

# Four-, Five-, and Six-Membered Silylhydrazine-Ring Systems<sup>†</sup>

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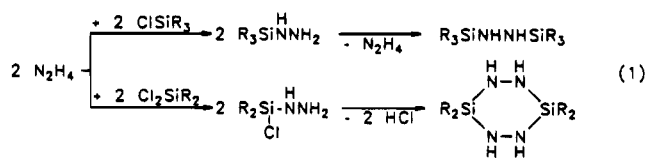
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Silylhydrazines (RR'R''SiNHNH<sub>2</sub>, 1–3) and the six-membered-ring [(Me<sub>2</sub>CH)<sub>2</sub>SiNHNH]<sub>2</sub> (4) are formed in reaction of fluorosilanes with lithiated hydrazine. N,N'-Bis(silyl)hydrazines with different silyl groups are obtained in reactions of lithated 1, [(CMe<sub>3</sub>)<sub>2</sub>SiMeNHNH<sub>2</sub>], with F<sub>2</sub>Si(CHMe<sub>2</sub>)<sub>2</sub> [(CMe<sub>3</sub>)<sub>2</sub>SiMeNHNHSiF(CHMe<sub>2</sub>)<sub>2</sub>, 5] and of lithated 2, [(CMe<sub>3</sub>)<sub>2</sub>-SiFNHNH<sub>2</sub>], with chlorosilanes [(CMe<sub>3</sub>)<sub>2</sub>SiFNHNHSiMe<sub>3</sub>R, R = Me (6) and CMe<sub>3</sub> (7)]. [(Me<sub>2</sub>-HC)<sub>2</sub>N]<sub>2</sub>SiFNHNH<sub>2</sub> (3) reacts with BuLi to give a five-membered cyclic silylhydrazine, (NHSiR<sub>2</sub>)<sub>2</sub>NNH<sub>2</sub> (8), and LiF. 8 isomerizes above its melting point, and the six-membered-ring (R<sub>2</sub>SiNHNH)<sub>2</sub>, R = N(CHMe<sub>2</sub>)<sub>2</sub> (9), is formed. The reaction of 5–7 with BuLi leads to the formation of six-membered rings, (R<sub>2</sub>SiNHNHR')<sub>2</sub> [R = CHMe<sub>2</sub>, R' = SiMe(CMe<sub>3</sub>)<sub>2</sub> (10); R = CMe<sub>3</sub>, R' = SiMe<sub>3</sub> (11), R' = SiMe<sub>2</sub>CMe<sub>3</sub> (12)], and LiF. Fluorine–chlorine exchange occurs in the reaction of lithated 5 with ClSiMe<sub>3</sub>. FSiMe<sub>3</sub> and the four-membered cyclic silylhydrazine [(CMe<sub>3</sub>)<sub>2</sub>SiMeNHSi(CHMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (13) are obtained by thermal LiCl elimination from the resulting salt. The crystal structures of 12 and 13 have been determined and are discussed.

## Introduction

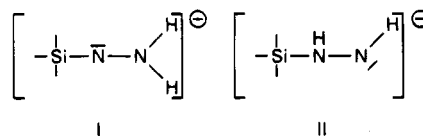
The syntheses of the first acyclic and cyclic silylhydrazines were reported by Aylett<sup>1</sup> and Wannagat<sup>2–4</sup> in 1956–1958. Two main methods for preparing them were developed.<sup>4</sup> The first is the treatment of a hydrazine with a halosilane, and the second, the treatment of a lithiated hydrazine with a halosilane. The reaction of iodosilane with hydrazine yields the tetrasilylhydrazine,<sup>1</sup> while chlorotrimethylsilane gives N,N'-bis(trimethylsilyl)hydrazine.<sup>2</sup> Primary silylhydrazines with R = Me, Et, or Pr cannot be isolated, as they immediately undergo further condensation to bis(silyl)hydrazines with elimination of hydrazine.<sup>2–4</sup> For the isolated Ph<sub>3</sub>SiNHNH<sub>2</sub>, this condensation occurs under more drastic conditions at 90 °C. Dichlorosilanes react with hydrazine to form only six-membered rings together with polymers (eq 1).<sup>4,5</sup>

In 1993 a series of acyclic and cyclic (hydridosilyl)hydrazines were prepared from the corresponding chloro- and bromosilanes and hydrazines in the presence of Et<sub>3</sub>N as an auxiliary base.<sup>6,7</sup> Recently we were able to show that primary and fluoro-functional silylhydrazines



can be kinetically stabilized by the use of bulky *tert*-butyl groups.<sup>8,9</sup> Lithium derivatives of these hydrazines allow a stepwise synthesis of cyclic silylhydrazines.<sup>8–10</sup>

The lithium derivative of (di-*tert*-butylmethylsilyl)hydrazine<sup>9</sup> crystallizes as a hexamer with Li<sup>+</sup> ions bound side-on and end-on. The crystal structure of this compound exhibits two tautomeric silylhydrazide units I and II.



This phenomenon accounts for the isomerizations during secondary substitutions.<sup>11</sup> Because only six-membered rings are formed in the reaction of hydrazine with dichlorosilanes, the results of this X-ray analysis gave us reason to examine the products formed via salt

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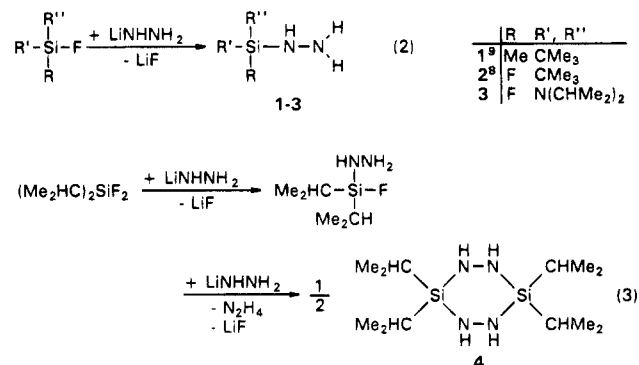
(10) Clegg, W.; Haase, M.; Hluchy, H.; Klingebiel, U.; Sheldrick, G. M. *Chem. Ber.* **1993**, *116*, 290–298.

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elimination from lithiated fluoro-functional mono- and bis(silyl)hydrazines.

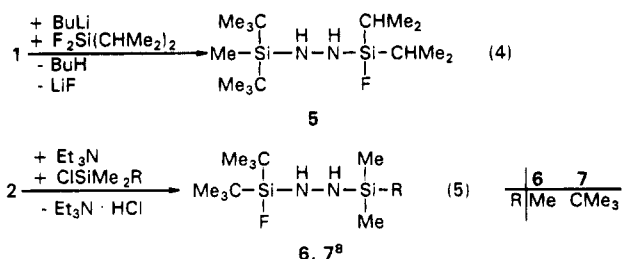
### Results and Discussion

As appropriate precursors for cyclic silylhydrazines, we chose the acyclic silylhydrazines 1–3, which can be obtained from the reaction of fluorosilanes with lithiated hydrazine (eq 2).<sup>8,9</sup> Compounds 1–3 are thermally very



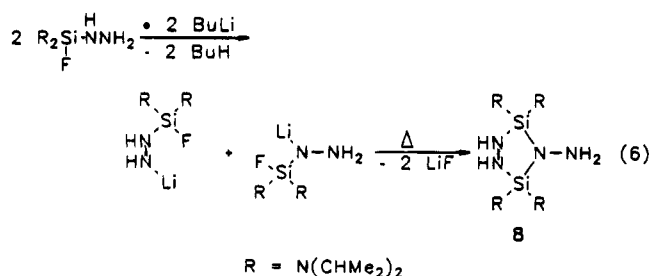
stable. Below 200 °C they do not tend to decompose with formation of HF or N<sub>2</sub>H<sub>4</sub>. The same reaction using difluorodiisopropylsilane leads to the formation of the six-membered-ring 4 and N<sub>2</sub>H<sub>4</sub>, respectively. No formation of HF is observed. This means that the reaction proceeds via the mono(silyl)hydrazine, which is then lithiated<sup>8</sup> (eqs 2 and 3).

Different preparative routes were chosen for the synthesis of the bis(silyl)hydrazines 5 and 6. Lithiated 1<sup>9</sup> was transformed into 5 by reacting with difluorodiisopropylsilane (eqs 4 and 5). As lithiated 2 readily



forms a six-membered ring and LiF at 5 °C,<sup>8</sup> we performed the substitution of 2 with chlorotrimethylsilane and chloro-*tert*-butyldimethylsilane, forming 6 and 7 in presence of NEt<sub>3</sub> to react with the HCl formed.

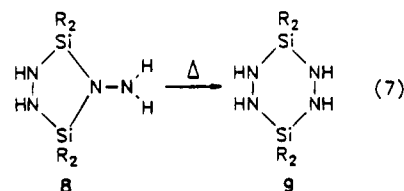
In the reaction of the mono(silyl)hydrazine 3 with *n*BuLi in a 1:1 molar ratio, colorless crystals with a melting point of 184 °C were obtained from *n*-hexane at 0 °C. The reaction product did not contain the expected six-membered ring, which was found in the analogous reaction of 2,<sup>8</sup> but, as proved by NMR and IR investigations, consisted of a disilatriazole 8 (eq 6).



The <sup>1</sup>H NMR spectrum showed two signals in the NH range with same intensity, and the IR spectrum also showed NH– and NH<sub>2</sub> vibrations. The mechanism of formation of 8, which is unique regarding its functionality, becomes clear with the result of the X-ray analysis of lithiated 1.<sup>9</sup> As mentioned above, two tautomers, >SiNLiNH<sub>2</sub> and >SiNHLiNH, exist in the solid state here. LiF elimination from fluoro-functional units in this case leads to the formation of a five-membered ring (eq 6).<sup>10</sup> Unfortunately we did not get single crystals of the lithium derivative of 2 and, therefore, obtained no information about the mechanism for an X-ray structural analysis.

Silicon–nitrogen chemistry is rich in rearrangements.<sup>11–13</sup> In general, the term “silatropy” is defined as the tendency of silyl groups to be bonded to the most electronegative element of the molecule. Anionic silyl group migration also occurs when the molecule consists of differently polarized atoms of the same kind. In cyclic molecules this arrangement leads to expansion or contraction of the ring.<sup>12,13</sup>

The thermodynamically more stable molecule related to 8 would contain the initially expected six-membered ring with equivalent N atoms. While S<sub>N</sub>2 mechanisms dominate in reactions of silicon-containing compounds, isomerism has to be partly thermally activated. When 8 is dissolved in refluxing *n*-hexane, and crystallized at room temperature, or held briefly above its melting point (184 °C), the structural isomer 9 is formed (eq 7).



Ring expansions from four- to five-membered rings in silicon hydrazine chemistry have already been found in anionic rearrangements of 1-amino-1,3-diaza-2,4-disilacyclobutanes to 1,2,4-triaza-3,5-disilacyclopentanes.<sup>10</sup>

One possibility for the preparation of silylhydrazine rings is salt elimination from lithiated *N*-silyl-*N'*-(fluorosilyl)hydrazines. Theoretically, the formation of four- or six-membered rings would be possible. We examined the LiF elimination of the Li derivatives from 5–7. Colorless crystalline compounds were isolated.

The appearance of <sup>29</sup>Si-NMR upfield signals points to the formation of six-membered rings (eq 8). This thesis was supported by an X-ray analysis of 12.

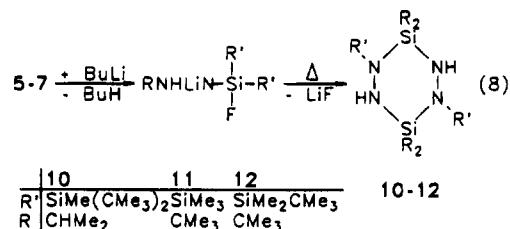


Figure 1 shows the structure of compound 12. Table 1 lists selected bond lengths and angles; Table 2 atomic

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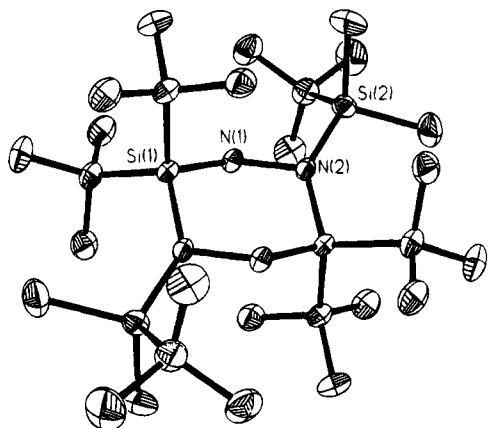


Figure 1. Structure of 12.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 12<sup>a</sup>

Si(1)—N(1)	1.744(1)	Si(1)—N(2) <sup>i</sup>	1.750(1)
N(1)—N(2)	1.480(2)	N(1)—H(1)	0.88(2)
Si(2)—N(2)	1.748(1)		
N(1)—Si(1)—N(2) <sup>i</sup>	108.0(1)	N(2)—N(1)—Si(1)	128.6(1)
N(2)—N(1)—H(1)	106(1)	Si(1)—N(1)—H(1)	115(1)
N(1)—N(2)—Si(2)	109.7(1)	N(1)—N(2)—Si(1) <sup>i</sup>	109.4(1)
Si(2)—N(2)—Si(1) <sup>i</sup>	140.7(1)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (i)  $-x + 1, -y + 1, -z$ .

Table 2. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{Å}^2 \times 10^3$ ) for 12

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Si(1)	5765(1)	3842(1)	-798(1)	19(1)
N(1)	4222(1)	3766(1)	701(1)	21(1)
C(1)	4791(2)	3155(1)	-1650(1)	27(1)
C(11)	6100(2)	2507(2)	-2671(2)	40(1)
C(12)	3518(2)	4313(2)	-2350(2)	35(1)
C(13)	3801(2)	2024(2)	-617(2)	36(1)
C(2)	7832(2)	2712(1)	-416(1)	25(1)
C(21)	7614(2)	1211(2)	370(2)	37(1)
C(22)	9281(2)	2753(2)	-1677(2)	36(1)
C(23)	8370(2)	3215(2)	442(2)	32(1)
Si(2)	3481(1)	3291(1)	3294(1)	25(1)
N(2)	4010(1)	4439(1)	1665(1)	20(1)
C(3)	2594(2)	4265(2)	4487(2)	40(1)
C(4)	5354(2)	2002(2)	3798(2)	43(1)
C(5)	1820(2)	2285(2)	3588(2)	32(1)
C(51)	1053(3)	1689(2)	5105(2)	52(1)
C(52)	383(2)	3211(2)	2957(2)	43(1)
C(53)	2587(2)	1058(2)	3087(2)	44(1)

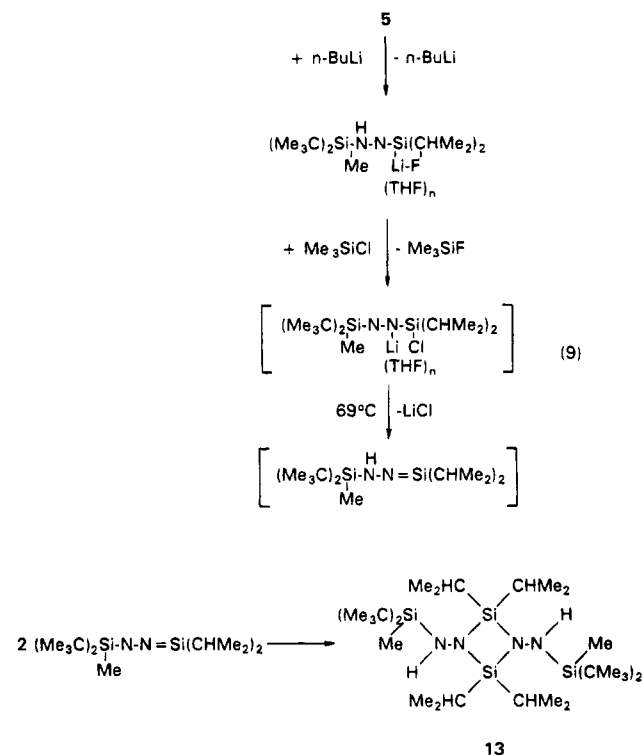
<sup>a</sup> *U*(eq) is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

coordinates and equivalent isotropic displacement parameters for 12. The molecule has an inversion center in the middle of the ring.

In contrast to a similar hydrazine six-membered ring,<sup>14</sup> 12 has a chair conformation. Due to the inversion center, the atoms N(2), Si(1), N(2a), and Si(1a) lie exactly in one plane. The atoms N(1) and N(1a) are 0.47 Å above and below this plane, respectively. The sum of angles at N(2) amounts to 359.8°. This nitrogen atom, in contrast to the NH-functional N(1) with 349.9° is sp<sup>2</sup>-hybridized. The angle Si(2)—N(2)—Si(1) of 140.7° is comparatively increased. The average Si—N and N—N bond distances are 1.747 and 1.48 Å, close to the expected values of 1.74 Å for Si—N and 1.45 Å for N—N.<sup>15</sup>

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A cyclization with formation of a four-membered ring has not been achieved via LiF elimination from lithiated (fluorosilyl)hydrazines. We tried to prepare a lithiated (chlorosilyl)hydrazine using a property of some lithiated (fluorosilyl)amines, which do not react with Me<sub>3</sub>SiCl by substitution at the N atoms but by halogen exchange.<sup>16,17</sup> A quantitative fluorine–chlorine exchange occurs in the reaction of the Li derivative of 5 with ClSiMe<sub>3</sub> at 0 °C, and Me<sub>3</sub>SiF and LiCl are formed. The resulting silahydrazone was isolated as the (2 + 2) cycloaddition product 13 (eq 9). Consequently, Me<sub>3</sub>SiCl as a fluorine–chlorine exchange reagent affords chlorination of the Li derivative of 5 with the formation of Me<sub>3</sub>SiF (eq 9).<sup>16,17</sup>



The structure of the first silylhydrazine four-membered ring has been confirmed by X-ray analysis. 13 is a structural isomer of the six-membered-ring 10. Suitable crystals for X-ray analysis were obtained after a 2-week crystallization process, by slowly condensing the *n*-hexane solvent in an ice-cooled trap.

Figure 2 shows the result of the X-ray analysis of 13. Table 3 contains selected bond lengths and angles; Table 4 atomic coordinates and equivalent isotropic displacement parameters for 13. The central four-membered SiN ring is strictly planar, and the molecule possesses an inversion center. The atom N(2) is 0.63 Å below the ring, so the ring N atom is not planar in contrast to that in the cyclodisilazanes. The sum of the angles in this case is 350.1°.

## Experimental Section

All experiments were performed in oven-dried glassware under purified nitrogen or argon using standard inert-

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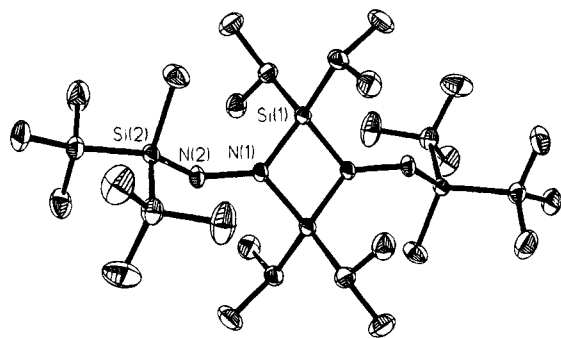


Figure 2. Structure of 13.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 13<sup>a</sup>

Si(1)—N(1)	1.755(1)	Si(1)—N(1) <sup>i</sup>	1.757(1)
N(1)—N(2)	1.444(1)	N(2)—Si(2)	1.730(1)
N(1)—Si(1)—N(1) <sup>i</sup>	84.3(1)	N(2)—N(1)—Si(1)	128.6(1)
N(2)—N(1)—Si(1) <sup>i</sup>	125.8(1)	Si(1)—N(1)—Si(1) <sup>i</sup>	95.7(1)
N(1)—N(2)—Si(2)	125.2(1)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (i)  $-x + 1, -y + 1, -z + 1$ .

Table 4. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{Å}^2 \times 10^3$ ) for 13

	x	y	z	U(eq) <sup>a</sup>
Si(1)	4939(1)	5998(1)	4097(1)	18(1)
C(1)	3434(2)	6460(1)	3155(1)	25(1)
C(11)	2039(2)	5609(2)	3578(2)	32(1)
C(12)	2838(2)	7945(2)	3041(2)	37(1)
C(2)	6412(2)	7284(1)	3404(1)	26(1)
C(21)	7683(2)	7205(2)	4093(2)	35(1)
C(22)	7151(2)	7275(2)	1953(2)	41(1)
N(1)	4222(1)	5656(1)	5771(1)	18(1)
N(2)	2761(1)	6154(1)	6585(1)	20(1)
Si(2)	2479(1)	7592(1)	7285(1)	19(1)
C(3)	3364(2)	7342(1)	8703(1)	27(1)
C(31)	3435(3)	8665(2)	9176(2)	49(1)
C(32)	2478(3)	6393(2)	9843(2)	52(1)
C(33)	5044(2)	6734(2)	8264(2)	50(1)
C(4)	264(2)	7977(1)	7719(1)	26(1)
C(41)	-254(2)	9108(2)	8547(2)	38(1)
C(42)	-609(2)	6754(2)	8453(2)	38(1)
C(43)	-254(2)	8439(2)	6486(2)	49(1)
C(5)	3461(2)	8988(2)	6114(2)	35(1)

<sup>a</sup> U(eq) is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

atmosphere and vacuum-line techniques. The *n*-hexane and THF solvents were dried over Na and distilled under nitrogen prior to use. All NMR spectra were obtained on either a Bruker-WP-80 or AM-250 spectrometer and were recorded in  $\text{CDCl}_3$  with  $\text{SiMe}_4$  and  $\text{C}_6\text{F}_6$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{19}\text{F}$ ) as internal and  $\text{MeNO}_2$  ( $^{15}\text{N}$ ) as external references. Mass spectra were obtained on a Varian CH-5 mass spectrometer. The data are reported in mass to charge units (*m/e*) followed by their relative intensities in parentheses. Infrared spectra were measured on a Perkin-Elmer infrared spectrophotometer.

The progress of the reactions was monitored by  $^1\text{H}$ - and  $^{19}\text{F}$ -NMR spectroscopy. The purity of the compounds was measured by NMR spectroscopy and if possible analyzed by gas chromatography.

**(Fluorobis(diisopropylamino)silyl)hydrazine (3).** To a solution of 3.2 g of anhydrous hydrazine (0.1 mol) in 100 mL of *n*-hexane was slowly added at room temperature 62.5 mL of *n*-BuLi (1.6 M solution in *n*-hexane, 0.1 mol). The reaction mixture was refluxed for 1 h and cooled to room temperature. After 50 mL of THF and 26.6 g of difluorobis-(diisopropylamino)silane (0.1 mol) had been added, the mixture was heated under reflux for 36 h and for a further 36 h at 90 °C, after distilling off excess solvent. **3** was separated from

LiF by condensing the product and solvents into a cooled trap in vacuo. **3** was then distilled in vacuo to give a pure sample.

$\text{C}_{12}\text{H}_{31}\text{FN}_4\text{Si}$  (278.49): yield 70%; bp 70 °C/0.01 mbar; MS (EJ) *m/z* (%) = 278 (32),  $\text{M}^+$ . NMR:  $^1\text{H}$ ,  $\delta = 1.04$   $\text{CHMe}_2\text{Me}_b$ , 12H (d, d,  $^3J_{\text{HH}} = 6.6$  Hz,  $^5J_{\text{HF}} = 0.8$  Hz), 1.07  $\text{CHMe}_2\text{Me}_b$ , 12H (d, d,  $^3J_{\text{HH}} = 6.6$  Hz,  $^5J_{\text{HF}} = 0.7$  Hz), 2.77 NH, 1H, 3.02  $\text{NH}_2$ , 2H, 3.27  $\text{CHMe}_2$ , 4H (sept, d,  $^3J_{\text{HH}} = 6.6$  Hz,  $^4J_{\text{HF}} = 0.8$  Hz);  $^{13}\text{C}$ ,  $\delta = 23.73$   $\text{CHC}_a\text{C}_b$  (d,  $^4J_{\text{CF}} = 0.9$  Hz), 24.82  $\text{CHC}_a\text{C}_b$  (d,  $^4J_{\text{CF}} = 1.8$  Hz), 44.60  $\text{CHC}_a\text{C}_b$  (d,  $^3J_{\text{CF}} = 0.6$  Hz), 44.61  $\text{CHC}_a\text{C}_b$  (d,  $^3J_{\text{CF}} = 0.6$  Hz);  $^{19}\text{F}$ ,  $\delta = 27.91$ ;  $^{15}\text{N}$ ,  $\delta = -333.06$   $\text{NH}_2$  (t, d,  $^1J_{\text{NH}} = 66.9$  Hz,  $^3J_{\text{NF}} = 4.9$  Hz),  $-325.55$  NH (d, d,  $^1J_{\text{NH}} = 83.4$  Hz,  $^2J_{\text{NF}} = 10.2$  Hz);  $^{29}\text{Si}$ ,  $\delta = -46.64$   $\text{SiF}$  (d,  $^1J_{\text{SiF}} = 235.1$  Hz). Anal. Calc: C, 51.75; H, 11.19. Found: C, 52.04; H, 11.54.

**3,3,6,6-Tetraisopropyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (4).** A 3.2-g amount of anhydrous hydrazine (0.1 mol) was reacted in 150 mL of *n*-hexane/50 mL of THF with 62.5 mL of *n*-BuLi (1.6 M solution in *n*-hexane, 0.1 mol) and heated under reflux for 1 h to complete the lithiation. A 12.4-g amount of difluorodisopropylsilane (0.1 mol) was added at  $-30$  °C and the reaction mixture again heated under reflux for 1 h. The product was separated from LiF in vacuo. **4** crystallized after distillation.

$\text{C}_{12}\text{H}_{32}\text{N}_4\text{Si}_2$  (288.59): yield 24%; bp 88 °C/0.01 mbar; MS (EJ) *m/z* (%) = 288 (22),  $\text{M}^+$ . NMR:  $^1\text{H}$ ,  $\delta = 0.75$  CH, 4H (sept,  $^3J_{\text{HH}} = 6.8$  Hz), 0.92  $\text{CHMe}_2$ , 24H (d,  $^3J_{\text{HH}} = 6.8$  Hz), 2.64 NH, 4H;  $^{13}\text{C}$ ,  $\delta = 12.81$   $\text{CHC}_2$ , 17.71  $\text{CHC}_2$ ;  $^{29}\text{Si}$ ,  $\delta = 0.58$ . Anal. Calc: C, 49.94; H, 11.17. Found: C, 49.51; H, 11.01.

**N-(Di-tert-butylmethylsilyl)-N'-(fluorodisopropylsilyl)hydrazine (5).** A 5.7-g amount of  $1^{\circ}$  (0.03 mol) was monolithiated with an equimolar amount of *n*-BuLi (1.6 M solution in *n*-hexane, 18.8 mL, 0.03 mol) in 50 mL of *n*-hexane/10 mL of THF at room temperature. After the mixture was stirred for 1 h, 3.7 g of difluorodisopropylsilane (0.03 mol) was slowly added at  $-20$  °C. The reaction occurred at 0 °C during slow warming to room temperature. After refluxing for 1 h, **5** was separated from LiF in vacuo and purified by distillation.

$\text{C}_{15}\text{H}_{37}\text{FN}_2\text{Si}_2$  (320.65): yield 86%; bp 72 °C/0.01 mbar, MS (EJ) *m/z* (%) = 320 (26),  $\text{M}^+$ . NMR:  $^1\text{H}$ ,  $\delta = 0.09$   $\text{SiMe}$ , 3H (d,  $^6J_{\text{HF}} = 0.5$  Hz), 0.98  $\text{SiCMe}_3$ , 18H, 1.04–1.07  $\text{SiCHMe}_2$ , 14H, 2.60 NH, 1H (d,  $^3J_{\text{HF}} = 3.2$  Hz), 3.06 NH, 1H;  $^{13}\text{C}$ ,  $\delta = -9.49$   $\text{SiC}$  (d,  $^5J_{\text{CF}} = 2.0$  Hz), 10.82  $\text{CHC}_a\text{C}_b$  (d,  $^2J_{\text{CF}} = 18.7$  Hz), 17.33  $\text{CHC}_a\text{C}_b$ , 17.39  $\text{CHC}_a\text{C}_b$  (d,  $^3J_{\text{CF}} = 1.1$  Hz), 20.51  $\text{SiCC}_3$ , 28.42  $\text{SiCC}_3$ ;  $^{19}\text{F}$ ,  $\delta = 1.23$ ;  $^{29}\text{Si}$ ,  $\delta = -1.68$   $\text{SiF}$  (d,  $^1J_{\text{SiF}} = 306.7$  Hz), 10.25 Si (d,  $^4J_{\text{SiF}} = 0.7$  Hz). Anal. Calc: C, 56.19; H, 11.63. Found: C, 56.02; H, 11.49.

**4-Amino-3,3,5,5-tetrakis(diisopropylamino)-1,2,4-triaza-3,5-disilacyclopentane (8).** An 8.4-g amount of **3** (0.03 mol) was lithiated at 0 °C in 50 mL of *n*-hexane/THF by the slow addition of 18.8 mL of *n*-BuLi (1.6 M solution in *n*-hexane, 0.03 mol). After 2 h the reaction mixture was warmed to room temperature. To ensure a complete reaction, the mixture was stirred under reflux for a further 2 h. At 0 °C **8** crystallized directly from this solution.

$\text{C}_{24}\text{H}_{60}\text{N}_6\text{Si}_2$  (516.98): yield 75%; mp 183 °C, MS (EJ) *m/z* (%) = 516 (100),  $\text{M}^+$ . IR ( $\text{cm}^{-1}$ ): 3378, 1592  $\text{NH}_2$ , 3258 NH. NMR:  $^1\text{H}$ ,  $\delta = 1.25$   $\text{CHMe}_2\text{Me}_b$ , 24H, (d,  $^3J_{\text{HH}} = 6.6$  Hz), 1.27  $\text{CHMe}_2\text{Me}_b$ , 24H (d,  $^3J_{\text{HH}} = 6.6$  Hz), 2.38 NH, 2H, 2.79 NH, 2H, 3.74  $\text{CHMe}_2$ , 8H (sept,  $^3J_{\text{HH}} = 6.6$  Hz);  $^{13}\text{C}$ ,  $\delta = 25.21$   $\text{NCC}_2$ , 26.00  $\text{NCC}_2$ , 45.20 NC;  $^{15}\text{N}$ ,  $\delta = -330.71$  NH,  $-324.90$   $\text{NH}_2$ ;  $^{29}\text{Si}$ ,  $\delta = -35.67$ . Anal. Calc: C, 55.76; H, 11.70. Found: C, 55.41; H, 11.49.

**3,3,6,6-Tetrakis(diisopropylamino)-1,2,4,5-tetraaza-3,6-disilacyclohexane (9).** A 5.2-g amount of **8** (0.01 mol) was stirred at ca. 190 °C, above its melting point, for 1 h and dissolved in refluxing *n*-hexane after cooling to room temperature. The six-membered ring started to crystallize when the *n*-hexane solution reached room temperature.

$\text{C}_{24}\text{H}_{60}\text{N}_6\text{Si}_2$  (516.98): yield 95%; mp 128 °C; MS (EJ) *m/z* (%) = 516 (9),  $\text{M}^+$ . IR ( $\text{cm}^{-1}$ ): 3382 NH. NMR:  $^1\text{H}$ ,  $\delta = 1.15$   $\text{CHMe}_2$ , 48H (d,  $^3J_{\text{HH}} = 6.8$  Hz), 2.60 NH, 4H, 3.46 CH, 8H;

$^{13}\text{C}$ ,  $\delta = 23.28 \text{ CC}_2$ , 44.84 NC;  $^{15}\text{N}$ ,  $\delta = -325.11 \text{ NH}$ ;  $^{29}\text{Si}$ ,  $\delta = -37.75$ . Anal. Calc: C, 55.76; H, 11.70. Found: C, 55.54; H, 11.53.

**Six-Membered-Rings 10–12.** A 3.2-g amount of **5** (0.01 mol), 2.6 g of **6**<sup>8</sup> (0.01 mol), or 3.1 g of **7**<sup>8</sup> (0.01 mol) was lithiated in 50 mL of *n*-hexane/THF with <sup>*n*</sup>BuLi (1.6 M solution in *n*-hexane, 6.3 mL, 0.01 mol) and heated to reflux for 2 h. The ring systems crystallized at 0 °C from the reaction mixture and were purified by recrystallization from *n*-hexane.

**1,4-Bis(di-*tert*-butylmethylsilyl)-3,3,6,6-tetraisopropyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (10).** C<sub>30</sub>H<sub>72</sub>N<sub>4</sub>Si<sub>4</sub> (601.29): yield 70%; mp 254 °C; MS (EJ) *m/z* (%) = 600 (100), M<sup>+</sup>. NMR:  $^1\text{H}$ ,  $\delta = 0.10 \text{ SiMe}$ , 6H, 1.05–1.35 CHMe<sub>2</sub>, 28H, 1.26 CMe<sub>3</sub>, 36H;  $^{13}\text{C}$ ,  $\delta = -5.48 \text{ SiCH}_3$ , 14.30 SiCH, 18.69 SiC(CH<sub>3</sub>)<sub>2</sub>, 19.76 SiC(CH<sub>3</sub>)<sub>2</sub>, 30.65 SiCC<sub>3</sub>;  $^{29}\text{Si}$ ,  $\delta = -11.74 \text{ SiCHMe}_2$ , 4.62 SiCH<sub>3</sub>. Anal. Calc: C, 59.93; H, 12.07. Found: C, 60.07; H, 12.22.

**3,3,6,6-Tetra-*tert*-butyl-1,4-bis(trimethylsilyl)-1,2,4,5-tetraaza-3,6-disilacyclohexane (11).** C<sub>22</sub>H<sub>56</sub>N<sub>4</sub>Si<sub>4</sub> (489.05): yield 10%; mp 318 °C; MS (EJ) *m/z* (%) = 488 (30), M<sup>+</sup>. NMR:  $^1\text{H}$ ,  $\delta = 0.28 \text{ SiMe}_3$ , 18H, 1.10 SiCMe<sub>3</sub>, 36H, 2.47 NH, 2H;  $^{13}\text{C}$ ,  $\delta = 2.18 \text{ SiC}_3$ , 22.08 SiCC<sub>3</sub>, 29.79 SiCC<sub>3</sub>;  $^{29}\text{Si}$ ,  $\delta = -4.42 \text{ SiCMe}_3$ , 3.27 SiMe<sub>3</sub>. Anal. Calc: C, 54.03; H, 11.54. Found: C, 53.94; H, 11.37.

**3,3,6,6-Tetra-*tert*-butyl-1,4-bis(*tert*-butyldimethylsilyl)-1,2,4,5-tetraaza-3,6-disilacyclohexane (12).** C<sub>28</sub>H<sub>68</sub>N<sub>4</sub>Si<sub>4</sub> (573.23): yield 50%; mp 215 °C; MS (EJ) *m/z* (%) = 572 (64), M<sup>+</sup>. NMR:  $^1\text{H}$ ,  $\delta = 0.22 \text{ SiMe}$ , 12H, 1.07 Si<sub>b</sub>CMe<sub>3</sub>, 18H, 1.12 Si<sub>a</sub>CMe<sub>3</sub>, 36H, 2.61 NH, 2H;  $^{13}\text{C}$ ,  $\delta = -1.10 \text{ SiC}$ , 20.33 Si<sub>b</sub>CC<sub>3</sub>, 22.26 Si<sub>a</sub>CC<sub>3</sub>, 29.14 Si<sub>b</sub>CC<sub>3</sub>, 30.47 Si<sub>a</sub>CC<sub>3</sub>;  $^{29}\text{Si}$ ,  $\delta = -6.73 \text{ Si}_a$ , 3.78 Si<sub>b</sub>.

**2,2,4,4-Tetraisopropyl-1,3-bis(di-*tert*-butylmethylsilyl)amino-1,3-diaza-2,4-disilacyclobutane (13).** A 3.2-g amount of **5** (0.01 mol) in 30 mL of *n*-hexane/THF was transformed into the lithium derivative by slow addition of 6.3 mL of <sup>*n*</sup>BuLi (1.6 M solution in *n*-hexane, 0.01 mol) at 0 °C. After the mixture was stirred for 0.5 h at this temperature, 1.1 g of Me<sub>3</sub>SiCl (0.01 mol) was added. The reaction mixture was slowly warmed to room temperature, and the formation of Me<sub>3</sub>SiF was monitored by  $^{19}\text{F}$ -NMR spectroscopy. After the mixture was stirred for a further 3 h and refluxed for 0.5 h, the product was separated from LiCl by condensing in a cold trap in vacuo. **13** can be recrystallized from *n*-hexane.

C<sub>30</sub>H<sub>72</sub>N<sub>4</sub>Si<sub>4</sub> (601.29): yield 60%; mp 210 °C; MS (EJ) *m/z* (%) = 600 (100), M<sup>+</sup>. NMR:  $^1\text{H}$ ,  $\delta = 0.21 \text{ SiMe}$ , 6H, 1.09

SiCMe<sub>3</sub>, 36H, 1.32–1.34 SiCHMe<sub>2</sub>, 28H, 2.47 NH, 2H;  $^{13}\text{C}$ ,  $\delta = 7.31 \text{ SiC}$ , 15.52 SiCHC<sub>2</sub>, 18.89 SiCHC<sub>2</sub>, 20.18 SiCC<sub>3</sub>, 29.01 SiCC<sub>3</sub>;  $^{29}\text{Si}$ ,  $\delta = 5.03 \text{ Si}_a$ , 14.97 Si<sub>b</sub>.

**X-ray Structure Determination of 12 and 13.** Data were collected on a Siemens-Stoe-AED diffractometer with monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Collection temperature<sup>18</sup> was  $-70 \text{ }^\circ\text{C}$  for **12** and  $-120 \text{ }^\circ\text{C}$  for **13**. The structures were solved by direct methods<sup>19</sup> and refined against  $F^2$ .<sup>20</sup> All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms bonded to carbon atoms, the riding model was used. The hydrogen atoms at the nitrogen atoms were refined freely. The *R*-values are defined as  $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4)^{1/2}$  and  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

Crystal data for **12**: C<sub>28</sub>H<sub>68</sub>N<sub>4</sub>Si<sub>4</sub>, *M<sub>r</sub>* = 573.2, triclinic, space group *P* $\bar{1}$ , *a* = 8.603(2) Å, *b* = 10.831(2) Å, *c* = 11.352(2) Å,  $\alpha = 65.90(1)^\circ$ ,  $\beta = 69.59(1)^\circ$ ,  $\gamma = 72.28(1)^\circ$ , *V* = 888.6(3) Å<sup>3</sup>, *Z* = 1,  $\rho_{\text{calcd}} = 1.071 \text{ Mg m}^{-3}$ ,  $\mu = 0.189 \text{ mm}^{-1}$ , *F*(000) = 320, crystal size (mm) 0.4 × 0.5 × 0.5, 4854 measured reflections in the range of  $8^\circ < 2\theta < 55^\circ$ , 4092 unique reflections, 4091 reflections used for the refinement of 178 parameters, goodness of fit 1.061, *R1* = 0.037 (for  $F < 4\sigma(F)$ ), *wR2* = 0.105 (for all data), maximum/minimum residual electron density 0.45/−0.37 e Å<sup>3</sup>.

Crystal data for **13**: C<sub>30</sub>H<sub>72</sub>N<sub>4</sub>Si<sub>4</sub>, *M<sub>r</sub>* = 601.3, triclinic, space group *P* $\bar{1}$ , *a* = 8.961(2) Å, *b* = 10.211(2) Å, *c* = 10.994(2) Å,  $\alpha = 80.08(1)^\circ$ ,  $\beta = 73.35(1)^\circ$ ,  $\gamma = 82.56(1)^\circ$ , *V* = 945.9(3) Å<sup>3</sup>, *Z* = 1,  $\rho_{\text{calcd}} = 1.055 \text{ Mg m}^{-3}$ ,  $\mu = 0.181 \text{ mm}^{-1}$ , *F*(000) = 336, crystal size (mm) 0.6 × 0.7 × 0.7, 6383 measured reflections in the range of  $8^\circ < 2\theta < 55^\circ$ , 4362 unique reflections, 4356 reflections used for the refinement of 187 parameters, goodness of fit 1.034, *R1* = 0.038 (for  $F > 4\sigma(F)$ ), *wR2* = 0.114 (for all data), maximum/minimum residual electron density 0.44/−0.41 e Å<sup>3</sup>.

**Supplementary Material Available:** For **12** and **13** tables of data collection parameters, displacement parameters, bond distances and angles, and hydrogen coordinates and *U* values (8 pages). Ordering information is given on any current masthead page.

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