Metallation of Multifunctional Secondary Amines: the Structural Characterisation of the Tripodal Lithium Amides $\{H_3CC[CH_2N(Li)R]_3\}_3$†

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A series of trifunctional amines of the type $H_3CC(CH_2NHR)_3$ [R = CH_3 **2**, C_2H_5 **3**, $CH(CH_3)_2$ **4**, $SiH(CH_3)_2$ **5** or $Si(CH_3)_3$ **6**] has been prepared and lithiated with *n*-butyllithium in hydrocarbon solvents. The tripodal lithium amides were found to be dimeric both in solution and in the solid state. Single-crystal X-ray structure analyses of $\{H_3CC[CH_2N(Li)CH(CH_3)_2]_3\}_2$ **9** and $\{H_3CC[CH_2N(Li)Si(CH_3)_3]_3\}_2$ **11** have established the central Li_6N_6 core in the molecular species. The geometrical requirements of the Li–N array cause a considerable distortion of the hydrocarbon skeleton which links the nitrogen centres.

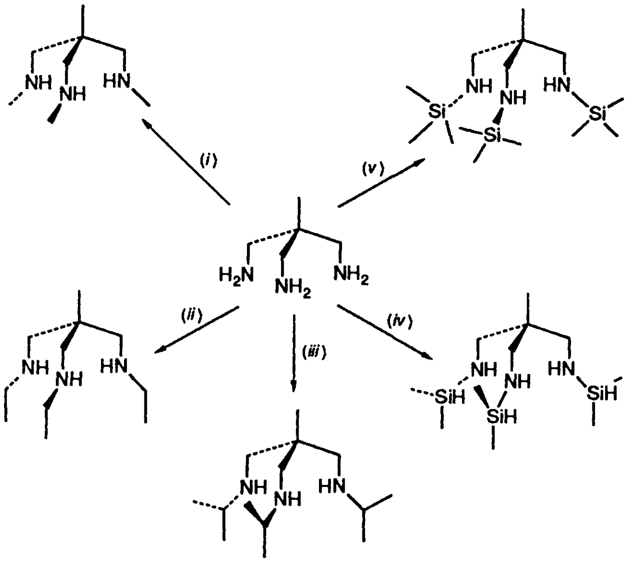
Structural investigations of amidolithium compounds have established a remarkable variety of forms of aggregation for these species in the solid state[1] as well as in solution[2] and have inspired a number of theoretical investigations into the nature of their structures.[3] These appear to be primarily controlled by the steric demands of the organic moieties attached to the nitrogen atoms as well as the presence of additional ligands. Apart from the basic interest in the bonding and structural chemistry of these species, the general interest in this area originates from the role lithium amides play as mild deprotonating reagents in organic synthesis as well as in the preparation of amides of other metals.[4] The elucidation of their structures both in the solid state and in solution may offer some insight into the origins of their reactive behaviour.

While the aggregation of lithium amides derived from monofunctional secondary amines leads to structures in which the Li–N framework displays an energetically (in the simplest approach: electrostatically) almost optimised geometry, the configurational flexibility in lithiated multifunctional amines should be restricted by the constraints imposed by the hydrocarbon skeleton linking the amino groups. Indeed, the structures of multifunctional amides studied to date have revealed patterns of aggregation which are significantly distinct from the well established structural forms in the lithium amide aggregates of metallated monofunctional amines.[5,6]

There has recently been considerable interest in the development of tripodal amides for use in the stabilisation of early transition-metal centres which have one remaining reactive site.[7] In order to achieve this, the synthesis of new, readily accessible, ligand systems as well as an insight into the structural chemistry of the alkali-metallated precursors is essential. Here we report the synthesis of a series of trifunctional amines and their corresponding trilithium amides and discuss their solid-state structures in the light of the principles outlined above.

Results and Discussion

Synthesis of Trifunctional Lithium Amides.—We have studied the metallation reactions of triamines of the type $H_3CC(CH_2NHR)_3$ [R = CH_3 **2**, C_2H_5 **3**, $CH(CH_3)_2$ **4**, $SiH(CH_3)_2$ **5** or $Si(CH_3)_3$ **6**] which are derived from the known primary amine $H_3CC(CH_2NH_2)_3$ **1**.[8] They are obtained in moderate to high yields by the synthetic routes outlined in Scheme 1.[9–12]



Scheme 1 Representation of the conversion of compound **1** into **2**–**6**. (*i*) (*a*) $ClCO_2Et–Na_2CO_3$, (*b*) $LiAlH_4$–thf; (*ii*) (*a*) $(CH_3CO)_2O$, (*b*) $[Me_3O]BF_4–CH_2Cl_2$, (*c*) $NaBH_4$–EtOH;[10] (*iii*) acetone–$NaBH_4$–H^+;[11] (*iv*) $SiMe_2HCl–NEt_3$;[12] (*v*) $SiMe_3Cl–NEt_3$[12]

From the reaction of $H_3CC(CH_2NHR)_3$ with 3 molar equivalents of *n*-butyllithium in hydrocarbon solvents the corresponding trilithium salts $[H_3CC(CH_2NLiR)_3]_2$ **7**–**11** may be isolated in moderate to high yields (60–95%) as colourless crystalline solids. While the lithiation of **2**–**5** is readily achieved at sub-ambient temperatures, the complete metallation of **6** leading to **11** required more vigorous reaction conditions. This may be due to the steric bulk of the trimethylsilyl groups in the free amine. Steric shielding may also be the reason for an increased chemical stability of the trilithium salt **11** in comparison to the other species studied. **CAUTION**: Compounds **7** and **8** were found to be pyrophoric solids which have to be handled with some care, while **11** may be exposed to air for short periods of time without significant decomposition. All the amides prepared could be sublimed at 100 °C and 10^{-4} Torr, although only with considerable decomposition, and generally thermally decompose above *ca.* 150 °C.

X-Ray Crystallographic Study of Compounds **9** *and* **11**.—Single-crystal X-ray structure analyses of compounds **9** and **11**

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: Torr ≈ 133 Pa.

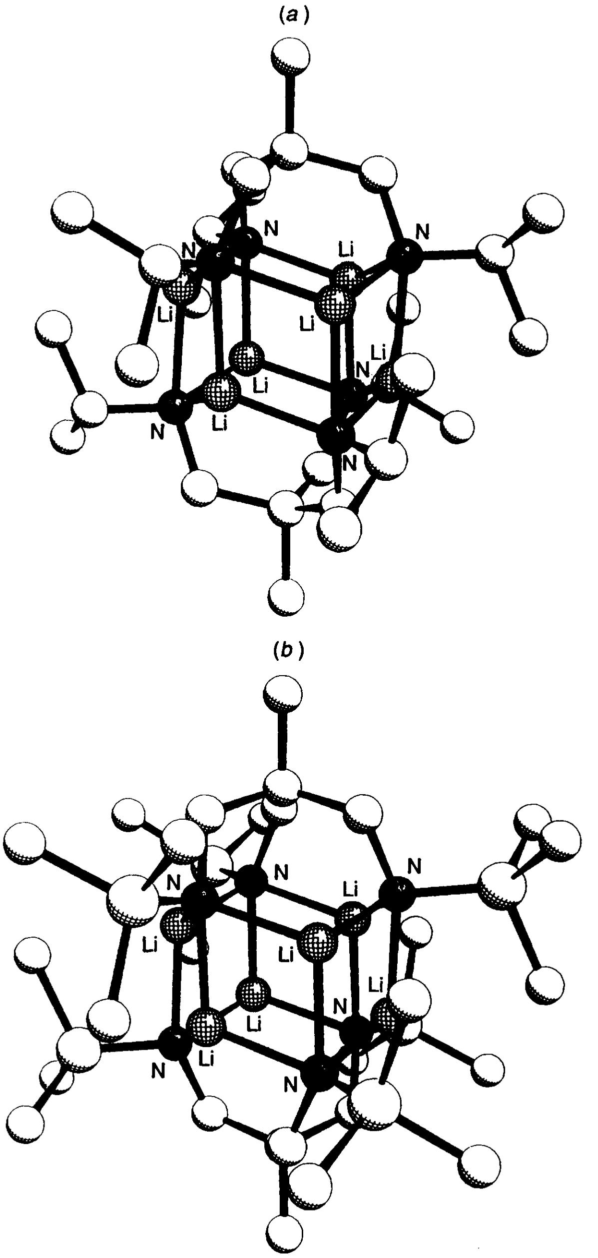

Fig. 1 The molecular structures of the dimeric compounds **9** (*a*) and **11** (*b*) in the solid state. For clarity, the atom numbering is restricted to the Li and N atoms

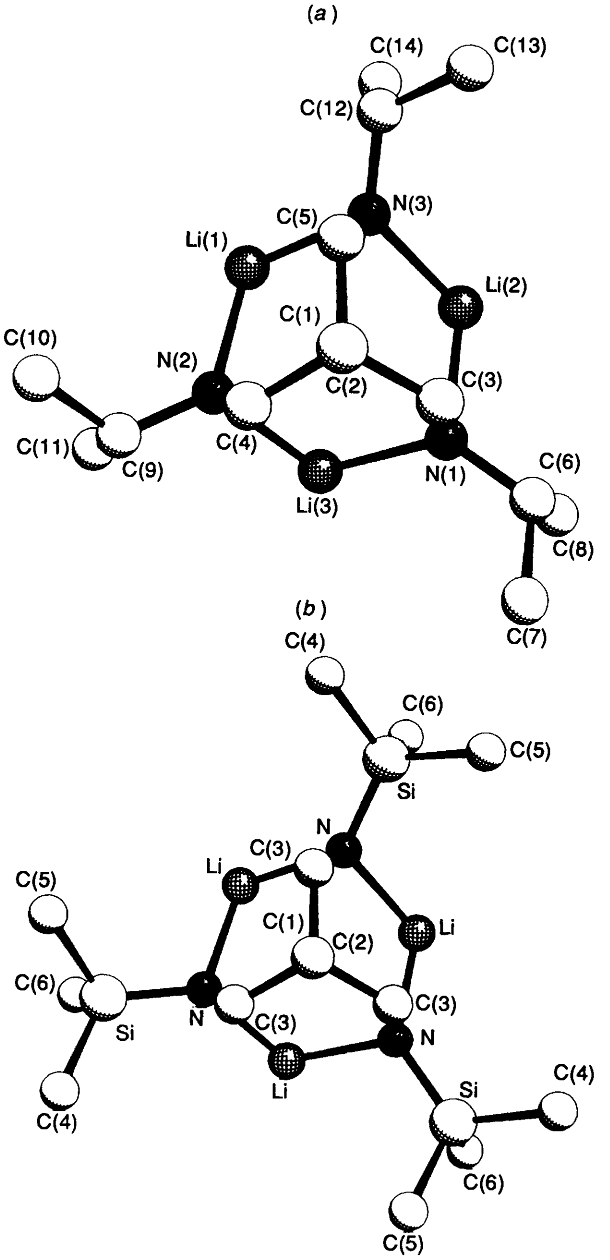

Fig. 2 The structural monomers of compounds **9** (*a*) and **11** (*b*) viewed along the three-fold molecular axis. In the crystals of **11** this coincides with the crystallographic three-fold axis

have established their dimeric structures in the solid state, and they should therefore be formulated as $\{H_3CC[CH_2N(Li)CH(CH_3)_2]_3\}_2$ and $\{H_3CC[CH_2N(Li)Si(CH_3)_3]_3\}_2$, respectively. Their molecular structures are depicted in Fig. 1, while Fig. 2 gives a view of the adamantane-like structure of one half of **9** and **11** along the idealised molecular three-fold axis (which in the crystal structure of **11** coincides with the crystallographic axis).

The principal bond distances and angles of compounds **9** and **11** are listed in Tables 1 and 2. In the case of **11** the point-group symmetry of the molecule (D_{3d}) is reflected in the space group symmetry ($R\bar{3}$) of its crystal, while **9** is slightly distorted from its idealised trigonal point symmetry in the solid and crystallises in the less-symmetrical monoclinic space group *C*2/*c*. Since the symmetry of **11** makes detailed analysis of the structure straightforward we shall concentrate on this species and point out significant structural differences of **9** wherever they occur.

Their respective centre piece comprises two puckered $(LiN)_3$ rings related to each other by a centre of inversion and linked to each other to form a Li_6N_6 cage reminiscent of the structural arrays found by Wade, Snaith and co-workers[13] in a number of iminolithium compounds of the type $(RR'C{=}NLi)_6$. While stacking of $(LiN)_n$ rings is thought to be a common feature in the structures of the latter class of compounds, monofunctional *amidolithiums* $(RR'NLi)_n$ generally do not form stacked structures. This is due to the fact that in cyclic systems such as $\{[(CH_3)_3Si]_2NLi\}_3$ the substituents project above and below the $(LiN)_3$ ring planes inhibiting a close vertical approach of the rings.[14c] For these species the formation of two-dimensional ladder structures is therefore favoured, the only exception being $[H_2C(CH_2)_5NLi]_6$ which forms a cyclic lithium amide ladder to give a structure with a similar topology to that of the $(LiN)_6$ cores of **9** and **11**.[15]

Whereas stacked arrays of rings are thus the exception for simple lithium amides, the presence of a hydrocarbon skeleton linking the nitrogen centres in multifunctional amides restricts the freedom of aggregation of the amido functions and may favour structural patterns which are otherwise rarely observed.

Table 1 Comparison of the principal bond distances (Å) in compounds **9** and **11**

9		**11**	
N(1)–C(3)	1.482(3)	N–C(3)	1.496(5)
N(2)–C(4)	1.477(4)		
N(3)–C(5)	1.481(4)		
N(1)–C(6)	1.494(3)	Si–N	1.725(4)
N(2)–C(9)	1.476(4)		
N(3)–C(12)	1.481(4)		
N(1)–Li(3)	1.982(6)	N–Li	2.010(4)
N(2)–Li(1)	1.976(6)		
N(3)–Li(2)	1.981(5)		
N(1)–Li(2)	2.003(6)	N–Li′	2.014(4)
N(2)–Li(3)	2.013(5)		
N(3)–Li(1)	2.019(6)		
N(1)–Li(1′)	2.105(5)	N–Li″	2.092(4)
N(2)–Li(2′)	2.098(5)		
N(3)–Li(3′)	2.106(5)		

Table 2 Comparison of the principal bond angles (°) in compounds **9** and **11**

9		**11**	
C(3)–N(1)–C(6)	105.4(2)	Si–N–C(3)	108.1(3)
C(4)–N(2)–C(9)	105.6(2)		
C(5)–N(3)–C(12)	105.6(2)		
Li(1)–N(2)–Li(3)	105.1(2)	Li–N–Li′	105.6(2)
Li(1)–N(3)–Li(2)	104.9(2)		
Li(2)–N(1)–Li(3)	104.6(2)		
Li(1)–N(2)–Li(2′)	70.0(2)	Li–N–Li″	69.7(2)
Li(2)–N(3)–Li(3′)	70.0(2)		
Li(3)–N(1)–Li(1′)	69.7(2)		
Li(1)–N(3)–Li(3′)	69.7(2)	Li′–N–Li″	69.8(2)
Li(2)–N(1)–Li(1′)	70.0(2)		
Li(3)–N(2)–Li(2′)	69.6(2)		
C(3)–C(2)–C(4)	114.3(2)	C(3)–C(2)–C(3′)	113.1(3)
C(4)–C(2)–C(5)	114.1(2)		
C(3)–C(2)–C(5)	114.2(3)		
N(2)–Li(1)–N(3)	116.0(2)	N–Li–N′	114.7(2)
N(3)–Li(2)–N(1)	116.7(3)		
N(2)–Li(3)–N(1)	116.2(3)		
N(1)–Li(3)–N(3′)	110.1(2)	N–Li–N″	110.0(2)
N(2)–Li(1)–N(1′)	109.7(2)		
N(3)–Li(2)–N(2′)	110.1(2)		
N(1)–Li(2)–N(2′)	109.8(2)	N′–Li–N″	110.1(2)
N(3)–Li(1)–N(1′)	109.5(3)		
N(2)–Li(3)–N(3′)	109.5(2)		

Indeed, the geometry of each monomer in the structure of compound **11** may be understood as being a compromise between the steric constraints due to the $H_3CC(CH_2)_3$ unit linking the three nitrogen centres and the structural requirements of a $(LiN)_3$ ring. This is best appreciated by comparison with $\{[(CH_3)_3Si]_2NLi\}_3$ in which the three N and Li atoms form a planar ring in which the two-co-ordinate lithium atoms are screened by the bulky $(CH_3)_3Si$ groups.[14] The Li–N distances in this structure range from 1.98 to 2.02 Å. Given an approximate Li–N distance of 2 Å as well as the relative orientation of the N atoms, such a planar arrangement is impossible in **11** (or **9**), and the three Li atoms are forced out of the plane of the amido functions into sterically more exposed positions, generating a distorted adamantane-type cage, a novel feature in the structural chemistry of lithium amides. The mutual steric strain the hydrocarbon skeleton and the (primarily ionic!) $(LiN)_3$ unit exert on each other is reflected in the considerable deviation of the bond angles C(3)–C(2)–C(3′) and C(2)–C(3)–N [113.1(3) and 120.0(4)° respectively] from the expected value for sp^3-hybridised carbon. The same effect is observed in the structure of **9** in which the respective average angles were found to be 114.2 and 119.8°.

The exposed situation of the lithium atoms in the monomeric $H_3CC[CH_2N(Li)Si(CH_3)_3]_3$ unit enables their co-ordination by a third donor atom which in donor solvents such as tetrahydrofuran (thf) is achieved by a solvent molecule.[16] Lithiation in hydrocarbon solvents, however, leads to dimerisation of two of these units to form the central Li/N framework, a situation also found by Bürger and co-workers[5,6] in the structures of the dimeric tris(lithioamido)silanes. This generates a remarkable co-ordination environment of the amido-nitrogen in both compounds of which there are few examples known to date* and which is shown in Fig. 3.

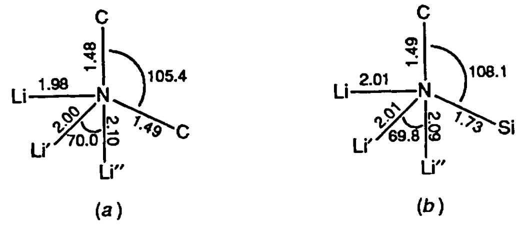

Fig. 3 Schematic representation of the detailed co-ordination environment of the hyperco-ordinate amido-N atoms in compounds **9** (*a*) and **11** (*b*)

In addition to the alkyl/silyl moieties of the secondary amide, three Li atoms are grouped around the nitrogen at almost equal distance [**11**: within the $(LiN)_3$ ring, *d*(Li–N) = 2.010(4) and *d*(Li′–N) = 2.014(4); between the $(LiN)_3$ rings, *d*(Li″–N) = 2.092(4) Å] generating the hyperco-ordinate nitrogen centre. The interbond angles suggest that, while C(3), Si and Li lie approximately at the vertices of a tetrahedron centred at the nitrogen atom, the fourth position is 'shared' by Li′ and Li″ (Li′–N–Li″ 69.8°). The situation is similar in the structure of compound **9**, the equivalent angle having an average value of 70.0°.

Studies of the Lithium Amides in Solution.—In view of the dimeric structure of compounds **9** and **11** in the solid lithium salts, it was of interest to investigate the behaviour of the lithium amides in solution, especially since this is the form in which they would be used in further chemical conversions. In the case of **7**–**10**, the ^1H, ^{13}C and ^7Li NMR spectra recorded in C_6D_6 at 25 °C display only one set of signals which is compatible with a trigonal molecular symmetry. That this situation is retained at low temperatures was established for **9** and **10** at 200 K in $C_6D_5CD_3$ which left the spectra essentially unchanged. On the other hand, the use of *e.g.* $[^2H_8]$thf as solvent leads to considerable temperature-dependent spectral changes due to adduct formation. Since the latter are not yet fully understood the details of these investigations will be reported elsewhere.[16]

Among the amides studied **11** proved to be a special case. Whereas saturated solutions in C_6D_6 prepared at ambient temperatures were too dilute to permit NMR spectroscopy, spectra could readily be obtained from supersaturated solutions prepared by briefly heating the sample to 70 °C and then cooling it to 25 °C. Here, however, the presence of two additional species in minor quantity (<20%) was detected [$\delta(^7Li)$ −0.47, −2.20; external reference LiI–water], along with the major component [$\delta(^7Li)$ −0.69] the other spectral data of which resemble those of **7**–**10**.

The poor solubility of compounds **7**, **8** and **11** in benzene at temperatures near its freezing point prohibited cryoscopic molecular weight determinations, however **9** and **10** were found to be suitable for the method. For these compounds a degree of aggregation of 1.90 ± 0.1 (**9**) (effective molecular weight 495 ± 25) and 1.95 ± 0.1 (**11**) (effective molecular weight 604 ± 30) was found which confirms their dimeric structure in solution.

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* The lithium amides reported in refs. 5, 6 and 15 display this type of co-ordination environment of the nitrogen. Five-co-ordinate nitrogen has also been observed in a number of sodium amides.[17]

Given the NMR spectroscopic results for **7**–**11** as well as the cryoscopic weight determinations of **9** and **10** in benzene, it is not unreasonable to assume a dimeric structure for all these species, not only in the solid state but likewise in solution.

Conclusion

The aim of this study was to establish the nature of a new class of lithiated trifunctional amines which may find general use as amido ligands in the co-ordination chemistry of early transition metals. The novel structural building block observed for the monomer, the trilithioadamantane-type cage, has been found to be part of a dimeric aggregate with a central Li_6N_6 framework the geometrical requirements of which impose a severe strain on the hydrocarbon moieties within the molecule. In reactions with transition-metal halide complexes this stable entity would have to be broken apart in order to permit the co-ordination of the amide to the metal centre. Investigations into the detailed chemistry of such conversions are currently underway.

Experimental

All experiments involving lithium amides were carried out under an inert-gas atmosphere of dry argon using standard (Schlenk) glassware which was flame-dried before use. The solvents used for the lithiations were dried over Na or Na/K alloy, distilled and saturated with argon. The deuteriated solvents used for the NMR spectroscopic measurements were dried over 4 Å molecular sieves. Proton and ^{13}C NMR spectra were recorded on Bruker AC 200 (at 200 and 50.3 MHz, respectively) and AMX 400 (at 400 and 100.6 MHz, respectively) spectrometers, the ^{29}Si and ^{7}Li NMR spectra on a Bruker AC 200 spectrometer (at 39.76 and 77.77 MHz, respectively) with tetramethylsilane and LiI–water (external) as references. Infrared spectra were recorded on Perkin Elmer 1420 and Bruker IFS 25 FT spectrometers. The C, H and N analyses were carried out in the microanalytical laboratory of the chemistry department at Würzburg. The cryoscopic molecular weight determinations of compounds **9** and **11** in benzene were carried out as described in the literature for similar systems.[1f]

The compound $H_3CC(CH_2NH_2)_3$ **1** was prepared from $H_3CC(CH_2OH)_3$ according to a literature procedure;[8] all other chemicals were obtained commercially and used without further purification.

1,1,1-*Tris(methylaminomethyl)ethane* **2**.—To an ice-cold saturated aqueous solution ($100\ cm^3$) of K_2CO_3, $H_3CC(CH_2NH_2)_3$ **1** (5 g, 0.0427 mol) and $ClCO_2Et$ (18 g, 0.1659 mol) were added and the reaction mixture stirred for 20 h. During this time the solution was slowly warmed from 0 to 25 °C. The product separated as a yellow oil which was extracted with diethyl ether ($3 \times 50\ cm^3$). The combined ether fractions were evaporated leaving the tris(urethane) $H_3CC(CH_2NHCO_2Et)_3$ as a light yellow glassy residue. NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), 0.78 (s, CH_3C), 1.20 [t, CH_3CH_2O, $^3J(HH)$ = 7.1], 2.83 [d, CH_2NH, $^3J(HH_N)$ = 7.8 Hz] and 4.06 (q, OCH_2CH_3); $^{13}C\text{-}\{^1H\}$ (50.3 MHz), δ 14.6 (CH_3CH_2O), 18.5 (CH_3C), 41.1 (CCH_3), 43.9 (CH_2N), 60.9 (OCH_2CH_3) and 157.8 ($NHCO_2Et$). The crude product was dissolved in dry thf ($50\ cm^3$) and slowly added to a suspension of $LiAlH_4$ (10 g, 0.263 mol) in thf ($80\ cm^3$). After the complete addition of the urethane the reaction mixture was stirred under reflux for 15 h, then cooled externally with an ice-bath and carefully hydrolysed with water ($10\ cm^3$), 15% NaOH ($10\ cm^3$) and again water ($30\ cm^3$). The cream-coloured aluminium hydroxide formed was extracted with thf ($5 \times 50\ cm^3$), the fractions combined and the solvent removed under vacuum. The residual light yellow oil was distilled at 0.1 Torr yielding 5.6 g (82%) of compound **2** as a colourless liquid; b.p. 45 °C (0.1 Torr). NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 0.64 (s, H_3CC), 2.13 (s, H_3CN) and 2.22 (s, H_2CN); $^{13}C\text{-}\{^1H\}$ (100.6 MHz), δ 21.5 (CH_3C), 37.1 (CH_3N), 37.6 (CH_3C) and 59.8 (CH_2N). IR (neat): 3275m (br), 2960s (sh), 2930s, 2850s, 2795s, 1470s, 1450m, 1395m and 1095m cm^{-1} (Found: C, 60.40; H, 13.40; N, 25.95. Calc. for $C_8H_{21}N_3$: C, 60.35; H, 13.30; N, 26.40%).

1,1,1-*Tris(ethylaminomethyl)ethane* **3**.—The compound $H_3CC(CH_2NH_2)_3$ (2 g, 0.0171 mol) was added dropwise to $(CH_3CO)_2O$ ($20\ cm^3$) and the reaction mixture was subsequently stirred for 6 h at room temperature. On addition of diethyl ether ($100\ cm^3$) the amide precipitated as a white powder. The suspension was stirred for 15 h, the solid filtered off and washed with diethyl ether. The amide which was formed almost quantitatively (yield of crude product 95–100%) was dissolved in dry dichloromethane ($100\ cm^3$). To the solution was added 8 g of $[Me_3O]BF_4$ and the reaction mixture was stirred at 25 °C for 40 h. The solvent was removed and the residue partially dissolved in absolute ethanol ($150\ cm^3$). Solid $NaBH_4$ (5 g, 0.1316 mol) was slowly added to the reaction mixture which was externally cooled with a salt/ice-bath. After stirring at room temperature for 20 h and hydrolysis with water ($15\ cm^3$) and 15% NaOH ($10\ cm^3$), the solvent was removed *in vacuo* and the residue extracted with benzene ($3 \times 30\ cm^3$). The organic solvent was evaporated and the oily residue distilled at 0.1 Torr yielding compound **3** (2 g, 58%) as a colourless liquid, b.p. 52 °C (0.1 Torr). NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 0.70 (s, CH_3C), 0.88 [t, CH_3CH_2, $^3J(HH)$ = 7.1 Hz], 2.32 (s, CCH_2N) and 2.35 (q, CH_2CH_3); $^{13}C\text{-}\{^1H\}$ (100.6 MHz), δ 15.0 (CH_3CH_2), 21.6 (CH_3C), 37.4 (CCH_3), 44.6 (CH_2CH_3) and 57.1 (CCH_2N). IR (neat): 3260m (br), 2960vs, 2925s, 2890s, 2870m, 2820s, 1465s, 1450s, 1375m, 1120vs (br) and 725m (br) cm^{-1} (Found: C, 65.40; H, 13.20; N, 20.90. Calc. for $C_{11}H_{27}N_3$: C, 65.60; H, 13.50; N, 20.85%).

1,1,1-*Tris(isopropylaminomethyl)ethane* **4**.—The compound $H_3CC(CH_2NH_2)_3$ **1** (2 g, 0.0171 mol) was dissolved in a solution of $NaO_2CCH_3{\cdot}3H_2O$ (5.4 g) in acetic acid ($17\ cm^3$), acetone ($20\ cm^3$) and water ($40\ cm^3$) which was externally cooled to 0 °C. Over a period of 1.5 h, $NaBH_4$ (8 g, 0.2105 mol) was added in small portions. After the addition was complete the solution was warmed to 25 °C and stirred for another 30 min. Sodium hydroxide (15%) was added until a pH of 12 was obtained, the aqueous phase extracted with diethyl ether ($4 \times 100\ cm^3$), the ether fractions combined and dried over Na_2SO_4. After evaporation of the solvent the residue was distilled at 0.1 Torr yielding compound **4** (3.8 g, 92%) as a colourless liquid, b.p. 62 °C (0.1 Torr). NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 0.79 (s, CH_3C), 0.95 [d, $(CH_3)_2CH$, $^3J(HH)$ = 6.5 Hz], 2.42 (s, CCH_2N) and 2.60 [spt, $CH(CH_3)_2$]; $^{13}C\text{-}\{^1H\}$ (100.6 MHz), δ 21.6 (CH_3C), 22.6 [$(CH_3)_2CH$], 36.9 CCH_3), 48.8 [$CH(CH_3)_2$] and 54.6 (CH_2N). IR (neat): 3250m (br), 2960vs, 2925s, 2875m, 2835m, 1465s, 1380s, 1170s and 725m (br) cm^{-1} (Found: C, 68.90; H, 13.75; N, 17.10. Calc. for $C_{14}H_{33}N_3$: C, 69.05; H, 13.60; N, 17.25%).

1,1,1-*Tris(dimethylsilylaminomethyl)ethane* **5** *and* 1,1,1-*Tris(trimethylsilylaminomethyl)ethane* **6**.—The compound $H_3CC(CH_2NH_2)_3$ **1** (2 g, 0.0171 mol) and triethylamine (5.2 g, 0.0515 mol) were dissolved in dry diethyl ether ($60\ cm^3$). The appropriate amount (0.0515 mol) of chlorisilane dissolved in diethyl ether ($40\ cm^3$) was added dropwise to the solution which was externally cooled to < 5 °C. The reaction mixture was subsequently stirred for 3 h at room temperature, the solid $[NEt_3H]Cl$ formed in the reaction filtered off through a G-3 frit and the ether evaporated *in vacuo*. The residue was subjected to vacuum distillation yielding the respective trissilylamine (3.8 g, 76% for **5** and 4.9 g, 86% for **6**).

Compound **5**: b.p. 58 °C (0.2 Torr). NMR ($CDCl_3$, 25 °C): ^1H (200 MHz), δ 0.11 [d, $(CH_3)_2SiH$, $^3J(HH_{Si})$ = 3.0], 0.64 (s, CH_3C), 2.49 [d, CCH_2N, $^3J(HH_N)$ = 6.8] and 4.65 [dspt, $NHSiH(CH_3)_2$, $^3J(HH_N)$ = 2.2, $^3J(HH_{Si})$ = 3.0 Hz]; $^{13}C\text{-}\{^1H\}$ (100.6 MHz), δ −1.4 [$Si(CH_3)_2$], 19.4 (CH_3C), 41.3

Table 3 Crystallographic data for compounds **9** and **11**

	9	**11**
Formula	$C_{28}H_{60}Li_6N_6$	$C_{28}H_{72}Li_6N_6Si_6$
M	522.476	703.078
Crystal size/mm	0.3 × 0.3 × 0.25	0.5 × 0.4 × 0.4
Crystal system	Monoclinic	Rhombohedral
Space group	*C*2/*c* (no. 15)	$R\bar{3}$ (no. 148)
Cell dimensions determination	23 reflections, 11 < θ < 14°	23 reflections, 10 < θ < 15°
a/Å	19.30(3)	12.278(1)
b/Å	11.128(6)	12.278(1)
c/Å	19.90(2)	25.376(1)
β/°	130.36(4)	
U/Å^3	3257	3312
Z	4	3
D_c/g cm^{-3}	1.063	1.057
F(000)	1152	1152
μ/cm^{-1}	0.6	2.1
Scan method	ω–θ	ω–2θ
2θ/°	50	60
h, k, l ranges	0–23, 0–13, −23 to 23	0–17, 0–17, −35 to 35
Total no. of reflections	3125	2431
No. unique	3026	2154
No. observed [$F_o > 3\sigma(F_o)$]	1567	960
No. of parameters	181	106
R	0.068	0.054
R′	0.072	0.059
Reflection parameter ratio	8.66	9.06
Residual electron density/e Å^{-3}	+0.264, −0.279	+0.316, −0.282

(*C*CH$_3$) and 48.0 (CH$_2$N); ^{29}Si (39.76 MHz), δ −8.8 [dm, $^1J(^{29}$SiH) = 191.8 Hz]. IR (neat): 3408m (br), 2956s, 2900m, 2860m, 2120s, 2088s, 1464m, 1400m, 1252s, 1092vs (br), 928s, 900vs, 836m, 756m, 732m and 624w cm^{-1} (Found: C, 45.15; H, 11.20; N, 14.40. Calc. for $C_{11}H_{33}N_3Si_3$: C, 45.30; H, 11.40; N, 14.40%).

Compound **6**: b.p. 85 °C (0.5 Torr). NMR (CDCl$_3$, 25 °C): ^{1}H (400 MHz), δ 0.05 [s, (CH$_3$)$_3$Si], 0.71 (s, CH$_3$C) and 2.50 [d, CH$_2$NH, ^3J(HH$_N$) = 7.3 Hz], ^{13}C-{^{1}H} (100.6 MHz), δ 0.2 [(CH$_3$)$_3$Si], 19.7 (*C*H$_3$C), 40.3 (*C*CH$_3$) and 47.6 (CH$_2$N); ^{29}Si-{^{1}H} (39.76 MHz), δ 3.2. IR (neat): 3400m (br), 2950vs, 2890s, 2850m, 1465m, 1450m, 1395s, 1285m, 1248s, 1135s, 1095vs, 745m, 680m and 615w cm^{-1} (Found: C, 50.30; H, 11.85; N, 12.30. Calc. for $C_{14}H_{39}N_3Si_3$: C, 50.40; H, 11.75; N, 12.65%).

Lithiation of Amines **2–5** *and Isolation of the Corresponding Trilithium Salts* **7–10**. *General Procedure*.—A stirred solution of the amine (3 mmol) in pentane (30 cm^3) was cooled to −50 °C and LiBu^n (9 mmol, 3.6 cm^3 of a 2.5 mol dm^{-3} solution in hexane) was slowly added. The reaction mixture was warmed to room temperature and stirred until the evolution of butane had subsided. After gentle refluxing for *ca.* 30 min the solvent volume was decreased to 10 cm^3 and the solution stored at −60 °C. The corresponding lithium salts were isolated as colourless microcrystalline solids. Melting points could not be obtained since decomposition occurred above 180 °C. While ^{7}Li NMR spectroscopy indicated an essentially quantitative conversion in every case, the yields given refer to the isolated solid.

Compound **7**: yield 67%. NMR (C$_6$D$_6$, 25 °C): ^{1}H (200 MHz), δ 1.07 (s, CH$_3$C), 2.33 (s, CH$_3$N) and 3.04 (s, CH$_2$N), ^{13}C-{^{1}H} (50.3 MHz), δ 31.3 (*C*H$_3$C), 42.5 (CH$_3$N), 43.7 (*C*CH$_3$) and 74.5 (CH$_2$N); ^{7}Li (77.77 MHz), δ −1.76 (Found: C, 53.30; H, 10.10; N, 23.30. Calc. for $C_{16}H_{36}Li_6N_6$: C, 54.25; H, 10.25; N, 23.75%).

Compound **8**: yield 63%. NMR (C$_6$D$_6$, 25 °C): ^{1}H (200 MHz), δ 1.06 [t, C*H*$_3$CH$_2$, ^3J(HH) = 7.1 Hz], 1.08 (s, CH$_3$C), 2.76 (q, C*H*$_2$CH$_3$) and 3.12 (s, CH$_2$N); ^{13}C-{^{1}H} (50.3 MHz), δ 15.1 (*C*H$_3$CH$_2$), 32.3 (*C*H$_3$C), 43.3 (*C*CH$_3$), 52.0 (*C*H$_2$CH$_3$) and 71.7 (CH$_2$N); ^{7}Li (77.77 MHz), δ −0.85 (Found: C, 60.00; H, 10.90; N, 19.00. Calc. for $C_{22}H_{48}Li_6N_6$: C, 60.30; H, 11.05; N, 19.15%).

Compound **9**: yield 82%. NMR (C$_6$D$_6$, 25 °C): ^{1}H (200 MHz), δ 1.02 (s, CH$_3$C), 1.19 [d, (C*H*$_3$)$_2$CH, ^3J(HH) = 6.2 Hz], 2.80 [spt, C*H*(CH$_3$)$_2$] and 3.01 (s, CH$_2$N); ^{13}C-{^{1}H} (50.3 MHz), δ 23.2 [(*C*H$_3$)$_2$CH], 33.2 (*C*H$_3$C), 42.6 (*C*CH$_3$), 53.4 [*C*H(CH$_3$)$_2$] and 64.2 (CH$_2$N); ^{7}Li (77.77 MHz), δ −0.74 (Found: C, 64.30; H, 11.55; N, 16.20. Calc. for $C_{28}H_{60}Li_6N_6$: C, 64.35; H, 11.60; N, 16.05%).

Compound **10**: yield 80%. NMR (C$_6$D$_6$, 25 °C): ^{1}H (200 MHz), δ 0.28 [d, (C*H*$_3$)$_2$SiH, ^3J((HH$_{Si}$) = 3.0 Hz] 0.62 (s, CH$_3$C), 3.22 (s, CH$_2$N) and 4.32 [spt, *H*Si(CH$_3$)$_2$]; ^{13}C-{^{1}H} (50.3 MHz), δ −2.0 [(CH$_3$)$_2$SiH], 29.8 (*C*H$_3$C), 44.1 (*C*CH$_3$) and 58.2 (CH$_2$N); ^{7}Li (77.77 MHz), δ −0.77; ^{29}Si (39.76 MHz), δ −16.4 (Found: C, 42.60; H, 9.60; N, 13.20. Calc. for $C_{22}H_{60}Li_6N_6Si_6$: C, 42.70; H, 9.75; N, 13.60%).

Lithiation of Compound **6** *and Isolation of* **11**.—The compound H$_3$CC[CH$_2$NHSi(CH$_3$)$_3$]$_3$ **6** (0.8 g, 2.4 mmol) in toluene (20 cm^3) was cooled to −20 °C. To the stirred solution LiBu^n (7.2 mmol, 2.8 cm^3 of a 2.5 mol dm^{-3} solution in hexane) was slowly added. The reaction mixture was warmed to room temperature and subsequently stirred at 90 °C for 15 min. On slow cooling the lithium salt crystallised in large, rhombohedrally shaped, colourless crystals. Isolated yield: 0.8 g (95%). NMR (C$_6$D$_6$, 25 °C): ^{1}H (200 MHz), δ 0.44 [s, (CH$_3$)$_3$Si], 0.89 (s, CH$_3$C) and 3.23 (s, CH$_2$N); ^{13}C-{^{1}H} (50.3 MHz), δ 1.9 [(CH$_3$)$_3$Si], 32.0 (*C*H$_3$C), 45.4 (*C*CH$_3$) and 59.2 (CH$_2$N); ^{7}Li (77.77 MHz), δ −0.69; ^{29}Si (39.76 MHz), δ 2.1 (Found: C, 47.45; H, 10.60; N, 12.25. Calc. for $C_{28}H_{72}Li_6N_6Si_6$: C, 47.85; H, 10.35; N, 11.95%).

Determination and Refinement of the Structures of Compounds **9** *and* **11**.—Both compounds crystallise as clear colourless crystals of which those of **9** are irregularly block-shaped (from pentane) while those of **11** have a regular rhombohedral habit (from toluene). For the data collection small crystals were sealed under argon in Lindemann capillaries. The respective space groups and cell constants were determined on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ 0.709 30 Å) which was subsequently used for the data collection. Data collection was carried out for both crystals at a temperature of 223 K. Cell constants were obtained by a least-squares fit of 23 high-angle reflections using the CAD centring routines and are listed along with other crystallographic data and data collection parameters in Table 3. The crystal stability and orientation was checked by measuring standard reflections every hour. All calculations were perfomed on a Micro-VAX computer using the program package SDP[18] from Enraf-Nonius.

For compound **9** intensity data were corrected for Lorentz and polarisation effects. An empirical absorption correction (ψ-scan method) was applied, the minimum transmission being 87.82% (maximum 99.69%). The structure was solved by direct methods (SHELXS 86).[19] Atomic coordinates (Table 4) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (unit weights). The positions of all hydrogen atoms were calculated according to ideal geometry (C–H 0.95 Å) and were taken for the structure-factor calculation.

For compound **11** intensity data were corrected for Lorentz and polarisation effects. During the measurement the crystal showed a total loss of intensity of 6.2%, which was corrected with the program DECAY.[18] No absorption correction was performed. The structure was solved by Patterson methods (SHELXS 86).[19] Atomic coordinates (Table 5) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (unit weights). All hydrogen atoms

Table 4 Positional parameters with estimated standard deviations (e.s.d.s) in parentheses for compound **9**

Atom	*x*	*y*	*z*
N(1)	0.1612(2)	−0.0013(4)	0.3397(2)
N(2)	0.0087(2)	−0.1515(3)	0.3399(2)
N(3)	0.0099(2)	0.1530(3)	0.3399(2)
C(1)	0.2045(3)	0.0000(6)	0.5568(2)
C(2)	0.1364(2)	0.0000(5)	0.4546(2)
C(3)	0.1958(2)	0.0274(5)	0.4297(2)
C(4)	0.0952(3)	−0.1278(4)	0.4295(2)
C(5)	0.0684(3)	0.1006(4)	0.4297(2)
C(6)	0.2411(2)	0.0106(5)	0.3444(2)
C(7)	0.3115(3)	−0.0899(5)	0.3956(3)
C(8)	0.2105(2)	0.0169(5)	0.2513(2)
C(9)	−0.0208(2)	−0.2714(4)	0.3445(2)
C(10)	−0.0556(3)	−0.2764(5)	0.3955(3)
C(11)	−0.0958(3)	−0.3228(4)	0.2511(3)
C(12)	−0.0310(3)	0.2619(4)	0.3443(2)
C(13)	0.0346(3)	0.3670(5)	0.3953(3)
C(14)	−0.1121(3)	0.3056(5)	0.2515(3)
Li(1)	−0.0623(4)	−0.0010(8)	0.2989(4)
Li(2)	0.0796(4)	0.1416(7)	0.2988(4)
Li(3)	0.0796(4)	−0.1418(7)	0.2983(4)

Table 5 Positional parameters with e.s.d.s in parentheses for compound **11**

Atom	*x*	*y*	*z*
Si	0.099 35(9)	0.768 4(1)	0.107 09(5)
N	0.219 8(3)	0.735 2(3)	0.112 8(1)
C(1)	0.333	0.667	−0.017 6(3)
C(2)	0.333	0.667	0.043 5(3)
C(3)	0.278 4(3)	0.750 5(3)	0.059 6(2)
C(4)	0.142 8(4)	0.920 0(4)	0.073 4(3)
C(5)	−0.037 4(5)	0.647 7(5)	0.068 2(2)
C(6)	0.040 0(4)	0.773 7(5)	0.174 2(2)
Li	0.161 0(6)	0.559 0(6)	0.138 2(3)

could be located in the Fourier difference map and were refined isotropically. Hydrogen atoms H(1), H(3A) and H(3B) were refined with fixed thermal parameters.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

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