

The diverse reactions of the silylene $\text{Si}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4-1,2]$ with $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ and $\text{K}[\text{N}(\text{SiMe}_3)_2]^\dagger$

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The silylene $\text{Si}[(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4-1,2]$ **1** inserts into the Li–Si bond of $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ to afford the new silyllithium compound $\text{Li}[(1)\text{Si}(\text{SiMe}_3)_3](\text{thf})_2$ **2**, whereas **1** with $\text{K}[\text{N}(\text{SiMe}_3)_2]$ yields the amidopotassium compound $\text{K}[\text{N}(\text{SiMe}_3)_2]\{(1)\text{Si}(\text{SiMe}_3)_3\}(\text{thf})_x$ [$x = 0$ (**3a**) or 3 (**3b**)]; the X-ray structures of the crystalline mononuclear complex **2** and the polymeric aggregate **3a** are reported, and NMR spectra show that in solution **2** is in equilibrium with its factors.

We report the first examples of reactions of a divalent, two-coordinate group 14 element compound EX_2 , which with an anionic reagent MX' yield four-coordinate E-atom adducts. For the present, they relate to systems in which EX_2 is the thermally stable silylene **1** and MX' is $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ **A** or $\text{K}[\text{N}(\text{SiMe}_3)_2]$. Although these reactions took place under mild conditions, their outcome was different (Scheme 1). Thus, the 1:1-adduct was the product of insertion in the former case, but a rearranged product in the latter. They were isolated as (i) the crystalline, mononuclear bis(thf)[(silyl)silyl]lithium complex **2**; and (ii) the solid bis(thf)potassium amide **3**, which upon recrystallisation gave the polymeric neutral donor-free potassium amide **3a** and the tris(thf) complex **3b**. The molecular structures of **2**, **3a** and **3b** have been determined;‡ discussion of **3b** is deferred to the full paper, as is the formation of the Li analogue of **3** from $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ and **1**.

Each of the yellow (**2**) or colourless (**3** and **3b**) complexes gave satisfactory microanalyses. The EI-mass spectra of **3** and **3a** were identical and, as for **2**, the major m/z peaks corresponded to the appropriate fragments: $[\text{anion}]^+$ and $[\text{anion} - \text{Bu}^t]^+$.

In solution, the lithium complex **2** was shown to be in equilibrium with its precursors, as demonstrated particularly clearly by VT $^{29}\text{Si}\{^1\text{H}\}$ -NMR spectra. Thus, dissociation was complete at ambient temperature, but was negligible at 213 K; a $^1J(^{29}\text{Si}^7\text{Li})$ was not observed, probably due to the fast exchange process. Complex **3b** retained its structural integrity at 298 K. The data, with those for **1**,¹ $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$,²

Table 1 ^{29}Si NMR spectroscopic chemical shifts for **1–3** and related compounds

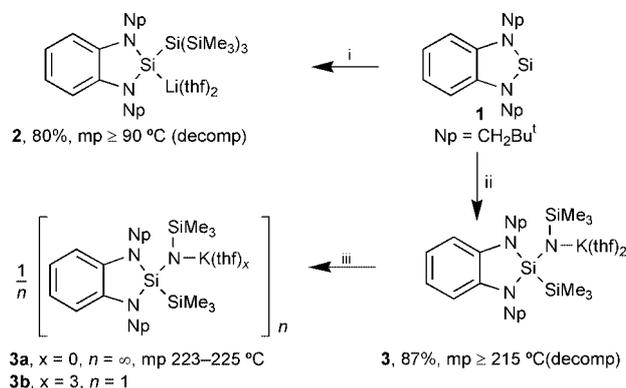
Complex (conditions ^a)	$\delta(^{29}\text{Si})$		
	α -Si	β -Si	γ -Si
$[\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})_3]^2$ A	–189.4	–5.2	
1	96.2		
2	60.1	–9.35	–4.5
	[94.5 (1)	–5.3]	
3a	–19.5	–23.0	–26.2
$\text{Li}[\text{N}(\text{SiMe}_3)_2]\{\text{Si}(\text{SiMe}_3)_3\}^3$ B	–7.1	–49.3	–18.0
$\text{Li}[\text{Si}(\text{Ph})(\text{NEt}_2)_2](\text{thf})_3^4$ C	27.9		

^a Solvent (T/K): **A**, C_7D_8 (298); **1**, C_6D_6 (298); **2**, C_7D_8 -thf (213, [298]); **3a**, C_7D_8 -thf (298); **B**, C_6D_6 (303); **C**, thf (273).

$\text{Li}[\text{N}(\text{SiMe}_3)_2]\{\text{Si}(\text{SiMe}_3)_3\}^3$ **B** and $\text{Li}[\text{Si}(\text{Ph})(\text{NEt}_2)_2](\text{thf})_3$,⁴ are shown in Table 1.

Complex **2** (Fig. 1) has the lithium atom in a three-coordinate, distorted trigonal-planar environment. The silyl anion is pyramidal at the Si(1) atom with respect to its contiguous Si(2), N(1) and N(2) atoms; the sum of the angles subtended by these three neighbouring atoms is low, 295.4° , as a consequence of the small bite angle of the adjacent chelating ligand; cf. 307.2° in $\text{Li}[\text{Si}(\text{SiMe}_3)_3](\text{thf})_3$ **A**² and 309.8° in $\text{Li}[\text{Si}(\text{Ph})(\text{NEt}_2)_2](\text{thf})_3$ **C**.⁴ The Li–Si(1) distance of $2.609(4)$ Å in **2** is slightly shorter than the $2.644(12)$ Å in **A** or $2.732(7)$ Å in **B**. The Si(1)–Si(2) bond length of $2.493(1)$ in **2** is longer than the mean Si_α – Si_β bond length of $2.330(2)$ Å in **A**. The mean Si–N bond length of $1.801(3)$ Å in **2** [$1.800(4)$ Å in **3a**] is longer than the $1.75(1)$ Å in **1**, and the N(1)–Si(1)–N(2) bond angle of $87.25(8)^\circ$ is slightly more acute than the $88.2(1)^\circ$ in **1**, or the $88.15(6)^\circ$ in **3a**.

The potassium amide **3a** comprises mononuclear units (Fig. 2), each linked to its neighbours by close $\text{K}\cdots\text{C}'(17)\text{H}_3$ [$3.268(2)$ Å] and $\text{K}\cdots\eta^3\text{-C}_6\text{H}_4$ [mean $\text{K}\cdots\text{C}'(o, m, m')$ 3.17 Å] contacts (Fig. 3). Similar intermolecular contacts are known in various potassium amides and alkyls.⁵ Associated with $\text{K}\cdots\text{C}'(17)\text{H}_3$ is



Scheme 1 Synthesis of the alkali metal complexes **2**, **3**, **3a** and **3b**. Reagents and conditions: i, $[\text{Li}\{\text{Si}(\text{SiMe}_3)_3\}(\text{thf})_3]$, C_6H_{14} , -30°C ; ii, $\frac{1}{2}$ $[\text{K}[\text{N}(\text{SiMe}_3)_2]]$, thf, -30°C ; C_6H_{14} -thf, 0°C (**3a**), -25°C (**3b**); iii, **3a** (at ca. 20°C), **3b** (at -25°C) recrystallised from hexane-thf solution.

† No reprints available.

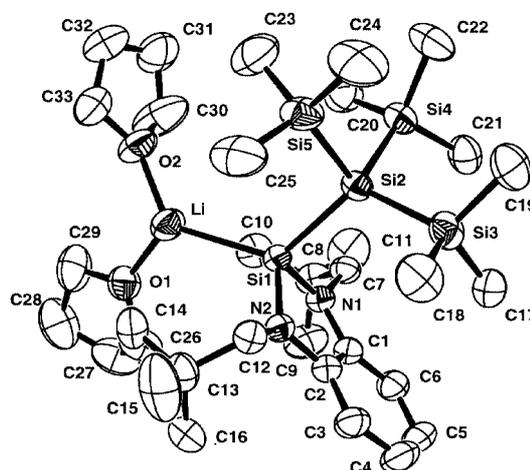


Fig. 1 Crystal structure of **2**.

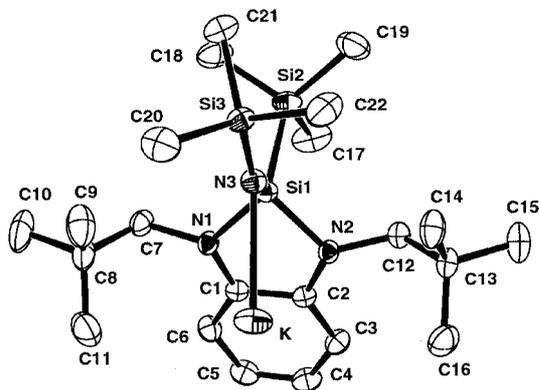


Fig. 2 Crystal structure of **3a**.

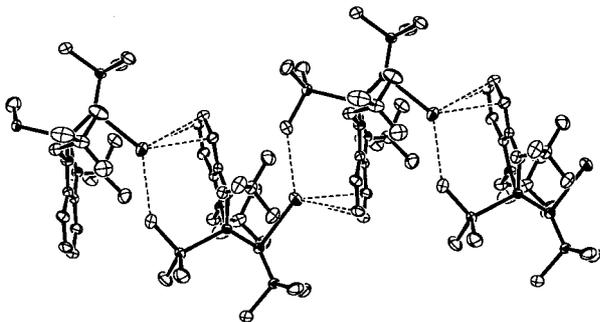
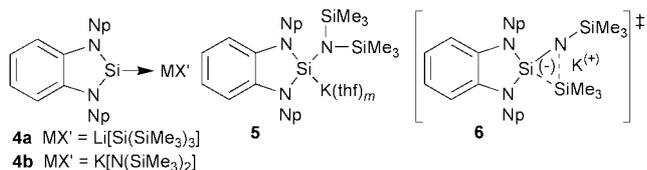


Fig. 3 Intermolecular contacts in **3a**.

the narrower Si(1)–Si(2)–C(17) angle of 105.84(7)°, compared with the mean of Si(1)–Si(2)–C(18 or 19) of 113.7(3)°. The amido nitrogen atom N(3) is in a planar environment, the Si(1)–N(3)–Si(3) angle of 144.40(9)° being only *ca.* 10° narrower than that in the separated [N(SiPh₃)₂][−] anion of [Li(12-crown-4)₂][N(SiPh₃)₂][−]·thf,⁶ but much wider than the 136(1)° in [K{N(SiMe₃)₂}(thf)₂].⁷ The N–Si bond lengths of 1.64(1) Å in the latter is close to the 1.6302(13) Å for Si(1)–NK in **3a**, but is significantly shorter than the Si(3)–NK bond length, 1.6739(14) Å. The N–K distance of 2.6938(14) Å in **3a** is unexceptional; *cf.* 2.70(2) Å in {K{N(SiMe₃)₂}(thf)₂}.⁷

The pathways to **2** or **3**, from **1** and Li[Si(SiMe₃)₃](thf)₃ or K[N(SiMe₃)₂], probably require that in the first step the silylene **1** behaves as a nucleophile yielding the appropriate adduct



X₂E:MX' (**4a** or **4b**). Complex **2** is presumed to arise from **4a** by insertion of X' into the E–M bond, and a similar step from **4b** would yield **5**. Complex **3** is believed to be formed by a final Me₃Si shift from the N to Si, either from **5** (a 1,2-shift; *cf.* the transition state **6**) or **4b** (a 1,3-shift). Although anionic trimethylsilyl shifts are well documented,⁸ this, we believe, is the first N→Si example. Precedents for X₂E:MX' adducts in group 14 element chemistry include (i) silylene–(Ni⁰ or Pt^{II}) complexes such as [Ni(**1**)₄] and *trans*-[Pt{(1)Cl₂}₂(1)₂]⁹ and (ii) carbene–(MX') complexes such as [Li{C[N(Bu)⁺CHCHN–Bu⁺]}{η⁵-C₅H₂(SiMe₃)₃-1,2,4}]¹⁰ and [K{C[N(Pr⁺)(CH₂)₃N–Pr⁺]}{μ-N(SiMe₃)₂}]₂,¹¹ and (iii) stannylene–MCp complexes such as SnCp₂(μ-Cp)Na from SnCp₂ + NaCp.¹² Alternative EX₂/MX' reactions have led to X/X' exchange as in (i) SnCp₂ +

LiN(SiMe₃)₂ yielding Sn(Cp)[N(SiMe₃)₂](μ-Cp)Li(pmdeta),¹³ and (ii) SnCp*₂ + Li[CH(SiMe₃)₂] affording Sn[CH(SiMe₃)₂]₂ + LiCp*.¹⁴ Insertion reactions of **1** into O–H, C–I, Ge^{II}–N, Sn^{II}–C, Sn^{II}–N or Pb^{II}–N bonds have been reported, as with M'[N(SiMe₃)₂]₂ to give M'[1{N(SiMe₃)₂}]₂ (M' = Sn **7** or Pb).¹⁵ The rearrangement **5**→**3** cannot be due to the lability of the anion {(1){N(SiMe₃)₂}[−], since it is found in **7** as a ligand. We suggest that **3** may be favoured, at least in part, by the strong Si–Si bond, as evident by its short [2.359(1) Å in **3a**] bond length, comparable with the av. Si–Si bond distance of 2.379 Å in **2**. However, according to bond dissociation energy data a migration of Me₃Si from nitrogen to silicon is unexpected.¹⁶ The facile dissociation of **2** is probably due to steric constraints, consistent with the long Si–Si(SiMe₃) bond of 2.493(1) Å and the narrow N–Si–Si angles, av. 103.9(6)°.

The present results significantly extend the already substantial boundaries of silylene reaction types. From work in progress, we anticipate that several new silicon-centred ligands [(1)X'][−] (that in **2** being a forerunner) will become available for use for a wide range of metals, and that the exceedingly bulky amido ligand present in **3** will find a useful role.

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Notes and references

‡ *Crystallographic data*: for **2**: C₃₃H₆₉LiN₂O₂Si₅, *M* = 673.29, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 12.8306(11), *b* = 18.4336(13), *c* = 18.7237(15) Å, β = 96.161(4)°, *U* = 4402.8(6) Å³, *Z* = 4, μ = 0.19 mm^{−1}, *T* = 173(2) K, 7659 unique reflections (*R*_{int} = 0.060), *R*₁ = 0.052 for 5962 reflections with *I* > 2σ(*I*), *wR*₂ = 0.138 for all reflections.

3a: C₂₂H₄₄KN₃Si₃, *M* = 473.97, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 13.4645(4), *b* = 12.7533(3), *c* = 16.5858(3) Å, β = 91.759(2)°, *U* = 2846.7(1) Å³, *Z* = 4, μ = 0.33 mm^{−1}, *T* = 173(2) K, 6689 unique reflections (*R*_{int} = 0.044), *R*₁ = 0.039 for 5363 reflections with *I* > 2σ(*I*), *wR*₂ = 0.097 for all reflections.

CCDC 182/1688. See <http://www.rsc.org/suppdata/cc/b0/b003833o/> for crystallographic files in .cif format.

- B. Gehrhus, P. B. Hitchcock, M. F. Lappert, J. Heinicke, R. Boese and D. Bläser, *J. Organomet. Chem.*, 1996, **521**, 211.
- A. Heine, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *Inorg. Chem.*, 1993, **32**, 2694.
- M. Westerhausen and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1993, **619**, 1053.
- A. Kawachi and K. Tamao, *J. Am. Chem. Soc.*, 2000, **122**, 1919.
- E.g.*, see K. W. Klinkhammer, *Eur. J. Chem.*, 1997, **3**, 1418; W. Clegg, S. Kleditzsch, R. E. Mulvey and P. O'Shaughnessy, *J. Organomet. Chem.*, 1998, **558**, 193.
- H. Chen, R. A. Bartlett, H. V. R. Dias, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1989, **111**, 4338.
- A. M. Domingos and G. M. Sheldrick, *Acta Crystallogr., Sect. B.*, 1974, **30**, 517.
- A. G. Brook and A. R. Bassindale, *Molecular Rearrangements of Organosilicon Compounds*, in *Rearrangements in Ground and Excited States*, Academic Press, New York, 1980, vol. 2.
- B. Gehrhus, P. B. Hitchcock, M. F. Lappert and H. Maciejewski, *Organometallics*, 1998, **17**, 5599.
- A. J. Arduengo, M. Tamm, J. C. Calabrese, F. Davidson and W. J. Marshall, *Chem. Lett.*, 1999, 1021.
- R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen and M. J. Quayle, *Chem. Commun.*, 1999, 241.
- D. R. Armstrong, M. J. Duer, M. G. Davidson, D. Moncrieff, C. A. Russell, C. Stourton, A. Steiner, D. Stalke and D. S. Wright, *Organometallics*, 1997, **16**, 3340.
- M. A. Paver, C. A. Russell, D. Stalke and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1993, 1349.
- P. Jutz and B. Hielscher, *Organometallics*, 1986, **5**, 2511.
- B. Gehrhus, P. B. Hitchcock and M. F. Lappert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2514.
- R. Becerra and R. Walsh, *Thermochemistry*, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, Chichester, 1998, vol. 2.