

Note

Synthesis and characterisation of [AlMe_n{Si(SiMe₃)₃}_{3-n}(thf)] (n = 1 or 2)

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Abstract

The crystalline compounds [AlMe_n{Si(SiMe₃)₃}_{3-n}(thf)] [n = 2 (**1**) or 1 (**2**)] were prepared from the lithium silyl [Li{Si(SiMe₃)₃}(thf)₃] (**A**) and the appropriate methylaluminium chloride [AlCl_{3-n}Me_n] in thf. The X-ray structure of **1** is reported. Unlike **A** or a magnesium silyl [Mg{Si(SiMe₃)₃}₂(thf)₂] (**B**), neither **1** nor **2** underwent an insertion reaction with an α-H-free nitrile.
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1. Introduction

The tris(trimethylsilyl)silyl (hereafter “silyl”; elsewhere, also, “hypersilyl”) ligand [Si(SiMe₃)₃][−] has featured in much interesting chemistry. The compound Li[Si(SiMe₃)₃], originally obtained from Si(SiMe₃)₄ and LiMe [1], was characterised as the tris(thf) adduct [2]; its potassium analogue was later made from Si(SiMe₃)₄ and KOBu^t [3]. The X-ray structure of [Li{Si(SiMe₃)₃}(thf)₃] (**A**) has been published [4]. Compound **A** has been widely used as a silyl ligand transfer agent for *inter alia* Zn[Si(SiMe₃)₃]₂ [5], [Mg{Si(SiMe₃)₃}₂(thf)₂] (**B**) [6], [Al(tmp)₂{Si(SiMe₃)₃}] [7] and [AlEt{Si(SiMe₃)₃}(μ-Et)]₂ [8]; while [K{Si(SiMe₃)₃}(thf)₂] was employed as a precursor to [Al{Si(SiMe₃)₃}-X₂(thf)] (X = Cl, Br, I) [9].

2. Results and discussion

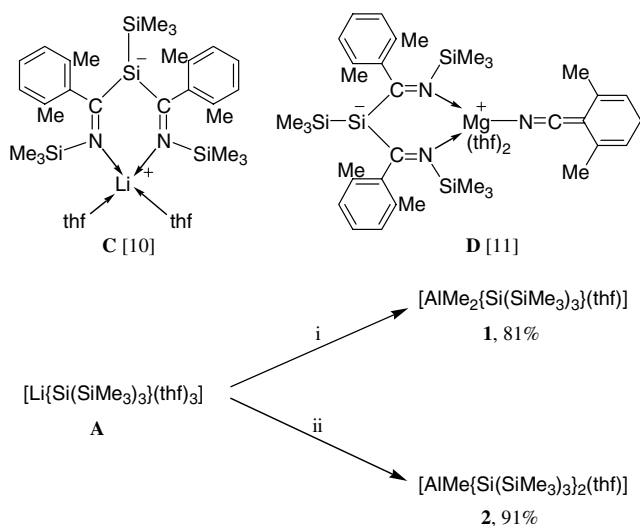
Our interest in silylaluminium compounds arose from the discovery that the alkali metal and magnesium compounds, including **A** and **B**, upon treatment with 2,6-dimethyl(cyano)benzene gave interesting metal 3-sila-

β-diketiminates including the crystalline compounds **C** [10] and **D** [11]. We therefore sought two methylaluminium silyls as potential precursors to corresponding 3-sila-β-diketiminates.

The two crystalline mononuclear methylaluminium silyls **1** and **2** were prepared in good yield, as shown in Scheme 1. Each was characterised by satisfactory microanalysis (C, H, N) and ¹H NMR spectra, and compound **1** also by its X-ray molecular structure. Attempts to obtain good quality crystals of **2** for X-ray analysis were hampered by its extremely high solubility in Et₂O, thf, PhMe or C₅H₁₂, such that crystals isolated from a concentrated solution dissolved in the co-crystallised solvent.

The ²⁹Si{¹H} NMR spectrum of **1** in C₆D₆ failed to reveal a signal between 80 and −200 ppm for the ²⁹Si nucleus adjacent to the aluminium atom, attributed to broadening of the signal due to coupling with ²⁷Al. The ²⁹Si (of the SiMe₃ moieties) and ²⁷Al signals for **1** were found at similar frequencies as in the NMR spectra of [Al(tmp)₂{Si(SiMe₃)₃}] (at δ −7.9 and +186, respectively) [7], which also failed to record a value for the α-Si. However, such data for the α-Si were observed at δ −81 ± 0.3 ppm for the compounds [Al{Si(SiMe₃)₃}-X₂(thf)] (X = Cl, Br, I) with the SiMe₃ value at δ −8.4 ± 0.3 ppm [9].

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Scheme 1. Reagents: (i) AlClMe_2 , C_6H_{14} ; (ii) AlCl_2Me , $\text{C}_6\text{H}_{14}/\text{Et}_2\text{O}$.

The molecular structure of the crystalline compound **1** is shown as an ORTEP representation in Fig. 1. Selected bond lengths and angles are listed in Table 1 together with corresponding data for the sterically closely similar compound $[\text{AlX}_2\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})]$ [9]. The AlX_2 moiety has a more positive aluminium atom in the latter ($\text{X} = \text{Cl}$) than in **1** ($\text{X} = \text{Me}$); hence it is not surprising that both the $\text{Al-Si}(1)$ and Al-O distances are longer in **1**.

Attempts at derivatisation of each of the compounds **1** and **2**, by treatment with the α -H-free nitrile PhCN , $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{CN}$ or Bu^tCN , failed to reveal any insertion of the latter into the Al-Me or Al-Si bond. ^1H NMR spectra in PhMe-d_8 showed minor shifts of ^1H NMR signals of **1** or **2**, which may have been due to some displacement of coordinated thf by the nitrile. In contrast to the observation of C_2H_4 polymerisation activity by cationic methylaluminium amidinates such as $[\text{AlMe}\{\text{N}(\text{Pr}^i)\text{C}(\text{Me})\text{NPr}^i\}][\text{B}(\text{C}_6\text{F}_5)_4]$ [12], neither **1** nor **2** in presence of MAO showed any reaction with C_2H_4 under ambient conditions.

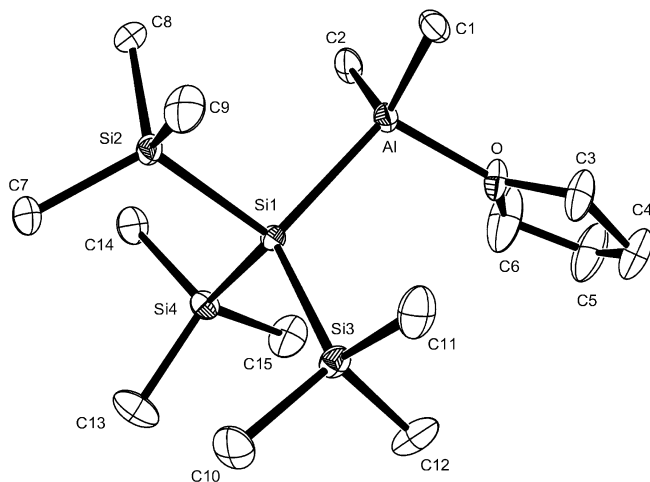


Fig. 1. ORTEP representation of the molecular structure of **1** (20% ellipsoids).

Table 1
Selected bond lengths (Å) and angles (°) for $[\text{Al}\{\text{Si}(\text{SiMe}_3)_3\}\text{X}_2(\text{thf})]$ ($\text{X} = \text{Me}$ (**1**), Cl [9])

	$\text{X} = \text{Me}$ (1)	$\text{X} = \text{Cl}$ [9]
$\text{Al-Si}(1)$	2.4747(16)	2.4101(13)
Al-X	1.978(5), 1.988(4)	2.1443(8), 2.1545(9)
Al-O	1.929(3)	1.8668(4)
$\text{Si}(1)\text{-Si}$	2.3336(13), 2.3419(14), 2.3432(15)	2.3380(8), 2.3453(10), 2.3527(9)
$\text{O-Al-Si}(1)$	107.79(12)	111.93(6)
O-Al-X	101.67(19), 101.77(17)	100.94(5), 101.46(5)
X-Al-X	117.0(2)	110.23(4)
$\text{Al-Si}(1)\text{-Si}$	103.77(6), 112.39(6), 115.34(6)	104.14(4), 111.14(4), 111.91(3)

3. Experimental

All manipulations were carried out under argon using standard Schlenk and vacuum line techniques. Hexane and pentane were dried using sodium-potassium alloy. Diethyl ether was dried and distilled from sodium benzophenone and stored over a sodium mirror. $[\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})_3]$ was prepared by a literature procedure [3]; the 1 molar solutions of $\text{AlCl}_{3-n}\text{Me}_n$ in hexane were purchased (Aldrich). The NMR spectra were recorded at 293 K in C_6D_6 on Bruker DPX 300 (300.1 MHz for ^1H , 75.5 MHz for ^{13}C) or AMX 500 (49.7 MHz for ^{29}Si and 131.31 MHz for ^{27}Al) and referenced internally to residual solvent resonances (^1H , ^{13}C) or externally (^{29}Si using SiMe_4 ; ^{27}Al using aqueous AlCl_3 with a D_2O lock). The electron impact mass spectrum of **1** was taken on a solid sample using a Kratos MS 80 RF instrument. Elemental analyses were carried out by Medac Ltd., UK, Brunel University.

3.1. Preparation of $[\text{AlMe}_2\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})]$ (**1**)

A solution of AlClMe_2 (1 M in hexane, 9.29 cm^3 , 9.29 mmol) was added dropwise to a stirred suspension of $[\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})_3]$ (**A**) (4.37 g, 9.28 mmol) in pentane (30 cm^3) at ambient temperature. After ca. 14 h the mixture was filtered. The filtrate was concentrated and stored at -30°C for 1 day, yielding white crystals of compound **1** (2.83 g, 81%) (Anal. Calc. for $\text{C}_{15}\text{H}_{41}\text{AlOSi}_4$: C, 47.8; H, 10.97. Found: C, 49.6; H, 10.31%), decomposition 116°C . ^1H NMR: δ -0.31 (br s, 6H, AlMe_2), 0.41 (s, 27H, $\text{Si}\{\text{SiMe}_3\}_3$), 1.03 (m, 4H, thf), 3.46 (m, 4H, thf); $^{13}\text{C}\{^1\text{H}\}$ NMR: δ -4.58 (AlMe_2), 4.47 (SiMe_3), 25.08 (thf), 71.22 (thf); $^{29}\text{Si}\{^1\text{H}\}$ NMR: δ -8.71 ($\text{Si}\{\text{SiMe}_3\}_3$); $^{27}\text{Al}\{^1\text{H}\}$ NMR: δ 190 ($\Delta\omega^{1/2}$ 3.3 Hz). EI-MS: m/z , assignment (%) 304 $[\text{AlMe}_2\{\text{Si}(\text{SiMe}_3)_3\}]^+$ (52), 289 $[\text{AlMe}\{\text{Si}(\text{SiMe}_3)_3\}]^+$ (66), 232 $[\text{Si}(\text{SiMe}_3)_2\text{SiMe}_2]^+$ (100).

3.2. Preparation of $[\text{AlMe}\{\text{Si}(\text{SiMe}_3)_3\}_2(\text{thf})]$ (**2**)

A solution of AlCl_2Me (1 M in hexane, 1.79 cm^3 , 1.79 mmol) was added dropwise to a stirred solution of **A**

Table 2
Crystal data and structure refinement for **1**

Empirical formula	C ₁₅ H ₄₁ AlOSi ₄
Formula weight	376.82
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 ₁ (No. 33)
<i>a</i> (Å)	19.5787(8)
<i>b</i> (Å)	12.9138(7)
<i>c</i> (Å)	9.9808(5)
<i>V</i> (Å ³)	2523.5(2)
<i>Z</i>	4
<i>d</i> _{calc} (Mg/m ³)	0.99
μ (Mo K α) (mm ⁻¹)	0.27
Reflections collected	9000
Independent reflections (<i>R</i> _{int})	4104 (0.060)
Reflections with <i>I</i> > 2 σ (<i>I</i>)	3456
Data/restraints/parameter	4104/1/191
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.049, <i>wR</i> ₂ = 0.110
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.064, <i>wR</i> ₂ = 0.120

(1.69 g, 3.59 mmol) in diethyl ether (20 cm³) at ambient temperature. The mixture was stirred for *ca.* 1 h, whereafter volatiles were removed *in vacuo* and the residue was extracted into pentane (2 × 30 cm³). The extract was concentrated and cooled at –30 °C for 2 days, yielding white crystals of compound **2** (0.88 g, 91%), m.p. 58–60 °C (Anal. Calc. for C₂₃H₆₅AlOSi₈: C, 45.3; H, 10.75. Found: C, 46.1; H, 10.26%). ¹H NMR: δ –0.10 (s, 3H, AlMe), 0.41 (s, 54H, Si{SiMe₃}₃), 1.28 (m, 4H, thf), 3.57 (m, 4H, thf); ¹³C{¹H} NMR: δ –4.53 (AlMe), 4.43 (SiMe₃), 25.09 (thf), 71.23 (thf).

4. Crystal data and refinement details for **1**

Diffraction data were collected on a Enraf-Nonius Kappa-CCD diffractometer using monochromated Mo K α radiation, λ 0.71073 Å at 173(2) K. The crystal was coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The structure was refined on all *F*² using SHELXL-97 [13]. An absorption correction was applied using MULTISCAN. The illustration of Fig. 1 used ORTEP-3 for Windows (20% ellipsoids). Further details are in Table 2.

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Appendix A. Supplementary material

CCDC 651715 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.08.018](https://doi.org/10.1016/j.jorganchem.2007.08.018).

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