Metal Complexes of Sulphur Ligands. Part VII.[1] Reaction of *mer*-Trichlorotris(dimethylphenylphosphine)rhodium(III) with *NN*-Dimethyldithiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and *O*-Ethyl Dithiocarbonate (Xanthate) Ligands

By **David J. Cole-Hamilton** and **T. Anthony Stephenson,*** Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reactions of the complex *mer*-[RhCl$_3$(PMe$_2$Ph)$_3$], (I), with excess of (S–S)$^-$ ion [(S–S)$^-$ = $^-$S$_2$CNMe$_2$, $^-$S$_2$PMe$_2$, $^-$S$_2$PPh$_2$, $^-$S$_2$COEt] have been thoroughly studied. On shaking in methanol for 10 min, the complexes *mer*-[RhCl$_2$(S–S)(PMe$_2$Ph)$_3$], (IV), are formed which contain a unidentate dithio-acid group. Recrystallisation of complexes (IV) from non-polar solvents gives *trans*-[RhCl$_2$(S–S)(PMe$_2$Ph)$_2$], (II). For (S–S)$^-$ = $^-$S$_2$PMe$_2$ or $^-$S$_2$PPh$_2$, further recrystallisation gives small amounts of the *cis–cis–cis*-isomers (VII). Conversely, for (S–S)$^-$ = $^-$S$_2$CNMe$_2$ or $^-$S$_2$COEt, reaction of complexes (IV) with NaBPh$_4$ in methanol gives some *mer*-[RhCl(S–S)(PMe$_2$Ph)$_3$]BPh$_4$, (V), as well as (II). However, reaction of complex (I) with excess of (S–S)$^-$ heated under reflux in ethanol for 60 min, followed by addition of Y (Y = BPh$_4^-$ or PF$_6^-$) to the filtrate, gives high yields of *cis*-[Rh(S–S)$_2$(PMe$_2$Ph)$_2$]Y [III; (S–S)$^-$ = $^-$S$_2$CNMe$_2$, $^-$S$_2$PMe$_2$, or $^-$S$_2$PPh$_2$]. Reaction of the complex *mer*-[RhCl$_3$(PMePh$_2$)$_3$] with NaS$_2$CNMe$_2$,2H$_2$O in ethanol gives both *cis*- and *trans*-[Rh(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$]Y [(III) and (VI) respectively]. In contrast, reaction of complex (I) with KS$_2$COEt gives *mer*-[RhCl(S$_2$CO)(PMe$_2$Ph)$_3$] (X), K[RhCl$_2$(S$_2$CO)(PMe$_2$Ph)$_2$] (XI), and *trans*- and *cis*-[Rh(S$_2$CO)(S$_2$COEt)(PMe$_2$Ph)$_2$] [(XII) and (XIII) respectively], which can be separated by chromatography. The complexes have been characterised by elemental analyses and i.r. and n.m.r. spectroscopy (^{1}H and ^{31}P), and a detailed mechanism for the overall reaction is postulated.

PREVIOUS papers in this series have been concerned with an examination of dithio-acid complexes of palladium,[2-5] platinum,[3-5] and ruthenium [1,6,7] and, in particular, those complexes with ligands containing Group VB donor atoms (L) have been thoroughly studied. All these metals are characterised by the possession of a stable bivalent oxidation state and, in addition, form complexes which are fairly labile. Thus, with palladium and platinum, complexes of the type [M(S-S)$_2$L] and [M(S-S)L$_2$](S-S) are formed, which exhibit (to date) seven different types of intra- and inter-molecular rearrangement reactions which can be monitored by various spectroscopic techniques. Complexes formed with ruthenium of type *cis*-[Ru(S-S)$_2$L$_2$] also exhibit rearrangement reactions, which have been interpreted as arising from facile interconversion of optical enantiomers *via* ruthenium–sulphur bond rupture [for (S-S)$^-$ = $^-$S$_2$PMe$_2$] and rotation about the C=N bond at elevated temperatures for (S-S)$^-$ = $^-$S$_2$CNMe$_2$.

In view of these results it was decided to extend our studies to rhodium, where complexes of the bivalent oxidation state are comparatively rare [8] and where, in general, complexes are less labile than those formed with ruthenium.[8,9] The results of this detailed investigation are presented below.

RESULTS AND DISCUSSION

Because of our previous success in generating dithio-complexes by replacement of chloro-groups in various ruthenium-(II) and -(III) tertiary phosphine and phosphite complexes by reactions with various alkali-metal dithio-acid salts,[6] we decided to use the same methods in this work. This method has already been employed with some success for the synthesis of other complexes of rhodium containing dithio-acid ligands, *viz.*: [Rh(S$_2$PR$_2$)$_3$] (R = Ph,[10] Et,[11] or F [12]); [Rh(S$_2$CNR$_2$)$_3$] (R = Me,[13-15] Et,[13,14] or Bu^n [13]); [Rh(S$_2$CR)$_3$] (R = Ph or PhCH$_2$);[16] NH$_4$[Rh(S$_2$CPh)$_2$Cl$_2$];[16] [Rh{S$_2$P(OEt)$_2$}$_3$];[17] [Rh(S$_2$CNR$_2$)$_3$PPh$_3$] (R = Me [15] or Et [18]); [Rh(S$_2$CNMe$_2$)(PPh$_3$)$_2$];[15] [Rh(S$_2$CNR$_2$)(CO)$_2$] (R = Me or Et);[14] [Rh(S$_2$CNMe$_2$)(CO)PPh$_3$];[15] [Rh(S$_2$CNMe$_2$)$_3$(CO)PPh$_3$];[15] {Rh(S$_2$PPh$_2$)PPh$_3$}$_2$;[19] [Rh(S$_2$PPh$_2$)$_3$PPh$_3$];[18] [Rh{S$_2$P(OEt)$_2$}$_3$(PPh$_3$)$_3$];[18] [Rh(S$_2$CNEt$_2$)$_2$(PPh$_3$)$_2$]BF$_4$;[18] and [Rh(S$_2$PF$_2$)(CO)$_2$]$_2$.[20] The alternative method of preparing these complexes, namely by direct reaction of free ligand with complexes

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TABLE 1

Analytical data for some rhodium complexes

Complex		Colour	M.p. (t/°C)	Found (%)				Calc. (%)				Λ [a]
				C	H	N	Cl	C	H	N	Cl	
trans-$[RhCl_2(S_2CNMe_2)(PMe_2Ph)_2]$	(II)	Orange	207—208	39·9	4·9	2·6	12·5	40·0	4·9	2·5	12·5	
cis-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]BPh_4$	(III)	Yellow	178—180	58·7	5·7	2·8		58·9	5·8	3·0		64·8 (3·5)
cis-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]PF_6$	(III)	Yellow	204—206	34·6	4·5	3·7		34·6	4·5	3·7		77·4 (10·5)
mer-$[RhCl_2(S_2CNMe_2)(PMe_2Ph)_3]$	(IV)	Orange	189—195 (decomp.)	45·4	5·5	1·7		45·8	5·5	2·0		
mer-$[RhCl(S_2CNMe_2)(PMe_2Ph)_3]BPh_4$	(V)	Yellow	176—178	61·4	5·9	1·3	3·8	61·7	6·0	1·4	3·6	50·0 (10·2)
trans-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]BPh_4$	(VI)	Yellow	192—195	62·4	5·6	2·7		63·3	5·5	2·6		53·2 (5·4)
trans-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]PF_6$	(VI)	Yellow	>230	43·3	4·3	3·1		43·2	4·3	3·2		68·1 (8·7)
$[Rh(S_2CNMe_2)_2(PMePh_2)_2]BPh_4$ [b]	(III), (VI)	Yellow		62·1	5·6	2·4		63·3	5·5	2·6		
cis-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]BPh_4$	(III)	Yellow	110—112	63·8	5·2			64·2	5·2			74·0 (2·0)
cis-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]PF_6$	(III)	Orange	128—130	47·3	4·2			47·0	4·1			74·0 (10·5)
cis–cis–cis-$[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$	(VII)	Orange	208—210	48·0	4·5			48·1	4·6			
cis-$[Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4$	(III)	Yellow	72—73	57·2	5·9			55·7	5·7			49·2 (9·2)
mer-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_3]$	(IV)	Orange	140—142 (decomp.)	43·9	5·8			43·8	5·5			
trans-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$	(II)	Orange	235—237 (decomp.)	37·8	4·9		12·5	37·6	4·9		12·4	
cis–cis–cis-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$	(VII)	Orange	184—186	37·8	4·9			37·6	4·9			
trans-$[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$	(II)	Orange	228—229 (decomp.)	48·1	4·8			48·1	4·6			
mer-$[RhCl(S_2CO)(PMe_2Ph)_3]$	(X)	Orange	150—155 (decomp.)	45·9	5·2			46·5	5·1			
$K[RhCl_2(S_2CO)(PMe_2Ph)_2]$	(XI)	Yellow	195 (decomp.)	34·9	3·8			35·1	3·8			64·0 (5·2)
trans-$[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$	(XII)	Yellow	150—153 (decomp.)	40·5	4·6			40·5	4·6			
cis-$[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$	(XIII)	Yellow	172—173 (decomp.)	40·6	4·7			40·5	4·6			
trans-$[RhCl_2(S_2COEt)(PMe_2Ph)_2]$	(II)	Orange	155—157	40·1	4·8		12·2	39·9	4·7		12·5	
mer-$[RhCl_2(S_2COEt)(PMe_2Ph)_3]$	(IV)	Orange	120—123 (decomp.)	45·4	5·5		10·3	45·6	5·4		10·0	
mer-$[RhCl(S_2COEt)(PMe_2Ph)_3]BPh_4$	(V)	Orange	89—91	59·6	5·8			61·7	5·8			

[a] In Ω^{-1} cm^2 mol^{-1}; measured in $MeNO_2$ at 298 K; conc. (10^{-4}M) in parentheses. [b] Mixture of *cis*- and *trans*-isomers (^{1}H n.m.r. evidence).

TABLE 2

I.r. spectra (cm^{-1}) of various rhodium dithio-acid complexes (shoulders in italics)

Complex		ν(RhCl)	Dithio-acid ligand absorptions
mer-$[RhCl_3(PMe_2Ph)_3]$	(I)	339, 313, 273	
mer-$[RhCl_2(S_2CNMe_2)(PMe_2Ph)_3]$	(IV)	339, 319	1 432 [a]
mer-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_3]$	(IV)	342, 309	601 [b]
mer-$[RhCl_2(S_2COEt)(PMe_2Ph)_3]$	(IV)	342, 312	1 200 [c]
trans-$[RhCl_2(S_2CNMe_2)(PMe_2Ph)_2]$	(II)	332, 320	1 520br [a]
trans-$[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$	(II)	340, 330	645, 580 [d]
cis–cis–cis-$[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$	(VII)	339, 312	630, 576 [d]
trans-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$	(II)	*330*, 321	589 [e]
cis–cis–cis-$[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$	(VII)	330, 318	580 [e]
trans-$[RhCl_2(S_2COEt)(PMe_2Ph)_2]$	(II)	338, 325	1 240 [c]
mer-$[RhCl(S_2CNMe_2)(PMe_2Ph)_3]BPh_4$	(V)	320	1 549br [a]
mer-$[RhCl(S_2COEt)(PMe_2Ph)_3]BPh_4$	(V)	342	1 258br [c]
mer-$[RhCl(S_2CO)(PMe_2Ph)_3]$	(X)	312	1 680br,[f] 1 600 [f]
$K[RhCl_2(S_2CO)(PMe_2Ph)_2]$	(XI)	320	1 640,[f] 1 610 [f]
trans-$[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$	(XII)		1 670br,[f] 1 592,[f] 1 248 [c]
cis-$[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$	(XIII)		1 680br,[f] 1 598,[f] 1 255 [c]
cis-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]BPh_4$	(III)		1 540br [a]
cis-$[Rh(S_2CNMe_2)_2(PMe_2Ph)_2]PF_6$	(III)		1 540br [a]
cis-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]BPh_4$	(III)		572 [d,g]
cis-$[Rh(S_2PPh_2)_2(PMe_2Ph)_2]PF_6$	(III)		572 [d,g]
cis-$[Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4$	(III)		577 [e]

[a] ν(CN) ($^-S_2CNMe_2$) (refs. 15 and 26). [b] Band for unidentate S_2PMe_2 (refs. 5 and 6). [c] ν(C–O) ($^-S_2COEt$); D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, **11**, 305 and refs. therein. [d] Bands for bidentate $^-S_2PPh_2$ (refs. 3 and 6). [e] Band for bidentate $^-S_2PMe_2$ (refs. 5 and 6). [f] ν(C=O)($^{2-}S_2CO$); J. P. Fackler, jun., and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631. [g] Higher-energy band positions masked by BPh_4^- or PF_6^- vibrations.

already containing the dithio-acid ligands, has also been used, but less frequently, *e.g.* in the preparation of [Rh(S$_2$PF$_2$)(CO)L] (L = PPh$_3$, AsPh$_3$, or SbPh$_3$) from {Rh(S$_2$PF$_2$)(CO)$_2$}$_2$ and L.[20]

In this work, reaction of the complex *mer*-[RhCl$_3$(PMe$_2$Ph)$_3$], (I),[21] with an excess of alkali-metal or ammonium dithio-acid salt under reflux for 1 h led to formation of several different products in every case. These products were separated by fractional recrystallisation or dry-column chromatography,[22] or, in general, each was synthesised as the sole product by slight changes in the conditions of reaction. Analytical data for all these new complexes are given in Table 1 and spectroscopic properties in Tables 2 and 3.

TABLE 3

^{1}H N.m.r. data for various rhodium complexes (in CDCl$_3$)

Complex		T/K	τ Value[a]		
			Dithio-ligand	Methyl groups of phosphine	Phenyl groups
mer-[RhCl$_3$(PMe$_2$Ph)$_3$]	(I)	301		8·04 (t) (8·0),[b] 8·70 (d) (11·0) [c]	2·3—3·2
mer-[RhCl$_2$(S$_2$CNMe$_2$)(PMe$_2$Ph)$_3$]	(IV)	301	6·83 (s)	8·02 (t) (8·0),[b] 8·76 (d) (12·0) [c]	2·2—3·0
mer-[RhCl$_2$(S$_2$PMe$_2$)(PMe$_2$Ph)$_3$]	(IV)	301	7·72 (d) (13·0) [c]	7·88 (t) (8·0),[b] 8·74 (d) (11·0) [c]	2·2—3·2
mer-[RhCl$_2$(S$_2$COEt)(PMe$_2$Ph)$_3$]	(IV)	301	5·47 (q) (7·0),[d] 8·56 (t) (7·0) [d]	8·18 (t) (8·0),[b] 8·80 (d) (11·0) [c]	2·3—3·2
mer-[RhCl(S$_2$CNMe$_2$)(PMe$_2$Ph)$_3$]BPh$_4$	(V)	301	7·14 (s), 7·45 (s)	8·20 (t) (7·5),[b] 8·34 (t) (7·5),[b] 8·72 (d) (10·5) [c]	2·0—3·3
mer-[RhCl(S$_2$CO)(PMe$_2$Ph)$_3$]	(X)	301		7·98 (t) (7·5),[b] 8·33 (t) (7·5),[b] 8·85 (d) (10·0) [c]	2·2—3·4
trans-[RhCl$_2$(S$_2$CNMe$_2$)(PMe$_2$Ph)$_2$]	(II)	301	6·54 (s)	8·31 [e] (11·0) [b]	2·2—2·8
trans-[RhCl$_2$(S$_2$PMe$_2$)(PMe$_2$Ph)$_2$]	(II)	301	7·98 (d) (13·0) [c]	8·32 [e] (11·0) [b]	2·2—2·8
trans-[RhCl$_2$(S$_2$PPh$_2$)(PMe$_2$Ph)$_2$]	(II)	301		8·34 [e] (11·0) [b]	2·2—2·8
trans-[RhCl$_2$(S$_2$COEt)(PMe$_2$Ph)$_2$]	(II)	301	5·50 (q) (7·0,) [d] 8·66 (t) (7·0) [d]	8·29 [e] (11·0) [b]	2·2—2·8
cis–cis–cis-[RhCl$_2$(S$_2$PMe$_2$)(PMe$_2$Ph)$_2$]	(VII)	301	7·52 (d) (13·0),[c] 8·26 (d) (13·0) [c]	8·10 [e] (11·0),[b] 8·29 [e] (11·0) [b]	2·4—3·2
K[RhCl$_2$(S$_2$CO)(PMe$_2$Ph)$_2$] [f]	(XI)	301		8·22 (t) (8·0) [b]	2·0—2·9
trans-[Rh(S$_2$CO)(S$_2$COEt)(PMe$_2$Ph)$_2$]	(XII)	301	6·30 (q) (7·0),[d] 8·90 (t) (7·0) [d]	8·16 (t) (7·0) [b]	2·4—2·8
cis-[Rh(S$_2$CO)(S$_2$COEt)(PMe$_2$Ph)$_2$]	(XIII)	301	5·44 (q) (7·0),[d] 8·57 (t) (7·0) [d]	8·24 (d) (9·0),[c] 8·35 (d) (9·0),[c] 8·48 (d) (9·5),[c] 8·53 (d) (9·0) [c]	2·6—3·2
cis-[Rh(S$_2$PMe$_2$)$_2$(PMe$_2$Ph)$_2$]BPh$_4$	(III)	301	7·86 (d) (13·0),[c] 8·30 (d) (13·0) [c]	8·32 [e] (8·0),[b] 8·42 [e] (8·0) [b]	2·4—3·4
cis-[Rh(S$_2$PPh$_2$)$_2$(PMe$_2$Ph)$_2$]BPh$_4$	(III)	301		8·38 [e] (10·0),[b] 8·48 [e] (10·0) [b]	2·0—3·2
cis-[Rh(S$_2$PPh$_2$)$_2$(PMe$_2$Ph)$_2$]PF$_6$	(III)	301		8·22 [e] (10·0),[b] 8·28 [e] (10·0) [b]	2·0—3·2
cis-[Rh(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_2$]BPh$_4$	(III)	301	6·96 (s), 7·00 (s)	8·46 [e] (8·0),[b] 8·56 [e] (8·0) [b]	2·4—3·3
		333	6·93 (s), 6·96 (s)	8·45 [e] (10·0),[b] 8·50 [e] (10·0) [b]	
cis-[Rh(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_2$]PF$_6$	(III)	227	6·63 (s), 6·65 (s)	8·32 [e] (9·5),[b] 8·38 [e] (9·5) [b]	2·6—3·2
		264	6·67 (s), 6·68 (s)	8·34 [e] (9·5),[b] 8·38 [e] (10·5) [b]	
		301	6·71 (s)	8·37 [e] (9·5) [b]	
trans-[Rh(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$]BPh$_4$	(VI)	301	7·60 (s)	7·92 (t) (6·5) [b]	2·4—3·4
trans-[Rh(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$]PF$_6$	(VI)	301	7·33 (s)	7·90 (t) (7·0) [b]	2·3—3·2
cis-[Rh(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$]BPh$_4$ [g]	(III)	301	7·22 (s), 7·40 (s)	8·18 [e] (8·0) [b]	2·4—3·4
cis-[Rh(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$]PF$_6$ [g]	(III)	301	7·00 (s), 7·27 (s)	8·08 [e] (8·0) [b]	2·3—3·2

s = Singlet, d = doublet, t = triplet, and q = quartet.

[a] ±0·01. [b] Since $H_nPP^1H_n{}^1$ type spectrum, coupling constant is $|J_{PH} + J_{PH}'|$ in Hz. [c] J_{PH} in Hz. [d] $J_{CH_3-CH_2}$ in Hz. [e] Pseudo-doublet. [f] Measured in (CD$_3$)$_2$CO. [g] Spectrum obtained from mixture of *cis*- and *trans*-isomers.

NN-*Dimethyldithiocarbamato-complexes*.— Heating complex (I) under reflux with an excess of NaS$_2$CNMe$_2$,2H$_2$O in ethanol for 1 h led to formation of two products. These were readily separated, since one of them, [RhCl$_2$(S$_2$CNMe$_2$)(PMe$_2$Ph)$_2$] (II), is insoluble in cold ethanol whereas the other is very soluble. After removal of complex (II), the other was precipitated in high yield as a yellow crystalline complex by addition of excess of NaBPh$_4$ or NH$_4$PF$_6$. The latter salts are strongly conducting in CH$_2$Cl$_2$ and analyse for [Rh(S$_2$CNMe$_2$)$_2$(PMe$_2$Ph)$_2$]Y (III; Y = BPh$_4^-$ or PF$_6^-$). Longer reaction times in ethanol led exclusively to product (III) on addition of Y.

However, when a suspension of complex (I) and NaS$_2$CNMe$_2$,2H$_2$O was shaken in methanol for 10 min, the orange methanol-insoluble [RhCl$_2$(S$_2$CNMe$_2$)(PMe$_2$Ph)$_3$], (IV), was formed, but on recrystallisation from dichloromethane–hexane this was converted into (II). When (IV) was shaken in methanol with a mixture of NaBPh$_4$ and PMe$_2$Ph for 24 h, (II) was again formed together with a new complex [RhCl(S$_2$CNMe$_2$)(PMe$_2$Ph)$_3$]BPh$_4$, (V). Attempts to prepare the latter directly from complex (I) by reaction with NaS$_2$CNMe$_2$,2H$_2$O, NaBPh$_4$, and PMe$_2$Ph proved abortive; instead, the yellow conducting solid [RhCl$_2$(PMe$_2$Ph)$_4$]BPh$_4$ [23] formed which, on setting aside in CDCl$_3$ for 48 h, reverted to (I) and free PMe$_2$Ph.

Finally, when the complex *mer*-[RhCl$_3$(PMePh$_2$)$_3$] was used instead of (I) long-term reaction in ethanol heated under reflux with excess of NaS$_2$CNMe$_2$,2H$_2$O, followed by addition of NaBPh$_4$, gave *two* ionic complexes, both of formula [Rh(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$]BPh$_4$, (III) and (VI), together with very small amounts of [Rh(S$_2$CNMe$_2$)$_3$]. Similar complexes [Rh(S$_2$CNMe$_2$)$_2$(PMePh$_2$)$_2$]PF$_6$ were formed on addition of NH$_4$PF$_6$.

Diphenyl- and Dimethyl-phosphinodithioato-complexes.—When complex (I) was heated under reflux in ethanol for 60 min with an excess of NH$_4$S$_2$PPh$_2$, addition of excess of NaBPh$_4$ or NH$_4$PF$_6$ led to precipitation of the

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[21] P. R. Brookes and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1079.

[22] B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

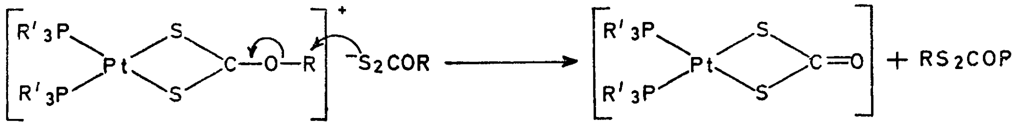
[23] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1693.

expected $[Rh(S_2PPh_2)_2(PMe_2Ph)_2]Y$ (III; $Y = BPh_4^-$ or PF_6^-). In addition, very small amounts of an ethanol-insoluble complex analysing for $[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$, (VII), were obtained. However, when the reaction was carried out using $NaS_2PMe_2,2H_2O$, the analogous complexes were not formed; instead, a red solid of uncertain composition was obtained which exhibited variable analyses (carbon and hydrogen) each time the reaction was attempted. The ^1H n.m.r. spectrum of this material contained only broad peaks, which were temperature invariant. The broadness of these signals probably arises from a paramagnetic impurity since the substance exhibited a weak e.s.r. signal {*cf.* the preparation of $[RhCl(PPh_3)_3]$ [24]}. The complex $[Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4$, (III), was, however, prepared as a yellow microcrystalline solid either by excluding oxygen completely from the reaction in ethanol or by reaction of *fac*-$[RhCl_3(PMe_2Ph)_3]$ [21] with excess of $NaS_2PMe_2,2H_2O$ in acetone, followed by addition of $NaBPh_4$. The compound is, in fact, stable both in the solid state and in solution; however, a red solution is rapidly formed when the complex is dissolved in ethanol or methanol in the presence of excess of $NaS_2PMe_2,2H_2O$ and air.

Short-term reactions between complex (I) and $NaS_2PMe_2,2H_2O$ or $NH_4S_2PPh_2$ also differed slightly from one another. The dimethylphosphinodithioato-ion behaved like the *NN*-dimethyldithiocarbamato-ion, giving, after shaking for 10 min in methanol, orange $[RhCl_2(S_2PMe_2)(PMe_2Ph)_3]$ (IV), which, on recrystallisation from deuteriochloroform–hexane, gave $[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$, (II). Recrystallisation of the latter from hot toluene gives mainly (II), together with a small amount of another complex, (VII), with the same analytical data but different spectral properties. In contrast, shaking complex (I) and $NH_4S_2PPh_2$ in ethanol for 10 min gave only $[RhCl_2(S_2PPh_2)(PMe_2Ph)_2]$, (II). The latter complex had different spectral properties from (VII), although recrystallisation from hot ethanol gave small amounts of (VII).

Finally, attempts to prepare the complex $[RhCl(S_2PMe_2)(PMe_2Ph)_3]BPh_4$ by reaction between $[RhCl_2(S_2PMe_2)(PMe_2Ph)_3]$ (IV), $NaBPh_4$, and PMe_2Ph in methanol yielded only $[Rh(O_2)(PMe_2Ph)_4]BPh_4$ (VIII),[25] or, if oxygen was excluded, a mixture of $[RhCl_2(PMe_2Ph)_4]BPh_4$ (IX) [23] and $[RhCl_2(S_2PMe_2)(PMe_2Ph)_2]$, (II). Compound (VIII) was also formed as the sole product from reaction of $[Rh(S_2PMe_2)_3]$, PMe_2Ph, and $NaBPh_4$.

O-Ethyl Dithiocarbonate (*Xanthate*) *and Dithiocarbonate Complexes*.—The reaction of KS_2COEt with complex (I) led to an even wider range of products than those found with the other dithio-ligands, since there is the added possibility of attack on a co-ordinated xanthate ligand by a nucleophile to yield dithiocarbonato-complexes [equation (1)].[4] Thus, when complex (I) was heated under reflux in ethanol with excess of KS_2COEt for 60 min, no fewer than four different complexes, which were separated by dry-column chromatography, were isolated. Analytical and spectroscopic analyses indicated the formulations $[RhCl(S_2CO)(PMe_2Ph)_3]$ (X), $K[RhCl_2(S_2CO)(PMe_2Ph)_2]$ (XI), and two isomers of $[Rh(S_2CO)(S_2COEt)(PMe_2Ph)_2]$, (XII) and (XIII). However, when the reaction was carried out in a less-polar solvent such as acetone or ethanol–chloroform, *none* of these products was obtained but, instead, orange $[RhCl_2(S_2COEt)(PMe_2Ph)_2]$, (II), was isolated.



(1)

As for $(S-S)^- = {}^-S_2CNMe_2$, shaking complex (I) and KS_2COEt in methanol for 10 min gave the dark orange $[RhCl_2(S_2COEt)(PMe_2Ph)_3]$, (IV), which yielded (II) on recrystallisation from hot methanol or chloroform–hexane. This interconversion was also affected by heating (IV) to its melting point (120—123 °C), whereupon PMe_2Ph was evolved and the orange residue consisted largely of compound (II).

Finally, when complex [IV; $(S-S)^- = {}^-S_2COEt$] was shaken in ethanol with excess of $NaBPh_4$ for several weeks, a small amount of $[RhCl(S_2COEt)(PMe_2Ph)_3]BPh_4$, (V), was deposited. The latter complex was also prepared in high yield by reaction of (I) and KS_2COEt (1 : 1 molar ratio) in methanol heated under reflux for 60 min, followed by addition of $NaBPh_4$. Longer reaction times (5 h) gave yellow solutions from which compounds (X) and (XIII) were isolated.

Spectroscopic Properties of the Dithio-acid Complexes.—*I.r. spectra.* Group theory predicts three i.r.-active $\nu(RhCl)$ stretching vibrations for complex (I) and Brookes and Shaw [21] assign these to the peaks at 339, 313, and 273 cm^{-1}, with the band at lowest energy arising (predominantly) from the stretch of the rhodium–chloride bond *trans* to a PMe_2Ph group. Thus, analysis of the Rh–Cl stretching region of some of these new complexes should yield information about their structures. Also, earlier work in this and other laboratories suggests that the position of the sulphur-ligand absorption bands should give some information about the mode of bonding of the dithio-acid group.

For each of the complexes (IV), the $\nu(RhCl)$ region was similar to that of (I) (Table 2) except that the lowest band had disappeared, indicating that the chloride ion *trans* to phosphine has been replaced. This

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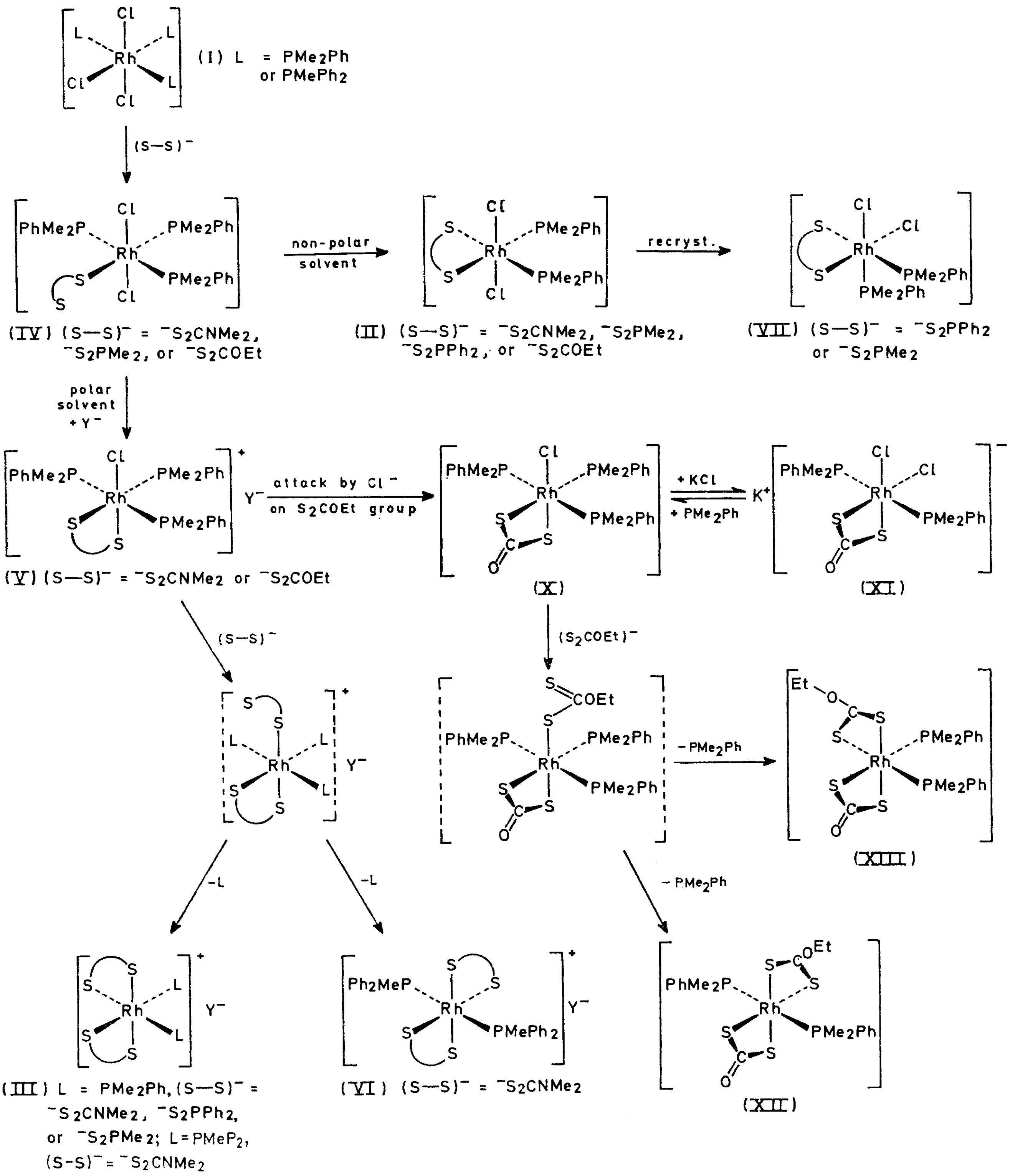
[24] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[25] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685.



Scheme

Compounds shown in broken square brackets were not isolated is in agreement with the larger *trans*-labilising effect of PMe_2Ph compared to chloride ion and with the results of other exchange reactions carried out by Brookes and Shaw.[21] In addition, for $(S{-}S)^- = {}^-S_2PMe_2$ the absorption at 601 cm^{-1},[5,6] and for $(S{-}S)^- = {}^-S_2CNMe_2$ the position of ν(CN) below 1 470 cm^{-1},[15,26] both suggest that the sulphur ligands are co-ordinated through only one sulphur atom.

Since there was little change in the ν(RhCl) region from complexes (IV) to (II), and since all the dithio-ligand absorptions now have characteristic frequencies for bidentate co-ordination (see Table 2), it seems reasonable to infer that the chloro-groups remain mutually *trans* and that chelation of the dithio-ligand occurs with concomitant loss of a PMe_2Ph group. From an i.r. standpoint, there was very little difference between the ν(RhCl) region or between the ν(PS) region for complexes (II) and (VII), although other parts of their i.r. spectra and their ^1H n.m.r. spectra are substantially different (see later).

The remaining complexes all appeared to contain only chelated dithio-groups and had only one or no ν(RhCl) bands and, hence, little stereochemical information can be gleaned from i.r. studies. N.m.r. spectroscopy has, however, proved an invaluable tool in assigning structures to all these complexes.

N.m.r. spectra. The only differences between ^1H n.m.r. spectra of complexes (IV) and (I) were that dithio-ligand resonances occurred in the former and that positions of the triplet and doublet arising from the phosphine groups were very slightly different (Table 3), presumably because of different shielding effects of the dithio-ligands from that of chloride ion. In agreement with the i.r. data, this confirms the structure of these complexes (Scheme), since if either of the other chloride ions had been replaced the plane of symmetry passing through the three phosphorus atoms would have been removed and, because of hindered rotation about the rhodium–phosphorus bonds, two triplets would arise from the methyl groups of the mutually *trans* phosphine ligands {*cf.* *cis*-$[RuCl_2(CO)(PMe_2Ph)_3]$ [27]}.

In fact, ^1H n.m.r. spectra of the complexes [V; $(S{-}S)^- = {}^-S_2CNMe_2$] and (X) did show two triplets arising from the *trans*-phosphine groups, indicating that there is no plane of symmetry through these phosphines and hence (V) is assigned the structure shown in the Scheme. Further evidence that complex [V; $S{-}S)^- = {}^-S_2CNMe_2$] has the structure shown stems from the fact that, at 301 K, there were two resonances arising from methyl groups on the dithiocarbamato-ligand which can only be explained if there is no plane of symmetry perpendicular to the S_2CN plane in the molecule and if rotation about the C=N bond is hindered. Since the two resonances remained sharp up to 320 K, it appears that free rotation about the C=N bond is not occurring, even at this temperature. Complex (X) is most probably formed from [V; $(S{-}S)^- = {}^-S_2COEt$] by attack of a previously displaced chloride ion on the co-ordinated *O*-ethyl dithiocarbonato-group.

Complexes (II) showed only one dithio-ligand resonance in each case, together with one $H_6PP'H'_6$ pseudo-doublet * which arises from the PMe_2Ph groups. Since $J_{PP'}$ was small and there was only one phosphine methyl resonance, the phosphine groups must be mutually *cis* and the phosphorus atoms must lie on the plane of symmetry of the molecule. The sulphur ligand must also have planes of symmetry both in the S–Rh–S plane and also perpendicular to it since, if any of these were absent, either the complex with $(S{-}S)^- = {}^-S_2CNMe_2$ or ${}^-S_2PMe_2$ would give rise to *two* dithio-ligand resonances. Thus, the only possible structure for these complexes is that with *trans*-chloride groups (as suggested by i.r. studies).

Since ^1H n.m.r. spectra of the complex [VII; $(S{-}S)^- = {}^-S_2PMe_2$] contained no triplet pattern, the complex cannot contain *trans*-PMe_2Ph groups. The only possible structure for this isomer is one containing *cis*-chlorides and -phosphines. This structure should exhibit four phosphine methyl doublets but only two were observed (Table 3). This could be due to fast rotation about the metal–phosphorus bonds at room temperature but, since solutions used for this n.m.r. study were very weak [because of the small yield of (VII)], it is possible that further small splittings were obscured by the high noise level. Further support for the correctness of this *cis–cis–cis*-isomer formulation for complex (VII) comes from recent studies of the isomerisation reaction of $[RuCl_2(CO)_2(EPh_3)_2]$ (E = P or As) where recrystallisation of *trans*-$[RuCl_2(CO)_2(EPh_3)_2]$ gives the more stable *cis–cis–cis*-isomer.[29]

The ^1H n.m.r. spectrum of complex (XI) consisted of broad peaks in the phenyl region, together with a single sharp triplet at τ 8·22. This can only occur if the phosphine groups are mutually *trans* (' virtually coupled ' triplet with large $J_{PP'}$).[28] A possible mode of formation of this rather unusual complex is by attack of potassium chloride, formed from reaction of (I) and KS_2COEt on (X). The PMe_2Ph group released could then attack (XI) to reproduce (X) with loss of potassium chloride. Since both complexes were found in the reaction mixture, it seems probable that in the presence of excess of KCl and PMe_2Ph an equilibrium is set up between the two complexes.

^1H N.m.r. spectra of the two complexes (XII) and (XIII) both contained quartet and triplet signals in positions expected for an OEt group, but the pattern arising from the methyl groups on the two phosphines

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* A ' pseudo-doublet ' is a sharp doublet with additional signal intensity situated between the doublet. This spectral pattern is indicative of a small, but non-zero, $J_{PP'}$ value when compared to $|J_{PH} + J_{PH'}|$.[28]

[26] D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 1152 and refs. therein.

[27] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.

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

[29] R. B. James and L. D. Markham, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 373; L. Ruiz-Ramírez, T. A. Stephenson, and E. S. Switkes, *J.C.S. Dalton*, 1973, 1770.

was quite different in each case. Complex (XII) exhibited a single ' virtually coupled ' triplet indicative of *trans*-phosphines, whereas (XIII) showed four doublets which suggests that the two phosphine groups are mutually *cis* and in different chemical environments and that there is hindered rotation about the rhodium–phosphorus bonds. A similar phosphine methyl pattern is observed for one isomer of the complex $[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2CO}]$.[6] For complex (XIII), the proton-noise-decoupled $^{31}\mathrm{P}$ n.m.r. spectrum showed two resonances (indicating the phosphorus atoms are magnetically inequivalent) each split into a doublet of doublets by coupling to the rhodium-103 nucleus and the other phosphorus atom. The $^{103}\mathrm{Rh}$ n.m.r. spectrum of complex (XIII) was also measured by decoupling the proton spectrum. Each peak arising from a methyl group in the $^{1}\mathrm{H}$ n.m.r. spectrum was rather broad (2—3 Hz) due to $^{103}\mathrm{Rh}$–$^{1}\mathrm{H}$ coupling and, hence, irradiation in the rhodium range of frequencies sharpened some of the signals but not others. In this way, the rhodium spectrum may be seen to consist of four resonances, *i.e.* a doublet of doublets arising from coupling to two inequivalent phosphorus atoms. The only structure consistent with all this information is that shown in the Scheme.

Complexes (III) $[(\mathrm{S{-}S})^- = {}^-\mathrm{S_2CNMe_2}$, $\mathrm{Y = BPh_4^-}$ or $\mathrm{PF_6^-}$; $(\mathrm{S{-}S})^- = {}^-\mathrm{S_2PMe_2}$, $\mathrm{Y = BPh_4^-}]$ all had low-temperature $^{1}\mathrm{H}$ n.m.r. spectra consistent with *cis*-phosphines and hindered rotation about the rhodium–phosphorus bonds, namely two resonances corresponding to the methyl groups on the dithio-ligands and two pseudo-doublets arising from the phosphine methyl groups. The $^{1}\mathrm{H}$ n.m.r. spectrum of the complex *cis*-$[\mathrm{Rh(S_2PMe_2)_2(PMe_2Ph)_2]BPh_4}$ was temperature invariant in chlorobenzene up to 360 K, but above this temperature all the peaks began to broaden and the solution darkened, indicating that decomposition had probably occurred. Thus, unlike the related *cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2}]$ complex, the inversion process *cis*-$\Delta \rightleftharpoons$ *cis*-Λ is very slow on the n.m.r. time scale. The complexes *cis*-$[\mathrm{Rh(S_2CNMe_2)_2(PMe_2Ph)_2]Y}$ ($\mathrm{Y = BPh_4^-}$ or $\mathrm{PF_6^-}$) both gave rise to a single doublet in the proton-noise-decoupled $^{31}\mathrm{P}$ n.m.r. spectrum due to coupling with the $^{103}\mathrm{Rh}$ nucleus and this coupling was found to be temperature invariant in each case. In contrast, the $^{1}\mathrm{H}$ n.m.r. spectrum of the $\mathrm{PF_6^-}$ salt showed marked variations with temperature giving only a singlet for the ${}^-\mathrm{S_2CNMe_2}$ resonance and a doublet for the phosphine methyl resonance at 300 K. However, the way in which this equivalence of the phosphine methyl groups is realised is rather strange since, on raising the temperature, rather than broadening of the signals followed by coalescence into a broad peak which then sharpens to a single resonance [the established pattern for dynamic mechanism involving, for example, C=N bond rotations or optical isomerisations (see refs. 1 and 6)], the resonances gradually moved closer together *without broadening* until they were coincident. Further elevation of the temperature did not affect the spectrum. Unpublished work [30] indicates that the complex *cis*-$[\mathrm{Os(S_2CNMe_2)_2(PMe_2Ph)_2}]$ shows similar variable-temperature $^{1}\mathrm{H}$ n.m.r. spectra.

The only type of mechanism that could give rise to this behaviour is one in which the chemical environments of the two methyl groups on one phosphine ligand become more equivalent at higher temperatures, without any exchange of methyl groups between the two environments (since no coalescence phenomenon was observed). One such mechanism could arise from the fact that at low temperatures (when rotation about the metal–phosphorus bond is slow) there will be one * or more preferred discrete orientations of the phosphine moiety with respect to the rest of the complex. These preferred orientations will be determined by a combination of steric and electronic factors. Since there is no symmetry element of the complex that incorporates the metal–phosphorus bond, under these conditions the environments of the two methyl groups on one phosphine ligand will be different and two different signals will therefore be seen in the $^{1}\mathrm{H}$ n.m.r. spectrum.

Now, when the orientation of the phosphine ligand differs from that preferred, each methyl group will be in a different chemical environment from that in the preferred configuration. Thus, as the temperature is raised and the rate of rotation about the metal–phosphorus bond is increased, each methyl group will spend less time in its preferred environment and more in other environments. Its chemical shift will then be an average of the chemical shifts of each environment, weighted according to the amount of time spent in each environment. When, at higher temperatures, the phosphine group is rotating freely, each methyl group will spend an equal amount of time in *all* environments; hence, the average environment of each is the same and a single resonance is expected. This argument applies to both the phosphine ligands in the complex since they are related to one another by rotation about the two-fold axis and, hence, whatever happens to one phosphine group will be exactly analogous to what happens to the other.†

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* In this instance there is probably only one preferred rotamer, since further cooling does not give rise to the additional signals which would be expected if, when no rotation is possible, the phosphine group has more than one preferred configuration.

† Closer examination of the phosphine methyl region in the $^{1}\mathrm{H}$ n.m.r. spectra of the complexes *cis*-$[\mathrm{Ru(S_2CNMe_2)_2(PMe_2Ph)_2}]$ and *cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)CO}]$ reveals that exactly the same type of behaviour occurs and not, as previously recorded,[6] a coalescence behaviour. However, for the phosphine methyl groups of the complex *cis*-$[\mathrm{Ru(S_2PMe_2)_2(PMe_2Ph)_2}]$, coalescence does occur as previously stated [1,6] and this can be attributed to *exchange* of the environments of the methyl groups on *different* phosphine groups by means of the *facile* optical-isomerism process discussed in these papers. Then, the discrepancy between the activation energy ($\Delta G^{\ddagger}$) for this inversion reaction, as calculated by lineshape analysis of methyl resonances of the dithio-ligands (*i.e.* 63·4 kJ mol^{-1}), and that calculated from the coalescence temperature of the pseudo-triplets arising from the phosphine methyl groups (57·4 kJ mol^{-1}) is explicable on the basis that the coalescence approach assumes a small linewidth compared with the separation of the peaks. In this case, the assumption is invalid since the linewidth of each pseudo-triplet is *ca.* 12·0 Hz and their separation only *ca.* 13·0 Hz.

[30] D. J. Cole-Hamilton and T. A. Stephenson, unpublished work.

It is important to note that exchange of the environments of the methyl groups does not occur in this process since, although at different times, each may occupy the same position relative to the non-phosphine part of the molecule, their environment with respect to the orientation of the other methyl group and the phenyl group attached to the phosphorus atom will always be different.

Finally, the ionic complexes formed by long-term reaction between (I; L = $PMePh_2$) and $NaS_2CNMe_2,2H_2O$ are, as expected, geometrical isomers of $[Rh(S_2CNMe_2)_2(PMePh_2)_2]Y$. Thus, ^1H n.m.r. spectra of complexes (VI; Y = BPh_4^- or PF_6^-) consisted of one $^-S_2CNMe_2$ resonance and a 'virtually coupled' triplet phosphine methyl resonance, whereas (III), which could not be satisfactorily separated from the *trans*-isomer, had two $^-S_2CNMe_2$ resonances and one pseudo-doublet phosphine resonance in each case. The fact that the *trans*-isomer is formed more readily when the phosphine is $PMePh_2$ rather than PMe_2Ph can presumably be attributed to the greater steric size of $PMePh_2$. It should be noted at this point that the analogous complex $[Rh(S_2CNEt_2)_2(PPh_3)_2]BF_4$ has been assigned a *trans*-stereochemistry [18] and, although no evidence is cited to support this assignment, the result is consistent with the still greater steric size of triphenylphosphine. Thus, this combination of i.r. and n.m.r. studies, together with the various interconversions of complexes noted earlier, can be used to suggest a probable stereochemical path for the overall reaction between complex (I) and the various dithio-acid ligands and this is outlined in the Scheme.

Conclusion.—The reactions between *mer*-$[RhCl_3(PMe_2Ph)_3]$, (I), and the various dithio-acid ligands can be seen to proceed in a stepwise manner and, as expected, the oxidation state of three is maintained in all the complexes formed. The latter are indeed much less labile than their ruthenium analogues, but this is probably due mainly to the fact that many of them are ionic. Hence, the positive charge on the metal atom will tend to make the metal–ligand bonds stronger and it is probably this fact, rather than any large intrinsic differences in lability of the co-ordination spheres of rhodium(III) and ruthenium(II), which accounts for the difference in behaviour. It is very probable that reactions of the dithio-acid ligands with *mer*-$[RuCl_3(PMe_2Ph)_3]$ also proceed as above, but the combination of such factors as the tendency to form ruthenium(II) complexes under the reducing conditions present, the greater lability of ruthenium compared to rhodium, and the paramagnetism of most ruthenium(III) species make satisfactory characterisation of any ruthenium(III) intermediates a difficult task.

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 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. ^1H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer and ^{31}P n.m.r. spectra on a Varian XL100 spectrometer operating in the pulse and Fourier-transform mode at 40·5 MHz (^{31}P chemical shifts are given in p.p.m. to high frequency of 85% H_3PO_4). Heteronuclear-decoupling experiments were carried out on the HA-100 spectrometer using a second radio-frequency field provided by a Schlumberger FS30 frequency synthesiser. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. M.p.s were determined with a Köfler hot-stage microscope and are uncorrected.

Rhodium trichloride trihydrate (Johnson, Matthey Ltd), dimethylphenylphosphine (B.D.H.), methyldiphenylphosphine (Strem), $NaS_2CNMe_2,2H_2O$ (Ralph Emanuel), and KS_2COEt (B.D.H.) were obtained as indicated. Sodium dimethylphosphinodithioate was prepared as described earlier [31] and ammonium diphenylphosphinodithioate from Ph_2PS_2H [32] and ammonia in benzene. The complexes *mer*-$[RhCl_3(PMe_2Ph)_3]$ (I), *fac*-$[RhCl_3(PMe_2Ph)_3]$, and *mer*-$[RhCl_3(PMePh_2)_3]$ were synthesised by published methods.[21]

Preparations.— trans-*Dichloro*(NN-*dimethyldithiocarbamato*)*bis*(*dimethylphenylphosphine*)*rhodium*(III), (II) *and* cis-*bis*(NN-*dimethyldithiocarbamato*)*bis*(*dimethylphenylphosphine*)*rhodium*(III) *tetraphenylborate*, (III). Complex (I) (0·25 g) and excess of $NaS_2CNMe_2,2H_2O$ (0·25 g) were heated under reflux in ethanol (20 cm^3) for 60 min and the resulting orange solution was cooled and filtered. The residue was well washed with water to remove sodium chloride and then with ethanol and pentane to give the orange *solid* (II) (0·07 g, 30%). The yellow filtrate was treated with excess of $NaBPh_4$ in ethanol, and the resulting yellow precipitate filtered off, washed with water, ethanol, and pentane, and then recrystallised from dichloromethane–ethanol to give complex (III) (0·20 g, 51%). ^{31}P N.m.r. spectrum of (III) in $CDCl_3$: 4·5 p.p.m. (doublet, J_{RhP} 112 Hz). When complex (I) and $NaS_2CNMe_2,2H_2O$ were heated under reflux in ethanol for 16 h, only (III) (0·35 g, 92%) was isolated on addition of $NaBPh_4$.

cis-*Bis*(NN-*dimethyldithiocarbamato*)*bis*(*dimethylphenylphosphine*)*rhodium*(III) *hexafluorophosphate*, (III), was similarly prepared except that excess of NH_4PF_6 was added to the yellow ethanolic solution. No immediate precipitation occurred but large orange *crystals* were deposited when the solution was left for 3 days. These were filtered off, and washed with water, ethanol, and pentane to give complex (III) (0·30 g, 98%). ^{31}P N.m.r. spectrum in $CDCl_3$: 4·57 (doublet) (J_{RhP} 114); −147·2 p.p.m. (heptet, J_{PF} 727 Hz).

cis- *and* trans-*Bis*(NN-*dimethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)*rhodium*(III) *tetraphenylborate*, (III) and (VI). These complexes were prepared as above, by heating under reflux *mer*-$[RhCl_3(PMePh_2)_3]$ (0·20 g) and excess of $NaS_2CNMe_2,2H_2O$ (0·15 g) in ethanol (20 cm^3) for 16 h. Addition of $NaBPh_4$ then gave an immediate yellow precipitate consisting of a mixture of the *cis*- and *trans*-isomers (III) and (VI) (^1H n.m.r. and analytical evidence). On setting aside the filtrate, yellow microcrystals of the pure *trans*-isomer (VI) were deposited. Total yield 90% (*cis* : *trans* ratio *ca.* 1·5 : 1·0).

Similarly, *cis*- and *trans*-$[Rh(S_2CNMe_2)_2(PMePh_2)_2]PF_6$,

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[32] W. A. Higgins, D. W. Vogel, and W. G. Craig, *J. Amer. Chem. Soc.*, 1955 **77**, 1864.

(III) and (VI), were prepared from *mer*-[$\mathrm{RhCl_3(PMePh_2)_3}$] and $\mathrm{NaS_2CNMe_2,2H_2O}$ followed by addition of excess of $\mathrm{NH_4PF_6}$. The yellow crystals that separated first were the pure *trans*-isomer (VI) (^{1}H n.m.r. evidence). Later batches were orange and consisted of a mixture of *cis*- and *trans*-isomers. Total yield *ca.* 70%.

mer-*Dichloro*(NN-*dimethyldithiocarbamato*)*tris*(*dimethylphenylphosphine*)*rhodium*(III), (IV). A suspension of complex (I) (0·25 g) was shaken with excess of $\mathrm{NaS_2CNMe_2,2H_2O}$ (0·20 g) in methanol (25 cm^3) for 10 min. The resulting orange *solid* (IV) was filtered off and washed with water, methanol, and pentane (0·25 g, 88%). Recrystallisation from dichloromethane–hexane gave *trans*-[$\mathrm{RhCl_2(S_2CNMe_2)(PMe_2Ph)_2}$], (II).

mer-*Chloro*(NN-*dimethyldithiocarbamato*)*tris*(*dimethylphenylphosphine*)*rhodium*(III) *tetraphenylborate*, (V). The complex *mer*-[$\mathrm{RhCl_2(S_2CNMe_2)(PMe_2Ph)_3}$] (0·23 g), $\mathrm{NaBPh_4}$ (0·36 g), and $\mathrm{PMe_2Ph}$ (0·20 cm^3) were shaken in methanol for 24 h under a nitrogen atmosphere. The resulting mixture of orange and yellow solids was treated with hot ethanol to leech out the yellow solid. On cooling, this solution gave yellow *crystals* which were recrystallised from methanol to give (V) (0·20 g, 55%). The remaining orange solid, which was insoluble in hot ethanol, was *trans*-[$\mathrm{RhCl_2(S_2CNMe_2)(PMe_2Ph)_2}$], (II).

cis–cis–cis-*Dichlorobis*(*dimethylphenylphosphine*)(*diphenylphosphinodithioato*)*rhodium*(III), (VII), *and* cis-*bis*(*dimethylphenylphosphine*)*bis*(*diphenylphosphinodithioato*)-*rhodium*(III) *tetraphenylborate*, (III). Complex (I) (0·30 g) and excess of $\mathrm{NH_4S_2PPh_2}$ (0·40 g) were heated under reflux in ethanol (20 cm^3) for 60 min. Filtration of the hot solution left a very small amount of orange *crystals* of (VII), which were purified by washing with water, methanol, and pentane. The orange filtrate was treated with excess of $\mathrm{NaBPh_4}$ to give an immediate orange precipitate (III), which was recrystallised from dichloromethane–methanol to remove any $\mathrm{NH_4BPh_4}$ (0·46 g, 80%). The complex *cis*-[$\mathrm{Rh(S_2PPh_2)_2(PMe_2Ph)_2]PF_6}$, (III), was similarly prepared except that the orange ethanolic solution was treated with excess of $\mathrm{NH_4PF_6}$ and the complex separated slowly as large orange crystals (0·40 g, 80%). The $\mathrm{BPh_4^-}$ salt was also obtained in a pure state by dissolving the $\mathrm{PF_6^-}$ salt in methanol and adding excess of $\mathrm{NaBPh_4}$.

trans-*Dichlorobis*(*dimethylphenylphosphine*)(*diphenylphosphinodithioato*)*rhodium*(III), (II). Complex (I) (0·20 g) and $\mathrm{NH_4S_2PPh_2}$ (0·20 g) were shaken in ethanol (25 cm^3) for 10 min. Excess of starting material was filtered off and, after 3 days, large crystals of the *complex* were formed in the filtrate. These were filtered and washed with diethyl ether and pentane (yield 0·11 g, 50%). Recrystallisation from ethanol gave a mixture of mainly (II) and small amounts of the *cis–cis–cis*-isomer (VII) (i.r. evidence).

cis-*Bis*(*dimethylphenylphosphine*)*bis*(*dimethylphosphinodithioato*)*rhodium*(III) *tetraphenylborate*, (III). Complex (I) (0·30 g) and $\mathrm{NaS_2PMe_2,2H_2O}$ (0·35 g) were heated under reflux in degassed ethanol (20 cm^3) for 1 h with dry oxygen-free nitrogen continuously bubbling through the mixture. The resulting orange solution was cooled (under a nitrogen atmosphere) and $\mathrm{NaBPh_4}$ (0·20 g) added. The resulting yellow *solid* was filtered off under a nitrogen atmosphere and washed with water, ethanol, and pentane (yield 0·30 g, 61%). Omission of nitrogen from the reaction gave a red solution from which a red solid was precipitated by addition of excess of $\mathrm{NaBPh_4}$. This material had different analyses from ostensibly the same preparation, *e.g.* C, 51·2; H, 5·6 and C, 37·3; H, 4·7%. However complex (III) was also prepared by treating under reflux *fac*-[$\mathrm{RhCl_3(PMe_2Ph)_3}$] (0·07 g) and excess of $\mathrm{NaS_2PMe_2,2H_2O}$ (0·06 g) in acetone–chloroform (50 : 50 v/v) (25 cm^3) for 60 min. By evaporating to dryness, dissolving in $\mathrm{CH_2Cl_2}$, filtering off excess of $\mathrm{NaS_2PMe_2,2H_2O}$, again evaporating to dryness, dissolving in methanol, and adding excess of $\mathrm{NaBPh_4}$, complex (III) was obtained as yellow microcrystals.

mer-*Dichlorotris*(*dimethylphenylphosphine*)(*dimethylphosphinodithioato*)*rhodium*(III), (IV). This complex was prepared by shaking (I) (0·40 g) and $\mathrm{NaS_2PMe_2,2H_2O}$ (0·24 g) in methanol (40 cm^3) for 10 min (0·41 g, 90%). Recrystallisation from deuteriochloroform–hexane gave trans-*dichlorobis*(*dimethylphenylphosphine*)(*dimethylphosphinodithioato*)*rhodium*(III), (II). This complex was also obtained by shaking (I) (0·30 g) and $\mathrm{NaS_2PMe_2,2H_2O}$ (0·30 g) in ethanol (20 cm^3) for 2 days. The orange crystals were filtered from the red-brown solution and washed with water, ethanol, and pentane (0·22 g, 80%). Recrystallisation of complex (II) from toluene gave mainly (II) together with small quantities of *cis–cis–cis*-[$\mathrm{RhCl_2(S_2PMe_2)(PMe_2Ph)_2}$], (VII).

Reactions.—mer-[$\mathrm{RhCl_2(S_2PMe_2)(PMe_2Ph)_3}$], (IV), *with* $\mathrm{NaBPh_4}$ *and* $\mathrm{PMe_2Ph}$. Complex (IV) (0·32 g), $\mathrm{NaBPh_4}$ (0·32 g), and $\mathrm{PMe_2Ph}$ (0·10 cm^3) were shaken in degassed ethanol under a nitrogen atmosphere for 2 days to give a yellow precipitate of cis-*dichlorotetrakis*(*dimethylphenylphosphine*)*rhodium*(III) *tetraphenylborate*, (IX), purified by washing several times with water, methanol, diethyl ether, and pentane (yield 0·43 g, 80%), m.p. 145—147 °C (Found: C, 64·1; H, 6·3. Calc. for $\mathrm{C_{56}H_{64}BCl_2P_4Ru}$: C, 64·3; H, 6·1%). The same complex was also formed by reaction of a mixture of (I), $\mathrm{NaS_2CNMe_2,2H_2O,NaBPh_4}$, and $\mathrm{PMe_2Ph}$. ^{1}H N.m.r. spectrum ($\mathrm{CH_2Cl_2}$) (233 K): τ 8·26 (' triplet ') ($|J_{\mathrm{PH}} + J_{\mathrm{PH'}}|$ 48); 8·94 (' doublet ') ($|J_{\mathrm{PH}} + J_{\mathrm{PH'}}|$ 40 Hz); (313 K) 8·40 (singlet); Ph resonance at τ 1·4—3·6. Complex (IX) rearranged to (I) and free $\mathrm{PMe_2Ph}$ on standing in $\mathrm{CDCl_3}$ for 48 h.

When the reaction between complex (IV), $\mathrm{NaBPh_4}$, and $\mathrm{PMe_2Ph}$ was carried out in the presence of air, the white solid cis-*tetrakis*(*dimethylphenylphosphine*)(*dioxygen*)-*rhodium*(I) *tetraphenylborate*, (VIII), was formed (0·40 g, 80%) {ν(O–O) at 841, 860 cm^{-1}; *cf.* 841, 870 cm^{-1} for [$\mathrm{Ru(O_2)(PMe_2Ph)_4]ClO_4}$}.[25] The same complex was formed when [$\mathrm{Rh(S_2PMe_2)_3}$] was treated with excess of $\mathrm{PMe_2Ph}$ in the presence of $\mathrm{NaBPh_4}$, m.p. 129—130 °C (Found: C, 66·2; H, 6·6. Calc. for $\mathrm{C_{56}H_{64}BO_2P_4Ru}$: C, 66·8; H, 6·4%). ^{1}H N.m.r. spectrum ($\mathrm{CH_2Cl_2}$) (300 K): τ 8·88 (' triplet ') ($|J_{\mathrm{PH}} + J_{\mathrm{PH'}}|$ 7); 8·99 (' doublet ') ($|J_{\mathrm{PH}} + J_{\mathrm{PH'}}|$ 8 Hz); Ph resonance at τ 2·2—3·6.

Potassium O-*ethyl dithiocarbonate* (*xanthate*) *with complex* (I). Complex (I) (0·30 g) and excess of $\mathrm{KS_2COEt}$ (0·30 g) were heated under reflux in ethanol for 60 min and the resulting yellow solution filtered hot in order to remove potassium chloride. It was then evaporated to dryness and the yellow oil dissolved in $\mathrm{CH_2Cl_2}$. Excess of $\mathrm{KS_2COEt}$ was filtered off and the solution allowed to stand whereupon yellow needle-shaped *crystals* of *potassium dichlorobis*(*dimethylphenylphosphine*)(*dithiocarbonato*)*rhodate*(III), (XI), were deposited (0·02 g, 7%). These were filtered off and recrystallised from dichloromethane–methanol. The yellow filtrate was placed on an alumina dry column and eluted with $\mathrm{CH_2Cl_2}$ to give three poorly resolved bands coloured yellow, orange, and yellow respectively. Each band was extracted with diethyl ether and then hexane added. Slow evaporation of these solutions gave crystals in each case. The first yellow band gave trans-*bis(dimethylphenylphosphine)(dithiocarbonato)*(O-*ethyl dithiocarbonato)rhodium*(III), (XII) (0·05 g, 17·5%). The orange band gave mer-*chlorotris(dimethylphenylphosphine)(dithiocarbonato)rhodium*(III), (X) (0·05 g, 16%), and the second yellow band yielded cis-*bis(dimethylphenylphosphine)(dithiocarbonato)*(O-*ethyl dithiocarbonato)rhodium*(III), (XIII) (0·10 g, 35%). ^{31}P N.m.r. spectrum of complex (XIII) in $CDCl_3$: 9·13 (doublet of doublets); 0·46 p.p.m. (doublet of doublets); J_{P_1Rh} 118, J_{P_2Rh} 110, $J_{P_1P_2}$ 18 Hz.

When the initial ethanolic solution was allowed to evaporate slowly, the first product to crystallise out was (XIII) (0·20 g, 70%). Then a mixture of complexes (XIII) and (X) were deposited followed by small amounts of pure (X) (0·05 g, 16%). When complex (I) (0·30 g) and KS_2COEt (0·08 g, 1 : 1·05 molar ratio) were heated under reflux in ethanol for 5 h and the resulting yellow solution worked-up as before, two bands were eluted containing (X) (0·05 g, 16%) and (XIII) (0·02 g, 7%). However, when complex (I) (0·30 g) and excess of KS_2COEt (0·30 g) were shaken in acetone (25 cm^3) for 16 h and the resulting orange solution evaporated to dryness (after removing KCl by filtration), recrystallisation of the orange oil from dichloromethane–hexane gave orange crystals of trans-*dichlorobis(dimethylphenylphosphine)*(O-*ethyl dithiocarbonato)rhodium*(III), (II) (0·20 g, 72%). This complex was also prepared by carrying out the same reaction in a solution of ethanol–chloroform heated under reflux and working up the orange solution in the same way. Reaction of complex (II) with KS_2COEt gave (XIII).

When complex (I) (0·30 g) and KS_2COEt (0·30 g) were shaken in methanol (25 cm^3) for 10 min the orange complex mer-*dichlorotris(dimethylphenylphosphine)*(O-*ethyl dithiocarbonato)rhodium*(III), (IV) (0·30 g, 88%) was deposited. Recrystallisation of this complex from methanol (or chloroform–hexane) gave *trans*-$[RhCl_2(S_2COEt)(PMe_2Ph)_2]$, (II). Finally, when the complex *mer*-$[RhCl_2(S_2COEt)(PMe_2Ph)_3]$, (IV) (0·12 g), was shaken for 4 weeks in ethanol (20 cm^3) with $NaBPh_4$ (0·12 g), a small amount of orange mer-*chlorotris(dimethylphenylphosphine)*(O-*ethyldithiocarbonato)rhodium*(III) *tetraphenylborate*, (V), was deposited (0·02 g, 9·5%). However, this complex was also prepared in high yield by reaction of (I) (0·37 g) with KS_2COEt (0·09 g, 1 : 1 molar ratio) in methanol (20 cm^3) heated under reflux for 60 min followed by addition of excess of $NaBPh_4$. Recrystallisation of the resulting yellow solid from dichloromethane–methanol gave (V) as orange microcrystals (0·45 g, 80%).

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