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Journal of Organometallic Chemistry 651 (2002) 150–156

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Erratum

The stable silylene $Si[(NCH_2{}^tBu)_2C_6H_4\text{-}1,2]$: insertion into Li–C or Li–Si bonds of lithium alkyls LiR or $[Li\{Si(SiMe_3)_3\}(THF)_3]$ $[R = Me, {}^tBu$ or $CH(SiMe_3)_2]$☆

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Abstract

The new crystalline amino-functionalised lithium silyls $Li[Si\{(NCH_2{}^tBu)_2C_6H_4\text{-}1,2\}R](L)$ [$R = Si(SiMe_3)_3$ (sisyl), $L = (THF)_2$ (**2**); $R = Me$, $L = (OEt_2)_2$ (**3**); $R = {}^tBu$, $L = (THF)_3$ (**4a**) or $THF(OEt_2)$ (**4b**); $R = CH(SiMe_3)_2$, $L = (THF)_2$ (**5**)] have been obtained in high yield from the silylene $Si[(NCH_2{}^tBu)_2C_6H_4\text{-}1,2]$ and Li–R under mild conditions. A by-product in the reaction leading to **4** was the crystalline disilane $[1,2\text{-}C_6H_4(NCH_2{}^tBu)_2({}^tBu)Si]_2$ (**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; Sisyls

1. Introduction

There are only few examples known of nucleophilic addition reactions of an alkali metal (M′) organic compound M′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 (M = Si, Ge, 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 unusually led to a product of insertion of MX_2 into the M′–Y bond. The majority have dealt with a Sn(II) or, less often a Pb(II), MX_2 substrate.

Treatment of $SnCp^*_2$ ($Cp^* = C_5Me_5$) with LiMe afforded LiCp* and a mixture of $(SnMe_2)_n$ oligomers; $Li[SnCp^*_2Me]$ was presumed to be a labile intermediate, since quenching the reaction mixture at low temperature with CD_3I gave $SnCp^*_2(CD_3)Me$ [2]. Addition of NaCp to MCp_2 yielded $[Na(pmdeta)(\mu\text{-}Cp)MCp_2]$ ($Cp = C_5H_5$, M = Sn or Pb) [3]. The adduct $[Li(pmdeta)(\mu\text{-}Cp)SnCp\{N(SiMe_3)_2\}]$, obtained from $Li[N(SiMe_3)_2]$ and $SnCp_2$, was regarded as a model intermediate for a nucleophilic displacement at a Sn(II) centre [4]. Likewise, the alkali metal metallate(II) complexes $[Li(THF)_4][Sn(C_{13}H_9)_3]$ [5], $[Li(THF)\{\mu\text{-}N{=}C({}^tBu)\text{-}Ph\}_3M]$ (M = Sn or Pb) [6,7], $[Li(THF)(\mu\text{-}2\text{-}C_5H_4N\text{–}C,N)_3M]$ [8] (M = Sn or Pb; the Sn compound was trapped by addition of ^nBuBr [8a]), $[Li(THF)_2\{\mu\text{-}N(H)R'\}_2Sn\{N(H)R'\}]$ [9] and $[Li(NMe_2)_3Sn]_\infty$ [10] were obtained from three equivalents of LiR and the appropriate MCp_2 or MCp^*_2 substrate [$R = C_{13}H_9$ (fluorenyl), $N{=}C({}^tBu)Ph$, $2\text{-}C_5H_4N$, $N(H)R'$ or NMe_2; $R' = C_6H_4OMe\text{-}2$]; their formation probably proceeded by an initial nucleophilic displacement of successive Cp^- or Cp^{*-} ligands (these being good leaving groups) and subsequent addition of LiR to MR_2. Likewise, the reaction of $Sn[N(SiMe_3)_2]_2$ with three equivalents of $Na[Si(SiMe_3)_3]$ led to the toluene solvate $[Na(CH_2Ph)Sn\{Si(SiMe_3)_3\}_3]$ [11].

Further examples relate to the formation of $[K(dme)_2(\mu\text{-}OR)_2Sn(OR)]$ [12a] or $[Li(\mu\text{-}OAr)_2Sn(OAr)]$ [12b], obtained from, respectively, $[Sn(OR)(\mu\text{-}OR)]_2$ and

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☆ PII of original article: S0022-328X(01)01273-6

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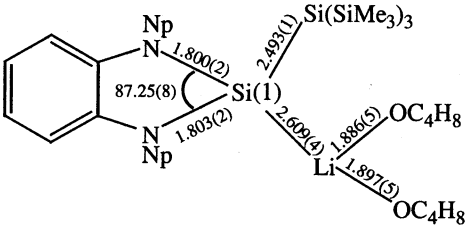
PII: S0022-328X(02)01315-3

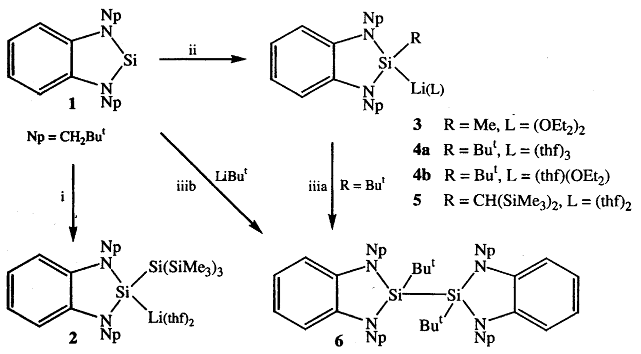
2 KOR or $SnCl_2$ and 3 LiOAr (R = $SiPh_3$ or $SiMe_2^tBu$; Ar = $C_6H_3Ph_2$-2,6).

It is noteworthy that in *none* (but see Ref. [11]) of the above reactions was a mononuclear two-coordinate MX_2 compound the substrate. On the other hand, there are just two such reports involving a thermally robust carbene. The addition of $K[N(SiMe_3)_2]$ or Li[η^5-$C_5H_2(SiMe_3)_3$-1,2,4] to $C[N(^iPr)(CH_2)_3N^iPr]$ or $C[N(R)CHCHNR]$ gave [K{μ-$N(SiMe_3)_2$}-($C\{N(^iPr)(CH_2)_3N^iPr\}$)]$_2$ [13] or [Li{η^5-$C_5H_2(SiMe_3)_3$-1,2,4}($C\{N(R)CHCHNR\}$)] [14], respectively (R = ^{t}Bu, 1-adamantyl or 2,4,6-trimethylphenyl).



2a, av. N-Si(1)-Li 115.3(3)°, Σ Si(1) 295.4°

Recently, we briefly described the first such reactions of a silylene, Scheme 1 [15]. Thus, the thermally robust silylene Si[$(NCH_2^tBu)_2C_6H_4$-1,2] (**1**) (abbreviated as Si(NN)) was found to insert into the Li–Si bond of [Li{$Si(SiMe_3)_3$}$(THF)_3$] [16] to give the new, crystalline X-ray-characterised silyllithium compound [Li{(**1**)$Si(SiMe_3)_3$}$(THF)_2$] (**2**) (which dissociated in solution), whereas $K[N(SiMe_3)_2]$ with **1** in THF gave the novel, crystalline amidopotassium compound **A**; the latter was believed to have been formed by rearrangement of the intermediates (NN)Si → $K[N(SiMe_3)_2]$ and/or K[Si(NN)$N(SiMe_3)_2$] (Eq. (1), Np = CH_2^tBu). (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, ^{t}Bu or $CH(SiMe_3)_2$]. 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) [Li{$Si(SiMe_3)_3$}$(THF)_3$], hexane, −30 °C; (ii) for **3**, LiMe, Et_2O, −30 °C; for **4**, Li^{t}Bu, hexane, −30 °C; for **5**, Et_2O, −30 °C; (iii) (a) decomposition, or by-product of (ii); (b) for **2a**, av. N–Si(1)–Li, 115.3(3)°; ΣSi(1) 295.4°.

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 sisyl Li[$Si(SiMe_3)_3$] or alkyl LiR [R = Me, ^{t}Bu or $CH(SiMe_3)_2$], 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 microanalysis and multinuclear ^{1}H-, ^{13}C-, ^{7}Li-, ^{29}Si-NMR and EI mass spectra. Each was thermally stable at ambient temperature, with **3** (m.p. (dec.) ≥41 °C) the most labile. This robustness is in contrast with previously reported amino-functionalised silyllithium compounds, which are only stable below 0 °C (cf. Li{$Si(NEt_2)_nPh_{3-n}$} [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 = ^{t}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^{t}Bu. As a probe of the decomposition of **4**, the less hindered homologue **3** was dissolved in C_6D_6–DMSO-d_6 and its fate monitored at ca. 60 °C by ^{1}H-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**), 291.88 (**4a**) and 294.15° (**4b**)] compared with that in $[Li\{Si(Ph)_2(NPh_2)\}(THF)_3]$ (**B**) (309.8°) [18] or $[Li(SiPh_3)(THF)_3]$ (**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 $Li(sp^2)$–Si distances in **3** [2.604(6) Å] and **4b** [2.619(9) Å] are shorter than the $Li(sp^3)$–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 $C_6H_4(NCH_2^tBu)_2$-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 $[(Et_2N)_2RSi]_2$, $R = CMe_2^iPr$, ^{t}Bu [20] and Ph [21], respectively; or with 2.4081(11) Å of $[\{\overline{N(Bu^t)(CH_2)_2NBu^t\}HSi}]_2$ [22].

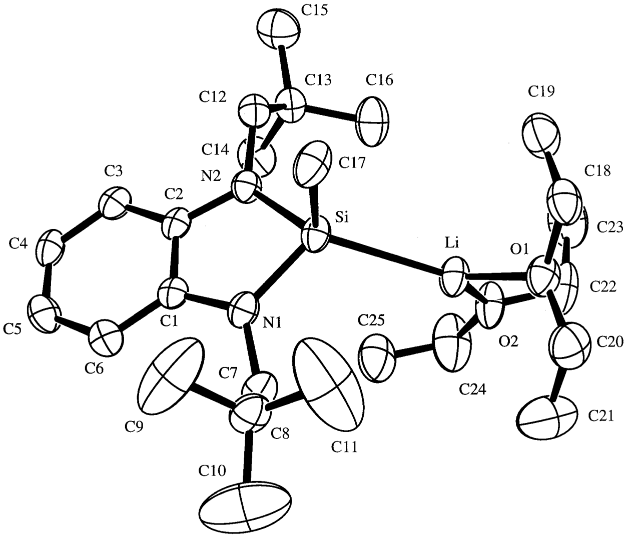


Fig. 1. Molecular structure with atom labelling for compound **3**.

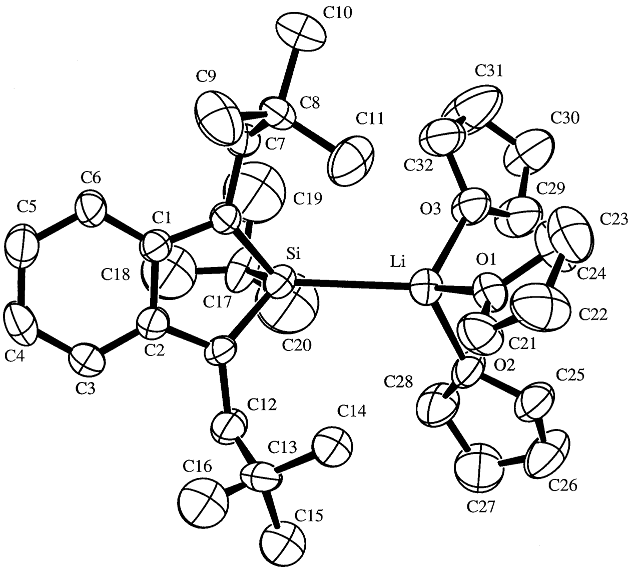


Fig. 2. Molecular structure with atom labelling for compound **4a**.

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 $^{29}Si\{^1H\}$- and selected $^{13}C\{^1H\}$-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 $[1,2\text{-}C_6H_4(NCH_2^tBu)_2]Si(I)Me$ (**7**) [23]. The ^{29}Si 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 ^{t}Bu or $CH(SiMe_3)_2$. These data are also available for comparison with those for $LiSiPh_2(NEt_2)$ (δ 19.3), $LiSiPh(NEt_2)_2$ (δ 27.9), $ClSiPh_2(NEt_2)$ (δ −6.8) and $ClSiPh(NEt_2)_2$ (δ −18.8) [17,18]. It has been suggested that amino substituents at a silicon atom have a deshielding effect on δ [^{29}Si]; a view supported by computational data on appropriate silyllithium compounds [24]. The δ [^{13}C] 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

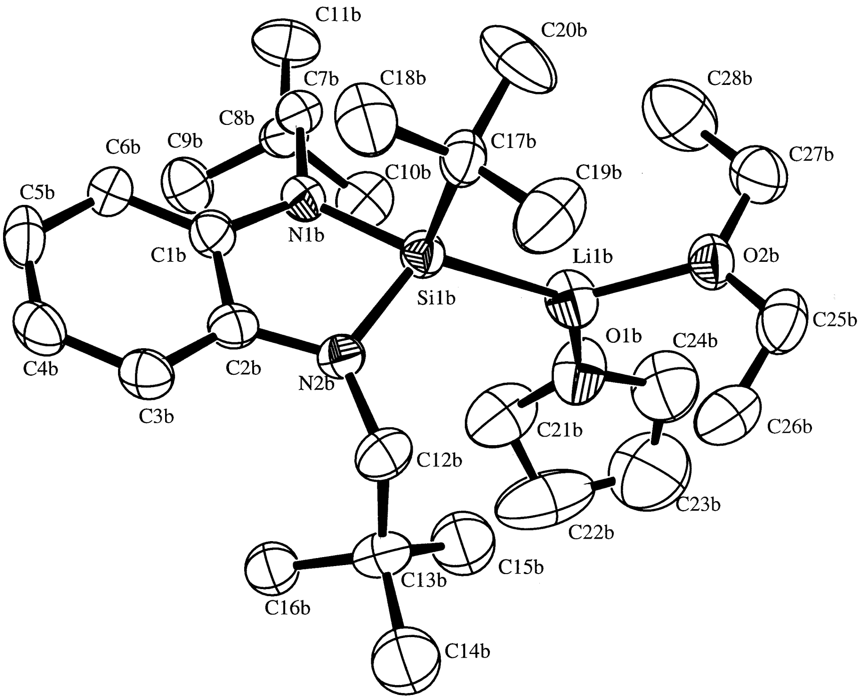


Fig. 3. Molecular structure with atom labelling for compound **4b**.

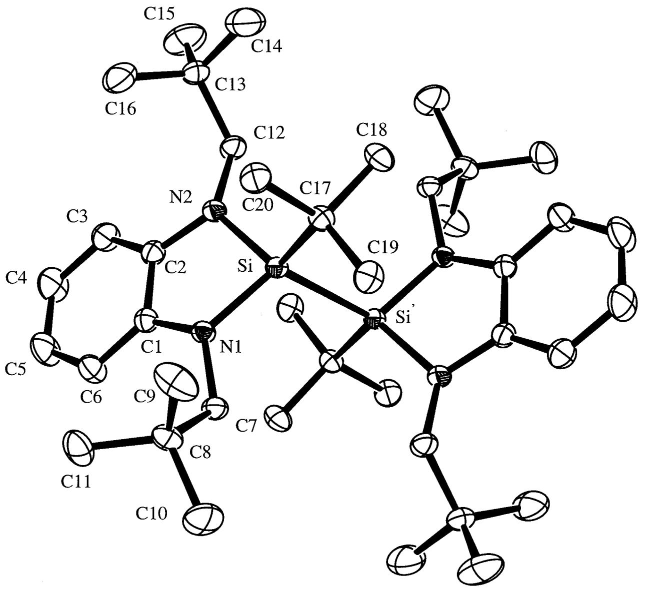


Fig. 4. Molecular structure with atom labelling for compound **6**.

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

	3	**4a**	**4b** [a]	**6** [b]
Bond lengths				
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)		
Bond angles				
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).

the *meta*-carbons, whereas the reverse trend is noted for the *ipso*-carbons.

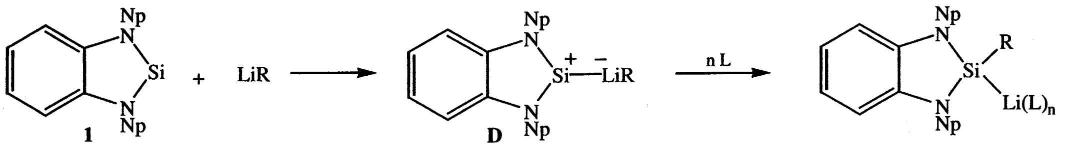
Variable temperature ^{29}Si-NMR spectra of the sisylsilyllithium compound **2** revealed that it readily dissociated into its factors in solution. Thus, at 298 K in toluene–toluene-d_8 the ^{29}Si-NMR chemical shifts were at δ 91.1, -5.8 and -180.75, which are close to the values of **1** (δ 96.9) and $[\mathrm{Li}\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{THF})_3]$ (δ -5.3 and -185.4) [25]. Upon cooling the solution of **2** to 198 K, the ^{29}Si signals were observed as a quartet at δ 59.9 [$^1J(^{29}\mathrm{Si}-^7\mathrm{Li}) = 63$ 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 ^{1}H-NMR CH_2 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 ^{29}Si-NMR spectroscopic data are available for comparison with the values of δ 54.0 and 17.8

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

	δ ($^{13}C_{ipso}$)	δ ($^{13}C_{ortho}$)	δ ($^{13}C_{meta}$)	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

recorded for $[\overline{\mathrm{Si}\{\mathrm{N}(^t\mathrm{Bu})(\mathrm{CH}_2)_2\mathrm{N}}{}^t\mathrm{Bu}\}]^{2-}$ and $[\{^t\mathrm{Bu}\overline{\mathrm{N}(\mathrm{CH}_2)_2\mathrm{N}(^t\mathrm{Bu})\}\mathrm{Si}}]_2^{2-}$, respectively [26].

The pathway to compounds **2**–**5** from **1**+LiR [R = $Si(SiMe_3)_3$, Me, ^{t}Bu or $CH(SiMe_3)_2$] 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 $[Ln(\eta^5\text{-}C_5H_5)_3]$ (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 [17a,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, ^{13}C and ^7Li) and AMX 500 (^{29}Si), 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. $[\{C_6H_4(NCH_2^tBu)_2\text{-}1,2\}Si\{Si(SiMe_3)_3\}Li(THF)_2]$ (**2**)*

A solution of $[Li\{Si(SiMe_3)_3\}(THF)_3]$ (prepared from $Si(SiMe_3)_4$–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 $C_{33}H_{69}LiN_2O_2Si_5$: C, 58.9; H, 10.33; N, 4.16%. ^7Li-NMR ($CD_3C_6D_5$): δ 1.07 (298 K), 0.37 (228 K); for ^1H- and $^{29}Si\{^1H\}$-NMR spectroscopic data refer to Section 2.

*3.3. $[\{C_6H_4(NCH_2^tBu)_2\text{-}1,2\}Si(Me)Li(Et_2O)_2]$ (**3**)*

A solution of LiMe (LiBr stabilised) (1.94 ml, 2.91 mmol, 1.5 M in Et_2O) 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 $C_{24}H_{49}LiN_2O_2Si$: C, 67.5; H, 11.11; N, 6.30%. ^1H-NMR (C_6D_6–d^8-THF): δ 0.44 (s, 3H, CH_3), 1.2 (s, 18H, CH_3), 1.09 (t, 12H, Et_2O), 3.23, 3.27, 3.34 and 3.38 (AB-type, 4H, CH_2), 3.25 (q, 8H, Et_2O) and 6.74–6.79 (m, 4H, phenyl). ^7Li-NMR (C_6D_6–d^8-THF): δ −2.43. $^{13}C\{^1H\}$-NMR (C_6D_6–d^8-THF): δ 13.57 (CH_3), 15.52 (Et_2O), 29.86 ($C\mathit{Me}_3$), 34.86 ($\mathit{C}Me_3$), 59.50 (CH_2), 65.85 (Et_2O), 106.76, 114.49 and 147.84 (phenyl). $^{29}Si\{^1H\}$-NMR (C_6D_6–d^8-THF): δ 53.8. EIMS; *m/z*: 289 ($[M-Li(Et_2O)_2]^+$, 100%).

*3.4. $[\{C_6H_4(NCH_2^tBu)_2\text{-}1,2\}Si(^tBu)Li(THF)_3]$ (**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 Et_2O 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 Et_2O. The extract was filtered and concentrated in vacuo affording the mixed THF–Et_2O complex **4a/4b**. Anal. Found: C, 68.5; H, 10.45; N, 5.47. Calc. for $[C_{32}H_{59}LiN_2O_3Si]/[C_{28}H_{53}LiN_2O_2Si]$ (THF–Et_2O complex): C, 69.3; H, 10.86; N, 5.39%. ^{1}H-NMR (C_6D_6–d^8-THF): δ 0.99 (s, 9H, CH_3), 1.16 (s, 18H, CH_3), 1.45 (m, 12H, THF), 3.37, 3.42 and 3.58 (AB-type, one signal hidden under THF, 4H, CH_2), 3.52 (m, 12H, THF) and 6.60 (m, 4H, phenyl). ^{7}Li-NMR (C_6D_6–d^8-THF): δ −2.43. $^{13}C\{^1H\}$-NMR (C_6D_6–d^8-THF): δ 25.69 (THF), 29.99 and 30.04 (Si*CMe*$_3$ and C*Me*$_3$), 30.87 (Si*C*Me$_3$), 35.93 (*C*Me$_3$), 56.19 (CH_2), 67.98 (THF), 105.89, 113.82 and 147.68 (phenyl). $^{29}Si\{^1H\}$-NMR (C_6D_6–d^8-THF): δ 47.5. EIMS; *m*/*z*: 332 ($[M-Li(THF)_3]^+$, 74%), 275 ($[M-Li(THF)_3-{}^tBu]^+$, 100%).

3.5. $[\{C_6H_4(NCH^t_2Bu)_2\text{-}1,2\}Si\{CH(SiMe_3)_2\}Li(OEt_2)]$ (**5**)

A solution of $Li[CH(SiMe_3)_2]$ (0.28 g, 1.68 mmol) in Et_2O (10 ml) was added slowly to a stirred solution of **1** (0.46 g, 1.68 mmol) in Et_2O (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.) ≥205 °C. Anal. Found: C, 61.2; H, 9.89; N, 5.58. Calc. for $C_{27}H_{55}LiN_2OSi_3$: C, 63.0; H, 10.77; N, 5.44%. ^{1}H-NMR (C_6D_6–d^8-THF): δ −0.81 (s, 1H, CH), 0.24 (s, 18H, $SiCH_3$), 1.07 (t, 6H, Et_2O), 1.12 (s, 18H, CH_3), 3.14, 3.19, 3.24 and 3.29 (AB-type, 4H, CH_2), 3.24 (q, 4H, Et_2O) and 6.59 (m, 4H, phenyl). ^{7}Li-NMR (C_6D_6–d^8-THF): δ −2.5. $^{13}C\{^1H\}$-NMR (C_6D_6–d^8-THF): δ 4.48 ($SiCH_3$), 15.52 (Et_2O), 20.15 (CH), 30.06 (C*Me*$_3$), 35.53 (*C*Me$_3$), 56.93 (CH_2), 65.88 (Et_2O), 106.88, 114.16 and 146.99 (phenyl). $^{29}Si\{^1H\}$-NMR (C_6D_6–d^8-THF): δ 48.0 and −4.2 ($SiMe_3$). EIMS; *m*/*z*: 434 ($[M-Li(Et_2O)]^+$, 30%), 377 ($[M-Li(Et_2O)-{}^tBu]^+$, 67%).

3.6. $[\{C_6H_4(NCH^t_2Bu)_2\text{-}1,2\}Si(^tBu)]_2$ (**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 $C_{40}H_{70}N_4Si_2$: C, 72.4; H, 10.64; N, 8.45%. ^{1}H-NMR (C_6D_6–d^8-THF): δ 1.04 (s, 18H, CH_3), 1.07 (s, 9H, CH_3) 2.90, 2.95, 3.01 and 3.06 (AB-type, 4H, CH_2) and 6.60–6.80 (m, 4H, phenyl). $^{13}C\{^1H\}$-NMR (C_6D_6–d^8-THF): δ 20.43 (s, Si*C*Me$_3$), 24.99 (SiC*Me*$_3$), 30.97 (C*Me*$_3$), 34.14 (*C*Me$_3$), 56.68 (CH_2), 110.84, 117.74 and 142.69 (phenyl). $^{29}Si\{^1H\}$-NMR (333 K, C_6D_6–d^8-THF): δ 16.6. EIMS; *m*/*z*: 662 ($[M]^+$, 12%), 331 ($[M1/2]^+$, 100%), 275.

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

	3	**4a/b**	**6**
Empirical formula	$C_{25}H_{49}LiN_2O_2Si$	$[C_{32}H_{59}LiN_2O_3Si]/[C_{28}H_{53}LiN_2O_2Si]$	$C_{40}H_{70}N_4Si_2$
Formula weight	444.69	1039.60	663.18
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$ (No. 19)	*Cc* (No. 9)	$P\bar{1}$ (No. 2)
Unit cell dimensions			
a (Å)	9.863(2)	18.9384(4)	10.1881(3)
b (Å)	16.967(8)	10.3931(3)	10.3795(3)
c (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)
U (Å^3)	2891.2(16)	6641.3(3)	995.77(5)
Z	4	4	1
μ (Mo–K$_\alpha$) (mm^{-1})	0.102	0.10	0.12
Total reflections	5542	23 818	11 010
Independent reflections	5065 [R_{int} = 0.051]	8962 [R_{int} = 0.067]	4709 [R_{int} = 0.032]
Reflections with $I > 2\sigma(I)$	3411	6561	4103
R_1 [$I > 2\sigma(I)$]	0.066	0.069	0.049
wR (all data)	0.165	0.193	0.148

4. Crystal data and refinements details

Data were collected using monochromated Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ 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 ^{t}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.

Acknowledgements

We are grateful to the EPSRC for the award of an Advanced Fellowship to B.G., the Royal Society for a K.S. Wong Fellowship to X.C., the Free University of Amsterdam for support to J.C.S., and to Dr A.G. Avent for the ^{29}Si-NMR spectroscopic data.

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