Intramolecular Rearrangement of Organosilyl Groups in Silylamines: A Combined Experimental−Theoretical Study

Christoph Matthes,[†] M. Noltemeyer,[†] U. Klingebiel,*[,†] and Stefan Schmatz*[,‡]

Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany, and Institut für Physikalische Chemie, Georg-August-Universität Göttingen,
Tammannstrasse 6, D-37077 Göttingen, Germany

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The lithium salt of $Me_3CSiMe_2NH_2$ reacted with halosilanes to give the bis(silyl)amines **1**−**3**, $Me_3CSiMe_2NHSiMe_2R$ (**1**: R = H, **2**: R = Me, **3**: R = CMe_3), which form lithium salts with BuLi. **4**, the lithium salt of **1**, crystallized as the trimer via the Li−N bond. Halosilanes reacted with lithiated bis(silyl)amines to give tris(silyl)amines **5**−**9**, $RSiMe_2N(SiMe_2Hal)SiMe_2R'$ (**5**: R, R′ = Me, Hal = Cl; **6**: R, R′ = Me, Hal = F; **7**: R = CMe_3, R = Me, Hal = Cl; **8**: R = CMe_3, R′ = Me, Hal = F; **9**: R, R′ = CMe_3, Hal = F). The ammonolysis of **5** and **7** led to the formation of the NH_2-substituted compounds **10** and **11**, $RSiMe_2N(SiMe_3)SiMe_2NH_2$ (**10**: R = Me, **11**: R = CMe_3). The fluorine-containing compounds (**6**, **8**, **9**) reacted with $LiNH_2$ to give the 1,3,5-trisila-2,4-diazanes **12**−**14**, $RSiMe_2{-}NH{-}SiMe_2{-}NH{-}SiMe_2R'$ (**12**: R, R′ = Me; **13**: R = Me, R′ = CMe_3; **14**: R, R′ = CMe_3). **10** and **12** as well as **11** and **13** are structural isomers. **12** and **13** are the result of a 1,3-silyl group migration in solution at low temperatures. Thermally the 1,3-silyl group migration occurred above 200 °C for **10** and at 130 °C using **11**. Quantum-chemical calculations on the thermal isomerization process reveal a two-step mechanism, whereas the anionic isomerization occurs via a single transition state at lower temperatures. **10** and **12** form the same lithium salt (**15**), $(Me_3SiNH{-}SiMe_2{-}NLi(THF){-}SiMe_3)_2$. In the reaction of **15** with $FSiMe_2CMe_3$ or of the lithiated compounds of **13** with $ClSiMe_3$ $(Me_3Si)_2NSiMe_2NHSiMe_2CMe_3$ (**16**) was obtained (eq 8). Starting from **15**, the reaction again includes a 1,3-silyl group migration from one nitrogen to the other. In the reaction of lithiated **14** with $ClSiMe_3$ substitution occurred and **17** was obtained. Crystal structures of **4** and **15** are presented, and the mechanisms of the rearrangements are discussed.

1. Introduction

The discovery of the easy migration of silyl groups in anionic and neutral molecules has been a milestone in the chemistry of inorganic molecules.[1−4] Silyl group migration has been applied to the synthesis of isomeric compounds as well as to stabilizing elements in lower coordination.[5,6]

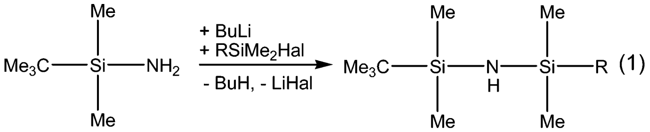
During the last years we studied migrations of hydrogen atoms and silyl groups in the chemistry of silyl hydrazines,[7,8] silyl hydroxylamines,[9,10] cyclosilazanes,[11] and aminosiloxanes both experimentally and by quantum-chemical calculations. It was found that in such isomerization reactions hydrogen atoms can migrate from a silicon to a nitrogen atom,[9] from a carbon to a nitrogen atom,[8] and from one nitrogen to another nitrogen atom.[8]

Silyl groups are usually bonded to the more electronegative atom in the rearranged molecule. They migrate, for example, from a nitrogen to an oxygen atom,[10] but also the other way around, from a nitrogen to a nitrogen atom,[11] partly via dyotropic transition states[9] or iminosilenes, and they can insert into N−O[9] or N−N bonds[7,8] with formation of silyl aminosiloxanes[9] or cyclosilazanes.[7]

In order to provide suitable compounds as precursors for polymer-pyrolysis materials, we prepared aminosilanes and again isolated products formed by silyl group migrations. This encouraged us to study the isomerization mechanism of these reactions in more detail.

2. Results and Discussion

tert-Butyldimethylsilylamine is easily lithiated with BuLi. The lithium salt thus formed reacts with halosilanes to give the unsymmetrically substituted bis(silyl)amines **1**−**3** (eq 1).



$$Me_3C{-}SiMe_2{-}NH_2 \xrightarrow[-\ BuH,\ -\ LiHal]{+\ BuLi,\ +\ RSiMe_2Hal} Me_3C{-}SiMe_2{-}NH{-}SiMe_2{-}R \quad (1)$$

1 - 3

	1	**2**[12]	**3**[13]
R	H	Me	CMe_3
Hal	Cl	Cl	F

1−**3** also form lithium salts on reaction with BuLi. The lithium salt of **1** (**4**) was isolated and purified by distillation

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* Corresponding authors. E-mail: uklinge@gwdg.de; sschmat@gwdg.de.

[†] Institut für Anorganische Chemie.

[‡] Institut für Physikalische Chemie.

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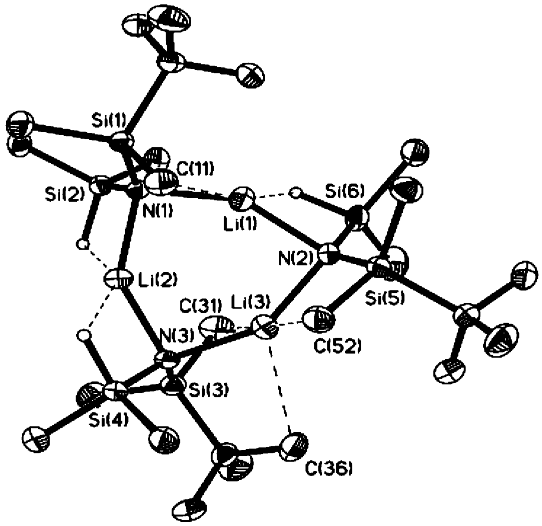
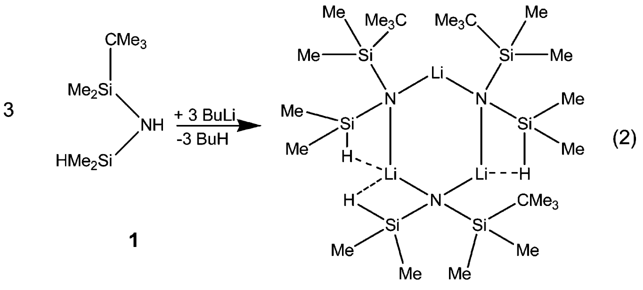


Selected bond lengths [Å] and angles [deg.].

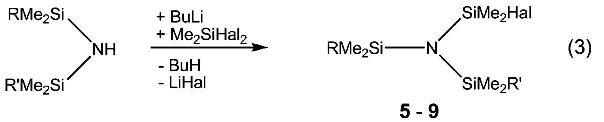
Li(1)-N(1)	1.992(3)	Li(2)-N(1)	1.975(2)	Li(3)-N(2)	2.007(3)
Li(1)-N(2)	2.045(3)	Li(2)-N(3)	2.004(3)	Li(3)-N(3)	2.009(3)
H(2)- Li(2)	2.239(1)	H(4)- Li(2)	2.168(1)	H(6)- Li(1)	2.093(2)
H(2)- Si(2)	1.436(1)	H(4)- Si(2)	1.437(2)	H(6)- Si(6)	1.465(2)
N(1)-Li(1)-N(2)	148.63(13)	N(1)-Li(2)-N(3)	141.64(14)	N(2)-Li(3)-N(3)	148.04(14)
Li(2)-N(1)-Li(1)	94.99(11)	Li(3)-N(2)-Li(1)	88.75(10)	Li(2)-N(3)-Li(3)	95.43(11)
Si(2)-N(1)-Li(2)	92.16(9)	Si(6)-N(2)-Li(1)	86.86(8)	Si(4)-N(3)-Li(2)	89.78(9)
Si(2)-N(1)-Li(1)	116.06(9)	Si(5)-N(2)-Li(3)	99.35(9)	Si(3)-N(3)-Li(3)	101.31(9)
Si(2)-N(1)-Si(1)	127.06(7)	Si(6)-N(2)-Si(5)	125.43(6)	Si(4)-N(3)-Si(3)	127.08(6)

Figure 1. Crystal structure of **4** with 50% probability thermal ellipsoids.

and crystallization (eq 2). The tris(silyl)amines **5**−**9** were prepared in situ by the reaction of lithiated bis(silyl)amines with halosilanes (eq 3).



1 **4**



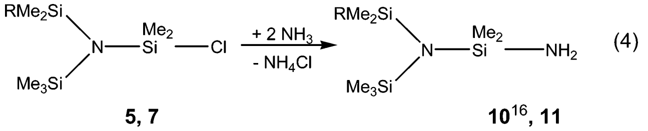
5 - 9

	5[14]	**6**[15]	**7**	**8**	**9**
R	Me	Me	CMe$_3$	CMe$_3$	CMe$_3$
R'	Me	Me	Me	Me	CMe$_3$
Hal	Cl	F	Cl	F	F

2.1. X-ray Structure of 4. Crystals of **4** were obtained from a solution of *n*-hexane. **4** crystallizes as the trimer in the space group *P*1. The Li−N bond lengths vary from 1.97 to 2.04 Å. With the Li−H contact smaller than 2.24 Å the lithium ions are four- (Li(2)), three- (Li(1)), and two-coordinated (Li(3)). Li(1) has contact to one and Li(2) to two hydridic hydrogen atoms of the SiMe$_2$H groups.

Due to this asymmetry the six-membered ring is not planar. The distances of the Li and N atoms from the least-squares are measured as follows: N(1) +0.025 Å, N(2) +0.045 Å, N(3) −0.106 Å, Li(1) −0.113 Å, Li(2) +0.087 Å, Li(3) +0.062 Å.

2.1.1. Reactions of the Si−Cl Functional Tris(silyl)amines 5 and 7 with Ammonia. The ammonolyses of SiCl units containing tris(silyl)amines **5** and **7** led to the formation of amino functional tris(silyl)amines (eq 4), which can be distilled in vacuo without NH$_3$ condensation.



5, 7 **10**[16]**, 11**

	10[16]	**11**
R	Me	CMe$_3$

2.1.2. Isomerizations of Si−F Functional Tris(silyl)amines (6, 8, 9) in Reactions with LiNH$_2$. Starting with fluoro functional tris(silyl)amines (**6**, **8**, **9**), the strong Si−F bond prevents the analogous ammonolysis. Attempts to prepare the NH$_2$ compound using LiNH$_2$ led to the formation of 1,3,5-trisila-2,4-diazanes (**12**, **13**, **14**[17]) below 50 °C (eq 5).

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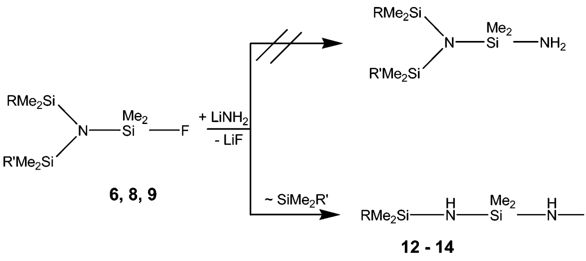


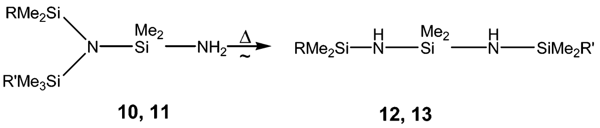
(5)

	12	13	14[17]
R	Me	CMe$_3$	CMe$_3$
R'	Me	Me	CMe$_3$

14 also can be prepared by the reaction of NHLiSiMe$_2$CMe$_3$ with Me$_2$SiHal$_2$.[17]

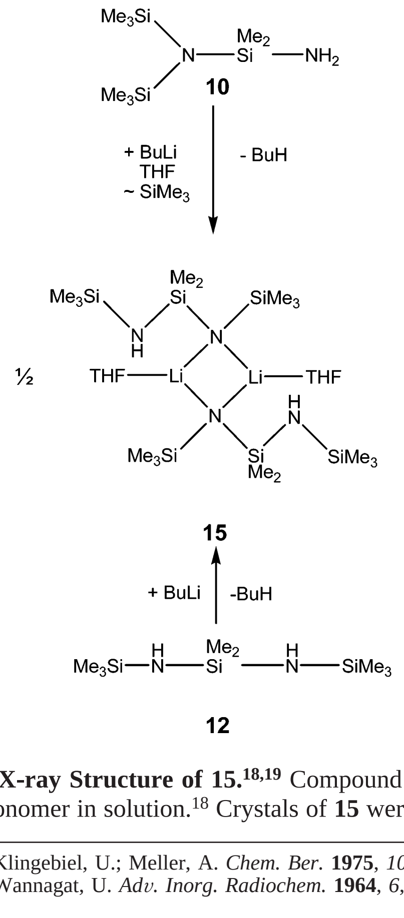
12 is a structural isomer of compound **10**, and **13** is the respective isomer of **11**. They were obtained via 1,3-silyl group migration from the (Me$_3$Si)$_2$N and the Me$_3$CSiMe$_2$−N−SiMe$_3$ group, respectively, to the NH$_2$ group. It was observed the other way around for a hydrogen of the NH$_2$ group (eq 6).

Thermally, the isomerization of **10** to **12** occurred above 200 °C[16] and that of **11**−**13** at 130 °C. **11** and **13** are present in equal amount, as derived from ^{1}H NMR data, at 120 °C. At 130 °C the rearrangement is complete.



(6)

With butyllithium, **10** as well as **12** reacted already at 0 °C, forming an amide, which was characterized as the dimer (**15**) via the Li−N bond (eq 7).



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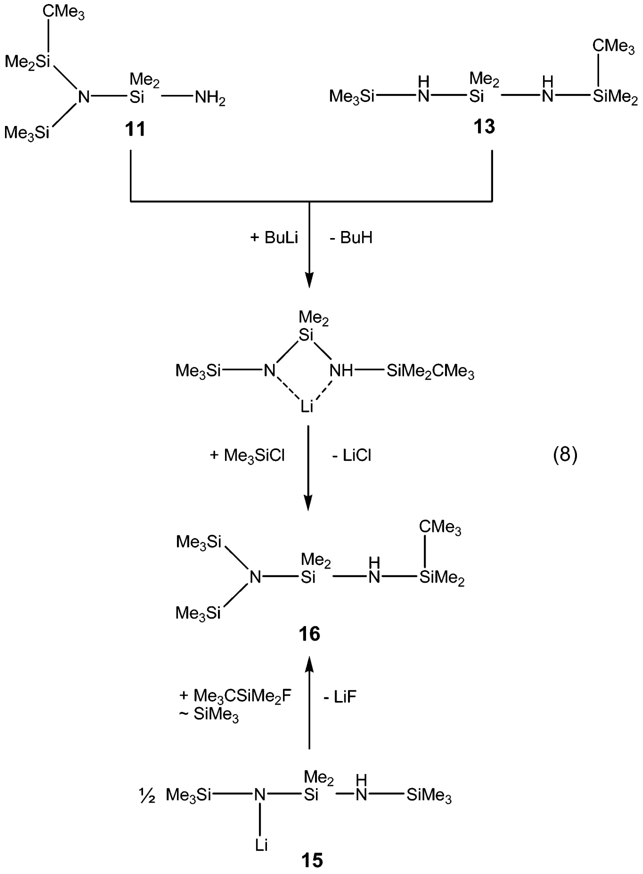
2.2. X-ray Structure of 15.[18,19] Compound **15** is described as a monomer in solution.[18] Crystals of **15** were obtained from a solution of THF. Compound **15** (Figure 2) crystallizes in the monoclinic space group $P2_1/n$. According to the results of the X-ray structure analysis **15** crystallizes as the dimer via the Li−N bond and forms an essentially planar four-membered ring in the crystal. The deviation of the atoms from the least-squares plane is as indicated, measured in Å.

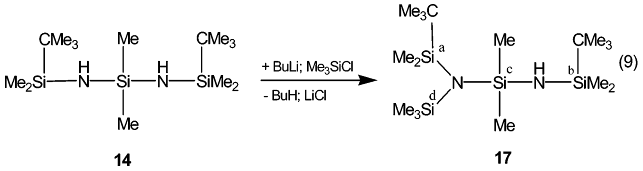
Because of the bulky silyl groups, the endocyclic angles at the N atoms are unusually small. The lithium atoms are 3-fold coordinated, but have contacts to the NH proton. The Li−H distances vary by about 0.39 Å. The NH protons were ideally positioned with constraints.[20,21]

2.2.1. Synthesis of the 1,3,5-Trisila-2,4-diazane 16. The lithium salt of **11** or **13** reacted with ClSiMe$_3$ by substitution at the NSiMe$_3$ group. The 1,1,3,5-tetrasilazane **16** is formed for steric but also for thermodynamic reasons. The ^{15}N NMR of **13** shows two resonances, −353.8 ppm for the NSiMe$_3$ nitrogen and −346.2 ppm for the NSiMe$_2$CMe$_3$ nitrogen.



(8)

In the reaction of **15** with FSiMe$_2$CMe$_3$ again **16** is obtained. A 1,3-silyl group migration has occurred. No rearrangement is observed in the reaction of lithiated **14** with ClSiMe$_3$. The substitution product **17** is formed (eq 9).



(9)

17 was characterized by NMR spectroscopy through $J_{^{29}\mathrm{Si}^{15}\mathrm{N}}$ and $J_{^{29}\mathrm{Si}^{13}\mathrm{C}}$ coupling constants and its ^{1}H−^{13}C 2D-NMR spectrum.

The easy thermal and anionic isomerizations of the silylamines encouraged us to carry out quantum-chemical calculations of the rearrangements.

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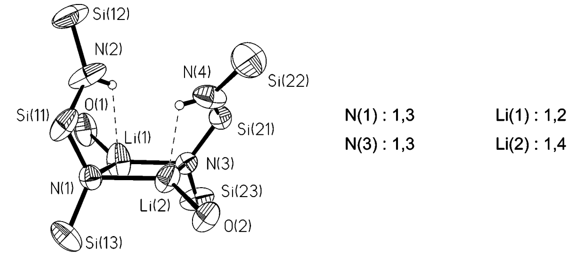

Selected bond lengths [Å] and angles [deg]:

N(1)-Li(1)	1.987(6)	N(3)- Li(2)	2.065(6)	H(2)-Li(1)	1.985(3)
N(1)-Li(2)	2.060(6)	N(3)-Li(1)	1.958(7)	H(4)-Li(2)	2.375(3)
N(1)-Si(11)	1.676(3)	N(3)-Si(21)	1.667(3)		
N(1)-Si(13)	1.683(3)	N(3)-Si(23)	1.683(2)		
N(1)-Li(1)-N(3)	109.1(3)	Li(1)-N(1)-Li(2)	74.0(2)	Li(1)-N(3)-Li(2)	74.5(2)
N(1)-Li(2)-N(3)	102.3(3)	Li(1)-N(1)-Si(11)	109.9(3)	Li(1)-N(3)-Si(23)	123.5(3)
Si(12)-N(2)-Si(11)	133.1 (2)	Si(11)-N(1)-Si(13)	124.5(15)	Si(23)-N(3)-Si(21)	123.8(15)
		Si(13)-N(1)-Li(2)	110.5(2)	Si(23)-N(3)-Li(2)	129.0(2)

Figure 2. Crystal structure of **15** with 50% probability thermal ellipsoids. Methyl groups are omitted for clarity.

2.3. Quantum-Chemical Study. To understand the formation of the rearranged molecules **12** and **13** from **10** and **11** in the framework of unimolecular isomerization processes, quantum-chemical calculations have been carried out. In particular, the experimental observation has to be explained that **11** reacts already at moderate temperature (130 °C) while the rearrangement of **10** occurs only at temperatures > 200 °C.

We have studied both the lithium salt, silylamide **A** (Figure 3), and the silylamines **C** (Figure 5). As in our previous work on related silicon-containing compounds,[7−11] we made use of density functional theory in its B3LYP variant. The B3LYP hybrid method[22] combines the Becke three-parameter exchange functional[23] with the Lee, Yang, and Parr[24] correlation functional.

The 6-31G(d,p) basis set was used throughout the calculations, which were performed using the program suite Gaussian03.[25]

The structures were fully optimized covering the full configuration space of the system. The minima and first-order saddle points were confirmed by analysis of the Hessian matrices, and zero-point vibrational energy (E_{zp}) effects were included within the harmonic oscillator rigid rotor model. The intrinsic reaction coordinate (IRC) method[26] was employed to identify the saddle points and intermediate products.

The structure of the lithium salt **A** (Figure 3) shows nearly planar surroundings of the central nitrogen atom with an N−SiNH bond length of 1.826 Å and a considerably shorter Si−NH bond (1.704 Å). Starting from **A**, the isomerization proceeds via a single dyotropic transition state (**TS**). This very constrained **TS** structure is possible due the small size of the lithium atom. In **TS**, the migrating trimethylsilyl group or *tert*-butyldimethylsilyl group, respectively, is coordinated to both nitrogen atoms; the same situation is given for the lithium atom (see Figure 3). The nonplanar $(Si-N)_2$ ring exhibits distances $r(N-SiMe_2) = 1.763$ Å, $r(Me_2Si-NH) = 1.738$ Å, $r(HN-SiMe_3) = 2.035$ Å, and $r(SiMe_3-N) = 2.002$ Å, so that the $(Si-N)_2$ skeleton has approximately C_s-symmetry. The Li−N distances [$r(N-Li) = 2.084$ Å; $r(Li-NH) = 1.939$ Å] are very close to the corresponding Si−N data for the migrating silyl group, allowing for the existence of the ionic transition state.

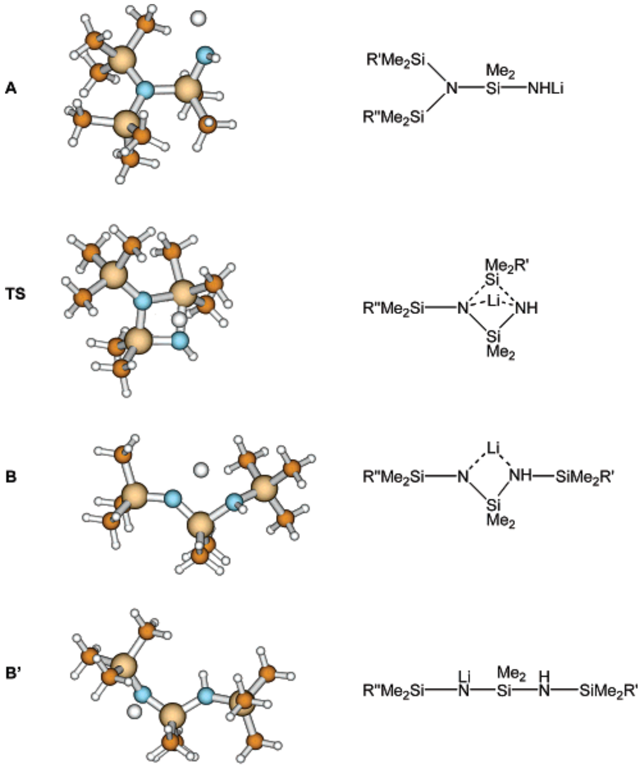

Figure 3. Calculated [B3LYP/6-31G(d,p)] structures of reactant (**A**), dyotropic transition state (**TS**), and products (**B**, **B′**) for the anionic unimolecular isomerization.

The energy diagram (Figure 4) shows that product **B** [−26.5 (−27.0) kcal mol^{-1}; energies including E_{zp} are given in parentheses] is more stable than **B′** [−15.3 (−16.7) kcal mol^{-1}] because, here, the lithium atom coordinates to both nitrogen atoms, rendering this structure particularly stable. Both products **B** and **B′** can be formed directly from **TS**, where in the latter case the N−Si and the Li−NH bond break simultaneously. The distances of the four-membered ring structure in **B** are $r(HN-Si) = 1.849$ Å, $r(Si-N) = 1.683$ Å, $r(Li-N) = 1.839$ Å, and $r(HN-Li) = 2.038$ Å. In **B′**, the $HN-SiMe_2$ bond is considerably shortened (1.756 Å), while $r(Si-N) = 1.692$ Å is almost unchanged; the N−Li distance is calculated to be 1.809 Å.

The calculated activation energy for this one-step unimolecular process amounts to only 6.9 (6.4) kcal mol^{-1}. Thus, the rearrangement occurs already below room temperature. Accordingly, the primary structure **A** could not be isolated.

In the corresponding silylamines, the situation is more complicated. For the unimolecular rearrangement to proceed in a single step, a hydrogen atom must be involved in a dyotropic transition state. Due to the small size of this atom, the necessary structure is not possible for steric reasons if the other bridging atom is the large silicon atom. Instead, the neutral rearrangement involves *two* transition states and an intermediate product. Silylamine **C** is characterized by four relatively similar Si−N bond lengths (terminal: 1.780 and 1.781 Å; central: 1.785 Å; $Si-NH_2$ 1.746 Å; for R′ = Me = R″). Starting from silylamine **C**, the isomerization proceeds via transition state **TS1**, which

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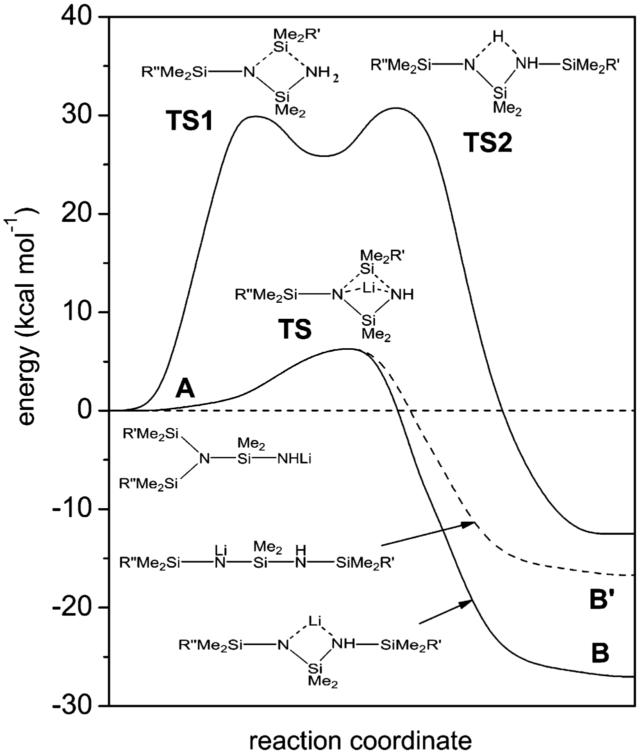

Figure 4. Energy diagram for the anionic rearrangement **A** → **B** (**B′**) [R′ = Me = R″; B3LYP/6-31G(d,p) data including E_{zp}]. The corresponding curve for the neutral two-step isomerization is also displayed for comparison (cf. Figure 6).

includes a bridging silyl group. As can be seen from Figure 5, this structure corresponds to a “late” transition state because the new bond to the second nitrogen atom (1.942 Å) is already formed, while the old bond (2.402 Å) is broken. The N−SiMe$_2$ bond length is 1.660 Å, while the SiMe$_2$−NH distance is considerably longer (1.887 Å). Following this transition state in the reaction pathway, an intermediate compound **D** is formed through the migration of the trimethylsilyl or *tert*-butyldimethylsilyl group, respectively, from the nitrogen atom to the NH$_2$ group. Species **D** is described as a zwitterionic compound with a 2-fold coordinated negatively charged amido nitrogen ion and a 4-fold coordinated positively charged amino nitrogen ion. The former nitrogen atom has almost linear coordination (angle Si−N$^-$−Si 168.9°), while the latter shows tetrahedral surroundings. The charges are strongly delocalized via the Si−N−Si−N−Si backbone so that the zwitterionic structure is an artifact of the Lewis formula. The natural charges from a natural bond analysis are (in atomic units) $q(N^-) = -1.78$ and $q(N^+) = -1.23$; thus, the difference is only 0.55 and not 2 as appears from the Lewis formula. The N$^-$−SiMe$_2$ bond is shortened to 1.606 Å, whereas the SiMe$_2$−NH$_2$ distance has become considerably longer (2.028 Å). The terminal Si−N bond with the amido nitrogen measures only 1.681 Å, indicating strong double-bond character.

Starting from **D**, the reaction proceeds via a second transition state (**TS2**), which is characterized by a four-membered Si−N−H−N ring system. The intermediate stabilizes itself in an intramolecular migration of one of the NH$_2$ hydrogen atoms to the other nitrogen atom. Comparable to **TS1**, the N−SiMe$_2$ bond measures 1.668 Å, while the SiMe$_2$−NH bond length amounts to 1.919 Å. The distances of the bridging H atom to the nitrogen atom are 1.473 Å (H- - -N) and 1.234 Å (H···NH), indicating an “early” transition state. The angles in the planar four-membered ring structure amount to 128.7° (N---H···N), 85.8° (N−Si−N), 74.5° (Si−N- - -H), and 71.0° (H···NH−Si) with a sum of angles of 360°.

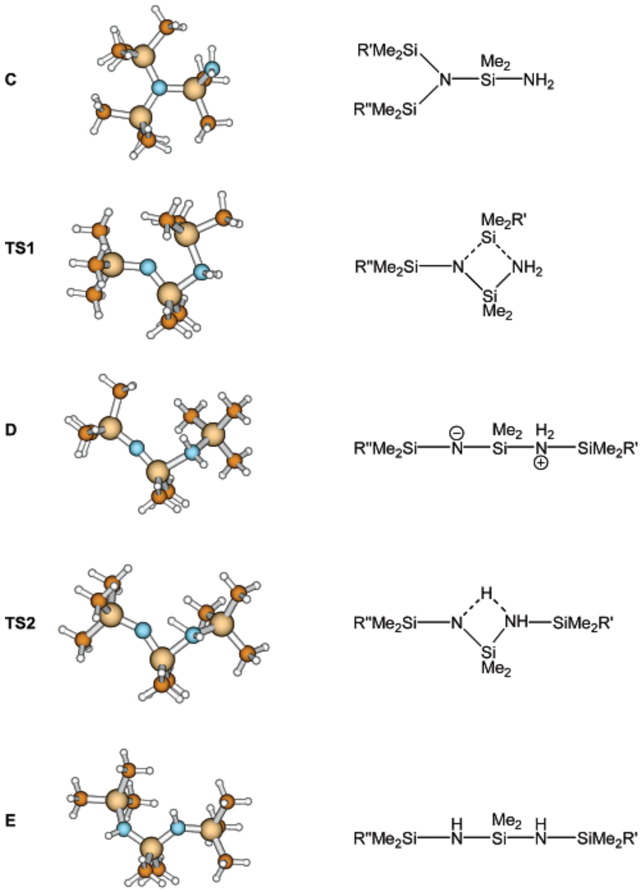

Figure 5. Calculated [B3LYP/6-31G(d,p)] structures of reactant (**C**), transition states (**TS1**, **TS2**), intermediate (**D**), and product (**E**) in the neutral rearrangement (R′ = Me = R″).

Finally, the trisilazane **E** is formed. The compound has very similar Si−N bond lengths (outer 1.758 Å; inner 1.750 Å). Due to the higher activation energy on the order of 30 kcal mol^{-1} with respect to the anionic rearrangement (Figures 3, 4), **C** can be isolated at room temperature.

Note that the zero-point vibrational energy has a considerable effect on **TS2**. This is due to the high modulus of the imaginary frequency of the transitional normal mode. For the symmetric reactant **11**, the second barrier is slightly higher and thus rate-determining.

The quantum-chemical calculations also show the easier migration of the *tert*-butyldimethylsilyl group (**11**, R′ = Me, R″ = tBu) compared to the trimethylsilyl group (**10**, R′ = Me = R″). Starting from **11**, two alternative pathways are possible (see Figure 6) because in the first step either the Me$_3$Si or the tBuMe$_2$Si group can migrate. The final products after the hydrogen shift are identical. As can be seen from Figure 6, the barrier height for both steps is smaller for the reaction of the unsymmetrically substituted reactant. This is due to electronic stabilization through the electron-rich tBuMe$_2$Si substituent. If the larger substituent migrates, the barrier for the first step is slightly lower, and the same holds for tBu in the side chain where the larger substituent also stabilizes the transition state. On the other hand, the energetic position of **TS2** (hydrogen migration) is hardly affected. In **10**, the first step is more rate-determining according to our B3LYP/6-31G(d,p) calculations.

For the symmetrically tBuMe$_2$-substituted reactant, the energetic effect is even more pronounced. Here, the overall barrier

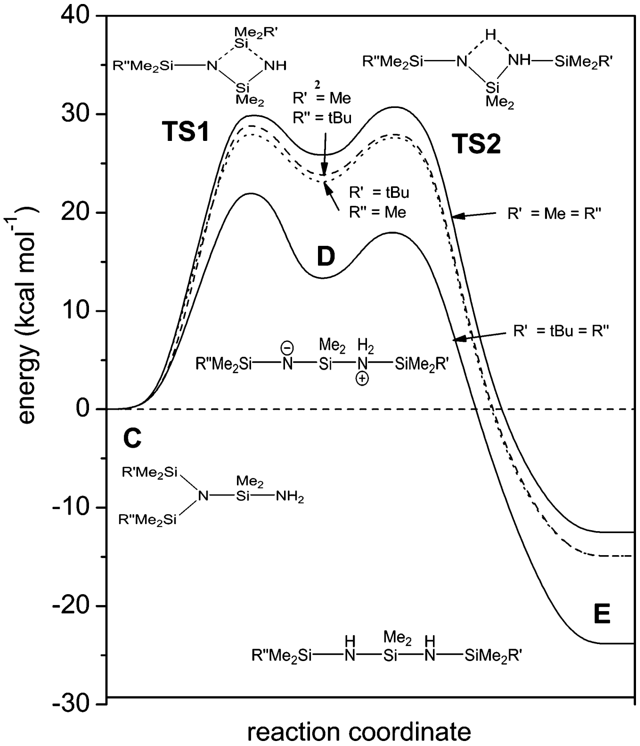

Figure 6. Energy diagram for the neutral rearrangement **C** → **E** [B3LYP/6-31G(d,p) data including E_{zp}]. The two symmetric cases R′ = Me = R″ and R′ = tBu = R″ as well as the asymmetric case are shown; in the latter, two pathways are possible (R′ = Me, R″ = tBu; R′ = tBu, R″ = Me).

has dramatically lowered and both transition states are almost equal in energy. A synergic effect occurs by the presence of two electron-rich substituents. Surprisingly, the effect is also seen in **TS2**. Besides the electronic influence there might also be sterical effects from the two tBu groups. Experimentally, the doubly tBu-substituted compound could not be isolated so far.

To study the influence of the size of the basis set, we carried out B3LYP/6-311G(2d,p) single-point energy calculations on the B3LYP/6-31G(d,p) geometries. The results, which are quoted in Table 2, indicate only very slight changes that do not affect the conclusions given above.

3. Conclusion

Starting from a silylamine, bis- and tris(silyl)amines were prepared. The lithium salt of *tert*-butyldimethylsilyl(dimethylsilyl)amine crystallizes as a trimer with two-, three-, and four-coordinated lithium ions. Depending on the reaction pathway, isomeric silylamines and trisiladiazanes, obtained by a 1,3-silyl group migration, are isolated. The silyl group migration could be proved by the crystal structure of a dimeric lithium-1,3,5-trisila-4-aza-2-amide. To understand the isomerization processes, quantum-chemical calculations have been carried out.

4. Experimental Section

All reactions were conducted under an argon or nitrogen atmosphere. Mass spectra were taken on a Finnigan MAT 8200-spectrometer or a Finnigan MAT 95-spectrometer. NMR spectra were recorded in $CDCl_3$, lithium salts in C_6D_6 (TMS int), on either a Bruker AM 250, a MSL-400, or an AVANCE 500 DRX spectrometer.

The reaction processes were controlled by ^{1}H and ^{19}F NMR spectroscopy.

***tert*-Butyldimethylsilyl(dimethylsilyl)amine (1).** Amino-*tert*-butyldimethylsilane (65.5 g, 0.5 mol) was reacted with 195 mL of nBuLi (24% in *c*-hexane, 0.5 mol) and heated at reflux for 1 h to complete the lithiation. The cooled mixture (−35 °C) was added to 60 mL of chlorodimethylsilane (0.5 mol) at −35 °C. After 2 h the mixture was heated at reflux for 3 h. The product (85.05 g, 0.45 mol, 90% yield) was separated from LiCl in vacuo and purified by distillation (bp 32 °C/10 mbar). $C_8H_{23}NSi_2$ (189.44 g/mol): ^{1}H NMR: δ 0.05 (s, SiCMe$_3$*Me*$_2$, 6H), 0.11 (d, $^3J_{HH} = 3.1$ Hz, SiH*Me*$_2$, 6H), 0.86 (s, C*Me*$_3$, 9H,), 4.70 (septd, $^3J_{HH} = 3.1$ Hz, $^3J_{HH} = 1.3$ Hz, Si*H*Me$_2$). ^{13}C NMR: δ −3.02 (qq, $^1J_{CH} = 118.2$ Hz, $^3J_{CH} = 1.8$ Hz, SiCMe$_3$*Me*$_2$), 1.25 (dqq, $^1J_{CH} = 119.7$ Hz, $^2J_{CH} = 10.8$ Hz, $^3J_{CH} = 1.0$ Hz, SiH*Me*$_2$), 18.25 (s, Si*C*Me$_3$Me$_2$), 26.26 (qq, $^3J_{CH} = 119.1$ Hz, $^3J_{CH} = 5.6$ Hz, SiC*Me*$_3$Me$_2$). ^{15}N NMR: δ −366.78 (dd, $^1J_{NH} = 66.9$ Hz, $^2J_{NH} = 5.9$ Hz, *N*H). ^{29}Si NMR: δ −11.96 (s, *Si*Me$_2$H), 8.92 (s, *Si*CMe$_3$Me$_2$). MS (EI, 70 eV): *m*/*z* (%) 132 (100) $[M - C_4H_9]^+$. Anal. Calcd: C, 50.72; H, 12.24. Found: C, 51.21; H, 12.78.

Lithium (*tert*-Butyldimethylsilyldimethylsilyl)amide (4). A 37.8 g sample of **1** (0.2 mol) was lithiated in 100 mL of *n*-hexane with 78 mL of nBuLi (24% in *c*-hexane, 0.2 mol) and heated at reflux for 1 h to complete the lithiation. The lithium salt was separated from *n*-hexane and *c*-hexane in vacuo and purified by distillation (95% yield, bp 108 °C/0.01 mbar). The distillation product was a solid that was recrystallized from *n*-hexane to obtain single crystals. $(C_8H_{22}LiNSi_2)_3$ (3 × 195.38 g/mol): ^{1}H NMR (C_6D_6): δ 0.07 (s, Si(CMe$_3$)(C*H*$_3$)$_2$, 6H), 0.29 (d, $^3J_{HH} = 3.1$, Si(C*H*$_3$)$_2$H, 6H), 0.95 (s, Si(C[C*H*$_3$]$_3$)Me$_2$, 9H), 4.62 (s, Si(CH$_3$)$_2$*H*, 1H). ^{7}Li NMR: δ 0.72. ^{13}C NMR: δ 0.33 (s, Si(CMe$_3$)(*C*H$_3$)$_2$), 4.93 (s, Si(*C*H$_3$)$_2$H), 19.36 (s, Si(*C*Me$_3$)Me$_2$), 27.84 (s, Si(C[*C*H$_3$]$_3$)Me$_2$). ^{29}Si NMR: δ −22.11 (s, *Si*Me$_2$), −1.11 (s, *Si*(CMe$_3$)Me$_2$).

(*tert*-Butyldimethylsilyl(chlorodimethylsilyl)trimethylsilyl)amine (7). A 41.8 g sample of lithium (*tert*-butyldimethylsilyl)(trimethylsilyl)amide in 100 mL of *n*-hexane was slowly added to an equimolar amount of 24 mL of dichlorodimethylsilane (0.2 mol) and stirred for 3 h at reflux. **7** (29.5 g, 50%) was separated from LiCl by condensing the crude product and solvent into a cooled trap in vacuo. **7** was purified by distillation (50% yield, bp 30 °C/0.01 mbar). $C_{11}H_{30}ClNSi_3$ (296.07 g/mol): ^{1}H NMR (CDCl$_3$): δ 0.24 (s, SiCMe$_3$*Me*$_2$, 6H), 0.30 (s, Si*Me*$_3$, 9H), 0.60 (s, SiCl*Me*$_2$, 6H), 0.92 (s, SiC*Me*$_3$Me$_2$, 9H). ^{13}C NMR: δ 2.43 (s, SiCMe$_3$*Me*$_2$), 6.23 (s, Si*Me*$_3$), 9.44 (s, SiCl*Me*$_2$), 20.01 (s, Si*C*Me$_3$Me$_2$), 28.12 (s, SiC*Me*$_3$Me$_2$). ^{29}Si NMR: δ 5.86 (s, *Si*Me$_3$) 10.49 (s, *Si*CMe$_3$Me$_2$), 13.26 (s, *Si*ClMe$_2$). MS (EI, 70 eV): *m*/*z* (%) 280 (30) $[M - CH_3]^+$, 238 (100) $[M - C_4H_9]^+$. Anal. Calcd: C, 44.62; H, 10.21. Found: C, 44.78; H, 10.38.

(*tert*-Butyldimethylsilyl(fluorodimethylsilyl)trimethylsilyl)amine (8) and Bis(*tert*-butyldimethylsilyl)fluorodimethylsilylamine (9). A 40.6 g portion of (*tert*-butyldimethylsilyl)(trimethylsilyl)amine (0.2 mol) or 49.0 g of (bis[*tert*-butyldimethylsilyl])amine (0.2 mol) was lithiated with 78 mL of nBuLi (24% in *c*-hexane, 0.2 mol) and heated at reflux for 3 h to complete the lithiation. The mixtures were added to 19.2 g of difluorodimethylsilane (0.2 mol) in 100 mL of THF at −35 °C. Then the mixture was heated at reflux for 3 h. The products (54.1 g, 0.2 mol, 97% yield (**8**), 62.3 g, 0.2 mol, 97% yield (**9**)) were separated from LiF by condensing the crude products and solvents into a cooled trap in vacuo. The products were purified by distillation (bp 58 °C/0.1 mbar (**8**), bp 69 °C/0.01 mbar (**9**)).

8: $C_{11}H_{30}FNSi_3$ (279.6 g/mol). ^{1}H NMR (CDCl$_3$): δ 0.18 (d, $^5J_{HF} = 2.0$ Hz, SiCMe$_3$*Me*$_2$, 6H), 0.20 (d, $^5J_{HF} = 0.5$ Hz, Si*Me*$_3$, 9H), 0.29 (d, $^3J_{HF} = 7.8$ Hz, SiF*Me*$_2$, 6H), 0.89 (d, $^6J_{HF} = 1.0$ Hz, SiC*Me*$_3$Me$_2$, 9H). ^{13}C NMR: δ 0.92 (d, $^4J_{CF} = 4.5$ Hz, SiCMe$_3$*Me*$_2$), 4.05 (d, $^2J_{CF} = 18.4$ Hz, SiF*Me*$_2$), 5.27 (d, $^4J_{CF} = 1.4$ Hz, Si*Me*$_3$), 19.73 (s, Si*C*Me$_3$Me$_2$), 27.87 (d, $^5J_{CF} = 1.9$ Hz, SiC*Me*$_3$Me$_2$). ^{19}F NMR: δ 34.39 (sept, $^3J_{FH} = 7.8$ Hz, Si*F*Me$_2$). ^{29}Si NMR: δ 1.22 (d, $^3J_{SiF} = 5.2$ Hz, *Si*Me$_3$) 8.99 (d, $^3J_{SiF} = 2.9$ Hz, *Si*CMe$_3$Me$_2$),

Table 1. Energetics (in kcal mol^{-1}) for the Neutral Rearrangements[a]

R′	R″	**C**	**TS1**	**D**	**TS2**	**E**
Me	Me	0.0 (0.0)	30.7 (30.1)	26.4 (25.7)	34.9 (31.1)	−11.2 (−12.5)
tBu	Me	0.0 (0.0)	29.1 (28.4)	24.0 (22.7)	32.1 (27.9)	−13.2 (−14.9)
Me	tBu	0.0 (0.0)	29.8 (29.2)	24.4 (23.5)	32.4 (28.2)	−13.2 (−14.9)
tBu	tBu	0.0 (0.0)	23.5 (22.4)	14.9 (13.0)	23.2 (18.3)	−21.5 (−23.8)

[a] Results from B3LYP/6-31G(d,p) calculations. Data in parentheses include zero-point vibrational energy effects.

Table 2. Energetics (in kcal mol^{-1}) for the Neutral Rearrangements[a]

R′	R″	**C**	**TS1**	**D**	**TS2**	**E**
Me	Me	0.0 (0.0)	29.8 (−0.9)	27.3 (0.9)	35.7 (0.8)	−11.2 (0.0)
tBu	Me	0.0 (0.0)	28.9 (−0.2)	24.3 (0.3)	32.3 (0.2)	−13.7 (−0.5)
Me	tBu	0.0 (0.0)	29.6 (−0.2)	24.7 (0.3)	32.6 (0.2)	−13.7 (−0.5)
tBu	tBu	0.0 (0.0)	23.7 (0.2)	14.5 (−0.4)	22.8 (−0.4)	−22.3 (−0.8)

[a] Results from B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d,p) calculations. Values in parentheses indicate the difference from the corresponding data given in Table 1.

9.58 (d, $^1J_{\mathrm{SiF}} = 268.8$ Hz, $Si\mathrm{FMe_2}$). MS (EI, 70 eV): *m/z* (%) 264 (30) $[\mathrm{M} - \mathrm{CH_3}]^+$, 222 (100) $[\mathrm{M} - \mathrm{C_4H_9}]^+$. Anal. Calcd: C, 47.25; H, 10.81. Found: C, 47.85; H, 11.10.

9: $\mathrm{C_{14}H_{36}FNSi_3}$ (321.70 g/mol). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.23 (d, $^5J_{\mathrm{HF}} = 1.2$ Hz, $\mathrm{SiCMe_3}Me_2$, 6H), 0.36 (d, $^3J_{\mathrm{HF}} = 7.8$ Hz, $\mathrm{SiF}Me_2$, 12H), 0.86 (d, $^6J_{\mathrm{HF}} = 0.8$ Hz, $\mathrm{C}Me_3$, 18H). ^{13}C NMR: δ 2.51 (d, $^4J_{\mathrm{CF}} = 3.1$ Hz, $\mathrm{SiCMe_3}Me_2$), 5.06 (d, $^2J_{\mathrm{CF}} = 18.5$ Hz, $\mathrm{SiF}Me_2$), 20.02 (s, $\mathrm{Si}C\mathrm{Me_3Me_2}$), 28.82 (d, $^5J_{\mathrm{CF}} = 1.6$ Hz, $\mathrm{SiC}Me_3\mathrm{Me_2}$). ^{19}F NMR: δ 36.57 (sept, $^3J_{\mathrm{FH}} = 7.8$ Hz, $\mathrm{Si}F\mathrm{Me_2}$). ^{29}Si NMR: δ 9.03 (d, $^3J_{\mathrm{SiF}} = 3.5$ Hz, $Si\mathrm{CMe_3Me_2}$), 9.74 (d, $^1J_{\mathrm{SiF}} = 268.5$ Hz, $Si\mathrm{FMe_2}$). MS (EI, 70 eV): *m/z* (%) 306 (15) $[\mathrm{M} - \mathrm{CH_3}]^+$, 264 (100) $[\mathrm{M} - \mathrm{C_4H_9}]^+$. Anal. Calcd: C, 52.27; H, 11.28. Found: C, 52.92; H, 11.79.

(Aminodimethylsilyl(*tert*-butyldimethylsilyl)trimethylsilyl)-amine (11). To 30.0 g of **7** (0.1 mol) in 100 mL of diethyl ether was added 0.2 mol of ammonia at 0 °C. After 3 h stirring at ambient temperature, the mixture was separated from ammonium chloride by a frit. The product was purified by distillation (13.4 g, 0.05 mol, 97% yield, bp 81 °C/2.2 mbar). $\mathrm{C_{11}H_{32}N_2Si_3}$ (276.64 g/mol): ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.21 (s, $\mathrm{SiCMe_3}Me_2$, 6H), 0.23 (s, $\mathrm{SiNH_2}Me_2$, 6H), 0.25 (s, $\mathrm{Si}Me_3$, 9H), 0.98 (s, $\mathrm{SiC}Me_3\mathrm{Me_2}$, 9H). ^{13}C NMR: δ 2.70 (s, $\mathrm{SiCMe_3}Me_2$), 5.93 (s, $\mathrm{SiNH_2}Me_2$), 6.37 (s, $\mathrm{Si}Me_3$), 20.05 (s, $\mathrm{Si}C\mathrm{Me_3Me_2}$), 28.53 (s, $\mathrm{SiC}Me_3\mathrm{Me_2}$). ^{15}N NMR: δ −354.53 (t, $^1J_{\mathrm{NH}} = 74.2$ Hz, $N\mathrm{H_2}$). ^{29}Si NMR: δ −5.96 (s, $Si\mathrm{NH_2Me_2}$), 0.60 (s, $Si\mathrm{Me_3}$), 6.28 (s, $Si\mathrm{CMe_3Me_2}$). MS (EI, 70 eV): *m/z* (%) 261 (15) $[\mathrm{M} - \mathrm{CH_3}]^+$, 219 (100) $[\mathrm{M} - \mathrm{C_4H_9}]^+$. Anal. Calcd: C, 47.72; H, 11.66. Found: C, 48.34; H, 11.98.

1-*tert*-Butyl-1,1,3,3,5,5,5-heptamethyl-1,3,5-trisila-2,4-diazane (13). A 13.8 g (0.05 mol) sample of **11** was heated at 130 °C for 12 h (**13b**).

1,5-Di(*tert*-butyl)-1,1,3,3,5,5-hexamethyl-1,3,5-trisila-2,4-diazane (14[16]). A 2.3 g sample of lithium amide (0.1 mol) and 50 mL of THF were added to an equimolar amount of **8** (27.9 g) or **9** (32.1 g). After stirring at reflux for 24 h, the mixtures were separated from LiF by condensing the crude products and solvents into a cooled trap. **13** (28.6 g, 0.1 mol, 90% yield) and **14** (28.9 g, 0.1 mol, 90% yield) were purified by distillation (**13** bp 83 °C/2.2 mbar, **14** 60 °C/0.01 mbar).

13: $\mathrm{C_{11}H_{32}N_2Si_3}$ (276.64 g/mol): ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0,10 (s, $\mathrm{SiCMe_3}Me_2$, 6H), 0.13 (s, $\mathrm{Si}Me_3$, 9H), 0.16 (s, $\mathrm{Si(NH)_2}Me_2$, 6H), 0.91 (s, $\mathrm{SiC}Me_3\mathrm{Me_2}$, 9H). ^{13}C NMR: δ −2.41 (s, $\mathrm{SiCMe_3}Me_2$), 2.58 (s, $\mathrm{Si}Me_2$), 4.08 (s, $\mathrm{Si(NH)_2}Me_2$), 18.03 (s, $\mathrm{Si}C\mathrm{Me_3Me_2}$), 26.32 (s, $\mathrm{SiC}Me_3\mathrm{Me_2}$). ^{15}N NMR: δ −353.78 (d, $^1J_{\mathrm{NH}} = 65.5$ Hz, $\mathrm{Si}N\mathrm{HMe_3}$), −346.15 (d, $^1J_{\mathrm{NH}} = 66.5$ Hz, $\mathrm{Si}N\mathrm{HCMe_3Me_2}$). ^{29}Si NMR: δ −6.90 (s, $Si\mathrm{(NH)_2Me_2}$), 1.21 (s, $Si\mathrm{Me_3}$), 6.67 (s, $Si\mathrm{CMe_3Me_2}$). MS (EI, 70 eV): *m/z* (%) 261 (15) $[\mathrm{M} - \mathrm{CH_3}]^+$, 219 (100) $[\mathrm{M} - \mathrm{C_4H_9}]^+$. Anal. Calcd: C, 47.72; H, 11.66. Found: C, 49.01; H, 12.32.

2-Lithium-1,1,1,3,3,5,5,5-octamethyl-1,3,5-trisila-4-aza-2-amide-THF-adduct (15). A 23.4 g amount of **10** or **12** (0.1 mol) in 100 mL of *n*-hexane was monolithiated with 39 mL of nBuLi (24% in

Table 3. Crystal Data and Structure Refinement for 4 and 15

	4	**15**
empirical formula	$\mathrm{C_{24}H_{66}Li_3N_3Si_6}$	$\mathrm{C_{24}H_{66}Li_2N_4O_2Si_6}$
fw	586.16	625.23
temperature	133(2) K	133(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
unit cell dimens	$a = 11.7389(6)$ Å, $\alpha = 74.400(4)°$ $b = 12.6241(7)$ Å, $\beta = 72.498(4)°$ $c = 15.2141(8)$ Å, $\gamma = 65.080(4)°$	$a = 12.224(3)$ Å, $\alpha = 90°$ $b = 25.357(6)$ Å, $\beta = 98.855(9)°$ $c = 13.059(3)$ Å
volume	1.92352(18) nm^3	3.9996 (17) nm^3
Z	2	4
density (calcd)	1.012 Mg/m^3	1.038 Mg/m^3
absorp coeff	0.233 mm^{-1}	0.233 mm^{-1}
$F(000)$	648	1376
cryst size	0.40 × 0.20 × 0.20 mm^3	1.00 × 0.50 × 0.50 mm^3
θ range for data collection	1.80 to 24.80°	1.61 to 27.69°
index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-17 \le l \le 17$	$-15 \le h \le 15$, $-32 \le k \le 27$, $-16 \le l \le 16$
no. of reflns collected	28073	55974
no. of indep reflns	6583 [R(int) = 0.0399]	9216 [R(int) = 0.0584]
completeness to $\theta = 27.69°$	99.5%	98.4%
max. and min. transmn	0.9548 and 0.9125	0.8926 and 0.8008
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	6583/0/355	9216/273/359
goodness-of-fit on F^2	1.054	1.067
final R indices [$I > 2\sigma(I)$]	R1 = 0.0269, wR2 = 0.0754	R1 = 0.0814, wR2 = 0.2173
R indices (all data)	R1 = 0.0317, wR2 = 0.0773	R1 = 0.1010, wR2 = 0.2364
largest diff peak and hole	0.323 and −0.197 e Å^{-3}	0.793 and −0.787 e Å^{-3}

c-hexane, 0.1 mol) and heated at reflux for 1 h to complete the lithiation. The product was separated from the solvents in vacuo. Single crystals were isolated by recrystallization from THF.

1-*tert*-Butyl-1,1,3,3,5,5,5-heptamethyl-4-trimethylsilyl-1,3,5-trisila-2,4-diazane (16) and 1,5-Di(*tert*-butyl)-1,1,3,3,5,5-hexamethyl-2-trimethylsilyl-1,3,5-trisila-2,4-diazane (17). A 0.02 mol amount of **13** (5.6 g) or **14** (6.4 g) was lithiated with 7.8 mL of nBuLi (24% in *c*-hexane, 0.02 mol) and heated at reflux for 2 h to complete the lithiation. The mixtures were treated with 0.02 mol of chlorotrimethylsilane and heated at reflux for 3 h. The products and solvents (**16a**: 3.48 g, 50% yield; **17**: 3.9 g, 0.01 mol, 50% yield) were separated from LiCl by condensing into a cooled trap and purified by distillation (**16**: bp 58 °C/0.01 mbar, **17**: 82 °C/0.01 mbar). **16b**: 23.4 g of **10** (0.1 mol) was lithiated in 100 mL of *n*-hexane with 39 mL of nBuLi (24% in *c*-hexane, 0.1 mol) and heated at reflux for 1 h to complete the lithiation. The mixture was treated with an equimolar amount of *tert*-butyldimethylfluorosilane (13.4 g) and heated at reflux for 8 h. The mixture was separated from LiF by condensing the product and solvents in a cooling trap in vacuo. **16** (3.48 g, 0.01 mol, 10% yield) was purified by distillation.

16: $C_{14}H_{40}N_2Si_4$ (348 g/mol). ^{1}H NMR: δ 0.11 (Si-(CMe$_3$)(C$_3$)$_2$, 6H), 0.27 (Si-(CH_3)$_3$, 18H), 0.31 ((N)(NH)-Si-(CH_3)$_2$, 6H), 0.91 (Si-(C[CH_3]$_3$)Me$_2$, 9H). ^{13}C NMR: δ −2.20 (Si-(CMe$_3$)(CH$_3$)$_2$), 5.78 (Si−(CH$_3$)$_3$), 7.21 ((N)(NH)-Si-(CH$_3$)$_2$), 18.01 (Si-(C[CH$_3$]$_3$)-Me$_2$), 26.40 (Si-(C[CH$_3$]$_3$)Me$_2$). ^{15}N NMR: δ −350.15 (d , *N*H, $^1J_{NH}$ = 64.9). ^{29}Si NMR: δ −5.32 ((N)(NH)-*Si*-Me$_2$), 1.91 (*Si*-Me$_3$), 6.81 (*Si*-(CMe$_3$)Me$_2$). MS (EI, 70 eV): *m*/*z* (%) 333 (30) [M − Me]$^+$, 291 (100) [M − Bu]$^+$. Anal. Calcd: C, 52.24; H, 11.56. Found: C, 52.78; H, 11.93.

17: $C_{17}H_{46}N_2Si_4$ (390 g/mol). ^{1}H NMR: δ 0.05 (Si^b-(CMe$_3$)-(CH_3)$_2$; 6H), 0.22 (Si^a-(CMe$_3$)(CH_3)$_2$, 6H), 0.26 (Si-(CH_3)$_3$, 9H), 0.28 ((N)(NH)-Si-(CH_3)$_2$, 6H), 0.88 (Si^b-(C[CH_3]$_3$)Me$_2$, 9H), 0.94 (Si^a-(C[CH_3]$_3$)Me$_2$, 9H). ^{13}C NMR: δ −2.35 (Si^b-(CMe$_3$)(CH$_3$)$_2$), 2.90 (Si^1-(CMe$_3$)(CH$_3$)$_2$), 6.79 (Si-(CH$_3$)$_3$), 8.08 ((N)(NH)-Si-(CH$_3$)$_2$), 17.87 (Si^b-(C[CH$_3$]$_3$)Me$_2$), 20.17 (Si^a-(C[CH$_3$]$_3$)Me$_2$), 26.32 (Si^b-(C[CH$_3$]$_3$)Me$_2$), 28.48 (Si^a-(C[CH$_3$]$_3$)Me$_2$). ^{15}N NMR: δ −349.59 (d, *N*H, $^1J_{NH}$ = 64,9). ^{29}Si NMR: δ −4.31 ((N)(NH)-*Si*-Me$_2$), 2.55 (*Si*-Me$_3$), 6.08 (*Si*^{a}-(CMe$_3$)Me$_2$), 7.69 (*Si*^{a}-(CMe$_3$)Me$_2$). MS (EI, 70 eV): *m*/*z* (%) 375 (15) [M − Me]$^+$, 333 (100) [M − Bu]$^+$.

$J^{15}N^{29}Si(b) = J^{29}Si(b)^{15}N = 11.7$ Hz, $J^{15}N^{29}Si(c) = J^{29}Si(c)^{15}N = 15.2$ Hz, $J^{13}C(2Me)^{29}Si(a) = J^{29}Si(a)^{13}C(2Me) = 53.7$ Hz, $J^{13}C(CMe3)^{29}Si(a) = J^{29}Si(a)^{13}C(CMe3) = 62.6$ Hz, $J^{13}C(2Me)^{29}Si(b) = J^{29}Si(b)^{13}C(2Me) = 54.6$ Hz, $J^{13}C(CMe3)^{29}Si(b) = J^{29}Si(b)^{13}C$-(CMe3) = 61.6 Hz, $J^{13}C^{29}Si(c) = J^{29}Si(c)^{13}C = 64.0$ Hz, $J^{13}C^{29}Si(c) = J^{29}Si(c)^{13}C = 56.6$ Hz

X-ray Structure Determination of 4 and 15. The data of **4** were collected on a Bruker SMART and of **15** on a STOE IPDS2 diffractometer with Mo Kα radiation. The structures were solved and refined using the SHELX program suite.[20,21]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 618433 (**4**) and CCDC 618434 (**15**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge Cb1 1EZ, UK [fax: (int.) +44-1223/336-033, e-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available: Crystallographic data (CIF) for the structures reported in this paper are available free of charge via the Internet at http://pubs.acs.org.

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