Metal Complexes of Sulphur Ligands. Part 18.[1] Reaction of Tris- and Tetrakis-(tertiary phosphine)dichlororuthenium(II) Complexes with Various Dithioacid Ligands †

By **Wilma J. Sime** and **T. Anthony Stephenson,*** Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of $[RuCl_2L_4]$ [L = $PPh(OMe)_2$ or $PMePh_2$] and $[RuCl_2(PEtPh_2)_3]$ with various alkali-metal dithioacid salts gives, under all conditions, the complexes $[Ru(S-S)_2L_2]$ [S–S = $S_2PR'_2$ (R′ = Me or Ph), S_2COMe, or $S_2CNR'_2$ (R′ = Me or Et)]. In contrast, the products of reaction of *cis*-$[RuCl_2(PMe_2Ph)_4]$ and $[RuCl_2\{PPh_2(OR)\}_3]$ (R = Me or Et) with these dithioacid anions are very sensitive to reaction conditions. For example, shaking with $Na[S_2PR'_2]$ in benzene gives the yellow complexes $[RuCl(S_2PR'_2)L_3]$ which readily rearrange to the red five-co-ordinate cations $[Ru(S_2PR'_2)L_3]^+$ in alcoholic media. In contrast, shaking with $K[S_2COMe]$ gives the six-co-ordinate $[Ru(S_2COMe)_2L_3]$ (with uni- and bi-dentate S_2COMe co-ordination), which on heating rearrange irreversibly to $[Ru(S_2COMe)_2L_2]$. Reaction of $[RuCl_2(PMe_2Ph)_4]$ with $Na[S_2CNR'_2]\cdot xH_2O$ for very short periods in ethanol gives $[Ru(S_2CNR'_2)(PMe_2Ph)_4]^+$, whereas in benzene $[Ru(S_2CNR'_2)_2(PMe_2Ph)_3]$ are formed. All these complexes have been fully characterised by elemental analyses and ^1H and $^{31}P-\{^1H\}$ n.m.r. spectroscopy, and a general mechanism for the formation of $[Ru(S-S)_2L_2]$ from $[RuCl_2L_n]$ (n = 3 or 4) is proposed.

REACTIONS of $[RuCl_2L_3]$ (L = PPh_3 or $PEtPh_2$) and *mer*-$[RuCl_3(PMe_2Ph)_3]$ with various dithioacid ligands have previously been reported. In *all* cases the products obtained were the six-co-ordinate ruthenium(II) complexes $[Ru(S-S)_2L_2]$ [S–S = $S_2PR'_2$ (R′ = Me, Et, or Ph), $S_2CNR'_2$ (R = Me, Et, or Ph), or S_2COMe] containing bidentate dithioacid groups and, in most instances, *cis* tertiary phosphine ligands.[2]

In this paper we report the reactions of more $[RuCl_2L_3]$ [L = $PPh_2(OMe)$ [3,4] or $PPh_2(OEt)$ [3,4]] and $[RuCl_2L_4]$ [L = $PPh(OMe)_2$,[3,4] PMe_2Ph,[5,6] or $PMePh_2$ [5,7]] complexes with various alkali-metal dithioacid salts M[S–S] [S–S = $S_2PR'_2$ (R′ = Me or Ph), S_2COMe, or $S_2CNR'_2$ (R′ = Me or Et)]. Again the final products were $[Ru(S-S)_2L_2]$ complexes but, in some instances, several *intermediate* products were isolated and characterised, and on the basis of these data a general reaction mechanism for the formation of $[Ru(S-S)_2L_2]$ has been proposed.[8]

RESULTS AND DISCUSSION

(*a*) *Diphenyl- and Dimethyl-phosphinodithioato-complexes.*—Prolonged heating under reflux of $[RuCl_2\{PPh_2(OR)\}_3]$ (R = Me or Et) with an excess of $Na[S_2PMe_2]\cdot 2H_2O$ in alcohol produced a brown solution from which, for R = Me, no solid could be isolated, but where for R = Et a small amount of red-brown crystals analysing for $[Ru(S_2PMe_2)_2\{PPh_2(OEt)\}_2]$ (Table 1) was obtained. The i.r. spectrum contained a band at 588 cm^{-1} indicating bidentate co-ordination of the $[S_2PMe_2]^-$ group,[9] and the ^{31}P n.m.r. spectrum in $CDCl_3$ at 303 K (Table 2) consisted of two triplets at δ 140.76 and 86.70 p.p.m. assigned to the phosphinite and $[S_2PMe_2]^-$ groups respectively. The ^1H n.m.r. spectrum at 301 K contained a doublet at 1.43 p.p.m. due to the methyl groups of $[S_2PMe_2]^-$ and resonances at 3.30 and 1.20 p.p.m. from $PPh_2(OEt)$. Unfortunately, at lower temperatures, the spectrum became very broad and thus the isomeric form could not be determined. Similarly, pro-

---

† No reprints available.

[1] Part 17, J. A. Goodfellow, T. A. Stephenson, and M. C. Cornock, *J.C.S. Dalton*, 1978, 1195.

[2] For detailed references, see D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 739.

[3] W. J. Sime and T. A. Stephenson, *J. Organometallic Chem.*, 1977, **124**, C23.

[4] W. J. Sime, Ph.D. Thesis, University of Edinburgh, 1977.

[5] P. W. Armit and T. A. Stephenson, *J. Organometallic Chem.*, 1973, **57**, C80.

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

[7] P. W. Armit, Ph.D. Thesis, University of Edinburgh, 1977.

[8] W. J. Sime and T. A. Stephenson, *Inorg. Nuclear Chem. Letters*, 1977, **13**, 311.

[9] D. F. Steele and T. A. Stephenson, *J.C.S. Dalton*, 1973, 2124.

TABLE 1

Analytical data for some ruthenium(II) dithioacid complexes

Complex	Analysis (%)						M[a]
	Found			Calc.			
	C	H	N	C	H	N	
$[RuCl(S_2PMe_2)\{PPh_2(OMe)\}_3]$	55.5	5.0		55.2	5.0		
$[RuCl(S_2PMe_2)\{PPh_2(OEt)\}_3]$	55.5	5.4		55.5	5.4		
$[RuCl(S_2PMe_2)(PMe_2Ph)_3]$	46.6	5.7		46.2	5.8		744 (775)
$[Ru(S_2PMe_2)\{PPh_2(OMe)\}_3][BPh_4]$	65.1	5.4		65.4	5.4		
$[Ru(S_2PPh_2)\{PPh_2(OMe)\}_3][BPh_4]$	68.2	5.2		68.3	5.2		
$[Ru(S_2PMe_2)\{PPh_2(OEt)\}_3][BPh_4]$	64.9	5.6		64.2	5.6		
$[Ru(S_2PPh_2)\{PPh_2(OEt)\}_3][BPh_4]$	68.9	5.3		68.9	5.5		
$[Ru(S_2PMe_2)(PMe_2Ph)_3][BPh_4]$	62.3	6.1		62.6	6.1		492 (479)[b]
$[Ru(S_2PPh_2)(PMe_2Ph)_3][BPh_4]$	66.3	5.8		66.5	5.8		
$[Ru(S_2PMe_2)_2\{PPh_2(OEt)\}_2]$	46.8	5.2		47.3	5.2		
$[Ru(S_2PMe_2)_2\{PPh(OMe)_2\}_2]$	35.5	4.8		34.7	4.9		688 (691)
$[Ru(S_2PPh_2)_2\{PPh(OMe)_2\}_2]$	51.0	4.6		51.1	4.5		
$[Ru(S_2COMe)_2\{PPh_2(OMe)\}_3]$	52.5	4.9		53.4	4.7		
$[Ru(S_2COMe)_2\{PPh_2(OEt)\}_3]$	53.9	5.1		54.9	5.1		
$[Ru(S_2COMe)_2(PMe_2Ph)_3]$	45.6	5.3		46.0	5.3		726 (729)
$[Ru(S_2COMe)_2(PMePh_2)_2]$	50.5	4.5		50.4	4.5		
$[Ru(S_2COMe)_2(PEtPh_2)_2]$	51.4	4.8		51.6	4.8		
$[Ru(S_2COMe)_2\{PPh_2(OMe)\}_2]$	49.1	4.3		48.4	4.3		
$[Ru(S_2CNMe_2)(PMe_2Ph)_4][BPh_4]$	65.3	6.3	1.4	64.2	6.2	1.5	612 (546)[b]
$[Ru(S_2CNEt_2)(PMe_2Ph)_4][BPh_4]$	65.0	6.5	1.3	65.3	6.6	1.2	
$[Ru(S_2CNMe_2)_2(PMe_2Ph)_3]$	47.5	5.9	3.6	47.7	5.9	3.7	683 (755)
$[Ru(S_2CNMe_2)_2\{PPh_2(OMe)\}_3]$	53.8	5.2	3.1	54.7	5.2	2.8	
$[Ru(S_2CNMe_2)\{PPh_2(OMe)\}_3][BPh_4]$	64.7	5.2	1.3	66.6	5.4	1.2	
$[Ru(S_2CNEt_2)\{PPh_2(OMe)\}_3][BPh_4]$	65.6	5.4	1.2	67.0	5.6	1.2	
$[Ru(S_2CNMe_2)_2\{PPh_2(OMe)\}_2]$	50.0	4.9	4.0	49.8	4.9	3.6	
$[Ru(S_2CNEt_2)_2\{PPh_2(OMe)\}_2]$	52.0	5.3	3.1	52.1	5.5	3.4	
$[Ru(S_2CNMe_2)_2\{PPh(OMe)_2\}_2]$	37.8	4.9	4.0	37.7	4.8	4.0	
$[Ru(S_2CNEt_2)_2\{PPh(OMe)_2\}_2]$	42.0	5.5	3.7	42.3	5.7	3.8	
$[Ru(S_2CNMe_2)_2(PMePh_2)_2]$	51.6	5.1	3.5	51.8	5.1	3.8	
$[Ru(S_2CNEt_2)_2(PMePh_2)_2]$	52.9	5.5	3.3	54.2	5.7	3.5	
$[Ru(S_2CNMe_2)_2(PEtPh_2)_2]$	53.3	5.3	3.4	53.1	5.4	3.6	
$[Ru(S_2CNEt_2)_2(PEtPh_2)_2]$	57.1	5.9	3.2	55.3	6.0	3.4	

[a] Measured osmometrically at 37 °C in $CHCl_3$; calculated values are given in parentheses. [b] Half actual molecular weight since complex is a 1 : 1 electrolyte.

TABLE 2

Phosphorus-31 n.m.r. data (proton noise-decoupled) for some ruthenium dithioacid complexes in $CDCl_3$

Complex	T/K	δ[a]/p.p.m.	
		$[S_2PR'_2]^-$	Other resonances[b]
$[RuCl(S_2PMe_2)(PMe_2Ph)_3]$	213	93.90[c]	AB_2 pattern [ν_A 20.38, ν_B 16.06; ^2J(AB) 33.0]
$[RuCl(S_2PMe_2)\{PPh_2(OMe)\}_3]$	298	96.65[d]	139.67[d]
$[RuCl(S_2PMe_2)\{PPh_2(OEt)\}_3]$	298	109.38[d]	140.42[d]
$[Ru(S_2PMe_2)(PMe_2Ph)_3][BPh_4]$	298	110.31 (q)	32.36 (d) [^3J(PP) 3.6]
$[Ru(S_2PPh_2)(PMe_2Ph)_3][BPh_4]$	298	104.26[d]	32.29[d]
$[Ru(S_2PMe_2)\{PPh_2(OMe)\}_3][BPh_4]$	298	111.58 (q)	144.85 (d) [^3J(PP) 4.4]
$[Ru(S_2PPh_2)\{PPh_2(OMe)\}_3][BPh_4]$	298	103.96[d]	144.95[d]
$[Ru(S_2PMe_2)\{PPh_2(OEt)\}_3][BPh_4]$	298	109.90 (q)	141.53 (d) [^3J(PP) 4.7]
$[Ru(S_2PPh_2)\{PPh_2(OEt)\}_3][BPh_4]$	298	102.52 (q)	141.39 (d) [^3J(PP) 4.2]
$[Ru(S_2PMe_2)_2\{PPh_2(OEt)\}_2]$	303	86.70 (t)	140.76 (t) [^3J(PP) 6.0]
$[Ru(S_2PMe_2)_2\{PPh(OMe)_2\}_2]$	298	88.83 (t)	170.54 (t) [^3J(PP) 6.8]
$[Ru(S_2PPh_2)_2\{PPh(OMe)_2\}_2]$	298	89.47 (t)	170.97 (t) [^3J(PP) 6.3]
$[Ru(S_2COMe)_2(PMe_2Ph)_3]$	298		AB_2 pattern [ν_A 7.62, ν_B 10.61; ^2J(AB) 30.3]
$[Ru(S_2COMe)_2\{PPh_2(OMe)\}_3]$	298		AB_2 pattern [ν_A 136.70, ν_B 138.89; ^2J(AB) 35.0]
$[Ru(S_2COMe)_2\{PPh_2(OEt)\}_3]$	298		AB_2 pattern [ν_A 132.64, ν_B 135.06; ^2J(AB) 34.8]
$[Ru(S_2COMe)_2\{PPh_2(OMe)\}_2]$	298		146.51 (s)
$[Ru(S_2COMe)_2(PMePh_2)_2]$	218		30.89 (s)
$[Ru(S_2COMe)_2(PEtPh_2)_2]$	218		50.32 (s),[e] 44.31 (s)[f]
$[Ru(S_2CNMe_2)(PMe_2Ph)_4][BPh_4]$	298		6.02 (t), −3.68 (t) [^2J(PP) 27.0]
$[Ru(S_2CNEt_2)(PMe_2Ph)_4][BPh_4]$	298		5.12 (t), −3.32 (t) [^2J(PP) 28.0]
$[Ru(S_2CNMe_2)_2(PMe_2Ph)_3]$	298		AB_2 pattern [ν_A 14.19, ν_B 11.48; ^2J(AB) 29.5]
$[Ru(S_2CNMe_2)_2\{PPh_2(OMe)\}_3]$	218		143.80[d]
$[Ru(S_2CNMe_2)\{PPh_2(OMe)\}_3][BPh_4]$	218		145.47 (s)
$[Ru(S_2CNEt_2)\{PPh_2(OMe)\}_3][BPh_4]$	218		145.54 (s)
$[Ru(S_2CNMe_2)_2\{PPh_2(OMe)\}_2]$	298		147.57 (s)
$[Ru(S_2CNEt_2)_2\{PPh_2(OMe)\}_2]$	298		148.37 (s)
$[Ru(S_2CNEt_2)_2(PMePh_2)_2]$	298		31.40 (s)
$[Ru(S_2CNMe_2)_2(PEtPh_2)_2]$	218		54.42 (s),[e] 45.76 (s)[f]
$[Ru(S_2CNEt_2)_2(PEtPh_2)_2]$	218		54.11 (s),[e] 45.82 (s)[f]
$[Ru(S_2CNMe_2)_2\{PPh(OMe)_2\}_2]$	298		176.15 (s)
$[Ru(S_2CNEt_2)_2\{PPh(OMe)_2\}_2]$	298		176.64 (s)

[a] Chemical shifts reported to high frequency of 85% H_3PO_4; s = singlet, d = doublet, t = triplet, and q = quartet. [b] From tertiary phosphine, phosphinite, or phosphonite ligands. [c] Multiplet resembling unsymmetrical quartet. [d] Broad. [e] Decreases in intensity with increasing temperature. [f] Increases in intensity with increasing temperature.

longed reaction of *cis*-[RuCl$_2$(PMe$_2$Ph)$_4$] with Na[S$_2$PMe$_2$]·2H$_2$O produced yellow crystals, shown by ^{31}P and ^{1}H n.m.r. spectroscopy to be identical to those obtained from *mer*-[RuCl$_3$(PMe$_2$Ph)$_3$], *viz.* *cis*-[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$].[2]

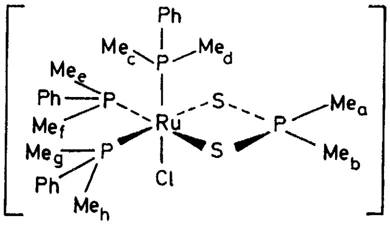
However, shaking [RuCl$_2$(PMe$_2$Ph)$_4$] or [RuCl$_2${PPh$_2$(OR)}$_3$] in methanol (R = Me) or ethanol (R = Et) with Na[S$_2$PR'$_2$] (R' = Me or Ph) for a short time produced red conducting solutions, which on addition of Na[BPh$_4$] precipitated red solids analysing closely for [Ru(S$_2$PR'$_2$)L$_3$][BPh$_4$]. The i.r. spectra contained bands at *ca.* 580 cm^{-1} consistent with bidentate [S$_2$PR'$_2$]$^-$ co-ordination and conductivity measurements in acetone indicated 1 : 1 electrolytes (see Experimental section). The latter result suggested monomeric structures in solution and this was supported by molecular-weight studies in CHCl$_3$ on [Ru(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$][BPh$_4$] (Table 1). The presence of a monomeric structure in the solid state has been confirmed by the results of a preliminary *X*-ray analysis on [Ru(S$_2$PPh$_2$)(PMe$_2$Ph)$_3$][BPh$_4$].[10] The cation has a distorted square-pyramidal geometry as found (and predicted) for several other five-co-ordinate ruthenium(II) complexes.[11]

The ^{31}P-{^{1}H} n.m.r. spectrum of [Ru(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$][BPh$_4$] in CDCl$_3$ at 298 K consisted of a doublet at 32.36 p.p.m. [^3J(PP) 3.6 Hz] due to the PMe$_2$Ph groups which, because of ready intramolecular scrambling, are rendered equivalent and thus equally coupled to the [S$_2$*P*Me$_2$]$^-$ group, and a quartet at 110.31 p.p.m. due to the [S$_2$*P*Me$_2$]$^-$ group coupled equally to the three PMe$_2$Ph groups. Similarly, the ^{1}H n.m.r. spectrum at 301 K consisted of a doublet [^2J(PH) 13 Hz] due to the [S$_2$PMe$_2$]$^-$ methyl groups (equivalent because of ready PMe$_2$Ph scrambling) and a ' pseudo-triplet ' * pattern from the PMe$_2$Ph methyl groups. Neither the ^{31}P or ^{1}H n.m.r. spectra changed on cooling to 213 K indicating that intramolecular scrambling was still rapid at these temperatures.

If [RuCl$_2${PPh$_2$(OR)}$_3$] or [RuCl$_2$(PMe$_2$Ph)$_4$] was shaken with Na[S$_2$PMe$_2$]·2H$_2$O in benzene, however, yellow non-conducting solids analysing for [RuCl(S$_2$PMe$_2$)L$_3$] were obtained. These were fairly stable in CHCl$_3$ or CH$_2$Cl$_2$, but, in methanol or ethanol, red solutions containing the [Ru(S$_2$PMe$_2$)L$_3$]$^+$ cations were formed immediately. The ^{31}P-{^{1}H} n.m.r. spectrum of [RuCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$] at 213 K in CDCl$_3$ consisted of an unsymmetrical quartet centred at 93.90 p.p.m. ([S$_2$PMe$_2$]$^-$ group) and an AB$_2$ pattern [ν_A 20.38, ν_B 16.06 p.p.m.; ^2J(AB) 33.0 Hz] (PMe$_2$Ph groups). At 298 K the AB$_2$ pattern broadened and a singlet appeared at 21.26 p.p.m. corresponding to [Ru$_2$Cl$_3$(PMe$_2$Ph)$_6$]Cl, formed presumably by the slow decomposition of [RuCl(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$] in chlorinated solvents.

The ^{1}H n.m.r. spectrum at 233 K in CDCl$_3$ contained two doublets at 1.19 and 2.17 p.p.m. which both collapsed at the same ^{31}P n.m.r. frequency (*viz.* 95.5 p.p.m.†) indicating that they arise from the methyl groups of [S$_2$PMe$_2$]$^-$. There was also a doublet at 1.60 p.p.m. (decoupling ^{31}P n.m.r. frequency = 19.5 p.p.m.) and a broad resonance at 1.88 p.p.m. due to the P*Me*$_2$Ph groups. At 298 K only a broad resonance at 1.70 p.p.m. was observed, indicating that, on the one hand, all the PMe$_2$Ph groups and, on the other, the methyls of [S$_2$PMe$_2$]$^-$ had become equivalent.

These low-temperature ^{1}H n.m.r. data are consistent with structure (I) in which the [S$_2$PMe$_2$]$^-$ methyl groups are inequivalent; the doublet at 1.60 p.p.m. is assigned to methyl groups (c) and (d) attached to the PMe$_2$Ph group *trans* to Cl$^-$ whereas the broad resonance at 1.88 p.p.m. is ascribed to the methyls on the two PMe$_2$Ph groups *trans* to the dithioacid ligand. The equivalence of all the tertiary phosphine methyl groups [and also Me(a) and Me(b)] at higher temperatures is tentatively rationalised by postulating ready Ru–S bond cleavage to generate five-co-ordinate intermediates, followed by re-formation to produce various six-co-ordinate isomers.



(I)

Reaction between [RuCl$_2${PPh(OMe)$_2$}$_4$] and Na[S$_2$PR'$_2$] (R' = Me or Ph) under all these conditions, however, produced in both cases only [Ru(S$_2$PR'$_2$)$_2${PPh(OMe)$_2$}$_2$]. The ^{1}H n.m.r. spectrum at 301 K of [Ru(S$_2$PMe$_2$)$_2${PPh(OMe)$_2$}$_2$] exhibited a ' pseudo-triplet ' pattern at 3.60 p.p.m. and a broad resonance at 1.80 p.p.m. As the temperature was decreased, the pseudo-triplet split into two and the broad resonance sharpened, such that at 213 K the spectrum contained two pseudo-triplets (decoupling to give two singlets at the same ^{31}P n.m.r. frequency) at 3.42 and 3.58 p.p.m. and two doublets (also decoupling at the same ^{31}P n.m.r. frequency) at 1.71 and 2.12 p.p.m. This low-temperature spectrum is consistent with a *cis* configuration and the mechanism of interconversion of optical isomers which occurred at higher temperatures is probably identical to that established earlier for other *cis*-[Ru(S$_2$PMe$_2$)$_2$L$_2$] complexes.[12]

(*b*) O-*Methyl Dithiocarbonato-complexes*.—Shaking

---

* A ' pseudo-triplet ' pattern consists of a sharp doublet with a broad hump of comparable intensity situated between the doublet and signifies a relatively large J(PP) compared to the $|J$(PH) + J(PH)$'|$ value {*cf.* *cis*-[Ru(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$] [2]}.

† The irradiation frequencies are different from the frequencies of the ^{31}P nuclei obtained from the Fourier-transform spectrum because the former are obtained from the HA-100 spectrometer (with Schlumberger FS30 frequency-synthesiser attachment) whereas the latter were directly measured on the XL100 spectrometer and these have slightly different reference frequencies.

[10] C. L. Jones, G. H. W. Milburn, and L. Sawyer, personal communication.

[11] For detailed references, see P. R. Hoffman and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221.

[12] D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 754.

$[RuCl_2\{PPh_2(OR)\}_3]$ (R = Me or Et) or $[RuCl_2(PMe_2Ph)_4]$ with excess of $K[S_2COMe]$ in methanol produced yellow non-conducting solids analysing for $[Ru(S_2COMe)_2L_3]$. The i.r. spectra contained several bands in the 1 000—1 200 cm^{-1} region indicating the presence of co-ordinated $[S_2COMe]^-$ groups, and the ^{31}P-$\{^1H\}$ n.m.r. spectrum at 298 K (for L = PMe_2Ph) consisted of an AB_2 pattern, confirming the presence of three PMe_2Ph groups. The ^1H n.m.r. spectrum of this complex in $CDCl_3$ at 301 K contained two resonances at 3.92 and 3.65 p.p.m. ($[S_2COMe]^-$) indicating the presence of both uni- and bidentate $[S_2COMe]^-$ ligands. The spectrum also showed pseudo-triplet and doublet resonances in the intensity ratio 2 : 1 (PMe_2Ph groups) (Table 3). The doublet could be assigned to a PMe_2Ph group *trans* to the unidentate dithioacid ligand and the pseudo-triplet to the two *cis* PMe_2Ph groups, each *trans* to a sulphur of the bidentate ligand.

TABLE 3

Hydrogen-1 n.m.r. data for some ruthenium dithioacid complexes in $CDCl_3$

Complex	T/K	δ ±0.01 p.p.m.[a]	
		Dithio-ligand	Other resonances
$[RuCl(S_2PMe_2)(PMe_2Ph)_3]$	233	2.17 (d), 1.19 (d) [^2J(PH) 12.5]	1.60 (d) [^2J(PH) 8.0], 1.88,[b] 7.28—7.36 (m)
$[RuCl(S_2PMe_2)\{PPh_2(OMe)\}_3]$	301	1.36 (d) [^2J(PH) 12.0]	3.20,[b] 7.10—7.60 (m) [c]
$[RuCl(S_2PMe_2)\{PPh_2(OEt)\}_3]$	301	1.52 (d) [^2J(PH) 12.0]	1.25 (t) [^3J(HH) 7.0], 3.36,[b] 7.20—7.40 (m) [c]
$[Ru(S_2PMe_2)(PMe_2Ph)_3][BPh_4]$	301	1.82 (d) [^2J(PH) 13.0]	1.37 (pt) (N 8.0), 6.96—7.50 (m) [c]
$[Ru(S_2PMe_2)\{PPh_2(OMe)\}_3][BPh_4]$	301	1.44 (d) [^2J(PH) 12.5]	3.12 (pt) (N 11.5), 6.98—7.50 (m) [c]
$[Ru(S_2PMe_2)\{PPh_2(OEt)\}_3][BPh_4]$	301	1.36 (d) [^2J(PH) 13.0]	1.19 (t), 3.40,[b] 6.94—7.50 (m) [c]
$[Ru(S_2PMe_2)_2\{PPh_2(OEt)\}_2]$	301	1.43 (d) [^2J(PH) 12.0]	1.20 (t) [^3J(HH) 7.0], 3.30,[b] 6.80—7.50 (m) [c]
$[Ru(S_2PMe_2)_2\{PPh(OMe)_2\}_2]$	213	1.71 (d), 2.12 (d) [^2J(PH) 13.0]	3.42 (pt), 3.58 (pt) (N 12.0), 7.36—7.70 (m) [c]
$[Ru(S_2COMe)_2(PMe_2Ph)_3]$	301	3.65 (s), 3.92 (s)	1.83 (pt) (N 8.0), 1.19 (d) [^2J(PH) 7.5], 7.30—7.60 (m) [c]
$[Ru(S_2COMe)_2\{PPh_2(OMe)\}_3]$	301	3.33 (s), 3.46 (s)	3.22 (pt) (N 11.0), 3.10 (d) [^2J(PH) 10.5], 7.00—7.60 (m) [c]
$[Ru(S_2COMe)_2\{PPh_2(OEt)\}_3]$	301	2.96 (s), 3.33 (s)	3.00—3.40 (m),[d] 1.31 (t), 1.26 (m),[e] 7.10—7.50 (m) [c]
$[Ru(S_2COMe)_2\{PPh_2(OMe)\}_2]$	301	3.71	3.22 (pt) (N 11.0), 7.10—7.40 (m) [c]
$[Ru(S_2COMe)_2(PMePh_2)_2]$	301	3.81 (s)	1.88 (pt) (N 7.5), 7.18 (m) [c]
$[Ru(S_2COMe)_2(PEtPh_2)_2]$	301	3.72 (s), 3.85 (s)	2.30,[b] 0.60 (m), 7.18 (m) [c]
$[Ru(S_2CNMe_2)(PMe_2Ph)_4][BPh_4]$	301	2.37 (s)	1.76 (pt) (N 6.5), 1.17 (t) (N 5.0), 7.00—7.45 (m) [c]
$[Ru(S_2CNEt_2)(PMe_2Ph)_4][BPh_4]$	301	2.90 (q), 0.82 (t) [^3J(HH) 7.0]	1.72 (pt) (N 6.5), 1.27 (t) (N 5.0), 6.98—7.44 (m) [c]
$[Ru(S_2CNMe_2)_2(PMe_2Ph)_3]$	301	2.90 (s), 3.49 (s)	1.96,[b] 1.07 (d) [^2J(PH) 8.0], 7.31 (m) [c]
$[Ru(S_2CNMe_2)_2\{PPh_2(OMe)\}_2]$	301	3.02 (s), 3.10 (s)	3.30 (pt) (N 11.0), 7.20—7.60 (m) [c]
$[Ru(S_2CNEt_2)_2\{PPh_2(OMe)\}_2]$	301	3.44 (q), 3.60 (q), 1.06 (t), 1.09 (t), [^3J(HH) 7.0]	3.22 (pt) (N 11.0), 7.20—7.60 (m) [c]
$[Ru(S_2CNEt_2)_2(PMePh_2)_2]$	301	3.57,[f] 1.07 (t) [^3J(HH) 7.0]	1.78 (pt) (N 4.0), 7.10—7.40 (m) [c]
$[Ru(S_2CNMe_2)_2(PEtPh_2)_2]$	301	2.72 (s),[g] 2.91 (s), 3.11 (s)	0.56 (m), 2.10,[h] 2.50,[h] 7.00—7.40 (m) [c]
$[Ru(S_2CNEt_2)_2(PEtPh_2)_2]$	301	3.10—3.90,[i] 1.1 [j]	0.56 (m), 2.10,[h] 2.50,[h] 7.00—7.40 (m) [b]
$[Ru(S_2CNMe_2)_2\{PPh(OMe)_2\}_2]$	301	2.91 (s), 3.04 (s)	3.48 (t), 3.61 (t) (N 7.50), 7.30—7.50 (m) [c]

[a] pt = Pseudo-triplet, m = multiplet. $N = |J(PH) + J(PH)'|$, J values in Hz. [b] Broad. [c] Phenyl group resonances. [d] Overlapping quartets. [e] Contains at least one triplet. [f] ABM_3 spin system, four overlapping quartets. [g] Less intense than other two singlets and therefore assigned to less-stable isomer. [h] Symmetrical multiplet. [i] Several overlapping quartets. [j] At least two triplets at 1.01 and 1.18 p.p.m. were observed.

If $[Ru(S_2COMe)_2\{PPh_2(OMe)\}_3]$ was heated under reflux in the presence of $K[S_2COMe]$, orange-yellow crystals of $[Ru(S_2COMe)_2\{PPh_2(OMe)\}_2]$ were produced. The ^{31}P-$\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at 298 K consisted of a singlet at 146.51 p.p.m. while the ^1H n.m.r. contained a singlet at 3.71 p.p.m. ($[S_2COMe])^-$ and a pseudo-triplet at 3.22 p.p.m. (PMe_2Ph) suggesting a *cis* configuration.

An intractable yellow oil was obtained from the reaction between $[RuCl_2\{PPh(OMe)_2\}_4]$ and excess of $K[S_2COMe]$, but shaking $[RuCl_2(PMePh_2)_4]$ and $[RuCl_2(PEtPh_2)_3]$ with excess of $K[S_2COMe]$ in alcohol produced $[Ru(S_2COMe)_2L_2]$. For $[Ru(S_2COMe)_2(PMePh_2)_2]$ the ^{31}P and ^1H n.m.r. spectra at both 218 and 298 K were consistent with a *cis* configuration. However, for $[Ru(S_2COMe)_2(PEtPh_2)_2]$, the ^{31}P-$\{^1H\}$ n.m.r. spectrum at 218 K in $CDCl_3$ consisted of two singlets of equal intensity, at 50.32 and 44.31 p.p.m. As the temperature was increased the singlet at 44.31 p.p.m. increased in intensity at the expense of the other and this process was irreversible. The ^1H n.m.r. spectrum in $CDCl_3$ at 301 K, containing $[S_2COMe]^-$ resonances at 3.72 and 3.85 p.p.m.,* also indicated the presence of two species.

The most likely explanation is the presence of both the *cis* and *trans* isomers, one of which is more stable at higher temperatures than the other.† A similar situation occurred for $[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$ when both *cis* and *trans* isomers were formed on reaction of *mer*-$[RuCl_3(PMe_2Ph)_3]$ with $Na[S_2CNMe_2]\cdot 2H_2O$ in methanol. On warming in solution the *trans* isomer was irreversibly converted into the *cis* isomer.[2]

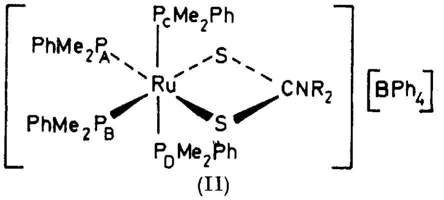
(*c*) *Dialkyldithiocarbamato-complexes*.—Reaction of *cis*-$[RuCl_2(PMe_2Ph)_4]$ with an excess of $Na[S_2CNR'_2]\cdot xH_2O$ (R' = Me or Et) for a *very short time* in ethanol produced pale yellow conducting solutions, which on addition of $Na[BPh_4]$ precipitated white solids analysing for

---

* The resonance at 3.85 p.p.m. was more intense and therefore most likely originated from the same species as that producing the singlet at 44.31 p.p.m. in the ^{31}P n.m.r. spectrum.

† The methyl and methylene resonances in the ^1H n.m.r. spectrum were complex and it was not possible to determine which isomeric form was predominant.

$[Ru(S_2CNR'_2)(PMe_2Ph)_4][BPh_4]$. Conductivity measurements in CH_2Cl_2 were consistent with 1 : 1 electrolytes while the i.r. spectra contained a band at *ca.* 1 500 cm^{-1} indicating the presence of a co-ordinated $[S_2CNR'_2]^-$ ligand and molecular-weight measurements in $CHCl_3$ supported a monomeric structure. The ^{31}P-{^1H} n.m.r. spectra in $CDCl_3$ at 298 K showed two triplets as expected for structure (II). Furthermore, the ^1H n.m.r. spectrum of $[Ru(S_2CNMe_2)(PMe_2Ph)_4][BPh_4]$ in $CDCl_3$ at 301 K contained a singlet at 2.37, pseudo-triplet at 1.76, and 1 : 2 : 1 triplet at 1.27 p.p.m. in the intensity ratio 1 : 2 : 2, assigned to the $[S_2CNMe_2]^-$, the *cis* phosphines (P_A and P_B), and the *trans* phosphines (P_C and P_D) respectively.

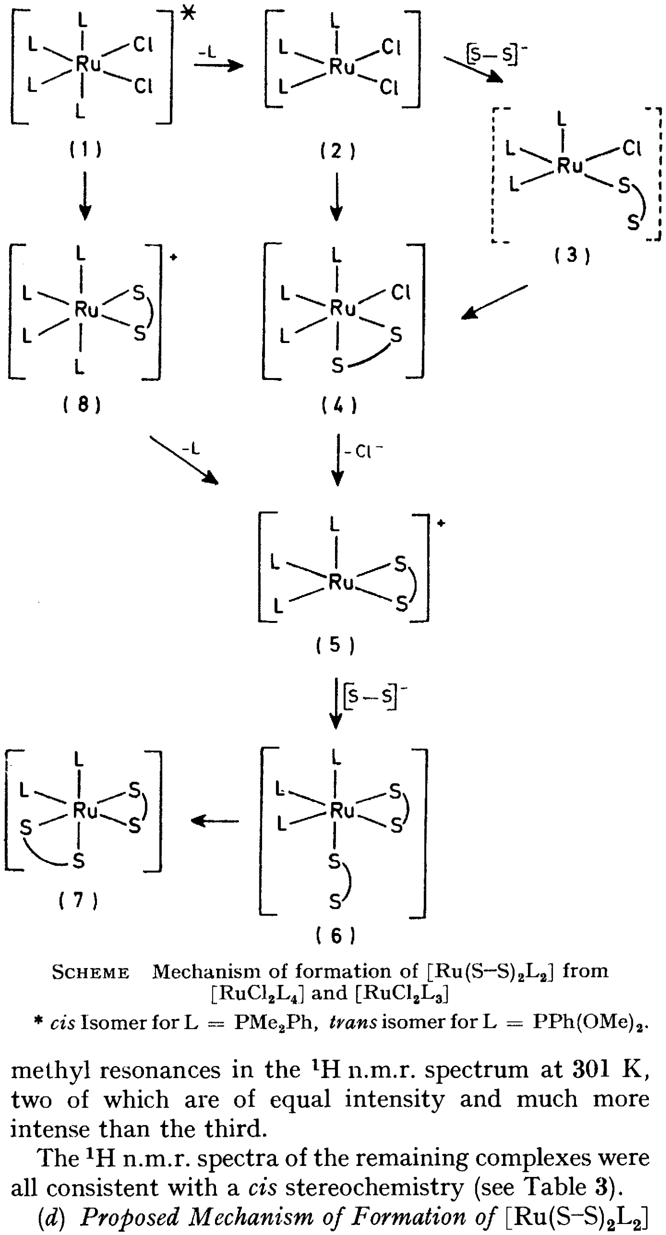


(II)

The reaction between $[RuCl_2(PMe_2Ph)_4]$ and $Na[S_2CNMe_2]\cdot 2H_2O$ in benzene, however, produced a bright yellow non-conducting solid analysing for $[Ru(S_2CNMe_2)_2(PMe_2Ph)_3]$. The ^{31}P-{^1H} n.m.r. spectrum in $CDCl_3$ at 298 K exhibited an AB_2 pattern [ν_A 14.19, ν_B 11.48 p.p.m.; ^2J(AB) 29.5 Hz] and the ^1H n.m.r. spectrum under the same conditions contained two singlets at 3.49 and 2.90 (assigned to uni- and bi-dentate $[S_2CNMe_2]^-$ groups respectively), two overlapping ' pseudo-doublets ' * at 1.96 arising from the two phosphine groups *trans* to bidentate $[S_2CNMe_2]^-$, and a doublet at 1.07 p.p.m. from the phosphine ligand *trans* to the unidentate group. This complex was also precipitated as yellow crystals on prolonged reaction of $[RuCl_2(PMe_2Ph)_4]$ with $Na[S_2CNMe_2]\cdot 2H_2O$ in methanol. The reaction presumably does not give $[Ru(S_2CNMe_2)_2(PMe_2Ph)_2]$ because of the insolubility of $[Ru(S_2CNMe_2)_2(PMe_2Ph)_3]$ in methanol.

When $[RuCl_2\{PPh_2(OMe)\}_3]$ was shaken with an excess of $Na[S_2CNR'_2]\cdot xH_2O$ (R' = Me or Et) in ethanol, *cis*-$[Ru(S_2CNR'_2)_2\{PPh_2(OMe)\}_2]$ (isomer confirmed by ^{31}P and ^1H n.m.r. evidence) was the major product, together with a small amount of the $[Ru(S_2CNR'_2)\{PPh_2(OMe)\}_3]^+$ cation which was trapped out by addition of $Na[BPh_4]$. In benzene the major product was $[Ru(S_2CNMe_2)\{PPh_2(OMe)\}_3]$ shown by ^{31}P n.m.r. spectroscopy to be partially converted into $[Ru(S_2CNMe_2)_2\{PPh_2(OMe)\}_2]$ in solution.

As for the other dithioacid ligands, treatment of $[RuCl_2L_4]$ [L = $PMePh_2$ or $PPh(OMe)_2$] and $[RuCl_2(PEtPh_2)_3]$ with $Na[S_2CNR'_2]\cdot H_2O$ *under all conditions* gave only $[Ru(S_2CNR_2)_2L_2]$. All the ^{31}P-{^1H} n.m.r. spectra {except for $[Ru(S_2CNMe_2)_2(PMePh_2)_2]$ which was too insoluble for either ^{31}P or ^1H n.m.r. studies} consisted of a singlet except those of $[Ru(S_2CNR'_2)_2(PEtPh_2)_2]$ which contained two singlets, the higher-frequency signals decreasing in intensity as the temperature was increased from 213 to 298 K. This suggested, as for $[Ru(S_2COMe)_2(PEtPh_2)_2]$, an irreversible isomerisation, which was shown for $[Ru(S_2CNMe_2)_2(PEtPh_2)_2]$ to be from the *trans* to the *cis* isomer by means of the relative intensities of the three $[S_2CNMe_2]^-$ methyl resonances in the ^1H n.m.r. spectrum at 301 K, two of which are of equal intensity and much more intense than the third.



SCHEME Mechanism of formation of $[Ru(S{-}S)_2L_2]$ from $[RuCl_2L_4]$ and $[RuCl_2L_3]$

* *cis* Isomer for L = PMe_2Ph, *trans* isomer for L = $PPh(OMe)_2$.

The ^1H n.m.r. spectra of the remaining complexes were all consistent with a *cis* stereochemistry (see Table 3).

(*d*) *Proposed Mechanism of Formation of* $[Ru(S{-}S)_2L_2]$ *from* $[RuCl_2L_n]$ (*n* = 3 *or* 4).—In view of the above results, in which several intermediates produced in the formation of $[Ru(S{-}S)_2L_2]$ have been isolated, a reaction scheme for the formation of $[Ru(S{-}S)_2L_2]$ from $[RuCl_2L_n]$ (*n* = 3 or 4) can now be proposed (Scheme).

Thus for $[RuCl_2L_3]$ (2) the initial step is probably replacement of one of the chloride ions by a dithioacid ligand to give the intermediate (3) followed by rapid

---

* A ' pseudo-doublet ' is a sharp doublet with small additional signal intensity situated between the doublet. This spectral pattern is indicative of a small, but non-zero, $J(PP')$ value when compared to $|J(PH) + J(PH)'|$.[13]

[13] R. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

attack of the dangling sulphur atom on the vacant co-ordination site to produce (4). Complex (4) is stable in benzene when $[S\text{-}S]^- = [S_2PR'_2]^-$ but in alcohol it loses chloride ion and is converted into the cation (5) which can then react with more $Na[S_2PR'_2]$ to give (6). However, (4) is not stable in benzene in the presence of stronger nucleophiles such as $[S_2COMe]^-$ and $[S_2CNR'_2]^-$ which replace the chloride ion to produce (6), although in polar solvents, for $[S\text{-}S]^- = [S_2CNR_2]^-$, the initial step in this process is the formation of the cation (5). The final step in this mechanism is then attack of the free sulphur atom with loss of L to give (7).

For $[RuCl_2L_4]$ (1) the reaction with $Na[S_2PR'_2]$ follows the same path as that of $[RuCl_2L_3]$ and it seems reasonable, therefore, to assume that loss of an L group occurs prior to reaction with the dithioacid ligand. However, reaction with $Na[S_2CNR'_2]\cdot xH_2O$ in alcohol produced the cationic species (8) containing four L groups, which is probably formed by rapid attack of the more nucleophilic $[S_2CNR'_2]^-$ ligand on $[RuCl_2L_4]$, prior to loss of L. Subsequent loss of L and reaction with $[S_2CNR'_2]^-$ yields (6) which, because of its insolubility in alcohol, is precipitated out and further reaction does not occur. Treatment of $[RuCl_2(PMe_2Ph)_4]$ with $K[S_2COMe]$ produced only (6) and, therefore, since (6) is formed by both paths, it is not possible to determine which one is operative in this case.

Finally, the isolation of several intermediate products in the reactions of $[RuCl_2(PMe_2Ph)_4]$ and $[RuCl_2\{PPh_2(OR)\}_3]$ (R = Me or Et) with dithioacid ligands, as opposed to the corresponding reactions of $[RuCl_2L_4]$ [L = $PMePh_2$ or $PPh(OMe)_2$] and $[RuCl_2(PEtPh_2)_3]$ which yield only $[Ru(S\text{-}S)_2L_2]$, is presumably a reflection of the stronger Ru–P bonds in the former complexes. Hence the last step of the mechanism, which involves cleavage of a Ru–P bond, is slow so that the intermediate complexes containing three phosphorus-donor groups are fairly long-lived and can readily be isolated. On the other hand, for complexes containing weaker Ru–P bonds, the tendency to lose an L group is much greater and any intermediates will quickly rearrange to form $[Ru(S\text{-}S)_2L_2]$ (7).

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. Molecular weights were determined on a Mechrolab vapour-pressure osmometer (model 301A) calibrated with benzil. 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. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature attachment. Heteronuclear decoupling experiments were carried out on this spectrometer using a radiofrequency field provided by the Schlumberger FS30 frequency synthesiser. Phosphorus-31 n.m.r. spectra (proton noise-decoupled) were recorded on a Varian Associates XL-100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz. Chemical shifts are reported in p.p.m. to high frequency of 85% H_3PO_4. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Conductivity measurements were made at 298 K using a model 310 Portland Electronics conductivity bridge. Data were obtained over a range of concentrations (2×10^{-3}—5×10^{-3} mol dm^{-3}) and a plot of Λ(equivalent conductance) against $c^{\frac{1}{2}}$ (concentration in equivalents dm^{-3}) gave a straight line which on extrapolation to $c^{\frac{1}{2}} = 0$ gave Λ_0. A subsequent plot of $\Lambda_0 - \Lambda$ against $c^{\frac{1}{2}}$ gave a straight line whose gradient is a function of the ionic charges.[14] Thus, the gradients obtained for various samples were compared with those for known 1 : 1 and 2 : 1 electrolytes and hence the electrolyte type could be determined.

Materials.—Ruthenium trichloride trihydrate (Johnson, Matthey), $Na[S_2CNR'_2]\cdot xH_2O$ (R = Me or Et; Ralph Emanuel), $Na[S_2PMe_2]\cdot 2H_2O$,[15] $Na[S_2PPh_2]$,[15] and $K[S_2COMe]$ [16] were prepared by standard literature methods. The various $[RuCl_2L_n]$ (n = 3 or 4) complexes were prepared as described elsewhere.[3-7] All the reactions were carried out in degassed solvents under an atmosphere of nitrogen.

Diaryl- or Dialkyl-phosphinodithioato-complexes.—*Chlorotris(dimethylphenylphosphine)(dimethylphosphinodithioato)ruthenium*(II). The compounds $[RuCl_2(PMe_2Ph)_4]$ (0.20 g) and $Na[S_2PMe_2]\cdot 2H_2O$ (0.20 g) were shaken in benzene (20 cm^3) for 1 h. The resulting yellow solution was filtered to remove any unchanged $Na[S_2PMe_2]\cdot 2H_2O$ and the benzene removed to give the complex as yellow *crystals* which were washed with water and dried *in vacuo*, m.p. 178—180 °C, $\nu(PS_2)$ at 600 cm^{-1}.

Chloro(dimethylphosphinodithioato)tris(methyl diphenylphosphinite)ruthenium(II). The compounds $[RuCl_2\{PPh_2(OMe)\}_3]$ (0.20 g) and $Na[S_2PMe_2]\cdot 2H_2O$ (0.20 g) were shaken in benzene (20 cm^3) for 1 h, and the resulting yellow solution was filtered and reduced in volume to *ca*. 5 cm^3. Addition of light petroleum (b.p. 60—80 °C) then precipitated a yellow *solid* which was filtered off, washed with water, and dried *in vacuo*, m.p. 91—93 °C, $\nu(PS_2)$ at 595 cm^{-1}.

Similarly, *chloro(dimethylphosphinodithioato)tris(ethyl diphenylphosphinite)ruthenium*(II) was prepared from $[RuCl_2\{PPh_2(OEt)\}_3]$, m.p. 116—118 °C, $\nu(PS_2)$ at 595 cm^{-1}.

Tris(dimethylphenylphosphine)(dimethylphosphinodithioato)ruthenium(II) *tetraphenylborate*. The compounds $[RuCl_2(PMe_2Ph)_4]$ (0.20 g) and $Na[S_2PMe_2]\cdot 2H_2O$ (0.20 g) were shaken in methanol (20 cm^3) for 5 min to give a red solution. After filtering to remove any unchanged $Na[S_2PMe_2]\cdot 2H_2O$, a solution of $Na[BPh_4]$ (0.20 g) in methanol (5 cm^3) was added and the red *crystals* formed were filtered off and washed with water and diethyl ether, m.p. 149—151 °C, $\nu(PS_2)$ at 580 cm^{-1}. Gradient of plot of $\Lambda_0 - \Lambda$ against $c^{\frac{1}{2}}$ = 192 (for $[Ru_2Cl_3\{PPh_2(OMe)\}_6][BPh_4]$, 155; $[Ru(\eta\text{-}C_6H_6)(NH_3)_3][PF_6]_2$, 350). Similarly, reaction with $Na[S_2PPh_2]$ produced red crystals of *tris(dimethylphenylphosphine)(diphenylphosphinodithioato)ruthenium*(II) *tetraphenylborate*, m.p. 160—162 °C, $\nu(PS_2)$ at 570 cm^{-1}.

(Dimethylphosphinodithioato)tris(methyl diphenylphosphinite)ruthenium(II) *tetraphenylborate*, m.p. 184—186 °C, $\nu(PS_2)$ at 580 cm^{-1} (conductivity gradient in acetone = 215), and *diphenylphosphinodithioatotris(methyl diphenylphosphinite)ruthenium*(II) *tetraphenylborate*, m.p. 150—152 °C, $\nu(PS_2)$ at 570 cm^{-1}, were prepared as red-brown and orange-brown solids respectively by shaking $[RuCl_2\{PPh_2(OMe)\}_3]$

---

[14] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.

[15] R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.*, 1971, **10**, 2710.

[16] D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **11**, 233.

with $Na[S_2PR_2]$ in methanol for 5 min, followed by addition of $Na[BPh_4]$ in methanol to the resulting red solutions. Similarly, *(dimethylphosphinodithioato)tris(ethyl diphenylphosphinite)ruthenium*(II) *tetraphenylborate*, m.p. 116—118 °C, ν(PS_2) at 580 cm^{-1}, and *(diphenylphosphinodithioato)tris(ethyl diphenylphosphinite)ruthenium*(II) *tetraphenylborate*, m.p. 174—176 °C, ν(PS_2) at 570 cm^{-1}, were prepared as red-brown and orange-brown solids respectively.

Bis(dimethylphosphinodithioato)bis(ethyl diphenylphosphinite)ruthenium(II). The compounds $[RuCl_2\{PPh_2(OEt)\}_3]$ (0.20 g) and $Na[S_2PMe_2]\cdot 2H_2O$ (0.20 g) were heated under reflux in ethanol (20 cm^3) for 2 h to give a brown solution. On standing for 3 d a small amount of yellow-brown crystals was deposited, m.p. 230 °C, ν(PS_2) at 588 cm^{-1}.

Bis(dimethyl phenylphosphonite)bis(dimethylphosphinodithioato)ruthenium(II). The compounds $[RuCl_2\{PPh(OMe)_2\}_4]$ (0.20 g) and $Na[S_2PMe_2]\cdot 2H_2O$ (0.20 g) were heated under reflux in methanol (40 cm^3) for 1 h to give a bright yellow solution. After reducing in volume to *ca.* 15 cm^3 and leaving for 1 h, yellow crystals were deposited, filtered off, washed with water, and dried *in vacuo*, m.p. 207—209 °C, ν(PS_2) at 580 cm^{-1}. Similarly *bis(dimethyl phenylphosphonite)bis(diphenylphosphinodithioato)ruthenium*(II), m.p. 211—213 °C, was prepared by reaction of $[RuCl_2\{PPh(OMe)_2\}_4]$ with $Na[S_2PPh_2]$.

O-*Methyl Dithiocarbonato-complexes.*—*Tris(dimethylphenylphosphine)bis(*O*-methyl dithiocarbonato)ruthenium*(II). The compounds $[RuCl_2(PMe_2Ph)_4]$ (0.20 g) and $K[S_2COMe]$ (0.20 g) were shaken in methanol (30 cm^3) for 2 h during which time lemon-yellow crystals of the complex were deposited. These were filtered off and washed with water and diethyl ether, m.p. 123—125 °C. *Tris(methyl diphenylphosphinite)bis(*O*-methyl dithiocarbonato)ruthenium*(II), m.p. 111—113 °C, and *tris(ethyl diphenylphosphinite)bis(*O*-methyl dithiocarbonato)ruthenium*(II), m.p. 106—108 °C, were prepared similarly from $[RuCl_2\{PPh_2(OR)\}_3]$ (R = Me or Et) respectively.

*Bis(methyl diphenylphosphinite)bis(*O*-methyl dithiocarbonato)ruthenium*(II). The complex $[Ru(S_2COMe)_2\{PPh_2(OMe)\}_3]$ (0.20 g) was heated under reflux in CH_2Cl_2 (20 cm^3) containing $K[S_2COMe]$ (0.05 g) for 1 h to give an orange-yellow solution. Methanol (10 cm^3) was added and the dichloromethane allowed to evaporate off over 2 d to produce orange crystals, m.p. 85—87 °C.

*Bis(methyldiphenylphosphine)bis(*O*-methyl dithiocarbonato)ruthenium*(II). The compounds $[RuCl_2(PMe_2Ph)_4]$ (0.20 g) and $K[S_2COMe]$ (0.20 g) were shaken in methanol for 12 h. The bright yellow *solid* obtained was filtered off and washed with water and diethyl ether, m.p. 163—165 °C. *Bis(ethyldiphenylphosphine)bis(*O*-methyl dithiocarbonato)ruthenium*(II) was prepared similarly as a yellow solid from $[RuCl_2(PEtPh_2)_3]$, m.p. 147—149 °C.

Dialkyldithiocarbamato-complexes.— *(Dimethyldithiocarbamato)tetrakis(dimethylphenylphosphine)ruthenium*(II) *tetraphenylborate*. The compounds $[RuCl_2(PMe_2Ph)_4]$ (0.20 g) and $Na[S_2CNMe_2]\cdot 2H_2O$ (0.20 g) were shaken in methanol for 5 min. After filtering, $Na[BPh_4]$ (0.20 g) was added, and the white precipitate filtered off and washed with methanol and diethyl ether, m.p. 154—156 °C, ν(CN) at 1 525 cm^{-1}, conductivity gradient in CH_2Cl_2 = 185. Similarly, *(diethyldithiocarbamato)tetrakis(dimethylphenylphosphine)ruthenium*(II) *tetraphenylborate*, ν(CN) at 1 492 cm^{-1}, was prepared using $Na[S_2CNEt_2]\cdot 3H_2O$.

Bis(dimethyldithiocarbamato)tris(dimethylphenylphosphine)ruthenium(II).—The compounds $[RuCl_2(PMe_2Ph)_4]$ (0.20 g) and $Na[S_2CNMe_2]\cdot 2H_2O$ (0.20 g) were shaken in benzene (20 cm^3) for 1 h. The resulting yellow solution was reduced in volume to *ca.* 5 cm^3 and light petroleum added to precipitate a yellow *solid*, ν(CN) at 1 510 cm^{-1}. *Bis(dimethyldithiocarbamato)tris(methyl diphenylphosphinite)ruthenium*(II) was prepared similarly from $[RuCl_2\{PPh_2(OMe)\}_3]$, m.p. 95—97 °C, ν(CN) at 1 500br cm^{-1}.

(Dimethyldithiocarbamato)tris(methyl diphenylphosphinite)ruthenium(II) *tetraphenylborate*. The compounds $[RuCl_2\{PPh_2(OMe)\}_3]$ (0.20 g) and $Na[S_2CNMe_2]\cdot 2H_2O$ (0.20 g) were shaken in methanol (20 cm^3) for 10 min to give an orange solution. Addition of $Na[BPh_4]$ (0.20 g) produced an orange-pink solid which was filtered off, leaving a yellow filtrate. Recrystallisation of the solid from CH_2Cl_2–MeOH gave yellow crystals of $[Ru_2Cl_3\{PPh_2(OMe)\}_6][BPh_4]$ (identified by ^1H n.m.r. spectroscopy) but on further standing the remaining red solution gave red *crystals* of the complex, ν(CN) at 1 510 cm^{-1}. The yellow filtrate on slowly evaporating to half its volume produced orange-yellow crystals of *bis(dimethyldithiocarbamato)bis(methyl diphenylphosphinite)ruthenium*(II), m.p. 194—196 °C, ν(CN) at 1 510 cm^{-1}. Similarly, reaction with $Na[S_2CNEt_2]\cdot 3H_2O$ gave *(diethyldithiocarbamato)tris(methyl diphenylphosphinite)ruthenium*(II) *tetraphenylborate* as red crystals, ν(CN) at 1 480 cm^{-1}, and *bis(diethyldithiocarbamato)bis(methyl diphenylphosphinite)ruthenium*(II) as yellow crystals, m.p. 170—172 °C, ν(CN) at 1 482 cm^{-1}.

Bis(dimethyldithiocarbamato)bis(dimethyl phenylphosphonite)ruthenium(II). The compounds $[RuCl_2\{PPh(OMe)_2\}_4]$ (0.20 g) and $Na[S_2CNMe_2]\cdot 2H_2O$ (0.20 g) were heated under reflux in methanol for 1 h. The solution was filtered and the solvent allowed to evaporate off slowly to give yellow *crystals*, m.p. 178—180 °C, ν(CN) at 1 520 cm^{-1}. Reaction with $Na[S_2CNEt_2]\cdot 3H_2O$ yielded yellow crystals of *bis(diethyldithiocarbamato)bis(dimethyl phenylphosphonite)ruthenium*(II), m.p. 125—127 °C, ν(CN) at 1 482 cm^{-1}. The complexes *bis(dimethyldithiocarbamato)bis(methyldiphenylphosphine)ruthenium*(II), m.p. 229—231 °C, ν(CN) at 1 515 cm^{-1}, *bis(diethyldithiocarbamato)bis(methyldiphenylphosphine)ruthenium*(II), m.p. 84—86 °C, ν(CN) at 1 485 cm^{-1}, *bis(dimethyldithiocarbamato)bis(ethyldiphenylphosphine)ruthenium*(II), m.p. 133—135 °C, ν(CN) at 1 515 cm^{-1}, and *bis(diethyldithiocarbamato)bis(ethyldiphenylphosphine)ruthenium*(II), m.p. 152—154 °C, ν(CN) at 1 480 cm^{-1} were all obtained as yellow solids by shaking $[RuCl_2(PMePh_2)_4]$ (0.20 g) and $[RuCl_2(PEtPh_2)_3]$ (0.20 g) respectively with $Na[S_2CNMe_2]\cdot 2H_2O$ (0.20 g) and $Na[S_2CNEt_2]\cdot 3H_2O$ (0.20 g) in methanol (30 cm^3). The complexes were filtered off and washed with water and diethyl ether.

We thank Johnson, Matthey Ltd. for generous loans of ruthenium trichloride trihydrate, the S.R.C. for support (to W. J. S.), Dr. A. S. F. Boyd and Mr. J. R. A. Millar for obtaining the ^{31}P and ^1H n.m.r. spectra respectively, and the Department of Chemistry, Glasgow University, for the use of their Mechrolab osmometer.

[8/385 *Received, 2nd March,* 1978]