

Journal of Organometallic Chemistry, 419 (1991) 171–180
 Elsevier Sequoia S.A., Lausanne
 JOM 22080

Silylphosphinites and their complexation to manganese. Crystal structure of *cis*-MnBr(CO)₄[P(4-CH₃C₆H₄)₂OSiMe₃]

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(Received June 3rd, 1991)

Abstract

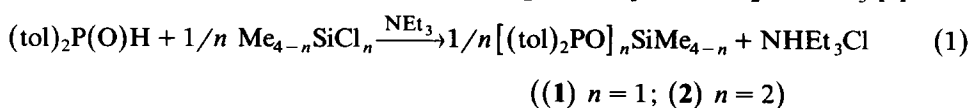
The new silylphosphinites, (4-CH₃C₆H₄)₂POSiMe₃(L) and [(4-CH₃C₆H₄)₂PO]₂SiMe₂(L-L) have been synthesised along with the manganese complexes *cis*-MnBr(CO)₄L, *trans,mer*-MnBr(CO)₃L₂ and *fac*-MnBr(CO)₃(L-L). The results of a single crystal X-ray diffraction study of *cis*-MnBr(CO)₄L are also reported.

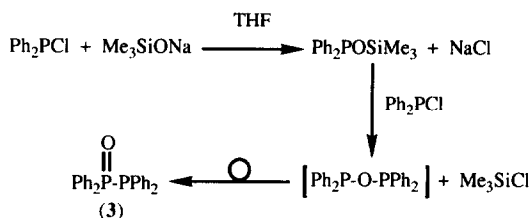
Although the coordination chemistry of functionalised organophosphorus ligands has been widely investigated [1], relatively little is known about the chemistry of transition metal coordinated phosphinite compounds (R₂POR'; R' = alkyl, aryl, ...) [2]. These compounds are of interest since the presence of both hard (oxygen) and soft (phosphorus) donor atoms may allow the coordination of two disparate metals to a single R₂PO-unit; for instance an oxophilic, early transition metal bound to oxygen and a later metal coordinated to phosphorus. In this regard, the trimethylsilyl substituted phosphinites R₂POSiMe₃, are particularly attractive given the lability of the Me₃Si-function of other Me₃SiX compounds (X = OSiMe₃, OMe, OEt, ORcO₃, SSiMe₃, C₅Me₅) in reactions with early transition metal halides [3]. Here we report our initial studies on the synthesis and coordination chemistry of two silylated phosphinites, (tol)₂POSiMe₃ (**1**) and [(tol)₂PO]₂SiMe₂ (**2**) (tol = 4-CH₃C₆H₄) in which only the phosphorus atoms are coordinated to the metal.

Results and discussion

Synthesis of silylphosphinites

The silylphosphinites (tol)₂POSiMe₃ (**1**) and [(tol)₂PO]₂SiMe₂ (**2**) are readily prepared in high yield (typically 70–90%) by the reaction of (tol)₂P(O)H with Me₃SiCl or Me₂SiCl₂ respectively in the presence of triethylamine (eq. 1); a procedure similar to that used to prepare Ph₂POSiMe₃ and ⁿBu₂POSiMe₃ [4].





Scheme 1.

If less than the stoichiometric amount of $(\text{tol})_2\text{P}(\text{O})\text{H}$ is used in the synthesis of **2**, an intermediate phosphinite is observable by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy with a single resonance at δ 103.4 ppm (benzene- d_6). We believe this species to be $(\text{tol})_2\text{POSiMe}_2\text{Cl}$ since upon further treatment with $(\text{tol})_2\text{P}(\text{O})\text{H}$ and NEt_3 it is completely converted to **2**.

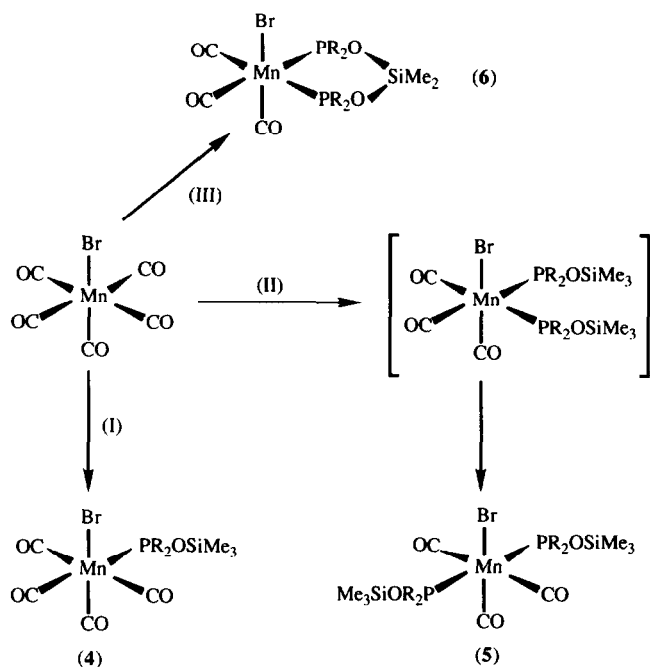
Both **1** and **2** are clear, viscous liquids which hydrolyze readily upon exposure to moist air, in both cases regenerating $(\text{tol})_2\text{P}(\text{O})\text{H}$. Full spectroscopic data for **1** and **2** are collected in Table 1 where it can be seen that the phosphorus nuclei resonate at δ 97.1 and 99.3 ppm respectively in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, consistent with a three coordinate phosphinite structure $\text{R}_2\text{POR}'$, rather than the four coordinate phosphine oxide form, $\text{R}_2\text{P}(\text{O})\text{R}'$ [5]; therefore it was anticipated that these phosphinite compounds would act as phosphorus donors towards suitable metal centres (*vide infra*).

We have investigated other potential routes to silylphosphinite compounds but have not been able to improve upon that described above (eq. 1). For example, the reaction between Ph_2PCl and Me_3SiONa proceeds smoothly in THF solvent at room temperature to afford the known compound $\text{Ph}_2(\text{O})\text{PPPh}_2$ (**3**) [6] in 79% isolated yield. Particularly characteristic is a strong band at 1180 cm^{-1} in the IR spectrum (Nujol) due to stretching of the $(\text{P}=\text{O})$ bond and an AX pattern with resonances at δ 36.4 and -22.2 ppm ($J(\text{P}-\text{P})$ 228 Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum supportive of an unsymmetrical diphosphine compound with one phosphorus atom in a four coordinate environment the other a three coordinate environment and a direct phosphorus-phosphorus bond [7]. Presumably the desired product from this reaction, $\text{Ph}_2\text{POSiMe}_3$, is formed initially but reacts rapidly with Ph_2PCl in an Arbuzov type reaction as shown in Scheme 1. Similar condensation reactions have been noted previously [8].

Since it was reported that the silylphosphinite $(\text{CF}_3)_2\text{POSiMe}_3$ could be isolated quantitatively following prolonged reflux of $(\text{CF}_3)_2\text{PCl}$ in $(\text{Me}_3\text{Si})_2\text{O}$ solvent [9], we attempted to extend this reaction to other chlorodiorganophosphines but found the analogous reaction between Ph_2PCl and $(\text{Me}_3\text{Si})_2\text{O}$ led only to the isolation of $\text{Ph}_2(\text{O})\text{PPPh}_2$ in low (15%) yield.

Reactions of silylphosphinites with $\text{MnBr}(\text{CO})_5$

Compound **1** reacts smoothly with $\text{MnBr}(\text{CO})_5$ (1 equiv.) at room temperature in toluene solvent to afford a mixture of *cis*- $\text{MnBr}(\text{CO})_4(\text{P}(\text{tol})_2\text{OSiMe}_3)$ (**4**), *trans*, *mer*- $\text{MnBr}(\text{CO})_3(\text{P}(\text{tol})_2\text{OSiMe}_3)_2$ (**5**) and unreacted $\text{MnBr}(\text{CO})_5$ (Scheme 2) from which orange **4** could be selectively crystallised in 34% yield by addition of petroleum ether (ca. 3 vol. equivs.) and cooling to -30°C . In the ^{31}P NMR spectra of **4** and **5** the phosphorus resonances are shifted to higher frequency of uncom-



Scheme 2. (I); one equiv. $\text{R}_2\text{POSiMe}_3$, (II); two equivs. $\text{R}_2\text{POSiMe}_3$, (III); one equiv. $[\text{R}_2\text{PO}]_2\text{SiMe}_2$; $\text{R} = 4\text{-CH}_3\text{C}_6\text{H}_4$. All reactions performed in toluene solvent at room temperature.

plexed **1** (Table 1), a trend consistent with that observed for other phosphinite ligands [10]. The resonances are also significantly broadened ($\Delta_{1/2}$ ca. 100 Hz (**4**) and 45 Hz (**5**)) due to the quadrupolar effects of the ^{55}Mn nucleus ($I = 5/2$). Infrared spectroscopy (CH_2Cl_2 solution) reveals three bands in the $\nu(\text{CO})$ region for **4** in a pattern characteristic of a *cis*- $\text{MnX}(\text{CO})_4\text{L}$ compound with local C_s symmetry [11] and this geometry has been confirmed by a single crystal X-ray diffraction analysis (*vide infra*).

The $\nu(\text{CO})$ values for **4** fall between those reported for *cis*- $\text{MnBr}(\text{CO})_4(\text{P}^n\text{Bu}_3)$; 2083, 2004 and 1949 cm^{-1} and *cis*- $\text{MnBr}(\text{CO})_4(\text{PPh}_3)$; 2101, 2012 and 1965 cm^{-1} (both in CHCl_3 solution) [11], suggesting $(\text{tol})_2\text{POSiMe}_3$ to possess a stereoelectronic character intermediate to those of P^nBu_3 and PPh_3 in this system.

Compound **4** is stable to moist air in the solid state for at least 24 h at ambient temperature but is significantly more sensitive in solution generating *cis*- $\text{MnBr}(\text{CO})_4(\text{P}(\text{tol})_2\text{OH})$ upon hydrolysis [12]. Furthermore, thermolysis of a toluene solution of **4** at 100°C for over 16 h did not appear to result in Me_3SiBr elimination but the only phosphorus containing product observed after this time was **5**.

Although it did not prove possible to isolate **5** completely free of **4** from the above reaction, yellow crystalline **5** can be synthesised in 71% isolated yield by the reaction of $\text{MnBr}(\text{CO})_5$ with two equivalents of **1** at room temperature. The *trans,mer* geometry is supported by the observation of three $\nu(\text{CO})$ infrared absorption bands in a weak, very strong, strong pattern [13] and a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta\ 144.7\text{ ppm}$ but has yet to be confirmed by X-ray diffraction. Like **4**, complex **5** is stable in moist air for several hours under ambient conditions in the solid state. We were unable to observe any of the alternative *cis, fac*

Table 1

Analytical and spectroscopic data for compounds 1–6

Compound ^a	IR ^b	NMR ^c
1 Clear liquid	945s, br ν (POSi)	¹ H{ ³¹ P} ^d : 7.59 [d, 4H, <i>J</i> (H–H) 8, Ar- <i>H_o</i>]; 6.98 [d, 4H, <i>J</i> (H–H) 8, Ar- <i>H_m</i>]; 2.02 [s, 6H, Ar- <i>CH₃</i>]; 0.20 [s, 9H, Si(<i>CH₃</i>) ₃] ^e . ³¹ P{ ¹ H}: 97.1 [s]. ¹³ C{ ¹ H}: 142.1 [d, <i>J</i> (P–C) 20, Ar- <i>C_i</i>]; 138.9 [s, Ar- <i>C_o</i>]; 130.2 [d, <i>J</i> (P–C) 23, Ar- <i>C_o</i>]; 129.5 [d, <i>J</i> (P–C) 3, Ar- <i>C_m</i>]; 21.2 [s, Ar- <i>CH₃</i>]; 1.1 [d, <i>J</i> (P–C) 2, Si(<i>CH₃</i>) ₃].
2 Clear liquid	935s, br ν (POSi)	¹ H{ ³¹ P} ^d : 7.54 [d, 8H, <i>J</i> (H–H) 8, Ar- <i>H_o</i>]; 6.95 [d, 8H, <i>J</i> (H–H) 8, Ar- <i>H_m</i>]; 2.05 [s, 12H, Ar- <i>CH₃</i>]; 0.33 [s, 6H, Si(<i>CH₃</i>) ₂] ^f . ³¹ P{ ¹ H}: 99.3 [s]. ¹³ C{ ¹ H}: 141.4 [d, <i>J</i> (P–C) 20, Ar- <i>C_i</i>]; 139.0 [s, Ar- <i>C_o</i>]; 130.3 [d, <i>J</i> (P–C) 25, Ar- <i>C_o</i>]; 129.3 [m, <i>J</i> (P–C) 7, Ar- <i>C_m</i>] ^g ; 21.4 [s, Ar- <i>CH₃</i>]; 0.1 [s, Si(<i>CH₃</i>) ₂]. ³¹ P{ ¹ H}: 36.4 [d, <i>J</i> (P–P) 228, R ₂ (O)P]; –22.2 [d, <i>J</i> (P–P) 228, R ₂ P].
3 Colourless solid C, 74.35 (74.61); H, 5.25 (5.22)	1180s ν (P–O)	¹ H{ ³¹ P} ^d : 7.73 [d, 4H, <i>J</i> (H–H) 8, Ar- <i>H_o</i>]; 6.88 [d, 4H, <i>J</i> (H–H) 8, Ar- <i>H_m</i>]; 1.95 [s, 6H, Ar- <i>CH₃</i>]; 0.03 [s, 9H, Si(<i>CH₃</i>) ₃] ^h . ³¹ P{ ¹ H}: 132.5 [s].
4 Orange solid C, 45.65 (45.89) H, 4.05 (4.23)	2087s, sp, 2003s, br, 1957s, br ν (CO)	¹ H{ ³¹ P} ^d : 7.98 [d, 8H, <i>J</i> (H–H) 8, Ar- <i>H_o</i>]; 6.95 [d, 8H, <i>J</i> (H–H) 8, Ar- <i>H_m</i>]; 1.97 [s, 12H, Ar- <i>CH₃</i>]; 0.17 [s, 18H, Si(<i>CH₃</i>) ₃] ⁱ . ³¹ P{ ¹ H}: 144.7 [s].
5 Yellow solid C, 54.50 (53.95); H, 5.75 (5.63)	2032w, 1950vs, 1914s ν (CO)	¹ H{ ³¹ P}: 9.94 [m, 4H, <i>J</i> (H–H) 8, Ar- <i>H_o</i>]; 7.67 [m, 4H, <i>J</i> (H–H) 8, Ar- <i>H_o</i>]; 6.95 [m, 8H, Ar- <i>H_m</i>]; 1.97 [s, 12H, Ar- <i>CH₃</i>]; 0.67 [s, 3H, Si- <i>CH₃</i>]; –0.10 [s, 3H, Si- <i>CH₃</i>] ^j . ³¹ P{ ¹ H}: 137.7 [s].
6 Yellow solid C, 53.60 (53.89); H, 4.60 (4.66)	2026s, 1957s, 1913s, ν (CO)	

^a Microanalysis as: Found (calc.) in %. ^b In cm^{–1} with w = weak, s = strong, vs = very strong, sp = sharp, br = broad. Data collected as thin films (1 and 2), Nujol mull (3) or as a solution in CH₂Cl₂ (4, 5 and 6).

^c Given as: chemical shift (δ) [multiplicity, relative intensity, *J* in Hz, assignment]. All data collected at room temperature in benzene-*d*₆ except 3 (chloroform-*d*). ^d The proton resonances in the aryl region form an AA'BB' system in which *J*(A–B) is much greater than all other *J*'s resulting in a pattern resembling an AB system. Shifts and couplings have been calculated on the basis of the latter.

^e *J*(²⁹Si–H) 6. ^f *J*(²⁹Si–H) 8. ^g Pattern is a five line multiplet from a virtually coupled AXX' spin system with [*J*(A–X) + *J*(A–X')] 7. ^h *J*(²⁹Si–H) 7. ⁱ *J*(²⁹Si–H) 7. ^j No coupling to ²⁹Si resolved.

or *cis,mer* isomers in the synthesis of 5, but monitoring the reaction of 4 with excess 1 by ³¹P{¹H} NMR spectroscopy (benzene-*d*₆) revealed an intermediate manganese phosphinite complex with a single resonance at δ 135.6 ppm which appeared to be produced before significant quantities of 5 were seen but upon complete consumption of 4 comprised less than 10% of the product mixture (> 90% being 5). It is possible that this species is the thermodynamically less stable *cis,fac* isomer.

A *cis,fac* geometry is favoured by the chelating diphosphinite 2, one equivalent of which reacts with MnBr(CO)₅ to yield MnBr(CO)₃{[P(tol)₂O]₂SiMe₂} (6) in 50% yield (Scheme 2). The observations of three strong ν (CO) bands in the IR spectrum (CH₂Cl₂), a single resonance at δ 137.7 in the ³¹P{¹H} NMR spectrum and diastereotopic methyl groups on the silicon atom (¹H NMR) are supportive of the *cis,fac* geometry [13]. Coupling to the quadrupolar ⁵⁵Mn nucleus results in broadening of the ³¹P resonance ($\Delta_{1/2}$ ca. 65 Hz) in the room temperature ³¹P{¹H} NMR spectrum. Complexes of molybdenum with the related diphosphinites [Ph₂PO]₂Si-

MeR (R = Me, Ph) have been reported recently from the reaction of $[\text{NHEt}_3][\text{cis-Mo}(\text{CO})_4\{\text{Ph}_2\text{PO}\}_2\text{H}]$ with MeRSiCl_2 in the presence of NEt_3 [14].

The molecular structure of cis-MnBr(CO)₄(P(tol)₂OSiMe₃) (4)

The molecular structure is displayed in Fig. 1, and selected intramolecular distances and angles and atomic coordinates are reproduced in Tables 2 and 3, respectively.

As suggested from the IR data, **4** possesses a distorted octahedral structure with a *cis* disposition of bromo and phosphinite ligands. Similar geometries have been reported for other $\text{MnBr}(\text{CO})_4\text{L}$ complexes [15]. Figure 1b shows the conformation adopted by the phosphinite ligand which presumably reflects a compromise between having the bromine atom fully staggered with respect to the phosphorus phenyl substituents and preventing the trimethylsiloxy moiety eclipsing the carbonyl C(3)–O(3): this results in a torsional angle of $22.2(2)^\circ$ between the vectors P(1)–O(5) and Mn(1)–C(3).

The average C–O (110.8(23) pm) and Mn–C (185.0(18) pm) distances are unexceptional; the Mn–Br bond length of 250.3(4) pm is comparable to that reported for *cis*- $\text{MnBr}(\text{CO})_4(\text{C}=\text{PPh}_3)$ (250.7(8) pm) [15b] and the Mn–P bond is only slightly shorter (by ca. 7 pm) than that reported for *cis*- $\text{MnCl}(\text{CO})_4(\text{PPh}_3)$ [15a]. The presence of differential *trans* influences between carbonyl, bromo and phosphinite ligands is presumably reflected in the distances Mn(1)–C(1)/C(4) (187.8(11) pm average), Mn(1)–C(3) (180.6(7) pm) and Mn(1)–C(2) (183.8(7) pm) which are supportive of a *trans* influence order $\text{CO} > (\text{tol})_2\text{POSiMe}_3 > \text{Br}$.

Within the phosphinite ligand itself the average substituent angle subtended at phosphorus is $103.8(7)^\circ$, significantly less than the sp^3 tetrahedral angle of 109.5° but comparable to that found for coordinated PPh_3 in $[\text{Au}(\text{PPh}_3)_3]^+$ (103.8°) [16]. The trimethylsilyl group is somewhat disordered, resulting in large esd values and making a detailed discussion of these parameters inappropriate. Although a search of the Cambridge Crystallographic Database revealed a number of alkylphosphinite complexes, no examples of monodentate silylphosphinite complexes appear to have

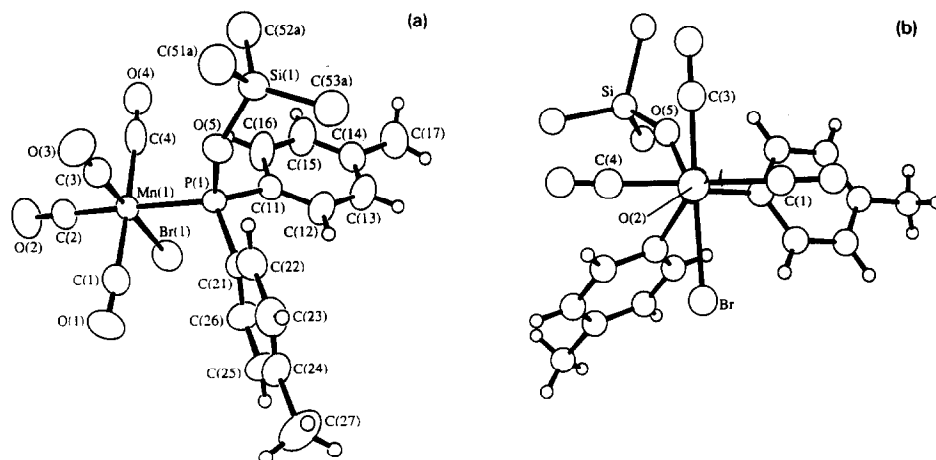


Fig. 1. (a) The molecular structure of **4**; (b) view along O(2)–C(2)–Mn(1)–P(1) vector.

Table 2

Selected bond lengths (pm) and angles (°) for **4**

Br(1)–Mn(1)	250.3(4)	P(1)–Mn(1)–Br(1)	87.9(1)
P(1)–Mn(1)	232.3(3)	C(1)–Mn(1)–P(1)	91.1(2)
C(1)–Mn(1)	186.7(6)	C(2)–Mn(1)–P(1)	175.1(1)
C(2)–Mn(1)	183.8(7)	C(3)–Mn(1)–Br(1)	177.2(1)
C(3)–Mn(1)	180.6(7)	C(3)–Mn(1)–C(1)	91.2(3)
C(4)–Mn(1)	188.9(7)	C(4)–Mn(1)–Br(1)	93.7(2)
		C(4)–Mn(1)–C(1)	178.2(2)
		C(4)–Mn(1)–C(3)	88.4(3)
		C(1)–Mn(1)–Br(1)	86.7(2)
C(11)–P(1)	184.0(4)	C(2)–Mn(1)–Br(1)	87.6(2)
C(21)–P(1)	182.5(4)	C(2)–Mn(1)–C(1)	90.3(3)
O(5)–P(1)	158.5(5)	C(3)–Mn(1)–P(1)	90.4(2)
		C(3)–Mn(1)–C(2)	94.2(3)
		C(4)–Mn(1)–P(1)	90.7(2)
		C(4)–Mn(1)–C(2)	87.9(3)
O(5)–Si(1)	167.6(5)		
C(51)–Si(1)	190.5(35)	C(11)–P(1)–Mn(1)	119.7(2)
C(52)–Si(1)	188.5(53)	C(21)–P(1)–C(11)	103.2(2)
C(53)–Si(1)	185.3(11)	O(5)–P(1)–C(11)	105.1(2)
		C(21)–P(1)–Mn(1)	114.7(2)
		O(5)–P(1)–Mn(1)	109.4(2)
		O(5)–P(1)–C(21)	103.1(2)
		C(12)–C(12)–P(1)	120.1(2)
C(17)–C(14)	152.6(7)	C(17)–C(14)–C(13)	120.0(3)
C(27)–C(24)	152.1(7)	C(16)–C(11)–P(1)	119.4(2)
		C(17)–C(14)–C(15)	119.9(3)
		Si(1)–O(5)–P(1)	147.0(2)
		C(22)–C(21)–P(1)	120.8(2)
		C(27)–C(24)–C(23)	120.9(4)
		C(26)–C(21)–P(1)	119.2(2)
		C(27)–C(24)–C(25)	119.1(4)
O(1)–C(1)	113.3(6)		
O(2)–C(2)	112.8(6)	O(1)–C(1)–Mn(1)	176.5(4)
O(3)–C(3)	113.3(6)	O(3)–C(3)–Mn(1)	178.8(4)
O(4)–C(4)	103.8(6)	O(2)–C(2)–Mn(1)	178.3(4)
		O(4)–C(4)–Mn(1)	175.9(4)

been reported, thus making direct comparisons difficult. Nonetheless, the phosphorus–aryl distances P(1)–C(11) (184.0(4) pm) and P(1)–C(21) (182.5(4) pm) in **4** are within the range commonly found for coordinated diphenylphosphinite ligands [17] and the P(1)–O(5) bond length of 158.5(5) pm falls at the short end of the range for analogous distances in other phosphinite complexes (ca. 158–165 pm) [18]. This latter may reflect differences in hybridisation of the oxygen atom, which should in turn manifest itself in variations within the P–O–R angle. Indeed, the P(1)–O(5)–Si(1) angle of 147.0(2)° in **4** (cf. Mo–O–Si = 146.6(4)° in [MoS₃(OSiMe₃)][–] [19]) is significantly above the normally observed range of ca. 119–128° found in Ph₂POR (R = Me, Et) complexes [17a,18a,20], consistent with a P–O bond comprising a greater oxygen *s*-orbital contribution.

Table 3

Atomic coordinates for **4** ($\times 10^4$)

	x	y	z
Mn(1)	389.0(6)	6162.0(5)	2372.4(5)
Br(1)	1648.1(5)	7949.0(5)	2121.0(4)
P(1)	-1561(1)	7603(1)	3200(1)
Si(1)	-4465(1)	7330(1)	2858(1)
C(11)	-1910(3)	9217(2)	2623(2)
C(12)	-2601(3)	10230(2)	3338(2)
C(13)	-3008(3)	11424(2)	2881(2)
C(14)	-2726(3)	11605(2)	1709(2)
C(15)	-2036(3)	10592(2)	994(2)
C(16)	-1628(3)	9398(2)	1451(2)
C(17)	-3210(6)	12902(5)	1207(5)
C(21)	-1702(3)	7873(2)	4712(2)
C(22)	-2762(3)	7526(2)	5508(2)
C(23)	-2854(3)	7742(2)	6660(2)
C(24)	-1887(3)	8305(2)	7016(2)
C(25)	-828(3)	8652(2)	6220(2)
C(26)	-735(3)	8436(2)	5068(2)
C(27)	-1993(9)	8585(5)	8264(4)
O(5)	-2883(3)	7055(3)	3157(2)
C(1)	948(4)	5870(4)	3767(4)
O(1)	1338(4)	5644(4)	4588(3)
C(2)	1991(5)	5138(4)	1663(4)
O(2)	2984(4)	4535(4)	1213(3)
C(3)	-549(5)	4895(4)	2625(4)
O(3)	-1128(4)	4092(3)	2765(3)
C(4)	-133(5)	6413(4)	942(4)
O(4)	-389(4)	6483(3)	144(3)

Experimental

All reactions and manipulations were carried out under dry nitrogen by standard Schlenk and vacuum-line techniques. Solvents were pre-dried over either sodium wire, calcium chloride or 4 Å molecular sieves before reflux and distillation from sodium/benzophenone (THF, 40–60 °C petroleum ether), sodium metal (toluene) or calcium hydride (CH_2Cl_2) under an atmosphere of argon and were deoxygenated before use. Elemental analyses were performed by the Microanalytical Laboratory in this department. Infrared spectra were recorded between KBr windows on a Perkin–Elmer 257 Grating Spectrophotometer. NMR spectra were recorded on JEOL FX90Q, JEOL FX100 or Bruker AM 400 instruments. Spectra were referenced internally using the residual solvent resonance (^1H and ^{13}C) relative to tetramethylsilane at 0 ppm or referred to 85% H_3PO_4 (^{31}P). Me_3SiCl , NEt_3 , Me_2SiCl_2 , $(\text{Me}_3\text{Si})_2\text{O}$, benzene- d_6 and Ph_2PCl were purchased from Aldrich and were either distilled from calcium hydride (Me_3SiCl , Me_2SiCl_2), purified by passage down a short column of basic (Brockmann Grade I) alumina (NEt_3 , $(\text{Me}_3\text{Si})_2\text{O}$, benzene- d_6), or distilled (Ph_2PCl) prior to use. The compounds, $(\text{tol})_2\text{P}(\text{O})\text{H}$ [21] and $\text{MnBr}(\text{CO})_5$ [22] were prepared according to published procedures.

Synthesis of $(\text{tol})_2\text{POSiMe}_3$ (1)

Me_3SiCl (0.34 g, 3.1 mmol) was added from syringe to a stirred solution of $(\text{tol})_2\text{P(O)H}$ (0.52 g, 2.3 mmol) and NEt_3 (0.32 g, 3.2 mmol) in toluene (25 cm³) at room temperature in a glass ampoule (100 cm³ capacity) fitted with a Teflon tap. Upon addition the mixture warmed slightly and a precipitate formed immediately. After 6 h stirring at room temperature the mixture was heated to 80 °C for 12 h. Upon cooling to room temperature the mixture was filtered and the gelatinous filter cake washed liberally with light petroleum ether (40 cm³). Subsequent removal of all volatiles *in vacuo* afforded $(\text{tol})_2\text{POSiMe}_3$ as a clear liquid, shown to be > 95% pure by $^1\text{H}\{^{31}\text{P}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, which proved suitable for synthetic work without further purification. Yield, 0.55 g (80%).

Synthesis of $[(\text{tol})_2\text{PO}]_2\text{SiMe}_2$ (2)

Me_2SiCl_2 (0.12 g, 0.93 mmol) was added at room temperature to a mixture of $(\text{tol})_2\text{P(O)H}$ (0.43 g, 1.87 mmol) and NEt_3 (0.20 g, 1.98 mmol) in toluene (25 cm³) in a glass ampoule (100 cm³ capacity) fitted with a Teflon tap. Immediate precipitation occurred. After stirring for 16 h at room temperature the mixture was heated to 80 °C for 6 h. Upon cooling, the mixture was filtered and the residue washed with light petroleum ether (50 cm³). The filtrate and washings were combined and all volatiles removed *in vacuo* to leave $[(\text{tol})_2\text{PO}]_2\text{SiMe}_2$ as a clear viscous liquid that proved sufficiently pure for further work. Yield, 0.35 g (72%).

Reaction of Ph_2PCl with Me_3SiONa . Synthesis of $\text{Ph}_2(\text{O})\text{PPPh}_2$ (3)

A solution of Me_3SiONa (0.56 g, 5.0 mmol) in THF (25 cm³) was added dropwise at room temperature to a solution of Ph_2PCl (1.1 g, 5.0 mmol) in THF (10 cm³). Within several seconds the solution became cloudy as a gelatinous precipitate formed. After stirring for 24 h at room temperature the mixture was filtered, the residue washed with light petroleum ether (30 cm³) and the volatiles removed to afford 3 as a white solid. Recrystallisation from toluene gave analytically pure, colourless crystals of $\text{Ph}_2(\text{O})\text{PPPh}_2$. Yield, 0.76 g (79% based on Ph_2PCl).

Reaction of Ph_2PCl with $(\text{Me}_3\text{Si})_2\text{O}$

A mixture of Ph_2PCl (1.0 g, 4.5 mmol) and $(\text{Me}_3\text{Si})_2\text{O}$ (3.68 g, 22.7 mmol) was heated to 100 °C in a thick walled glass ampoule fitted with a Teflon tap. After ca. 16 h white crystals were seen lining the vessel walls and after 2 d were visible in the bulk solution. After 5 d the mixture was cooled to room temperature and light petroleum ether added (ca. 10 cm³) resulting in the precipitation of a white solid. This solid was isolated by filtration, washed with petroleum ether (10 cm³) and dried *in vacuo*. IR and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies identified the solid as $\text{Ph}_2(\text{O})\text{PPPh}_2$. Yield, 0.13 g (15% based on Ph_2PCl).

Synthesis of *cis*- $\text{MnBr}(\text{CO})_4(\text{P}(\text{tol})_2\text{OSiMe}_3)$ (4)

A solution of $(\text{tol})_2\text{POSiMe}_3$ in toluene (0.96 cm³, 0.38 M, 0.36 mmol) was added at room temperature to a stirred suspension of $\text{MnBr}(\text{CO})_5$ (0.10 g, 0.36 mmol) in toluene (10 cm³). The mixture was stirred for 12 h whereupon it was filtered and the filtrate concentrated to a deep orange solution (ca. 3 cm³). This solution was layered with light petroleum ether (ca. 9 cm³) and cooled to -30 °C for > 24 h affording orange crystals of *cis*- $\text{MnBr}(\text{CO})_4(\text{P}(\text{tol})_2\text{OSiMe}_3)$. Yield, 67 mg (34%).

Synthesis of *trans,mer*- $\text{MnBr}(\text{CO})_3(\text{P}(\text{tol})_2\text{OSiMe}_3)_2$ (**5**)

To a stirred suspension of $\text{MnBr}(\text{CO})_5$ in toluene (0.10 g, 0.36 mmol in 15 cm³) at room temperature was added a solution of $(\text{tol})_2\text{POSiMe}_3$ in toluene (4.73 cm³, 0.154 M, 0.73 mmol). The remaining solid dissolved to a yellow solution. After stirring for 16 h the solution was filtered and carefully concentrated to a deep orange solution (3 cm³), layered with light petroleum ether (5 cm³) and cooled to -78°C to afford yellow crystals of *trans,mer*- $\text{MnBr}(\text{CO})_3(\text{P}(\text{tol})_2\text{OSiMe}_3)_2$ which were isolated, washed with cold (-30°C) petroleum ether and dried in *vacuo*. Yield, 0.21 g (71%).

Synthesis of *fac*- $\text{MnBr}(\text{CO})_3\{[\text{P}(\text{tol})_2\text{O}]_2\text{SiMe}_2\}$ (**6**)

A toluene solution of $[(\text{tol})_2\text{PO}]_2\text{SiMe}_2$ (4.29 cm³, 0.17 M, 0.73 mmol) was added to a stirred suspension of $\text{MnBr}(\text{CO})_5$ (0.20 g, 0.73 mmol) in toluene (ca. 15 cm³) at room temperature. The remaining solid dissolved to a yellow solution within 5 min. After stirring for a further 12 h the solution was filtered, concentrated to ca. 3 cm³ and cooled to -35°C for 48 h to afford the product as yellow crystals, which were washed with cold (-30°C) light petroleum ether (10 cm³) and dried in *vacuo*. Yield 0.27 g (51%).

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 ψ scans.

The structure was determined *via* standard heavy atom (for the Br atom) and Fourier techniques and was refined by full-matrix least-squares using the SHELX program system [23]. All non-hydrogen atoms were refined with anisotropic thermal parameters with the exception of the methyl substituents of the $\{-\text{SiMe}_3\}$ groups. These were found to be rotationally disordered (about the $\text{O}(5)-\text{Si}(1)$ vector) over three positions and so the carbon atom in each position refined with an isotropic thermal parameter and an occupancy factor of 1/3. The phenyl groups were treated as rigid bodies with idealised hexagonal symmetry ($\text{C}-\text{C} = 139.5$ pm). All hydrogen atoms were included in calculated positions ($\text{C}-\text{H} = 96$ pm) and were refined with an overall isotropic thermal parameter. The weighting scheme $w^{-1} = [\sigma^2(F_o) + 0.0004(F_o)^2]$ was used. Final non-hydrogen atomic co-ordinates are given in Table 3.

Complete lists of bond length and angles, a tables of anisotropic thermal parameters, and lists of structure factors are available from the authors.

Crystal data

$\text{C}_{21}\text{H}_{23}\text{BrMnO}_5\text{PSi}$, $M = 549.31$, triclinic, $P\bar{1}$, a 1014.46(11), b 1079.35(11), c 1201.84(13) pm, α 87.727(7), β 78.696(8), γ 78.049(6)°, $U = 1.265(2)$ nm⁻³, $Z = 2$, $D_x = 1.45$ g cm⁻³, $\lambda(\text{Mo-K}_\alpha) = 71.069$ pm, $\mu = 21.61$ cm⁻¹, $F(000) = 555.98$.

Data collection

Scan widths $1.05^\circ + \alpha$ -doublet splitting, scan speeds $1.5\text{--}8.0^\circ \text{ min}^{-1}$, $4.0 < 2\theta < 50.0^\circ$. 4103 Data collected, 3223 with $I > 2.0\sigma(I)$ considered observed, $T = 200$ K.

Structure refinement

Number of parameters = 263, $R = 0.0373$, $R_w = 0.0403$.

Acknowledgment

We wish to thank Dr. I.J. Hart and Mr. J.P. Mitchell for helpful comments.

References

- 1 T.B. Rauchfuss, in L.S. Pignolet (Ed.), *Homogeneous Catalysis with Metal Phosphine Complexes*, Plenum, New York, 1983.
- 2 D.M. Roundhill, R.P. Sperline and W.B. Beaulieu, *Coord. Chem. Rev.*, 26 (1978) 263.
- 3 (a) V.C. Gibson, A. Shaw and D.N. Williams, *Polyhedron*, 8 (1989) 549; (b) V.C. Gibson, T.P. Kee and A. Shaw, *Polyhedron*, 9 (1990) 2293; (c) V.C. Gibson and T.P. Kee, *J. Chem. Soc., Chem. Commun.*, (1989) 656; (d) V.C. Gibson and T.P. Kee, unpublished results; (e) G.H. Llinas, M. Mena, F. Palacios, P. Royo and R. Serrano, *J. Organomet. Chem.*, 340 (1988) 37.
- 4 (a) K. Issleib and B. Walther, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 88; (b) F. Mares, W.J. Boyle and A.M. Corbo, *J. Catal.*, 107 (1987) 407.
- 5 K. Moedritzer, *J. Inorg. Nucl. Chem.*, 22 (1961) 19.
- 6 J. McKechnie, D.S. Payne and W. Sim, *J. Chem. Soc.*, (1965) 3500.
- 7 D.G. Gorenstein (Ed.), *Phosphorus-31 NMR: Principles and Applications*, Academic Press, New York, 1984, Chap. 18.
- 8 V.I. Foss, B.A. Solobenko and I.F. Lutsenko, *Zh. Obshch. Khim.*, 49 (1979) 2418.
- 9 A.B. Burg and J.S. Basi, *J. Am. Chem. Soc.*, 90 (1968) 3361.
- 10 R.T. DePue, D.B. Collum, J.W. Ziller and M.R. Churchill, *J. Am. Chem. Soc.*, 107 (1985) 2131.
- 11 R.J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, 84 (1962) 2495.
- 12 A.L. Langton and T.P. Kee, unpublished results.
- 13 R.J. Angelici, F. Basolo and A.J. Poe, *J. Am. Chem. Soc.*, 85 (1963) 2215.
- 14 G.M. Gray and K.A. Redmill, *J. Organomet. Chem.*, 280 (1985) 105.
- 15 (a) H. Vahrenkamp, *Chem. Ber.*, 104 (1971) 449; (b) S.Z. Goldberg, E.N. Duesler and K.N. Raymond, *Inorg. Chem.*, 11 (1972) 1397; (c) M. Green, J.R. Moss, I.W. Nowell and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1972) 1339.
- 16 C.A. Tolman, *Chem. Rev.*, 77 (1977) 313.
- 17 (a) E. Lindner, G. Von Au, H.-J. Eberle and S. Hoehne, *Chem. Ber.*, 115 (1982) 513; (b) D.R. Powell and R.A. Jacobson, *Cryst. Struct. Commun.*, 9 (1980) 1023.
- 18 (a) S. Vastas, L. Marko and A.L. Rheingold, *J. Organomet. Chem.*, 372 (1989) 141; (b) R.P. Gould, C.L. Jones, W.J. Sime and T.A. Stephenson, *J. Chem. Soc., Dalton Trans.*, (1977) 669; (c) G.M. Gray, F.P. Fish, D.K. Srivastava, A. Varshney, M.J. Van der Woerd and S.E. Ealick, *J. Organomet. Chem.*, 385 (1990) 49.
- 19 Y. Do, E.D. Simhon and R.H. Holm, *Inorg. Chem.*, 24 (1985) 1831.
- 20 (a) N.J. Taylor and A.J. Carty, *J. Chem. Soc., Dalton Trans.*, (1976) 799; (b) T.V. Ashworth, O.C. Liles and E. Singleton, *Organometallics*, 3 (1984) 1851.
- 21 B.B. Hunt and B.C. Saunders, *J. Chem. Soc.*, (1957) 2413.
- 22 M.H. Quick and R.J. Angelici, *Inorg. Synth.*, 19 (1979) 160.
- 23 G.M. Sheldrick, *SHELX76*, Program System for X-Ray Structure Determination, University of Cambridge, 1976.