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 [RuCl₂(PPh₃)₃] with [Ru(CO)Cl₂(dmf)(PPh₃)₂] in acetone (1:1 molar ratio) (dmf = NN-dimethylformamide) gives a high yield of [(Ph₃P)₂CIRuCl₃Ru(CO)(PPh₃)₂]·2Me₂CO, supporting the mechanism proposed earlier for formation of the analogous thiocarbonyl complex. Extensions of this type of coupling reaction to form [(Ph₃P)₂BrRuBrCl₂Ru(CO)(PPh₃)₂]·Me₂CO and [(Ph₃P)₂ClRuBr₂ClRu(CO)(PPh₃)₂]·Me₂CO are also described. Recrystallisation of [Ru(CO)Cl2(dmf)(PPh3)2] from MeOH–CH2Cl2 gives [Ru(CO)Cl2(HOMe)(PPh3)2] (4), and prolonged refluxing of the latter in dichloromethane-light petroleum (b.p. 60-80 °C) produces displacement of a PPh₂ group with formation of an isomeric mixture of $[(Ph_3P)CI(OC)RuCl_3Ru(CO)(PPh_3)_2]$ (5). The same isomeric mixture, together with [{Ru(CO)Cl₂(PPh₃)₂}₂], is also formed by reaction of PPh₃ with [PPh₃(CH₂Ph)]- $[Ru(C_2H_8)(CO)Cl_3]$ (2:1 molar ratio). Treatment of (5) with Na[BPh_4] and PPh_3 in CH_2Cl_2 gives a high yield of $[(Ph_3P)_4(OC)RuCl_3Ru(CO)(PPh_3)_2][BPh_4]$ (6). This cation is also formed, together with (5), by prolonged shaking of (4) in ethanol, whereas treatment of (4) with [AsPh_4]Cl·HCl in acetone gives [AsPh_4][Ru(CO)Cl_3-(PPh₃)₂]·Me₂CO (7). Related complexes are described, starting from [Ru(CS)Cl₂(dmf)(PPh₃)₂]. Finally, all this information is used to suggest detailed rearrangement mechanisms in the [RuCl₂(PPh₃)₃]-CS₂, [PPh₃(CH₂Ph)]- $[\operatorname{Ru}(C_7H_8)(\operatorname{CO})CI_3]$ -2PPh₃, and the closely related $[\operatorname{Ru}X_2(\operatorname{PR}_3)_n]$ - $[\operatorname{Ru}_2X_3(\operatorname{PR}_3)_6]X$ (X = Cl or Br; n = 3 or 4) systems.

In an earlier paper¹ we examined the reaction of [RuCl₂(PPh₃)₃] with carbon disulphide and showed that the three products [{Ru(CS)Cl₂(PPh₃)₂}₂] (1), [Ru(η^2 -CS₂)- $Cl(PPh_3)_3$ 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)Cl₂(PPh₃)₂]' possibly formed by elimination of PPh₃S from (2)] with [RuCl₂-(PPh₃)₃]. A competing reaction was dimerisation of $[\operatorname{Ru}(\operatorname{CS})\operatorname{Cl}_2(\operatorname{PPh}_3)_2]$ ' to give (1).

Because of our inability to isolate the '[Ru(CS)Cl₂- $(PPh_3)_2$]' 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 detail⁴ 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 [RuCl₂(PPh₃)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 [RuCl₂(PPh₃)₃] (1:1 molar ratio), deep red crystals of [(Ph₃P)₂ClRuCl₃Ru- $(CO)(PPh_3)_2$]·2Me₂CO [v(CO) at 1 951 cm⁻¹] were isolated in high vield. Confirmation of this formulation is based on the fact that it is isomorphous with [(Ph₃P)₂ClRuCl₃Ru-(CS)(PPh₃)₂] (3), and its ¹H-decoupled ³¹P n.m.r. spectrum in CDCl₃ 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_a groups *cis* to Cl⁻ and the lower-frequency quartet from the two PPh₃ groups cis to CS. The values of ${}^{2}I(PP)$ (37.5 and 24.6 Hz respectively) are consistent with those observed elsewhere ' 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 [RuBr₂(PPh₃)₃] and [Ru(CO)Cl₂(dmf)-(PPh₃)₂] in acetone (1:1 molar ratio) gave deep red crystals, which analyse closely for the expected [(Ph₃P)₂BrRuBrCl₂-Ru(CO)(PPh₃)₂]·Me₂CO [v(CO) at 1 952 cm⁻¹]. Similarly, reaction of [RuCl₂(PPh₃)₃] and [RuBr₂(CO)(dmf)(PPh₃)₂]⁶ produced a red solid, analysing closely for the expected $[(Ph_3P)_2ClRuBr_2ClRu(CO)(PPh_3)_2]$ ·Me₂CO $[\nu(CO)$ at 1953 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 v(RuCl)]. However, the ³¹P n.m.r. spectra in CDCl₃ at 303 or 213 K were identical, consisting of two complex patterns of resonances between 46-52 and

⁴ Some of this work has been reported in a preliminary communication: P. W. Armit and T. A. Stephenson, J. Organometal-lic Chem., 1974, 73, C33. ⁵ T. A. Stephenson and G. Wilkinson J. Lawra, Nuclear Chem.

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

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

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

[†] A related reaction is the formation of [(Ph₃P)₂ClRuCl₃Ru- $(PPh_3)_2(PF_3)$ from $[RuCl_2(PPh_3)_3]$ and PF_3 (2:1 molar ratio) ⁸ which, presumably, involves initial formation of an intermediate [RuCl₂(PPh₃)₂(PF₃)],' followed by coupling with unsuch as ' changed $[\operatorname{RuCl}_2(\operatorname{PPh}_3)_2]$. Similarly, coupling of species such as $[\operatorname{RuCl}_2(\operatorname{PPh}_3)_2]$. Similarly, coupling of species such as $[\operatorname{RuCl}_2(\operatorname{N}_2)(\operatorname{PPh}_3)_2]$ and $[\operatorname{RuCl}_2(\operatorname{PPh}_3)_3]$ could be invoked to explain the formation of $[(\operatorname{Ph}_3\operatorname{P}_2\operatorname{CIRuCl}_3\operatorname{Ru}(\operatorname{N}_2)(\operatorname{PPh}_3)_2]$ from [RuCl₂(PPh₃)₄] and N₂ in a reverse-osmosis cell.⁹

¹ Part I, 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.

 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)Cl₂(dmf)(PPh₃)₂] in solution in the absence of $[RuCl_2(PPh_3)_3]$ is also of some interest. Thus, recrystallisation of this product from MeOH-CH₂Cl₂ under mild conditions was claimed to give the five-coordinate [Ru(CO)Cl₂(PPh₃)₂],⁶ but our recent reinvestigation 10 of this product indicates that it should be reformulated as the six-co-ordinate [Ru(CO)Cl₂(HOMe)- $(PPh_3)_2$ [v(CO) at 1 940 cm⁻¹ (CH₂Cl₂)]. On the evidence of far-i.r. spectra [v(RuCl) at ca. 330 cm⁻¹] and ³¹P n.m.r. spectra at 303 K in CDCl₃ (singlet at ca. 34 p.p.m.), both these solvates are considered to have configuration (4) with trans-chlorides and trans-phosphines.



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 CH₂Cl₂

Three geometrical isomers are possible for (5) and the ³¹P 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 ${}^{2}I(PP)$ values (ca. 25 Hz) are consistent with cis-phosphines bound to Ru^{II}. Support for this interpretation comes from the

TABLE	E 1	
Assignment of isomeric forms of $[(Ph_3P)Cl(OC)R$	$uCl_3Ru(CO)(PPh_3)_2$ to ^{31}P	n.m.r. resonances
³¹ P n.m.r. (CDCl ₃ at 213 K), δ/p.p.m		
Taoman .	Charles 111	

Isomer
Isomer
Singlet position
Singlet position
Singlet position
AB Position
AB Position
AB Position

$$AB Position$$

 $AB Position$
 $AB Position$

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)Cl₂- $(PPh_3)_2$] isomers, formed by dimerisation of (4; S = MeOH). However, examination of the ³¹P n.m.r. spectrum of this material clearly shows that this double-chloridebridged dimer is not formed to any significant extent. At 213 K in CDCl₃ (Figure 1) the ³¹P n.m.r. spectrum consisted

† 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 ³¹P 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.

very recent synthesis by similar methods of the related $[(F_3P)(Ph_3P)CIRuCl_3Ru(PPh_3)_2(PF_3)]$, where a combination of ³¹P and ¹⁹F 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

A reinterpretation of the nature of the products from the reaction of [PPh3(CH2Ph)][Ru(C7H8)(CO)Cl3] and PPh3 (1:2 molar ratio) in CH₂Cl₂ is also appropriate at this junction. Earlier,¹⁰ we formulated the product as a mixture of [{Ru(CO)Cl₂(PPh₃)₂}₂] isomers (which could not

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



δ/p.**p.m**

FIGURE 1 Phosphorus-31 n.m.r. spectrum in CDCl₃ at 213 K of the product from reaction of [Ru(CO)Cl₂(HOMe)(PPh₃)₂], and dichloromethane-light petroleum (b.p. 60—80 °C)

shows that in addition to the doubly-bridged isomers (strong singlets at 17.2 and 25.5 p.p.m. *cf.* [{Ru(CS)Cl₂-(PPh₃)₂]₂] (1),^{1,*} 31.3 p.p.m.) there is a substantial amount of the [(Ph₃P)Cl(OC)RuCl₃Ru(CO)(PPh₃)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).

When $[Ru(CO)Cl_2(HOMe)(PPh_3)_2]$ was shaken for several hours in more polar solvents, such as Me₂CO or EtOH, with an equimolar amount of PPh₃ a pale yellow solid was precipitated, whose i.r. spectrum (Nujol) contained two $\nu(\rm CO)$ bands at 1978br and 1928 cm^-1. The $^{31}\rm P$ n.m.r. spectra at 243 K in CDCl₃ reveal the products to be mixtures containing both $[Ru(CO)Cl_2(PPh_3)_2S]$ [S = MeOH or Me₂CO (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)Cl₂(PPh₃)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 Me₂CO. The same mixture of products was obtained when the reaction was repeated without free PPh3 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

* In ref. 1, a ³¹P 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 PPh₃O.

additional AB quartet in the ³¹P 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 PPh₃ and Na[BPh₄] and shaken in either CH₂Cl₂, Me₂CO, 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) $[\nu(CO)$ at 1 976 cm⁻¹ (Nujol)]. Support for this formulation is obtained from the ³¹P n.m.r. spectrum in CDCl₃ 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 $[(Ph_3P)_2CIRuCl_3Ru(CO)(PPh_3)_2]$, 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 CH₂Cl₂ and its far-i.r. spectrum showed no band indicative of terminal $\nu(RuCl)$. Thus, this evidence clearly indicates that the cationic dimer (6) is formed both directly from



δ/p.p.m

FIGURE 2 Phosphorus-31 n.m.r. spectrum in CDCl₃ at 303 K of the product from reaction of [PPh₃(CH₂Ph)][Ru(C₇H₈)(CO)Cl₃] and 2 PPh₃

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.



 \dagger 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.

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Finally, when $[Ru(CO)Cl_2(HOMe)(PPh_3)_2]$ (4) was treated with $[AsPh_4]Cl$ ·HCl in Me₂CO the anionic $[AsPh_4][Ru(CO)-Cl_3(PPh_3)_2]$ ·Me₂CO (7) [v(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 ³¹P n.m.r. studies. However, the far-i.r. spectrum of (7) contained a strong peak at 320 cm⁻¹ indicative of a *trans*-RuCl₂ 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).

Thiocarbonyl Complexes.—The success of coupling [Ru-(CO)Cl₂(dmf)(PPh₃)₂] and [RuCl₂(PPh₃)₃] to give a high yield of [Ru₂(CO)Cl₄(PPh₃)₄] strongly supports the proposed RuCl₃Ru(CS)(PPh₃)₂)·0.5CH₂Cl₂. A small amount of this complex (Me₂CO solvate) has been prepared previously ¹ by shaking [{Ru(CS)Cl₂(PPh₃)₂}] in degassed Me₂CO for several days. Unlike the analogous CO complex, the ³¹P 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 ³¹P 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 $[\operatorname{Ru}_2(\operatorname{CS})\operatorname{Cl}_4(\operatorname{PPh}_3)_3]$ complexes has been produced was obtained by its reaction with Na[BPh₄] and PPh₃ in $\operatorname{CH}_2\operatorname{Cl}_2$ which gave a high yield of $[(\operatorname{Ph}_3\operatorname{P})_2(\operatorname{SC})\operatorname{RuCl}_3\operatorname{Ru}(\operatorname{CS})-(\operatorname{PPh}_3)_2][\operatorname{BPh}_4]$ (6). The ³¹P n.m.r. spectrum in CDCl₃ at 213 K consisted of a sharp quartet centred at 37.5 p.p.m. $[J(\operatorname{PP}) 27.0, \delta_{AB} 86.8 \text{ Hz}]$. A small amount of this cation, together with the $[\operatorname{Ru}_2(\operatorname{CS})\operatorname{Cl}_4(\operatorname{PPh}_3)_3]$ isomeric mixture, was also formed when $[\operatorname{Ru}(\operatorname{CS})\operatorname{Cl}_2(\operatorname{HOMe})(\operatorname{PPh}_3)_2]$ was shaken in EtOH with an equimolar amount of PPh₃ for several hours.

DISCUSSION

A summary of the preparative methods for the various dimeric complexes of Ru^{II} reported in this paper is given

TABLE 2

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

 $[\operatorname{RuYCl}_{2}(\operatorname{HOMe})(\operatorname{PPh}_{3})_{2}] \xrightarrow{(i)-(iii)} \operatorname{Mainly} [\operatorname{Ru}_{2}Y_{2}Cl_{4}(\operatorname{PPh}_{3})_{3}] \text{ isomeric mixture and, for } Y = CO, \text{ trace amounts of } [\{\operatorname{RuYCl}_{2}(\operatorname{PPh}_{3})_{2}\}_{2}] \\ [\operatorname{RuYCl}_{2}(\operatorname{HOMe})(\operatorname{PPh}_{3})_{2}] \xrightarrow{(iv)} \operatorname{Mainly} [\operatorname{Ru}Y_{2}Cl_{2}(\operatorname{PPh}_{3})_{3}] \text{ isomeric mixture and } [\operatorname{Ru}_{2}Y_{2}Cl_{3}(\operatorname{PPh}_{3})_{4}]CI \text{ and, } for Y = CO, \text{ trace amounts of } [\{\operatorname{RuYCl}_{2}(\operatorname{PPh}_{3})_{2}\}_{2}] \\ [\operatorname{RuCl}_{2}(\operatorname{PPh}_{3})_{3}] + \operatorname{CS}_{2} \xrightarrow{(iii)} [\operatorname{Ru}_{2}(\operatorname{CS})Cl_{4}(\operatorname{PPh}_{3})_{4}] (39\%), \quad [\operatorname{Ru}(\eta-\operatorname{CS}_{2})\operatorname{Cl}(\operatorname{PPh}_{3})_{3}]CI (3\%)_{1}, \quad [\operatorname{Ru}(\eta-\operatorname{CS}_{3})\operatorname{Cl}(\operatorname{PPh}_{3})_{3}]CI (3\%)_{1}, \quad [\operatorname{Ru}(\operatorname{CS})Cl_{2}-\operatorname{CS})CI(\operatorname{PPh}_{3})_{3}]CI (3\%)_{1}, \quad [\operatorname{Ru}(\eta-\operatorname{CS}_{3})\operatorname{CL}(\operatorname{PDh}_{3})_{3}]CI (3\%)_{1}, \quad [\operatorname{Ru}(\operatorname{CS})CL_{2}-\operatorname{CS})CI(\operatorname{PDh}_{3})_{3}]CI (3\%)_{1}, \quad [\operatorname{Ru}(\eta-\operatorname{CS}_{3})\operatorname{CL}(\operatorname{PDh}_{3})_{3}]CI (3\%)_{1}, \quad [\operatorname{Ru}(\eta-\operatorname{CS}_{3})_{3}]CI (3\%)_{1}, \quad [\operatorname{Ru}$

 $[PPh_{3}(CH_{2}Ph)][Ru(C_{7}H_{8})(CO)Cl_{3}] + 2PPh_{3} \xrightarrow{(1), (11)} [Ru_{2}(CO)_{2}Cl_{4}(PPh_{3})_{3}] \text{ isomeric mixture } (33\%) \text{ and } [\{Ru(CO)Cl_{2}(PPh_{3})_{2}\}_{2}] \xrightarrow{(67\%)} (67\%)$

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 $[RuCl_2(PPh_3)_2]$ -CS₂ reaction, we found that reaction of $[{Ru(CS)Cl_2(PPh_3)_2}]$ with refluxing dmf gave $[Ru(CS)Cl_2(dmf)(PPh_3)_2]$ [ν (CS) at 1 275 cm⁻¹ (Nujol)], whose ³¹P n.m.r. spectrum at 303 K in CDCl₃ (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 Me₂CO (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 fari.r. and ³¹P 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 $[(Ph_3P)Cl(SC)-$ 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.

We suggest that the mode of dimerisation is very dependent on the stereochemistry of either the starting material or the reactive intermediate. For $[RuYCl_2-(HOMe)(PPh_3)_2]$, ³¹P 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 PPh₃ 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*-PPh₃ groups. Support for this statement comes from the X-ray structure

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of [RuCl₂(PPh₃)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 [{RuCl₂(PPh₃)₂}₂], shown by ³¹P n.m.r. studies ^{2,7} to contain cis-PPh₃ groups. Therefore, a likely structure for the five-co-ordinate intermediate in the [RuCl2-(PPh₃)₃]-CS₂ reaction is (8), formed by elimination of PPh_3S from either $[Ru(\eta^2-CS_2)Cl(PPh_3)_3]Cl$ and/or $[RuCl_2(PPh_3)_3(SCS)]$ (see Scheme 1 *).

A similar mechanism (Scheme 2) can be proposed to explain the products from the [PPh₃(CH₂Ph)][Ru(C₇H₈)-(CO)Cl₃]-2PPh₃ reaction. As discussed fully in ref. 10, it is reasonable to postulate that an intermediate containing an η^2 -C₇H₈ group is first formed and this then reacts further with PPh₃ to give [Ru(CO)Cl₃- $(PPh_3)_2$ of structure (9). Analogous complexes $[PPh_3]$ -(CH₂Ph)][Ru(CO)Cl₃L₂] of this stereochemistry have been characterised for $L = AsPh_3$, SMe₂, 2,2'-bipyridyl, etc.¹⁰ However, for (9) the combination of the high

It is then proposed that (8) will undergo three com-



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 $(-Cl^-)$

peting 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)Cl₂- $(PPh_3)_2$ [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 dimerse with concomitant chloride-ion displacement to give [Ru₂(CS)₂- $Cl_3(PPh_3)_4$ [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)].

trans influence of PPh3, 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)Cl₂(PPh₃)₂] (10) containing cis-PPh₃ groups. As for the analogous CS intermediate, this can either dimerise without phosphine loss to form [{Ru(CO)Cl₂- $(PPh_3)_{2}_{2}$ or isomerise to a species (11) with transphosphines which, in turn, dimerises with concomitant PPh₃ loss to form [Ru₂(CO)₂Cl₄(PPh₃)₃]. In this instance the proportion of the latter is considerably higher (33%) than in the [RuCl₂(PPh₃)₃]-CS₂ reaction, because there is no [RuCl₂(PPh₃)₃] present to remove

- 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.

- A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, 14, 365.
 For a full discussion of ligand cone angles see C. A. Tolman, J. Amer. Chem. Soc., 1970, 92, 2956.

^{*} Isomers (8), (10), and (11) are written with essentially squarepyramidal 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 d⁶ complexes.

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

of Ru-L and Ru-X bonds and on the polarity of the solvent medium.

The reason why five-co-ordinate complexes (or sixco-ordinate solvates) with trans-PPh₃ groups dimerise to form triple-chloride-bridged complexes with concomitant PPh₃ loss whereas those with *cis*-PPh₃ groups form double-chloride-bridged dimers without PPh₃ loss is attributed to the high *trans* influence of PPh₃ and the consequent electronic instability of *trans*-Ru(PPh₃)₂ compared to *cis*-Ru(PPh₃)₂ arrangements.* The driving force for all these rearrangements is presumably the 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 ³¹P n.m.r. AB₂ 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 $[{RuCl(HOEt)_2(PEtPh_2)_3}_2]Cl_2$. The disappearance of this ³¹P n.m.r.



SCHEME 2 (a) PPh₃; (b) $-C_7H_8$; (c) $-Cl^-$; (d) dimerisation; (e) isomerisation; (f) dimerisation ($-PPh_3$)

high stability of six-co-ordinate ruthenium(II) $(4d^6)$ complexes.

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 = PR₃; 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 pattern above 220 K in CDCl_3 with formation of $[\text{RuCl}_2(\text{PEtPh}_2)_3], [\text{Ru}_2\text{Cl}_4(\text{PEtPh}_2)_5], [\text{Ru}_2\text{Cl}_3(\text{PEtPh}_2)_6]$ -Cl, and PEtPh_2^2 is then readily rationalised by postulating nucleophilic displacement of solvent by chloride ion to form $[\text{RuCl}_2(\text{PEtPh}_2)_3]$, 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.

* 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 250-4000 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% H₃PO₄. 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 $[{Ru(CS)-Cl_2(PPh_3)_2}_2]$ were prepared as described elsewhere.

(a) Carbonyl Complexes.—Tri- μ -chloro-a-carbonyl-g-chlorotetrakis(triphenylphosphine)diruthenium(II)-acetone (1/2). The complexes [RuCl₂(PPh₃)₃] (0.12 g) and [Ru(CO)Cl₂-(dmf)(PPh₃)₂] (0.10 g) were heated under reflux for 2.5 h in degassed Me₂CO (30 cm³) 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 cm³ (0.13 g, 69%), m.p. 170— 171 °C (decomp.) [v(CO) at 1 951 cm⁻¹, v(CO) (acetone) at 1 710 cm⁻¹ (Nujol)] (Found: C, 61.7; H, 4.7; Cl, 9.4. Calc. for C₇₉H₇₂Cl₄O₃P₄Ru₂: C, 61.6; H, 4.8; Cl, 9.3%); ³¹P n.m.r. (CDCl₃ at 298 K) 48.0 (q) and 40.3 (q) p.p.m. [J(P¹P²) 37.5, J(P³P⁴) 24.6; δ (P¹P²) 97.7, δ (P³P⁴) 74.2 Hz].

μ-Bromo-di-μ-chloro-a-bromo-g-carbonyl-tetrakis(triphenylphosphine)diruthenium(II)-acetone (1/1). The complex [RuBr₂(PPh₃)₃] (0.12 g) and [Ru(CO)Cl₂(dmf)(PPh₃)₂] (0.08 g) were heated together under reflux for 3 h in degassed Me₃CO (30 cm³) under an atmosphere of nitrogen. The solution was then cooled and the deep red *precipitate* was filtered aff and washed with diethyl ether (0.10 g, 56%), m.p. 159-160 °C (decomp.) [v(CO) at 1 952 cm⁻¹; v(CO) (acetone) at ! 710 cm⁻¹ (Nujol)] (Found: C, 59.0; H, 4.4; Br, 10.0; Cl, 4.6. Calc. for C₇₆H₆₆Br₂Cl₂O₂P₄Ru₂: 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 [RuCl₂(PPh₃)₃] (0.11 g) and [RuBr₂(CO)(dmf)-(PPh₃)₂] (0.10 g) to give deep red crystals of the product (0.085 g, 51%), m.p. 160—162 °C (decomp.) [v(CO) at 1 953 cm⁻¹; v(CO) (acetone) at 1 710 cm⁻¹ (Nujol)] (Found: C, 58.5; H, 4.3; Br, 10.0; Cl, 4.6. Calc. for C₇₆H₆₆Br₂-Cl₂O₂P₄Ru₂: 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.

 $\label{eq:carbonyldichloro(methanol)bis(triphenylphosphine)ruthen-ium(11). The complex [Ru(CO)Cl_2(dmf)(PPh_3)_2] ^6 [^{31}P n.m.r. (CDCl_3 at 303 K) 33.9 (s) p.p.m.; v(RuCl) at 330 cm^{-1}] was recrystallised from hot CH_2Cl_2-MeOH to give the$

yellow *product* which was washed with diethyl ether (Found: C, 60.3; H, 4.3; Cl, 9.1. Calc. for $C_{38}H_{34}Cl_2$ - $O_2P_2Ru:$ C, 60.5; H, 4.5; Cl, 9.4%); ³¹P n.m.r. (CDCl₃ at 303 K) 34.5 (s) p.p.m. [ν (CO) at 1 931 and 1 921 cm⁻¹ (Nujol); 1 940 cm⁻¹ (CH₂Cl₂)]; ν (RuCl) at 333 cm⁻¹. At 213 K, singlets in the ³¹P 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(triphenylphos-The complex [Ru(CO)Cl₂phosphine)diruthenium(II). (HOMe)(PPh₃)₂] was dissolved in CH₂Cl, 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 CH₂Cl₂ to evaporate slowly. The resulting orange solid was redissolved in CH₂Cl₂, light petroleum (b.p. 60-80 °C) was added, and the process repeated to give pale orange crystals of the *broduct* which were filtered off and washed with EtOH and diethyl ether, m.p. 247 °C [v(CO) at 1 960br cm⁻¹ (Nujol)] (Found: C, 58.7; H, 4.1. Calc. for C₅₆H₄₅Cl₄- $O_2P_3Ru_2$: C, 56.7; H, 3.8%); ³¹P n.m.r. (CDCl₃ 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)Cl₂(HOMe)(PPh₃)₂] (see Figure 1).

Reaction of [PPh₃(CH₂Ph)][Ru(C₇H₈)(CO)Cl₃] and PPh₃. The complex (0.24 g) and PPh₃ (0.20 g, 1:1 molar ratio) were dissolved in CH₂Cl₂ (100 cm³) 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 [PPh₃(CH₂Ph)]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)], ³¹P n.m.r. (CDCl₃ at 303 K) as shown in Figure 2 (Found: C, 59.8; H, 4.2. Calc. for mixture of [{Ru(CO)Cl₂(PPh₃)₂] and [(Ph₃P)Cl-(OC)RuCl₃Ru(CO)(PPh₃)₂] (67:33): C, 59.8; H, 4.0%).

 $Tri-\mu-chloro-bis [carbonylbis (triphenylphosphine) ruth enium-bis [carbonylbis (triphenylbis (triphenylphosphine) ruth enium-bis [carbonylbis (triphenylbis (trip$ (II)] tetraphenylborate. The [(Ph₃P)Cl(OC)RuCl₃Ru(CO)-(PPh₃)₂] isomeric mixture (0.12 g), Na[BPh₄] (0.034 g), and PPh_{3} (0.026 g) were shaken together in degassed $CH_{2}Cl_{2}$ (25 cm³) 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 [v(CO) at 1 976 cm⁻¹ (Nujol)] (Found: C, 66.7; H, 4.9. Calc. for C₉₈H₈₀BCl₃O₂P₄Ru₂: C, 67.9; H, 4.6%); ³¹P n.m.r. in CDCl₃ at 213 K, 40.8 (q) p.p.m., $J(P_AP_B)$ 27.1, $\delta(P_AP_B)$ 113.3 Hz [$\Lambda(1 \times 10^{-3} \text{ mol dm}^{-3})$ in $CH_2Cl_2 = 30 \text{ S cm}^2$ mol⁻¹]. The complex [Ru₂(CO)₂Cl₃(PPh₃)₄]Cl was also formed by shaking [Ru(CO)Cl₂(HOMe)(PPh₃)₂] in either Me₂CO or EtOH for 3 h (³¹P n.m.r. evidence) with or without free PPh₃ 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)Cl₂-(HOMe)(PPh₃)₂] (0.10 g) was suspended in degassed Me₂CO (30 cm³) and treated with a two-fold excess of [AsPh₄]Cl·HCl together with PPh₃ (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 [v(CO) at 1 918 cm⁻¹; v(CO) (acetone) at 1 710 cm⁻¹ (Nujol)] (Found: C, 64.1; H, 4.7; Cl, 9.0. Calc. for C₆₄H₅₆AsCl₃O₂P₂Ru: C, 64.0; H, 4.7; Cl, 8.9%) [A(1 × 10⁻³ mol dm⁻³) in CH₂Cl₂ = 45 S cm² mol⁻¹]. (b) Thiocarbonyl Complexes.—Dichloro(NN-dimethylformamide)thiocarbonylbis(triphenylphosphine)ruthenium(II). The complex [{Ru(CS)Cl₂(PPh₃)₂}] (0.20 g) was heated under reflux in degassed NN-dimethylformamide (15 cm³) 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 C₄₀H₃₇Cl₂NOP₂RuS: C, 59.0; H, 4.6; N, 1.7%); ³¹P n.m.r. (CDCl₃ at 303 K) 30.2 (s) p.p.m.

 $Tri-\mu$ -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 Me₂CO (30 cm³) 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 ³¹P n.m.r. spectrum of the products in CDCl₃ at 298 K (see ref. 2).

Dichloro(methanol) thio carbonylbis(triphenylphosphine)-

ruthenium(11). 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), v(CS) at 1 280 cm⁻¹, v(RuCl) at 332 cm⁻¹; ³¹P n.m.r. (CDCl₃ at 303 K) 30.7 (s) p.p.m.

 $Tri-\mu$ -chloro-a-chloro-gh-dithiocarbonyl-tris(triphenylphosphine)diruthenium(II)-dichloromethane (2/1). The complex

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[Ru(CS)Cl₂(HOMe)(PPh₃)₂] was dissolved in CH₂Cl₂ and light petroleum (b.p. 60—80 °C) was added. The yellow solution was placed on a water-bath and the CH₂Cl₂ 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 [v(CS) at 1 300br cm⁻¹ (Nujol)] (Found: C, 52.7; H, 3.7. Calc. for C_{56.5}H₄₆Cl₅P₃Ru₂S₂: C, 53.8; H, 3.6%). ³¹P N.m.r. (in CDCl₃ 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 [Ru₂(CS)₂Cl₄(PPh₃)₃] isomeric mixture (0.08 g), Na[BPh₄] (0.022 g), and PPh₃ (0.018 g) were shaken in degassed CH₂Cl₂ (20 cm³) 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 C₉₈H₈₀BCl₃P₄Ru₂S₂: C, 66.7; H, 4.5%); ³¹P n.m.r. (in CDCl₃ 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 CH₂Cl₂ = 32 S cm² 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 ³¹P n.m.r. spectra.

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

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