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SYNTHESES AND CRYSTAL STRUCTURES OF THE DIMERS OF A BIS(LITHIOAMINO)- AND A TRIS(LITHIOAMINO)-SILANE CONTAINING ELECTRON-DEFICIENT Li_4N_4 AND Li_6N_6 CLUSTERS

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Summary

The syntheses of $[\text{t-BuN(H)}]_3\text{SiPh}$ and $\{[\text{t-BuN(Li)}]_3\text{SiPh}\}_2$ (IV) are described, and their ^{1}H NMR, infrared and Raman spectra are reported. Crystals of $\{[\text{t-BuN(Li)}]_2\text{SiMe}_2\}_2$ (III) belong to the space group $C2/c$ with a 18.799(5), b 8.963(3), c 18.672(5) Å, β 112.19(2)°, $Z = 4$ and $R = 0.084$. There is a Li_4 bisphenoid at the core of the dimers, the two pairs of Li_3 faces being linked by the two N–Si–N bridges. The molecular symmetry is roughly $\bar{4}2m$ (D_{2d}) although only two-fold crystallographic symmetry is required. The dimers IV are centered on $\bar{1}$ symmetry sites of the space group $P\bar{1}$ with a 10.234(2), b 10.406(2), c 11.476(3) Å, α 61.43(1), β 82.16(1), γ 73.28(1)°, $Z = 1$ and $R = 0.057$. Each nitrogen atom is bonded to a Li_3 face of a Li_6 trigonal antiprism with the Si atoms over the remaining two unbridged faces. The overall symmetry approaches $\bar{3}m$ (D_{3d}). Factors determining the shapes of the Li_4N_4 and Li_6N_6 clusters of III and IV, respectively, are discussed.

Introduction

Oligomerization of *N*-metallated aminosilanes is well known. Whereas cyclic (e.g. $[\text{LiN(SiMe}_3)_2]_n$: $n = 2$ [1]; $n = 3$ [2,3]) or polymeric (e.g. $[\text{NaN(SiMe}_3)_2]_\infty$ [4]) structures with electron precise N → Li_2/Na_2 bonding have been found for $N(SiMe_3)_2$ derivatives, *N*-metallation of di- and tri-aminosilanes has afforded novel main group cluster compounds with electron-deficient N → Li_3/Na_3 bridging. Structural studies of $\{[\text{Me}_3\text{SiN(Na)}]_2\text{SiMe}_2\}_3$ (I) [5] and $\{[\text{Me}_3\text{SiN(Li)}]_3\text{SiR}\}_2$ (II) (a, R = Me; b, R = t-Bu; c, R = Ph) [6] have established their respective trimeric and dimeric natures in the solid state. While the cores of both I and II contain six metal atoms, their geometries are distinctly different. For I, five Na atoms are arranged in a distorted trigonal-bipyramidal fashion about the sixth while trigonal antiprismatic arrays of Li atoms are found for II. Whereas both N → Na_2 and

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$Na \rightarrow Na_3$ bonding is exhibited by I, only $N \rightarrow Li_3$ interactions are found in the more symmetric Li_6N_6 fragments of II. These Li_6N_6 fragments are related to an icosahedron which has been distorted so as to shorten the Li–N bonds while relaxing the Li...Li and N...N contacts.

Nitrogen coordination does not lead to coordinately saturated metal atoms, and possible $SiMe_3$–Na and $SiMe_3$–Li interactions were noted. Since such contacts are believed to contribute to the stability of a given metal amide structure [7], the effect of t-Bu and Me_3Si substituents on the structure and bonding in these compounds is of interest. Thus X-ray studies have been performed on $\{[t\text{-BuN(Li)}]_2SiMe_2\}_2$ (III) and $\{[t\text{-BuN(Li)}]_3SiPh\}_2$ (IV), and the results are reported below. Compound III was generated (but not isolated) more than twenty years ago [8], but the preparations of IV and the parent amine $[t\text{-BuN(H)}]_3SiPh$ (V) are described here for the first time. Physical properties of these compounds are also discussed.

Synthesis and properties

The dilithio derivative of dimethylbis(t-butylamino)silane (III) was first prepared by Fink [8] and used for the synthesis of cyclodisilazanes. Subsequently it was employed in the synthesis of four-membered siladiazametallacycles $Me_2Si(N\text{-}t\text{-}Bu)_2M$ with M = Ti [9,10], Zr [11], Sn [12], Pb [13] as well as diazasilaphosphetidines [14], though to our knowledge it has never been characterized.

The synthesis of III is easily achieved by the lithiation of $Me_2Si[t\text{-BuN(H)}]_2$ [8] with BuLi in petroleum ether; after removal of the solvent, III is isolated by sublimation in vacuo in a yield of 72%. Some of its physical properties and the NMR spectra are set out in Table 1.

The triaminosilane $PhSi[t\text{-BuN(H)}]_3$ (V) has not previously been mentioned in the literature. It was obtained in a two-step synthesis starting from $PhSiCl_3$ and $t\text{-BuNH}_2$ (eq. 1, 2):

$$PhSiCl_3 + 4\ t\text{-BuNH}_2 \rightarrow 2\ t\text{-BuNH}_3Cl + \underset{\text{(VI)}}{PhSi(Cl)[t\text{-BuN(H)}]_2} \qquad (1)$$

$$VI + t\text{-BuN(H)Li} \rightarrow LiCl + V \qquad (2)$$

The yields of reactions 1 and 2 were 65 and 77%, respectively. Lithiation of V

TABLE 1

PHYSICAL PROPERTIES AND NMR SPECTRA OF COMPOUNDS III TO VI

	M.p. (°C)	B.p. (°C/Torr)	^{1}H NMR (δ(^{1}H)(ppm) [a]			δ(^{7}Li) (ppm) [b]
			$SiMe_2$	SiPh	t-Bu	
III	≥110 (dec.)	$90/10^{-3}$ (subl.)	0.32		1.24	1.9
IV	≥235 (dec.)	$180/10^{-3}$ (subl.)		7.35 8.52	1.42	2.4
V	-	96–98/1		7.22 7.69	1.17	-
VI	42	114–115/1		7.18 7.60	1.17	-

[a] III and IV in C_6D_6, int. std. TMS, V and VI in CCl_4, int. std. TMS. [b] In n-hexane, ext. std. aqueous LiI.

with BuLi afforded colourless crystals of IV which slowly precipitated from solution. Physical properties and NMR data are set out in Table 1. Infrared and Raman data are given in the Experimental. The ^{7}Li NMR spectra of solutions prepared from BuLi and the respective amine indicate that multilithiation occurs even at relatively low BuLi/amine ratios. Thus ^{7}Li signals at 1.8 and 1.9 ppm are observed from a solution prepared from BuLi and $Me_2Si(t\text{-}BuNH)_2$ in a 1/1 ratio, the former signal disappearing upon further addition of BuLi. Similarly, V and BuLi 1/1 give rise to signals at 1.8, 2.4 and 3.0 ppm, the signal at 2.4 ppm belonging to IV.

III, IV and V are colourless, crystalline solids, and compounds III–VI are soluble in non-polar organic solvents. III and IV are rapidly decomposed by oxygen and water.

X-ray structural determinations

Crystals of III and IV were grown from solutions in petroleum ether and sealed in glass capillaries under argon. Following preliminary photographic studies, cell constants and intensity data were determined with a Siemens AED 1 diffractometer

TABLE 2

CRYSTALLOGRAPHIC DATA

	III	IV
Formula	$\{[t\text{-}BuN(Li)]_2SiMe_2\}_2$	$\{[t\text{-}BuN(Li)]_3SiPh\}_2$
M	428.56	678.76
Space group	$C2/c$	$P\bar{1}$
a (Å)	18.799(5)	10.234(2)
b (Å)	8.963(3)	10.406(2)
c (Å)	18.672(5)	11.476(3)
α (°)	90.00	61.43(1)
β (°)	112.19(2)	82.16(1)
γ (°)	90.00	73.28(1)
Z	4	1
D_x (g/cm^3)	0.977	1.096
T (°C)	23	24
Quadrants	hkl, $\bar{h}kl$ $hk\bar{l}$, $\bar{h}k\bar{l}$	hkl, $h\bar{k}l$ $hk\bar{l}$, $h\bar{k}\bar{l}$
2θ-limits (°)	4–55	4–55
Reflections measured	7353	6288
Unique reflections	3356	5976
Unique $F \geqq 4\sigma(F)$	2317	4599
μ(Mo-K_α) (cm^{-1})	1.3	1.1
Crystal size (mm)	0.22×0.43×1.04	0.39×0.40×1.28
Transmission	0.934–0.973	0.946–0.964
Monitor correction	0.993–1.005	1.000–1.006
Parameters	144	282
$\lvert\xi/\sigma\rvert_{max}$	0.15	0.05
Final $\Delta\rho$(e/Å^3)	0.38 to −0.30	0.42 to −0.20
R [a]	0.084/0.117	0.057/0.074
R_w [a]	0.107/0.110	0.076/0.078

[a] $R = \Sigma\Delta/\Sigma|F_0|$, $R_w = [\Sigma w\Delta^2/\Sigma w|F_0|^2]^{1/2}$, $\Delta = ||F_0| - |F_c||$, $w = 1/(\sigma^2(F) + 0.0004F^2)$, first value for $F \geqq 4\sigma(F)$, second with all unique reflections.

TABLE 3

POSITIONAL AND EQUIVALENT [a] ISOTROPIC THERMAL PARAMETERS FOR III

Atom	x	y	z	U
Si	0.37473(5)	0.5714(1)	0.12613(5)	0.0585(4)
N(1)	0.4028(1)	0.4653(3)	0.2096(1)	0.052(1)
N(2)	0.4612(1)	0.6656(3)	0.1509(1)	0.053(1)
C(1)	0.3439(3)	0.4651(6)	0.0326(2)	0.103(2)
C(2)	0.2920(2)	0.6998(6)	0.1142(3)	0.109(2)
C(3)	0.3548(2)	0.3511(5)	0.2276(2)	0.074(2)
C(4)	0.3972(3)	0.2931(7)	0.3087(3)	0.134(3)
C(5)	0.2775(4)	0.405(1)	0.2189(5)	0.205(6)
C(6)	0.3433(6)	0.2185(8)	0.1747(5)	0.231(7)
C(7)	0.4794(2)	0.7779(4)	0.1029(2)	0.072(2)
C(8)	0.5577(4)	0.8397(8)	0.1446(4)	0.168(4)
C(9)	0.4723(6)	0.7194(8)	0.0250(4)	0.236(7)
C(10)	0.4225(5)	0.9048(8)	0.0795(6)	0.221(7)
Li(1)	0.4956(3)	0.4531(6)	0.3110(3)	0.056(2)
Li(2)	0.5588(3)	0.6780(7)	0.2445(3)	0.062(2)

[a] $U = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star \bar{a}_i \cdot \bar{a}_j$.

TABLE 4

POSITIONAL AND EQUIVALENT [a] ISOTROPIC THERMAL PARAMETERS FOR IV

Atom	x	y	z	U
Si	0.86809(4)	0.21703(5)	0.86337(4)	0.0361(2)
N(1)	0.8095(1)	0.1405(2)	1.0276(1)	0.0439(6)
N(2)	0.8904(1)	0.0723(1)	0.8196(1)	0.0434(6)
N(3)	1.0334(1)	0.2238(1)	0.8796(1)	0.0434(6)
C(1)	0.6901(2)	0.2020(2)	1.0906(2)	0.0561(8)
C(2)	0.6907(3)	0.3531(3)	1.0807(3)	0.094(2)
C(3)	0.5553(2)	0.2235(3)	1.0344(3)	0.097(2)
C(4)	0.6913(3)	0.0877(4)	1.2394(3)	0.111(2)
C(5)	0.8383(2)	0.0616(2)	0.7120(2)	0.0569(9)
C(6)	0.6854(3)	0.0638(3)	0.7295(3)	0.097(2)
C(7)	0.9140(3)	−0.0935(3)	0.7188(3)	0.099(2)
C(8)	0.8603(4)	0.1815(4)	0.5752(2)	0.100(2)
C(9)	1.1145(2)	0.3329(2)	0.8022(3)	0.075(1)
C(10)	1.1082(3)	0.3849(4)	0.6542(3)	0.141(2)
C(11)	1.2645(3)	0.2579(3)	0.8448(4)	0.123(2)
C(12)	1.0750(4)	0.4692(4)	0.8300(6)	0.177(4)
C(13)	0.7488(2)	0.4088(2)	0.7494(2)	0.0490(7)
C(14A)	0.7581(5)	0.5362(6)	0.7636(8)	0.062(2)
C(15A)	0.6788(6)	0.6809(6)	0.6886(9)	0.080(3)
C(16A)	0.597(1)	0.708(1)	0.594(1)	0.084(4)
C(17A)	0.580(1)	0.5952(9)	0.5798(7)	0.088(4)
C(18A)	0.6605(7)	0.4457(6)	0.6557(7)	0.067(2)
C(14B)	0.7693(7)	0.5476(7)	0.687(1)	0.077(3)
C(15B)	0.674(1)	0.6775(9)	0.608(1)	0.100(4)
C(16B)	0.547(1)	0.674(1)	0.590(1)	0.079(5)
C(17B)	0.5187(7)	0.533(1)	0.6450(9)	0.076(4)
C(18B)	0.6139(6)	0.4035(7)	0.7257(8)	0.061(3)
Li(1)	0.9116(3)	−0.0622(4)	1.1818(3)	0.051(1)
Li(2)	1.0125(3)	−0.1559(4)	0.9317(3)	0.054(1)
Li(3)	1.1881(3)	0.0341(3)	1.0012(3)	0.052(1)

[a] $U = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^\star a_j^\star \bar{a}_i \cdot \bar{a}_j$.

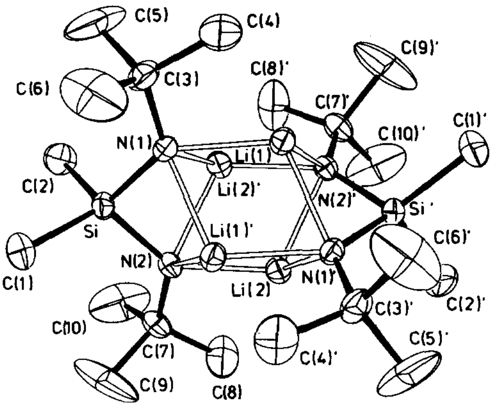

Fig. 1. A perspective drawing of $\{[\text{t-BuN(Li)}]_2\text{SiMe}_2\}_2$ with 20% probability thermal ellipsoids.

employing Zr-filtered Mo-K_α (λ 0.71073 Å) radiation as described previously [6]. Crystal data and details of the data collection are given in Table 2.

The Si atom and its nearest neighbours were located by multisolution direct methods for III and by Patterson techniques for IV. The remaining non-hydrogen atoms were taken from electron density maps. After anisotropic refinement of these atoms, hydrogen atoms were included in calculated positions (C–H 0.95 Å, H–C–H 109.5°, phenyl H on external C–C–C bisector), assigned group isotropic thermal parameters, and allowed to ride on their respective carbon atoms. For IV, a second orientation was found for the phenyl group, and the two groups were refined as if they possessed a common *ipso* carbon; the final value for the occupancy parameter, 0.539(9), indicated essentially 50/50 disorder for this group. Full-matrix least squares refinement converged in both cases, and further details of the refinements are listed in Table 2. Positional parameters are given in Tables 3 and 4, and the numbering schemes are defined in Figs. 1 and 2. The final difference Fourier syntheses were void of chemically significant features. The data were corrected for

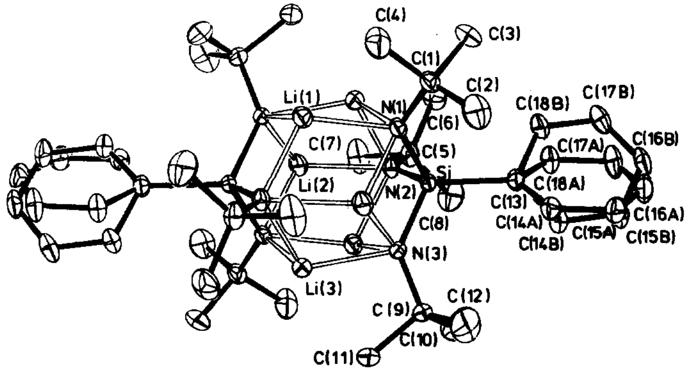

Fig. 2. A perspective drawing of $\{[\text{t-BuN(Li)}]_3\text{SiPh}\}_2$ with 20% probability thermal ellipsoids.

absorption, but no extinction corrections were deemed necessary *. Despite the high thermal motion in III and disorder in IV, it was not considered necessary to carry out refinement in the alternative non-centrosymmetic space groups. Programs used included SHELX-76 [15] and ORTEP-II [16].

Description of the crystal structures

{[t-BuN(Li)]$_2$SiMe$_2$}$_2$ (III)

Compound III crystallizes as discrete dimeric molecules. Each dimer is located on a crystallographic two-fold axis and possesses approximately $\bar{4}2m$ (D_{2d}) symmetry, the S_4 axis coinciding with the Si–Si′ vector. A bisphenoid of lithium atoms is found at the core of III, the two Li(1)–Li(2) type edges (2.852(8) Å) being much longer than the average of the other four (2.32(2) Å). Each nitrogen atom is engaged in $N \rightarrow Li_3$ bonding, and each $[N(t\text{-}Bu)]_2SiMe_2$ species spans two Li_3 triangles which are fused along a long Li–Li edge. The dihedral angle formed by the normals to each such pair of Li_3 faces is 77.7(5)°, an angle, so much smaller than the tetrahedral angle (109.47°), indicating a considerable flattening of the Li_4 moieties across the long edges.

In line with the above-mentioned molecular symmetry, the dihedral angle between the normals to the planes defined by N(1),N(2),Li(1),Li(2) and C(3),N(1), Si,N(2),C(7) (both planar within 0.02 Å) is only 4.5(5)°, and these planes are essentially perpendicular to their two-fold related counterparts (dihedral angles of 89.5(5) and 89.6(5)°, respectively). Thus the atoms of the Li_4N_4 fragment occupy the vertices of a dodecahedron. Interestingly the two other structurally investigated compounds containing Li_4N_4 fragments, $(Ph_2C{=}NLi \cdot NC_5H_5)_4$ (VII) [17] and $[Li\overline{NCMe_2(CH_2)_3C}Me_2]_4$ (VIII) [18], display pseudocubane and planar eight-membered ring geometries, respectively. In accord with the Li–N bonding in III and VII being electron-deficient (five-coordinated nitrogen) but electron-precise in VIII (four-coordinate nitrogen) the mean Li–N distances in III (2.073 Å) and VII (2.090 Å) are longer than in VIII (2.00 Å). Bond distances and angles are given in Tables 5 and 6.

Considering the Li–N bonding to each fused pair of Li_3 faces in III, the distances to the unfused corners (Li(1) and Li(2) in the asymmetric unit) are on average shorter (2.02(2) Å) than those to the fused corners (2.10(2) Å). Nevertheless the projection of the nitrogen atoms on each Li_3 face lies slightly to the fused-edge side of their mid-points (Fig. 3). Thus the N–Si–N bridge is even too small to span ideally two Li_3 faces of these flattened Li_4 bisphenoids, and the trend in the Li–N bond distances probably results from the fact that the fused edge of the two Li_3 triangles cannot contract as far as the other edges.

Further contraction appears to be prohibited by the non-bonded contacts Si–Li(1′) and Si–Li(2′) (average 2.48(4) Å). These are surprisingly short in the light of the Si–Li distances in $(LiSiMe_3)_6$, average 2.69(6) Å [19], and $[Me_3SiLi(TMEDA)]_2TMEDA$, 2.70(1) Å [20]. Thus a small N–Si–N bond angle (95.3(1)°) is

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* F_0, F_c lists, tables of hydrogen coordinates and anisotropic thermal parameters may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, by quoting the deposit number CSD-51716, the names of the authors, and the literature reference.

TABLE 5

SELECTED DISTANCES (Å) IN $\{[\text{t-BuN(Li)}]_2\text{SiMe}_2\}_2$

Si-N(1)	1.729(3)	C(7)-C(8)	1.489(6)	N(1)-Li(1)	2.036(6)
Si-N(2)	1.733(3)	C(7)-C(9)	1.505(6)	N(1)-Li(2)	2.003(6)
Si-C(1)	1.878(4)	C(7)-C(10)	1.508(8)	Li(1)-Li(2)	2.852(8)
Si-C(2)	1.879(4)	C(4)-Li(1)	2.328(9)	Li(1)-Li(1)'	2.35(1)
N(1)-C(3)	1.485(4)	C(8)-Li(2)	2.355(9)	Li(1)-Li(2)'	2.320(8)
N(2)-C(7)	1.470(4)	N(1)-Li(1)' [a]	2.089(7)	Li(2)-Li(2)'	2.30(1)
C(3)-C(4)	1.512(6)	N(1)-Li(2)'	2.103(7)	Si-Li(1)'	2.507(6)
C(3)-C(5)	1.481(7)	N(2)-Li(1)'	2.087(6)	Si-Li(2)'	2.456(6)
C(3)-C(6)	1.508(8)	N(2)-Li(2)'	2.129(6)		

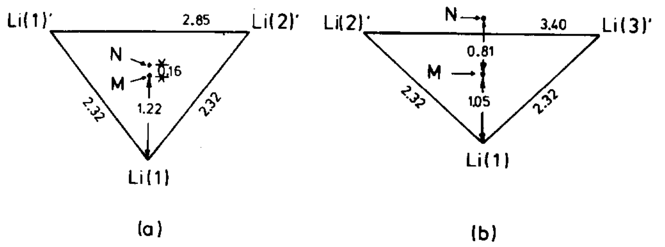
[a] Coordinates of primed atoms are related to those in the asymmetric unit by x', y', $z' = 1 - x$, y, $0.5 - z$.

TABLE 6

SELECTED BOND ANGLES (°) IN $\{[\text{t-BuN(Li)}]_2\text{SiMe}_2\}_2$

N(1)-Si-N(2)	95.3(1)	Si-N(1)-Li(1)' [a]	81.5(2)
C(1)-Si-C(2)	104.5(2)	Si-N(1)-Li(2)'	79.1(2)
N(1)-Si-C(1)	116.1(2)	Si-N(2)-Li(1)'	81.5(2)
N(1)-Si-C(2)	113.6(2)	Si-N(2)-Li(2)'	78.2(2)
N(2)-Si-C(1)	115.1(2)	C(3)-N(1)-Li(1)	97.6(3)
N(2)-Si-C(2)	112.6(2)	C(7)-N(2)-Li(2)	98.4(3)
Si-N(1)-C(3)	125.4(2)	C(3)-N(1)-Li(1)'	133.0(3)
Si-N(2)-C(7)	125.5(2)	C(3)-N(1)-Li(2)'	132.6(3)
N(1)-C(3)-C(4)	109.2(3)	C(7)-N(2)-Li(1)'	133.0(3)
N(2)-C(7)-C(8)	110.3(3)	C(7)-N(2)-Li(2)'	133.3(3)
N(1)-C(3)-C(5)	114.0(4)	Li(1)'-N(1)-Li(2)'	85.8(2)
N(1)-C(3)-C(6)	110.1(4)	Li(1)'-N(2)-Li(2)'	85.1(2)
N(2)-C(7)-C(9)	113.2(4)	Li(1)-N(1)-Li(1)'	69.3(2)
N(2)-C(7)-C(10)	113.1(4)	Li(1)-N(1)-Li(2)'	68.1(2)
C(4)-C(3)-C(5)	110.2(5)	Li(2)-N(2)-Li(1)'	69.1(2)
C(4)-C(3)-C(6)	106.0(5)	Li(2)-N(2)-Li(2)'	67.5(3)
C(5)-C(3)-C(6)	107.0(6)	N(1)'-Li(1)-N(2)'	75.5(2)
C(8)-C(7)-C(9)	110.1(5)	N(1)'-Li(2)-N(2)'	74.4(2)
C(8)-C(7)-C(10)	108.9(5)	N(1)-Li(1)-N(1)'	110.4(3)
C(9)-C(7)-C(10)	100.8(6)	N(1)-Li(1)-N(2)'	110.8(3)
Si-N(1)-Li(1)	136.9(2)	N(2)-Li(2)-N(1)'	111.5(3)
Si-N(2)-Li(2)	135.9(2)	N(2)-Li(2)-N(2)'	112.2(3)

[a] See Table 5.



(a) (b)

Fig. 3. Average dimensions (Å) of the Li_3 faces in III (a) and IV (b). Midpoints and projection of the bridging nitrogen atom are denoted by M and $\dot{N}$ respectively. Atom numbering is given solely for orientational purposes.

required to relieve Si–Li repulsion. This angle is more like that in spirocyclic $\mathrm{M[(N(t\text{-}Bu)_2SiMe_2]_2}$ compounds (M Ti, 92.4(2)°; M = Zr, 94.8(1)° [11]) than that in the sodio derivative I, 111.9(7)°.

The spirocyclic compounds possess both average Si–N distances and C–Si–N angles (M = Ti: 1.742(10) Å, 130.5(5)°; M = Zr: 1.753(2) Å, 130.0(2)°) which are in general significantly larger than those in III (1.731(3) Å and 125.4(2)°). On the other hand, shorter central Si–N bond lengths, 1.712(3) Å, are found in the planar Si–N–Si–N–Si fragment of I which contains two five-coordinate nitrogen atoms. Even the Si–N–Si angles in this fragment, 125.7(2)°, agree excellently with the average C–N–Si bond angle in III. While the central Si–N distances in the other Si–N–Si–N–Si units of I are comparably short, these units are grossly non-planar, possess both four- and five-coordinate nitrogen atoms, and display both smaller (122.6(2)°) and larger (140.0(2)°) Si–N–Si bond angles.

Each of the three crystallographically independent $\mathrm{Me_3SiN}$ groups in I is oriented differently with respect to the corresponding central Si–N linkage, an observation consistent with the low barrier expected for internal rotation of the $\mathrm{Me_3SiN}$ groups. In III, both t-BuN fragments have the same conformation. Within the constraints of normal t-BuN valencies, this conformation requires that one methyl group of each t-Bu moiety is brought as close as possible to a lithium atom. Furthermore, the locations assumed for the hydrogen atoms place two of them in bridging positions between each Li–C contact. The mean Li–C distance (2.34(2) Å) is comparable to those reported for analogous interactions in $\mathrm{Li\{Al[NC(t\text{-}Bu)_2]_4\}}$ (2.37(2) Å) [21], but is much longer than those in $\mathrm{LiBMe_4}$ (2.189(5) Å) [22].

Large torsional motion about the N–C bonds leads to an apparent shortening of the C–C bonds lengths of III. A slight tilt of the t-Bu groups towards the center of the molecule is indicated by the fact that the average N–C–C angle in the Si,N,C planes (109.8(8)°) is smaller than the out-of-plane angles (113(2)°). This tilt tightens the Li–Me contacts.

TABLE 7

SELECTED DISTANCES (Å) IN $\mathrm{\{[t\text{-}BuN(Li)]_3SiPh\}_2}$

Si–N(1)	1.755(1)	N(1)–Li(1)	2.083(3)	Si–C(13)	1.929(2)
Si–N(2)	1.751(1)	N(2)–Li(2)	2.160(3)	C(13)–C(14A)	1.441(5)
Si–N(3)	1.752(1)	N(3)–Li(3)	2.126(3)	C(13)–C(18A)	1.338(5)
N(1)–C(1)	1.476(2)	N(1)–Li(2)′ [a]	2.009(4)	C(14A)–C(15A)	1.383(7)
N(2)–C(5)	1.473(2)	N(1)–Li(3)′	1.989(4)	C(15A)–C(16A)	1.34(1)
N(3)–C(9)	1.464(2)	N(2)–Li(1)′	1.997(4)	C(16A)–C(17A)	1.31(1)
C(1)–C(2)	1.523(3)	N(2)–Li(3)′	1.995(4)	C(17A)–C(18A)	1.420(8)
C(1)–C(3)	1.515(3)	N(3)–Li(1)′	2.030(4)	C(13)–C(14B)	1.336(6)
C(1)–C(4)	1.545(3)	N(3)–Li(2)′	1.965(4)	C(13)–C(18B)	1.465(6)
C(5)–C(6)	1.544(4)	C(4)–Li(1)	2.552(5)	C(14B)–C(15B)	1.382(9)
C(5)–C(7)	1.545(3)	C(7)–Li(2)	2.488(5)	C(15B)–C(16B)	1.36(2)
C(5)–C(8)	1.504(3)	C(11)–Li(3)	2.434(5)	C(16B)–C(17B)	1.40(1)
C(9)–C(10)	1.521(5)	Li(1)–Li(2)′	2.315(5)	C(17B)–C(18B)	1.383(7)
C(9)–C(11)	1.534(3)	Li(1)–Li(3)′	2.316(5)		
C(9)–C(12)	1.531(5)	Li(2)–Li(3)′	2.328(5)		

[a] Coordinates of primed atoms are related to those in the asymmetric unit by x', y', $z' = 2 - x$, $-y$, $2 - z$.

{[t-BuN(Li)]$_3$SiPh}$_2$ (IV)

Compound IV crystallizes as discrete dimers centered on points of crystallographic inversion symmetry. While the nearly 50/50 orientational disorder might suggest that an ordered non-centrosymmetric structure in space group *P*1 is possible, the core of the structure is obviously so centrosymmetric that a refinement in *P*1 would not be warranted. Inspection of intermolecular contacts revealed that the cavities occupied by the phenyl groups are compatible with the disorder model. The assumption of a common *ipso* atom for the two disordered rings, which was made in order to facilitate refinement, leads to slightly distorted ring geometries which should be regarded as artifacts of the model.

In a complete analogy to the structures of II, compound IV possesses a trigonal-antiprismatic Li_6 core, with the nitrogen atoms of the two PhSi[N(t-Bu)]$_3$ moieties in bridging positions over six Li_3 faces. Disregarding the phenyl groups, the highest symmetry obtainable for such a structure is $\bar{3}m$ (D_{3d}), and inspection of the bond distances and angles in Tables 7 and 8, respectively, reveals that this symmetry is

TABLE 8

SELECTED BOND ANGLES (°) IN {[t-BuN(Li)$_3$]$_3$SiPh}$_2$

N(1)–Si–N(2)	103.98(8)	Si–N(2)–Li(1)′	84.1(1)
N(1)–Si–N(3)	103.32(7)	Si–N(2)–Li(3)′	84.0(1)
N(2)–Si–N(3)	105.17(8)	Si–N(3)–Li(1)′	83.1(1)
C(13)–Si–N(1)	112.54(8)	Si–N(3)–Li(2)′	85.0(1)
C(13)–Si–N(2)	115.65(8)	C(1)–N(1)–Li(1)	105.0(1)
C(13)–Si–N(3)	114.86(8)	C(5)–N(2)–Li(2)	101.5(1)
Si–N(1)–C(1)	130.6(1)	C(9)–N(3)–Li(3)	100.4(1)
Si–N(2)–C(5)	134.4(1)	C(1)–N(1)–Li(2)′	114.0(2)
Si–N(3)–C(9)	133.8(1)	C(1)–N(1)–Li(3)′	119.9(2)
N(1)–C(1)–C(2)	113.4(2)	C(5)–N(2)–Li(1)′	117.8(2)
N(1)–C(1)–C(3)	113.2(2)	C(5)–N(2)–Li(3)′	115.4(2)
N(2)–C(5)–C(6)	112.1(2)	C(9)–N(3)–Li(1)′	106.7(2)
N(2)–C(5)–C(8)	114.0(2)	C(9)–N(3)–Li(2)′	125.2(2)
N(3)–C(9)–C(10)	112.2(2)	Li(2)′–N(1)–Li(3)′	117.8(2)
N(3)–C(9)–C(11)	112.4(3)	Li(1)′–N(2)–Li(3)	115.1(2)
N(1)–C(1)–C(4)	108.1(2)	Li(1)′–N(3)–Li(2)′	116.5(2)
N(2)–C(5)–C(7)	108.1(2)	Li(1)–N(1)–Li(2)′	68.9(2)
N(3)–C(9)–C(12)	109.1(2)	Li(1)–N(1)–Li(3)′	69.3(2)
C(2)–C(1)–C(3)	107.3(2)	Li(2)–N(2)–Li(1)′	67.6(2)
C(2)–C(1)–C(4)	107.6(2)	Li(2)–N(2)–Li(3)′	68.0(2)
C(3)–C(1)–C(4)	107.0(2)	Li(3)–N(3)–Li(1)′	67.7(1)
C(6)–C(5)–C(7)	105.9(2)	Li(3)–N(3)–Li(2)′	69.2(2)
C(6)–C(5)–C(8)	109.0(2)	N(2)′–Li(1)–N(3)′	87.4(2)
C(7)–C(5)–C(8)	107.4(2)	N(1)′–Li(2)–N(3)′	87.6(2)
C(10)–C(9)–C(11)	107.4(3)	N(1)′–Li(3)–N(2)′	87.8(2)
C(10)–C(9)–C(12)	110.5(3)	N(1)–Li(1)–N(2)′	110.6(2)
C(11)–C(9)–C(12)	104.9(3)	N(1)–Li(1)–N(3)′	108.8(2)
Si–N(1)–Li(1)	124.3(1)	N(2)–Li(2)–N(1)′	107.1(2)
Si–N(2)–Li(2)	124.0(1)	N(2)–Li(2)–N(3)′	108.3(2)
Si–N(3)–Li(3)	124.4(1)	N(3)–Li(3)–N(1)′	108.7(2)
Si–N(1)–Li(2)′ [a]	83.6(1)	N(3)–Li(3)–N(2)′	108.5(2)
Si–N(1)–Li(3)′	84.0(1)		

[a] See Table 7.

approximated quite well. For comparative purposes, reference will be made to appropriately averaged parameters of IV and the phenyl derivative IIc in the subsequent discussion.

The Li_6 antiprism in IV has six long edges, 3.40(3) Å, which define the two Li_3 faces directly below the silicon atoms, and six short edges, 2.320(7) Å. These dimensions are significantly shorter than those in IIc, 3.53(1) and 2.395(5) Å, respectively. Nevertheless, the Li–N distances in these two compounds are essentially identical; that is, those in the Si–N–C planes are longer (IV: 2.12(4) Å; IIc: 2.11 (2) Å) than those inclined to these planes (IV: 2.00(2) Å; IIc: 2.03(2) Å).

The reversal of the trend in these Li–N distances compared to that of III reflects the dispositions of the Si atoms. Since each Si atom of IV is supended over the middle of a face adjacent to those being spanned rather than over the edge of the bridged faces as in III, the projection of each nitrogen atom upon the plane of the bridged Li_3 face is located much further from the midpoint and from the furthest corner than in III (Fig. 3).

Longer Si–N bonds (1.753(2) Å) and smaller N–Si–N bond angles (104.2(10)°) are found in IV (IIc: 1.733(6) Å, 106.5(5)°); even so, three identical Si–Li contacts are formed on each side of the molecule in both structures (IV: 2.515(3) Å; IIc: 2.51(2) Å). This is made possible by the fact that the lithium atoms in IV lie 0.08(1) Å closer to the molecular three-fold axis than they do in IIc. In IV, the Si–N–C bond angles (130.6(1)–134.4(1)°) are generally smaller than the Si–N–Si bond angles in IIc (134.1(2)–140.1(2)°). In both structures the smallest angle is found for the t-Bu or $SiMe_3$ group lying furthest from the planes of the phenyl rings.

In both structures, the rotameter defined by each Me_3CNSi or Me_3SiNSi group is that which allows formation of one short Li–Me contact (IV: 2.49(6) Å; IIc: 2.56(10) Å). These interactions, though appreciably longer, are analogous to those described above for III. As in III, a tilt of the t-Bu groups towards the molecular center of IV is indicated by the in-plane N–C–C angles (108.4(6)°) being smaller than the out-of-plane angles (112.9(8)°). The analogous tilts in IIc are markedly greater, as shown by the 106.6(4) and 115(1)° values for the corresponding angles.

Discussion

The structures of III and IV are consistent with their high solubilities in non-coordinating solvents but greater reactivity in etheral solutions. Irrespective of our terminology used in describing these compounds, the Li–N bonds are undoubtedly fairly ionic. Each amide nitrogen has only two electron pairs for use in its three Li–N bonds. Since Li–N bonding can provide at best only four electrons for each lithium valence shell, the lithiums are coordinately unsaturated and thus potential reactive centers. However, all the lithium coordination positions are blocked either by Li–N bonds or by pendant methyl groups. While the methyl surfaces of these dimers favour their dissolution in non-polar solvents, dissociation to monomers is a likely prerequisite for the formation of a reactive species. Similarly, lithium coordination by a Lewis base must lead to a breakdown of the lithium-nitrogen clusters and thus to a generation of more open (and therefore more reactive) species.

The only dramatic structural effect caused by replacing the $SiMe_3$ fragments of IIc by t-Bu groups is the shrinking of the Li_6 antiprism. The dimensions of these antiprisms are apparently determined by a delicate balance between Li–N attraction and N...N, Li...Li and Li...Si repulsions. In particular, the structure of III underscores the importance of Li...Si repulsions. Although each of the six edges of the Li_4 bisphenoids are doubly bridged by nitrogen atoms, those two edges closest to the silicon atoms are substantially (0.53(2) Å) longer.

Classification of the Li...Li interactions is not straightforward. To the extent that Li–N bonding is ionic, the Li...Li contacts must be electrostatically repulsive. That comparatively short Li...Li distances can exist in ionic substances is shown by the Li_2O structure [23], in which, after conversion from X to Å units, these distances are 2.316 Å. On the other hand, we can find no structural feature of III or IV which arises solely from any type of Li...Li interaction. Thus while these distances are considerably shorter than the bonds in Li_2 (2.67 Å) or in the metal (3.04 Å), they appear to have no stereochemical influence.

Replacement of $SiMe_3$ groups by t-Bu groups does not lead to appreciably shorter Li–Me interactions in IV. That considerably shorter Li–Me contacts are possible for analogously bonded lithium atoms is demonstrated by the structure of III. Comparison of the structures of II showed that these interactions were tightened by an opening of the $Si-N-SiMe_3$ bond angles [6]. The corresponding $Si-N-CMe_3$ angles in IV are smaller than those in IIc. Furthermore, comparison of N–Si–C and N–C–C bond angles shows that the $NSiMe_3$ groups are more readily distorted than the N-t-Bu groups in directions which lead to shortening of the Li–Me contacts.

Experimental

Synthesis

Bis(t-butylamino)dimethylsilane was prepared as described in ref. 8.

Bis(t-butyl-N-lithioamino)-dimethylsilane (III). A solution of 10.12 g (50 mmol) bis(t-butylamino)dimethylsilane in 50 ml petroleum ether was treated with 100 mmol LiBu in 100 ml n-hexane, and the mixture was heated under reflux for 2 h. The solvent was then removed and the residue sublimed in vacuo, yield 72%. Anal.: Found: Li, 6.3; N, 12.8. $C_{10}H_{24}Li_2N_2Si$ calcd.: Li, 6.48; N, 13.07%. Raman: 102m, 141w, 174s, 214s, 241vs, 283vw, 349w, 363w, 381w, 430m, 472vw, 525s, 535s, 652m, 696w, 745s, 798s, 841w, 899vs, 956w, 1026w, 1139w, 1155vw, 1210vs, 1447w, 1465m cm^{-1}. IR: 521s, 643m, 679vw, 727vs, 758m, 777vw, 792w, 820vw, 831vs, 890w, 976vw, 1009vs, 1026s, 1157sh, 1190vs, 1209m, 1246m cm^{-1}.

Bis(t-butylamino)phenylchlorosilane (VI). A solution of 43.2 g (0.2 mol) $PhSiCl_3$ in 40 ml petroleum ether was slowly added to a solution of 87.8 g (1.2 mol) $t-BuNH_2$ in 500 ml petroleum ether. The mixture was heated under reflux for 2 h then filtered. The solvent was evaporated off and the residue distilled in vacuo; yield 65%. Anal.: Found: C, 12.5; N, 9.6. $C_{14}H_{25}ClN_2Si$ calcd.: C, 12.44; N, 9.83%. Raman: 169w, 204w, 224m, 267w, 278s, 369sh, 384m, 433vw, 484w, 513m, 625m, 682sh, 690s, 720vw, 749vw, 825m, 849vw, 913m, 925w, 1000vs, 1031s, 1118m, 1165vw, 1194m, 1223vs, 1447m, 1467w, 1569w, 1590m, 2867w, 2908w, 2947vw, 2967vw, 3055s cm^{-1}. IR: 369vw, 386m, 415vw, 431s, 481s, 510vs, 538vs, 550s, 632w, 690w, 705s, 729vs, 744s, 822vs, 843vs, 911vw, 923m, 1001m, 1034vs, 1118vs, 1170vw, 1201sh, 1224m, 1309m, 1365vs, 1380vs, 1401vw, 1431s, 1471vs, 1594s, 2870s, 2908vw, 2942sh, 2970vs, 3058m, 3077s, 3386s (ν NH) cm^{-1}.

Tris(t-butylamino)phenylsilane (V). A solution of 30.4 g (0.42 mol) $t-BuNH_2$ in

250 ml petroleum ether was metallated at 0°C with 0.42 mol LiBu in 360 ml n-hexane. A solution of 119 g (0.42 mol) VI in 100 ml petroleum ether was then added, and the mixture was heated under reflux for 2 h then filtered. The solvent was evaporated off and the residue distilled in vacuo; yield 77%. Anal.: Found.: C, 66.4; H, 10.9; N, 13.0. $C_{18}H_{35}N_3Si$ calcd.: C, 67.23; H, 10.97; N, 13.07%. Raman: 163s, 191w, 226s, 263w, 356m, 395vw, 496m, 541vw, 622m, 671vs, 748vw, 801s, 854w, 905s, 919m, 1002vs, 1029s, 1110m, 1157w, 1196s, 1218s, 1444s, 1466s, 1568w, 1588s cm^{-1}. IR: 431m, 481m, 502vw, 540s, 702s, 724s, 747sh, 802w, 832w, 841m, 1015vs, 1036sh, 1109s, 1157vw, 1196s, 1233vs, 1307w, 3393m (ν NH) cm^{-1}.

Tris(t-butyl-N-lithioamino)phenylsilane (IV). A solution of 0.78 g (2.4 mmol) V in 1 ml petroleum ether was metallated with 7.2 mmol LiBu in 5 ml n-hexane. After 1 h colourless crystals of IV separated. Anal. Found: Li, 5.9; N, 12.6. $C_{18}H_{32}Li_3N_3Si$ calcd.: Li, 6.13; N, 12.38%. Raman: 226s, 270w, 280s, 431vw, 470vw, 518s, 545vw, 622m, 648m, 713m, 783s, 886s, 1004vs, 1030s, 1087m, 1154w, 1201s, 1457s, 1470s, 1565m, 1585s cm^{-1}. IR: 431m, 515vw, 534w, 567w, 641m, 668w, 722vs, 738vw, 776s, 891m, 976s, 1006s, 1020w, 1088m, 1201s cm^{-1}.

For spectra see ref. 6.

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