1-Oxa-3-aza-2,4-disilacyclobutanes − Synthesis, X-ray Structures, and Reactivity

Uwe Klingebiel,*[a] M. Noltemeyer[a]

Keywords: Silicon / Structure elucidation / Silanes / Small ring systems

Lithium aminodi(*tert*-butyl)silanolate reacts with F_3SiR to give the aminosiloxane $(Me_3C)_2SiNH_2–O–SiF_2R$ [**1**; R = 2,4,6-$(tBu)_3C_6H_2$]. In the reaction of **1** with BuLi a four-membered (Si–O–Si–NH) ring system **2** is formed [$–(Me_3C)_2Si–O–SiFR–NH–$]. The amino-1,3-disiloxane $RSiF_2–NH–Si(CMe_3)_2–O–SiF_2R$ (**3**) is obtained from dilithiated amino(di-*tert*-butyl)silanol and F_3SiR. Compound **1** reacts with BuLi with formation of a dimeric lithium derivative through the Li–N bond (**4**). In **4** the transannular Si···Si distance was found to be 237.2 pm, which is the shortest distance so far found between two silicon atoms contained in four-membered rings. Compound **4** reacts with $Me_3SiOSO_2CF_3$ with substitution of the lithium by the Me_3Si group to give **5**.

Introduction

In silicon chemistry it is possible to stabilize compounds with two or three OH or NH_2 groups bonded to one silicon atom, in contrast to carbon chemistry. The first silanediols and -diamines were described by Sommer and Tyler in the fifties.[1] Silanetriols and -triamines followed about thirty years later.[2−4] We succeeded in preparing stable halosilanols,[5] (e.g. chlorosilanols) from the reaction of silanediols with PCl_5, accompanied by formation of HCl and $POCl_3$. The reaction of di-*tert*-butyl-dichlorosilane with ammonia proceeds with complete cleavage of hydrogen chloride to afford the amino-di-*tert*-butylsilanol, the only aminosilanol known so far,[2,6] which is stable towards self-reaction [Equation (1)].

$$R_2Si(OH)_2 \xrightarrow[-\,HCl,\,-\,POCl_3]{+\,PCl_5} R_2Si(OH)Cl \xrightarrow[-\,NH_4Cl]{+\,2\,NH_3} R_2Si(OH)NH_2 \quad (1)$$

The kinetic stabilization of the aminosilanol led to the stepwise synthesis of numerous acyclic and cyclic organosilicon compounds.[7] After lithiation of the aminosilanol,[6] treatment with a halosilane always results in attachment of the new organosilicon group to the oxygen atom; aminosiloxanes are formed [Equation (2)]. Lithiation of these aminosiloxanes normally leads again to the bonding of lithium to the oxygen atom. In this case aminosilanolates of type I are formed. This means that in the lithiation reaction the silyl substituent on the oxygen atom is displaced by the Lewis acidic lithium, so that an O → N silyl group migration is observed.[8] This rearrangement can be prevented by bulky groups [Equation (2)]. Siloxaneamides of type II are then formed. Therefore the success of the substitution of the silyl groups determines which isomer is obtained.[8] In reactions with other halosilanes silylamino-1,3-disiloxanes are obtained.

In attempting to obtain cyclic products by salt elimination from isomeric lithium compounds we isolated eight-membered (Si−O−Si−N) rings [Equation (2)].[9,10] Lithium derivatives of type I are found to be very stable; they can be distilled without decomposition.[11] However, they are direct precursors of four-membered (Si−O−Si−N) rings when catalytic amounts (1−5%) of fluorosilanes are added to a solution of the lithium compounds.[8,12]

In this paper we describe the preparation of 1-[amino-1,1-di(*tert*-butyl)]-3-[2,4,6-tri(*tert*-butyl)phenyl]-3,3-difluoro-1,3-disiloxane, its cyclisation to the first (Si−NH−Si−O) four-membered ring system, and the formation of its lithium derivative.

Results and Discussions

In preparative ring chemistry bulky groups lead to the formation of small ring compounds. In order to prepare a fluoro-functionalized Si(F)−O−Si−N(H) four-membered ring system we used the bulky $Si(CMe_3)_2$ and $F_2SiC_6H_2(CMe_3)_3$ units. The lithiated aminodi(*tert*-butyl)silanol[6] reacts with 2,4,6-tri(*tert*-butyl)phenyltrifluorosilane to yield the aminosiloxane **1** [Equation (3)], which is stable against HF or NH_3 condensation.

Our attempts to isolate the lithium derivative of **1** in the reaction of **1** and BuLi were unsuccessful, LiF elimination occurred and the 1-aza-3-oxa-2,4-disilacyclobutane **2** was obtained [Equation (4)].

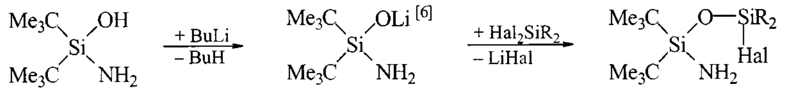
Crystal Structure of 2

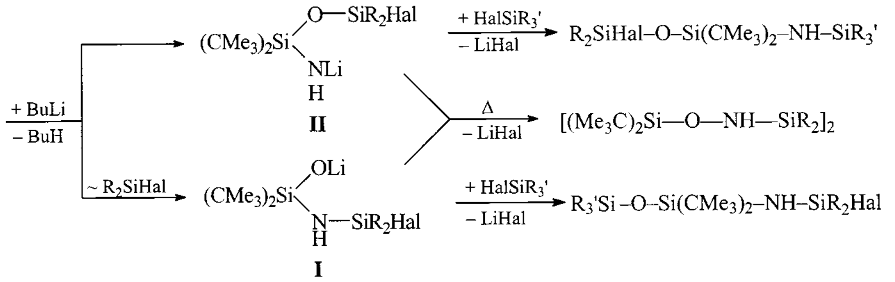
Colorless crystals of **2** with space group $P\bar{1}$ were obtained from a saturated solution of *n*-hexane. The atoms N(1), Si(1), O(1) and Si(2) of the molecule form a planar four-membered ring, but there are some irregularities as follows. At the oxygen and the nitrogen atoms there is a slight open-

---

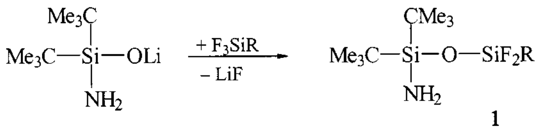
[a] Institut für Anorganische Chemie der Georg-August-Universität Göttingen,
Tammannstraße 4, 37077 Göttingen, Germany
E-mail: uklinge@gwdg.de

1434−1948/01/0707−1889 $ 17.50+.50/0





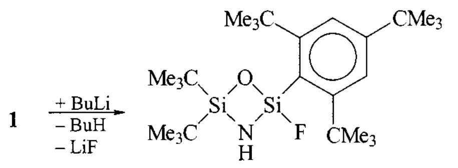
(2)



(3)

1

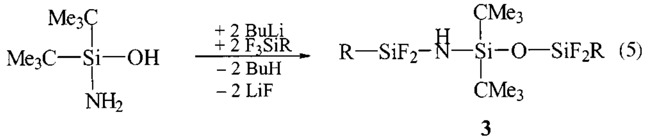
R = 2,4,6-(CMe$_3$)$_3$C$_6$H$_2$



(4)

2

ing of the Si(1)−O(1)−Si(2) angle (93.42°) and the Si(1)−N(1)−Si(2) angle (94.03°), which is accompanied by a contraction of the angles at the other ring atoms [N(1)−Si(1)−O(1) = 87.15°; N(1)−Si(2)−O(1) = 85.4°]. The Si(1)−O(1) (167.2 pm), and the Si(2)−O(1) (170.2 pm) bond lengths are lengthened. The Si(1)−N(1) (166.6 pm) and Si(2)−N(1) (169.1 pm) bonds are short, even shorter than the Si−O bonds. In order to see if there is any O/NH split occupancy of O(1) re-refinements of O/NH occupancies were carried out on both sites. However, strong correlation with ADPS leads to unstable refinement. Also, no hydrogen atoms could be located in the difference maps and riding models had to be used throughout. The Si···Si nonbonding distance in the ring is 245.6 pm, the corresponding N···O distance is 230.1 pm. These short distances illustrate that the ring atoms in a four-membered ring as strained as this one are forced to approach each other to an extraordinary extent. The C(1) atom of the aryl group is found to have no planar environment: the sum of the angles at C(1) amounts to 355.7°. Figure 1 shows the structure of compound **2**.



(5)

3

R = 2,4,6-C$_6$H$_2$(CMe$_3$)$_3$

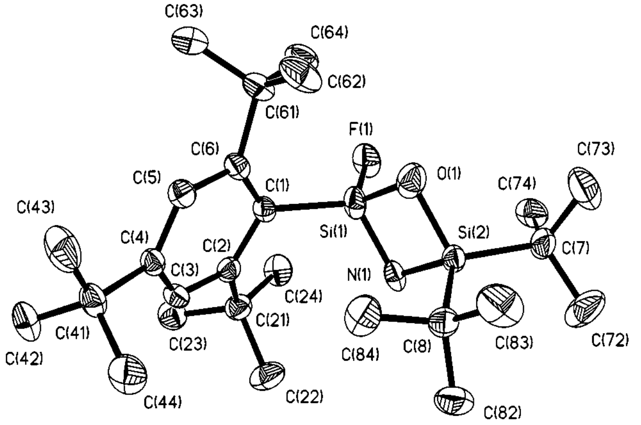
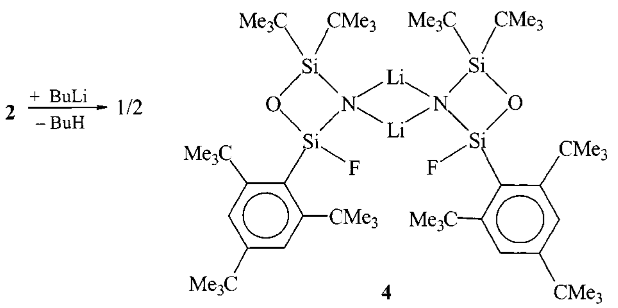


Figure 1. Structure of **2**; selected bond lengths [pm] and angles [°]: Si(1)−F(1) 158.81(13), Si(1)−N(1) 166.6(2), Si(1)−O(1) 167.2(2), Si(1)−C(1) 186.3(2), Si(1)−Si(2) 245.56(10), Si(2)−N(1) 169.1(2), Si(2)−O(1) 170.2(2), Si(2)−C(7) 188.3(2); F(1)−Si(1)−N(1) 111.17(9), F(1)−Si(1)−O(1) 111.30(8), N(1)−Si(1)−O(1) 87.15(9), F(1)−Si(1)−C(1) 114.70(8), N(1)−Si(1)−C(1) 114.73(9), O(1)−Si(1)−C(1) 114.78(9), N(1)−Si(2)−O(1) 85.40(10), Si(1)−O(1)−Si(2) 93.42(10), Si(1)−N(1)−Si(2) 94.03(10)

Disilylation of the aminosilanol is possible by starting from the dilithium derivative according to Equation (5):

Crystal Structure of 4

The lithium compound **4** is obtained in high yields [Equation (6)] from the reaction of **2** with BuLi, thus confirming the structure of **4**.



(6)

4

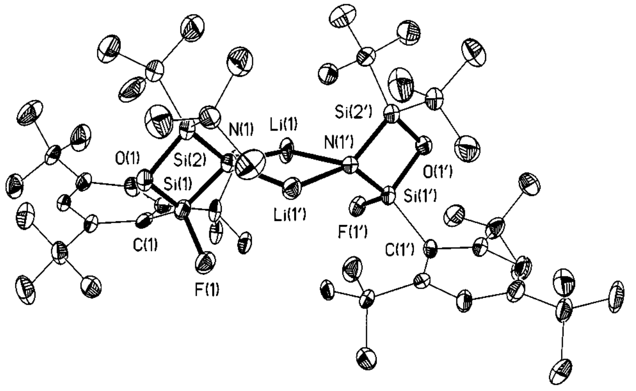


Figure 2. Structure of **4**; selected bond lengths [pm] and angles [°]: Si(1)−F(1) 161.8(4), Si(1)−O(1) 166.7(5), Si(1)−N(1) 172.1(6), Si(1)−C(1) 187.6(7), Si(1)−Si(2) 237.2(3), Si(2)−O(1) 169.6(5), Si(2)−N(1) 174.3(6), Si(2)−C(8) 190.1(8), Li(1)−N(1) 195.1(12), Li(1)−N(1′) 203.5(13), Li(1)−Li(1′) 232(2), N(1)−Li(1′) 201.5(13), Si(1′)−F(1′) 160.5(5), Si(1′)−O(1′) 166.7(5), Si(1′)−N(1′) 172.9(6), Si(1′)−Si(2′) 237.3(3), Si(2′)−O(1′) 169.8(5), Si(2′)−N(1′) 173.5(6), Li(1′)−N(1′) 195.4(12); F(1)−Si(1)−O(1) 110.8(2), F(1)−Si(1)−N(1) 109.1(2), O(1)−Si(1)−N(1) 92.6(3), O(1)−Si(1)−Li(1′) 102.1(3), N(1)−Si(1)−Li(1′) 37.9(3), O(1)−Si(2)−N(1) 90.9(3), N(1)−Li(1)−N(1′) 107.7(6), N(1)−Li(1)−Li(1′) 55.5(4), Si(1)−N(1)−Si(2) 86.4(3), Li(1)−N(1)−Li(1′) 71.5(5), Si(1)−O(1)−Si(2) 89.7(2), O(1′)−Si(2′)−N(1′) 91.1(3), N(1′)−Li(1′)−N(1) 108.4(6), Si(1′)−N(1′)−Si(2′) 86.5(3), Li(1′)−N(1′)−Li(1) 71.0(5), Si(1′)−O(1′)−Si(2′) 89.7(2)

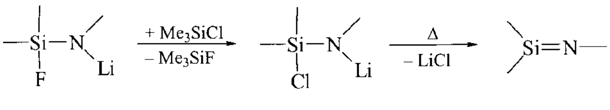
Compound **4** crystallizes from *n*-hexane as a dimer in the space group *C*2/*c* (Figure 2) Again the crystal structure shows some irregularities. The dimer of **4** is formed from a four-membered $(Li-N)_2$ ring system, which is not entirely planar but folded by 10.7° across the Li···Li line. The Si−O−Si−N rings have an angle of 86° to the central $(LiN)_2$ ring and of 5.8° to each other. The *tert*-butyl groups and therefore the aryl group and the fluorine atom are in *cis* positions. The sum of the angles around C(1) amounts to 355.1°. In contrast to compound **2**, the Si−O distances here are shorter than the Si−N distances. Now the ring angles at Si(1) (92.6°) and Si(2) (90.9°) are above 90° and the angles at O(1) (89.7°) and N(1) (86.4°) are smaller than 90°. This brings the Si(1) and Si(2) atoms into a close approximation. The Si···Si nonbonding distance in the ring is only 237.2 pm, which as far as we are aware is the shortest nonbonding Si···Si contact found so far. The transannular O···N distance is found to be 245.1 pm. The bonding properties of such small four-membered rings containing two opposite silicon atoms have been investigated by various theoretical methods[5,13−16]. Table 1 shows examples of known rings. The presence of a transannular σ bond has been excluded, in agreement with the very small Si···Si coupling constant.[17] Grev and Schäfer have explained the short Si···Si contacts in terms of an "unsupported π bond", which lies in the plane of the ring.[15]

The bulky groups at this lithiated fluorine-containing ring system motivated us to test the possibility of a LiF elimination. In the eighties and nineties we were successful in the preparation of iminosilanes in the following reaction [Equation (7)]:

Table 1. Geometric parameters of $[R_2Si-X]_2$ four-membered rings; X = CR_2', NR′ and O

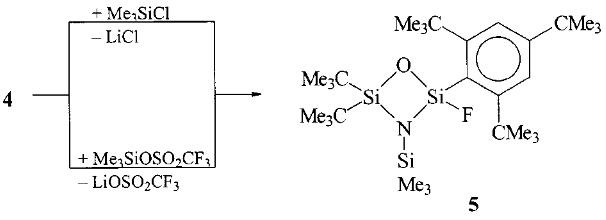
	Si−X [pm]	Si···Si [pm]
$[H_2Si-C(CMe_3)_2]_2$[a]	190.3	270.3
$[H_2Si-CH_2]_2$ [b]	188.8	259.2
$[Cl_2Si-NCMe_3]_2$[c]	171.1	245.0
$[F_2Si-NCMe_3]_2$[d]	170.6	241.3
$[Mes_2Si-O]_2$[e]	167.0	239.0
$[F_2Si-NSiMe(CMe_3)_2]_2$[f]	170.7	237.8
4[g]		237.2

[a] Crystal structure, see ref.[18] − [b] Gas-phase structure, see ref.[19] − [c] Crystal structure, see ref.[20] − [d] Gas-phase structure, see ref.[20] − [e] Crystal structure, see ref.[17] − [f] Crystal structure, see ref.[21] − [g] This work.



(7)

In the analogous reaction of **4** with Me_3SiCl, however, we isolated the silyl-substituted compound **5**, which was also obtained from the reaction of **4** and $Me_3Si-O-SO_2-CF_3$ [Equation (8)].



(8)

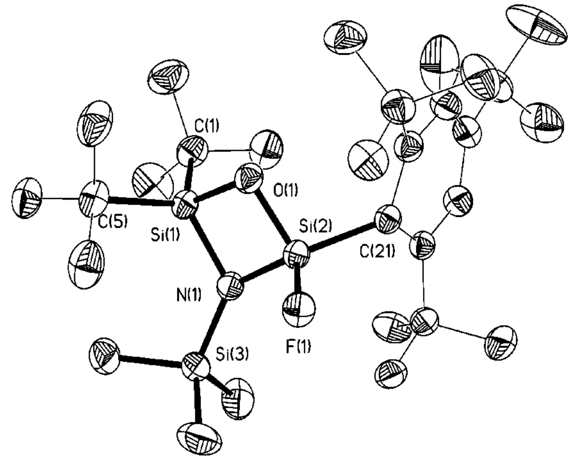


Figure 3. Structure of **5**; selected bond lengths [pm] and angles [°]: Si(1)−O(1) 167.56(12), Si(1)−N(1) 177.41(14), Si(1)−C(1) 189.9(2), Si(1)−C(5) 190.4(2), Si(1)−Si(2) 244.53(7), Si(2)−F(1) 159.38(10), Si(2)−O(1) 165.32(12), Si(2)−N(1) 175.26(14), Si(3)−N(1) 174.80(14); O(1)−Si(1)−N(1) 88.07(6), F(1)−Si(2)−O(1) 113.60(6), F(1)−Si(2)−N(1) 107.73(6), O(1)−Si(2)−N(1) 89.51(6), Si(3)−N(1)−Si(2) 137.28(8), Si(3)−N(1)−Si(1) 128.32(8), Si(2)−N(1)−Si(1) 87.79(6), Si(2)−O(1)−Si(1) 94.54(6)

Crystal Structure of 5

Crystals of **5** were obtained from a THF solution. It crystallizes in the space group *Pbcn* (Figure 3). The ring system of **5** resembles the ring system of **2**. The ring angles at the Si atoms are smaller than 90° and the angles at the N and O atoms are larger, although in **5** the Si−N bonds are much longer than in **2** and than the Si−O bonds. The transannular Si···Si distance is 244.5 pm. Compound **5** has a planar (O−Si−N−Si) four-membered ring. The sum of the angles around the N atom is 353.39°, indicating a slightly trigonal environment. The C(21) atom deviates slightly from the plane, as well [ΣC(21) = 356.26°]. The angle between the four-membered ring and Si(3) amounts 21.3°.

Experimental Section

All experiments were performed in oven-dried glassware using standard inert atmosphere and vacuum-line techniques. The NMR spectra were recorded in $CDCl_3$ (**1**, **3**) or C_6D_6 (**2**, **4**, **5**) with $SiMe_4$ and C_6F_6 (^1H, ^{13}C, ^{19}F, ^{29}Si) as internal and $MeNO_2$ (^{15}N) as external references. The progress of the reactions was monitored by ^{19}F NMR spectroscopy. The compounds were isolated analytically pure.

1-[Aminodi(*tert*-butyl)]-3-{[2,4,6-tri(*tert*-butyl)phenyl]difluoro}1,3-disiloxane (1): To a solution of $(Me_3C)_2Si(NH_2)OLi$ (5.4 g, 0.03 mol) in 50 mL THF was slowly added at room temperature 2,4,6-$(CMe_3)_3C_6H_2SiF_3$ (9.9 g, 0.03 mol) in 20 mL THF. The reaction mixture was refluxed for 1 h and cooled to room temperature. Compound **1** was separated from LiF by condensing into a cooled trap in vacuo and then distilled to give a pure sample, which crystallized. − Yield 88%, b.p. 155 °C/0.03 mbar, m.p. 88 °C. − ^1H NMR: $\delta = 1.00$ ($SiCMe_3$), 1.35 (4-C_6CMe_3), 1.54 (2,6-C_6CMe_3), 7.44 (C_6H_2). − ^{13}C NMR: $\delta = 20.05$ (SiC), 27.95 ($SiCC_3$), 31.36 (4-C_6CC_3) 33.45 (t, $^5J_{CF} = 2.7$ Hz, 2,6-C_6CC_3), 34.96 (4-C_6C), 39.01 (2,6-C_6C), 117.53 (t, $^2J_{CF} = 23.7$ Hz, F_2SiC), 123.07 (3,5-C_6), 152.05 (4-C_6), 160.81 (t, $^3J_{CF} = 1.3$ Hz, 2,6-C_6). − ^{19}F NMR: $\delta = 46.7$. − ^{29}Si NMR: $\delta = -73.50$ (t, $J_{SiF} = 248.9$ Hz, SiF_2), −7.66 ($SiNH_2$). − MS (EI): *m*/*z* (%) = 470 (1) $[M - CH_3]^+$, 428 (28) $[M - C(CH_3)_3]^+$. − $C_{26}H_{49}F_2NOSi_2$ (485.85): calcd. C 64.28, H 10.16; found C 64.42, H 10.34.

1-Oxa-3-aza-2,4-disilacyclobutane (2): A solution of **1** (4.8 g, 0.01 mol) in a mixture of 50 mL *n*-hexane and 5 mL THF was treated with 6.25 mL of *n*BuLi (1.6 M solution in *n*-hexane, 0.01 mol). The reaction occurred at room temperature. After stirring for 2 h the solvents were condensed into a cooled trap. Compound **2** crystallized from *n*-hexane. − Yield 90%, m.p. 130 °C. − ^1H NMR: $\delta =$ 0.60 ($SiCMe_3$), 1.10 ($SiCMe_3$), 1.38 (4-C_6CMe_3), 1.45 (d, $^5J_{HF} =$ 1.0 Hz, 2,6-C_6CMe_3), 1.65 (d, $^5J_{HF} = 1.2$ Hz, 2,6-C_6CMe_3), 7.34 (d, $^5J_{HF} = 1.4$ Hz, 3,5-C_6H), 7.45 (d, $^5J_{HF} = 1.4$ Hz, 3,5-C_6H). −

Table 2. Crystal data and data collections parameters for **2**, **4** and **5**

	2	**4**	**5**
Empirical formula	$C_{26}H_{48}FNOSi_2$	$C_{54}H_{98}F_2Li_2N_2O_{250}Si_4$	$C_{29}H_{56}FNOSi_3\cdot0.5THF$
Molecular mass [g/mol]	465.83	979.58	538.02
Temperature [K]	150(2)	150(2)	200(2)
Wave length [pm]	71.073	71.073	71.073
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	*C*2/*c*	*Pbcn*
Unit cell dimensions	$a = 1032.6(3)$ pm	$a = 4182.3(28)$ pm	$a = 1989.7(3)$ pm
	$b = 1048.7(3)$ pm	$b = 1368.2(9)$ pm	$b = 1633.03(15)$ pm
	$c = 1332.4(6)$ pm	$c = 2968.1(17)$ pm	$c = 2078.4(3)$ pm
	$\alpha = 89.76(3)°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 86.95(4)°$	$\beta = 133.97(3)°$	$\beta = 90°$
	$\gamma = 86.93(2)°$	$\gamma = 90°$	$\gamma = 90°$
Volume [nm^3]	1.4387(8)	12.2245(135)	6.7532(15)
Z	2	8	8
Density (calculated) [Mg/m^3]	1.075	1.065	1.058
Absorption coefficient [mm^{-1}]	0.146	0.141	0.166
F(000)	512	4288	2368
Crystal size [mm]	1.00 × 1.00 × 1.00	0.60 × 0.50 × 0.30	0.80 × 0.70 × 0.60
θ range for data collection	3.56 to 25.00°	3.54 to 20.02°	3.64 to 25.04°
Index ranges	$-12 < h < 12$	$-32 < h < 40$	$-23 < h < 23$
	$-12 < k < 12$	$-13 < k < 13$	$-19 < k < 19$
	$-14 < l < 15$	$-28 < l < 28$	$-24 < l < 24$
Reflections collected	6545	6935	11920
Independent reflections	5042 [*R*(int) = 0.0254]	5690 [*R*(int) = 0.0631]	5960 [*R*(int) = 0.0631]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5037/0/295	5666/0/618	5950/0/334
Goodness-of-fit on F^2	1.057	1.061	1.061
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0501$	$R1 = 0.0716$	$R1 = 0.0380$
	$wR2 = 0.1312$	$wR2 = 0.1688$	$wR2 = 0.1020$
R indices (all data)	$R1 = 0.0565$	$R1 = 0.1189$	$R1 = 0.0459$
	$wR2 = 0.1401$	$wR2 = 0.2237$	$wR2 = 0.1116$
Largest diff. peak and hole	0.532 and −0.334 e.Å^{-3}	0.598 and −0.414 e·Å^{-3}	0.283 and −0.240 e·Å^{-3}

^{13}C NMR: δ = 20.94 (d, $^4J_{CF}$ = 3.6 Hz, Si*C*C$_3$), 20.97 (Si*C*C$_3$), 21.42 (SiC*C*$_3$), 26.65 (SiC*C*$_3$) 31.21 (4-C$_6$C*C*$_3$), 32.93 (d, $^5J_{CF}$ = 1.5 Hz, 2,6-C$_6$C*C*$_3$), 32.98 (d, $^5J_{CF}$ = 0.6 Hz, 2,6-C$_6$C*C*$_3$), 34.70 (4-C$_6$*C*), 38.97 (d, $^4J_{CF}$ = 1.1 Hz, 2,6-C$_6$*C*$_2$), 38.98 (d, $^4J_{CF}$ = 1.1 Hz, 2,6-C$_6$*C*), 122.35 (d, $^2J_{CF}$ = 35.3 Hz, FSiC), 122.15 (d, $^3J_{CF}$ = 1.9 Hz, 2,6-C$_6$), 123.12 (d, $^3J_{CF}$ = 1.8 Hz, 2,6-C$_6$), 151.52 (4-C$_6$), 157.90 (d, $^4J_{CF}$ = 0.4 Hz ,3,5-C$_6$), 159.78 (d, $^4J_{CF}$ = 0.3 Hz, 3,5-C$_6$). − ^{15}N NMR: δ = −339.80 (d, $^2J_{NF}$ = 3.9 Hz). − ^{19}F NMR: δ = 54.5. − ^{29}Si NMR: δ = −47.20 (d, J_{SiF} = 313.35 Hz, SiF), 9.78 (d, $^3J_{SiF}$ = 2.32 Hz). − MS (EI): *m*/*z* (%) = 465 (7) [M$^+$], 408 (100) [M − CMe$_3$$^+$]. − C$_{26}H_{48}$FNOSi$_2$ (465.85): calcd. C 67.04, H 10.39; found C 67.39, H 10.70.

1-Di(*tert*-butyl)-1-{[2,4,6-tri(*tert*-butyl)phenyl]difluorosilylamino}-3-[difluoro-2,4,6-tri(*tert*-butyl)phenyl]-1,3-disiloxane (3): To a solution of (Me$_3$C)$_2$Si(NH$_2$)OLi (1.8 g, 0.01 mol) in 50 mL THF was added 6.25 mL of *n*BuLi (1.6 M solution in *n*-hexane). The reaction mixture was heated under reflux for 1 h, cooled to room temperature and mixed with 2,4,6-(CMe$_3$)$_3$C$_6$H$_2$SiF$_3$ (6.6 g, 0.02 mol) in 20 mL THF. The mixture was heated under reflux for a further 2 h. The formation of **3** was monitored by ^{19}F NMR spectroscopy. Compound **3** was separated from LiF by condensing the product and solvents into a cooled trap in vacuo. It was then distilled in vacuo and recrystallized from *n*-hexane to give a pure sample. − Yield 75%, b.p. 210 °C/0.01 mbar, m.p. 158 °C. − ^{1}H NMR: δ = 1.12 (SiCMe$_3$), 1.30, 1.31 (4-C$_6$CMe$_3$), 1.47, 1.51 [2,6-C$_6$(CMe$_3$)$_2$] 7.38, 7.40 (C$_6$H$_2$). − ^{13}C NMR: δ = 21.09 (SiC), 27.61 (SiC*C*$_3$), 31.11, 31.30 (4-C$_6$C*C*$_3$), 33.20 (t, $^5J_{CF}$ = 2.43 Hz, 2,6-C$_6$*C*$_3$), 33.58 (t, $^5J_{CF}$ = 2.12 Hz, 2,6-C$_6$C*C*$_3$), 34.68, 34.69 (4-C$_6$*C*), 38.67, 38.99 (2,6-C$_6$*C*$_2$), 116.85 (t, $^2J_{CF}$ = 23.24 Hz, 1-C$_6$) 119.5 (t, $^2J_{CF}$ = 20.18 Hz, 1-C$_6$), 122.78, 122.95 (3,5-C$_6$), 151.73, 151.96 (4-C$_6$), 160.67 (t, $^3J_{CF}$ = 1.3 Hz, 2,6-C$_6$), 160.78 (t, $^2J_{CF}$ = 1.2 Hz, 2,6-C$_6$). − ^{19}F NMR: δ = 47.40 (OSiF$_2$), 49.37 (d, $^3J_{HF}$ = 6.45 Hz, NHSiF$_2$). − ^{29}Si NMR: δ = −74.09 (t, J_{SiF} = 250.5 Hz, OSiF$_2$), −48.32 (t, J_{SiF} = 341.4 Hz, NSiF$_2$), −5.41 (pquint, $^3J_{SiF}$ = 0.91 Hz, SiCMe$_3$). − MS (EI): *m*/*z* (%) = 795 (1) [M$^+$], 738 (100) [M − C$_4$H$_9$$^+$]. − C$_{44}H_{77}F_4$NOSi$_3$ (796.35): calcd. C 66.36, H 9.75; found C 66.43, H 9.87.

Lithium 4,4-di(*tert*-butyl)-2-fluoro-2-[2,4,6-tri(*tert*-butyl)phenyl]-1-oxa-3-aza-2,4-disilacyclobutane (4): A solution of **2** (4.6 g, 0.01 mol) in 30 mL *n*-hexane was treated with 6.25 mL of *n*BuLi (1.6 M solution in *n*-hexane, 0.01 mol). The lithiation occurred at room temperature, was monitored by ^{19}F NMR spectroscopy, and finished after 2 h. Compound **4** was separated from solvent in vacuo and crystallized from *n*-hexane as a dimer. − Yield 95%. − ^{1}H NMR: δ = 1.00, 1.17 (SiCMe$_3$), 1.30 (4-C$_6$CMe$_3$), 1.55, 1.57 (2,6-C$_6$CMe$_3$), 7.40 (C$_6$H$_2$). − ^{13}C NMR: δ = 20.80, 21.07 (Si*C*C$_3$), 27.90, 28.07 (SiC*C*$_3$), 31.24 (4-C$_6$C*C*$_3$), 33.81 (2,6-C$_6$C*C*$_3$), 34.59 (4-C$_6$C), 39.40 (2,6-C$_6$C$_2$), 122.60 (2,6-C$_6$), 125.26 (d, $^2J_{CF}$ = 20.72 Hz, FSiC), 150.92 (4-C$_6$), 161.22 (3,5-C$_6$). − ^{19}F NMR: δ = 60.53. − ^{29}Si NMR: δ = −52.16 (d, J_{SiF} = 248.11 Hz, SiF), −1.08 (SiC$_2$).

4,4-Di(*tert*-butyl)-2-fluoro-3-trimethylsilyl-2-[2,4,6-tri(*tert*-butyl)-phenyl]-1-oxa-3-aza-2,4-disilacyclobutane (5): Compound **4** (4.7 g, 0.01 mol) in 50 mL THF was mixed with Me$_3$SiOSO$_2$CF$_3$ (2.2 g, 0.01 mol). In an exothermic reaction LiOSO$_2$CF$_3$ and **5** were formed. LiOSO$_2$CF$_3$ was removed by filtration through a frit and **5** crystallized from the THF solution. − Yield 95%, m.p. 112 °C. − ^{1}H NMR: δ = 0.23 (SiMe$_3$), 0.58 (SiCMe$_3$), 1.13 (SiCMe$_3$), 1.26 (4-C$_6$CMe$_3$), 1.45 [d, $^6J_{HF}$ = 1.13 Hz, 2,6-C$_6$(CMe$_3$)$_2$], 7.26 (C$_6$H$_2$). − ^{13}C NMR: δ = 4.75 (SiC$_3$), 21.80 (d, $^4J_{CF}$ = 3.48 Hz, Si*C*C$_3$), 22.74 (Si*C*C$_3$), 26.88 (SiC*C*$_3$), 27.85 (SiC*C*$_3$), 31.10 (4-C$_6$C*C*$_3$), 33.25 [d, $^5J_{CF}$ = 1.46 Hz, 2,6-C$_6$(C*C*$_3$)], 34.42 (4-C$_6$C), 39.19 (d, $^4J_{CF}$ = 1.15 Hz, 2,6-C$_6$*C*$_2$), 121.43 (d, $^2J_{CF}$ = 36.20 Hz, FSiC), 121.64 (d, $^3J_{CF}$ = 1.2 Hz, 2,6-SiC$_6$), 150.80 (4-C$_6$), 159.67 (3,5-C$_6$). − ^{19}F NMR: δ = 57.10. − ^{29}Si NMR: δ = −49.03 (d, J_{SiF} = 326.9 Hz, SiF), −4.34 (d, $^3J_{SiF}$ = 1.5 Hz, SiMe$_3$), 12.85 (d, $^3J_{SiF}$ = 2.0 Hz, SiCMe$_3$). − MS (EI): *m*/*z* (%) = 537 (12) [M$^+$], 480 (100) [M − CMe$_3$$^+$]. − C$_{29}H_{55}$FNOSi$_3$ (537.02): calcd. C 64.86, H 10.32; found C 64.69, H 10.02.

X-ray Structure Determination of 2, 4 and 5: The data in Table 2 were collected on a STOE AED2 four circle diffractometer with Mo-K_α radiation. The structures were solved and refined using the SHELX program suite.[22] The data of **4** were measured only to a resolution of Θ = 20 degrees.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151335 (**2**), -151336 (**4**) and -151337 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for support of this work.

---

[1] L. H. Sommer, L. J. Tyler, *J. Am. Chem. Soc.* **1954**, *76*, 1030−1034.

[2] P. D. Lickiss, *Adv. Inorg. Chem.* **1995**, *42*, 147−262.

[3] K. Ruhlandt-Senge, R. A. Bartlett, M. M. Olmstead, P. P. Power, *Angew. Chem.* **1993**, *105*, 459−461; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 425−427.

[4] R. Murugavel, M. Bhattadarjee, H. W. Roesky, *Appl. Organomet. Chem.* **1999**, *13*, 227−243.

[5] O. Graalmann, U. Klingebiel, *J. Organomet. Chem.* **1984**, *275*, C1−C4.

[6] O. Graalmann, U. Klingebiel, W. Clegg, M. Haase, G. M. Sheldrick, *Angew. Chem.* **1984**, *96*, 904−905; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 891−892.

[7] U. Klingebiel, S. Schütte, D. Schmidt-Bäse, in *The Chemistry of Inorganic Ring Systems* (Ed.: R. Steudel), Elsevier, Amsterdam, **1992**, 75−99.

[8] D. Schmidt-Bäse, U. Klingebiel, *J. Organomet. Chem.* **1989**, *364*, 313−321.

[9] E. Egert, M. Haase, U. Klingebiel, C. Lensch, D. Schmidt, G. M. Sheldrick, *J. Organomet. Chem.* **1986**, *315*, 19−25.

[10] O. Graalmann, U. Klingebiel, M. Meyer, *Chem. Ber.* **1986**, *119*, 872−877.

[11] S. Walter, U. Klingebiel, M. Noltemeyer, *Chem. Ber.* **1992**, *125*, 783−788.

[12] K. Dippel, U. Klingebiel, G. M. Sheldrick, D. Stalke, *Chem. Ber.* **1987**, *120*, 611−616.

[13] Y. Appeloig, in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai and Z. Rappaport), Part 1, Wiley, Chichester, **1989**, p. 1213.

[14] M. O'Keefe, G. V. Gibbs, *J. Phys. Chem.* **1985**, *89*, 4574.

[15] R. S. Grev, H. F. Schäfer, III, *J. Am. Chem. Soc.* **1987**, *109*, 6577.

[16] A. Savin, H. J. Flad, H. W. Preuss, H. G. von Schnering, *Angew. Chem.* **1992**, *104*, 185−186; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 185−186.

[17] R. West, *Angew. Chem.* **1987**, *99*, 1231−1241; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1201−1211.

[18] M. Jendras, Dissertation Univ. Göttingen, **2000**.
[19] B. Rempfer, G. Pfafferott, H. Oberhammer, N. Auner, J. E. Boggs, *Acta Chem. Scand., Ser. A* **1988**, *42*, 352.
[20] C. Brönnecke, R. Herbst-Irmer, U. Klingebiel, P. Neugebauer, M. Schäfer, H. Oberhammer, Chem. Ber.,/*Recueil* **1997**, *130*, 835−837.
[21] B. Tecklenburg, U. Klingebiel, M. Noltemeyer, D. Schmidt-Bäse, *Z. Naturforsch. B: Chem. Sci.* **1992**, *47*, 855−860.
[22] G. M. Sheldrick, The SHELX-97 manual, Universität Göttingen, **1997**.

Received October 3, 2000
[I00401]