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Syntheses and Characterizations of a New Bulky Disilazane and Two Lithium Disilazides

Lauren M. Atagi,[1a] David M. Hoffman,*[,1a] and David C. Smith[1b]

Department of Chemistry, University of Houston, Houston, Texas 77204, and Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Reaction of dimethylamine with $Cl_3SiN(H)SiMe_3$ in hexane solution at 25 °C gave the bulky disilazane $[(Me_2N)_3Si]N(H)SiMe_3$ in 73% yield. Reaction of $[(Me_2N)_3Si]N(H)SiMe_3$ with *n*-butyllithium in benzene at 0 °C produced the lithium complex $[(Me_2N)_3Si]N(Li)SiMe_3$ in 82% yield. $LiN[Si(NMe_2)_3]_2$ was prepared in 92% yield from the reaction of $HN(SiCl_3)_2$ and 7 equiv of $LiNMe_2$ in hexane. $LiN[Si(NMe_2)_3]_2$ is converted to the amine (83% yield) by reaction with $[H_2NMe_2]Cl$ in THF. The new compounds were characterized spectroscopically, and the X-ray crystal structures of $[(Me_2N)_3Si]N(Li)SiMe_3$ and $LiN[Si(NMe_2)_3]_2$ were determined. $[(Me_2N)_3Si]N(Li)SiMe_3$ and $LiN[Si(NMe_2)_3]_2$ are dimeric in the solid state, forming four-membered Li_2N_2 rings. In both cases dimethylamido groups bridge between silicon and lithium, giving three-coordinate lithium in $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$ and four-coordinate lithium in $\{LiN[Si(NMe_2)_3]_2\}_2$. Crystal data at −50 °C (Mo Kα radiation, $\lambda = 0.710\ 73$ Å): $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$, $C_{18}H_{54}N_8Li_2Si_4$, $a = 8.594(2)$ Å, $b = 17.185(3)$ Å, $c = 22.045(4)$ Å, $\beta = 95.29(2)°$, monoclinic, space group $C2/c$, $Z = 4$, $R = 0.045$; $\{LiN[Si(NMe_2)_3]_2\}_2$, $C_{24}H_{72}N_{14}Li_2Si_4$, $a = 16.634(4)$ Å, $b = 21.169(7)$ Å, $c = 23.924(8)$ Å, orthorhombic, space group *Pbca*, $Z = 8$, $R = 0.044$.

We recently demonstrated that dialkylamido complexes, such as $Si(NMe_2)_4$, are promising precursors to nitride thin films.[2] On this basis, we reasoned that transition metal and main group disilazide complexes in which the silicon has dialkylamido substituents (e.g., $[N(Si(NMe_2)_3)_2]^-$) are potential precursors to ternary silicon nitride films. Bulky disilazide ligands are known to stabilize main group and transition metal complexes with low coordination numbers,[3] an important consideration in making volatile compounds for deposition studies. As part of our synthetic studies, we report here the syntheses of a new bulky disilazane, $[(Me_2N)_3Si]N(H)SiMe_3$, and the potential disilazide ligand reagents $[(Me_2N)_3Si]N(Li)SiMe_3$ and $LiN[Si(NMe_2)_3]_2$. X-ray crystal structures of the unsolvated lithium salts show that they are dimers in the solid state with unusual lithium coordination geometries.

Experimental Section

General Procedures. Reactions were performed under argon or nitrogen by using standard Schlenk line techniques or a glovebox. Solvents were dried by using standard techniques,[4] dimethylamine (Matheson) was used directly from the cylinder, dimethylamine hydrochloride (Aldrich) was recrystallized from benzene before use, lithium dimethylamide was prepared from *n*-butyllithium (Strem) and dimethylamine, and 1,1,1-trichloro-3,3,3-trimethyldisilazane[5] was prepared by published methods. $HN(SiCl_3)_2$ was synthesized in low yield (≈20%) by slowly adding ammonia to $SiCl_4$, as reported in the literature.[6] A mass flow controller was used to monitor the rate of ammonia addition.

Proton and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively. ^1H NMR are reported as δ (multiplicity, number of H's, assignment). Chemical shifts are referenced to solvent peaks or tetramethylsilane. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

$[(Me_2N)_3Si]N(H)SiMe_3$ (1). To a stirred solution of $Cl_3SiN(H)SiMe_3$ (7.0 g, 31 mmol) in hexane (220 mL) was added slowly dimethylamine (ca. 30 mL/min) so that there was no reflux. The solution warmed slightly, and the dimethylamine was added until no further warming was observed (2.5 h). A white precipitate ($[H_2NMe_2]Cl$) was allowed to settle overnight under an argon atmosphere. The solution was filtered from the white solids, and the solids were rinsed with an additional 30 mL of hexane. The volatiles were removed *in vacuo* from the filtrate. The crude product was vacuum-distilled (70 °C, <10 mTorr) to give $[(Me_2N)_3Si]N(H)SiMe_3$ as a colorless liquid (5.6 g, 73% yield). ^1H NMR (C_6D_6): 2.50 (s, 18H, $Si[N(CH_3)_2]_3$), 1.5 (broad lump, 1H, N*H*), 0.88 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR: 38.2 (s, $Si[N(CH_3)_2]_3$), 2.2 (s, $Si(CH_3)_3$). IR (neat, KBr): $\nu_{NH} = 3376$ (m) cm^{-1}; 2970 (s), 2879 (s), 2789 (s), 1485 (m), 1464 (m) 1450 (m), 1410 (w), 1292 (s), 1250 (s), 1180 (s), 1071 (m), 990 (s), 937 (s), 880 (s), 837 (s), 788 (m), 714 (s), 686 (m), 613 (m) cm^{-1}. Anal. Calcd for $Si_2N_4C_9H_{28}$: C, 43.50; H, 11.35; N, 22.55. Found: C, 43.05; H, 11.45; N, 22.26.

$[(Me_2N)_3Si]N(Li)SiMe_3$ (2). A hexane solution of *n*-BuLi (2.5 mL of a 1.6 M solution, 4 mmol) was added via an addition funnel to a solution of **1** (1.00 g, 4 mmol) in benzene (12 mL) at 0 °C. After the addition was complete, the mixture was allowed to warm to room temperature and then stirred for 1 h. The volatiles were removed *in vacuo* to leave sticky colorless crystals (84 g, 82% yield). The crystals decompose when dried (*vide infra*), precluding a satisfactory analysis. ^1H NMR (C_6D_6): 2.50 (s, 18H, $Si[N(CH_3)_2]_3$), 0.25 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 39.6 (s, $Si[N(CH_3)_2]_3$), 4.2 (s, $Si(CH_3)_3$). IR (neat, KBr): 2943 (s), 2876 (s), 2826 (s), 2778 (s), 1481 (w), 1462 (m), 1283 (s), 1242 (m), 1230 (w), 1182 (s), 1155 (s), 1051 (s), 982 (s), 957 (m), 895 (w), 862 (s), 818 (s), 754 (m), 694 (m), 660 (m), 600 (m) cm^{-1}.

$LiN[Si(NMe_2)_3]_2$ (3). A solution of $HN(SiCl_3)_2$ (2.00 g, 7 mmol) in hexane (60 mL) was added over a period of 1 h to a stirring solution of $LiNMe_2$ (2.70 g, 53 mmol). Gas evolution ($HNMe_2$) was observed, and the solution was stirred under an argon atmosphere overnight. The white solids were filtered off and rinsed with hexane (2 × 10 mL). The filtrate was reduced *in vacuo* to give $LiN[Si(NMe_2)_3]_2$ as a white solid (2.21 g, 92% yield). ^1H NMR (C_6D_6): 2.54 (s, 36H, $2\ Si[N(CH_3)_2]_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): 39.5 (s, $2\ Si[N(CH_3)_2]_3$). IR (Nujol mull, KBr): 2785 (s), 1287 (m), 1184 (m), 1146 (w), 1071 (m), 989 (s), 947 (m), 853 (w), 772 (m), 706 (m), 665 (m), 592 (w) cm^{-1}. Anal. Calcd for $Si_2N_7C_{12}LiH_{36}$: C, 42.20; H, 10.62; N, 28.71. Found: C, 41.91; H, 10.74; N, 28.95.

$HN[Si(NMe_2)_3]_2$. A solution of $LiN[Si(NMe_2)_3]_2$ (1.00 g, 2.9 mmol) and dimethylamine hydrochloride (0.26 g, 3.2 mmol) in THF (30 mL) was stirred in a bomb at room temperature overnight. The volatiles were removed from the reaction, the gooey residue was extracted with hexane (3 × 15 mL), and the extract was filtered. The volatiles were removed *in vacuo* to give a clear liquid. Vacuum distillation (85 °C, *ca.* 10 mTorr)

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(1) (a) University of Houston. (b) Los Alamos National Laboratory.

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Table I. Selected Crystallographic Data and Structural Parameters for $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$ (**2**) and $\{LiN[Si(NMe_2)_3]_2\}_2$ (**3**)

	2	**3**
formula	$C_{18}H_{54}N_8Li_2Si_4$	$C_{24}H_{72}N_{14}Li_2Si_4$
fw	509.04	683.34
temp, °C	−50	−50
a, Å	8.594(2)	16.634(4)
b, Å	17.185(3)	21.169(7)
c, Å	22.045(4)	23.924(8)
β, deg	95.29(2)	
V, Å^3	3242	8424
space group	*C*2/*c* (No. 15)	*Pbca* (No. 61)
Z	4	8
D_{calc}, g cm^{-3}	1.04	1.08
μ, cm^{-1}	1.97	1.69
R, R_w[a]	0.045, 0.034	0.044, 0.038

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = \sigma(F)^{-2}$.

gave a colorless liquid (0.81 g, 83% yield). ^1H NMR (C_6D_6): 2.54 (s, 36H, $Si[N(CH_3)_2]_3$), 0.4 (broad s, 1H, N*H*).

X-ray Crystallography. Colorless crystals of **2** and **3** were grown by removing the solvent *in vacuo* from a benzene solution (**2**) or slowly evaporating the solvent from a hexane solution (**3**). The air-sensitive crystals were handled under mineral oil. They were mounted on the goniometer in a random orientation under a stream of dry nitrogen gas. Data were collected at −50 °C on a Nicolet R3m/V automatic diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were measured using the ω-scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant variation. During data reduction, Lorentz and polarization corrections were applied; however, no corrections for absorption were made due to the low absorption coefficients.

The Laue symmetry for **2** was determined to be 2/*m*, and from the systematic absences the space group was shown to be either *Cc* or *C*2/*c*. Since the unitary structure factors displayed centric statistics, space group *C*2/*c* was assumed. The structure was solved using the SHELXTL direct methods program, which revealed the positions of all the non-hydrogen atoms in the asymmetric unit, consisting of one-half molecule situated about a 2-fold axis. The Laue symmetry for **3** was determined to be *mmm*, and the space group was shown unambiguously to be *Pbca*. The structure was solved using the SHELXTL direct methods program, which revealed the positions of most of the non-hydrogen atoms; remaining atoms were located in subsequent difference Fourier syntheses. All non-hydrogen atoms in **2** and **3** were refined anisotropically, and all isotropic hydrogen atoms were placed in calculated positions and constrained to riding motion. No unusually high correlations were noted between any of the variables in the final cycle of full-matrix least squares refinement, and all shift/esd ratios were less than 0.1. The final difference maps for **2** and **3** showed maximum peaks of about 0.25 e/Å^3. Details of the data collection and refinement are listed in Table I, and atomic coordinates are listed in Tables II (**2**) and III(**3**).

Results

The results of this study are summarized in Scheme I. The X-ray crystal structures of **2** and **3** were determined.

Discussion

Synthesis. The sodium derivative of **3** was synthesized previously from $HN[Si(NMe_2)_3]_2$ and $NaNH_2$.[7] We originally planned to prepare **3** similarly by deprotonating $HN[Si(NMe_2)_3]_2$, but we were not able to synthesize the amine cleanly by the published procedures (from $HN(SiCl_3)_2$ and $HNMe_2$). The synthesis of **3** from $HN(SiCl_3)_2$ and $LiNMe_2$ (Scheme I) conveniently bypasses the need to isolate the amine. In this regard, the conversion of **3** quantitatively to $HN[Si(NMe_2)_3]_2$ by reaction with dimethylamine hydrochloride may be important in future studies.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$ (**2**)

	x	*y*	*z*	*U*(eq)[a]
Si(1)	5515(2)	6882(1)	1329(1)	48(1)
Si(2)	3429(2)	5521(1)	1533(1)	58(1)
N(1)	4558(4)	6293(2)	1771(1)	40(1)
N(2)	7195(4)	7180(2)	1803(2)	41(1)
N(3)	4475(5)	7696(3)	1110(2)	74(2)
N(4)	6172(5)	6451(3)	703(2)	76(2)
Li	3630(8)	6376(4)	2574(3)	45(3)
C(1)	8756(5)	7198(3)	1569(2)	64(2)
C(2)	7049(5)	7857(3)	2196(2)	70(2)
C(3)	5199(7)	8380(4)	848(3)	128(4)
C(4)	2816(6)	7784(3)	1087(2)	83(3)
C(5)	5705(7)	6690(4)	84(2)	114(4)
C(6)	7148(7)	5768(4)	728(3)	106(3)
C(7)	4520(6)	4584(3)	1506(3)	91(3)
C(8)	2271(6)	5641(3)	777(2)	89(3)
C(9)	1958(5)	5359(3)	2113(2)	72(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $\{LiN[Si(NMe_2)_3]_2\}_2$ (**3**)

	x	*y*	*z*	*U*(eq)[a]
Si(1)	1843(1)	3949(1)	7187(1)	31(1)
Si(2)	2473(1)	2642(1)	6876(1)	37(1)
Si(3)	2952(1)	4245(1)	5165(1)	26(1)
Si(4)	1348(1)	3567(1)	4997(1)	30(1)
N(1)	2187(2)	3392(2)	6744(2)	27(1)
N(2)	2134(2)	3841(2)	5372(1)	24(1)
N(3)	1263(2)	4492(2)	6780(2)	30(2)
N(4)	2590(3)	4381(2)	7508(2)	42(2)
N(5)	1189(3)	3659(2)	7690(2)	49(2)
N(6)	3168(2)	2462(2)	6332(2)	32(2)
N(7)	1682(3)	2112(2)	6824(2)	50(2)
N(8)	2975(3)	2483(2)	7491(2)	50(2)
N(9)	3714(2)	4104(2)	5673(2)	28(2)
N(10)	2813(2)	5049(2)	5136(2)	34(2)
N(11)	3358(2)	3990(2)	4536(2)	36(2)
N(12)	536(2)	3551(2)	5481(2)	34(2)
N(13)	1493(3)	2814(2)	4753(2)	40(2)
N(14)	1004(3)	4010(2)	4433(2)	39(2)
Li(1)	1440(5)	3781(4)	6110(3)	35(3)
Li(2)	2839(5)	3397(4)	5994(3)	32(3)
C(1)	488(3)	4712(3)	7002(2)	50(2)
C(2)	1655(3)	5026(2)	6490(2)	45(2)
C(3)	3375(3)	4135(3)	7656(2)	62(3)
C(4)	2438(4)	4995(3)	7773(2)	69(3)
C(5)	553(3)	3216(3)	7559(3)	78(3)
C(6)	1100(4)	3920(3)	8251(2)	77(3)
C(7)	3995(3)	2714(2)	6363(2)	45(2)
C(8)	3183(3)	1837(2)	6077(2)	49(2)
C(9)	1026(3)	2161(3)	6435(3)	64(3)
C(10)	1645(4)	1518(3)	7115(3)	98(3)
C(11)	3601(3)	2007(3)	7557(2)	72(3)
C(12)	2651(4)	2644(3)	8043(2)	96(3)
C(13)	4553(3)	3991(3)	5484(2)	44(2)
C(14)	3757(3)	4474(3)	6190(2)	46(2)
C(15)	3475(3)	5503(2)	5160(3)	60(3)
C(16)	2053(3)	5352(2)	5000(2)	48(2)
C(17)	3754(2)	4394(3)	4130(2)	64(3)
C(18)	3471(3)	3328(3)	4398(2)	60(3)
C(19)	−50(3)	3030(3)	5491(2)	56(2)
C(20)	126(3)	4146(3)	5618(2)	54(2)
C(21)	1933(4)	2331(2)	5048(3)	67(3)
C(22)	1112(3)	2555(3)	4255(2)	66(3)
C(23)	170(3)	4009(3)	4249(2)	57(2)
C(24)	1505(3)	4236(3)	3981(2)	65(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Compounds **2** and **3** are hydrocarbon soluble, which allowed us to isolate solvent-free crystals. In the case of **2**, crystallization occurs directly from the filtered reaction mixture (Scheme I) upon removing the benzene solvent *in vacuo*. The sticky crystals

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Scheme I

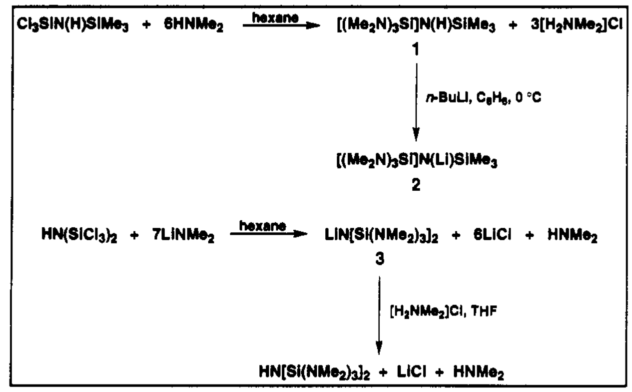

Table IV. Selected Bond Distances (Å) and Angles (deg) for $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$ (**2**)

Bond Distances					
Si(1)–N(1)	1.672(4)	Si(1)–N(2)	1.788(3)	Si(1)–N(4)	1.709(5)
Si(1)–N(3)	1.705(5)	Si(2)–N(1)	1.699(4)	N(1)–Li′	2.029(7)
Li···Li′	2.406(14)	N(1)–Li	2.013(8)	N(2)–Li′	2.115(8)

Bond Angles			
N(1)–Si(1)–N(2)	104.4(2)	Si(1)–N(1)–Si(2)	126.2(2)
Si(1)–N(1)–Li	136.5(3)	Si(1)–N(1)–Li′	89.2(3)
Si(2)–N(1)–Li′	130.9(3)	Li–N(1)–Li′	73.1(3)
N(1)–Li–N(1′)	106.3(3)	N(1)–Li–N(2′)	143.2(4)
N(1′)–Li–N(2′)	82.3(3)	Si(2)–N(1)–Li	93.8(3)
Si(1)–N(2)–Li′	83.7(2)		

Table V. Selected Bond Distances (Å) and Angles (deg) for $\{LiN[Si(NMe_2)_3]_2\}_2$ (**3**)

Bond Distances					
Si(1)–N(1)	1.686(4)	Si(1)–N(3)	1.788(4)	Si(4)–N(13)	1.714(4)
Si(1)–N(4)	1.725(5)	Si(1)–N(5)	1.734(5)	Si(4)–N(14)	1.740(4)
Si(2)–N(1)	1.687(4)	Si(2)–N(6)	1.782(4)	Si(4)–N(2)	1.688(4)
Si(2)–N(7)	1.732(5)	Si(2)–N(8)	1.725(5)	Si(4)–N(12)	1.779(4)
Si(3)–N(2)	1.682(4)	Si(3)–N(9)	1.782(4)	Si(3)–N(10)	1.719(4)
Si(3)–N(11)	1.737(4)	N(1)–Li(1)	2.126(9)	N(1)–Li(2)	2.097(9)
N(2)–Li(1)	2.114(9)	N(2)–Li(2)	2.114(9)	N(3)–Li(1)	2.217(9)
N(6)–Li(2)	2.209(9)	N(12)–Li(1)	2.182(9)	N(9)–Li(2)	2.225(9)
Li(1)···Li(2)	2.479(11)				

Bond Angles			
Si(1)–N(1)–Si(2)	129.5(2)	Si(1)–N(1)–Li(1)	88.8(3)
Si(2)–N(1)–Li(1)	131.5(3)	Si(1)–N(1)–Li(2)	135.2(3)
Si(2)–N(1)–Li(2)	91.1(3)	Li(1)–N(1)–Li(2)	71.9(3)
Si(3)–N(2)–Si(4)	130.2(2)	Si(3)–N(2)–Li(1)	135.8(3)
Si(4)–N(2)–Li(1)	90.1(3)	Si(3)–N(2)–Li(2)	89.1(3)
Si(4)–N(2)–Li(2)	130.6(3)	Li(1)–N(2)–Li(2)	71.8(3)
Si(1)–N(3)–Li(1)	83.4(3)	Si(2)–N(6)–Li(2)	85.1(3)
Si(3)–N(9)–Li(2)	83.2(3)	Si(4)–N(12)–Li(1)	85.6(3)
N(1)–Li(1)–N(2)	107.5(4)	N(1)–Li(1)–N(3)	80.0(3)
N(2)–Li(1)–N(3)	129.4(4)	N(1)–Li(1)–N(12)	143.9(4)
N(2)–Li(1)–N(12)	79.2(3)	N(3)–Li(1)–N(12)	123.9(4)
N(1)–Li(2)–N(2)	108.6(4)	N(1)–Li(2)–N(6)	79.0(3)
N(2)–Li(2)–N(6)	142.6(4)	N(1)–Li(2)–N(9)	129.5(4)
N(2)–Li(2)–N(9)	79.8(3)	N(6)–Li(2)–N(9)	124.6(4)

can be dried under vacuum for only a short time (<1 h) because more extensive drying produces a white insoluble material. Curiously, the crystals can be stored slightly "wet" with hexane or benzene in a tightly closed flask under inert atmosphere with no apparent decomposition over a period of months. In contrast to **2**, the lithium salt **3** is stable *in vacuo* at temperatures up to 100 °C for 12 h.

Structural Characterization. Selected bond distances and angles taken from X-ray crystallographic studies are given in Tables IV (**2**) and V(**3**). A table of structural data for lithium disilazides is given in Table VI for comparison.[8,9]

Table VI. Selected Structural Parameters for Lithium Disilazides

compd	Li coord no.	Li–N, Å (av)	Si–N, Å (av)	∠SiNSi, deg (av)	ref
$[LiN(SiMe_3)_2]_2$^{a}	2	1.99(3)	1.712(7)	129.8(1.7)	8a
$[LiN(SiMe_3)_2]_3$	2	2.00(1)	1.729(5)	118.6(3)	8b
$[LiN(SiMe_3)_2{\cdot}Et_2O]_2$	3	2.055(3)	1.705(2)	121.2(2)	8c
$[LiN(SiMe_3)_2{\cdot}THF]_2$	3	2.025(9)	1.689(4)	122.3(4)	8d
$LiN(SiMePh_2)_2{\cdot}$2THF	3	1.949(6)	1.671(1)	132.3(1)	8e
$LiN(SiPh_3)_2{\cdot}$2THF	3	1.998(7)	1.666(1)	140.5(2)	8e
$\{[(Me_2N)_3Si]N(Li)$-$SiMe_3\}_2$^{b}	3	2.021(8)	1.699(4)^c 1.672(4)^d	126.2(2)	
$\{LiN[Si(NMe_2)_3]_2\}_2$^{b}	4	2.113(9)	1.686(4)^d	129.9(3)	
$LiN(SiMe_3)_2{\cdot}$12-crown-4	5	1.965(4)	1.681(2)	123.5(1)	8f
$LiN(SiMePh_2)_2{\cdot}$12-crown-4	5	2.064(14)	1.667(3)	133.9(4)	8e

^{a} Electron diffraction data. ^{b} This work; distances and angles are for nitrogen atoms in the Li_2N_2 ring. ^{c} N(1)–$SiMe_3$. ^{d} From Si of $Si(NMe_2)_3$ groups to the nitrogens in the Li_2N_2 ring.

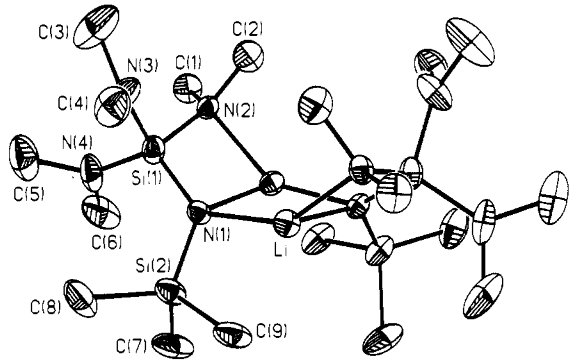

Figure 1. Plot of $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$ (**2**) showing the atom-numbering scheme used in the tables (30% probability level). Hydrogen atoms are omitted for clarity.

Complex **2** is a dimer in the solid state (Figure 1) with a crystallographic 2-fold axis. The lithium atom is surrounded by three nitrogens, two from the Li_2N_2 ring and one from a dimethylamido group bridging between silicon and lithium. The lithium atoms are in a highly distorted environment with N–Li–N angles ranging from 82.3(3) to 143.2(4)°. There is a 10.1° angle between the two N–Li_2 components of the Li–N(1)–Li′–N(1′) ring. This distorted ring contrasts with those found in alkali metal derivatives of hexamethyldisilazide where the M_2N_2 rings are essentially square and planar.[8a] The Li–N distances in the central four-membered ring are the same within experimental error and are comparable to values for analogous disilazides containing three-coordinate lithium atoms (Table VI). The Li–N bond distance to the bridging dimethylamido nitrogen is ca. 0.09

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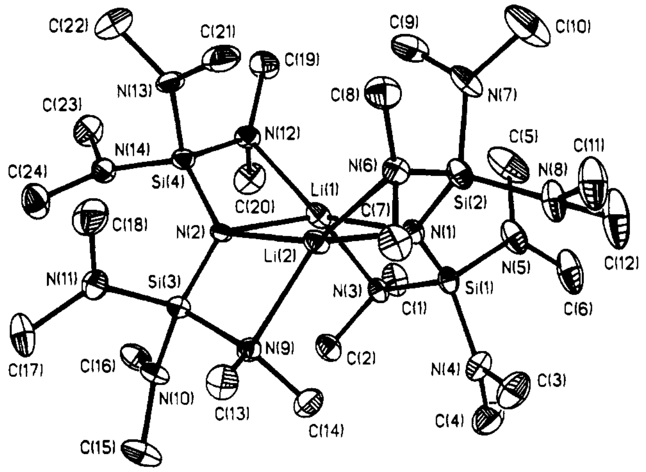

Figure 2. Plot of $\{LiN[Si(NMe_2)_3]_2\}_2$ (3) showing the atom-numbering scheme used in the tables (30% probability level). Hydrogen atoms are omitted for clarity.

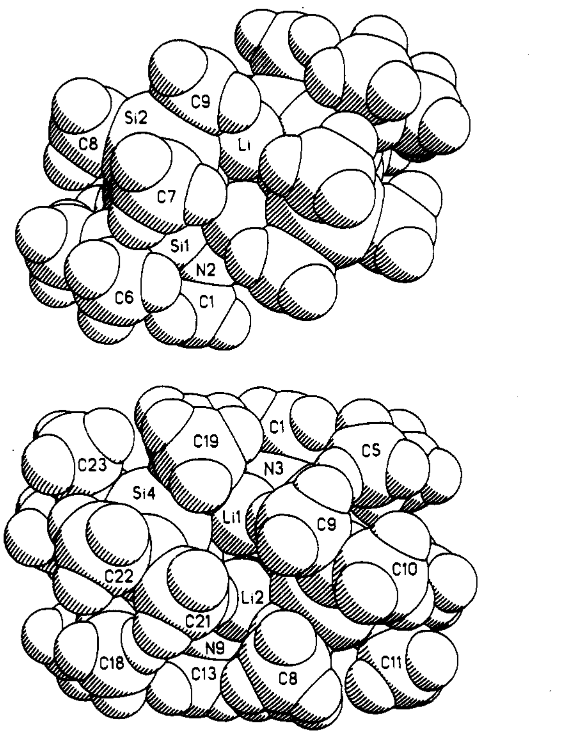

Figure 3. Space-filling drawings of (top) $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$ (2) and (bottom) $\{LiN[Si(NMe_2)_3]_2\}_2$ (3).

Å longer than the core Li–N bonds, suggesting a weaker interaction of the dimethylamido ligand with the lithium atom.

In the molecule the bridging dimethylamido groups are on one side of the Li_2N_2 ring and the two $SiMe_3$ groups are on the other. It is not clear why this arrangement is adopted since an antifacial arrangement with respect to the Li_2N_2 ring would presumably minimize steric interactions. Space-filling models do not suggest a clear reason for the counterintuitive coordination.

Complex 3 is a dimer in the solid state (Figure 2) with virtual D_2 symmetry. The central four-membered Li_2N_2 ring is nearly planar, with only a 4.5° angle between the two $N-Li_2$ components. The lithium atoms are coordinated to the two nitrogens of the Li_2N_2 ring and two nitrogens from the bridging amido groups, producing a highly distorted tetrahedral environment. The Li–N distances in the central ring are equivalent by the 3σ criterion, and on average are ca. 0.10 Å shorter than the Li–N distances within the external rings. Both sets of Li–N bond distances are longer than the corresponding distances in **2** (average difference ca. 0.09 Å), perhaps due to the greater steric congestion in **3**. In complexes **2** and **3** the Si–N distances are similar to those observed in other cyclic lithium disilazide structures and the Si–N–Si angles fall within the range of observed values (Table VI).

Preliminary reactivity studies suggest that **2** and **3** are less reactive than lithium hexamethyldisilazide. We attribute this to the dimethylamido coordination to lithium which protects the Li–N ring bonds and precludes reactivity. This is evident in space-filling drawings of **2** and **3** (Figure 3) which show that the lithium atoms occupy a cavity surrounded by methyl groups.

Conclusion

We have prepared a new bulky disilazane, $[(Me_2N)_3Si]N(H)SiMe_3$, and two new lithium disilazides, $[(Me_2N)_3Si]N(Li)SiMe_3$ and $LiN[Si(NMe_2)_3]_2$. Crystal structures of the lithium salts show that the compounds are dimers with unusual lithium coordination environments and $Li(\mu\text{-}NMe_2)Si$ groups. Use of the lithium salts to introduce the novel disilazides as ligands in transition metal and main group compounds may prove difficult because of the encapsulation of the Li–N bonds by the dimethylamido groups. Reactivity studies involving these compounds and attempts to prepare other alkali metal derivatives are in progress.

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Supplementary Material Available: A textual presentation of the experimental crystallographic details, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, and least-squares planes, and packing diagrams for $\{[(Me_2N)_3Si]N(Li)SiMe_3\}_2$ and $\{LiN[Si(NMe_2)_3]_2\}_2$ (35 pages). Ordering information is given on any current masthead page. Tables of observed and calculated structure factors can be obtained from the authors.