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Synthesis and structures of crystalline dilithium diamides and aminolithium amides derived from *N*,*N*′-disubstituted 1,2-diaminobenzenes or 1,8-diaminonaphthalene

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Received 10th May 2001, Accepted 16th August 2001
First published as an Advance Article on the web 15th October 2001

The crystalline dilithium diamides $[Li_2(\mu\text{-}\mathbf{A})]_2$ **1**, $[Li(\mu\text{-}\mathbf{A})\{\mu\text{-}Li(thf)(\mu\text{-}thf)\}]_2$ **2**, $[Li(thf)_2(\mu\text{-}\mathbf{A})Li(thf)]$ **3**, $[\{Li(tmen)\}_2(\mu\text{-}\mathbf{A})]$ **4**, $[\{Li(\mu\text{-}\mathbf{A}')(thf)_2\}(\mu\text{-}Li)]_2$ **5**, $[\{Li(tmen)\}_2(\mu\text{-}\mathbf{A}'')]$ **6**, $[\{Li(\mu\text{-}\mathbf{B}')(thf)\}(\mu\text{-}Li)]_2$ **7**, $[\{Li(tmen)\}_2\{\mu\text{-}N\overline{Si(Me)_2C_{10}H_6N}\text{-}1,8\}]$ **9** and $[\{Li(tmen)\}_2(\mu\text{-}\mathbf{B})]$ **13** and aminolithium amides $[Li\{(\mu\text{-}\overline{NC_{10}H_6NH}\text{-}1,8)\overline{SiMe_2}\}(OEt_2)]_2$ **8**, $[Li(tmen)_2\{N\overline{Si(Me)_2C_{10}H_6NH}\text{-}1,8\}]$ **12** and $[Li(tmen)\{\mu\text{-}N\overline{Si(Me)_2C_{10}H_6NH}\text{-}1,8\}]$ **15** have been prepared from the appropriate $H_2(\mathbf{A})$, $H_2(\mathbf{A}')$, $H_2(\mathbf{A}'')$, $H_2(\mathbf{B}')$ or $H_2(\mathbf{B})$ [**A** = 1,2-$\{N(SiMe_3)\}_2C_6H_4$, **A**′ = 1,2-$\{N(CH_2Bu^t)\}_2C_6H_4$, **A**″ = 1,2-$\{N(SiMe_2CH{=}CH_2)\}_2C_6H_4$, **B** = 1,8-$\{N(SiMe_3)\}_2C_{10}H_6$ and **B**′ = 1,8-$\{N(CH_2Bu^t)\}_2C_{10}H_6$], $LiBu^n$ and (except for **1**) the chosen neutral coligand (thf, tmen or Et_2O). The X-ray structures of **1**–**8** are presented and further evidence for **9** and **13** is provided by converting them into derivatives: $Me_2\overline{Si\{N(R')C_{10}H_6NR'}\text{-}1,8\}$ (R′ = Me **10** or H **11**) from **9** and $[Zr(\eta^5\text{-}C_5H_5)_2(\mathbf{B})]$ **14** from **13**. The formation, from $H_2(\mathbf{B})$ and $LiBu^n$ under appropriate and mild conditions, of *N*-lithio- or dilithio-derivatives **8**, **12** and **15** of the tricyclic anions $[1,8\text{-}\{\overline{NSi(Me)_2C_{10}H_6NH}\}]^-$ or $[1,8\text{-}\{\overline{NSi(Me)_2C_{10}H_6N}\}]^{2-}$ is especially noteworthy.

Introduction

We have a long standing interest in the chemistry of metal and non-metal amides,[1] for which the corresponding lithium amides are particularly useful precursors. Our most recent contribution in this area relates to lithium complexes containing the ligand $[N(Ph)R]^-$ (R = $SiMe_3$ or CH_2Bu^t), including the X-ray-characterised crystalline complexes $[Li\{N(Ph)SiMe_3\}]_4$,[2] $[(Li\{\mu\text{-}N(Ph)R\text{-}trans\})(\mu\text{-}tmen)]$,[3] and $[Li\{\mu\text{-}N(Ph)CH_2Bu^t\}(OEt_2)]_2$.[3] As an extension, we have been exploring some aspects of the chemistry of complexes containing diamido ligands. Particularly relevant to the present paper are **A**, **A**′, **A**″, **B**, **B**′, **C** and **C**′. These have featured in the following crystalline metal complexes : $[Mg(\mathbf{A})]_2$,[4] $[Ga(\mathbf{A})]_2$,[5] $[\overline{Ga(\mathbf{A})\{C_6H_4CH_2NMe_2}\text{-}2\}]$,[5] $[Ge(\mathbf{A})]$,[6] $[\{Sn(\mathbf{A})\}_2(\mu\text{-}tmen)]$,[7] $[\{ZrCl_2(\mathbf{A})\}(\mu\text{-}tmen)]$,[8] $[\{Zr(NMe_2)(\mathbf{A}$ or $\mathbf{A}'')(\mu\text{-}NMe_2)\}_2]$,[8] $[ZrCl_2(\mathbf{A}'')]$,[8] $[\{M(Cl)(\mathbf{A}'')(\mu\text{-}Cl)(thf)\}_2]$ (M = Ti or Zr),[8] $[MCl_n(\mathbf{A})\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,2\}]$ (n = 1 and M = Zr or Hf; or n = 2 and M = Ta),[9] $[\{Mo(\mathbf{A})(NPh)(\mu\text{-}NPh)\}_2]$,[10] $[MoX_2(\mathbf{A})(NPh)L_n]$ (n = 1 and X = Cl; or n = 0 and X = Me, CH_2Bu^t, CH_2Ph, CH_2SiMe_3 or Ph),[10] $[Mo(\mathbf{A})(NPh)\{C(H)R\}]$ (R = $SiMe_3$ or Bu^t),[10] various tungsten complexes containing the $W(\mathbf{A})(NPh)$ moiety,[11] $[Li(thf)_{1\text{ or }2}\text{-}Tl(\mathbf{B})]$,[12,13] $[Li(thf)Mg(Br)(thf)(\mathbf{B})]$,[14] $[(AlMe_2)_2(\mu\text{-}\mathbf{B})]$,[15] $[In(\mathbf{B})(thf)]_2$,[13] $[TiCl_2(\mathbf{B})]$,[15,16] $[Zr(\mathbf{B})_2]$,[15] $[SiCl_2(\mathbf{C}$ or $\mathbf{C}')]$[17] and $[\{Sn(\mathbf{C}$ or $\mathbf{C}')(\mu\text{-}O)\}_3]$.[17] The ligand **A**′ has had a central role in developing the chemistry of the first X-ray-characterised silylene Si(**A**′);[18a] for the latest paper, see our review.[18b] Most of these metal or silicon complexes were obtained from the appropriate dilithio derivative, generally prepared *in situ*. Crystallographic structural data on such compounds are rare, being restricted to $[\{Li(\mu\text{-}\overline{B(thf)\}Li}]_2$ **D**,[12] $[\{Li(hmpa)\}_2(\mu\text{-}\mathbf{B})]$ **E** (hmpa = hexamethylphosphoramide),[14] $[(\{Li(\mu\text{-}\mathbf{B})(tmen)\}Li)_2(\mu\text{-}tmen)]$ **F**,[14] and $[\{Li(thf)\}_2(\mu\text{-}\mathbf{C}$ or $\mathbf{C}')]$ **G**.[17]

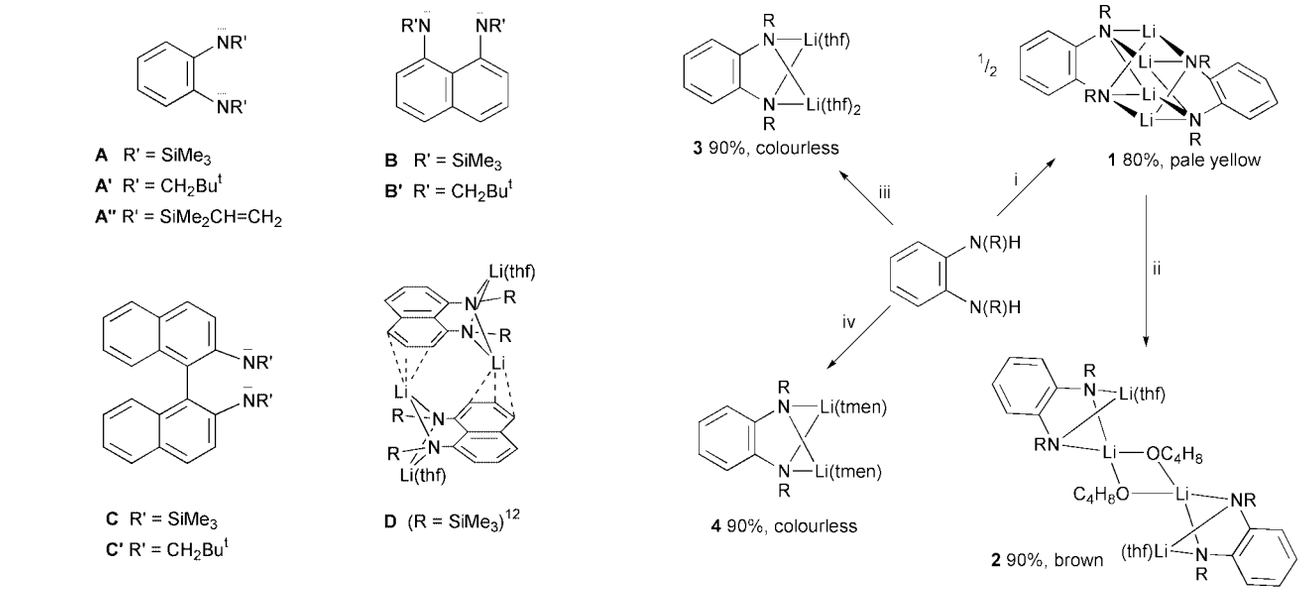
Results and discussion

We present data on (i) the synthesis (**1**–**7**, **9** and **13**) and X-ray structures (**1**–**7**) of the crystalline dilithium compounds $[Li_2(\mu\text{-}\mathbf{A})]_2$ **1**, $[Li(\mu\text{-}\mathbf{A})\{\mu\text{-}Li(thf)(\mu\text{-}thf)\}]_2$ **2**, $[Li(thf)_2(\mu\text{-}\mathbf{A})Li(thf)]$ **3**, $[\{Li(tmen)\}_2(\mu\text{-}\mathbf{A})]$ **4**, $[\{Li(\mu\text{-}\mathbf{A}')(thf)_2\}(\mu\text{-}Li)_2]_2$ **5**, $[\{Li(tmen)\}_2(\mu\text{-}\mathbf{A}'')]$ **6**, $[\{Li(\mu\text{-}\mathbf{B}')(thf)\}(\mu\text{-}Li)]_2$ **7**, $[\{Li(tmen)\}_2\{\mu\text{-}N\overline{Si(Me)_2C_{10}H_6N}\text{-}1,8\}]$ **9** and $[\{Li(tmen)\}_2(\mu\text{-}\mathbf{B})]$ **13**; and (ii) the synthesis (**8**, **12** and **15**) and X-ray structure (**8**) of the crystalline complexes $[Li\{(\mu\text{-}\overline{NC_{10}H_6NH}\text{-}1,8)\overline{SiMe_2}\}(OEt_2)]_2$ **8**, $[Li(tmen)_2\{N\overline{Si(Me)_2C_{10}H_6NH}\text{-}1,8\}]$ **12** and $[Li(tmen)\{\mu\text{-}N\overline{Si(Me)_2C_{10}H_6NH}\text{-}1,8\}]$ **15**. Additionally, (iii) we provide evidence for compounds **9** and **13** by converting them into derivatives: $Me_2\overline{Si\{N(R')C_{10}H_6NR'}\text{-}1,8\}$ (R′ = Me **10** or H **11**) from **9** and $[Zr(\eta^5\text{-}C_5H_5)_2(\mathbf{B})]$ **14** from **13**. Each of the compounds **8**, **12** and **15** contains a tricyclic nucleus derived from **B** by joining the nitrogen atoms by an $SiMe_2$ bridge.

The syntheses in good yield of the four diamidodilithium compounds **1**–**4**, derived from the ligand **A**, are summarised in Scheme 1. The neutral coligand-free tetranuclear complex $[Li_2(\mu\text{-}\mathbf{A})]_2$ **1** was obtained (step i of Scheme 1) from 1,2-bis(trimethylsilylamino)benzene[5] [≡ $H_2(\mathbf{A})$] and n-butyllithium (2 mol) in hexane. Addition of a stoichiometric amount of thf (Li : thf in 1 : 1 ratio) to compound **1** afforded (step ii of Scheme 1) the tetranuclear complex **2**, of molecular formula $Li_4(\mathbf{A})_2(thf)_4$. With an excess of thf, however, the product was the binuclear complex **3**, having molecular formula $Li_2(\mathbf{A})(thf)_3$. The binuclear tmen adduct **4**, of molecular formula $Li_2(\mathbf{A})(tmen)_2$, was obtained (step iv of Scheme 1) by using tmen in place of thf.

The starting materials for the diamidodilithium compounds **5** and **6** were 1,2-bis(neopentylamino)benzene [≡ $H_2(\mathbf{A}')$] and

DOI: 10.1039/b104135p

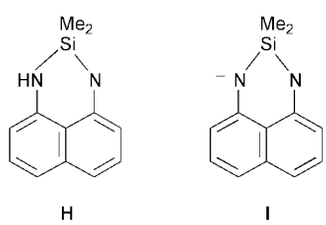


Scheme 1 Synthesis of the crystalline compounds **1**–**4** (R = $SiMe_3$). *Reagents and conditions*: i, $LiBu^n$, C_6H_{14}, *ca.* 20 °C; ii, thf, reflux then cool; iii, $LiBu^n$, C_6H_{14}, thf excess, *ca.* 20 °C, then concentrated and crystallisation (C_5H_{12}); iv, $LiBu^n$, C_6H_{14}, Et_2O, tmen, 0 °C.

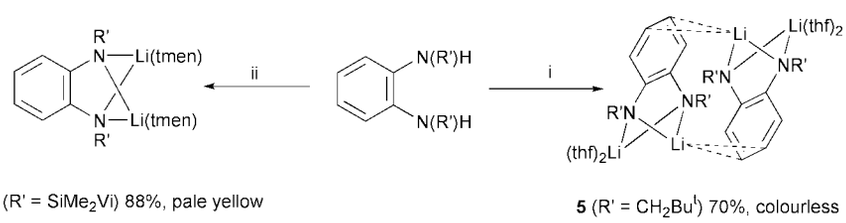
1,2-bis(dimethylvinylsilylamino)benzene [≡ H_2(**A**″)],[8] respectively. Although H_2(**A**′) has been extensively used by us in the context of Group 14 element chemistry,[7,18] details of its synthesis from 1,2-diaminobenzene and successively pivaloyl chloride with triethylamine and Li[AlH_4] are only now described (see Experimental section). The synthesis in good yield of the tetranuclear complex [{Li(μ-**A**′)(thf)$_2$}(μ-Li)]$_2$ **5** and the dinuclear [{Li(tmen)}$_2$(μ-**A**″)] **6** are summarised in Scheme 2. Compound **5** was obtained (step i of Scheme 2) from H_2(**A**′), n-butyllithium (2 mol) in hexane and thf, while **6** was produced (step ii of Scheme 2) from H_2(**A**″), 2 $LiBu^n$ in hexane and 2 tmen.

1,8-Bis(neopentylamino)naphthalene H_2(**B**′) was the precursor to the dilithiodiamide **7**, Scheme 3. The diamine H_2(**B**′), obtained from 1,8-diaminonaphthalene by successive *N*,*N*′-bis(acylation) and Li[AlH_4] reduction (steps i and ii of Scheme 3), was treated with n-butyllithium (2 mol) and an excess of thf to yield (step iii of Scheme 3) the tetranuclear compound [{Li(μ-**B**′)(thf)}(μ-Li)]$_2$ **7**.

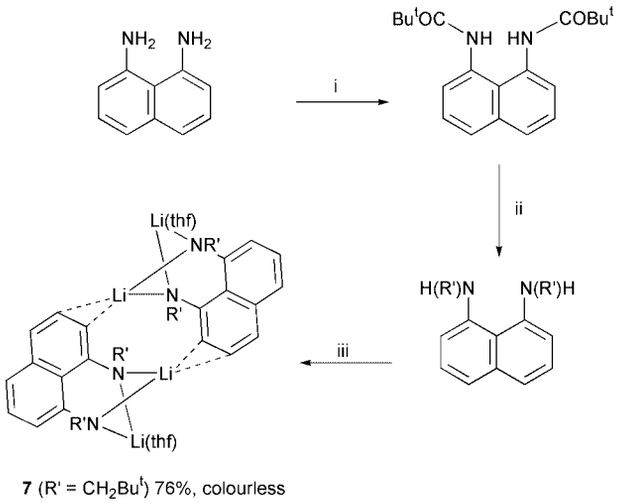
Each of the compounds **8**–**15** was obtained directly or indirectly from 1,8-diaminonaphthalene and thence to the *N*,*N*′-bis(trimethylsilyl) derivative H_2(**B**), Scheme 4.[12–15] The latter was here prepared by heating $(H_2N)_2C_{10}H_6$-1,8 and hexamethyldisilazane (2 equivalents) with a trace of chlorotrimethylsilane. Despite the mild reaction conditions, fragmentation of the moiety **B** was surprisingly facile and led in high yields to the crystalline mono- or di-lithium amides containing either the tricyclic monoanion **H** (**8**, **12** and **15**) or dianion **I** (**9**). On the other hand, such a transformation was not inevitable; the dilithium compound [{Li(tmen)}$_2$(**B**)] **13** was accessible from H_2(**B**) under carefully controlled conditions.



Treatment of H_2(**B**) with an equimolar portion of n-butyllithium in hexane yielded (step i of Scheme 4) the dinuclear lithium monoamide [Li{(μ-$\overline{NC_{10}H_6NH\text{-}1,8}$)$SiMe_2$}-($OEt_2$)]$_2$ **8**. Addition of tmen to **8** gave (step x of Scheme 4) [Li(tmen){μ-$\overline{NSi(Me)_2C_{10}H_6NH\text{-}1,8}$}] **15**. Using H_2(**B**) and 3 equivalents each of $LiBu^n$ and tmen gave (step ii of Scheme 4) [{Li(tmen)}$_2${μ-$\overline{NSi(Me)_2C_{10}H_6N\text{-}1,8}$}] **9**, which with 2 MeI



Scheme 2 Synthesis of the crystalline compounds **5** and **6**. *Reagents and conditions*: i, $LiBu^n$, C_6H_{14} and thf to precipitate in C_6H_6; ii, $LiBu^n$, C_6H_{14}, Et_2O, tmen, 0 °C.

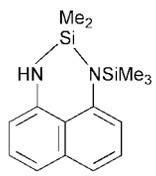


Scheme 3 Synthesis of the crystalline compound **7** (R′ = CH_2Bu^t). *Reagents and conditions*: i, $Bu^tC(O)Cl$, Et_3N, thf, reflux; ii, $Li[AlH_4]$, thf, reflux; iii, $LiBu^n$, C_6H_{14}, reflux, then thf (excess).

or 2 HCl yielded $Me_2Si\{N(Me)C_{10}H_6NMe\text{-}1,8\}$ **10** or $Me_2Si\{N(H)C_{10}H_6NH\text{-}1,8\}$ **11**, respectively. However, H_2(**B**) with 2 $LiBu^n$ and 2 tmen led (v in Scheme 4) to $[Li(tmen)_2\{NSi(Me)_2C_{10}H_6NH\text{-}1,8\}]$ **12**. The tricyclic compound **11** was also obtained (step vii of Scheme 4) from 1,8-diaminonaphthalene, $SiCl_2Me_2$ and 2 NEt_3. From solid H_2(**B**) and 2.7 $LiBu^n$ in hexane at 0 °C and then addition of tmen (step viii of Scheme 4), the product was $[\{Li(tmen)\}_2$(**B**)] **13**, which was derivatised (step ix of Scheme 4) by addition of zirconium(IV) chloride to give $[Zr(\eta^5\text{-}C_5H_5)_2$(**B**)] **14**.

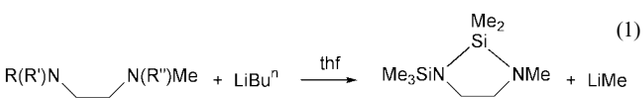
There are a number of features of the reactions in Scheme 4 which are noteworthy: (i) the selective monolithiation of H_2(**B**) to afford the monolithium amides **8** and **12** of the monoanion **H**; (ii) the selective dilithiation of H_2(**B**) under different conditions to give the dilithium diamides of either the dianion **B** (**13**) or **I** (**9**); (iii) the facile ring closure observed leading to the $SiMe_2$-bridged compounds containing the tricyclic nuclei **H** or **I**; and (iv) the reluctance (under similarly mild conditions) to lithiation of compound **11**, using $LiBu^n$(tmen) or $LiBu^n$ in diethyl ether, to afford soluble products.

A possible pathway for the cyclisation leading to derivatives of the 1,3-diaza-2-silaphenanthrenes H(**H**) and H_2(**I**) may have involved initial mono *N*-lithiation of H_2(**B**), followed by LiMe extrusion and concomitant formation of the intermediate **J**.



J

Cleavage of the remaining N–$SiMe_3$ bond of **J** using $LiBu^n$ with tmen is presumed to have yielded successively **12** or **9**, whereas **8** was formed with $LiBu^n$ in Et_2O. Although the proposed cleavage of a Si–N bond by an carbanion is unusual,[19,20] there is a precedent, namely the reaction shown in eqn. (1);[21] moreover, the 1,2,2-trimethyl-3-trimethylsilyl-1,3-

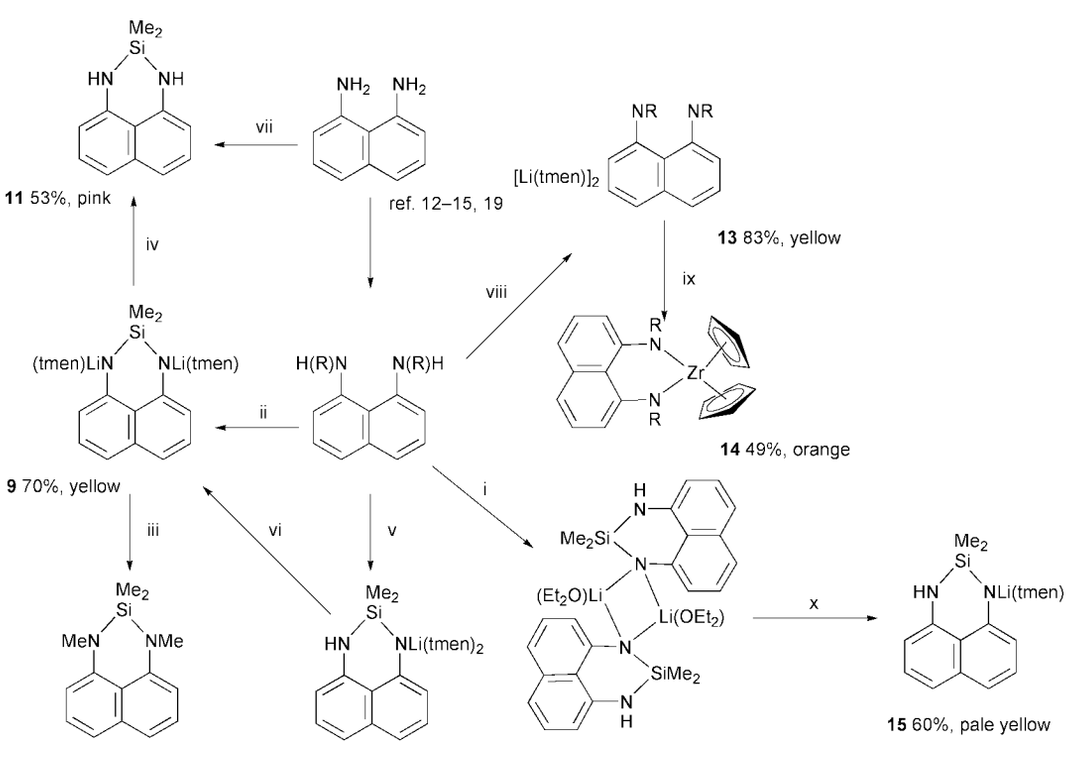


(1)

R′ = $SiMe_3$ = R, R″ = H;
or R′ = H, R″ = $SiMe_3$ = R

diazasilacyclopentane was obtained even if a catalytic quantity of $LiBu^n$ was used, whence the coproduct was methane.

As to item (iv), the inaccessibility of the base-stabilised lithium amides **8**, **12** or **15** or the dilithium diamide **9** from **11** and $LiBu^n$ in presence of tmen or Et_2O is consistent with the notion that for compounds containing both N–H and N–Si bonds (*cf.*



Scheme 4 Synthesis of the crystalline compounds **8**–**15** (R = $SiMe_3$). *Reagents and conditions*: i, $LiBu^n$, C_6H_{14}, *ca.* 20 °C, then precipitate + Et_2O; ii, 3 $LiBu^n$, C_6H_{14}, 0 °C, then 3 tmen; iii, 2 MeI, Et_2O, 0 °C; iv, 2 HCl, Et_2O, 0 °C; v, 2 $LiBu^n$, 2 tmen, C_6H_{14}, 0 °C; vi, 2 $LiBu^n$, C_6H_{14}, 0 °C; vii, $SiCl_2Me_2$, 2 NEt_3, PhMe, reflux; viii, 2.7 $LiBu^n$ in C_6H_{14} added to solid at 0 °C, then 2 tmen; ix, $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$, Et_2O, 0 °C; x, tmen, PhMe, 0 °C.

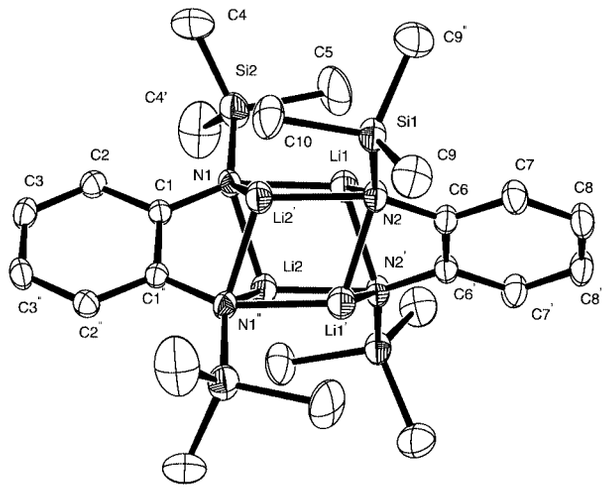
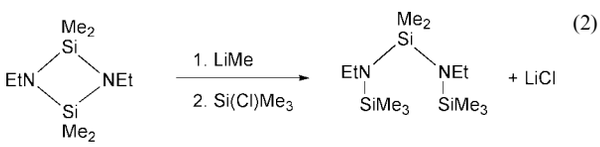


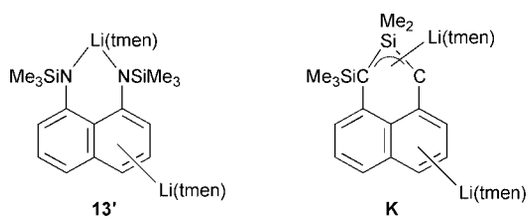
Fig. 1 Molecular structure of compound **1**.

J) the preferred reaction with a lithium alkyl is N–Si rather than N–H cleavage. As support for this postulate, we draw attention to the contrasting behaviour of two related cyclodisilazanes $\overline{Si(Me)_2N(R')Si(Me)_2}NR''$ with respect to successively adding LiMe and $Si(Cl)Me_3$ under identical conditions; whereas ring-opening was observed in one case, eqn. (2) (R′ = Et = R″), the other (R′ = $SiMe_3$, R″ = H) was unreactive.[22]



(2)

The ^{1}H NMR spectra of each of the dilithium diamides **1**–**7** was consistent with their crystal structures (see below). This



was also the case for the proposed structures of **9**, **12**, **13** and **15**. The ^{7}Li NMR spectra at ambient temperature showed single signals for **4**, **6**, **7**, **9**, **12** and **15**, but two for **1**, **2**, **3**, **5** and **13**. For **1**–**6**, these data are consistent with their crystal structures, but it may well be that their solution structures are more complicated and may in some cases involve equilibria between two or more species. For **13**, the signals at δ 3.4 and 3.7 are tentatively attributed to structure **13′**. This is based on analogy with compound **K**, readily obtained from the isoelectronic $[Li(tmen)]_2[\{C(H)SiMe_3\}_2C_{10}H_6$-1,8] by loss of methane.[23]

Crystal structures of the dilithium diamides 1–7 and the lithium amide 8

The molecular structures of the dilithium diamides **1**–**7** are illustrated in Figs. 1–7, respectively. Selected bond distances and angles are listed in Tables 1–7.

The molecule $[Li_2(\mu$-**A**$)]$ **1** lies on two intersecting mirror planes (Fig. 1, Table 1). The nitrogen and lithium atoms are arranged in a twisted cube. The rings N(1)Li(1)N(2)Li(2)′, N(1)″Li(2)N(2)′Li(1)″ and Li(2)′N(2)Li(1)″N(1)″, N(1)Li(1)-N(2)′Li(2) are planar (the sum of the endocyclic angles in each ring being 359.9°, with a torsion angle of 1.6°). The N(1)Li(2)N(1)″Li(2)′ and N(2)Li(1)N(2)′Li(1)″ rings are puckered, with torsion angles of 33.9 and 33.5°, respectively. Each of the lithium atoms is coordinated by the three adjacent nitrogen atoms [Li–N distances range from 2.028(3) to 2.087(4) Å] and by one of the carbon atoms of an $SiMe_3$ group [Li···CH_3 2.270(8) Å], the mean angle subtended at the Li atom by these being 109°. The lithium atoms have an additional close contact to the two *ipso*-carbon atoms of 2.403(4) and 2.412(4) Å.

Table 1 Selected bond lengths [Å] and angles [°] for **1**

Li(1)–N(2)	2.028(3)	Li(2)–N(1)	2.036(3)
Li(1)–N(1)	2.087(4)	Li(2)–N(2)′	2.082(4)
N(2)–Li(1)–N(2)′	87.22(17)	C(1)–N(1)–Li(1)	149.86(17)
N(2)–Li(1)–N(1)	108.72(15)	Li(2)–N(1)–Li(1)	71.17(13)
N(1)″–Li(2)–N(1)	86.68(16)	C(6)–N(2)–Li(1)	86.31(13)
N(1)–Li(2)–N(2)′	108.59(14)	Li(1)″–N(2)–Li(1)	82.35(19)
C(1)–N(1)–Li(2)	86.51(12)	C(6)–N(2)–Li(2)′	150.06(17)
Li(2)–N(1)–Li(2)′	82.83(18)	Li(1)–N(2)–Li(2)′	71.43(13)

Symmetry transformations used to generate equivalent atoms: ′ $x, y, -z + 3/2$; ″ $-x, y, z$.

Table 2 Selected bond lengths [Å] and angles [°] for **2**

Li(1)–O(1)	1.897(11)	Li(2)–N(1)	2.070(9)
Li(1)–N(1)	1.962(11)	Li(2)–N(2)	2.077(10)
Li(1)–N(2)	1.968(10)	Li(2)–O(2)	2.086(10)
Li(2)–O(2)′	2.067(9)		
N(1)–Li(1)–N(2)	86.7(5)	N(1)–Li(2)–O(2)	119.1(4)
O(2)′–Li(2)–N(1)	128.8(5)	N(2)–Li(2)–O(2)	124.1(4)
O(2)′–Li(2)–N(2)	123.9(4)	Li(1)–N(1)–Li(2)	80.7(4)
N(1)–Li(2)–N(2)	81.1(4)	Li(1)–N(2)–Li(2)	80.4(4)
O(2)′–Li(2)–O(2)	85.2(4)		

Symmetry element ′ is $-x + 1, -y + 1, -z + 1$.

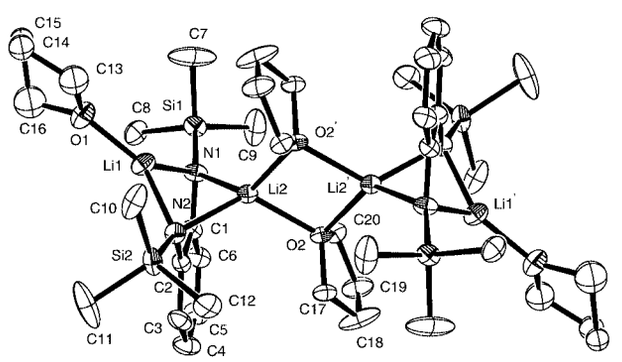


Fig. 2 Molecular structure of compound **2**.

The crystals of $[Li(\mu$-**A**$)\{\mu$-Li(thf)$(\mu$-thf$)\}]_2$ **2** diffracted poorly (Fig. 2, Table 2). The oxygen atom of the terminal thf ligand, O(1), was modelled as two alternative sets of ring carbon atoms with bond length constraints and isotropic displacement parameters. The dimeric molecule **2** is centrosymmetric. Each of the central lithium atoms, Li(2) and Li(2)′, is four-coordinate (the mean angle subtended at each being 110°), the two atoms are bridged by the thf oxygen atoms O(2) and O(2)′. Each of the terminal lithium atoms, Li(1) and Li(1)′, is three-coordinated, being bound to the two nitrogen atoms of the ligand **A** and an oxygen atom of the terminal thf ligand; the sum of the three angles subtended at Li is 359.6°. The terminal and bridging Li–O bond distances are slightly different, 1.897(10) and a mean of 2.08, respectively. The lithium atom Li(1) has a close contact to the *ipso*-carbon atoms of 2.36(1) Å. The Li(1)N(1)Li(2)N(2) ring is puckered, the torsion angle being 41.5° and Li(2)–N(1 or 2) and Li(1)–N(1 or 2) bond lengths being 2.074(10) (mean) and 1.965(10) Å (mean), respectively.

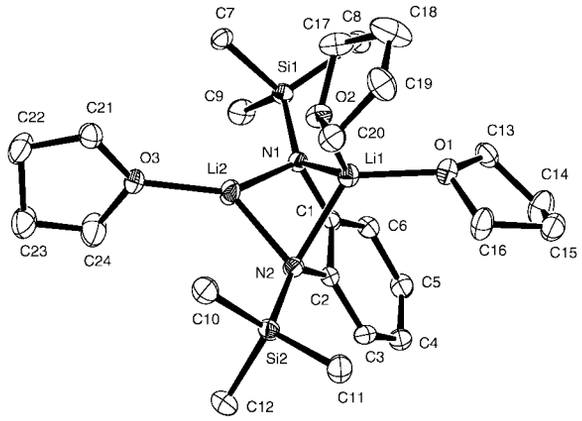


Fig. 3 Molecular structure of compound **3**.

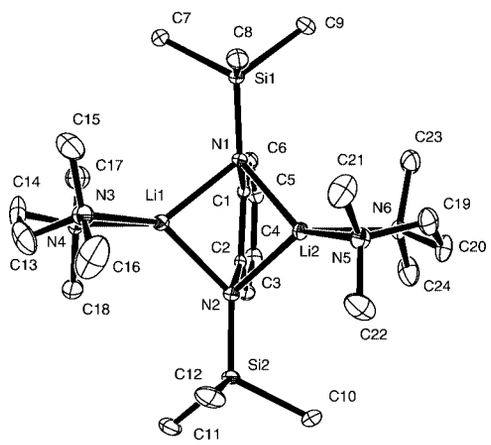


Fig. 4 Molecular structure of compound **4**.

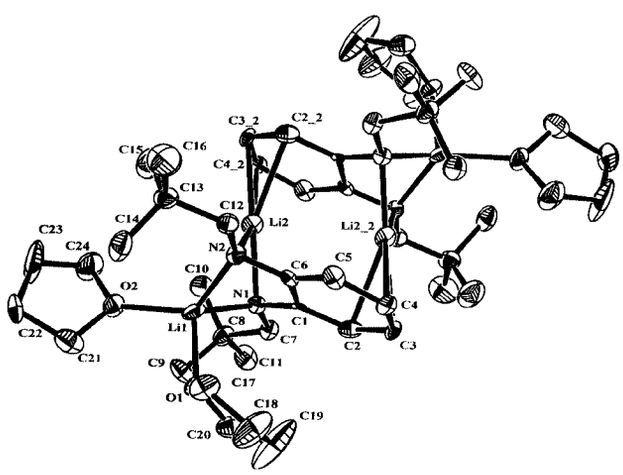


Fig. 5 Molecular structure of compound **5**.

There are two independent molecules of [Li(thf)$_2$(μ-**A**)Li(thf)] **3** in the unit cell, with similar geometry (Fig. 3, Table 3). The two lithium atoms are bridged by the two nitrogen atoms of the ligand **A**. The Li(1)N(1)Li(2)N(2) ring is puckered, with a torsion angle of *ca.* 44°. One of the lithium atoms, Li(1), is four-coordinate [average angle subtended at Li(1) is 109.4°] whereas the Li(2) atom is in a three-coordinate environment [the sum of the angles at Li(2) is 354.6°]. Each lithium atom is equidistant to N(1) and N(2), but Li(1)–N(1 or 2) > Li(2)–N(1 or 2) by *ca.* 0.1 Å. The lithium atom Li(1) has close contacts to the two *ipso*-carbon atoms: 2.404(8) and 2.487(8) Å. The Li–O bond distances are slightly longer for Li(1) [mean 1.947(7) and 1.947(7) Å] than Li(2) [1.897(7) and 1.915(7) Å].

Table 3 Selected bond lengths [Å] and angles [°] for **3**

O(1)–Li(1)	1.934(7)	O(1B)–Li(1B)	1.941(7)
O(2)–Li(1)	1.959(7)	O(2B)–Li(1B)	1.953(7)
O(3)–Li(2)	1.897(7)	O(3B)–Li(2B)	1.915(7)
N(1)–Li(2)	1.954(7)	N(1B)–Li(2B)	1.968(7)
N(1)–Li(1)	2.081(7)	N(1B)–Li(1B)	2.072(7)
N(2)–Li(2)	1.971(8)	N(2B)–Li(2B)	1.980(7)
N(2)–Li(1)	2.098(7)	N(2B)–Li(1B)	2.109(7)
Li(2)–N(1)–Li(1)	73.1(3)	Li(2B)–N(1B)–Li(1B)	78.0(3)
Li(2)–N(2)–Li(1)	72.4(3)	Li(2B)–N(2B)–Li(1B)	76.9(3)
O(1)–Li(1)–O(2)	104.3(3)	O(1B)–Li(1B)–O(2B)	104.0(3)
N(1)–Li(1)–N(2)	80.0(3)	N(1B)–Li(1B)–N(2B)	80.5(3)
N(1)–Li(2)–N(2)	86.4(3)	N(1B)–Li(2B)–N(2B)	86.3(3)

Table 4 Selected bond lengths [Å] and angles [°] for **4**

N(1)–Li(1)	2.076(7)	N(1)–Li(2)	2.056(7)
N(2)–Li(2)	2.063(7)	N(2)–Li(1)	2.078(7)
N(3)–Li(1)	2.136(8)	N(4)–Li(1)	2.265(8)
N(5)–Li(2)	2.209(7)	N(5)–Li(2)	2.209(7)
N(1)–Li(1)–N(2)	82.4(3)	N(3)–Li(1)–N(4)	82.7(3)
N(1)–Li(2)–N(2)	83.2(3)	N(5)–Li(2)–N(6)	83.8(3)
Li(2)–N(1)–Li(1)	87.8(3)	Li(2)–N(2)–Li(1)	87.6(3)

Table 5 Selected bond lengths [Å] and angles [°] for **5**

Li(1)–O(1)	2.021(13)	Li(2)–N(1)	2.060(13)
Li(1)–O(2)	2.003(14)	Li(2)–N(2)	2.103(14)
Li(1)–N(1)	2.003(15)	Li(2)–C(3′)	2.361(13)
Li(1)–N(2)	1.993(14)	Li(2)–C(4′)	2.380(14)
O(1)–Li(1)–N(1)	109.8(7)	O(2)–Li(1)–N(2)	124.4(7)
O(1)–Li(1)–O(2)	101.8(6)	N(1)–Li(1)–N(2)	83.1(5)
O(2)–Li(1)–N(1)	125.9(7)	N(1)–Li(2)–N(2)	79.1(5)

The two nitrogen atoms N(1) and N(2) of the ligand **A** are members of the puckered Li(1)N(1)Li(2)N(2) ring of the molecule [{Li(tmen)}$_2$(μ-**A**)] **4**, with a torsion angle of 33° (Fig. 4, Table 4). The Li(1 or 2)–N(1 or 2) bond distances are closely similar at 2.067 ± 0.012 Å, and are shorter than Li(1 or 2)–N(3, 4 or 5, 6) of 2.20 ± 0.06 Å.

The dimeric molecule [{Li(μ-**A**′)(thf)$_2$}(μ-Li)]$_2$ **5** lies across a crystallographic inversion centre (Fig. 5, Table 5). Each monomeric unit has a puckered Li(1)N(1)Li(2)N(2) ring, with a torsion angle of 38°; the Li–N distances are slightly longer for Li(2) [mean 2.080(10) Å] than Li(1) [mean 1.998(10) Å]. The two lithium atoms Li(2) bridge the two rings; the four-coordination for the Li(2) atoms is completed by close contacts to the atoms C(3) and C(4) of 2.361(13) and 2.380(14) Å, respectively, and has more remote contacts to the *ipso*-carbon atoms of 2.400(14) Å. The four-coordinate lithium atom Li(1) has bonds to O(1) and O(2) of 2.021(13) and 2.003(14), respectively.

There are two independent molecules of [{Li(tmen)}$_2$(μ-**A**″)] **6** in the unit cell, one in a general position and the other lying on a crystallographic mirror plane (Fig. 6, Table 6). The geometric skeletal parameters of the molecules **4** and **6** are closely similar. It is evident that the pendant vinyl group at each silicon atom of **6** has little influence.

The dimeric molecule [{Li(μ-**B**′)(thf)}(μ-Li)]$_2$ **7** lies across an inversion centre (Fig. 7, Table 7). Each monomeric unit has a puckered Li(1)N(1)Li(2)N(2) ring with a torsion angle of 24.4°; the unusually short Li–N distances are very slightly longer for Li(2) [1.98(2) Å] than Li(1) [1.95(2) Å]. The two lithium atoms Li(2) and Li(2)′ bridge the two rings; the four-coordination of these lithium atoms is completed by close contacts to C(8′ or 8) of 2.364(8) Å and C(9′ or 9) of 2.416(8) Å. Each of the three-coordinate lithium atoms Li(1) and Li(1)′ is joined to just one thf ligand, the Li–O bond being short, 1.883(8) Å; the sum of the angles subtended at Li(1) is 338°.

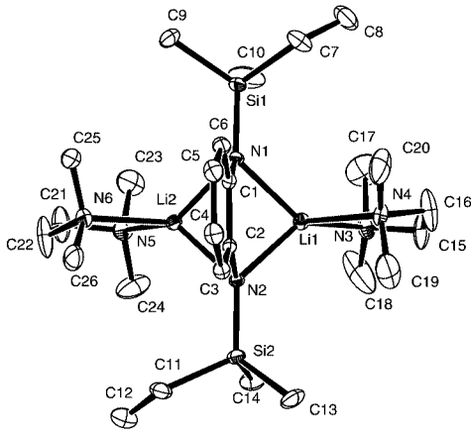


Fig. 6 Molecular structure of compound **6**.

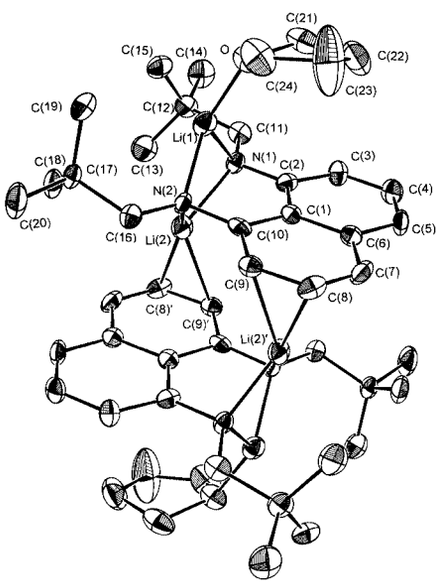


Fig. 7 Molecular structure of compound **7**.

In Table 8 are summarised the general features relating to the molecular structures of the crystalline dilithium diamides **1**–**7**, together with those for **D**,[12] **E**,[14] **F**,[14] and **G**.[17] Each has one or more LiNLi′N′ puckered rings, with the endocyclic angles at the nitrogen atoms somewhat more acute than those at lithium; the distances of each lithium atom to the two attached nitrogen atoms are generally slightly different. There are close Li · · · Li′ and Li or Li′ · · · C_{ipso} contacts (these being arranged almost orthogonally), but this is probably an inevitable consequence of the geometrical constraints. The C–C distances in the 1,2-diamidobenzene ligands **A**, **A′** and **A″** in compounds **1**–**6** are longest and shortest for the 1,2- [1.440(5) Å in **3** to 1.469(1) Å in **5**] and 4,5- [1.353(12) Å in **5** to 1.382(4) Å in **1**] bonds, respectively. Likewise, in the 8,9-diamidonaphthalene ligand **B′** of **7**, the 1,9- and 8,9-C–C bonds are the longest, 1.485(5) and 1.455(7) Å, respectively; the 3,4- and 5,6-C–C bonds are the shortest, 1.353(8) and 1.345(8), respectively. The N–C *ipso* bonds are short for the bridging ligands **A′** in **5** [mean 1.37(1) Å] and **B′** in **7** [1.38(1) Å]; whereas in **1** they are the longest [1.42(1) Å] and in **2**–**4** and **6** they range from 1.39 to 1.41 Å.

The molecular structure of the crystalline monoamidolithium complex $[Li\{(\mu\text{-}NC_{10}H_6NH\text{-}1,8)SiMe_2\}(OEt_2)]_2$ **8** is illustrated in Fig. 8, selected bond distances and angles being listed in Table 9. The molecule is dimeric, and there are two independent monomeric units in the asymmetric unit, each residing over a crystallographic centre of inversion. As such, the LiNLi′N′ rings are constrained to be planar. The bond

Table 6 Selected bond lengths [Å] and angles [°] for **6**

N(1)–Li(1)	2.078(11)	N(2)–Li(2)	2.078(9)
N(1)–Li(2)	2.062(9)	N(3)–Li(1)	2.206(10)
N(2)–Li(1)	2.072(10)	N(4)–Li(1)	2.183(9)
C(1)–N(1)–Li(1)	90.4(4)	Li(1)–N(1)–Li(2)	87.0(4)
C(1)–N(1)–Li(2)	85.5(4)	Li(1)–N(2)–Li(2)	86.7(4)
C(1)–N(1)–Si(1)	125.1(4)	Li(1)–N(1)–Si(1)	126.5(3)
C(2)–N(2)–Li(1)	90.7(4)	Li(2)–N(1)–Si(1)	129.1(3)
C(2)–N(2)–Li(2)	85.4(4)	Li(1)–N(2)–Si(2)	129.4(4)
C(2)–N(2)–Si(2)	123.8(3)	Li(2)–N(2)–Si(2)	127.5(3)

Table 7 Selected bond lengths [Å] and angles [°] for **7**

Li(1)–O	1.883(8)	Li(2)–Ni(1)	1.979(10)
Li(1)–N(1)	1.941(8)	Li(2)–N(2)	1.977(8)
Li(1)–N(2)	1.952(10)		
N(1)–Li(1)–N(2)	90.0(3)	Li(1)–N(1)–Li(2)	85.6(4)
N(1)–Li(2)–N(2)	88.2(3)	Li(1)–N(2)–Li(2)	85.4(4)

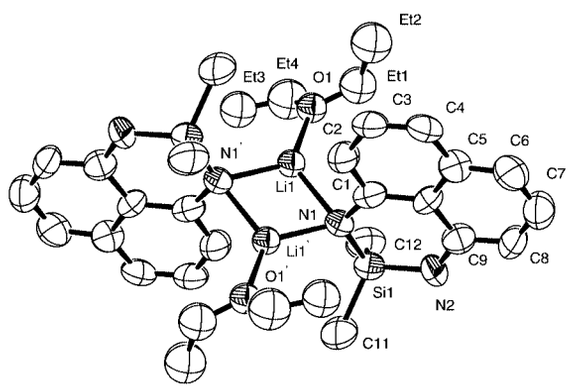


Fig. 8 Molecular structure of compound **8**.

lengths and angles are unremarkable. There is a molecule of solvent in the lattice. However, it is so disordered that no sensible model could be refined. As a result of the high thermal motion observed for this and for the coordinated diethyl ether molecules, the crystal scattered poorly and blocked least-squares refinement methods were used.

Experimental

All manipulations were carried out under argon or *in vacuo* using standard Schlenk techniques. Solvents were pre-dried over sodium wire, distilled from sodium–potassium alloy (pentane, hexane and toluene) and sodium–benzophenone (diethyl ether and tetrahydrofuran) and stored over molecular sieves (4 Å). Deuteriated solvents were likewise stored over such molecular sieves and degassed prior to use. Triethylamine, chloro(trimethyl)silane, chloro(dimethyl)vinylsilane, hexamethyldisilazane, lithium aluminium hydride, pivaloyl chloride and n-butyllithium in hexanes (1.6 mol dm^{-3}, FMC corporation), were commercial samples used without further purification. The NMR solution spectra were recorded on Bruker AC 250 (for ^1H, ^{13}C and ^7Li for compounds **1**, **5** and **7**), DPX 300 (for ^1H, ^{13}C and ^7Li for compounds **2**–**4** and **6**), WP 80 (for ^1H **10** and **11** and ^1H and ^7Li for compounds **9**, **12**, **13** and **15**) or AMX 500 (^{29}Si) instruments and referenced internally (^1H, ^{13}C) or externally (using aqueous $LiNO_3$ with a D_2O lock for ^7Li, or $SiMe_4$ for ^{29}Si). Unless otherwise stated, all NMR spectra were examined at 293 K in C_6D_6 and, except for ^1H, were proton-decoupled. Electron impact mass spectra were taken on a Kratos MS 80 RF instrument. The IR spectra were measured on solid samples as "Nujol" mulls using a Perkin-Elmer 1720

Table 8 General features relating to the molecular structures of **1**–**7** and **D**–**G**

Molecule	No. of diamido ligands	Nature of diamido ligands	Coligands	No. of Li atoms	Li coordn. environment	N^- coordn. environment	Further comments
D[12]	2	chel., bridg. bridg. *via* η^3	$(thf)_2$	4	$(2\ N + 1\ O)_2$ $[2\ N + 3\ C\ (\eta^3)]_2$	$(2\ Li + 1\ C + 1\ Si)_4$	μ-Li
E[14]	1	chel., bridg.	$(hmpa)_2$	2	$(2\ N + 1\ O)_2$	$(2\ Li + 1\ C + 1\ Si)_2$	
F[14]	2	chel., bridg.	$(\eta^2\text{-tmen})_2$ μ-tmen	4	$[2N + 2\ N\ (tmen)]_2$ $[2\ N + 1\ N\ (tmen)]_2$	$(2\ Li + 1\ C + 1\ Si)_4$	μ-tmen
G[17]	1	chel., bridg.	$(thf)_2$	2	$(2\ N + 1\ O)_2$	$(2\ Li + 1\ C + 1\ C\ or\ Si)_2$	
1	2	chel., bridg.	—	4	$(3\ N)_4$	$(3\ Li + 1\ C + 1\ Si)_4$	Homoleptic $(Li\cdots C_{ipso})_2$ $(Li\cdots CH_3)_2$
2	2	chel., bridg.	$(thf)_2$ $(\mu\text{-thf})_2$	4	$(2\ N + 1\ O)_2$ $(2\ N + 2\ O)_2$	$(2\ Li + 1\ C + 1\ Si)_4$	μ-thf $(Li\cdots C_{ipso})_2$
3	1	chel., bridg.	$(thf)_2$ thf	2	2 N + 2 O 2 N + 1 O	$(2\ Li + 1\ C + 1\ Si)_2$	sym. $Li\cdots C_{ipso}$
4	1	chel., bridg.	$(tmen)_2$	2	$[2\ N + 2\ N\ (tmen)]_2$	$(2\ Li + 1\ C + 1\ Si)_2$	
5	2	chel., bridg., bridg. *via* η^2	$(thf)_2$	4	$(2\ N + 1\ O)_2$ $[2\ N + 2\ C\ (\eta^2)]_2$	$(2\ Li + 1\ C + 1\ O)_4$	$(Li\cdots C_{ipso})_2$
6	1	chel., bridg.	$(tmen)_2$	2	$[2\ N + 2\ N\ (tmen)]_2$	$(2\ Li + 1\ C + 1\ Si)_2$	
7	2	chel., bridg., bridg. *via* η^2	$(thf)_2$	4	$(2\ N + 1\ O)_2$ $[2\ N + 2\ C\ (\eta^2)]_2$	$(2\ Li + 1\ C + 1\ C)_4$	$(Li\cdots C_{ipso})_2$

Table 9 Selected bond lengths [Å] and angles [°] for **8**

Li(1)–O(1)	1.94(2)	Li(1)–N(1)′	2.00(2)
Li(2)–O(2)	1.93(2)	Li(2)–N(3)	2.01(2)
Li(1)–N(1)	2.03(2)	Li(2)–N(3)″	2.06(2)
N(1)–Li(1)–N(1)′	106(1)	Li(1)–N(1)–Li(1)′	74(1)
N(3)–Li(2)–N(3)′	107(1)	Li(2)–N(3)–Li(2)″	73(1)

Symmetry transformations used to generate equivalent atoms: ′ $1 - x, -y, 1 - z$. ″ $1 - x, -y, 2 - z$.

instrument. Elemental analyses (calculated data are for empirical formulae) were carried out by Medac Ltd, UK. Melting points are uncorrected.

Preparations

$[Li_2(\mu\text{-A})]_2$ 1. n-Butyllithium in n-hexane (3.5 cm^3 of a 1.6 mol dm^{-3} solution, 5.7 mmol) was added dropwise to a solution of 1,2-bis(trimethylsilylamino)benzene[5] (0.73 g, 2.9 mmol) in hexane (20 cm^3) at *ca.* 20 °C. The mixture was set aside for *ca.* 2 h. Filtration yielded the pale yellow solid **1** (0.63 g, 80%) (Found: C, 53.6; H, 8.63; N, 8.85. $C_6H_{11}LiNSi$ requires C, 54.5; H, 8.39; N, 10.59%), mp 104–105 °C, which was washed with hexane and dried *in vacuo*. ^{1}H NMR: δ 0.30 (s, 18 H, $SiMe_3$), 6.11 (m, 2 H, C_6H_4), 6.70 (m, 2 H, C_6H_4); ^{13}C NMR: δ 3.3 ($SiMe_3$), 113.9, 119.8, 152.9 and 154.0 (C_6H_4); ^{7}Li NMR δ 4.3, 3.3; ^{29}Si NMR: δ −12.6. MS (EI) *m*/*z* (%, assignment), 502 (15, $[H_2(\mathbf{A})]_2^+$), 430 (5, $[\{H_2(\mathbf{A})\}_2 - SiMe_3]^+$), 324 (10), 252 (65, $[H_2(\mathbf{A})]^+$), 221 (15, $[H_2(\mathbf{A}) - 2Me - H]^+$), 149 (50, $[H_2(\mathbf{A}) - 2Me - SiMe_3]^+$), 72 (75, $[SiMe_3 - H]^+$) and 42 (100).

$[Li(\mu\text{-A})\{\mu\text{-Li(thf)}(\mu\text{-thf})\}]_2$ 2. n-Butyllithium in n-hexane (6 cm^3 of a 1.6 mol dm^{-3} solution, 9.6 mmol) was added dropwise to a solution of 1,2-bis(trimethylsilylamino)benzene (1.20 g, 4.76 mmol) in hexane (60 cm^3) at *ca.* 20 °C. Tetrahydrofuran (0.69 g, 9.57 mmol) was added and the turbid mixture was heated until a clear solution was obtained. Concentration yielded light brown crystals of **2** (1.81 g, 90%) (Found: C, 58.8; H, 9.26; N, 6.99. $C_{10}H_{19}LiNOSi$ requires C, 58.8; H, 9.37; N, 6.86%), mp 86–88 °C. ^{1}H NMR: δ 0.42 (s, 18 H, $SiMe_3$), 1.16 (s, 8 H, CH_2CH_2O), 3.36 (s, 8 H, OCH_2), 6.80 (m, 2 H, C_6H_4), 7.10 (m, 2 H, C_6H_4); ^{13}C NMR: δ 2.9 ($SiMe_3$), 25.2 (CH_2CH_2O), 68.4 (OCH_2), 115.9, 118.0 and 150.7 (C_6H_4); ^{7}Li NMR: δ 2.9, 0.9; ^{29}Si NMR: δ −11.0. MS (EI) *m*/*z* (%, assignment), 535 (55, $[Li_5(\mathbf{A})_2]^+$), 528 (60, $[Li_4(\mathbf{A})_2]^+$), 513 (35, $[Li_4(\mathbf{A})_2 - Me]^+$), 271 (100, $[Li_3(\mathbf{A})]^+$), 263 (65, $[Li_2(\mathbf{A})]^+$), 249 (65, $[\mathbf{A} - H]^+$), 236 (20, $[\mathbf{A} - NH]^+$), 73 (20, $[SiMe_3]^+$) and 40 (15).

$[Li(thf)_2(\mu\text{-A})Li(thf)_2]$ 3. n-Butyllithium in n-hexane (6.5 cm^3 of a 1.6 mol dm^{-3} solution, 10.4 mmol) was added dropwise to a solution of 1,2-bis(trimethylsilylamino)benzene (1.25 g, 5.03 mmol) in thf (80 cm^3) at *ca.* 20 °C. The yellow solution was set aside for *ca.* 2 h. Solvent was removed *in vacuo*. The residual white solid was crystallised from n-pentane, yielding colourless needles of compound **3** (2.13 g, 90%) (Found: C, 59.0; H, 8.74; N, 5.65. $C_{24}H_{46}Li_2N_2O_3Si_2$ requires C, 59.9; H, 9.65; N, 5.83%), mp 103–105 °C. ^{1}H NMR: δ 0.46 (s, 18 H, $SiMe_3$), 1.23 (s, 12 H, CH_2CH_2O), 3.40 (s, 12 H, OCH_2), 6.79 (m, 2 H, C_6H_4), 7.01 (m, 2 H, C_6H_4); ^{13}C NMR: δ 3.0 ($SiMe_3$), 25.3 (CH_2CH_2O), 68.3 (OCH_2), 115.8, 117.6 and 150.5 (C_6H_4); ^{7}Li NMR: δ 1.2 and 0.9; ^{29}Si NMR: δ −11.8. MS (EI) *m*/*z* (%, assignment), 502 (10, $[H_2(\mathbf{A})_2]^+$), 324 (50), 252 (55, $[H_2(\mathbf{A})]^+$), 237 (15, $[H_2(\mathbf{A}) - Me]^+$), 221 (60, $[H_2(\mathbf{A}) - 2Me - H]^+$), 149 (45, $[H_2(\mathbf{A}) - 2Me - SiMe_3]^+$), 134 (15, $[H_2(\mathbf{A}) - 3Me - SiMe_3]^+$), 73 (100, $[SiMe_3]^+$).

$[\{Li(tmen)\}_2(\mu\text{-A})]$ 4. n-Butyllithium in n-hexane (7.0 cm^3 of a 1.6 mol dm^{-3} solution, 11.2 mmol) was added dropwise to a solution of 1,2-bis(trimethylsilylamino)benzene (1.30 g, 5.15 mmol) in diethyl ether (*ca.* 100 cm^3) at 0 °C. The solution was set aside for *ca.* 30 min at 0 °C and then *ca.* 2 h at *ca.* 20 °C. 1,2-Bis(dimethylamino)ethane (1.20 g, 10.32 mmol) was added. After *ca.* 2 h the solution was concentrated, yielding colourless crystals of compound **4** (2.35 g, 90%) (Found: C, 57.9; H, 11.13; N, 16.94. $C_{12}H_{27}LiN_3Si$ requires C, 58.0; H, 10.96; N, 16.91%), mp 175–180 °C. ^{1}H NMR: δ 0.40 (s, 18 H, $SiMe_3$), 1.76 (s, 8 H, NCH_2), 1.92 (s, 24 H, NMe_2), 6.75 (m, 2 H, C_6H_4), 7.01 (m, 2 H, C_6H_4); ^{13}C NMR: δ 4.7 ($SiMe_3$), 46.7 (NCH_2), 57.1 (NMe_2), 115.1, 118.5 and 150.8 (C_6H_4); ^{7}Li NMR: δ 0.6; ^{29}Si NMR: δ −14.2. MS (EI) *m*/*z* (%, assignment), 502 (15, $[H_2(\mathbf{A})_2]^+$), 324 (10), 252 (25, $[H_2(\mathbf{A})]^+$), 221 (10, $[H_2(\mathbf{A}) - 2Me - H]^+$), 149 (20, $[H_2(\mathbf{A}) - 2Me - SiMe_3]^+$), 73 (40, $[SiMe_3]^+$) and 58 (100, $[SiMe_2]^+$).

1,2-Bis(neopentylamino)benzene, $H_2(\mathbf{A}')$. Pivaloyl chloride (50.5 cm^3, 0.41 mol) in diethyl ether (200 cm^3) was added dropwise with stirring to a solution of 1,2-diaminobenzene (21.6 g, 0.20 mol) and triethylamine (58.5 cm^3, 0.42 mol) in diethyl ether (800 cm^3). The mixture was heated under reflux while being stirred for 6 h. Water (*ca.* 300 cm^3) was added to the mixture at ambient temperature. The precipitate of $C_6H_4[N(H)C(O)Bu^t]_2$-

1,2 (44.0 g, 80%), mp 174–175 °C, was filtered off, washed several times with water and dried for 12 h in an oven at 100 °C. ^{1}H NMR (C_6D_6): δ 1.27 (s, 18 H, Me), 7.09–7.32 (m, 4 H, C_6H_4), 8.28 (s, 2 H, NH); ^{13}C NMR: δ 27.6 (C*Me*$_3$), 39.3 (*C*Me$_3$), 125.9 and 131.1 (C_6H_4), 178.1 (CO). MS (EI) *m*/*z* (%, assignment): 276 (35, $[C_6H_4[NH\{C(O)Bu^t\}]_2]^+$).

Solid 1,2-bis(pivaloylamino)benzene (44.0 g, 0.16 mol) was added in small portions to a stirring suspension of lithium tetrahydroaluminate (12.0 g, 0.32 mol) in thf (1000 cm^3). The mixture was heated under reflux with stirring for 6 h and then was carefully hydrolysed. The mixture was filtered and the precipitate was washed with diethyl ether. The combined filtrate and washings were dried (Na_2SO_4) and solvent was removed *in vacuo*. The residue was purified either by crystallisation from hexane or distillation. The compound H_2(**A′**) (32.0 g, 86%) had mp 53–54 °C. ^{1}H NMR (C_6D_6): δ 1.07 (s, 18 H, Me), 2.87 (s, 4 H, CH_2), 3.35 (s, 2 H, NH) 6.7–6.8 (m, 4 H, C_6H_4); ^{13}C NMR: δ 27.8 (C*Me*$_3$), 56.4 (CH_2), 119.15, 112.1 and 138.3 (C_6H_4). MS (EI) *m*/*z* (%, assignment): 248 (55, $[H_2(\mathbf{A}')]^+$).

[{Li(μ-A′)(thf)$_2$}(μ-Li)]$_2$ 5. n-Butyllithium in n-hexane (12.5 cm^3 of a 1.6 mol dm^{-3} solution, 20.1 mmol) was added dropwise to a solution of 1,2-bis(neopentylamino)benzene (2.50 g, 10.0 mmol) in hexane (*ca.* 50 cm^3) at *ca.* 20 °C. After stirring for *ca.* 2 h, the mixture was filtered. The pale yellow precipitate was washed with n-hexane and dried *in vacuo* to yield an off-white solid. Colourless crystals of compound **5** (70%) were obtained by slow addition of thf to a refluxing solution of the off-white solid in hexane and then allowing the solution to cool slowly to *ca.* 20 °C. ^{1}H NMR: δ 1.22 (s, 18 H, Me), 1.13 (brs, 4 H, C*H*$_2$CH$_2$O), 2.98 and 3.20 (brs, 4 H, C*H*$_2$Bu^t) 3.44 (brs, 4 H, OCH$_2$), 6.15 (m, 2 H, C_6H_4), 6.46 (m, 2 H, C_6H_4); ^{7}Li NMR: δ 1.2, −4.0; ^{29}Si NMR: δ: −20.5.

[{Li(tmen)}$_2$(μ-A″)] 6. n-Butyllithium in n-hexane (3.4 cm^3 of a 1.6 mol dm^{-3} solution, 5.44 mmol) was added dropwise to a solution of 1,2-bis{(dimethylvinylsilyl)amino}benzene[8] (0.78 g, 2.73 mmol) and 1,2-bis(dimethylamino)ethane (0.83 cm^3, 5.46 mmol) in hexane (40 cm^3) at 0 °C. The mixture was stirred for *ca.* 20 h at 20 °C, then filtered. Concentration of the filtrate yielded pale yellow crystals of compound **6** (1.25 g, 88%) (Found: C, 59.9; H, 10.37; N, 16.14. $C_{13}H_{27}LiN_3Si$ requires C, 60.0; H, 10.65; N, 16.24%). ^{1}H NMR (toluene-d$_8$): δ 0.31 (s, 12 H, SiMe$_2$), 1.77 (s, 8 H, NCH$_2$), 1.88 (s, 24 H, NMe$_2$), 5.72 (dd, 2 H, $^2J_{HH}$ = 4.15, $^3J_{HH\text{-}trans}$ = 20.25, CH=CH$_2$), 5.85 (dd, 2 H, $^2J_{HH}$ = 4.15, $^3J_{HH\text{-}cis}$ = 18.33, CH=C*H*$_2$), 6.89 (m, 2 H, C_6H_4), 6.52 (m, 2 H, C_6H_4), 6.61 (dd, 2 H, $^3J_{HH\text{-}trans}$ = 20.25, $^3J_{HH\text{-}cis}$ = 18.33 Hz, C*H*=CH$_2$); ^{13}C NMR: δ −1.5 (SiMe$_2$), 45.9 (NCH$_2$), 57.0 (NMe$_2$), 121.2 (CH=*C*H$_2$), 127.4 (*C*H=CH$_2$), 136.8, 135.5 and 131.3 (C_6H_4); ^{7}Li NMR: δ −1.7; ^{29}Si NMR: δ −20.5. MS (EI) *m*/*z* (%, assignment): 276 (100, $[H_2(\mathbf{A}'')]^+$).

H$_2$(B) (*cf.* refs. 12–15, 19). A mixture of 1,8-diaminonaphthalene (20.0 g, 126.42 mmol), hexamethyldisilazane (53.7 cm^3, 252.8 mmol) and chloro(trimethyl)silane (4 drops) was heated under reflux at 140 °C for 1 d. Volatiles were removed *in vacuo*. Distillation of the residue afforded the pale yellow liquid H_2(**B**) (27.83 g, 73%), bp 123 °C/0.1 Torr. ^{1}H NMR (toluene-d$_8$): δ 0.20 (s, 18 H, SiMe$_3$), 3.20 (brs, 2 H, NH), 5.9–6.2 (m, 2 H, $C_{10}H_6$), 6.8–7.0 (m, 4 H, $C_{10}H_6$).

H$_2$(B′). Pivaloyl chloride (10.0 g, 82.0 mmol) was slowly added to 1,8-diaminonaphthalene (5.0 g, 31.6 mmol) and triethylamine (10.0 g, 99.0 mmol) in thf (200 cm^3) at *ca.* 20 °C. The reaction mixture was heated under reflux for *ca.* 2 h. The mixture was filtered. Removal of solvent from the filtrate *in vacuo*, washing the residue with pentane and then crystallisation from thf yielded colourless needles of 1,8-bis(pivaloylamino)naphthalene (9.9 g, 96%) (Found: C, 73.7; H, 8.09; N, 8.54. $C_{10}H_{13}NO$ requires C, 73.6; H, 8.03; N, 8.58%), mp 240–244 °C. ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 18 H, Bu^t), 7.38–7.70 (m, 6 H, $C_{10}H_6$), 8.31 (s, 2 H, NH). MS (EI) *m*/*z* (%, assignment): 326 (22, $[C_{10}H_6[NH\{C(O)Bu^t\}]_2]^+$), 224 (73).

1,8-Bis(pivaloylamino)naphthalene (5.0 g, 15.0 mmol) was added in small portions to a stirred suspension of lithium tetrahydroaluminate (1.2 g, 31.0 mmol) in thf (*ca.* 200 cm^3). The reaction mixture was heated under reflux for *ca.* 12 h and then was carefully hydrolysed. The mixture was filtered and the precipitate was washed with thf. The combined filtrate and washings were separated. The organic layer was dried (Na_2SO_4) and solvent was removed *in vacuo*. The residue was purified by distillation and afforded colourless crystals of H_2(**B′**) (4.2 g, 92%) (Found: C, 80.6; H, 10.13; N, 9.26. $C_{10}H_{15}N$ requires C, 80.5; H, 10.13; N, 9.39%). ^{1}H NMR: δ 0.91 (s, 18 H, Bu^t), 2.74 (s, 4 H, CH_2), 5.37 (s, 2 H, NH), 6.58–7.37 (m, 6 H, $C_{10}H_6$); ^{13}C NMR: δ 28.1 [C(*C*H$_3$)$_3$], 31.8 [*C*(CH$_3$)$_3$], 58.5 (*C*H$_2$Bu^t), 108.0, 119.7, 126.5, 137.7 and 147.7 ($C_{10}H_6$). MS (EI) *m*/*z* (%, assignment): 298 (52, $[H_2(\mathbf{B}')]^+$), 241 (100, $[H_2(\mathbf{B}') - Bu^t]^+$.

[{Li(μ-B′)(thf)}(μ-Li)]$_2$ 7. n-Butyllithium in n-hexane (4.3 cm^3 of a 1.6 mol dm^{-3} solution, 6.9 mmol) was added dropwise to a solution of 1,8-bis(neopentylamino)naphthalene (2.0 g, 6.7 mmol) in hexane (*ca.* 50 cm^3) at *ca.* 20 °C. The mixture was heated to a gentle reflux while thf was added by syringe until the precipitate had dissolved. Slow cooling to ambient temperature then at 0 °C yielded colourless crystals of compound **7** (1.95 g, 76%) (Found: C, 77.2; H, 10.4. $C_{24}H_{36}Li_2N_2O$ requires C, 75.4; H, 9.49%). ^{1}H NMR: δ 0.94 (m, 4 H, C*H*$_2$CH$_2$O), 1.16 (s, 18 H, Bu^t), 3.09 (s, 4 H, C*H*$_2$Bu^t), 3.11 (m, 4 H, CH$_2$O), 6.40 (d, 2 H, $C_{10}H_6$, $^3J_{HH}$ = 7.6), 7.05 (d, 2 H, $C_{10}H_6$, $^3J_{HH}$ = 7.2 Hz), 7.44 (pseudo-t, 2 H, $C_{10}H_6$); ^{13}C NMR: δ 25.0 (*C*H$_2$CH$_2$O), 29.6 [C*Me*$_3$], 32.5 [*C*Me$_3$], 65.5 (*C*H$_2$Bu^t), 68.3 (CH$_2$O), 101.0, 112.1, 118.6, 139.9 and 160.3 ($C_{10}H_6$); ^{7}Li NMR: δ 1.08.

[Li{(μ-NC$_{10}$H$_6$NH-1,8)SiMe$_2$}(OEt$_2$)]$_2$ 8. n-Butyllithium in n-hexane (13.8 cm^3 of a 1.6 mol dm^{-3} solution, 22.1 mmol) was slowly added to a solution of 1,8-bis(trimethylsilylamino)-naphthalene (6.68 g, 22.1 mmol) in hexane (*ca.* 30 cm^3) at *ca.* 20 °C. The mixture was stirred for 3 h, then filtered. To the pale yellow precipitate, dried *in vacuo*, diethyl ether was added with stirring until a clear solution was obtained. After 10 d, the large colourless crystals of compound **8** (4.78 g, 75%), mp 232–235 °C were collected by filtration, washed with cold hexane and dried in a stream of argon. ^{1}H NMR (toluene-d$_8$): δ 0.27 (s, 6 H, SiMe$_2$), 0.78 (t, 6 H, OCH$_2$C*H*$_3$), 2.90 (q, 4 H, OC*H*$_2$CH$_3$), 6.1–6.3 (m, 2 H, $C_{10}H_6$), 7.0–7.2 (m, 4 H, $C_{10}H_6$); ^{7}Li NMR: δ 0.4

[{Li(tmen)}$_2${μ-NSi(Me)$_2$C$_{10}$H$_6$N-1,8}] 9. A solution of n-butyllithium in n-hexane (57.0 cm^3 of a 1.6 mol dm^{-3} solution, 91.2 mmol) was slowly added to a stirred solution of 1,8-bis(trimethylsilylamino)naphthalene (9.2 g, 30.4 mmol) in n-hexane (40 cm^3) at 0 °C yielding a pale yellow precipitate. Slow addition of 1,2-bis(dimethylamino)ethane (13.8 cm^3, 91.2 mmol) resulted in the mixture becoming bright yellow. The mixture was filtered. The precipitate was washed with hexane and dried *in vacuo* affording bright yellow, amorphous, compound **9** (9.8 g, 70%) (Found: C, 62.2; H, 9.2; N, 17.8. $C_{24}H_{44}Li_2N_6Si$ requires C, 62.9; H, 9.7; N, 18.3%), mp 137–141 °C. ^{1}H NMR (toluene-d$_8$): δ 0.28 (s, 6 H, SiMe$_2$), 1.76 (brs, 32 H, tmen), 6.0–6.2 (m, 2 H, $C_{10}H_6$), 6.7–7.0 (m, 4 H, $C_{10}H_6$); ^{7}Li NMR: δ 0.6.

Me$_2$Si{N(Me)C$_{10}$H$_6$NMe-1,8} 10. A solution of iodomethane (1.40 g, 9.9 mmol) in diethyl ether (10 cm^3) was slowly added to a stirred solution of compound **9** (2.22 g, 4.84 mmol) in diethyl ether (40 cm^3) at 0 °C. The pale yellow reaction mixture was stirred at *ca.* 20 °C for 4 h, then filtered. Volatiles were removed from the filtrate *in vacuo*. The residue was extracted into n-hexane. The yellow extract was concentrated and cooled at −30 °C yielding colourless crystals of compound **10** (0.87 g,

75%) (Found: C, 69.6; H, 7.6; N, 11.4. $C_{14}H_{18}N_2Si$ requires C, 69.4; H, 7.5; N, 11.6%), which was washed with pentane and dried *in vacuo*. ^{1}H NMR (toluene-d_8): δ 0.30 (s, 6 H, $SiMe_2$), 2.0 (brs, 6 H, NMe), 6.0–6.2 (m, 2 H, $C_{10}H_6$), 6.9–7.1 (m, 4 H, $C_{10}H_6$). MS (EI) *m*/*z* (assignment): 242 ([**10**]$^+$).

$Me_2Si\{N(H)C_{10}H_6NH$-1,8$\}$ 11. Dichloro(dimethyl)silane (11.5 cm^3, 94.8 mmol) and triethylamine (26.4 cm^3, 189.7 mmol) were added to a solution 1,8-diaminonaphthalene (15.0 g, 94.8 mmol) in toluene (200 cm^3) at *ca.* 20 °C. The mixture was heated under reflux for 4 h yielding a pink solution and a white precipitate. Toluene was removed *in vacuo* and the residue was extracted with diethyl ether (*ca.* 200 cm^3). Volatiles were removed from the extract *in vacuo*. The residue was washed with light petroleum ether (bp 60–80 °C, 2 × 50 cm^3) yielding the pink, amorphous compound **11** (10.8 g, 53%) (Found: C, 67.3; H, 6.6; N, 12.9. $C_{12}H_{14}N_2Si$ requires C, 67.2; H, 6.6; N, 13.1%), mp 121–124 °C, which was dried *in vacuo*. ^{1}H NMR (toluene-d_8): δ −0.10 (s, 6 H, $SiMe_2$), 3.10 (brs, 2 H, NH), 6.07 (m, 2 H, $C_{10}H_6$; X part of ABX with $J_{(AX)}$ = 7.3 and $J_{(BX)}$ = 1.2), 7.05 (m, 4 H, $C_{10}H_6$; AB part of ABX with $J_{(AB)}$ = 8.2 Hz); IR, $\nu_{(NH)}$ 3360 s. MS (EI) *m*/*z*: 302 ([**11**]$^+$).

$[Li(tmen)_2\{NSi(Me)_2C_{10}H_6NH$-1,8$\}]$ 12. A solution of H_2(**B**) (1.61 g, 5.3 mmol) was added slowly with stirring to a solution of n-butyllithium in n-hexane (6.7 cm^3 of a 1.6 mol dm^{-3} solution, 10.72 mmol) and 1,2-bis(dimethylamino)ethane (1.6 cm^3, 10.7 mmol) in hexane at 0 °C. After *ca.* 3 h the pale yellow solution was concentrated and filtered. The filtrate upon cooling at −30 °C afforded pale yellow crystals of compound **12** (1.95 g, 81%), mp 123–127 °C, which were dried *in vacuo*. ^{1}H NMR (toluene-d_8): δ 0.30 (s, 6 H, $SiMe_2$), 1.70 (brs, 32 H, tmen), 3.16 (brs, 1 H, NH), 6.0–6.2 (m, 2 H, $C_{10}H_6$), 6.8–7.4 (m, 4 H, $C_{10}H_6$); ^{7}Li NMR: δ 0.7.

$[\{Li(tmen)\}_2(\mu$-B$)]$ 13. n-Butyllithium in n-hexane (70.1 cm^3 of a 1.6 mol dm^{-3} solution, 112.1 mmol) was added slowly with stirring to H_2(**B**) (12.41 g, 41.01 mmol) at 0 °C. A yellow precipitate was immediatly observed. Slow addition of 1,2-bis(dimethylamino)ethane (16.9 cm^3, 111.9 mmol) caused a darkening of the yellow colour. The mixture was stirred at *ca.* 20 °C for 4 h. The volatiles were removed *in vacuo*. The residue was extracted with diethyl ether (60 cm^3). The extract was concentrated and cooled yielding the yellow amorphous compound **13** (17.85 g, 83%) which was dried *in vacuo*. ^{1}H NMR (toluene-d_8): δ 0.30 (s, 18 H, $SiMe_3$), 1.63 (brs, 32 H, tmen), 6.4–6.8 (m, 2 H, $C_{10}H_6$), 6.9–7.0 (m, 4 H, $C_{10}H_6$); ^{7}Li NMR: δ 3.4, 3.7.

$[Zr(\eta^5$-$C_5H_5)_2$(B$)]$ 14. The reaction between the dilithium diamide **13** and an equivalent portion of $[Zr(\eta^5$-$C_5H_5)_2Cl_2]$ in diethyl ether at 0 °C afforded the orange, crystalline complex **14** (49%) (Found: C, 60.0; H, 6.8; N, 5.2. $C_{26}H_{34}N_2Si_2Zr$ requires C, 59.8; H, 6.6; N, 5.4%), mp > 240 °C (decomp.), which was dried *in vacuo*. ^{1}H NMR (toluene-d_8): δ 0.3 (s, 18 H, $SiMe_3$), 5.5 (s, 10 H, C_5H_5), 6.2–6.4 (m, 2 H, $C_{10}H_6$), 6.8–7.1 (m, 4 H, $C_{10}H_6$).

$[Li(tmen)\{\mu$-$NSi(Me)_2C_{10}H_6NH$-1,8$\}]$ 15. 1,2-Bis(dimethylamino)ethane (0.59 cm^3, 3.91 mmol) was added slowly with stirring to a solution of compound **8** (1.10 g, 1.91 mmol; prepared *in situ* as described above) in toluene (20 cm^3) at 0 °C. The pale yellow solution was stirred at *ca.* 20 °C for 2 h. Volatiles were removed *in vacuo* and the residue was extracted with diethyl ether (40 cm^3). The pale yellow extract was concentrated and filtered. The filtrate was cooled to −30 °C affording pale yellow crystals of compound **15** (0.75 g, 60%) (Found: C, 63.8; H, 8.1; N, 16.1. $C_{18}H_{29}LiN_4Si$ requires C, 64.3; H, 8.7; N, 16.7%), which was dried *in vacuo*. ^{1}H NMR (toluene-d_8): δ 0.21 (s, 6 H, $SiMe_2$), 1.63 (brs, 16 H, tmen), 3.42 (brs, 1 H, NH), 6.2 (brs, 4 H, $C_{10}H_6$); ^{7}Li NMR: δ 0.0.

Table 10 Crystal data and refinement for the diamidodilithium compounds **1**–**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{24}H_{44}Li_4N_4Si_4$	$C_{40}H_{76}Li_4N_4O_4Si_4$	$C_{24}H_{46}Li_2N_2O_3Si_2$	$C_{24}H_{54}Li_2N_6Si_2$	$C_{48}H_{84}Li_4N_4O_4$	$C_{26}H_{54}Li_2N_6Si_2$	$C_{48}H_{72}Li_4N_4O_2$	$C_{36}H_{54}Li_2N_4O_3Si_2$
M	528.7	817.2	480.7	496.8	809.0	520.8	764.9	660.78
T/K	173(2)	173(2)	173(2)	173(2)	173(2)	293(2)	173(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Cncm* (no. 63)	*Pbca* (no. 61)	*Pbca* (no. 61)	$P2_1$ (no. 4)	$P2_1/n$ (no. 14)	$Cmc2_1$ (no. 36)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	15.7489(7)	10.7906(7)	17.8015(7)	9.813(5)	10.122(5)	36.532(11)	10.465(2)	17.550(6)
b/Å	13.7919(4)	17.7715(9)	27.9629(9)	16.812(3)	16.769(6)	16.972(10)	16.733(9)	10.110(9)
c/Å	14.8525(5)	25.8104(14)	23.7088(5)	10.872(2)	14.714(4)	16.030(5)	13.887(4)	21.036(6)
β/°	90	90	90	116.20(3)	97.82(3)	90	111.83(2)	99.40(3)
U/Å^3	3226.1(2)	4949.5(5)	11801.8(6)	1609.3(9)	2475(2)	9939(7)	2257(1)	3682(1)
Z	4	4	16	2	2	12	2	4
μ/mm^{-1}	0.20	0.16	0.14	0.13	0.60	0.13	0.60	0.13
Unique reflections, R_{int}	2054, 0.055	2994, 0.102	7079, 0.094	2931, 0.022	3170, 0.03	6301, —	4138, 0.04	3916, 0.045
Reflections with $I > 2\sigma(I)$	1655	2190	5069	2519	1461	4507	1913	1745[a]
R_1 ($I > 2\sigma(I)$)	0.042	0.087	0.061	0.046	0.076	0.074	0.073	0.074[a]
wR_2 (all data)	0.113	0.238	0.158	0.113	—	0.223	—	0.073[a]

[a] $I > 3\sigma(I)$.

Crystallography

Data were collected on an Enraf-Nonius KappaCCD (**1**–**3**) or CAD4 (**4**–**8**) diffractometer, using monochromated Mo-Kα radiation [λ 0.71073 Å]. Crystals were mounted on the diffractometer under a stream of cold nitrogen gas (**1**–**5** and **7**) or were sealed in a Lindemann capillary under argon (**6** and **8**). For **1**–**4** and **6**, refinement was based on all F^2 using SHELXL-97[24]; for **5** and **7** refinement was on F for reflections with $I > 2\sigma(I)$, using MOLEN;[25] whilst for **8** refinement was on F for reflections with $I > 3\sigma(I)$ using SHELX-76.[26] Further details for **1**–**8** are found in Table 10.

CCDC reference numbers 168078–168085.

See http://www.rsc.org/suppdata/dt/b1/b104135p/ for crystallographic data in CIF or other electronic format (for **1**–**4** and **6**).

Acknowledgements

We thank the European Commission for the award of Marie Curie fellowships to S.D. and P.G.M., EPSRC for a studentship for S.M.H. and fellowships for C.D. and B.G. and other support. This paper is dedicated to Professor Hansgeorg Schnöckel as a mark of admiration and (for M.F.L.) friendship.

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