

Metal Complexes of Sulphur Ligands. Part 10.¹ Reaction of *mer*-Trichlorotris(dimethylphenylphosphine)osmium(III) with Dimethyldithiocarbamate, Dimethyl- and Diphenyl-phosphinodithioate, and *O*-Ethyl Dithiocarbonate Ligands

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

Reactions of the complex *mer*-[OsCl₃(PMe₂Ph)₃] (1) with excess of [S-S]⁻ ion (S-S⁻ = S₂CNMe₂⁻, S₂PMe₂⁻, S₂PPh₂⁻, or S₂COEt) have been thoroughly studied. For [S₂CNMe₂]⁻, refluxing in methanol for 90 min gives a high yield of *cis*-[Os(PMe₂Ph)₂(S₂CNMe₂)₂] (2), whereas shaking in methanol gives *mer*-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (3). Reaction of (3) with Na[S₂CNMe₂]⁻·2H₂O in refluxing ethanol gives (2) together with small amounts of *fac*-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (5) and *fac*-[Os(OEt)(PMe₂Ph)₃(S₂CNMe₂)] (6), whereas with K[S₂COEt] these three complexes and *cis*-[Os(PMe₂Ph)₂(S₂CNMe₂)(S₂COEt)] (4) are formed. Similarly, for [S-S]⁻ = S₂PMe₂⁻ or S₂PPh₂⁻, reaction with (1) in refluxing ethanol gives *cis*-[Os(PMe₂Ph)₂(S₂PR₂)₂] [R = Me (7) or Ph (8)]. However, shaking in methanol gives paramagnetic *mer*-[OsCl₂(PMe₂Ph)₃(S₂PR₂)] [R = Me (9) or Ph (10)]. Recrystallisation of (9) from boiling benzene gives *trans*-[OsCl₂(PMe₂Ph)₂(S₂PMe₂)] (11), whereas prolonged standing in cold benzene gives a purple oil containing the cation [OsCl(PMe₂Ph)₃(S₂PMe₂)⁺ (12) together with (1) and brown crystalline *mer*-[OsCl(PMe₂Ph)₃(S₂PMe₂)] (13). Carbonylation of (7) in refluxing ethanol in the presence of sulphur gives *cis*-[Os(CO)(PMe₂Ph)(S₂PMe₂)₂] (14) together with a brown oil containing PMe₂PhS and a complex of probable formula [Os(CO)₂(PMe₂Ph)(S₂PMe₂)₂] (15). In the presence of PMe₂Ph, carbonylation of (7) gives [Os(CO)(PMe₂Ph)(S₂PMe₂)₂] (16) whereas in cold CH₂Cl₂-C₆H₁₄ a different isomeric form of [Os(CO)(PMe₂Ph)₂(S₂PMe₂)₂] (17) is produced. In contrast, reaction of (1) with K[S₂COEt] under all conditions gives only *mer*-[OsCl(PMe₂Ph)₃(S₂COEt)] (18). The complexes have been characterised by elemental analyses and mass, i.r., and n.m.r. spectroscopy (¹H and ³¹P), and detailed mechanisms for the overall reaction and the carbonylation of (7) are postulated.

In Part 7 of this series² the investigation of the reactions of *mer*-[RhCl₃(PMe₂Ph)₃] with dithioacid ligands gave considerable insight into the possible nature of some of the paramagnetic intermediates which might be formed in the preparation of *cis*-[Ru(PMe₂Ph)₂(S₂PR₂)₂] (R = Me or Ph) from *mer*-[RuCl₃(PMe₂Ph)₃].³ However, because of the stability of rhodium(III) complexes with respect to reduction to Rh^{II}, no information could be gleaned about the step at which reduction to Ru^{II} occurs or the nature of any ruthenium(II) intermediates. It was therefore felt, since osmium has stable oxidation

¹ Part 9, D. J. Cole-Hamilton, T. A. Stephenson, and D. R. Robertson, *J.C.S. Dalton*, 1975, 1260.

² D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 1818.

states of both II and III and is also less labile than ruthenium in both of these oxidation states,⁴ that an investigation of the reactions of *mer*-[OsCl₃(PMe₂Ph)₃] with dithioacid ligands might shed some extra light on the mechanism of formation of *cis*-[Ru(PMe₂Ph)₂(S₂PR₂)₂] from *mer*-[RuCl₃(PMe₂Ph)₃].

With the exception of a very recent paper on osmium dialkyldithiocarbamates and *O*-alkyl dithiocarbonates,⁵ very little work has been published on osmium

³ D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 739.

⁴ See W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals,' Interscience, London, 1967.

⁵ P. B. Critchlow and S. D. Robinson, *J.C.S. Dalton*, 1975, 1367.

complexes containing dithioacid ligands. Earlier examples include the synthesis of $[\text{Os}(\text{S}_2\text{CNR}_2)_3]$ from the reaction of $[\text{NH}_4]_2[\text{OsCl}_6]$ with $\text{Na}[\text{S}_2\text{CNR}_2]$,⁶ a brief mention of $[\text{OsO}_2(\text{S}_2\text{CNR}_2)_2]$,⁷ and $[\text{OsCl}(\text{bipy})_2(\text{S}_2\text{CN}(\text{CH}_2)_5)]$ (bipy = 2,2'-bipyridyl) from the interaction of $[\text{OsCl}_2(\text{bipy})_2]$ and $\text{K}[\text{S}_2\text{CN}(\text{CH}_2)_5]$.⁶

Analytical data for the new complexes are given in Table I and spectroscopic properties in Tables 2—4.

Dimethyldithiocarbamate-complexes.—When complex (1) was heated under reflux with excess of $\text{Na}[\text{S}_2\text{CNMe}_2] \cdot 2\text{H}_2\text{O}$ in ethanol for 90 min, a yellow complex of composition $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNMe}_2)_2]$ (2) was isolated in

TABLE I
Analytical data for some osmium dithioacid complexes

Complex	Colour	M.p. ($\theta_c/^\circ\text{C}$)	Analysis (%)						$\mu_{\text{eff.}}/ \text{B.M.}$
			Found			Calc.			
			C	H	N	C	H	N	
<i>mer</i> - $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ (9)	Purple	140—142	39.8	4.9		39.0	4.9		1.82
<i>mer</i> - $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PPh}_2)]$ (10)	Purple	104—105	46.6	4.6		46.7	4.7		1.81
<i>trans</i> - $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)]$ (11)	Red	207—210 ^b	32.6	4.3		32.6	4.2		1.97
<i>mer</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ (13)	Brown	198—200	39.9	4.7		40.8	5.1		
<i>mer</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (3)	Yellow	140—150 ^b	42.6	5.3	1.7	42.7	5.1	1.8	
<i>fac</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (5)	Yellow	172—174 ^b	42.4	5.2	1.9	42.7	5.1	1.8	
<i>fac</i> - $[\text{Os}(\text{OEt})(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (6)	Yellow	206—210 ^b	41.5	5.2	1.7	45.3	5.7	1.8	
<i>mer</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{COEt})]$ (18)	Orange	123—125	42.5	5.2		42.6	5.0		
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (7)	Orange	189—190 ^b	33.5	4.9		33.5	4.8		
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PPh}_2)_2]$ (8)	Orange	238 ^b	49.5	4.5		49.7	4.4		
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNMe}_2)_2]$ (2)	Yellow	172—174	37.5	4.9	4.1	37.4	4.8	4.0	
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{COEt})]$ (4)	Orange	84—86	37.1	4.6	1.8	37.3	4.7	2.0	
<i>cis</i> - $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (14)	Yellow	120—122	25.8	3.8		25.7	3.8		
$[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (16)	Yellow	155—158 ^b	34.0	4.7		33.9	4.6		

^a Obtained in CH_2Cl_2 at 301 K by Evans' method. 1 B.M. $\approx 9.27 \times 10^{-24}$ A m². ^b Decomposition.

TABLE 2
I.r. spectra (cm^{-1}) of various osmium dithioacid complexes as mulls

Complex	$\nu(\text{OsCl})$	Dithioacid ligand absorptions	Others
<i>mer</i> - $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ (1)	350m, 312s, 270m		
<i>mer</i> - $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ (9)	350w, 310s	600vs, ^a	
<i>mer</i> - $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PPh}_2)]$ (10)	350w, 318m	645s, ^a 540s ^a	
<i>trans</i> - $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)]$ (11)	300s, br	528m ^b	
<i>mer</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ (13)	340w	580m ^b	
<i>mer</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (3)	348w	1 510m ^c	
<i>fac</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (5)	330vw	1 505m ^c	
<i>fac</i> - $[\text{Os}(\text{OEt})(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (6)		1 515m ^c	1 040vs ^d
<i>mer</i> - $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{COEt})]$ (18)	350w	1 250vs ^e	
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (7)		583m ^b	
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PPh}_2)_2]$ (8)		608w, ^b 571vs ^b	
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNMe}_2)_2]$ (2)		1 510vs, br ^c	
<i>cis</i> - $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNMe}_2)(\text{S}_2\text{COEt})]$ (4)		1 520m, br, ^c 1 230s, br ^c	
<i>cis</i> - $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (14)		580s ^b	1 908vs ^f
$[\text{Os}(\text{CO})_2(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (15)		600vs, ^{a,g}	2 010s, ^f 1 950s ^f
$[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (16)		602s, ^a 570m ^b	1 923vs ^f
$[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (17)		602s, ^a 575m ^b	1 942vs, ^f 1 923vs, ^f [1 941vs, ^{f,h}

^a Band(s) for unidentate $[\text{S}_2\text{PR}_2]^-$ (J. M. C. Alison, T. A. Stephenson, and R. O. Gould, *J. Chem. Soc. (A)*, 1971, 3690; D. F. Steele and T. A. Stephenson, *J. C.S. Dalton*, 1973, 2124). ^b Bands for bidentate $[\text{S}_2\text{PR}_2]^-$ (refs. as in a). ^c $\nu(\text{CN})$ (bidentate $[\text{S}_2\text{CNMe}_2]^-$) (D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. (A)*, 1969, 1152, and refs. therein; C. O'Connor, J. D. Gilbert, and G. Wilkinson, *ibid.*, p. 84). ^d $\nu(\text{C}-\text{O})$ (of OEt⁻ group). ^e $\nu(\text{C}-\text{O})$ ($[\text{S}_2\text{COEt}]^-$ group) (D. Coucouvanis, *Progr. Inorg. Chem.*, 1970, 11, 305 and refs. therein). ^f $\nu(\text{CO})$. ^g Mixture of (14) and (15) so lower $\nu(\text{PS})$ is masked. ^h In CDCl_3 solution.

RESULTS AND DISCUSSION

It is reported that *mer*- $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ can be prepared either by reaction of OsO_4 with PMe_2Ph in hydrochloric acid or, in low yield, by refluxing $[\text{NH}_4]_2[\text{OsCl}_6]$ with excess of PMe_2Ph in 2-methoxyethanol.⁸ We have found that quantitative yields of the complex are obtained in the latter reaction by addition of concentrated HCl to the mixture and by prolonging the reflux for 16 h. The reactions of *mer*- $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ (1) with various dithioacid anions are described below.

⁶ R. A. Bozis, *University Microfilms*, 72-14,064 (*Chem. Abs.*, 1972, 77, 108887y).

⁷ L. F. Shvydka, Yu. I. Usatenko, and F. M. Tulyupa, *Zhur. neorg. Khim.*, 1975, 18, 756.

80% yield and the remaining solution was shown (by t.l.c.) to contain small quantities of three other coloured compounds together with some white tetramethylthiuram disulphide. Shaking the two reactants in methanol for 10 min produced a single yellow complex of formula $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (3), white $\text{S}_2(\text{SCNMe}_2)_2$, and a very small quantity of (2). When, however, this latter reaction was carried out in the presence of excess of PMe_2Ph , the previously known, pale yellow, complex $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_4]$ ⁹ was isolated and this was

⁸ J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc. (A)*, 1968, 2636.

⁹ J. Chatt, G. J. Leigh, and R. L. Richards, *J. Chem. Soc. (A)*, 1970, 2243.

oxidised quantitatively to *mer*-[OsCl₃(PMe₂Ph)₃] and PMe₂PhO on standing in CDCl₃ {*cf.* the reaction of

refluxing ethanol in the absence of excess of PMe₂Ph to produce, after 90 min, (2) together with the three other coloured complexes obtained earlier. In this instance, (2) was only obtained in 50% yield.

TABLE 3
Main peaks in the mass spectrum of
mer-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (3) at 200 °C

<i>m/e</i> of ¹⁹² Os peak ^a	Probable ion
795	[OsCl ₂ (PMe ₂ Ph) ₃ (S ₂ CNMe ₂) ⁺
761	[OsCl(PMe ₂ Ph) ₃ (S ₂ CNMe ₂) ⁺
708	[Os(PMe ₂ Ph) ₂ (S ₂ CNMe ₂) ₂ ⁺
658	[OsCl ₂ (PMe ₂ Ph) ₂ (S ₂ CNMe ₂) ⁺
623	[OsCl(PMe ₂ Ph) ₂ (S ₂ CNMe ₂) ⁺
570	[Os(PMe ₂ Ph)(S ₂ CNMe ₂) ₂ ⁺
520	[OsCl ₂ (PMe ₂ Ph)(S ₂ CNMe ₂) ⁺
485	[OsCl(PMe ₂ Ph)(S ₂ CNMe ₂) ⁺
458 ^b	708 → 570
432	[Os(S ₂ CNMe ₂) ₂ ⁺
354	[Os(PMe ₂ Ph) ₂ (S ₂ CNMe ₂) ₂ ²⁺
328 ^b	570 → 432

^a All the peaks showed the characteristic osmium isotopic pattern. ^b Metastable.

[RhCl₂(PMe₂Ph)₄]⁺ with CDCl₃ to give *mer*-[RhCl₃(PMe₂Ph)₃]²⁺.

Reaction of (3) with K[S₂COEt] in refluxing ethanol again produced several compounds, four of which were the same as those obtained from the reaction of (3) with Na[S₂CNMe₂·2H₂O] and the fifth was an orange compound of higher R_F value than the others. In this case, the five compounds were separated on a dry alumina column,¹⁰ and, after recrystallisation, shown to have the following composition in decreasing order of R_F value: [Os(PMe₂Ph)₂(S₂CNMe₂)(S₂COEt)] (4), (1), [OsCl(PMe₂Ph)₃(S₂CNMe₂)] (5) [but with different spectral properties from (3)], [Os(OEt)(PMe₂Ph)₃(S₂CNMe₂)] (6), and a red oil which was not successfully recrystallised or identified.

The stereochemistries of these complexes are discussed later but it is of interest to note that, although reaction of (3) with Na[S₂CNMe₂·2H₂O] does give rise

TABLE 4
Hydrogen-1 n.m.r. data for various osmium(II) dithioacid complexes (in CDCl₃)

Complex	T/K	Dithio-ligand	δ ^a /p.p.m. Phosphine Me groups	Phenyl groups	Other resonances
<i>mer</i> -[OsCl(PMe ₂ Ph) ₃ (S ₂ PMe ₂)] (13)	301	1.53 (d) (14.5) ^b	2.0 (t) (8.0), ^c 1.82 (t) (8.5), ^c 1.36 (d) (10.5) ^b	7.9—7.0	
<i>mer</i> -[OsCl(PMe ₂ Ph) ₃ (S ₂ CNMe ₂)] (3)	301	3.08 ^d	1.80 (s), 1.66 (s), 1.34 (d) (7.0) ^b	7.6—6.6	
<i>fac</i> -[OsCl(PMe ₂ Ph) ₃ (S ₂ CNMe ₂)] (5)	301	2.90 (s)	2.00 ^e (8.0), ^c 1.97 ^e (9.0), ^c 1.55 (d) (12.0) ^b	7.8—6.8	
<i>fac</i> -[Os(OEt)(PMe ₂ Ph) ₃ (S ₂ CNMe ₂)] (6)	253	2.76 (s)	1.98 ^e (7.0), ^c 1.96 ^e (7.0), ^c 1.35 (d) (8.0) ^b	7.8—6.7	4.64 (q), 1.33 (t), (7.0) ^f
	301	2.79 (s)	1.92 ^e (8.0), ^c 1.32 (d) (8.0) ^b	7.8—6.7	4.61 (q), 1.28 (t), (7.0) ^f
<i>mer</i> -[OsCl(PMe ₂ Ph) ₃ (S ₂ COEt)] (18)	301	4.30 (q) (7.0), ^f 1.43 (t) (7.0) ^f	1.82 (t) (6.5), ^c 1.65 (t) (6.5), ^c 1.41 (d) (8.5) ^b	7.6—6.8	
<i>mer</i> -[OsBr(PMe ₂ Ph) ₃ (S ₂ COEt)] (19)	301	4.20 (q), ^f 1.39 (t) (7.0) ^f	1.85 (t) (6.5), ^c 1.75 (t) (6.5), ^c 1.50 (d) (8.0) ^b	7.6—6.6	
<i>cis</i> -[Os(PMe ₂ Ph) ₂ (S ₂ PMe ₂) ₂] (7)	273	2.10 (d) (12.5), ^b 1.68 (d) (12.5) ^b	1.71 ^e (8.5), ^c 1.64 ^e (8.5) ^c	7.3—6.7	
	333	1.89 ^d	1.67 ^e (8.5) ^c	7.3—6.7	
<i>cis</i> -[Os(PMe ₂ Ph) ₂ (S ₂ PPh ₂) ₂] (8)	301		1.57 ^e (12.5) ^c	8.1—6.7	
<i>cis</i> -[Os(PMe ₂ Ph) ₂ (S ₂ CNMe ₂) ₂] (2)	253	3.25 (s), 3.18 (s)	1.62 ^e (8.0), ^c 1.54 ^e (8.0) ^c	7.3—6.9	
	313	3.16 (s)	1.60 ^e (8.5), ^c 1.55 ^e (8.5) ^c	7.3—6.9	
<i>cis</i> -[Os(CO)(PMe ₂ Ph)(S ₂ PMe ₂) ₂] (14)	233	2.15 (d) (12.5), ^b 1.96 (d) (12.5) ^b 1.93 (d) (12.5), ^b 1.48 (d) (12.5) ^b	2.04 (d) (9.5), ^b 2.02 (d) (9.5) ^b	7.7—6.3	
	333	2.09 (d) (13.0), ^b 1.89 (d) (12.5) ^b 1.44 (d) (12.5) ^b	1.97 (d) (9.5) ^b	7.7—6.3	
[Os(CO) ₂ (PMe ₂ Ph)(S ₂ PMe ₂) ₂] (15)	301	2.09 (d) (11.0), ^b 2.07 (d) (12.0) ^b 1.21 (d) (12.5) ^b	2.09 (d) (11.0), ^b 2.02 (d) (10.0) ^b	8.1—7.9	
[Os(CO)(PMe ₂ Ph) ₂ (S ₂ PMe ₂) ₂] (16)	301	1.91 (d) (12.0), ^b 1.00 (d) (12.0) ^b	2.21 (t) (7.0) ^b	7.8—7.2	
[Os(CO)(PMe ₂ Ph) ₂ (S ₂ PMe ₂) ₂] (17)	301	2.06 (d) (12.5), ^b 2.02 (d) (12.0) ^b 2.01 (d) (12.5), ^b 1.46 (d) (12.0) ^b	1.78 (d) (9.5), ^b 1.74 (d) (9.5) ^b 1.62 (d) (9.5) ^b	7.6—6.8	

s = singlet, d = doublet, t = triplet, q = quartet.

^a ± 0.001. ^b *J*(PH) in Hz. ^c Since H₆PP'H₆' type spectrum, coupling constant is |*J*(PH) + *J*(PH')| in Hz. ^d Broad singlet. ^e pseudo-doublet. ^f *J*(CH₃-CH₂) in Hz.

Attempts to prepare complexes of formula [Os(PMe₂Ph)₃(S₂CNMe₂)₂] by shaking (3) with Na[S₂CNMe₂·2H₂O] in the presence of excess of PMe₂Ph were unsuccessful, giving only unchanged starting material. However, (3) did react with Na[S₂CNMe₂·2H₂O] in

to the formation of (2), the yield of (2) (50%) is not as high as from the reaction of *mer*-[OsCl₃(PMe₂Ph)₃] (1) with Na[S₂CNMe₂·2H₂O] (80%). Thus, although (3)

¹⁰ For details see B. Loev and M. M. Goodman, *Chem. and Ind.*, 1967, 2026.

may be an intermediate in the formation of (2) from (1), a parallel path which does not involve (3) as an intermediate must also be operating to form (2). The mechanistic implications of this observation are discussed later.

Diphenyl- and Dimethyl-phosphinodithioato-complexes.—As for dithiocarbamate, reactions of (1) with excess of $\text{Na}[\text{S}_2\text{PMe}_2] \cdot 2\text{H}_2\text{O}$ or $[\text{NH}_4][\text{S}_2\text{PPh}_2]$ in refluxing ethanol led to the formation of orange solutions from which crystalline complexes of formula $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PR}_2)_2]$ [$\text{R} = \text{Me}$ (7) or Ph (8)] may be isolated in high yield. Solutions of these complexes rapidly turn green in the presence of air and, as with *cis*- $[\text{Ru}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$,³ broadening of the previously sharp ^1H n.m.r. signals is observed, indicating that oxidation to a paramagnetic species is probably occurring. Again as for the ruthenium complexes, sharp peaks appeared in these spectra after several weeks but these clearly arise from non-metal-containing decomposition products since the ruthenium and osmium spectra were superimposable and one of the doublets in the spectrum is assignable to PMe_2PhS . During one of the preparations of (7), a pale yellow solid was also isolated. This is the well known $[\text{Os}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ which is formed when (1) is heated under reflux in aqueous ethanol.⁸

As with *mer*- $[\text{RhCl}_3(\text{PMe}_2\text{Ph})_3]$,² shaking (1) with excess of $\text{Na}[\text{S}_2\text{PMe}_2] \cdot 2\text{H}_2\text{O}$ in methanol produced a complex of formula $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ (9). In this case, the complex is purple and a reaction time of 90 min (*cf.* 10 min for Rh ²) was required for complete conversion. The analogous complex $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PPh}_2)]$ (10) was also prepared by reaction of (1) in CH_2Cl_2 with a methanolic solution of $\text{Na}[\text{S}_2\text{PPh}_2]$, followed by evaporation of the CH_2Cl_2 and collection of the methanol-insoluble product. Since (10) is more difficult to prepare than (9) and less amenable to ^1H n.m.r. studies, its reactions were not investigated further but those of (9) were studied in some detail.

Thus, (9) was recovered unchanged when it was recrystallised rapidly from dichloromethane-*n*-hexane in the cold (*cf.* the facile formation of *trans*- $[\text{RhCl}_2(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)]$ on recrystallisation of *mer*- $[\text{RhCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ ²), but when the solution was warmed and allowed to stand quantitative conversion into red *mer*- $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ occurred, whilst prolonged reaction of (9) with PMe_2Ph in cold CH_2Cl_2 produced a yellow solution from which $[\text{Os}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ was isolated. Recrystallisation of (9) from boiling benzene in air gave a red complex of formula $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)]$ (11) together with some PMe_2PhO , whereas when (9) was allowed to stand in cold benzene for 2 weeks, three compounds were isolated from the resulting brown solution by fractional crystallisation with *n*-hexane. These were a purple strongly conducting oil, which is thought to contain the cation $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]^+$ (12), a brown crystalline solid of formula $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PMe}_2)]$ (13), and *mer*- $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ (1). Longer reaction times in cold benzene (4 weeks) produced only (13) and (1). Finally, shaking (9) in acetone for several

days again produced a highly conducting purple oil, as well as (1), but, in this instance, no (13).

As in the case of *cis*- $[\text{Ru}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$,³ $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (7) reacted with carbon monoxide under mild conditions. Thus, reaction of (7) with CO in refluxing ethanol, in the presence of a small amount of elemental sulphur, produced a complex of formula $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ (14) together with a brown oil which contained (*i.r.* and *n.m.r.* evidence) both PMe_2PhS and a complex with two *cis*-CO groups, of probable formula $[\text{Os}(\text{CO})_2(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ (15). When the carbonylation reaction was carried out in the presence of excess of PMe_2Ph , a yellow crystalline complex of formula $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ was exclusively formed. Finally, reaction of (7) with CO in cold CH_2Cl_2 - C_6H_{14} gave another yellow complex, probably also of formula $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$, which rapidly becomes green on air exposure and whose structure will be discussed later.

O-Ethyl Dithiocarbonato-complexes.—The reaction of (1) with $\text{K}[\text{S}_2\text{COEt}]$ is rather different from those with the other dithioacid anions studied since both refluxing the reactants in ethanol for 1 h or shaking them in methanol for 10 min produced only one complex which has the formula $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{COEt})]$ (18). Attempts to persuade this complex to react further with either $\text{K}[\text{S}_2\text{COEt}]$ or $\text{Na}[\text{S}_2\text{CNMe}_2] \cdot 2\text{H}_2\text{O}$ were abortive yielding only unchanged starting materials in both cases. An attempt to prepare the complex $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{COEt})_2]$ by reaction of *mer*- $[\text{OsBr}_3(\text{PMe}_2\text{Ph})_3]$ with $\text{K}[\text{S}_2\text{COEt}]$ was also fruitless since, although no solid product could be isolated, a ^1H n.m.r. spectrum of the resulting orange oil indicated that $[\text{OsBr}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{COEt})]$ (19) was the only identifiable product.

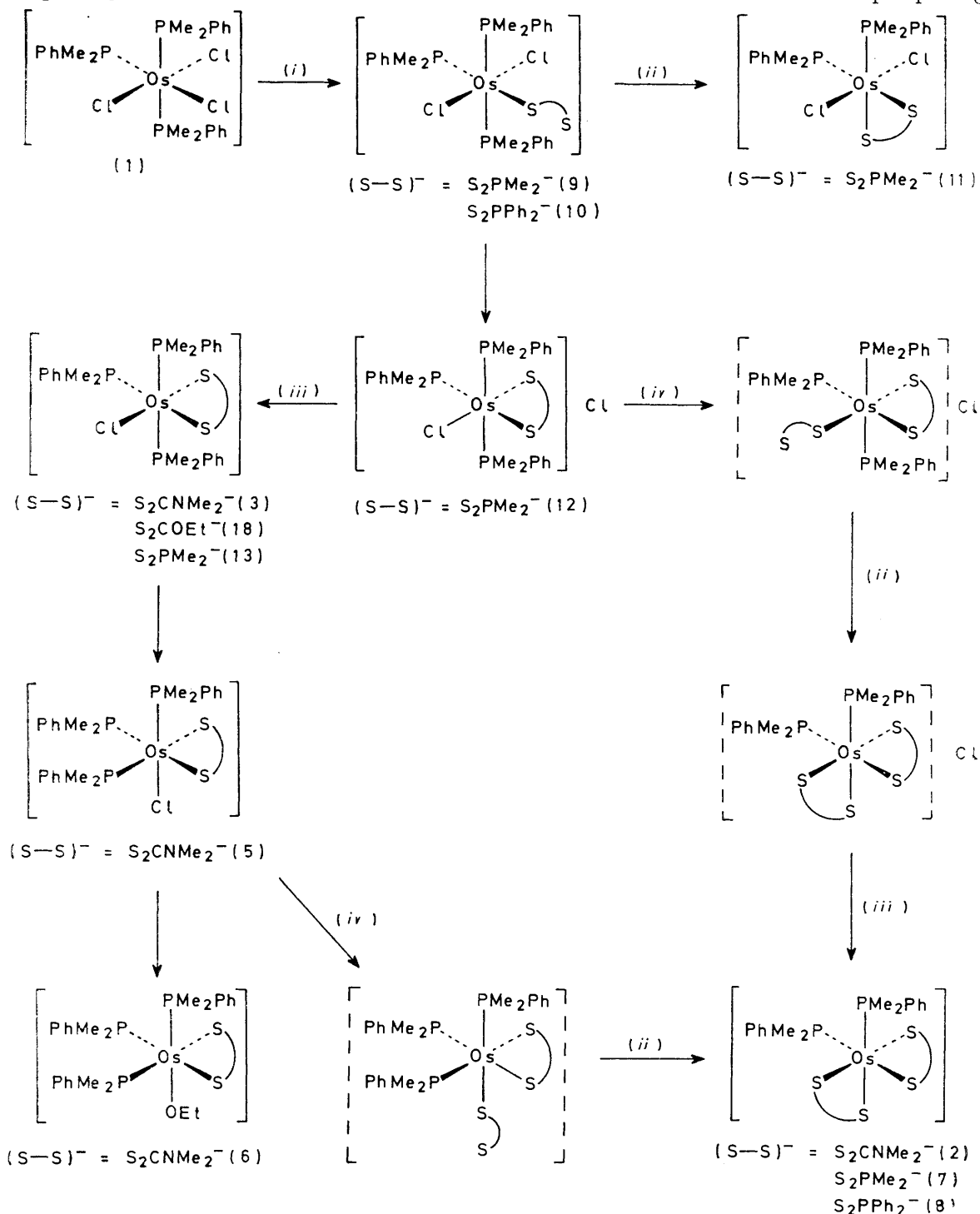
Spectroscopic Properties of the Dithioacid Complexes.—*I.r. spectra.* Like *mer*- $[\text{RhCl}_3(\text{PMe}_2\text{Ph})_3]$,² *mer*- $[\text{OsCl}_3(\text{PMe}_2\text{Ph})_3]$ has three *i.r.*-active $\nu(\text{OsCl})$ stretching vibrations and these are assigned to the absorptions at 350, 312, and 270 cm^{-1} (Table 2). Again, by analogy with the rhodium complex, the band of lowest energy (270 cm^{-1}) is assigned as arising predominantly from the Os-Cl bond *trans* to the highest *trans*-influence ligand (PMe_2Ph). Then, the two absorptions at 350 and 312 cm^{-1} are assigned as arising predominantly from the symmetric (ν_{sym}) and asymmetric (ν_{asym}) Cl-Os-Cl stretching vibrations. Although the exact assignment of these two absorption frequencies to ν_{sym} and ν_{asym} is not possible, since in a molecule of this size mixing with other vibrations of the same symmetry will occur,¹¹ this region may be used as a 'fingerprint' in assigning stereochemistries to related molecules.

Analysis of the $\nu(\text{OsCl})$ region of $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PR}_2)]$ ($\text{R} = \text{Me}$ or Ph) (Table 2) indicates that in both cases the chloride ion *trans* to phosphine has been removed, as expected in view of the greater *trans* influence of PMe_2Ph compared to chloride. This fact, coupled with the observations that absorptions in the $\nu(\text{PS})$

¹¹ See D. M. Adams, 'Metal Ligand and Related Vibrations,' E. Arnold, London, 1967.

region indicate that only unidentate $[S_2PR_2]^-$ groups are present and that $[RhCl(PMe_2Ph)_3(S_2PMe_2)]$ has a meridional configuration,² leads to the conclusion that complexes (9) and (10) have the structure shown in Scheme 1. The complex $[OsCl_2(PMe_2Ph)_2(S_2PMe_2)]$ (11) has a strong absorption at 300 cm^{-1} indicative of a *trans*- $OsCl_2$ arrangement.

The similar $\nu(OsCl)$ of complexes (13), (3), and (18), all of which have formula $[OsCl(PMe_2Ph)_3(S-S)]$ ($S-S^- = S_2PMe_2^-$, $S_2CNMe_2^-$, and S_2COEt^- respectively), indicate that these complexes probably have a common stereochemistry. Since the other isomer of $[OsCl(PMe_2Ph)_3(S_2CNMe_2)]$ (5) has a lower $\nu(OsCl)$, it is likely that here the chloride ion is *trans* to a phosphine group,



SCHEME 1 Proposed mechanism for the reaction of *mer*- $[OsCl_3(PMe_2Ph)_3]$ (1) with $[S-S]^-$ (complexes shown in broken square brackets were not isolated). (i) $-Cl^-$; (ii) $-PMe_2Ph$; (iii) $+e^-$; (iv) $[S-S]^-$

whilst the other complexes (13), (3), and (18) have a meridional configuration (see Scheme 1). The other complexes, apart from those containing CO, all have dithioacid absorptions characteristic of bidentate coordination (Table 2) and little information as to their stereochemistries can be gleaned from their i.r. spectra, although the presence of a $\nu(\text{CO})$ stretching vibration at $1\ 030\ \text{cm}^{-1}$ in $[\text{Os}(\text{OEt})(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (6) is in the region expected for an ethoxy-group directly bound to a metal ($1\ 000$ – $1\ 100\ \text{cm}^{-1}$).¹²

For the carbonyl-containing species, although the 500 – $700\ \text{cm}^{-1}$ region in their i.r. spectra is complicated by the presence of carbonyl bending modes, it can be seen from Table 2 that the two complexes of formula $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ [(16) and (17)] as well as $[\text{Os}(\text{CO})_2(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ (15) probably contain both uni- and bi-dentate $[\text{S}_2\text{PMe}_2]^-$ groups and that (15) has the two CO groups in a *cis* configuration [having two $\nu(\text{CO})$]. The higher value of $\nu(\text{CO})$ for (17) compared to the other two monocarbonyl complexes indicates that the CO group in (17) may be *trans* to PMe_2Ph {cf. $[\text{Ru}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (D) in ref. 3}. Finally, the absence of a peak at $600\ \text{cm}^{-1}$ in the i.r. spectrum of $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ indicates that this complex probably does not contain unidentate $[\text{S}_2\text{PMe}_2]^-$ groups.

Mass spectra. The mass spectra of $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ (14) and $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (16) were identical since (16) readily loses PMe_2Ph at high temperatures to form (14). Their mass spectra showed well defined, intense, osmium isotope patterns which correspond to $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]^+$ (608),* $[\text{Os}(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]^+$ (580), $[\text{Os}(\text{S}_2\text{PMe}_2)_2]^+$ (442), and $[\text{Os}(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]^{2+}$ (290), as well as several weaker patterns corresponding to loss of methyl groups and large metastable-ion signals at m/e 560 and 347 which correspond to loss of CO from $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]^+$ and of PMe_2Ph from $[\text{Os}(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]^+$ respectively.

The mass spectrum of $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (3) is also of interest since it not only showed the parent ion and fragmentation pattern corresponding to this complex, but also those for two other complexes, $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNMe}_2)_2]$ (2) and $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (9) (Table 3). Since there is no evidence for (2), or an isomer of (2), in the ^1H n.m.r. spectrum of (3) and since the relative intensities of the mass-spectral signals arising from these two complexes are comparable in two different samples, it seems likely that (2) is formed from (3) under the extreme conditions present in the mass spectrometer ($200\ ^\circ\text{C}$). However, since the intensities of the mass-spectral signals arising from $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (9) vary considerably relative to those of (3) from one sample to another, it is likely that this

* Numbers in parentheses refer to m/e of the ^{192}Os peak.

† 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, $J(\text{PP}')$ value when compared to $|J(\text{PH}) + J(\text{PH}')|$.¹⁴

complex is an impurity in (3). This is quite possible since the mode of preparation of (3) is similar to that of (9), and the presence of this osmium(III) impurity might also explain the broadness of the signals observed in the ^1H n.m.r. spectrum of (3) (see below).

Hydrogen-1 n.m.r. spectra. The ^1H n.m.r. spectra of *mer*- $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{PR}_2)]$ [$\text{R} = \text{Me}$ (9) or Ph (10)] and of *trans*- $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)]$ (11) all showed ill defined contact-shifted resonances from which very little structural information may be obtained. These spectra are indicative of paramagnetic species, and solution magnetic moments obtained by Evans' method¹³ (see Table 1) lie well within the range expected for one unpaired electron and are consistent with the formulation of these complexes as containing Os^{III} . However, the structures of (9), (10), and (11) as indicated by their i.r. spectra are consistent with those of the analogous diamagnetic rhodium(III) complexes² as well as with their modes of preparation, which involve replacement of the most labile chloride ion in (1) by a unidentate $[\text{S}-\text{S}]^-$ ligand [(9) and (10)] followed by chelation of this dithioacid ligand with concomitant loss of phosphine to form (11) (see Scheme 1). The remaining complexes are all diamagnetic and gave rise to sharp n.m.r. signals from which their structures in solution may be unequivocally assigned (Table 4). The methyl groups on the phosphine ligands of $[\text{OsX}(\text{PMe}_2\text{Ph})_3(\text{S}-\text{S})]$ [$\text{X} = \text{Cl}$, $\text{S}-\text{S}^- = \text{S}_2\text{PMe}_2^-$ (13) or S_2COEt^- (18); $\text{X} = \text{Br}$, $\text{S}-\text{S}^- = \text{S}_2\text{COEt}^-$ (19)] gave rise to two virtually coupled triplets and a sharp doublet in their ^1H n.m.r. spectra. This, together with only one methyl doublet from the $[\text{S}_2\text{PMe}_2]^-$ group of (13), confirms that these complexes have the meridional structure shown in Scheme 1.

At low temperature, the ^1H n.m.r. spectra of $[\text{OsX}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ [$\text{X} = \text{Cl}$ (5) or OEt (6)] consisted of two pseudo-doublets † and a sharp doublet arising from the phosphine methyl groups as well as a sharp singlet from the dithiocarbamate methyl groups. For (6), there were also a quartet and a triplet arising from the OEt group. This indicates that the complexes do not contain mutually *trans* phosphine groups and hence must have a facial configuration (Scheme 1). Then, the phosphines *trans* to the sulphur atoms are chemically equivalent giving rise to the pseudo-doublets, and there are two such pseudo-doublets since there is no plane of symmetry through the Os–P bonds. The phosphine *trans* to X is unique, giving rise to a single methyl doublet.

The ^1H n.m.r. spectrum of $[\text{OsCl}(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ (3) is more difficult to interpret since, although immediately after the solution was made up the resonances were relatively sharp, they rapidly broadened. This is presumably because the complex is rapidly oxidised in air or because a paramagnetic impurity is present in the

¹² W. J. Reagan and C. H. Brubaker, *Inorg. Chem.*, 1970, **9**, 827.

¹³ D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

¹⁴ R. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

solution.* Complex (3) is assigned a *mer* configuration on the basis of heteronuclear-decoupling studies and because it is different from (5) which is definitely the *fac* isomer. Irradiation in the ^{31}P resonance region produced sharpening of the slightly broad singlets at δ 1.80 and 1.66 p.p.m. which indicates that these are separate resonances with some P-H coupling. Irradiation at a different frequency in the same region decoupled the doublet at δ 1.34 p.p.m. to a singlet and thus it is most likely that the ^1H n.m.r. spectrum of the phosphine methyl groups is similar to those of the *mer* complexes (13), (18), and (19) and that (3) also has this *mer* configuration.

The low-temperature ^1H n.m.r. spectra of $[\text{Os}(\text{PMe}_2\text{-Ph})_2(\text{S-S})_2]$ [$\text{S-S} = \text{S}_2\text{PMe}_2^-$ (7), S_2PPh_2^- (8), or $\text{S}_2\text{CNMe}_2^-$ (2)] are all consistent with *cis* stereochemistry, although the non-equivalence of the methyl groups of (8) was not seen even at 213 K. As for *cis*- $[\text{Ru}(\text{PMe}_2\text{-Ph})_2(\text{S}_2\text{PMe}_2)_2]$,³ the two doublets arising from the $[\text{S}_2\text{PMe}_2]^-$ groups of (7) broadened and coalesced on warming, but in this case the coalescence temperature was *ca.* 328 K and the fast-exchange limit was not reached in CDCl_3 . The two pseudo-doublets from the phosphine methyl groups also coalesced on warming to give a sharp signal at higher temperatures. This behaviour is again attributed to rapid interconversion of the two possible optical isomers of (7)¹⁵ and rates together with related activation parameters for the inversion in CDCl_3 and C_6H_6 are given in Table 5. Since there is negligible difference in ΔH^\ddagger for the inversion on changing the solvent from CDCl_3 to C_6H_6 , it is unlikely that a

doublets from the phosphine methyl groups gradually moved together without broadening. This behaviour is similar to that found for *cis*- $[\text{Ru}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{-CNMe}_2)_2]$ ^{3,15} and *cis*- $[\text{Rh}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{CNMe}_2)_2][\text{BPh}_4]^-$ ² and cannot be explained in terms of a metal-centred inversion, but rather by separate processes involving increases in the rates of rotation about the C \cdots N bonds of the $[\text{S}_2\text{CNMe}_2]^-$ ligands and coincidental equivalence of the signals from different rotamers at higher temperatures.

The low-temperature ^1H n.m.r. spectrum of $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ (14) consisted of six doublets arising from the six inequivalent methyl groups in the molecule indicating *cis* stereochemistry (see Scheme 2). However, on warming, the two doublets arising from the methyl groups on the phosphine (c and c') became coincident, but also, more surprisingly, two of the dithioacid doublets (b and b') move together until at *ca.* 283 K they were exactly coincident. The large doublet so formed broadened on further heating, which presumably indicates that the chemical shifts of these two doublets are no longer identical. Phosphorus-31 decoupling studies indicate that these two doublets arise from two methyl groups attached to the same phosphorus atom (presumably with one of the methyl groups *syn* to CO), and the only explanation for this behaviour appears to be that small structural changes occur on warming the complex and these give rise to different shielding effects on the two methyl groups at different temperatures.†

The presence of a triplet from the methyl groups of the

TABLE 5
Rates and activation parameters for the inversion process *cis* $\Delta \rightleftharpoons$ *cis* Λ for $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$

Solvent	$\log_{10}(h/s^{-1})$ at 298 K	E^\ddagger kJ mol $^{-1}$	ΔH_{298}^\ddagger kJ mol $^{-1}$	ΔS_{298}^\ddagger J K $^{-1}$ mol $^{-1}$	ΔG_{298}^\ddagger kJ mol $^{-1}$
CDCl_3	0.50 ± 0.04	94.0 ± 4	91.5 ± 4	72 ± 18	70.1 ± 0.2
C_6H_6	-0.20 ± 0.10	93.4 ± 4	91.0 ± 4	57 ± 12	74.1 ± 0.1

solvent-assisted process is operating here.^{16,17} However, the large positive ΔS^\ddagger values together with the comparable values of the activation parameters for the inversions of *cis*- $[\text{M}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (M = Ru or Os) in benzene suggest that a similar mechanism to that shown in Scheme 2b (ref. 1) is operating for the inversion of *cis*- $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ in both CDCl_3 and C_6H_6 .

On increasing the temperature, the ^1H n.m.r. spectrum of (2) also underwent interesting changes. The two $[\text{S}_2\text{CNMe}_2]^-$ methyl singlets coalesced to give a sharp singlet at higher temperatures, whilst the two pseudo-

* A weak e.s.r. signal was observed in the solid, but since its position is not reproducible it is probably due to a small amount of paramagnetic impurity rather than to any inherent paramagnetism of the complex itself. The nature of this impurity is unclear although the presence of $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]^-$ in the mass spectrum of (3) (Table 3) could indicate that $[\text{OsCl}_2(\text{PMe}_2\text{Ph})_3(\text{S}_2\text{CNMe}_2)]$ is the impurity, but this could also be formed in the mass spectrometer.

† Since the four-membered rings in *cis*- $[\text{Ru}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PET}_2)_2]$ are not planar in the solid state,¹⁸ it may be that this is also the case at low temperature for *cis*- $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ in solution, and that on warming fast 'inversion' of these rings occurs which fortuitously causes equal shielding effects of the two methyl groups on one $[\text{S}_2\text{PMe}_2]^-$ ligand at 283 K.

phosphines and two doublets from the $[\text{S}_2\text{PMe}_2]^-$ methyl groups in the ^1H n.m.r. spectrum of $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (16) is consistent with a structure containing *trans* phosphines, as shown in Scheme 2, provided that there is free rotation about the metal-phosphorus bonds. For the analogous $[\text{Ru}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ (complex C, Figure 8 in ref. 3) the ^1H n.m.r. spectrum indicates that rotation about the Ru-P bonds is slow at room temperature. Another important difference between these two complexes is that, whereas at elevated temperatures the ruthenium complex readily loses PMe_2Ph to give *cis*- $[\text{Ru}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$,³ (16) may be kept in solution at 323 K for several hours or may be recovered unchanged on recrystallisation from $\text{CH}_2\text{-Cl}_2\text{-C}_6\text{H}_{14}$. This is presumably a reflection of the greater inertness of Os^{II} compared to Ru^{II} .

¹⁵ D. J. Cole-Hamilton and T. A. Stephenson, *J.C.S. Dalton*, 1974, 754.

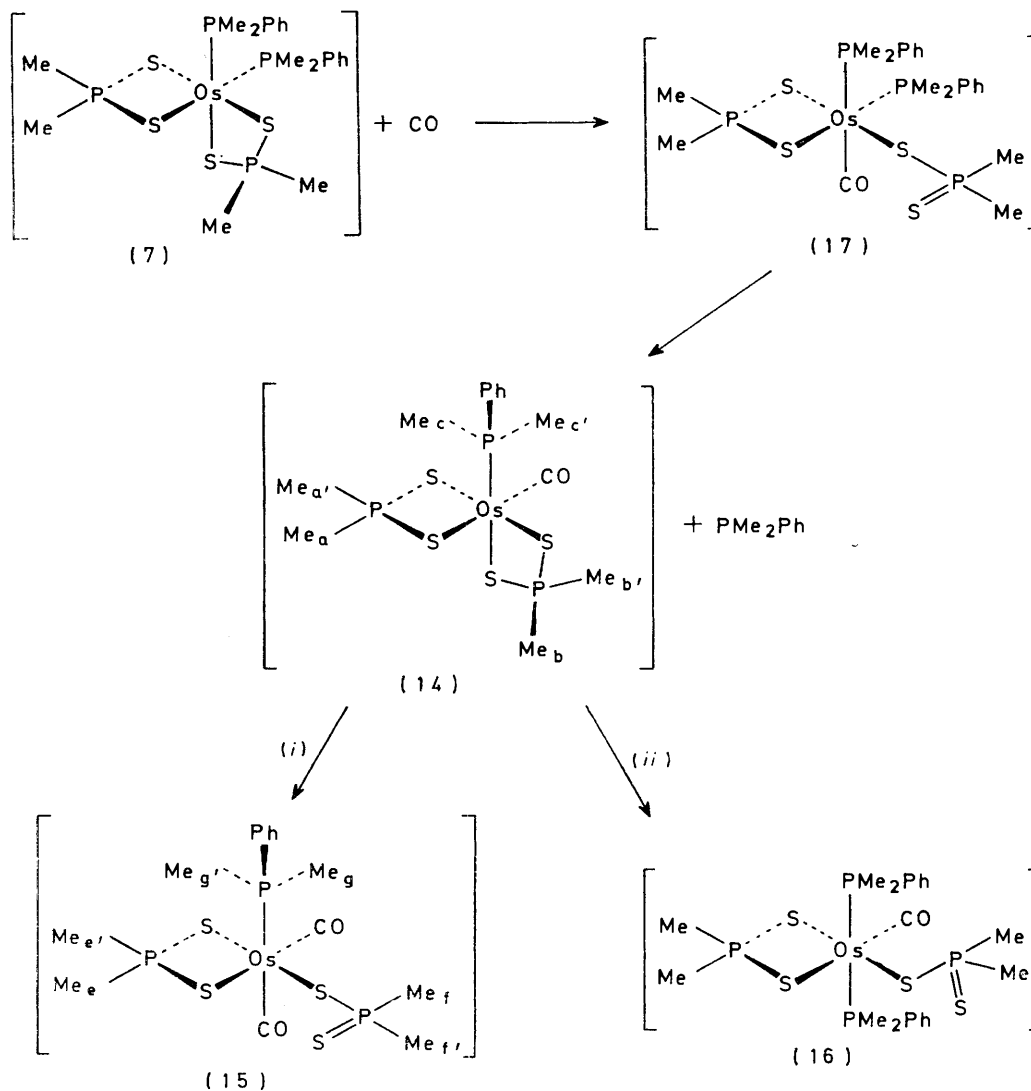
¹⁶ D. A. Case and T. J. Pinnavia, *Inorg. Chem.*, 1971, 10, 482.

¹⁷ A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, 1970, 92, 7061.

¹⁸ J. D. Owen and D. J. Cole-Hamilton, *J.C.S. Dalton*, 1974, 1867.

The other isomer of $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (17) gave rise to seven doublets in the ^1H n.m.r. spectrum and, apart from small changes in chemical shift, this spectrum was temperature invariant up to 323 K and again showed no detectable decomposition at this temperature. Phosphorus-31 decoupling studies indicate that the doublet at δ 1.74 p.p.m., which has twice the intensity of the other doublets, is composed of two accidentally degenerate resonances from methyl groups

cis- $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ in the presence of sulphur show that it consists of a mixture of (14), PMe_2PhS , and complex (15) whose n.m.r. spectrum is given in Table 4. The best interpretation of this spectrum is that the complex contains one PMe_2Ph ligand, in which the methyl groups are inequivalent, and two $[\text{S}_2\text{PMe}_2]^-$ ligands in one of which the methyl groups are inequivalent whilst in the other they are equivalent. We assign this complex the structure shown in Scheme 2



SCHEME 2 Proposed mechanism of carbonylation of *cis*- $[\text{Os}(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (7). (i) CO; (ii) PMe_2Ph

on different phosphine ligands. Thus, all the methyl groups in this complex are inequivalent, and in view of the similarity of preparation of this complex and that of $[\text{Ru}(\text{CO})(\text{PMe}_2\text{Ph})_2(\text{S}_2\text{PMe}_2)_2]$ (complex D, Figure 8 in ref. 3) as well as the similarity in their spectroscopic properties (17) is assigned the structure shown in Scheme 2.

Finally, ^{31}P decoupling studies on the ^1H n.m.r. spectrum of the brown oil obtained from carbonylation of

because this fits the evidence and is the most likely dicarbonyl to be formed from further carbonylation of *cis*- $[\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})(\text{S}_2\text{PMe}_2)_2]$ (14). It is also the only isomer with no plane of symmetry through the Os-P bond in which there is a methyl group *syn* to PMe_2Ph on the bidentate $[\text{S}_2\text{PMe}_2]^-$ ligand, which is required to explain the large shift to low frequency of one of these methyl groups (e'). Since the osmium atom in this complex is a chiral centre, the two methyl groups of the

unidentate $[\text{S}_2\text{PMe}_2]^-$ ligand would be expected to be inequivalent [as in (17)], but in this case it appears that the chemical-shift difference is only very small.

Stereochemical Path for Conversion of mer-[OsCl₃(PMe₂Ph)₃] into cis-[Os(PMe₂Ph)₂(S-S)₂].—Since the only complex obtainable from the reaction of (1) with $\text{K}[\text{S}_2\text{COEt}]$ is *mer*-[OsCl(PMe₂Ph)₃(S₂COEt)], it is clear that this complex does not react with $\text{K}[\text{S}_2\text{COEt}]$ and that the chloride ion in this complex is inert. This indicates that the sulphur atom of the $[\text{S}_2\text{COEt}]^-$ moiety has a low *trans* effect and is not able to labilise the chloride ion *trans* to it to any large extent. Although little information is available on the *trans* effects of sulphur-containing ligands, work on the reactions of *fac*-[Cr(NO)(OH₂)₃(S-S)] [S-S⁻ = S₂CNR₂⁻, S₂COR⁻, or S₂PR₂⁻] with Lewis bases¹⁹ has shown that the *trans* effects of these dithioacid ligands are low but of comparable magnitude. Thus, since *mer*-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (3) reacts with [S-S⁻] to give *cis*-[Os(PMe₂Ph)₂(S₂CNMe₂)(S-S⁻)] [S-S⁻ = S₂CNMe₂⁻ (2) or S₂COEt⁻ (4)], the mechanism of these reactions cannot involve direct displacement of chloride ion by [S-S⁻]. However, since *fac*-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (5) is also obtained from these reactions, it is probable that they proceed by isomerisation of (3) to give (5) followed by displacement of Cl⁻ by [S-S⁻] since in the *fac* isomer the chloride ion is *trans* to the high *trans*-effect ligand, PMe₂Ph. The formation of *fac*-[Os(OEt)(PMe₂Ph)₃(S₂CNMe₂)] (6) is then explained as arising from inter-action of (5) with solvent ethanol and loss of HCl gas.

As has already been noted, the reaction of (1) with $\text{Na}[\text{S}_2\text{CNMe}_2] \cdot 2\text{H}_2\text{O}$ gives higher yields of (2) than does the corresponding reaction of (3). This can only mean that another path which does not involve (3) as an intermediate is operative in the formation of (2) from (1). This path probably involves ionic osmium(III) intermediates with the reduction to Os^{II} occurring as the last step (see Scheme 1).

Since *mer*-[OsCl(PMe₂Ph)₃(S₂PMe₂)] (13) is only formed on prolonged standing of *mer*-[OsCl₂(PMe₂Ph)₃(S₂PMe₂)] (9) in non-polar solvents and since no (13) but only a purple ionic oil and (1) are formed from (9) in polar solvents, it seems likely that the formation of *cis*-[Os(PMe₂Ph)₂(S₂PMe₂)₂] (7) from (1) in refluxing ethanol does not involve (13) as an intermediate but rather goes by the path which involves osmium(III) cations. Then, the purple ionic oil probably contains [OsCl(PMe₂Ph)₃(S₂PMe₂)⁺ (12), and the formation of (1) on allowing (9) to stand in polar or non-polar solvents is easily explained since the chloride ion released in the formation of (12) from (9) might then attack (9) to release $[\text{S}_2\text{PMe}_2]^-$ and give *mer*-[OsCl₃(PMe₂Ph)₃] (1).

It still remains to explain why neither of the paths shown in Scheme 1 is open to the reaction of (1) with $\text{K}[\text{S}_2\text{COEt}]$ in refluxing ethanol. The latter is thought to be excluded because the strongly reducing nature of

$[\text{S}_2\text{COEt}]^-$ causes reduction to Os^{II} before [OsCl(PMe₂Ph)₃(S₂COEt)]⁺ can react with more $[\text{S}_2\text{COEt}]^-$. Since it is well documented that the ease with which isomerisations of complexes occur is dependent on the substituents in the molecule,²⁰ we propose that *mer*-[OsCl(PMe₂Ph)₃(S₂COEt)] (18) isomerises less readily to its *fac* isomer than does (3) and that, in fact, harsher conditions than refluxing in ethanol are required to effect this isomerisation for (18) and thus to allow further reaction to occur.

EXPERIMENTAL

Microanalyses were by the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the 250–4 000 cm⁻¹ region on a Perkin-Elmer 457 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Solution spectra were recorded in potassium bromide cells. Mass spectra were obtained on an A.E.I. MS9 spectrometer and conductivity measurements on a Portland Electronics 310 conductivity bridge. Hydrogen-1 n.m.r. spectra and solution magnetic moments (Evans' method)¹³ were obtained on a Varian Associates HA-100 spectrometer and ³¹P n.m.r. spectra on a Varian XL-100 spectrometer operating in the pulse and Fourier-transform mode at 40.5 MHz (³¹P chemical shifts are given in p.p.m. to high frequency of 85% H₃PO₄). Kinetic line-shape analysis on *cis*-[Os(PMe₂Ph)₂(S₂PMe₂)₂] was made as described elsewhere.¹⁵ Heteronuclear-decoupling experiments were carried out on the HA-100 spectrometer using a second radio-frequency field provided by a Schlumberger FS30 frequency synthesiser. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Materials.—Ammonium hexachloro-osmate(IV) (Johnson, Matthey Ltd), carbon mono-oxide (Air Products), dimethylphenylphosphine (B.D.H.), $\text{Na}[\text{S}_2\text{CNMe}_2] \cdot 2\text{H}_2\text{O}$ (Ralph Emanuel), and $\text{K}[\text{S}_2\text{COEt}]$ (B.D.H.) were obtained as indicated. Sodium dimethylphosphinodithioate, and sodium and ammonium diphenylphosphinodithioate were prepared as described earlier.² All the solutions were degassed before use and reactions were carried out under a nitrogen atmosphere unless otherwise stated.

Preparations.—*mer-Trichlorotris(dimethylphenylphosphine)osmium(III)* (1).—The salt $[\text{NH}_4]_2[\text{OsCl}_6]$ (2.0 g) and PMe₂Ph (3 cm³) were heated under reflux in 2-methoxyethanol (50 cm³) containing concentrated HCl (5 cm³) for 16 h. The resulting red solution was filtered hot to remove $[\text{NH}_4]\text{Cl}$ and allowed to crystallise. The red crystals were collected and washed with water, ethanol, and n-pentane (3.0 g, 93%).

mer-Tribromotris(dimethylphenylphosphine)osmium(III). The complex *mer*-[OsCl₃(PMe₂Ph)₃] (0.35 g) and LiBr (2.0 g) were heated under reflux in ethanol (20 cm³) for 36 h and allowed to cool. The resulting purple needles were filtered off and washed with water, ethanol, and n-pentane (0.30 g, 72%).

mer-Dichlorotris(dimethylphenylphosphine)(diphenylphosphinodithioato)osmium(III) (10). Solutions of (1) (0.15 g) in CH₂Cl₂ (15 cm³) and Na[S₂PPh₂] (0.20 g) in methanol (10 cm³) were mixed and after passing nitrogen the purple solution was evaporated to half its volume. The purple

¹⁹ See O. I. Kondrat'eva, A. D. Troitskaya, N. A. Chadaeva, G. M. Usacheva, and A. E. Ivantsov, *Zhur. obschei Khim.*, 1973, **43**, 2087 and refs. therein.

²⁰ J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391.

product was collected and washed with water, methanol, and n-pentane (0.10 g, 51%).

mer-Dichlorotris(dimethylphenylphosphine)(dimethylphosphinodithioato)osmium(II) (9). Complex (1) (0.30 g) and $\text{Na}[\text{S}_2\text{PMe}_2]\cdot 2\text{H}_2\text{O}$ (0.30 g) were shaken in methanol (25 cm³) for 90 min. The resulting purple crystals were collected and washed with water, methanol, and n-pentane (0.31 g, 92%). Slow recrystallisation of (9) from CH_2Cl_2 - C_6H_{12} gave red crystals of (1).

mer-Chloro(dimethyldithiocarbamato)tris(dimethylphenylphosphine)osmium(II) (3), from (1) (0.30 g) and $\text{Na}[\text{S}_2\text{CNMe}_2]\cdot 2\text{H}_2\text{O}$ (0.25 g) in methanol (25 cm³) for 10 min as yellow crystals (0.22 g, 69%), and mer-chlorotris(dimethylphenylphosphine)(O-ethyl dithiocarbonato)osmium(II) (18), from (1) (0.15 g) and $\text{K}[\text{S}_2\text{COEt}]$ (0.10 g) in methanol (15 cm³) for 10 min and evaporation to near dryness as orange crystals (0.11 g, 70%), were similarly prepared. Complex (18) was also prepared by refluxing (1) (0.15 g) with $\text{K}[\text{S}_2\text{COEt}]$ (0.10 g) in ethanol (20 cm³) for 60 min, evaporating to dryness, and recrystallising the orange oil from CH_2Cl_2 - C_6H_{14} (0.10 g, 62%). Phosphorus-31 n.m.r. in CDCl_3 at 303 K: (3) AB₂ pattern with ν_A -39.8, ν_B -37.8 p.p.m., δ_{AB} 81.0 Hz, and J_{AB} 11.1 Hz; (18) AB₂ pattern with ν_A -37.3, ν_B -38.8 p.p.m., δ_{AB} 61.7 Hz, and J_{AB} 18.2 Hz.

mer-Bromotris(dimethylphenylphosphine)(O-ethyl dithiocarbonato)osmium(II) (19). The complex mer-[OsBr₃(PMe₂Ph)₃] (0.10 g) and $\text{K}[\text{S}_2\text{COEt}]$ (0.07 g) were heated under reflux in ethanol (15 cm³) for 60 min and the orange solution was evaporated to dryness. The resulting orange oil could not be recrystallised.

mer-Chlorotris(dimethylphenylphosphine)(dimethylphosphinodithioato)osmium(II) (13).—The complex mer-[OsCl₂(PMe₂Ph)₃(S₂PMe₂)₂] (9) (0.10 g) was dissolved in benzene (5 cm³) and allowed to stand in air for 2 weeks. Addition of n-hexane to the solution then precipitated a purple oil (12) from which the brown solution was decanted and allowed to crystallise slowly. The complex precipitated in low yield as brown needles and after filtration the filtrate deposited red crystals of (1). When the reaction was allowed to proceed for 4 weeks, no purple oil was formed but approximately equal molar ratios of (13) and (1). The purple oil (12) may also be prepared by allowing mer-[OsCl₂(PMe₂Ph)₃(S₂PMe₂)₂] (9) to stand in acetone in the presence of air for several days; (12) and (1) were then the sole products.

trans-Dichlorobis(dimethylphenylphosphine)(dimethylphosphinodithioato)osmium(II) (11). This complex was prepared by refluxing mer-[OsCl₂(PMe₂Ph)₃(S₂PMe₂)₂] (0.07 g) in benzene (10 cm³) for 30 min and evaporating to near dryness. The red needles were collected and washed with n-pentane (0.063 g, 97%).

cis-Bis(dimethylphenylphosphine)bis(dimethylphosphinodithioato)osmium(II) (7). Complex (1) (0.60 g) and $\text{Na}[\text{S}_2\text{PMe}_2]\cdot 2\text{H}_2\text{O}$ (0.50 g) were heated under reflux in ethanol (25 cm³) for 60 min. The orange solution was cooled with nitrogen bubbling through it and the resulting orange crystals were collected and washed with water, ethanol, and n-pentane (0.40 g, 66%). On one occasion, the filtrate deposited a small quantity of yellow [Os₂Cl₃(PMe₂Ph)₆]Cl.

Similarly prepared were cis-bis(dimethylphenylphosphine)bis(diphenylphosphinodithioato)osmium(II) (8) from (1) (0.15 g) and $[\text{NH}_4][\text{S}_2\text{PPh}_2]$ (0.20 g) as orange crystals (0.10 g; 50%) and cis-bis(dimethyldithiocarbamato)bis(dimethyl-

phenylphosphine)osmium(II) (2) from (1) (0.10 g) and $\text{Na}[\text{S}_2\text{CNMe}_2]\cdot 2\text{H}_2\text{O}$ (0.10 g) in ethanol (10 cm³) for 90 min, as yellow crystals (0.08 g, 80%). A thin-layer chromatograph of the filtrate from (2) (toluene on alumina) showed four weak bands, one of which corresponded to (2). Complex (2) was also prepared by the reaction of mer-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (3) (0.026 g) with $\text{Na}[\text{S}_2\text{CNMe}_2]\cdot 2\text{H}_2\text{O}$ (0.02 g) in refluxing ethanol (5 cm³) for 90 min, the yellow solid crystallising out on cooling (0.01 g, 37%). T.l.c. (toluene on alumina) of the resulting solution showed four bands of approximately equal intensity, identical in R_F values and colours to those obtained from the reaction of (1) with $\text{Na}[\text{S}_2\text{CNMe}_2]\cdot 2\text{H}_2\text{O}$. Thus, the total yield of (2) was ca. 50%.

cis-(Dimethyldithiocarbamato)bis(dimethylphenylphosphine)(O-ethyl dithiocarbonato)osmium(II) (4), fac-chloro(dimethyldithiocarbamato)tris(dimethylphenylphosphine)osmium(II) (5), and fac-(dimethyldithiocarbamato)tris(dimethylphenylphosphine)ethoxo-osmium(II) (6). The complex mer-[OsCl(PMe₂Ph)₃(S₂CNMe₂)] (3) (0.147 g) and $\text{K}[\text{S}_2\text{COEt}]$ (0.031 g) were heated under reflux in ethanol (15 cm³) for 90 min. T.l.c. of the resulting orange solution (toluene on alumina) revealed that it consisted of five complexes, four of which were identical to those produced in the reaction of (1) with $\text{Na}[\text{S}_2\text{CNMe}_2]\cdot 2\text{H}_2\text{O}$, and the fifth orange band was of higher R_F value than the other four. After evaporation of the solution to dryness, the orange oil was dissolved in toluene and eluted from a dry alumina column with toluene. The five bands were washed off with diethyl ether and after evaporation to dryness the complexes were recrystallised from CH_2Cl_2 - C_6H_{14} . The products in order of decreasing R_F value were (4) (orange), (2) (yellow), (5) (yellow), and (6) (yellow). The band of lowest R_F value produced an orange oil whose identity is unknown.

cis-Carbonyl(dimethylphenylphosphine)bis(dimethylphosphinodithioato)osmium(II) (14). The complex cis-[Os(PMe₂Ph)₂(S₂PMe₂)₂] (7) (0.10 g) and sulphur (0.01 g) were heated under reflux in ethanol (15 cm³), with CO bubbling, for 30 min. The yellow solution was cooled, filtered through celite, and evaporated to dryness. The resulting yellow oil was recrystallised from CH_2Cl_2 - C_6H_{14} to give a brown oil which contained (15), (14), and PMe_2PhS . The yellow supernatant was decanted and allowed to crystallise to give the product as yellow crystals (0.04 g, 47%).

Carbonylbis(dimethylphenylphosphine)bis(dimethylphosphinodithioato)osmium(II) (16). The complex cis-[Os(PMe₂Ph)₂(S₂PMe₂)₂] (7) (0.10 g) and PMe_2Ph (0.20 cm³) were carbonylated in refluxing ethanol (15 cm³) for 30 min. On cooling, the resulting yellow solution gave yellow crystals of the product (0.07 g, 67%).

Carbonylbis(dimethylphenylphosphine)bis(dimethylphosphinodithioato)osmium(II) (17). The complex cis-[Os(PMe₂Ph)₂(S₂PMe₂)₂] (7) (0.05 g) was carbonylated in CH_2Cl_2 - C_6H_{14} (1 : 1 v/v) at room temperature for 2 min. The solvent was evaporated by passing nitrogen and the yellow solid was collected in quantitative yield.

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