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Attachment to manganese or cobalt of a bulky tri(organosilyl)methyl ligand containing an NMe_2 or an OMe donor group

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Abstract

The organolithium compound $Li(THF)_2\{C(SiMe_3)_2(SiMe_2NMe_2)\}$ reacted with one equivalent of $MnCl_2$ to give $[Mn(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ (**4**) and with 0.5 equivalent of $MnCl_2$ to give $Mn\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2$ together with a small amount of the Mn^{III} compound $[Mn(\mu\text{-}O)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ (**6**) formed by adventitious admission of air. With $CoBr_2$, the compound $[Co(\mu\text{-}Br)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ (**7**) was obtained. The reaction between the lithium compound $Li(THF)_2\{C(SiMe_3)_2(SiMe_2OMe)\}$ and $MnCl_2$ in THF gave $[Mn(THF)(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2OMe)\}]_2$ (**5**). The crystal structures of compounds **4**, **5**, **6** and **7** were determined. Compounds **4** and **5** are the first manganese analogues of Grignard reagents containing Mn–C σ-bonds to be characterised in the solid state. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organomanganese; Organocobalt; Bulky ligands; Grignard analogues

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1. Introduction

During the past 20 years, we and others have made extensive studies of the chemistry of organometallic compounds of Main Group and lanthanide elements containing ligands of the 'trisyl' type, i.e. with a central carbon atom bearing three organosilyl substituents [1–3]. Corresponding derivatives of the transition elements have proved to be more difficult to isolate; the only authenticated compounds are the dialkylmanganese $Mn\{C(SiMe_3)_3\}_2$ (**1**) [4], the ate complexes $[Li(THF)_4][Mn_3\{C(SiMe_3)_3\}_3Cl_4(THF)]$ (**2**) [5,6] and $Li(THF)_3(\mu\text{-}Cl)Mn\{C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$ (**3**) (THF = tetrahydrofuran) [7], an incompletely characterised cobalt compound with a structure like that of **2** [5] and the very recently described compound $Fe\{C(SiMe_3)_3\}_2$ [8].

$Mn\{C(SiMe_3)_3\}_2$

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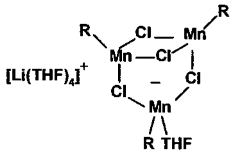
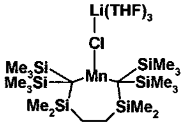


2 R = $C(SiMe_3)_3$



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In our hands, reactions of $LiC(SiMe_3)_3{\cdot}2THF$ with a range of transition metal halides gave black (probably metallic) precipitates and intractable mixtures but we found that we could isolate a series of compounds containing the bidentate ligand $C(SiMe_3)_2(SiMe_2\text{-}C_5H_4N\text{-}2)$ [9,10]. Since this appeared to prevent reduction to metallic particles by stabilising low valent organometallic compounds, we decided to look at the synthesis of transition metal derivatives containing the ligands $C(SiMe_3)_2(SiMe_2Y)$ (Y = NR_2 [11,12] or OR [13–17]), which we had recently made available, in the expectation that coordination by the group Y would lead to isolable organometallic products.

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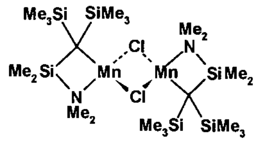

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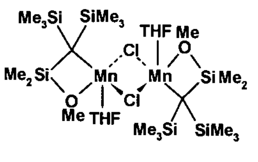

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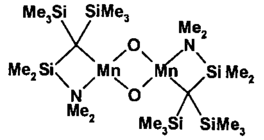

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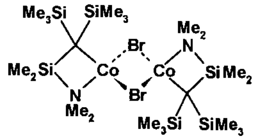

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In this paper we describe some initial results, including the crystal structures of the Mn^{II} compounds $[Mn(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ (**4**) and $[Mn(THF)(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2OMe)\}]_2$ (**5**), and the Mn^{III} derivative $[Mn(\mu\text{-}O)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ (**6**). Organomanganese halides RMnX have been employed as reagents in organic chemistry for over 60 years [18,19], particularly for the syntheses of a wide range of functionalised ketones [20–23], but they have always been prepared in situ from Grignard reagents and manganese halides and used without isolation. The compounds **4** and **5** are, as far as we are aware, the first σ-bonded compounds to be characterised in the solid state. The structures of the cyclopentadienyl derivatives $[Mn(PEt_3)Cl(C_5H_4Me)]_2$ [24,25], the alkylmanganese phosphanide $[Mn(\mu\text{-}PBu^t_2)(CH_2CMe_3)]_2$, and the aryloxide $[Mn(\mu\text{-}OAr)(CH_2CMe_2Ph)]_2$ ($Ar = C_6H_2Bu^t_3$-2,4,6) [26] have, however, been determined.

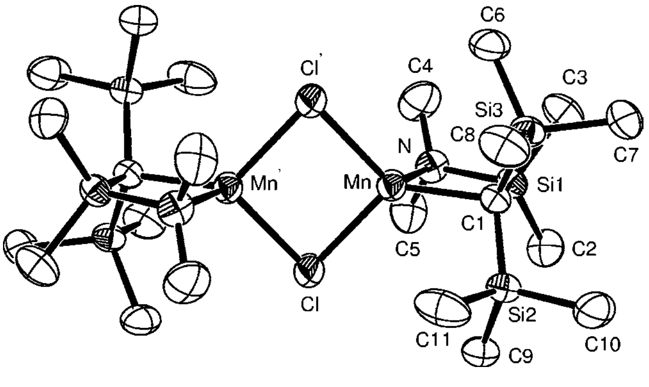


Fig. 1. Molecular structure of $[Mn(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ (**4**).

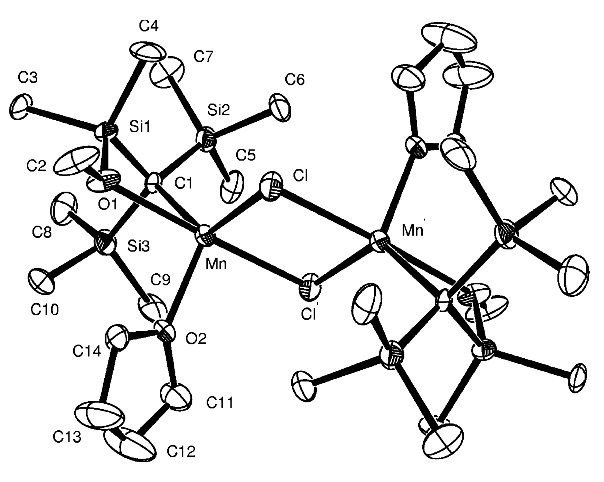
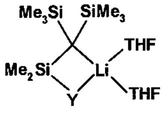


Fig. 2. Molecular structure of $[Mn(THF)(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2OMe)\}]_2$ (**5**).

The compound $[Co(\mu\text{-}Br)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2$ (**7**) has also been obtained. We are aware of only one other structurally characterised σ-bonded organocobalt(II) compound of this general type, viz $[Co(THF)(\mu\text{-}Br)\{C_6H_3(C_6H_2Me_3\text{-}2,4,6)_2\text{-}2,6\}]_2$ (**8**) [27] but the σ-bonded Co^{III} compounds $CoMe_2X(PMe_3)_3$ (X = Br or I) have been reported [28].

2. Results and discussion

2.1. Organometal(II) halides



$Mn\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2$

Y = NMe2 9; Y = OMe 11 **10**

The organolithium compound $Li(THF)_2C(SiMe_3)_2SiMe_2NMe_2$ (**9**) reacted with $MnCl_2$ in 1:1 mole ratio to give the alkylmanganese chloride **4** and in 2:1 mole ratio to give $Mn\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2$ (**10**). The reaction between $Li(THF)_2\{C(SiMe_3)_2(SiMe_2OMe)\}$ (**11**) and $MnCl_2$ in THF gave the methoxy compound **5**. The organocobalt(II) halide **7** was obtained from reaction of **9** with a molar equivalent of $CoBr_2$. We made several attempts with what appeared to be well-formed crystalline samples to obtain analytical data for compounds **4** and **5** but the carbon values were variable and low. Since similar difficulties were encountered in previous work on organomanganese halides [7,9] we think that the problems stem from the sensitivity of this class of compounds towards oxidation by traces of air. The presence of **4** was shown by a high-resolution mass spectrum and confirmed by an X-ray structure determination. The ^1H-NMR spectrum shows three broad overlapping peaks with concentration-dependent chemical shifts, but in view of the incomplete resolution and the low C analysis the presence of impurities cannot be completely ruled out. Compounds **5** and **7** were also isolated as crystalline solids and characterised by X-ray studies.

The molecules of all three compounds are centrosymmetric and their structures, shown in Figs. 1–3, contain planar rings comprising two metal and two halogen

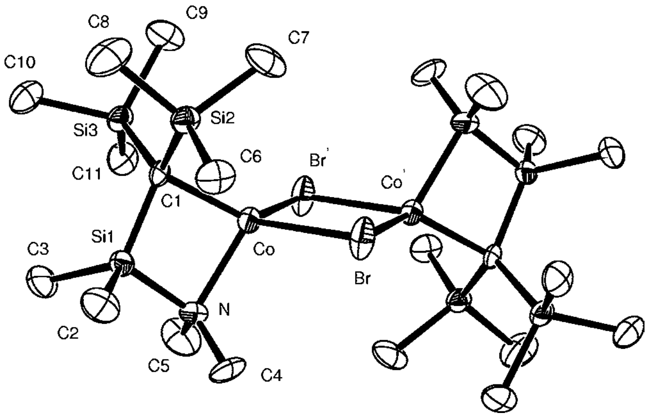


Fig. 3. Molecular structure of [Co(μ-Br){C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$)}]$_2$ (**7**).

atoms. The donor groups Y (= NMe$_2$ or OMe) of the organosilyl-substituted ligands are bound to the metal centres. The bond lengths and angles together with those in the Mn^{III} compound **6** are given in Table 1 and show that the ligand configuration is similar throughout the series. In each compound the Si(1)–C(1) bonds are shorter than the Si(2,3)–C(1) bonds and all Si–C(1) bonds are shorter than the Si–Me bonds. The C–M–N angles (81–86°) are similar to those found previously in C(SiMe$_3$)$_2$(SiMe$_2$NMe$_2$) derivatives [11,12].

We first consider the halides **4** and **7**. The NMCSi rings (M = Mn or Co) are planar (sum of angles 360.0° in **4** and 359.7° in **7**) and the NMCSi planes are approximately perpendicular to the M$_2$X$_2$ planes (X = Cl or Br) so that the configuration at the metal is distorted tetrahedral. The M–N are longer than the

Table 1

Bond lengths (Å) and angles (°) in [M(μ-X){C(SiMe$_3$)$_2$(SiMe$_2$Y)}]$_2$ (M = Mn or Co, X = Cl, Br or O, Y = NMe$_2$ or OMe)

	4	**5**	**6**	**7**
Bond lengths				
M–C	2.150(3)	2.204(11)	2.128(3)	2.065(8)
M–Y	2.201(2)	2.450(8) [a]	2.101(2)	2.087(7)
M–X	2.4398(9)	2.464(4)	1.845(2)	2.478(2)
M–X′ [b]	2.4152(9)	2.513(4)	1.803(2)	2.445(2)
Si–Y	1.831(3)	1.672(8)	1.814(2)	1.834(8)
Si(1)–C(1)	1.849(3)	1.822(12)	1.840(3)	1.849(8)
Si(2,3)–C(1) [c]	1.869(3)	1.851(12)	1.862(3)	1.873(8)
Si–Me [c]	1.879(3)	1.875(13)	1.874(3)	1.880(9)
N,O–C [c]	1.488(4)	1.420(13)	1.478(4)	1.472(12)
Bond angles				
C(1)–M–Y	82.06(10)	70.4(4)	81.37(10)	85.7(3)
C–M–X	127.15(70	127.5(3)	172.15(10)	125.9(2)
C–M–X′ [b]	132.34(7)	114.3(3)	100.10(10)	127.1(2)
Y–M–X	106.74(7)	87.1(2)	90.82(9)	107.4(2)
Y–M–X′ [b]	111.37(7)	174.3(2)	178.41(10)	116.6(2)
X–M–X′ [b]	93.74(3)	87.4(1)	87.72(10)	94.18(6)
M–X–M′ [b]	86.26(3)	92.61(12)	92.28(10)	85.82(6)
Y-Si(1)–C(1)	101.82(12)	100.5(5)	97.95(12)	100.1(3)
Y-Si(1)–C(2,3)	107.37(14) [c]	111.4(5),105.0(5) [d]	107.75(14) [c]	107.6(4) [c]
C(1)–Si–C(2,3)	117.91(14) [c]	115.6, 118.0(5) [d]	119.04(15) [c]	118.6(4) [c]
C(1)–Si–Me	112.14–114.36(15)	112.6–118.0(5)	111.27–119.06(15)	110.9 – 119.1(4)
Me–Si–Me	103.0–107.3(2)	103.7–107.1(6)	102.2–108.9(2)	103.5 – 107.1(5)
C–N–C	109.1(3)		108.4(2)	108.5(8)
Si–N,O–C	116.9(2) [c]	125.1(7)	118.16(19) [c]	117.3(7) [c]
C–N,O–M	111.6, 113.4(2)	135.6(8)	109.66(15) [c]	111.2, 114.1(6)
Si(1)–Y–M in ring	87.49(10)	88.3(3)	91.11(10)	86.8(3)
Si(1)–C–Si(2)	119.41(14)	115.2(6)	115.45(15)	120.5(4)
Si(2)–C–Si(3)	114.04(14)	112.8(6)	117.82(15)	112.8(4)
Si(1)–C–Si(3)	114.75(14)	113.6(6)	116.68(15)	115.1(4)
Si(1)–C–M	88.59(11)	92.6(5)	89.53(12)	87.1(3)
Si(2)–C–M	105.71(12)	114.2(5)	105.96(13)	106.4(3)
Si(3)–C–M	110.47(12)	106.5(5)	105.93(13)	111.3(4)
Dihedral angle M$_2$X$_2$–NMC	88	48	1	85

[a] Mn–O(2) 2.166(7), O(2)–Mn–C(1) 119.5(4), O(2)–Mn–O(1) 87.3(3), O(2)–Mn–Cl 105.4(2), O(2)–Mn–Cl′ 92.9(2).

[b] Symmetry transformation to generate equivalent atoms: $-x$, $-y$, $-z$.

[c] Mean value (estimated S.D.'s of individual measurements in parentheses). No individual value differs significantly from the mean.

[d] Atoms attached to Si(1) are labelled C(3) and C(4).

Table 2
X-ray structure determinations

	4	**5**	**6**	**7**
Chemical formula	$C_{22}H_{60}Cl_2Mn_2N_2Si_6$	$C_{28}H_{70}Cl_2Mn_2O_4Si_6$	$C_{22}H_{60}Mn_2N_2O_2Si_6$	$C_{22}H_{60}Br_2Co_2N_2Si_6$
Formula weight	702.04	820.2	663.1	798.9
T (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ no. 2	$P2_1/n$ no. 14	$P\bar{1}$ no. 2	$P\bar{1}$ no. 2
a (Å)	9.1797(13)	9.231(3)	9.1461(16)	9.135(5)
B (Å)	9.2643(12)	24.919(6)	9.2708(160)	9.255(4)
c (Å)	13.4980(15)	9.737(3)	12.6958(18)	13.496(8)
α (°)	75.390(8)	90	92.749(13)	73.35(4)
β (°)	79.430(7)	103.28(2)	103.092(13)	78.31(4)
γ (°)	60.845(6)	90	118.350(14)	60.85(4)
U (Å^3)	967.6(2)	2179.9(11)	907.4(3)	952.0(9)
Z	1	2	1	1
μ (mm^{-1})	0.99	0.90	0.91	3.17
R_1 wR_2 $I>2\sigma(I)$	0.039, 0.108	0.087, 0.145	0.038, 0.086	0.072, 0.196
All data	0.049, 0.114	0.215, 0.198	0.056, 0.094	0.104, 0.226
Measured/independent reflections R_{int}	3368/3368	3236/3029/0.142	3178/3178	3315/3315
Reflections with $I>2\sigma(I)$	2862	1391	2523	2397

M–C bonds, as found previously [12] for the gallium compound $GaCl_2\{C(SiMe_3)_2(SiMe_2NMe_2)\}$; in contrast, in the analogous aluminium compound **12** and $Li(THF)_2\{C(SiMe_3)_2(SiMe_2NMe_2)\}$ (**9**) the M–N are shorter than the M–C bonds indicating that coordination of nitrogen is stronger to Li and Al than to the divalent transition metals. The Si–N bond lengths in **4** [1.831(3) Å] and **7** [1.834(8) Å] are not as long as that [1.875(2) Å] in the compound **12**, again reflecting the fact that the nitrogen lone pair is less firmly bound to the transition metal than it is to aluminium.

There is a significant difference between the Mn–Cl and the Mn–Cl′ bonds in **4** (or the Co–Br and Co–Br′ bonds in **7**) as expected since the ligand is not symmetrically disposed about the MCSiN plane. Few data for Mn–Cl bonds involving tetrahedral Mn^{II} have been reported [29]. The bonds in **4** [2.4152(9) and 2.4398(9) Å] are shorter than those [2.528(4)–2.5749(6) Å] in $(\mu\text{-}Cl)_2$-bridges between octahedral Mn^{II} centres [30,31], but similar to those in the cage anion of **2** [2.468(4)–2.495(4) Å] and to the bond [2.4105(15) Å] between three-coordinate Mn^{II} and Cl in **3** [7]. The Mn–C bond in **4** [2.150(3) Å] is similar to those in **2** [2.17(2) Å] or the terminal bonds in the compound $[Mn\{C_6H_2Me_3\text{-}2,4,6\}_2]_3$ (**13**) [2.11(1) Å] [32] and longer than those [2.01(3)–2.108(2) Å] in the two-coordinate compounds $Mn\{C(SiMe_3)_3\}_2$ (**1**) [4], $Mn\{CH_2CMe_3\}_2$ [33], $Mn\{CH(SiMe_3)_2\}_2$ [34] or $Mn\{C_6H_2Bu^t_3\text{-}2,4,6\}_2$ [35]. The mass spectrum of **4** showed a strong peak attributed to the molecular ion, indicating that the dimeric species found in the solid state is present in the gas phase also.

The Co–Br [2.478(2) and 2.445(2) Å] and Co–C bonds [2.065(8) Å] in compound **7** are similar to those [Co–Br 2.480(2) and 2.495(2) Å; Co–C 2.053(8) Å] in the aryl derivative **8** [27]. For comparison, the Co^{II}–C bonds in $Co(TMEDA)R_2$ [$R = CH_2SiMe_3$ or CH_2CMe_3; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine] and related compounds range from 2.024(7) to 2.154(8) Å, and Co–N(TMEDA) bonds from 2.179(7) to 2.213(5) Å [36]. The latter are significantly longer than the Co–N bonds [2.087(7) Å] in **7**.

The methoxo derivative **5** is similar to **4** but the manganese is five- rather than four-coordinate. The configuration at the metal is that of a distorted trigonal bipyramid with the bond to the OMe group and the longer of the two Mn–Cl bonds axial. The carbon and chlorine atoms are twisted out of the equatorial plane. A similar configuration is found in the Yb [14], Sm [15], Sn and Pb [16] derivatives studied previously (in the Group 14 derivatives one equatorial position is occupied by a lone pair). The bite angle of the chelating ligand [70.4(4)°] is similar to those found [66–69°] previously. The Mn–THF bond [2.166(7) Å] is normal [cf. 2.16(2) Å in $Mn\{N(SiMe_3)_2\}_2\cdot THF$ and 2.226(5) Å in $Mn\{N(SiMe_3)_2\}_2\cdot 2THF$] [37,38] but the Mn–OMe bond [2.450(8) Å] is exceptionally long (cf. Mn^{II}–O 2.03–2.09 Å in tetrahedral and ca. 2.22 Å in octahedral environments [29]. A similar pattern is observed in the compound $[YbI(OEt_2)\{C(SiMe_3)_2(SiMe_2OMe)\}]_2$, in which the Yb–$OEt_2$ is shorter than the Yb–OMe distance, reflecting the fact that the OMe group is only weakly bound (compare $AlCl_2\{C(SiMe_3)_2(SiMe_2NMe_2)\}$ (**12**) in which the nitrogen is bound to aluminium [12] and $[AlCl_2\{C(SiMe_3)_2(SiMe_2OMe)\}(THF)]$ in which the methoxy oxygen is readily displaced from the Al coo;rdination sphere by THF [17]). The Si–O bond [1.672(8) Å] in **5** is longer than most Si–O-alkyl bonds

[39] but similar in length to those found previously in $\text{C(SiMe}_3)_2(\text{SiMe}_2\text{OMe})$ derivatives [14–17], including $\text{Zn}\{\text{C(SiMe}_3)_2(\text{SiMe}_2\text{OMe})\}_2$ in which there is no significant coordination of O to Zn [40]. The Mn–Cl bond lengths in **5** are longer than those in **4** and only a little shorter than those quoted for bonding between Cl and octahedral Mn^{II} centres [30–32]. The Mn–C bonds in **5** are also longer than those in **4**. The Mn···Mn distance [3.598(4) Å] is considerably longer than that [2.811(1) Å] in the dimeric amide $[\text{Mn}\{\text{N(SiMe}_3)_2\}_2]_2$, (**14**) [41,42] or the aryl derivative **13**; however, the magnetic moment [3.73 μ_B at 296 K] is lower than that (4.18 μ_B) for a compound containing two independent Mn^{II} centres, indicating possible antiferromagnetic interaction within the Mn_2Cl_2 core. The moment for **5** is similar to those in the amide **14** (3.34 μ_B at 296 K), the trimer **13** (3.65 μ_B at 299 K [32]) or the ate complex **2** (3.8 μ_B).

The structures of compounds **4**, **5**, and **7** are similar to the halide-bridged structures of Grignard reagents crystallised in the presence of donor solvents [43,44]. Since the ionic radii of $\text{Mg}^{2+}$and Co^{2+} are similar [27], the similarity of the structures of compounds of the type RMX is not surprising.

*2.2. The dialkylmanganese **10** and the Mn^{III} compound **6***

The reaction between MnCl_2 and two equivalents of the lithium compound **9** gave colourless crystals of an exceedingly air-sensitive compound, which was identified from its C, H analyses and high-resolution mass spectrum as the dialkylmanganese **10**. The magnetic susceptibility ($\mu_{\text{eff}} = 5.44\ \mu_B$) was consistent with the presence of a d^5 high-spin metal centre like those in the two-coordinate dialkylmanganese **1** and related compounds [4,33–35]. Crystals of **10** were not suitable for an X-ray study, so it is not possible to determine whether the nitrogen atom is coordinated to the manganese. There is no precedent for a dialkylmanganese with two chelated organic groups.

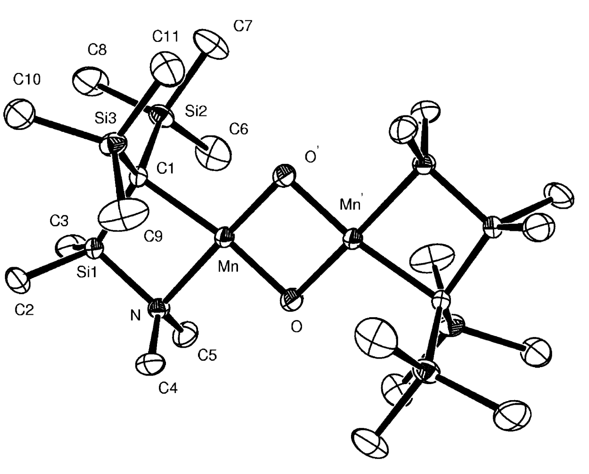


Fig. 4. Molecular structure of $[\overline{\text{Mn}(\mu\text{-O})\{\text{C(SiMe}_3)_2(\text{SiMe}_2\text{N}}\text{Me}_2)\}]_2$ (**6**).

In an experiment with THF as solvent a very few air-sensitive crystals were obtained. One of these gave excellent X-ray data (Table 2), which showed that the product was the Mn^{III} compound **6**. It is most probable that this was formed by oxidation of **4** after the accidental admission of air. Compound **6** could have been formed by the oxidation of **10** but the good analytical data for **10** suggest that the dialkylmanganese is less susceptible towards oxidation than the alkylmanganese halide **4**, which is less crowded at the metal centre. The source of the oxygen in **6** could also be the THF solvent but this is considered to be unlikely in view of the ready isolation of THF adducts such as **3** or **5**.

We have been unable to obtain analytical or spectroscopic data for **6** because of the small amount available but its structure is shown in Fig. 4. The molecules consist of centrosymmetric bridged dimers in which the configuration of the ligand is very similar to those in the halides **4**, **5**, and **7**. There is no sign of extra electron density in the vicinity of the oxygen atom, indicating that the compound is an oxygen-bridged Mn^{III} rather than a hydroxide-bridged Mn^{II} derivative. This conclusion is confirmed by the fact that the coordination at Mn is square-planar, as expected for a d^4 complex, rather than tetrahedral as expected, and commonly found, for d^5 compounds [44,45]. The Mn^{III}–C distance [2.128(3) Å] is significantly shorter than the Mn^{II}–C distance in compound **4**. Mn–C distances in other square-planar Mn^{III} compounds are 2.041(5)–2.122(4) Å in $[\text{Li(TMEDA)}_2][\text{MnMe}_4]$ [46] or $\text{Li}_2[\text{MnMe}_3(\text{O})]$ (the latter obtained as a double salt with the 4-methyl-2-penten-2,4-diolate dianion [47]) and 2.089(8) Å in $\text{Mn}\{\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}\}\text{Br}_2(\text{PMe}_3)_2$ [48,49]. The Mn^{III}–O distances [1.845(2) and 1.803(2) Å] are shorter than those in $\text{Li}_2[\text{MnMe}_3(\text{O})]$ [1.913(4) Å] and in Mn^{III}–Mn^{IV} derivatives containing the cations $[\text{Mn}_2\text{O}_2\text{L}_2]^{3+}$ [L = 2 bipy or $\text{N(CH}_2\text{CH}_2\text{NMe}_2)_3$], which, like **6**, have a central Mn_2O_2 core [1.847(4)–1.856(4) Å] [50,51]. The Mn–O bond opposite nitrogen in **6** is considerably shorter than that opposite carbon, reflecting the difference between the *trans* influences of the NMe_2 and the CSi_3 centres. A similar effect is observed in the d^4 Cr^{II} compound $[\overline{\text{Cr}(\mu\text{-Cl})\{\text{C(SiMe}_3)_2(\text{SiMe}_2\text{C}_5\text{H}_4\text{N}}\text{-2})\}]_2$ [9]. The Mn–N distance [2.101(2) Å] is significantly shorter than that in **4**. It is also shorter than the Mn–C distance, indicating that the Mn^{III} centre in **6** binds the nitrogen lone pair more strongly than the Mn^{II} centre in **4**. The Mn^{III}–N distances in the cations $[\text{Mn}_2\text{O}_2\text{L}_2]^{3+}$ range from 2.101(5) to 2.344(5) Å [50,51].

As far as we are aware, no other neutral compounds of the type RMnO with four-coordinate square–planar Mn^{III} have been reported [44]. The reactions of several alkyl(cyclopentadienyl)manganese(III) derivatives have been described, though their structures have not been determined [52,53]. The structurally characterised compound $MnMe(C_6H_4CH_2NMe_2)_2$ is, like **6**, stabilised by internal coordination; the Mn^{III}–C distances [2.050(4)–2.068(3) Å] are shorter and the Mn–N distances [2.218(3)–2.259(3) Å] longer than the corresponding distances in **6** [54]. We have not had the opportunity to determine the source of the oxygen in **6** or to find a high yield synthesis, but its isolation and structural characterisation suggest that the controlled oxidation of organometallic compounds of Mn^{II} would be worthy of study.

3. Experimental

Air and moisture were excluded as far as possible from all reactions by use of Schlenk techniques, flame-dried glassware, and argon as blanket gas. In mass spectral assignments $R = C(SiMe_3)_2(SiMe_2Y)$. Compounds **9** [12] and **11** [13,17] were made as described previously. Magnetic moments were determined by the Evans' method without a diamagnetic correction [55,56].

3.1. $[Mn(\mu\text{-}Cl)C(SiMe_3)_2(SiMe_2NMe_2)]_2$ (**4**)

A solution of **9** (1.1 g, 2.7 mmol) in THF (30 ml) was added to a stirred suspension of $MnCl_2$ (0.34 g, 2.7 mmol) in THF (15 ml) at −78 °C and the mixture was allowed to warm to room temperature (r.t.). The solvent was removed under vacuum and the solid residue extracted with hexane. The pale yellow extract was filtered and its volume reduced to 7 ml. The solution was kept at 5 °C to give colourless crystals of **4** (0.9 g, 95%), m.p. 237–242 °C. MS: *m*/*z* 700.1527 (30, $C_{22}H_{60}Cl_2N_2Mn_2Si_6$ (M_2) calc. 700.1510), 685 (10, M_2–Me), 350 (60, M), 335 (100, M–Me), 315 (15, M–Cl), 230 [80, $Me_2Si{=}C(SiMe_2NMe_2)SiMe_2$], 129 (50, $Me_2Si{=}CHSiMe_2$), 102 (30, $SiMe_2NMe_2$), 73 (70), 59 (30).

3.2. $Mn\{C(SiMe_3)_2(SiMe_2NMe_2)\}_2$ (**10**)

A solution of **9** (7.4 mmol) in toluene (40 ml) was added dropwise to a stirred suspension of $MnCl_2$ (0.43 g, 3.4 mmol) in toluene (15 ml) at −18 °C. The mixture was allowed to warm to r.t. and the solvent was removed in vacuum to leave a brown solid, which was extracted with hexane. The yellow extract was filtered and its volume reduced to 10 ml. It was then kept at 5 °C to give colourless crystals of **10** (1.8 g, 72%) m.p. 136–140 °C. Anal. Calc. for $C_{22}H_{60}MnN_2Si_6$ C, 45.9; H, 10.4; N, 4.9. Found: C, 45.4; H, 10.3; N, 4.5%. MS *m*/*z* 575.2754 ($C_{22}H_{60}MnN_2Si_6$ calc. 575.2753), 560 (5, M–Me), 315 (100, RMn), 230 (30), 187 [50, $Me_2Si{=}C(SiMe_2H)SiMe_2$], 129 (20), 102 (13), 73 (40). $\mu_{eff} = 5.44\ \mu_B$.

3.3. $[Mn(\mu\text{-}O)C(SiMe_3)_2(SiMe_2NMe_2)]_2$ (**6**)

A solution of **9** (2.9 mmol) in THF (20 ml) was added to a suspension of $MnCl_2$ (0.18 g, 1.4 mmol) in THF (10 ml) at −16 °C and the mixture was allowed to warm to r.t. The solvent was removed under vacuum to leave a solid, which was extracted with hexanes. The yellow extract was filtered and concentrated and kept at 5 °C to give pale brown crystals of **6**. There was insufficient material for C and H analyses but the structure was established by an X-ray study.

3.4. $[Co(\mu\text{-}Br)C(SiMe_3)_2(SiMe_2NMe_2)]_2$ (**7**)

A solution of **9** (0.47 g, 1.1 mmol) in THF (25 ml) was added dropwise to a stirred solution of $CoBr_2$ (0.25 g, 1.0 mmol) in THF (20 ml) at −12 °C. The mixture was allowed to warm to r.t., the solvent removed under vacuum and the residue extracted with hexane. The extract was filtered and its volume reduced to 5 ml. The solution was kept at 5 °C to give dark green crystals (0.45 g, 50%), m.p. 107–111 °C. Anal. Calc. for $C_{22}H_{60}Br_2Co_2N_2Si_6$: C, 33.0, H, 7.5; N, 3.5. Found: C, 32.8, H, 7.5; N, 3.4%. $\mu_{eff} = 2.66\ \mu_B$. The reaction between **9** (1.4 mmol) and $CoBr_2$ (0.7 mmol) under similar conditions gave the same product **7**.

3.5. $[Mn(THF)(\mu\text{-}Cl)\{C(SiMe_3)_2(SiMe_2OMe)\}]_2$ (**5**)

A solution of **11** (0.8 g, 2.0 mmol) in THF (20 ml) was added dropwise with stirring to $MnCl_2$ (0.16 g, 1.0 mmol) in THF (10 ml) at −10 °C. The stirred mixture was allowed to warm to r.t. overnight, the solvent then removed under vacuum, and the residue extracted with hexanes (25 ml). The pale yellow extract was filtered, then concentrated to 5 ml and kept at 5 °C to give light brown crystals (0.52 g, 63%) suitable for an X-ray study, m.p. 290 °C (with dec., becoming black at 310 °C). Anal. Calc. for $C_{28}H_{70}Cl_2Mn_2O_4Si_6$; C, 41.0; H, 8.6. Found: C, 38.5; H, 8.7%. MS *m*/*z* 322 [10, RMnCl–Me, $R = C(SiMe_3)_2(SiMe_2OMe)$], 247 (10, R), 233 (100, RH–Me), 217 [70, $Me_2Si{=}C(SiMe_2OMe)\text{-}SiMe_2$)]. $\mu_{eff} = 3.73\ \mu_B$.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 172755–172758 for compounds **4**, **5**, **6**, and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2

1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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