Carbonyl Complexes of Iron, Cobalt, and Nickel with Tris(trimethylsilylmethyl)phosphine †

By **Andrew T. T. Hsieh** and **Geoffrey Wilkinson**,* Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

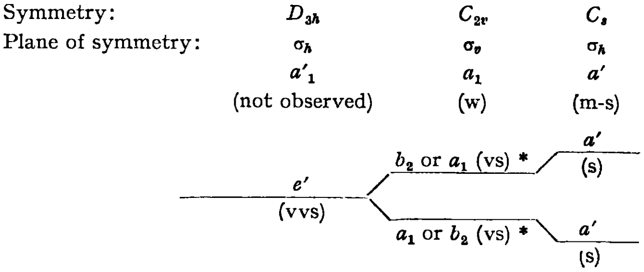
Tris(trimethylsilylmethyl)phosphine (siphos) reacts with iron, cobalt, and nickel carbonyls under various conditions to give the series of new complexes, $Fe(CO)_3(siphos)_2$, $Fe(CO)_4(siphos)$, $[Co(CO)_3(siphos)_2][Co(CO)_4]$, $[Co(CO)_3(siphos)]_2$, and $Ni(CO)_3(siphos)$. The mercurials, $Hg[Fe(CO)_2(NO)(siphos)]_2$, $Hg[Co(CO)_4]_2$, and $XHgCo(CO)_3(siphos)$ (X = Cl and Br), and the thallium complex, $Tl[Co(CO)_3(siphos)]_3$, have also been prepared. Their structures are discussed on the basis of their i.r. and n.m.r. spectra. The cobalt–carbonyl complexes react with halogenated solvents to give the dimeric complex, $[CoCl(CO)_2(siphos)]_2$, which is the first dicarbonylmonophosphine complex of cobalt(I).

THE ability of tris(trimethylsilylmethyl)phosphine (siphos) to form stable complexes with most transition metals has been recently demonstrated, and several carbonyl-containing complexes have been isolated and characterised.[1] Reactions of siphos with various metal carbonyls have now been investigated and herein we report some of its more stable derivatives with carbonyls of iron, cobalt, and nickel.

RESULTS AND DISCUSSION

Iron Complexes.—In as much as tris(trimethylsilylmethyl)phosphine is sensitive to heat and, to a lesser extent, u.v. light, attempts at direct carbonyl substitution with pentacarbonyliron under these conditions result only in the formation of decomposition products. However, the disubstituted complex, $Fe(CO)_3(siphos)_2$, can be obtained by briefly heating dodecacarbonyltri-iron with the phosphine.

Like most of the closely related complexes, *trans*-$Fe(CO)_3L_2$ (L = PEt_3 [2] or PPh_3 [3]), the i.r. spectrum of $Fe(CO)_3(siphos)_2$ shows a single carbonyl stretching absorption in Nujol; in chloroform, however, three are observed. Thus, its solution spectrum bears a close resemblance to that of *trans*-$Fe(CO)_3(PEt_3)_2$ in chloroform,[4] except that the intense lower-frequency e' mode (in D_{3h} geometry) is split into a doublet. Such splitting may be associated with a deviation from linearity in the P–Fe–P axis (*i.e.* with symmetry of the molecule lowered to C_{2v} or C_s), thus lifting the degeneracy of the e' mode with concomitant appearance of the weak higher-frequency a'_1 mode, which is i.r. inactive in the D_{3h} environment. The correlation diagram for the carbonyl stretching modes in various possible configurations is given in the Scheme together with the relative intensities in parentheses. That the complex has a symmetry lower than D_{3h} and most probably, C_{2v}, is further substantiated by its ^1H n.m.r. spectrum which consists of a doublet for the methylene protons; a triplet pattern would be expected if the P–Fe–P axis is linear.



* The order of this pair is unknown.[4]

Although the pure monosubstituted complex, $Fe(CO)_4$-siphos, could not be isolated from the reaction of nonacarbonyldi-iron with tris(trimethylsilylmethyl)phosphine, its formation is indicated by its ^1H n.m.r. spectrum in which the coupling constant, $|^2J + {}^4J|$(P–H), for the methylene doublet changes from 1·2 Hz for the free phosphine [1] to 11·2 Hz for the complex, and further by its i.r. spectrum in the carbonyl stretching region which consists of a pattern typical of complexes of the type $LFe(CO)_4$ with C_{3v} structure.[4]

Bis(tricarbonylnitrosyliron)mercury reacts with tertiary phosphines, arsines, and stibines, L, to yield complexes of formula $Hg[Fe(CO)_2(NO)L]_2$,[5-7] whereas pyridine, *p*-anisyl isocyanide,[5] or tris(dimethylamino)-phosphine [6] gives a deposition of metallic mercury along with a variety of products. With tris(trimethylsilylmethyl)phosphine, the substituted complex, $Hg[Fe(CO)_2(NO)(siphos)]_2$, is obtained in essentially quantitative yield. Its solution i.r. spectrum exhibits four carbonyl stretching and two nitrosyl stretching absorptions. The existence of linear trimetallic systems has been well established by recent *X*-ray structural studies on some transition metal complexes of mercury,[8-10] and a staggered C_2 structure, (Ia) with a linear PFeHgFeP skeleton has been postulated for the related complexes, $Hg[Fe(CO)_2(NO)L]_2$ (L = phosphines, arsines, and

---

† No reprints available.

[1] A. T. T. Hsieh, J. D. Ruddick, and G. Wilkinson, *J.C.S. Dalton*, 1972, 1966.

[2] A. Reckziegel and M. Bigorgne, *J. Organometallic Chem.*, 1965, **3**, 341.

[3] F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1960, 1440.

[4] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, London, 1967, p. 97.

[5] W. Hieber and W. Klingshirn, *Z. anorg. Chem.*, 1963, **323**, 292.

[6] R. B. King, *Inorg. Chem.*, 1963, **2**, 1275.

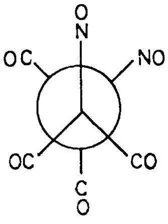
[7] M. Casey and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2258.

[8] A. T. T. Hsieh and M. J. Mays, *Internat. Rev. Sci.*, *Inorg. Chem. Series I*, 1972, **6**, 43.

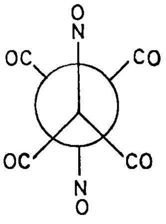
[9] W. Clegg and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1971, 3572.

[10] M. L. Katcher and G. L. Simon, *Inorg. Chem.*, 1972, **11**, 1651.

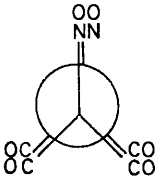
stibines).[7] For complexes of this type, four conformers are possible with a linear PFeHgFeP axis as shown below together with their i.r. ν(CO) and ν(NO) activities



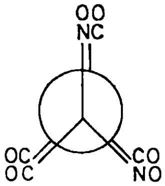
(Ia)



(Ib)



(IIa)



(IIb)

Symmetry:	C_2	C_{2h}	C_{2v}	C_2
Activity: ν(CO)	$2a + 2b$	$a_u + b_u$	$a_1 + b_1 + b_2$	$2a + 2b$
ν(NO)	$a + b$	b_u	$a_1 + b_1$	$a + b$

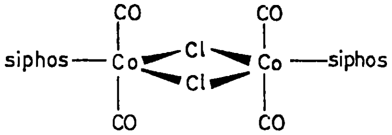
predicted on the basis of group theory. Thus, for the tris(trimethylsilylmethyl)phosphine complex, the C_{2h} (Ib) and the C_{2v} (IIa) structure may be excluded since they are expected to show respectively, two and three carbonyl stretching absorptions. Although the skew conformation (Ia) appears to be the more likely structure, it is impossible to distinguish the two C_2 structures (Ia and IIb) from one another on the basis of its i.r. spectrum. Further physical data such as its molecular weight, n.m.r. spectrum, and dipole moment could not be determined because of its limited solubility.

Cobalt Complexes.—Octacarbonyldicobalt(0) reacts with tris(trimethylsilylmethyl)phosphine in light petroleum or diethyl ether at 0° to furnish the orange-yellow, air-sensitive complex, $[Co(CO)_3(siphos)_2][Co(CO)_4]$, the ionic character of which has been confirmed by conductivity measurements. Four carbonyl stretching absorptions are observed in its solution i.r. spectrum and the intense, broad peak at 1888 cm^{-1} may be unambiguously assigned to that of the tetracarbonylcobaltate(—I) anion. The three higher-frequency carbonyl absorptions may then be attributed to those of the cation, which is isoelectronic and most probably, isostructural with the iron complex, $Fe(CO)_3(siphos)_2$. Its ^1H n.m.r. spectrum could not be obtained since it is rapidly decomposed by most organic solvents such as alcohols and halogenomethanes (*vide infra*). The triphenylphosphine and several other related ionic complexes of the type $[Co(CO)_3L_2][Co(CO)_4]$ have previously been described.[11,12]

At temperatures above 50°, the non-ionic complex, $[Co(CO)_3(siphos)]_2$, is the major product of the reaction between octacarbonyldicobalt and tris(trimethylsilylmethyl)phosphine. This reaction has previously been employed in the preparation of complexes of the type $[Co(CO)_3L]_2$ (L = tertiary phosphine or arsine),[12-15] most of which exist in solution predominantly as the unbridged isomer, although the solutions of some, especially those with L = PEt_3,[13] PMe_2Ph,[14] and $AsEt_3$,[15] have been shown to contain an equilibrium mixture of the bridged and unbridged forms.* In the case of the tris(trimethylsilylmethyl)phosphine complex, however, its i.r. spectrum indicates that the bridging isomers * are present both in the solid state and in solution. Further studies on this complex including n.m.r. spectroscopy were precluded by the limited solubility and low stability in various solvents.

Addition of four moles of tris(trimethylsilylmethyl)phosphine to a solution of dodecacarbonyltetracobalt(0) in light petroleum leads to the formation of the complex $[Co(CO)_3(siphos)]_2$ without evolution of carbon monoxide. An analogous reaction with triphenylphosphine has been reported.[16]

It has been well established [17] that the reaction of octacarbonyldicobalt with various 1,1,1-trihalogenoalkanes produces complexes of formula $RCCo_3(CO)_9$ (R = organic group or halogen). In contrast, solutions of both the complexes $[Co(CO)_3(siphos)_2][Co(CO)_4]$ and $[Co(CO)_3(siphos)]_2$, in halogenated solvents evolve carbon monoxide at room temperature, and in the case with carbon tetrachloride, the major product of the reaction is the emerald green, diamagnetic complex, $CoCl(CO)_2$(siphos), along with traces of the cluster, $ClCCo_3(CO)_9$. The chlorodicarbonyl-complex, which is also obtained in lower yield from the corresponding reaction with chloroform, exhibits two terminal carbonyl stretching absorptions in its i.r. spectrum and a poorly resolved doublet for the methylene protons of the phosphine in its ^1H n.m.r. spectrum. It is dimeric in chloroform and thus may have the chlorine-bridged D_{2h} structure (III), for which group theory predicts two i.r. active carbonyl stretching vibrations ($b_{1u} + b_{3u}$). This effectively five-co-ordinate complex is yet another example of cobalt(I) complexes in the trigonal bipyramidal configuration. It is noteworthy that no cobalt(I) complexes of the general



(III)

---

* For a description of the various possible bridged and unbridged structures, see ref. 15.

[11] A. Sacco and M. Freni, *Ann. Chim.* (*Italy*), 1958, **48**, 218; *J. Inorg. Nuclear Chem.*, 1958, **8**, 566; and references therein.

[12] W. Hieber and W. Freyer, *Chem. Ber.*, 1958, **91**, 1230; 1960, **93**, 462; and references therein.

[13] G. Capron-Cotigny and R. Poilblanc, *Bull. Soc. chim. France*, 1967, 1440.

[14] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1135; and references therein.

[15] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1665.

[16] W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1259.

[17] G. Palyi, F. Piacenti, and L. Marko, *Inorg. Chim. Acta, Rev.*, 1970, **4**, 109.

formula $CoX(CO)_2L$ (X = halogen and L = phosphine) have been reported albeit the square planar rhodium(I) analogue, *trans*-$RhCl(CO)_2PPh_3$, has been prepared from the stoicheiometric reaction of di-μ-chlorotetracarbonyldirhodium(I) with triphenylphosphine.[18,19] Treatment of the green chloroform solution of the chlorodicarbonyl-complex with nitrogen- or oxygen-donors such as pyridine and methanol gives light orange to yellow-brown solutions from which no stable adducts could be isolated. Attempts to isolate the complex $CoCl(CO)_2(siphos)_2$, which is akin to the known triphenylphosphine complex,[20] by a similar bridge-splitting reaction with tris(trimethylsilylmethyl)phosphine result only in an intractable mess.

Reduction of the substituted complex $[Co(CO)_3(siphos)]_2$, with sodium amalgam affords the extremely air-sensitive salt, $NaCo(CO)_3(siphos)$, the i.r. spectrum of which contains a broad carbonyl stretching absorption in tetrahydrofuran. It is isoelectronic and perhaps isostructural with the nickel complex, $Ni(CO)_3(siphos)$ (*vide infra*). Acidification of the anion gives a mixture of products including the dimer, $[Co(CO)_3(siphos)]_2$, presumably formed from the thermally unstable hydride, $HCo(CO)_3(siphos)$, which we failed to detect by spectroscopic techniques.

Treatment of the tricarbonyltris(trimethylsilylmethyl)phosphinecobaltate anion with mercury(II) cyanide in aqueous solution furnishes an essentially quantitative yield of the mercurial, $Hg[Co(CO)_3(siphos)]_2$, which is also prepared from the parent compound, $Hg[Co(CO)_4]_2$, by direct carbonyl substitution with tris(trimethylsilylmethyl)phosphine at room temperature. For both its solution and solid-state i.r. spectra, two carbonyl stretching absorptions are observed and are consistent with, but do not distinguish between the D_{3h} and the D_{3d} structures with linear $HgCo_2$ moieties. This as well as other related complexes of the type, $Hg[Co(CO)_3L]_2$ (L = tertiary phosphines, arsines, stibines, and phosphites) [16,21,22] all of which show similar i.r. spectra, may well adopt the D_{3d} structure as found for the triethylphosphine complex $Hg[Co(CO)_3PEt_3]_2$ by *X*-ray crystallographic analysis.[23] These complexes undergo exchange (or redistribution) reactions with mercury(II) halides according to the equation:[22,24-27]

$$Hg[Co(CO)_3L]_2 + HgX_2 \rightleftharpoons 2XHgCo(CO)_3L \quad (1)$$

and the tris(trimethylsilylmethyl)phosphine complex is no exception. The ^1H n.m.r. spectra of the yellow crystalline complexes, $XHgCo(CO)_3(siphos)$ (X = Cl and Br), exhibit a doublet for the methylene protons of the phosphine, and two carbonyl stretching absorptions are observed in their i.r. spectra, indicating that the geometry of the $HgCo(CO)_3(siphos)$ moiety is retained in these molecules. For this C_{3v} structure with a linear XHgCoP skeleton, two carbonyl stretching modes ($a_1 + e$) are expected on the basis of group theory.

The interaction of thallium(I) salts with transition metal carbonylate anions (R^-) has been recently shown to yield either the thallium(I) or thallium(III) complexes, equation (2), depending on the relative stability of one

$$3Tl^+ + 3R^- \longrightarrow 3Tl\text{-}R \rightleftharpoons 2Tl^0 + Tl^{III}R_3 \quad (2)$$

with respect to the other.[28-30] Thus, thallium(I) nitrate reacts with sodium pentacarbonylmanganate(−I) in water to give only the thallium(III) complex, $Tl[Mn(CO)_5]_3$,[28] whereas both thallium(I) and thallium(III) complexes with the transition metal groups, $C_5H_5(CO)_3M$ (M = Mo or W) and $Co(CO)_4$, could be isolated.[30] Treatment of the tricarbonyltris(trimethylsilylmethyl)phosphinecobaltate(−I) anion with thallium(I) nitrate in water leads to the formation of the deep red thallium(III) complex, $Tl[Co(CO)_3(siphos)]_3$, together with a deposition of thallium metal. Similar complexes of the type, $Tl[Co(CO)_3L]_3$ (L = phosphine, *etc.*), have been prepared although an analogous reaction with tetracarbonylcobaltate(−I) anion gives the yellow thallium(I) complex, $TlCo(CO)_4$.[30] The tris(trimethylsilylmethyl)phosphine complex, which is monomeric in benzene, is also obtained by reacting the phosphine with the parent complex, $Tl[Co(CO)_4]_3$. Its i.r. spectrum shows only two carbonyl stretching absorptions and is consistent with a D_{3h} arrangement of the cobalt atoms around the thallium metal. Of particular interest is its ^1H n.m.r. spectrum which consists of a broad doublet for the methylene protons, and a sharp doublet for the methyl protons of the phosphine. These splittings are tentatively associated with the long range thallium–proton couplings with $^6J(^{203,205}Tl\text{-}H) = 3{\cdot}0$ Hz and $^6J(^{203,205}Tl\text{-}H) = 40{\cdot}1$ Hz. The lack of separation between the ^{203}Tl and ^{205}Tl splittings may be attributed to the similarity in the magnetogyric ratios of these isotopes. The phosphorus–proton couplings could not be obtained visually owing to the broadness of the methylene signals.

Nickel Complex.—The reaction between tetracarbonylnickel and tris(trimethylsilylmethyl)phosphine takes place slowly at room temperature to furnish only the monosubstituted complex, $Ni(CO)_3(siphos)$, when an

---

[18] P. Uguagliati, G. Deganello, L. Busetto, and U. Belluco, *Inorg. Chem.*, 1969, **8**, 1625.

[19] G. Deganello, P. Uguagliati, B. Crociani, and U. Belluco, *J. Chem. Soc.* (*A*), 1969, 2726.

[20] M. Bressan, *Inorg. Chem.*, 1970, **9**, 1733.

[21] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1018; and references therein.

[22] J. Neuman and A. R. Manning, *J.C.S. Dalton*, 1972, 241.

[23] R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

[24] F. Bonati, S. Cenini, and R. Ugo, *J. Chem. Soc.* (*A*), 1967, 932.

[25] O. Kahn, J. Henrion, and G. Bouquet, *Bull. Soc. chim. France*, 1967, 3547.

[26] A. Ragni, E. F. Trogu, and G. Peyronel, *Ann. Chim.* (*Italy*), 1968, **58**, 768.

[27] B. J. Aylett and J. M. Campbell, *J. Chem. Soc.* (*A*), 1969, 1910.

[28] A. T. T. Hsieh and M. J. Mays, *J. Organometallic Chem.*, 1972, **38**, 243.

[29] H.-J. Haupt and F. Neumann, *J. Organometallic Chem.*, 1971, **33**, C56.

[30] A. T. T. Hsieh and M. J. Mays, to be published.

TABLE 1

I.r. spectra of the complexes in the carbonyl stretching region (2150—1800 $\mathrm{cm^{-1}}$)

Complex	Solvent	ν(CO)/$\mathrm{cm^{-1}}$
$\mathrm{Fe(CO)_3(siphos)_2}$	Nujol	1856vs,br
	$\mathrm{CHCl_3}$	1945vw, 1847vs, 1834s,sh
$\mathrm{Fe(CO)_4(siphos)}$	$\mathrm{C_6H_6}$ [a]	2020ms, 1955ms, 1927vs
$\mathrm{Hg[Fe(CO)_2(NO)(siphos)]_2}$	Nujol [b]	1997w, 1969w, 1922m, 1906vs
	$\mathrm{CHCl_3}$ [c]	2049mw, 1976m, 1947ms, 1908vs
$\mathrm{[Co(CO)_3(siphos)_2][Co(CO)_4]}$	Nujol	2055w, 2002mw,sh, 1980s, 1973s, 1895s,sh, 1875vs
	$\mathrm{CHCl_3}$ [d]	2058vw, 1992s,sh, 1982s, 1888vs,br
$\mathrm{[Co(CO)_3(siphos)]_2}$	Nujol	2057vw, 2001ms,sh, 1989s, 1968s, 1943mw, 1889vs
	$\mathrm{CHCl_3}$ [d]	2068vw, 2033w, 1979s, 1969s, 1890vs
$\mathrm{[CoCl(CO)_2(siphos)]_2}$	Nujol	2051vw, 1973vs
	$\mathrm{CHCl_3}$	2060w, 1986vs
$\mathrm{NaCo(CO)_3(siphos)}$	THF	1914vs,br
$\mathrm{Hg[Co(CO)_3(siphos)]_2}$	Nujol	1979m, 1929vs, 1894m
	THF	*ca.* 1974vs, 1933m
$\mathrm{ClHgCo(CO)_3(siphos)}$	Nujol	2021mw, 1959s, 1938vs
	$\mathrm{CHCl_3}$	2028w, 1962vs
$\mathrm{BrHgCo(CO)_3(siphos)}$	Nujol	2018w, 1957s, 1943vs
	$\mathrm{CHCl_3}$	2025w, 1960vs
$\mathrm{Tl[Co(CO)_3(siphos)]_3}$	n-Hexane	1981w, 1946s
$\mathrm{Ni(CO)_3(siphos)}$	Nujol	2063ms, 1986vs
	n-Hexane	2064m, 1989vs

[a] Absorptions due to traces of $\mathrm{Fe_3(CO)_{12}}$ have been subtracted. [b] ν(NO): 1716s, 1703vs, $\mathrm{cm^{-1}}$. [c] ν(NO): **1745m,sh; 1711vs** $\mathrm{cm^{-1}}$. [d] In freshly prepared solutions and measured within $\frac{1}{2}$ min.

TABLE 2

^{1}H N.m.r. spectra of the complexes

Complex	Solvent	τ ($\mathrm{CH_3}$)	τ ($\mathrm{CH_2}$)	$\lvert ^2J + {}^4J\rvert$ (P–H) [a]
$\mathrm{Fe(CO)_3(siphos)_2}$	$\mathrm{C_6D_6}$	9·71(s)	8·30(d)	11·0
$\mathrm{Fe(CO)_4(siphos)}$	$\mathrm{C_6D_6}$	9·93(s)	8·78(d)	11·2
$\mathrm{[CoCl(CO)_2(siphos)]_2}$	$\mathrm{CDCl_3}$	9·89(s)	8·82(d) br	*ca.* 8
$\mathrm{ClHgCo(CO)_3(siphos)}$	$\mathrm{CDCl_3}$	9·90(s)	8·68(d)	14·1
$\mathrm{BrHgCo(CO)_3(siphos)}$	$\mathrm{CDCl_3}$	9·91(s)	8·83(d)	14·0
$\mathrm{Tl[Co(CO)_3(siphos)]_3}$	$\mathrm{C_6D_6}$	9·94(d) [b]	9·08 [c]	*b, c*
$\mathrm{Ni(CO)_3(siphos)}$	$\mathrm{CDCl_3}$	9·88(s)	8·92(d)	8·4

[a] In Hz. [b] $^6J(^{203,205}\mathrm{Tl–H})$ = 3·0 Hz; see text. [c] Broad doublet of doublets: $^4J(^{203,205}\mathrm{Tl–H})$ = 40·1 Hz; see text.

excess of the phosphine is used. Unlike the corresponding reaction with triphenylphosphine,[31–33] the disubstituted complex is not formed on prolonged reaction or when treated under reflux. The presence of two carbonyl stretching absorptions in its i.r. spectrum and a doublet resonance for the methylene protons of the phosphine clearly indicate a C_{3v} structure.

TABLE 3

Analytical data

Complex	Colour	M.p. (°)	Found				Required			
			C	H	P	*M*	C	H	P	*M*
$\mathrm{Fe(CO)_3(siphos)_2}$	Pale yellow	168—171 dec.	44·7	9·2	8·7	700 [a]	44·7	9·2	8·5	724·9
$\mathrm{Hg[Fe(CO)_2(NO)(siphos)]_2}$ [b]	Orange-yellow	>180 dec.	31·6	6·6	5·8	*c*	31·4	6·2	5·8	
$\mathrm{[Co(CO)_3(siphos)_2][Co(CO)_4]}$	Orange-yellow	127—128 dec.	40·9	7·7	7·2	*c*	41·4	7·4	6·9	
$\mathrm{[Co(CO)_3(siphos)]_2}$	Orange-brown	123 dec.	41·0	7·4	7·2	*c*	41·3	7·6	7·1	
$\mathrm{[CoCl(CO)_2(siphos)]_2}$	Emerald green	102	37·8	7·5	8·4	860 [d]	37·9	7·5	8·0	885·8
$\mathrm{Hg[Co(CO)_3(siphos)]_2}$	Yellow	225 [e]	34·2	6·3	6·0	*c*	33·6	6·2	5·8	
$\mathrm{ClHgCo(CO)_3(siphos)}$	Bright yellow	>147 dec.	27·3	5·2	4·5		26·8	4·9	4·6	
$\mathrm{BrHgCo(CO)_3(siphos)}$	Intense yellow	143 [e]	25·4	4·8	3·9		25·2	4·6	4·3	
$\mathrm{Tl[Co(CO)_3(siphos)]_3}$	Dark red	>85 dec.	36·1	6·9	6·0	1490	35·7	6·6	6·1	1510·7
$\mathrm{Ni(CO)_3(siphos)}$	Cream	>145 dec.	41·4	7·7	7·2		41·4	7·6	7·1	

[a] In benzene. [b] Found: N, 3·0; Calcd.: N, 2·6%. [c] Insufficiently soluble. [d] In chloroform. [e] Decomposed without melting.

EXPERIMENTAL

I.r. spectra in the carbonyl stretching region (2150—1800 $\mathrm{cm^{-1}}$) were recorded on a Perkin-Elmer 257 spectrophotometer on $\times 2\frac{1}{2}$ or $\times 10$ scale expansion and were calibrated against carbon monoxide (Table 1); spectra in other regions were taken on a Perkin-Elmer 457 spectrophotometer. The samples were prepared as mulls in Nujol between KBr plates or in dry organic solvents in 0·1, 0·5, or 1·0 mm balanced cells with NaCl windows. ^{1}H N.m.r. spectra (Table 2) were registered on a Perkin-Elmer R12A or R14 spectrometer operating at 60 or 100 MHz respectively and using TMS as internal reference. Molecular weights were measured with a Hitachi–Perkin-Elmer 115 osmometer. M.p.s were determined using an Electrothermal hot-stage apparatus, and are uncorrected. Elemental analyses (Table 3) were carried out by the Microanalytical Department of this laboratory.

All manipulations especially those involving the free phosphine were performed in the absence of air and solvents were dried and degassed before use. Tris(trimethylsilylmethyl)phosphine [34] and the carbonyl com-

[31] W. Reppe and W. Schweckendiek, *Annalen*, 1948, **560**, 104.

[32] L. S. Meriwether and M. Fiene, *J. Amer. Chem. Soc.*, 1959, **81**, 4200.

[33] M. Bigorgne and A. Zelwer, *Bull. Soc. chim. France*, **1960**, 1986.

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

plexes, $Fe_2(CO)_9$,[35] $Fe_3(CO)_{12}$,[35,36] $Hg[Fe(CO)_3NO]_2$,[35,37] $Co_4(CO)_{12}$,[35,38] $Hg[Co(CO)_4]_2$,[39] and $Tl[Co(CO)_4]_3$ [30,40] were prepared as described in the literature; others were all commercial products and were used without further purification.

Iron Complexes

Tricarbonylbis[tris(trimethylsilylmethyl)phosphine]iron(0).—A mixture of dodecacarbonyltri-iron (0·52 g, 1·03 mmol) and siphos (1·0 g, 3·42 mmol) in light petroleum (b.p. 60—80°, 40 ml) was heated under gentle reflux for 20 min. The solution was filtered and evaporated under reduced pressure to give the *complex* (0·31 g, 25% based on siphos) as pale yellow plates (from methanol).

Tetracarbonyltris(trimethylsilylmethyl)phosphineiron(0).—A suspension of nonacarbonyldi-iron (0·75 g, 2·06 mmol) in light petroleum (b.p. 40—60°, 25 ml) was stirred at 40—50° with siphos (0·59 g, 2·02 mmol) until all the carbonyl had dissolved (*ca.* ½ h). The solution was filtered and all the volatile materials (containing pentacarbonyliron) were removed *in vacuo*. The *complex* (*ca.* 0·8 g) was contaminated by traces of dodecacarbonyltri-iron (as evident from its i.r. spectrum), separation from which could not be effected by chromatographic and crystallisation techniques.

Bis[dicarbonylnitrosyltris(trimethylsilylmethyl)phosphine-iron]mercury(II).—A mixture of bis(tricarbonylnitrosyliron)mercury (0·46 g, 0·85 mmol) and siphos (0·5 g, 1·71 mmol) in light petroleum (b.p. 30—40°, 25 ml) was stirred at room temperature for 4 h during which the orange-yellow *product* precipitated out in virtually quantitative yield. It was filtered, washed well with light petroleum (b.p. 30—40°), and dried *in vacuo*. It is insoluble in most common solvents.

Cobalt Complexes

Tricarbonylbis[tris(trimethylsilylmethyl)phosphine]cobalt(I) *Tetracarbonylcobaltate*(−I).—A solution of siphos (0·72 g, 2·46 mmol) in light petroleum (b.p. 30—40°, 30 ml) or diethyl ether (25 ml) was added in several portions to solid octacarbonyldicobalt (0·42 g, 1·21 mmol) cooled in an ice–water bath. After stirring for 2 h at 0°, the orange-yellow *complex* (9·9 g, 91%) was filtered, washed twice with light petroleum (b.p. 30—40°, 10 ml each), and dried *in vacuo*.

A $0{\cdot}503 \times 10^{-3}$M solution of the complex in acetone had a molar conductivity of $121{\cdot}5\ \Omega^{-1}\ cm^2\ mol^{-1}$, which varied with time.

Hexacarbonylbis[tris(trimethylsilylmethyl)phosphine]di-cobalt(0).—(a) *From octacarbonyldicobalt.* A solution of octacarbonyldicobalt (1·71 g, 5·0 mmol) in light petroleum (b.p. 60—80°, 50 ml) was treated with a solution of siphos (2·93 g, 10·0 mmol) in the same solvent (25 ml). A vigorous reaction ensued at room temperature and after 10 min when it had more or less subsided, the mixture was warmed under gentle reflux for *ca.* ½ h. The orange-brown *complex* (3·5 g, 80%) was filtered from the cooled reaction mixture, washed twice with light petroleum (b.p. 30—40°, 10 ml each), and dried *in vacuo*.

(b) *From dodecacarbonyltetracobalt.* A solution of siphos (1·13 g, 3·85 mmol) in light petroleum (b.p. 30—40°, 50 ml) was stirred with solid dodecacarbonyltetracobalt (0·55 g, 0·96 mmol) until all the black solid had dissolved to form a flocculent yellow-brown precipitate of the *product* (1·11 g, 66%) which was treated as in (a).

Reaction of Tricarbonylbis[tris(trimethylsilylmethyl)phosphine]cobalt(I) *Tetracarbonylcobaltate*(−I) *with Carbon Tetrachloride.*—A suspension of $[Co(CO)_3(siphos)_2][Co(CO)_4]$ (0·45 g, 0·5 mmol) in carbon tetrachloride (15 ml) was stirred at room temperature until gas evolution had subsided. After stirring for a further ½ h, the solution was filtered and the solvent was removed under reduced pressure. Repeated extraction of the residue with light petroleum (b.p. 30—40°) afforded a red burgundy-coloured solution from which the complex, $ClCCo_3(CO)_9$ (52 mg; identified by its i.r. spectrum), was obtained as maroon *needles* (from light petroleum, b.p. 30—40°). The remaining green solid was crystallised from chloroform–light petroleum (b.p. 80—100°) to give emerald green *prisms* (0·395 g) of the complex, $CoCl(CO)_2(siphos)$.

The reaction of *hexacarbonylbis[tris(trimethylsilylmethyl)-phosphine]dicobalt* with carbon tetrachloride or chloroform was similarly carried out.

Sodium Tricarbonyltris(trimethylsilylmethyl)phosphine-cobaltate(−I).—A solution of $[Co(CO)_3(siphos)]$, (0·305 g, 0·35 mmol) in 30 ml of dry tetrahydrofuran was vigorously agitated with sodium amalgam (1—2%, 10 ml) for 1 h. After removing the amalgam, the pale yellow solution was centrifuged and evaporated *in vacuo* to give the *complex* in essentially quantitative yield.

Bis[tricarbonyltris(trimethylsilylmethyl)phosphinecobalt]-mercury(II).—(a) *From hexacarbonylbis[tris(trimethylsilyl-methyl)phosphine]dicobalt.* Solid $NaCo(CO)_3(siphos)$, prepared as above from $[Co(CO)_3(siphos)]_2$ (0·47 g, 0·54 mmol), was dissolved in water (25 ml) and treated with an aqueous solution of mercury(II) cyanide (0·139 g, 0·55 mmol). The dense yellow precipitate was filtered, washed well with water, and dried *in vacuo* over phosphoric oxide for 1 h. Crystallisation from hot toluene gave yellow *needles* of the complex (0·55 g, 95%).

(b) *From bis(tetracarbonylcobalt)mercury.* A mixture of $Hg[Co(CO)_4]_2$ (0·85 g, 1·57 mmol) and siphos (0·92 g, 3·15 mmol) in light petroleum (b.p. 30—40°, 50 ml) was stirred for 1 h. The yellow precipitate was filtered and treated as in (a) to give the *complex* (1·63 g, 97%) as yellow needles (from hot toluene).

Chloro[tricarbonyltris(trimethylsilylmethyl)phosphine-cobalt]mercury(II).—A mixture of $Hg[Co(CO)_2(siphos)]_2$ (0·422 g, 0·394 mmol) and mercury(II) chloride (0·107 g, 0·394 mmol) in acetone (20 ml) was warmed until all the solid had dissolved. The solution was filtered and evaporated under reduced pressure to give pale yellow *prisms* (from methanol) of the complex (0·52 g, 98%).

The *bromo*-complex was similarly prepared as bright yellow prisms.

Tris[tricarbonyltris(trimethylsilylmethyl)phosphinecobalt]-thallium(III).—(a) *From hexacarbonylbis[tris(trimethylsilyl-methyl)phosphine]dicobalt.* Solid $NaCo(CO)_3(siphos)$, prepared as above from $[Co(CO)_3(siphos)]_2$ (0·6 g, 0·69 mmol), was dissolved in water (20 ml) and treated with an aqueous solution of thallium(I) nitrate (0·373 g, 1·40 mmol). The

---

[35] R. B. King, 'Organometallic Syntheses,' Vol. I, Academic Press, New York, 1965

[36] R. B. King and F. G. A. Stone, *Inorg. Synth.*, 1963, **7**, 193.

[37] W. Hieber and H. Beutner, *Z. anorg. Chem.*, 1963, **320**, 101.

[38] R. Ercoli, P. Chini, and M. Massi-Mauri, *Chim. Ind.* (*Italy*), 1959, **41**, 132.

[39] J. M. Burlitch and A. Ferrari, *Inorg. Chem.*, 1970, **9**, 563.

[40] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1586.

voluminous dark brown to almost black precipitate was filtered, washed well with water and dried *in vacuo* over phosphorus(V) oxide for 1 h. (**Caution.** Prolonged drying often results in the formation of pyrophoric materials.) The solid was repeatedly extracted with 10 ml portions of light petroleum (b.p. 30—40°) until the extract was no longer coloured. The combined extract solution was filtered and evaporated to dryness to give dark red *prisms* (from acetone–light petroleum, b.p. 30—40°) of the complex (0·66 g, 95%).

(b) *From tris(tetracarbonylcobalt)thallium.* A mixture of $Tl[Co(CO)_4]_3$ (0·33 g, 0·46 mmol) and siphos (0·405 g, 1·38 mmol) in light petroleum (b.p. 30—40°, 25 ml) was stirred for 2 h at room temperature. The blood red solution was filtered and treated as in (a) to give the *complex* (0·61 g, 88%) as dark red prisms.

Nickel Complex

Tricarbonyltris(trimethylsilylmethyl)phosphinenickel(0).— In a typical experiment, an excess of tetracarbonylnickel (3·0 ml) and siphos (0·90 g, 3·07 mmol) in light petroleum (b.p. 30—40°, 50 ml) was stirred at room temperature for 10 h. The colourless solution was filtered and evaporated *in vacuo*. Crystallisation from a small volume of light petroleum (b.p. 30—40°) gave silky *flakes* of the complex (1·04 g, 78%) on cooling to −30°.

The reactions involving excess of phosphine, or refluxing over a longer period were essentially analogous.

We are indebted to the sponsors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research.

[2/2278 *Received, 3rd October*, 1972]