Acyclic and Cyclic Silylaminohydrazines

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The reaction of H_2N–NH_2 with $ClSiMe_2N(SiMe_3)_2$ in a molar ratio 1 : 2 gave the bis(silylamino) hydrazine $[HNSiMe_2$–$N(SiMe_3)_2]_2$ (**1**). Compound **1** forms a monomeric dilithium salt with BuLi. From *n*-hexane $(Me_3Si$–$NSiMe_2$–$NLiSiMe_3)_2$ (**2**) crystallizes while from THF $[Me_3Si$–$NSiMe_2$–$NLi(THF)SiMe_3]_2$ (**3**) precipitates. Compounds **2** and **3** are formed from **1** *via* a silyl group migration. In the rearranged salts, the silyl groups are bonded at the hydrazino nitrogen atoms. Hydrolysis of **2** led to the formation of $(Me_3Si$–N–$SiMe_2$–$NHSiMe_3)_2$ (**4**) which is a structural isomer of **1**. Ring closure occurs in reactions of **2** or **3** with $F_3B \cdot OEt_2$ or SiF_4. The seven-membered rings $(Me_3Si$–N–$SiMe_2$–$NSiMe_3)_2BF$ (**5**) and $(Me_3Si$–$NSiMe_2$–$NSiMe_3)_2SiF_2$, (**6**) were isolated as the products. The crystal structures of **2**, **3** and **5** have been determined.

Key words: Silylhydrazines, Silyl Group Migration, Isomers, Ring Closure Reactions

Introduction

The syntheses of the first silylhydrazines were described by Aylett [1] and Wannagat [2] in 1956 – 1958. Two main methods for the preparation of these compounds have since been developed [3]: the reaction of halosilanes (Hal: Cl, Br, I) with a) hydrazines and b) lithium hydrazides. Especially lithium derivatives of silyl hydrazines have shown a large variety of substitution and oxidation reactions. In 1964 Baley and West discovered the migration of silyl groups from one nitrogen atom to the other in silyl hydrazines [4, 5]. In the meantime, silyl group migration has been applied to the synthesis of isomeric compounds, as well as to stabilizing elements in lower coordination numbers [3, 6, 7]. During the last years we studied migrations of hydrogen atoms and silyl groups in the chemistry of silazanes [8] and silyl hydrazines [6, 9] both experimentally and by quantum-chemical calculations [10]. It was found that in such isomerization reactions hydrogen atoms can migrate from a carbon to a nitrogen atom [3, 6] and from one nitrogen to another atom [6].

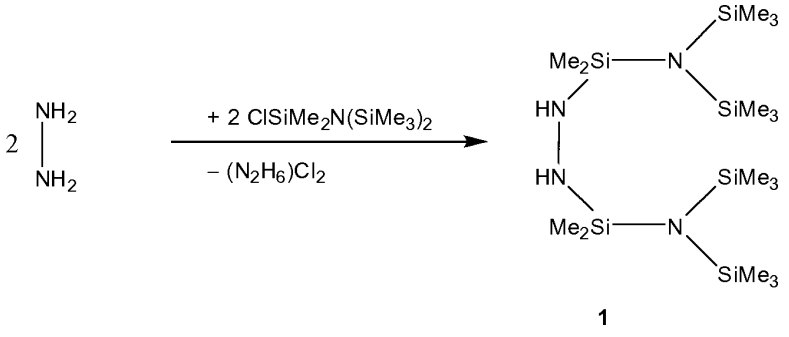
Silyl groups are usually bonded to the more electronegative atom in the rearranged molecule, but migration from a nitrogen to another nitrogen atom was also observed [8], partly *via* dyotropic transition states or *via* iminosilenes [9, 11]. In addition, silyl groups can become inserted into N–N bonds [6, 9] leading to the formation of cyclosilazanes [9].

In spite of the successful use of lithium hydrazides in chemistry, the first crystal structure determinations of these reagents were published as late as in the 1990's [3, 6, 12]. The crystal structures of solely silyl-substituted hydrazides often show unexpected features. Hexameric, tetrameric, trimeric, dimeric and monomeric hydrazides have been described [3, 6, 12 – 16]. The lithium ions in these oligomers are coordinated (side on / end on) to the N–N unit in different modes. The degree of oligomerization decreases with increasing bulkiness of the silyl substituents. The reactivity of lithium hydrazides gives access to acyclic and cyclic hydrazines, which can also be silylamino-substituted.

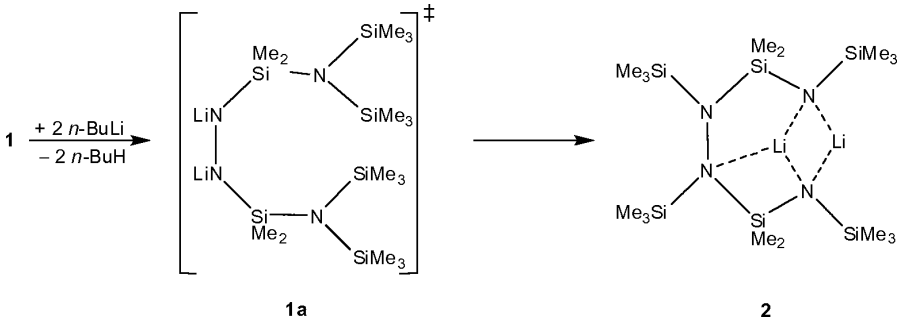
In this paper we present the synthesis of an *N*,*N*′-bis[bis(silyl)amino-dimethylsilyl] hydrazine, **1**, and show for the first time that the lithiation of such hydrazines can lead to a silyl group migration from the amine to the hydrazine nitrogen atom. This isomerization on the stage of the dilithium salt allows the synthesis of a structural isomer of **1** after reaction with water, and the synthesis of seven-membered ring compounds in reactions with trifluoroborane and tetrafluorosilane.

Results and Discussion

In the presence of triethylamine or upon using two equivalents of hydrazine as hydrogen chloride scaven-



(1)



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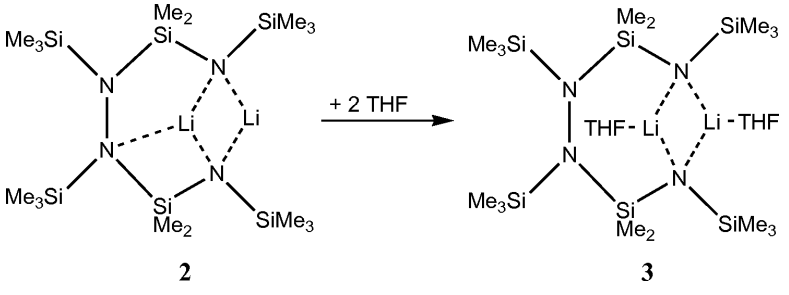
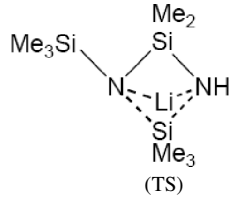


(3)

ger, anhydrous hydrazine reacts with bis(trimethylsilyl)(chlorodimethyl)amine to give the *N*,*N*′-bis[(bis(trimethylsilyl)amino-dimethylsilyl]hydrazine, **1** (Eq. 1).

No thermal isomerization *via* silyl group migration occurs below 270 °C (the decomposition temperature of **1**). With two equivalents of butyllithium **1** reacts already at 0 °C forming an amide, which was characterized as the monomer **2** (Eq. 2).

The dilithiated hydrazine **1a** was not detected in this reaction. This means that the lithium cations have become attached to the strongest donor centers of the molecule and have displaced the silyl groups there already at low temperatures. In the rearranged salt the Me_3Si groups are bonded to the hydrazine nitrogen atoms. Quantum-chemical calculations in our previous work on related silicon-nitrogen-containing compounds have shown that the N–Si bonds and the Li–N



(TS)

contacts are broken simultaneously in these reactions. The isomerization proceeds *via* a single dyotropic transition state (TS) [10].

This very constrained TS structure is possible due to the small size of the lithium cation [10, 11]. In the TS the migrating silyl group and the lithium cation are coordinated to both nitrogen atoms. The calculated activation energy for this one-step unimolecular process amounts to only 6 – 7 kcal mol^{-1}. Thus the rearrangement occurs already below r. t.

Li1–N3	195.7(4)	Li2···C1A	252.4(5)	Si3–N1	174.9(2)
Li1–N4	199.3(4)	C1···Li2A	252.4(5)	Si4–N2	175.4(2)
Li1–N2	216.7(4)	Si1–N4	168.6(2)	Si2–N2	178.6(2)
Li2–N4	200.9(4)	Si1–C1	189.5(3)	Si5–N1	178.1(2)
Li2–N3	201.9(5)	Si1–C5	187.0(2)	Si5–N3	168.5(2)
Si6–N3	169.6(2)	Si1–C10	187.2(3)	N1–N2	150.0(2)
N3–Li1–N4	105.8(2)	N3–Li1–N2	94.2(3)	N4–Li1–N2	83.8(5)
N4–Li2–N3	102.9(2)	N4–Li2–C1A	131.6(2)	N3–Li2–C1A	124.5(5)
N2–N1–Si3	116.2(1)	N2–N1–Si5	116.7(7)	Si3–N1–Si5	126.5(4)
N1–N2–Si4	117.4(3)	N1–N2–Si2	116.2(3)	Si4–N2–Si2	125.7(6)
N1–N2–Li1	107.7(6)	Si4–N2–Li1	89.9(3)	Si2–N2–Li1	81.2(0)
Si1–C1–Li2A	174.3(2)				

Table 1. Selected bond lengths (pm) and angles (deg) for **2**.

Si1–N1	169.4(1)	Si5–N4	168.1(2)	N1–Li2	198.3(3)
Si2–N1	168.7(2)	Si5–N3	177.9(2)	N1–Li1	202.5(3)
Si2–N2	178.0(1)	Si6–N4	169.2(2)	N2–N3	151.3(2)
Si3–N2	176.3(1)	O1–Li1	195.0(3)	N4–Li1	197.4(3)
Si4–N3	176.6(1)	N4–Li2	202.0(3)		
Si2–N1–Si1	127.8(0)	Li2–N1–Li1	80.2(3)	Si4–N3–Si5	122.8(1)
Si2–N1–Li2	108.3(9)	N3–N2–Si3	119.2(9)	N2–N3–Si5	115.7(8)
Si1–N1–Li2	113.2(8)	N3–N2–Si2	114.9(5)	O1–Li1–N1	138.6(0)
Si2–N1–Li1	97.3(4)	Si3–N2–Si2	123.0(7)	O1–Li1–N4	121.2(8)
Si1–N1–Li1	119.1(5)	N2–N3–Si4	119.2(1)	N4–Li1–N1	99.5(1)

Table 2. Selected bond lengths (pm) and angles (deg) for **3**.

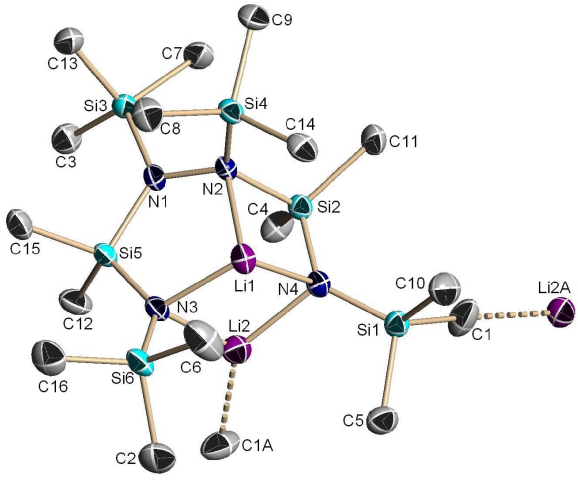


Fig. 1. Molecular structure of **2** in the crystal.

The dilithium salt **2** was isolated and purified by distillation. Single crystals of **2** were obtained from a solution in *n*-hexane at r. t. In the reaction of **2** with THF the dilithium salt **3** was formed as colorless crystals from *n*-hexane/THF. The crystals were dissolved in C_6D_6, and their NMR spectra revealed the presence of one molecule of THF coordinated to each lithium atom (Eq. 3).

*Crystal and molecular structure of **2***

Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. Fig. 1 shows a plot of the molecular structure, Table 1 summarizes selected bond lengths (pm) and angles (deg).

The amide nitrogen atoms N3 and N4 together with the two lithium atoms Li1 and Li2 form a four-membered $(Li–N)_2$ ring. In addition, Li1 is coordinated to the nitrogen atom N2 of the hydrazine unit (Li1–N2 = 216.7(4) pm) creating a four-membered (LiN_2Si) and a five-membered (LiN_2SiN) ring.

The Li1–N2 contact generates a tetrahedral environment of the hydrazine nitrogen atom N2. By contrast, the three-coordinated hydrazine nitrogen atom N1 is bound to only three other atoms and has a planar environment ($\Sigma°N1 = 359.5°$). The Si–N bonds of the amine nitrogen atoms are about 10 pm longer in comparison to those with the amide nitrogen atoms. The angles at the nitrogen atoms of the four-membered $(Li–N)_2$ ring, *e. g.* Li1–N4–Li2 = 74.4(1)°, are extremely small compared *e. g.* to the angle Si1–N4–Si2 = 130.6(1)°.

The monomers of **2** are connected *via* lithium-carbon contacts Li2A–C1 and Li2–C1A (Fig. 2) to form chains. This contact lengthens the Si–C bonds involved, *e. g.* Si1–C1 = 189.5(3) pm, as compared to Si1–C5 = 187.0(2) pm.

*Crystal and molecular structure of **3***

Compound **3** crystallizes as a monomer in the triclinic space group $P\bar{1}$ with $Z = 2$ (Fig. 3). Table 2 contains imoportant bond lengths (pm) and angles (deg).

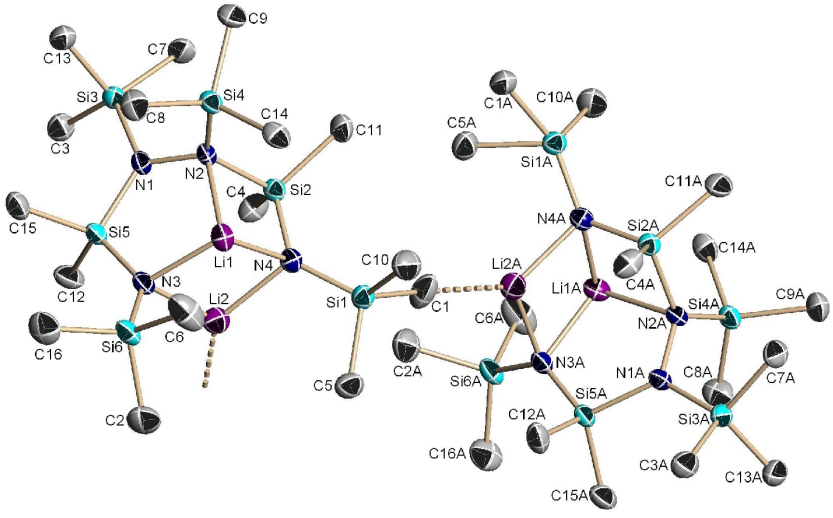
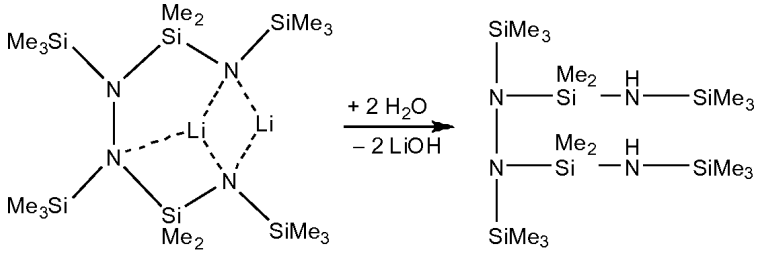


Fig. 2. Part of the extended chain structure of **2** in the crystal.



2 **4** (4)

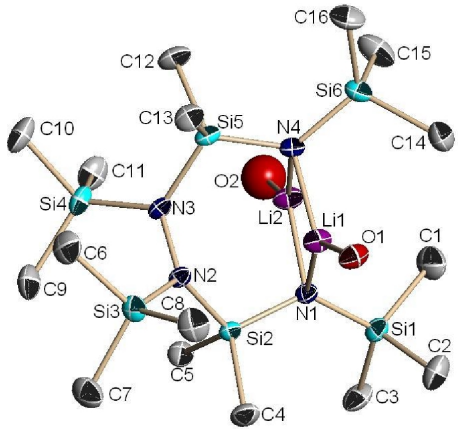


Fig. 3. Molecular structure of **3** in the crystal.

In the bicyclic compound **3** each lithium ion is coordinated by a THF molecule. This leads – compared to compound **2** – to a loss of intramolecular lithium-hydrazine and intermolecular lithium-methyl contacts. The two rings of **3** are nearly perpendicular to each other (87°). The environments of all the lithium atoms and hydrazine nitrogen atoms are nearly planar (Σ°Li1 = 359.4°, Σ°Li2 = 359.8°, Σ°N2 = 357.3°, Σ°N3 = 357.8°).

For electrostatic reasons, the Si–N bonds of the silicon to the hydrazine nitrogen atoms are about 10 pm longer than those to the amide nitrogen atoms.

*Hydrolysis of compound **3***

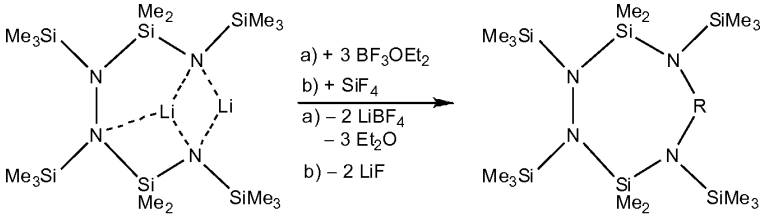
The dilithium salt **2** and its THF adduct **3** react quantitatively with water in a molar ratio 1 : 2 to give **4**, which is a structural isomer of **1** (Eq. 4).

*Bora- and silacycloheptanes **5** and **6***

The dilithium salt **2** reacts with $F_3B \cdot OEt_2$ or SiF_4 to form the cycloheptanes **5** and **6**, respectively (Eq. 5). The ring closure reactions require careful monitoring with ^{19}F NMR. **5** and **6** can be isolated by vacuum distillation (> 130 °C, 0.01 mbar), but can also be purified by crystallization.

B1–F1	136.4(3)	Si1–N4	172.7(2)	Si3–N1	178.1(2)
B1–N1	143.3(3)	Si1–N1	175.6(2)	Si4–N2	177.5(2)
B1–N2	144.8(3)	Si2–N3	173.8(2)	Si5–N3	175.6(2)
N3–N4	149.0(2)	Si2–N2	175.1(2)	Si6–N4	174.8(2)
F1–B1–N1	114.8(2)	F1–B1–N2	114.2(2)	N1–B1–N2	130.9(2)
B1–N1–Si1	123.3(8)	B1–N1–Si3	113.3(4)	Si1–N1–Si3	122.5(6)
B1–N2–Si2	116.3(7)	B1–N2–Si4	114.4(6)	Si2–N2–Si4	125.6(6)
N4–N3–Si2	116.2(4)	N4–N3–Si5	116.9(2)	Si2–N3–Si5	126.6(9)
N3–N4–Si1	111.7(7)	N3–N4–Si6	117.4(0)	Si1–N4–Si6	129.6(6)
N1–Si1–N4	108.4(4)	N2–Si2–N3	108.6(0)		

Table 3. Selected bond lengths (pm) and angles (deg) of **5**.



2 R = BF (**5**), SiF_2 (**6**) (5)

During attempts to obtain single crystals of **5** from diethyl ether it was found that **5** is a chromophoric compound. It changes its color in $(C_2H_5)_2O$ from colorless at r. t. to blue-green below 0 °C.

Crystal and molecular structure of ***5***

The 1-bora-2,4,5,7-tetraaza-3,6 disilacycloheptane **5** crystallizes from *n*-hexane in the monoclinic space group $P2_1/n$ with $Z = 4$ (Fig. 4, Table 3). The boron and nitrogen atoms of **5** have, with exception of N(2), [Σ°N2 = 356.6°], a nearly planar environment: Σ°B1 = 359.3°, Σ°N3 = 359.9°, Σ°N4 = 358.8°. The shortest Si–N bonds are found to be the endocyclic hydrazine nitrogen-silicon bonds (Si2–N3 = 173.8(2) pm, Si1–N4 = 172.7(2) pm) whereas the exocyclic amino-silicon bonds are elongated (Si1–N3 = 178.1(2) pm, Si2–N4 = 177.5(2) pm).

The side-on view of the ring system **5** shows a twist conformation, which allows the nitrogen and boron atoms to have a planar environment [Fig. 4 (b)].

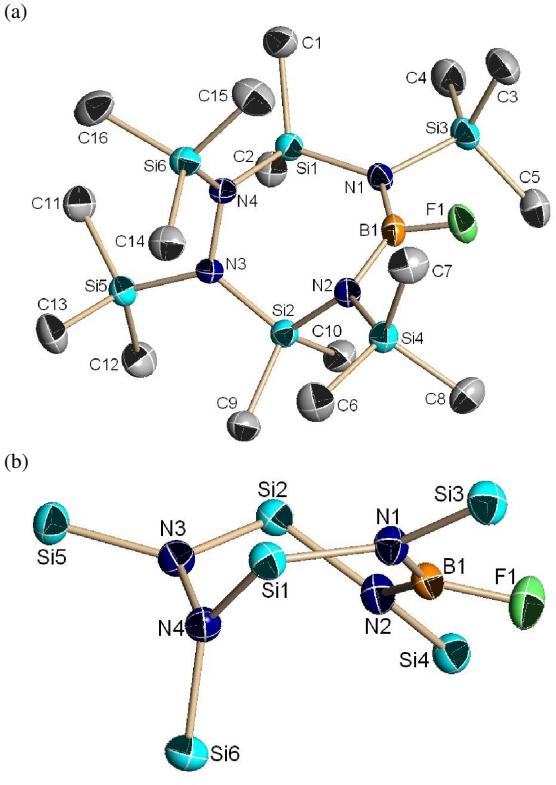


Fig. 4. (a) Molecular structure of **5** in the crystal; (b) side-on view of **5**.

Conclusion

Starting from bis(trimethylsilyl)amino-dimethylchlorosilane and hydrazine, an *N*,*N*′-bis[bis(silyl)-amino]silylhydrazine (**1**) was prepared and converted to a dilithium salt, which crystallizes from *n*-hexane as a monomer containing a $(LiN)_2$ ring system. The reaction involves a silyl group migration as demonstrated by the crystal structure of **2**. The hydrolysis of **2** leads to the formation of **4**, a structural isomer of **1**. Seven-

membered rings (**5**, **6**) are formed in reactions of **2** with BF_3 and SiF_4.

Experimental Section

All reactions were conducted under an argon or nitrogen atmosphere. Mass spectra were recorded on Finnigan MAT 8200 or MAT 95 spectrometers. NMR spectra were generally recorded in $CDCl_3$, lithium salts in C_6D_6, (internal TMS as standard) on Bruker AM 250, MSL-400 or AVANCE 500 DRX spectrometers. The progress of the reactions was controlled by ^1H and ^{19}F NMR spectroscopy, respectively.

*N,N′-Bis[bis(trimethylsilylamino)dimethylsilyl]hydrazine (**1**)*

To 32 g of hydrazine (1 mol) in 250 mL of diethyl ether kept at low temperature (0 °C) was added an equimolar amount of chlorodimethylsilyl-bis(trimethylsilyl)amine (1 mol). The mixture was stirred and heated under reflux for 5 h. Then the hydrochloride was separated using a glass filter. The silylhydrazine **1** was purified by distillation. Yield: 84 %; b. p. 113 °C/001 mbar. – MS (EI, 70 eV): *m/z* (%) = 468 (30) $[M]^+$. – ^1H NMR ($CDCl_3$): δ = 0.18 ($Si(CH_3)_2$, 12 H), 0.19 ($Si(CH_3)_3$, 36 H), 2.28 (NH, 2H). – ^{13}C NMR: δ = 2.82 (SiC_2), 5.47 (SiC_3). – ^{15}N NMR: δ = −323.96 (NH, d, $^1J_{NH}$ = 76.6 Hz). – ^{29}Si NMR: δ = −4.51 ($Si(CH_3)_2$), 1.98 ($Si(CH_3)_3$).

*N,N′-Bis[(trimethylsilyl-lithiumamido)dimethylsilyl]-trimethylsilylhydrazine (**2**)*

A 46.7 g sample of **1** (0.1 mol) in 100 mL of *n*-hexane was treated with 0.2 mol *n*-C_4H_9Li (15 % in *n*-hexane), and the mixture was heated under reflux for 1 h to complete the lithiation. The dilithium salt was separated from *n*-hexane *in vacuo* and purified by distillation (95 % yield; b. p. 124 °C/0.01 mbar). The distillation product was a solid which was re-crystallized from *n*-hexane to obtain single crystals. **3** was obtained by crystallization of **2** from THF. Yield: 95 %; m. p. 95 °C. – ^1H NMR (C_6D_6): δ = 0.12 ($LiNSi(CH_3)_3$, 18H), 0.15 ($NNSi(CH_3)_3$, 18H), 0.31 ($Si(CH_3)_2$, 12H). – ^7Li NMR: δ = 1.46. – ^{13}C NMR: δ = 3.39 ($LiNSiC_3$), 5.69 ($NNSiC_3$), 7.66 (SiC_2). – ^{29}Si NMR: δ = −12.86 (LiNSi), −5.87 ($SiMe_2$), 6.74 (NNSi).

*N,N′-Bis(1-trimethylsilylamino)dimethylsilyl-N,N′-bis(trimethylsilyl)hydrazine (**4**)*

Dilithium salt **2** (9.6 g, 0.02 mol) was dissolved in 50 mL of *n*-hexane. Distilled water was added (0.72 g, 0.04 mol), and the solution was stirred for 2 h. The *n*-hexane and the crude product were removed from LiOH *in vacuo*. Subsequent distillation yielded **4** as a colorless liquid. Yield 94 %; b. p. 104 °C/0.01 mbar. – MS (EI): *m/z* (%) = 451 (30) $[M–CH_3]^+$. – ^1H NMR ($CDCl_3$): δ = 0.15 ($NHSi(CH_3)_3$, 18H), 0.28 ($NNSi(CH_3)_3$, 18H), 0.33 ($Si(CH_3)_2$, 12H). – ^{13}C NMR: δ = 3.20 ($NHSiC_3$), 3.81 ($NNSiC_3$), 7.49 (SiC_2). – ^{29}Si NMR: δ = −0.08 (SiC_2), 8.80 (NHSi), 9.21 (NNSi).

*1-Fluoro-2,4,5,7-tetrakis(trimethylsilyl)-3,3,6,6-tetramethyl-1-bora-2,4,5,7-tetraaza-3,6-disila-cycloheptane (**5**)*

In a 250 mL Schlenk flask, dilithium salt **1** (14.0 g, 0.3 mol) was dissolved in 150 mL of *n*-hexane. Trifluoroborane-diethyl ether (12.8 g, 0.9 mol) was added to the solution. With stirring, the reaction mixture was heated under reflux for 4 h. The salt $LiBF_4$ formed during the reaction was filtered off, and diethyl ether and *n*-hexane were evaporated under vacuum. The product was purified by distillation and re-crystallized from *n*-hexane to obtain single crystals. Yield 40 %; b. p. 133 °C/0.01 mbar, m. p. 93 °C. – MS (EI, 70 eV): *m/z* (%) = 494 (100) $[M]^+$, 479 (80) $[M–CH_3]^+$. – ^1H NMR ($CDCl_3$): δ = 0.23 ($NNSi(CH_3)_3$, 18H), 0.29 ($FBNSi(CH_3)_3$, d, $^5J_{HF}$ = 2.3 Hz, 18H), 0.33 ($Si(CH_3)_2$, 12H). – ^{11}B NMR: δ = 26.58. – ^{13}C NMR: δ = 3.20 ($NNSiC_3$), 3.85 ($FBNSiC_3$, d, $^4J_{CF}$ = 4.3 Hz), 5.17 (SiC_2, d, $^4J_{CF}$ = 1.9 Hz). – ^{29}Si NMR: δ = −1.37 (SiC_2, d, $^3J_{SiF}$ = 7.4 Hz), 5.40 (FBNSi, d, $^3J_{SiF}$ = 10.9 Hz), 9.34 (NNSi).

*1,1-Difluoro-2,4,5,7-tetrakis(trimethylsilyl)-3,3,6,6-tetramethyl-2,4,5,7-tetraaza-1,3,6-trisila-cycloheptane (**6**)*

To 14.0 g of **1** (0.3 mol) in 200 mL of *n*-hexane at −70 °C was added 3.4 g of SiF_4 (0.33 mol) with stirring. With continued stirring the reaction mixture was allowed to warm to r. t. overnight. The cycloheptane was separated from LiF by condensing the product and the *n*-hexane into a cooled trap *in vacuo*. **6** was purified by distillation. Yield 42 %; b. p. 136 °C/0.01 mbar. – MS (EI, 70 eV): *m/z* (%) = 530 (100) $[M]^+$, 515 (80) $[M–CH_3]^+$. – ^1H NMR ($CDCl_3$): δ = 0.13 ($NNSi(CH_3)_3$, 18H), 0.25 ($F_2SiNSi(CH_3)_3$, t, $^5J_{HF}$ = 1.1 Hz, 18H), 0.32 ($Si(CH_3)_2$, t, $^5J_{HF}$ = 1.3 Hz, 12H). – ^{13}C NMR: δ = 2.60 ($NNSiC_3$, t, $^4J_{CF}$ = 4.3 Hz), 4.06 ($NSiC_3$, t, $^4J_{CF}$ = 4.3 Hz), 5.34 (SiC_2, t, $^4J_{CF}$ = 1.9 Hz). – ^{19}F NMR: δ = 48.32. – ^{29}Si NMR: δ = −61.08 (SiF_2, t, J_{SiF} = 232.1 Hz), 0.48 (SiC_2, t, $^3J_{SiF}$ = 1.4 Hz), 9.24 ($NNSiC_3$).

X-Ray structure determination

The data were collected on a Stoe IPDS II diffractometer (graphite-monochromatized MoK_α radiation, λ = 0.71073 Å) by use of ω scans at −140 °C. The structures were solved by Direct Methods and refined on F^2 using all reflections with SHELX-97 [17]. Most non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. One THF molecule in structure **3** is disordered in two positions and was refined

Table 4. Crystal structure data for **2**, **3** and **5**.

	2	**3**	**5**
Formula	$C_{16}H_{48}Li_2N_4Si_6$	$C_{24}H_{64}Li_2N_4O_2Si_6$	$C_{16}H_{48}BFN_4Si_6$
M_r	479.00	623.21	494.93
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$
a, Å	10.0319(5)	10.0539(5)	9.0894(6)
b, Å	16.8421(7)	11.4456(6)	18.3316(11)
c, Å	17.3218(7)	17.6115(9)	18.1063(10)
α, deg	90	93.441(4)	90
β, deg	90	98.782(4)	96.033(5)
γ, deg	90	108.991(4)	90
V, Å^3	2926.7(2)	1880.74(17)	3000.2(3)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.087	1.100	1.096
μ(MoK_α), mm^{-1}	0.295	0.247	0.295
F(000), e	1048	684	1080
hkl range	$-11 \le h \le 11$	$-11 \le h \le 12$	$-10 \le h \le 10$
	$-19 \le k \le 19$	$-14 \le k \le 13$	$-21 \le k \le 21$
	$-20 \le l \le 20$	$-21 \le l \le 21$	$-21 \le l \le 21$
Refl. measured	32972	16133	46401
Refl. unique	5005	7206	5185
R_{int}	0.0703	0.0252	0.0871
Param. refined	280	354	269
$R(F)/wR(F^2)$ (all refl.)	0.0326 / 0.0619	0.0455 / 0.0947	0.0611 / 0.0594
x(Flack)	−0.04(9)	–	–
GoF (F^2)	0.970	1.039	1.034
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.214 / −0.197	0.476 / −0.299	0.207 / −0.231

with fixed occupancies of 0.5. Details of the crystal structure dermination are summarized in Table 4.

CCDC 08252 (**2**), 708250 (**3**), and 708251 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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