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2-Lithiumamide-2-fluoro-1,3-diaza-2,4-disilacyclobutanes – Syntheses, Reactions, Structures

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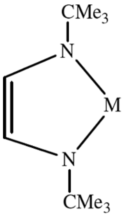
Abstract. The cyclodisilazane $Me_2Si(NCMe_3)_2SiF_2$ (**1**) reacts with lithium salts of ammonia (**2**), hydrazine (**3**) and amines (**4–10**) to give the stable compounds $Me_2Si(NCMe_3)_2SiFNHR$ (R = H (**2**), NH_2 (**3**) CMe_3 (**4**), $C_{10}H_{15}$ (**5**), 3,5-$C_6H_3Me_2$ (**6**), 2,4,6-$C_6H_2Me_3$ (**7**), 2,6-$C_6H_3(CHMe_2)_2$ (**8**), C_6F_5 (**9**), $Si(CMe_3)_2Ph$ (**10**)). Compounds **2–10** show no condensation reactions with formation of NH_3, N_2H_4, or amines. Dilithiummethylenediamide reacts with **1** to give the ethylenediamine coupled ring system **11** or spirocyclic compound **12**. Compounds **2**, **3**, **4** form the spirocyclic systems **13–15** in reactions with *n*-C_4H_9Li. A partly hydrolysed lithium salt (**16**) was isolated as tetramer containing a central Li_6O octahedron. The lithium salts of **5** (**17**), **9** (**19**) and **10** (**20**) were isolated as monomers (**17**, **19**) or dimer, respectively, via an (LiN)-four-membered ring (**20**). Crystal structures of **3**, **9**, **13–17**, **19** and **20** are reported.

1 Introduction

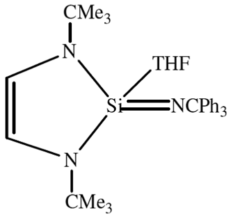
Developing the molecular chemistry of low-coordinate compounds containing heavier group 14, 15 or 16 elements has to be regarded as one of the most fruitful recent innovations in inorganic chemistry, in spite of the fact that such compounds were considered to be unstable and synthetically inaccessible.[1–3] The multiple bonded systems of nitrogen and sulfur[1] or phosphorus[2] first prepared in the 1970s, are more stable than those of silicon.[3–5] The first iminosilenes were reported in the mid-1980s. The difference in electronegativity of silicon (1.8) and nitrogen (3.0) gives the iminosilenes an ylidic nature, which makes them susceptible to oligomerisation and dimerisation. However, monomers can be kinetically stabilised by the presence of bulky substituents which are also useful for the synthesis of stable silylenes.[6] Following the discovery of analogous carbenes I by *Arduengo* and co-workers,[7] the group of *R. West* described the synthesis of stable silylenes in 1994.[8]

Using this silylene in the reaction with triphenylmethylazide provides a novel method for the synthesis of iminosilenes III.[8] The chemistry of divalent silicon compounds dates from 1986,[9–11] whereas germylenes and stannylenes were already well known.[12–14] At the time *M. Veith* used the dilithium salt $Me_2Si(NLiCMe_3)_2$ in reactions with MCl_2(M = Ge,Sn) and obtained the germylene IV and stannylene V as stable compounds.

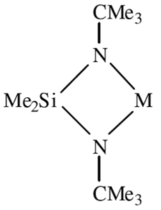


M= C(I) [7], Si(II) [8],

I, II



III



M= Ge (IV), Sn (V)

The corresponding silylene, in contrast, was reported to decompose near 77 K.[15]

We succeeded in preparing the 2,2-di-fluoro-1,3-diaza-2,4-disilacyclobutane and present in this paper its first reactions, which led to stable amino- and hydrazino-fluorosubstituted ring compounds, unusual lithium salts, and spirocyclic rings. Thermal LiF-cleavage from 2-lithiumamido-2-fluoro-1,3-diaza-2,4-disilacyclobutanes led to iminosilene which was proven to exist in solution.

2 Results and Discussion

2.1 1,3-Di-tert-butyl-difluoro-4,4-dimethyl-1,3-diaza-2,4-disilacyclobutane (1)

The synthetic pathway for **1** is shown in Equation (1). The bis(tertbutylamino)-dimethylsilane[13,16] reacts with *n*-BuLi in a molar ratio 1:2 to give the dilithium salt which forms the ring compound **1** in the reaction with SiF_4.

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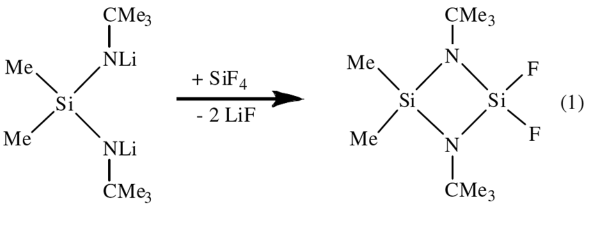


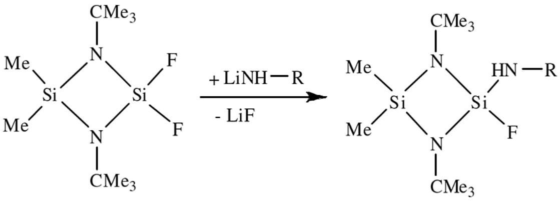
(1)

1

Compound **1** is a thermally stable liquid and can be distilled without decomposition.

2.2 1-Amino-and 1-Hydrazino-1-fluoro-1,3-diaza-2,4-disilacyclobutanes (2–10)

In contrast to other halosilanes the strong Si–F-bond energy allows a successive substitution of the fluorine atoms with nitrogen atoms. The reactions of **1** with lithiumamides lead to the formation of **2–10**, (Equation (2)). The ring system of **1** stabilises even the NH_2- and $NHNH_2$-substituted compounds **2** and **3**. The typical condensation and formation of NH_3 or H_2NNH_2 was not observed.



(2)

2-10

	2	**3**	**4**	**5**	**6**	**7**
R	H	NH_2	CMe_3	$C_{10}H_{15}$	3,5-$C_6H_3Me_2$	2,4,6-$C_6H_2Me_3$

	8	**9**	**10**
R	2,6-$C_6H_3(CHMe_2)_2$	C_6F_5	$Si(CMe_3)_2Ph$

2.2.1 Crystal Structure of 3

Colourless crystals of **3** were grown from *n*-hexane. Figure 1 depicts the molecular structure.

Compound **3** crystallises in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell. The Si–N–Si angles of the four-membered ring are larger and the N–Si–N ring angles are smaller than 90°. The four-membered ring is planar and the exocyclic nitrogen atoms have a planar environment. The average length of the Si–N-bonds in neighbourhood to the fluorine atom are 2.5 pm larger than in neighbourhood to the $SiMe_2$-unit. The eight molecules of the unit cell are connected through NH-bridges (Figure 2).

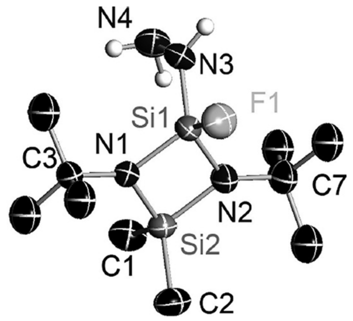


Figure 1. Crystal structure of **3**. Selected bond lengths /pm and angles /°: Si(1)–F(1) 162.5, Si(2)–N(1) 173.9, Si(1)–N(1) 170.8, Si(2)–N(3) 173.3, N(1)–Si(1)–N(2) 87.57, N(2)–Si(2)–N(1) 85.71, Si(1)–N(1)–Si(2) 93.35, N(4)–N(3)–Si(1) 120.7, C(3)–N(1)–Si(1) 133.0.

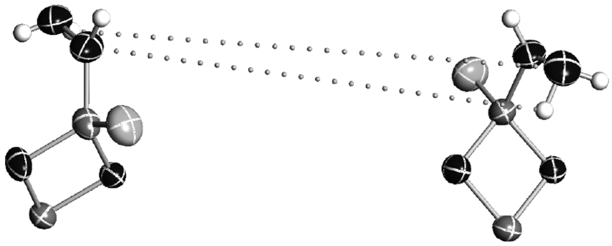


Figure 2. NH bridges between the molecules of **3**.

2.2.2 Crystal Structure of 9

Compound **9** crystallised from *n*-hexane in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The crystal structure obtained is shown in Figure 3.

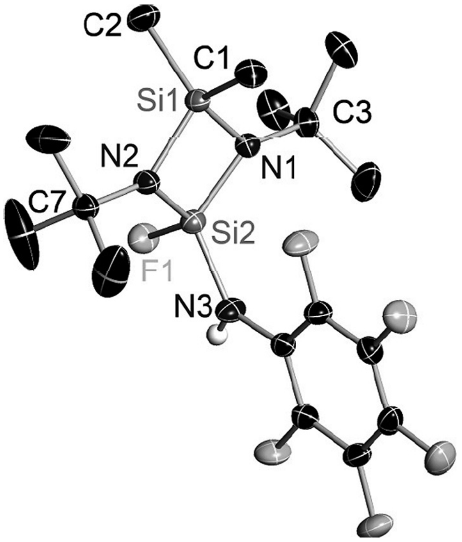


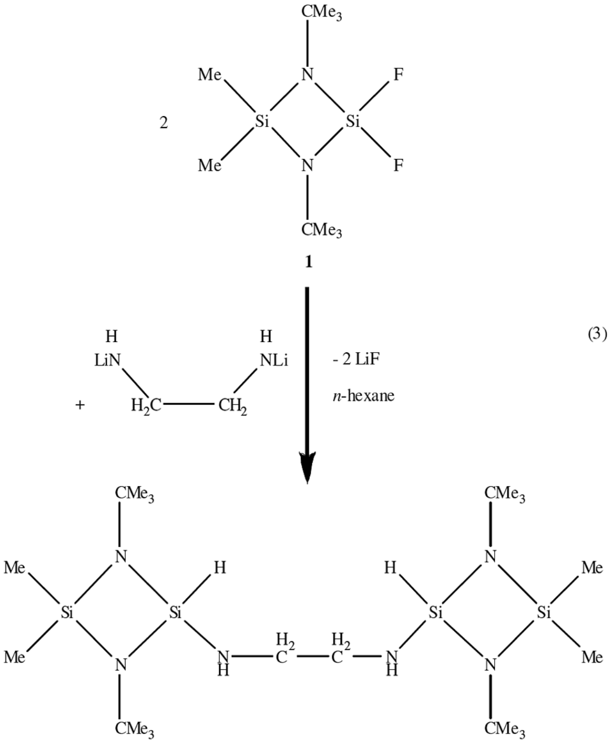
Figure 3. Crystal structure of **9**. Selected bond lengths /pm and angles /°: Si(1)–N(1) 175.1, Si(1)–N(2) 175.6, Si(2)–F(1) 159.9, Si(2)–N(1) 169.5, Si(2)–N(2) 170.0, Si(2)–N(3) 173.4. N(1)–Si(1)–N(2) 85.8, F(1)–Si(2)–N(1) 114.9, F(1)–Si(2)–N(3) 95.9, N(1)–Si(2)–N(3) 121.8, C(3)–N(1)–Si(2) 133.8, Si(2)–N(1)–Si(1) 92.5.

The four-membered ring system of **9** is planar. The Si–N-ring bonds are rather different. Caused by the electron-withdrawing effect of the CF- and SiF-unit, the Si–N bond lengths

Si(2)–N(1) (169.4 pm) and Si(2)–N(2) (170.0 pm) are more than 5 pm shorter than the Si(1)–N(1) and Si(1)–N(2) bond lengths.

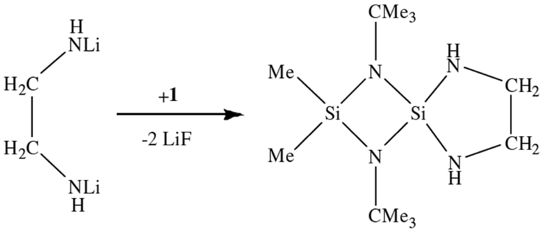
2.3 Acyclic and Spirocyclic Ethylenediamines of 1

Depending on the reaction conditions the dilithium-ethylenediamide reacts with **1** in a molar ratio 1:2 to give the ethylenediamine coupled ring system **11** or in a molar ratio 1:1 the spirocyclic compound **12** (Equation (3), Equation (4)).



(3)

11



(4)

12

Bulky substituted difluorosilanes are necessary to stabilise the NH-functional five-membered 1,3-diaza-2-silacyclopentane. The first compound of this composition was published in 2004.[17] Giving an excess of **1** to the diamide allows the isolation of **11** (Equation (3)) and the reverse order with equimolar amounts leads to the formation of the spirocyclic compound **12** (Equation (4)).

2.4 Spirocyclic Compounds 13–15

The amino and hydrazine substituted cyclodisilazanes **2**–**10** react with lithium organyls like n-C_4H_9Li giving the respective lithium salts. The thermal stability of the lithium amido-fluoro compounds increases with the bulkiness of the amino groups. By a thermally induced LiF-elimination the lithium salts show the typical reaction behaviour of iminosilenes. [2+2] cycloadditions and en-reactions are observed.[4,18] Whereas in reactions with n-C_4H_9Li **2** and **3** form spirocyclic compounds already in solution at 60–70 °C, the lithium salt of **4** is stable up to 200 °C (Equation (5), Equation (6)).

Single crystals of **13**–**15** were obtained from n-hexane and X-ray structure determinations were carried out.

*2.4.1 Crystal Structure of **13***

Compound **13** crystallises from n-hexane in the space group $P2_1/n$ with two molecules in the unit cell. The nitrogen atoms have a planar environment. The Si_2N_2 planes are perpendicular towards each other (Figure 4).

*2.4.2 Crystal Structure of **14***

The structure of **14** was confirmed by X-ray structure analysis (Figure 5), though the poor quality of the crystals led to rather high R-values and the structural parameters have to be taken with caution. Therefore the structure is not discussed in detail.

*2.4.3 Crystal Structure of **15***

Compound **15** crystallises from n-hexane in the orthorhombic space group $Pmn2_1$ with two molecules in the unit cell (Figure 6).

All nitrogen atoms have a planar environment. The four-membered rings are also planar. However, the Si(2)–N(3)–Si(3)–N(4) ring system has angles of 122.29° relative to the other four-membered rings.

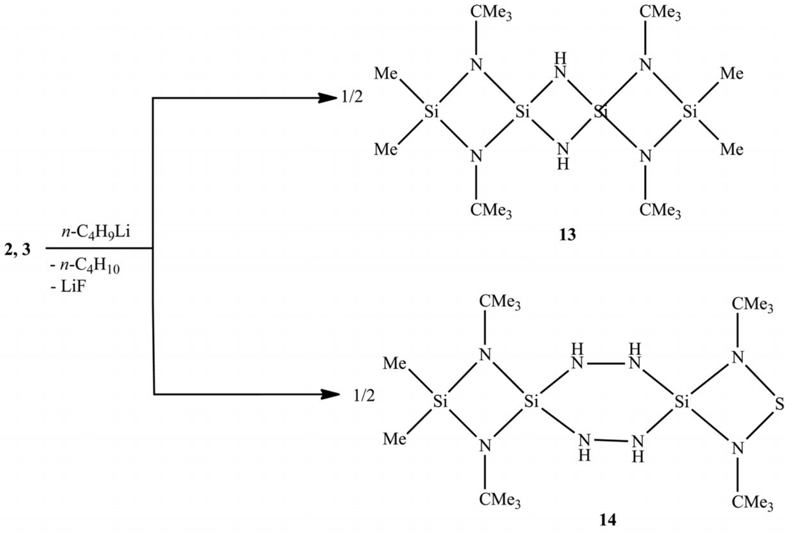
2.5 Lithium Salts of 4 (16), 5(17), 6(18), 9(19), 10(20)

*2.5.1 Crystal Structure of the Li_2O-Coordinated Tetrameric Lithium Salt of **4(16)***

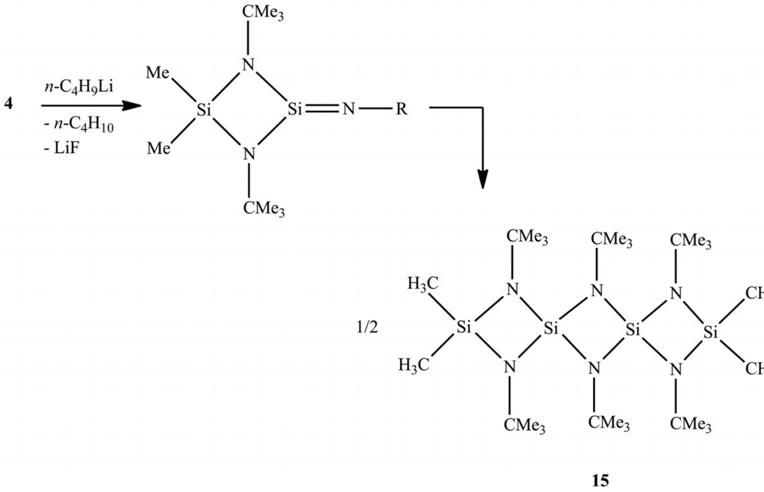
In the residual solid matter of **15** the partly hydrolysed lithium salt of **4**(**16**) was isolated as tetramer containing a central Li_6O octahedron (Equation (7)).

Compound **16** crystallises in the space group $P\bar{4}2_1c$ with two molecules in the unit cell (Figure 7).

The four-membered $(Si–N)_2$-rings are planar. The N–Si–N angles are smaller than 90° and the angles around the nitrogen atoms are larger than 90°. Because of the lithium interaction with the fluorine atom, the Si–F bond is measured with 166.4 pm. The silicon amide bond length (167.3 pm) is about 6.5 pm shorter than the average silicon amine bond length (173.7 pm). The equatorial Li–O contacts are shorter (188.0 pm) compared with the axial Li–O distances (194.5 pm). The axial Li–O–Li angle is exact 180° whereas the equatorial Li–O–Li angles were determined to be 92.9°.



(5)



(6)

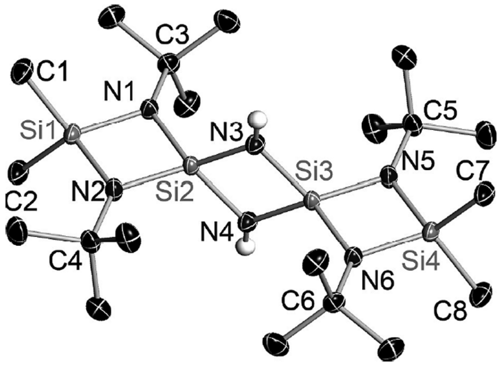


Figure 4. Crystal structure of **13**. Selected bond lengths /pm and angles /°: Si(2)–N(1) 173.61, Si(1)–N(1) 173.72, Si(1)–C(1) 186.72, Si(2)–N(3) 173.35, N(2)–Si(1)–N(1) 86.25, N(3)–Si(2)–N(2) 122,87, N(2)–Si(2), N(1) 86.34, C(3)–N(1)–Si(2) 134.34, C(3)–N(1)–Si(1) 131.01, Si(2)–N(1)–Si(1) 93.65, N(4)–Si(2)–N(3) 84.52,N(3)–Si(2)–N(1) 122.70, Si(2)–N(3)–Si(3) 95.48.

Compounds like **5**–**10** form stable lithium salts in reactions with n-C_4H_9Li (Equation (8)). We succeeded in isolating single crystals of the salts **17**, **19**, **20**.

Depending on the bulkiness of the substituent R and the solvent the lithium salts crystallise as monomers (**17**, **19**) or dimer held together by two Li–N contacts or by two Li–F contacts (**20**).

*2.5.2 Crystal Structure of **17***

The adamantylamide substituted cyclodisilazane crystallises from THF/TMEDA at room temperature in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Figure 8).

The (Si–N)-ring system of **17** is planar. The sums of the angles around the nitrogen atoms are $\Sigma°N(1) = 354{,}6$ and $\Sigma°N(2) = 357.9$, respectively. The structure shows that TMEDA and not THF coordinates the lithium ion. A spirocycle with the two silicon atoms and the lithium ion is formed. The angle between the Si(2)–N(3)–F–Li-ring and the $(SiN)_2$ ring as well as the five-membered TMEDA–Li-ring is 126.9°. The Si–N-ring bond lengths involving the Si(1) atom are about 2 pm shorter than the ones involving Si(2). The siliconamide bond is even more than 10 pm shorter than the Si(2)–N-bond.

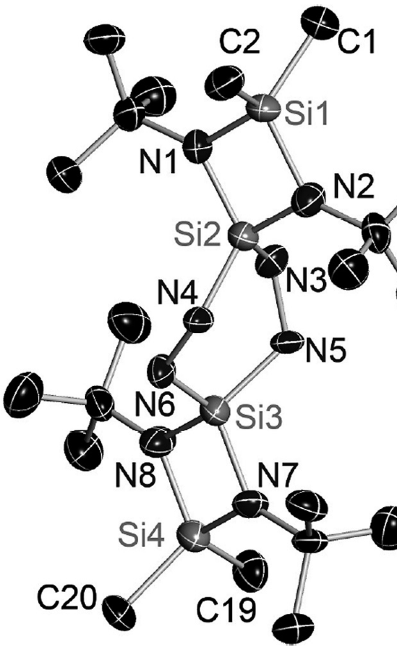


Figure 5. Crystal structure of **14**. Selected bond lengths /pm and angles /°: Si(1)–N(1) 175.7, Si(2)–N(1) 172.4, Si(2)–N(3) 173.4, N(3)–N(5) 145.4, N(2)–Si(1)–N(1) 86.2, N(4)–Si(2)–N(3)103.2, N(1)–Si(2)–N(3) 111.8.

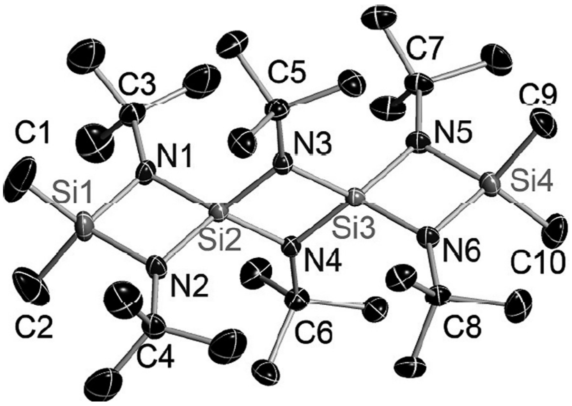
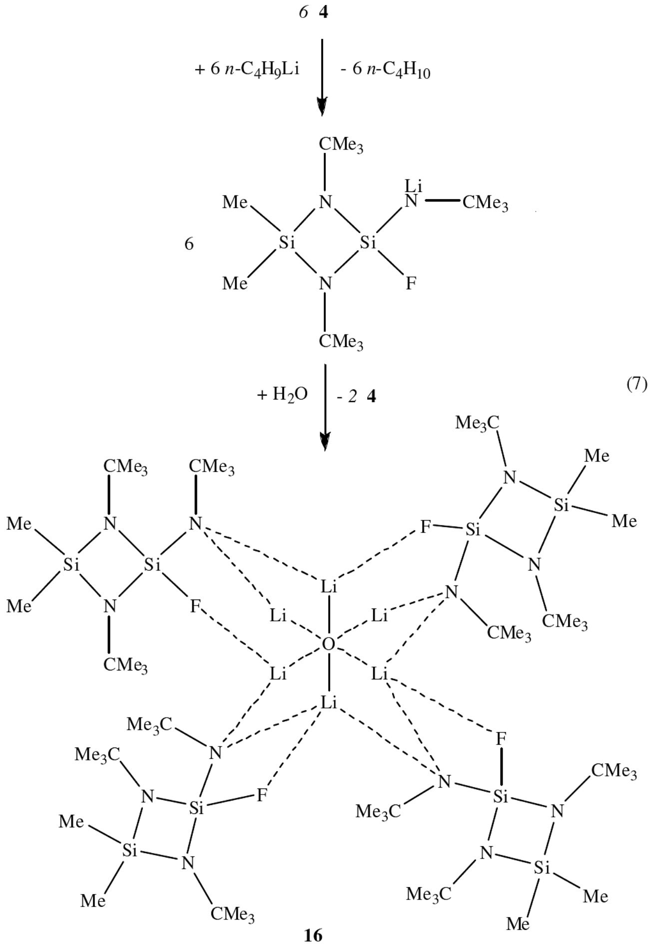


Figure 6. Crystal structure of **15**. Selected bond lengths /pm and angles /°: Si(3)–N(5) 175.2, Si(2)–N(3) 174.7, Si(1)–N(2) 173.6, N(1)–C(12) 148.4, Si(1)–N(1)–Si(2) 93.49, Si(1)–N(1)–C(3) 126.90, Si(2)–N(1)–C(3) 139.60, Si(2)–N(4)–C(6) 132.73, Si(2)–N(4)–Si(3) 94.68, Si(3)–N(4)–C(6) 132.59.

2.5.3 Crystal Structure of ***19***

The pentafluoroaniline substituted cyclodisilazane reacts with n-C_4H_9Li to give its lithium salt (**19**). The crystal structure determination of **19**, which was crystallised from a solution of THF and TMEDA, shows lithium coordinated by one TMEDA, the fluorine atom of silicon and the anilide ion. The Li···F interaction with F–Si is short and no interactions with ortho F–C of the C_6F_5 group were observed (Figure 9).[4,18]

Compound **19** crystallises with Z = 4 in the monoclinic space group $P2_1/n$.



16

(7)

2.5.4 Crystal Structure of ***20***

Crystallising the lithium salt of **10** from n-hexane led to the formation of a dimer. Two salts formed a central $(LiF)_2$ ring system. The central moiety consists of three four-membered rings: the two (Si–N–Li–F) and the $(Li--F)_2$ rings (Figure 10). The silicon atoms of the (SiNLiF)-rings exhibit shorter Si–N bonds than the other two silicon atoms possibly due to the relatively weak Si–Li interaction.

3 Crystallographic Experiments

Suitable crystals were mounted on a glass fibre and data were collected with an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å) at 133(2) K. The data were integrated with Xarea. The structures were solved by Direct Methods (SHELXS-97) and refined by full-matrix least square methods against F^2 (SHELXL-97).[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model unless they were found and refined freely. Crystallographic details can be found in Table 1 and Table 2. Three of the crystal structures have relatively high R-values. In the case of structure **3** and structure **19** this is due to the disorder of tBu groups, which are basically free to rotate. Even though the respective

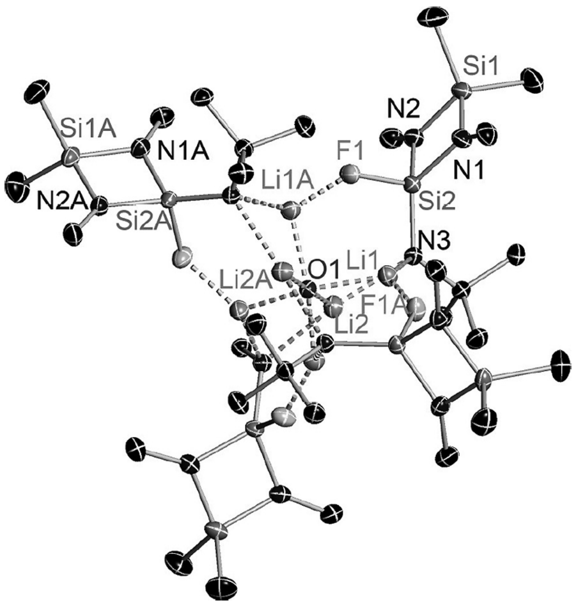
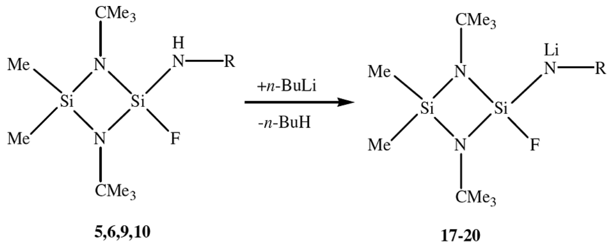


Figure 7. Crystal structure of **16**. Selected bond lengths /pm and angles /°: Si(1)–N(1) 173.76, Si(1)–C(2) 186.69, Si(2)–F 166.43, OLi(2) 188.0, O–Li(1) 194.15, Si(2)–N(3) 167.27, Si(2)–N(1) 174.44, F–Li(5) 186.8, N(1)–C(3) 146.62, N(3)–C(5) 148.60, N(3)–Li(1) 203.4, N(3)–Li(6) 219.09, N(1)–Si(1)–N(2) 86.68, Li(6)–O–Li(4) 103.07, Li(4)–O–Li(1) 180.0, F–Si(2)–N(3) 99.47, C(3)–N(1)–Si(1) 131.22, F–Si(2)–N(2) 108.40, C(3)–N(1)–Si(2) 134.69, N(3)–Si(2)–N(1) 126.2, Si(1)–N(1)–Si(2) 93.07, N(2)–Si(2)–N(1) 86.71, C(4)–N(2)–Si(2) 136.01, Si(2)–F–Li(5) 144.07, Li(6)–O–Li(5) 92.93, C(5)–N(3)–Si(2), 122.91, C(5)–N(3)–Li(6) 117.93, Si(2)–N(3)–Li(6) 102.80.



(8)

	5(17)	6(18)	9(19)	10(20)
R	$C_{10}H_{16}$	3,5-C_6Me_2	C_6F_5	$Si(CMe_3)_2C_6H_5$

disorders could be modelled, it was necessary to use restraints on carbon–carbon distances and displacement factors to reach chemically sensible solutions. Such disorders of *t*Bu groups are rather typical and do not affect the structural quality of the remaining molecule. In the case of structure **14** the problem is entirely different. Here the diffraction of the crystal was rather weak. This led to an increase in the total exposure and measurement time. Due to this, ice was building up around the crystal causing additional diffuse diffraction, increasing all *R*-values for this structure. Consequently, the poor *R*-values for this compound are rather a measurement issue than a structural issue. Nevertheless, the metric values of these three structural analyses have to be taken with caution and those from **14** are not discussed here.

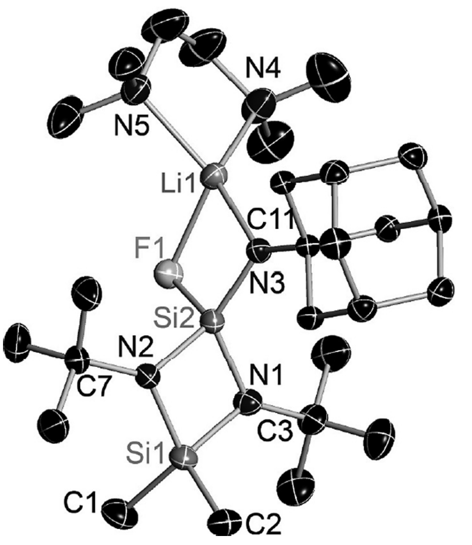


Figure 8. Crystal structure of **17**. Selected bond lengths /pm and angles /°: Si(1)–N(2) 172.68, Si(1)–N(1) 172.8, Si(1)–C(1) 186.8, Si(2)–N(3) 163.7, Si(2)–F 165.9, Si(2)–N(1) 174.0, Si(2)–N(2) 174.7 F–Li 207.6, N(3)–C(11) 144.5, N(3)–Li 192.2, N(4)–Li 208.3, N(5)–Li 213.6, N(2)–Si(1)–N(1) 87,0, N(1)–Si(1)–C(1) 114.7, N(3)–Si(2)–N(1) 128.0, N(1)–Si(2)–N(2) 86.0, C(9)–N(1)–Si(1) 132.7, Si(1)–N(1)–Si(2) 93.5, N(3)–Li–F 76.6, N(3)–Li–N(4) 131.7, F–Li–N(4) 115.2, N(4)–Li–N(5) 85.9.

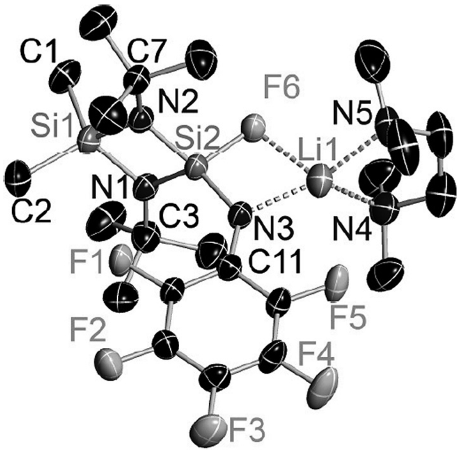


Figure 9. Crystal structure of **19**. Selected bond lengths /pm and angles /°: Si(1)–N(1) 173.8, Si(2)–F(6) 164.9, Si(2)–N(3) 166.3, Si(2)–N(1) 171.6, F(6)–Li(1) 206.0, N(3)–Li(1) 199.1, N(4)–Li(1) 146.6, N(5)–Li(1) 208.2, N(1)–Si(1)–N(2) 86.6, N(1)–Si(1)–C(2) 116.2, F(6)–Si(2)–N(3) 95.2, F(6)–Si(2)–N(2) 110.1, N(1)–Si(2)–N(2) 88.1, Si(2)–F(6)–Li(1) 94.2, Si(2)–N(2)–Si(1) 92.6, Si(2)–N(3)–Li(1) 96.3, C(20)–N(5)–Li(1) 99,0, N(3)–Li(1)–F(6) 74.2, N(3)–Li(1)–N(5) 132.8, F(6)–Li(1)–N(5) 110.8, N(5)–Li(1)–N(4) 88.4.

Complete crystallographic data are deposited at the Cambridge Crystallographic Data Centre, where they can be downloaded free of charge from www.ccdc.cam.ac.uk/data_request/cif (CCDC numbers are 788782–788791).

4 Conclusions

The 1,3-di-tert-butyl-2,2-difluoro-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane, $Me_2Si(NCMe_3)_2SiF_2$ (**1**) was synthe-

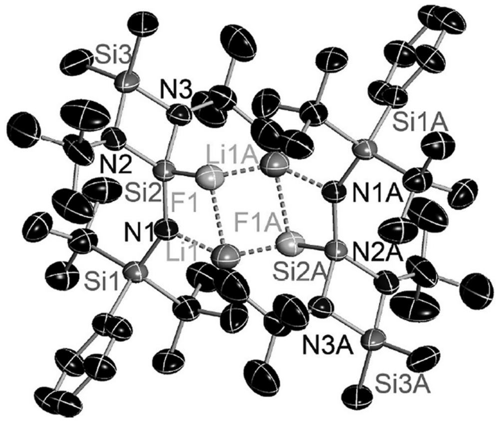


Figure 10. Crystal structure of **20**. Selected bond lengths /pm and angles /°: Si(1)–N(1) 169.5, Si(2)–N(1) 163.7, Si(2)–F(1) 169.3, Si(2)–N(2) 170.4, Si(2)–N(3) 172.0, Si(2)–Li(1) 273.3, F(1)–Li(1A) 179.7, F(1)–Li(1) 229.9, N(1)–Li(1) 190.2, Li(1)–F(1A) 179.7. N(1)–Si(2)–F(1) 99.41, N(1)–Si(2)–N(2) 129.19, F(1)–Si(2)–N(2)106.97, N(1)–Si(2)–N(3) 126.17, F(1)–Si(2)–N(3) 105.39, N(2)–Si(2)–N(3) 87.55, N(1)–Si(2)–Li(1) 43.14, F(1)–Si(2)–Li(1) 56.93, N(2)–Si(2)–Li(1) 143.86, N(3)–Si(2)–Li(1) 126.51, Si(2)–F(1)–Li(1A) 148.1, Si(2)–F(1)–Li(1) 84.97, Li(1A)–F(1)–Li(1) 97.4, Si(2)–N(1)–Si(1) 144.82, Si(2)–N(1)–Li(1) 100.8, Si(1)–N(1)–Li(1) 114.3, F(1A)–Li(1)–N(1) 145.8, F(1A)–Li(1)–F(1) 82.6, N(1)–Li(1)–F(1) 73.7, F(1A)–Li(1)–Si(2)114.7, N(1)–Li(1)–Si(2) 36.04, F(1)–Li(1)–Si(2)38.10, F(1A)–Li(1)–Li(1A) 47.47.

sised and for the first time used as starting material in preparation of substitution compounds, rings, and lithium salts. Starting from lithium amides and hydrazide the amine and hydrazine substituted ring compounds **2–11** were isolated. Compounds **2–11** are thermally stable and do not condensate with formation of amines or hydrazine. Spirocyclic compounds (**12–15**) are isolated in reactions of **1** with dilithium ethylenediamide (**12**) or of **2** (**13**), **3** (**14**) and **4** (**15**) respectively with n-C_4H_9Li. A partly hydrolysed lithium salt of **4** (**16**) was isolated as tetramer containing a central Li_6O octahedron. The lithium salts of **5** (**17**) and **9** (**19**) crystallise from a solution of n-hexane, THF and TMEDA as monomers and the one of **10** (**20**) from n-hexane as dimer. The thermally induced LiF-elimination of lithiated **4** shows the [2+2] cycloaddition of an iminosilene.[4,18]

5 Experimental Section

All experiments were performed in oven-dried glassware under purified nitrogen or argon using standard inert atmosphere and vacuo-line techniques. All NMR spectra were obtained with a Bruker AM-250, MSL–400, or Avance 500 spectrometer with $SiMe_4$ as internal reference or $MeNO_2$ as external reference. The mass spectra were reported in mass to charge units (m/z). The NMR spectra confirmed the purity of the compounds.

1,3-Di-tert-butyl-2,2-difluoro-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (1)

To a suspension of bis(tert-butyl-amino)-dimethylsilane (0.1 mol) in THF (20 mL) and n-hexane (80 mL) n-C_4H_9Li (0.2 mol, 23 % in n-hexane) was added. The reaction mixture was heated to reflux for 1 h and afterwards cooled to –20 °C. SiF_4 (0.12 mol) was added to the suspension of the dilithium salt during 2 h. Compound **1** was separated from LiF in vacuo. The clear liquid obtained was fractionally distilled for purification. $C_{10}H_{24}F_2N_2Si_2$ (266.5), yield 93 %; b.p. 57 °C (3 mbar). **MS** (EI): m/z (%) 251(100) $[M – Me]^+$. **^{1}H NMR:** $\delta = 0.35$ Si–$(CH_3)_2$, 6 H, 1.17 N–$C(CH_3)_3$, 18H. **^{13}C NMR:** $\delta = 3.76$ Si–$(CH_3)_2$ (t, $^4J_{CF} = 2.7$ Hz), 33.56 $NC(CH_3)_3$ (t, $^4J_{CF} = 0.7$ Hz), 49.78 N–

Table 1. Crystallographic data for the structural analyses of **3**, **9**, **13**, and **14**.

	3	9	13	14
Empirical formula	$C_{10}H_{27}FN_4Si_2$	$C_{16}H_{25}F_6N_3Si_2$	$C_{20}H_{50}N_6Si_4$	$C_{20}H_{48}N_8Si_4$
CCDC-No.	788782	788783	788784	788785
T /K	133(2)	133(2)	133(2)	133(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a /Å	6.3702(13)	8.5840(17)	6.3296(13)	10.602(2)
b /Å	16.963(3)	9.4406(19)	12.101(2)	12.442(3)
c /Å	30.505(6)	13.230(3)	18.623(4)	13.749(3)
α /°		85.34(3)		110.42(3)
β /°	93.70(3)	76.04(3)	97.30(3)	111.78(3)
γ /°		79.82(3)		92.78(3)
V /Å^3	3289.4(11)	1023.3(4)	1414.9(5)	1545.0(5)
Z	8	2	2	2
$D_{calcd.}$ /g·cm^{-3}	1.125	1.394	1.143	1.103
μ /mm^{-1}	0.214	0.232	0.229	0.214
$F(000)$	1216	448	536	560
θ range /°	1.37–25.84	1.59–27.00	2.01–26.94	1.74–27.02
Data/restraints/parameters	6340/60/295	4399/0/267	3051/0/236	6701/0/306
Reflections collected/unique/R_{int}	28852/6340/0.1092	9457/4399/0.0374	12554/3051/0.0429	14791/6701/0.1216
$R1, wR2[I > 2\sigma(I)]$$^{a)}$	0.0716, 0.1725	0.0387, 0.1001	0.0344, 0.0802	0.1338, 0.3075
$R1$, $wR2$ (all data)$^{a)}$	0.1319, 0.1969	0.0499, 0.1049	0.0467, 0.0845	0.2380, 0.3654
GoF	0.937	1.042	1.063	1.015
$\Delta\rho$(max),$\Delta\rho$(min) /e·Å^{-3}	0.839, –0.574	0.494, –0.456	0.404, –0.197	1.082, –0.526

a) $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Table 2. Crystallographic data for the structural analyses of **15**–**17**, **19**, and **20**.

	15	**16**	**17**	**19**	**20**
Empirical formula	$C_{28}H_{66}N_6Si_4$	$C_{56}H_{132}F_4Li_6N_{12}OSi_8$	$C_{26}H_{55}FLiN_5Si_2$	$C_{22}H_{40}F_6LiN_5Si_2$	$C_{48}H_{94}F_2Li_2N_6Si_6$
CCDC-No.	788786	788787	788788	788789	788791
T /K	133(2)	133(2)	133(2)	133(2)	133(2)
Crystal system	orthorhombic	tetragonal	monoclinic	monoclinic	monoclinic
Space group	$Pmn2_1$	$P\bar{4}2_1c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a /Å	12.485(3)	17.937(3)	10.390(2)	11.269(2)	11.450(2)
b /Å	13.604(3)	17.937(3)	30.091(6)	20.926(4)	18.955(4)
c /Å	10.726(2)	12.560(3)	10.509(2)	12.880(3)	14.322(3)
β /°			106.35(3)	105.58(3)	106.69(3)
V /Å^3	1821.8(6)	4041.2(11)	3152.8(11)	2925.9(10)	2977.4(10)
Z	2	2	4	4	2
$D_{\text{calcd.}}$ /g·cm^{-3}	1.092	1.095	1.095	1.252	1.088
μ /mm^{-1}	0.189	0.183	0.140	0.179	0.181
F(000)	664	1452	1144	1168	1064
θ range /°	2.21–26.94	1.61–27.03	1.35–25.85	1.91–27.06	1.83–27.02
Data/restraints/ parameters	3621/4/207	4369/0/208	6060/0/331	6349/0/372	6478/21/313
Reflections collected/ unique/R_{int}	9985/3621/0.0454	40200/4369/0.0455	17600/6060/0.0317	17010/6349/0.1013	26075/6478/0.0502
$R1$,$wR2$[$I > 2\sigma(I)$]$^{a)}$	0.0389, 0.0997	0.0248, 0.0629	0.0457, 0.1127	0.0751, 0.1952	0.0674, 0.1632
$R1$, $wR2$ (all data)$^{a)}$	0.0446, 0.1020	0.0262, 0.0635	0.0607, 0.1191	0.1013, 0.2125	0.0983, 0.1750
GoF	1.076	1.076	1.022	0.988	1.163
$\Delta\rho$(max),$\Delta\rho$(min) /e·Å^{-3}	0.400, –0.309	0.253, –0.159	0.967, –0.526	0.836, –0.604	0.548, –0.500

a) $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

C(CH$_3$)$_3$ (t, $^3J_{CF}$ = 1.7 Hz). **^{19}F NMR:** δ = 29.07 Si–F$_2$. **^{29}Si NMR:** δ = –77.81 Si–F$_2$ (t, $^1J_{SiF}$ = 268.6 Hz), –4.28 Si–(CH$_3$)$_2$ (t, $^3J_{SiF}$ = 2.1 Hz).

Amino-, Hydrazino, and Ethylenediamino Compounds 2–12

In the synthesis of **2**–**12** the freshly prepared lithium amides (**2, 4**–**10**), lithiumhydrazide (**3**) (0.1 mol each), respectively dilithium ethylenediamide (**11**) (0.5 mol) in THF (50 mL) and *n*-hexane (50 mL) were given dropwise to **1** (0.1 mol) in *n*-hexane (50 mL) at 0 °C. The synthesis of **12** occurred in a molar ration 1:1 in a reverse reaction of dilithium ethylenediamide and **1**.

The mixtures were heated to reflux for 3 h, afterwards cooled to room temperature. Afterwards the products were separated from LiF in vacuo. The clear liquids of **2**, **4**, **8**, **9**, **12** obtained were fractionally distilled in vacuo. The solid products **3**, **5**, **6**, **7**, **10**, **11** were recrystallised from *n*-hexane.

2-Amino-1,3-di-tert-butyl-2-fluoro-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (2)

$C_{10}H_{26}FN_3Si_2$ (263.5), yield 86 %; b.p. 60 °C (0.8 mbar). **MS** (EI): *m*/*z* (%) 248 (100) [M – Me]$^+$. **^{1}H NMR:** δ = 0.28 Si–C$_B$H$_3$, 3 H, 0.30 Si–C$_A$H$_3$, 3 H, 1.17 C(CH$_3$)$_3$, 18H. **^{13}C NMR:** δ = 4.29 Si–C$_A$, (d, $^4J_{CF}$ = 6.7 Hz), 4.53 Si–C$_B$ (d, $^4J_{CF}$ = 0.9 Hz), 33.70 N–C(CH$_3$)$_3$ (d, $^4J_{CF}$ = 0.6 Hz), 49.67 N–C(CH$_3$)$_3$ (d, $^3J_{CF}$ = 1.7 Hz). **^{19}F NMR:** δ = 32.85 (t, $^3J_{FH}$ = 9.5 Hz). **^{29}Si NMR:** δ = –56.32 Si–(NH$_2$)F (d, $^1J_{SiF}$ = 257.6 Hz), –5.97 Si–(CH$_3$)$_2$ (d, $^3J_{SiF}$ = 0.5 Hz).

1,3-Di-tert-butyl-2-fluoro-2-(silylhydrazino)-1,3-diaza-2,4-disila-cyclobutane (3)

$C_{10}H_{27}FN_4Si_2$ (278.5), yield 71 %, m.p. 59 °C. **MS** (EI): *m*/*z* (%) 263 (100) [M – Me]$^+$. **^{1}H NMR:** δ = 0.29 Si–C$_A$H$_3$ (dd, $^4J_{HH}$ = 6.47, $^5J_{HF}$ = 0.45 Hz), 3 H, 0.32 Si–C$_B$H$_3$ (dd, $^4J_{HH}$ = 6.47, $^5J_{HF}$ = 0.45 Hz), 3 H, 1.17 N–(C(CH$_3$)$_3$, 18H. **^{13}C NMR:** δ = 4.14 Si–C$_B$ (d, $^4J_{CF}$ = 0.81), 4.37 Si–C$_A$ (d, $^4J_{CF}$ = 6.72), 33.64 N–C(CH$_3$)$_3$, 49.64 N–C(CH$_3$)$_3$ (d, $^3J_{CF}$ = 1.60 Hz). **^{19}F NMR**: δ = 23.68. **^{29}Si NMR:** δ = –55.97 SiF (d, $^1J_{SiF}$ = 265.73 Hz), –5.62 Si(CH$_3$)$_2$. **^{15}N NMR**: δ = –335.72 N–H$_2$ (d, $^3J_{NF}$ = 1.43 Hz), –330.10 N–H (d, $^2J_{NF}$ = 17.10 Hz), –312.29 N–C(CH$_3$)$_3$ (d, $^2J_{NF}$ = 4.37 Hz).

1,3-Di-tert-butyl-2-tert-butylamino-2-fluoro-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (4)

$C_{14}H_{34}FN_3Si_2$ (319.6), yield 52 %, b.p. 57 °C (0.02 mbar), **MS** (EI): *m*/*z* (%) 304 (100) [M – Me]$^+$. **^{1}H NMR:** δ = 0.24 Si–C$_B$H$_3$ (d, $^4J_{HH}$ = 0.5 Hz), 3 H, 0.31 Si–C$_A$H$_3$ (d, $^4J_{HH}$ = 0.5 Hz), 3 H, 1.19 N–C(CH$_3$)$_3$, 18 H, 1.25 NHC(CH$_3$)$_3$ (d, $^5J_{HF}$ = 0.6 Hz), 9H. **^{13}C NMR:** δ = 3.87 Si–C$_A$ (d, $^4J_{CF}$ = 6.7 Hz), 5.09 Si–C$_B$ (d, $^4J_{CF}$ = 0.9 Hz), 33.03 NH–C(CH$_3$)$_3$ (d, $^4J_{CF}$ = 1.0 Hz), 33.89 Si2N–C(CH$_3$)$_3$ (d, $^4J_{CF}$ = 0.7 Hz), 49.01 Si2N–C(CH$_3$)$_3$ (d, $^3J_{CF}$ = 2.4 Hz), 49.88 (d, $^3J_{CF}$ = 1.7 Hz). **^{19}F NMR:** δ = 33.70 (d, $^3J_{FH}$ = 4.9 Hz). **^{29}Si NMR:** δ = –61.89 SiF (d, $^1J_{SiF}$ = 258.8 Hz), –6.52 Si(CH$_3$)$_2$.

1,3-Di-tert-butyl-2-adamantylamino-2-fluoro-1,3-diaza-2,4-disila-cyclobutane (5)

$C_{20}H_{40}FN_3Si_2$ (397), yield 82 %, m.p. 79 °C. **MS** (EI): *m*/*z* (%) 382 (100) [M – Me]$^+$. **^{1}H NMR:** δ = 0.25 Si–C$_B$H$_3$, 3 H, 0.31 Si–C$_A$H$_3$, 3 H, 1.20 NC$_{C,D}$(CH$_3$)$_3$, 9 H, 1.60 C*(6,8,10)*–H$_2$, 6 H, 1.80 C*(2,3,4)*–H2, (d, $^5J_{HF}$ = 2.70 Hz), 6 H, 2.01 C*(5,7,9)*–H, 3H. **^{13}C NMR:** δ = 3.97 Si–C$_B$ (d, $^4J_{CF}$ = 6.71 Hz), 5.07 Si–C$_A$, 29.90 C*(6,8,10)*, 33.92 N–C(CH$_3$)$_3$, 36.35 C*(5,7,9)*, 46.51 C(2,3,4) (d, $^4J_{CF}$ = 3.50 Hz), 49.27 N–C$_C$(CH$_3$)$_3$ (d, $^3J_{CF}$ = 0.013 Hz), 49.88 NC$_D$(CH$_3$)$_3$ (d, $^3J_{CF}$ = 0.014 Hz). **^{19}F NMR:** δ = 34.86 SiF (d, $^3J_{FH}$ = 5.75 Hz). **^{29}Si NMR:** δ = –61.14 SiF (d, $^1J_{SiF}$ = 260.13 Hz), –6.62 Si(CH$_3$)$_2$. **^{15}N NMR:** δ = –315.35 N–H (d, $^2J_{NF}$ = 10.81 Hz), –307.23 NC(CH$_3$)$_3$ (d, $^2J_{NF}$ = 4.40 Hz).

1,3-Di-tert-butyl-2-fluoro-2-(3,5-dimethylanilino)-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (6)

$C_{18}H_{34}FN_3Si_2$ (367.7), yield 66 %, m.p. 56 °C, **MS** (EI): *m/z* (%) 352 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.43 Si–C_BH_3, 3 H, 0.54 Si–C_AH_3, 3 H, 1.18 N–(C(CH_3)$_3$, 18 H, 2.26 C(*3,5*)–CH_3 (q, $^6J_{HH}$ = 0.6 Hz), 6 H, 3.84 NH, 1 H, 6.47 C(*4*)H, 1 H, 6.59 C(*3, 5*)H, 2H. **^{13}C NMR:** δ = 3.63 Si–C_A (d, $^4J_{CF}$ = 6.5 Hz), 4.94 Si–C_B (d, $^4J_{CF}$ = 0.8 Hz), 21.25 C(*3,5*)–CH_3, 33.51 N–(C(CH_3)$_3$ (d, $^4J_{CF}$ = 0.7 Hz), 49.95 N–C(CH_3)$_3$ (d, $^3J_{CF}$ = 1.7 Hz), 115.09 C(*2,6*) (d, $^4J_{CF}$ = 0.7 Hz), 120.82 C(*4*), 138.35 C(*3,5*), 144.48 C(*1*) (d, $^3J_{CF}$ = 6.0 Hz). **^{19}F NMR:** δ = 2.83. **^{29}Si NMR:** δ = –63.13 SiF (d, $^1J_{SiF}$ = 260.4 Hz), –4.59 Si(CH_3)$_2$.

1,3-Di-tert-butyl-2-fluoro-2-(2,4,6-trimethylanilino)-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (7)

$C_{19}H_{36}FN_3Si_2$ (381.7), yield 59 %, m.p. 54 °C, **MS** (EI): *m/z* (%) 366 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.36 Si–C_BH_3, 3 H, 0.38 Si–C_AH_3, 3 H, 1.10 N–(C(CH_3)$_3$, 18 H, 2.15 $C_{2,6}$–CH_3, 6 H, 2.20 C_4–CH_3, 3 H, 3.27 NH, 1 H, 6.78 $C_{3,5}$ H, 2H. **^{13}C NMR:** δ = 3.45 Si–C_A (d, $^4J_{CF}$ = 6.4 Hz), 5.17 Si–C_B (d, $^4J_{CF}$ = 0.9 Hz), 19.71 $C_{2,6}$–CH_3 (d, $^5J_{CF}$ = 1.1 Hz), 20.39 C_4–CH_3, 33.48 N–C(CH_3)$_3$, (d, $^4J_{CF}$ = 0.8 Hz), 49.81 N–C(CH_3)$_3$ (d, $^3J_{CF}$ = 1.7 Hz), 128.76 C(*2,6*) (d, $^4J_{CF}$ = 0.5 Hz), 129.05 C(*3,5*), 130.07 C(*4*), 138.53 C(*1*) (d, $^3J_{CF}$ = 3.3 Hz). **^{19}F NMR:** δ = 37.76 SiF ($^3J_{FH}$ = 3.2 Hz). **^{29}Si NMR:** δ = –61.94 SiF (d, $^1J_{SiF}$ = 267.1 Hz), –4.08 Si(CH_3)$_2$.

1,3-Di-tert-butyl-2-fluoro-2-(2,6-diisopropylanilino)-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutane (8)

$C_{22}H_{42}FN_3Si_2$ (423.8), yield 44 %, b.p. 119 °C (0.1 mbar), **MS** (EI): *m/z* (%) 408 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.35 Si–C_BH_3, 3 H, 0.38 Si–C_AH_3, 3 H, 1.07 N–C(CH_3)$_3$, 18 H, 1.21 CH(CH_3)$_2$ (d, $^3J_{HH}$ = 6.8 Hz), 12 H, 3.54 CH(CH_3)$_2$ ($^3J_{HH}$ = 6.8 Hz), 2 H, 3.25 NH, 1 H, 7.05 $C_{3,5}$ H, 2 H, 7.07 C_4 H, 1H. **^{13}C NMR:** δ = 3.70 Si–C_A (d, $^4J_{CF}$ = 6.4 Hz), 5.21 Si–C_B (d, $^4J_{CF}$ = 0.9 Hz), 23.59 CH(CH_3)$_2$, 20.39 CH(CH_3)$_2$ (d, $^5J_{CF}$ = 0.8 Hz), 33.48 N–C(CH_3)$_3$ (d, $^4J_{CF}$ = 0.9 Hz), 49.65 N–C(CH_3)$_3$ (d, $^3J_{CF}$ = 1.8 Hz), 122.80 C(*4*), 122.93 C(*3, 5*), 138.08 C(*2, 6*) (d, $^4J_{CF}$ = 2.1 Hz), 141.53 C(*1*) (d, $^3J_{CF}$ = 0.7 Hz). **^{19}F NMR:** δ = 39.29 SiF (d, $^3J_{FH}$ = 3.9 Hz). **^{29}Si NMR:** δ = –61.96 SiF (d, $^1J_{SiF}$ = 271.2 Hz), –3.62 Si(CH_3)$_2$. **^{15}N NMR:** δ = –328.14 NH (d, $^2J_{NF}$ = 11.1 Hz), –308.58 N–(CH_3)$_3$ (d, $^2J_{NF}$ = 3.8 Hz).

1,3-Di-tert-butyl-2-fluoro-2-(2,3,4,5,6-pentafluoroanilino)-1,3-diaza-2,4-disila-cyclobutane (9)

$C_{16}H_{25}F_6N_3Si_2$ (429.58), yield 78 %, b.p. 78 °C/ (0.02 mbar), **MS** (EI): *m/z* (%) 414.2 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.37 Si–C_AH_3, 3 H, 0.39 Si–C_BH_3, 3 H, 1.12 NC(CH_3)$_3$, 18 H, 3.85 N–H, 1H. **^{13}C NMR:** δ = 3.06 Si–C_A (dt, $^4J_{CF}$ = 8.40, $^7J_{CF}$ = 1.94 Hz), 4.69, 33.62 N–C(CH_3)$_3$, 49.94 N–(C(CH_3)$_3$ (d, $^3J_{CF}$ = 1.62 Hz), 121.33 C(*2, 6*) (m), 132.89 C(*4*) (m), 136.56 C(*3, 5*) (m), 139.90 C(*1*) (m). **^{19}F NMR:** δ = –35.47 SiF (t, $^5J_{FF}$ = 5.80 Hz), 2.53 F*(2,6)* (m), 7.46 F*(3,5)* (m), 7.89 F*(4)* (tt, $^3J_{FF}$ = 27.64, $^4J_{FF}$ = 10.52, $^7J_{FF}$ = 5.73 Hz). **^{29}Si NMR:** δ = –64.16 SiF (d, $^1J_{SiF}$ = 262.63 Hz), –2.86 Si(CH_3)$_2$. **^{15}N NMR:** δ = –333.17 N–H (dt, $^2J_{NF}$ = 20.16, $^3J_{NF\mathit{ortho}}$ = 1.72 Hz), –309.09 N–C(CH_3)$_3$ (dt, $^2J_{NF}$ = 5.02, $^5J_{NF\mathit{ortho}}$ = 0.99 Hz).

1,3-Di-tert-butyl-2-fluoro-2-(di-tert-butyl-phenyl-silylamino)-1,3-diaza-2,4-disila-cyclobutane (10)

$C_{22}H_{48}FN_3Si_3$ (457.31), yield 56 %, m.p. 120 °C. **^{1}H NMR:** δ = 0.47 Si–C_BH_3, 3 H, 0.52 Si–C_AH_3, 3 H, 1.25 Si–C(CH_3)$_2$Ph, 6 H, 1.32 N–C(CH_3)$_3$, 9 H, 7.16 C(*3, 5*)H, 1 H, 7.22 C(*4*)H, 1 H, 7.91 C(*2, 6*)H, 1 H, 7.95 C(*1*)H, 1H. **^{13}C NMR:** δ = 4.55 Si–C_BH_3 (d, $^4J_{CF}$ = 0.10 Hz), 5.25 Si–C_AH_3, 20.72 Si–C(CH_3)$_3$, 29.18 Si–C(CH_3)$_3$, 34.13 N–C(CH_3)$_3$, 50.01 N–C(CH_3)$_3$ (d, $^3J_{CF}$ = 1.67 Hz), 126.87 C(*3, 5*) (d, $^5J_{CF}$ = 1.5 Hz), 129.05 C(*4*), 135.96 C(*2, 6*) (d, $^6J_{CF}$ = 2.15 Hz), 136.46 C(*1*) d, $^4J_{CF}$ = 20.52 Hz). **^{19}F NMR:** δ = 44.87 SiF (d, $^1J_{SiF}$ = 12.16 Hz). **^{29}Si NMR:** δ = –58.35 SiF (d, $^1J_{SiF}$ = 268.05 Hz), –14.22 Si–C(CH_3)$_3$ (d, $^3J_{SiF}$ = 0.57 Hz), –5.46 Si(CH_3)$_2$.

Bis(1,3-di-tert-butyl-2-fluoro-4,4-dimethyl-1,3-diaza-2,4-disila-cyclobutan)-2-ethylenediamine (11)

$C_{22}H_{54}F_2N_6Si_4$ (553.1), yield 20 %, m.p. 195 °C, **MS** (EI): *m/z* (%) 537 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.26 Si–C_BH_3, 6 H, 0.30 Si–C_AH_3, 6 H, 1.15 N–C(CH_3)$_3$, 36 H, 1.29 NH, 2 H, 2.86 CH_2, 4H. **^{13}C NMR:** δ = 4.22 Si–C_A (d, $^4J_{CF}$ = 6.7 Hz), 4.50 Si–C_B (d, $^4J_{CF}$ = 0.7 Hz), 33.71 N–C(CH_3)$_3$ (d, $^4J_{CF}$ = 0.5 Hz), 44.15 CH_2 (d, $^3J_{CF}$ = 3.0 Hz), 49.55 N–C(CH_3)$_3$ (d, $^3J_{CF}$ = 1.7 Hz). **^{29}Si NMR:** δ = –57.80 SiF (d, $^1J_{SiF}$ = 260.0 Hz), –6.17 Si(CH_3)$_2$. **^{15}N NMR:** δ = –353.812 NH (d, $^2J_{NF}$ = 12.8 Hz), –309.70 NC(CH_3)$_3$ (d, $^2J_{NF}$ = 4.5 Hz).

1,3-Di-tert-butyl-1,3,5,8-tetraaza-2,4-disilaspiro[3,4]octane (12)

$C_{12}H_{30}N_4Si_2$ (286.6), yield 17 %, b.p. 95 °C (0.09 mbar), m.p. 49 °C, **MS** (EI): *m/z* (%) 271 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.21 Si(CH_3)$_2$, 6 H, 1.13 N–C(CH_3)$_3$, 18 H, 3.11 CH_2, 4H. **^{13}C NMR:** δ = 4.71 Si–(CH_3)$_2$, 33.69 N–C(CH_3)$_3$, 42.18 CH_2, 49.32 N–C(CH_3)$_3$. **^{29}Si NMR:** δ = –38.46 Si–N_4, –7.66 Si(CH_3)$_2$. **^{15}N NMR:** δ = –356.49 NH.

Spirocyclic Compounds 13–15

A solution of the amino (**2**, **4**) or hydrazino (**3**) compounds (0.1 mol) in *n*-hexane (100 mL) was cooled to 0 °C and *n*-C_4H_9Li (0.1 mol, 23 % in *n*-hexane) was added. The mixture was warmed to reflux for 2 h and compounds **13** and **14** were separated from LiF in vacuo and analytically pure obtained by recrystallisation from *n*-hexane. In the case of **15** it was necessary to temper the formed lithium salt of **4** to 200 °C to separate it from LiF. The mixture was solved in *n*-hexane (100 mL) under reflux and afterwards cooled. The formed crystals of **13**–**15** were recrystallised from *n*-hexane.

Compound (13)

$C_{20}H_{50}N_6Si_4$ (486), m.p. 91 °C, **MS** (EI): *m/z* (%) 471 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.31 Si–(CH_3)$_2$, 12 H, 1.27 N–C(CH_3)$_3$, 36H. **^{13}C NMR:** δ = 5.52 Si–(CH_3)$_2$, 34.16 N–C(CH_3)$_3$, 49.77 NC(CH_3)$_3$. **^{29}Si NMR:** δ = –58.84 Si–N, –8.46 Si(CH_3)$_2$.

Compound (14)

$C_{20}H_{52}N_8Si_4$ (516), yield 30 %, **MS** (EI): *m/z* (%) 502 (100) $[M - Me]^+$.

Compound (15)

$C_{28}H_{66}N_6Si_4$ (598), yield 24 %, m.p. 184 °C, **MS** (EI): *m/z* (%) 583 (100) $[M - Me]^+$. **^{1}H NMR:** δ = 0.37 Si–(CH_3)$_2$, 12 H, 1.36 N–C_A(CH_3)$_3$, 36 H, N–(C_B(CH_3)$_3$ 18H. **^{13}C NMR:** δ = 6.36 Si–(CH_3)$_2$, 34.40 N–$C_B(CH_3)_3$, 35.25 $NC_A(CH_3)_3$, 50.69 N–$C_B(CH_3)_3$, 51.08 N–$C_A(CH_3)_3$. **^{29}Si NMR:** δ = –61.90 Si–N_4, –7.04 $Si(CH_3)_2$. **^{15}N NMR:** δ = –314.27 N–$C_A(CH_3)_3$, –303.74 N–$C_B(CH_3)_3$.

Lithium Salts of 4 (16), 5 (17), 6 (18), 9 (19), 10 (20)

In the residual solid matter of **15** the partly hydrolysed lithium salt of **4** (**16**) was isolated and cleaned by recrystallisation from *n*-hexane. In the reaction of **5**–**10** (0.1 mol) in *n*-hexane (100 mL) with *n*-C_4H_9Li (0.1 mol, 23 % in *n*-hexane) the lithium salts **17**–**20** were formed at room temperature. The purification of **17**–**20** was carried out by recrystallisation in *n*-hexane and THF. To dissolve them it was necessary to give TMEDA (0.1 mol) to the adamantly compound **17** and the pentafluoroanilino compound **19**.

Lithium Salt of Partly Hydrolysed 1,3-Di-tert-butyl-2-tert-butylamino-2-fluoro-4,4-dimethyl-1,3-diaza-2,4-disilacyclobutane (16)

$C_{56}H_{132}F_4Li_6N_{12}OSi_8$ (1332.10), yield 25 %, m.p. 87 °C. **^{1}H NMR**: δ = 0.36 Si–$(CH_3)_2$, 6 H, 1.36 N–$C(CH_3)_3$, 9 H, 1.53 N–$C(CH_3)_3$exo, 18H. **^{13}C NMR:** δ = 4.55 Si–C_B, 5.71 Si–C_A, 35.33 N–$C(CH_3)_3$, 50.15 N–$C(CH_3)_3$. **^{29}Si NMR:** δ = –55.57 SiF (d, $^1J_{SiF}$ = 227.16 Hz), –7.85 Si–$(CH_3)_2$. **^{15}N NMR:** δ = –307.89 N1–$C(CH_3)_3$ring (d, $^2J_{NF}$ = 4.22 Hz), 306.03 N2–$C(CH_3)_3$exo (d, $^2J_{NF}$ = 6.82 Hz). **^{19}F NMR:** δ = –34.05 SiF. **^{7}Li NMR:** δ = 1.10 LiN, 1.81 LiF.

Lithium-1,3-di-tert-butyl-2-adamantylamino-2-fluoro-1,3-diaza-2,4-disila-cyclobutane TMEDA Adduct (17)

$C_{26}H_{56}FLiN_5Si_2$ (513), yield 63 %, m.p. 97 °C. **^{1}H NMR:** δ = –0.30 Si–C_BH_3, 3 H, 0.49 Si–C_AH_3, 3 H, 1.29 *N*–$C(CH_3)_3$, 9 H, 1.49 N–$C(CH_3)_2$–CH_2, 6 H, 1.54 C(6,8,10)–H2, 6 H, 1.81 C(2,3,4)–H2, 6H (d, $^5J_{HF}$ = 2.97 Hz), 2.00 N–$C(CH_3)_2$–CH_2, 4 H, 2.23 C(5,7,9), 3H. **^{13}C NMR:** δ = –4.21 Si–C_A (d, $^4J_{CF}$ = 6.59 Hz), 5.77 Si–C_B (d, $^4J_{CF}$ = 1.10 Hz), 31.80 N–$C(CH_3)_3$ (d, $^4J_{CF}$ = 0.5 Hz), 44.15 CH_2 (d, $^3J_{CF}$ = 3.0 Hz), 49.55 C(6,8,10), 34.98 N–$C(CH_3)_3$, 38.02 C(5,7,9), 46.65 N–$C(CH_3)_3$–CH_2, 50.03 N–$C_c(CH_3)_3$ (d, $^3J_{CF}$ = 1.95 Hz), 50.15 N–$C_D(CH_3)_3$ (d, $^3J_{CF}$ = 1.66 Hz), 52.26, C(2,3,4), 56.71 N–$(CH_3)_3$–CH_2. **^{29}Si NMR:** δ = –63.00 SiF (d, $^1J_{SiF}$ = 213.55 Hz), –11.51 $Si(CH_3)_2$. **^{15}N NMR:** δ = –305.26 N–$C(CH_3)_3$ (d, $^2J_{NF}$ = 6,36 Hz). **^{19}F NMR:** δ = –30.23 SiF. **^{7}Li NMR:** δ = 0.71 (d, $^1J_{LiF}$ = 6.32 Hz).

Lithium-1,3-di-tert-butyl-2-fluoro-4,4-dimethyl-2-(3,5-dimethylanilino)-1,3-diaza-2,4-disila-cyclobutan THF Adduct (18)

$(C_{22}H_{41}FLiN_3OSi_2)_2$ (2 × 445.7), yield 83 %, m.p. 74 °C. **1H NMR:** δ = 0.47 Si–C_BH_3, 3 H, 0.58 Si–C_AH_3, 3 H, 1.24 O–$(CH_2$–$CH_2)_2$, 4H (t, $^3J_{HH}$ = 6.4 Hz), 1.32 N–$(C(CH_3)_3$, 18 H, 1.26 C–CH_3, 6 H, 3.32 C–CH_3, 4H (t, $^3J_{HH}$ = 6.4), 6.41 C(*4*)–H, 6.99 C(*3,5*)–H, 2H. **^{13}C NMR:** δ = 4.49 Si–C_A (d, $^4J_{CF}$ = 7.1 Hz), 5.35 Si–C_B, 21.66 C–CH_3, 25.22 O–$(CH_2$–$CH_2)_2$, 34.22 N–$C(CH_3)_3$, 49.90 N–$(C(CH_3)_3$ (d, $^3J_{CF}$ = 1.66 Hz), 68.12 O–$(CH_2$–$CH_2)_2$, 118.71 C(*2,6*), 122.33 C(*4*), 137.93 C(*3,5*), 157.20 C(*1*) (d, $^3J_{CF}$ = 13,0 Hz). **^{19}F NMR:** δ = 36.61 SiF **^{29}Si NMR:** δ = –55.71 (d, $^1J_{SiF}$ = 238.0 Hz), –7.68 $Si(CH_3)_2$. **^{7}Li NMR:** δ = 0.96.

Lithium-1,3-di-tert-butyl-2-fluoro-2-(di-tert-butyl-phenylsilyl-amino)- 1,3-diaza-2,4-disila-cyclobutane (20)

1H NMR: from thf, δ = 0.08 Si–$(CH_3)_2$, 0.27 Si–$C(CH_3)_2$, 0.32 N–$C(CH_3)_2$. **^{13}C NMR**: δ = 4.76 Si–$(CH_3)_2$ (d, $^4J_{CF}$ = 0.095 Hz), 22.61 Si–$C(CH_3)_2$, 34.64 N–$C(CH_3)_3$, 50.11 N–$C(CH_3)_3$ (d, $^3J_{CF}$ = 0.027 Hz), 128.00 –C_6H_5 (m). **^{19}F NMR:** δ = 42.90 SiF (q, $^4J_{NF}$ = 34.04 Hz). **^{29}Si NMR:** δ = –60.81 SiF (d, $^1J_{SiF}$ = 231.42 Hz), –13.99 Si–$C(CH_3)_2$ (d, $^3J_{SiF}$ = 16.98 Hz), –8.72 Si–$(CH_3)_2$. **^{7}Li NMR:** δ = 0.14 (d, $^1J_{LiF}$ = 0.099 Hz).

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