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The first structurally characterised oligosilylmagnesium compound

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Abstract

The crystalline magnesium compounds $Mg[Si(SiMe_3)_3]_2(thf)_2$ (**1**) and $MgBr[Si(SiMe_3)_3](thf)_2$ (**2**) are obtained in high yield from $MgBr_2$ and the Li or K sisyl in appropriate stoichiometry in Et_2O or thf; NMR spectra and X-ray crystal data for **1** and **2** confirm their structures; for **1:** Mg–Si 2.682(2) Å, Si–Mg–Si′ 131.19(15)°. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of silyl anions is a rapidly developing field [1]. Attention has largely focused on alkali metal silyls. As in carbanion chemistry, where Grignard reagents or MgR_2 compounds are sometimes the reagents of choice, silylmagnesium compounds may also offer advantages over alkali metal silyls. Examples of in situ–prepared silylmagnesium halides (e.g. from $LiSiMe_2Ph + MgBr_2$) for several organic reactions have shown improved control, compared with silyllithiums, of regio- [2a], stereo- [2b] or diastereo- [2c,d] selectivity. A second generation of silyl anions are the oligosilyls [3], among which the sisyl, $^{-}Si(SiMe_3)_3$, has been prominent. An in situ-prepared ‘sisyl-Grignard reagent’ [from [4] $Li[Si(SiMe_3)_3](thf)_3 + MgBr_2$] has been used, in preference to the sisyllithium reagent, to effect sila-Peterson reactions, e.g. $Me_2CO \rightarrow CH_2{=}C(Me)[Si(SiMe_3)_2]_2C(H)Me_2$ via $(Me_3Si)_2Si{=}CMe_2$ [5].

The present paper results from complementary interests of our three groups on oligosilylmetal compounds, including (a) new routes to potassium complexes [6]; (b) sisyl derivatives of early transition metals [7]; and (c) migratory insertion reactions of nitriles or isonitriles into $Li[Si(SiMe_3)_3](thf)_3$ [8]; in each area sisylmagnesium compounds were required.

2. Results and discussion

The synthesis and structure of the first well characterised crystalline sisylmagnesium compounds $Mg[Si(SiMe_3)_3]_2(thf)_2$ (**1**) and $MgBr[Si(SiMe_3)_3](thf)_2$ (**2**) are reported. Compound **1** was prepared (i or ii in Scheme 1) from $MgBr_2 + 2M[Si(SiMe_3)_3](thf)_n$ [$M = Li$ and $n = 3$, or $M = K$ and $n = 2$; the latter obtained [6] from $Si(SiMe_3)_4 + KOBu^t$ in thf]. Using this sisylpotassium compound and an equivalent portion of $MgBr_2$, the sisyl-Grignard reagent **2** was isolated (iii in Scheme 1). The quantitative nature of the reactions was verified by following their course by ^{29}Si-NMR spectroscopy at ambient temperature. Alternatively, crystalline compound **2** was synthesised either (iv in Scheme 1) by addition of a solution of $Li[Si(SiMe_3)_3](thf)_3$ in diethyl ether to an equivalent portion of $MgBr_2$ suspended in Et_2O, or (v in Scheme 1) in C_6D_6 solution from $MgBr_2$ and **1**.

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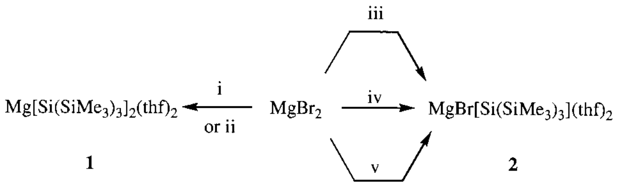


Scheme 1. Synthesis of the sisylmagnesium compounds **1** and **2**. Reagents and solvents (at ambient temperature): (i) 2Li[Si-$(SiMe_3)_3$]$(thf)_3$, Et_2O; (ii) 2K[Si(Si$(SiMe_3)_3$)]$(thf)_2$, thf; (iii) K[Si-$(SiMe_3)_3$]$(thf)_2$, thf; (iv) Li[Si$(SiMe_3)_3$]$(thf)_3$, Et_2O; (v) **1**, Et_2O, C_6D_6 (NMR experiment).

The crystalline compound **1** was thermally stable and did not melt below 200°C. In C_6D_6 solution, however, it very slowly eliminated hexakis(trimethylsilyl)disilane **3** [previously obtained [9] from $PbCl_2 + 2Li[Si(SiMe_3)_3][(thf)_3]$, Eq. (1), $\delta[^1H]$ 0.24, as established by monitoring the ^{1}H-NMR spectrum in C_6D_6 at ambient temperature, revealing a ratio of **1**:**3** of 1:0.06 after 1 h but 1:0.4 after 7 d. Nevertheless, the thf ligands in **1** are firmly bound, although under EI MS conditions a strong signal from **1**, assigned to the thf-free cation, was observed.

$$Mg[Si(SiMe_3)_3]_2(thf)_2 \xrightarrow{C_6D_6} (Me_3Si)_3Si\text{-}Si(SiMe_3)_3 + 2\,thf + Mg \quad (1)$$

The molecular structure of the crystalline complex **1** is illustrated in Fig. 1. The molecule lies on a two-fold symmetry axis. The Mg atom and its attached Si atoms have distorted tetrahedral configurations, the widest angles being Si(1)–Mg–Si(1)′ [131.19(15)°] and Mg–Si(1)–Si′ [av. 115.2°] and the narrowest O–Mg–O′ [92.0(3)°] and Si′–Si(1)–Si″ [av. 102.8°]. The Mg–Si bond length of 2.682(2) Å is unexceptional. The only Mg–Si compounds for which X-ray data are available are of (a) the bis-trimethylsilyls: $Mg(SiMe_3)_2(LL)$ [LL = dme [10a], tmeda [10b] or 1,3-$(Me_2N)_2C_3H_6$ [10c], having Mg–Si bond lengths 2.630(2), av. 2.628(4) and av. 2.660(2) Å and Si–Mg–Si′ bond angles 125.2(1), 115.3(1) and 119.7(1)°, respectively]; and (b) $MgBr(SiMe_3)L$ [L = tmeda {a 'loose'–(μ-Br)$_2$–dimer, Mg–Br ca. 2.53 and Mg–Br 3.21 Å} or pmdeta], having similar Mg–Si bond lengths of 2.630(4) and 2.651(6) Å, respectively [11]. The Si–Si′ bond lengths and Si′–Si–Si″ bond angles in **1** are similar to those found in the alkali metal sisyls $[M\{\mu\text{-}Si(SiMe_3)_3\}]_2$ (M = Li, Na, K, Rb or Cs) (also termed 'hypersilyls') [12] or $LiSi(SiMe_3)_3(thf)_3$ [4].

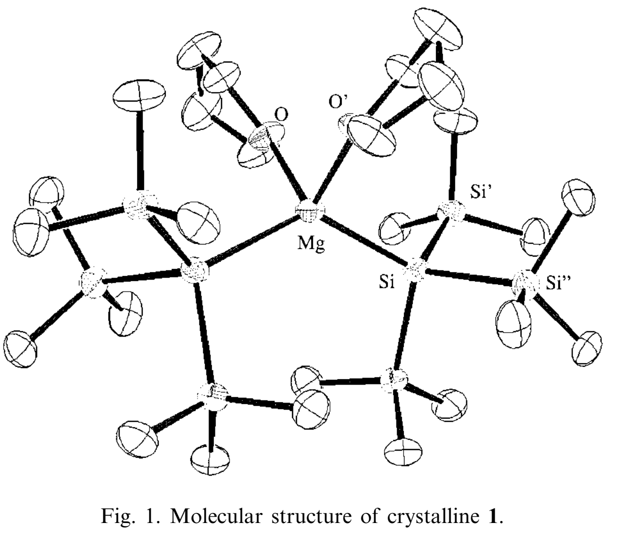
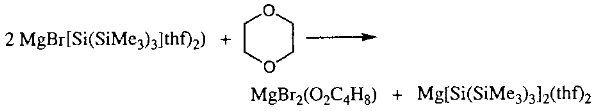


Fig. 1. Molecular structure of crystalline **1**.

Compound **2**, like **1**, was obtained as a colourless, analytically pure solid that melted sharply, and showed satisfactory NMR spectral features. The EI mass spectrum was identical to that of **1**, indicating that under these conditions it underwent a Schlenk — type conversion into **1**. Likewise, as in the case of conventional Grignard reagents, addition of 1,4-dioxane to **2** afforded **1**, Eq. (2). The rate of this process was monitored by ^{1}H-NMR spectroscopy, as illustrated in Fig. 2.



$$2\,MgBr[Si(SiMe_3)_3]thf)_2) + C_4H_8O_2 \longrightarrow MgBr_2(O_2C_4H_8) + Mg[Si(SiMe_3)_3]_2(thf)_2 \quad (2)$$

A specimen of **2**, prepared according to (iv) in Scheme 1 was crystallized from diethyl ether. Single crystals were obtained. An X-ray diffraction analysis revealed a unit cell containing not only the molecule **2**, but also another in which in place of two thf molecules, there was one thf and one diethyl ether; another crystal had one thf and further residual electron density. The refinement converged at ca. $R = 12\%$; this was adequate merely to confirm its mononuclear nature (Fig. 3) having one sisyl and one bromide ligand attached to a distorted tetrahedrally coordinated magnesium atom.

Oligosilylmagnesium compounds are likely to open up new chemistry and the present results on sisyl derivatives offer, we believe, a firm foundation.

3. Experimental

3.1. Synthesis of $Mg[Si(SiMe_3)_3]_2(thf)_2$ (**1**)

$MgBr_2(OEt_2)$ (0.803 g, 3.11 mmol) was added to an in situ-generated solution of $K[Si(SiMe_3)_3](thf)_2$ (6.23 mmol) in thf (10 ml) at ambient temperature. The mixture was stirred for 1 h. Solvent was removed in vacuo and pentane (3 × 10 ml) was added. The filtrate was concentrated and set aside at −30°C for 2 d yielding white crystals of **1** (1.75 g, 85%). (Found: C, 45.2; H, 10.32. $C_{26}H_{70}MgO_2Si_8$ requires C, 47.04; H, 10.63%). NMR spectral data in C_6D_6 at 298 K (^{1}H 500 MHz, ^{13}C 125.7 MHz, ^{29}Si 99.3 MHz) ^{1}H: δ 3.74 (m, 8H), 1.32 (m, 8H), 0.46 (s, 54H); $^{13}C\{^1H\}$: δ 70.23, 25.53, 5.85; $^{29}Si\{^1H\}$: δ −6.4, −171.9; for. EI-MS, 70

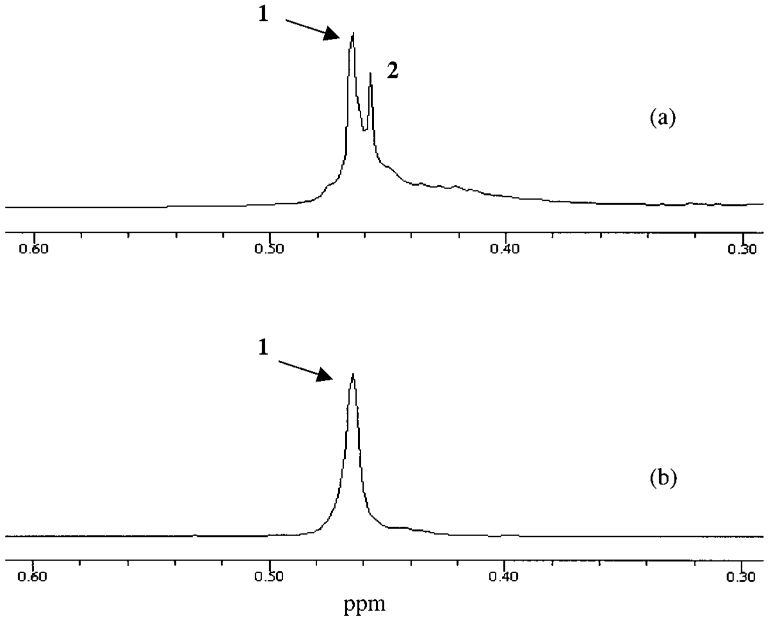


Fig. 2. Time dependent ^{1}H-NMR spectral studies on reaction (2) in C_6D_6; for (a), after 10 min at 20°C; δ 0.465 for **1** and δ 0.457 for **2** (ratio of **1**:**2** = 1:1.2); for (b), after 20 min at 20°C; δ 0.465 for **1**.

eV: *m*/*z* (%): 518 $[M-2thf]^+$ (58), 503 $[M-Me]^+$ (20), 271 $[MgSi(SiMe_3)_3]^+$ (95), 247 $[Si(SiMe_3)_3]^+$ (88), 173 $[Si(SiMe_3)_3]^+$ (100), 73 $[SiMe_3]^+$ (86).

The crystalline compound **1**, having essentially identical spectral properties, was also prepared by addition of $Li[Si(SiMe_3)_3](thf)_3$ (1.68 g, 3.6 mmol) in Et_2O (50 ml) to a stirred suspension of $MgBr_2$ (0.33 g, 1.8 mmol) in Et_2O (30 ml) at −80°C. The mixure was stirred for 16 h at ambient temperature. Dioxane (0.5 ml) was added and the solution stirred for a further 5 min; the solvent was then removed in vacuo and the residue was extracted into pentane (50 ml). The extract was concentrated and cooled at −30°C for 1 d, yielding white crystals of **1** (1.27 g, 53%).

3.2. *Synthesis of $MgBr[Si(SiMe_3)_3](thf)_2$ (**2**)*

$MgBr_2(OEt_2)$ (1.61 g, 6.23 mmol) was added to an in situ-generated solution of $K[Si(SiMe_3)_3](thf)_2$ (6.23 mmol) in thf (20 ml) at ambient temperature. The yellow solution was immediately decolourised and a white precipitate was formed. The mixture was stirred for 1 h, solvent was removed in vacuo and pentane (3 × 10 ml) was added. The filtrate was set aside for 2 d at −30°C yielding white crystals of **2** (2.81 g, 91%). Found: C, 40.6; H, 8.57. $C_{17}H_{43}MgO_2Si_4$ requires C, 41.2; H, 8.74%). NMR spectral data in C_6D_6 or C_4D_8O (for ^{13}C) at 298 K (^1H 500 MHz, ^{13}C 125.7 MHz, ^{29}Si 99.3 MHz). ^1H: δ 3.82 (m, 8H), 1.53 (m, 8H), 0.40 (s, 27H); $^{13}C\{^1H\}$: δ 67.80, 25.47, 4.59; $^{29}Si\{^1H\}$: δ −6.5, −168.7. M.p. 198–201°C.

Compound **2** was also prepared by addition of $Li[Si(SiMe_3)_3](thf)_3$ (1.15 g, 2.4 mmol) in Et_2O (20 ml) to a stirred suspension of $MgBr_2$ (0.45 g, 2.4 mmol) in Et_2O (20 ml) at ambient temperature. The mixture was stirred for 15 h, Solvent was removed in vacuo and the residue was extracted into Et_2O (60 ml). The extract was concentrated and cooled at −30°C for 2 d, yielding white crystals of **2** (0.80 g, 68%).

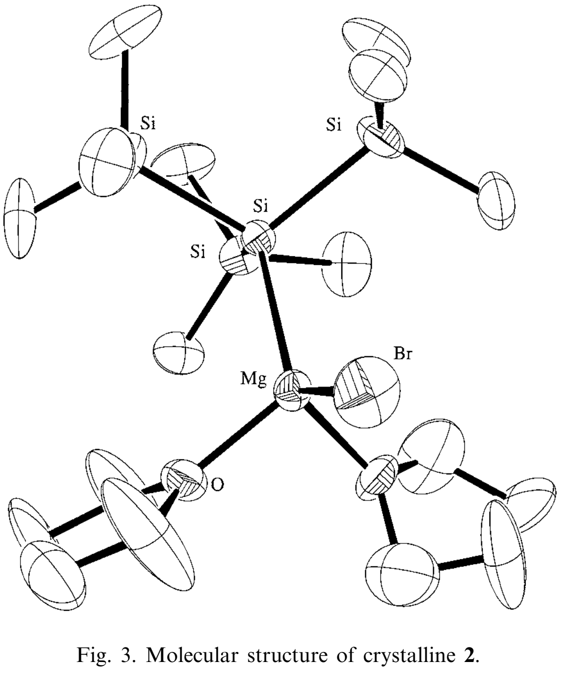


Fig. 3. Molecular structure of crystalline **2**.

3.3. Reaction of $MgBr[Si(SiMe_3)_3](thf)_2$ (2) with 1,4-dioxane

Dioxane (0.05 g, 0.53 mmol, 0.04 ml) was added to a saturated solution of **2** (0.35 g, 0.52 mmol) in pentane (20 ml) and the mixture was stirred for 30 min. The solvent was removed in vacuo and the product was extracted into pentane (40 ml); white crystals of **1** (0.28 g, 83%) were isolated after 2 d at −30°C.

3.4. Crystallographic data for *1* and *2*

Single crystals of **1** were obtained from pentane at −30°C. The following data were derived. $C_{26}H_{70}MgO_2Si_8 \cdot C_5H_{12}$, $M = 736.0$, monoclinic, space group $C2/c$ (No.15), $a = 18.6893(6)$, $b = 15.4235(5)$, $c = 18.6904(3)$ Å, $\beta = 115.8604(3)°$, $V = 4848.1(2)$ Å^3, $Z = 4$, λ(Mo–K$_\alpha$) 0.71069 Å, $\mu = 0.27$ mm^{-1}. Data were collected at 175(2) K on a SMART (Siemens) CCD area detector, 1483 observed reflections $[I > 3\sigma(I)]$, $R_{\text{int}} = 0.042$, $wR_2 = 0.045$, CCDC reference number 141763. An independent, essentially identical, structural determination was carried out by Dr P.B. Hitchcock, Sussex, using an Enraf–Nonius CAD4 instrument who also carried out the analysis on **2**. Single crystals of **2** were obtained from a pentane–diethyl ether solution at −30°C. Data were collected at 173 K, 7134 observed reflections $[I > 4\sigma(I)]$, $R_{\text{int}} = 0.113$.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 141763 for compound **1**. Copies of this information can 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).

See http://www.rsc.org./suppdata/cc/2000/ for crystallographic data in.cif format for **1**.

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