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Preparation, crystal structure, and reactivity of bis{tris(trimethylsilyl)methyl}magnesium

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Abstract

Heating of the lithium magnesate [Li(THF)$_2$(μ-Br)$_2$Mg(Tsi)(THF)] (Tsi = (Me$_3$Si)$_3$C) under vacuum gives the dialkylmagnesium compound Mg(Tsi)$_2$, the first two-coordinate magnesium derivative to have been structurally characterized in the solid state. The compound is remarkably thermally stable, not decomposing (or melting) when heated to 350°C. It has a very low reactivity, failing to react in toluene with, for example, CO$_2$, Me$_3$SiCl, Me$_2$SiHCl, MeI, BCl$_3$ or CH$_3$COCl, and even with neat CH$_3$COCl at its boiling point. It does react, though fairly slowly, with I$_2$ in toluene to give TsiI, and more rapidly with Br$_2$ to give TsiBr, and with an excess of PhSO$_2$Cl in toluene at 100°C to give TsiCl. It decomposes quickly in the air, and reacts readily with MeOH in toluene to give TsiH without formation of detectable amounts of the intermediate TsiMgOMe, and with O$_2$ in toluene.

Key words: Silicon; Magnesium; Crystal structure

1. Introduction

We previously briefly reported the preparation and structural characterization of the novel two-coordinate dialkylmagnesium compound [Mg{C(SiMe$_3$)$_3$}$_2$], **1**, and a preliminary study of its reactivity towards electrophiles [1]. We present below a more detailed account, in which the group (Me$_3$Si)$_3$C is frequently denoted by the symbol Tsi.

$$\underset{\mathbf{1}}{[\mathrm{Mg\{C(SiMe_3)_3\}_2}] \equiv \mathrm{Tsi_2Mg}}$$

$$\underset{\mathbf{2}}{[\mathrm{Li(THF)_2(\mu\text{-}Br)_2Mg\{C(SiMe_3)_3\}(THF)}]}$$

2. Results and discussion

Compound **1** was made from the complex **2**, which was prepared by reaction of 'TsiLi' (for the actual composition of this reagent see ref. 2) and MgBr$_2$ in Et$_2$O [3]. When **2** was heated at 170°C at 0.08 Torr the dialkylmagnesium compound **1** slowly sublimed out. It was found to be remarkably thermally stable, not decomposing (or melting) below 350°C in a sealed capillary tube; it is thus even more stable than the related mercury derivative Tsi$_2$Hg, which decomposes at *ca.* 300°C after melting at *ca.* 270°C [4].

3. Crystal structure

Recrystallization from toluene gave crystals of **1** suitable for an X-ray diffraction study. The structure of the molecule, which is centrosymmetric, is shown in Fig. 1, and bond lengths and angles are listed in Table 1. Compound **1** is the only two-coordinate magnesium compound to have been structurally characterized in the solid state, but the structure of bis(neopentyl)magnesium in the gas phase has been determined by electron diffraction [5]; the Mg–C bond lengths in the two compounds, 2.116(2) and 2.126(6) Å are virtually identical (and probably somewhat shorter than those in [Li(THF)$_2$(μ-Br)$_2$Mg(Tsi)(THF)] (2.19(3)) [1], [TsiMg(μ-Br)$_3$Mg(THF)$_3$] (2.16(2)) [6] and [EtMgBr.(Et$_2$O)$_2$] (2.15(1)) Å [7]), in all of which the relevant Mg atom is four-coordinate. Solid dimethyl-and diethyl-magnesium

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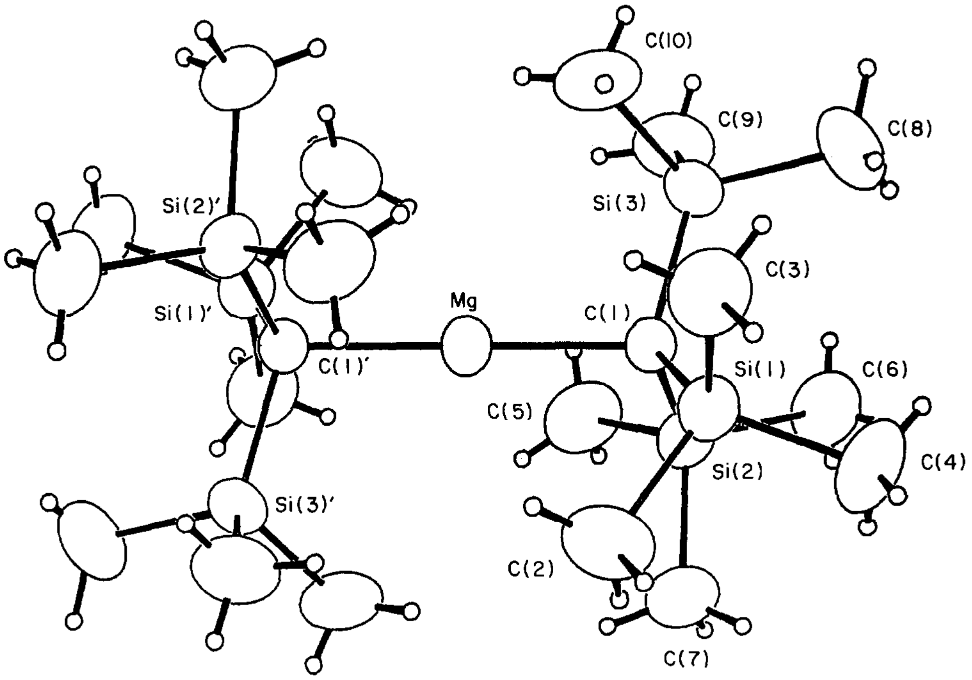

Fig. 1. The centrosymmetric structure of 1.

have been shown by powder diffraction studies to be polymeric [8], and bis(neopentyl)magnesium is trimeric in benzene [9]. Compound 1 is isomorphous with the related compounds $M(Tsi)_2$, M = Mn [10], Hg [11], or Zn [12].

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, which is well below the distance of 4.0 Å given by twice the van der Waals radius of the Me group, but the two $(Me_3Si)_3C$ groups mesh together (interlock) so that no C · · · · C distance involving different $(Me_3Si)_3C$ groups is below 4.0 Å. The absence of serious steric interaction between the two groups also shows up in the fact that, as in Tsi_2M with M = Zn [11] or Mn [10], the C–Si bonds are rather similar in length (mean C–Si 1.877(3) Å, mean Si–Me 1.881(4) Å), whereas in many TsiX compounds in which X is bulky, *e.g.* $TsiSiMe_2Ph$ [13], $TsiBPh_2$ [14], and $[Li(THF)_4][\{Cd[C(SiMe_3)_3]\}_3(\mu\text{-}Br)_3(\mu\text{-}Br)] \cdot 0.5C_6H_{12}$ [3], the central C–Si bonds are markedly longer than the peripheral Si–Me bonds. However, as is usual in TsiX compounds, the steric strain is mainly accommodated by opening of the Si–C–Si angles (mean 112.6°) and closing of the Me–Si–Me angles (mean 105.4°). It it noteworthy that the internal strain within a Tsi ligand outweighs any steric repulsion by the other such ligand, so that the Me_3Si groups lie in towards the Mg atom, with a mean Si–C–Mg angle of 106.1°.

TABLE 1. Intramolecular distances (Å) and angles (°) in $Mg\{C(SiMe_3)_3\}_2$ with estimated standard deviations in parentheses

a) Bonds			
Si(1)–C(1)	1.882(2)	Si(1)–C(2)	1.882(3)
Si(1)–C(3)	1.883(4)	Si(1)–C(4)	1.873(3)
Si(2)–C(1)	1.877(3)	Si(2)–C(5)	1.891(4)
Si(2)–C(6)	1.874(3)	Si(2)–C(7)	1.881(2)
Si(3)–C(1)	1.872(2)	Si(3)–C(8)	1.873(3)
Si(3)–C(9)	1.890(4)	Si(3)–C(10)	1.885(3)
Mg–C(1)	2.116(2)		
b) Angles			
C(1)–Si(1)–C(2)	111.5(1)	C(1)–Si(1)–C(3)	114.9(1)
C(1)–Si(1)–C(4)	113.7(1)	C(2)–Si(1)–C(3)	102.9(2)
C(2)–Si(1)–C(4)	107.7(1)	C(3)–Si(1)–C(4)	105.3(2)
C(1)–Si(2)–C(5)	110.9(1)	C(1)–Si(2)–C(6)	114.9(1)
C(1)–Si(2)–C(7)	113.8(1)	C(5)–Si(2)–C(6)	106.7(2)
C(5)–Si(2)–C(7)	104.5(1)	C(6)–Si(2)–C(7)	105.3(1)
C(1)–Si(3)–C(8)	114.8(1)	C(1)–Si(3)–C(9)	114.2(1)
C(1)–Si(3)–C(10)	110.5(1)	C(8)–Si(3)–C(9)	105.3(2)
C(8)–Si(3)–C(10)	107.1(2)	C(9)–Si(3)–C(10)	104.0(1)
Si(1)–C(1)–Si(2)	112.89(8)	Si(1)–C(1)–Si(3)	112.7(1)
Si(1)–C(1)–Mg	106.79(9)	Si(2)–C(1)–Si(3)	112.2(1)
Si(2)–C(1)–Mg	106.0(1)	Si(3)–C(1)–Mg	105.55(7)

4. Reactivity

Compound 1 is very remarkably thermally stable, not decomposing (or melting) when heated to 350°C in a sealed tube.

Crystals of compound **1** decomposed within a few minutes, however, when exposed to the air on a filter paper, to give a white powder and leave a liquid spot on the paper. In solution in toluene it reacted rapidly with MeOH to give TsiH. When a deficiency of MeOH was used a mixture of TsiH and unchanged **1** was formed; ^{1}H NMR spectroscopic monitoring gave no indication of the presence of the intermediate TsiMgOMe, which is not surprising since removal of one Tsi group will greatly ease the approach to the Mg atom, making TsiMgOMe much more reactive than **1**.

Complete reaction occurred when a solution of **1** in toluene was kept under oxygen for 4 h, and an oil separated. The ^{1}H NMR spectrum of the solution above the oil showed that no **1** remained; the presence of a single sharp peak in the Me_3Si region, at δ 0.13, enhanced on addition of TsiH, suggested that the latter was the main product, but removal of the solvent left a sticky solid, whereas TsiH is a liquid. The properties of the solid were consistent with its being mainly TsiOH, but it was not positively identified.

Because we hoped that **1** might be a useful reagent for transfer of Tsi groups to metal centres in a solvent other than an ether, which can give rise to side products or to unwanted etherates, we examined its reactions mainly in toluene. It underwent no reaction with Me_3SiCl, Me_2SiHCl, MeI, BCl_3, or CH_3COCl in this solvent at 22–25°C, or even with neat CH_3COCl at its boiling point. It did, however, react slowly with $PhSO_2Cl$ in toluene at 100°C to give TsiCl (not the $TsiO_2SPh$ we had hoped for). There was no reaction when **1** was treated with $MgBr_2$ in $Et_2O–C_6D_6$, indicating either that the Schlenk equilibrium lies well over towards the dialkylmagnesium species or, more likely, that steric hindrance makes the reaction too slow to allow establishment of the thermodynamically favoured species. Compound **1** did react with a 1 molar equiv. of iodine in toluene at room temperature. The iodine colour mainly disappeared within a few hours, though after 3 days it was still faintly present; the ^{1}H NMR spectrum showed that **1** and TsiI were present in a ratio of *ca.* 1 : 2. When 2 molar equiv. of iodine were used, all of **1** was converted into TsiI. Reaction with a 1 molar proportion of bromine in toluene at room temperature was faster, as judged by the rate of decolorization; after 2 days the colourless solution contained **1** and TsiBr in 1 : 2 molar ratio. Again it is evident that TsiMgX (X = Br or I) is much more reactive than Tsi_2Mg.

The unreactivity of **1** even towards such a powerful electrophile as acetyl chloride is not really surprising, since the metal atom is very effectively surrounded by Me groups. Indeed, it is perhaps more surprising that H_2O, MeOH, O_2, Br_2 and I_2 are able to reach the C–Mg bond. It seems unlikely that **1** will ever find use as a reagent for attachment of a Tsi group to a carbon or metal centre, but in principle it could be used to remove traces of, for example, HCl or Cl_2 from CH_3COCl, Me_3SiCl, or $PhSO_2Cl$, of EtOH from ethyl acetate, or of H_2O from acetone, and perhaps even of O_2 from such liquids or from gaseous CO_2.

5. Experimental details

5.1. General

Reactions and manipulations were carried out under argon and/or by Schlenk or vacuum line techniques. Solvents were dried by standard methods.

5.2. NMR spectra

Chemical shifts in the ^{1}H NMR spectra were determined relative to internal Me_4Si; usually the spectrum was recorded in its absence and re-recorded after its addition. Identities of products were confirmed where necessary by addition of authentic samples and re-recording of the spectrum.

5.3. Preparation of Tsi_2Mg, 1

1,2-Dibromoethane (26.2 mmol) was added slowly to a stirred mixture of Mg turnings (0.63 g, 26 mmol) and Et_2O (25 cm^3) at 0°C. Stirring was continued until all the Mg had disappeared (*ca.* 2 h) and the solvent was then removed to leave a white powder. A solution of TsiLi (12.5 mmol) in THF (30 cm^3) was added; reaction occurred rapidly, but the mixture was nevertheless stirred overnight at room temperature (*ca.* 20°C). The solvent was removed under reduced pressure, and the residue extracted with Et_2O (100 cm^3). The extract was filtered through Celite and the solvent removed under reduced pressure. The white solid obtained was heated at 170°C/0.08 Torr to give a sublimate (which passed through a plug of glass wool). This was recrystallized from toluene to give colourless plates of **1** (3.6 g; 60% based on amount of TsiLi taken), m.p. > 350°C; δ(H) (in toluene) 0.27; δ(C) (in toluene-d^8) 7.2 ppm (CH_3; quaternary carbon not observed); δ(Si) (in toluene-d^8) -7.4 ppm; m/z 486 (3%, M), 471 (3, M–Me), 255 (100, M–Tsi).

5.4. Reactions of 1

5.4.1. With MeOH

A solution of **1** (0.20 mmol) in toluene (1.0 cm^3) was mixed with one of MeOH (0.10 mmol) in toluene (1.0 cm^3), and the ^{1}H NMR spectrum was recorded as soon as possible (within 2 min). This showed that only **1** and TsiH, in *ca.* 1 : 1 ratio, were present.

When the procedure was repeated but with 0.21

mmol of MeOH, the spectrum revealed that only TsiH was present.

5.4.2. *With CO_2*

An NMR tube was flushed with a carefully dried CO_2 gas and a solution of **1** (0.14 mmol) in toluene-d^8 (0.8 cm^3) was introduced. The solution was left at 60°C under a positive pressure of CO_2 for 3 h, after which the ^1H NMR spectrum showed that only unchanged **1** and a trace of TsiH were present.

5.4.3. *With O_2*

A solution of **1** (50 mg) in toluene (2 cm^3) was stirred under O_2 (1 atm.) for 4 h. The clear solution was drawn off from the oil that had separated and its ^1H NMR spectrum was recorded, showing that no **1** remained. The spectrum contained, in addition to several small peaks in the range δ 0–0.5, a large peak at δ 0.13, which compares with values of δ 0.13 and δ 0.11 observed for TsiOH and TsiH in this solvent [16]. The toluene was removed from the solution under vacuum to leave a sticky solid, which gave a single sharp peak at δ 0.11 in $CDCl_3$ (the shift reported for TsiOH in this solvent [17]. The IR spectrum of a thin film of the sticky solid contained a broad band centred at 3400 cm^{-1}, consistent with (but not diagnostic of) a CO–H bond. Unfortunately an authentic sample of TsiOH was not available for comparison.

5.4.4. *With I_2*

(i) Solid iodine (0:10 mmol) was added to a solution of **1** (0.10 mmol) in toluene (2 cm^3) under argon. When the mixture was stirred at room temperature the colour had largely disappeared within a few hours, but even after 3 days the solution was still slightly pink. The clear solution was taken off from the solid that had separated and its ^1H NMR spectrum was recorded. This showed the presence off two large peaks, at δ 0.29 and 0.26, of approximately equal height, which were assigned to **1** and TsiI respectively.

(ii) When the above experiment was repeated but with a 2 molar proportion of iodine (*i.e.* 0.20 mmol) and for 2 days only, the solution contained only TsiI.

5.4.5. *With Br_2*

When the procedure described under (i) above was repeated but with Br_2 (0.10 mmol) in place of I_2, the colour disappeared more quickly. After 1 day the ^1H NMR spectrum showed the presence of **1** (δ 0.29) and TsiBr (δ 0.14) in a 1:2 molar ratio.

5.4.6. *With CH_3COCl*

(i) A solution of **1** (50 mg, 0.10 mmol) and CH_3COCl (0.10 mmol) in toluene (2 cm^3) was kept at room temperature for 3 days during which no visible change occurred. The ^1H NMR spectrum recorded after this time showed that only unchanged **1** and a little TsiH were present.

(ii) A mixture of **1** (50 mg) and CH_3COCl (2 cm^3) was boiled under reflux for 3 h and then evaporated to dryness under vacuum. The residue was dissolved in C_6D_6 and the ^1H NMR spectrum recorded. This showed that only unchanged **1** and a trace of TsiH were present.

5.4.7. *With BCl_3*

A solution of **1** (0.10 mmol) and BCl_3 (0.10 mmol) in toluene (2 cm^3) was kept for 15 h at room temperature. The ^1H NMR spectrum after this time showed that only **1** and a trace of TsiH were present.

5.4.8. *With Me_3SiCl, Me_2HSiCl, or MeI*

A solution of **1** (0.15 mmol) and the relevant halide (0.15 mmol) in toluene (2 cm^3) was kept at 25°C for 4 days. The ^1H NMR spectrum of the solution after this time showed that only the unchanged reagents were present.

5.4.9. *With $PhSO_2Cl$ (experiment by A.J. Jaggar).*

A solution of **1** (0.43 g, 0.88 mmol) and $PhSO_2Cl$ (2.1 mmol) in toluene (5 cm^3) was kept at 100°C for 8 h. The ^1H NMR spectrum after this time showed that some **1** still remained. Additional $PhSO_2Cl$ (1.0 mmol) was added and the mixture kept at 100°C for a further 4 h, after which no **1** remained. The solution was filtered to remove the magnesium salts and the precipitate was washed with toluene (2 × 5 cm^3). The filtrate and washings were combined and the solvent removed under vacuum at room temperature. The ^1H NMR spectrum of the residue showed in the Si–Me region only the signals from TsiCl and a trace of TsiH, but there were small peaks in the aryl-H region, probably from residual $PhSO_2Cl$.

5.4.10. *With $MgBr_2$*

A mixture of **1** (0.2 mmol) and $MgBr_2$ (0.2 mmol) in a 9/1 mixture of Et_2O and C_6D_6 (3 cm^3) was kept in a sealed NMR tube at 25°C for 5 h. There was no change in the ^1H NMR spectrum.

5.5. *Crystal structure determination*

Crystal data for **1**: $C_{20}H_{54}MgSi_6$, $M = 487.5$, triclinic, space group $P\bar{1}$, a = 9.093(7), b = 9.308(2), c = 11.907(4) Å, $\alpha = 68.52(2)°$, $\beta = 74.26(5)$, $\gamma = 58.98(4)$, $U = 807.1$ Å^3, $Z = 1$, $D_c = 1.00$ g cm^{-1}, $F(000) = 270$, monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, μ = 2.8 cm^{-1}.

A crystal *ca.* 0.4 × 0.4 × 0.4 mm^3, sealed in a capil-

TABLE 2. Fractional atomic coordinates ($\times 10^4$) for $Mg\{C(SiMe_3)_3\}_2$ with estimated standard deviations in parentheses

	x	*y*	*z*
Si(1)	−845.5(7)	1415.2(7)	−2761.1(5)
Si(2)	1589.3(7)	2348.3(7)	−2058.8(6)
Si(3)	2817.0(8)	−1412.9(8)	−2100.3(6)
Mg	0	0	0
C(1)	945(2)	633(2)	−1852(2)
C(2)	−2972(3)	2761(4)	−2022(3)
C(3)	−1195(3)	−339(3)	−2902(2)
C(4)	−572(4)	2723(4)	−4358(2)
C(5)	2546(3)	1930(3)	−679(3)
C(6)	3189(4)	2563(4)	−3404(3)
C(7)	−249(4)	4574(3)	−2234(3)
C(8)	3437(5)	−1480(4)	−3721(3)
C(9)	4838(3)	−1943(4)	−1544(3)
C(10)	2377(4)	−3325(3)	−1212(3)

lary under argon, was used for data collection on an Enraf-Nonius CAD4 diffractometer. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 25°$ were measured by a θ-2θ scan with a scan width $\Delta\theta = (0.8 + 0.35 \tan \theta)°$. Each reflection was given a rapid pre-scan at 1° $\min^{-1}$ in θ, where reflections with $I/\sigma(I)$ less than 1 were coded as unobserved. The remainder were rescanned subject to a maximum $I/\sigma(I)$ of 50 or maximum recording times of 60 seconds. Every 30 min two standard reflections were monitored and showed no significant variation. After correction for Lorentz and polarization effects but not for absorption, 2444 reflections with $|F^2| > \sigma(F^2)$ were used for the structure analysis. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.04I)^2]^{1/2}/\mathrm{Lp}$.

The unit cell is isomorphous with that of $Mn\{C(SiMe_3)_3\}_2$, so the coordinates of the Mn structure were used and refined by full matrix least squares with anisotropic temperature factors.

The hydrogen atoms were placed at calculated positions but then refined by full matrix least squares isotropically. Refinement converged at $R = 0.045$, $R' = 0.060$ with weighting scheme $w = 1/\sigma^2(F)$, and all final shift to error ratios were < 4.4. A final difference map was everywhere < 0.23 e A^{-3}. The structure solution and refinement were carried out on MicroVax computer using the Enraf-Nonius SDP-PLUS Program Package.

Atomic coordinates are listed in Table 2. Data for C–H bonds and a table of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (see ref. 1).

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