

# The Crystal Structure of Bis{tris(trimethylsilyl)methyl}magnesium: an Example of Two-co-ordinate Magnesium in the Solid State

Salih S. Al-Juaid, Colin Eaborn,\* Peter B. Hitchcock, Catherine A. McGeary, and J. David Smith\*

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

The lithium–magnesium complex  $[\text{Li}(\text{thf})_2(\mu\text{-Br})_2\text{Mg}\{\text{C}(\text{SiMe}_3)_3\}\text{thf}]$  (thf = tetrahydrofuran) decomposes on heating in vacuum to give  $[\text{Mg}\{\text{C}(\text{SiMe}_3)_3\}_2]$ , which is monomeric; this is the first characterisation of a two-co-ordinate magnesium compound in the solid state.

We are not aware of any single crystal *X*-ray diffraction study of an unsolvated dialkylmagnesium. Dimethyl-<sup>1</sup> and diethylmagnesium<sup>2</sup> have been shown by powder diffraction to be polymeric, and bis(neopentyl)magnesium (1), though monomeric in the gas phase,<sup>3</sup> is trimeric in benzene.<sup>4</sup>

The compound  $\text{RLi} [\text{R} = \text{C}(\text{SiMe}_3)_3]$  (2) reacts with anhydrous magnesium(II) bromide to give the bridged lithium–magnesium complex (3).<sup>5</sup> We have now shown that complex (3) decomposes on heating in vacuum to give the dialkyl derivative  $\text{Mg}\{\text{C}(\text{SiMe}_3)_3\}_2$  (4).† An *X*-ray study‡ shows that (4) is monomeric, and we believe that this is the first example of two-co-ordinate magnesium in the solid state.

The dialkyl compound (4) is isomorphous with the compounds  $\text{R}_2\text{M}$  [ $\text{M} = \text{Mn}$  (5)<sup>6</sup> or  $\text{Hg}$  (6)<sup>7</sup>], and the centrosymmetrical molecule is shown in Figure 1. The Mg–C distance is almost the same as that found by electron diffraction<sup>3</sup> [2.126(6) Å] in (1) where there is less intramolecular steric hindrance. This suggests that the  $(\text{Me}_3\text{Si})_3\text{C}$  groups in (4) are accommodated without weakening of Mg–C bonds:§ indeed there is no carbon–carbon distance involving different  $(\text{Me}_3\text{Si})_3\text{C}$  groups which is less than 4.0 Å (twice the van der Waals radius of the methyl group). However, the two  $(\text{Me}_3\text{Si})_3\text{C}$  groups interlock as they do in (5): the distance between the two planes defined by C(2), C(5), and C(10) and C(2'), C(5'), and C(10') is only 2.97 Å. The carbon–silicon

bonds in (4), like those in (5), are all similar in length, in contrast to corresponding bonds in the ions  $\text{MR}_2^-$  ( $\text{M} = \text{Li}$ ,  $\text{Cu}$ , or  $\text{Ag}$ ), in which the C–Si are shorter than the Si–Me bonds. The Si–C–Si and Me–Si–Me angles are similar to those in other  $(\text{Me}_3\text{Si})_3\text{C}$  derivatives, and, as expected,<sup>5</sup> the Mg–C–Si–C torsion angles show that each  $\text{SiMe}_3$  group is twisted from the staggered configuration, making the  $(\text{Me}_3\text{Si})_3\text{C}$  groups chiral. The quality of the *X*-ray data for (4) shows that molecules of the *meso* form (*i.e.* with left- and right-handed groups in the same molecule) pack in a highly regular fashion; there is no indication of the disorder which so often bedevils crystal structure determinations of compounds containing  $(\text{Me}_3\text{Si})_3\text{C}$  groups.

The dialkylmagnesium (4) has potential as a reagent for transfer of  $(\text{Me}_3\text{Si})_3\text{C}$  groups to suitable substrates in the absence of donor solvents such as ether or thf which sometimes cause complications when reagent (2) is used, or as a selective alkylating agent. In preliminary experiments, no reaction was detected with  $\text{Me}_3\text{SiCl}$ ,  $\text{Me}_2\text{HSiCl}$ , or  $\text{MeI}$  after 4 days in toluene at 25 °C; reactions with more electrophilic halides are being explored. With water or methanol at 25 °C

† 1,2-Dibromoethane (26.2 mmol) was added to a stirred slurry of magnesium turnings (0.63 g, 26 mmol) in  $\text{Et}_2\text{O}$  (25  $\text{cm}^3$ ) at 0 °C. The white solid obtained on removal of solvent was treated with (2) (25 mmol) in thf (30  $\text{cm}^3$ ). The solution was stirred overnight at 20 °C, the solvent then evaporated, the product extracted into  $\text{Et}_2\text{O}$  (100  $\text{cm}^3$ ), the extract filtered, and the solvent removed. The residue was heated at 170 °C/0.08 Torr and the sublimate which passed through a glass wool plug was recrystallised from toluene to give colourless plates of (4) [3.6 g, 60% yield based on (2)], m.p. > 350 °C. A satisfactory C analysis could not be obtained, probably because of formation of magnesium carbide. N.m.r. ( $\text{C}_6\text{D}_5\text{-CD}_3$  relative to  $\text{SiMe}_4$ )  $\delta_{\text{H}}$ : 0.23;  $\delta_{\text{C}}$ : 7.1 ( $\text{SiMe}_3$ );  $\delta_{\text{Si}}$  –7.4 p.p.m.;  $m/z$  486 (3%,  $[\text{M}]^+$ ), 471 (3,  $[\text{M} - \text{Me}]^+$ ), 255 (100,  $[\text{M} - \text{R}]^+$ ).

‡ Crystal data for (4):  $\text{C}_{20}\text{H}_{54}\text{MgSi}_6$ ,  $M = 487.5$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.093(7)$ ,  $b = 9.308(2)$ ,  $c = 11.907(4)$  Å,  $\alpha = 68.52(2)^\circ$ ,  $\beta = 74.26(5)^\circ$ ,  $\gamma = 59.98(4)^\circ$ ,  $U = 807.1$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.00$  g  $\text{cm}^{-3}$ ,  $F(000) = 270$ , monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 2.8$   $\text{cm}^{-1}$ . Data from a crystal of size 0.4 × 0.4 × 0.4 mm were collected on a CAD4 diffractometer; 2444 reflections with  $2 < \theta < 25^\circ$  and with  $|F|^2 > \sigma|F|^2$  were used for the structure analysis. Refinement, by full-matrix least-squares with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen, converged at  $R = 0.045$  and  $R_w = 0.060$ . The Enraf-Nonius SDP-Plus Program was used. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ A survey of Mg–C distances in the Cambridge Crystallographic Data Base shows that most two-centre-two-electron bonds are in the range 2.1–2.2 Å, irrespective of the co-ordination numbers of carbon and magnesium.

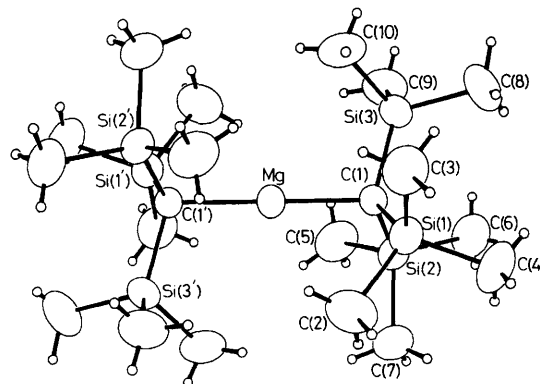
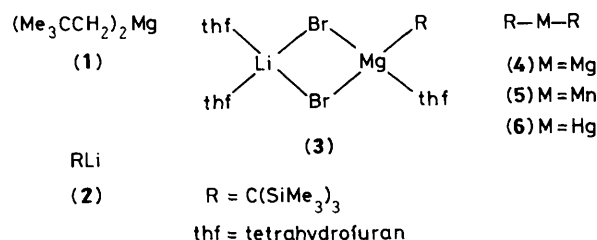


Figure 1. The structure of (4). Mean bond distances and angles: Mg–C 2.116(2), C–Si 1.877(3), Si–Me 1.881(4) Å; Si–C–Si 112.6(1), Me–Si–Me, 105.4(2)°.

(4) gave  $(\text{Me}_3\text{Si})_3\text{CH}$  without any indication of formation of intermediates  $\text{RMgOR}$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ).

When (4) (1 equiv.) was sealed with  $\text{MgBr}_2$  (1 equiv.) in ether- $\text{C}_6\text{D}_6$  (9:1) in an n.m.r. tube for 5 h at  $25^\circ\text{C}$  no change was observed in  $^1\text{H}$  or  $^{13}\text{C}$  n.m.r. spectra, showing that the Schlenk equilibrium to give  $\text{RMgBr}$  was either established very slowly (as expected for compounds with very large R) or, less probably, lies well over to the side of (4).

We thank the S.E.R.C. for support and the Government of Saudi Arabia for a scholarship (to S. S. Al-J.).

Received, 14th October 1988; Com. 8/04091E

## References

- 1 E. Weiss, *J. Organomet. Chem.*, 1964, **2**, 314.
- 2 E. Weiss, *J. Organomet. Chem.*, 1965, **4**, 101.
- 3 E. C. Ashby, L. Fernholt, A. Haaland, R. Seip, and R. C. Smith, *Acta Chem. Scand., Ser. A.*, 1980, **34**, 213.
- 4 R. A. Andersen and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 809.
- 5 N. H. Buttrus, C. Eaborn, M. N. A. El-Kheli, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, and K. Tavakkoli, *J. Chem. Soc., Dalton Trans.*, 1988, 381.
- 6 N. H. Buttrus, C. Eaborn, P. B. Hitchcock, J. D. Smith, and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1985, 1380.
- 7 F. Glockling, N. S. Hosmane, V. B. Mahale, J. J. Swindall, L. Magos, and T. J. King, *J. Chem. Res.*, 1977, (S) 116, (M) 1201.