

The stable silylene $\text{Si}[(\text{NCH}_2^t\text{Bu})_2\text{C}_6\text{H}_4-1,2]$: insertion into Li–C or Li–Si bonds of lithium alkyls LiR or $[\text{LiSi}(\text{SiMe}_3)_3(\text{THF})_3]$ [$\text{R} = \text{Me}, ^t\text{Bu}$ or $\text{CH}(\text{SiMe}_3)_2$]

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Abstract

The new crystalline amino-functionalised lithium silyls $\text{Li}[\text{Si}\{(\text{NCH}_2^t\text{Bu})_2\text{C}_6\text{H}_4-1,2\}\text{R}](\text{L})$ [$\text{R} = \text{Si}(\text{SiMe}_3)_3$ (sisyl), $\text{L} = (\text{THF})_2$ (**2**); $\text{R} = \text{Me}$, $\text{L} = (\text{OEt}_2)_2$ (**3**); $\text{R} = ^t\text{Bu}$, $\text{L} = (\text{THF})_3$ (**4a**) or $\text{THF}(\text{OEt}_2)$ (**4b**); $\text{R} = \text{CH}(\text{SiMe}_3)_2$, $\text{L} = (\text{THF})_2$ (**5**)] have been obtained in high yield from the silylene $\text{Si}[(\text{NCH}_2^t\text{Bu})_2\text{C}_6\text{H}_4-1,2]$ and Li–R under mild conditions. A by-product in the reaction leading to **4** was the crystalline disilane $[1,2\text{-C}_6\text{H}_4(\text{NCH}_2^t\text{Bu})_2(^t\text{Bu})\text{Si}]_2$ (**6**). Each of **2–6** was fully characterised by microanalysis, multinuclear NMR spectra and X-ray structures. Each of the compounds **3–6** was thermally stable in solution, whereas the sisyl derivative **2** retained its integrity only at low temperatures, being completely dissociated into its factors at ambient temperature. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Amino-functionalised silyl anions; Lithium; Alkyls; Silyls

1. Introduction

There are only few examples known of nucleophilic addition reactions of an alkali metal (M') organic compound $\text{M}'\text{Y}$ to a thermally stable carbene CX_2 (but Li^nBu has been added to a phosphino(silyl)carbene [1a]; for reviews, see Ref. [1b]) or a Group 14 metal(II) homologue MX_2 ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ or Pb). (The group X has frequently been a cyclopentadienyl; strictly, such MCp_2 compounds are not metallenes, this term being best restricted to a two-coordinate MX_2 complex.) These have rarely led to a product of insertion of MX_2 into the $\text{M}'\text{–Y}$ bond. The majority have dealt with a $\text{Sn}(\text{II})$ or, less often a $\text{Pb}(\text{II})$, MX_2 substrate.

Treatment of SnCp_2^* ($\text{Cp}^* = \text{C}_5\text{Me}_5$) with LiMe afforded LiCp^* and a mixture of $(\text{SnMe}_2)_n$ oligomers; $\text{Li}[\text{SnCp}_2^*\text{Me}]$ was presumed to be a labile intermediate, since quenching the reaction mixture at low temperature with CD_3I gave $\text{SnCp}_2^*(\text{CD}_3)\text{Me}$ [2]. Addition of

NaCp to MCp_2 yielded $[\text{Na}(\text{pmdeta})(\mu\text{-Cp})\text{MCp}_2]$ ($\text{Cp} = \text{C}_5\text{H}_5$, $\text{M} = \text{Sn}$ or Pb) [3]. The adduct $[\text{Li}(\text{pmdeta})(\mu\text{-Cp})\text{SnCp}\{\text{N}(\text{SiMe}_3)_2\}]$, obtained from $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ and SnCp_2 , was regarded as a model intermediate for a nucleophilic displacement at a $\text{Sn}(\text{II})$ centre [4]. Likewise, the alkali metal metallate(II) complexes $[\text{Li}(\text{THF})_4][\text{Sn}(\text{C}_{13}\text{H}_9)_3]$ [5], $[\text{Li}(\text{THF})\{\mu\text{-N}=\text{C}(\text{Bu})\text{Ph}\}_3\text{M}]$ ($\text{M} = \text{Sn}$ or Pb) [6,7], $[\text{Li}(\text{THF})(\mu\text{-}2\text{-C}_5\text{H}_4\text{N}\text{-C},\text{N})_3\text{M}]$ [8] ($\text{M} = \text{Sn}$ or Pb ; the Sn compound was trapped by addition of $^n\text{BuBr}$ [8a]), $[\text{Li}(\text{THF})_2\{\mu\text{-N}(\text{H})\text{R}'\}_2\text{Sn}\{\text{N}(\text{H})\text{R}'\}]$ [9] and $[\text{Li}(\text{NMe}_2)_3\text{Sn}]_\infty$ [10] were obtained from three equivalents of LiR and the appropriate MCp_2 or MCp_2^* substrate [$\text{R} = \text{C}_{13}\text{H}_9$ (fluorenyl), $\text{N}=\text{C}(\text{Bu})\text{Ph}$, $2\text{-C}_5\text{H}_4\text{N}$, $\text{N}(\text{H})\text{R}'$ or NMe_2 ; $\text{R}' = \text{C}_6\text{H}_4\text{OMe-}2$]; their formation probably proceeded by an initial nucleophilic displacement of successive Cp^- or $\text{Cp}^{* -}$ ligands (these being good leaving groups) and subsequent addition of LiR to MR_2 . Likewise, the reaction of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ with three equivalents of $\text{Na}[\text{Si}(\text{SiMe}_3)_3]$ led to the toluene solvate $[\text{Na}(\text{CH}_2\text{Ph})\text{Sn}\{\text{Si}(\text{SiMe}_3)_3\}_3]$ [11].

Further examples relate to the formation of $[\text{K}(\text{dme})_2(\mu\text{-OR})_2\text{Sn}(\text{OR})]$ [12a] or $[\text{Li}(\mu\text{-OAr})_2\text{Sn}(\text{OAr})]$

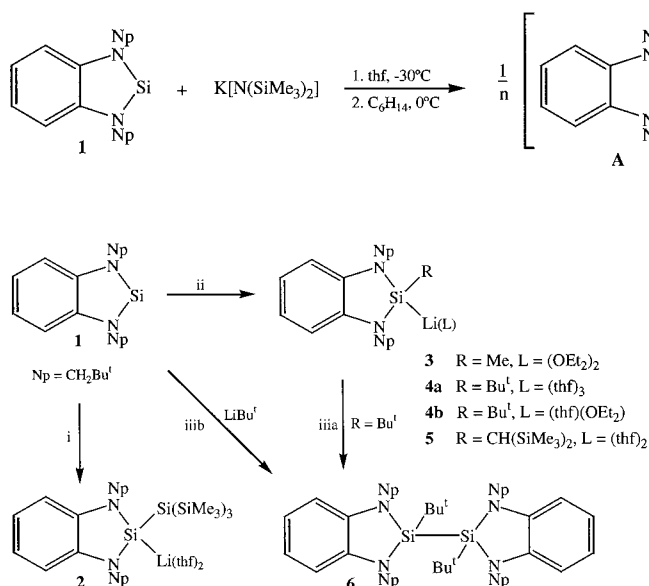
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[12b], obtained from, respectively, $[\text{Sn}(\text{OR})(\mu\text{-OR})_2]$ and 2KOR or SnCl_2 and 3LiOAr (R = SiPh₃ or SiMe₂Bu; Ar = C₆H₃Ph₂-2,6).

It is noteworthy that in *none* (but see Ref. [11]) of the above reactions was a mononuclear two-coordinate MX₂ compound the substrate. On the other hand, there are just two such reports involving a thermally robust carbene. The addition of $\text{K}[\text{N}(\text{SiMe}_3)_2]$ or $\text{Li}[\eta^5\text{-C}_5\text{H}_2(\text{SiMe}_3)_3\text{-1,2,4}]$ to $\text{C}[\text{N}(\text{Pr})(\text{CH}_2)_3\text{N}(\text{Pr})]$ or $\text{C}[\text{N}(\text{R})\text{CHCHNR}]$ gave $[\text{K}\{\mu\text{-N}(\text{SiMe}_3)_2\}\text{-}(\text{C}\{\text{N}(\text{Pr})(\text{CH}_2)_3\text{N}(\text{Pr})\})_2]$ [13] or $[\text{Li}\{\eta^5\text{-C}_5\text{H}_2(\text{SiMe}_3)_3\text{-1,2,4}\}(\text{C}\{\text{N}(\text{R})\text{CHCHNR}\})]$ [14], respectively (R = 'Bu, 1-adamantyl or 2,4,6-trimethylphenyl).

Recently, we briefly described the first such reactions of a silylene, Scheme 1 [15]. Thus, the thermally robust silylene $\text{Si}[(\text{NCH}_2\text{Bu})_2\text{C}_6\text{H}_4\text{-1,2}]$ (**1**) (abbreviated as Si(NN)) was found to insert into the Li–Si bond of $[\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}(\text{THF})_3]$ [16] to give the new, crystalline X-ray-characterised silyllithium compound $[\text{Li}\{\text{1}\}\text{Si}(\text{SiMe}_3)_3\}(\text{THF})_2]$ (**2**) (which dissociated in solution), whereas $\text{K}[\text{N}(\text{SiMe}_3)_2]$ with **1** in THF gave the novel, crystalline amidopotassium compound **A**; the latter was believed to have been formed by rearrangement of the intermediates $(\text{NN})\text{Si} \rightarrow \text{K}[\text{N}(\text{SiMe}_3)_2]$ and/or $\text{K}[\text{Si}(\text{NN})\text{N}(\text{SiMe}_3)_2]$ (Eq. (1), Np = CH₂Bu). (Reactions of a wider range of alkali metal amides with **1** will be described in due course.) We now provide: (i) full details on the synthesis and characterisation of **2**; and (ii) extensions of such silylene insertion reactions into the domain of lithium alkyls LiR [R = Me, 'Bu or CH(SiMe₃)₂]. This study is a continuation of our exploration of the chemistry of stable bis(amino)silylenes [17a]; for another review, see Ref. [17b].

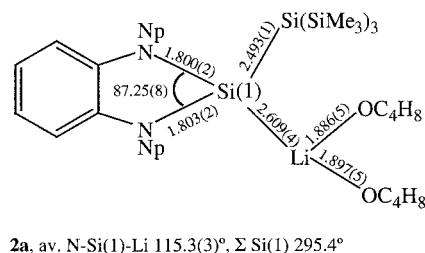


Scheme 1. Reagents and conditions: (i) $[\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}(\text{THF})_3]$, hexane, -30°C ; (ii) for **3**, LiMe, Et₂O, -30°C ; for **4**, Li'Bu, hexane, -30°C ; for **5**, Et₂O, -30°C ; (iii) (a) decomposition.

2. Results and discussion

The silylene **1** inserted under very mild conditions into the Li–Si (step i in Scheme 1) or Li–C (step ii in Scheme 1) bond of the lithium silyl $\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}$ or alkyl LiR [R = Me, 'Bu or CH(SiMe₃)₂], respectively. Each of the yellow (**2**) or colourless (**3–5**), crystalline, new silyllithium compounds was obtained in good yield (ca. 80%) and was characterised by satisfactory micro-analysis and multinuclear ¹H-, ¹³C-, ⁷Li-, ²⁹Si-NMR and EI mass spectra. Each was thermally stable at ambient temperature, with **3** (m.p. (dec.) $\geq 41^\circ\text{C}$) the most labile. This robustness is in contrast with previously reported amino-functionalised silyllithium compounds, which are only stable below 0°C (cf. $\text{Li}\{\text{Si}(\text{NEt}_2)_n\text{Ph}_{3-n}\}$ [18]). However, in solution, compound **4** (containing **4a** and **4b**) may have slowly decomposed, as evident from the isolation in low yield of disilane **6**, from the experiment (step ii in Scheme 1, R = 'Bu) leading to **4**. Compound **6** may have resulted from the homolysis of **4** (step iii(a) of Scheme 1), or (step iii(b) of Scheme 1) it may have been a by-product of the reaction between **1** and Li'Bu. As a probe of the decomposition of **4**, the less hindered homologue **3** was dissolved in C₆D₆–DMSO-*d*₆ and its fate monitored at ca. 60°C by ¹H-NMR spectroscopy; the spectrum was unchanged over several hours. The pathway to **6** warrants further examination.

The molecular structures of compounds **3**, **4a**, **4b** and **6** are shown in Figs. 1–4, respectively, and selected bond lengths and bond angles are given in Table 1. The structure of **2** was reported previously [15], key geometric parameters being illustrated in **2a**.



The asymmetric unit of crystalline **4** contains two different molecules: the tris(THF) adduct **4a** and the THF–(diethyl ether) adduct **4b**. In each of the molecules **3**, **4a** and **4b** the silyl anion is pyramidal at the silicon atom with respect to its contiguous N(1), N(2) and C(17) atoms; the sum of the three angles subtended by these three atoms at Si is low [295.52 (3),

Table 1
Selected bond lengths (Å) and bond angles (°) for **3**, **4a**, **4b** and **6**

	3	4a	4b ^a	6 ^b
<i>Bond lengths</i>				
Si–Li	2.604(6)	2.724(9)	2.619(9)	
Si–C(17)	1.922(4)	1.978(6)	1.970(5)	1.8996(15)
Si–N(1)	1.79(4)	1.806(4)	1.803(4)	1.7748(12)
Si–N(2)	1.811(3)	1.808(4)	1.804(4)	1.7615(12)
Li–O(1)	1.911(7)	2.040(10)	1.904(9)	
Li–O(2)	1.893(7)	1.995(10)	1.948(11)	
Li–O(3)		2.028(10)		
<i>Bond angles</i>				
N(1)–Si–N(2)	87.19(15)	85.88(19)	87.05(19)	91.42(6)
N(1)–Si–C(17)	107.73(19)	102.9(2)	103.2(2)	114.30(6)
N(2)–Si–C(17)	100.6(17)	103.1(3)	103.9(2)	112.87(6)
N(1)–Si–Li[Si']	116.8(2)	121.0(3)	122.4(3)	[113.54(5)]
N(2)–Si–Li[Si']	125.6(2)	122.2(2)	121.0(3)	[113.96(5)]
C(17)–Si–Li[Si']	114.7(2)	116.4(3)	114.7(3)	[109.82(5)]

^a In Fig. 3, labels denoted with 'b'.

^b Si–Si' 2.465(7).

Table 2
Selected ¹³C{¹H}- and ²⁹Si{¹H}-NMR spectroscopic data for **1**, **3–7**

	δ (¹³ C _{<i>ipso</i>})	δ (¹³ C _{<i>ortho</i>})	δ (¹³ C _{<i>meta</i>})	δ (²⁹ Si)
1	141.48	110.67	118.48	96.9
3	147.84	106.76	114.49	53.8
4	147.68	105.89	113.82	47.5
5	146.99	106.88	114.16	48.0
6	142.7	110.8	117.7	16.6
7	139.61	110.68	118.98	–8.9

291.88 (**4a**) and 294.15° (**4b**) compared with that in [Li{Si(Ph)₂(NPh₂)}(THF)₃] (**B**) (309.8°) [18] or [Li(SiPh₃)(THF)₃] (**C**) (303.8°) [19], and is a result of the small bite angle [N(1)–Si–N(2) (85.9–87.2°)] of the chelating ligand. The lithium atoms in **3** and **4b** are in a distorted trigonal planar environment, as also is the case for **2** [ΣLi 356.9 (**2**), 360 (**3**), 359.6° (**4b**)], whereas **4a** has a four-coordinate lithium atom. The Li(sp²)–Si distances in **3** [2.604(6) Å] and **4b** [2.619(9) Å] are shorter than the Li(sp³)–Si bonds of **4a** [2.724(9) Å], **B** [2.732(7) Å] [18] or **C** [2.672(9) Å] [19]. The carbon atom C(17) α to silicon in **4a** or **4b** lies in the plane that bisects the C₆H₄(NCH₂Bu)₂-1,2 moiety; for **3**, however, it slightly deviates, as judged by the significant variation in the two N(1 or 2)–Si–C(17) bond angles, an effect attributed to the transoid disposition of its neopentyl groups.

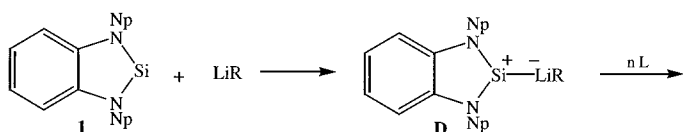
The centrosymmetric disilane molecule **6** has its inversion centre as the mid-point of the Si–Si' bond; its length of 2.465(7) Å may be compared with 2.539(2), 2.476(9) and 2.391(6) Å of the disilanes [(Et₂N)₂RSi]₂, R = CMe₂Pr, 'Bu [20] and Ph [21], respectively; or with 2.4081(11) Å of [N(Bu')(CH₂)₂NBu']HSi]₂ [22].

It is interesting to compare some geometrical features of **6** with those of **3**, **4a** and **4b**. In contrast to these, the silicon atom Si (and Si') in **6** is in only a slightly distorted tetrahedral environment, as shown by the much wider (by ca. 10°) N(1 or 2)–Si–C(17) but narrower N(1 or 2)–Si–Si'(or Li) (by ca. 6°) and C(17)–Si–Si'(or Li) (by ca. 5°) angles. As a consequence, the sum of the angles at Si subtended by N(1), N(2) and C(17) is much greater (318.59°) in **6** than in **3**, **4a** or **4b**, and is closer to the ideal tetrahedral value of 328°. The Si–N(1 or 2) bond lengths in **6** are slightly shorter than in **3**, **4a** or **4b** and the N(1)–Si–N(2) bond angle is significantly wider in **6** than in these three lithium silyls; while in the parent silylene **1**, the av. Si–N(1 or 2) bond distance is 1.75(1) Å and the N(1)–Si–N(2) angle is 88.2(1)° [23].

The ²⁹Si{¹H}- and selected ¹³C{¹H}-NMR spectral data for compounds **3–6** are summarised in Table 2, together with such data on the silylene **1** [23] and its iodomethane adduct [1,2-C₆H₄(NCH₂Bu)₂](Si(I)Me) (**7**) [23]. The ²⁹Si chemical shifts for **3–5** were at unusually high frequency compared with values for covalent Si(IV) compounds and highest for **3**, consistent with the weaker electron-releasing effect of Me than 'Bu or CH(SiMe₃)₂. These data are also available for comparison with those for LiSiPh₂(NEt₂) (δ 19.3), LiSiPh(NEt₂)₂ (δ 27.9), ClSiPh₂(NEt₂) (δ –6.8) and ClSiPh(NEt₂)₂ (δ –18.8) [17,18]. It has been suggested that amino substituents at a silicon atom have a deshielding effect on δ [²⁹Si]; a view supported by computational data on appropriate silyllithium compounds [24]. The δ [¹³C] values for the aromatic carbon nuclei of **3**, **4** and **5** were found at lower frequency than in **1**, **6** and **7** for the *ortho*-carbons and less clearly for the *meta*-carbons, whereas the reverse trend is noted for the *ipso*-carbons.

Variable temperature ²⁹Si-NMR spectra of the silyllithium compound **2** revealed that it readily dissociated into its factors in solution. Thus, at 298 K in toluene–toluene-*d*₈ the ²⁹Si-NMR chemical shifts were at δ 91.1, –5.8 and –180.75, which are close to the values of **1** (δ 96.9) and [Li{Si(SiMe₃)₃}(THF)₃] (δ –5.3 and –185.4) [25]. Upon cooling the solution of **2** to 198 K, the ²⁹Si signals were observed as a quartet at δ 59.9 [¹J(²⁹Si–⁷Li) = 63 Hz] and singlets at δ –9.9 and –154.5, assigned to the silicon nuclei α, γ and β to the lithium atom of **2**, respectively. The ¹H-NMR CH₂ signal of **2** (in toluene-*d*₈) was found at δ 3.52 at 343 K (cf. δ 3.58 for **1**), which at 208 K split into an AB-type quartet (δ 3.38, 3.35, 3.11 and 3.09), consistent with the structure of the undissociated compound **2**. The present ²⁹Si-NMR spectroscopic data are available for comparison with the values of δ 54.0 and 17.8 recorded for [Si{N('Bu)(CH₂)₂N'Bu}]²⁻ and [Bu'–N(CH₂)₂N(Bu')Si]₂²⁻, respectively [26].

The pathway to compounds **2–5** from **1** + LiR [R = Si(SiMe₃)₃, Me, ^tBu or CH(SiMe₃)₂] probably proceeds via an intermediate donor–acceptor adduct **D**, followed by subsequent intramolecular insertion of **1** into the Li–R bond, Eq. (2). Adducts such as **D** have previously been found in reactions between **1** and [Ln(η⁵-C₅H₅)₃] (Ln = Y or Yb) [27]. The silylene **1** has also been observed to behave as a donor to a Ni(0), Pt(0) or Pt(II) centre [28]; and similar adducts have been proposed as intermediates in the insertion of **1** into Ge(II)–N, Sn(II)–C, Sn(II)–N or Pb(II)–N bonds [17,29,30].



The present results introduce an alternative strategy (cf. Ref. [18]) towards the synthesis of functionalised silyllithium compounds. Furthermore, we anticipate that the lithium compounds **2–5** will be useful ligand transfer reagents for a wide range of metals.

3. Experimental

3.1. General procedures

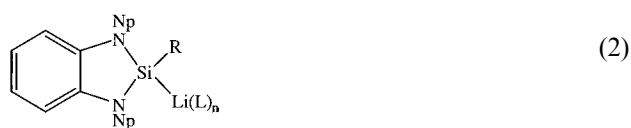
All operations and manipulations were carried out under purified Ar, by conventional Schlenk techniques. Solvents were dried and degassed before use. Microanalyses were carried out by Medac Ltd (Brunel University). The NMR spectra were recorded (at 298 K) using Bruker instruments: Bruker DPX 300 (¹H, ¹³C and ⁷Li) and AMX 500 (²⁹Si), and referenced internally to residual solvent resonances (data in δ). Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and were uncorrected.

3.2. [¹C₆H₄(NCH^tBu)₂-1,2]Si{Si(SiMe₃)₃}Li(THF)₂ (**2**)

A solution of [Li{Si(SiMe₃)₃}](THF)₃ (prepared from Si(SiMe₃)₄–LiMe in THF [16]) (0.79 g, 1.68 mmol) in hexane (10 ml) was slowly added to a stirred solution of **1** (0.46 g, 1.68 mmol) in hexane at –30 °C. The mixture was warmed to ambient temperature and stirred for 5 h, then filtered. The yellow filtrate was concentrated in vacuo and cooled at –25 °C affording yellow crystals of **2** (0.9 g, 80%), m.p. (dec.) ≥ 90 °C. Anal. Found: C, 56.8; H, 10.1; N, 4.05. Calc. for C₃₃H₆₉LiN₂O₂Si₅: C, 58.9; H, 10.33; N, 4.16%. ⁷Li-NMR (CD₃C₆D₃): δ 1.07 (298 K), 0.37 (228 K); for ¹H- and ²⁹Si{¹H}-NMR spectroscopic data refer to Section 2.

3.3. [¹C₆H₄(NCH^tBu)₂-1,2]Si(Me)Li(Et₂O)₂ (**3**)

A solution of LiMe (LiBr stabilised) (1.94 ml, 2.91 mmol, 1.5 M in Et₂O) was added slowly to a stirred solution of **1** (0.80 g, 2.91 mmol) in ether (20 ml) at –30 °C. The mixture was warmed to ambient temperature and stirred for 5 h, then filtered. The filtrate was concentrated and cooled at –25 °C yielding colourless crystals of **3** (0.98 g, 76%), m.p. (dec.) ≥ 41 °C. Anal. Found: C, 66.6; H, 10.82; N, 6.71. Calc. for C₂₄H₄₉LiN₂O₂Si: C, 67.5; H, 11.11; N, 6.30%. ¹H-NMR



(C₆D₆-*d*⁸-THF): δ 0.44 (s, 3H, CH₃), 1.2 (s, 18H, CH₃), 1.09 (t, 12H, Et₂O), 3.23, 3.27, 3.34 and 3.38 (AB-type, 4H, CH₂), 3.25 (q, 8H, Et₂O) and 6.74–6.79 (m, 4H, phenyl). ⁷Li-NMR (C₆D₆-*d*⁸-THF): δ –2.43. ¹³C{¹H}-NMR (C₆D₆-*d*⁸-THF): δ 13.57 (CH₃), 15.52 (Et₂O), 29.86 (CMe₃), 34.86 (CMe₃), 59.50 (CH₂), 65.85 (Et₂O), 106.76, 114.49 and 147.84 (phenyl). ²⁹Si{¹H}-NMR (C₆D₆-*d*⁸-THF): δ 53.8. EIMS; *m/z*: 289 ([M – Li(Et₂O)₂]⁺, 100%).

3.4. [¹C₆H₄(NCH^tBu)₂-1,2]Si(^tBu)Li(THF)₃ (**4**)

A solution of Li^tBu (1.48 ml, 2.51 mmol, 1.7 M in pentane) was added slowly to a stirred solution of **1** (0.69 g, 2.51 mmol) in *n*-hexane (20 ml) at –30 °C. The mixture was warmed to ambient temperature and stirred for 5 h. The solvent was removed from the cloudy pale yellow mixture in vacuo and the residue was extracted into THF. The extract was filtered and reduced to about 1 ml and Et₂O was added. Cooling at –25 °C afforded colourless crystals of **4** (1.09 g, 78%), m.p. (dec.) ≥ 77 °C. In another reaction, the THF was removed completely in vacuo and the remaining solid was extracted into Et₂O. The extract was filtered and concentrated in vacuo affording the mixed THF–Et₂O complex **4a/4b**. Anal. Found: C, 68.5; H, 10.45; N, 5.47. Calc. for [C₃₂H₅₉LiN₂O₃Si]/[C₂₈H₅₃LiN₂O₂Si] (THF–Et₂O complex): C, 69.3; H, 10.86; N, 5.39%. ¹H-NMR (C₆D₆-*d*⁸-THF): δ 0.99 (s, 9H, CH₃), 1.16 (s, 18H, CH₃), 1.45 (m, 12H, THF), 3.37, 3.42 and 3.58 (AB-type, one signal hidden under THF, 4H, CH₂), 3.52 (m, 12H, THF) and 6.60 (m, 4H, phenyl). ⁷Li-NMR (C₆D₆-*d*⁸-THF): δ –2.43. ¹³C{¹H}-NMR (C₆D₆-*d*⁸-THF): δ 25.69 (THF), 29.99 and 30.04 (SiCMe₃ and CMe₃), 30.87 (SiCMe₃), 35.93 (CMe₃), 56.19 (CH₂), 67.98 (THF), 105.89, 113.82 and 147.68 (phenyl). ²⁹Si{¹H}-NMR (C₆D₆-*d*⁸-THF): δ 47.5. EIMS; *m/z*: 332 ([M – Li(THF)₃]⁺, 74%), 275 ([M – Li(THF)₃ – ^tBu]⁺, 100%).

Table 3
Crystal data and structure refinement parameters for compounds **3**, **4** and **6**

	3	4a/b	6
Empirical formula	C ₂₅ H ₄₉ LiN ₂ O ₂ Si	[C ₃₂ H ₅₉ LiN ₂ O ₃ Si]/[C ₂₈ H ₅₃ LiN ₂ O ₂ Si]	C ₄₀ H ₇₀ N ₄ Si ₂
Formula weight	444.69	1039.60	663.18
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)	<i>Cc</i> (No. 9)	<i>P</i> $\bar{1}$ (No. 2)
Unit cell dimensions			
<i>a</i> (Å)	9.863(2)	18.9384(4)	10.1881(3)
<i>b</i> (Å)	16.967(8)	10.3931(3)	10.3795(3)
<i>c</i> (Å)	17.277(4)	33.7686(6)	10.6264(3)
α (°)	90	90	88.865(2)
β (°)	90	92.287(1)	83.978(2)
γ (°)	90	90	63.062(2)
<i>U</i> (Å ³)	2891.2(16)	6641.3(3)	995.77(5)
<i>Z</i>	4	4	1
μ (Mo–K α) (mm ⁻¹)	0.102	0.10	0.12
Total reflections	5542	23 818	11 010
Independent reflections	5065 [<i>R</i> _{int} = 0.051]	8962 [<i>R</i> _{int} = 0.067]	4709 [<i>R</i> _{int} = 0.032]
Reflections with <i>I</i> > 2 σ (<i>I</i>)	3411	6561	4103
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.066	0.069	0.049
<i>wR</i> (all data)	0.165	0.193	0.148

3.5. [$\{C_6H_4(NCH_2Bu)_{2-1,2}\}Si\{CH(SiMe_3)_2\}Li(OEt_2)$] (**5**)

A solution of Li[CH(SiMe₃)₂] (0.28 g, 1.68 mmol) in Et₂O (10 ml) was added slowly to a stirred solution of **1** (0.46 g, 1.68 mmol) in Et₂O (20 ml) at –30 °C. The mixture was warmed to ambient temperature, stirred for 24 h, then concentrated to about 5 ml in vacuo, and hexane was added. The mixture was filtered and cooled at –25 °C yielding colourless crystals of **5** (0.72 g, 83%), m.p. (dec.) \geq 205 °C. Anal. Found: C, 61.2; H, 9.89; N, 5.58. Calc. for C₂₇H₅₅LiN₂O₃Si₃: C, 63.0; H, 10.77; N, 5.44%. ¹H-NMR (C₆D₆-*d*⁸-THF): δ –0.81 (s, 1H, CH), 0.24 (s, 18H, SiCH₃), 1.07 (t, 6H, Et₂O), 1.12 (s, 18H, CH₃), 3.14, 3.19, 3.24 and 3.29 (AB-type, 4H, CH₂), 3.24 (q, 4H, Et₂O) and 6.59 (m, 4H, phenyl). ⁷Li-NMR (C₆D₆-*d*⁸-THF): δ –2.5. ¹³C{¹H}-NMR (C₆D₆-*d*⁸-THF): δ 4.48 (SiCH₃), 15.52 (Et₂O), 20.15 (CH), 30.06 (CMe₃), 35.53 (CMe₃), 56.93 (CH₂), 65.88 (Et₂O), 106.88, 114.16 and 146.99 (phenyl). ²⁹Si{¹H}-NMR (C₆D₆-*d*⁸-THF): δ 48.0 and –4.2 (SiMe₃). EIMS; *m/z*: 434 ([M – Li(Et₂O)]⁺, 30%), 377 ([M – Li(Et₂O) – 'Bu]⁺, 67%).

3.6. [$\{C_6H_4(NCH_2Bu)_{2-1,2}\}Si('Bu)_2$] (**6**)

Compound **6** was isolated in a very small amount during the crystallisation of compound **4**, m.p. (dec.) = 275 °C. Anal. Found: C, 71.0; H, 10.41; N, 8.25. Calc. for C₄₀H₇₀N₄Si₂: C, 72.4; H, 10.64; N, 8.45%. ¹H-NMR (C₆D₆-*d*⁸-THF): δ 1.04 (s, 18H, CH₃), 1.07 (s, 9H, CH₃) 2.90, 2.95, 3.01 and 3.06 (AB-type, 4H, CH₂) and

6.60–6.80 (m, 4H, phenyl). ¹³C{¹H}-NMR (C₆D₆-*d*⁸-THF): δ 20.43 (s, SiCMe₃), 24.99 (SiCMe₃), 30.97 (CMe₃), 34.14 (CMe₃), 56.68 (CH₂), 110.84, 117.74 and 142.69 (phenyl). ²⁹Si{¹H}-NMR (333 K, C₆D₆-*d*⁸-THF): δ 16.6. EIMS; *m/z*: 662 ([M]⁺, 12%), 331 ([M/2]⁺, 100%), 275.

4. Crystal data and refinements details

Data were collected using monochromated Mo–K α radiation, λ = 0.71073 Å, with the crystal under a stream of cold nitrogen gas, on a CAD4 diffractometer for **3** or a Nonius KappaCCD diffractometer for **4** and **6**.

For both molecules **4a** and **4b**, some 'Bu groups have the methyl C atoms disordered and these C atoms were left isotropic and distance constraints (SADI) applied. In the figures only one set of alternative methyl sites is included.

The program used for structure refinement was SHELXL 97 [31]. Further details are in Table 3.

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