

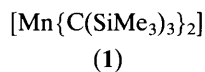
Preparation and Crystal Structure of a Two-co-ordinate Manganese Compound, Bis[tris(trimethyl)silylmethyl]manganese

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The product of the reaction between MnCl_2 and tris(trimethylsilyl)methyl-lithium in 1:2 molar ratio in tetrahydrofuran is the monomeric species $[\text{Mn}\{\text{C}(\text{SiMe}_3)_2\}]$, the first two-co-ordinate manganese compound to be characterized.

We recently described the compound $[\text{Li}(\text{thf})_4][\text{Mn}_3\text{Tsi}_3\text{Cl}_4(\text{thf})]$ [thf = tetrahydrofuran; Tsi = $(\text{Me}_3\text{Si})_3\text{C}$], which was obtained from the reaction between MnCl_2 and TsiLi^\dagger in 1:1 mol ratio.¹ By use of these same reagents in 1:2 mol ratio we have now obtained the dialkylmanganese compound, $[\text{Mn}(\text{Tsi})_2]$ (1), as a monomeric species which we believe to be the first two co-ordinate manganese compound characterised.



Compound (1) was made by adding a solution of TsiLi^2 (18.3 mmol, based on this monomeric formulation) in thf (20 cm^3) dropwise under argon to a stirred slurry of MnCl_2 (1.15 g, 9.14 mmol) in thf (15 cm^3) at -78°C . The mixture was stirred at -78°C for 2 h then overnight at room temperature. The thf was removed under vacuum and the residue was extracted several times with hot heptane. The combined extracts were filtered, concentrated, and cooled, to give plate-like pale yellow, air-sensitive crystals (ca. 65% yield).

Crystal data. $\text{C}_{20}\text{H}_{54}\text{Si}_6\text{Mn}$, $M = 518.1$, triclinic, space group $P\bar{1}$, $a = 9.033(3)$, $b = 9.337(4)$, $c = 11.910(4)$ Å. $\alpha =$

$68.43(4)$, $\beta = 74.38(3)$, $\gamma = 59.99(4)^\circ$, $Z = 1$, $D_c = 1.07$ g cm^{-3} , monochromated Mo- K_α radiation, $\mu = 6.2$ cm^{-1} . $R = 0.066$, $R' = 0.070$ for 2091 unique reflections with $I > \sigma(I)$, measured on an Enraf-Nonius CAD-4 diffractometer in the range $2 < \theta < 25^\circ$.[‡]

The structure of (1), with the atom numbering, is shown in Figure 1. The molecule lies across an inversion centre, and so the co-ordination at Mn is strictly linear and the $\text{C}(\text{SiMe}_3)_3$ groups are staggered about the C-M-C direction. The Tsi groups have roughly C_3 symmetry, with C(2), C(5), and C(10) closest to manganese. The distance between the planes C(2), C(5), C(10) and C(2'), C(5'), C(10') is ca. 3.0 Å, and, since the van der Waals radius of a methyl group is ca. 2.0 Å, it is evident that the Tsi groups virtually interlock, and effectively fill the space around the Mn, precluding any increase in the co-ordination at that atom. (Indeed, since there must be severe steric hindrance to the approach of a reagent to the manganese atom or to the directly attached carbon atoms, and to any increase in the co-ordination number of the manganese, it is perhaps surprising that the compound is so sensitive to air.) This close approach of the Me groups from the two $\text{C}(\text{SiMe}_3)_3$ ligands is associated with opening of the $\text{Me}_3\text{Si-C-}$

[†] For simplicity we represent tris(trimethylsilyl)methyl-lithium as TsiLi , although it is known to be an ionic species $[\text{Li}(\text{thf})_4][\text{Li}(\text{Tsi})_2]$ (see refs. 2 and 5).

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

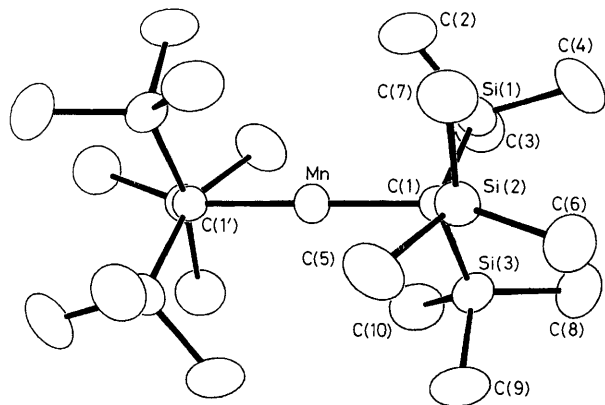


Figure 1. Crystal structure of (1), showing the atom numbering. Mean bond lengths and angles: Mn–C(1) 2.102(4), C(1)–Si 1.881(8), Si–Me 1.883(9) Å; Si–C(1)–Si 112.3(2), C(1)–Si–Me 113.1(16), Me–Si–Me 105.6(17)°.

SiMe₃ angles [to 112.3(3)°] to minimise strain within these ligands.

The structure of (1) is very similar to that of the corresponding mercury compound Hg(Tsi)₂,³ and to the structures of the anions [M(Tsi)₂][−], where M = Li,² Cu,⁴ or Ag.⁵ The Mn–C distance, 2.102(4) Å, falls in the range of M–C distances in those related species [viz., ca. 2.14 (M = Hg), 2.18 (M = Li and Ag), and 2.05 Å (M = Cu)]. The Mn–C distance is also similar to the mean Mn–C distance (2.17 Å) in [Mn₃Tsi₃Cl₄(thf)][−], and to the distance for Mn–C terminal bonds [2.12(1) Å] in [Mn(mesityl)₂]₃, which has a linear array of Mn atoms linked by electron-deficient aryl bridges.⁶ The mean Me₃Si–C distance, 1.883(9) Å, is the same as the mean Me–Si distance, 1.881(8) Å; in other neutral Tsi–metal or –metalloid derivatives the Me₃Si–C bonds are longer than the Me–Si bonds, but the opposite seems to be the case for the anions [M(Tsi)₂][−] with M = Li, Cu, or Ag.

Compound (1) is believed to be the first recognised two-coordinate manganese compound. The diorganomanganese compounds (MnR₂)_n with R = CH₂CMe₂Ph (*n* = 2), C₆H₂Me₃-2,4,6 (*n* = 3), or CH₂CMe₃ (*n* = 4), and polymeric

[Mn(CH₂SiMe₃)₂]_n all have structures in which the manganese is three- or four-coordinate.⁷ In mononuclear manganese compounds three-coordinate is rare, and only [Mn{N(SiMe₃)₂}(thf)]⁸ and [Li{MnN(SiMe₃)₂(OCBu₃)₂}]⁹ have been characterized.

Compound (1) has a magnetic moment (determined by Evans' method¹⁰) of ca. 5.1 μ_B, somewhat lower than the value (5.9 μ_B) expected for a high spin d⁵ species. It melts at 290 °C (there is some sublimation above ca. 250 °C), and after being taken to 290 °C then cooled it remelts on heating at 290 °C. At 315 °C the liquid goes black, indicating some decomposition. Compound (1) thus has a high thermal stability, and both the melting point and the decomposition temperature are remarkably close to those of the M(Tsi)₂ compounds with M = Zn, Cd, and Hg.¹¹

We thank the S.E.R.C. for support, and N. H. B. thanks the Ministry of Higher Education, Iraq, for the award of a postgraduate scholarship.

Received, 30th May 1985; Com. 749

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