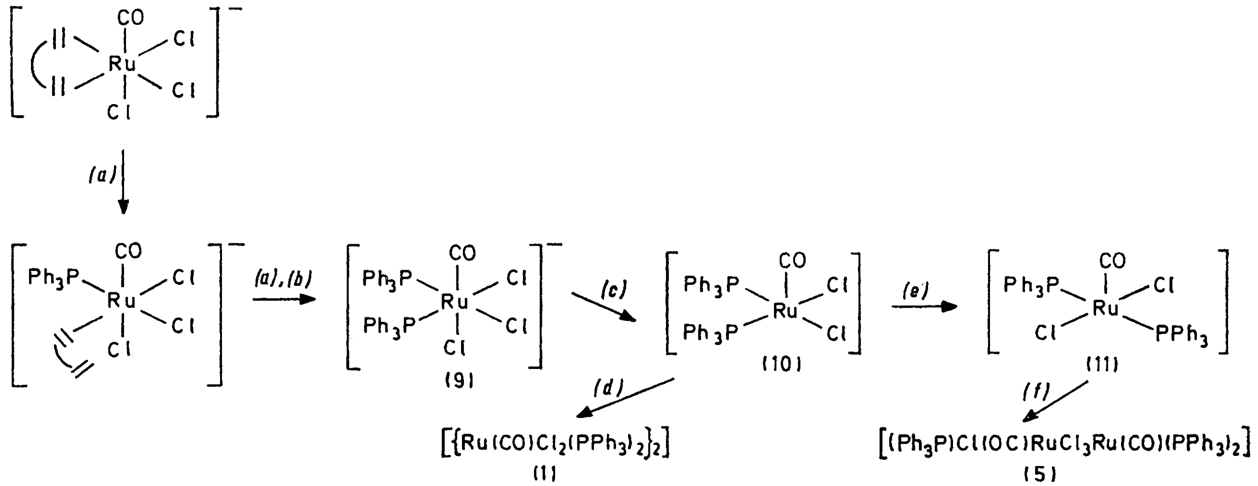
[14] J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 375.

[15] A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.

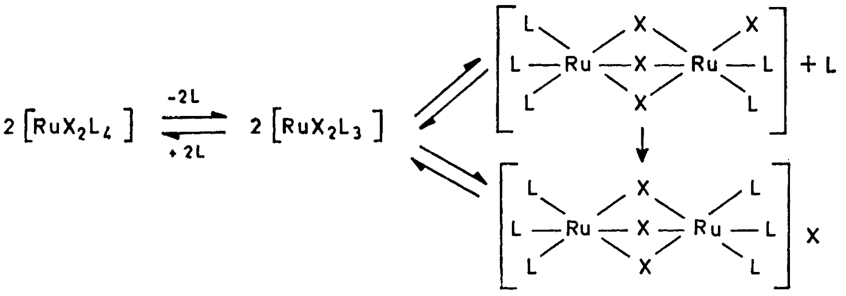
[16] For a full discussion of ligand cone angles see C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

either of the $[Ru(CO)Cl_2(PPh_3)_2]$ isomers by generating $[Ru_2(CO)Cl_4(PPh_3)_4]$.

The reason why five-co-ordinate complexes (or six-co-ordinate solvates) with *trans*-PPh_3 groups dimerise to form triple-chloride-bridged complexes with concomitant PPh_3 loss whereas those with *cis*-PPh_3 groups form double-chloride-bridged dimers without PPh_3 loss is attributed to the high *trans* influence of PPh_3 and the consequent electronic instability of *trans*-$Ru(PPh_3)_2$ compared to *cis*-$Ru(PPh_3)_2$ arrangements.* The driving force for all these rearrangements is presumably the high stability of six-co-ordinate ruthenium(II) ($4d^6$) complexes.



SCHEME 2 (*a*) PPh_3; (*b*) $-C_7H_8$; (*c*) $-Cl^-$; (*d*) dimerisation; (*e*) isomerisation; (*f*) dimerisation ($-PPh_3$)



SCHEME 3

Finally, the observations presented in this paper strongly suggest that the detailed mechanism proposed by us in ref. 2 for the related rearrangement reactions of $[RuX_2L_n]$ ($L = PR_3$; $X = Cl$ or Br; $n = 3$ or 4) complexes is incorrect. Thus, instead of dimerisation to a double-halide-bridged complex $[\{RuX_2L_3\}_2]$ followed by intramolecular displacement by halide ion of either L to give $[Ru_2X_4L_5]$ or X^- to give $[Ru_2X_3L_6]X$ (see Scheme, ref. 2), it is now suggested (Scheme 3) that direct dimerisation of $[RuX_2L_3]$ to form either $[Ru_2X_4L_5]$ or $[Ru_2X_3L_6]X$ occurs accompanied by concomitant loss of either L or X^- groups respectively. The amount of each product formed depends on the relative strengths of Ru–L and Ru–X bonds and on the polarity of the solvent medium.

This revised mechanism is then consistent with the observations in this paper and also the earlier inability [2] to obtain evidence for the proposed $[\{RuCl_2L_3\}_2]$ intermediate (except for $L = PEtPh_2$). In fact, further studies reveal that the product giving rise to the ^{31}P n.m.r. AB_2 pattern (Figure 4, ref. 2) is not neutral $[\{RuCl_2(PEtPh_2)_3\}_2]$ but a cationic complex of probable formula $[RuCl(HOEt)_2(PEtPh_2)_3]Cl$ or $[\{RuCl(HOEt)(PEtPh_2)_3\}_2]Cl_2$. The disappearance of this ^{31}P n.m.r. pattern above 220 K in $CDCl_3$ with formation of $[RuCl_2(PEtPh_2)_3]$, $[Ru_2Cl_4(PEtPh_2)_5]$, $[Ru_2Cl_3(PEtPh_2)_6]Cl$, and $PEtPh_2$ [2] is then readily rationalised by postulating nucleophilic displacement of solvent by chloride ion to form $[RuCl_2(PEtPh_2)_3]$, which then undergoes the facile rearrangement steps shown in Scheme 3. This mechanism, in retrospect, is more reasonable than the previously postulated intramolecular rearrangements of a six-co-ordinate dimer, since d^6 complexes of this co-ordination number are invariably kinetically inert.

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* *Note added in proof.* Additional experimental evidence for this suggestion is the isolation of $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$, from a solution thought to contain $[Ru(CO)Cl_2(PMe_2Ph)_2]$ with *cis*-PMe_2Ph groups (C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J.C.S. Dalton*, 1976, 953).

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the 250—4 000 cm^{-1} region on Perkin-Elmer 457 and 225 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates and in the 150—400 cm^{-1} region on a Beckman RIIC IR 720 far-i.r. spectrometer using pressed Polythene discs. Phosphorus-31 n.m.r. 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. Conductivity measurements were made on a Portland Electronics model 310 conductivity bridge. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Ruthenium(III) trichloride trihydrate (Johnson, Matthey Ltd), carbon monoxide (Air products), triphenylphosphine (B.D.H.), sodium tetraphenylborate (B.D.H.), and carbon disulphide (Fisons) were obtained as indicated. The complexes $[RuX_2(PPh_3)_3]$,[5] $[RuX_2(CO)(dmf)(PPh_3)_2]$ (X = Cl or Br),[6] $[PPh_3(CH_2Ph)][Ru(C_7H_8)(CO)Cl_3]$,[10] and $[\{Ru(CS)Cl_2(PPh_3)_2\}_2]$ [1] were prepared as described elsewhere.

(a) *Carbonyl Complexes.—Tri-μ-chloro-*a*-carbonyl-*g*-chloro-tetrakis(triphenylphosphine)diruthenium*(II)*–acetone* (1/2). The complexes $[RuCl_2(PPh_3)_3]$ (0.12 g) and $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ (0.10 g) were heated under reflux for 2.5 h in degassed Me_2CO (30 cm^3) under an atmosphere of nitrogen. The solution was then cooled and the deep red crystals of *product* were filtered off and washed with diethyl ether. Further crystals of the complex were obtained by evaporation of the filtrate to *ca.* 10 cm^3 (0.13 g, 69%), m.p. 170—171 °C (decomp.) [ν(CO) at 1 951 cm^{-1}, ν(CO) (acetone) at 1 710 cm^{-1} (Nujol)] (Found: C, 61.7; H, 4.7; Cl, 9.4. Calc. for $C_{79}H_{72}Cl_4O_3P_4Ru_2$: C, 61.6; H, 4.8; Cl, 9.3%); ^{31}P n.m.r. ($CDCl_3$ at 298 K) 48.0 (q) and 40.3 (q) p.p.m. [$J(P^1P^2)$ 37.5, $J(P^3P^4)$ 24.6; $\delta(P^1P^2)$ 97.7, $\delta(P^3P^4)$ 74.2 Hz].

*μ-Bromo-di-μ-chloro-*a*-bromo-*g*-carbonyl-tetrakis(triphenylphosphine)diruthenium*(II)*–acetone* (1/1). The complex $[RuBr_2(PPh_3)_3]$ (0.12 g) and $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ (0.08 g) were heated together under reflux for 3 h in degassed Me_2CO (30 cm^3) under an atmosphere of nitrogen. The solution was then cooled and the deep red *precipitate* was filtered off and washed with diethyl ether (0.10 g, 56%), m.p. 159—160 °C (decomp.) [ν(CO) at 1 952 cm^{-1}; ν(CO) (acetone) at 1 710 cm^{-1} (Nujol)] (Found: C, 59.0; H, 4.4; Br, 10.0; Cl, 4.6. Calc. for $C_{76}H_{66}Br_2Cl_2O_2P_4Ru_2$: C, 58.2; H, 4.2; Br, 10.2; Cl, 4.5%); far-i.r. spectrum 317s, 304m, 280s, 270brs, 260m, 250w, 244w, 236m, 228m, and 180brw cm^{-1}.

*Di-μ-bromo-μ-chloro-*a*-carbonyl-*g*-chloro-tetrakis(triphenylphosphine)diruthenium*(II)*–acetone* (1/1) was prepared as above using $[RuCl_2(PPh_3)_3]$ (0.11 g) and $[RuBr_2(CO)(dmf)(PPh_3)_2]$ (0.10 g) to give deep red crystals of the *product* (0.085 g, 51%), m.p. 160—162 °C (decomp.) [ν(CO) at 1 953 cm^{-1}; ν(CO) (acetone) at 1 710 cm^{-1} (Nujol)] (Found: C, 58.5; H, 4.3; Br, 10.0; Cl, 4.6. Calc. for $C_{76}H_{66}Br_2Cl_2O_2P_4Ru_2$: C, 58.2; H, 4.2; Br, 10.2; Cl, 4.5%); far-i.r. spectrum 317vs, 304w, 280 (sh), 270brs, 260m, 250w, 244w, 236m, 228m, and 180brm cm^{-1}.

Carbonyldichloro(methanol)bis(triphenylphosphine)ruthenium(II). The complex $[Ru(CO)Cl_2(dmf)(PPh_3)_2]$ [6] [^{31}P n.m.r. ($CDCl_3$ at 303 K) 33.9 (s) p.p.m.; ν(RuCl) at 330 cm^{-1}] was recrystallised from hot CH_2Cl_2–MeOH to give the yellow *product* which was washed with diethyl ether (Found: C, 60.3; H, 4.3; Cl, 9.1. Calc. for $C_{38}H_{34}Cl_2O_2P_2Ru$: C, 60.5; H, 4.5; Cl, 9.4%); ^{31}P n.m.r. ($CDCl_3$ at 303 K) 34.5 (s) p.p.m. [ν(CO) at 1 931 and 1 921 cm^{-1} (Nujol); 1 940 cm^{-1} (CH_2Cl_2)]; ν(RuCl) at 333 cm^{-1}. At 213 K, singlets in the ^{31}P n.m.r. spectrum were found at 35.9 and 37.0 p.p.m. for dmf and MeOH solvents respectively.

*Tri-μ-chloro-*ag*-dicarbonyl-*b*-chloro-tris(triphenylphosphine)diruthenium*(II). The complex $[Ru(CO)Cl_2(HOMe)(PPh_3)_2]$ was dissolved in CH_2Cl_2 and light petroleum (b.p. 60—80 °C) was added. The yellow solution was warmed gently on a water-bath for several hours to allow the CH_2Cl_2 to evaporate slowly. The resulting orange solid was redissolved in CH_2Cl_2, light petroleum (b.p. 60—80 °C) was added, and the process repeated to give pale orange crystals of the *product* which were filtered off and washed with EtOH and diethyl ether, m.p. 247 °C [ν(CO) at 1 960br cm^{-1} (Nujol)] (Found: C, 58.7; H, 4.1. Calc. for $C_{56}H_{45}Cl_4O_2P_3Ru_2$: C, 56.7; H, 3.8%); ^{31}P n.m.r. ($CDCl_3$ at 213 K) (Figure 1) given in Table 1. The slightly high carbon and hydrogen analyses are due to the presence of some unchanged $[Ru(CO)Cl_2(HOMe)(PPh_3)_2]$ (see Figure 1).

Reaction of $[PPh_3(CH_2Ph)][Ru(C_7H_8)(CO)Cl_3]$ *and* PPh_3. The complex (0.24 g) and PPh_3 (0.20 g, 1 : 1 molar ratio) were dissolved in CH_2Cl_2 (100 cm^3) and the solution was heated under reflux under a nitrogen atmosphere for 12 h. The resulting pale orange solution was reduced in volume and diethyl ether was added to give a white precipitate of $[PPh_3(CH_2Ph)]Cl$. The remaining solution was treated with pentane to give a pale orange *solid* [ν(CO) at 2 029m, 1 993s, and 1 960s cm^{-1} (Nujol)], ^{31}P n.m.r. ($CDCl_3$ at 303 K) as shown in Figure 2 (Found: C, 59.8; H, 4.2. Calc. for mixture of $[\{Ru(CO)Cl_2(PPh_3)_2\}_2]$ and $[(Ph_3P)Cl(OC)RuCl_3Ru(CO)(PPh_3)_2]$ (67 : 33): C, 59.8; H, 4.0%).

Tri-μ-chloro-bis[carbonylbis(triphenylphosphine)ruthenium(II)] *tetraphenylborate*. The $[(Ph_3P)Cl(OC)RuCl_3Ru(CO)(PPh_3)_2]$ isomeric mixture (0.12 g), $Na[BPh_4]$ (0.034 g), and PPh_3 (0.026 g) were shaken together in degassed CH_2Cl_2 (25 cm^3) under nitrogen for 50 h. The solution was evaporated to dryness, triturated with MeOH, and the resulting *solid* was filtered off and washed with water, MeOH, and diethyl ether (0.14 g, 80%), m.p. 124—126 °C [ν(CO) at 1 976 cm^{-1} (Nujol)] (Found: C, 66.7; H, 4.9. Calc. for $C_{98}H_{80}BCl_3O_2P_4Ru_2$: C, 67.9; H, 4.6%); ^{31}P n.m.r. in $CDCl_3$ at 213 K, 40.8 (q) p.p.m., $J(P_AP_B)$ 27.1, $\delta(P_AP_B)$ 113.3 Hz [$\Lambda(1 \times 10^{-3}$ mol dm^{-3}) in CH_2Cl_2 = 30 S cm^2 mol^{-1}]. The complex $[Ru_2(CO)_2Cl_3(PPh_3)_4]Cl$ was also formed by shaking $[Ru(CO)Cl_2(HOMe)(PPh_3)_2]$ in either Me_2CO or EtOH for 3 h (^{31}P n.m.r. evidence) with or without free PPh_3 present. In these reactions, the $[Ru_2(CO)_2Cl_4(PPh_3)_3]$ isomeric mixture and trace amounts of $[\{Ru(CO)Cl_2(PPh_3)_2\}_2]$ were also found.

Tetraphenylarsonium carbonyl(trichloro)bis(triphenylphosphine)ruthenate(II)*–acetone* (1/1). The complex $[Ru(CO)Cl_2(HOMe)(PPh_3)_2]$ (0.10 g) was suspended in degassed Me_2CO (30 cm^3) and treated with a two-fold excess of $[AsPh_4]Cl{\cdot}HCl$ together with PPh_3 (*ca.* 0.01 g). The mixture was shaken for 4 h when orange yellow *crystals* of the product precipitated. These were filtered off, washed with water, MeOH, and diethyl ether, and dried *in vacuo* at 40 °C (0.13 g, 70%), m.p. 155—158 °C [ν(CO) at 1 918 cm^{-1}; ν(CO) (acetone) at 1 710 cm^{-1} (Nujol)] (Found: C, 64.1; H, 4.7; Cl, 9.0. Calc. for $C_{64}H_{56}AsCl_3O_2P_2Ru$: C, 64.0; H, 4.7; Cl, 8.9%) [$\Lambda(1 \times 10^{-3}$ mol dm^{-3}) in CH_2Cl_2 = 45 S cm^2 mol^{-1}].

(b) *Thiocarbonyl Complexes.—Dichloro*(NN-*dimethylformamide*)*thiocarbonylbis*(*triphenylphosphine*)*ruthenium*(II). The complex [{Ru(CS)Cl_2(PPh_3)$_2$}$_2$] (0.20 g) was heated under reflux in degassed *NN*-dimethylformamide (15 cm^3) under nitrogen for 3 h. The resulting yellow solution was reduced in volume and diethyl ether was added to precipitate the pale yellow *solid*, m.p. 168—170 °C [ν(CS) at 1 275 cm^{-1}, ν(CO) (dmf) at 1 640 cm^{-1}, ν(RuCl) at 325 cm^{-1} (Nujol)] (Found: C, 57.5; H, 4.5; N, 1.7. Calc. for $C_{40}H_{37}Cl_2NOP_2RuS$: C, 59.0; H, 4.6; N, 1.7%); ^{31}P n.m.r. ($CDCl_3$ at 303 K) 30.2 (s) p.p.m.

*Tri-μ-chloro-*a*-chloro-*g*-thiocarbonyl-tetrakis*(*triphenylphosphine*)*diruthenium*(II). The complexes [$RuCl_2$(PPh_3)$_3$] (0.19 g) and [Ru(CS)Cl_2(dmf)(PPh_3)$_2$] (0.16 g) were heated under reflux for 4 h in degassed Me_2CO (30 cm^3) under an atmosphere of nitrogen. On cooling the solution, the red *solid* was deposited together with some unchanged [Ru(CS)Cl_2(dmf)(PPh_3)$_2$]. Proof of the formation of (3) was obtained from the ^{31}P n.m.r. spectrum of the products in $CDCl_3$ at 298 K (see ref. 2).

Dichloro(*methanol*)*thiocarbonylbis*(*triphenylphosphine*)*ruthenium*(II). The complex [Ru(CS)Cl_2(dmf)(PPh_3)$_2$] was recrystallised from hot CH_2Cl_2–MeOH to give yellow *crystals* which were washed with MeOH, m.p. 182—184 °C (Found: C, 57.8; H, 4.5. Calc. for $C_{38}H_{34}Cl_2OP_2RuS$: C, 59.3; H, 4.4%); i.r. spectrum (Nujol) 3 460 and 1 030 cm^{-1} (co-ordinated MeOH), ν(CS) at 1 280 cm^{-1}, ν(RuCl) at 332 cm^{-1}; ^{31}P n.m.r. ($CDCl_3$ at 303 K) 30.7 (s) p.p.m.

*Tri-μ-chloro-*a*-chloro-*gh*-dithiocarbonyl-tris*(*triphenylphosphine*)*diruthenium*(II)*-dichloromethane* (2/1). The complex [Ru(CS)Cl_2(HOMe)(PPh_3)$_2$] was dissolved in CH_2Cl_2 and light petroleum (b.p. 60—80 °C) was added. The yellow solution was placed on a water-bath and the CH_2Cl_2 allowed to evaporate off slowly over a period of 24 h to give yellow *crystals* which were filtered off and washed with diethyl ether, m.p. 264 °C [ν(CS) at 1 300br cm^{-1} (Nujol)] (Found: C, 52.7; H, 3.7. Calc. for $C_{56.5}H_{46}Cl_5P_3Ru_2S_2$: C, 53.8; H, 3.6%). ^{31}P N.m.r. (in $CDCl_3$ at 213 K): isomer (5a) 49.7 (s) and 37.0 (q) p.p.m. (J_{AB} 26.0; δ_{AB} 15.0 Hz); isomers (5b) and (5c) 51.8 (s) and 35.8 (q) p.p.m. (J_{AB} 26.0; δ_{AB} 71.4 Hz) and a very weak singlet at 50.9 p.p.m. and weak resonances between 36 and 38 p.p.m.

Tri-μ-chloro-bis[*thiocarbonylbis*(*triphenylphosphine*)*ruthenium*(II)] *tetraphenylborate*. The [Ru_2(CS)$_2$$Cl_4$($PPh_3$)$_3$] isomeric mixture (0.08 g), Na[BPh_4] (0.022 g), and PPh_3 (0.018 g) were shaken in degassed CH_2Cl_2 (20 cm^3) under nitrogen for 48 h. The orange-yellow solution was evaporated to dryness and triturated with MeOH to give an orange-yellow *solid* which was filtered off and washed with water, MeOH, and diethyl ether, m.p. 118—120 °C [ν(CS) at 1 290 cm^{-1} (Nujol)] (Found: C, 66.5; H, 4.6. Calc. for $C_{93}H_{80}BCl_3P_4Ru_2S_2$: C, 66.7; H, 4.5%); ^{31}P n.m.r. (in $CDCl_3$ at 213 K) 37.5 (q) p.p.m., $J(P_AP_B)$ 27.0; $\delta(P_AP_B)$ 86.8 Hz [Λ(1×10^{-3} mol dm^{-3}) in CH_2Cl_2 = 32 S cm^2 mol^{-1}].

We thank Johnson, Matthey Ltd for generous loans of ruthenium(III) trichloride, the S.R.C. for the award of research studentships (to P. W. A. and W. J. S.), and Dr. A. S. F. Boyd for obtaining the ^{31}P n.m.r. spectra.

[6/613 *Received*, 31*st March*, 1976]