New Thiocarbonyl Complexes of Ruthenium

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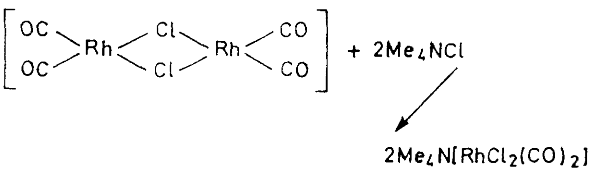
Reaction of the complex $[RuCl_2(CS)(PPh_3)_2]_2$, (I), with MCl–HCl in acetone leads to chloride-bridge cleavage with formation of $M[RuCl_3(CS)(PPh_3)_2]$ ($M = Ph_4As^+$, $Ph_3(PhCH_2)P^+$, or Et_4N^+), (II). A reinvestigation of the reaction between the complex $[RuCl_2(PPh_3)_3]$ and CS_2 reveals that, in addition to the previously reported $[RuCl(\eta\text{-}CS_2)(PPh_3)_3]Cl$ and (I), another thiocarbonyl complex, (III), with very similar physicochemical properties to (I) is also formed. Full analytical data and ^{31}P n.m.r. studies, together with an *X*-ray crystallographic study, show that complex (III) is the tri-μ-chloro-species $[(PPh_3)_2ClRuCl_3Ru(CS)(PPh_3)_2]$. Although no evidence has been found for conversion of complex (I) into (III), prolonged shaking of an acetone solution of (I) gives a small amount of $[(PPh_3)(CS)ClRuCl_3Ru(CS)(PPh_3)_2],Me_2CO$, (IV). Reaction of complex (III) with concentrated hydrochloric acid gives paramagnetic $[(PPh_3)Cl_2RuCl_3Ru(CS)(PPh_3)_2],2Me_2CO$, (V), which contains ruthenium in formal oxidation states of (III) and (II).

THERE are now a large number of publications discussing syntheses and characterisation of neutral complexes of ruthenium(II), particularly those with ligands such as tertiary phosphines, carbonyl, and various organic molecules. Recent years have also produced an increasing amount of work on cationic ruthenium(II) complexes containing these types of ligand.[1] However, relatively few anionic ruthenium(II) complexes of this type have been prepared other than those containing nitrosyl[2] and, more recently, carbonyl groups, *e.g.* $[RuX_3(CO)_3]^-$,[3] $[RuX_4(CO)_2]^{2-}$,[3-5] and $[RuX_4CO(H_2O)]^{2-}$ (X = Cl, Br, or I).[3,6] In particular, only three papers on anionic tertiary phosphine (or phosphite) complexes of ruthenium(II) appear to have been published, none of which involve ' conventional ' methods of preparation; *e.g.* the well known complex $[Ru_2Cl_3L_6]Cl$,[7] on heating in methyl acetate at 60 °C, gives $[Ru_2Cl_3L_6][RuCl_3L_3]$ ($L = PEt_2Ph$).[8] Similar diamagnetic complexes have been reported for the ligands $L = P(OEt)_3$, $P(OMe)Ph_2$, and $P(OEt)_2Ph$, obtained by direct reaction of $RuCl_3$ with L (although the authors inadvertently formulated them as $[RuCl_4L_2]^-$ anions, which would be paramagnetic[9]). A recent note[10] gives the results of a reinvestigation of the reaction between the complex $[Ru(CO)_3(PPh_3)_2]$ and methyl iodide which, instead of the previously reported $[Ru(CO)_2(PPh_3)_2I(Me)]$, gives $PPh_3Me[RuI_3(CO)_2PPh_3]$. The same anionic complex could be made from $[RuI_2(CO)_2(PPh_3)_2]$ and methyl iodide.

Several years ago, one of us[11] reported that a convenient synthesis of the ruthenium(III) anions $[RuX_4L_2]^-$ (X = Cl or Br; $L = PPh_3$, $AsPh_3$, *etc.*) was through methanol displacement by halide ion from the complex $[RuX_3L_2MeOH]$. Similar ruthenium(III) anions with L = pyridine (py),[12] or aniline[13] or L_2 = ethylenediamine (en),[14] 2,2′-bipyridyl (bipy),[15] and *o*-phenylenebis-(dimethylarsine)[16] are also known. Unfortunately, our attempts to prepare the corresponding $[RuX_4(PPh_3)_2]^{2-}$ ions by reaction of $[RuX_2(PPh_3)_{3\text{ or }4}]$ with Ph_4AsX–HX also gave $[RuX_4(PPh_3)_2]^-$.[11] [The detailed mechanism of this apparent ' oxidation ' on addition of hydrogen halides is not known at present although a ruthenium(IV) hydrido-intermediate may be involved.] An alternative route used successfully in rhodium and platinum chemistry to synthesise anionic complexes is by cleavage of halide-bridged dimeric species with halide ion, *e.g.* as in eqation (1).[17] We have recently reported the use of this type of reaction to synthesise the first anionic ruthenium diene complexes $[RuX_3(CO)(C_7H_8)]^-$ (X = Cl or Br; C_7H_8 = bicyclo[2.2.1]hepta-2,5-diene) *via* $[RuX_2CO(C_7H_8)]_n$.[18] These complexes are very useful precursors for the preparation of a range of new anionic complexes of type $[RuX_3COL_2]^-$ ($L = AsPh_3$, $SbPh_3$, py, Me_2S, CH_2CHCN, *etc.*), although, to date, attempts to prepare tertiary phosphine anions by this method have been unsuccessful; instead complexes such



(1)

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[1] For example, see W. Hieber, V. Frey, and P. John, *Chem. Ber.*, 1967, **100**, 1961; G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2146; P. G. Douglas, R. D. Feltham, and H. G. Metzger, *J. Amer. Chem. Soc.*, 1971, **93**, 84; R. A. Zelonka, and M. C. Baird *Canad. J. Chem.*, 1972, **50**, 3063; B. F. Cavit, K. R. Grundy, and W. R. Roper, *J.C.S. Chem. Comm.*, 1972, 60; J. R. Sanders, *J.C.S. Dalton*, 1973, 743; L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *ibid.*, p. 1770.

[2] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1967, 1144; M. Mukaida, *Bull. Chem. Soc. Japan*, 1970, **43**, 3805 and references therein.

[3] M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372.

[4] J. Halpern, B. R. James, and A. L. W. Kemp, *J. Amer. Chem. Soc.*, 1966, **88**, 5142.

[5] R. Colton and R. H. Farthing, *Austral. J. Chem.*, 1967, **20**, 1283.

[6] J. Halpern and A. L. W. Kemp, *J. Amer. Chem. Soc.*, 1966, **88**, 5147.

[7] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

[8] R. H. Prince and K. A. Raspin, *J. Inorg. Nuclear Chem.*, 1969, **31**, 695; K. A. Raspin, *J. Chem. Soc.* (*A*), 1969, 461.

[9] B. Jezowska-Trzebiatowska, H. Ratajczak, P. Sobota, and R. Tyka, *Bull. Acad. polon. Sci.*, *Ser. Sci. chim.*, 1972, **20**, 869.

[10] J. Jeffery and R. J. Mawby, *J. Organometallic Chem.*, 1972, **40**, C42.

[11] T. A. Stephenson, *J. Chem. Soc.* (*A*), 1970, 889.

[12] J. Souček, *Coll. Czech. Chem. Comm.*, 1962, **27**, 960

[13] D. L. Key, L. F. Larkworthy, and J. E. Salmon, *J .Chem. Soc.* (*A*), 1971, 2583.

[14] J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1967, 546.

[15] F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Austral. J. Chem.*, 1963, **16**, 42.

[16] R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 1958, 567, 572.

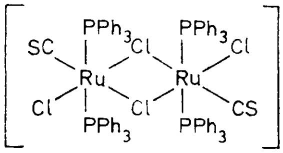
[17] L. M. Vallarino, *Inorg. Chem.*, 1965, **4**, 161; D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.

[18] T. A. Stephenson, E. S. Switkes, and L. Ruiz-Ramirez, *J.C.S. Dalton*, 1973, 2112.

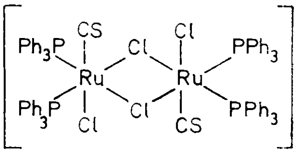
as $[\mathrm{RuCl_2CO(PPh_3)_2}]_2$ and $[\mathrm{RuCl_2(PMe_2Ph)_2(C_7H_8)}]$ are preferentially formed.[19] However, another halide-bridged dimer already containing triphenylphosphine groups is $[\mathrm{RuCl_2(CS)(PPh_3)_2}]_2$, (I), prepared by Gilbert *et al.* from $[\mathrm{RuCl_2(PPh_3)_3}]$ and $\mathrm{CS_2}$.[20] In the present paper, reactions of complex (I) with halide ion are described, together with results of a careful reinvestigation of the $[\mathrm{RuCl_2(PPh_3)_3}]$–$\mathrm{CS_2}$ reaction. A preliminary account of the first part of this work has been presented elsewhere.[21]

RESULTS AND DISCUSSION

In accordance with the method of Gilbert *et al.*,[20] the complex $[\mathrm{RuCl_2(PPh_3)_3}]$ [22] in carbon disulphide was heated under reflux under an atmosphere of nitrogen for 5 min to give a deep red solution. After cooling the solution, filtration gave a small amount of a dark red, crystalline, solid readily identified as $[\mathrm{RuCl}(\eta\text{-}\mathrm{CS_2})(\mathrm{PPh_3})_3]\mathrm{Cl}$ (*ca.* 8% yield). The red filtrate was concentrated *in vacuo* and then treated with excess of diethyl ether,* giving a purple-red precipitate and red ethereal solution. The precipitate was well washed with diethyl ether and dried *in vacuo* (*ca.* 16% yield). This precipitate is almost certainly a sample of the complex $[\mathrm{RuCl_2(CS)(PPh_3)_2}]_2$, (I), as established by full elemental analyses (C, H, P, Cl, and S) and osmometric molecular-weight measurement in benzene (see Experimental section). Furthermore, in agreement with the data in ref. 20, it is diamagnetic, non-conducting (in $\mathrm{CH_2Cl_2}$), completely soluble in benzene, dichloromethane, chloroform, and acetone, and, although quite air stable in the former, rapidly turns greenish brown in acetone solution. Its i.r. spectrum [ν(CS) at 1 290 cm^{-1}] and m.p. [165—166 °C (decomp.)] were very similar to those reported earlier.

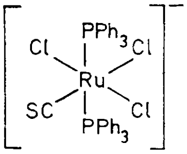


(Ia)

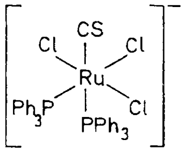


(Ib)

When complex (I) was dissolved in degassed acetone and shaken under an atmosphere of nitrogen with excess of $\mathrm{Ph_4AsCl,HCl}$ for several days, slow conversion to a red crystalline precipitate of $\mathrm{Ph_4As[RuCl_3CS(PPh_3)_2],2Me_2CO}$, (II), occurred. The same anion was obtained by using either benzyltriphenylphosphonium chloride or tetraethylammonium chloride together with concentrated hydrochloric acid. In the absence of acid, no reaction occurred. These diamagnetic complexes are 1 : 1 electrolytes ($\mathrm{CH_2Cl_2}$) and i.r. spectra show characteristic cation bands, triphenylphosphine, and a thiocarbonyl band at 1 272 cm^{-1} (Nujol). Although they are not sufficiently soluble for either ^{1}H or ^{31}P n.m.r. studies, the presence of a strong i.r. band at 320 cm^{-1} is characteristic of a *trans*-$\mathrm{RuCl_2}$ arrangement,[23] consistent with either structure (IIa) or (IIb).



(IIa)



(IIb)

At this juncture, the only discrepancy with the work of Gilbert *et al.* was our consistently low yield of complex (I) (16 as against 70% in ref. 20). Therefore, in order to remedy this, we removed most of the solvent from the red ethereal solution and added excess of light petroleum (b.p. 60—80 °C), which gave a pinkish red precipitate, (III) (*ca.* 40% yield). The same material was obtained in a more crystalline form (maroon red) when the ethereal solution was set aside for *ca.* 15 min. Both samples were then insoluble in diethyl ether. At first sight complex (III) appeared identical to the initial precipitate (I). Thus, the complex is diamagnetic, non-conducting ($\mathrm{CH_2Cl_2}$), completely soluble in benzene, dichloromethane, and chloroform, analyses closely for $[\mathrm{RuCl_2(CS)(PPh_3)_2}]_2$ (C, H, P, and Cl), and is dimeric in benzene. The complex melts at 167—168 °C and its i.r. spectrum is virtually identical to (I) except that ν(CS) occurs at 1 284 cm^{-1} and there are slight differences below 400 cm^{-1} (see Experimental section).

However, closer examination revealed that (I) and (III) were not the same complex. Thus, benzene or chloroform solutions of complex (III) rapidly darkened when exposed to air. Furthermore, complex (III), although transiently soluble in acetone, rapidly precipitated from this solution as an acetone solvate [ν(CO) 1 705, ν(CC) 1 221 cm^{-1}]. Sulphur analyses on complex (III) consistently gave values 50% lower than found for (I); ^{31}P n.m.r. studies revealed that (I) and (III) had quite different spectra and, finally, reaction of (III) and $\mathrm{Ph_4AsCl,HCl}$ did not give $\mathrm{Ph_4As[RuCl_3CS(PPh_3)_2]}$. It is interesting to note that when light petroleum (b.p. 60—80 °C) was used instead of diethyl ether as precipitating solvent, both complexes (I) and (III) were immediately precipitated (^{31}P n.m.r. evidence) and were readily separated by a few minutes shaking in degassed acetone.

By means of the liquid-diffusion method[24] using a dichloromethane–acetone solvent, crystals of complex (III) were obtained suitable for *X*-ray analysis. This structure determination, which is reported in full in the following paper,[25] has unequivocally established that

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* In ref. 20 the word ether is used which we have taken to mean diethyl ether, not light petroleum.

[19] L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J. Organometallic Chem.*, 1973, **49**, C77.

[20] J. D. Gilbert, M. C. Baird, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2198.

[21] T. A. Stephenson and E. S. Switkes, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 805.

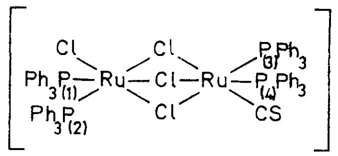
[22] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[23] See M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741.

[24] For method see G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, New York, 1968, p. 64.

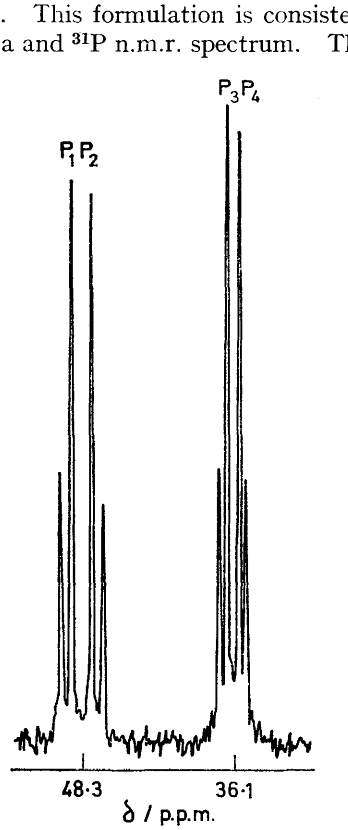
[25] A. J. F. Fraser and R. O. Gould, following paper.

complex (III) has the molecular composition $[(PPh_3)_2ClRuCl_3Ru(CS)(PPh_3)_2]$, *i.e.* a tri-μ-chloro-complex with



(III)

one CS group. This formulation is consistent with the analytical data and ^{31}P n.m.r. spectrum. The spectrum

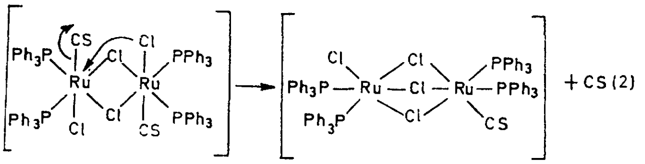


^{31}P N.m.r. spectrum of complex (III) measured in $CDCl_3$ (chemical shifts are in p.p.m. to high frequency of 85% H_3PO_4) at 298 K

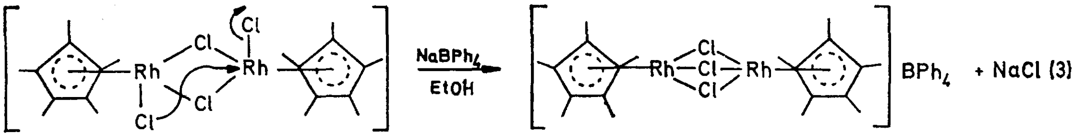
shown in the Figure can be readily interpreted as two AB quartets centred at 48·3 and 36·1 p.p.m. In contrast, the ^{31}P n.m.r. spectrum of complex (I) in C_6H_6–C_6D_6 consisted of a strong singlet at 24·4 p.p.m. and a weak singlet at 31·3 p.p.m. which disappeared when the solution was set aside for several days. In $CDCl_3$, the singlet at 31·3 p.p.m. was more intense. A possible explanation of these observations is formation of two isomers (Ia) and (Ib) with the *trans*-form favoured in benzene and the *cis* form in chloroform. Irrespective of the detailed interpretation of these observations, the similarity in position of the higher-field quartet in complex (III) with the strong singlet of (I) in $CDCl_3$ suggests that this quartet arises from the PPh_3 groups numbered (3) and (4) which are *cis* to the thiocarbonyl group.

Complex (III) represents another example of the increasing number of ruthenium complexes which contain a $RuCl_3Ru$ bridging unit. Earlier examples are $[L_3RuCl_3RuL_3]Cl$ (L = PEt_2Ph, *etc.*)[7] (although this structure has not been verified by *X*-ray analysis), $[Ru_2Cl_3L_6][RuCl_3L_3]$ (L = PEt_2Ph),[8] $[(PEt_2Ph)_2ClRuCl_3Ru(PEt_2Ph)_3]$ made by heating $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in methyl acetate at 120 °C,[26] and the paramagnetic $[(PBu^n_3)_2(Cl)RuCl_3RuCl(PBu^n_3)_2]$ made from $RuCl_3$ and PBu^n_3.[27] A very recent example is the complex $[(PPh_3)_2ClRuCl_3Ru(N_2)(PPh_3)_2]$ made from $[RuCl_2(PPh_3)_4]$[22] and molecular nitrogen by the novel technique of reverse osmosis,[28] and closely related examples are $[(PPh_3)_2ClRuCl_3Ru(N_2B_{10}H_8SMe_2)(PPh_3)_2]$[29] and $[(CO)_2(SnCl_3)RuCl_3Ru(CO)_3]$ made from $Ru_3(CO)_{12}$ and $SnCl_4$.[30] Details of the structural relations of (III) to these complexes are presented in the following paper.[25]

It is tempting to speculate that complex (III) is formed *via* (I) perhaps by intramolecular rearrangement involving displacement of a thiocarbonyl group by chloride ion [equation (2)]. A related rearrangement



reaction has been reported by Kang and Maitlis [equation (3)].[31] A study of the relative yields of complexes (I) and (III) as a function of reaction time would appear at first sight to support this hypothesis. Thus, increasing the time of reaction from 2 to 60 min increased the yield of complex (III) and decreased that of (I). However, further experiments showed that on heating complex (I) under reflux in CS_2 for up to 10 h, none of the triply bridged species was produced. Similarly, there was no evidence for conversion of complex (I) into (III) in acetone, benzene, or chloroform solutions.



However, when complex (I) was shaken in degassed acetone for several days, a very small amount of golden-

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[26] N. W. Alcock and K. A. Raspin, *J. Chem. Soc.* (*A*), 1968, 2108; R. H. Prince and K. A. Raspin, *ibid.*, 1969, 612.

[27] J. K. Nicholson, *Angew. Chem. Internat. Edn.*, 1967, **6**, 264; G. Chioccola, J. J. Daly, and J. K. Nicholson, *ibid.*, 1968, **7**, 131; G. Chioccola and J. J. Daly, *J. Chem. Soc.* (*A*), 1968, 1981.

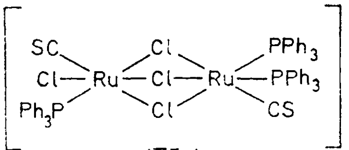
[28] L. W. Gosser, W. H. Knoth, and G. W. Parshall, *J. Amer. Chem. Soc.*, 1973, **95**, 3436.

[29] W. H. Knoth, *J. Amer. Chem. Soc.*, 1972, **94**, 104.

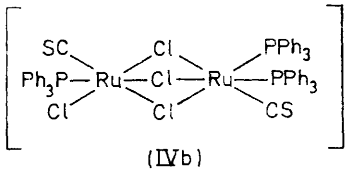
[30] M. Elder and D. Hall, *J. Chem. Soc.* (*A*), 1970, 245.

[31] J. W. Kang and P. M. Maitlis, *J. Organometallic Chem.*, 1971, **30**, 127.

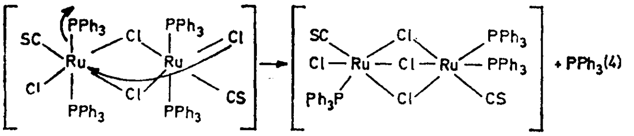
yellow crystals were deposited. The i.r. spectrum of this material showed evidence of solvent acetone, thiocarbonyl [ν(CS) 1 300 cm^{-1}], and triphenylphosphine. The far-i.r. spectrum had bands at 326, 288, and 259 cm^{-1}, which may indicate both terminal and bridging chloride ligands, and the complex is diamagnetic (Evans' method). A possible formulation consistent with this evidence and the analytical data is $[(PPh_3)(CS)ClRuCl_3Ru(CS)(PPh_3)_2],Me_2CO$, (IV) {*cf.* $[(PEt_2Ph)_2ClRuCl_3Ru(PEt_2Ph)_3]$ [26]}. The ^{31}P n.m.r. spectrum of complex (IV) in $CDCl_3$ consisted of two strong peaks at 48·1 and 37·7 p.p.m. of relative intensity 1 : 2.* The positions of these resonances were close to those found for complex (III), thus supporting the proposed formulation. The resonance arising from the two PPh_3 groups was only slightly split in this instance, indicating only a small chemical difference between these two phosphorus atoms, and therefore we tentatively attribute these signals to isomer (IVa). In addition, two other much weaker peaks at 50·2 and 35·5 p.p.m. of relative intensity 1 : 2 also occurred in some samples. We tentatively attribute these to isomer (IVb) since, in this instance, the more intense resonance appears to exhibit a greater splitting of the central peak compared to that observed for the resonance at 37·7 p.p.m. This suggests a bigger chemical-shift difference between the two phosphorus atoms, which might arise if these atoms were *cis* to a PPh_3 and Cl (or CS) group respectively [as in complexes (III) and (IVb)] rather than to a Cl and a CS group [as in complex (IVa)]. The mechanism of formation of complex (IV) from (I) could involve intramolecular displacement of a PPh_3 group by chloride ion [equation (4)].



(IVa)



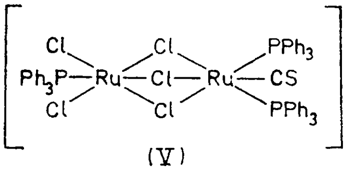
(IVb)



(Ia) (IVa)

At this juncture, it must therefore be concluded that complexes (I) and (III) are probably formed by competing reactions from $[RuCl_2(PPh_3)_3]$ or $[RuCl(\eta\text{-}CS_2)(PPh_3)_3]Cl$. A speculative mechanism could involve elimination of Ph_3PS from the cationic complex (as demonstrated in ref. 20) with formation of the complex $[RuCl_2CS(PPh_3)_2]$. This five-co-ordinate species might then undergo dimerisation to give complex (I) or combine with unreacted '$RuCl_2(PPh_3)_2$' {the dissociation product from $[RuCl_2(PPh_3)_3]$ (see ref. 22)} to give (III). Such a mechanism (which is difficult to prove, particularly for these thiocarbonyl complexes) might explain why complex (III) was not observed by earlier workers. A similar mechanism involving intermediates such as $[RuCl_2(N_2)(PPh_3)_2]$ and '$RuCl_2(PPh_3)_2$' could also be invoked to explain formation of the complex $[(PPh_3)_2ClRuCl_3Ru(N_2)(PPh_3)_2]$ from $[RuCl_2(PPh_3)_4]$ and molecular nitrogen.[28] †

Finally, although (III) does not react with Ph_4AsCl,HCl to give a ruthenium(II) anionic complex, it does react slowly in acetone with concentrated hydrochloric acid to give a sparingly soluble orange-brown solid. This material is sharp melting (234 °C), non-conducting (CH_2Cl_2), and its i.r. spectrum was very similar to that of complex (III), except for ν(CS) at 1 303 and 1 297 cm^{-1} and small differences in the far-i.r. region. However, the complex is paramagnetic (strong e.s.r. signals) and analysed closely (C, H, and Cl) for $[(PPh_3)Cl_2RuCl_3Ru(CS)(PPh_3)_2],2Me_2CO$, (V). This formulation is supported by the magnetic moment of 2·00 B.M. per dimer, obtained on a Faraday balance at 292 K {*cf.* $[(PBu^n_3)_2ClRuCl_3RuCl(PBu^n_3)_2]$ with $\mu_{eff.}$ = 1·50 B.M. per dimer [27]}, and the formation of complex (V) from (III) is readily explained by invoking intermolecular displacement of a PPh_3 group by chloride ion.



(V)

It is hoped that current work on the reaction of other $[RuX_2(PR_3)_3]$ (X = Cl or Br; PR_3 = $PEtPh_2$, PEt_2Ph, *etc.*) [32] complexes with CS_2 will help to clarify further the various rearrangement reactions exhibited by this interesting class of compounds.

EXPERIMENTAL

Microanalyses were by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4 000—250 cm^{-1} on a Perkin-Elmer 225 grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. ^1H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer and ^{31}P n.m.r. spectra on a Varian Associates XL100 spectrometer with a 12 in wide gap magnet operating in the pulse and Fourier transform mode at 40·5 MHz. Magnetic susceptibilities

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* *Note added in proof:* These assignments are supported by the ^{31}P n.m.r. spectrum in $CDCl_3$ at 298 K of the isomorphous $[(PPh_3)_2ClRuCl_3Ru(CO)(PPh_3)_2]Me_2CO$ complex which has two AB quartets centred at 48·0 and 40·3 p.p.m.

† *Note added in proof:* This mechanism is supported by the high yield synthesis of $[(PPh_3)_2ClRuCl_3Ru(CO)(PPh_3)_2],Me_2CO$ from reaction of $[RuCl_2(CO)(PPh_3)_2(dmf)]$ and $[RuCl_2(PPh_3)_3]$ (1 : 1 mole ratio) in acetone-dmf = *NN'*-dimethylformamide).

[32] For method of preparation, see P. W. Armit and T. A. Stephenson, *J. Organometallic Chem.*, 1973, **57**, C80.

were measured by Faraday (solid) and Evans' n.m.r. methods (solution).[33] Conductivity measurements were obtained on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Köfler hot-stage microscope and are uncorrected.

Ruthenium(III) trichloride trihydrate (Johnson, Matthey Ltd), carbon disulphide (Fisons), tetraphenylarsonium chloride–hydrochloride (Koch–Light), tetraethylammonium chloride (B.D.H.), and benzyltriphenylphosphonium chloride (Alfa Inorganics) were obtained as indicated. The complex $[RuCl_2(PPh_3)_3]$ was prepared as described earlier.[22]

Reaction of Dichlorotris(triphenylphosphine)ruthenium(II) *with Carbon Disulphide*.—The complex $[RuCl_2(PPh_3)_3]$ (0·19 g) was heated under reflux for 5 min in degassed CS_2 (30 cm^3) under an atmosphere of nitrogen. The solution was then cooled in ice in a stream of nitrogen. Filtration of the deep red solution gave a red crystalline residue (0·016 g, 8%), m.p. 175—176 °C. This material initially contained some CS_2 of solvation [$\nu(CS_2)$ at 1 515 cm^{-1}] but this was removed by gentle suction. The product was then identical (i.r. spectrum and analysis) to that reported earlier,[20] *i.e.* $[RuCl(\eta\text{-}CS_2)(PPh_3)_3]Cl$ (Found: C, 64·0; H, 4·2. Calc. for $C_{55}H_{45}Cl_2P_3RuS_2$: C, 63·8; H, 4·4%).

The remaining red solution was concentrated on a rotary evaporator to *ca.* 5 cm^3 and then treated with excess of diethyl ether to give a microcrystalline purple-red solid and a red solution. The solid was shaken with degassed acetone for *ca.* 10 min (virtually all soluble), filtered, and the solvent removed. The residue was redissolved in degassed benzene leaving a small undissolved amount of the complex $[RuCl(\eta\text{-}CS_2)(PPh_3)_3]Cl$ (i.r. evidence). Removal of benzene, followed by washing with diethyl ether, then gave *di-μ-chloro-bis[chloro(thiocarbonyl)bis(triphenylphosphine)ruthenium*(II), (I) (0·024 g, 16%), m.p. 165—166 °C (decomp.), $\nu(CS)$ at 1 290 cm^{-1} [Found: C, 60·3; H, 4·2; Cl, 9·3; P, 8·7; S, 4·2. *M*(in C_6H_6) 974. Calc. for $C_{74}H_{60}Cl_4P_4Ru_2S_2$: C, 60·0; H, 4·1; Cl, 9·5; P, 8·4; S, 4·3%. *M* 1 480]. This complex is completely soluble in benzene, dichloromethane, chloroform, and acetone, but rapidly oxidises in the latter giving a greenish brown solution. As reported earlier,[20] it appears stable to oxidation in the other solvents. The complex is non-conducting in dichloromethane and diamagnetic. ^{31}P N.m.r. spectrum: (C_6H_6–C_6D_6) 24·4 (singlet) (s); 31·3 (singlet) (w); ($CDCl_3$) 31·3 (singlet) p.p.m. I.r. spectrum (400—250 cm^{-1}) (Nujol): 330—320m (broad); 260w cm^{-1}.

Removing the diethyl ether immediately from the remaining red solution and then adding excess of light petroleum (b.p. 60—80 °C) gave a further pinkish red precipitate which, after washing well with acetone to remove any of the complex $[RuCl_2(CS)(PPh_3)_2]_2$, left *tri-μ-chloro-[chlorobis(triphenylphosphine)ruthenium*(II)]*[thiocarbonylbis(triphenylphosphine)ruthenium*(II)], (III) (0·057 g, 39%), m.p. 167—168 °C, $\nu(CS)$ at 1 284 cm^{-1} [Found: C, 60·7; H, 4·3; Cl, 9·4; P, 8·5; S, 2·3. *M* (in C_6H_6) 1 423. Calc. for $C_{73}H_{60}Cl_4P_4Ru_2S$: C, 61·0; H, 4·2; Cl, 9·9; P, 8·6; S, 2·2%. *M* 1 436]. The same complex separated out in smaller yield when the diethyl ether solution was set aside for a few minutes. This complex is also completely soluble in benzene, dichloromethane, and chloroform, but only slightly soluble in acetone. Although the complex is quite stable in acetone suspension, it is rapidly oxidised in benzene and the other solvents. The complex is non-conducting (CH_2Cl_2) and diamagnetic. ^{31}P N.m.r. spectrum: (C_6H_6–C_6D_6) 48·8 (quartet); 35·2 (quartet) ($J_{P_1P_2}$ 38·1, $J_{P_3P_4}$ 24·4, $\delta_{P_1P_2}$ 124·9, $\delta_{P_3P_4}$ 43·8); ($CDCl_3$) 48·3 (quartet); 36·1 (quartet) p.p.m., ($J_{P_1P_2}$ 37·4, $J_{P_3P_4}$ 24·6, δP_1P_2 94·0, δP_3P_4 54·9 Hz). I.r. spectrum (400—250 cm^{-1}) (Nujol): 318s; 308msh; and 260m cm^{-1}.

The same products were also obtained by treating the initial CS_2 solution (after filtering off $[RuCl(\eta\text{-}CS_2)(PPh_3)_3]Cl$) with light petroleum (b.p. 60—80 °C). In this instance, *both* thiocarbonyl complexes were immediately precipitated and were separated by shaking with degassed acetone for 10—15 min. Under these conditions, complex (III) separates out with an acetone molecule of solvation [$\nu(CO)$ at 1 705, $\nu(CC)$ at 1 221 cm^{-1}] which can be removed by prolonged pumping at room temperature.

Finally, the relative percentages of the complexes $[RuCl(\eta\text{-}CS_2)(PPh_3)_3]Cl$, (I) and (III) were dependent on the time of reaction. Thus, after only 2 min, percentage yields were 5, 24, and 50, after 5 min, 8, 16, and 39, and after 60 min, 11, 9, and 47 respectively. This clearly indicates that the yields of η-CS_2 and mono(CS) complexes increase with time, whereas that of the bis(CS) complex decreases with time.

Preparations.— *Tri-μ-chloro-[chloro(thiocarbonyl)(triphenylphosphine)ruthenium*(II)]*[thiocarbonylbis(triphenylphosphine)ruthenium*(II)]*–acetone* (1/1), (IV). Complex (I) was shaken in degassed acetone for several days to give a very small amount of golden-yellow *crystals*, m.p. 264 °C [$\nu(CS)$ at 1 300, $\nu(CO)$ at 1 708 cm^{-1}] (Found: C, 53·5; H, 3·7. Calc. for $C_{59}H_{51}Cl_4OP_3Ru_2S_2$: C, 52·5; H, 3·7%]. ^1H N.m.r. spectrum ($CDCl_3$): τ 2·8 (phenyl); 7·9 (acetone). ^{31}P N.m.r. spectrum ($CDCl_3$): 48·1 (singlet), 37·7 (broad) [isomer (IVa)]; 50·2 (singlet), 35·5 p.p.m. (doublet) [isomer (IVb)]. I.r. spectrum (400—250 cm^{-1}) (Nujol): 326s; 288s; and 259m cm^{-1}.

Tri-μ-chloro-[dichloro(triphenylphosphine)ruthenium(III)]*-[thiocarbonylbis(triphenylphosphine)ruthenium*(II)]*–acetone* (1/2), (V). The acetone solvate of complex (III) (0·12 g) was suspended in degassed acetone (18 cm^3) and shaken with concentrated hydrochloric acid (3·0 cm^3) for several days. The resulting orange-brown *solid* was then filtered off and washed with water, acetone, and light petroleum (b.p. 60—80 °C)/(0·07 g, 66%), m.p. 234 °C, $\nu(CS)$ at 1 303, and 1 297, $\nu(CO)$ at 1 710, and $\nu(CC)$ at 1 223 cm^{-1} (Found: C, 55·2; H, 4·2; Cl, 12·8. Calc. for $C_{61}H_{57}Cl_5O_2P_3Ru_2S$: C, 55·2; H, 4·3; Cl, 13·4%). The complex is sparingly soluble in CH_2Cl_2, non-conducting, gives strong e.s.r. signals (g_1 2·43, g_2 1·75), and has a magnetic moment of 2·00 B.M. per dimer at 292 K (solid). I.r. spectrum (400—250 cm^{-1}) (Nujol): 339vs; 286m; and 260m cm^{-1}. The same complex was obtained using a mixture of Ph_4AsCl,HCl and HCl.

Tetraphenylarsonium trichloro(thiocarbonyl)bis(triphenylphosphine)ruthenate(II)*–acetone* (1/2). Complex (I) (0·31 g) was dissolved in degassed acetone (60 cm^3) and shaken with excess of Ph_4AsCl,HCl (1·2 g) under an atmosphere of nitrogen for 5 days. The red *crystals* which formed were collected, washed with small amounts of ethanol and pentane, and dried *in vacuo* (40 °C), m.p. 180—183 °C, $\nu(CS)$ at 1 272, and $\nu(CO)$ at 1 712 cm^{-1} (Found: C, 62·8; H, 4·7; S, 2·6. Calc. for $C_{67}H_{62}AsCl_3O_2P_2RuS$: C, 63·1; H, 4·9; S, 2·5%) [$\Lambda(10^{-3}M)$ in CH_2Cl_2 = 34·8 Ω^{-1} cm^2 mol^{-1}].

Benzyltriphenylphosphonium trichloro(thiocarbonyl)bis(triphenylphosphine)ruthenate(II). Complex (I) (0·12 g) was dissolved in degassed acetone (60 cm^3) and shaken with excess of Ph_3PhCH_2PCl (1·5 g) and concentrated hydrochloric acid (0·30 cm^3) for 5 days under an atomosphere of

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[33] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

nitrogen. The red precipitate was then collected and washed with small amounts of acidified acetone to remove Ph_3PhCH_2PCl, then with acetone and pentane, m.p. 190—195 °C, ν(CS) at 1 272 cm^{-1} (Found: C, 66·4; H, 4·7. Calc. for $C_{62}H_{52}Cl_3P_3RuS$: C, 65·9; H, 4·7%) [Λ(10^{-3}M) in CH_2Cl_2 = 20·1 Ω^{-1} cm^2 mol^{-1}].

Tetraethylammonium trichloro(thiocarbonyl)bis(triphenylphosphine)ruthenate(II). This complex was prepared as above using excess of Et_4NCl and a small amount of conc. HCl (Found: C, 58·1; H, 5·1; N, 1·9. Calc. for $C_{45}H_{50}Cl_3NP_2RuS$: C,59·6; H, 5·6; N, 1·6%).

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