Silylmethyl and related complexes

VIII *. Bis[bis(trimethyl)silylmethyl]manganese(II): its synthesis, properties, and crystal structures of its tetrahydrofuran and bis(dimethylphosphino)ethane adducts **

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Abstract

Treatment of the manganese dialkyl MnR_2 [R = $CH(SiMe_3)_2$], prepared from anhydrous $MnCl_2$ and LiR in Et_2O, with tetrahydrofuran (THF), yielded the crystalline complex [$MnR_2(THF)$] (1). It was also obtained from $MnCl_2$ and [$MgR(\mu\text{-Cl})(THF)$]$_2$ in THF. Treatment of 1 with (Me_2PCH_2)$_2$ (DMPE) afforded [$MnR_2(DMPE)$] (2). Selected bond lengths and angles for 1 (2 in brackets) are Mn–C 2.06(2) [2.17(1)] and Mn–O 2.19(2) [Mn–P 2.775(4)] Å, C–Mn–C' 160.1(9) [141.4(7)], O–Mn–C 100.0(6)° [P–Mn–C 98.7(4) and 112.1(3), and P–Mn–P' 74.4(1)°]. Compound 1 is also a monomer in n-C_5H_{12}. Its magnetic behaviour is consistent with high spin Mn(II), and its EPR spectrum (like that of 2) at ambient temperature in THF showed a broad singlet (g_{av} = 2.005 for 1). Various reactions of complex 1 have been carried out: PMe_3 gave [$MnR_2(PMe_3)_2$], ArOH gave $Mn(OAr)_2$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4), and M[$N(SiMe_3)_2$]$_2$ gave MR_2(M = Sn or Pb) (providing particularly convenient route to these Group 14 metal alkyls).

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* For Part VII, see ref. 1. No reprints available.
** Dedicated to Professor Gordon Stone, in recognition of his important contributions to organometallic chemistry. M.F.L., his friend over many years, also wishes to pay tribute to his pivotal role in British science during the past three decades.

Introduction

Earlier parts of this series have dealt with silylmethyl derivatives of d-block elements and indium. The bis(trimethylsilyl)methyl ligand $\overline{C}H(SiMe_3)_2$ ($\equiv \overline{R}$) has featured prominently, as in the X-ray-characterised [MR_3] {M = In [1] or Cr [2]}. A related series concerned (i) subvalent Group 14 metal compounds, including the crystalline Ge_2R_4. Sn_2R_4 [3], and PbR_2 [4], (ii) the solution species $\dot{M}R_3$ (M = Si, Ge, or Sn) [5], and (iii) the gaseous $\ddot{M}R_2$ (M = Ge or Sn) [6].

Other bis(trimethylsilyl)methyls of metals and non-metals having no other anionic coligand for which diffraction data are available are LiR (a monomer in the vapour [7], but a linear polymer in the crystal [8]), LiR(PMDETA) (PMDETA = [$Me_2NCH_2CH_2]_2NMe$) [9], $(MgR_2)_\infty$ [10], M_2R_4 (M = Al [11], Ga [12a], or In [12b]), [LnR_3] (Ln = La or Sm [13]), and [UR_3] [14]; and EPR data unequivocally established that element-centred radicals $\dot{M}R_2$ (M = P or As) [15] are indefinitely stable in toluene at ambient temperature.

The structures of manganese(II) dialkyls and diaryls and some of their tertiary phosphine adducts have attracted recent attention; selected data are included in Table 1. Only one homoleptic compound, $(MnR'_2)_n$, has been demonstrated (X-ray) to be monomeric in the crystal [$n = 1$, R' = $C(SiMe_3)_3$] [16], but two others have been shown to adopt a similar linear CMnC configuration in the gas phase (at ca. 120°C and 10^{-1} Torr): R' = CH_2Bu^t [17] or R' = R = $CH(SiMe_3)_2$ [18]. Solution molecular weight measurements indicated that $n = 1$ for R' = R [18], $n = 2$ for R' = CH_2CMe_2Ph [19], $n = 3$ for R' = $C_6H_2Me_3$-2,4,6 [20], $n = 4$ for R' = CH_2Bu^t [19], and $n = \infty$ for R' = CH_2SiMe_3 [19]; X-ray data have indicated that in each of the oligomers ($n \geqslant 2$) each pair of manganese atoms has a pair of bridging $\overline{R}'$, ligands, but no numerical data on the three alkyls have been published. Several tertiary phosphine adducts such as [$Mn(CH_2CMe_2Ph)_2(PMe_3)_2$] [22], [{$MnR'(\mu$-R')$(PMe_3)$}$_2$] (R' = CH_2SiMe_3) [21], and [{$Mn(C_6H_{11})(\mu$-$C_6H_{11})$}$_2(\mu$-DMPE)] [29] are well established, Table 1.

For many of the complexes listed in Table 1 the EPR spectra were recorded, and for the most part these showed a broad signal in solution, with g_{av} ca. 2.0, consistent with a high spin d^5 metal configuration. Magnetic moment measurements supported this assignment, although for some complexes antiferromagnetic behaviour was postulated. The most detailed study has been of MnR_2, the magnetic susceptibility of which from 5 to 240 K was shown to follow the Curie–Weiss law, with $\mu_{eff} = 5.49$ BM, indicative of a monomeric high spin species [18]. For [Mn{C-($SiMe_3)_3$}$_2$], μ_{eff} was determined in C_6H_6 solution by Evans' NMR method to be 5.1 BM [16]; similar data were obtained for [$MnR'_2(DMPE)$] [R' = CH_2SiMe_3 (5.6 BM) or R' = CH_2Ph (5.9 BM)] [22]. Lower values were recorded for $Mn(CH_2Bu^t)_2$ (3.9 BM) [19], $Mn(C_6H_2Me_3$-3,4,6)$_2$ (3.69 BM), $Mn(C_6H_4NMe_2$-$o)_2$ (2.6 BM) [23], and [$MnMe_2(DMPE)$] (2.4 BM) [25], but on the basis of EPR data there were still designated as high spin d^5 complexes. By contrast, [$\overline{Mn(\overline{CH_2C_6H_4CH_2}}$-$o)(DMPE)$], has been judged to be low spin on the basis of its magnetic moment of 1.7 BM (g_{av} 2.049) [22].

Experimental

Materials and procedures

All manipulations were carried out under vacuum or high purity dinitrogen or

argon. Solvents were dried and distilled over sodium under dinitrogen. Anhydrous $MnCl_2$ was purchased from Aldrich Chemical Company and used without further purification. The neutral ligand-free complex MnR_2 was prepared as described previously [18]. Microanalyses were carried out by Butterworth Laboratories Ltd. Solution magnetic moments were measured by Evans' method in C_6D_6. EPR spectra were recorded using a Varian 104 spectrometer.

Preparation of [Mn{CH(SiMe₃)₂}₂(THF)] (1)

A solution of $[MgR(\mu\text{-}Cl)(THF)]_2$ [R = $CH(SiMe_3)_2$], prepared from RCl (10.0 g, 51.4 mmol) and magnesium powder (2.5 g, 0.10 mol) in THF [6], was added to a suspension of $MnCl_2$ (3.20 g, 25.3 mmol) in THF (10 cm³) at ca. 20°C. When the addition was completed, the mixture was stirred for ca. 18 h at ca. 20°C. The solvent was removed under reduced pressure and the residual yellow-pink solid was sublimed at 120°C and 10^{-1} Torr to give the white crystalline complex 1 (8.20 g,

Table 1

Selected X-ray (or GED) structural data on neutral manganese(II) alkyls

R'; n in [$(MnR'_2)_n$]; or $MnR'_2(L)_x$	Mn co-ordination number	⟨Mn–C⟩ (Å)	C–Mn–C (°)	Ref.
CH_2Bu^t; 1 (GED)	2	2.104(6)	180 [a]	17
$CH(SiMe_3)_2$(≡ R); 1 (GED)	2	2.01(3)	180 [a]	18
$C(SiMe_3)_3$; 1 [b]	2	2.102(4)	180	16
CH_2CMe_2Ph; 2 [c,d]	3+	[h]	[h]	19
$C_6H_2Me_3$-2,4,6; 3	3,4	2.11(1) t 2.20(2) b 2.34(1) b	122.1(4) [h] 130.2(5) [i]	20
CH_2Bu^t; 4 [c]	3,4	[h]	[h]	19
CH_2SiMe_3; ∞ [c]	4	[h]	[h]	19
[$MnR_2(THF)$] (1)	3	2.06(2)	160.1(9)	this work
[$MnR_2(DMPE)$] (2)	4	2.17(1)	141.4(7)	this work
[$Mn(CH_2C_6H_4CH_2\text{-}o)(DMPE)_2$] [e]	6	2.117(6)	84.7(2)	22
[$Mn(CH_2CMe_2Ph)_2(PMe_3)_2$] [f]	4	2.149(6)	137.9	22
[{$MnR'(\mu\text{-}R')(PMe_3)$}$_2$] [g]	4+	2.111(3) t 2.208(3) b 2.369(5) b		21
[{$Mn(CH_2SiMe_3)$-$(\mu\text{-}CH_2SiMe_3)(PMePh_2)$}$_2$]	4+	2.117(5) t 2.193(5) b 2.389(5) b		21
[{$\overline{Mn(CH_2C_6H_4NMe_2\text{-}o)}$-$(CH_2C_6H_4NMe_2\text{-}o)$}$_2$]	5	2.18 t		23
[{$Mn(C_6H_{11})(\mu\text{-}C_6H_{11})$}$_2(\mu\text{-}DMPE)$]	4	2.12(1) t 2.256(9) b 2.327(9) b		24

[a] Assumed. [b] ⟨Si–C⟩ 1.881(8) Å. [c] Unpublished work, cited in ref. 19; chain structure with $(\mu\text{-}R')_2$. [d] Evidence for η^2-Ph bonding to Mn. [e] Mn–P 2.230(2) Å (*trans* to P) and 2.298(3) Å (*trans* to C), P–Mn–P 83.2(2)°. [f] ⟨Mn–P⟩ 2.633(4) Å, P–Mn–P 96.2°. [g] R' = CH_2SiMe_3, CH_2Bu^t, or CH_2Ph (data cited in table refer to R' = CH_2SiMe_3); the abbreviations "t" and "b" refer to terminal and bridging, respectively; there is a close Mn···H contact [2.29(6) Å] involving a bridging CH_2; the compound [{$MnR'(\mu\text{-}R')(PMePh_2)$}$_2$] (R' = CH_2SiMe_3) has a similar structure. [h] Not available. [i] These refer to C(t)–Mn–C(b); the abbreviations "t" and "b" refer to terminal and bridging, respectively.

72%), m.p. 70–72°C. Compound **1** was recrystallised from pentane to give X-ray-quality single crystals. Found: C, 46.8; H, 10.4 $C_{18}H_{46}MnOSi_4$ calc.: C, 48.5; H, 10.4%. Mass spectrum (m/e; $e = 1$) [assignment]: 445 $[P]^+$, 373 $[P - THF]^+$, 358 $[MnR - Me]^+$, 215 $[MnR]^+$, 73; $\mu_{eff} = 5.89$ BM. The solution molecular weight (found: 364) by Signer's method was consistent with monomeric formulation (calc. 373). The EPR spectrum in THF at ambient temperature, like that of **2** and **3**, showed a broad singlet centred at $g = 2.005$.

Preparation of [MnR_2(DMPE)] (2)

The diphosphine ($Me_2PCH_2CH_2PMe_2$) (DMPE) (0.5 g, 3.3 mmol) was added to a solution of $[MnR_2(THF)]$ (**1**) (1.26 g, 2.8 mmol) in pentane (50 cm^3) at ca. 20°C. The colourless solution was stirred for 1 h at ca. 20°C then concentrated to ca. 20 cm^3 in vacuo and cooled, to afford colourless crystals of complex **2** (0.90 g, 61%), m.p. 125–128°C. Found: C, 43.9; H, 10.3; P., 11.85. $C_{20}H_{54}MnP_2Si_4$ calc.: C, 43.4; H, 10.5; P, 12.4%. Mass spectrum (m/e, $e = 1$) [assignment]: 373 $[P - DMPE]^+$, 358 $[MnR_2 - Me]^+$, 214 $[MnR]^+$, 73; $\mu_{eff} = 2.83$ BM.

Preparation of [MnR_2(PMe_3)_2] (3)

Trimethylphosphine (0.85 g, 11.1 mmol) was added to $[MnR_2(THF)]$ (**1**) (2.20 g, 4.94 mmol) in n-pentane (50 cm^3) at ca. 20°C. The colourless solution was concentrated to ca. 30 cm^3 then cooled to -30°C, to yield colourless crystals of complex **3** (2.31 g, 78%), m.p. 105°C. Mass spectrum (m/e, $e = 1$) [assignment]: 373 $[P - 2PMe_3]^+$, 358 $[MnR_2 - Me]^+$, 214 $[MnR]^+$, 73.

Reaction of [MnR_2(THF)] (1) with 4-Me 2,6-Bu^t_2-C_6H_2OH

A solution of complex **1** (1.10 g, 2.5 mmol) in hexane (50 cm^3) was treated with the phenol (1.10 g, 5 mmol) at 20°C. After 2 h stirring the pink mixture was filtered. The filtrate was concentrated and cooled, to give pale pink crystals of $Mn(OAr)_2$ (0.78 g, 64%), m.p. ca. 150°C dec., μ_{eff} 2.20 BM.

Reaction of [MnR_2(THF)] (1) with Sn[N(SiMe_3)_2]_2

A solution of the tin(II) amide (1.44 g, 3.3 mmol) in pentane (30 cm^3) was added to a solution of complex **1** (1.46 g, 3.3 mmol) in pentane (15 cm^3) at ca. -10°C. The deep red solution was set aside for ca. 2 h at 20°C, then concentrated and cooled, to afford deep red crystals of Sn_2R_4 (1.01 g, 71%), m.p. 113–114°C, authentic [6] ^{1}H and ^{119}Sn NMR spectra. Further concentration and cooling of the mother liquor afforded colourless, crystalline $[(Mn\{N(SiMe_3)_2\}\{\mu\text{-}N(SiMe_3)_2\})_2]$ [26].

Reaction of [MnR_2(THF)] (1) with Pb[N(SiMe_3)_2]_2

By a similar procedure to that used for Sn_2R_4, crystalline PbR_2 [4] (64%) was obtained from complex **1** (0.75 g, 1.7 mmol) and the lead(II) amide (1.0 g, 1.9 mmol).

Reaction of [MnR_2(THF)] (1) with PbCl_2

A solution of complex **1** (0.31 g, 0.70 mmol) in hexane (20 cm^3) was added to a suspension of $PbCl_2$ (0.23 g, 0.83 mmol) in C_6H_{14} (100 cm^3) at ca. 20°C. The

mixture was stirred for 36 h and then filtered. The deep purple filtrate was freed from solvent in vacuo. The purple residue was PbR_2 (0.28 g, 64%).

X-Ray data collection, structure determination, and refinement for [MnR₂(THF)] (1) and [MnR₂(DMPE)] (2) [in brackets]

Crystalline $C_{18}H_{46}MnOSi_4$ [$C_{20}H_{54}MnP_2Si_4$], $M = 445.9$ [523.9], is monoclinic [orthorhombic] with a 18.158(1) [34.648(3)], b 10.414(3) [18.574(1)], c 15.443(1) [10.221(6)] Å, $\beta = 93.66(6)°$; U 2914.1 [6577.7] Å^3, $Z = 4$ [8], D_c 1.01 [1.06] g cm^{-3}, μ(Mo-K_α) 6.0 [6.3] cm^{-1}, space group $C2/c$ [$Fdd2$]. The lattice parameters were determined from a least-squares refinement of the angular settings of 25 [25] reflections with $\theta = 11°$ [11°], accurately centred on an Enraf-Nonius CAD-4 diffractometer.

A crystal of dimensions ca. $0.3 \times 0.25 \times 0.22$ [$2.0 \times 1.0 \times 1.0$] mm was sealed in a thin-walled capillary under an atmosphere of argon. Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation, $\lambda = 0.71069$ Å.

Intensities for unique reflections with $2 < \theta < 20$ [$2 < \theta < 23°$] were measured by the $\theta/2\theta$ technique with a scan width of $\Delta\theta = (0.8 + 0.35 \tan \theta)°$ [$(1.0 + 0.35 \tan \theta)$]°, and a maximum scan time of one minute. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarisation effects and not for absorption; after averaging any equivalent reflections, 816 [932] reflections with $(F^2) > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02\ I)^2]^{1/2}/Lp$.

Non-hydrogen atoms were located using routine heavy atom methods and refined with anisotropic temperature factors by full matrix least-squares. For **1** hydrogen atoms were omitted. For **2** hydrogen atoms were held fixed at calculated positions (C–H = 1.08 Å) with isotropic temperature factors of $B = 6.0$ Å^2. For **1**, the THF ligand was disordered with alternative positions for the carbon atoms, although only one set could be refined. Refinement converged at $R = 0.11$ [0.074], $R' = 0.13$ [0.082]; the maximum shift/error was 0.2 [0.4] and the weighting scheme was $w = 1/\sigma^2(F)$. For **2** the opposite absolute structure gave $R = 0.076$, $R' = 0.084$.
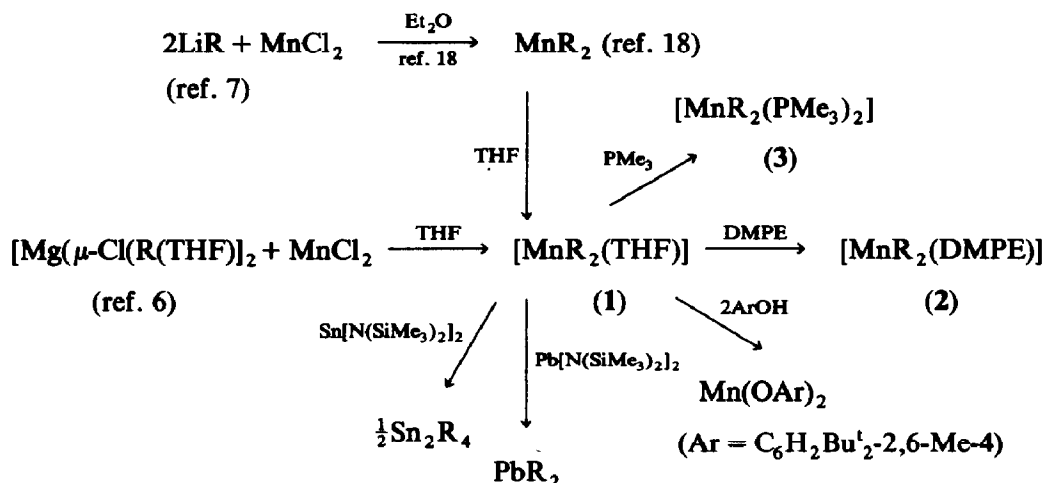
The structure solutions and refinements were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for the neutral atoms were taken from ref. 27.

The atomic coordinates, anisotropic temperature factors, and torsional angles are available on request from the Cambridge Crystallographic Data Centre, Cambridge CB2 1EW, U.K.

Results and discussion

1. Synthesis of [MnR₂(THF)] (1) and [MnR₂(DMPE)] (2) and some reactions of complex 1

The preparation of [MnR₂(THF)] (**1**) was accomplished by treating MnR_2 with tetrahydrofuran, or from the reaction between anhydrous manganese(II) chloride and the Grignard reagent $[Mg(\mu\text{-Cl})R(THF)]_2$ in THF, as indicated in Scheme 1, which also summarises some of the reactions of **1**. The compound $Mn(OAr)_2$ (Ar = $C_6H_2Bu^t_2$-2,6-Me-4) is related to its analogues (Ar = $C_6H_3Bu^t_2$-2,6 or

$$2LiR + MnCl_2 \xrightarrow[\text{ref. 18}]{\text{Et}_2\text{O}} MnR_2 \text{ (ref. 18)}$$

(ref. 7)

$$[MnR_2(PMe_3)_2]$$

THF | PMe_3 ↗ (3)

$$[Mg(\mu\text{-}Cl(R(THF)]_2 + MnCl_2 \xrightarrow{\text{THF}} [MnR_2(THF)] \xrightarrow{\text{DMPE}} [MnR_2(DMPE)]$$

(ref. 6)   Sn[N(SiMe_3)_2]_2 / (1) \ 2ArOH   (2)

Pb[N(SiMe_3)_2]_2

$$Mn(OAr)_2$$

$$\tfrac{1}{2}Sn_2R_4$$

$$(Ar = C_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$$

$$PbR_2$$

Scheme 1. The synthesis of the dialkylmanganese(II) complex [MnR_2(THF)] [R = CH(SiMe_3)_2] (1), and some of its reactions.

$C_6H_2Bu^t_3$-2,4,6) prepared previously from $Mn[N(SiMe_3)_2]_2$ and the appropriate phenol [28].

The chemistry of [MnR_2(THF)] (1) appears to be governed by (i) its energetically low-lying LUMO, (ii) the relatively ready steric access to the Lewis acid metal site by a nucleophile, and (iii) the low Mn–C bond strength. Thus, each of the reagents PMe_3, $Me_2PCH_2CH_2PMe_2$ (DMPE), ArOH (Ar = $C_6H_2Bu^t_2$-2,6-Me-4), and $M[N(SiMe_3)_2]_2$ (M = Sn or Pb) behaved as a *P*-, *O*-, or *N*-centred nucleophile. Despite the fact that tetrahydrofuran is displaced in each of the reactions of complex 1 shown in Scheme 1, the THF ligand in 1 is firmly bound to manganese. This is evident from the observation that complex 1 sublimes unchanged at ca. 120°C and 10^{-1} Torr, even though the THF-free alkyl MnR_2 can be made by another route [18]. Similarly, $(MgR_2)_2(\mu\text{-dioxane})$ is sublimable (at 160°C and 10^{-3} Torr) [6]. By contrast, THF is readily removed from $[Mn\{N(SiMe_3)_2\}_2(THF)]$ by pumping in vacuo [26].

The reactions of complex 1 could doubtless be significantly extended to include other (a) bases B [yielding $MnR_2(B)_n$], such as tertiary amines or phosphines; (b) protic compounds HA [yielding MnA_2 or $Mn(A)R$], such as alcohols, secondary or primary amines, cyclopentadienes, alkynes, or thiols; and (c) unsaturated compounds X=Y or X=Y=Z [yielding $Mn\{(XY)R\}_2$ or $Mn\{Y(X)ZR\}_2$] such as alkenes or heterocumulenes. Finally, (d) complex (1) may prove to be a useful agent for transferring the ligand $\overline{R}$ from Mn to another metal site; the yield of PbR_2 obtained from 1 and PbX_2 [X = Cl or $N(SiMe_3)_2$] is certainly superior to that achieved previously [4].

2. Magnetic susceptibility of [MnR_2(THF)] (1) (measurements by R.A. Andersen and D.J. Berg)

The measurements were carried out at 5 and 40 kG and from $T = 5$ to $T = 280$ K with an S.H.E. model 905 superconducting magnetometer (SQUID), as outlined in ref. 18. Corrected $1/\chi_M$ values were fitted to $1/\chi_M = (T - \theta)/C$ ($\mu = 2.828 \ C^{1/2}$).

Complex 1 exhibited Curie–Weiss behaviour between 5 and 280 K, with no significant field dependence. The average moment of $\mu = 5.58$ BM is reasonable for
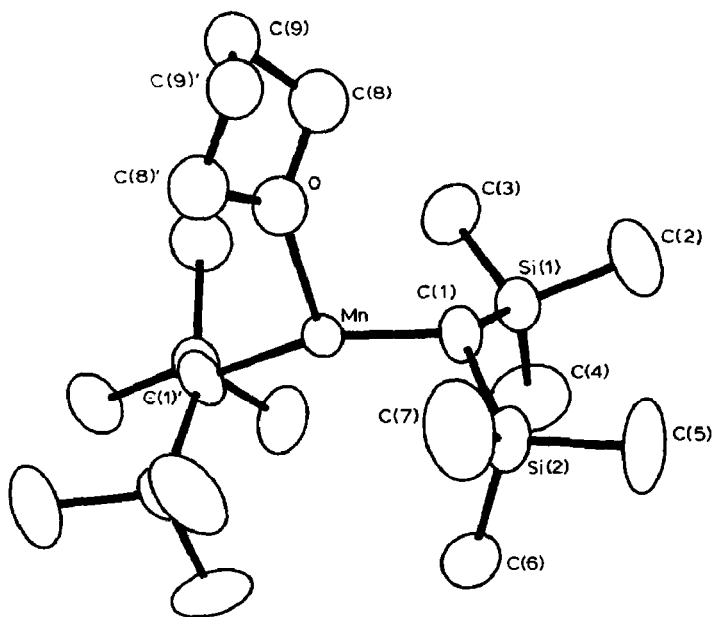
Fig. 1. The molecular structure and atom numbering scheme for [MnR$_2$(THF)] (1).

high spin manganese(II), and the small value of θ indicates that the sample is magnetically dilute (5.61 BM with $\theta = -2$ at 5 kG, and 5.55 BM with $\theta = -3$ at 40 kG).

3. X-Ray structures of [MnR$_2$(THF)] (1) and [MnR$_2$(DMPE)] (2)

The molecular structure and atom numbering scheme for each of complexes **1** and **2** is shown in Figs. 1 and 2, respectively. Both molecules lie on crystallographic
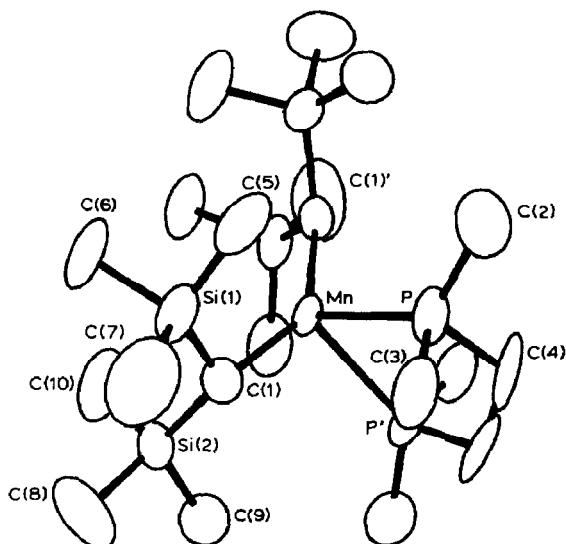

Fig. 2. The molecular structure and atom numbering scheme for [MnR$_2$(DMPE)] (2).

Table 2

Bond lengths (Å) and angles (degrees), with estimated stand: deviations in parentheses, for [MnR$_2$(THF)] (1)

Bonds

Mn–C(1)	2.06(2)	Mn–O	2.19(2)
Si(1)–C(1)	1.83(2)	Si(1)–C(2)	1.93(3)
Si(1)–C(3)	1.88(3)	Si(1)–C(4)	1.79(3)
Si(2)–C(1)	1.85(2)	Si(2)–C(5)	1.95(2)
Si(2)–C(6)	1.88(3)	Si(2)–C(7)	1.88(3)
C(9)–C(9)'	1.37(6)	O–C(8)	1.51(5)
C(8)–C(9)	1.53(7)		

Angles

C(1)–Mn–C(1)'	160.1(9)	O–Mn–C(1)	100.0(6)
Si(1)–C(1)–Si(2)	117(1)	C(1)–Si(1)–C(2)	111(1)
C(1)–Si(1)–C(3)	106(1)	C(1)–Si(1)–C(4)	115(1)
C(2)–Si(1)–C(3)	110(1)	C(2)–Si(1)–C(4)	106(2)
C(3)–Si(1)–C(4)	110(1)	C(1)–Si(2)–C(5)	116(1)
C(1)–Si(2)–C(6)	113(1)	C(1)–Si(2)–C(7)	107(1)
C(5)–Si(2)–C(6)	106(1)	C(5)–Si(2)–C(7)	105(1)
C(6)–Si(2)–C(7)	109(1)	Mn–O–C(8)	131(2)
O–C(8)–C(9)	100(3)	C(8)–O–C(8)'	98(3)
Mn–C(1)–Si(1)	112.3(9)	Mn–C(1)–Si(2)	114.1(9)
C(8)–C(9)–C(9)'	90(4)		

': at symmetry element $-x$, y, $\frac{1}{2} - z$.

Table 3

Bond lengths (Å) and angles (degrees), with estimated standard deviations in parentheses, for [MnR$_2$(DMPE)] (2)

Bonds

Mn–C(1)	2.168(12)	Mn–P	2.775(4)
P–C(2)	1.81(2)	P–C(3)	1.82(2)
P–C(4)	1.873(14)	Si(1)–C(1)	1.825(14)
Si(1)–C(5)	1.90(2)	Si(1)–C(6)	1.87(2)
Si(1)–C(7)	1.89(2)	Si(2)–C(1)	1.868(13)
Si(2)–C(8)	1.88(2)	Si(2)–C(9)	1.86(2)
Si(2)–C(10)	1.87(2)	C(4)–C(4)'	1.42(2)

Angles

P–Mn–P'	74.4(1)	P–Mn–C(1)	98.7(4)
C(1)–Mn–C(1)'	141.4(7)	P'–Mn–C(1)	112.1(3)
Mn–P–C(2)	127.6(7)	Mn–P–C(3)	111.7(6)
Mn–P–C(4)	106.3(5)	C(2)–P–C(3)	101.7(8)
C(2)–P–C(4)	103.8(8)	C(3)–P–C(4)	103.1(8)
C(1)–Si(1)–C(5)	114.0(7)	C(1)–Si(1)–C(6)	114.4(7)
C(1)–Si(1)–C(7)	112.2(8)	C(5)–Si(1)–C(6)	103.6(8)
C(5)–Si(1)–C(7)	104.9(8)	C(6)–Si(1)–C(7)	106.9(9)
C(1)–Si(2)–C(8)	114.5(9)	C(1)–Si(2)–C(9)	113.2(7)
C(1)–Si(2)–C(10)	114.1(8)	C(8)–Si(2)–C(9)	103.4(9)
C(8)–Si92)–C(10)	106(1)	C(9)–Si(2)–C(10)	104.3(8)
Mn–C(1)–Si(1)	115.0(6)	Mn–C(1)–Si(2)	116.2(6)
Si(1)–C(1)–Si(2)	113.9(7)	P–C(4)–C(4)'	112(1)

': at symmetry element $\bar{x}$, $\bar{y}$, $\bar{z}$.

Table 4

Final atomic coordinates ($\times 10^4$), with estimated standard deviations in parentheses, for [MnR$_2$(THF)] (1)

	x	y	z
Mn	0	1818(4)	2500
Si(1)	1555(4)	2856(7)	3377(5)
Si(2)	1327(4)	2895(7)	1341(5)
O	0	−285(19)	2500
C(1)	1109(10)	2161(21)	2387(11)
C(2)	2606(14)	2583(37)	3428(21)
C(3)	1142(16)	1998(29)	4301(16)
C(4)	1436(20)	4549(23)	3490(21)
C(5)	2358(12)	3307(30)	1205(20)
C(6)	797(14)	4411(24)	1093(18)
C(7)	1077(16)	1681(32)	470(16)
C(8)	486(26)	−1237(47)	3002(32)
C(9)	−18(27)	−2412(39)	2941(26)

two-fold rotation axes. Selected geometric parameters are included in Table 1 for comparison with similar data on other manganese(II) alkyls or aryls. More complete sets of bond distances and angles are found in Tables 2 and 3, and final fractional coordinates are in Tables 4 and 5.

Complex 1 is unusual in being a crystalline mononuclear three-co-ordinate manganese(II) complex, with Mn in a trigonal planar environment, C–Mn–C' 160.1(9)° and O–Mn–C 100.0(6)°. The isoelectronic compound [Mn{N-(SiMe$_3$)$_2$}$_2$(THF)] (μ_{eff} 5.91 BM) has a similar geometry [26], with both Mn and N probably (inaccurate structure) in trigonal planar environments; with the following selected bond distances and angles ⟨Mn–N⟩ 1.99(2), Mn–O 2.16(2), and ⟨N–Si⟩ 1.69(2) Å, N–Mn–N' 145 and 150, and N–Mn–O 101–113°. There is also similarity with the quasi-isoleptic magnesium complex MgR$_2$(OEt$_2$), which has Mg in a

Table 5

Final atomic coordinates ($\times 10^4$), with estimated standard deviations in parentheses, for [MnR$_2$(DMPE)] (2)

	x	y	z
Mn	0	0	0
P	481(1)	−107(2)	2162(4)
Si(1)	649(1)	1055(2)	−1538(5)
Si(2)	−194(1)	1607(2)	−1517(5)
C(1)	184(4)	1047(6)	¬702(13)
C(2)	868(6)	−741(8)	2424(21)
C(3)	718(5)	747(8)	2525(17)
C(4)	158(4)	−243(90	3610(12)
C(5)	992(5)	315(10)	−985(16)
C(6)	619(5)	925(10)	−3348(15)
C(7)	922(6)	1920(10)	−1256(23)
C(8)	−34(7)	2545(11)	−1954(25)
C(9)	−626(5)	1760(8)	−476(18)
C(10)	−392(5)	1203(12)	−3056(17)

trigonal planar environment, with the following selected bond distances and angles: $\langle Mg-C \rangle$ 2.17(1), $\langle C-Si \rangle$ 1.86(2), and Mg–O 2.07(1) Å; C–Mg–C′ 146.6(5), C–Mg–O 106.7(3)° [29].

The complexes [MnR$_2$(DMPE)] (**2**) and [Mn(CH$_2$CMe$_2$Ph)$_2$(PMe$_3$)$_2$] [22] have similar structures, based on a distorted tetrahedral manganese environment, although the P–Mn–P′ angles are rather different, viz. 74.4(1) and 96.2°, respectively, and the Mn–C and Mn–P bond lengths are ca. 0.15 Å longer for **2**. The only other mononuclear Mn(II) DMPE complex for which structural data are available is the low spin [Mn($\overline{\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2}$-o)(DMPE)], containing six-co-ordinate manganese, which, surprisingly, has a rather wider P–Mn–P angle of 83.2° [22].

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