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SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF THE SILYLATED DIPHOSPHITES $[(R^1O)_2PO]_2SiR^2R^3$ (R^1 = Me, Et; R^2, R^3 = Me, Ph, H, CH=CH_2). CRYSTAL STRUCTURE OF $[MnBr(CO)_3\{P(OMe)_2O\}_2SiMe_2]$

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Abstract—A convenient, general, high yield synthesis of the novel, silylated diphosphites $[(R^1O)_2PO]_2SiR^2R^3$ by reaction of the secondary phosphites $(R^1O)_2P(=O)H$ (R^1 = Me, Et) with $Cl_2SiR^2R^3$ ($R^2 = R^3$ = Me; $R^2 = R^3$ = Ph; R^2 = Me, R^3 = Ph; R^2 = Me, R^3 = CH=CH_2; R^2 = Me, R^3 = H) in the presence of NEt_3 is described. The relative rates of reaction are sensitive to the nature of the substituents on both phosphorus and silicon and follow the order [SiMeH] > [$SiMe_2$] > [SiMe(CH=CH_2)] > [SiMePh] > [$SiPh_2$] for both R^1 = Me, Et and R^1 = Me > R^1 = Et for all pairs with the same silicon substituents. ^{31}P NMR spectroscopic data suggest that the nature of the silicon substituents has only a small effect on through-bond electronic induction or hybridization at the phosphorus atoms of the free diphosphites. Complexation of these diphosphites to transition metals, of the form $MX(CO)_3[P(OMe)_2O]_2SiR^2R^3$ (M = Mn, X = Br; M = Mo, X = CO), stabilizes the ligand towards hydrolysis compared to the uncoordinated diphosphites. There is some correlation between the ^{13}C NMR shifts of the carbonyl ligands and the stereoelectronic character of the silicon substituents in $MX(CO)_3[P(OMe)_2O]_2SiR^2R^3$, suggesting that the electron-releasing properties of the diphosphite ligands increase in the order [$SiPh_2$] < [SiMePh] = [SiMe(CH=CH_2)] < [$SiMe_2$]. The crystal structure of $MnBr(CO)_3[P(OMe)_2O]_2SiMe_2$ has been determined. The compound exists as discrete, distorted octahedral monomers in which the diphosphite ligand occupies *cis* coordination sites and the six-membered chelate ring has an unusual "chaise longue" conformation.

Although chelating tertiary phosphine ligands have been widely exploited in the coordination and organometallic chemistry of the transition elements,[1] relatively few studies have been conducted with chelating tertiary phosphites.[2] Recent research into the transition-metal catalysed hydroformylation[3] and dimerization[4] of alkenes and dienes, respectively, has demonstrated that highly electron-withdrawing and/or sterically-demanding tertiary phosphites are among the most active cocatalysts for these reactions. Subsequently, more recent interest has focused on chelating diphosphites, particularly those containing chelating diollato substituents[5,6] where it has been shown that complexes of transition metals containing such diphosphites as ligands are active alkene hydroformylation[7] and hydrocyanation catalysts.[5]

We are currently investigating the chemistry of silylated organophosphorus compounds[8] and have, in the course of this work, synthesized a range of novel, silylated diphosphites of the form $[(R^1O)_2PO]_2SiR^2R^3$ where R^1, R^2 and R^3 can be variously methyl, ethyl, phenyl, hydrido or vinyl. The syntheses are convenient, proceed in high yield and use inexpensive starting materials. This report describes full details of the synthesis and spectroscopic characterization of a range of silylated diphosphites and some aspects of their coordination chemistry: part of this work has been briefly communicated.[8b]

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Table 1. Quantities and yields for diphosphite syntheses (all reactions were performed in toluene solvent at room temperature and the reaction times quoted are not necessarily optimized)

Reagents (mmol)			Reaction time (h)	Product	Yield (%)
$(R^1O)_2P(O)H$	$Cl_2SiR^2R^3$	NEt_3			
5.45	2.73	7.50	48	**1**	96
5.45	2.73	14.35	96	**2**	81
5.45	2.73	7.50	48	**3**	99
5.45	2.73	14.35	48	**4**	87
5.45	2.73	7.50	20	**5**	91
3.88	1.94	4.95	48	**6**	78
3.88	1.94	14.35	96	**7**	87
3.88	1.94	14.35	96	**8**	82
3.88	1.94	14.35	48	**9**	85
3.88	1.94	5.32	20	**10**	85

RESULTS AND DISCUSSION

Synthesis and characterization of the diphosphites $[(R^1O)_2PO]_2SiR^3R^3$

The reaction between the secondary phosphites $(R^1O)_2P({=}O)H$ (R^1 = Me, Et) and the dichlorodiorganosilanes, $Cl_2SiR^2R^3$ ($R^2 = R^3$ = Me; $R^2 = R^3$ = Ph; R^2 = Me, R^3 = Ph; R^2 = Me, R^3 = $CH{=}CH_2$; R^2 = Me, R^3 = H), in toluene solvent in the presence of excess NEt_3 proceeds smoothly at ambient temperature to afford the silylated diphosphites $[(R^1O)_2PO]_2SiR^2R^3$ as clear, mobile liquids in high yields (Table 1 and Scheme 1). The products were found to be satisfactory for synthetic studies without further purification.

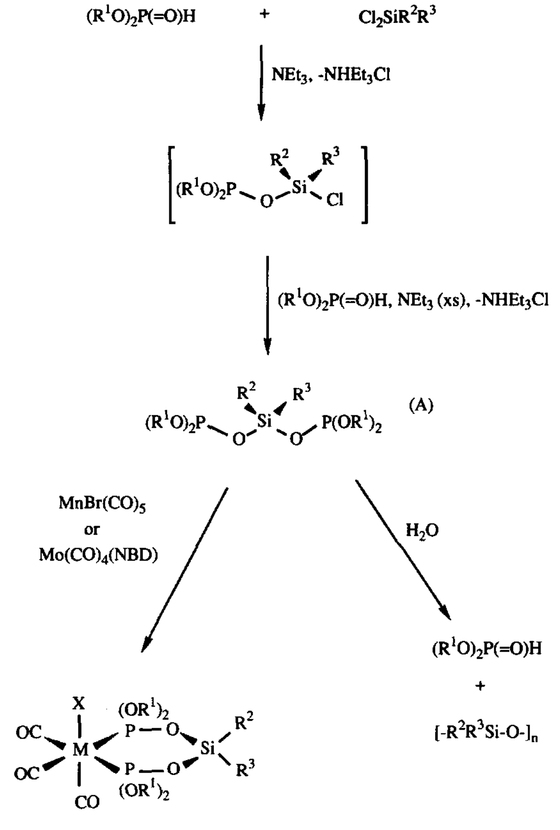
If the reactions are quenched too early or if insufficient NEt_3 is used, other organophosphorus compounds can be observed by ^{31}P NMR spectroscopy (Table 2), which we presume to be the intermediate monophosphites of the form $(R^1O)_2POSiR^2R^3Cl$ since upon subsequent treatment with $(RO)_2P({=}O)H$ and NEt_3 these species are completely converted to the corresponding diphosphites. In all cases, the ^{31}P resonances for these intermediate monophosphites are located at a higher frequency than those for the corresponding diphosphites.[9] Attempts to shorten reaction times by increasing the reaction temperatures (80°C; *ca* 24 h) leads to the formation of by-products, most prevalent in the methoxo series, with new ^{31}P resonances in the region expected for four-coordinate phosphorus species of the form $[R_3P({=}O)]$. Since these resonances remain singlets (albeit broadened) in the fully coupled ^{31}P NMR spectrum, we presume that the R groups are either methyl or methoxo groups rather than hydrogen.

With the exception of **5** and **10** all the diphosphites are stable indefinitely at ambient temperature in a dry nitrogen atmosphere under normal laboratory light; **5** and **10**, however, take on a yellow colouration when left to stand for several hours at room temperature even in the absence of oxygen and moisture; shielding the samples from laboratory light does not prevent this discolouration. New ^{31}P resonance signals, at δ 129.0 and 124.9 ppm (benzene-d_6), are seen to accompany the process, but their identities remain unknown. We presume that the instability of these two diphosphites is linked to the presence of the Si—H units since these moieties are known to be reactive towards alkoxo residues[10] similar to those present

Table 2. $^{31}P\{^1H\}$ NMR data for $(R^1O)_2POSiR^2R^3Cl$

R^1	R^2	R^3	$^{31}P\{^1H\}$ (ppm)[a]
Me	Me	Me	127.7
Me	Ph	Ph	127.3
Me	Me	Ph	127.6
Me	Me	$CH{=}CH_2$	127.4
Me	Me	H	128.3
Et	Me	Me	126.7
Et	Ph	Ph	126.1
Et	Me	Ph	126.3
Et	Me	$CH{=}CH_2$	126.5
Et	Me	H	127.4

[a] Reactions of $(R^1O)_2P({=}O)H$ (4 mmol) and $Cl_2SiR^2R^3$ (3 mmol) in the presence of NEt_3 (8 mmol) were performed in toluene solvent, filtered after 5.5 h (2 h in the case of R^3 = H) and analysed, without further treatment, by $^{31}P\{^1H\}$ NMR spectroscopy in protio toluene at 298 K with external C_6D_6 as a reference.



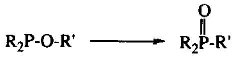
M = Mn; X = Br; R^1 = Me; R^2 = Me; R^3 = Me; **11**
M = Mn; X = Br; R^1 = Me; R^2 = Ph; R^3 = Ph; **12**
M = Mn; X = Br; R^1 = Me; R^2 = Me; R^3 = Ph; **13**
M = Mo; X = CO; R^1 = Me; R^2 = Me; R^3 = Me; **14**
M = Mo; X = CO; R^1 = Me; R^2 = Ph; R^3 = Ph; **15**
M = Mo; X = CO; R^1 = Me; R^2 = Me; R^3 = Ph; **16**
M = Mo; X = CO; R^1 = Me; R^2 = Me; R^3 = $-CH=CH_2$; **17**

Scheme 1. Synthesis and reactivity of diphosphites **1–10**.

R^1	R^2	R^3	(A)
Me	Me	Me	**1**
Me	Ph	Ph	**2**
Me	Me	Ph	**3**
Me	Me	$CH{=}CH_2$	**4**
Me	Me	H	**5**
Et	Me	Me	**6**
Et	Ph	Ph	**7**
Et	Me	Ph	**8**
Et	Me	$CH{=}CH_2$	**9**
Et	Me	H	**10**

in **5** and **10**. All the diphosphites hydrolyse upon exposure to moist air over the course of several hours (between 3 and 20 h) at ambient temperature to reform $(R^1O)_2P({=}O)H$ (by ^{31}P NMR spectroscopy) and presumably oligosiloxanes of the form $[-R^2R^3Si-O-]_n$ (which were not isolated or characterized). The relative degree of sensitivity towards hydrolysis appears to be a function of the size of the silicon substituents; compounds **5** and **10** (both having R^2 = Me and R^3 = H) react significantly faster than the others. This is consistent with the well-documented S_N2-Si hydrolysis mechanism in which initial attack of H_2O on the silicon atom affords a five-coordinate intermediate whose stability is strongly influenced by the steric environment around silicon.[11]

All the diphosphites display a single, sharp resonance in their $^{31}P\{^1H\}$ NMR spectra (Table 3) in the region expected for tertiary phosphite compounds.[12] This provides good evidence for the presence of three-coordinate, trivalent phosphorus atoms in these compounds as opposed to the isomeric four-coordinate, pentavalent form which could arise via a formal 1,2-shift (Scheme 2).



Scheme 2.

This is further supported by the absence of a strong, broad band in the 1250–1299 cm^{-1} region of their IR spectra due to $\nu(P{=}O)$ [cf. $\nu(P{=}O)$ = 1265 cm^{-1} in $(MeO)_2P({=}O)H$ and $\nu(P{=}O)$ = 1255 cm^{-1} in $(EtO)_2P({=}O)H$]. Instead, **1–10** have strong absorptions in the region 925–990 cm^{-1} assignable to $\nu(P-O-Si)$. In addition, **5** and **10** have bands at 2175 and 2185 cm^{-1}, respectively, due to $\nu(Si-H)$ with the corresponding bending vibrations appearing at 890 and 885 cm^{-1}.[13]

The nature of the substituents on silicon in both series (methoxo and ethoxo) has little effect upon the ^{31}P resonances (in each series the shift range covers *ca* 1 ppm), suggesting that the bond hybridization and through-bond electronic inductive effects at phosphorus are only slightly sensitive to the substitution on silicon. Interestingly it is the compounds with the most electron-withdrawing silicon substituents (**2** and **7**, for which $R^2 = R^3$ = Ph) which possess the lowest frequency resonances, possibly indicating that the more electronegative substituents on silicon promote greater *s*-character in the phosphorus lone-pair. Consequently, the more electron-releasing silicon substituents should promote greater *p*-character of the phosphorus lone-pair and hence make the diphosphite more electron-releasing in a complex. This latter hypothesis is supported by ^{13}C NMR data for the complexes **14–17** (*vide infra*).

The methoxo hydrogens of diphosphites **1–5** appear as virtual coupled multiplets in the ^1H NMR spectra, forming the A/A′ and M/M′ parts of $A_6A'_6XX'$ (**1** and **2**) or $A_3A'_3M_3M'_3XX'$ (**3–5**) spin systems for which the two magnetically inequivalent

Table 3. Spectroscopic data for compounds 1–17

Compound	IR[a]	^{31}P{^{1}H} NMR[b]	^{1}H and ^{13}C{^{1}H} NMR[c]
1	940(s)[d]	126.6	^{1}H: 3.29 [m, 12H, J(P—H) 11, CH_3O—], 0.22 [s, 6H, (CH_3)$_2$Si][e] ^{13}C: 47.72 [m, ^2J(P—C) 9.3, ^6J(P—C) −0.8, CH$_3$O—],[f] 0.60 [t, ^3J(P—C) 1.7, (CH$_3$)$_2$Si]
2	950(s)[d]	126.2	^{1}H: 7.8–7.2 (m, 10H, Ph—H), 3.31 [m, 12H, J(P—H) 11, CH_3O—] ^{13}C: 134.8 (s, Ph—C_o), 133.3 (s, Ph—C_{ipso}), 131.1 (s, Ph—C_p), 128.3 (s, Ph—C_m), 48.1 [m, ^2J(P—C) 12.0, ^6J(P—C) −3.3, CH$_3$O—][g]
3	940(s)[d]	126.3	^{1}H: 7.7 (m, 2H, Ph—H_o), 7.2 (m, 3H, Ph—$H_{m/p}$), 3.30 [m, 6H, J(P—H) 10, CH_3O—], 3.29 [m, 6H, J(P—H) 10, CH_3O—], 0.51 (s, 3H, CH_3Si) ^{13}C: 134.84 (s, Ph—C_{ipso}), 133.80 (s, Ph—C_o), 130.82 (s, Ph—C_p), 128.28 (s, Ph—C_m), 47.94 [m, J(P—C) 10, CH$_3$O—], 47.90 [m, J(P—C) 10, CH$_3$O—], −0.51 (s, CH$_3$Si)
4	978(s)[d]	126.2	^{1}H: 6.0–5.8 [m, 3H, J(H—H) 19.4, 15.2, 4.3 CH_2═CH—],[h] 3.273 [m, 6H, J(P—H) 10, CH_3O—], 3.272 [m, 6H, J(P—H) 10, CH_3O—], 0.29 (s, 3H, CH_3Si) ^{13}C: 135.42 (s, CH$_2$═CH—),[k] 134.47 (s, CH$_2$═CH—),[i] 47.85 [m, J(P—C) 8, CH$_3$O—], −1.10 (s, CH$_3$Si)
5	2175(s)[j] 950(s)[d] 890(s)[l]	126.8	^{1}H: 4.88 [m, 1H, ^3J(H—H) 2, ^3J(P—H) 3, Si—H],[k] 3.28 [m, 12H, J(P—H) 10, CH_3O—], 0.21 [d, 3H, ^3J(H—H) 2, CH_3Si] ^{13}C: 47.95 [m, J(P—C) 8, CH$_3$O—], 47.91 [m, J(P—C) 8, CH$_3$O—], 0.20 (s, CH$_3$Si)
6	925(s)[d]	125.3	^{1}H: 3.74 [m, 8H, J(P—H) 8, ^3J(H—H) 7, CH$_3$CH_2O—], 1.07 [t, 12H, ^3J(H—H) 7, CH_3CH$_2$O—], 0.23 [s, 6H, (CH_3)$_2$Si] ^{13}C: 56.96 [m, ^2J(P—C) 10.2, ^6J(P—C) −0.1, CH$_3$$CH_2$O—], 17.09 [m, ^3J(P—C) 7.3, ^7J(P—C) −2.2, CH$_3$CH$_2$O—],[m] 0.85 [t, ^3J(P—C) 3.6, (CH$_3$)$_2$Si]
7	930(s)[d]	124.8	^{1}H: 7.8–7.0 (m, 10H, Ph—H), 3.80 [m, 8H, J(P—H) 7, ^3J(H—H) 7, CH$_3$CH_2O—], 1.04 [t, 12H, ^3J(H—H) 7, CH_3CH$_2$O—] ^{13}C: 135.00 (s, Ph—C_o), 133.70 (s, Ph—C_{ipso}), 130.92 (s, Ph—C_p), 128.23 (s, Ph—C_m), 57.40 [m, ^2J(P—C) 11.9, ^6J(P—C) −2.6, CH$_3$$CH_2$O—][n] 17.00 [m, J(P—C) 5.2, CH$_3$CH$_2$O—]
8	928(s)[d]	125.3	^{1}H: 7.75–7.73 (m, 2H, Ph—H_o), 7.21–7.19 (m, 3H, Ph—$H_{m/p}$), 3.77 [m, 8H, J(P—H) 12, CH$_3$CH_2O—], 1.07 [t, 6H, ^3J(H—H) 7, CH_3CH$_2$O—], 1.06 [t, 6H, ^3J(H—H) 7, CH_3CH$_2$O—], 0.55 (s, 3H, CH_3Si) ^{13}C: 135.26 (s, Ph—C_{ipso}), 133.87 (s, Ph—C_o), 130.69 (s, Ph—C_p), 128.17 (s, Ph—C_m), 57.23 [m, J(P—C) 9, CH$_3$$CH_2$O—], 57.18 [m, J(P—C) 8, CH$_3$$CH_2$O—], 17.04 (s, CH$_3CH_2$O—), 17.01 (s, CH$_3CH_2$O—), −0.29 (s, CH$_3$Si)
9	980(s)[d]	125.3	^{1}H: 6.1–5.9 [m, 3H, J(H—H) 18.7, 16.2, 4.1, CH_2═CH—],[j] 3.74 [m, 8H, ^3J(H—H) 7, CH$_3$CH_2O—], 1.06 [m, 12H, ^3J(H—H) 7, J(P—H) 0.5, CH_3CH$_2$O—], 0.33 (s, 3H, CH$_3$Si) ^{13}C: 135.04 (s, CH$_2$═CH—),[i] 134.98 (s, CH$_2$═CH—),[i] 57.13 [m, J(P—C) 9, CH$_3$$CH_2$O—], 17.07 [m, J(P—C) 4, CH$_3$CH$_2$O—], −0.83 (s, CH$_3$Si)
10	2185(s)[j] 930(s)[d] 885(s)[l]	125.9	^{1}H: 4.95 [m, 1H, ^3J(H—H) 2, ^3J(P—H) 2.4, Si—H],[k] 3.74 [m, 8H, ^3J(H—H) 7, CH$_3$CH_2O—], 1.07 [t, 12H, ^3J(H—H) 7, CH_3CH$_2$O—], 0.24 [d, 3H, ^3J(H—H) 2, CH_3Si] ^{13}C: 57.28 [m, J(P—C) 9, CH$_3$$CH_2$O—], 17.04 [m, J(P—C) 5, CH$_3$CH$_2$O—], 0.53 (s, CH$_3$Si)
11	2050(s,sp) 1981(s,br) 1941(s,br)	149.3 (+22.7)	^{1}H: 3.67 [m, 6H, J(P—H) 11, CH_3O—], 3.24 [m, 6H, J(P—H) 11, CH_3O—], 0.46 (s, 3H, CH_3Si), 0.02 (s, 3H, CH_3Si)
12	2048(s,sp) 1980(s,br) 1941(s,br)	149.9 (+23.7)	^{1}H: 8.0–7.1 (m, 10H, Ph—H), 3.69 [m, 6H, J(P—H) 11, CH_3O—], 3.18 [m, 6H, J(P—H) 11, CH_3O—]

Table 3—*continued*

Compound	IR[a]	$^{31}P\{^1H\}$ NMR[b]	^1H and $^{13}C\{^1H\}$ NMR[c]
13	2050(s,sp) 1982(s,br) 1943(s,br)	149.3 (+23.0)	^{1}H: 7.5–7.2 (m, 5H, Ph—*H*), 3.71 [m, 6H, *J*(P—H) 10, $\mathrm{C}H_3\mathrm{O}$—], 3.17 [m, 6H, *J*(P—H) 11, $\mathrm{C}H_3\mathrm{O}$—], 0.80 (s, 3H, $\mathrm{C}H_3\mathrm{Si}$)
14	2042(s,sp) 1945(s,sh) 1922(s,br)	148.8 (+22.2)	^{1}H: 3.29 [m, 12H, *J*(P—H) 13, $\mathrm{C}H_3\mathrm{O}$—], 0.12 [s, 6H, $(\mathrm{C}H_3)_2\mathrm{Si}$] ^{13}C: 212.91 [m, *J*(P—C) 25.6, $C\mathrm{O}_{trans}$],[o] 207.89 [t, ^{2}*J*(P—C) 13.7, $C\mathrm{O}_{cis}$], 50.27 (s, $C\mathrm{H_3O}$—), 0.14 [s, $(C\mathrm{H}_3)_2\mathrm{Si}$]
15	2041(s,sp) 1945(s,sh) 1925(s,br)	149.4 (+23.2)	^{1}H: 7.8 (m, 4H, Ph—H_o), 7.2 (m, 6H, Ph—$H_{m/p}$), 3.32 [m, 12H, *J*(P—H) 12, $\mathrm{C}H_3\mathrm{O}$—] ^{13}C: 212.68 [m, *J*(P—C) 27.1, $C\mathrm{O}_{trans}$],[o] 207.57 [t, ^{2}*J*(P—C) 13.5, $C\mathrm{O}_{cis}$], 134.61 (s, Ph—C_o), 131.71 (s, Ph—C_p), 131.57 (s, Ph—C_{ipso}), 128.49 (s, Ph—C_m), 50.59 (s, $C\mathrm{H_3O}$—)
16	2042(s,sp) 1945(s,sh) 1921(s,br)	148.8 (+22.5)	^{1}H: 7.4 (m, 2H, Ph—H_o), 7.0 (m, 3H, Ph—$H_{m/p}$), 3.16 [m, 6H, *J*(P—H) 12, $\mathrm{C}H_3\mathrm{O}$—], 3.04 [m, 6H, *J*(P—H) 12, $\mathrm{C}H_3\mathrm{O}$—], 0.10 (s, 3H, $\mathrm{C}H_3\mathrm{Si}$) ^{13}C: 212.82 [m, *J*(P—C) 24.7, $C\mathrm{O}_{trans}$],[o] 208.21 [t, ^{2}*J*(P—C) 13.0, $C\mathrm{O}_{cis}$], 207.41 [t, ^{2}*J*(P—C) 13.8, $C\mathrm{O}_{cis}$], 133.52 (s, Ph—C_o), 132.96 (s, Ph—C_{ipso}), 131.55 (s, Ph—C_p), 128.48 (s, Ph—C_m), 50.50 (s, $C\mathrm{H_3O}$—), 50.43 (s, $C\mathrm{H_3O}$—], −1.20 (s, $C\mathrm{H_3Si}$)
17	2041(s,sp) 1948(s,sh) 1923(s,br)	148.3 (+22.1)	^{1}H: 6.14 (m, 3H, $\mathrm{C}H_2\mathrm{{=}CH}$—), 3.56 [m, 12H, *J*(P—H) 13, $\mathrm{C}H_3\mathrm{O}$—], 0.48 (s, 3H, $\mathrm{C}H_3\mathrm{Si}$) ^{13}C: 212.82 [m, *J*(P—C) 26.1, $C\mathrm{O}_{trans}$],[o] 207.91 [t, ^{2}*J*(P—C) 13.6, $C\mathrm{O}_{cis}$], 207.63 [t, ^{2}*J*(P—C) 13.7, $C\mathrm{O}_{cis}$], 137.18 (s, $C\mathrm{H_2{=}CH}$—), 132.38 (s, $\mathrm{CH_2{=}}C\mathrm{H}$—), 50.40 (s, $C\mathrm{H_3O}$—), 50.35 (s, $C\mathrm{H_3O}$—), 1.40 (s, $C\mathrm{H_3Si}$)

[a] Recorded as thin films (**1–10**) or solutions in CH_2Cl_2 (**11–17**). For **11–17**, only *v*(CO) bands are reproduced. All absorptions reported as cm^{-1} with relative intensities as s (strong), sp (sharp), br (broad), sh (shoulder).

[b] In benzene-d_6 at 298 K. Coordination chemical shifts (Δ_c) in parentheses, defined as δ(complex)–δ(free ligand).

[c] In benzene-d_6 at 298 K.

[d] *v*(POSi).

[e] *J*(Si—H) 7.

[f] ^{4}*J*(P—P) 3.6 Hz, calculated as in ref. 14.

[g] ^{4}*J*(P—P) 3.0 Hz, calculated as in ref. 14.

[h] Strongly coupled ABC pattern.

[i] Assigned by an Attached Proton Test pulse sequence.

[j] *v*(Si—H).

[k] ^{1}*J*(^{29}Si—H) 254.

[l] δ(Si—H)

[m] ^{4}*J*(P—P) 2.9 Hz, calculated as in ref. 14.

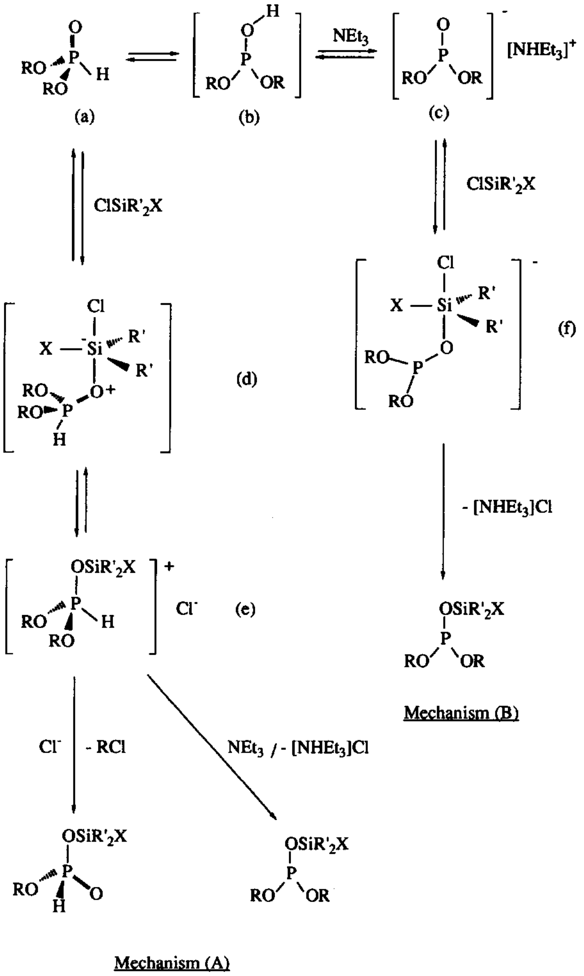
[n] ^{4}*J*(P—P) 4.6 Hz, calculated as in ref. 14.

[o] The A portion of an AXX′ spin system. *Trans* indicates the carbonyl ligand *trans* to a phosphorus atom.

phosphorus atoms form the XX′ part. From these spectra, values of [*J*(AX)+*J*(AX′)] can be obtained directly and vary from 10 to 12 Hz (see Table 3). Since *J*(AX) for $(MeO)_2POSiMe_3$ is 11 Hz (in an A_6X spin system), it is probable that the values of *J*(AX′) for **1–5** are of the order 1–2 Hz. The methoxo carbons also display virtual coupling in the $^{13}C\{^1H\}$ NMR spectra; the signals for **1** and **2** appearing as five-line multiplets (in an AXX′ spin system) from which it has proved possible to extract full coupling information as described by Redfield *et al.*[14] (Table 3). The values of ^{4}*J*(P—P) for **1** and **2** (3.6 and 3.0 Hz, respectively) are of a similar magnitude to the ^{4}*J*(P—P) value reported for $Ph_2P(CH_2)_3PPh_2$ (1 Hz).[15] For compounds **3–5**, the presence of different silicon substituents renders the geminal methoxo groups inequivalent and separate, virtually coupled multiplets can be observed for these carbon and hydrogen nuclei in most of the NMR spectra. Diphosphites **6–10** also display second-order coupling patterns for the ethyl methylene hydrogen and carbon nuclei, some of the latter signals being sufficiently well resolved after Gaussian multiplication to enable full coupling information to be calculated (Table 3).

Possible mechanisms of formation of the diphosphites $[(R^1O)_2PO]_2SiR^2R^3$

It has been reported in the patent literature[16] that reactions of secondary phosphites with Cl_2SiMe_2 in the absence of a base at elevated temperatures lead to products of the form $[(RO)HP({=}O)]_2SiMe_2$, presumably resulting from nucleophilic attack of chloride ions on an incipient phosphonium salt $[(RO)_2HPOSiMe_2Cl]^+$ (e), formed via the five-coordinate intermediate (d) as illustrated in Scheme 3 (a similar mechanism has been proposed for the trimethylsilylation of secondary phosphites[17] and although the phosphonium salt is not observed directly in these reactions, salts of the form $[(Me_2N)_3POSiMe_3]^+X^-$ (X = Br, I) can be isolated from stoichiometric mixtures of $(Me_2N)_3P{=}O$ and Me_3SiX[18]). We anticipate that a similar mechanism will operate in the presence of a base such as NEt_3, where now deprotonation of the intermediate phosphonium salts $[(RO)_2HPOSiR'_2X]^+$ (e) [$X = Cl$, $OP(OR)_2$] occurs in preference to the S_N2 reaction of the chloride ion on the phosphorus-bound alkoxo group [mechanism (A) in Scheme 3]. A possible alternative mechanism (B) would involve reaction of the three-coordinate tautomer (b) or its triethylammonium salt (c) with Cl_2SiR_2 in a direct S_N2-Si reaction (Scheme 3). In the absence of base, the equilibrium between (a) and (b) lies far to the side of (a) for both R = Me and R = Et, since signals due only to the four-coordinate phosphorus species are observed in the room temperature ^{31}P NMR spectra and IR spectroscopy reveals no evidence for species containing hydroxyl groups. Furthermore, we observed that the addition of 10 equivalents of NEt_3 to a solution of $(MeO)_2P({=}O)H$ in toluene did not result in the appearance of resonances assignable to either (b) or (c) in the ^{31}P NMR spectrum. The resonance for (a) is unbroadened, shifted to low frequency by 0.54 ppm [δ 10.64 for pure $(MeO)_2P({=}O)H$ in toluene] and the $^1J(P{-}H)$ coupling increased by 4 Hz [$^1J(P{-}H) = 685$ Hz for pure $(MeO)_2P({=}O)H$ in toluene] upon the introduction of NEt_3. This behaviour is inconsistent with the formation of either (b) or (c) and contrasts with stronger bases such as NaH for which the phosphito salt is strongly favoured.[19] Therefore, although it is possible that a very small equilibrium concentration of either (b) or (c) could be actively involved in the reaction, we have no evidence for this at present. The observation that the rates of formation of **1**–**5** (R = Me) are faster than those of **6**–**10** (R = Et) may suggest that the intermediate phosphonium salts $[(MeO)_2HPOSiR_2X]^+$ are stronger acids than $[(EtO)_2HPOSiR_2X]^+$. Moreover, when the syntheses of **1**–**10** are performed under standard conditions (see footnote to Table 2 for procedure), it is found that for both R^1 = Me and Et the relative rates of reaction depend upon the silicon substituents in the following order: [SiMeH] > [$SiMe_2$] > [$SiMe(CH{=}CH_2)$] > [SiMePh] > [$SiPh_2$], presumably reflecting the degree of steric congestion in, and hence ease of formation of, the five-coordinate intermediates (d).



Scheme 3. Possible mechanisms of reaction of $(RO)_2P({=}O)H$ with $ClSiR'_2X$ [$X = Cl$, $OP(OR)_2$ or $OP({=}O)H(OR)$; R = Me, Et; R′ = Me, Ph, H, $CH{=}CH_2$].

Transition metal complexes of the diphosphites $[(R^1O)_2PO]_2SiR^2R^3$

Both $MnBr(CO)_5$ and $Mo(CO)_4(NBD)$ (NBD = norbornadiene) react smoothly with the silylated diphosphites to afford complexes of the form

$[MX(CO)_3\{P(OMe)_2O\}_2SiR^2R^3]$ (M = Mn, X = Br; M = Mo, X = CO) (see Scheme 1 and Experimental). The facial geometry of the orange–yellow manganese complexes **11**–**13** is supported by the observation of three strong bands in the IR spectrum assignable to $\nu(CO)$ vibrations,[20] a single resonance [broadened due to coupling with the quadrupolar ^{55}Mn ($I = 5/2$) nucleus] in their $^{31}P\{^1H\}$ NMR spectra and has been confirmed in the case of **11** by a single-crystal X-ray diffraction study (*vide infra*). We were not able to isolate manganese complexes with the diphosphites **4** and **5**; only oils were obtained which we presume, in the case of diphosphite **4**, to contain the desired complex on the basis of the similarity of solution IR [$\nu(CO)$ at 2050, 1980 and 1940 cm^{-1}] and $^{31}P\{^1H\}$ NMR (δ 149.8 ppm) parameters to those of **11**–**13**. With diphosphite **5**, IR spectroscopy revealed that the Si—H unit was not retained in the products, possibly the result of reaction with the Mn—Br moiety since it is known that silanes are readily halogenated.[21] Similarly, we were unable to isolate solid products from the reactions of **4** and **5** with $Mo(CO)_4(NBD)$; again only oils were obtained.

Within the series of manganese complexes **11**–**13**, the $\nu(CO)$ vibrations show little sensitivity (range *ca* 2 cm^{-1}) to the nature of the silicon substituents; presumably the carbonyl bonds are too remote to register significant changes in the ligand backbone six bonds distant. Similar insensitivity is also found in the molybdenum series **14**–**17**, although in these complexes it is possible to resolve only three of the expected four ($2A_1+B_1+B_2$) $\nu(CO)$ vibrations. Several silyl diphosphinite complexes of the form $[Mo(CO)_4\{PPh_2O\}_2SiMeR]$ (R = Me, Et, Ph and CH_2Cl) have been reported recently[22] (although the syntheses of these complexes did not involve preparing the free diphosphinites) and correlations between various NMR parameters discussed in detail.[23] A comparison of the IR data of **14**–**17** with the above diphosphinite complexes reveals that the latter have consistently lower frequency $\nu(CO)$ vibrations (by *ca* 10–15 cm^{-1}) suggesting that the diphosphinite ligands $[Ph_2PO]_2SiR^2R^3$ generate a more electron-rich metal centre than the diphosphites $[(R^1O)_2PO]_2SiR^2R^3$ in this system. This is further supported by the observation that the ^{13}C resonances of the carbonyl carbon nuclei *trans* to the phosphorus atoms are higher in frequency (by *ca* 2 ppm) for $[Mo(CO)_4\{PPh_2O\}_2SiMeR]$ (R = Me, Et, Ph and CH_2Cl) than for **14**–**17**, consistent with the model of carbonyl bonding whereby increasing the electron density on the metal results in a greater degree of M—L π-back-donation and a greater contribution of the paramagnetic screening term to nuclear shielding which in turn leads to higher frequency carbonyl chemical shifts.[24] Furthermore, within the series **14**–**17** the ^{13}C resonances of the carbonyl carbon nuclei increase in the order $[SiPh_2] < [SiMePh] = [SiMeCH{=}CH_2] < [SiMe_2]$, indicating that the electron-donating abilities of the diphosphites follow the same order. However, given the very narrow spread of chemical shifts a more detailed analysis may be imprudent. The ^{31}P coordination chemical shifts of compounds **11**–**17** range from +22.1 to +23.7 ppm and compare favourably to those found in several bis(diphenylphosphino)propane complexes (+20 to +35 ppm) which also contain six-membered chelate rings.[25]

The complexes **14**–**17** are more stable towards hydrolysis than the free diphosphites (the former remaining unchanged upon exposure to moist air in benzene-d_6 solution over 48 h at room temperature), presumably reflecting a more constrained environment around the silicon atoms in the complexes thus making it harder for silicon to achieve the necessary five-coordinate geometry involved in an S_N2-Si hydrolysis mechanism.[11]

The molecular structure of $[MnBr(CO)_3\{P(OMe)_2O\}_2SiMe_2]$ (**11**)

Two independent molecules (molecule 1 and molecule 2) are found in the unit cell, the molecular structures for which differ primarily in the conformation of one of the phosphorus-coordinated methoxo groups as shown in Fig. 1 (see also Experimental). Lists of bond distances and angles for both molecules are reproduced in Tables 4 and 5, respectively. The complex exists as a slightly distorted, octahedral monomer with a facial arrangement of the carbon monoxide ligands. The Mn—Br bond length of 252.8(5) pm [252.7(5) pm in molecule 2] is *ca* 2 pm longer than that found in *cis*-$MnBr(CO)_4[P(4\text{-}CH_3C_6H_4)_2OSiMe_3]$[8a] possibly reflecting the more electron-rich character of the manganese centre in **11**. Furthermore, the Mn—P bond lengths range from 225.5(6) to 226.6(6) pm and are *ca* 6 pm shorter than the corresponding distance in $MnBr(CO)_4[P(4\text{-}CH_3C_6H_4)_2OSiMe_3]$, which contains less electronegative substituents on the phosphorus atom. The greater *trans* influence of the phosphite ligand over bromine results in longer Mn—C bonds to the carbon monoxide ligands *trans* to phosphorus. A bite angle of 89.5(2)° [88.2(2)° in molecule 2] for the disphosphite ligand is within the range found for other chelating diphosphorus ligands which form six-membered chelate rings.[26] Of particular interest is the conformation of the chelate ring which appears to differ significantly from the "chair type" conformations commonly

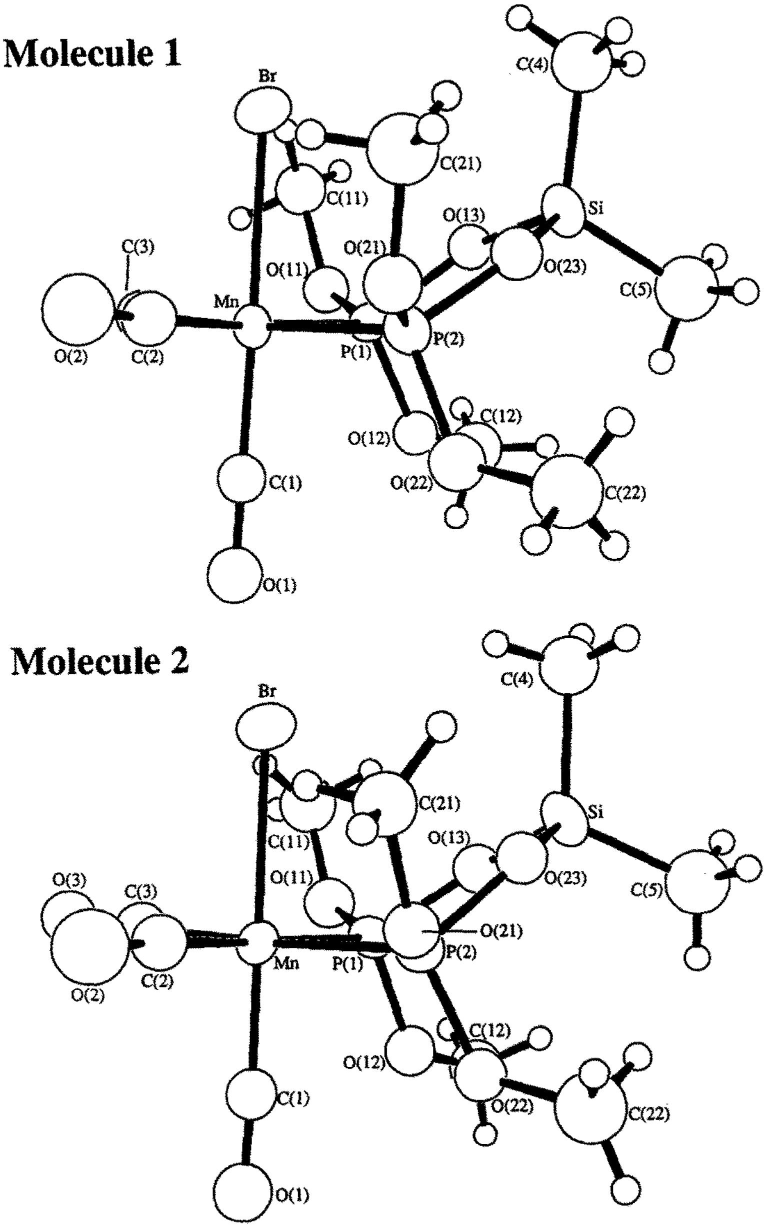


Fig. 1. Molecular structure of $MnBr(CO)_3[P(OMe)_2O]_2SiMe_2$ (**11**) (two independent molecules in the unit cell).

found in complexes containing the formally analogous ligand $Ph_2P(CH_2)_3PPh_2$(dppp).[26] The conformation in **11** is similar to that found in the complex $[Mo(CO)_4\{PPh_2O\}_2SiMe^tBu]$,[27] which the authors described as a "chaise longue", except that the "back-rest" is formed by the atoms {P(1)—Mn—P(2)} in **11** but by the atoms {O—Si—O} in the molybdenum complex. The methoxo groups on each phosphorus are close to eclipsing each other; the dihedral angle between the planes O(11)—P(1)—O(12) and O(21)—P(2)—O(22) is 13.98° (14.99° in molecule 2). Within the chelate ring, the five atoms P(1)—O(13)—Si—O(23)—P(2) lie approximately in a plane with the largest deviation being that due to O(13) (*ca* 11 pm in both molecules 1 and 2). The angle between this plane and that formed by the atoms P(1)—Mn—P(2) is 147.5° (143.9° in molecule 2). The relative importance of steric and electronic factors in determining chelate-ring conformations in ligands of this type is not yet clear, although crystallographic studies are now beginning to provide a basis set of data through which the effects of controlled ligand modifications can be correlated.

Table 4. Bond lengths (pm) for **11**

Molecule 1			
Br(1)—Mn(1)	252.8(5)	P(1)—Mn(1)	225.8(5)
P(2)—Mn(1)	225.5(6)	C(1)—Mn(1)	180.2(15)
C(2)—Mn(1)	183.3(16)	C(3)—Mn(1)	180.9(16)
O(11)—P(1)	160.6(12)	O(12)—P(1)	159.0(11)
O(13)—P(1)	158.9(11)	O(21)—P(2)	159.7(11)
O(22)—P(2)	159.0(12)	O(23)—P(2)	157.6(11)
O(13)—Si(1)	165.2(11)	O(23)—Si(1)	167.3(11)
C(4)—Si(1)	180.4(17)	C(5)—Si(1)	182.1(20)
O(1)—C(1)	112.8(15)	O(2)—C(2)	112.1(17)
O(3)—C(3)	114.9(18)		
C(11)—O(11)	141.5(17)	C(12)—O(12)	146.2(18)
C(21)—O(21)	142.8(18)	C(22)—O(22)	144.3(21)
Molecule 2			
Br(1)—Mn(1)	252.7(5)	P(1)—Mn(1)	226.6(6)
P(2)—Mn(1)	226.6(6)	C(1)—Mn(1)	178.0(15)
C(2)—Mn(1)	183.4(16)	C(3)—Mn(1)	182.7(17)
O(11)—P(1)	157.3(12)	O(12)—P(1)	158.4(12)
O(13)—P(1)	159.2(11)	O(21)—P(2)	159.1(11)
O(22)—P(2)	157.1(11)	O(23)—P(2)	160.3(11)
O(13)—Si(1)	165.8(11)	O(23)—Si(1)	165.4(11)
C(4)—Si(1)	184.5(17)	C(5)—Si(1)	180.7(20)
O(1)—C(1)	116.5(16)	O(2)—C(2)	112.6(18)
O(3)—C(3)	113.9(17)		
C(21)—O(21)	142.5(17)	C(22)—O(22)	142.6(19)
C(11)—O(11)	141.7(18)	C(12)—O(12)	147.6(20)

EXPERIMENTAL

All manipulations of air- and/or moisture-sensitive compounds were carried out under dry nitrogen using Schlenk and cannula techniques. Solvents were pre-dried over either sodium wire, calcium chloride or 4 Å molecular sieves before reflux and subsequent distillation under argon from a suitable drying agent (given in parentheses): THF, diethyl ether and pentane (sodium benzophenone ketyl), toluene (sodium metal) and dichloromethane (calcium hydride). All solvents were deoxygenated before use. Elemental analyses were performed by the Microanalytical Laboratory of this department. IR spectra were recorded between KBr windows using a Perkin–Elmer 257 grating spectrophotometer. NMR spectra were obtained on JEOL FX90Q, JEOL FX100 and Bruker AM400 instruments. Benzene-d$_6$ was dried by passage down a column of basic alumina (Brockmann Grade I) and was deoxygenated before use. Spectra were referenced internally using the residual solvent resonance for ^1H (C_6D_6, 7.15 ppm) and ^{13}C (C_6D_6, 128.0 ppm) relative to tetramethylsilane at 0 ppm, and externally for ^{31}P using 85% H_3PO_4 as 0 ppm. All spectra are reported at 298 K; the ^{13}C and ^{31}P spectra being run under conditions of broad-band ^1H decoupling unless noted otherwise. The compounds $(R^1O)_2P(=O)H$, $Cl_2SiR^2R^3$ and norbornadiene (NBD) were purchaed from commercial sources and were distilled prior to use. Triethylamine was purified by passage down a short column of basic alumina (Brockmann Grade I). $MnBr(CO)_5$[28] and $Mo(CO)_4(NBD)$[29] were prepared and purified using published procedures.

General synthesis of $[(R^1O)_2PO]_2SiR^2R^3$

The specific details relating to the preparations of **1**–**10** are presented in Table 1, but the general procedure is the same for each: $Cl_2SiR^2R^3$ was added dropwise at ambient temperature to a stirred mixture of $(R^1O)_2P(O)H$ and NEt_3 in toluene solvent. After stirring for an appropriate amount of time (see Table 1), the mixture was filtered and the residue washed liberally with pentane. The filtrate and combined washings were then reduced *in vacuo* to a liquid residue in which is invariably suspended small quantities of the $NHEt_3Cl$ salt. Extraction of the liquid into pentane, filtration and subsequent removal of the volatiles under reduced pressure afforded the products as clear mobile liquids. We have found that both pentane and THF are acceptable substitutes for toluene in these syntheses, although the reactions are generally slower in THF possibly due to competition between $(RO)_2P(=O)H$ and the solvent for coordination sites on silicon (see Scheme 3 for possible mechanisms).

Synthesis of fac-$[MnBr(CO)_3\{P(OMe)_2O\}_2SiMe_2]$ (**11**)

A solution of **1** (2.28 cm^3, 0.32 M solution, 0.73 mmol) in toluene was added to a suspension of $MnBr(CO)_5$ (0.2 g, 0.73 mmol) in toluene (10 cm^3) at room temperature. Within 5 min, the remaining yellow solid had dissolved to an orange solution. After stirring overnight the mixture was filtered, concentrated under reduced pressure and cooled to −35°C to afford the product **11** as yellow crystals which were isolated, washed with pentane and dried *in vacuo*. Yield 0.21 g, 59%. Found: C, 21.8; H, 3.7. Calc. for $C_9H_{18}O_9SiP_2MnBr$: C, 21.8; H, 3.7%. A similar synthetic procedure was used to prepare **12** and **13**. Yields **12**, 42%; **13**, 49%. Found for **12**:

Table 5. Bond angles (°) for **11**

	Molecule 1		
P(1)—Mn(1)—Br(1)	88.8(2)	P(2)—Mn(1)—Br(1)	87.6(2)
P(2)—Mn(1)—P(1)	89.5(2)	C(1)—Mn(1)—Br(1)	177.9(4)
C(1)—Mn(1)—P(1)	93.3(5)	C(1)—Mn(1)—P(2)	92.2(5)
C(2)—Mn(1)—Br(1)	87.1(5)	C(2)—Mn(1)—P(1)	175.6(4)
C(2)—Mn(1)—P(2)	88.7(6)	C(2)—Mn(1)—C(1)	90.8(7)
C(3)—Mn(1)—Br(1)	89.1(5)	C(3)—Mn(1)—P(1)	89.9(5)
C(3)—Mn(1)—P(2)	176.6(5)	C(3)—Mn(1)—C(1)	91.2(7)
C(3)—Mn(1)—C(2)	91.7(7)		
O(11)—P(1)—Mn(1)	119.6(5)	O(12)—P(1)—Mn(1)	112.6(4)
O(12)—P(1)—O(11)	100.8(6)	O(13)—P(1)—Mn(1)	116.9(4)
O(13)—P(1)—O(11)	100.7(6)	O(13)—P(1)—O(12)	103.8(6)
O(21)—P(2)—Mn(1)	118.2(5)	O(22)—P(2)—Mn(1)	112.1(5)
O(22)—P(2)—O(21)	101.0(6)	O(23)—P(2)—Mn(1)	118.0(5)
O(23)—P(2)—O(21)	100.4(6)	O(23)—P(2)—O(22)	104.9(6)
O(23)—Si(1)—O(13)	106.6(6)	C(4)—Si(1)—O(13)	110.7(8)
C(4)—Si(1)—O(23)	108.3(7)	C(5)—Si(1)—O(13)	108.1(8)
C(5)—Si(1)—O(23)	108.2(8)	C(5)—Si(1)—C(4)	114.6(9)
O(1)—C(1)—Mn(1)	179.7(5)	O(2)—C(2)—Mn(1)	177.9(13)
O(3)—C(3)—Mn(1)	178.3(13)		
C(11)—O(11)—P(1)	121.8(9)	C(12)—O(12)—P(1)	123.9(9)
Si(1)—O(13)—P(1)	134.8(6)	C(21)—O(21)—P(2)	124.2(11)
C(22)—O(22)—P(2)	121.2(11)	Si(1)—O(23)—P(2)	136.3(6)
	Molecule 2		
P(1)—Mn(1)—Br(1)	89.0(2)	P(2)—Mn(1)—Br(1)	89.1(2)
P(2)—Mn(1)—P(1)	88.2(2)	C(1)—Mn(1)—Br(1)	179.2(4)
C(1)—Mn(1)—P(1)	90.6(6)	C(1)—Mn(1)—P(2)	91.5(5)
C(2)—Mn(1)—Br(1)	88.9(5)	C(2)—Mn(1)—P(1)	176.6(4)
C(2)—Mn(1)—P(2)	89.1(5)	C(2)—Mn(1)—C(1)	91.6(7)
C(3)—Mn(1)—C(2)	91.7(7)	C(3)—Mn(1)—Br(1)	86.4(5)
C(3)—Mn(1)—P(1)	90.8(6)	C(3)—Mn(1)—P(2)	175.4(4)
C(3)—Mn(1)—C(1)	93.0(7)		
O(21)—P(2)—Mn(1)	119.3(5)	O(22)—P(2)—Mn(1)	111.7(5)
O(22)—P(2)—O(21)	100.9(6)	O(23)—P(2)—Mn(1)	117.0(4)
O(23)—P(2)—O(21)	101.3(6)	O(23)—P(2)—O(22)	104.5(6)
O(11)—P(1)—Mn(1)	120.8(5)	O(12)—P(1)—Mn(1)	110.6(5)
O(12)—P(1)—O(11)	100.0(6)	O(13)—P(1)—Mn(1)	117.4(5)
O(13)—P(1)—O(11)	101.0(6)	O(13)—P(1)—O(12)	104.6(6)
O(23)—Si(1)—O(13)	107.8(6)	C(4)—Si(1)—O(13)	110.0(7)
C(4)—Si(1)—O(23)	109.0(7)	C(5)—Si(1)—O(13)	109.3(8)
C(5)—Si(1)—O(23)	107.1(8)	C(5)—Si(1)—C(4)	113.5(9)
O(1)—C(1)—Mn(1)	177.1(13)	O(2)—C(2)—Mn(1)	177.4(14)
O(3)—C(3)—Mn(1)	176.5(13)		
C(11)—O(11)—P(1)	125.4(11)	C(12)—O(12)—P(1)	123.4(10)
Si(1)—O(13)—P(1)	136.5(6)	C(21)—O(21)—P(2)	122.1(9)
C(22)—O(22)—P(2)	121.9(10)	Si(1)—O(23)—P(2)	132.4(6)

C, 36.7; H, 3.6. Calc. for $C_{19}H_{22}O_9SiP_2MnBr$: C, 36.8; H, 3.6%. Found for **13**: C, 30.1; H, 3.6. Calc. for $C_{14}H_{20}O_9SiP_2MnBr$: C, 30.2; H, 3.6 %.

Synthesis of $Mo(CO)_4[P(OMe)_2O]_2SiMe_2$ (**14**)

A solution of $[(MeO)_2PO]_2SiMe_2$ in pentane (1.58 cm^3, 0.34 M solution, 0.54 mmol) was added to $Mo(CO)_4(NBD)$ (0.16 g, 0.53 mmol) dissolved in pentane (10 cm^3). The resulting yellow solution became cloudy within seconds and then lightened in colour after 1 h stirring at room temperature. After 24 h at room temperature, the mixture was filtered, the filtrate concentrated to 2 cm^3 and then cooled to −78°C for *ca* 15 min at which point a pale yellow crystalline solid formed. Upon warming the vessel to −35°C, colourless crystals of the desired product formed over the course of *ca* 1 h. These were collected and dried *in vacuo*. Yield 0.26 g, 76%. Found: C, 25.0; H, 3.9. Calc. for $C_{10}H_{18}O_{10}SiP_2Mo$: C, 24.8; H, 3.7%. Compound **17** was prepared in an analogous manner, but could only be isolated as an oil (see Results and Discussion).

Synthesis of $[Mo(CO)_4\{P(OMe)_2O\}_2SiPh_2]$ (**15**)

A solution of $[(MeO)_2PO]_2SiPh_2$ in pentane (2.24 cm^3, 0.24 M solution, 0.54 mmol) was added to $Mo(CO)_4(NBD)$ (0.16 g, 0.53 mmol) dissolved in pentane (10 cm^3). The resulting pale yellow solution began to turn cloudy within seconds of diphosphite addition, and a white, powdery precipitate was observed to settle out after *ca* 1 h. After stirring at room temperature for a further 4 h, the supernatant was decanted off and the solid residue redissolved in CH_2Cl_2. Subsequent cooling of this solution to −35°C for several hours afforded the product as colourless crystals. Yield 0.25 g, 77%. Found: C, 39.6; H, 3.6. Calc. for $C_{20}H_{22}O_{10}SiP_2Mo$: C, 39.5; H, 3.6%.

Synthesis of $Mo(CO)_4[P(OMe)_2O]_2SiMePh$ (**16**)

A solution of $[(MeO)_2PO]_2SiMePh$ in pentane (1.68 cm^3, 0.31 M solution, 0.52 mmol) was added to $Mo(CO)_4(NBD)$ (0.15 g, 0.50 mmol) dissolved in pentane (10 cm^3). After 10 min at room temperature the initially pale yellow solution became lighter and after 1 h a brown precipitate was observed. The mixture was filtered after 6 h stirring at room temperature and all volatiles removed under reduced pressure to afford a white solid. This solid was redissolved in the minimum of CH_2Cl_2 (*ca* 2 cm^3) and layered with pentane (5 cm^3). Subsequent cooling of this solution to −35°C afforded the product as colourless crystals. Yield 0.22 g, 79%. Found: C, 33.2; H, 3.8. Calc. for $C_{15}H_{20}O_{10}SiP_2Mo$: C, 33.0; H, 3.7%.

Single crystal X-ray diffraction analysis

All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω–θ scan mode using graphite monochromated Mo-K_α radiation. The data set was corrected for absorption semi-empirically using azimuthal psi scans.

The structure was determined by direct methods using SHELXS[30] and was refined by full-matrix least-squares refinement using the SHELX 76 program system.[31] The solution gave two independent molecules in the asymmetric part of the unit cell which were found to differ principally by a rotation of *ca* 15° of one of the methoxo groups [O(21)—C(21)] of the phosphite chelate. Due to the limited amount of data, only the heaviest atoms were assigned anisotropic thermal parameters; all other non-hydrogen atoms were included in calculated positions (C—H = 96 pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o)+0.0004(F_o)^2]^{-1}$ was used. Final non-hydrogen atomic coordinates are given in Table 4.

Crystal data. $C_9H_{18}BrMnO_9P_2Si$, $M = 495.11$, orthorhombic, space group $P2_12_12_1$, $a = 887.0(1)$, $b = 1548.0(3)$, $c = 2785.0(3)$ pm, $U = 3.8240(9)$ nm^3, $Z = 2$, $D_x = 1.71$ Mg m^{-3}, $\mu = 21.61$ cm^{-1}, $F(000) = 1983.93$.

Data collection. $4.0 < 2\theta < 50.0°$, 3829 data collected, 2741 with $I > 2.0\sigma(I)$ considered observed, $T = 240$ K.

Structure refinement. Number of parameters = 272, $R = 0.0570$, $R_w = 0.0596$.

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REFERENCES

1. (a) C. A. McAuliffe, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Ch. 14. Pergamon, Oxford (1978); (b) L. H. Pignolet (Editor), *Homogeneous Catalysis with Metal–Phosphine Complexes*. Plenum Press, New York (1983).
2. Much early work, however, has been done with related chelating ligands such as the diphosphonites $[(RO)_2PCH_2]_2$ and the pyrophosphites $(RO)_2POP(OR)_2$. See, for example: (a) R. B. King and W. M. Rhee, *Inorg. Chem.* 1978, **17**, 2961; (b) F. A. Cotton, R. J. Haines, B. E. Hanson and J. C. Seku-

towski, *Inorg. Chem.* 1978, **17**, 2010; (c) R. Carreno, V. Riera and M. A. Ruiz, *J. Organomet. Chem.* 1991, **419**, 163.

3. P. W. N. M. Van Leeuwen and C. F. Roobeek, *J. Organomet. Chem.* 1983, **258**, 343.
4. P. W. N. M. Van Leeuwen and C. F. Roobeek, *Tetrahedron* 1981, **37**, 1973.
5. (a) M. J. Baker, K. N. Harrison, A. G. Orpen, P. G. Pringle and G. Shaw, *J. Chem. Soc., Chem. Commun.* 1991, 803; (b) M. J. Baker and P. G. Pringle, *J. Chem. Soc., Chem. Commun.* 1991, 1292.
6. (a) J. R. Bleeke, A. J. Donaldson and W.-J. Peng, *Organometallics* 1988, **7**, 33; (b) D. J. Wink, T. J. Kwok and A. Yee, *Inorg. Chem.* 1990, **29**, 5006.
7. Union Carbide Euro. Pat., 214622 A2 (1988): *Chem. Abstr.* 1987, **107**, 25126m.
8. (a) K. M. Cooke, T. P. Kee, A. L. Langton and M. Thornton-Pett, *J. Organomet. Chem.* 1991, **419**, 171; (b) T. P. Kee and M. T. Patel, *Polyhedron* 1992, **11**, 135.
9. We have also observed that the ^{31}P NMR resonances of the monophosphites $(RO)_2POSiR'_3$ generally occur at high frequency compared with those of the corresponding diphosphites $[(RO)_2PO]_2SiR'_2$; N. Greene and T. P. Kee, unpublished results.
10. K. Hayashi, J. Iyoda and I. Shiihara, *J. Organomet. Chem.* 1967, **10**, 81.
11. D. A. Armitage, in *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone and E. W. Abel), Ch. 9.1, p. 15. Pergamon Press, New York (1982).
12. D. G. Gorenstein (Editor), *Phosphorus-31 NMR: Principles and Applications*, Ch. 18. Academic Press, New York (1984).
13. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th edn, p. 175. John Wiley, New York (1981).
14. D. A. Redfield, J. H. Nelson and L. W. Cary, *Inorg. Nucl. Chem. Lett.* 1974, **10**, 727.
15. I. J. Colquhoun and W. McFarlane, *J. Chem. Soc., Dalton Trans.* 1982, 1915.
16. (a) A. Tzschach, K. Kellner, U. Thust, P. Kemter, E. Hillert and C. Fieseler, D.D.R. Pat., 247,825 A1 (1987): *Chem. Abstr.* 1987, **108**, 182213a; (b) K. Kellner, L. Rodewald, A. Tzschach, U. Thust and P. Kemter, D.D.R. Pat., 270,076 A1 (1989): *Chem. Abstr.* 1989, **112**, 139574q.
17. R. Rabinowitz, *J. Org. Chem.* 1963, **28**, 2975.
18. J. Chojnowski, M. Cypryk and J. Michalski, *J. Organomet. Chem.* 1978, **161**, C31.
19. K. Moedritzer, *J. Inorg. Nucl. Chem.* 161, **22**, 19.
20. R. J. Angelici, F. Basolo and A. J. Poe, *J. Am. Chem. Soc.* 1963, **85**, 2215.
21. M. P. Doyle and C. T. West, *J. Am. Chem. Soc.* 1975, **97**, 3777.
22. G. M. Gray and K. A. Redmill, *J. Organomet. Chem.* 1985, **280**, 105.
23. G. M. Gray and K. A. Redmill, *Magnet. Reson. Chem.* 1986, **24**, 519.
24. G. M. Bodner and L. J. Todd, *Inorg. Chem.* 1974, **13**, 1335.
25. (a) T. G. Appleton, M. A. Bennett and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.* 1976, 439; (b) B. R. James, D. Mahajan, S. J. Rettig and G. M. Williams, *Organometallics* 1983, **2**, 1452; (c) M. F. Hallam, N. D. Howells, D. M. P. Mingos and R. W. M. Wardle, *J. Chem. Soc., Dalton Trans.* 1985, 845.
26. (a) M. R. Churchill and S. A. Bezman, *Inorg. Chem.* 1973, **12**, 531; (b) N. F. Cole, F. A. Cotton, G. L. Powell and T. J. Smith, *Inorg. Chem.* 1983, **22**, 2618; (c) W. L. Steffen and G. J. Palenik, *Inorg. Chem.* 1976, **15**, 2432; (d) Q. B. Bao, A. L. Rheingold and T. B. Brill, *Organometallics* 1986, **5**, 2259; (e) G. J. Palenik, M. Mathew, W. L. Steffen and G. Beran, *J. Am. Chem. Soc.* 1975, **97**, 1059.
27. G. M. Gray, F. P. Fish, D. K. Srivastava, A. Varshney, M. J. van der Woerd and S. E. Ealick, *J. Organomet. Chem.* 1990, **385**, 49.
28. M. H. Quick and R. J. Angelici, *Inorg. Synth.* 1979, **19**, 160.
29. M. A. Bennett, L. Pratt and G. Wilkinson, *J. Chem. Soc.* 1961, 2037.
30. G. M. Sheldrick, SHELXS 86, Program System for X-Ray Structure Solution, University of Göttingen, F.R.G. (1986).
31. G. M. Sheldrick, SHELXS 76, Program System for X-Ray Structure Determination, University of Cambridge, Cambridge, U.K. (1976).