

Synthesis and structures of crystalline lithium 1-azaallyls and a 1,3-diazaallyl derived from $\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_3-n(\text{OMe})_n)\}$ ($n = 1$ or 2) and $\text{Li}\{\text{CH}(\text{SiMe}_2\text{OMe})_2\}$ and RCN ($\text{R} = {}^t\text{Bu}, \text{Ph}, 2,5\text{-Me}_2\text{C}_6\text{H}_3, \text{or Ad}$)

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Abstract

Crystalline $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OMe})\text{C}({}^t\text{Bu})\text{C}(\text{H})(\text{SiMe}_3)\}_2]$ (**5**), $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OMe})\text{C}(\text{Ph})\text{C}(\text{H})(\text{SiMe}_3)\}_2]$ (**6**), $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OMe})\text{C}(\text{C}_6\text{H}_3\text{Me}_2-2,5)\text{C}(\text{H})(\text{SiMe}_3)\}(\text{TMEDA})](7)$, $[\text{Li}\{\text{N}(\text{SiMe}(\text{OMe})_2)\text{C}({}^t\text{Bu})\text{C}(\text{H})(\text{SiMe}_3)\}(\text{THF})_2]$ (**8**), $[\text{Li}\{\text{N}(\text{SiMe}(\text{OMe})_2)\text{C}(\text{Ph})\text{C}(\text{H})(\text{SiMe}_3)\}(\text{TMEDA})]$ (**9**) and $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OMe})\text{C}({}^t\text{Bu})\text{C}(\text{H})(\text{SiMe}_2\text{OMe})\}_2]$ (**10**) were readily obtained at ambient temperature from (i) $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})\}_8]$ (**1**) and an equivalent portion of RCN ($\text{R} = {}^t\text{Bu}$ (**5**), Ph (**6**) or $2,5\text{-Me}_2\text{C}_6\text{H}_3$ (**7**)); (ii) $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}(\text{OMe})_2)\}_\infty]$ (**2**) and an equivalent portion of ${}^t\text{BuCN}$ (**8**) or PhCN (**9**); and (iii) $[\text{Li}\{\text{CH}(\text{SiMe}_2\text{OMe})_2\}_\infty]$ (**3**) and one equivalent of ${}^t\text{BuCN}$ (**10**). Reactions (i) and (ii) were regiospecific with $\text{SiMe}_{3-n}(\text{OMe})_n > \text{SiMe}_3$ in 1,3-migration from C (in **1** or **2**) \rightarrow N. The 1-azaallyl ligand was bound to the lithium atom as a terminally bound κ^1 -enamido (**8** and **10**), a bridging η^3 -1-azaallyl (**6**), or a bridging κ^1 -enamido (**5**). The stereochemistry about the C=C bond was *Z* for **5**, **8** and **10** and *E* for **7**. X-ray data are provided for **5**, **6**, **7**, **8** and **10** and multinuclear NMR spectra data in C_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$ for each of **5–10**.

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1. Introduction

We have a long-standing interest in trimethylsilyl-substituted hydrocarbyl ligands, including alkyls, allyls, 1-azaallyls, and cyclopentadienyls: for the most recent references on these four types, see Refs. [1–4], respectively. The present paper is a contribution to 1-azaallylmetal chemistry, a topic which we recently reviewed [5] and specifically to new lithium compounds.

Lithium 1-azaallyls have received much attention, from organic chemists, as useful synthons, but for this role they have generally been prepared in situ and rarely structurally identified. They react with various electrophiles to give C–C bond-forming products rather than

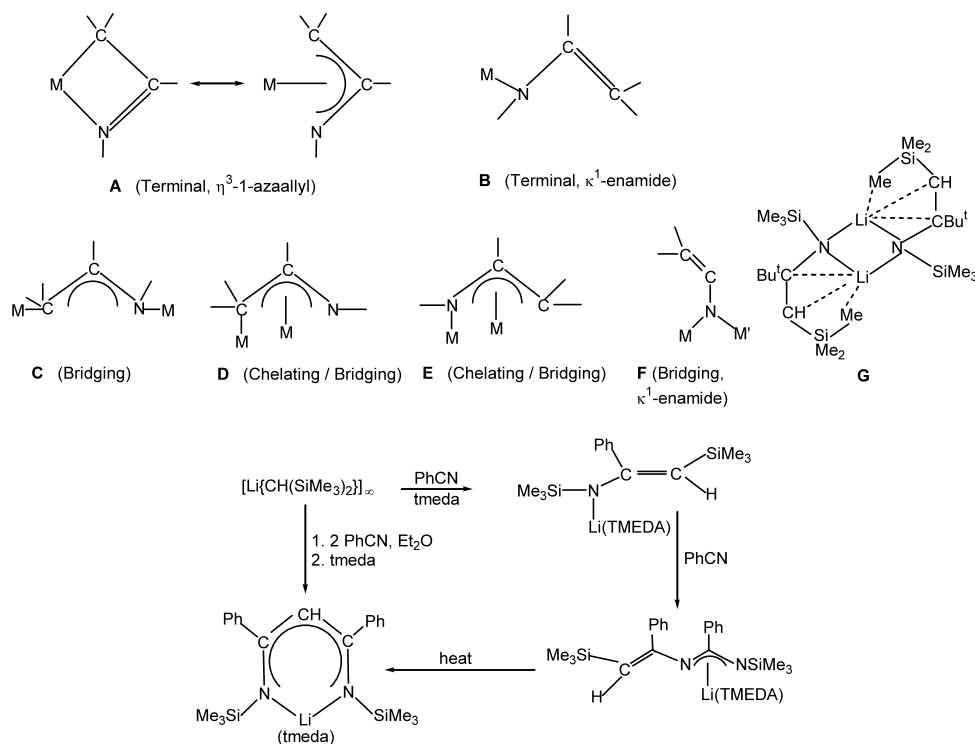
(unlike lithium enolates) undergoing proton transfer [6,7]. Examples of such reactions include controlled aldol condensation reactions and regioselective α -functionalisation of ketones.

In our review [5], we noted that the 1-azaallyl ligand may bind to a metal in one of six major ways, A–F, the major distinction, as far as bonding in the ligand is concerned, is between the ligand being a coordinated η^3 -1-azaallyl or the tautomeric κ^1 -enamido. While C–E show the bridging mode for η^3 -1-azaallyl ligation, the same possibilities are in principle available for the κ^1 -enamido tautomer, as in F.

Our entry into the 1-azaallylmetal field came in 1994, with the discovery that $[\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}_\infty]$ with ${}^t\text{BuCN}$ gave the crystalline $[\text{Li}\{\text{N}(\text{SiMe}_3)\text{C}({}^t\text{Bu})\text{C}(\text{H})(\text{SiMe}_3)\}_2]$ (**G**), in which the bonding is of type E [8]. The reactions of $[\text{Li}\{\text{CH}(\text{SiMe}_3)_2\}_\infty]$ with less bulky α -H-free organic cyanides proved to be more complicated, as summarised

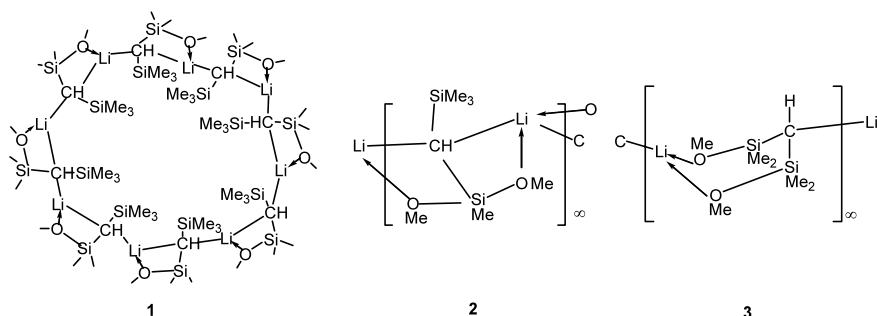
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in [Scheme 1](#) for the case of PhCN [9]; in the absence of a strong neutral coligand the presumed 1-azaallyllithium reagent reacted with a second PhCN molecule. These 1:2

The synthesis of the crystalline **1–3** have recently been reported [1]; their structures are illustrated schematically below.

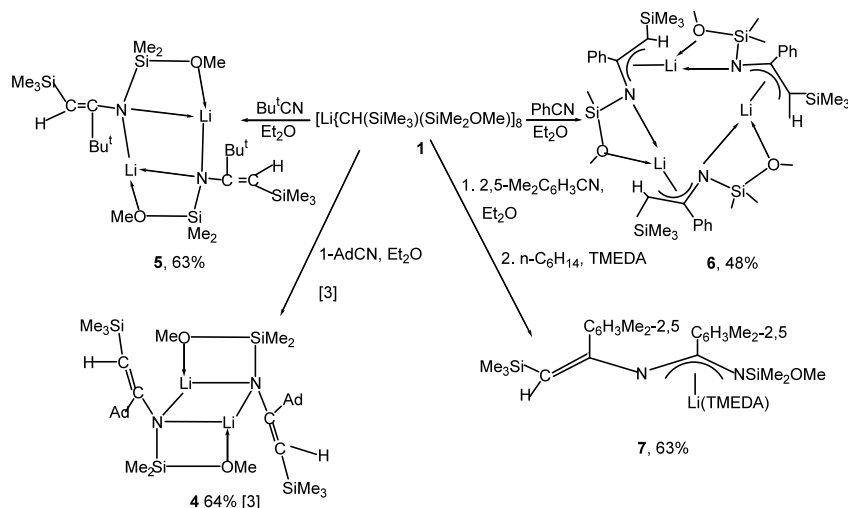


products were believed to have formed via 1, 3-Me₃Si migration from C→N, and concomitant C–C bond formation for **F** and further reaction of **F** as either a C- or N-centered nucleophile with PhCN generating the β-diketiminato or the thermodynamically less stable 1,3-diazaallyl, respectively.

We now report on the 1:1 reactions between (i) [Li{CH(SiMe₃)(SiMe₂OMe)}]₈ (**1**), [Li{CH(SiMe₃)(SiMe(OMe)₂)}]_∞ (**2**), or [Li{CH(SiMe₂OMe)₂}]_∞ (**3**) and (ii) ^tBuCN (**1–3**), PhCN (**1** and **2**), 2,5-Me₂C₆H₃CN (**1**) or AdCN (**1**) (AdCN = 1-adamantanecarbonitrile).

2. Results and discussion

In a preliminary communication [3] we showed that **1** + AdCN gave the crystalline dimeric lithium enamide **4** (see [Scheme 2](#)), thus demonstrating that its formation involves (i) regioselectivity, with 1,3-migration of the SiMe₂OMe rather than the SiMe₃ group, and (ii) preference of the coordinated enamido tautomer; and (iii) stereoselectivity, **4** being the Z-isomer [3]. In this paper, we extend the study to the further reactions of **1–3** with the organic cyanides ^tBuCN, PhCN and 2,5-



Scheme 2.

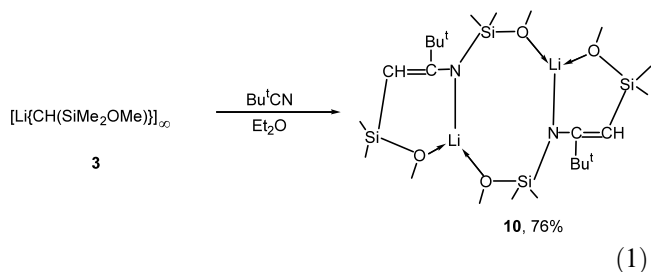
$Me_2C_6H_3CN$ to give the new crystalline compounds **5**–**10**; X-ray diffraction data on **5**–**8** and **10** are provided.

2.1. Reactions of the lithium alkyls $[Li\{CH(SiMe_3)(SiMe_{3-n}(OMe)_n)\}]_x$ ($n = 1$ and $x = 8$ (**1**), $n = 2$ and $x = \infty$ (**2**)) and $[Li\{CH(SiMe_2OMe)_2\}]_\infty$ (**3**) with α -H-free nitriles

Treatment of $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**1**) [1] with an equivalent portion of 1-adamantanecarbonitrile, 2-methyl-2-cyanopropane, cyanobenzene, or 2,5-dimethylcyanobenzene (and subsequently TMEDA) in diethyl ether at ambient temperature afforded the crystalline, colourless dimeric lithium enamide **4** [3] or **5**, the yellow trimeric 1-azaallyllithium compound **6**, and the colourless mononuclear 1,3-diazaallyllithium-TMEDA adduct **7**, respectively. These data are summarised in Scheme 2. The different outcome between **4**, **5** and **6** on the one hand and **7** on the other has a precedent (see Scheme 1) [9]. We suggest that in the course of the reaction $1 \rightarrow 7$, the intermediate may have been the enamidolithium compound $Li\{N(SiMe_2OMe)C(C_6H_3Me_2-2,5)C(H)(SiMe_3)\}$ which reacted faster than **1** with 2,5- $Me_2C_6H_3CN$.

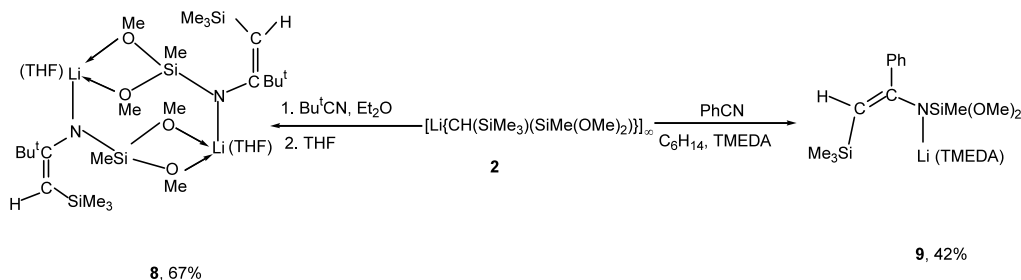
In a similar fashion, from $[Li\{CH(SiMe_3)(SiMe(OMe)_2)\}]_\infty$ (**2**) and an equivalent portion of 2-

methyl-2-cyanopropane (in diethyl ether and extraction of the solvent-free residue with THF) or benzonitrile (in *n*-hexane and TMEDA) the product was the colourless, crystalline, dimeric enamidolithium-THF adduct **8** or the pale yellow, powdery enamido-lithium-TMEDA adduct **9**, as summarised in Scheme 3. Likewise, $[Li\{CH(SiMe_2OMe)_2\}]_\infty$ (**3**) and 2-methyl-2-cyanopropane in diethyl ether yielded the crystalline, colourless, dimeric enamidolithium compound **10**, Eq. (1). The yields cited for compounds **5**–**10** relate to purified isolated products and were not optimised, but in the case of **6** and **9**, there were significant β -diketiminato co-products (which will be described in a subsequent publication).



(1)

Compounds **5**–**10** were characterised by microanalyses and multinuclear NMR spectra in C_6D_6 , $C_6D_5CD_3$ or C_6D_6/C_5D_5N , which were consistent with the struc-



Scheme 3.

tures of the crystalline compounds **5–8** and **10**, see Section 2.2 and the formula shown in Scheme 3 for **9**.

2.2. The X-ray structures of the crystalline compounds **5–8** and **10**

The molecular structure of **4** has been published [3]; the selected geometric parameters are shown in Fig. 1.

The molecular structures of the new 1-azaallyllithium compounds **5**, **6**, **7**, **8** and **10** are shown in Figs. 2–6, respectively, and selected geometric parameters are listed in Tables 1–5, respectively.

Crystalline **5**, like **4** [3], is a centrosymmetric dimer. It has a rhomboidal (LiN)₂ core (with the endocyclic angles at the lithium atoms wider than those at the nitrogen atoms), which is the centre of a fused tricyclic ladder structure, Fig. 2. The outer planar four-membered LiNSiO rings have endocyclic angles varying from 76.49(17)° at Li to 100.12(10)° at Si. As a result of the intramolecular coordination of the MeO groups to the lithium atoms, the Li–N bond is longer than the Li–N'. The 1-azaallyl ligand is bound to the lithium atoms in

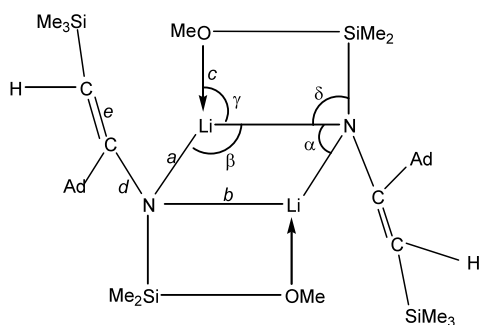


Fig. 1. Selected geometrical parameters for **4** [3]: $a = 1.977(3)$, $b = 2.179(3)$, $c = 1.917(3)$, $d = 1.401(2)$, $e = 1.353(2)$ Å; $\alpha = 75.9(2)$, $\beta = 104.1(2)$, $\gamma = 77.4(1)$, $\delta = 87.1(1)$ °.

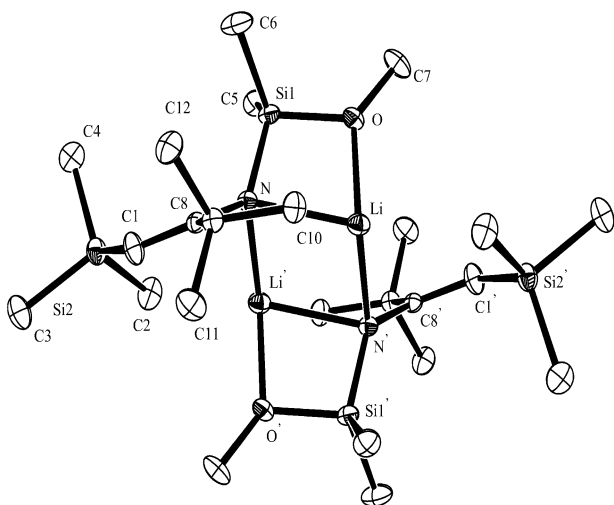


Fig. 2. Molecular structure and atom numbering scheme for $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OMe})\text{C}(\text{t-Bu})\text{C}(\text{H})(\text{SiMe}_3)\}_2]$ (**5**).

mode F (bridging κ^1 -enamido) and the hydrogen atoms and the *tert*-butyl groups are arranged in a cisoid manner about each C=C bond. These features are both qualitatively and quantitatively similar for **4** [3] and **5**.

Crystalline **6** has a central (LiN)₃ core with Li–N bond lengths in the narrow range 2.015(2) to 2.104(4) Å and endocyclic bond angles at the lithium atoms of 142.5(2) to 147.9(2)° much wider than those at the nitrogen atoms, 92.88(17) to 97.81(17)°, Fig. 3. Each Li–N edge is part of a planar LiNSiO ring, with endocyclic angles ranging from 77.80(6)° at Li to

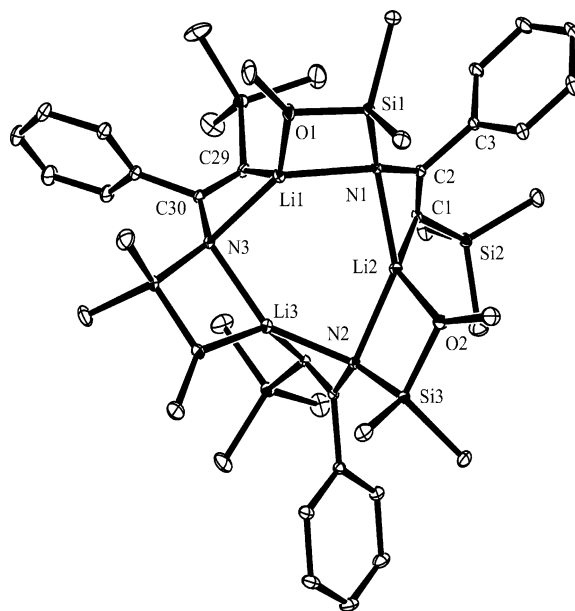


Fig. 3. Molecular structure and atom numbering scheme for $[\text{Li}\{\text{N}(\text{SiMe}_2\text{OMe})\text{C}(\text{Ph})\text{C}(\text{H})(\text{SiMe}_3)\}_2]$ (**6**).

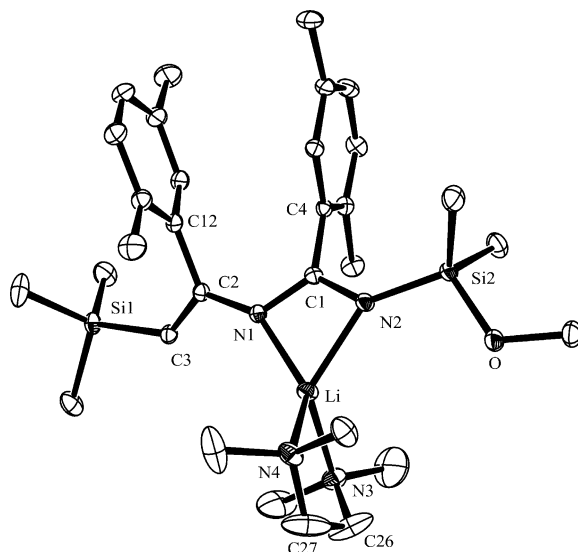


Fig. 4. Molecular structure of $[\text{Li}\{\text{N}(\text{Si}_2\text{OMe})\text{NC}_6\text{H}_3\text{Me}_2\text{-3,5C}(\text{H})(\text{SiMe}_3)\}(\text{TMEDA})]$ (**7**).

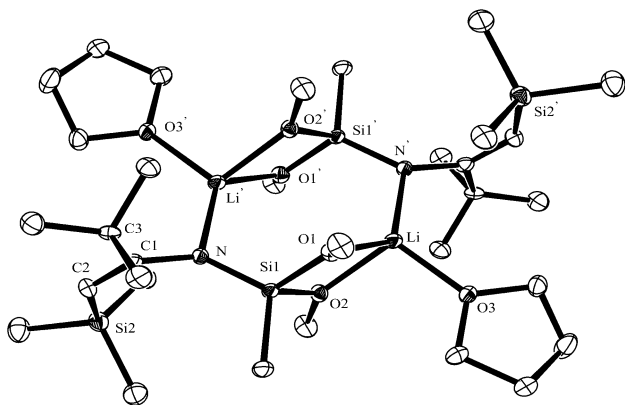


Fig. 5. Molecular structure and atom numbering scheme for $[\text{Li}\{\text{N}(\text{SiMe}(\text{OMe})_2)\text{C}(\text{'Bu})\text{C}(\text{H})(\text{SiMe}_3)\}(\text{THF})_2]$ (**8**).

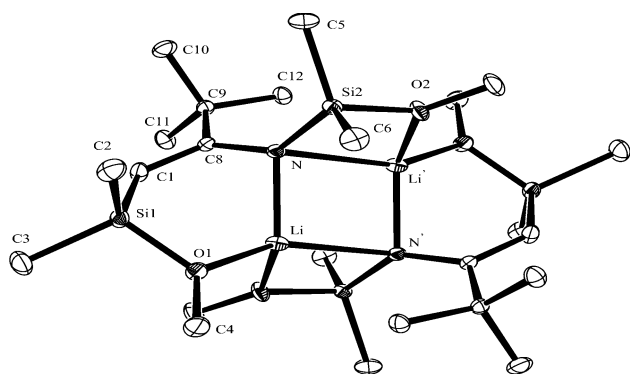


Fig. 6. Molecular structure and atom numbering scheme for $[\text{Li}\{\text{N}(\text{SiMe}_3)\text{C}(\text{'Bu})\text{C}(\text{H})(\text{SiMe}_3)\}(\text{THF})_2]$ (**7**).

Table 1
Selected bond lengths (Å) and angles (°) for **5**

Bond lengths			
Li–O	1.912(5)	Si(1)–O	1.690(2)
Li–N'	1.971(4)	Si(2)–C(1)	1.843(3)
Li–N	2.227(5)	N–C(8)	1.400(3)
Si(1)–N	1.667(2)	C(1)–C(8)	1.345(4)
Bond angles			
O–Li–N'	137.4(3)	C(8)–C(1)–Si(2)	132.5(2)
O–Li–N	76.49(17)	C(1)–C(8)–N	122.7(2)
C(8)–N–Si(1)	130.27(16)	C(1)–C(8)–C(9)	118.7(2)
N'–Li–N	104.07(19)	N–C(8)–C(9)	118.6(2)
N–Si(1)–O	100.12(10)		

96.84(9)° at Si. The geometric parameters relating to the bridging of the 1-azaallyl ligands to the lithium atoms are consistent with the bonding mode C, i.e., bridging η^3 -1-azaallyls, as evident from the Li–N, Li–C $_{\alpha}$, Li–C $_{\beta}$ and C $_{\alpha}$ –C $_{\beta}$ bond lengths, Table 2.

Crystalline **7** is a mononuclear 1,3-diazapentadienyl-lithium-TMEDA adduct, in which the ligand is bound to the metal in a chelating 1,3-diazaallyl fashion, Fig. 4. The only crystallographically characterised mononuclear analogue $[\text{Li}\{\text{N}(\text{Ph})\text{C}(\text{SiMe}_3)\text{NC}(\text{Ph})\text{C}(\text{H})(\text{SiMe}_3)\}(\text{OEt}_2)_2]$, Fig. 7 [9] has rather similar geometric

Table 2
Selected bond lengths (Å) and angles (°) for **6**

Bond lengths			
Li(1)–O(1)	1.908(4)	Si(2)–C(1)	1.845(2)
Li(1)–N(3)	2.036(4)	Si(3)–O(2)	1.683(2)
Li(1)–N(1)	2.104(4)	Si(3)–N(2)	1.703(2)
Li(1)–C(30)	2.265(5)	Si(4)–C(15)	1.842(2)
Li(2)–O(2)	1.928(4)	Si(5)–O(3)	1.680(2)
Li(2)–N(1)	2.015(4)	Si(5)–N(3)	1.706(2)
Li(2)–N(2)	2.070(4)	Si(6)–C(29)	1.845(3)
Li(2)–C(2)	2.241(4)	N(1)–C(2)	1.383(3)
Li(3)–O(3)	1.913(4)	N(2)–C(16)	1.374(3)
Li(3)–N(2)	2.030(4)	N(3)–C(30)	1.376(3)
Li(3)–N(3)	2.084(4)	C(1)–C(2)	1.359(3)
Li(3)–C(16)	2.249(4)	C(15)–C(16)	1.366(3)
Si(1)–O(1)	1.678(2)	C(29)–C(30)	1.371(4)
Si(1)–N(1)	1.697(2)		
Bond angles			
O(1)–Li(1)–N(3)	127.5(2)	N(3)–Li(3)–C(15)	113.65(19)
O(1)–Li(1)–N(1)	77.80(16)	C(2)–N(1)–Si(1)	129.85(15)
N(3)–Li(1)–N(1)	143.1(2)	C(16)–N(2)–Si(3)	127.59(15)
O(1)–Li(1)–C(29)	136.8(2)	C(30)–N(3)–Si(5)	126.55(16)
N(1)–Li(1)–C(29)	67.50(14)	C(2)–C(1)–Si(2)	135.52(19)
N(1)–Li(1)–C(29)	115.0(2)	C(2)–C(1)–Li(2)	69.41(16)
O(2)–Li(2)–N(1)	126.7(2)	Si(2)–C(1)–Li(2)	130.68(15)
O(2)–Li(2)–N(2)	78.56(15)	C(1)–C(2)–N(1)	122.6(2)
N(1)–Li(2)–N(2)	142.5(2)	C(16)–C(15)–Si(4)	131.54(18)
O(2)–Li(2)–C(1)	138.4(2)	C(16)–C(15)–Li(3)	69.45(16)
N(1)–Li(2)–C(1)	66.91(14)	Si(4)–C(15)–Li(3)	132.31(15)
N(2)–Li(2)–C(1)	114.97(19)	C(15)–C(16)–N(2)	123.3(2)
O(3)–Li(3)–N(2)	125.0(2)	C(30)–C(29)–Si(6)	130.03(19)
O(3)–Li(3)–N(3)	78.24(16)	C(30)–C(29)–Li(1)	70.78(17)
N(2)–Li(3)–N(3)	147.9(2)	Si(6)–C(29)–Li(1)	130.12(16)
O(3)–Li(3)–C(15)	136.8(2)	C(29)–C(30)–N(3)	124.0(2)
N(2)–Li(3)–C(15)	66.76(14)		

Table 3
Selected bond lengths (Å) and angles (°) for **7**

Bond lengths			
Li–N(1)	1.996(4)	N(1)–C(1)	1.332(3)
Li–N(2)	2.044(4)	N(1)–C(2)	1.406(3)
Li–N(4)	2.067(4)	N(2)–C(1)	1.328(3)
Li–N(3)	2.076(4)	C(2)–C(3)	1.348(3)
Bond angles			
N(1)–Li–N(2)	68.41(4)	N(2)–C(1)–N(1)	117.22(18)
N(4)–Li–N(3)	88.03(16)	C(3)–C(2)–N(1)	120.28(19)
C(1)–N(1)–C(2)	124.16(18)	C(2)–C(3)–Si(1)	130.15(18)

parameters, except that the N–C-bond length in **7** is significantly longer, Table 3.

There are two independent dinuclear molecules, each lying on an inversion centre, in the unit cell of the dinuclear compound **8**, with essentially the same geometry, Fig. 5; hence data for only one are listed in Table 4.

The molecule has two outer planar $\overline{\text{LiOSiO}}$ four-membered rings with endocyclic angles varying from 70.9(3)° at Li to 100.6(3)° at one of the two bridging methoxy oxygen atoms. The two rings are members of

Table 4
Selected bond lengths (Å) and angles (°) for **8**

<i>Bond lengths</i>			
Li–O(3)	1.965(8)	Si(1)–O(2)	1.675(3)
Li–O(2)	2.005(8)	Si(1)–O(1)	1.678(3)
Li–N'	2.016(8)	Si(2)–C(2)	1.859(6)
Li–O(1)	2.073(8)	N–C(1)	1.408(6)
Si(1)–N	1.634(4)	C(1)–C(2)	1.323(7)
<i>Bond angles</i>			
O(3)–Li–O(2)	104.9(4)	Si(1)–O(2)–Li	100.6(3)
O(3)–Li–N'	122.3(4)	C(1)–N–Si(1)	133.8(3)
O(2)–Li–N'	117.9(4)	Si(1)–N–Li'	111.6(3)
O(3)–Li–O(1)	102.2(4)	C(2)–C(1)–N	122.1(5)
O(2)–Li–O(1)	70.9(3)	C(2)–C(1)–C(3)	118.6(4)
N'–Li–O(1)	126.6(4)	N–C(1)–C(3)	119.2(4)
O(2)–Si(1)–O(1)	89.83(17)	C(1)–C(2)–Si(2)	129.3(4)
Si(1)–O(1)–Li	97.8(3)		

Table 5
Selected bond lengths (Å) and angles (°) for **10**

<i>Bond lengths</i>			
Li–O(2)'	1.919(3)	Si(2)–N	1.6607(13)
Li–O(1)	1.995(3)	Si(2)–O(2)	1.6782(12)
Li–N	2.009(3)	N–C(8)	1.3770(19)
Li–N'	2.475(3)	C(1)–C(8)	1.363(2)
Si(1)–O(1)	1.6779(12)	C(8)–C(9)	1.556(2)
Si(1)–C(1)	1.8231(16)		
<i>Bond angles</i>			
O(2)'–Li–O(1)	106.36(14)	Si(1)–O(1)–Li	107.70(10)
O(2)'–Li–N	128.48(15)	Si(2)–O(2)–Li'	103.22(10)
O(1)–Li–N	104.11(13)	C(8)–N–Si(2)	135.33(11)
O(2)'–Li–N'	71.08(10)	C(8)–C(1)–Si(1)	127.06(13)
O(1)–Li–N'	152.42(14)	C(1)–C(8)–N	122.36(14)
N–Li–N'	97.84(11)	C(1)–C(8)–C(9)	118.47(13)
O(1)–Si(1)–C(1)	106.61(7)	N–C(8)–C(9)	119.09(13)
N–Si(2)–O(2)	101.96(6)		

an $\overline{\text{LiNSiOLiNSiO}}$ macrocycle. The geometry about each four-coordinate lithium atom is completed by an oxygen atom of a THF ligand. Each 1-azaallyl ligand is bound to a lithium atom in mode **B** (terminal κ^1 -enamido). The Li–N and C_α – C_β bond lengths are shorter and the Li–OMe is longer than in **4** [3], **5**, or **6**, while the N– C_α bond length is similar to those in **4** [3] or **5** (**6** is significantly shorter). As in **5**, the hydrogen atoms and the *tert*-butyl groups in **8** are arranged in a cisoid manner about each C_α – C_β bond.

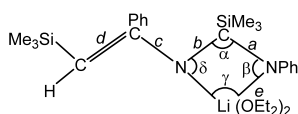


Fig. 7. Selected geometrical parameters for $[\text{Li}\{\text{N}(\text{Ph})\text{C}(\text{SiMe}_3)\text{N}\}\text{C}(\text{Ph})=\text{C}(\text{H})\text{SiMe}_3\}\text{(OEt}_2)]$ (**9**). $a = 1.326(6)$, $b = 1.355(6)$, $c = 1.379(6)$, $d = 1.352(7)$, $e = 1.353(2)$ Å; $\alpha = 113.2(7)$, $\beta = 89.5(4)$, $\gamma = 67.5(3)$, $\delta = 89.6(4)^\circ$.

Crystalline **10** is a centrosymmetric, fused tricyclic dimer, Fig. 6. Its inner core is an eight-membered $\overline{\text{LiNSiOLi}'\text{N}'\text{Si}'\text{O}'}$ ring, with short transannular Li...N' and Li'...N contacts of 2.475(3) Å; the endocyclic Li–N and Li–O bond lengths of 2.009(3) and 1.919(3) Å, respectively, Table 5, are similar to those in **6**.

Each Li–N edge is also a member of an outer six-membered $\overline{\text{LiNCCSiO}}$ ring. The endohexacyclic bond angles are 104.11(13), 96.84(12), 122.36(14), 127.06(13), 106.61(7) and 107.79(10)° at Li, N, C, C, Si, and O atoms, respectively; the Li–O bond length of 1.995(3) Å is significantly longer than in any of **4** [3], **5**, **6** or **8**. Although the N– C_α and C_α – C_β bond lengths of **10** are very similar to those in **6**, the transannular Li– C_α and Li– C_β contacts of 2.568 and 2.824 Å, respectively, are significantly longer than those in **6** (2.310 and 2.265 Å, respectively). Consequently we conclude that each 1-azaallyl ligand in **10** is bound to a lithium atom in mode **B** (terminal κ^1 -enamido); and, as in **5** and **8**, the hydrogen atom and the *tert*-butyl group are *cis* to one another about the $C_\alpha=C_\beta$ bond.

3. Conclusions

We have shown that one equivalent of each silylmethyl lithium reagent $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_{3-n}(\text{OMe})_n)\}_x]$ ($n = 1$ and $x = 8$ (**1**), $n = 2$ and $x = \infty$ (**2**)) and $[\text{Li}\{\text{CH}(\text{SiMe}_2\text{OMe})_2\}]_\infty$ (**3**) reacts readily with an α -H-free organic cyanide to afford the 1:1-insertion product **4** [3], **5**, **6**, **8**, and **10** and the 1:2 product **7**. Of these, the 1-azaallyllithium compounds **4**, **5**, **6** and **8** are formed from the C_1 -symmetric compounds **1** and **2**, as a result of carbanionic attack at $\text{RC}\equiv\text{N}$, involving C–C bond-formation and concomitant regioselective 1,3-shift of the appropriate $\text{SiMe}_{3-n}(\text{OMe})_n$ (rather than SiMe_3) group from C \rightarrow N. The formation of the 1,3-diazaallyllithium-TMEDA adduct **7** from **1** and 2,5-Me₂C₆H₃CN likewise shows $\text{SiMe}_2\text{OMe} > \text{SiMe}_3$ in migratory aptitude. The mode of bonding of the 1-azaallyl ligand to lithium is diverse: **B** (terminal κ^1 -enamido) in **8** and **10**, **C** (bridging η^3 -1-azaallyl) in **6**, and **F** (bridging κ^1 -enamido) in **4** [3] and **5**. The compounds **4** [3], **5**, **8** and **10** have the *Z*- and **7** has the *E*-stereochemistry about the C=C bond.

4. Experimental section

4.1. General

All manipulations were carried out under vacuum or argon using standard Schlenk and vacuum line techniques. Pentane, hexane, TMEDA, Et₂O, benzene-*d*₆, pyridine-*d*₅ and toluene-*d*₈ were dried and distilled

over sodium–potassium alloy and degassed prior to use. Tetrahydrofuran was distilled twice from sodium-benzophenone. Li^nBu (Aldrich) was a 1.6 M solution in hexane. Melting points were determined in sealed capillaries under argon on an electrothermal apparatus and are uncorrected. The NMR spectra were recorded using a WM-300 Bruker instrument at 300.13 (^1H), 75.42 (^{13}C) and 116.64 (^7Li) MHz or an AMX-500 Bruker spectrometer at 500.1 (^1H), 125.72 (^{13}C), 194.32 (^7Li), and 99.36 (^{29}Si) MHz at ambient probe temperature, referenced internally to residual solvent resonances (^1H , ^{13}C), or externally (^7Li , ^{29}Si) and, except for ^1H , were proton-decoupled. Electron impact mass spectra were taken on a Kratos MS 80 RF instrument. Elemental analyses (calculated data are for empirical formulas) were carried out by Medac Ltd., UK; as in our earlier studies of **1–3** [1], some of the data for carbon were low, attributed to incomplete combustion of CSi. The compounds $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})\}]_8$ (**1**), $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}(\text{OMe})_2)\}]_\infty$ (**2**), and $[\text{Li}\{\text{CH}(\text{SiMe}_2\text{OMe})_2\}]_\infty$ (**3**), were prepared by literature procedures [1]; in the following syntheses using **1–3** “mmol” is based on the empirical formula.

4.2. Synthesis of $[\text{Li}\{N(\text{SiMe}_2\text{OMe})C(^t\text{Bu})C(H)(\text{SiMe}_3)\}]_2$ (**5**)

$^t\text{BuCN}$ (0.22 cm^3 , 1.99 mmol) was added by syringe to a stirred solution of $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})\}]_8$ (**1**) (0.36 g, 1.98 mmol) in diethyl ether (45 cm^3) at room temperature. The resulting solution was stirred for 12 h. The volatiles were removed at 45 $^\circ\text{C}/10^{-2}$ Torr and the residue was ‘stripped’ twice with pentane and extracted into diethyl ether. The extract was filtered; the filtrate was concentrated and stored for a few weeks at -25°C , yielding the colourless, crystalline complex **5** (0.34 g, 64%), m.p. 90 $^\circ\text{C}$ (dec.). $^1\text{H-NMR}$ ($\text{C}_6\text{D}_5\text{CD}_3$): δ 0.15 (s, 9H, SiMe_3), 1.11 (s, 6H, SiMe_2), 3.14 (s, 3H, MeO), 4.51 (s, 1H, CH allylic). $^{13}\text{C-NMR}$: δ 0.63 (SiMe_3), 1.36 (SiMe_2), 31.78 (CMe_3), 41.01 (CMe_3), 49.72 (MeO), 97.98 (CH allylic). $^7\text{Li-NMR}$: δ -1.94 . $^{29}\text{Si-NMR}$: δ -8.66 (SiMe_3) and -4.06 (SiMe_2OMe). Anal. Calc. for $\text{C}_{12}\text{H}_{28}\text{LiNOSi}_2$: C, 54.3; H, 10.63; N, 5.27. Found: C, 52.9; H, 10.29; 5.21%.

4.3. Synthesis of $[\text{Li}\{N(\text{SiMe}_2\text{OMe})C(\text{Ph})C(H)(\text{SiMe}_3)\}]_3$ (**6**)

PhCN (0.52 cm^3 , 5.05 mmol) was added by syringe to a stirred solution of $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})\}]_8$ (**1**) (0.46 g, 2.53 mmol) in diethyl ether (ca. 55 cm^3) at 0 $^\circ\text{C}$. The resulting solution was stirred for 12 h at room temperature. The volatiles were removed in vacuo and ‘stripped’ twice with pentane. The residue was extracted with Et_2O (20 cm^3) and the extract was filtered. The filtrate was concentrated and stored for a few days at

-25°C ; the first crop of yellow crystals was filtered off. The filtrate was concentrated (to ca. 10 cm^3) and stored at -25°C for a few days, yielding pale yellow crystals of complex **6** (0.35 g, 48%), m.p., 140–143 $^\circ\text{C}$. $^1\text{H-NMR}$ (C_6D_6): δ -0.14 (s, 6H, SiMe_2OMe), 0.17 (s, 9H, SiMe_3), 3.22 (s, 3H, OMe), 4.68 (s, 1H, CH), 7.14 (m, 3H, Ph), 7.40 (d, 2H, Ph). $^{13}\text{C-NMR}$: δ 0.02 (SiMe_3), 1.65 (SiMe_2), 49.91 (OMe), 92.82 (CH), 127.36, 128.71 (Ph), 147.27 (*ipso-C*), 174.25 ($\text{C}=\text{N}$). $^7\text{Li-NMR}$: δ -1.44 . MS *m/z* (% and assignment, *M* denotes the monomer): 570 (11%, $[2\text{M}]^+$), 292 (100%, $[\text{M}+\text{Li}]^+$), 192 (77%), 162 (98%, $[\text{SiMe}_3+\text{SiMe}_2\text{OMe}]^+$), 89 (68%, $[\text{SiMe}_2\text{OMe}]^+$), 73 (54%, $[\text{SiMe}_3]^+$). Anal. Calc. for $\text{C}_{52}\text{H}_{72}\text{Li}_3\text{N}_3\text{O}_3\text{Si}_6$: C, 58.9; H, 8.47; N, 4.90. Found: C, 57.3; H, 8.67; N, 4.88%.

4.4. Synthesis of $[\text{Li}\{N(\text{SiMe}_2\text{OMe})C(\text{C}_6\text{H}_3\text{Me}_2-2,5)\text{NC}(\text{C}_6\text{H}_3\text{Me}_2-2,5)C(H)(\text{SiMe}_3)\}(\text{TMEDA})]$ (**7**)

2,5- $\text{Me}_2\text{C}_6\text{H}_3\text{CN}$ (0.39 cm^3 , 2.86 mmol) was added by syringe to a stirred solution of $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{OMe})\}]_8$ (**1**) (0.26 g, 1.43 mmol) in diethyl ether (20 cm^3) at 0 $^\circ\text{C}$. The resulting solution was stirred for 12 h at room temperature. The volatiles were removed in vacuo and the residue was extracted with hexane. Colourless, X-ray quality crystals of compound **7** (0.50 g, 63%), m.p. 78 $^\circ\text{C}$ (dec.) were obtained by recrystallisation from hexane/TMEDA. $^1\text{H-NMR}$ (C_6D_6): δ -0.08 (s, 9H, SiMe_3), 0.19 (s, 6H, SiMe_2), 1.62 (s, 4H, TMEDA), 1.87 (s, 12H, TMEDA), 2.08 (s, 12H, Me), 3.48 (s, 3H, OMe), 4.92 (s, 1H, CH), 6.80 (d, 4H, Ph), 6.95 (m, 2H, Ph). $^{13}\text{C-NMR}$: δ 0.24 (SiMe_3), 2.38 (SiMe_2), 20.12 (Me), 20.35 (Me), 20.84 (Me), 20.98 (Me), 45.23 (TMEDA), 49.74 (TMEDA), 52.68 (OMe), 98.07 (CH), 129.33, 129.58, 130.86, 143.49 (Ph), 145.22 (*ipso-C*), 170.24 ($\text{C}=\text{N}$). Anal. Calc. for $\text{C}_{51}\text{H}_{53}\text{LiN}_4\text{OSi}_2$: C, 66.3; H, 9.45; N, 9.98. Found: C, 66.0; H, 9.43; N, 10.12%.

4.5. Synthesis of $[\text{Li}\{N(\text{SiMe}(\text{OMe})_2)C(^t\text{Bu})C(H)(\text{SiMe}_3)\}(\text{THF})]_2$ (**8**)

$^t\text{BuCN}$ (0.32 cm^3 , 2.88 mmol) was added by syringe to a stirred solution of $[\text{Li}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}(\text{OMe})_2)\}]_\infty$ (**2**) (0.57 g, 2.88 mmol) in diethyl ether (45 cm^3) at 25 $^\circ\text{C}$. The resulting solution was stirred for 18 h. The volatiles were removed at 45 $^\circ\text{C}/10^{-2}$ Torr and the residue was extracted with THF and the extract was filtered. The filtrate was concentrated and stored for a few days at -25°C , yielding colourless crystals of compound **8** (0.68 g, 67%), m.p. 95 $^\circ\text{C}$ (dec.). $^1\text{H-NMR}$ ($\text{C}_6\text{D}_6/\text{C}_5\text{D}_5\text{N}$): δ 0.39 (s, 9H, SiMe_3), 0.51 (s, 3H, Me), 1.36 (s, 9H, ^tBu), 3.38 (s, 6H, OMe), 4.39 (s, 1H, CH). $^{13}\text{C-NMR}$: δ 2.35 (SiMe_3), 4.83 (SiMe), 31.33 (CMe_3), 40.99 (CMe_3), 49.75 (OMe), 86.26 (CH), 176.24 ($\text{C}=\text{N}$). MS: (*M* denotes the monomeric unit) *m/z* (% and assign-

ment): 288 (24%, $[M+Li]^+$), 224 (75%, $[M-^iBu]^+$), 105 (60%, $[SiMe(OMe)_2]^+$), 73 (87%, $[SiMe_3]^+$), 57 (98%, $[^iBu]^+$), 41 (100%, $[MeC=N]^+$), 29 (68%). Anal. Calc. for $C_{32}H_{72}Li_2N_2O_6Si_4$: C, 54.4; H, 10.26; N, 3.96. Found: C, 52.4; H, 10.22; N, 4.30%.

4.6. Synthesis of

$Li\{N(SiMe(OMe)_2)C(Ph)C(H)(SiMe_3)\}(TMEDA)$ (**9**)

PhCN (0.24 cm³, 2.33 mmol) was added by syringe to a solution of $[Li\{CH(SiMe_3)(SiMe(OMe)_2)\}]_{\infty}$ (**2**) (0.46 g, 2.33 mmol) in hexane/TMEDA (35 cm³/0.35 cm³, 2.33 mmol) at 0 °C. The solution immediately became yellow. The reaction mixture was stirred for 18 h at 25 °C, then decanted and the yellow precipitate was filtered off. Compound **9**, as a pale yellow powder (0.39 g, 42%), m.p. 83 °C (dec.) was obtained from the filtrate after removing the solvent and drying in vacuo. ¹H-NMR (C_6D_6): δ 0.21 (s, 9H, $SiMe_3$), 0.39 (s, 3H, $SiMe(OMe)_2$), 1.59, 1.72 (4H, 12H, *TMEDA*), 3.45 (s, 6H, *OMe*), 4.48 (s, 1H, *CH*); 7.08 (m, 3H, *Ph*), 7.58 (d, 2H, *Ph*). ¹³C-NMR: δ 1.87 ($SiMe_3$), 2.42 ($SiMe_2$), 45.16 (*TMEDA*), 48.95 (*TMEDA*), 50.02 (*OMe*), 88.24 (*CH*), 129.46, 130.82 (*Ph*), 143.34 (*ipso-C*), 171.16 (*C=N*). Anal. Calc. for $C_{20}H_{40}LiN_3O_2$: C, 66.5; H, 11.08; N, 11.63. Found: C, 64.8; H, 11.21; N, 11.60%.

4.7. Synthesis of

$[Li\{N(SiMe_2OMe)C(^iBu)C(H)(SiMe_2OMe)\}]_2$ (**10**)

^tBuCN (0.19 cm³, 1.72 mmol) was added by syringe to a stirred solution of $[Li\{CH(SiMe_2OMe)_2\}]_{\infty}$ (**3**) (0.34 g,

1.72 mmol) in diethyl ether (55 cm³) at 0 °C. The resulting solution was stirred for 24 h at room temperature. The volatiles were removed in vacuo and the residue was 'stripped' twice with pentane and extracted into Et₂O. The extract was filtered and the filtrate was concentrated and stored for a few days at -27 °C yielding colourless crystals of compound **10** (0.37 g, 76%), m.p., 172 °C, (dec.). ¹H-NMR (C_6D_6): δ 0.23 (s, 6H, $SiMe_2$), 0.27 (s, 6H, $SiMe_2$), 1.29 (s, 9H, CMe_3), 3.22, (s, 3H, *OMe*), 3.23 (s, 3H, *OMe*), 4.42 (s, 1H, *CH*), ¹³C-NMR: δ -0.30 ($SiMe_2$), 31.48 (CMe_3), 41.02 (CMe_3), 49.82 (*OMe*), 50.21 (*OMe*), 91.02 (*CH*). ⁷Li-NMR: δ -1.96. MS *m/z* (% and assignment): 281 (26%, $[M]^+$), 224 (100%, $[M-^iBu]^+$), 89 (24%, $[SiMe_2OMe]^+$). Anal. Calc. For $C_{12}H_{28}LiNO_2Si_2$: C, 51.2; H, 9.96; N, 4.98. Found: C, 49.9; H, 9.89; N, 4.94%.

4.8. X-ray structure determinations for compounds **5–8** and **10**

Data for the crystal structure determinations were collected on a Kappa CCD diffractometer, using a crystal coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 173(2) K or for **5** at 223(2) K. Crystal data and refinement details are listed in Table 6. The structures were solved by direct methods and refined using SHELXL-97 [10]. All non-H atoms were refined anisotropically; absorption corrections were not applied. There were two independent molecules of **8** in the unit cell, of very similar geometry; in Table 3 parameters for one only are listed. Drawings (Figs. 1–5) are by ORTEP-3 with 20% ellipsoids.

Table 6

Crystal data and structure refinement for **5–8** and **10**

Compound	5	6	7	8	10
Empirical formula	$C_{24}H_{56}Li_2N_2O_2Si_4$	$C_{42}H_{72}N_3O_3Si_6 \cdot (C_4H_{10}O)$	$C_{31}H_{53}LiN_4OSi_2$	$C_{32}H_{72}Li_2N_2O_6Si_4$	$C_{24}H_{56}Li_2N_2O_4Si_4$
Formula weight	530.95	930.51	560.89	707.16	562.95
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
<i>a</i> (Å)	9.4436(3)	14.2859(2)	10.3173(2)	10.5688(4)	9.8397(3)
<i>b</i> (Å)	9.7697(3)	20.2922(2)	12.0896(2)	24.9064(6)	10.0236(3)
<i>c</i> (Å)	11.2895(5)	21.1611(3)	15.3472(3)	16.5411(6)	10.2898(4)
α (°)	93.335(1)	90	76.183(1)	90	103.471(1)
β (°)	109.043(2)	92.420(2)	89.829(1)	94.835(2)	98.834(1)
γ (°)	115.732(2)	90	72.923(1)	90	114.149(1)
<i>V</i> (Å ³)	862.17(5)	6128.97(14)	1772.28(6)	4338.6(2)	864.43(5)
<i>Z</i>	1	4	2	4	1
<i>D</i> _{calc} (Mg m ⁻³)	1.02	1.01	1.05	1.08	1.08
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	0.19	0.17	0.13	0.17	0.20
Reflections collected	9022	44982	18831	32587	8569
Independent reflections	3001 [<i>R</i> _{int} = 0.065]	10331 [<i>R</i> _{int} = 0.053]	6126 [<i>R</i> _{int} = 0.058]	6264 [<i>R</i> _{int} = 0.080]	4047 [<i>R</i> _{int} = 0.036]
Reflections with <i>I</i> > 2σ(<i>I</i>)	2265	8330	5079	4588	3525
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.052	<i>R</i> ₁ = 0.051	<i>R</i> ₁ = 0.054	<i>R</i> ₁ = 0.080	<i>R</i> ₁ = 0.040
<i>R</i> indices (all data)	<i>wR</i> ₂ = 0.130	<i>wR</i> ₂ = 0.141	<i>wR</i> ₂ = 0.135	<i>wR</i> ₂ = 0.266	<i>wR</i> ₂ = 0.117

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data centre, CCDC no. 207352 for compound **5**, CCDC no. 207353 for compound **6**, CCDC no. 207351 for compound **7**, CCDC no. 207354 for compound **8**, CCDC no. 207355 for compound **10**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336003; e-mail: deposit@ccdc.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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