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Silylphosphinites and their complexation to manganese. Crystal structure of *cis*-$MnBr(CO)_4[P(4\text{-}CH_3C_6H_4)_2OSiMe_3]$

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Abstract

The new silylphosphinites, $(4\text{-}CH_3C_6H_4)_2POSiMe_3$(L) and $[(4\text{-}CH_3C_6H_4)_2PO]_2SiMe_2$(L–L) have been synthesised along with the manganese complexes *cis*-$MnBr(CO)_4L$, *trans,mer*-$MnBr(CO)_3L_2$ 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 (R_2POR'; 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 R_2PO-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 $R_2POSiMe_3$, are particularly attractive given the lability of the Me_3Si-function of other Me_3SiX compounds ($X = OSiMe_3$, OMe, OEt, $OReO_3$, $SSiMe_3$, C_5Me_5) in reactions with early transition metal halides [3]. Here we report our initial studies on the synthesis and coordination chemistry of two silylated phosphinites, $(tol)_2POSiMe_3$ (**1**) and $[(tol)_2PO]_2SiMe_2$ (**2**) (tol = $4\text{-}CH_3C_6H_4$) in which only the phosphorus atoms are coordinated to the metal.

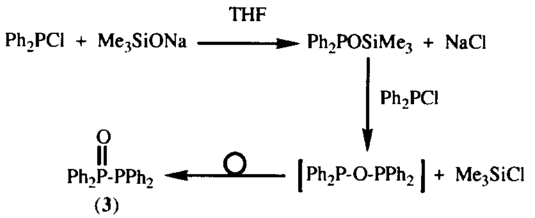
Results and discussion

Synthesis of silylphosphinites

The silylphosphinites $(tol)_2POSiMe_3$ (**1**) and $[(tol)_2PO]_2SiMe_2$ (**2**) are readily prepared in high yield (typically 70–90%) by the reaction of $(tol)_2P(O)H$ with Me_3SiCl or Me_2SiCl_2 respectively in the presence of triethylamine (eq. 1); a procedure similar to that used to prepare $Ph_2POSiMe_3$ and $^nBu_2POSiMe_3$ [4].

$$(tol)_2P(O)H + 1/n\ Me_{4-n}SiCl_n \xrightarrow{NEt_3} 1/n[(tol)_2PO]_nSiMe_{4-n} + NHEt_3Cl \qquad (1)$$

$$((\mathbf{1})\ n = 1;\ (\mathbf{2})\ n = 2)$$



Scheme 1.

If less than the stoicheiometric amount of $(tol)_2P(O)H$ is used in the synthesis of **2**, an intermediate phosphinite is observable by $^{31}P\{^1H\}$ NMR spectroscopy with a single resonance at δ 103.4 ppm (benzene-d_6). We believe this species to be $(tol)_2POSiMe_2Cl$ since upon further treatment with $(tol)_2P(O)H$ and NEt_3 it is completely converted to **2**.

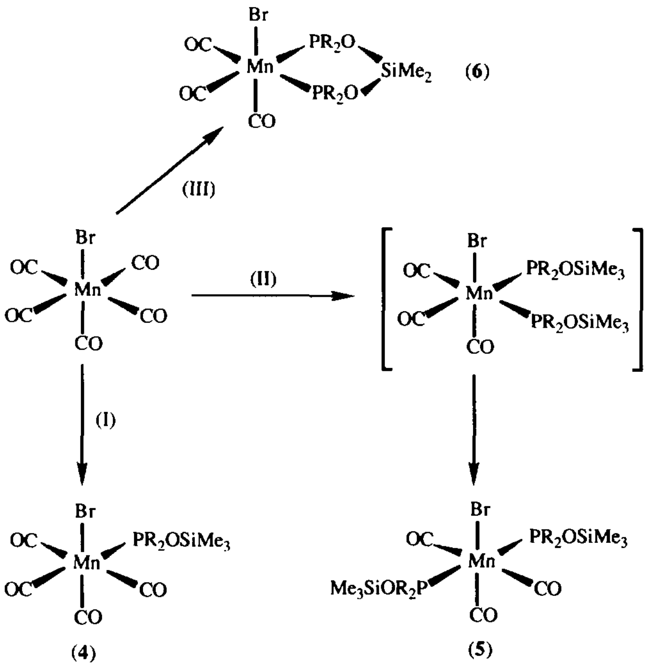
Both **1** and **2** are clear, viscous liquids which hydrolyze readily upon exposure to moist air, in both cases regenerating $(tol)_2P(O)H$. Full spectroscopic data for **1** and **2** are collected in Table 1 where it can be seen that the phosphorus nuclei resonate at δ 97.1 and 99.3 ppm respectively in the $^{31}P\{^1H\}$ NMR spectra, consistent with a three coordinate phosphinite structure R_2POR', rather than the four coordinate phosphine oxide form, $R_2P(O)R'$ [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 $Ph_2(O)PPPh_2$ (**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 (P=O) bond and an AX pattern with resonances at δ 36.4 and -22.2 ppm (J(P–P) 228 Hz) in the $^{31}P\{^1H\}$ 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, $Ph_2POSiMe_3$, 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 $(CF_3)_2POSiMe_3$ could be isolated quantitatively following prolonged reflux of $(CF_3)_2PCl$ in $(Me_3Si)_2O$ solvent [9], we attempted to extent this reaction to other chlorodiorganophosphines but found the analogous reaction between Ph_2PCl and $(Me_3Si)_2O$ led only to the isolation of $Ph_2(O)PPPh_2$ in low (15%) yield.

Reactions of silylphosphinites with MnBr(CO)$_5$

Compound **1** reacts smoothly with $MnBr(CO)_5$ (1 equiv.) at room temperature in toluene solvent to afford a mixture of *cis*-$MnBr(CO)_4(P(tol)_2OSiMe_3)$ (**4**), *trans, mer*-$MnBr(CO)_3(P(tol)_2OSiMe_3)_2$ (**5**) and unreacted $MnBr(CO)_5$ (Scheme 2) from which orange **4** could be selectivity 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. $R_2POSiMe_3$, (II); two equivs. $R_2POSiMe_3$, (III); one equiv. $[R_2PO]_2SiMe_2$; $R = 4\text{-}CH_3C_6H_4$. 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 ν(CO) region for **4** in a pattern characteristic of a *cis*-$MnX(CO)_4L$ compound with local C_s symmetry [11] and this geometry has been confirmed by a single crystal X-ray diffraction analysis (*vide infra*).

The ν(CO) values for **4** fall between those reported for *cis*-$MnBr(CO)_4(P^nBu_3)$; 2083, 2004 and 1949 cm^{-1} and *cis*-$MnBr(CO)_4(PPh_3)$; 2101, 2012 and 1965 cm^{-1} (both in $CHCl_3$ solution) [11], suggesting $(tol)_2POSiMe_3$ 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*-MnBr $(CO)_4(P(tol)_2OH)$ 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 $MnBr(CO)_5$ with two equivalents of **1** at room temperature. The *trans,mer* geometry is supported by the observation of three ν(CO) infrared absorption bands in a weak, very strong, strong pattern [13] and a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 144.7 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, J(H–H) 8, Ar-H_o]; 6.98 [d, 4H, J(H–H) 8, Ar-H_m]; 2.02 [s, 6H, Ar-CH_3]; 0.20 [s, 9H, Si(CH_3)$_3$] [e]. ^{31}P{^{1}H}: 97.1 [s]. ^{13}C{^{1}H}: 142.1 [d, J(P–C) 20, Ar-C_i]; 138.9 [s, Ar-C_p]; 130.2 [d, J(P–C) 23, Ar-C_o]; 129.5 [d, J(P–C) 3, Ar-C_m]; 21.2 [s, Ar-CH$_3$]; 1.1 [d, J(P–C) 2, Si(CH$_3$)$_3$].
2 Clear liquid	935s,br ν(POSi)	^{1}H{^{31}P} [d]: 7.54 [d, 8H, J(H–H) 8, Ar-H_o]; 6.95 [d, 8H, J(H–H) 8, Ar-H_m]; 2.05 [s, 12H, Ar-CH_3]; 0.33 [s, 6H, Si(CH_3)$_2$] [f]. ^{31}P{^{1}H}: 99.3 [s]. ^{13}C{^{1}H}: 141.4 [d, J(P–C) 20, Ar-C_i]; 139.0 [s, Ar-C_p]; 130.3 [d, J(P–C) 25, Ar-C_o]; 129.3 [m, J(P–C) 7, Ar-C_m] [g]; 21.4 [s, Ar-CH$_3$]; 0.1 [s, Si(CH$_3$)$_2$].
3 Colourless solid C, 74.35 (74.61); H, 5.25 (5.22)	1180s ν(P=O)	^{31}P{^{1}H}: 36.4 [d, J(P–P) 228, R$_2$(O)P]; −22.2 [d, J(P–P) 228, R$_2$$P$].
4 Orange solid C, 45.65 (45.89) H, 4.05 (4.23)	2087s,sp, 2003s, br, 1957s,br ν(CO)	^{1}H{^{31}P} [d]: 7.73 [d, 4H, J(H–H) 8, Ar-H_o], 6.88 [d, 4H, J(H–H) 8, Ar-H_m]; 1.95 [s, 6H, Ar-CH_3]; 0.03 [s, 9H, Si(CH_3)$_3$] [h]. ^{31}P{^{1}H}: 132.5 [s].
5 Yellow solid C, 54.50 (53.95); H, 5.75 (5.63)	2032w, 1950vs, 1914s ν(CO)	^{1}H{^{31}P} [d]: 7.98 [d, 8H, J(H–H) 8, Ar-H_o]; 6.95 [d, 8H, J(H–H) 8, Ar-H_m]; 1.97 [s, 12H, Ar-CH_3]; 0.17 [s, 18H, Si(CH_3)$_3$] [i]. ^{31}P{^{1}H}: 144.7 [s].
6 Yellow solid C, 53.60 (53.89); H, 4.60 (4.66)	2026s, 1957s, 1913s, ν(CO)	^{1}H{^{31}P}: 9.94 [m, 4H, J(H–H) 8, Ar-H_o]; 7.67 [m, 4H, J(H–H) 8, Ar-H_o]; 6.95 [m, 8H, Ar-H_m]; 1.97 [s, 12H, Ar-CH_3]; 0.67 [s, 3H, SiCH_3]; −0.10 [s, 3H, SiCH_3] [j]. ^{31}P{^{1}H}: 137.7 [s].

[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 CH$_2$Cl$_2$ (**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(^{29}Si–H) 6. [f] J(^{29}Si–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(^{29}Si–H) 7. [i] J(^{29}Si–H) 7. [j] No coupling to ^{29}Si resolved.

or *cis,mer* isomers in the synthesis of **5**, but monitoring the reaction of **4** with excess **1** by ^{31}P{^{1}H} 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 table *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)$_2$O]$_2$SiMe$_2$} (**6**) in 50% yield (Scheme 2). The observations of three strong ν(CO) bands in the IR spectrum (CH$_2$Cl$_2$), a single resonance at δ 137.7 in the ^{31}P{^{1}H} NMR spectrum and diastereotopic methyl groups on the silicon atom (^{1}H NMR) are supportive of the *cis,fac* geometry [13]. Coupling to the quadrupolar ^{55}Mn nucleus results in broadening of the ^{31}P resonance ($\Delta_{1/2}$ ca. 65 Hz) in the room temperature ^{31}P{^{1}H} NMR spectrum. Complexes of molybdenum with the related diphosphinites [Ph$_2$PO]$_2$Si-

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

The molecular structure of cis-*MnBr(CO)$_4$(P(tol)$_2$OSiMe$_3$) (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 MnBr(CO)$_4$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 trimethylsiloxo moiety eclipsing the carbonyl C(3)–O(3): this results in a torsional angle of 22.2(2)^0 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*-MnBr(CO)$_4$(C=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*-MnCl(CO)$_4$(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 CO > (tol)$_2$POSiMe$_3$ > Br.

Within the phosphinite ligand itself the average substituent angle subtended at phosphorus is 103.8(7) °, significantly less than the sp^3 tetrahedral angle of 109.5 ° but comparable to that found for coordinated PPh$_3$ in [Au(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

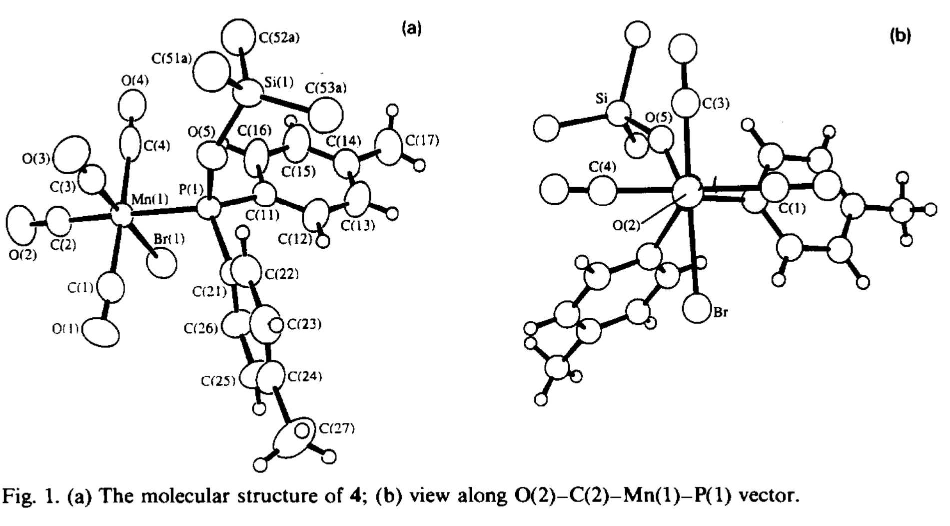


Fig. 1. (a) The molecular structure of 4; (b) view along O(2)–C(2)–Mn(1)–P(1) vector.

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)
O(5)–Si(1)	167.6(5)	C(4)–Mn(1)–C(2)	87.9(3)
C(51)–Si(1)	190.5(35)		
C(52)–Si(1)	188.5(53)	C(11)–P(1)–Mn(1)	119.7(2)
C(53)–Si(1)	185.3(11)	C(21)–P(1)–C(11)	103.2(2)
		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)
O(1)–C(1)	113.3(6)	C(27)–C(24)–C(25)	119.1(4)
O(2)–C(2)	112.8(6)		
O(3)–C(3)	113.3(6)	O(1)–C(1)–Mn(1)	176.5(4)
O(4)–C(4)	103.8(6)	O(3)–C(3)–Mn(1)	178.8(4)
		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. Nontheless, 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 $[MoS_3(OSiMe_3)]^-$ [19]) is significantly above the normally observed range of ca. 119–128° found in Ph_2POR (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 refered to 85% H_3PO_4(^{31}P). Me_3SiCl, NEt_3, Me_2SiCl_2, $(Me_3Si)_2O$, 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, $(Me_3Si)_2O$, benzene-d_6), or distilled (Ph_2PCl) prior to use. The compounds, $(tol)_2P(O)H$ [21] and $MnBr(CO)_5$ [22] were prepared according to published procedures.

Synthesis of $(tol)_2POSiMe_3$ *(1)*

Me_3SiCl (0.34 g, 3.1 mmol) was added from syringe to a stirred solution of $(tol)_2P(O)H$ (0.52 g, 2.3 mmol) and NEt_3 (0.32 g, 3.2 mmol) in toluene (25 cm^3) at room temperature in a glass ampoule (100 cm^3 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 cm^3). Subsequent removal of all volatiles *in vacuo* afforded $(tol)_2POSiMe_3$ as a clear liquid, shown to be $> 95\%$ pure by $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR spectroscopy, which proved suitable for synthetic work without further purification. Yield, 0.55 g (80%).

Synthesis of $[(tol)_2PO]_2SiMe_2$ *(2)*

Me_2SiCl_2 (0.12 g, 0.93 mmol) was added at room temperature to a mixture of $(tol)_2P(O)H$ (0.43 g, 1.87 mmol) and NEt_3 (0.20 g, 1.98 mmol) in toluene (25 cm^3) in a glass ampoule (100 cm^3 capacity) fitted with a Teflon tap. Immediate precipitation occured. 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 cm^3). The filtrate and washings were combined and all volatiles removed *in vacuo* to leave $[(tol)_2PO]_2SiMe_2$ 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* $Ph_2(O)PPPh_2$ *(3)*

A solution of Me_3SiONa (0.56 g, 5.0 mmol) in THF (25 cm^3) was added dropwise at room temperature to a solution of Ph_2PCl (1.1 g, 5.0 mmol) in THF (10 cm^3). 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 cm^3) and the volatiles removed to afford **3** as a white solid. Recrystallisation from toluene gave analytically pure, colourless crystals of $Ph_2(O)PPPh_2$. Yield, 0.76 g (79% based on Ph_2PCl).

Reaction of Ph_2PCl *with* $(Me_3Si)_2O$

A mixture of Ph_2PCl (1.0 g, 4.5 mmol) and $(Me_3Si)_2O$ (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 cm^3) resulting in the precipitation of a white solid. This solid was isolated by filtration, washed with petroleum ether (10 cm^3) and dried *in vacuo*. IR and $^{31}P\{^1H\}$ NMR spectroscopies identified the solid as $Ph_2(O)PPPh_2$. Yield, 0.13 g (15% based on Ph_2PCl).

Synthesis of cis-$MnBr(CO)_4(P(tol)_2OSiMe_3)$ *(4)*

A solution of $(tol)_2POSiMe_3$ in toluene (0.96 cm^3, 0.38 *M*, 0.36 mmol) was added at room temperature to a stirred suspension of $MnBr(CO)_5$ (0.10 g, 0.36 mmol) in toluene (10 cm^3). The mixture was stirred for 12 h whereupon it was filtered and the filtrate concentrated to a deep orange solution (ca. 3 cm^3). This solution was layered with light petroleum ether (ca. 9 cm^3) and cooled to −30 °C for > 24 h affording orange crystals of *cis*-$MnBr(CO)_4(P(tol)_2OSiMe_3)$. Yield, 67 mg (34%).

Synthesis of trans,mer-*$MnBr(CO)_3(P(tol)_2OSiMe_3)_2$ (5)*

To a stirred suspension of $MnBr(CO)_5$ in toluene (0.10 g, 0.36 mmol in 15 cm^3) at room temperature was added a solution of $(tol)_2POSiMe_3$ in toluene (4.73 cm^3, 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 cm^3), layered with light petroleum ether (5 cm^3) and cooled to −78 °C to afford yellow crystals of *trans,mer*-$MnBr(CO)_3(P(tol)_2OSiMe_3)_2$ which were isolated, washed with cold (−30 °C) petroleum ether and dried *in vacuo*. Yield, 0.21 g (71%).

Synthesis of fac-*$MnBr(CO)_3\{[P(tol)_2O]_2SiMe_2\}$ (**6**)*

A toluene solution of $[(tol)_2PO]_2SiMe_2$ (4.29 cm^3, 0.17 *M*, 0.73 mmol) was added to a stirred suspension of $MnBr(CO)_5$ (0.20 g, 0.73 mmol) in toluene (ca. 15 cm^3) 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 cm^3 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 cm^3) 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 $\{-SiMe_3\}$ groups. These were found to be rotationally disordered (about the O(5)–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 (C–C = 139.5 pm). All hydrogen atoms were included in calculated positions (C–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

$C_{21}H_{23}BrMnO_5PSi$, $M = 549.31$, 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}, $\lambda(Mo\text{-}K_\alpha) = 71.069$ pm, $\mu = 21.61$ cm^{-1}, $F(000) = 555.98$.

Data collection

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

Structure refinement

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

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