Metal Complexes of Tris(trimethylsilylmethyl)phosphine †

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Complexes of tris(trimethylsilylmethyl)phosphine (siphos) with ruthenium, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, cadmium, and mercury have been prepared and characterised by analysis and i.r. and n.m.r. spectroscopy. The formation of the unusual complex $RuCl_2(CO)_2[(Me_3SiCH_2)_2PMe]_2$ is described. Ethanolic sodium borohydride reacts with *trans*-MCl(CO)(siphos)$_2$ (M = Rh or Ir) in the presence of the phosphine to give the tetrahydroborate complexes, $M(BH_4)(CO)(siphos)_2$. With rhodium trichloride and tribromide, the dimeric $[RhCl_2(siphos)_2]_2$ and the monomeric *trans*-$RhBr_2$(siphos)$_2$ are obtained respectively; the latter shows i.r. and n.m.r. spectra similar to those of the corresponding palladium and platinum complexes.

THE use of trimethylsilylmethyl groups to stabilise transition metal alkyls,[1] together with current interest in bulky phosphines has prompted us to investigate the metal complexes of tris(trimethylsilylmethyl)phosphine (siphos). The phosphine was first prepared by Seyferth and only one metal complex, namely, (siphos)$HgCl_2$, has been previously described.[2]

During our studies we found that the phosphine readily decomposes under vigorous reaction conditions; several complexes of its decomposition products have been isolated but have not yet been fully characterised. Hence, most of the reactions described herein were performed under mild conditions and thus, the formation of a methylbis(trimethylsilymethyl)phosphine complex (*vide infra*) at room temperature is singularly remarkable. Intense i.r. absorptions at *ca.* 1250 and 840 cm^{-1} serve as an indication of the presence of the $P-CH_2SiMe_3$ grouping in a metal complex, while the presence of the P–Me grouping may be associated with an additional peak at 1300 cm^{-1}. The number of $SiMe_3$ protons can readily be determined from the n.m.r. spectrum since they normally occur as a singlet.

Like most alkyl and aryl phosphines, tris(trimethylsilylmethyl)phosphine absorbs atmospheric oxygen slowly in the solid state and more rapidly in solution to form the phosphine oxide, $(Me_3SiCH_2)_3PO$, which is characterised by its $\nu(P=O)$ at 1150 cm^{-1} in the i.r., spectrum. With carbon disulphide, a 1 : 1 adduct of formula $(Me_3SiCH_2)_3PCS_2$ is formed. The phosphine also forms a wide range of complexes with most transition and main-group metals, the representative complexes of which are described below.

Ruthenium Complexes.—Ethanolic hydrated ruthenium trichloride reacts with carbon monoxide to give a carbonyl-containing solution which, when treated with stoicheiometric quantities of tertiary phosphines, L, gives complexes of the types, $RuCl_2(CO)_2L_2$ and $RuCl_2(CO)L_3$.[3] Addition of tris(trimethylsilylmethyl)phosphine in excess to this carbonyl-containing solution yields only $RuCl_2(CO)_2$(siphos)$_2$, and the failure to form $RuCl_2(CO)$(siphos)$_3$ may be attributed to steric effects. The i.r. spectrum of $RuCl_2(CO)_2$(siphos)$_2$ exhibits a ν(RuCl) mode, suggesting a *trans*-phosphine structure (I; L = siphos), since related complexes (*e.g.* L = PEt_3, PMe_2Ph, PEt_2Ph, PBu_2Ph, and PPr-

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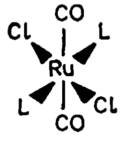
† No reprints available.

[1] W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

[2] D. Seyferth, *J. Amer. Chem. Soc.*, 1958, **80**, 1336.

[3] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466; J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.

$Ph_2)$[4] with this structure show ν(CO) in the range 1976—1999 cm^{-1} and ν(RuCl) in the region 320—350 cm^{-1}. Further evidence for this structure arises from its ^1H n.m.r. spectrum which contains a triplet methylene

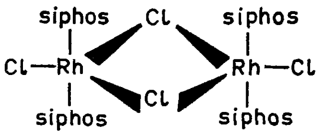


(I)

resonance; yet another example of an $X_6AA'X_6'$ spin system where $|J_{AA'}|$ is large and hence virtual coupling of A and X occurs.[5]

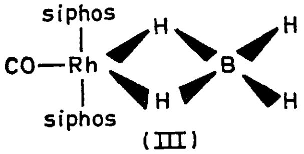
In marked contrast, the polymeric $Ru(CO)_2Cl_2$ reacts with tris(trimethylsilylmethyl)phosphine at room temperature to give the *methyl*phosphine complex, $RuCl_2(CO)_2[(Me_3SiCH_2)PMe]_2$. The similarity in the values of ν(CO) and ν(RuCl) to those of the corresponding tris(trimethylsilylmethyl)phosphine complex suggests an analogous structure [I; $L = (Me_3SiCH_2)_2PMe$]. That the phosphines are mutually *trans* is substantiated by its ^1H n.m.r. spectrum which shows a triplet for the phosphorus-bonded methyl protons due to virtual coupling of the trans-phosphines as $|^2J_{PP}|$ is large.[5] Lack of a plane of symmetry along any of the $P-CH_2$ axes results in the non-equivalence of the methylene protons, thus giving an AB spectrum (fully resolved at 100 MHz) in which each peak is further split into a triplet by virtual coupling of the two ^{31}P nuclei.

Rhodium and Iridium Complexes.—It has been recently shown that rhodium trichloride reacts with t-butylphosphines, L, to give monomeric rhodium(II) complexes of the type *trans*-$RhCl_2L_2$.[6] Under similar conditions, however, tris(trimethylsilylmethyl)phosphine affords a similar complex which is dimeric in benzene solution. A structure with bridging chlorine atoms and *trans*-phosphines, (II), is indicated by its ^1H n.m.r. spectrum. Its far i.r. spectrum exhibits ν(Rh–Cl) absorptions at 338 cm^{-1} (terminal) and at 274 cm^{-1} (bridging), lending further support to this D_{2h} structure for which group theory predicts one terminal and one bridging ν(Rh–Cl) mode that is i.r. active. In contrast, the corresponding reaction with rhodium tribromide gives a monomeric species which has an i.r. and n.m.r. spectrum very similar to those of the palladium complexes, *trans*-$PdX_2(siphos)_2$ (*vide infra*). Hence by analogy to the previously reported t-butylphosphine complexes,[6] a square *trans*-phosphine structure seems to be the most plausible for this bromo-complex. Both the chloro- and the bromo-complex have a magnetic moment (measured at 20°) of 1·5 B.M. per rhodium atom, a rather low value as compared with the 'spin-only' value for one unpaired electron. Similar anomaly has also been noted for related complexes.[6] The e.s.r. spectrum of the bromo-complex is consistent with such a formulation although it differs perceptibly from that of the chloro-complex, which is not at all surprising if the assigned structure, (II), is correct.



(II)

Tris(trimethylsilylmethyl)phosphine reacts with rhodium dicarbonyl chloride dimer to give the yellow *trans*-$RhCl(CO)(siphos)_2$ in almost quantitative yield. Treatment of the related triphenylphosphine complex, *trans*-$RhCl(CO)(PPh_3)_2$, with ethanolic sodium borohydride and an excess of triphenylphosphine gives the hydrido-complex, $RhH(CO)(PPh_3)_3$.[7] An analogous reaction with the tris(trimethylsilylmethyl)phosphine complex however, yields a boron-containing product. The absence of a high-field signal in its ^1H n.m.r. spectrum and the observation of strong i.r. absorptions at 2370 and 2385 cm^{-1}, which are characteristic of ν(B–H) vibrations,[8] together with a boron analysis indicate that it is indeed a tetrahydroborate complex; the possibility of it being a BH_2^- complex may be excluded since the complex reacts with hydrochloric acid to give four moles of hydrogen per rhodium atom. The compound is not ionic and its molecular weight is normal. Similar tetrahydroborate complexes of rhodium and iridium, *e.g.* $Rh(BH_4)(CO)(PPh_3)_2$ were reported during our studies.[8b]



(III)

It is noteworthy that the recently reported tetrahydrido-complex, $FeH_4(PBuPh_2)_3$, obtained by the reaction of iron(II) chloride with butyldiphenylphosphine and ethanolic sodium borohydride in the presence of hydrogen,[9] is doubtless also a tetrahydroborate complex, since its i.r. spectrum also contains absorptions around 2400 cm^{-1}.

Treatment of ethanolic chloroiridic acid with carbon monoxide produces a carbonyl-containing solution which reacts with tris(trimethylsilylmethyl)phosphine to form $IrHCl_2(CO)(siphos)_2$, the i.r. spectrum of which

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

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

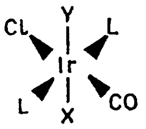
[6] C. Masters, W. S. McDonald, G. Raper, and B. L. Shaw, *Chem. Comm.*, 1971, 210; M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, 1969, **91**, 6266.

[7] D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2660.

[8] (*a*) B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1966, 182; (*b*) L. Vaska, W. V. Miller, and B. R. Flynn, *Chem. Comm.*, 1971, 1615.

[9] M. Arresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, 1971, **5**, 115.

shows a ν(Ir–H) absorption at 2180 cm^{-1} and a ν(CO) absorption at 2010 cm^{-1}. Its ^{1}H n.m.r. spectrum contains a high-field triplet resonance which is typical of a proton *trans* to a chlorine atom in an iridium(III) complex,[10] and indicates that the hydride is coupled to the two equivalent ^{31}P nuclei. The methylene protons constitute an AB spectrum (taken at 100 MHz) in which each line is further split into a triplet by virtual coupling with the mutually *trans* ^{31}P nuclei. The non-equivalence of the methylene protons is presumably caused by asymmetry about the Ir–P bonds brought about by the rather different magnetic environment of other ligands. These data and the similarity in spectral features to those of related iridium(III) complexes[10] favour the structure (IV; X = Cl, Y = H, L = siphos).



(IV)

In refluxing carbon tetrachloride, the hydrido-complex is readily converted to $IrCl_3(CO)(siphos)_2$ with the conceivable structure (IV; X = Y = Cl, L = siphos). The methylene proton resonance of this complex is just a triplet [*cf.* $IrHCl_2(CO)(siphos)_2$] because the Ir–P bonds contain a plane of symmetry.

The analogue of the Vaska complex, *trans*-$IrCl(CO)(siphos)_2$, is formed by the action of an equimolar quantity of sodium methoxide on $IrHCl_2(CO)(siphos)_2$. It undergoes oxidative addition reactions with organic halides such as methyl iodide, trifluoromethyl iodide, or *p*-toluene sulphonyl chloride to give adducts which probably have the structure (IV; X = halogen, Y = Me, CF_3, or *p*-$MeC_6H_4SO_2$) by analogy to those obtained with related complexes of iridium(I).[11] The ^{1}H n.m.r. spectra of the methyl- and trifluoromethyl-complex exhibit a triplet for the methylene protons in each case. The *p*-toluene sulphonyl group causes sufficient magnetic asymmetry in the complex rendering the methylene protons non-equivalent, and this results in an AB spectrum (taken at 100 MHz) further split by the ^{31}P nuclei into triplets.

The reaction of *trans*-$IrCl(CO)(siphos)_2$ with ethanolic sodium borohydride is entirely analogous to that of the rhodium analogue, forming the tetrahydroborate complex, $Ir(BH_4)(CO)(siphos)_2$.

Nickel, Palladium, and Platinum.—Nickel(II) bromide reacts with tris(trimethylsilylmethyl)phosphine in ethanol to give the dark red square complex, *trans*-$NiBr_2(siphos)_2$. In its ^{1}H n.m.r. spectrum, a slightly broadened 1 : 2 : 1 triplet is observed for the methylene protons, confirming the expected *trans*-configuration.

The reaction of sodium chloropalladite with the phosphine affords the complex, *trans*-$PdCl_2(siphos)_2$, which shows a ν(Pd–Cl) at 358 cm^{-1} in its far i.r. spectrum and a triplet methylene proton resonance in its n.m.r. spectrum. It undergoes metathesis with the appropriate halide or pseudohalide ions to produce complexes of the type, *trans*-$PdX_2(siphos)_2$ (X = Br, I, NCS, or N_3). That the thiocyanate complex is *N*-bonded is indicated by the chemical shift of the methylene protons (8·63), which is close to that in the azido-complex (8·57). There is considerable variation in the chemical shift of the methylene protons with changes in the anionic ligands. Thus, the difference in chemical shift for the methylene protons between the chloro- and iodo-complex, $\Delta\tau$, is 0·62. The corresponding $\Delta\tau$ for the methyl protons in complexes of the type, *trans*-$PdX_2(PMe_2Ph)_2$, is only 0·43,[12] although a slightly larger value (0·57) has been reported[13] for a similar shift in the chloro- and iodo-complex of the type, *trans*-$PdX_2(PMe_2Bu^t)_2$.

In view of the possibility of the well-known ortho-metallation in bulky arylphosphines[14] to form ring systems, similar attempts have been made by heating *trans*-$PdI_2(siphos)_2$ in a high boiling alcohol for prolonged periods. However, no cyclisation was observed and starting material was recovered unchanged even when the reaction was performed in the presence of triethylamine. The failure may be attributed to the rather long distances between any of the methyl protons and the metal atom, and to the somewhat unhindered rotation of the methyl groups and less significantly, of the trimethylsilyl group as a whole.

Tris(trimethylsilylmethyl)phosphine reacts with potassium chloroplatinite to give *trans*-$PtCl_2(siphos)$,[2] the i.r. spectrum of which contains the expected ν(Pt–Cl) at 332 cm^{-1}. Its ^{1}H n.m.r. spectrum shows a triplet for the methylene protons with two triplet satellites of $\frac{1}{4}$ intensity due to coupling with the 33% abundant ^{195}Pt. The complex exchanges slowly with iodide ion to yield *trans*-$PtI_2(siphos)_2$ but an attempt to prepare the azido-complex gave only the unchanged starting material.

Copper, Silver, and Gold Complexes.—Tris(trimethylsilylmethyl)phosphine reduces copper(II) chloride to give the copper(I) complex, (siphos)CuCl, which is also prepared by interaction of the phosphine with copper(I) chloride. As expected, a doublet n.m.r. signal is observed for the methylene protons. In the presence of an excess of the phosphine, $(siphos)_3CuCl$, may be isolated. Both complexes, especially the latter, dissociate considerably in polar solvents. Thus, repeated ether extraction of either of the complexes leads to

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[10] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 1887.

[11] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 53; A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1128.

[12] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

[13] B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 2976.

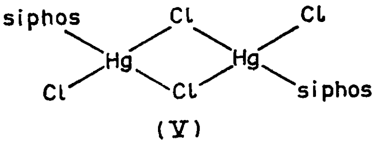
[14] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 3833; A. J. Cheney and B. L. Shaw, *J.C.S. Dalton*, 1972, 754.

almost quantitative recovery of the phosphine. The ^1H n.m.r. spectrum of (siphos)$_3$CuCl shows a doublet resonance for the methylene protons indicating that the phosphines are not mutually *trans* as in a square planar complex.

Silver perchlorate reacts with various proportions of tris(trimethylsilylmethyl)phosphine in methanol giving colourless light- and air-sensitive solutions from which attempts to isolate complexes of the type (siphos)$_n$-$Ag^+ClO_4^-$ ($n = 1$—4) have been unsuccessful. There is little or no reaction between silver halides and the phosphine presumably due to the low solubility of the silver salts in most organic solvents. However, the colourless (siphos)AgCl can be readily prepared by adding a saturated aqueous methanol (50%) solution of sodium chloride to a solution of silver perchlorate containing the phosphine. It is monomeric in chloroform and is light-sensitive.

Sodium tetrachloroaurate(III) is reduced by tris(trimethylsilylmethyl)phosphine in methanol to yield the air- and light-sensitive complex, (siphos)AuCl. Treatment of this complex with tin(II) chloride in the presence of the phosphine gives the colourless Au–Sn bonded complex, (siphos)$_2$AuSnCl$_3$.

Zinc, Cadmium, and Mercury.—Zinc(II) chloride forms a 1 : 2 adduct with tris(trimethylsilylmethyl)phosphine in methanol solution, while under similar conditions, cadmium(II) iodide gives a 1 : 1 adduct, which is monomeric in chloroform solution. The corresponding reaction with mercury(II) chloride and iodide, however, affords the dimeric (siphos)$_2$Hg$_2$Cl$_4$ and the trimeric (siphos)$_3$Hg$_3$I$_6$. They differ considerably in their i.r. spectra and may have the halogen-bridged structures (V) and (VI) respectively.



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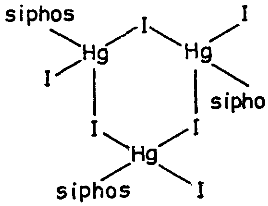

(VI)

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 257, 457, and 325 spectrophotometers in Nujol mills between KBr plates (4000—400 cm^{-1}) or Polythene discs (400—200 cm^{-1}). N.m.r. spectra were registered on a Perkin-Elmer R12A (at 60 MHz) or R14 (at 100 or 94·1 MHz) spectrometer using TMS as an internal reference, and the spectra are summarised in the Table. Molecular weights were measured with a Hitachi–Perkin-Elmer 115 instrument. M.p.s were determined in unsealed capillary tubes using an Electrothermal hot-stage apparatus, and are uncorrected. Magnetic measurements were made using the Evans modification of the Gouy balance. Elemental analyses were carried out by the Microanalytical Department of this laboratory and by Beller, West Germany. The analytical results are given in the Table.

All reactions involving the free phosphine were performed under an atmosphere of nitrogen. Tris(trimethylsilylmethyl)phosphine (siphos) was prepared by the action of phosphorus trichloride on trimethylsilylmethylmagnesium chloride in tetrahydrofuran–diethyl ether; the phosphine had the m.p. reported [2] and the following i.r. (Nujol mull) spectrum: 1413mw [$\delta_{as}(CH_3)$]; 1263s,sh, 1250vs [$\delta_s(CH_3) + \delta_{as}(CH_2)$]; 1090s [$\delta_s(CH_2)$]; 845vvs,br, 782vs, and 758s,sh [$\rho(CH_3) + \rho(CH_2)$]; 694s [$\nu_{as}(SiC_3)$]; and 632m [$\nu_s(SiC_3)$].

Ruthenium Complexes

Dichlorodicarbonylbis[tris(trimethylsilylmethyl)phosphine]ruthenium(II).—Carbon monoxide was bubbled through a refluxing solution of hydrated ruthenium trichloride (0·76 g) in ethanol (25 ml) for 14 h. The resulting red solution was treated with siphos (2·8 g) and the mixture was maintained at 60° for 1·5 h to give the complex (1·62 g) as yellow needles (from dichloromethane–methanol), ν(Ru–Cl): 341vs cm^{-1}.

Dichlorodicarbonylbis[methylbis(trimethylsilylmethyl)phosphine]ruthenium(II).—A suspension of pulverised dichlorodicarbonylruthenium(II) (0·86 g) and siphos (3·0 g) in methanol (30 ml) was stirred for 18 h to give the *product* (2·0 g) as yellow plates (from dichloromethane–methanol), ν(Ru–Cl): 355vs cm^{-1}.

Rhodium Complexes

Di-μ-chloro-dichlorobis[tris(trimethylsilylmethyl)phosphine]dirhodium(II).—A solution of hydrated rhodium trichloride (0·50 g) and siphos (1·6 g) in ethanol (20 ml) was left standing at room temperature for 20 h. Recrystallisation of the precipitate from dichloromethane–methanol gave orange prisms of the complex (0·40 g). At 20°, μ_{eff} = 1·51 B.M. per Rh atom.

trans-*Dibromobis[tris(trimethylsilylmethyl)phosphine]rhodium*(II).—A solution of hydrated rhodium trichloride (0·7 g) and lithium bromide (2·0 g) in ethanol (25 ml) was heated under reflux for 10 min and cooled. Siphos (2·0 g) was added and the mixture was set aside at room temperature for 4 h to give the product (1·6 g) as orange prisms (from dichloromethane–methanol). At 20°, μ_{eff} = 1·50 B.M.

trans-*Chlorocarbonylbis[tris(trimethylsilylmethyl)phosphine]rhodium*(I).—Addition of siphos (1·6 g) to a rapidly stirred suspension of di-μ-choro-tetracarbonyldirhodium(I) (0·53 g) in methanol (20 ml) precipitated the complex as yellow plates in almost quantitative yield; ν(Rh–Cl): 308m cm^{-1}.

trans-*Iodocarbonylbis[tris(trimethylsilylmethyl)phosphine]rhodium*(I).—The complex, *trans*-RhCl(CO)(siphos)$_2$ (0·2 g), and sodium iodide (0·5 g) in acetone (15 ml) was heated under reflux for 2 h. Removal of the solvent followed by washing with water gave the complex (0·2 g) as yellow plates (from ethanol).

Tetrahydroborato(carbonyl)bis[tris(trimethylsilylmethyl)phosphine]rhodium(I).—A solution of sodium borohydride (0·2 g) and the complex, *trans*-RhCl(CO)(siphos)$_2$ (0·55 g) in ethanol (30 ml) was stirred for 2 h. The precipitated complex was recrystallised from benzene–methanol to give pale yellow plates (0·2 g).

Reaction of Tetrahydroborato(carbonyl)bis[tris(trimethylsilylmethyl)phosphine]rhodium(I) *with Hydrochloric Acid*.—The complex (2·7 mg) in benzene (2·50 ml) was treated with methanolic hydrochloric acid (0·50 ml, 0·1N) at 30° in a Warburg apparatus evolving 16 µmol (required: 15 µmol) of hydrogen. In a second determination, 2·8 mg of the complex gave 17 µmol of hydrogen.

Iridium Complexes

Hydridodichlorocarbonylbis[tris(trimethylsilylmethyl)phosphine]iridium(III).—The colourless solution, obtained by carbonylation of chloroiridic acid (1·0 g) in refluxing ethanol (25 ml) for 20 h, was treated with siphos (2·1 g) and the mixture was maintained at 60° for 10 min and then filtered. Partial evaporation of the filtrate under reduced pressure gave the *product* (1·3 g) as colourless needles (from aqueous ethanol). ν(Ir–H); 2180mw: ν(Ir–Cl); 311m (*trans*-CO) and 257s (*trans*-H) cm^{-1}.

Tris(trimethylsilylmethyl)phosphine complexes

			Anatytical data								N.m.r. spectra[b]			Carbony stretching frequency	
			Found			Required									
Complex	Colour	M.p. (°C)	C	H	Other	M[a]	C	H	Other	M				Nujol mull	CHCl$_3$
RuCl$_2$(CO)$_2$(siphos)$_2$	Yellow	151—153	38·2	8·3	Cl, 8·8	854	38·4	8·2	Cl, 8·7	813	9·72	8·06t	10·1	1988	1986
RuCl$_2$(CO)$_2$[(Me$_3$SiCH$_2$)$_2$PMe]$_2$	Yellow	127—131 dec.	35·5	7·5	Cl, 10·8; P, 8·7	642	35·9	7·5	Cl, 10·6, P, 9·3	669	9·83	8·32[c]	10·0, 10·8	1996	1992
Rh$_2$Cl$_4$(siphos)$_4$	Yellow	128—131 dec.	37·7	8·9	Cl, 8·9	1486	37·9	8·8	Cl, 9·3	1518	9·76	8·30t	9·0		
trans-RhBr$_2$(siphos)$_2$	Orange yellow	134—135 dec.	36·2	8·3	Br, 18·9	769	35·0	7·9	Br, 18·9	848	9·77	8·13t	9·3		
trans-RhCl(CO)(siphos)$_2$	Yellow	138—142	40·6	9·0	Cl, 4·8	738	40·0	8·9	Cl, 4·7	752	9·70	8·34t	9·0	1951	
trans-RhI(CO)(siphos)$_2$	Yellow	126—135 dec.	35·6	7·9			35·6	7·9			9·72	8·13t	8·9	1953	
Rh(BH$_4$)(CO)(siphos)$_2$	Pale yellow	116—118 dec.	41·3	9·5	B, 1·8; P, 8·5	753	41·1	9·6	B, 1·5; P, 8·5	731	9·80	8·40t	9·1	1937	1940
IrHCl$_2$(CO)(siphos)$_2$	Colourless	129—136 dec.	34·1	7·3	Cl, 8·0	890	34·2	7·7	Cl, 8·1	877	9·77	7·98[e]	11·2, 10·5	2010	2012
trans-IrCl(CO)(siphos)$_2$	Yellow	122—124	35·6	8·2	Cl, 4·4	850	35·7	7·9	Cl, 4·2	842	9·70	8·22t	9·8	1937	1928
IrClI(CH$_3$)(CO)(siphos)$_2$	Yellow	158—159 dec.	31·8	7·4		963	31·8	7·1		983	9·75	7·83t	10·7	2010	
IrClI(CF$_3$)(CO)(siphos)$_2$	White	192—193 dec.	30·1	6·8		994	30·1	6·4		1037	9·73	7·70t	11·1	2040	
IrCl$_3$(CO)(siphos)$_2$	Colourless	165—167	30·8	7·4	Cl, 11·7		31·8	7·1	Cl, 11·3		9·74	7·91t	11·3	2040	2038[d]
Ir(BH$_4$)(CO)(siphos)$_2$	Pale yellow	105—125 dec.	36·5	8·6	B, 1·2; P, 7·7	795	36·6	8·6	B, 1·3; P, 7·6	820	9·80	8·27t	9·8	1922	1926[d],
trans-NiBr$_2$(siphos)$_2$	Dark red	148—153	36·0	8·2		805	35·9	8·3		8·04	9·62	8·41t	9·8		
trans-PdCl$_2$(siphos)$_2$	Yellow	175—180	37·9	8·5			37·5	8·7			9·70	8·41t	9·7		
trans-PdBr$_2$(siphos)$_2$	Yellow	181—183	34·0	7·7			33·9	7·8			9·71	8·22t	9·0		
trans-PdI$_2$(siphos)	Orange	168—173	30·7	7·0		926	30·5	7·0		945	9·69	7·79t	9·5		
trans-Pd(N$_3$)$_2$(siphos)$_2$	Yellow	168—171 dec.	36·7	8·3	N, 10·9	699	37·2	8·6	N, 10·8	775	9·70	8·57t	9·0		
trans-Pd(NCS)$_2$(siphos)$_2$	Pale yellow	168—170	38·5	8·0	N, 3·6	827	38·7	8·2	N, 3·5	807	9·73	8·63t	9·6		
trans-PtCl$_2$(siphos)$_2$	Pale yellow	170—172	33·8	7·7		842	33·9	7·8		851	9·72	8·39t	10·3		
trans-PtI$_2$(siphos)$_2$	Yellow	175—176	27·7	6·7			27·9	6·4			9·69	7·82t	10·2		
(siphos)CuCl	Colourless	130—134 dec.	36·0	8·2	P, 7·4; Cl, 9·0		36·8	8·5	P, 7·9; Cl, 9·1		9·76	8·90d	18·6		
(siphos)$_3$CuCl[g]	Colourless	169—172 dec.	43·1	9·9			44·2	10·2			9·74	9·33d	13·8		
(siphos)AgCl	Colourless	132—134	33·7	7·8	P, 7·3; Cl, 8·0	436[h]	33·0	7·6	P, 7·1; Cl, 8·1	436	9·77	8·93d	10·8		
(siphos)AuCl[i]	Colourless	166—168	27·0	6·3	P, 6·1; Cl, 7·3	504[h]	27·4	6·3	P, 5·9; Cl, 6·8	525	9·79	8·87d	14·9		
(siphos)$_2$AuSnCl$_3$[i]	Colourless	217—218	28·2	6·5	Cl, 11·0	1041[h]	28·6	6·6	Cl, 10·6	1007	9·60	8·53d	11·0		
(siphos)$_2$ZnCl$_2$[j]	Colourless	100—101 dec.	39·5	9·2	P, 7·8; Cl, 9·8		39·9	9·2	P, 8·6; Cl, 9·8		9·73	8·66d	14·2		
(siphos)CdI$_2$[j]	Colourless	>180°	22·0	5·1	P, 5·7; I, 38·9	680[h]	21·9	5·0	P, 4·7; I, 38·5	658	9·75	8·81d	8·8		
(siphos)$_2$Hg$_2$Cl$_4$	Colourless	176—177	25·6	5·9	Cl, 12·4	1040	25·5	5·9	Cl, 12·6	1128	9·79	8·16d	15·5		
(siphos)$_3$Hg$_3$I$_6$[i]	Colourless	245—248 dec.	19·2	4·8		2131	19·3	4·5		2241	9·87	8·60d	9·0		
siphos·CS$_2$	Bronze	137—138	42·4	8·9	P, 8·3; S, 18·2	359	42·3	9·0	P, 8·4; S, 17·4	369	9·76	8·34d	16·8		
IrCl$_2$(O$_2$SC$_6$H$_4$Me-*p*)(CO)(siphos)$_2$											9·71	7·90[k]	12·0		
(Me$_3$SiCH$_2$)$_3$P											9·88	9·30d	1·2		
(Me$_3$SiCH$_2$)$_3$PO[i]											9·80	8·82d	14·5		

[a] Measured in benzene unless otherwise stated. [b] Taken in C$_6$D$_6$ unless otherwise indicated; TMS used as internal reference. [c] AB pattern: $\Delta\tau$ 0·65; J(A–B) 14·5; τ(P–CH$_3$) 8·17; $|^2J + {}^4J|$(P–H) 6·5. [d] Taken in cyclohexane. [e] AB pattern: $\Delta\tau$ 0·35; J(A–B) 14·9; τ(Ir–H) 26·58t; ^2J(P–H) 12·7. [f] Decomposed in CHCl$_3$. [g] N.m.r. in CDCl$_3$: τ 9·79, 9·12d, 14·4. [h] Measured in dichloromethane. [i] N.m.r. taken in CDCl$_3$. [j] N.m.r. taken in CD$_3$OD. [k] AB pattern: $\Delta\tau$ 0·41; J(A–B) 14·0; τ(CH_3C$_6$H$_4$SO$_2$) 7·98.

Trichlorocarbonylbis[tris(trimethylsilylmethyl)phosphine]iridium(III).—A solution of IrHCl$_2$(CO)(siphos)$_2$ (0·1 g) in carbon tetrachloride (5 ml) was heated under reflux for 20 h and then evaporated to dryness. Recrystallisation of the crude product (quantitative yield) from methanol gave colourless *prisms*. ν(Ir–Cl): 329vs, 316s,sh, 306ms, cm^{-1}.

trans-*Chlorocarbonylbis[tris(trimethylsilylmethyl)phosphine]iridium*(I).—A methanol solution of sodium methoxide (1·0 ml, 0·65N) was added dropwise to a warm (70°) solution of IrHCl$_2$(CO)(siphos)$_2$ (0·54 g) in ethanol (20 ml), and the precipitated sodium chloride was filtered off. Concentration of the filtrate to a small volume gave the crude product (0·38 g) as yellow *needles* which were recrystallised from ethanol. ν(Ir–Cl): 301m cm^{-1}.

Chloroiodo(methyl)carbonylbis[tris(trimethylsilylmethyl)phosphine]iridium(III).—An approximately ten-fold excess of methyl iodide was added to the complex, *trans*-IrCl(CO)(siphos)$_2$ (0·05 g), in benzene (0·5 ml), and the mixture was set aside at 34° until the n.m.r. spectrum showed that the reaction was complete (*ca.* 2 h). Removal of the solvent and the excess of methyl iodide *in vacuo* gave the *product* as white microcrystals (from ethanol) in almost quantitative yield.

Chloroiodo(trifluoromethyl)carbonylbis[tris(trimethylsilylmethyl)phosphine]iridium(III).—A solution of *trans*-IrCl(CO)(siphos)$_2$ (0·055 g) in trifluoromethyl iodide (0·4 ml) was sealed in a tube and left in the dark at room temperature for 20 h. The tube was then opened and volatile materials were removed. Recrystallisation of the residue from benzene–methanol gave the *product* (0·050 g) as white needles.

Reaction of trans-*Chlorocarbonylbis[tris(trimethylsilylmethyl)phosphine]iridium*(I) *with Toluene*-p-*sulphonyl Chloride*.—A mixture of toluene-*p*-sulphonyl chloride (0·025 g) and *trans*-IrCl(CO)(siphos)$_2$ (0·060 g) in benzene (0·5 ml) was left standing at 34° until it became colourless (20 min). The n.m.r. spectrum showed that a 1 : 1 adduct had been formed but attempts to isolate the product led to extensive decomposition.

Tetrahydroborato(carbonyl)bis[tris(trimethylsilylmethyl)-phosphine]iridium(I).—A solution of sodium borohydride (0·2 g) in ethanol (15 ml) was added to a suspension of *trans*-IrCl(CO)(siphos)$_2$ (0·33 g) in ethanol (20 ml), and the mixture was stirred for 2 h. The precipitate was filtered and recrystallised from benzene–methanol to give pale yellow *plates* (0·24 g).

Nickel Complex

trans-*Dibromobis[tris(trimethylsilylmethyl)phosphine]-nickel*(II).—A mixture of siphos (2·0 g) and nickel(II) bromide hexahydrate (1·0 g) in ethanol (20 ml) was agitated for 3 h to give the *complex* (2·0 g) as dark red prisms (from ethanol).

Palladium Complexes

trans-*Dichlorobis[tris(trimethylsilylmethyl)phosphine]palladium*(II).—A mixture of sodium tetrachloropalladate(II) (0·5 g) and siphos (1·0 g) in ethanol (20 ml) was stirred for 1 h and the solvent was evaporated *in vacuo*. The product was thoroughly washed with water and then crystallised from hot ethanol as yellow *prisms* (1·0 g), ν(Pd–Cl): 358s cm^{-1}.

trans-*Dibromobis[tris(trimethylsilylmethyl)phosphine]-palladium*(II).—A mixture of *trans*-PdCl$_2$(siphos)$_2$ (0·07 g) and lithium bromide (0·3 g) was heated under reflux in acetone (15 ml) for 15 min. Removal of the solvent followed by washing with water gave the *complex* as yellow prisms (from ethanol) in essentially quantitative yield.

trans-*Di-iodobis[tris(trimethylsilylmethyl)phosphine]palladium*(II).—From a refluxing (10 min) mixture of *trans*-PdCl$_2$(siphos)$_2$ (0·2 g) and potassium iodide (0·5 g) in 2-methoxyethanol (10 ml), the product was isolated quantitatively as orange *prisms* (from ethanol). There was no evidence for the cyclisation of the phosphine ligand, even when heated in the presence of triethylamine for 25 h.

trans-*Dithiocyanatobis[tris(trimethylsilylmethyl)phosphine]palladium*(II).—The complex was similarly obtained as pale yellow *needles* using lithium thiocyanate in acetone, ν_{as}(NCS): 2095s cm^{-1}.

trans-*Diazidobis[tris(trimethylsilylmethyl)phosphine]palladium*(II).—Using sodium azide in aqueous solution, the *complex* was prepared as yellow prisms, $\nu_{as}(N_3)$: 2128m cm^{-1}.

Platinum Complexes

trans-*Dichlorobis[tris(trimethylsilymethyl)phosphine]-platinum*(II).—A solution of potassium tetrachloroplatinate(II) (0·5 g) in warm water (5 ml) was added to a solution of siphos (0·72 g) in warm methanol (10 ml), and the mixture was vigorously stirred for 1 h after which, the solvent was evaporated to about half its original volume and water (100 ml) was added. The precipitate was filtered, washed successively with water (10 ml) and light petroleum (b.p. 30—40°, 10 ml), and dried *in vacuo*. Recrystallisation from hot ethanol afforded pale yellow *prisms* (0·8 g) of the product, ν(Pt–Cl): 332s cm^{-1}.

trans-*Di-iodobis[tris(trimethylsilylmethyl)phosphine]platinum*(II).—A mixture of *trans*-PtCl$_2$(siphos)$_2$ (0·10 g) and sodium iodide (0·5 g) in acetone (12 ml) was heated under reflux for 2 h to give the *product* (0·12 g) as yellow hexagonal plates (from ethanol).

Copper Complexes

Chlorotris(trimethylsilylmethyl)phosphinecopper(I).— A mixture of siphos (0·50 g) and copper(I) chloride (0·144 g) in methanol (25 ml) was stirred for 15 min and added to water (*ca.* 150 ml). The white precipitate was filtered, washed with water (10 ml), and dried *in vacuo* over phosphoric oxide for 1·5 h. Crystallisation from a minimum volume of methanol gave the complex (0·38 g) as colourless prisms. The complex was also prepared in an analogous manner starting with copper(II) chloride.

Chlorotris[tris(trimethylsilylmethyl)phosphine]copper(I).—A mixture of siphos (5·66 g) and anhydrous copper(II) chloride (0·65 g) in methanol (100 ml) was stirred for $\frac{1}{2}$ h and concentrated to a small volume. The crystalline product was filtered and recrystallised from a minimum volume of methanol as large colourless *prisms* (2·75 g).

Silver and Gold Complexes

The preparations of the somewhat light-sensitive silver(I) and gold(I) complexes were performed in the dark. These complexes, which produce permanent stains (black for silver and maroon for gold) on clothings, skin, *etc.*, should be handled with **care**.

Chlorotris(trimethylsilylmethyl)phosphinesilver(I).—A mixture of silver perchlorate (0·38 g) and siphos (0·54 g) in methanol was stirred for 5 min and treated with a saturated solution of sodium chloride (0·15 g) in aqueous methanol (50%). The white, light-sensitive precipitate was centrifuged and dried *in vacuo* over phosphoric oxide for 1 h. Recrystallisation from a minimum volume of methanol gave the *complex* (0·41 g) as large colourless prisms.

Chlorotris(trimethylsilylmethyl)phosphinegold(I).— Solid siphos (1·47 g) was added to a solution of sodium tetrachloroaurate(III) dihydrate (1·0 g) in methanol (20 ml). After stirring for 1 h, the solvent was removed *in vacuo* and the residue was washed successively with water (20 ml), light petroleum (b.p. 30—40°, 20 ml), and cold diethyl ether (5 ml). Recrystallisation from hot ethanol gave the *complex* (0·62 g) as colourless prisms.

Trichlorostannatobis[tris(trimethylsilylmethyl)phosphine]-gold(I).—A mixture of (siphos)AuCl (0·130 g), tin(II) chloride (0·045 g) and siphos (0·078 g) in acetone (10 ml) was stirred for $\frac{1}{2}$ h and the solvent was removed under reduced pressure. The oily residue was triturated with diethyl ether–light petroleum (b.p. 30—40°) (1 : 1) and the liquor was subsequently discarded. The crystalline solid was recrystallised twice from methanol to give the *product* (0·15 g) as colourless prisms.

Zinc Complex

Dichlorobis[tris(trimethylsilylmethyl)phosphine]zinc(II).—A solution of copper(II) chloride (0·18 g) in methanol (20 ml) was shaken vigorously with a ten-fold excess of zinc dust for 1 h. The filtered colourless solution of zinc(II) chloride was treated with siphos (0·78 g) as a suspension in methanol (20 ml), and the mixture was stirred for 15 min. The solution was concentrated to a small volume and cooled to −20° to deposit colourless prisms of the *complex* (0·67 g), ν(Zn–Cl): 342s cm^{-1}.

Cadmium Complex

Di-iodobis[tris(trimethylsilylmethyl)phosphine]cadmium(II).—A suspension of cadmium(II) iodide (0·40 g) and siphos

(0·65 g) in 60% aqueous methanol (25 ml) was stirred for 3 h to give white microcrystals of the *product* (0·65 g).

Mercury Complexes

Di-μ-chloro-dichlorobis[tris(trimethylsilylmethyl)phosphine]-dimercury(II).[2]—A solution of mercury(II) chloride (0·31 g) in methanol (15 ml) was added to siphos (0·65 g) in the same solvent (25 ml). After stirring for 15 min, the solution was concentrated to give the *product* (0·6 g) as colourless needles (from methanol).

Tri-μ-iodo-tri-iodotris[tris(trimethylsilylmethyl)phosphine]-trimercury(II).—The *complex* was similarly prepared as colourless needles using mercury(II) iodide.

Miscellaneous

Tris(trimethylsilylmethyl)phosphine Oxide.—A stream of oxygen was passed through a warm solution of the phosphine (0·5 g) in ethanol (25 ml) to give colourless prisms of the *product* (0·32 g) after 1 h, ν(P=O): 1150s cm^{-1}; δ(P=O) (?): 430m cm^{-1}.

Reaction of Tris(trimethylsilylmethyl)phosphine with Carbon Disulphide.—Carbon disulphide (10 ml) was added to the phosphine (0·5 g) resulting in a red-brown solution which, after 5 min, was evaporated. Crystallisation of the residue from boiling diethyl ether gave the 1 : 1 *adduct* (0·5 g) as bronze-coloured needles (from chloroform–light petroleum). ν(C=S): 1047ms and 900w cm^{-1}.

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