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Reactions of $LiCHR_2$ and related lithium alkyls with α-H free nitriles and the crystal structures of eleven representative lithium 1,3-diazaallyls, 1-azaallyls and β-diketiminates

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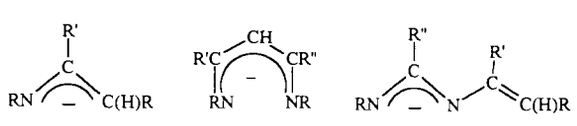
Received 27th March 2000, Accepted 19th May 2000
Published on the Web 30th June 2000

Reactions between bis(trimethylsilyl)methyllithium $LiCHR_2$ and a nitrile R′CN gave lithium 1-azaallyls, β-diketiminates or 1,3-diazaallyls. The products of related processes involving the lithium alkyl $LiCH_2R$, LiCH(R)Ph or $[Li(tmen)]_2[1,2\text{-}\{C(H)R\}_2C_6H_4]$ have also been obtained (R = $SiMe_3$ and R′ = Bu^t, Ph or C_6H_4Me-4). Analytical and spectroscopic data served to identify the following crystalline compounds: $[Li\{N(R)C(Bu^t)C(H)R\}(D)]_n$ [D absent and $n = 2$; D = tmen or dme and $n = 1$], $[Li\{N(R)C(Ph)C(H)R\}(D)]_n$ [D = tmen or pmdien and $n = 1$, or D = thf and $n = 2$], $[Li\{N(R)C(Ph)C(H)C(R'')NR\}(D)]_n$ [D absent, $n = 2$ and R″ = Ph (**4a**), C_6H_4Me-4 (**4b**) or Bu^t; or D = tmen, $(thf)_2$ (**9b**), NEt_3 or thf and NCPh and $n = 1$ and R″ = Ph], $[Li\{N(R)C(Ph)C(H)C(Ph)NR\}(D)Li(CHR_2)]$ [D = OEt_2 or thf], $[Li\{N(R)C(Ar)NC(Ph)=C(H)R\}(D)]_n$ [D = tmen, $n = 1$ and Ar = Ph or C_6H_4Me-4; or D = thf, $n = 2$ and Ar = Ph], $[Li\{N(Ph)C(R)NC(Ph)=C(H)R\}(tmen)]$, $[Li\{N(R)C(Bu^t)CH_2\}_2]$, $[Li\{N(R)C(Ph)=C(H)Ph\}(tmen)]$, and $[Li(tmen)]_2[1,2\text{-}\{N(R)C(Bu^t)CH\}_2C_6H_4]$. Each of the three classes of ligands has a diversity of ligating possibilities, functioning towards lithium variously in a terminal or bridging and mono- or bi-dentate fashion, the role of a neutral donor D often being crucial. For an isomeric pair, the lithium β-diketiminate was thermodynamically preferred over the 1,3-diazaallyl. From $[Li\{N(R)C(Bu^t)C(H)R\}]_2$ and successively CH_2Br_2 and $LiBu^n$, the further lithium 1-azaallyl compound $[Li\{N(R)C(Bu^t)C(H)C(H)(R)Bu^n\}]_2$ was obtained. From **4a** and CH_2Br_2 or $(BrCH_2)_2$ a bis(β-diketiminyl)-methane $CH_2[C\{C(Ph)NR\}C(Ph)N(H)R]_2$ or **9b** or β-diketimine HN(R)C(Ph)C(H)C(Ph)NR were obtained, while **4b** with successively $KOBu^t$ and H_2O gave the β-diketimine $HN(R)C(C_6H_4Me\text{-}4)C(H)C(C_6H_4Me\text{-}4)NR$. Mechanistic pathways are proposed, which involve Me_3Si migrations: from C to N or N to N; or, for the latter a 1,2-dyotropic Me_3Si/H exchange. The crystal structures of eleven of these compounds have been determined. Each of the new lithium compounds may in principle behave as an *N*-, *C*-, (*N*,*N*′)-, or (*N*,*C*)-centred nucleophile. Reactions demonstrating the first two alternatives for the β-diketiminate $[Li\{N(R)C(Ar)C(H)C(Ar)NR\}]_2$ are (i) those with water (Ar = C_6H_4Me-4) or $(BrCH_2)_2$ (Ar = Ph) which gave the diketimine N(R)C(Ar)C(H)C(Ar)N(H)R, whereas (ii) that with CH_2Br_2 (Ar = Ph) yielded $CH_2[\overline{C\{C(Ph)NR\}C}(Ph)N(H)R]_2$.

Introduction

In a series of communications we have shown that the interaction of a trimethylsilylmethyllithium reagent $Li[CH_{3-n}R_n]$ ($n = 1$, 2, or 3 and R = $SiMe_3$) and an α-hydrogen-free nitrile R′CN can yield a 1-azaallyl-, β-diketiminato- or 1,3-diazaallyllithium compound depending on *n*, the nature of R′, the stoichiometry and the absence or presence of a neutral co-ligand.[1–4] Furthermore, we have demonstrated that each of such ligands (illustrated below for the case of $n = 2$ in the delocalised mode as **A**, **B** and **C**, respectively) has a diversity of ligating



A **B** **C**

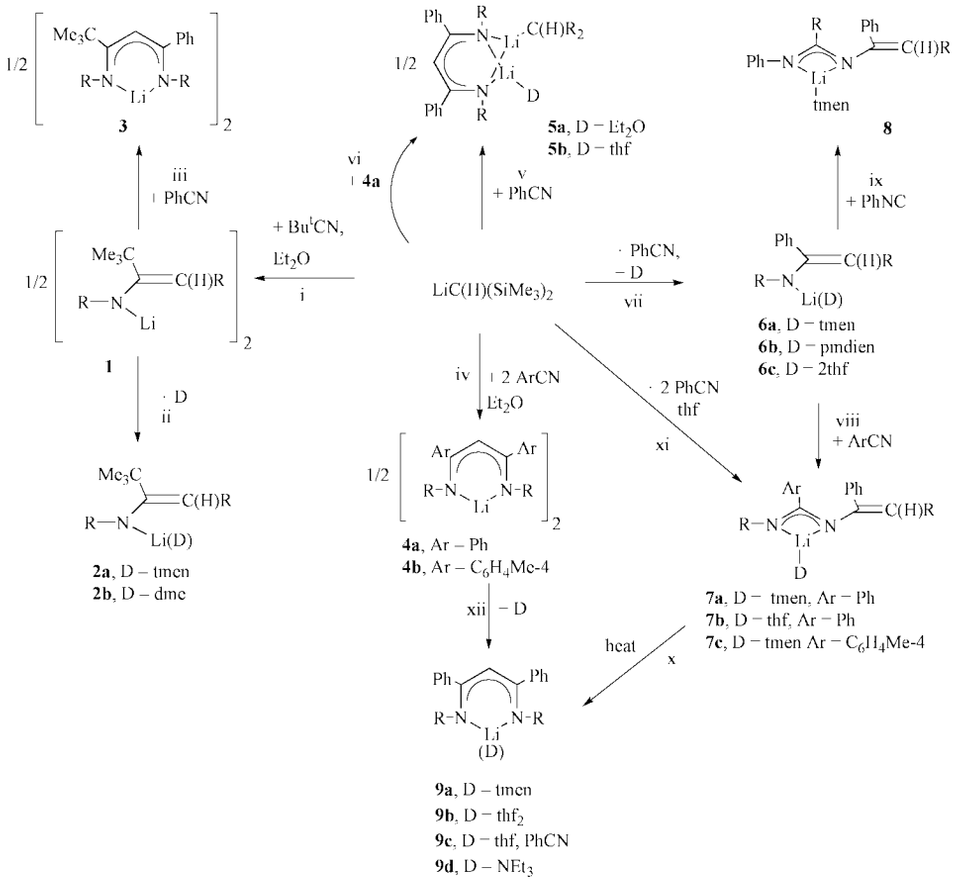
possibilities, functioning in a terminal or bridging fashion. The 1-azaallyl may bind to the metal in a chelating (η^3-1-azaallyl) or open chain (η^1-1-azaallyl or enamido) mode.

We have used these lithium compounds as ligand transfer agents, generating 1-azaallyls, β-diketiminates or 1,3-diazaallyls of various metals [*e.g.* there are papers on derivatives of K,[5,6] Cu^I,[7] Sn^{II},[6] Hg^{II},[6] and Au^I [7*b*]; this aspect,[8] as well as the reaction pathways to Li(**A**), Li(**B**) and Li(**C**),[9] have been reviewed. Some of the zirconium(IV) complexes, when treated with methylaluminoxane ($(MeAlO)_n$, MAO), were effective catalysts for olefin polymerisation.[9] Related chemistry has been based on the reactions of $[Li\{C(R)(R^1)(C_5H_4N\text{-}2)\}]_2$ or $[Li\{C(R)(R^1)(C_9H_6N\text{-}2)\}]_2$ with R^2CN;[10] some of the derived zirconium(IV) or hafnium(IV) complexes $[M\{N(R)C(R^2)C(R^1)(C_5H_4N\text{-}2$ or $C_9H_6N\text{-}2)\}_{4-m}Cl_m]$ were effective catalysts with MAO for the polymerisation of ethylene [R^1 = H or R (= $SiMe_3$), $R^2 = Bu^t$ or Ph and $m = 1$ or 2].[11] Further similar reactions were those between $Li_2[\eta^5\text{-}C_5H_4Si(Me)_2C(H)R]$ and 2 Bu^tCN in the absence or presence of tmen.[12]

The aim of this paper is to provide (i) full details of the material briefly described in the above mentioned communications,[1–4] (ii) extensions to related trimethylsilyl(methyl)-lithium–R′CN systems, and (iii) details of the crystal structures of eleven representative lithium 1-azaallyls, β-diketiminates and 1,3-diazaallyls.

Compounds related to the lithium 1-azaallyls and β-diketiminates here reported, but prepared by different routes include the following: $[Li\{\eta^3\text{-}CH_2{=}C(Bu^t)NPh\}(OEt_2)]_2$,[13] $[Li\{2,6\text{-}[C(H)R]_2C_5H_3N\}Li]$,[14] $[Li\{2\text{-}(CR_2)C_5H_4N\}(OEt_2)_n]_2$ ($n = 0$ or 1),[15] $[Li\{2\text{-}(CR_2)(C_5H_4N)\}(tmen)]$,[15] $[Li\{2\text{-}(CR_2)(C_5H_4N)\text{-}\{NC_5H_4[C(H)R_2]\text{-}2\}\}]$,[15] $[Li\{2\text{-}[C(H)R]C_5H_4N\}]$,[15] $[Li\{NC_5H_4){=}C(Ph)R\text{-}2\}(tmen)]$,[16] $[Li\{2\text{-}(CR_2)(C_5H_3NMe\text{-}6)\}(tmen)]$,[17] $[Li\{(C(H)R)(C_5H_3NCHR_2\text{-}6)\}(tmen)]$,[17] $[Li\{N(H){=}C(Bu^t)C(H)Pr^n\}(hmpa)]$,[18] $[Li\{(2\text{-}NC_5H_4)_2CH_2\}(thf)_2]$,[19] $[Li\{(2\text{-}NC_5H_4)_2CH_2\}]_2$,[19] and $[Li\{N(H)C(H)C(H)C(H)NH\}\{\mu\text{-}OP(NMe_2)_3\}]_2$.[20] The 1,3-diazaallyls presented in this paper belong

DOI: 10.1039/b002376k



Scheme 1

to the amidinates, a review of which, dealing with compounds such as the benzamidinate $[Li\{N(R)C(Ph)NR\}]_2$ is available.[21]

Results and discussion

The various reactions of $LiCHR_2$ (R = $SiMe_3$) with Bu^{t}CN and PhCN are summarised in Scheme 1. Treatment of $LiCHR_2$ with an equivalent portion of Bu^{t}CN in Et_2O or a hydrocarbon led (i in Scheme 1) in high yield to the 1:1 adduct, the lithium 1-azaallyl **1**. Use of two equivalents of Bu^{t}CN proceeded no further; affording the same product **1** after removal of solvents and heating the residue at 75 °C/10^{-2} mmHg for 14 h. It is possible that a presumably unstable Lewis base adduct **1**·*n*(NCBu^t) (*n* = 1 or 2), similar to **2a** and **2b**, had formed but dissociated at work-up. The tmen (**2a**) and dme (**2b**) adducts were, in contrast, much more stable and obtained (ii in Scheme 1) in high yield from **1** after addition of one equivalent of tmen or dme to **1** and subsequent recrystallisation from pentane. Treating **1** with the less bulky nitrile PhCN led (iii in Scheme 1) in a clean reaction to the lithium β-diketiminate **3**.

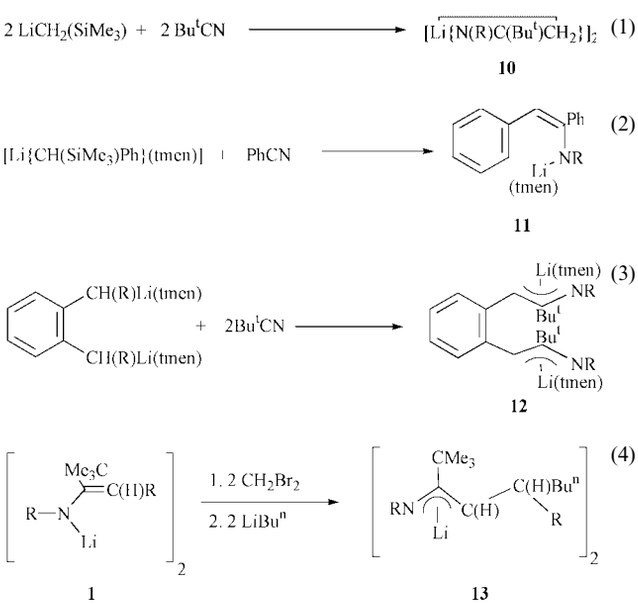
The reaction of $LiCHR_2$ with PhCN is much more complex than that with Bu^{t}CN. It was initially shown that treatment of these reagents at room temperature in Et_2O, independent of the ratio of $LiCHR_2$ to PhCN, gave (iv in Scheme 1) the lithium β-diketiminate **4**. Using a 1:1 ratio of reagents, there was no evidence for the formation of a lithium 1-azaallyl (an analogue of **1**) as an intermediate. Further investigation of this reaction showed that when it was performed in the presence of an excess of $LiCHR_2$ (1.5 fold to PhCN) at −78 °C in Et_2O, and the mixture worked up immediately after warming up to room temperature, the complex **5a**, a co-crystal of $LiCHR_2$ and the lithium β-diketiminate **4a** were obtained (v in Scheme 1) in moderate yield (45%), while the ^{1}H NMR spectrum of the mother liquor showed signals corresponding to a mixture of $LiCHR_2$ (as its Et_2O adduct) and $Li\{N(R)C(Ph)C(H)R\}$. Although we have not been able to separate this mixture into its individual components, **5a** was independently and conveniently produced (vi in Scheme 1) in satisfactory yield by dissolving $LiCHR_2$ and **4a** in the presence of a slightly larger than stoichiometric amount of Et_2O; its thf analogue **5b** was prepared from **5a** by replacing the co-ordinated Et_2O with thf.

Although our attempts to isolate the solvent-free lithium 1-azaallyl $Li\{N(R)C(Ph)C(H)R\}$, by variation of reaction conditions or stoichiometry of the reactants, have not been successful, it was discovered that the reaction of $LiCHR_2$ and PhCN in the presence of a stoichiometric amount of a neutral (chelating) electron donor such as tmen or pmdien led (vii in Scheme 1) in high yield to the donor-co-ordinated lithium 1-azaallyl complexes **6a** and **6b**. Use of the weaker electron-donor thf gave the corresponding thf complex **6c** in a much lower yield (32%), with the lithium β-diketiminate **4a** as a co-product. When the same reaction was carried out in the presence of a large excess of thf (thf as solvent) and at higher temperature **6c** was isolated in high yield (78%). Interestingly the reaction of **6a** with a second equivalent of PhCN gave not, as anticipated, the β-diketiminate **9a** (a donor adduct of **4a**) but instead (viii in Scheme 1) the lithium 1,3-diazaallyl **7a**, which is a regioisomer of **9a**. Treatment of **6a** with 4-MeC_6H_4CN or PhNC gave the 1,3-diazaallyls **7c** or **8**, while reaction of $LiCHR_2$ with 2 equivalents of PhCN in thf gave **7b** (viii, ix and xi, respectively in Scheme 1).

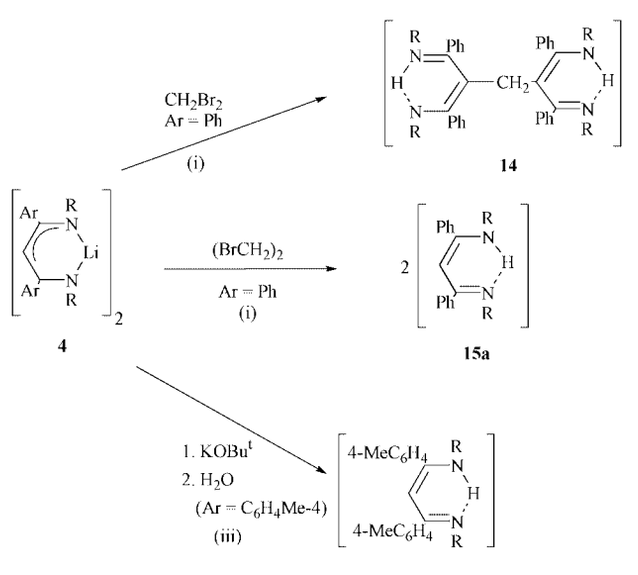
Investigation of the thermal stability of the 1,3-diazaallyl by heating a solution of compound **7b** in toluene-d_8 in a sealed NMR tube showed that it was converted (x in Scheme 1) within 5 min at 100 °C into the isomeric diketiminate **9b**, thus indicating that **9b** is the thermodynamically more stable isomer. A wider range of β-diketiminates **9** was easily prepared (xii in Scheme 1) on a preparative scale from **4a** by adding the appropriate neutral donor to the solvent-free compound **4**, followed by recrystallisation from a hydrocarbon solvent.

The colourless (**1**, **2**) or pale yellow (**6**) lithium 1-azaallyls were highly air-sensitive, extremely hydrocarbon-soluble compounds. The lithium 1,3-diazaallyls **7** and **8** and the lithium β-diketiminates **3**, **4**, **5** and **9** were, in contrast, yellow (**3**, **4**, **7**, **8**, **9a**, **9c**, **9d**), yellow-green (**9b**) or orange-red (**5**), but also soluble in hydrocarbons (except the solvent-free compounds **4** which were only moderately soluble) and slightly less air-sensitive than the 1-azaallyls.

The closely related lithium starting materials $LiCH_2R$, $[Li(tmen)]_2[\{1,2\text{-}CH(R)\}_2C_6H_4]$ and Li{CH(R)Ph}(tmen) behaved very similarly to $LiCHR_2$ with regard to their reactions with nitriles, as illustrated in eqns. (1)–(3) for the synthesis of the lithium-1-azaallyls **10**–**12**. The outcome of reaction (4) leading to the 1-azaallyllithium complex **13** was unexpected. The purpose of adding CH_2Br_2 to compound **1** was to generate a methylene-bridged bis(1-azaallyl) precursor. Since a crystalline complex was not obtained, n-butyllithium was added, yielding **13** in modest yield.



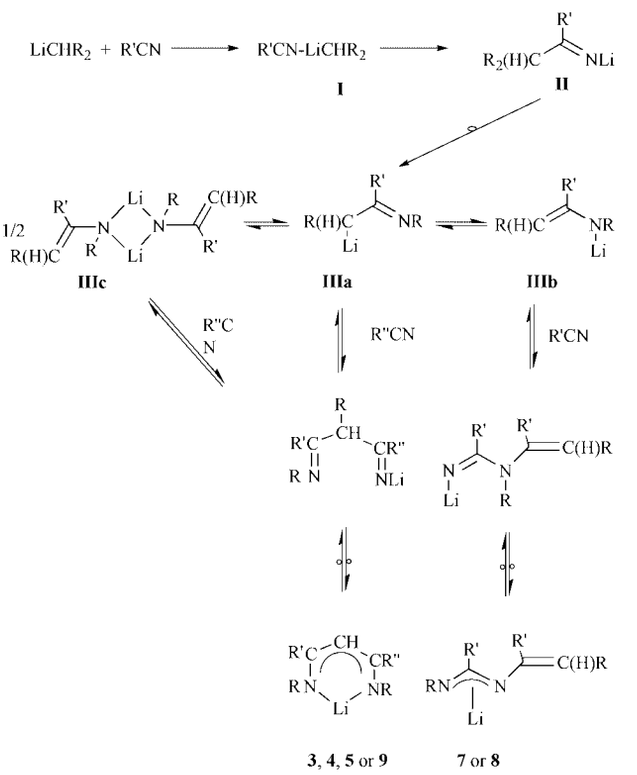
The β-diketiminatolithium compounds **4a** (Ar = Ph) and **4b** (Ar = C_6H_4Me-4) generally behaved as *N*-centred (ii or iii in Scheme 2, or reactions with metal halides [1,8,9,13]) nucleophiles, but exceptionally (i in Scheme 2) functioned as *C*-centred reagents.



Scheme 2 Some reactions of the β-diketiminatolithium compounds **4a** (Ar = Ph) and **4b** (Ar = C_6H_4Me-4) (R = $SiMe_3$).

Previously we suggested pathways to the lithium 1-azaallyl Li(**A**), β-diketiminate Li(**B**) and 1,3-diazaallyl Li(**C**) from $LiCHR_2$ and R′CN.[8] Thus, the formation of Li(**A**) was attributed to initial nucleophilic attack of the $^-CHR_2$ carbanion at the nitrile carbon atom followed by a 1,3-Me_3Si shift from carbon to nitrogen. Li(**A**) was proposed to be an intermediate along the reaction path to Li(**B**) or Li(**C**), depending on whether Li(**A**) behaved as a *C*- or *N*-centred nucleophile, respectively; a final 1,3-Me_3Si migration from C to N for Li(**B**) or N to N for Li(**C**) completed the reaction sequence.

The major features of these proposals seem to us still to be persuasive. However, some new experimental observations have come to light which need to be accommodated. These relate to (i) the role of a neutral coligand D, (ii) different ligand-to-metal bonding modes of Li(**A**) and Li(**A**)D (see **2** or **6** in Scheme 1) and (iii) the isomerism of Li(**B**) and Li(**C**). As for (i), we draw attention to the contrast between steps iv {Ar = Ph yielding $[Li(\mathbf{B})]_2$ **4**} and vii [giving Li(**A**)D **6**] of Scheme 1. Regarding (iii), it is now evident (step x of Scheme 1) that the β-diketiminates (*e.g.* **9a**) are the thermodynamically preferred isomers of the 1,3-diazaallyls (*e.g.* **7a**). We now propose the modified reaction pathways summarised in Scheme 3. This shows the initial formation of the donor–acceptor complex **I**, leading to the 1,2-insertion product the imidolithium compound **II**, which rearranges to the 1-azaallyllithium compound **III**.



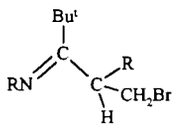
Scheme 3 Proposed reaction pathways from $LiCHR_2$ + R′CN to Li(**A**) (**III**; **1**, **2** or **6**), Li(**B**) (**3**, **4**, **5** or **9**) and Li(**C**) (**7** or **8**).

The formation of $[\overline{Li\{N(R)C(Bu^t)C}(H)C(H)RBu^n\}]_2$ **13**, from $[Li\{N(R)C(Bu^t)C(H)R\}]_2$ **1**, according to eqn. (4), requires further comment. It is likely that compound **1** behaves as a *C*-centred nucleophile generating **D**, which with $LiBu^n$ may first yield the dyotropic isomer **E** of **13**. The use of the various lithium 1-azaallyls, β-diketiminates and 1,3-diazaallyls as ligand transfer reagents with metal halides will be reported in later papers (see also refs. 5–7). The role of the lithium 1-azallyl **1** in phosphorus chemistry, yielding diazaphosphetidines such as **F** or cyclic phosphonium salts such as **G**, has been described.[22]

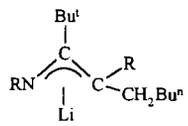
The 1-azallyl ligands are ambidentate nucleophiles; hence lithium derivatives are likely to exist in solution as a tautomeric mixture of a monomeric lithium iminoalkyl **IIIa**, a monomeric

Table 1 The effect of temperature and time on the products from the reaction between $LiCHR_2$ and 2 PhCN in thf

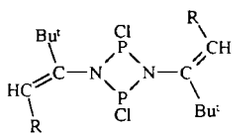
T/°C	*t*/min	Ratio of compound **9b** to **7b**
−78	120	78:22
0	60	53:47
65	5	5:95



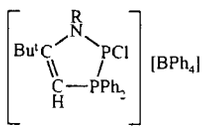
D



E



F



G

lithium enamide **IIIb** and, in most cases in the absence of a neutral donor, a dimeric species **IIIc**. These three species are expected to be in equilibrium with one another. Dimeric species **IIIc** have been established for crystalline complexes **1** and **6c** by single crystal X-ray diffraction studies. The lithium 1-azaallyl [Li{N(R)C(Ph)=CR_2}(thf)], related to **6c**,[4] was shown to be monomeric in the crystal and a low temperature ^{1}H NMR spectroscopic study provided no evidence for more than one species in solution. We suggest that **IIIa** is predominant in pentane or Et_2O solution at room temperature, since under these reaction conditions an excess of nitrile led to the formation of a β-diketiminate (**3**, **4**, **5**, or **9**). Use of a chelating donor such as tmen or pmdien, or refluxing in thf as solvent, is likely to increase the abundance of **IIIb**; the presence of a powerful neutral donor increases the ionicity of the lithium 1-azaallyl and therefore favours structure **IIIb**, in which the more electronegative nitrogen atom is the anionic centre. As a consequence, a lithium 1,3-diazaallyl (**7**) is favoured in strongly polar solvents (thf > Et_2O) over an isomeric β-diketiminate (**4** or **9**). As mentioned above (item iii) the lithium 1,3-diazaallyl **7a** was convertible into the thermodynamically more stable β-diketiminate **9a**. This process was very fast in toluene (conversion within 5 min at 100 °C) but much slower in thf (not fully completed after 1 week at 65 °C) and involves, we believe, an equilibrium between **7**, **IIIb**, **IIIa** and **4**. A cross-over experiment, in which a mixture of **7a** and **7c** was heated in toluene, was inconclusive; slow decomposition of the sample occurred and a mixture of unidentified products was obtained and not, as expected, a mixture of lithium β-diketiminates.

In a series of additional experiments $LiCHR_2$ was treated with PhCN (2 equivalents) in thf, varying both reaction time and temperature (Table 1). After a selected reaction time the solvent was removed and the residue analysed by NMR spectroscopy and shown to be a mixture of the lithium 1,3-diazaallyl **7b** and β-diketiminate **9b**. These results appear to contradict the earlier discussed notion of **9b** being thermodynamically more stable than **7b**, because the proportion of **7b** to **9b** increased with increasing temperature. A possible explanation is that there is a higher proportion of the dimeric species **IIIc** at lower temperatures, and that due to steric shielding of the nitrogen atoms **IIIc** behaves more as a *C*- than a *N*-centred nucleophile and therefore facilitates the formation of the lithium β-diketiminate **9b**. At higher temperature, on the other hand, the abundance of the monomer **IIIb** is increased, which behaving as a *N*-centred nucleophile affords **7b**. Refluxing for a longer period, or heating to a higher temperature, shifts the equilibrium back to **9b**.

Table 2 Characteristic NMR spectroscopic data for lithium 1-azaallyls, 1,3-diazaallyls and β-diketiminates

Compound	δ(^{7}Li)	δ(CH,[a] ^{1}H)	δ(*C*(H,R),[a] ^{13}C)	δ(*C*N, ^{13}C)
1	—	4.47	95.6	185.5
2a	0.34	4.02	83.4	185.6
2b	−0.62	4.06	83.6	184.8
6a	0.88	3.67	83.1	175.9
6b	0.79	3.53	84.1	176.3
6c	0.76	4.37	93.9	174.7
10	—	3.80/4.48	—	—
11	—	5.53	—	—
12	—	5.36	—	—
7a	1.89	4.45	108.2	164.2/175.0
7b	1.62	4.67	113.6	164.0/176.2
7c	1.90	4.43	107.9	164.3/175.3
8	1.54	4.79	96.7	154.1/165.7
3	—	5.85	—	—
4a	2.80	5.49	105.2	175.5
4b		5.69	106.9	176.5
5a	2.29	5.51	105.4	177.2
5b	2.34	5.09	105.4	176.8
9a	—	5.57	105.4	174.9
9b	2.65	5.34	105.3	175.7
9c	—	5.37	105.2	175.2
9d	—	5.60	105.6	175.8

[a] Olefinic proton or carbon.

NMR Spectroscopy

The NMR spectroscopic data on compounds **1**–**12** are summarised in Table 2. Use of ^{7}Li NMR spectroscopy provided a powerful tool for distinguishing between lithium 1-azaallyls (δ −0.6 to 0.9), lithium 1,3-diazaallyls (δ 1.6–1.9) and lithium β-diketiminates (δ 2.3–2.8) as the principal products of the reaction of $LiCHR_2$ with nitriles. Further help in the identification of the products came from ^{1}H NMR spectra, which showed characteristic, with the exception of compounds **11** and **12** (these have a very different backbone compared to the other compounds), resonances for the protons of the CH groups in the region of δ 3.5–4.5 (1-azaallyl), 4.4–4.7 (1,3-diazaallyl) and 5.1–5.9 (β-diketiminate). Additional support for the identification of a compound was provided by the ^{13}C NMR spectra; the lithium 1-azaallyls showed shift values at δ 85–96 (CH) and 175–186 (CN), as compared to values close to δ 105 (CH) and δ 175 (CN) in lithium 1,3-diazaallyls or β-diketiminates. A distinction between the latter two isomeric compounds was easily accomplished on the basis of the lower molecular symmetry of the former, which gave rise to two distinct CN signals (and also two for the Me_3Si groups), as compared with one signal for the β-diketiminates.

In order to establish the structures of the above twentythree crystalline lithium complexes more securely, single crystal X-ray diffraction studies were undertaken on eleven representative samples: **1**, **3**, **4a**, **5b**, **6c**, **7b**, **8**, **9a**, **9b**, **11** and **13**. The molecular structures of **1**,[2] **4a**[1] and **5b**[3] were described in preliminary communications. We now present such data on the remaining eight complexes, discuss trends and comment on bonding modes. Such problems have previously been discussed in the context of complexes of 1-azaallyls[7,23] or 1,3-diazaallyls[6] with other metals (Au^{I},[7b] Sn^{II},[6,23] Cu^{I},[7] K[6] and Hg^{II} [6]).

Crystal structures of representative lithium complexes

1,3-Diazaallyls [Li{N(R)C(Ph)NC(Ph)=CHR}(thf)]$_2$ 7b and [Li{N(Ph)C(R)NC(Ph)=CHR}(tmen)] 8. The molecular structures of compounds **7b** and **8** are illustrated in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 3. *N*,*N*′-Bis(trimethylsilyl)benzamidines HN(R)C(Ar)NR and their metal complexes containing the conjugate base [N(R)C(Ar)NR]$^-$ as ligand have been reviewed (R = $SiMe_3$, Ar = aryl group).[21] The 1,3-diazaallyllithium complexes **7b** and **8** belong

Table 3 Some important geometric data (bond lengths in Å, angles in °) for compounds **7b** and **8**

	7b	**8**
Li–N(1)	1.99(1)	2.025(9)
Li–N(2)	—	2.003(9)
Li–N(2′	1.99(1)	—
Li–D	1.89(1)	2.06(1)
		2.10(1)
C(1)–N(1)	1.302(7)	1.355(6)
C(1)–N(2)	1.364(7)	1.379(6)
N(1)–C(1)–N(2)	119.0(5)	113.2(4)
Co-ordination number at Li	3	4
Aggregation	Dimer	Monomer

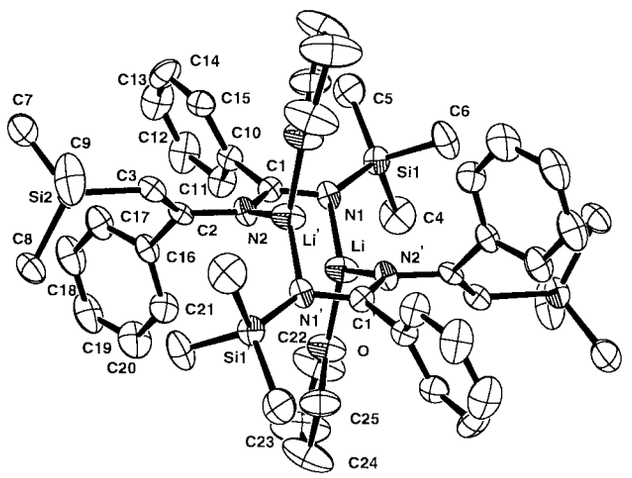


Fig. 1 Molecular structure of compound **7b**.

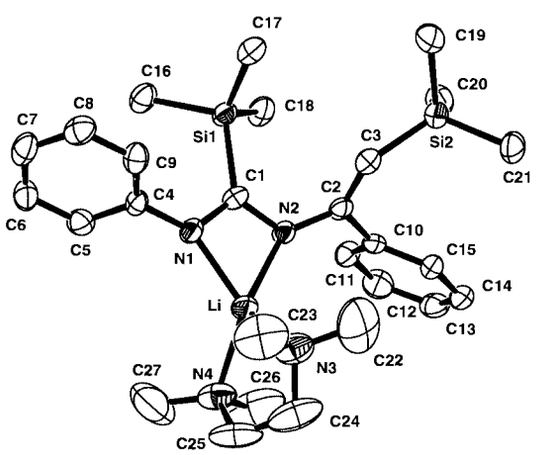


Fig. 2 Molecular structure of compound **8**.

to the latter class. They differ in that **7b** is dinuclear, while **8** is mononuclear. Although in both the 1,3-diazaallyl ligand is bidentate and the LiNCN core is planar (**8**) or almost planar (**7b**), in **8** it is chelating whereas in **7b** it is bridging. The molecular structure of **7b** may be compared with those of five other dinuclear amidinates [Li{N(R)C(C_6H_4Me-4)NR}(thf)$_2$] **H**,[24] [Li{N(R)C(Ph)NR}(NCC_6H_4Me-4)]$_2$ **I**,[25] [Li{N(Ph)C(Ph)N(Ph)}{OP(NMe_2)$_3$}]$_2$ **J**,[26] [Li{N(C_6H_4Me-4)C(H)NC_6H_4Me-4}(OEt)$_2$]$_2$ **K**[27] and [Li{N(Ph)C(Me)NPh}{μ-OP(NMe_2)$_3$}]$_2$ **L**[26] which like **7b** have an additional neutral ligand at each lithium atom; that of **8** is related to those of the mononuclear lithium amidinates [Li{N(Ph)C(Ph)NPh}(tmen)] **M**[27] and [Li{N(Ph)C(Ph)NPh}(pmdien)] **N**.[26] In each of **H**–**N** each NCNLi core is planar.

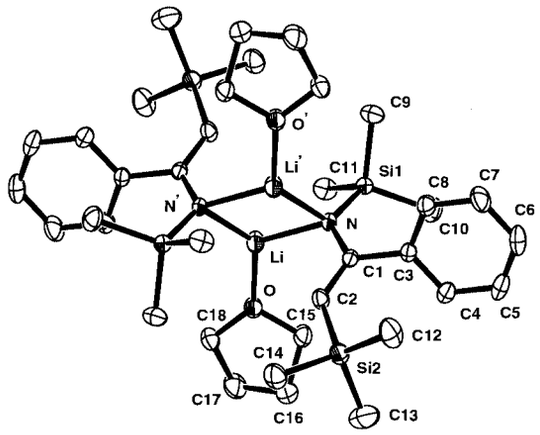


Fig. 3 Molecular structure of compound **6c**.

Complex **7b** is a centrosymmetric dimer. Each anionic ligand is bound to the two lithium atoms in a bridging manner. Although this is also the case for **H**–**K** (in **L** it is simply a chelate), **7b** is unique in having no close Li···N contact to a third nitrogen atom: Li–N(1) 1.989(11), Li–N(2) 1.985(11) and Li···N′ 3.26(1) Å. In contrast, the third shortest Li···N contact in **H**–**K** is 2.145(8), 2.260(9), 2.137(7) and 2.231(9) Å, respectively. The mean of the two shorter Li–N contacts in **7b** is 1.99(1) Å compared with 2.05(1), 2.06(1), 2.05(1) and 2.06(1) Å in **H**–**K**, respectively. The core in **7b** is an eight-membered $(LiNCN)_2$ ring in chair conformation. Each of the lithium, nitrogen, oxygen and endocyclic carbon atoms is in a distorted trigonal planar environment, the distortion being minimal at carbon. The widest angle at each lithium atom is that subtended by the two neighbouring nitrogen atoms, while the C–N–Li and C–O–C angles are the narrowest at the nitrogen or oxygen atoms, respectively.

In the mononuclear crystalline complex **8** the geometric parameters of the chelating LiNCN core are very similar to those found in **M**[27] or **N**.[26] Thus, the mean Li–N [2.014(9) Å] and C–N [1.367(6) Å] bond lengths are close to the 2.02(1) (**M**) or 2.13(11) Å (**N**) and 1.33(1) Å (**M** and **N**); *cf.*[28] also the mean Li–N distance of 2.04 Å in the LiNC(sp^2)N unit of [Li{NC_5H_3(NR)Me-2,6}(tmen)]. The angles subtended at Li, N (mean) and C are 67.5(3), 89.5(5) and 132.2(9)° for **8**, 67.6(2), 88.7(2) and 115.1(2)° for **M**,[27] and 64.4(2), 89.4(2) and 116.7(3)° for **N**.[26]

A comparison between the NCN fragments of the LiNCN unit of compounds **7b** and **8** shows there to be (i) a significant contraction from the C_{sp^2} value of the angle subtended at the carbon atom only for the mononuclear complex **8** [113.2(4)°], attributable to the chelate effect, and (ii) a more pronounced similarity in the two C–N distances for **8** (they are identical for **M**[27] and **N**[26]) than **7b**: $\Delta r = 0.029(6)$ Å for **8** and 0.062(7) Å for **7b**. In respect of (ii), **7b** also differs from the other binuclear complexes **H**–**L**. We conclude that **7b** is unique in containing the shortest [1.302(7) Å] and to a less marked extent the longest [1.364(7) Å] C–N bonds among this family of nine lithium 1,3 diazaallyls and hence the least degree of NCN π-electron delocalisation. These data may be compared with the single and double NC bonds lengths in the bis(hydrogen-bonded) dimer $[HN(Ph)C(Ph)NPh]_2$ of 1.369(8) and 1.310(8) Å, respectively.[29]

1-Azaallyls [Li{N(R)C(Bu^t)CHR}]$_2$ 1, [Li{N(R)C(Ph)CHR}(thf)]$_2$ 6c, [Li{N(R)C(Ph)C(H)Ph}(tmen)] 11 and [Li{N(R)C(Bu^t)CH(Bu^n)}]$_2$ 13. The molecular structure of complex **1**[2] is shown schematically while those of **6c**, **11** and **13** are illustrated in Figs. 3–5, respectively. Selected bond distances and angles are listed in Table 4.

The crystal structures of three lithium 1-azaallyls [Li{N(Ph)C(Bu^t)CH_2}(OEt$_2$)]$_2$ **O**,[13] [Li{N(Ph)(C(=CH[CH_2]$_3$$CH_2$)}(NHPr$_2^i$)]$_2$ **P**[30] and [Li{N(R)C(Bu^t)CH_2}]$_3$ **Q**[31] have previously

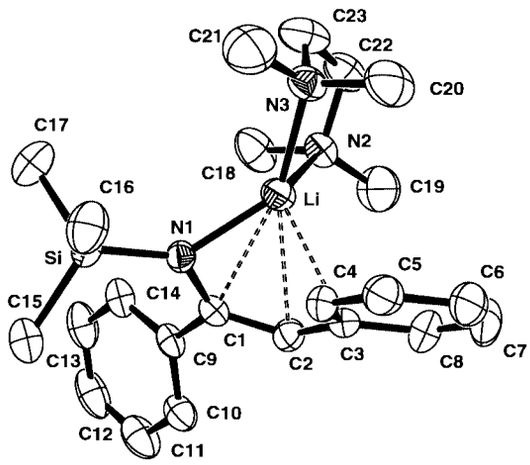
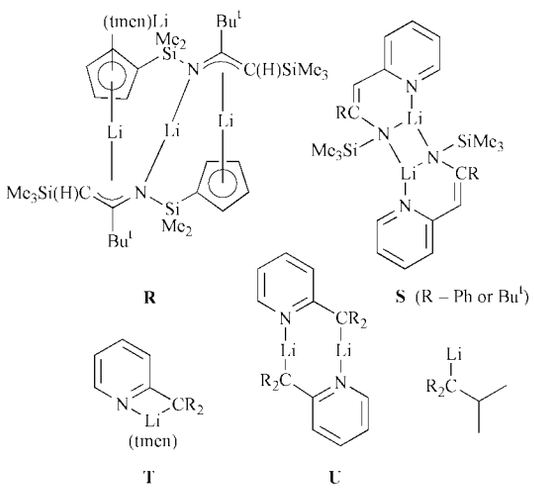
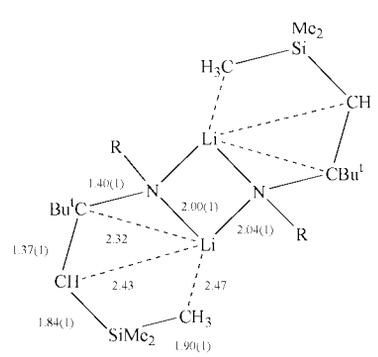


Fig. 4 Molecular structure of compound **11**.





1

been published and brief reference has been made to two others: the tetranuclear complex **R**[12] obtained from [Li{η-$C_5H_4Si(Me)_2C(H)R$}(tmen)]$_2$ and 2 Bu^{t}CN, and **S**.[10] Closely related compounds are the 2-pyridylmethyls,[14,17,32] pioneered by Raston and exemplified by **T** and **U**.[32a] They differ from the 1-azaallyls in that, unlike in the latter, the pyridyl nitrogen atom cannot bear a negative charge unless the ring loses its aromaticity, which almost invariably is not the case. Thus, the relationship of the 1-azaallyls to the 2-pyridylmethyls is analogous to that of allyls to benzyls.

The molecular structures of the dinuclear compounds **1**, **6c** and **13** resemble one another and also those of **O**[13] and **P**,[30] in that each is a centrosymmetric dimer containing as core a nearly planar LiNLiN ring, with the angles subtended at the nitrogen atoms narrower [73.0(4) (**1**), 74.1(1) (**6c**) and 72.7(4)° (**13**)] than those at the Li atoms [107.5(5) (**1**), 106.0(1) (**6c**) and 107.3(4)° (**13**)]. The Li–N distances are closely similar {2.00(1) and 2.04(1) Å (**1**), 2.051(3) and 2.063(3) Å (**6c**), 1.983(9) and 2.035(9) Å (**13**), 2.00(1) and 2.08(1) (**O**)[13] and 2.01(2) and 2.08(2) Å (**P**)[30]}. Whereas **1** and **13** are free of neutral coligands, each of the remainder has a single such molecule at each lithium atom. Complexes **1** and **13** have Li–C_α and Li–C_β distances which are within bonding range [2.43(1) and 2.32(1) (**1**), 2.36(1) and 2.27(1) Å (**13**)]; consequently **1** and **13** are formulated as η^3-1-azaallyllithium compounds. By contrast, complexes **6c**, **O**[13] and **P**,[30] which contain a neutral coligand at each lithium atom, have appreciably longer Li–C_α and Li–C_β contacts [3.01(1) and 2.62(1) (**6c**) and 2.99(2) and 2.57(1) Å (**O**)]; hence these are assigned as lithium enamides, *i.e.* η^1-1-azaallyllithium complexes.

Table 4 Some important geometric data (bond lengths in Å) for compounds **1**, **6c**, **11** and **13**

	1	**6c**	**11**	**13**
Li–N	2.02(1) av.	2.051(3)	1.983(4)	2.035(9)
Li–N′	1.99(1) av.	2.063(3)	—	1.983(9)
Li–C(1)	2.43(2)	2.622(3)	2.416(5)	2.27(1)
Li–C(2)	2.32(1)	3.011(3)	2.510(5)	2.36(1)
N–C(1)	1.397(7)	1.380(2)	1.361(3)	1.392(6)
C(1)–C(2)	1.368(7)	1.367(2)	1.381(3)	1.361(7)
Co-ordination number at Li	2–3	3	4–6	3–4
Aggregation	Dimer	Dimer	Monomer	Dimer

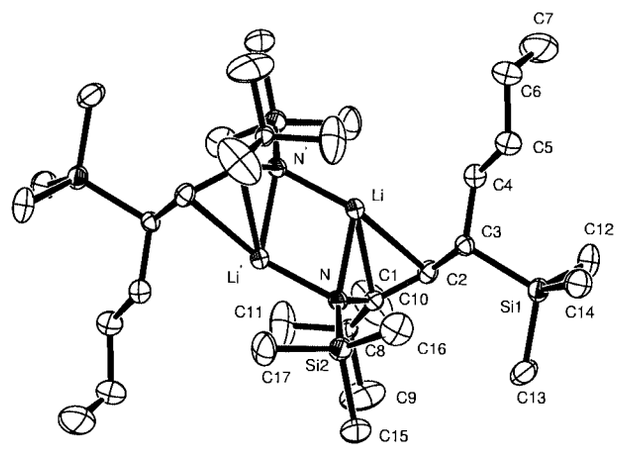


Fig. 5 Molecular structure of compound **13**.

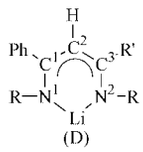
The molecular structures of the two mononuclear lithium compounds differ in that **11** is an enamide, whereas **S** is an η^3-1-azallyl, as evident from the Li–C_α and Li–C_β distances: 2.81(4) and 2.77(4) (**11**) and 2.23(2) and 2.32(2) Å (**S**)[4] Å. In both complexes the Li–N distances are rather short: 1.97(4) (**11**) and 1.93(2) (**S**) Å. For **11** this is particularly noteworthy since its lithium atom is more co-ordinatively saturated than that in **S**, having not only a bidentate coligand (tmen; *cf.* thf in **S**) but also short Li-C contacts to the *ipso*-[2.77(4) Å] and *ortho*-[2.56(4) Å] carbon atoms of the phenyl substituent of C_α.

The C–C and N–C bond distances of the 1-azaallyl ligands in these complexes (see Table 4) do not appear to be diagnostic as to the nature of their bonding mode.

β-Diketiminates [Li{N(R)C(Ph)C(H)C(Bu^t)NR}]$_2$ 3, [Li{N(R)C(Ph)C(H)C(Ph)NR}]$_2$ 4a, [Li{N(R)C(Ph)C(H)C(Ph)NR}(LiCHR$_2$)(thf)] 5b, [Li{N(R)C(Ph)C(H)C(Ph)NR}(tmen)] 9a and [Li{N(R)C(Ph)C(H)C(Ph)NR}(thf)$_2$] 9b. The molecular structures of complexes **4a**[1] and **5b**[3] are shown schematically while those of **3**, **9a**, and **9b** are illustrated in Figs. 6–8. Important bond distances and angles are summarised in Table 5.

The crystal structure of a lithium β-diketiminate [Li{N-(Ph)$(CH)_3$NPh}(μ-OP$(NMe_2)_3$}]$_2$ **V** has been published.[20] The

Table 5 Some important geometric data (bond lengths in Å, angles in °) on compounds **3**, **4a**, **5b**, **9a** and **9c** (R = $SiMe_3$)



3 R = $SiMe_3$, R' = Bu^t, no donor
4a R = $SiMe_3$, R' = Ph, no donor
5b R = $SiMe_3$, R' = Ph, D = $LiCHR_2(thf)$
9a R = $SiMe_3$, R' = Ph, D = tmen
9b R = $SiMe_3$ R' = Ph, D = $(thf)_2$

	3	**4a**	**5b**	**9a**	**9b** (av.)
Li–N(1)	1.97(2)	1.965(9)	2.01(2)	2.016(7)	2.02(2)
Li–N(2)	2.04(2)	1.952(10)	—	2.024(6)	2.02(2)
Li–N(1)′	2.17(2)	2.095(9)	2.01(2)	—	—
N(1)–C(1)	1.27(1)	1.337(6)	1.32(1)	1.326(4)	1.32(1)
N(2)–C(3)	1.33(1)	1.299(6)	1.32(1)	1.320(4)	1.32(1)
C(1)–C(2)	1.46(1)	1.394(7)	1.41(1)	1.408(4)	1.41(1)
C(2)–C(3)	1.41(5)	1.439(6)	1.41(1)	1.402(4)	1.41(1)
N(1)–Li–N(2)	100.0(7)	103.0(4)	94.4	97.3(3)	102.3(7)
Co-ordination number at Li	3	3	3	4	4
Aggregation	Dimer	Dimer	Monomer	Monomer	Monomer

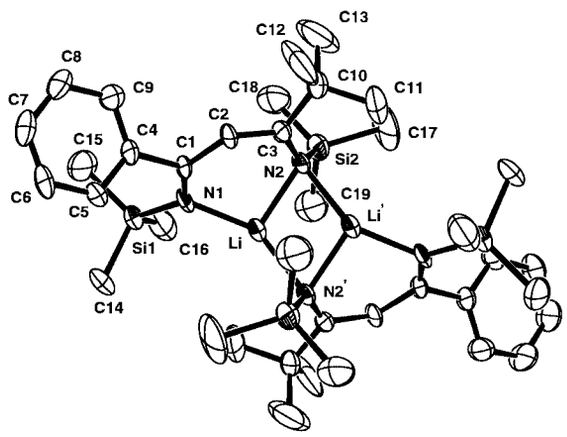
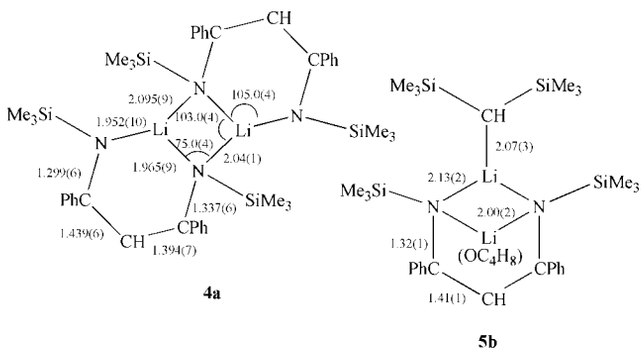


Fig. 6 Molecular structure of compound **3**.



bis(2-pyridyl)methyllithium compounds [Li{(2-$NC_5H_4)_2CH$}-$(thf)_2$] **W**, [Li{(2-$NC_5H_4)_2CH$}{(2-$NC_5H_4)_2CH_2$}] **X** and [Li{(2-$NC_5H_4)_2CH$}$_2$] **Y**[19] are closely related to lithium 1-azaallyls, while the complexes obtained from PhCN or Bu^tCN and an appropriate 2-pyridylmethyllithium precursor[10] are similarly related to lithium β-diketiminates.

The dinuclear complexes **3** and **4a**[1] differ only in the substituents (Ph, Bu^t in **3**, but Ph, Ph in **4a**) at the *C*(N) atoms. Each molecule is a centrosymmetric dimer built around a planar LiNLiN core, the angle at the lithium atom being wider [103.8(7) (**3**) and 105.0(4)° (**4a**)] than that at nitrogen [76.2(6) (**3**) and 75.0(4)° (**4a**)]. One of the nitrogen atoms is four-co-ordinate and bridging, the other is three-co-ordinate. The intramolecular Li–N_{sp^3} bond is slightly shorter [2.004(2) (**3**) and 1.965(9) Å (**4a**)] than the intermolecular Li–N_{sp^3} [2.17(2) (**3**) and 2.095(9) Å (**4a**)]. The β-diketiminato ligand has a marginally

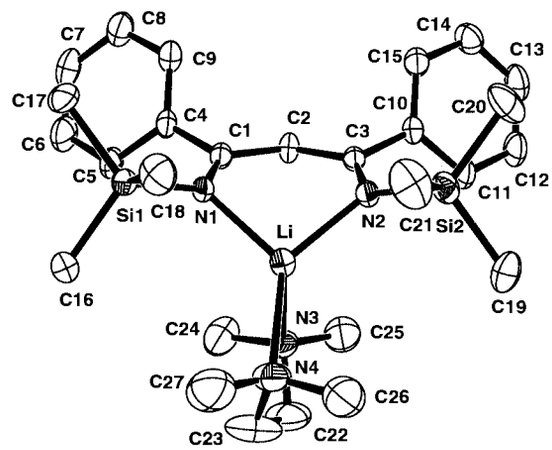


Fig. 7 Molecular structure of compound **9a**.

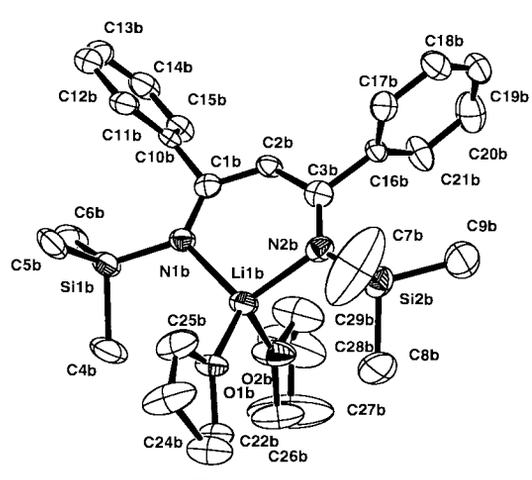


Fig. 8 Molecular structure of compound **9b**.

shorter Li–N_{sp^2} bond [1.973(15) Å (**3**) and 1.952(10) Å (**4a**)]. Within the LiNCCCN ring, the NCCC fragment is planar and there is some degree of π-electron delocalisation, although the pairs of N–C [1.271(11) and 1.333(11) Å (**3**) and 1.299(6) and 1.337(6) Å (**4a**)] and C–C bonds [1.460(11) and 1.415(11) Å (**3**) and 1.439(6) and 1.394(7) Å (**4a**)] are far from being identical. The lithium β-diketiminate **V**[20] differs from **3** and **4a** in that, although dinuclear, it has bridging hmpa ligands and thus it is

best considered with the mononuclear complexes. Complex **5b**[3] is distinct from **3**, **4a** and **V** in that it contains a single β-diketiminato ligand. Its skeleton is nearly planar and π-electron-delocalised. The two three-co-ordinate lithium atoms are on opposite sides of this plane; the Li–N distances are very similar.

The mononuclear complexes **9a** and **9b**, like **V**,[20] have a π-electron-delocalised and almost planar β-diketiminate skeleton, as evident by the essentially equivalent pairs of N–C [1.32(1) Å] and C–C [1.40(1) Å (**9a**), 1.39(1) and 1.42(1) Å (**9b**) and 1.39(1) Å (**V**)] bonds. The four-co-ordinate lithium atom in each molecule is about 0.7 Å out of this plane and the Li–N_{sp^2} distances are similar [2.02(1) Å in **9a** and **9b** and 2.04(2) Å in **V**].

Experimental

General procedures

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in C_6D_6, $C_6D_5CD_3$ or $CDCl_3$ at 298 K using the following Bruker instruments DPX 300 (^{1}H, 300.1; ^{13}C, 75.5; ^{7}Li, 116.6 MHz) and AMX 500 (^{1}H, 500.1; ^{13}C, 125.7; ^{7}Li, 194.3 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^{1}H and ^{13}C spectra. The ^{7}Li were referenced externally to LiCl. Unless otherwise stated all NMR spectra other than ^{1}H were proton-decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were recorded in sealed capillaries and are uncorrected. Elemental analyses (empirical formulae shown) were determined by Medac Ltd., Brunel University. In the experimental section, the abbreviation L for mass spectra denotes the ligand **A**, **B** or **C**.

Preparations

[Li{N(R)C(Bu^t)C(H)R}]$_2$ 1. *Method (i).* Bu^{t}CN (0.40 cm^3, 3.61 mmol) was added dropwise to a cooled (−20 °C) and stirred solution of $LiCHR_2$ (0.60 g, 3.61 mmol) in diethyl ether (*ca.* 15 cm^3). The resultant solution was warmed to room temperature and stirred overnight. The solvent was removed *in vacuo*. The residue was dried at room temperature (10^{-2} Torr) for 1 h and extracted with pentane (*ca.* 20 cm^3). The resultant extract was filtered. Concentrating the filtrate by slow evaporation of the solvent produced white crystals of compound **1** (0.98 g, 99%).

Method (ii). Bu^{t}CN (0.98 cm^3, 8.87 mmol) was added dropwise to a cooled (−20 °C) and stirred solution of $LiCHR_2$ (0.74 g, 4.46 mmol) in diethyl ether (*ca.* 25 cm^3). The mixture was warmed to room temperature and stirred for 14 h. The solvent was removed *in vacuo*; the residual solid was dried at 75 °C/10^{-2} Torr for 3 h and dissolved in hexane (*ca.* 15 cm^3), filtering to remove an insoluble impurity. The filtrate was concentrated and set aside for a few days at room temperature to give white crystals of compound **1** (0.98 g, 89%), mp (decomp.) 145–148 °C (Found: C, 58.0; H, 11.61; N, 5.74. $C_{12}H_{28}LiNSi_2$ requires C, 55.6; H, 11.91; N, 5.90%); ^{1}H NMR ($C_6D_5CD_3$) δ 0.16, 0.24 (s, $SiMe_3$), 1.11 (s, CMe_3) and 4.47 (s, CH); ^{13}C NMR ($C_6D_5CD_3$) δ 0.8, 4.8 (s, $SiMe_3$), 31.3 (s, C*Me*$_3$), 41.6 (s, *C*Me$_3$), 95.6 (s, CH) and 185.5 (s, CN).

[Li{N(R)C(Bu^t)C(H)R}(tmen)] 2a and [Li{N(R)C(Bu^t)C(H)R}(dme)] 2b. Compounds **2a** and **2b** were obtained from $LiCHR_2$ and Bu^{t}CN as described for **1**, except that reactions were carried out in C_5H_{12} with 1 equivalent of tmen or dme. Compound **1** (0.53 g, 2.12 mmol) and tmen (0.32 cm^3, 2.12 mmol) gave **2a** (0.71 g, 91.6%): ^{1}H NMR (C_6D_6) δ 0.33 (s, $SiMe_3$), 0.47 (s, $SiMe_3$), 1.34 (s, Bu^t), 1.58 (m, NCH_2), 1.85 (s, NMe) and 4.02 (s, CH); ^{7}Li NMR(C_6D_6) δ 0.34; ^{13}C NMR (C_6D_6) δ 1.8 (s, $SiMe_3$), 6.1 (s, $SiMe_3$), 31.2 (s, NMe), 40.6 (s, *C*Me$_3$), 46.1 (s, C*Me*$_3$), 56.4 (s, NCH_2), 83.4 (s, CH) and 185.6 (s, CN). Compound **2b**: mass spectrum *m*/*z* (%) 243 (20, $[HL]^+$), 228 (43, $[HL - Me]^+$) and 186 (79, $[HL - Bu^t]^+$); ^{1}H NMR (C_6D_6) δ 0.32 (s, $SiMe_3$), 0.47 (s, $SiMe_3$), 1.34 (s, Bu^t), 2.60 (m, OCH_2), 2.96 (s, OMe) and 4.06 (s, CH); ^{7}Li NMR(C_6D_6) δ −0.62; ^{13}C NMR (C_6D_6) δ 1.1 (s, $SiMe_3$), 5.7 (s, $SiMe_3$), 31.0 (s, C*Me*$_3$), 40.6 (s, *C*Me$_3$), 59.4 (s, OMe), 69.6 (s, OCH_2), 83.6 (s, CH) and 184.8 (s, CN).

[Li{N(R)C(Bu^t)C(H)C(Ph)NR}]$_2$ 3. Benzonitrile (0.4 g, 5.09 mmol) was slowly added to a solution of [Li{N-(R)C(Bu^t)CH(R)}]$_2$ **1** (1.33 g, 2.05 mmol) in Et_2O (30 cm^3) at *ca.* 25 °C. The resulting yellow solution was stirred for *ca.* 12 h. Volatiles were removed during 1 h at 90 °C/10^{-2} Torr. Crystallisation from hexane afforded yellow crystals of complex **3** (1.40 g, 81%) (Found: C, 63.4, H, 9.50; N, 7.68. $C_{19}H_{33}LiSi_2$ requires C, 64.7; H, 9.43; N, 7.94%). ^{1}H NMR (360 MHz, C_6D_6) δ 0.03 and 0.04 ($SiMe_3$, s, 9 H), 1.25 (Bu^t, d, 9 H), 5.85 (CH, s, 1 H), 7.07–7.13 (phenyl, m, 3 H) and 7.37 (phenyl, d, 2 H).

[Li{N(R)C(Ph)C(H)C(Ph)NR}]$_2$ 4a. PhCN (2.30 cm^3, 22.53 mmol) was added slowly by syringe to a cooled (0 °C) and stirred solution of $LiCHR_2$ (1.85 g, 11.15 mmol) in diethyl ether (50 cm^3). There was an immediate change from colourless to yellow. The resultant mixture was slowly warmed to room temperature and stirred for 2 h; the diethyl ether was removed *in vacuo*, and the resultant yellow-white solid heated to boiling, then cooled and filtered. The yellow precipitate was dried *in vacuo* and identified as compound **4a** (3.16 g, 76%), mp 167.5–171 °C (Found: C, 66.1; H, 8.32; N, 7.85. $C_{21}H_{29}LiN_2Si_2$ requires C, 67.7; H, 7.85; N, 7.52%); ^{1}H NMR (C_6D_6–C_4D_8O) δ −0.07, (s, $SiMe_3$), 5.49 (s, CH), 7.07–7.13 (m, Ph, 6 H) and 7.50–7.53 (m, Ph, 4 H); ^{13}C NMR (C_6D_6) δ 3.0 (s, $SiMe_3$), 105.2 (s, CH), 127.4, 127.8, 127.9 (s, *o*, *m*, *p*-C of Ph), 149.8 (s, *ipso*-C) and 175.5 (CN).

[Li{N(R)C(C_6H_4Me-4)C(H)C(C_6H_4Me-4)NR}]$_2$ 4b. Compound **4b** (1.09 g, 52%) (Found: C, 68.1; H, 8.66; N, 6.99. $C_{23}H_{35}LiN_2Si_2$ requires C, 69.0; H, 8.24; N, 7.00%) was prepared similarly, mp 188–191 °C. ^{1}H NMR ($C_6D_5CD_3$) δ 0.0 (s, $SiMe_3$), 2.07 (s, Me), 5.69 (s, CH), 6.93, 7.41 (d, Ph, 4 H). ^{13}C NMR ($C_6D_5CD_3$) δ 3.0 (s, $SiMe_3$), 21.2 (s, Me) 106.9 (s, CH), 128.2, 128.6 (s, *m*, *p*-C of Ph), 137.7, 140.0 (s, *ipso*-C) and 176.5 (CN).

Reaction of $LiCHR_2$ with PhCN. A solution of PhCN (0.30 g, 2.88 mmol) in Et_2O (10 cm^3) was added slowly to a solution of $LiCHR_2$ (0.72 g, 4.33 mmol) in Et_2O (30 cm^3) at −80 °C. The resulting yellow solution was allowed to warm to room temperature and stirred for 90 min. The solvent was removed *in vacuo*, the residue "stripped" with pentane (this procedure refers to adding the solvent and then removing it *in vacuo*) and then dissolved in pentane (45 cm^3). Filtration from a yellow precipitate (0.2 g) and cooling the filtrate gave yellow crystals of [Li{N(R)C(Ph)C(H)C(Ph)NR}]$_2$ **4a** (0.24 g, 44.7% based on PhCN). Concentration of the mother liquor yielded orange red crystals of compound **5a** (0.20 g, 23%), while further concentration gave colourless crystals which, according to ^{1}H NMR spectroscopic data, correspond to a mixture of $LiCHR_2$ and Li{N(R)C(Ph)C(H)R}.

[Li{N(R)C(Ph)C(H)C(Ph)NR}($LiCHR_2$)(OEt_2)] 5a. Pentane (10 cm^3) and Et_2O (0.1 cm^3) were added to a mixture of solid [Li{N(R)C(Ph)C(H)C(Ph)NR}]$_2$ **4a** (0.50 g, 0.67 mmol) and $LiCHR_2$ (0.22 g, 1.34 mmol). The resulting orange-red solution was concentrated. Cooling to −25 °C gave red crystals of compound **5a** (0.47 g, 57%). From the mother liquor another 0.19 g (21.9%) was obtained, mp (decomp.) 129 °C (Found: C, 62.9; H, 9.48; N, 4.72. $C_{29}H_{65}Li_2N_3OSi_4$ requires C, 62.7; H, 9.54; N,

4.57%); ^{1}H NMR (C_6D_6) δ −1.94 (s, $CHSi_2$), 0.05 (s, $NSiMe_3$), 0.36 (s, $SiMe_3$), 0.92 [t, CH_3 (Et_2O), $^3J(^1H–^1H)$ 7.1], 3.20 [q, CH_2 (Et_2O), $^3J(^1H–^1H)$ 7.1 Hz], 5.51 (s, CH), 7.03–7.14 (Ph, 6 H) and 7.44 (d, Ph, 4 H); ^{7}Li NMR (C_6D_6) δ 2.3; ^{13}C NMR (C_6D_6) δ 1.8 (s, $CHSi_2$), 3.0 (s, $NSiMe_3$), 5.7 (s, $SiMe_3$), 14.3 [s, CH_3 (Et_2O)], 65.9 [s, CH_2 (Et_2O)], 105.4 (s, CH), 127.4, 128.0, 128.8 (s, Ph), 148.0 (s, *ipso*-C) and 177.2 (s, CN).

[Li{N(R)C(Ph)C(H)C(Ph)NR}(LiCHR$_2$)(thf)] 5b. Compound **5a** (0.3 g, 0.49 mmol) was dissolved in a mixture of pentane (8 cm^3) and thf (0.1 cm^3). Volatiles were completely removed *in vacuo*; the residue was treated with pentane (20 cm^3). Filtration and concentration of the red filtrate gave upon cooling red crystals of compound **5b** (0.1 g, 33%); ^{1}H NMR (C_6D_6) δ −1.90 (s, $CHSi_2$), 0.05 (s, $NSiMe_3$), 0.396 (s, $SiMe_3$), 1.19 (m, thf), 3.40 (m, thf), 5.09 (s, CH), 7.09–7.12 (Ph, 6 H) and 7.48 (d, Ph, 4 H); ^{7}Li NMR (C_6D_6) δ 2.3; ^{13}C NMR (C_6D_6) δ 1.4 (s, $CHSi_2$), 2.8 (s, $NSiMe_3$), 5.9 (s, $SiMe_3$), 25.1 [s, CH_2 (thf)], 68.6 [s, OCH_2 (thf)], 105.4 (s, CH), 127.5–128.3 (s, Ph), 148.3 (s, *ipso*-C) and 176.8 (s, CN).

[Li{N(R)C(Ph)=C(H)R}(tmen)] 6a, [Li{N(R)C(Ph)=C(H)R}(pmdien)] 6b and [Li{N(R)C(Ph)=C(H)R}(thf)]$_2$ 6c. The procedure for the preparation of each of compounds **6a**–**6c** was very similar and is therefore reported in detail only for **6b**. A solution of PhCN (0.31 cm^3, 3.07 mmol) and pmdien (0.64 cm^3, 3.07 cm^3) in Et_2O (10 cm^3) was added dropwise to a solution of $LiCHR_2$ (0.51 g, 3.07 mmol) in Et_2O (20 cm^3). The mixture was allowed to warm to room temperature and stirred for 15 h. All volatiles were removed *in vacuo* and the residue was recrystallised from Et_2O to give colourless crystals of **6b** (1.23 g, 90%), mp (decomp.) 132 °C (Found: C, 61.6; H, 10.74; N, 12.47. $C_{23}H_{47}LiN_4Si_2$ requires C, 62.4; H, 10.74; N, 12.65%); mass spectrum *m*/*z* (%) 538 (75, $[LiL_2]^+$), 523 (20, $[LiL_2 - Me]^+$), 465 (10 $[LiL_2 - SiMe_3]^+$), 276 (100, $[Li_2L]^+$), 269 (56, $[LiL]^+$), 262 (65, $[L]^+$); ^{1}H NMR (C_6D_6) δ 0.08 (s, $SiMe_3$), 0.16 (s, $SiMe_3$), 1.74 (s, broad, NMe), 1.92 (s, NCH_2), 2.14 (s, NMe_2), 3.53 (s, CH), 7.15 (d, *p*-H of Ph), 7.24 [dt, *m*-H of Ph, $J(^1H–^1H)$ 6.8] and 7.57 [*o*-H of Ph, $J(^1H–^1H)$ 6.8 Hz]; ^{7}Li NMR(C_6D_6) δ 0.79; ^{13}C NMR (C_6D_6) δ 3.1 (s, $SiMe_3$), 4.7 (s, $SiMe_3$), 45.6 (s, NMe), 45.9 (s, NMe_2), 53.9 (s, NCH_2), 57.1 (NCH_2), 84.1 (s, CH), 126.0 (s, *p*-C), 127.3, 129.7 (s, *o*/*m*-C), 150.7 (s, *ipso*-C) and 176.3 (s, CN).

Similarly, compound **6a** (1.27 g, 85.6%) was obtained from $LiCHR_2$ (0.64 g, 3.85 mmol), PhCN (0.39 cm^3, 3.85 mmol) and tmen (0.58 cm^3, 3.85 mmol). It was recrystallised from pentane, mp (decomp.) 90 °C (Found: C, 60.9; H, 10.17; N, 11.48. $C_{20}H_{40}LiN_3Si_2$ requires C, 62.3; H, 10.45; N, 10.89%); mass spectrum *m*/*z* (%) 263 (40, $[HL]^+$), 248 (10, $[HL - Me]^+$), 186 (15, $[HL - Ph]^+$) and 176 (50, $[Me_3SiC{=}NPh]^+$); ^{1}H NMR (C_6D_6) δ 0.11 (s, $SiMe_3$), 0.22 (s, $SiMe_3$), 1.55 (s, NCH_2), 1.79 (s, NCH_3), 3.67 (s, CH), 7.09–7.20 (Ph, 3 H) and 7.49 [dd, *o*-H of Ph, $J(^1H–^1H)$ 6.6 Hz]; ^{7}Li NMR(C_6D_6) δ 0.88; ^{13}C NMR (C_6D_6) δ 2.6 (s, $SiMe_3$), 3.5 (s, $SiMe_3$), 45.5 (s, NCH_3), 56.2 (s, NCH_2), 83.1 (s, CH), 126.2–128.7 (s, *o*/*m*/*p*-C), 150.1 (s, *ipso*-C) and 175.9 (s, CN).

Likewise compound **6c** (0.35 g, 31.5%) was obtained from $LiCHR_2$ (0.54 g, 3.25 mmol), PhCN (0.33 cm^3, 3.25 mmol) and thf (0.52 cm^3, 3.25 mmol) and was recrystallised from pentane; the second crop of crystals (0.44 g) consisted of a mixture of Li{N(R)C(Ph)C(H)R} and **9b**. Compound **6c** was also prepared by addition of benzonitrile (2.9 cm^3, 28.42 mmol) to a boiling solution of $LiCHR_2$ (4.95 g, 29.79 mmol) in thf (70 cm^3) under reflux. The deep green mixture was stirred for 2 min and thf was removed *in vacuo*. The pale green residue was extracted into hexane (30 cm^3). Cooling at −30 °C afforded pale yellow crystals of compound **6c** (7.95 g, 78%) (Found: C, 62.2; H, 9.35; N, 3.96. $C_{18}H_{32}LiNOSi_2$ requires C, 63.3; H, 9.44; N, 4.10%); ^{1}H NMR (C_6D_6) δ 0.04 (s, $SiMe_3$, 9 H), 0.10 (s, $NSiMe_3$, 9 H), 1.36 (m, CH_2, 4 H), 3.69 (m, OCH_2, 4 H), 4.37 (s, CH), 7.10–7.17 (Ph, 3 H) and 7.40 [d, $J(^1H–^1H)$ 7.8 Hz, *o*-H of Ph, 2 H]. ^{7}Li NMR(C_6D_6) δ 0.76. ^{13}C NMR (C_6D_6) δ 2.1 [s, $SiMe_3$], 3.9 (s, $NSiMe_3$), 25.4 (s, CH_2), 68.8 (s, OCH_2), 94.0 (s, CH), 127.0 (s, *p*-Ph), 127.6 and 128.9 (s, *o*- and *m*-Ph), 148.4 (s, *ipso*-C) and 174.7 ppm (s, CN).

[Li{N(R)C(Ph)NC(Ph)=C(H)R}(tmen)] 7a. A mixture of PhCN (0.39 cm^3, 3.85 mmol) and tmen (0.58 cm^3, 3.85 mmol) in Et_2O (10 cm^3) was added dropwise to a solution of $LiCHR_2$ (0.64 g, 3.85 mmol) in Et_2O at −60 °C. The clear solution was warmed to room temperature and stirred for 15 h. The solvent was removed *in vacuo*; Et_2O (20 cm^3) and PhCN (0.39 cm^3, 3.85 mmol) were added and the solution stirred for 15 h. Removing the solvent and recrystallisation of the residue yielded pale yellow crystals of compound **7a** (1.42 g, 86%), mp (decomp.) 110 °C (Found: C, 65.3; H, 9.08; N, 11.38. $C_{27}H_{45}LiN_4Si_2$ requires C, 66.3, H, 9.28, N, 11.46%); ^{1}H NMR (C_6D_6) δ −0.10 (s, $SiMe_3$), 0.13 (s, $SiMe_3$), 1.63 (s, NCH_2), 1.85 (s, NCH_3), 4.45 (s, CH), 7.05–7.19 (Ph, 6 H), 7.43 [dd, *o*-H of Ph, $J(^1H–^1H)$ 8.1, 2 H], 7.51 [dd, *o*-H of Ph, $J(^1H–^1H)$ 8.0 Hz]; ^{7}Li NMR(C_6D_6) δ 1.89; ^{13}C NMR (C_6D_6) δ 1.2 (s, $SiMe_3$), 3.6 (s, $SiMe_3$), 45.3 (s, NCH_3), 56.2 (s, NCH_2), 108.2 (s, CH), 126.1–128.4 (s, Ph), 144.0, 147.2 (s, *ipso*-C), 164.2 (s, *C*=CH) and 175.0 (s, CN_2).

[Li{N(R)C(Ph)NC(Ph)=C(H)R}(thf)]$_2$ 7b. Benzonitrile (2 cm^3, 19.60 mmol) was added to a boiling solution of $LiCHR_2$ (1.37 g, 8.24 mmol) in thf (30 cm^3) under reflux. The orange solution was stirred for 5 min and the volatiles were removed *in vacuo*. The residual yellow solid was dissolved in hexane (20 cm^3); cooling at –30 °C afforded pale yellow crystals of compound **7b** (1.14 g, 31%), mp 145 °C (Found: C, 66.8; H, 8.22; N, 6.29. $C_{25}H_{37}LiN_2OSi_2$ requires C, 67.5; H, 8.29; N, 6.30%); mass spectrum *m*/*z* (%) 366 (17, $[½M - Li - thf]^+$), 351 (4, $[½M - Li - thf - Me]^+$), 293 (19, $[½M - Li - thf - SiMe_3]^+$) and 263 (82 $[½M - Li - thf - NSiMe_3 - Me]^+$); ^{1}H NMR ($C_6D_5CD_3$) δ −0.16 (s, $SiMe_3$), 0.01 (s, $NSiMe_3$), 1.14 (m, CH_2, 4 H), 3.60 (m, OCH_2, 4 H), 4.67 (s, CH), 6.92–7.17 (Ph, 8 H) and 7.26 (d, Ph, $J(^1H–^1H)$ 6.9 Hz, 2 H); ^{7}Li NMR ($C_6D_5CD_3$) δ 1.62; ^{13}C NMR ($C_6D_5CD_3$) δ 1.1 (s, $SiMe_3$), 3.2 (s, $NSiMe_3$), 25.8 (s, CH_2), 68.5 (s, OCH_2), 113.6 (s, CH), 119.5, 127.3, 127.7, 127.9, 128.2 and 129.0 (s, aromatic carbons), 143.3 (s, *ipso*-C), 145.3 (s, *ipso*-C), and 164.0, 176.2 (s, CN).

[Li{N(R)C(C$_6$H$_4$Me-4)NC(Ph)=C(H)R}(tmen)] 7c. Toluonitrile (0.31 cm^3, 2.6 mmol) was added at −30 °C to a solution of compound **6a** (1 g, 2.6 mmol) in Et_2O (30 cm^3). The mixture was allowed to warm to room temperature and stirred for 12 h. The solvent was removed *in vacuo,* the residue extracted into pentane and the extract filtered. Concentration of the filtrate and cooling gave yellow crystals of compound **7c** (0.79 g, 60%); ^{1}H NMR (C_6D_6) δ −0.10, 0.15 (s, $SiMe_3$), 1.65 (s, NCH_2), 1.86 (s, NCH_3), 2.14 (s, Me), 4.43 (s, CH), 6.98 [d, Ph, $J(^1H–^1H)$ 7.80, 2 H], 7.14 (m, Ph, 3 H), 7.36 [d, Ph, $J(^1H–^1H)$ 7.80] and 7.52 [d, Ph $^3J(^1H–^1H)$ 6.68 Hz, 2 H]; ^{7}Li NMR(C_6D_6) δ 1.90; ^{13}C NMR (C_6D_6) δ 1.2, 3.7 (s, $SiMe_3$), 21.2 (s, Me), 45.4 (s, NCH_3), 56.3 (s, NCH_2), 107.9 (s, CH), 119.5 (s, *ipso*-C), 126.6, 127.3, 128.1, 129.1, 129.7 (s, *o*-, *m*-, *p*-C), 135.8, 141.2, 147.4 (s, *ipso*-C), 164.3 (s, *C*=CH) and 175.3 (s, CN_2).

[Li{N(Ph)C(R)NC(Ph)=C(H)R}(tmen)] 8. A solution of phenyl isocyanide (0.20 g, 2.0 mmol) in pentane (10 cm^3) was slowly added to a solution of compound **6a** (0.77 g, 2.0 mmol) in pentane (30 cm^3) at −78 °C. After stirring for 3 h at this temperature the reaction mixture was allowed to warm slowly to room temperature and stirred for 8 h. All volatiles were removed *in vacuo* and the residue was recrystallised from pentane or methylcyclohexane to give compound **8** (0.51 g, 52%), mp (decomp.) 98 °C; elemental analysis was unsatisfactory due to incorporation of solvent; mass spectrum *m*/*z* (%) 366 (42,

[HL]$^+$), 351 (8, [HL − Me]$^+$), 293 (70, [HL − $SiMe_3$]$^+$), 191 (15, [(Ph)NC($SiMe_3$)NH]$^+$) and 176 (86, [$Me_3SiC{=}NPh$]$^+$); ^{1}H NMR (C_6D_6) δ 0.24 (s, $SiMe_3$), 0.45 (s, $SiMe_3$), 1.49 (s, NCH_2), 1.68 (s, NCH_3), 4.79 (s, CH), 6.95 [t, *p*-H of Ph, J(^{1}H–^{1}H) 7.2, 1 H], 7.04 [d, *o*-H of Ph, J(^{1}H–^{1}H) 7.2], 7.17–7.29 (Ph, 5 H) and 7.72 [dd, *o*-H of Ph, J(^{1}H–^{1}H) 6.8 Hz, 2 H]; ^{7}Li NMR(C_6D_6) δ 1.54; ^{13}C NMR (C_6D_6) δ 1.9 (s, $SiMe_3$), 4.2 (s, $SiMe_3$), 45.0 (s, NCH_3), 56.2 (s, NCH_2), 96.7 (s, CH), 120.7, 123.2, 127.1, 127.3, 128.9, 129.4 (s, *o*/*m*-C of Ph), 119.4, 146.9 (s, *ipso*-C), 154.1 (s, *C*=CH) and 165.7 (s, CN_2).

[Li{N(R)C(Ph)C(H)C(Ph)N(R)}(tmen)] 9a. Addition of tmen (2 cm^3, 1.3 mmol) to a stirred suspension of compound **4a** (0.35 g, 0.47 mmol) in hexane (30 cm^3) at *ca.* 25 °C immediately gave a clear solution. After stirring for 6 h this was concentrated to *ca*. 3 cm^3. Cooling to −30 °C afforded the yellow crystalline compound **9a** (0.4 g, 87%) (Found: C, 65.8; H, 9.09; N, 10.7. $C_{21}H_{29}LiN_2Si_2$ requires C, 66.3; H, 9.28; N, 11.5%); ^{1}H NMR (C_6D_6) δ − 0.12 (s, $SiMe_3$), 1.90 (s, NCH_2, 4 H), 2.01 (s, NMe, 12 H), 5.57 (s, CH), 7.10–7.33 (m, Ph, 6 H) and 7.62–7.67 (m, Ph, 4 H); ^{29}Si NMR (C_6D_6) δ −6.7, ^{13}C NMR (C_6D_6) δ 3.9 (s, $SiMe_3$), 46.9 (s, NCH_2), 57.8 (s, NMe), 105.4 (s, CH), 127.4–127.8 (s, *o*-, *m*-, *p*-C of Ph), 150.0 (s, *ipso*-C) and 174.9 (s, CN).

[Li{N(R)C(Ph)C(H)C(Ph)NR}(thf)$_2$] 9b. From compound **4a** (1.12 g, 3.01 mmol) in thf (20 cm^3) at room temperature, using procedures similar to those for **9a**, then recrystallisation from hexane, yellow-green crystals of compound **9b** (0.46 g, 30%) were obtained. When separated from the mother liquor these crystals lost thf rapidly. ^{1}H NMR ($C_6D_5CD_3$): δ −0.02 (s, $NSiMe_3$), 1.37 (m, CH_2, 8 H), 3.52 (m, OCH_2, 8 H), 5.34 (s, CH), 7.01–7.07 (Ph, 6 H) and 7.39 (Ph, 4 H). ^{7}Li NMR ($C_6D_5CD_3$) δ 2.65. ^{13}C NMR ($C_6D_5CD_3$) δ 3.2 (s, $NSiMe_3$), 25.7 (s, CH_2), 68.4 (s, OCH_2), 105.3 (s, CH), 127.5 (s, *p*-C of Ph), 128.3 and 129.2 (s, *o*- and *m*-Ph), 149.8 (s, *ipso*-C) and 175.7 (CN).

[Li{N(R)C(Ph)C(H)C(Ph)N(R)}(thf)(NCPh)] 9c. Likewise, from compound **4a** (1.0 g, 1.37 mmol) and PhCN (0.28 g, 2.7 mmol) in thf (50 cm^3) at 25 °C, there was obtained, after recrystallisation from toluene, compound **9c** (1.3 g, 90%). ^{1}H NMR ($C_6D_5CD_3$) δ 0.01 (s, $SiMe_3$), 1.34 (m, CH_2), 3.51 (m, OCH_2), 5.37 (s, CH), 6.60–7.15 (m, Ph, 9 H) and 7.43–7.50 (m, Ph, 6 H). ^{29}Si NMR ($C_6D_5CD_3$) δ −5.7 and 0.5. ^{13}C NMR ($C_6D_5CD_3$) δ 3.1 (s, $SiMe_3$), 25.5 (s, CH_2), 68.2 (s, OMe), 105.2 (s, CH), 127.1–132.6 (s, *o*-, *m*-, *p*-C of Ph and C≡N), 149.8 (s, *ipso*-C), 170.5, 175.2 (s, CN).

Li{N(R)C(Ph)C(H)C(Ph)N(R)}(NEt$_3$) 9d. A mixture of [Li{N(R)C(Ph)C(H)C(Ph)N(R)}]$_2$ **4a** (0.18 g, 0.24 mmol) and $LiCHR_2$ (0.08 g, 0.48 mmol) was dissolved in pentane (8 cm^3) and NEt_3 (0.05 cm^3). After cooling to −25 °C, yellow crystals of **9d** (0.1 g, 43.7%) were obtained. ^{1}H NMR (C_6D_6) δ 0.08 (s, $SiMe_3$), 0.90 [t, CH_3, J(^{1}H–^{1}H) 7.2], 2.52 [q, NCH_2, J(^{1}H–^{1}H) 7.2 Hz], 5.60 (s, CH) and 7.10–7.13 (Ph, 6 H), 7.54 (d, *o*-H of Ph). ^{13}C NMR (C_6D_6): δ 3.3 (s, $SiMe_3$), 10.4 (s, Me), 45.7 (s, NCH_2), 105.6 (s, CH), 127.6–128.7 (s, Ph), 149.1 (s, *ipso*-C) and 175.8 (s, CN).

[Li{N(R)C(Bu^t)CH$_2$}]$_2$ 10. Bu^{t}CN (2.21 cm^3, 20.0 mmol) was added dropwise to a stirred diethyl ether solution of $LiCH_2R$ (1.0 mol dm^{-3}, 20 cm^3) at *ca.* 25 °C. The resulting solution was stirred for 12 h. Volatiles were removed during 1 h at 70 °C/10^{-2} Torr. The residue was washed with pentane to give the white solid **10** (3.45 g, 97%) (Found: C, 58.6; H, 11.37; N, 7.33. $C_9H_{20}Li$ requires C, 61.0; H, 11.37; N, 7.90%); ^{1}H NMR (C_6D_6) δ 0.25 (s, $SiMe_3$), 1.15 (s, CMe_3), 3.80 (s, CH_2, 1 H), 4.48 (s, CH_2, 1 H) and 9.04 (m, Ph, 2 H).

[Li{N(R)C(Ph)=C(H)Ph}(tmen)] 11. PhCN (2.0 cm^3, 20 mmol) was added by syringe to Li{CH(R)Ph}(tmen) (5.7 g, 19.93 mmol) in pentane (*ca.* 30 cm^3) at ambient temperature. The mixture was stirred for 6 h. Filtration gave the yellow solid **11** (7.0 g, 90%) (Found: C, 70.8; H, 9.17; N, 10.26. $C_{23}H_{36}LiN_3Si$ requires C, 70.9; H, 9.31; N, 10.79%); ^{1}H NMR (C_6D_6) δ 0.31 (s, $SiMe_3$), 1.41 (s, NCH_2), 1.68 (s, NMe), 5.53 (s, CH), 6.79 [t, Ph, 1 H], 7.11 (m, Ph, 4 H), 7.23 (d, Ph, 2 H) and 8.12 (m, Ph, 2 H).

[Li(tmen)]$_2$[{1,2-N(R)C(Bu^t)C(H)}$_2$C$_6$H$_4$] 12. Bu^{t}CN (1.39 cm^3, 12.6 mmol) was added dropwise to a stirred solution of [Li(tmen)]$_2$[{1,2-CH(R)}$_2$C$_6$H$_4$] (3.1 g, 6.28 mmol) in Et_2O (*ca.* 40 cm^3) at 25 °C. The resulting orange solution was stirred for 12 h. Volatiles were removed at 90 °C/10^{-2} Torr, and the residue was extracted into hexane (*ca.* 50 cm^3). The filtered extract upon concentrating yielded yellow crystals of complex **12** (3.1 g, 75%); ^{1}H NMR (C_6D_6) δ 0.54 (s, $SiMe_3$), 1.53 (s, CMe_3), 1.69 (s, broad, tmen), 5.36 (s, CH), 6.92 (m, Ph, 2 H) and 9.04 (m, Ph, 2 H).

[Li{N(R)C(Bu^t)C(H)CH(R)Bu^n}]$_2$ 13. Dibromomethane (0.45 cm^3, 6.88 mmol) was added dropwise to a stirred solution of [Li{N(R)C(Bu^t)C(H)(R)}]$_2$ **1** (3.60 g, 6.88 mmol) in hexane (*ca.* 30 cm^3) at 25 °C. The resulting suspension was stirred for 12 h and filtered. n-Butyllithium (1.6 mmol dm^{-3} in hexane, 7 cm^3) was added to the filtrate at 25 °C; the solution was stirred for 4 h. Concentration yielded white crystals of compound **13** (0.60 g, 27%) (Found: C, 63.0; H, 11.78; N, 4.49. $C_{17}H_{38}LiNSi_2$ requires C, 64.1; H, 11.71; N, 4.40%); ^{1}H NMR (C_6D_6) δ 0.15 (s, $SiMe_3$), 0.33 (s, $SiMe_3$), 1.27 (s, CMe_3), 4.97 (d, CH), 0.92, 1.04 and 2.08 (Bu^n).

CH$_2$[C{C(Ph)NR}C(Ph)N(H)R]$_2$ 14. 1,2-Dibromoethane (0.34 g, 1.95 mmol) was added to a solution of [Li{N(R)C(Ph)C(H)C(Ph)NR}]$_2$ **4a** (1.32 g, 1.77 mmol) in hexane (*ca.* 20 cm^3). The mixture was refluxed for 10 h. The white precipitate of lithium bromide was filtered off. Concentrating the filtrate by slow evaporation of the solvent *in vacuo* gave yellow crystals of compound **14** (0.57 g, 43%), which were washed with hexane (*ca.* 5 cm^3) and dried *in vacuo*, mp 193–198 °C (Found: C, 67.9; H, 8.44; N, 7.41. $C_{43}H_{60}N_4Si_4$ requires C, 69.3; H, 8.12; N, 7.52%); ^{1}H NMR ($C_6D_5CD_3$) δ 0.08 (s, $SiMe_3$), 2.65 (s, CH_2), 6.67 (d, Ph, 4 H), 7.01 (m, Ph, 6 H) and 11.80 (s, NH); ^{13}C NMR ($C_6D_5CD_3$) δ 2.0 (s, $SiMe_3$), 33.1 (s, CH_2), 110.5 (s, CH), 127.6, 128.4, 129.3 (s, *o*-, *m*-, *p*-C of Ph), 142.9 (s, *ipso*-C) and 170.1 (s, CN).

HN(R)C(Ph)C(H)C(Ph)NR 15a. $BrCH_2CH_2Br$ (0.01 cm^3, 0.82 mmol) was added by syringe to a solution of K{N(R)-C(Ph)C(H)C(Ph)NR} [prepared from **4a** and KOBu^t (0.41 g, 1.01 mmol) in hexane (*ca*. 20 cm^3)]. The mixture was maintained at 50 °C for 5 h. After filtration, the filtrate was concentrated *in vacuo* to yield yellow needles of compound **15a** (0.36 g, 97%), mp 85–88 °C (Found: C, 68.9; H, 8.25; N, 7.82. $C_{21}H_{20}N_2Si_2$ requires C, 86.8; H, 8.25; N, 7.64%); ^{1}H NMR (C_6D_6) δ 0.04 (s, $SiMe_3$), 5.39 (s, CH), 6.99 (m, Ph, 6 H), 7.21 (m, Ph, 4 H) and 12.38 (s, NH); ^{13}C NMR (C_6D_6) δ 1.9 (s, $SiMe_3$), 102.8 (s, CH), 127.4, 128.9, 132.8 (s, *o*-, *m*-, *p*-C of Ph), 143.7 (s, *ipso*-C) and 170.7 (s, CN).

HN(R)C(C_6H_4Me-4)C(H)C(C_6H_4Me-4)NR 15b. A suspension of [Li{N(R)C(C_6H_4Me-4)C(H)C(C_6H_4Me-4)NR}]$_2$ **4b** (0.33 g, 0.44 mmol) in hexane (*ca.* 10 cm^3) was stirred under aerobic conditions until nearly all the solid had dissolved, changing from red to yellow. Slow evaporation of the solvent afforded yellow crystals of compound **15b** (0.31 g, 96%), mp 120–124 °C (Found: C, 70.1; H, 9.17; N, 7.22. $C_{23}H_{34}N_2Si_2$ requires C, 70.0; H, 8.78; N, 7.10%); ^{1}H NMR ($CDCl_3$) δ 0.06 (s, $SiMe_3$), 2.39 (s, Me), 5.28 (s, CH) 7.16, 7.28 (d, Ph, 2 H) and

Table 6 Crystal data and refinement for compounds **3**, **6c**, **7b**, **8**, **9a**, **9b**, **11** and **13**

	3	**6c**	**7b**	**8**	**9a**	**9b**	**11**	**13**
Formula	$C_{38}H_{66}Li_2N_4Si_4$	$C_{36}H_{64}Li_2N_2O_2Si_4$	$C_{50}H_{74}Li_2N_4O_2Si_4$	$C_{34}H_{59}LiN_4Si_2$	$C_{27}H_{45}LiN_4Si_2$	$C_{29}H_{45}LiN_2O_2Si_2$	$C_{23}H_{36}LiN_3Si$	$C_{34}H_{76}Li_2N_2Si_4$
M	705.2	683.1	889.4	587.0	488.8	516.8	389.6	639.2
T/K	293(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (non-st., no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	11.203(4)	9.781(1)	11.075(12)	13.688(4)	11.068(3)	10.189(5)	10.0529(3)	9.612(5)
b/Å	12.163(3)	10.239(3)	11.440(15)	20.777(8)	14.702(2)	21.686(5)	31.5904(10)	11.651(10)
c/Å	16.462(7)	10.416(2)	11.514(6)	14.787(2)	20.140(6)	22.163(9)	8.2296(2)	19.940(15)
α/°		92.49(2)	94.22(7)			86.25(3)		
β/°	94.04(3)	96.37(1)	93.81(7)	117.53(2)	105.22(2)	80.98(4)	111.457(3)	101.56(5)
γ/°		97.52(2)	110.94(8)			76.52(3)		
U/Å^3	2237.6	1026.0(4)	1352.0(9)	3729(2)	3162.4	4701(3)	2432.4(1)	2187.9
Z	2	1	1	4	4	6	4	2
μ/mm^{-1}	0.16	0.18	0.15	0.12	0.13	0.14	0.11	1.41
Reflections collected	4351	5962	3289	6819	4844	11482	12641	4692
Independent reflections	4145	5962	3289	6535	4594	11482	4263	4487
Reflections with $I > 2\sigma(I)$	1837	4592	2096	3339	2435	7900	2841	1898
$R1$ ($I > 2\sigma(I)$)	0.107	0.044	0.079	0.083	0.046	0.102	0.057	0.070
$wR2$ (all data)	—	0.114	0.234	0.225	—	0.298	0.153	—

12.08 (s, NH); ^{13}C NMR ($CDCl_3$) δ 1.8 (s, $SiMe_3$), 21.3 (s, Me), 102.1 (s, CH), 127.2, 128.6 (s, *m*-, *p*-C of Ph), 138.1, 140.5 (s, *ipso*-C) and 170.5 (s, CN).

Crystal data and refinement details

Data were collected on an Enraf-Nonius CAD4 diffractometer using monochromatic Mo-Kα or Cu-Kα radiation [λ 0.71073 Å or 1.5418 Å (**13**)]. Crystals were either sealed in a Lindemann capillary under argon or else directly mounted on the diffractometer under a stream of cold nitrogen gas. Cell dimensions were calculated from the setting angles for 25 reflections with $7 < \theta < 10°$. Intensities were measured by an ω–2θ scan. Corrections were made for Lorentz and polarisation effects and in the case of compound **13** for absorption correction (DIFABS).[33] The programs used for structure solutions and refinement were SHELXS 86[34] and SHELXL 93[35] (or MOLEN[36]). There was no crystal decay as measured by two standard reflections. Further details are found in Table 6.

CCDC reference number 186/2001.

See http://www.rsc.org/suppdata/dt/b0/b002376k/ for crystallographic files in .cif format.

Acknowledgements

We thank the Sir Run Run Shaw Foundation (studentship for D.-S. L.), SPECS-BIOSPECS (fellowship for D.-S. L.), E.P.S.R.C. (fellowship for M. L.) and the European Commission (Marie Curie fellowship for R. S.) for support.

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