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Journal of Organometallic Chemistry 689 (2004) 1342–1349

Journal of Organometallic Chemistry

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# Synthesis and structures of four crystalline lithium β-diketiminates derived from $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ and PhCN or $Bu^tCN$ and PhCN

Peter B. Hitchcock [a], Michael F. Lappert [a,*], Xue-Hong Wei [a,b]

[a] *Department of Chemistry, University of Sussex, Brighton, E. Sussex BN1 9QJ, UK*
[b] *The School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China*

Received 13 November 2003; accepted 14 January 2004

## Abstract

Treatment at ambient temperature in diethyl ether of one equivalent of $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**A**) with (i) two equivalents of PhCN, or (ii) successive equivalent portions of $Bu^tCN$ and PhCN gave from (i) $[Li(OEt_2)\{N\overline{SiMe_2C(Ph)C(H)C(Ph)N}\}]_4$ (**1**) and $[Li(OEt_2)\{N\overline{SiMe_2C(Ph)C(SiMe_3)C(Ph)N}\}]_2$ (**2**) as well as the known lithium 1-azaallyl $[Li\{N(SiMe_2OMe)C(Ph)CH(SiMe_3)\}]_3$, and from (ii) $[Li(THF)\{N\overline{SiMe_2C(Bu^t)C(H)C(Ph)N}\}]_4$ (**3**) The latter was also obtained from the known $[Li\{N(SiMe_2OMe)C(Bu^t)CH(SiMe_3)\}]_2$ and PhCN under similar conditions. Recrystallisation of **2** from THF/hexane afforded $[Li(THF)\{N\overline{SiMe_2C(Ph)C(SiMe_3)C(Ph)N}\}]_4$ (**2′**). X-ray diffraction data on **2**, **2′** and **3** are presented; data for **1** were only adequate to confirm its gross tetrameric structure. The particularly novel feature of these transformations of the lithium alkyl **A** into lithium β-diketiminates **1**, **2**, **2′** or **3** is that while the first 1,3-carbon to nitrogen shift from the α-carbon of **A** is both silicotropic and regiospecific (in so far as $SiMe_2OMe > SiMe_3$ in migratory aptitude), the second migration is indiscriminate: silicotropy yielding **1** or **3** but prototropy giving **2** (or **2′**). Consistent with these observations, the central carbon atom of the β-diketiminato ligand has significant carbanionic character in **2** or **2′**, attributed to its stabilisation by the exocyclic $Me_3Si$ at C2, whereas in **1** or **3** there is π-delocalisation.

*Keywords:* Lithium silylmethyls; beta-Diketiminates; Insertion reactions; X-ray structures

## 1. Introduction

Our interest in the reactions of alkali metal trimethylsilylmethyls with α-hydrogen-free nitriles dates back to 1994 [1], and is illustrated for the case of $Li[CH(SiMe_3)_2]$ with $Bu^tCN$ or PhCN in Scheme 1 [2]. The main features are: (i) $Bu^tCN$ only reacts in a 1:1 ratio with the lithium alkyl, whereas the less sterically hindered PhCN in the absence of a strong neutral donor gives a 1:2 PhCN adduct; (ii) the 1:1-adducts are 1-azaallyls, while the 1:2 adducts are β-diketiminates or the thermodynamically less stable isomeric 1,3-diazaallyls; and (iii) the reactions involve C–C-coupling and 1,3-$Me_3Si$ shifts from carbon to nitrogen. Each of these new metal complexes is a useful ligand transfer agent; the chemistry of metal 1-azaallyls [3] and β-diketiminates [4] has recently been reviewed.

In a foregoing paper, we extended the study *inter alia* to the reactions of $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**A**) [5] with an equivalent portion of $Bu^tCN$, or two equivalents of PhCN (or 2,5-$Me_2C_6H_3CN$) [6]; these reactions, as well as the corresponding one with AdCN (1-adamantanecarbonitrile) [7], are summarised in Scheme 2. The principal new disclosures were that (i) the migrations giving the lithium 1-azaallyls ($Bu^t$, Ph, Ad) or 1,3-diazaallyl (2,5-$Me_2C_6H_3$) were regioselective with $SiMe_2OMe > SiMe_3$ in migratory aptitude; (ii) the 1-azaallyl had a variety of bonding modes to Li [e.g., enamide (**B**) or $\eta^3$-1-azaallyl (**C**); (iii) the methoxy oxygen atom acted as either an intra-(**B**) or inter-(**C**)

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[*] Corresponding author. Fax: +44-1273-677-196.
*E-mail address:* m.f.lappert@sussex.ac.uk (M.F. Lappert).

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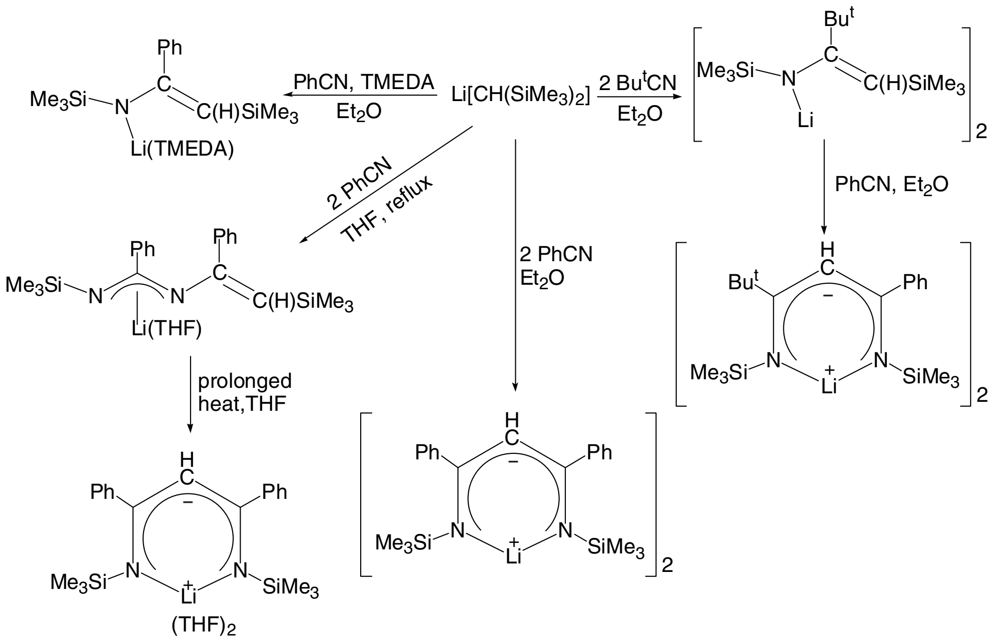
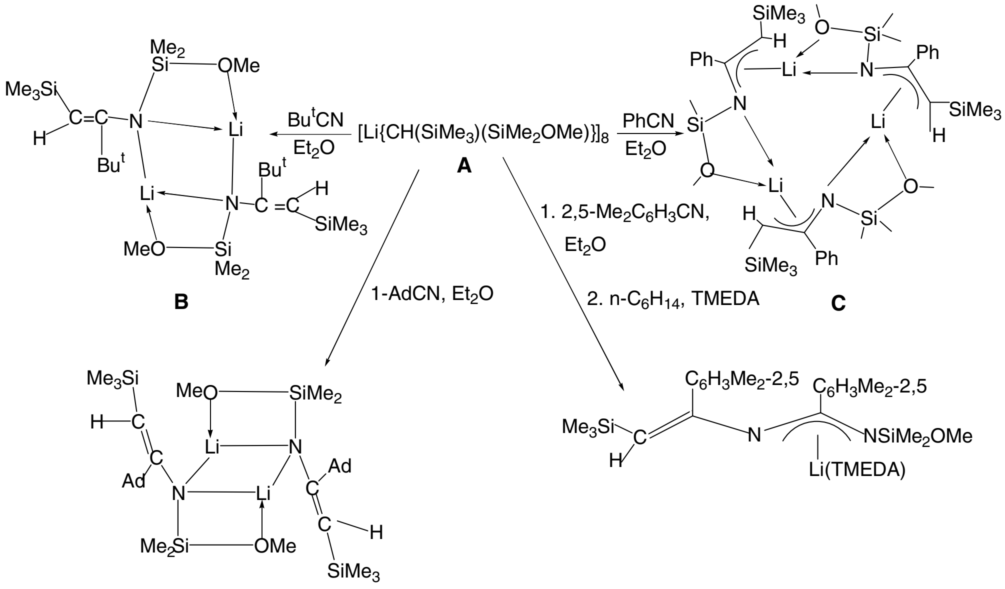
doi:10.1016/j.jorganchem.2004.01.011



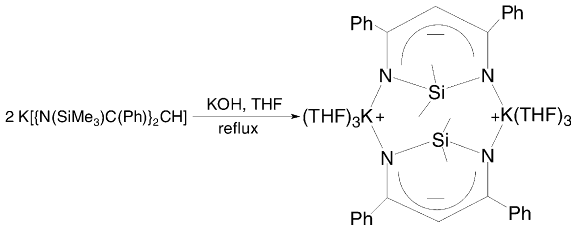
Scheme 1.



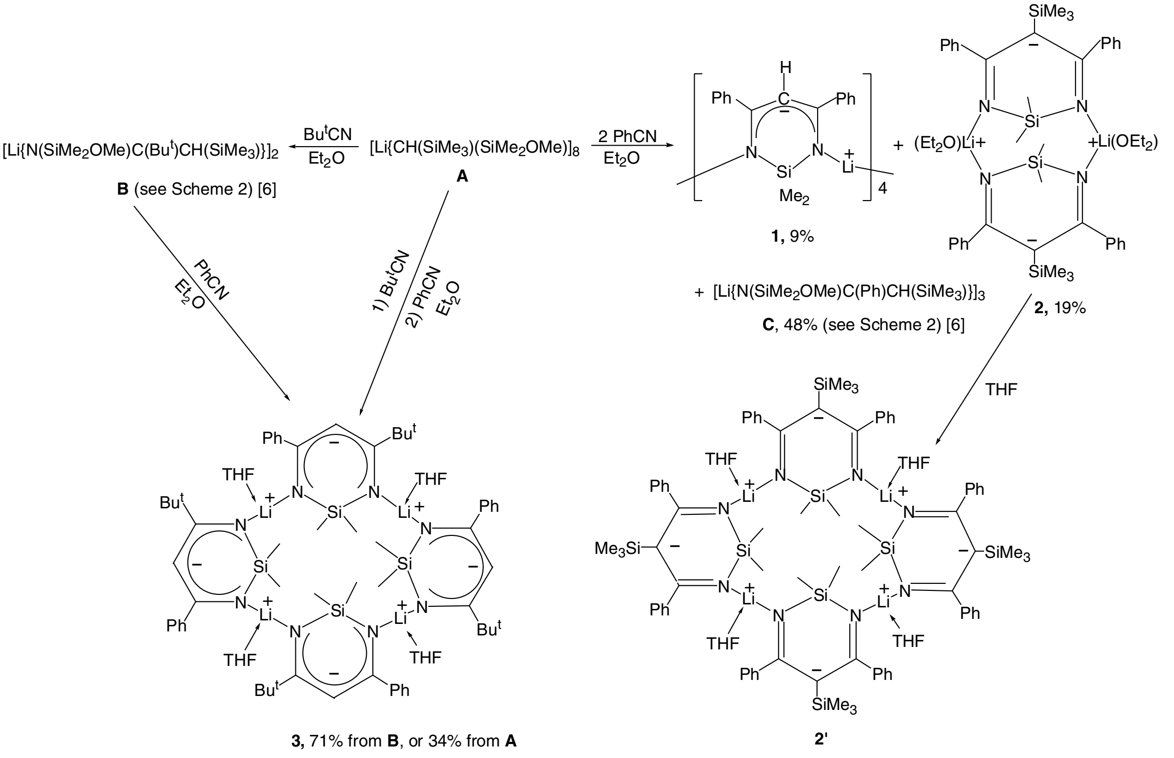
Scheme 2.

molecular donor site; (iv) the latter also had the effect of yielding the 1-azaallyl **C** as the principal (see Scheme 3) product from 1/8**A** + 2PhCN in $Et_2O$.

Metal *N*,*N*′-bis(trimethylsilyl)-β-diketiminates are readily desilylated. Relevant to the present study is the reaction shown in Eq. (1) ($2KOSiMe_3 + 2CH_4$ are the plausible coproducts), in which partial desilylation and N-Si(Me)$_2$-N′ ring closure of the β-diketiminate ligand was a further new development [8].



(1)



Scheme 3.

## 2. Results and discussion

### 2.1. Reactions of $[\mathrm{Li\{CH(SiMe_3)(SiMe_2OMe)\}}]_8$ (*A*) with $\mathrm{Bu^tCN}$ or PhCN

We now turn to some 1:2 (nitrile) reactions of the lithium alkyl **A** with $\mathrm{Bu^tCN}$ and PhCN, as summarised in Scheme 3; the yields refer to crystalline products and have not been optimised. While the reaction of 1/8**A** + 2PhCN in diethyl ether at 0 °C gave the lithium 1-azaallyl **C** as the principal product (Scheme 2) [6], significant portions of the lithium β-diketiminates **1** and **2** were also obtained; they were separated by fractional crystallisation, their solubilities in $\mathrm{Et_2O}$ decreasing in the sequence **C** > **2** > **1**. Treatment of 1/8(**A**) with successively $\mathrm{Bu^tCN}$ in diethyl ether at 0 °C and then PhCN at ca. 20 °C gave crystalline **3** in modest yield, but in good yield from the lithium 1-azaallyl **B** and PhCN at ca. 20 °C. Recrystallisation of **2** from THF/hexane yielded the crystalline lithium β-diketiminate **2′**.

Each of the crystalline complexes **1**, **2**, **2′** and **3** was yellow and, except for **2**, was characterised by elemental analysis, $^1$H- and $^{13}$C{$^1$H}-NMR solution spectra; $^{29}$Si{$^1$H}-NMR for **1** and $^7$Li{$^1$H}-NMR spectra for **2′** were also recorded. The structure of each of the crystalline complexes **2**, **2′** and **3** was established by single crystal X-ray diffraction. Crystals of **1**, obtained from $\mathrm{Et_2O}$, were of poor quality but the data were adequate to establish its tetrameric structure.

### 2.2. The X-ray structures of the crystalline compounds *2*, *2′* and *3*

The molecular structures of the new β-diketiminatolithium compounds **2**, **2′** and **3** are shown in Figs. 1–3, respectively, and selected geometric parameters are listed in Tables 1–3, respectively.

There are two independent dinuclear molecules, each lying on an inversion centre, in the unit cell of $[\mathrm{Li(OEt_2)}\{\overline{\mathrm{NSiMe_2C(Ph)C(SiMe_3)C(Ph)N}}\}]_2$ (**2**), with essentially the same geometry; hence data for only one is shown in Fig. 1 and Table 1. The central core comprises an almost coplanar six-membered LiNNLiNN ring. Each of the adjacent *N*,*N′*-$\mathrm{Me_2Si}$-bridged β-diketiminato ligands (which also bridge the two *N*,*N′*-nitrogen atoms) is boat-shaped, C2 and Si1 being ca. 0.24 and ca. 0.72 Å, respectively, out of the N1N2C1C3 plane. The exocyclic silicon atom Si2 is ca. 0.22 Å out of the C1C2C3 plane. The β-diketiminato ligand is symmetrically bonded, as evident by the closely similar pairs of Si1–N1(N2), C1–N1 or C3–N2, and C2–C1(3) bond lengths. The Li–N and Li–O bond lengths of 2.019 ± 0.008 and 1.941(3) Å, respectively are unexceptional. Each of the two lithium atoms is in a slightly distorted trigonal planar environment with the N1–Li–N2′ angle of 117.4(6)° slightly narrower than the contiguous O1–Li1–N1(or N2′) angles, 121.2 ± 0.2°.

The tetrameric molecule **2′** lies on a site of $\bar{4}$ symmetry, with the $\mathrm{Li_4}$ moiety having a fold angle of 82°

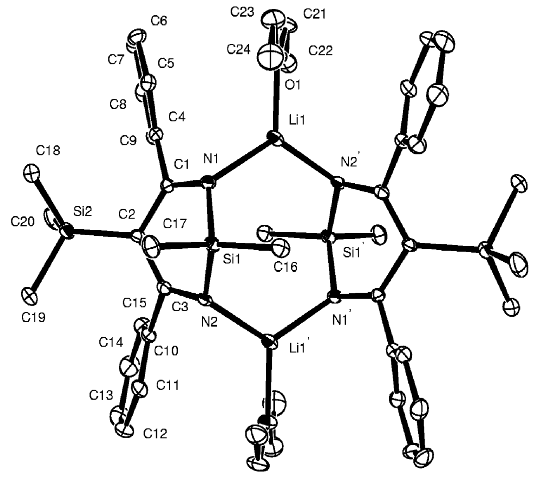


Fig. 1. Molecular structure and atom numbering scheme for $[\mathrm{Li(OEt_2)}\{\mathrm{N\overline{SiMe_2C(Ph)C(SiMe_3)C(Ph)N}}\}]_2$ (**2**).

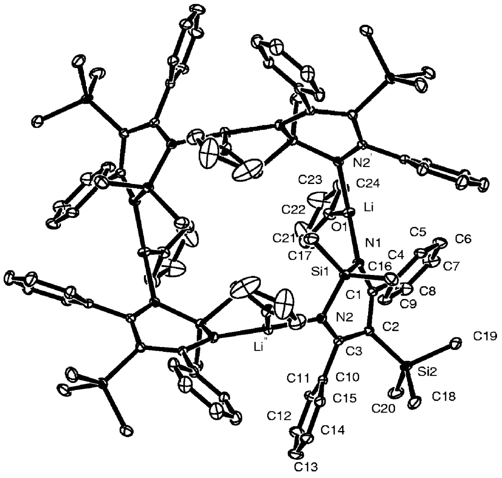


Fig. 2. Molecular structure and atom numbering scheme for $[\mathrm{Li(THF)}\{\mathrm{N\overline{SiMe_2C(Ph)C(SiMe_3)C(Ph)N}}\}]_4$ (**2′**).

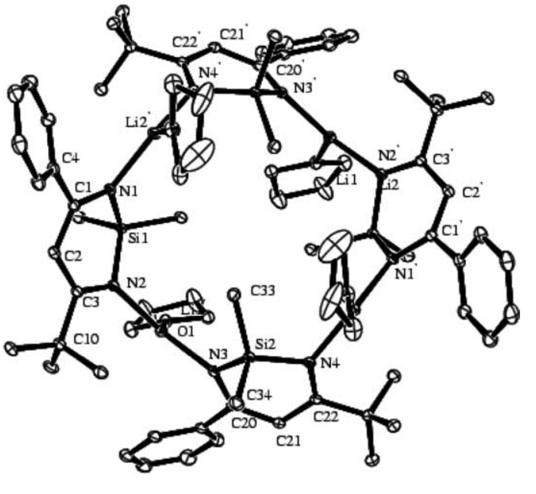


Fig. 3. Molecular structure and atom numbering scheme for $[\mathrm{Li(THF)}\{\mathrm{N\overline{SiMe_2C(Bu^t)C(H)C(Ph)N}}\}]_4$ (**3**).

Table 1
Selected bond lengths (Å) and angles (°) for **2**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Li1–O1 | 1.941(13) | Si2–C2 | 1.869(7) |
| Li1–N1 | 2.027(13) | N1–C1 | 1.320(8) |
| Li1–N2′ | 2.011(14) | C1–C2 | 1.455(9) |
| Si1–N1 | 1.742(6) | C2–C3 | 1.425(9) |
| Si1–N2 | 1.741(6) | C3–N2 | 1.323(9) |
| *Bond angles* | | | |
| O1–Li1–N2′ | 121.2(6) | C3–C2–C1 | 116.1(6) |
| O1–Li1–N1 | 121.4(7) | N2–C3–C2 | 127.8(6) |
| N2′–Li1–N1 | 117.4(6) | C1–N1–Si1 | 111.9(5) |
| N2–Si1–N1 | 104.1(3) | C3–N2–Si1 | 110.3(5) |
| N1–C1–C2 | 125.6(6) | | |

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

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Li–O1 | 1.947(7) | Si2–C2 | 1.880(3) |
| Li–N1 | 2.001(6) | N1–C1 | 1.312(5) |
| Li–N2′ | 2.021(6) | C1–C2 | 1.451(5) |
| Si1–N1 | 1.731(3) | C2–C3 | 1.435(5) |
| Si1–N2 | 1.735(3) | C3–N2 | 1.318(5) |
| *Bond angles* | | | |
| O1–Li–N2′ | 110.5(3) | C3–C2–C1 | 116.6(3) |
| O1–Li–N1 | 114.1(3) | N2–C3–C2 | 127.3(3) |
| N2′–Li–N1 | 132.4(3) | C1–N1–Si1 | 113.0(2) |
| N2–Si1–N1 | 105.42(14) | C3–N2–Si1 | 113.2(2) |
| N1–C1–C2 | 126.9(3) | | |

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

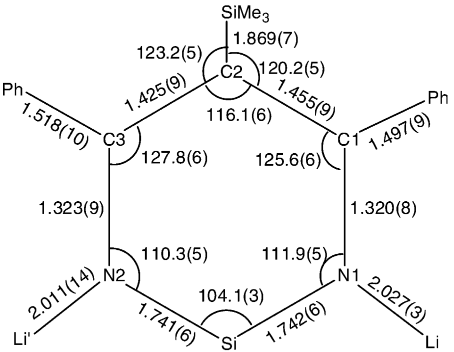
| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Li1–O1 | 1.939(7) | N1–C1 | 1.336(4) |
| Li1–N3 | 1.988(7) | C1–C2 | 1.408(5) |
| Li1–N2 | 2.006(7) | C2–C3 | 1.414(5) |
| Si1–N1 | 1.732(3) | C3–N2 | 1.328(4) |
| Si1–N2 | 1.734(3) | | |
| *Bond angles* | | | |
| O1–Li1–N3 | 111.2(3) | C3–C2–C1 | 123.4(3) |
| O1–Li1–N2 | 109.7(3) | N2–C3–C2 | 124.0(3) |
| N3–Li1–N2 | 137.3(3) | C1–N1–Si1 | 112.5(2) |
| N2–Si1–N1 | 108.19(14) | C3–N2–Si1 | 113.6(2) |
| N1–C1–C2 | 125.5(3) | | |

and the bridging β-diketiminato ligands alternately above and below adjacent Li atoms. Each of these ligands is boat-shaped; the atoms Si1 and C2 are ca. 0.63 and 0.19 Å, respectively, out of the N1C1C3N2 plane, and the exocyclic Si2 atom is ca. 0.30 Å out of the C1C2C3 plane. Like **2**, the β-diketiminato ligand is symmetrically bonded; the geometric parameters are closely similar in **2** and **2′** (Tables 1 and 2). The atoms N1N2Li1Li1′ are coplanar.

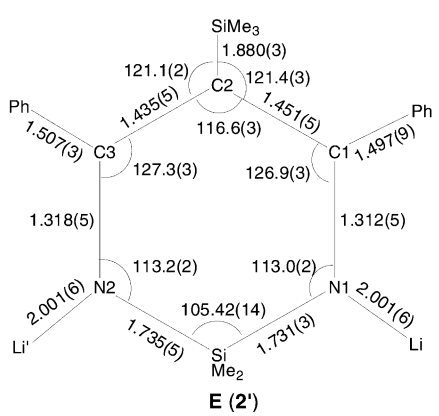
The tetrameric molecule **3** lies on a crystallographic 2-fold rotation axis. Each β-diketiminato ligand is boat-shaped with Si1 and C2 ca. 0.55 and 0.11 Å, respectively out of the N1C1C3N2 plane. The torsion angle between adjacent NCCN planes is 120°. The endocyclic geometric parameters of each β-diketiminato ligand differ from those of **2** (**D**) and **2′** (**E**) in being more clearly π-delocalised (see **F**), as in those of $[K(THF)_3\{N\overline{SiMe_2C(Ph)C(H)C(Ph)N}\}]_2$ (**G**) (see Eq. (1)) [8]. The Li–O and Li–N bond lengths in **2**, **2′** and **3** are closely similar.

### *2.3. Bonding in the β-diketiminato ligands of the crystalline compounds 2, 2′ and 3*

The evidence that the lithium bonding differs in β-diketiminates having an exocyclic C–$SiMe_3$ (**2** and **2′**) rather than a C–H (**3**) bond, as depicted in Scheme 3, is based on an analysis of selected geometrical parameters. While each is essentially $C_2$-symmetric: (i) the mean C–N bond lengths in **2** and **2′** are only very slightly shorter than in **3**, (ii) the mean C–C bond lengths in **2** and **2′** are significantly longer than in **3**, and (iii) the endocyclic bond angle at the central carbon atom is much narrower in **2** and **2′** than in **3**. These features are illustrated in **D** (**2**), **E** (**2′**), and **F** (**3**). Although the π-delocalised structure for **3** is shown as being distinct from the localised zwitterionic structures of **2** and **2′**, the difference may only be one of degree. Thus, we consider that each of **2** and **2′** has unquestionably a greater degree of carbanionic character at C2 than does **3**. Supporting this notion is the fact that each of **2** and **2′**, unlike **3**, has a neighbouring silicon atom (Si2), and it is long established that the effect of an α-silyl group is to stabilise an adjacent carbanion.

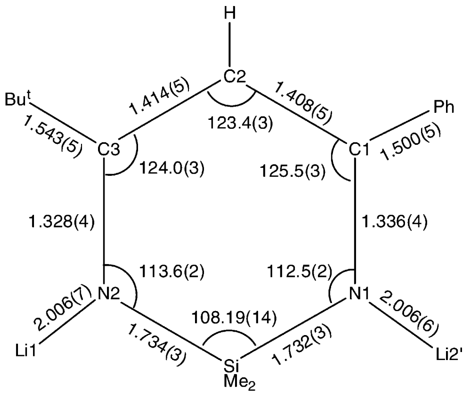


**D** (**2**)

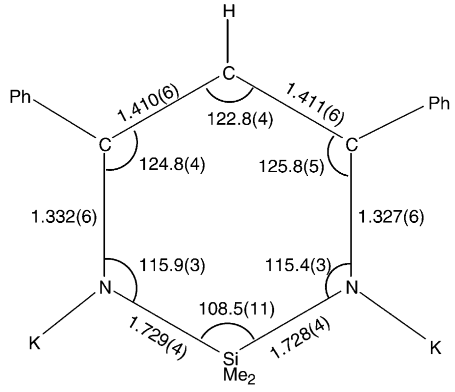


**E** (**2′**)

(2)



**F** (**3**)



**G** [8]

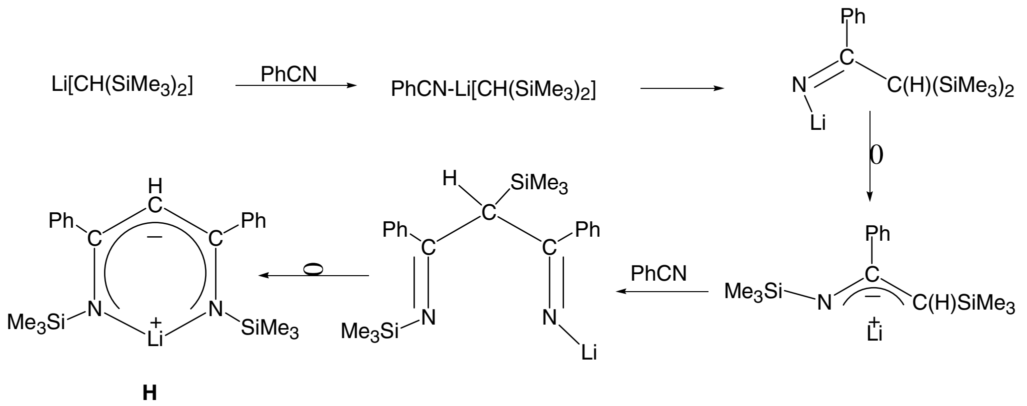
(3)

### *2.4. The reaction pathways to the lithium β-diketiminates 1, 2 and 2′*

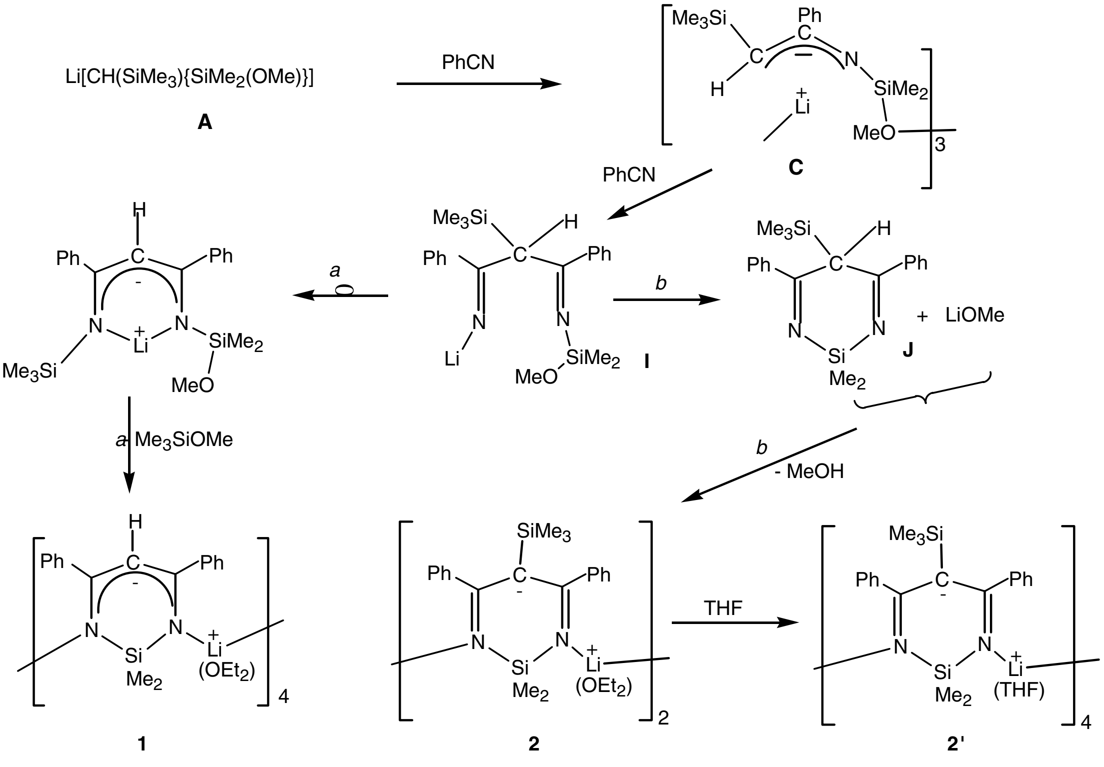
The formation of the lithium β-diketiminate **H** from $Li[CH(SiMe_3)_2]$ and 2PhCN was proposed to follow the pathway shown in Scheme 4, in which not only the first but also the second 1,3-carbon to nitrogen migration was silyl-selective [2].

The major new feature in the reactions of the lithium silylmethyl $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**A**) with benzonitrile (Scheme 3), as compared with the earlier observations on the corresponding reaction of $Li[CH(SiMe_3)_2]$ (Scheme 1), is the discovery that the products included two different lithium β-diketiminates. One of these had a central exocyclic C–H bond (**1**) and the other an exocyclic C–$SiMe_3$ bond (**2,** transformable into **2′**). Clearly the final 1,3-carbon to nitrogen migration was not silyl-selective, a prototropic shift yielding **2** and an $Me_3Si$ shift giving **1**. The proposed pathways (***a*** → **1**, ***b*** → **2**) are shown in Scheme 5.

The structure of the product **C** of the 1:1 PhCN insertion ($(SiMe_2OMe) > SiMe_3$ in migratory aptitude) has been established [6]. The next intermediate **I** is an analogue of the penultimate product of Scheme 4. The pathways from **I** are then believed to diverge: route *a*, yielding **1**, is closely similar to the silyl-selective process



Scheme 4.



Scheme 5.

shown as the final step of Scheme 4; as for *b*, it is proposed that **I** readily eliminates lithium methoxide to give the *N*,*N*′-dimethylsilyl-bridged β-diketimine **J**. In the final step, it is suggested that **J** is deprotonated by the strong base LiOMe, the reaction being favoured by the α-trimethylsilyl-stabilisation of the incipient carbanion of **2**. Further evidence is that the X-ray-characterised compound **J** has been made independently and shown to yield **2′** by treatment with $\mathrm{LiBu^n}$ in THF [9].

## 3. Conclusions

We have shown that one equivalent of the lithium reagent $[\mathrm{Li\{CH(SiMe_3)(SiMe_2OMe)\}}]_8$ (**A**) reacts readily with two equivalents of PhCN in $\mathrm{Et_2O}$ to give not only the known lithium 1-azaallyl $[\mathrm{Li\{N(SiMe_2OMe)C(Ph)C(H)(SiMe_3)\}}]_3$ **C** but also two different lithium β-diketiminates $[\mathrm{Li(OEt_2)\{\overline{NSiMe_2C(Ph)C(H)C(Ph)N}\}}]_4$ (**1**) and $[\mathrm{Li(OEt_2)\{\overline{NSiMe_2C(Ph)C(SiMe_3)C(Ph)N}\}}]_2$ (**2**). Recrystallisation of **2** from THF/hexane yielded $[Li(THF)\{N\overline{SiMe_2C(Ph)C(SiMe_3)C(Ph)N}\}]_4$ (**2′**). From one equivalent of **A** and successively Bu$^t$CN (1 mol) and PhCN (1 mol), the product was the lithium β-diketiminate $[Li(THF)\{N\overline{SiMe_2C(Bu^t)C(H)C(Ph)N}\}]_4$ (**3**) which was also obtained from equivalent portions of $[Li\{N(SiMe_2OMe)C(Bu^t)C(H)(SiMe_3)\}]_2$ (**B**) and PhCN. The X-ray structures of crystalline **2**, **2′** and **3** have been determined. Crystalline compound **1**, like **2′** and **3**, is a tetramer. The central exocyclic C–X bond in the β-diketiminato ligand of **1** and **3** has X = H; but, unexpectedly, for **2** and **2′**, X = $SiMe_3$. Pathways are suggested for the appropriate 1,3-carbon to nitrogen silico-(**1**, **3**) or proto-(**2**, **2′**)-tropic rearrangements. Consistent with these is the observed π-delocalised structure of the *N*,*N′*-$Me_2Si$- bridged β-diketiminato ligand of **3**; whereas the more localised structure of **2** and **2′**, with the central carbon atom having carbanionic character, is stabilised by the pendant $SiMe_3$ group.

## 4. Experimental

### 4.1. General

All manipulations were carried out under vacuum or argon using standard Schlenk and vacuum line techniques. Pentane, hexane, $Et_2O$, benzene-d$_6$, and $C_5D_5N$ were dried and distilled over sodium–potassium alloy and degassed prior to use. Tetrahydrofuran was distilled twice from sodium–benzophenone. LiBu$^n$ (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, in $C_6D_6$ unless otherwise stated, using a WM-300 Bruker instrument at 22 °C, referenced internally to residual solvent resouces ($^1$H, $^{13}$C) or externally ($^7$Li, $^{29}$Si), at 300.13 ($^1$H), 75.42 ($^{13}$C), 116.64 ($^7$Li) and 99.36 ($^{29}$Si) MHz and, except for $^1$H, 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 **A** [5], some of the data for carbon were low, attributed to incomplete combustion of CSi. The compound $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**A**) was prepared by the literature procedure [5].

### 4.2. Synthesis of $[Li(OEt_2)\{N\overline{SiMe_2C(Ph)C(H)C(Ph)N}\}]_4$ (1) $[Li(OEt_2)\{N\overline{SiMe_2C(Ph)C(SiMe_3)C(Ph)N}\}]_2$ (2), $[Li(THF)\{N\overline{SiMe_2C(Ph)C(SiMe_3)C(Ph)N}\}]_4$ (2′) and $[Li\{N(SiMe_2OMe)C(Ph)C(H)(SiMe_3)\}]_3$ (C)

PhCN (0.52 cm$^3$, 5.05 mmol) was added by syringe to a stirred solution of $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**A**) (0.46 g, 2.53 mmol) in diethyl ether (ca. 55 cm$^3$) at 0 °C. The resulting solution was stirred for 12 h at room temperature. The yellow precipitate was filtered off and dried in vacuo to give the yellow powder **1** (0.08 g, 9%), mp: 174 °C, (decomp.). $^1$H-NMR ($C_6D_6/C_5D_5N$): δ 0.55 (s, 6 H, Si $Me_2$), 6.76 (s, 1 H, C*H*), 7.14 (m, 6 H, Ar-*H*), 7.78 (d, 4 H, Ar-*H*); $^{13}$C-NMR: δ 3.45 (Si $Me_2$), 90.26 (*C*H), 126.81 (Ar-*C*; other signals were obscured by solvent signals), 141.23 (*ipso-C*), 174.32 (*C*=N); $^{29}$Si-NMR: δ 6.36. Anal. Calc. for $C_{17}H_{17}LiN_2Si$: C, 71.8; H, 5.98; N, 9.86. Found: C, 70.0; H, 5.91; N, 9.87%. (**1** was dissolved in a very large volume of diethyl ether; poor quality single crystals were obtained which showed **1** to be a tetramer with each lithium atom having one coordinated diethyl ether molecule). All volatiles from the filtrate were removed in vacuo and “stripped” twice with pentane. The residue was extracted with $Et_2O$ (ca. 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 of **2** (0.21 g, 19%) 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 **C** (0.35 g, 48%) (for details of its characterisation, see [6]). Recrystallisation of **2** from THF/hexane (1/10 cm$^3$) yielded good quality crystals of the yellow crystalline compound **2′**, mp, 168 °C, (decomp.). $^1$H-NMR: δ −0.28 (s, 9 H, Si $Me_3$), 0.36 (s, 6 H, Si $Me_2$), 1.41 (4 H THF, 3.55 (4 H, THF), 7.47 (m, 6 H, Ar-*H*), 7.83 (d, 4 H, Ph-*H*); $^{13}$C-NMR: δ −0.25 (Si $Me_3$), 0.57 (Si $Me_2$), (25.60, 68.52, THF), 84.64 (*C*$SiMe_3$), 125.84, 127.36, 129.24, 140.36 (*ipso C*), 172.28 (*C*=N); $^7$Li-NMR: δ 0.97. MS (*M* denotes the monomeric unit) *m*/*z* (% and assignment): 350 (35%, $[M-Li-THF+H]^+$), 293 (65%, $[M-Li-THF-SiMe_2+2H]^+$), 103 (60%, $[PhC{=}N]^+$), 72 (92%, $[THF]^+$), 42 (100%, $[Si–N]^+$). Anal. Calc. for $C_{24}H_{33}LiN_2OSi_2$: C, 67.3; H, 7.76; N, 6.54. Found: C, 67.0; H, 7.64; N, 6.47%.

### 4.3. Synthesis of $[Li(THF)\{N\overline{SiMe_2C(Bu^t)C(H)C(Ph)N}\}]_4$ (3)

Bu$^t$CN (0.15 cm$^3$, 1.35 mmol) was added by syringe to a stirred solution of $[Li\{CH(SiMe_3)(SiMe_2OMe)\}]_8$ (**A**) (0.24 g, 1.32 mmol) in diethyl ether (ca. 45 cm$^3$) at 0 °C. The resulting solution was stirred for 12 h at room temperature; PhCN (0.13 cm$^3$, 1.26 mmol) was added and stirring was continued for a further 12 h. The volatiles were removed in vacuo 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 yellow crystals of **3** (0.18 g, 34%), mp 86 °C (decomp.). $^1$H-NMR: δ 0.08 (s, 6 H, $SiMe_2$), 1.14 (s, 9 H, $CMe_3$), 5.86 (s, 1 H, C*H*), 7.03-7.15 (m, 3 H, Ar-*H*), 7.50 (m, 2 H, Ar-*H*); $^{13}$C-NMR: δ 3.53 ($SiMe_2$), 32.45 ($CMe_3$), 41.08 (*C*$Me_3$), 90.05 (*C* H), 125.43, 125.64, 126.96 (Ar-*C*), 146.62 (*ipso-C*), 177.68 (*C*=N). Anal.

Table 4
Crystal data and structure refinements for 2, 2′ and 3

| Compound | 2 | 2′ | 3 |
|---|---|---|---|
| Empirical formula | $C_{48}H_{70}Li_2N_4O_2\ Si_4$ | $C_{96}H_{132}Li_4N_8O_4\ Si_8(C_4H_8O)$ | $C_{76}H_{116}Li_4N_8O_4\ Si_4(C_4H_8O)$ |
| Formula weight | 861.32 | 2002.99 | 1634.30 |
| Crystal system | Triclinic | Tetragonal | Monoclinic |
| Space group | $P\bar{1}$ (No. 2) | $I\bar{4}$ (No. 82) | $C2/c$ (No. 15) |
| $a$ (Å) | 12.4303(4) | 21.3200(3) | 20.6047(4) |
| $b$ (Å) | 14.8455(6) | 21.3200(3) | 18.9128(2) |
| $c$ (Å) | 15.1847(6) | 14.4507(2) | 27.3652(3) |
| $\alpha$° | 83.907(2) | 90 | 90 |
| $\beta$° | 85.555(2) | 90 | 111.064(2) |
| $\gamma$° | 71.204(2) | 90 | 90 |
| $V$ (Å$^3$) | 2634.9(2) | 6568.5(2) | 9951.4(4) |
| $Z$ | 2 | 2 | 4 |
| $d_{calc}$ (mg m$^{-3}$) | 1.09 | 1.01 | 1.09 |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ (mm$^{-1}$) | 0.15 | 0.13 | 0.11 |
| Reflections collected | 20424 | 35101 | 44928 |
| Independent reflections | 7256 [$R_{int} = 0.100$] | 5762 [$R_{int} = 0.049$] | 8449 [$R_{int} = 0.102$] |
| Reflections with $I > 2\sigma(I)$ | 5381 | 5338 | 5144 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.108$ | $R_1 = 0.065$ | $R_1 = 0.075$ |
| $R$ indices (all data) | $_wR_2 = 0.256$ | $_wR_2 = 0.200$ | $_wR_2 = 0.208$ |

Calc. for $C_{15}H_{21}LiN_2Si$: C, 68.1; H, 8.01; N, 10.60. Found C, 66.6; H, 7.68; N, 9.85%. (**3** was also synthesised in good yield (71%) from **B** and PhCN using a closely similar procedure to that described above.).

### *4.4. X-ray structure determinations for compounds **2**, **2′** and **3***

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. Crystal data and refinement details are listed in Table 4. For **2′**, as well as the THF-solvate molecule in a general position, there was a weak residual density probably due to further very disordered solvate. For **3**, included in the refinement were two independent disordered THF-solvate molecules refined with distance constraints (SADI). 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. Drawings (Figs. 1–3) are by ORTEP-3 with 20% ellipsoids.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data centre, CCDC no. 223622 for compound **2,** CCDC no. 223623 for compound **2′**, CCDC no. 223624 for compound **3**. 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 http://www.ccdc.cam.ac.uk).

## Acknowledgements

We thank the Royal Society for the award of a Sino-British Fellowship for X.-H. W., and EPSRC for other support.

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