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Lithium Coordination in Chelating Silazanes of the General Formula $[X-Me_2Si-N-SiMe_2-X]_2Li_2$[†]

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New derivatives of hexamethyldisilazanelithium of the general formula $[X-Me_2Si-N-SiMe_2-X]_2Li_2$ (X = Ph (**2**), C_4H_3S (**3**), NMe_2 (**4**), NEt_2 (**5**), $N(H)^iPr$ (**6**), OPh (**7**), $OSiMe_3$ (**8**), C_4H_3O (**9**)) have been synthesized and characterized by spectroscopic means. All compounds except **3** have been subjected to X-ray structure determinations which reveal a common polycyclic arrangement with a central Li_2N_2 four-membered ring to which four similar LiNSiY rings are annealed along a common Li−N edge (Y can either be a carbon atom of a π-system (**2**, **3**), nitrogen (**4**−**6**) or oxygen (**7**−**9**)). The common four-membered polycyclic skeleton $Li_2N_2Si_4Y_4$ has a point symmetry of approximately D_2 (222) of which only C_2 (2) symmetry is retained in the crystals of **4**, **5**, **6**, and **9**, whereas all other derivatives have point symmetry C_1 (1). One of the compounds crystallizes in one enantiomeric form (**4**) in an acentric structure. All other compounds crystallize in centrosymmetric structures with the two enantiomers present in the crystal. The lithium atoms in **2**−**9** are present in a distorted tetrahedral environment constituted by two nitrogen and two Y atoms. From molecular mass determinations, the compounds seem to retain their dimeric nature in benzene, the NMR patterns being nevertheless more simple than expected from the crystal structures and indicate a dynamic behavior in solution. None of these compounds, so far, shows lithium motion in the solid state up to room temperature, although phase transitions seem to occur in compound **8** at higher temperatures (^{13}C SPE/MAS NMR evidence). Li−N distances in the central Li_2N_2 ring depend on the nature of donor groups Y: short Li−N bonds (2.024 Å) are found for the lithium atoms coordinated by organic π-systems together with relatively long Li−C bonds (2.53 Å in **2**), whereas longer Li−N bonds (2.07−2.085 Å) are encountered for the nitrogen donors with short Li−N "donor" bonds (2.157 (**4**), 2.163 (**5**), 2.121 Å (**6**)). If the donor atom (Y) is oxygen, the Li−O bonds can be either shorter than the Li−N bonds (**7**, Li−N 2.073, Li−O 1.978 Å; **9**, Li−N 2.076, Li−O 1.977 Å) or slightly longer (**8**, Li−N 2.021, Li−O 2.077 Å). It is remarkable that in the trimethylsilyloxy case **8** the Li−N distances are not equal within their standard deviations as observed in the other cases: two distances (average 1.96 Å) on opposite sides of the Li_2N_2 ring are much shorter than the remaining two (average 2.08 Å).

Introduction

Lithium atoms with a formal positive charge of +1 have been shown to be easily moved in ionic solid materials such as Li_3N when the crystal is brought in an electric field.[1,2] This lithium conduction, which is useful for solid-state batteries, is connected to a lithium mobility.[3] Recently, we were able to show that lithium mobility can also be encountered in crystals of a special lithium amide $[tBuO-SiMe_2-N-SiMe_2-OtBu]_2Li_2$ (**1**).[4] Compound **1**, which can be derived from $LiN(SiMe_3)_2$ by substituting one of the methyl groups on each silicon by *tert*-butoxy groups, forms several crystalline phases with increasing temperature. In the monoclinic low-temperature phase, the crystal is made up of an ordinary van der Waals packing of molecules, while in the tetragonal phase (phase transition occurring just below room temperature), the molecules show mobility with lithium atoms hopping within a definite trajectory. The lithium ions move in a concerted fashion within the molecules from one tetrahedral N_2O_2 hole to a similar unoccupied one, resulting in a rotational motion around the center of gravity of the molecules.

As this special crystalline state encountered in molecule **1**, which can be considered as a new state of matter (packing of molecules with lithium atoms moving inside the molecular skeleton), could be of more general interest, we have explored the structural features of a series of compounds which are all derived from hexamethyldisilazanelithium. We have replaced the *tert*-butoxy groups in compound **1** by aromatic or quasi aromatic π-systems such as phenyl or thienyl (**2**, **3**),

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[†] Dedicated to Prof. Dr. Hans von Schnering on his retirement.

(1) Rabenau, A. *Nachr. Chem. Technol. Lab.* **1978**, *26*, 310.

(2) Hartwig, P.; Weppner, W.; Wichelhaus, W.; Rabenau, A. *Angew. Chem.* **1982**, *92*, 72; *Angew. Chem., Int. Ed. Engl.* **1982**, *19*, 74.

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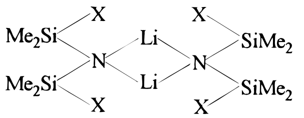
Scheme 1. Numbering of the Compounds Derived from $[X{-}Me_2SiNSiMe_2{-}X]_2Li_2$



X = OtBu (**1**)
X = Ph (**2**)
X = C_4H_3S (**3**)
X = NMe_2 (**4**)
X=N Et_2 (**5**)
X = $N(H)^iPr$ (**6**)
X = OPh (**7**)
X = $OSiMe_3$ (**8**)
X = C_4H_3O (**9**)

alkylnitrogen groups such as dimethylamino, diethylamino, and isopropylamino (**4**, **5**, **6**), and oxo ligands such as phenoxy (**7**), trimethylsilyloxy (**8**), and furyl (**9**).

A general survey of Li_2N_2-centered amide structures has been given by R. E. Mulvey and R. Snaith.[5] Nevertheless, to our knowledge, nobody has looked on the dynamical properties of lithium atoms in such molecules, especially in the solid state. Here, we report the exploration of similar compounds which differ in the basicity of the ancillary ligands. To find indications for lithium movements in solids, we have performed X-ray structure determinations at room temperature.

The numbering of the compounds assembled in this article is depicted in Scheme 1. It was anticipated that in all of the compounds the lithium atoms should be tetracoordinated by two nitrogen atoms and two other atoms of the different donors. In the case of the furyl ligand, two potential donor systems are present either the π-system or the oxygen atom. To identify any possible lithium movement in the solid, the crystal structures of all of the new derivatives were determined.

Synthesis. The lithiumamides **2**−**9** are synthesized from the corresponding disilazanes, which can be obtained directly[6] (eq 1) or by use of the chloroaminosilane $ClMe_2Si{-}N(H){-}SiMe_2Cl$[7−9] and by replacement of the chloro functions by anionic ligands (eq 2). These salt

$$2PhMe_2SiCl + 3NH_3 \rightarrow (PhMe_2Si)_2NH + 2NH_4Cl \qquad (1)$$

$$ClSiMe_2N(H)SiMe_2Cl + 2MX \rightarrow XSiMe_2N(H)SiMe_2X + 2MCl \qquad (2)$$

$$X = C_4H_3S,\ NMe_2,\ NEt_2,\ NH^iPr,\ OPh,\ C_4H_3O;\quad M = Li$$

$$X = OSiMe_3;\ M = Na$$

elimination reactions proceed well, and the corresponding amines can be obtained in reasonable yields. The exchange of the nitrogen-bonded hydrogen atom by lithium can be performed by different techniques using butyllithium or phenyllithium as the lithiating reagents (eq 3). For the synthesis of **6**, a stoichiometric amount of butyllithium has to be used to avoid further lithiation of the NH groups belonging to the $N(H)^iPr$ substituents. If this is followed, no side reaction is observed and the

$$X{-}SiMe_2N(H)SiMe_2{-}X + LiR \rightarrow {}^1/_2[X{-}SiMe_2NSiMe_2{-}X]_2Li_2 + HR \qquad (3)$$

$$R = CH_2{-}CH_2{-}CH_2{-}CH_3,\ Ph$$

$$X = Ph\ (\mathbf{2}),\ C_4H_3S\ (\mathbf{3}),\ NMe_2\ (\mathbf{4}),\ NEt_2\ (\mathbf{5}),\ N(H)^iPr\ (\mathbf{6}),\ OPh\ (\mathbf{7}),\ OSiMe_3\ (\mathbf{8}),\ C_4H_3O\ (\mathbf{9})$$

lithiation occurs selectively on the central nitrogen atom, as may be deduced from the NMR spectra.

The compounds **2**−**9** can be isolated by crystallization from mostly toluene solutions. They all form colorless crystals. As determined by cryoscopy (benzene), the compounds **2**, **4**, **5**, **7**, **8**, and **9** form dimers of the general formula $[X{-}SiMe_2NSiMe_2{-}X]_2Li_2$ in solution. Compared to the crystal structures, in which the highest point symmetry found is C_2 (vide infra), the ^1H, ^{13}C, and ^{29}Si NMR spectra of the solutions of the compounds are simple, indicating a higher global symmetry. The observations are discussed for compound **8** in more detail, similar arguments being true for the other derivatives (see Experimental Section). In each of the spectra (^1H, ^{13}C, ^{29}Si), only two resonances can be found, consistent with symmetrically equivalent dimethylsilyl and trimethylsilyl groups, respectively (the tertiary carbon atoms are not considered here). Assuming D_2 symmetry for the free molecule, there should, nevertheless, be two different resonances for the dimethylsilyl groups, the methyl ligands not being equivalent because of the specific orientations of the four-membered cycles (see crystallography discussion). In contrast to the solution ^{13}C NMR, the ^{13}C SPE/MAS NMR spectrum of crystalline **8** at room temperature exhibits three main resonances, one at δ 2.7 ppm for the trimethylsilyl groups and two at δ 5.0 and 7.1 ppm for the two distinctly different methyl groups of the Me_2Si unit. From these findings it is evident that the methyl groups coalesce in solution, probably due to a molecular motion which makes them symmetrically equivalent. The overall point symmetry of this movement must be at least compatible with D_{2d} ($-42m$), which is possible only if the lithium atoms are involved in the molecular dynamics. It can be anticipated that these movements should be similar to the ones observed in the crystalline derivative **1**.[4] It should, however, be pointed out that during these dynamic rearrangements, bond closures and openings should also be taken into account. For the amido compounds **4** and **5**, we have measured the variable-temperature ^1H NMR spectra. While the ^1H and ^{13}C NMR spectra of **4** remain unchanged down to 200 K, the single peak of the dimethylsilyl group of **5** splits into two singlets of equal intensity at 200 K. This could be considered as an important hint for a dynamic process in solution and parallels the findings for crystalline **1** (the lack of splitting in the spectrum of **4** could possibily be due to the smaller methyl groups on the nitrogen atoms). The dynamics in **6** could be similar to the ones found for compounds of the general formula $Me_2Si(NtBu)[N(H)tBu]MX_2$ (M = trivalent group 13 element; X = F, Cl, Br, Me) with inversions at the nitrogen atoms.[10]

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(6) Shostakovskii, M. F.; Kondrart′ev, Kh. I. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1956**, 811.

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Table 1. Crystal Data, Data Collection, and Refinement Parameters for 2 and 4−9

	2	**4**	**5**	**6**	**7**	**8**	**9**
Crystal Data							
formula	$C_{32}H_{44}Li_2N_2Si_4$	$C_{16}H_{48}Li_2N_6Si_4$	$C_{24}H_{64}Li_2N_6Si_4$	$C_{20}H_{56}Li_2N_6Si_4$	$C_{32}H_{44}Li_2N_2O_4Si_4$	$C_{20}H_{60}Li_2N_2O_4Si_8$	$C_{24}H_{36}Li_2N_2O_4Si_4$
mol wt	588.48	450.84	563.05	506.94	646.94	631.30	542.79
cryst syst	monoclinic	trigonal	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$	$P3_12$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$I2/a$
a (Å)	34.941(7)	10.430(6)	20.619(4)	9.732(6)	12.366(2)	17.46(2)	15.303(3)
b (Å)	13.652(3)	10.430(6)	10.840(2)	20.261(12)	13.262(3)	18.09(2)	11.105(2)
c (Å)	16.783(3)	24.20(2)	18.149(4)	17.826(12)	14.059(3)	18.09(2)	19.190(4)
α (deg)	90	90	90	90	71.74(3)	90	90
β (deg)	117.20(3)	90	116.05(3)	95.90(5)	72.99(3)	93.50(8)	106.94(3)
γ (deg)	90	120	90	90	65.34(3)	90	90
V (Å^3)	7120(3)	2280(3)	3644.4(13)	3496(4)	1954.6(7)	4289(7)	3119.6(1)
D_{calc} (g cm^{-3})	1.098	0.985	1.026	0.964	1.099	0.978	1.156
Z	8	3	4	4	2	4	4
F(000)	2540	744	1248	560	688	1376	1152
μ (mm^{-1})	0.189	0.985	0.184	0.093	0.185	0.272	0.220
cryst size (mm)	0.6 × 0.4 × 0.3	0.2 × 0.4 × 0.7	0.3 × 0.25 × 0.2	0.6 × 0.5 × 0.4	0.1 × 0.5 × 0.2	0.9 × 0.7 × 0.5	0.5 × 0.3 × 0.2
Data Collection							
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
θ_{min}, θ_{max} (deg)	2.35, 26.23	2.25, 25.01	2.26, 24.04	2.30, 24.00	1.84, 24.15	1.62, 23.89	2.30, 20.97
wavelength (Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
monochromator	graphite	graphite	graphite	graphite	graphite	graphite	graphite
diffractometer	Stoe/IPDS	Siemens/ Stoe AED2	Stoe/IPDS	Siemens/ Stoe AED2	Stoe/IPDS	Siemens/ Stoe AED2	Stoe/IPDS
scan type		$\omega-\theta$ scan		$\omega-\theta$ scan		$\omega-\theta$ scan	
total no. of data	27512	7518	14 015	2887	15 440	5609	4092
total no. of unique data	7009	2658	2706	1656	5775	5472	1214
R_{int}	0.0447	0.0446	0.0752	0.0415	0.046	0.0309	0.1073
obsd data ($I > 2\sigma(I)$)	4345	2251	2292	955	3945	3481	888
Refinement							
no. of refined params	525	128	164	143	397	325	164
final R indices [$I > 2\sigma(I)$]	R1 = 0.044 wR2 = 0.11	R1 = 0.035 wR2 = 0.09	R1 = 0.044 wR2 = 0.13	R1 = 0.044 wR2 = 0.09	R1 = 0.040 wR2 = 0.10	R1 = 0.060 wR2 = 0.15	R1 = 0.049 wR2 = 0.132
final R indices (all data)	R1 = 0.08 wR2 = 0.13	R1 = 0.04 wR2 = 0.10	R1 = 0.05 wR2 = 0.13	R1 = 0.10 wR2 = 0.12	R1 = 0.06 wR2 = 0.11	R1 = 0.10 wR2 = 0.18	R1 = 0.067 wR2 = 0.15
goodness-of-fit on F^2	1.026	0.935	1.040	1.031	0.965	1.025	1.013
min and max residual density, e Å^{-3}	0.183, −0.219	0.158, −0.155	0.242, −0.222	0.096, −0.115	0.188, −0.127	0.280, −0.240	0.220, −0.231

X-ray Structure Determinations and Discussion. The procedures for the X-ray structure determinations of **2** and **4**−**9** are described in the Experimental Section, while some important crystal data are assembled in Table 1. Crystals of **3** did not lead to a satisfactory structure model, probably due to statistical disorder respectively twinning; nevertheless, we could obtain the positions of the heavy atoms from which we concluded that the structure of **3** was similar to the other derivations. Interestingly the sulfur atoms did not coordinate to the lithium atoms which were found in close vicinity to the π-system of the thienyl ligand (Li···C = 2.49 Å). From inspection of the crystal constants together with the crystal systems and space groups it can be concluded that there are not two isomorphous or isotopic crystal structures present in this series, although from a chemical point of view the molecules are quite similar. The molecular packings of the compounds are in agreement with the principles of Kitaigorodski which hold for van der Waals interactions.[11] To evaluate the probability of solid-phase transitions at higher temperatures, the N···N vector of the molecules can be taken as a rough guide and its orientation to principal axes or diagonals of the crystal lattices can be determined (for **1** it can be shown that the orientations of the molecules in the monoclinic phase with respect to the N···N vector are almost identical to the orientations in the tetragonal phase).[4] From inspection, two structures show an orientation parallel to the axes: in **6** the N···N vectors are almost parallel to [010], and in **8** the N···N vectors of the molecules are almost parallel to either [110] or to [−110].

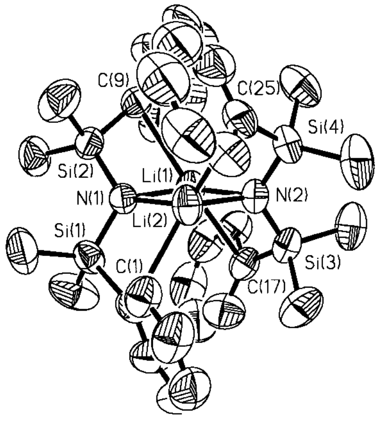

Figure 1. ORTEP view of [{Me$_2$Si(Ph)}$_2$N−Li]$_2$ (**2**). Thermal ellipsoids are drawn at the 30% probability level.

The perspective view of **2** is presented in Figure 1, while for the series of similar compounds **4** and **5** as well as **7** and **8**, only one of the two different types (**4** and **8**) is shown in Figures 2 and 4. The structure of the isopropylamine derivative **6** is represented in Figure

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(11) Kitaigorodskii, A. I. *Molecular Solids and Crystals*; Academic Press: New York, 1973.

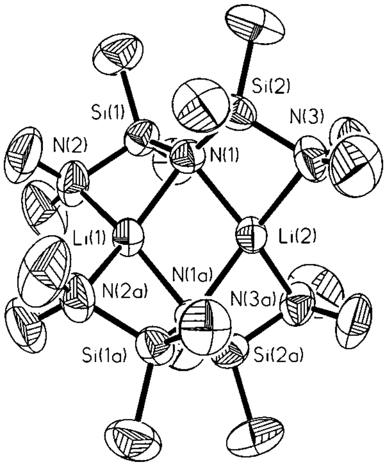

Figure 2. ORTEP view of $[\{Me_2Si(NMe_2)\}_2N-Li]_2$ (**4**). Thermal ellipsoids are drawn at the 30% probability level.

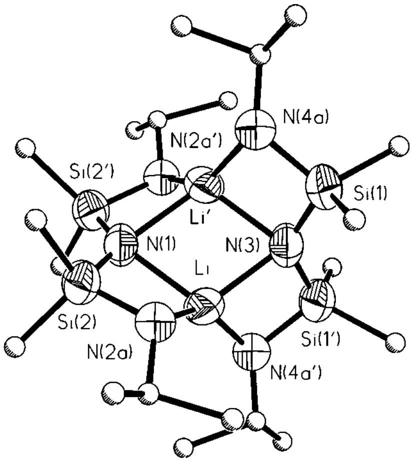

Figure 3. ORTEP view of $[\{Me_2Si(N(H)^iPr)\}_2N-Li]_2$ (**6**). Thermal ellipsoids are drawn at the 30% probability level.

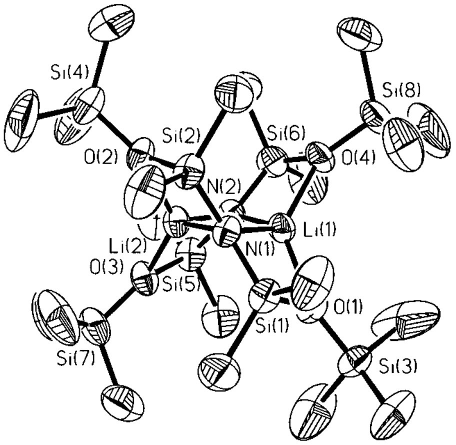

Figure 4. ORTEP view of $[\{Me_2Si(OSiMe_3)\}_2N-Li]_2$ (**8**). Thermal ellipsoids are drawn at the 30% probability level.

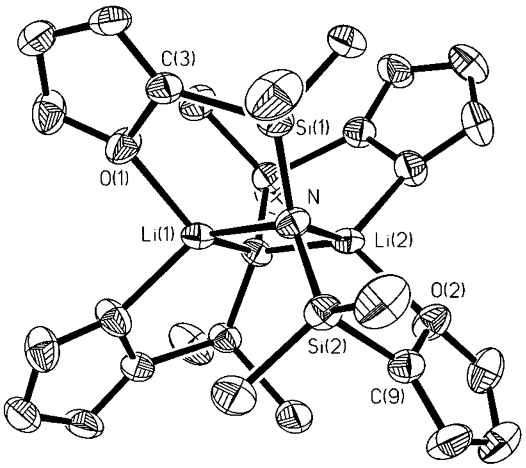

Figure 5. ORTEP view of $[\{Me_2Si(C_4H_3O)\}_2N-Li]_2$ (**9**). Thermal ellipsoids are drawn at the 30% probability level.

3, while the structure of the furyl derivative **9** is shown in Figure 5. From Figures 1−5 it is quite obvious that all of the molecular structures are very similar. The central backbone consists of a four-membered Li_2N_2 ring to which four similar four-membered LiNSiY (Y = C, N, O) rings (five-membered for **9**) are fused with a common Li−N edge. The lithium atoms are, thus, present in a distorted tetrahedral environment of two nitrogen and two Y atoms. The orientation of the LiNSiY cycles, in a rough approximation, can be described by the point symmetry D_2 (222), two of the axes running through the nitrogen or lithium atoms of the central ring. Nevertheless, none of the molecules retains this higher point symmetry in the crystal, the highest crystal symmetry C_2 (2) being observed for **4**, **5**, **6**, and **9** (the other molecules have C_1 (1) point symmetry in common). Because of the special polycyclic arrangement together with the point symmetry, all of the molecules (**2**−**9**) are chiral, crystallizing in enantiomeric pairs in the case of **2**, **5**, **6**, **7**, **8**, and **9**. The crystal structure of **4** is only built up of one enantiomeric form and is, thus, acentric. All molecules are dimers of the simple lithium amide formula and closely resemble the molecular structure of derivative **1**.[4]

The most important bond lengths and angles of the derivatives **2** and **4**−**9** are collected in Table 2. Before discussing the trends in these values, some comments have to be made regarding the Li−C interactions in **2**. The phenyl groups in **2** are not to be considered as simple "spectator ligands": they interact with the lithium atoms, as may be seen from the short distances of the α- and β-C atoms to the lithium atoms (2.53−2.77 Å). Comparable Li−C distances are found in compound $[N(CH_2-Ph)_2Li]_3$ where Li π bonding is assumed as well.[12] Furthermore, the C−C distances within the phenyl groups are systematically perturbed with long C−C distances for the α-, β-, and β'-C atoms and short distances for the C−C bonds that are at the extremities of the phenyl group. This bonding scheme could reflect a π-bonding to the lithium atoms of the highest occupied MO of the aromatic 6π system which has one nodal plane. As a matter of fact, the orientation of the phenyl groups with respect to the lithium atoms is such that the LiCα or LiCβ vectors are almost perpendicular to the phenyl plane (75−85°).

From inspection of Table 2, it can be followed that most of the Si−C, Si−N, and Si−O bonds are quite similar in the different derivatives. If differences are found, they can be correlated to either the different hybridization states of the elements or the different electronegativities of the ligands that are attached to the bonds under consideration.

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(12) Armstrong, D. R.; Mulvey, R. E.; Walker, G. T.; Barr, D.; Snaith, R.; Clegg, W.; Reed, D. *J. Chem. Soc., Dalton Trans.* **1988**, 617.

Table 2. Summary of Selected Bond Lengths (Å) and Angles (deg) for Lithium Compounds 2 and 4−9

{[PhSiMe$_2$]$_2$N−Li}$_2$ (**2**)							
Si(1)−N(1)	1.696(2)	N(2)−Li(2)	2.028(4)	C(2)−C(3)	1.393(4)	C(17)−C(22)	1.387(4)
Si(2)−N(1)	1.701(2)	Li(2)−C(1)	2.775(5)	C(3)−C(4)	1.350(5)	C(18)−C(19)	1.398(5)
Si(3)−N(2)	1.692(2)	Li(2)−C(2)	2.770(5)	C(4)−C(5)	1.361(5)	C(19)−C(20)	1.369(6)
Si(4)−N(2)	1.694(2)	Li(1)−C(9)	2.663(4)	C(5)−C(6)	1.391(5)	C(20)−C(21)	1.356(6)
Si(1)−C(1)	1.899(2)	Li(1)−C(10)	2.532(4)	C(9)−C(14)	1.394(4)	C(21)−C(22)	1.389(5)
Si(2)−C(9)	1.890(3)	Li(1)−C(17)	2.670(5)	C(9)−C(10)	1.397(4)	C(25)−C(26)	1.389(4)
Si(3)−C(17)	1.898(3)	Li(1)−C(18)	2.661(5)	C(10)−C(11)	1.390(5)	C(25)−C(30)	1.394(4)
Si(4)−C(25)	1.893(3)	Li(2)−C(26)	2.606(5)	C(11)−C(12)	1.350(9)	C(26)−C(27)	1.411(5)
N(1)−Li(2)	2.011(4)	Li(2)−C(25)	2.616(5)	C(12)−C(13)	1.346(8)	C(27)−C(28)	1.361(7)
N(1)−Li(1)	2.035(4)	C(1)−C(6)	1.386(4)	C(13)−C(14)	1.399(7)	C(28)−C(29)	1.334(7)
N(2)−Li(1)	2.022(4)	C(1)−C(2)	1.392(3)	C(17)−C(18)	1.386(4)	C(29)−C(30)	1.375(5)
N(1)−Si(1)−C(1)	109.67(9)	Si(2)−N(1)−Li(1)	100.55(13)	N(2)−Li(1)−N(1)	108.5(2)	N(1)−Li(2)−N(2)	109.2(2)
N(1)−Si(2)−C(9)	107.51(10)	Li(2)−N(1)−Li(1)	71.2(2)	N(1)−Li(1)−C(9)	74.84(14)	Si(1)−C(1)−Li(2)	73.59(11)
N(2)−Si(3)−C(17)	107.50(10)	Si(3)−N(2)−Li(1)	101.45(14)	N(2)−Li(1)−C(17)	74.87(14)	Si(2)−C(9)−Li(1)	76.43(11)
N(2)−Si(4)−C(25)	107.03(10)	Si(4)−N(2)−Li(2)	100.12(14)	N(2)−Li(2)−C(25)	75.7(2)	Si(4)−C(25)−Li(2)	76.95(12)
Si(1)−N(1)−Li(2)	101.90(14)	Li(1)−N(2)−Li(2)	71.1(2)	N(1)−Li(2)−C(1)	73.90(14)	Si(3)−C(17)−Li(1)	76.17(11)
{[(Me$_2$N)SiMe$_2$]$_2$N−Li}$_2$ (**4**)							
Si(1)−N(1)	1.660(2)	Si(2)−N(3)	1.764(3)	N(2)−Li(1)	2.154(4)		
Si(1)−N(2)	1.766(3)	N(1)−Li(2)	2.083(4)	N(3)−Li(2)	2.163(3)		
Si(2)−N(1)	1.676(2)	N(1)−Li(1)	2.087(4)	Li(1)−Li(2)	2.521(7)		
N(1)−Si(1)−N(2)	103.49(11)	Si(1)−N(1)−Si(2)	134.61(13)	Si(1)−N(2)−Li(1)	85.10(14)	N(1)−Li(1)−N(2)	78.77(9)
N(1)−Si(2)−N(3)	103.67(11)	Li(2)−N(1)−Li(1)	74.41(16)	Si(2)−N(3)−Li(2)	84.59(13)	N(1)−Li(2)−N(3)	79.28(9)
{[(Et$_2$N)SiMe$_2$]$_2$N−Li}$_2$ (**5**)							
Si(1)−N(1)	1.6895(16)	Si(2)−N(2)	1.7794(17)	N(2)−Li(1)	2.153(3)		
Si(1)−N(3)	1.787(2)	N(1)−Li(2)	2.079(3)	N(3)−Li(2)	2.173(3)		
Si(2)−N(1)	1.6894(17)	N(1)−Li(1)	2.081(3)	Li(1)−Li(2)	2.494(6)		
N(1)−Si(1)−N(3)	105.35(8)	Si(2)−N(1)−Li(1)	88.27(10)	Si(1)−N(3)−Li(2)	83.72(10)	N(1)$^{\#}$−Li(2)−N(1)	106.4(2)
N(1)−Si(2)−N(2)	105.56(8)	Li(2)−N(1)−Li(1)	73.68(15)	N(1)−Li(1)−N(1)$^{\#}$	106.2(2)	N(1)−Li(2)−N(3)	81.11(7)
Si(1)−N(1)−Li(2)	89.10(11)	Si(2)−N(2)−Li(1)	83.78(10)	N(1)−Li(1)−N(2)	81.43(7)		
{[(N(H)^{i}Pr)SiMe$_2$]$_2$N−Li}$_2$ (**6**)							
Si(1)−N(3)	1.666(2)	Si(2)−N(2A)	1.807(6)	Li−N(2A)	2.107(9)		
Si(1)−N(4A)	1.759(6)	N(1)−Li	2.076(6)	Li−Li$^{\#}$	2.496(13)		
Si(2)−N(1)	1.663(2)	N(3)−Li	2.063(6)	N(4A)−Li$^{\#}$	2.113(9)		
N(1)−Li−N(2A)	79.8(2)	Si(2)−N(2A)−Li	84.4(3)	Si(2)$^{\#}$−N(1)−Si(2)	130.7(2)	Si(1)−N(3)−Li	131.5(2)
N(3)−Li−N(4A)$^{\#}$	80.0(2)	Si(1)−N(4A)−Li$^{\#}$	85.3(3)	Li$^{\#}$−N(1)−Li	73.9(3)	Li$^{\#}$−N(3)−Li	74.4(3)
N(1)−Li−N(4A)$^{\#}$	124.7(4)	N(3)−Si(1)−N(4A)	103.1(2)	Si(1)$^{\#}$−N(3)−Si(1)	131.7(2)	N(3)−Li−N(1)	105.8(3)
N(2A)−Li−N(4A)$^{\#}$	144.7(5)	N(1)−Si(2)−N(2A)	101.2(2)	Si(1)−N(3)−Li	89.3(2)	N(3)−Li−N(2A)	120.7(4)
{[(PhO)SiMe$_2$]$_2$N−Li}$_2$ (**7**)							
Si(1)−N(1)	1.668(2)	Si(3)−O(3)	1.708(2)	Li(1)−N(2)	2.061(4)	Li(2)−N(1)	2.065(4)
Si(1)−O(1)	1.705(2)	Si(4)−N(2)	1.662(2)	Li(1)−N(1)	2.070(4)	Li(2)−N(2)	2.097(4)
Si(2)−N(1)	1.661(2)	Si(4)−O(4)	1.712(2)	Li(1)−Li(2)	2.552(6)		
Si(2)−O(2)	1.701(2)	Li(1)−O(3)	1.977(4)	Li(2)−O(2)	1.976(4)		
Si(3)−N(2)	1.663(2)	Li(1)−O(1)	1.984(4)	Li(2)−O(4)	1.976(4)		
O(3)−Li(1)−N(2)	78.74(14)	O(4)−Li(2)−N(1)	136.3(2)	Si(1)−N(1)−Li(1)	89.57(14)	Li(1)−N(2)−Li(2)	75.7(2)
O(1)−Li(1)−N(2)	135.4(2)	O(2)−Li(2)−N(2)	132.3(2)	Li(2)−N(1)−Li(1)	76.2(2)	Si(1)−O(1)−Li(1)	91.45(14)
O(3)−Li(1)−N(1)	132.7(2)	O(4)−Li(2)−N(2)	78.2(2)	Si(3)−N(2)−Si(4)	135.02(11)	Si(2)−O(2)−Li(2)	92.1(2)
O(1)−Li(1)−N(1)	78.9(2)	N(1)−Li(2)−N(2)	103.4(2)	Si(3)−N(2)−Li(1)	90.29(13)	Si(3)−O(3)−Li(1)	91.89(13)
N(2)−Li(1)−N(1)	104.5(2)	Si(2)−N(1)−Si(1)	130.96(11)	Si(4)−N(2)−Li(1)	129.9(2)	N(1)−Si(1)−O(1)	99.66(9)
O(3)−Li(1)−O(1)	131.6(2)	Si(2)−N(1)−Li(2)	90.2(2)	Si(3)−N(2)−Li(2)	124.2(2)	N(1)−Si(2)−O(2)	98.98(9)
O(2)−Li(2)−O(4)	132.7(2)	Si(1)−N(1)−Li(2)	131.8(2)	Si(4)−O(4)−Li(2)	92.11(13)	N(2)−Si(3)−O(3)	98.94(8)
O(2)−Li(2)−N(1)	78.4(2)	Si(2)−N(1)−Li(1)	130.1(2)	Si(4)−N(2)−Li(2)	89.36(14)	N(2)−Si(4)−O(4)	99.30(6)
{[(Me$_3$SiO)SiMe$_2$]$_2$N−Li}$_2$ (**8**)							
Si(1)−O(1)	1.579(4)	Si(5)−O(3)	1.621(4)	N(1)−Li(1)	1.943(8)	O(3)−Li(2)	2.053(8)
Si(1)−N(1)	1.740(4)	Si(5)−N(2)	1.674(4)	N(1)−Li(2)	2.073(8)	O(4)−Li(1)	2.087(8)
Si(2)−N(1)	1.652(4)	Si(6)−N(2)	1.673(4)	N(2)−Li(2)	1.981(8)	Li(1)−Li(2)	2.406(11)
Si(2)−O(2)	1.699(3)	Si(6)−O(4)	1.686(5)	N(2)−Li(1)	2.085(9)		
Si(3)−O(1)	1.631(4)	Si(7)−O(3)	1.636(4)	O(1)−Li(1)	2.150(9)		
Si(4)−O(2)	1.659(4)	Si(8)−O(4)	1.639(4)	O(2)−Li(2)	2.016(8)		
O(2)−Li(2)−O(3)	134.4(4)	O(3)−Li(2)−Si(2)	155.0(4)	Si(1)−O(1)−Li(1)	89.7(3)	N(1)−Li(1)−O(1)	77.0(3)
N(2)−Li(2)−N(1)	106.4(4)	Li(1)−N(1)−Li(2)	73.5(3)	Si(2)−O(2)−Li(2)	88.4(3)	N(2)−Li(1)−O(1)	133.9(4)
O(2)−Li(2)−N(1)	80.2(3)	Si(6)−N(2)−Si(5)	130.9(2)	Si(5)−O(3)−Li(2)	87.5(2)	O(4)−Li(1)−O(1)	136.8(4)
O(3)−Li(2)−N(1)	133.0(4)	Si(5)−N(2)−Li(2)	88.4(3)	Si(6)−O(4)−Li(1)	91.1(3)	N(2)−Li(2)−O(2)	126.0(4)
O(2)−Li(2)−Si(5)	142.4(4)	Si(6)−N(2)−Li(1)	91.5(3)	N(1)−Li(1)−N(2)	107.4(4)	N(2)−Li(2)−O(3)	79.7(3)
N(1)−Li(2)−Si(5)	133.5(4)	Si(5)−N(2)−Li(1)	132.6(3)	N(1)−Li(1)−O(4)	129.2(4)		
N(2)−Li(2)−Si(2)	124.0(4)	Li(2)−N(2)−Li(1)	72.5(3)	N(2)−Li(1)−O(4)	76.6(3)		
{[(C$_4$H$_3$O)SiMe$_2$]$_2$N−Li}$_2$ (**9**)							
Si(1)−N	1.700(4)	Si(2)−C(9)	1.870(6)	C(3)−O(1)	1.394(6)	O(1)−Li(1)	1.974(8)
Si(1)−C(3)	1.882(6)	N−Li(1)	2.080(8)	C(9)−O(2)	1.418(6)	Li(1)−Li(2)	2.520(17)
Si(2)−N	1.693(4)	N−Li(2)	2.073(8)	O(2)−Li(2)	1.980(8)		

Table 2 (Continued)

			$\{[(C_4H_3O)SiMe_2]_2N{-}Li\}_2$ (**9**)				
N−Si(1)−C(3)	108.4(2)	Li(1)−N−Li(2)	74.7(4)	C(3)−O(1)−Li(1)	110.3(4)	N#1−Li(1)−N	105.0(6)
N−Si(2)−C(9)	107.5(2)	O(1)−C(3)−Si(1)	117.0(3)	O(1)−Li(1)−N	98.60(15)		
Si(1)−N−Li(1)	102.2(2)	O(2)−C(9)−Si(2)	117.6(4)	O(2)−Li(2)−N	98.03(15)		
Si(2)−N−Li(2)	103.4(2)	C(9)−O(2)−Li(2)	107.7(4)	N#1−Li(2)−N	105.6(6)		

Table 3. Dimensions of the Li_2N_2 Ring in Compounds $[X{-}Me_2Si{-}N{-}SiMe_2{-}X]_2Li_2$ 1, 2, and 4−9 (Mean Values) as Well as Li−X Interactions

compound	X	Li−N (Å)	Li···Li (Å)	N···N (Å)	Li···X (Å, X in brackets)	sum of angles in ring Li_2N_2 (deg)
2	Ph	2.024(5)	2.355(5)	3.29(1)	2.55(3) (C)	360
4	NMe_2	2.085(3)	2.521(7)	3.32(1)	2.157(4) (N)	360
5	NEt_2	2.080(1)	2.494(6)	3.33(1)	2.163(8) (N)	360
6	$N(H)^iPr$	2.070(6)	2.496(1)	3.30(1)	2.121(5) (N)	360
1	OtBu	2.066(5)	2.47(1)	3.33(1)	2.008(8) (O)	359.9
7	OPh	2.073(6)	2.552(6)	3.27(1)	1.978(7) (O)	359.8
8	$OSiMe_3$	2.02(4)	2.41(1)	3.25(1)	2.08(5) (O)	359.9
9	OC_4H_3	2.076(5)	2.52(2)	3.30(1)	1.977(5) (O)	360

In Table 3 we have assembled the dimensions of the inner Li_2N_2 unit that are common to all derivatives **2** and **4**−**9** together with those determined for **1** in the monoclinic phase.[4] If the electron-donating groups X on the $X{-}SiMe_2{-}N{-}SiMe_2{-}X$ ligand interfere most effectively with the lithium atoms of the central Li_2N_2 ring (or in a charge model the electrostatic interaction of the group X is relevant for the more positively charged lithium atoms), we should have longer Li−N bonds together with a larger Li···Li distance and a smaller N···N separation. The contrary should be found if the interaction of the lithium atoms with X is of minor importance.

In all derivatives, the Li_2N_2 rings are almost planar (see the sum of the angles in the Li_2N_2 rings), although some of the rings have small tilt angles (**8** 2.8°). The majority of the Li_2N_2 cycles have a trapezoidal shape, while only **8** forms a parallelogram with two opposite sides being longer than the adjacent ones (see also Table 2). The smallest Li−N bond lengths together with small Li···Li distances are found for **2**, whereas long Li−N bond lengths with long Li···Li distances are found for derivatives **1**, **4**, **5**, **6**, **7**, and **9**. Compound **8** is exceptional as it displays a very short Li−N bond length when the mean value is considered. The N···N separation is generally less effected than expected from the model.

This comparison shows that the organic π system in compound **2** is the weakest Lewis base for the lithium centers and, thus, effects the Li−N bonding only to a small but noticeable extent, as can be seen above. The nitrogen and oxygen donors in **1**, **4**−**7**, and **9** do effectively bind to lithium, so that the Li−N bonding in the central ring is weakened and the Li···Li separation is increased. The oxygen derivatives **1**, **7**, and **9** have very small Li−O distances, which are even smaller than the Li−N distances in the central ring. It can be deduced that in these molecules a considerable charge must be located on the oxygen atoms of the *tert*-butoxy, phenoxy, and furyl group. Although the nitrogen donors in **4**, **5**, and **6** have a longer distance to the lithium atoms of the central Li_2N_2 ring compared to the oxygen derivatives **1**, **7**, and **9**, all molecules display longer Li−N distances within the Li_2N_2 cycle. This could be an effect of a better polarization of nitrogen compared to oxygen by the metallic centers; along the same lines, it is well-known that nitrogen compounds are better Lewis bases than the similar oxygen derivatives.

The special bonding in **8** is not surprising: the short Li−N bond correlates with a rather long Li−O distance. As the oxygen atoms in this compound are coordinated by two silicon atoms, they are poorly basic. Silicon is well-known to have effective bonding to oxygen,[13] which can be explained either by Si−O multiple bonding from charge separation or by $d\pi{-}p\pi$ bonding. The very different Li−N bond lengths in the inner Li_2N_2 cycle seem to indicate less ionic bonding in this compound compared to the other ones. It also could be a consequence of the fact, that the N···N separation is the shortest of all compounds **1**−**9** (see Table 3).

It is interesting to note that the oxygen of the furyl group in **9** is strongly coordinating to lithium (see Table 2) whereas the sulfur of the thienyl group in **3** is not involved in coordination to lithium (this can be unambiguously seen from the crystal data obtained so far).[14] This effect can be correlated to the different basicity of the oxygen and sulfur atom and is a consequence of hard and soft acids and bases.[15] Furthermore, the sulfur in the thienyl group is participating to a bigger extent in the π-system than the oxygen in the furyl group.[16]

The ^{13}C CP/MAS NMR spectrum of **8** has a pecularity in that it changes with increasing temperature (see Experimental Section). At 340 K, the spectrum becomes more simple with less resonances than expected from the crystal structure of **8**. This is an indication of a solid-phase transition; so far, we have not been able to study this effect by X-ray diffraction techniques.

Experimental Section

Preparation and handling of the described compounds was performed under rigorous exclusion of air and moisture in a nitrogen atmosphere. All solvents were dried with the appropriate drying agents and distilled. Melting points were determined by sealing single crystals of the compounds under an inert atmosphere inside melting point capillaries. Molec-

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ular weights were determined cryoscopically by the freezing-point depression of benzene. Elemental analyses (C, H, N) were performed on a LECO CHN 900 Elemental Analyzer. The NMR (^{1}H, ^{13}C, and ^{29}Si) spectra were recorded on Bruker AC-200 and AM-400 spectrometers and referenced relative to TMS. Samples were run at room temperature using C_6D_6 as the lock solvent. The derivatives of hexamethyldisilazane of the general formula $X-Me_2Si-N(H)-Me_2Si-X$ were prepared according to published procedures (X = Ph,[7] OPh,[9] $OSiMe_3$[17]), whereas the other derivatives were obtained by treating 1,3-dichloro-1,1,3,3-tetramethyldisilazanes with $LiNMe_2$,[18] $LiNEt_2$,[19] $LiN(H)^iPr$,[20] C_4H_3SLi,[21] and C_4H_3OLi[22] at −78 °C in THF. After the solution was warmed to room temperature, it was further stirred for 1 h. After filtration of lithium chloride, the 1,3-functionalized disilazane compounds were treated in situ with lithium reagents as described below.

General Procedures. Preparation of [{$Me_2Si(X)$}$_2$N−Li]$_2$ (X = Ph (2), C_4H_3S (3), NMe_2 (4), NEt_2 (5), $N(H)^iPr$ (6), $OSiMe_3$ (8), C_4H_3O (9)). A solution of 15% *n*-BuLi in *n*-hexane was added dropwise to a solution of the disilazane **[$Me_2Si(X)]_2NH$ (X = Ph, C_4H_3S, NMe_2, NEt_2, $N(H)^iPr$, $OSiMe_3$, C_4H_3O)** at 0 °C in *n*-hexane. After the reaction mixture was warmed to room temperature, it was heated 15 min under reflux. On concentrating the solution and cooling at −20 °C, the lithium compounds were isolated as colorless crystals in yields between 72% and 90%.

[{$Me_2Si(Ph)$}$_2$N−Li]$_2$ (2). Yield: 72%. Mp: 112 °C. ^{1}H NMR: δ 0.24 (s, 24H, $Si-CH_3$), 7.28−7.38 (m, 20H, Ar). ^{13}C NMR: δ 3.0 ($Si-CH_3$), 129.0, 132.9, 133.0, 142.8 (Ar). ^{29}Si NMR: δ −13.5. Anal. Calcd for $C_{32}H_{44}Li_2N_2Si_4$: C, 65.95; H, 7.56; N, 4.81. Found: C, 65.84; H, 7.77; N, 4.73. MW calcd 586; found, 586 (cryoscopy in benzene).

[{$Me_2Si(C_4H_3S)$}$_2$N−Li]$_2$ (3). Yield: 81%. Mp: 124 °C. ^{1}H NMR: δ 0.37 (s, 24H, $Si-CH_3$), 6.99−7.26 (m, 12H, C_4H_3S). ^{13}C NMR: δ 4.6 ($Si-CH_3$), 129.1, 131.1, 133.3, 142.4 (C_4H_3S). ^{29}Si NMR: δ −17.4. Anal. Calcd for $C_{24}H_{36}Li_2N_2S_4Si_4$: C, 47.49; H, 5.98; N, 4.61. Found: C, 47.63; H, 6.12; N, 4.67. MW calcd 607; found, 545 (cryoscopy in benzene).

[{$Me_2Si(NMe_2)$}$_2$N−Li]$_2$ (4). Yield: 89%. Sublimation point 90 °C (10^{-2} Torr). ^{1}H NMR: δ 0.18 (s, 12H, $Si-CH_3$), 2.27 (s, 12H, $N-CH_3$). ^{13}C NMR: δ 1.9 ($Si-CH_3$), 38.9 ($N-CH_3$). ^{29}Si NMR: δ −6.4. Anal. Calcd for $C_{16}H_{48}Li_2N_6Si_4$: C, 42.63; H, 10.73; N, 18.64. Found: C, 41.98; H, 10.67; N, 19.00. MW calcd, 451 (dimer); found, 438 (cryoscopy in benzene).

[{$Me_2Si(NEt_2)$}$_2$N−Li]$_2$ (5). Yield: 86%. Mp: 128 °C. ^{1}H NMR (room temperature): δ 0.32 (s, 12H, $Si-CH_3$), 1.01 (t, J = 7.0 Hz, 12H, $N-CH_2-C\mathbf{H}_3$), 2.85 (q, J = 7.0 Hz, 8H, $N-C\mathbf{H}_2-CH_3$). ^{1}H NMR (200 K, toluene-d_8): δ 0.39 (2, 6H, $Si-CH_3$), 0.47 (s, 6H, $Si-CH_3$). ^{13}C NMR: δ 4.1 ($Si-CH_3$), 13.0 ($N-CH_2-\mathbf{C}H_3$), 38.5 ($N-\mathbf{C}H_2-CH_3$). ^{29}Si NMR: δ −7.7. Anal. Calcd for $C_{24}H_{64}Li_2N_6Si_4$: C, 51.20; H, 11.46; N, 14.93. Found: C, 50.85; H, 11.23; N, 14.71. MW calcd, 562 (dimer); found, 502 (cryoscopy in benzene).

[{$Me_2Si(N(H)^iPr$}$_2$N−Li]$_2$ (6). Yield: 86%. Mp: 162 °C. ^{1}H NMR: δ 0.22 (s, 12H, $Si-CH_3$), 1.03 (d, 12H, $CH(C\mathbf{H}_3)_2$), 2.98 (sept, 2H, $C\mathbf{H}(CH_3)_2$. ^{13}C NMR: δ 4.6 ($Si-CH_3$), 28.3 ($C-\mathbf{C}H_3$), 44.1 ($\mathbf{C}-CH_3$). ^{29}Si NMR: δ −13.3. Anal. Calcd for $C_{20}H_{56}Li_2N_6Si_4$: C,47.39; H, 11.13; N, 16.58. Found: C, 47.37; H, 11.11; N, 16.45. MW calcd, 507 (dimer).

[{$Me_2Si(OSiMe_3)$}$_2$N−Li]$_2$ (8). Yield: 75%. Mp: 205 °C. ^{1}H NMR: δ 0.22 (s, 18H, $OSi-CH_3$), 0.28 (s, 12H, $Si-CH_3$). ^{13}C NMR: δ 2.2 ($OSi-CH_3$), 5.5 ($Si-CH_3$). ^{29}Si NMR: δ 10.1 ($OSi-CH_3$), −11.5 ($Si-CH_3$). Anal. Calcd for $C_{20}H_{60}Li_2N_2O_4Si_8$: C, 38.05; H, 9.58; N, 4.44. Found: C, 37.47; H, 9.19; N, 4.36. MW calcd, 701; found, 608 (cryoscopy in benzene). ^{13}C SPE/MAS NMR: Two selected spectra are discussed. At room temperature (293 K), crystalline **8** shows a lower symmetry, indicated by three signals, one signal for the trimethylsilyl group can be observed and a splitting of the dimethylsilyl group into two signals δ 2.7 ($Si(CH_3)_3$), 5.0 ($Si(CH_3)_2$), 7.1 ($Si(CH_3)_2$). With increasing temperature, **8** becomes more symmetrical and exhibits only two main resonances, at 353 K, δ 2.4 ($Si(CH_3)_3$), 5.3 ($Si(CH_3)_2$).

[{$Me_2Si(C_4H_3O)$}$_2$N−Li]$_2$ (9). Yield: 87%. Mp: 124 °C. ^{1}H NMR: δ 0.25 (s, 24H, $Si-CH_3$), 6.12 (dd, J_{HA-HM} = 3.3 Hz, J_{HM-HX} = 1.6 Hz, 4H, $C_4H_2\mathbf{H_M}O$), 6.28 (d, J = 3.3 Hz, 4H, $C_4H_2\mathbf{H_A}O$), 7.24 (d, J = 1.6 Hz, 4H, $C_4H_2\mathbf{H_X}O$). ^{13}C NMR: δ 4.8 ($Si-CH_3$), 110.7, 117.1, 144.0, 166.1 (C_4H_3O). ^{29}Si NMR: δ −19.1. Anal. Calcd for $C_{24}H_{36}Li_2N_2O_4Si_4$: C, 53.11; H, 6.68; N, 5.16. Found: C, 53.54; H, 6.70; N, 5.21. MW calcd 543; found, 528 (cryoscopy in benzene).

Preparation of [{$Me_2Si(OPh)$}$_2$N−Li]$_2$ (7). A solution of phenyllithium in cyclohexane/ether (ratio 70/30) was added to a solution of equimolar $[Me_2Si(OPh)]_2NH$ at room temperature. The mixture was stirred for 1 h. After removing the solvent under reduced pressure, the resulting yellowish oil could be crystallized from *n*-hexane. Yield: 75%. Mp: 103 °C. ^{1}H NMR: δ 0.36 (s, 12H, $Si-CH_3$), 7.23−7.68 (m, 10H, Ar). ^{13}C NMR: δ 3.40 ($Si-CH_3$), 119.9, 122.4, 130.0, 154.8 (Ar). ^{29}Si NMR: δ −1.7. Anal. Calcd for $C_{32}H_{44}Li_2N_2O_4Si_4$: C, 59.41; H, 6.86; N, 4.33. Found: C, 59.32; H, 6.90; N, 4.26. MW calcd, 647; found, 666 (cryoscopy in benzene).

Crystal Structures. The crystal structures of compounds **2** and **4**−**9** have been obtained from X-ray diffraction of single crystals. The most important parameters for the crystals and the structure determination have been assembled in Table 1. The structure of compound **6** could be only refined by using a split-atom model for the atoms belonging to the N−C bond of the aminoisopropyl groups. They show a 50% occupancy on two sites A and B. In Figure 3 only one of the split positions is shown.

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Supporting Information Available: Tables of crystallographic data, coordinates, thermal coefficients, bond distances, and bond angles and ORTEP diagrams of **2** and **4**−**9** (49 pages). Ordering information is given on any current masthead page.

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