(Di-*tert*-butylmethylsilyl)amide – a Building Block for Azasilacyclobutane Synthesis

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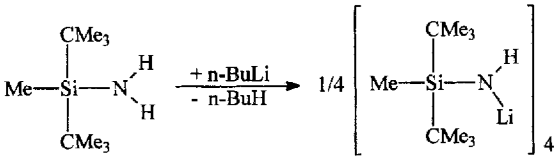
Di-*tert*-butylmethylsilylamide reacts with *n*-BuLi to give the tetrameric lithium di-*tert*-butylmethylsilylamide **1**. Reactions of lithium (di-*tert*-butylmethylsilyl)amide **1** with SiF_4 give the mono- (**2**), bis- (**3**), tris- (**4**), and tetrakis- (**5**) -[(di-*tert*-butylmethylsilyl)amino]silanes. Lithiated **3** reacts with Me_3SiCl to form (di-*tert*-butylmethylsilyl-trimethylsilyl)amino-(di-*tert*-butylmethylsilyl)amino-difluorosilane (**6**); the 1,3-diaza-2,4-disilacyclobutane **7** is obtained by LiF elimination. The lithium derivative of **6** (compound **8**) crystallizes with formation of a (SiFNLi) four-membered ring system. The ^{19}F-NMR spectrum proves that the Li–F bond fluctuates in solution. Reactions of **1** with $(Me_3Si)_2C(SiF_3)_2$ afford different products (**9**, **10**) by controlling the reaction sequence. An excess of **1** reacts to give a four-membered CSi_2N ring system, the 1-(di-*tert*-butylmethylsilyl)-2,4-bis-[(di-*tert*-butylmethylsilyl)-amino]-2,4-difluoro-3-bis(trimethylsilyl)-1-aza-2,4-disilacyclobutane (**9**), disubstitution with formation of bis[(di-*tert*-butylmethylsilyl)aminodifluorosilyl]bis(trimethylsilyl)methane (**10**) occurs in a molar ratio of 2:1. The cyclodisilazane **11** is obtained from dilithiated **10** in an intramolecular interconversion reaction. The crystal strucutres of **1**, **8**, **9**, and **11** are reported.

Reactions of fluorosilanes with amines are completely different from those of other halogenosilanes[1,2]. Fluorosilanes and amines form amine adducts[1,3]. Stronger bases like amides provide an opportunity to prepare acyclic aminosilanes and cyclosilazanes[2,4]. The use of bulky silylamino ligands was pioneered by Bürger and Wannagat for both main group and transition metals[1,5]. The extremely bulky di-*tert*-butylmethylsilyl group was used to stabilize an iminosilane[4,6], to prepare lithium derivatives of silylaminofluorosilanes[6,7], and to prepare a very small cyclodisilazane with a transannular Si–Si ring distance of 237.8 pm[8]. Molecular orbital ab initio calculations on model cyclosilazanes reveal a very large effect of the fluorine and silyl substituents on the Si···Si separation[9]. They also show that the (SiNSiN) ring is extremely flexible in respect of bending to the endocyclic N–Si–N bond angle. Steric interactions associated with the bulky substituents may therefore strongly influence the geometry of the ring. This gave rise to synthesis other four-membered ring systems with this bulky ligands.

In this paper we report that by starting from lithium (di-*tert*-butylmethylsilyl)amide we were able to isolate fluorinated silazanes, to characterize their lithium derivatives and to prepare cyclodisilazanes. We found that LiF elimination leads to the formation of isomeric rings. The reaction of $(Me_3Si)_2C(SiF_3)_2$ with lithium di-*tert*-butylmethylamide depends on the reaction conditions. Disubstitution, ring closure with formation of a SiN_2C cycle and with formation of a SiN_2Si cycle in an interconversion reaction occur.

Results and Discussion

(Di-*tert*-butylmethylsilyl)amine was found to react with *n*BuLi to give the tetrameric lithium derivative **1**.



(1)

1

Crystal Structure of 1

Figure 1 shows the crystal structure of **1**. In the asymmetric unit there is one quarter of a molecule. The lithium and nitrogen atoms form a distorted Li_4N_4 cubane. The lithium atoms are tricoordinated. They are additionally saturated by short Li–CH contacts.

The mono (**2**)-, bis (**3**)-, tris (**4**)-, and tetrakis (**5**) -(silylamino)silanes containing the bulky $R = SiMe(CMe_3)_2$ group on the nitrogen atom are obtained by the reaction of **1** with SiF_4 at −70 °C depending on the molecular ratio and the solvent.

The synthesis of the mono- and dilithium derivative of **3** was described recently[7]. Substitution and formation of **6** and LiCl occur in the reaction of the monolithium derivative with Me_3SiCl. The cyclodisilazane **7** is obtained by LiF elimination. The *cis* and *trans* isomers of **7** are formed in the ratio of 1:3.

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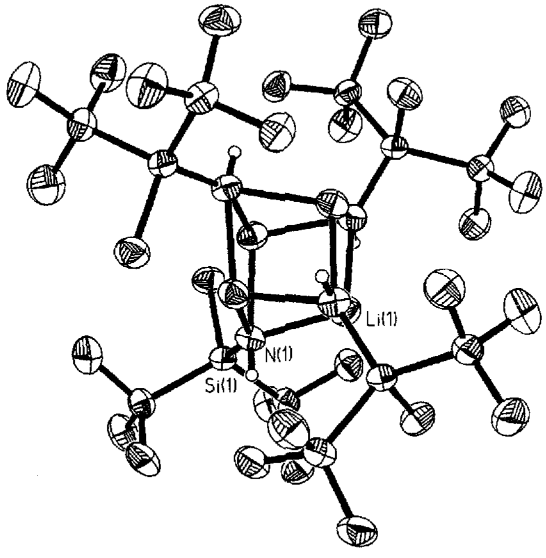
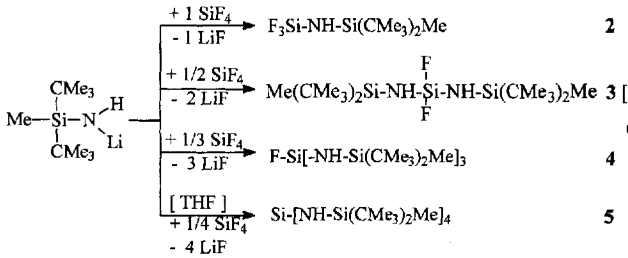
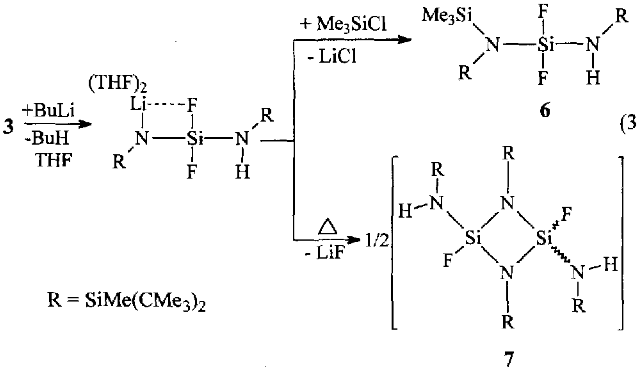
Figure 1. Structure of **1** in the crystal



Selected bond lengths [pm] and angles [°]: Li(1)–N(1) 203.9(8), Li(1)–N(1a) 204.1(8), Li(1)–N(1b) 205.0(8); N(1)–Li(1)–N(1a) 100.5(3), N(1)–Li(1)–N(1b) 100.2(3), N(1a)–Li(1)–N(1b) 109.6(4), Li(1)–N(1)–Li(1b) 76.3(4), Li(1)–N(1)–Li(1a) 76.1(3), Li(1b)–N(1)–Li(1a) 70.2(3).

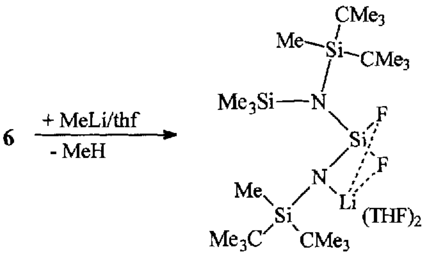


(2)



(3)

The reaction of **6** with methyllithium yields an amorphous solid which dissolved in THF forms colorless crystals of **8** at −18 °C.



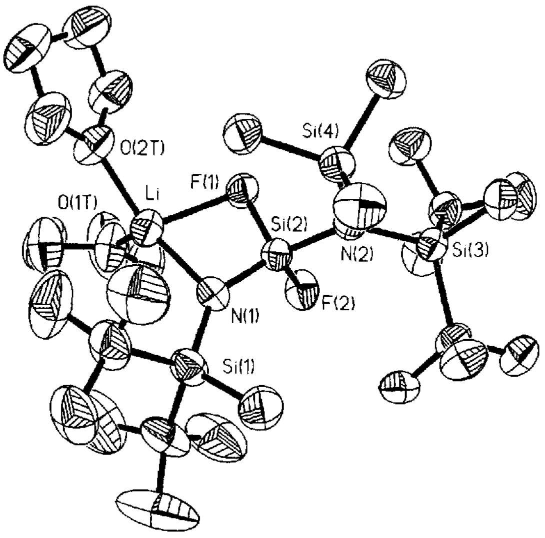
(4)

8

Crystal Structure of 8

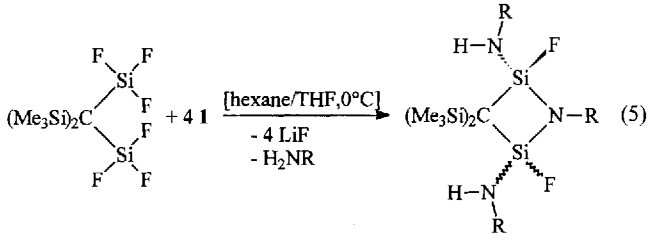
Compound **8** crystallizes from THF as a monomeric amide (Figure 2). According to the results of the X-ray structure analysis the coordination sphere of the lithium is made up of one fluorine atom, one nitrogen atom, and two THF molecules. Thus the FSiN skeleton brackets the lithium to form a planar four-membered ring[10]. The Li–F(1) contact effects a lengthening of the F(1)–Si(2) bond (164.6 pm) compared to the Si(2)–F(2) distance (160.5 pm). The Si(2)–N(1) (162.5 pm) distance lies in the range typical of Si–N double bonds. The Si(1)–N(1)–Si(2) angle is extended (143.8°) compared with the other Si–N–Si angles. ^{19}F-NMR experiments show equivalent fluorine atoms. The Li–F bond fluctuates in solution.

Figure 2. Structure of **8** in the crystal



Selected bond lengths [pm] and angles [°]: Si(2)–N(1) 162.5(4), Si(2)–F(1) 164.6(3), F(1)–Li 214.8(9), N(1)–Li 203.6(9), Si(1)–N(1) 168.7(4), Si(2)–N(2) 173.0(4), Si(2)–F(2) 160.5(3); N(1)–Si(2)–F(1) 103.7(2), F(2)–Si(2)–N(1) 115.0(2), N(1)–Si(2)–N(2) 125.2(2), F(2)–Si(2)–F(1) 97.9(2), F(2)–Si(2)–N(2) 105.0(2), F(1)–Si(2)–N(2) 106.3(2), Si(2)–N(1)–Li 92.3(3), Si(2)–N(1)–Si(1) 143.8(3), Si(1)–N(1)–Li 123.1(3), Si(2)–F(1)–Li 87.8(3), F(1)–Li–N(1) 75.8(3), Si(2)–N(2)–Si(4) 114.9(2), Si(4)–N(2)–Si(3) 120.7(2), Si(2)–N(2)–Si(3) 124.3(2).

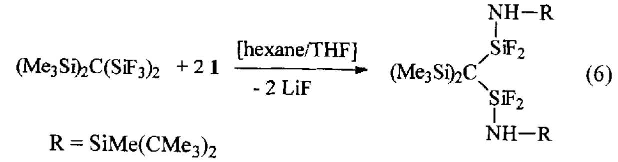
$(\mathrm{Me_3Si})_2\mathrm{C(SiF_3)_2}$[11] reacts with lithium (di-*tert*-butylmethylsilyl)amide (**1**) to give **9** or **10**, depending on the reaction sequence. First, a fourfold excess of **1** is dissolved in hexane/THF and bis(trifluorosilyl)bis(trimethylsilyl)methane is added slowly from a dropping funnel at 0 °C. In this way compound **9** is formed in *cis*/*trans* conformation (1:1) by lithium transfer and recovery of one equivalent of (di-*tert*-butylmethylsilyl)amine.



R = $\mathrm{SiMe(CMe_3)_2}$

9

If two equivalents of **1** are added to a solution of $(\mathrm{Me_3Si})_2\mathrm{C(SiF_3)_2}$ in *n*-hexane at room temperature the expected acyclic compound **10** is formed according to eq. (6).



$$(\mathrm{Me_3Si})_2\mathrm{C(SiF_3)_2} + 2\,\mathbf{1} \xrightarrow[-2\,\mathrm{LiF}]{[\mathrm{hexane/THF}]} (\mathrm{Me_3Si})_2\mathrm{C}\begin{matrix}\mathrm{NH{-}R}\\ |\\ \mathrm{SiF_2}\\ \mathrm{SiF_2}\\ |\\ \mathrm{NH{-}R}\end{matrix} \qquad (6)$$

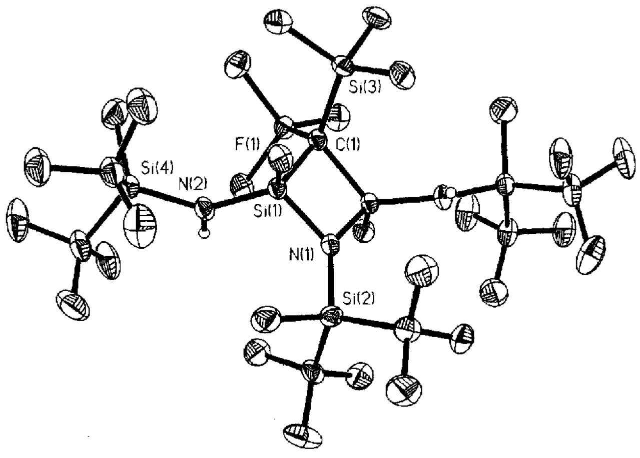
R = $\mathrm{SiMe(CMe_3)_2}$

10

Crystal Structure of 9

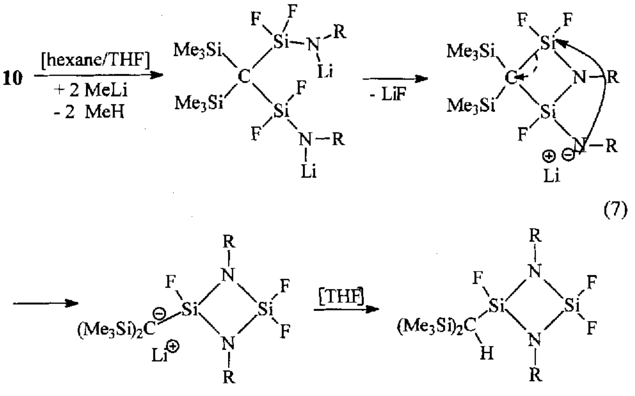
Figure 3 shows the crystal structure of **9**. There is a twofold axis along C(1) and N(1). Therefore, in contrast to other $\mathrm{SiN_2C}$ ring molecules[12], **9** has a planar ring with a planar arrangement around the N(1) atom [ΣN(1): 359.9°]. The long endocyclic C−Si bonds (188.1 pm) and shorter endocyclic N(1)−Si(1) bonds (173.0 pm) cause a small Si(1)−C(1)−Si(1a) angle (83.3°). The transannular Si···Si ring distance is 250.1 pm. The exocyclic Si(1)−N(2) bond is relatively short (169.9 pm). In the neighbourhood of the fluorine atom, the N(2)−Si(4) bond is in the normal range. The bulky $\mathrm{SiMe(CMe_3)_2}$ groups cause a widening of the Si(4)−N(2)−Si(1) angles.

Figure 3. Structure of **9** in the crystal



Selected bond lengths [pm] and bond angles [°]: C(1)−Si(1) 188.1(2), Si(1)−N(1) 173.0(2), Si(1)−F(1) 159.7(1), Si(1)−N(2) 169.9(2), C(1)−Si(3) 189.6(2), N(1)−Si(2) 176.8(2), N(2)−Si(4) 175.8(2); Si(1)−C(1)−Si(1a) 83.3(1), Si(1a)−C(1)−Si(3) 119.14(3), Si(1)−C(1)−Si(3) 110.80(3), Si(3a)−C(1)−Si(3) 111.4(1), N(1)−Si(1)−C(1) 92.05(9), N(2)−Si(1)−N(1) 116.54(7), F(1)−Si(1)−N(1) 110.11(5), N(2)−Si(1)−C(1) 123.85(7), F(1)−Si(1)−C(1) 109.77(5), F(1)−Si(1)−N(2) 104.10(7), Si(1a)−N(1)−Si(1) 92.6(1), Si(1)−N(1)−Si(2) 124.96(6), Si(1a)−N(1)−Si(2) 142.4(1), Si(1)−N(2)−Si(4) 141.4(1).

Treatment of **10** with two equivalents of MeLi yields the cyclodisilazane **11** in an intermolecular conversion as shown in eq. (7).



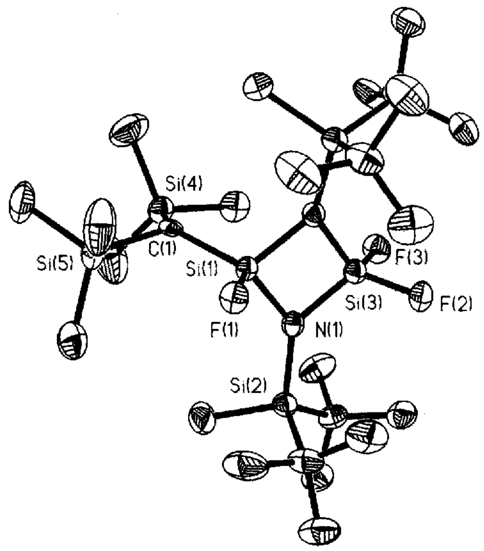
R = $\mathrm{SiMe(CMe_3)_2}$

11

Crystal Structure of 11

Figure 4 shows the crystal structure of **11**. There is a mirror plane through the atoms Si(1), Si(3), F(1), F(2), and F(3). The trifluorocyclodisilazane **11** has a planar (SiNSiN) four-membered ring. The sum of the angles around N(1) is 358.1°, so that the nitrogen atoms have essentially a planar environment. Replacement of the Si(3) atom by two fluorine atoms results in a significant shortening of the Si−N ring bonds. The endocyclic Si(3)−N bonds (170.4 pm) are considerably shorter than the endocyclic Si(1)−N bonds (175.5 pm) and the exocyclic N(1)−Si(2) bonds (176.6 pm). This contrasts with the situation in non-fluorine substituted 1,3-cyclodisilazanes[2]. The Si(3)−N(1)−Si(1) ring angles

Figure 4. Structure of **11** in the crystal



Selected bond lengths [pm] and bond angles [°]: Si(1)−N(1) 175.5(3), N(1)−Si(3) 170.4(3), Si(1)−F(1) 160.3(3), Si(1)−C(1) 186.3(6), Si(3)−F(2) 157.9(3), Si(3)−F(3) 158.4(3), N(1)−Si(2) 176.6(3), Si(1)−Si(3) 242.2(2); N(1)−Si(1)−N(1a) 89.4(2), F(1)−Si(1)−N(1) 108.9(1), N(1)−Si(1)−C(1a) 112.6(2), F(1)−Si(1)−C(1a) 106.1(2), C(1a)−Si(1)−Si(3) 135.8(2), N(1a)−Si(3)−N(1) 92.8(2), F(3)−Si(3)−N(1) 115.4(1), F(2)−Si(3)−N(1) 116.5(1), F(2)−Si(3)−F(3) 101.2(2), Si(3)−N(1)−Si(1) 88.9(1), Si(3)−N(1)−Si(2) 134.8(2), Si(1)−N(1)−Si(2) 134.4(2).

are smaller than 90° (88.9°) while the N(1)−Si(3)−N(1a) ring angle is larger than 90° (92.8°). The combined effects of the three fluorine atoms at silicon and of the two bulky silyl groups on the nitrogen atoms brings the ring silicon atoms in **11** into close proximity. The transannular Si−Si ring distance in **11** is 242.2 pm, a distance very close to that of a "normal" Si−Si single bond (ca. 235 pm).

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Experimental

All experiments were carried out with the exclusion of moisture under dry N_2 or Ar. − MS: CH-5 Varian. − NMR: 25% solutions in C_6D_6: TMS, C_6F_6 int., Bruker-WP-80 or AM-250. − The purity of the isolated compounds was determined by spectroscopy.

Tetrakis[lithium (Di-tert-butylmethylsilyl)amide] (**1**): To a solution of 17.34 g (0.1 mol) of $(Me_3C)_2MeSiNH_2$ in 40 ml of hexane was added 0.1 mol of *n*BuLi (23% in hexane). The crude product was refluxed for 2 h. **1** can be purified by recrystallization from hexane.

(Di-tert-butylmethylsilyl)(trifluorosilyl)amine (**2**), *Tris[(di-tert-butylmethylsilyl)amino]fluorosilane* (**4**), *and Tetrakis[(di-tert-butylmethylsilyl)amino]silane* (**5**): A solution of *n*BuLi (0.1 mol) in hexane (100 ml) was treated with di-*tert*-butylmethylamine (17.3 g, 0.1 mol), and the mixture was refluxed for 2 h. When the lithiation was complete the solution was cooled to −70 °C and either 10.4 g (0.1 mol) of SiF_4 for **2** or 3.5 g (0.03 mol) of SiF_4 for **4**, or 2.6 g (0.025 mol) of SiF_4 for **5** was introduced. Over a period of 10 h the mixture was allowed to warm up. The products were separated from LiF, **2** fractionally distilled, **4** and **5** purified by recrystallization from *n*-hexane. **2**: Yield: 15.9 g (62%), b.p. 31 °C/0.01 mbar; **4**: 13.2 g (70%), m.p. 204 °C; **5**: 14.9 g (83%), m.p. 213 °C.

[(Di-tert-butylmethylsilyl)amino][(di-tert-butylmethylsilyl)(trimethylsilyl)amino]difluorosilane (**6**): To a solution of 28.0 g (0.05 mol) of lithiated **3** in 100 ml of *n*-hexane/THF 5.43 g (0.05 mol) of chlorotrimethylsilane was added at 0 °C. The resulting mixture was stirred for 1 h at 0 °C and slowly warmed to 20 °C. The product was condensed at 0.01 mbar into a cooling trap and purified by distillation. Yield: 19.32 g (80%), b.p. 130 °C/0.02 mbar.

1,3-Bis(di-tert-butylmethylsilyl)-2,4-bis[(di-tert-butylmethylsilyl)amino]-2,4-difluorocyclosilazane (**7**): 28.0 g (0.05 mol) of lithiated **3** was heated to >100 °C. The formed **7** was condensed into a cooling trap and purified by distillation at 0.01 mbar. Yield: 15.2 g (72%) (*cis*/*trans* = 1:3), b.p. 212 °C/0.02 mbar, m.p. 232 °C.

Lithium [{Di-tert-butylmethylsilyl)(trimethylsilyl)amino}difluorosilyl](di-tert-butylmethylsilyl)amide−Bis(tetrahydrofuran) (**8**): To a solution of 4.8 g (0.01 mol) of **6** in 20 ml of hexane 0.01 mol of MeLi (5% in ether) was added, and the mixture was heated at reflux for 2 h. Compound **8** precipitated as an amorphous solid to which THF was added until it had redissolved. **8** crystallized at −18 °C. Yield: 6.01 g (95%), m.p. 78 °C.

1-(Di-tert-butylmethylsilyl)-2,4-bis[(di-tert-butylmethylsilyl)amino]-2,4-difluoro-3,3-bis(trimethylsilyl)-1-aza-2,4-disilacyclobutane (**9**): To a solution of 34.68 g (0.2 mol) of **1** in 40 ml of hexane a solution of 16.43 g (0.05 mol) of bis(trifluorosilyl)bis(trimethylsilyl)methane in 10 ml of hexane was added at 0 °C.The reaction mixture was refluxed for 30 min and separated from LiF. Solvent and excess of di-*tert*-butylsilylamine were removed by distillation. The residue was dissolved in 20 ml of hexane and crystallized at 7 °C. Yield: 21.52 g (56%) (*cis*/*trans* = 1:1), m.p. 197 °C.

Bis[{di-tert-butylmethylsilyl)amino}difluorosilyl]bis(trimethylsilyl)methane (**10**): To a solution of 16.43 g (0.05 mol) of bis(trifluorosilyl)bis(trimethylsilyl)methane in 30 ml of hexane a solution of 17.34 g (0.1 mol) of **1** in 20 ml of hexane was added dropwise at 20 °C. After addition of **1** the reaction mixture was heated for 1 h at reflux and the solvent removed by distillation. **10** was separated from LiF, purified by distillation, and crystallized from hexane at −18 °C. Yield: 17.19 g (56%), b.p. 174 °C/0.01 mbar, m.p. 102 °C.

2-[Bis(trimethylsilyl)methyl]-1,3-bis(di-tert-butylmethylsilyl)-2,4,4-trifluorocyclodisilazane (**11**): 0.01 mol of MeLi (5% in ether) was added dropwise to a solution of 6.35 g (0.01 mol) of **10** in 50 ml of hexane at room temp. The reaction mixture was stirred for further 2 h and concentrated in vacuo. Colorless crystals separated which were recrystallized from hexane. Yield: 2.83 g (46%), m.p. 203 °C.

1: B.p. 178 °C/0.01 mbar. − ^{1}H NMR (C_6D_6): $\delta = -0.06$ (s, $SiCH_3$, 12 H), 0.96 [s, $SiC(CH_3)_3$, 72 H]. − ^{7}Li NMR: $\delta = 2.37$. − ^{13}C NMR: $\delta = -4.14$ (s, $SiCH_3$), 20.62 [s, $Si\mathit{C}(CH_3)_3$] 29.09 (s, $SiC\mathit{C}H_3$). − ^{29}Si NMR: $\delta = 8.80$.

2: B.p. 31 °C/0.01 mbar. − MS (EI), *m*/*z* (%): 257 (0.8) [M^+], 200 (20) [$M - CMe_3]^+$. − ^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.15$ (qd, $^{5}J_{HF} = 1$, $^{4}J_{HH} = 0.5$ Hz, $SiCH_3$, 3 H), 0.98 [s, $SiC(CH_3)_3$, 18 H]. − ^{13}C NMR: $\delta = -8.30$ (q, $^{4}J_{CF} = 1.1$ Hz, $SiCH_3$), 19.94 [q, $^{4}J_{CF} = 0.5$ Hz, $Si\mathit{C}(CH_3)_3$], 27.55 [s, $SiC(\mathit{C}H_3)_3$]. − ^{19}F NMR: $\delta = 16.90$ (dq, $^{3}J_{FH} = 2$, $^{5}J_{FH} = 1$ Hz, SiF_3). − ^{29}Si NMR: $\delta = -3.35$ (q, $^{1}J_{SiF} = 203.5$ Hz, SiF_3), 10.56 [s, $SiC(CH_3)_3$]. − $C_9H_{22}F_3NSi_2$ (257.5): calcd. C 42.3, H 8.61; found C 43.1, H 8.91.

4: M.p. 204 °C. − MS (EI), *m*/*z* (%): 506 (100) [$M - CMe_3]^+$. − ^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.18$ (s, $SiCH_3$, 9 H), 0.65 (s, NH, 3 H), 0.99 [s, $C(CH_3)_3$, 54 H]. − ^{13}C NMR: $\delta = -5.80$ (s, $SiCH_3$), 20.68 [s, Si*C*$(CH_3)_3$], 29.09 [s, SiC$(CH_3)_3$]. – ^{15}N NMR: $\delta = -349.20$. – ^{19}F NMR: $\delta = 45.17$ (q, $^3J_{FH} = 5.1$ Hz). – ^{29}Si NMR: $\delta = -44.12$ (d, $^1J_{SiF} = 225.0$ Hz, SiF), 8.15 (d, $^3J_{SiF} = 1.2$ Hz, SiF). – $C_{27}H_{66}FN_3Si_4$ (564.2): calcd. C 57.48, H 11.78; found C 57.21, H 11.52.

5: M.p. 213 °C. – MS (EI), *m/z* (%): 659 (88) [M – $C(CH_3)_3]^+$. – ^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.11$ (s, $SiCH_3$, 12 H), 0.58 (s, NH, 4 H), 0.92 [s, $SiC(CH_3)_3$, 72 H]. – ^{13}C NMR: $\delta = -5.56$ (s, $SiCH_3$), 20.88 [s, Si*C*$(CH_3)_3$], 29.30 [s, SiC$(CH_3)_3$]. – ^{29}Si NMR: $\delta = -41.95$ (s, SiN_4), 7.22 (s, NHSi). – $C_{36}H_{88}N_4Si_5$ (717.6): calcd. C 60.26, H 12.36; found C 59.97, H 12.11.

6: B.p. 130°/0.02 mbar. – MS (EI), *m/z* (%): 467 (8) [M – Me]$^+$, 425 (100) [M – $CMe_3]^+$. – ^{1}H NMR ($CDCl_3$/TMS): $\delta = 0.13$ (t, $^5J_{HF} = 1.12$ Hz, $NSiCH_3$, 3 H), 0.31 (s, $NHSiCH_3$, 3 H), 0.33 [t, $^5J_{HF} = 0.74$ Hz, $NSi(CH_3)_3$, 9 H], 0.99 [s, $NHSiC(CH_3)_3$, 18 H], 1.04 [t, $^4J_{HF} = 0.62$ Hz, $NSiC(CH_3)_3$, 18 H]. – ^{13}C NMR: $\delta = -7.78$ (t, $^4J_{CF} = 1.60$ Hz, $NSiCH_3$), –1.84 (s, $NHSiCH_3$), 5.60 [t, $^4J_{CF} = 1.31$ Hz, $NSi(CH_3)_3$], 20.14 [s, NSi*C*$(CH_3)_3$], 22.05 [s, NHSi*C*$(CH_3)_3$], 28.06 [s, NHSiC$(CH_3)_3$], 29.57 [t, $^5J_{CF} = 2.00$ Hz, NSiC$(CH_3)_3$]. – ^{19}F NMR: $\delta = 42.70$. – ^{29}Si NMR: $\delta = -57.73$ (t, $^1J_{SiF} = 222.90$ Hz, SiF_2), 4.06 [t, $^3J_{SiF} = 1.39$ Hz, $NSi(CH_3)_3$], 10.92 (t, $^3J_{SiF} = 1.19$ Hz, $NSiCH_3$), 14.02 (s, $NHSiCH_3$). – $C_{21}H_{52}F_2N_2Si_4$ (483.0): calcd. C 52.22, H 10.85; found C 52.03, H 10.69.

7: M.p. 232 °C, b.p. 212 °C/0.02 mbar. – MS (EI), *m/z* (%): 723 (100) [M – $CMe_3]^+$. – ^{19}F NMR: ($C_6D_6/CDCl_3$/TMS): $\delta = 44.28$ (d, $^4J_{FF} = 14.0$ Hz, SiF, *cis*), 48.68 (d, $^4J_{FF} = 10.2$ Hz SiF, *trans*). – ^{29}Si NMR: $\delta = -62.28$ (dd, $^1J_{SiF} = 299.0$, $^3J_{SiF} = 5.6$ Hz, SiF, *cis*), –54.32 (dd, $^1J_{SiF} = 266.6$, $^3J_{SiF} = 5.0$ Hz, SiF, *trans*). – $C_{36}H_{86}F_2N_4Si_6$ (781.6): calcd. C 55.32, H 11.09; found C 55.18, H 10.92.

8: M.p. 78 °C. NMR (C_6D_6). – ^{1}H NMR: $\delta = 0.00$ (s, $SiCH_3$, 3 H), 0.22 (s, $NSiCH_3$, 3 H); 1.18 [s, $SiC(CH_3)_3$, 18 H], 1.23 [s, $SiC(CH_3)_3$, 18 H], 1.23 (THF, 12 H), 3.40 (THF, 12 H). – ^{7}Li NMR: $\delta = 0.28$. – ^{19}F NMR: $\delta = 49.26$ (s, SiF_2).

9: M.p. 197 °C. – MS (EI), *m/z* (%): 710 (100) [M – $CMe_3]^+$. – NMR ($CDCl_3$/TMS): ^{1}H NMR: $\delta = 0.19$ (s, $NHSiCH_3$, 12 H), 0.28 (s, $NSiCH_3$, 6 H), 0.25 [s, $Si(CH_3)_3$, 18 H], 0.26 [s, $Si(CH_3)_3$, 18 H], 1.02 [s, $NHSiC(CH_3)_3$, 72 H], 1.05 [s, $NSiC(CH_3)_3$, 18 H], 1.06 [s, $NSiC(CH_3)_3$, 18 H], 1.56 (s, NH, 2 H). – ^{13}C: $\delta = -3.29$ (s, $NHSiCH_3$), 4.61 [s, $Si(CH_3)_3$], 20.20 [s, NSi*C*$(CH_3)_3$], 20.25 [s, NHSi*C*$(CH_3)_3$], 28.71 [s, NSiC$(CH_3)_3$], 28.76 [s, NSiC$(CH_3)_3$], 28.96 [s, NHSiC$(CH_3)_3$], 29.55 [s, NHSiC$(CH_3)_3$]. – ^{19}F NMR: $\delta = 41.75$ (s, SiF, *trans*), 54.12 (s, SiF, *cis*). – ^{29}Si NMR: $\delta = -36.15$ (d, $^1J_{SiF} = 284.05$ Hz, SiF), –33.50 (d, $^1J_{SiF} = 283.87$ Hz, SiF), –3.05 (s, $Si(CH_3)_3$), –3.08 (s, $Si(CH_3)_3$), 7.92 (t, $^3J_{SiF} = 1.63$ Hz, $NSiCH_3$), 11.81 (d, $^3J_{SiF} = 0.91$ Hz, $NHSiCH_3$).

Table 1. Crystal data of **1**, **8**, **9**, and **11**

Structure	**1**	**8**	**9**	**11**
Empirical formula	$C_{36}H_{88}Li_4N_4Si_4$	$C_{29}H_{67}F_2LiN_2O_2Si_4$	$C_{34}H_{83}F_2N_3Si_7$	$C_{25}H_{61}F_3N_2Si_6$
Formula mass	717.22	633.15	768.66	615.30
Temperature [K]	153(2)	223(2)	153(2)	153(2))
Crystal system	tetragonal	monoclinic	orthorhombic	monoclinic
Space group	$I4_1/a$	$P2_1/n$	*Pbcn*	$P2_1/m$
a [pm]	1179.3(1)	985.5(2)	1698.7(2)	887.60(1)
b [pm]	1179.3(1)	2983.2(2)	1569.1(2)	2104.2(5)
c [pm]	3478.0(4)	1354.7(3)	1720.0(3)	1055.2(1)
β [°]	90	101.16(1)	90	111.40(1)
V [nm^3]	4.8370(8)	3.907(1)	4.585(1)	1.8348(5)
Z	4	4	4	2
*D*x [Mg/m^3]	0.985	1.076	1.114	1.114
μ [mm^{-1}]	0.149	0.187	0.242	0.259
F(000)	1600	1392	1696	672
Cryst. size [mm]	0.3 x 0.3 x 0.6	0.4 x 0.6 x 0.6	0.4 x 0.5 x 0.8	0.4 x 0.4 x 0.5
2θ range	7 - 50	7 - 45	7 - 50	7 - 45
Index range	$-1 \leq h \leq 13$	$-10 \leq h \leq 10$	$-20 \leq h \leq 20$	$-9 \leq h \leq 9$
	$-13 \leq k \leq 13$	$0 \leq k \leq 32$	$-18 \leq k \leq 18$	$-7 \leq k \leq 22$
	$-40 \leq l \leq 41$	$-14 \leq l \leq 14$	$-20 \leq l \leq 20$	$-11 \leq l \leq 11$
Reflect. coll.	2187	5124	9941	3659
Indep. reflect.	2116	5072	4051	2470
R_{int}	0.0167	0.0681	0.0658	0.0388
Data	2116	5032	4048	2464
Parameters	121	378	268	205
Restraints	1	0	265	16
S	1.069	1.090	1.045	1.062
*R*1 [I>2σ(I)]	0.0642	0.0727	0.0418	0.0447
*wR*2 [all data]	0.1624	0.2276	0.1165	0.1140
*g*1	0.0704	0.1056	0.0521	0.0386
*g*2	8.5393	5.7455	1.2829	1.7465
Largest diff. peak [enm^{-3}]	338	481	682	386
Largest diff. hole [enm^{-3}]	-315	-405	-286	-314

10: B.p. 174°C/0.01 mbar, m.p. 102°C. – MS (EI), *m/z* (%): 619 (14) [M – Me]$^+$, 577 (100) [M – CMe$_3$]$^+$. – ^{1}H NMR (CDCl$_3$/TMS): δ = 0.14 (t, $^5J_{HF}$ = 1.13 Hz, SiCH$_3$, 6H), 0.34 [t, $^5J_{HF}$ = 0.60 Hz, Si(CH$_3$)$_3$, 18H], 0.98 [s, SiC(CH$_3$)$_3$, 36H], 1.14 (s, NH, 2H). – ^{13}C NMR: δ = –8.11 (t, $^4J_{CF}$ = 0.88 Hz, SiCH$_3$), –3.21 [p, $^4J_{CF}$ = 1.13 Hz, Si(CH$_3$)$_3$], 4.17 (p, $^2J_{CF}$ = 11.19 Hz, CSi$_4$), 20.03 [s, Si*C*(CH$_3$)$_3$], 27.80 [s, SiC(*C*H$_3$)$_3$]. – ^{19}F NMR: δ = 46.65. – ^{29}Si NMR: δ = –36.85 (tt, $^1J_{SiF}$ = 261.51, $^3J_{SiF}$ = 4.41 Hz, SiF$_2$), –0.48 [p, $^3J_{SiF}$ = 1.83 Hz, Si(CH$_3$)$_3$], 11.91 (t, $^3J_{SiF}$ = 1.48 Hz, SiCH$_3$). – $C_{25}H_{62}F_4N_2Si_6$ (635.3): calcd. C 47.27, H 9.84; found C 47.38, H 9.96.

11: M.p. 203°C. – MS (EI), *m/z* (%): 557 (1) [M – CMe$_3$]$^+$. – ^{13}C NMR (C$_6$D$_6$): δ = –4.44 (s, SiCH$_3$), 3.33 [s, Si(CH$_3$)$_3$], 19.71 [Si*C*(CH$_3$)$_3$], 25.72 [SiC(*C*H$_3$)$_3$]. – ^{19}F NMR: δ = 38.46 (dd, $^2J_{FF}$ = 90.2, $^4J_{FF}$ = 6.5 Hz, SiF$_2$), 43.66 (d, $^2J_{FF}$ = 90.2 Hz, SiF$_2$), 45.41 (d, $^4J_{FF}$ = 7.0 Hz, SiF).

X-ray Structure Determination for **1**, **8**, **9**, and **11**[13]: Crystal data are summarized in Table 1. Data for **1**, **8**, and **11** were collected with a Stoe-Siemens-AED2 diffractometer and for **9** with a Stoe-Siemens-Huber diffractometer both with monochromated Mo-K_α radiation (λ = 71.073 pm). The structures were solved by direct methods[14]. All non-hydrogen atoms were refined anisotropically[15]. For the hydrogen atoms bound to carbon atoms the riding model was used. The hydrogen atoms bound to nitrogen in structures **1** and **9** were refined with distance restraints. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$. The R values are defined as $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/[\Sigma w F_o^4]^{0.5}$.

Structure **1** was successfully refined as a twin[16]. The twin matrix is 0 1 0 1 0 0 0 0 1. The higher symmetric tetragonal Laue group was shown to be emulated. The twinning factor refines to 0.342(3). In structure **9** the silyl group at Si(2) does not fulfil the symmetry of the twofold axis. This part of the structure was refined as disorder. The atoms were refined with distance restraints and restraints for the anisotropic displacement parameters. A refinement in acentric orthorhombic or monoclinic space groups also led to disordered models. In structure **11** C(1) and the carbon atoms at Si(5) do not fulfil the mirror symmetry. Again this part was refined as disorder with distance restraints and restraints for the anisotropic displacement parameters.

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