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Aminosilanolates as precursors of four- and eight-membered (SiNSiO)-rings

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Abstract

The amino-di-*tert*-butyl-silanol (**1**) crystallizes as a dimer. It forms sodium- and potassium aminosilanolates (**2**, **3**) in the solid state, which crystallize as hexagonal prisms. In the reaction of the alkali-aminosilanolates with halosilanes, 1-amino-1,3-disiloxanes $(Me_3C)_2Si(NH_2)$–O–SiRR′R″ are obtained; (**4**: R = R′ = CMe_3, R″ = H; **5**: R″ = Cl; **6**: R = Me, R′ = CMe_3, R″ = F; **7**: R = R′ = $NMeSiMe_3$, R″ = F; **8**: R = R′ = $NCHMe_2SiMe_3$, R″ = F; **9**: R = R′ = $N(CHMe_2)_2$, R″ = F). The formation of **5** is accompanied by two by-products, a six-membered $Si(SiO)_2NH$-ring (**10**) and a 1,3-diamino-1,3-disiloxane (**11**). The treatment of **6** with n-C_4H_9Li followed by LiF-elimination results in an eight-membered $(SiOSiN)_2$-ring (**13**), the analogous reaction of **7** and **8** leads to the formation of four-membered (SiOSiN)-rings (**14**, **15**). The results of the crystal structure determinations of **2**, **3**, **9** the lithium salt of **8** (**12**) and quantum chemical calculations for four-membered $R_2SiOSiNR'$-rings (R, R′ = H; R, R′ = Me; R, R′ = CMe_3) are reported.

Keywords: Silicon; Alkali-aminosilanolates; Aminosiloxanes; Structure elucidation; Density functional calculations

1. Introduction

In contrast to carbon chemistry in silicon chemistry a kinetic stabilization of compounds with two or three OH or NH_2 groups bonded to one silicon atom is possible [1–3]. Starting from di-*tert*-butylsilanediol we succeeded in preparing stable halosilanols, e.g. the chlorosilanol from the reaction of $(Me_3C)_2Si(OH)_2$ with PCl_5, accompanied by formation of HCl and $POCl_3$. The reaction of $(Me_3C)_2Si(OH)Cl$ with liquid ammonia affords amino-di-*tert*-butylsilanol, which is stable towards self-condensation (Eq. (1)) and an excellent building unit for acyclic and cyclic compounds with alternating SiOSiN-atoms [4].

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

The lithium salt of the aminosilanol crystallizes as a tetramer and forms a Li–O–cubane [4]. This explains why treatment of the aminosilanolate with halosilanes always results in attachment of the new silicon group to the oxygen atom and formation of 1-amino-1,3-disiloxanes.

Subsequent lithiation of these aminodisiloxanes normally leads to the bonding of lithium to the oxygen atom, which means an O → N silyl group migration has occurred, the silyl group at the oxygen has been displaced by the Lewis acidic lithium cation [5].

1-Amino-1,3-siloxanolates are formed (Eq. (2), type I). Using bulky silyl groups this rearrangement can be prevented and the lithiation leads to the formation of 1,3-disiloxaneamides (Eq. (2), type II).

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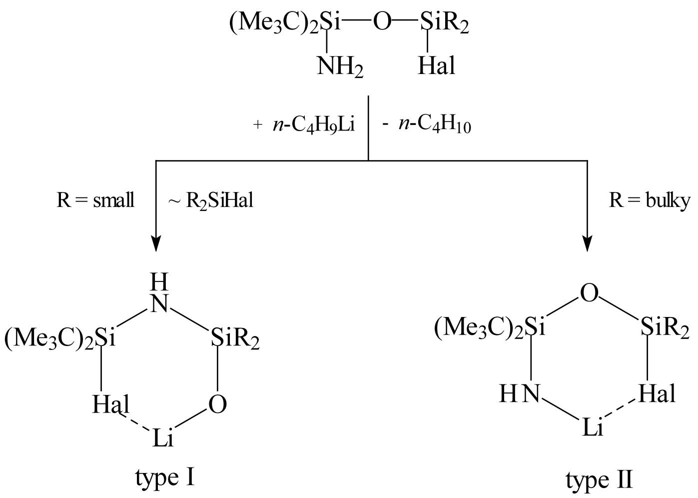


(2)

In salt elimination reactions from halofunctional compounds of type I eight-membered (SiOSiN)-rings are obtained. The analogous reactions of type II compounds lead to the formation of four-membered rings [6].

Very short transannular Si···Si-distances were found in these four-membered rings and in one anion of such a ring [6].

In this paper we describe the preparation and crystal structures of the aminosilanol $(Me_3C)_2Si(OH)NH_2$ (**1**) and its sodium (**2**) and potassium salts (**3**), present new aminosiloxanes (**6**–**9**) and the crystal structure of a lithium salt of a siloxanamide (**12**).

By salt elimination of fluorosilyl-functional compounds we succeeded in the syntheses of four-, six-, and eight-membered ring compounds. In order to understand the bonding properties and the short transannular Si···Si-distances of small four-membered (SiOSiN)-rings, quantum chemical calculations were carried out with neutral ring systems ($R_2SiO(NR')SiR_2$, R = H, Me; R′ = $SiMe_3$) and ring anions.

2. Results and discussion

2.1. *Crystal structure of amino-di-tert-butylsilanol (1)*

Colourless crystals of **1** were obtained from a saturated solution of CH_2Cl_2. Compound **1** is a nice example that in compounds with two basic atoms the less electronegative element, here the nitrogen, forms stronger hydrogen bridges leading to chains of dimers (Fig. 1). (NH···O 335.7, OH···N 284.9 pm).

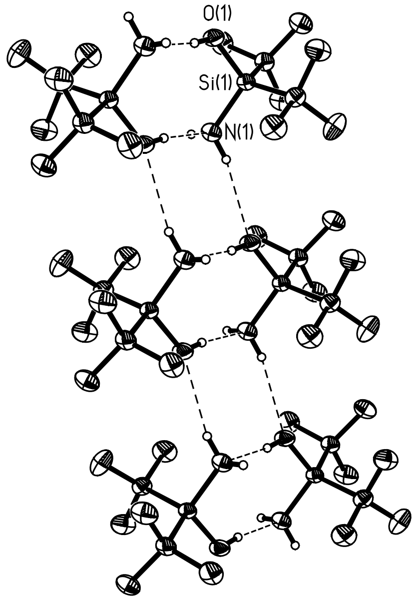
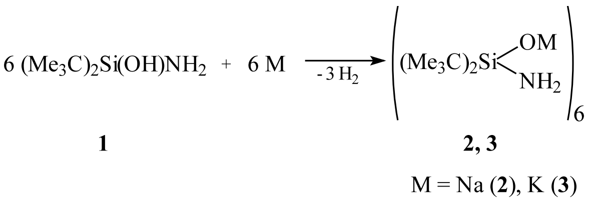


Fig. 1. Molecular structure of **1**; selected bond lengths (pm) and angles (°): Si(1)–O(1) 163.6(3), Si(1)–N(1) 174.6(4), Si(1)–C(1) 190.0(4), Si(1)–C(2) 190.3(4), O(1)–Si(1)–N(1) 109.2(2), O(1)–Si(1)–C(1) 109.8(2), N(1)–Si(1)–C(1) 106.5(2), O(1)–Si(1)–C(2) 104.0(2), N(1)–

2.2. *Synthesis and crystal structures of sodium (2) and potassium aminosilanolate (3)*

Aminosilanol **1** reacts with sodium or potassium in THF under formation of the salts **2** and **3** (Eq. (3)).



$$6\,(Me_3C)_2Si(OH)NH_2 + 6\,M \xrightarrow[-3\,H_2]{} \left((Me_3C)_2Si\begin{matrix}OM\\NH_2\end{matrix}\right)_6 \qquad (3)$$

1 **2, 3**

M = Na (**2**), K (**3**)

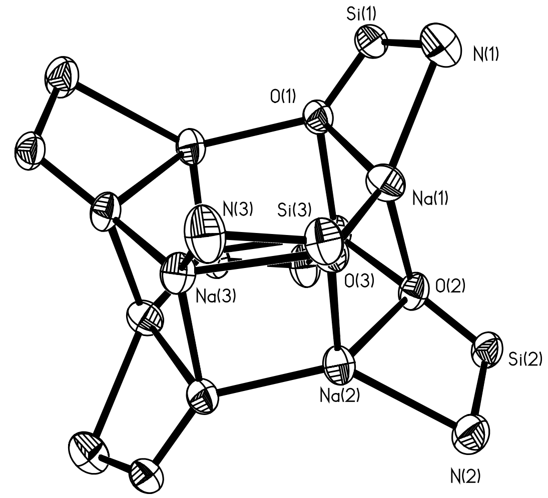


Fig. 2. Molecular structure of **2**; selected bond lengths (pm) and angles (°): Si(1)–O(1) 159.5(3), Na(1)–O(2) 229.0(3), Na(1)–N(1) 249.2(4), Si(1)–N(1) 176.2(4), Na(1)–O(3) 226.0(3), Na(1)–O(1) 241.6(3), O(1)–Si(1)–N(1) 106.9(2), O(3)–Na(1)–O(2) 98.1(1), O(3)–Na(1)–O(1) 128.9(1), O(2)–Na(1)–O(1) 94.3(1), O(3)–Na(1)–N(1) 136.0(1), O(2)–Na(1)–N(1) 123.1(1), O(1)–Na(1)–N(1) 66.7(1), Si(1)–O(1)–Na(2A) 138.3(2), Na(2A)–O(1)–Na(3A) 85.9(1), Si(1)–O(1)–Na(1) 96.5(1), Na(3A)–O(1)–Na(1) 81.3(1), Si(1)–N(1)–Na(1) 89.6(2).

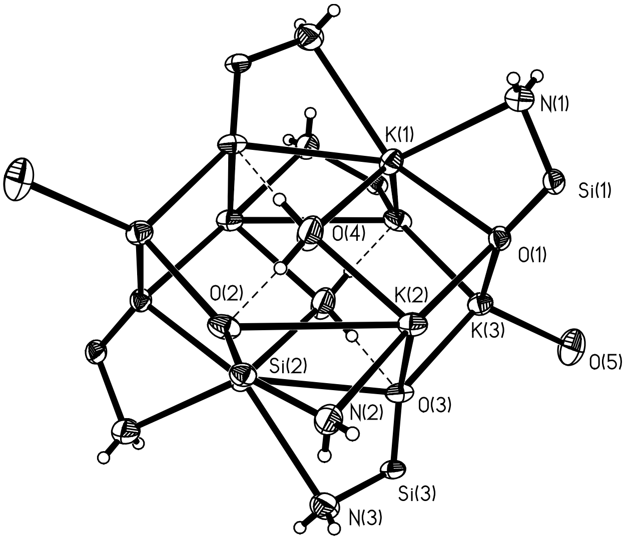


Fig. 3. Molecular structure of **3**; selected bond lengths (pm) and angles (°): K(3)–O(1) 260.13(16), K(3)–O(2 A) 266.04(13), K(3)–O(3) 272.7(2), O(3)–Si(3) 159.16(10), O(3)–K(2) 262.85(11), O(3)–K(1A) 322.19(16), Si(3)–N(3) 176.63(19), N(3)–K(1A) 302.27(16), K(2)–O(4) 262.80(13), K(2)–O(1) 265.3(2), K(2)–N(2) 294.7(2), N(2)–Si(2) 176.67(14), O(2)–K(1A) 270.37(13), O(1)–Si(1) 159.18(17), O(1)–K(1) 273.26(16), Si(1)–N(1) 176.27(18), N(1)–K(1) 295.87(19), O(4)–K(1) 274.1(2), O(1)–K(3)–O(2A) 92.53(5), O(1)–K(3)–O(5) 125.2(4), O(1)–K(3)–O(3) 91.50(6), O(5)–K(3)–O(3) 118.3(5), O(3)–K(3)–O(4A) 50.82(4), Si(3)–O(3)–K(2) 131.40(6), Si(3)–O(3)–K(3) 129.76(6), K(2)–O(3)–K(3) 86.86(5), O(3)–Si(3)–N(3) 110.29(7), O(4)–K(2)–O(3) 104.00(5), O(3)–K(2)–O(1) 92.57(5), O(3)–K(2)–N(2) 99.70(5), O(1)–K(2)–N(2) 165.77(5), Si(2)–N(2)–K(2) 107.78(7), O(2)–Si(2)–N(2) 109.22(8), K(3)–O(1)–K(2) 88.97(6), Si(1)–O(1)–K(1) 101.91(8), O(1)–Si(1)–N(1) 110.47(8), O(1)–K(1)–O(4) 88.10(5), O(1)–K(1)–N(1) 57.80(5), O(4)–K(1)–N(1) 116.83(6).

Salts **2** and **3** crystallize from THF as hexameric aminosilanolates and form a hexagonal prism (Figs. 2 and 3). The sodium respectively potassium and oxygen ions are connected to form two six-membered rings. The sodium structure is very asymmetrical. The coordination sphere of each metal ion is made up by three oxygen atoms and the nitrogen atom of the NH_2-group. The nitrogen thus brackets the Si–O–M skeleton to form a planar four-membered ring of a monomeric unit. Each sodium ion forms two shorter Na–O bonds (mean value 228.0 pm) and one longer bond (mean value 241.2 pm). The Na–N bonds are in the range of 248.8–252.7 pm. Due to the hygroscopic character of the potassium two water molecules are inserted in the hexamer of **3** and two potassium atoms coordinate additional THF molecules. Two potassium ions form two KOSiN rings and the remaining two only one such ring. The K–O distances in the hexamer vary from 260.1 to 363.2 pm. The K–N bonds are in between 294.7 and 302.3 pm. K(3)–O(3)–K(2)–O(1) form a four-membered ring. In contrast to the other potassium ions, which have a tetrameric environment, K(1) has a hexameric environment. K(3) binds three oxygen atoms of three different aminosilanolates and coordinates one THF molecule. K(2) binds two oxygen atoms and one NH_2 group of aminosilanolates and one oxygen of a water molecule. K(1) coordinates four O-atoms, one NH_2-group and one water molecule. Both H-atoms form H-bridges to silanolate–oxygen atoms. The $K\cdots OH_2$ bond between 262.8 and 274.1 pm while the $K\cdots O(CH_2)_2$ distance amounts to 270.3 pm.

*2.3. Synthesis of 1-amino-1,3-disiloxanes, **4**–**9***

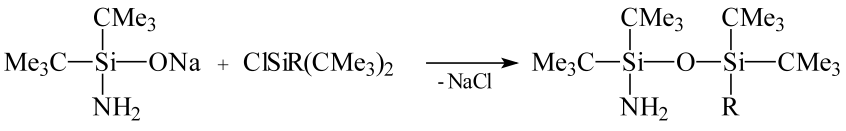
Alkali-aminosilanolates react smoothly with halosilanes to form 1-amino-1,3-disiloxanes (Eqs. (4) and (5)). The use of the lithium salt in reactions with fluorosilanes, and of the sodium derivative with chlorosilanes leads to higher yields.

The formation of the 1-amino-3-chloro-1,3-disiloxane (**5**) is accompanied by the formation of two by-products, **10** and **11** (Eq. (6)).

It is likely that **5** reacts with the sodium salt **2** in solution to give a 1,5-diamino-1,3,5-trisiloxane, which condenses to ammonia and a six-membered ring (**10**). The liberated ammonia substitutes the chlorine of **5** and as second product the 1,3-diamino-1,3-disiloxane (**11**) is formed.

*2.3.1. Crystal structure of 1-amino-1,1-di-tert-butyl-3-fluoro-3,3-bis(diisopropylamino)-1,3-disiloxan (**9**)*

The compound **9** crystallizes in the triclinic space group $P\bar{1}$. A molecule plot is shown in Fig. 4. The Si–

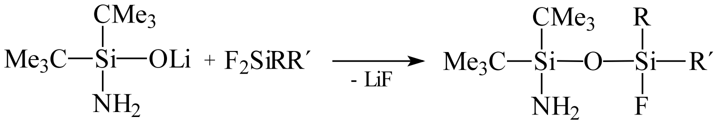


(4)

2

4, 5

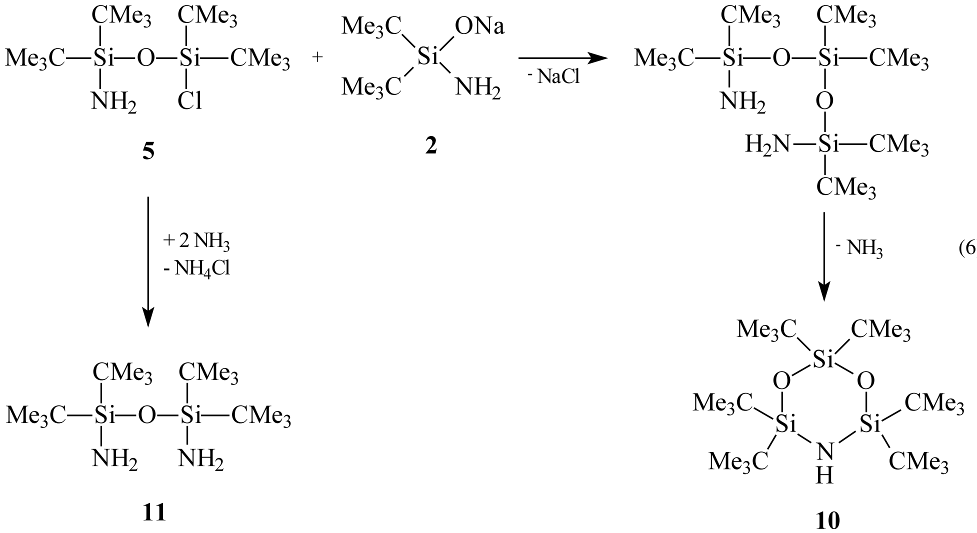
R = H (**4**), Cl (**5**)



(5)

6 - 9

	6	**7**	**8**	**9**
R	Me	$NMeSiMe_3$	$NCHMe_2SiMe_3$	$N(CHMe_2)_2$
R′	CMe_3	$NMeSiMe_3$	$NCHMe_2SiMe_3$	$N(CHMe_2)_2$



5 **2**

(6)

11 **10**

O–Si-angle is 148.5°. Due to the electron-withdrawing effect of the fluorine substituent at Si(2) the Si(2)–O(1) bond is shorter (162.1 pm) compared with Si(1)–O(1) (165.1 pm).

*2.4. Synthesis and crystal structure of N-1-lithiumamide-1,1-di-tert-butyl-3-fluoro-3,3-bis(isopropyltrimethylsilylamino)-1,3-disiloxane (**12**)*

Lithium salts of 1-amino-1,3-disiloxanes are excellent precursors of 1-silylamino-1,3-disiloxanes and four- or eight-membered ring systems. All lithium derivatives, which have been characterized by X-ray so far, show that the lithium cation is coordinated to the most electronegative atoms oxygen and if present fluorine. The 1-amino-3,3-bis(isopropylsilyl-amino)-1,3-disiloxane reacts with butyllithium to give compound **12** (Eq. (7)).

Compound **12** crystallizes from THF–*n*-hexane in the space group $P\bar{1}$ as a dimer (Fig. 5). It forms a tricyclic system consisting of two six-membered (Si_2ONLiF)-rings and a central $(LiN)_2$-four-membered ring.

The $(Li–N)_2$-ring system is not entirely planar but folded by 30.6° across the Li···Li-line. The hydrogen

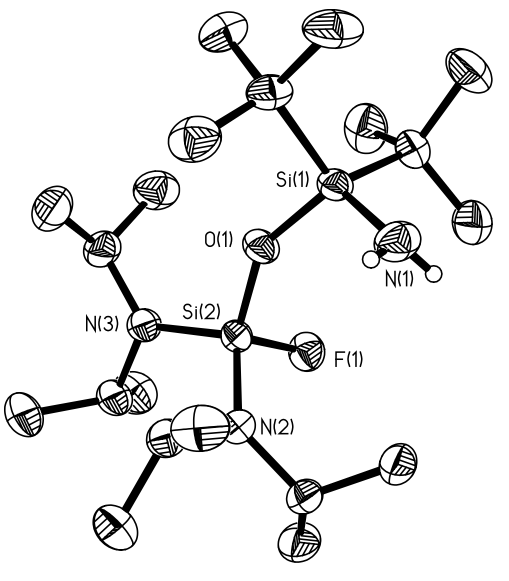


Fig. 4. Molecular structure of **9**; selected bond lengths (pm) and angles (°): Si(1)–C(1) 190.0 (2), Si(2)–F(1) 160.0(1), Si(2)–O(1) 162.1(1), Si(1)–O(1) 165.1(1), Si(2)–N(2) 170.3(1), Si(1)–N(1) 171.0(2), Si(2)–N(3) 170.2(1), O(1)–Si(1)–N(1) 112.85(7), N(1)–Si(1)–C(2) 105.20(8), N(1)–Si(1)–C(1) 107.39(9), O(1)–Si(2)–N(3) 108.93(7), O(1)–Si(1)–C(2) 105.55(7), O(1)–Si(2)–N(2) 115.83(7), O(1)–Si(1)–C(1) 108.31(7), Si(2)–O(1)–Si(1) 148.46(8), C(2)–Si(1)–C(1) 117.68(8), F(1)–Si(2)–N(3) 110.51(7), F(1)–Si(2)–N(2) 104.31(7), F(1)–Si(2)–O(1) 106.00(6).

atoms at N(1) and N(1)′ as well the fluorine atoms at Li(1) and Li(1′) are in *cis* position. In the crystal structure, the lithium cations are threefold coordinated with two nitrogen atoms and one fluorine atom. They have a nearly planar environment. The sum of the angles around Li(1) is 355.6° and around Li(1)′ 354.6°. The lithium cations have no contact to the oxygen atom, observed for the first time in such compounds. The lithiation of the oxygen, and therefore, the 1.3-silyl group migration from the oxygen to the nitrogen atom is prevented by the bulky $N(CHMe_2)SiMe_3$ substituents at the Si(2) atom. Hitherto known compounds with a (FSiNLiOSi)-skeleton crystallize under formation of eight-membered $(FSiNLi)_2$-rings.

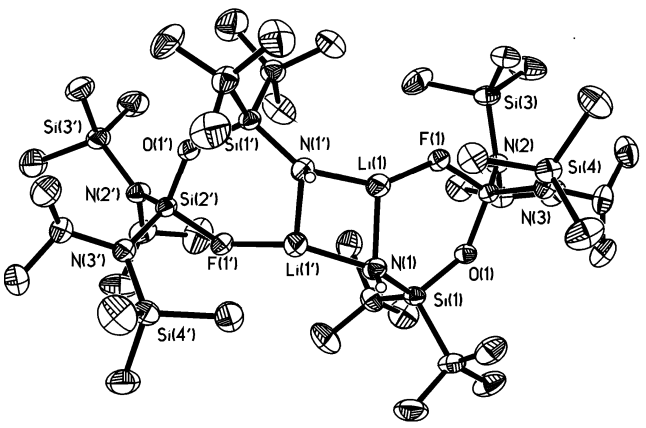
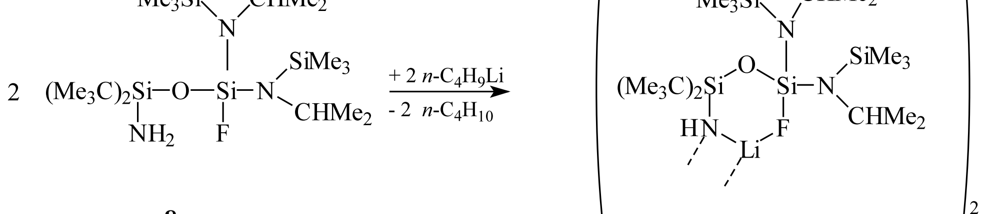


Fig. 5. Molecular structure of **12**; selected bond lengths (pm) and angles (°): Si(1)–O(1) 168.7(2), Si(1)–N(1) 168.8 (2), N(1)–Li(1) 199.7(4), Li(1)–F(1) 194.0(4), O(1)–Si(2) 160.7(2), F(1)–Si(2) 163.1(1), Si(2)–N(2) 171.6(2), N(2)–Si(3) 175.7(2), O(1)–Si(1)–N(1) 112.14(8), Si(1)–N(1)–Li(1′) 138.4(2), Si(1)–N(1)–Li(1) 120.2(1), Li(1′)–N(1)–Li(1) 74.2(2), F(1)–Li(1)–N(1′) 147.6(2), F(1)–Li(1)–N(1) 105.6(2), N(1′)–Li(1)–N(1) 102.4(2), Si(2)–F(1)–Li(1) 129.4(1), Si(2)–O(1)–Si(1) 140.84(9), O(1)–Si(2)–F(1) 105.11(7), O(1)–Si(2)–N(3) 114.84(8), F(1)–Si(2)–N(3) 103.69(7), O(1)–Si(2)–N(2) 110.89(8), F(1)–Si(2)–N(2) 105.43(7), Si(2)–N(2)–Si(3) 119.44(9), Si(2)–N(3)–Si(4) 130.0(1).

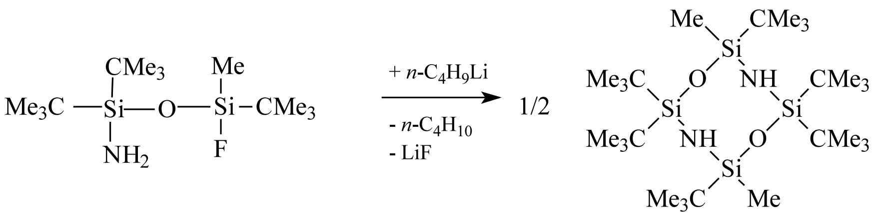
*2.5. 2,4,4,6,8,8-Hexa-tert-butyl-2,6-dimethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetra-silacyclooctane (**13**) and 1-aza-3-oxa-2,4-disilacyclobutanes (**14**, **15**)*

Depending on the bulkiness of the substituents, LiF-elimination from lithiated 1-amino-1,3-disiloxanes leads to eight- or four-membered (SiOSiN)-rings. The 1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (**13**) is obtained from lithiated **6** and the four-membered 1-aza-3-oxa-2,4-disilabutanes, **14** and **15** from lithiated **7** and **8** (Eq. (8)).

Compound **13** crystallizes in the space group $P\bar{1}$ and has a crown structure with the $SiMe_3$-groups in *cis* position. However, because of the low quality of the crystals it was not possible to distinguish between the O and N atoms of the ring skeleton. Therefore, no bond lengths and angles are presented. Hitherto only one

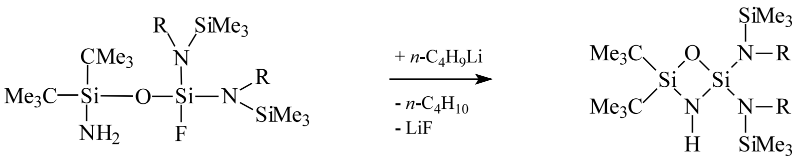


8 **12** (7)



6 **13**

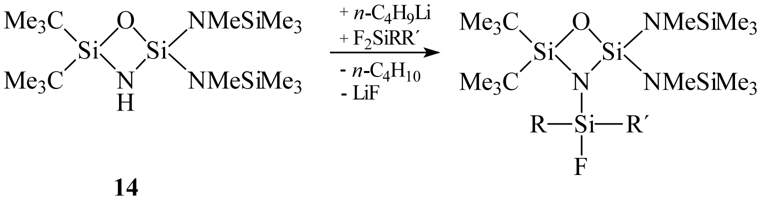
(8)



7, 8 **14, 15**

(9)

	7, 14	**8, 15**
R	Me	i-C_3H_7



14 **16, 17**

(10)

	16	**17**
R	Me	F
R′	Me	$NCMe_3(SiMe_3)$

(SiOSiNH)-four-membered ring and its lithium salt has been described.

Very short transannular Si···Si-distances are found in these compounds, especially in the anion. This caused us to carry out quantum chemical studies of these systems.

2.6. 1-Silyl-1-aza-3-oxa-2,4-disilacyclobutanes, **16** and **17**

The N–H unit of **14** reacts with butyllithium to give the lithium derivative and n-butane. With halosilanols, e.g. Me_2SiF_2 or $F_3SiN(CMe_3)SiMe_3$ it is possible to substitute the ring at the nitrogen atom and to obtain **16** and **17**.

2.7. Quantum chemical study of SiOSiN rings

The first structure of a SiOSiN four-membered ring was published by Klingebiel and Noltemeyer only in 2001 [6]. The dimeric lithium derivative exhibits a short transannular Si···Si distance of 237.2 pm. Theoretical calculations on four-membered rings containing two silicon atoms have been reported mainly for the unsubstituted cyclodisiloxane $(H_2SiO)_2$. The short silicon–silicon distance was explained in terms of the high polarity of the Si–O bond and the repulsion by the lone electron pairs at the oxygen atoms [7,8]. NMR spin-coupling constants indicate that the silicon atoms are not σ-bonded [9]. Grev and Schaefer proposed a residual π-bond (unsupported π-bond) [10].

To elucidate the structures of the four-membered SiOSiN rings, quantum chemical (density functional, DFT) calculations have been carried out for tetrafluorocycloaminodisiloxane, tetramethylcycloaminodisiloxane and tetra(*tert*-butyl)cycloaminodisiloxane. The structures of the stationary points on the potential energy hypersurface were fully optimized using Becke's three-parameter hybrid method with Becke's exchange func-

Table 1
Geometrical parameters of differently substituted $X_2Si(ONH)SiX_2$ four-membered rings

	r(Si···Si)	r(N···O)	r(Si–N)	r(Si–O)	α(N–Si–X)	α(O–Si–X)	α(X–Si–X)
X = F	242.6	237.6	172.3	167.3	117.3	114.1	105.1
X = Me	250.4	238.5	175.6	170.2	116.2	112.8	110.1
X = *tert*-butyl	255.8	236.8	177.0	171.6	120.3, 113.9	114.6, 108.4	111.4

Interatomic distances are given in pm, bond angles in degrees.

tional [11] and the Lee, Yang and Parr correlation functional [12] (B3LYP) as implemented in GAUSSIAN98 [13]. The structures were optimized employing the 6-31+G(d) basis set (162, 186 and 462 contracted Gaussian-type orbitals (cGTOs) for F_4HNOSi_2, $C_4H_{13}NOSi_2$ and $C_{16}H_{37}NOSi_2$, respectively). In order to confirm that true minima on the PES were found, the Hessian matrices at the stationary points were calculated.

The key geometric parameters for the three differently substituted (X = F, methyl, *tert*-butyl) four-membered rings are collected in Table 1.

The structures exhibit planar SiOSiNH units and twofold symmetry axes through the oxygen and nitrogen atoms. The nitrogen atom is sp^2 hybridized. While for the fluorine and methyl substituted compounds the planes perpendicular to the ring containing the C_2 axis and the Si···Si line, respectively, are symmetry elements, the bulky *tert*-butyl moieties distort the C_{2v} symmetry to a C_2-symmetric structure. Thus, the two Si–N–C and Si–O–C angles at the silicon atoms show different values at each silicon site. Note that the silicon and fluorine (or carbon) atoms do not lie in one plane as it is the case for symmetric $(SiO)_2$ and $(SiNH)_2$ four-membered rings. While the *cis*-torsional angle θ(X–Si–Si–X) amounts to 0° for X = F and Me, it is calculated to be 10° for *tert*-butyl substitutents. The *trans*-torsional angles are 173° for both X = F and Me, while two different *trans*-torsional angles (180 and 159°) are obtained for the bulky *tert*-butyl substituents.

Due to the electron-withdrawing effect of the fluorine atoms, the transannular Si···Si distance amounts to only 243 pm. The methyl groups are sterically more demanding as can be seen from the X–Si–X angles that become wider by 5°. The even bulkier *tert*-butyl groups cause a long Si···Si distance of 256 pm. In keeping with these changes, both the Si–N and Si–O bonds become longer from the fluorine to the *tert*-butyl substituted species. The transannular N···O distances, on the contrary, show only very small changes without a clear trend. Compared with methyl substitution, the *tert*-butyl groups exhibit two different N–Si–C angles where one angle is larger by about 4° and the other smaller by about 2°. For the O–Si–C angle the situation is similar, but one angle is smaller by ca. 4° and the other wider by 2° compared with the methyl substituted species.

Similar calculations have been performed for the (deprotonated) anions of the three compounds. The results are given in Table 2.

For different substitution, the same trends are observed as for the neutral species. However, all geometrical parameters discussed above show strong deviations from the neutral case. The lone electron pair at the nitrogen center causes that the transannular Si···Si distances are shortened by as much as 13.5, 15.0 and 16.4 pm for fluorine, methyl and *tert*-butyl substitution, respectively. The N···O interatomic distances are increased by 13.3, 13.6 and 13.9 pm, respectively. On average, the Si–N bonds are shorter by 5 pm while the Si–O bonds are longer by 4 pm. The Si–N–Si angles become smaller by 4° in the anionic species. The N–Si–X angles becomes slightly larger while the O–Si–X angles are decreased by about the same amount. While the O–Si–N angles becomes larger in the anions, the angles between the substitutents, α(X–Si–X), are decreased by 5.9, 5.5 and 4.3° compared with the neutral protonated species. The *trans*-torsional angles θ(X–Si–Si–X) are smaller in the anions (165° for X = F, 166° for X = Me). For the *tert*-butyl substituted species, the change is less pronounced (*cis*-torsional angle 11°, *trans*-torsional angles 177 and 155°).

Table 2
Geometrical parameters of differently substituted $X_2Si(ON)SiX_2^-$ anionic four-membered rings

	r(Si···Si)	r(N···O)	r(Si–N)	r(Si–O)	α(N–Si–X)	α(O–Si–X)	α(X–Si–X)
X = F	229.1	250.9	168.3	171.5	120.6	110.7	99.2
X = Me	235.4	252.1	170.7	174.2	119.0	109.8	104.6
X = *tert*-butyl	239.4	250.7	171.3	175.3	121.8, 115.8	112.9, 105.3	107.1

Interatomic distances are given in pm, bond angles in degrees.

3. Experimental

All experiments were performed in oven-dried glassware using standard inert atmosphere and vacuum-line techniques. The NMR spectra were recorded with $SiMe_4$ and C_6F_6 as internal and $MeNO_2$ as external references. The compounds were isolated analytically pure.

3.1. Compounds **2** and **3**

To a solution of **1** (8.75 g, 50 mmol) in 40 ml THF the corresponding alkalines were added. The mixture was heated for 1 h. Compounds **2** and **3** crystallized as single crystals at room temperature.

3.1.1. Sodium [amino-di-*tert*-butyl]silanolate (**2**)

Melting point (m.p.) 234 °C. Yield 25%. NMR (C_6D_6): ^1H δ 0.37 (NH_2, 12H), 1.07 (CMe_3, 108H); ^{13}C δ 5.82 (CMe_3), 20.42 (CMe_3); ^{29}Si δ −14.57; MS [EI, *m*/*z* (%)] 731 [100, 4 M−CMe_3^+], 337 [90, 2 M−CMe_3^+].

3.2. Compounds **4**, **5**, **10** and **11**

To an ice-cooled solution of $(Me_3C)_2SiNH_2ONa$ (13.7 g, 100 mmol) in a mixture of 30 ml *n*-hexane and 20 ml THF, 100 mmol $(Me_3C)_2SiHCl$ (**4**), respectively, $(Me_3C)_2SiCl_2$ (**5**) (17.8 g, respectively, 21.3 g) were added. After separating the solvent the reaction mixture was heated under reflux for 3 h. The products were condensed into a cooled trap. The formation of **5** is accompanied by the formation of two by-products (**10**, **11**). Compound **4**, **5** and **10** were purified by distillation, compound **11** crystallizes from *n*-hexane.

3.2.1. 1-Amino-1,1,3,3-tetra-*tert*-butyl-1,3-disiloxane (**4**)

Boiling point (b.p.) 60 °C/0.02 mbar. Yield 83%. NMR ($CDCl_3$): ^1H δ 0.61 (NH_2, 2H), 0.95 (CMe_3, 18H), 0.97 (CMe_3, 18H), 4.18 (SiH, 1H); ^{13}C δ 20.18 (CMe_3), 20.48 (CMe_3), 27.60 (CMe_3), 28.26 (CMe_3); ^{15}N δ −370.81 (t, $^1J_{NH} = 83.5$ Hz); ^{29}Si δ −12.46 (SiN), 5.17 (SiH); MS [EI, *m*/*z* (%)] 302 [2, M−Me^+], 260 [100, M−CMe_3^+].

3.2.2. 1-Amino-1,1,3,3-tetra-*tert*-butyl-3-chloro-1,3-disiloxane (**5**)

B.p. 160 °C/15 mbar. Yield 15%. NMR ($CDCl_3$): ^1H δ, 1.05 ($ClSiCMe_3$, 9H), 1.06 ($NSiCMe_3$, 18H), 1.23 ($ClSiCMe_3$, 9H); ^{13}C δ 20.06 ($NSiCMe_3$), 20.36 ($ClSiCMe_3$), 27.88 ($NSiCMe_3$), 28.14 ($ClSiCMe_3$); ^{29}Si δ −17.75 (SiN), −13.28 (SiCl); MS [EI, *m*/*z* (%)] 294 [27, M−CMe_3^+], 231 [3, M−$2(CMe_3)^+$].

3.2.3. 1,1,3,3,5,5-Hexa-*tert*-butyl-2-aza-4,6-dioxa-1,3,5-trisilacyclohexane (**10**)

M.p. 282 °C. Yield 45%. NMR ($CDCl_3$): ^1H δ 1.11 ($NOSiCMe_3$, 36H), 1.14 (O_2SiCMe_3, 18H); ^{13}C δ 21.91 (O_2SiCMe_3), 22.63 ($NOSiCMe_3$), 29.45 (O_2SiCMe_3), 29.48 ($NOSiCMe_3$); ^{29}Si δ −16.96 (SiO_2), −6.53 (SiNO); MS [EI, *m*/*z* (%)] 416 [100, M−CMe_3^+], 359 [2, M−$2(CMe_3)^+$].

3.2.4. 1,3-Diamino-1,1,3,3-tetra-*tert*-butyl-1,3-disiloxane (**11**)

Sub. 160 °C/15 mbar. Yield 34%. NMR ($CDCl_3$): ^1H δ 1.04 (CMe_3, 36H); ^{13}C δ 20.20 (CMe_3), 28.32 (CMe_3); ^{29}Si δ −12.43; MS [EI, *m*/*z* (%)] 332 [24, M^+], 275 [100, M−CMe_3^+].

3.3. Compounds **6**–**9**

To a solution of $(Me_3C)_2SiLiHNH_2$ (18.1 g, 100 mmol) in 50 ml *n*-hexane and 10 ml THF the corresponding fluorosilanes [$(Me_3C)MeSiF_2$ (13.8 g) (**6**), $(Me(SiMe_3)N)_2SiF_2$ (27.0 g) (**7**), $(Me_2CH(SiMe_3)N)_2SiF_2$ (32.6 g) (**8**), $((Me_2CH)_2N)_2SiF_2$ (26.6 g) (**9**)] were added.

The solvent was separated and the mixture was heated above 100 °C under reflux for 8 h. Compounds **6**–**9** were condensed into a cooled trap and obtained analytically pure by distillation in vacuo.

3.3.1. 1-Amino-1,1,3-tri-*tert*-butyl-3-fluoro-3-methyl-1,3-disiloxane (**6**)

B.p. 60 °C/0.01 mbar. Yield 74%. NMR ($CDCl_3$): ^1H δ 0.19 (d, FSiMe, $^3J_{HF} = 6.2$ Hz, 3H), 0.84 (NH_2, 2H), 0.97 (d, $FSiCMe_3$, $^4J_{HF} = 0.9$ Hz, 9H), 1.01 ($Si(CMe_3)_2$, 18H); ^{13}C δ −5.69 (d, FSiMe, $^2J_{CF} = 19.1$ Hz), 18.13 (d, $FSiCMe_3$, $^2J_{HF} = 16.31$ Hz), 19.67 (d, $NSiCMe_{3(a)}$, $^4J_{CF} = 0.6$ Hz), 19.69 (d, $NSiCMe_{3(b)}$, $^4J_{CF} = 0.4$ Hz), 25.39 ($NSiCMe_3$), 27.66 (d, $FSiCMe_3$, $^3J_{CF} = 0.4$ Hz); ^{19}F δ 18.46; ^{29}Si δ −10.95 (d, SiF, $^1J_{SiF} = 294.6$ Hz), −10.07 (d, SiN, $^3J_{SiF} = 0.7$ Hz); MS [EI, *m*/*z* (%)] 276 [2, M−Me^+], 236 [85, M−CMe_3^+].

3.3.2. 1-Amino-1,1-di-*tert*-butyl-3-fluoro-3,3-bis[methyl(trimethylsilyl)amino]-1,3-disiloxane (**7**)

B.p. 95 °C/0.02 mbar. Yield 76%. NMR ($CDCl_3$): ^1H δ 0.11 (d, SiMe, $^5J_{HF} = 0.9$ Hz, 18H), 0.80 (NH_2, 2H), 1.02 (CMe_3, 18H), 2.54 (d, NMe, $^4J_{HF} = 1.2$ Hz, 6H); ^{13}C δ −0.06 (d, SiMe, $^4J_{CF} = 2.0$ Hz), 19.83 (CMe_3), 27.77 (CMe_3), 30.38 (d, NMe, $^3J_{CF} = 1.1$ Hz); ^{19}F δ 34.34; ^{29}Si δ −63.79 (d, SiF, $^1J_{SiF} = 219.3$ Hz), −10.92 ($SiCMe_3$), 6.63 (SiMe); MS [EI, *m*/*z* (%)] 425 [5, M^+], 410 [10, M−Me^+], 368 [62, M−CMe_3^+].

Table 3
Crystal data and structure refinement for **1**, **2**, **3**, **9** and **12**

Compound	**1**	**2**	**3**	**9**	**12**
Empirical formula	$C_8H_{21}NOSi$	$C_{56}H_{136}N_6Na_6O_8Si_6$	$C_{56}H_{140}K_6N_6O_{10}S_6$	$C_{20}H_{48}FN_3OSi_2$	$C_{40}H_{102}F_2Li_2N_6O_2Si_8$
Formula weight	175.35	1328.19	1460.88	421.79	975.88
Temperature (K)	200(2)	220(2)	133(2)	203(2)	200(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$\mathrm{P}\bar{1}$
a (pm)	594.9(2)	1247.9(7)	1300.3(3)	984.6(2)	1072.8(2)
b (pm)	861.9(2)	1296.1(7)	1338.3(3)	1005.1(2)	1173.9(2)
c (pm)	1156.5(3)	1421.1(8)	1516.0(3)	1436.0(3)	2681.5(5)
α (°)	106.40(2)	115.00(3)	101.53(3)	75.35(3)	88.29(3)
β (°)	95.48(2)	94.80(3)	102.04(3)	71.38(3)	89.67(3)
γ (°)	102.89(1)	99.88(3)	118.20(3)°	78.92(3)	63.22(3)
Volume (nm^3)	0.5465(3)	2.021(2)	2.1332(8)	1.2933(5)	3.0133(9)
Z	2	1	1	2	2
Density (calculated) (Mg m^{-3})	1.066	1.092	1.137	1.083	1.076
Absorption coefficient (mm^{-1})	0.171	0.181	0.438	0.158	0.219
Crystal size (mm)	0.8 × 0.7 × 0.6	0.7 × 0.5 × 0.3	0.5 × 0.5 × 0.5	1.0 × 1.0 × 1.0	0.6 × 0.6 × 0.3
θ Range (°)	3.56–25.00	3.56–25.08	2.3–27.95	3.65–25.06	3.55–25.04
Reflections collected	1932	12 274	46 652	5034	11 403
Independent reflections	1908	7126	9972	4543	10 548
R_{int}	0.0829	0.680	0.0391	0.0393	0.0233
Data	1908	7126	9972	4543	10 548
Restraints	2	250	692	1	1
Parameter	118	465	575	267	581
Extinction coefficient				0.045(5)	
R_1 (all data)	0.0656	0.0638	0.0326	0.0432	0.0406
wR_2 ($I > 2\sigma(I)$)	0.2164	0.1865	0.0866	0.1240	0.1148
Largest difference peak and hole (10^3 e nm^{-3})	0.549 and −0.458	0.457 and −0.449	0.911 and −0.505	0.523 and −0.431	0.378 and −0.286

*3.3.3. 1-Amino-1,1-di-tert-butyl-3-fluoro-3,3-bis[isopropyl(trimethylsilyl)amino]-1,3-disiloxane (**8**)*

B.p. 112 °C/0.02 mbar. Yield 29%. NMR ($CDCl_3$): ^1H δ 0.18 (d, SiMe, $^5J_{HF} = 1.4$ Hz, 18H), 0.79 (NH_2, 2H), 1.02 (CMe_3, 18H), 1.24 (d, CH*Me*, $^3J_{HH} = 6.8$ Hz, 12H), 3.62 (dsep, C*H*Me, $^3J_{HH} = 6.8$ Hz, $^4J_{HF} = 0.7$ Hz, 2H); ^{13}C δ 3.76 (d, SiMe, $^4J_{CF} = 2.6$ Hz), 19.98 (*C*Me_3), 25.33 (d, CH$Me_{(a)}$, $^4J_{CF} = 1.1$ Hz), 26.25 (d, CH$Me_{(b)}$, $^4J_{CF} = 1.1$ Hz), 28.07 (d, CMe_3, $^4J_{CF} = 0.8$ Hz), 46.64 (*C*HMe); ^{19}F δ 45.36; ^{29}Si δ −63.89 (d, SiF, $^1J_{SiF} = 226.5$ Hz), −10.80 ($SiCMe_3$), 2.66 (d, SiMe, $^3J_{SiF} = 0.7$ Hz); MS [EI, *m/z* (%)] 481 [2, M^+], 466 [6, $M-Me^+$], 424 [22, $M-CMe_3^+$].

*3.3.4. 1-Amino-1,1-di-tert-butyl-3-fluoro-3,3-bis[(diisopropyl)amino]-1,3-disiloxane (**9**)*

B.p. 118 °C/0.01 mbar. Yield 43%. NMR ($CDCl_3$): ^1H δ 0.82 (NH_2, 2H), 1.05 (CMe_3, 18H), 1.15 (d, CH$Me_{(a)}$, $^3J_{HH} = 6.7$ Hz, 12H), 1.17 (d, CH$Me_{(b)}$, $^3J_{HH} = 6.7$ Hz, 12H), 3.40 (sep, C*H*Me, $^3J_{HH} = 6.7$ Hz, 4H); ^{13}C δ 2.07 (*C*Me_3), 24.20 (d, CH$Me_{(a)}$, $^4J_{CF} = 1.1$ Hz), 24.73 (d, CH$Me_{(b)}$, $^4J_{CF} = 1.5$ Hz), 28.12 (d, CMe_3, $^4J_{CF} = 0.9$ Hz), 44.91 (*C*HMe); ^{19}F δ 38.41; ^{29}Si δ −67.06 (d, SiF, $^1J_{SiF} = 230.1$ Hz), −11.25 (d, $SiCMe_3$, $^3J_{SiF} = 0.6$ Hz); ^{15}N δ −370.90 (t, NH_2, $^1J_{NH} = 73.0$ Hz); MS [EI, *m/z* (%)] 421 [1, M^+], 406 [3, $M-Me^+$], 378 [60, $M-CMe_3^+$].

*3.4. Bis[1-lithiumamido-1,1-di-tert-butyl-3-fluoro-3,3-bis[isopropyl(trimethylsilyl)amino]-1,3-disiloxane] (**12**)*

Compound **8** (20 mmol, 9.6g) in 30 ml *n*-hexane and 20 mmol *n*-butyllithium solved in *n*-hexane (23%) were heated under reflux for 1 h. After separating the solvent single crystals were obtained by recrystallization from THF.

*3.5. Compounds **13** and **14***

Compound **6** (29.1 g, 100 mmol) (**13**), respectively, **7** (42.5 g, 100 mmol) (**14**) were treated with *n*-butyllithium and heated under reflux for 1 h. After evaporating the solvent the mixture was heated up to 200 °C for 2 h. Compounds **6** and **7** were condensed into a cooled trap and purified by distillation in vacuo. Single crystals of **14** were obtained by recrystallization from THF.

*3.5.1. 2,4,4,6,8,8-Hexa-tert-butyl-2,6-dimethyl-1,5-diaza-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (**13**)*

B.p. 160 °C/0.01 mbar. Yield 23%. NMR ($CDCl_3$): ^1H δ 0.24 (SiMe, 3H), 0.28 (SiMe, 3H), 0.45 (NH, 2H), 0.98

$((CMe_3)_2$, 36H), 1.02 (CMe_3, 18H); ^{13}C δ −1.12 (SiMe), 1.52 (SiMe), 18.90 ($\mathit{C}Me_3$), 19.60 ($\mathit{C}Me_3$), 21.07 $((\mathit{C}Me_3)_2)$, 21.27 $((\mathit{C}Me_3)_2)$, 26.61 ($C\mathit{Me}_3$), 26.71 ($C\mathit{Me}_3$), 28.52 $((C\mathit{Me}_3)_2)$, 29.04 $((C\mathit{Me}_3)_2)$; ^{29}Si δ −24.01 (SiMe), −11.87 ($Si(CMe_3)_2$); MS [EI, *m/z* (%)] 546 [1, M^+], 531 [8, $M-Me^+$], 489 [100, $M-CMe_3^+$].

3.5.2. 2,2-Di-*tert*-butyl-4,4-bis[methyl(trimethylsilyl)amino]-1-aza-3-oxa-2,4-disilacyclobutane (**14**)

B.p. 82 °C/0.01 mbar. Yield 65%. NMR ($CDCl_3$): ^1H δ 0.07 (SiMe, 18H), 1.03 (CMe_3, 18H), 1.33 (NH, 1H), 2.55 (NMe, 6H); ^{13}C δ −0.25 (SiMe), 21.38 ($\mathit{C}Me_3$), 27.59 ($C\mathit{Me}_3$), 31.18 (NMe); ^{29}Si δ −40.09 ($\mathit{Si}(NMeSiMe_3)_2$), 5.29 (SiMe), 7.65 ($SiCMe_3$); MS [EI, *m/z* (%)] 405 [20, M^+], 390 [10, $M-Me^+$], 348 [100, $M-CMe_3^+$].

3.5.3. 2,2-Di-*tert*-butyl-4,4-bis[isopropyl(trimethylsilyl)amino]-1-aza-3-oxa-2,4-disilacyclobutane (**15**)

Compound **12** (48.7g, 100 mmol) was heated up to 200 °C over 2 h. The product was condensed in a cooled trap and purified by distillation in vacuo and recrystallization from *n*-hexane. B.p. 115 °C/0.02 mbar. Yield 12%. NMR ($CDCl_3$): ^1H δ 0.19 (SiMe, 18H), 0.83 (NH, 1H), 1.08 (CMe_3, 18H), 1.29 (d, $CH\mathit{Me}$, $^3J_{HH} = 6.7$ Hz, 12H), 3.45 (sep, $C\mathit{H}Me$, $^3J_{HH} = 6.7$ Hz, 2H); ^{13}C δ 4.51 (SiMe), 21.54 ($\mathit{C}Me_3$), 26.12 ($CH\mathit{Me}$), 27.99 ($C\mathit{Me}_3$), 46.48 ($\mathit{C}HMe$); ^{29}Si δ −48.20 ($\mathit{Si}(NMeSiMe_3)_2$), −0.47 ($SiCMe_3$), 8.18 (SiMe); MS [EI, *m/z* (%)] 461 [14, M^+], 446 [30, $M-Me^+$], 404 [66, $M-CMe_3^+$].

3.6. Compounds **16** and **17**

Compound **14** (10.1 g, 25 mmol) was treated with one equivalent *n*-butyllithium dissolved in *n*-hexane (23%) and heated under reflux for 1 h. Then 25 mmol (2.4 g) Me_2SiF_2 (**16**; −30 °C), respectively, $((Me_3C)SiMe_3N)SiF_3$ (5.7 g) (**17**; 20 °C) were added. The reaction mixture was condensed into a cooled trap. Compounds **16** and **17** were isolated by distillation in vacuo.

3.6.1. 2,2-Di-*tert*-butyl-1-(fluorodimethylsilyl)-4,4-bis[methyl(trimethylsilyl)amino]-1-aza-3-oxa-2,4-disilacyclobutane (**16**)

B.p. 120 °C/0.02 mbar. Yield 37%. NMR ($CDCl_3$): ^1H δ 0.13 ($SiMe_3$, 18H), 0.27 (d, $SiMe_2$, $^3J_{HF} = 6.8$ Hz, 6H), 1.09 (CMe_3, 18H), 2.59 (NMe, 6H); ^{13}C δ 0.02 ($SiMe_3$), 2.17 (d, $SiMe_2$, $^2J_{CF} = 19.3$ Hz), 22.05 ($\mathit{C}Me_3$), 28.01 (d, $C\mathit{Me}_3$, $^5J_{CF} = 0.8$ Hz), 31.67 (d, NMe, $^5J_{CF} = 1.5$ Hz); ^{19}F δ 30.21 (sep, SiF, $^3J_{HF} = 6.8$ Hz); ^{29}Si δ −42.12 (d, SiNMe, $^3J_{SiF} = 3.9$ Hz), 0.66 (d, SiF, $^1J_{SiF} = 266.1$ Hz), 6.26 ($SiCMe_3$), 8.52 (d, $SiMe_3$, $^5J_{SiF} = 2.3$ Hz; MS [EI, *m/z* (%)] 481 [25, M^+], 466 [20, $M-Me^+$], 424 [100, $M-CMe_3^+$].

3.6.2. 4,4-Bis[methyl(trimethylsilyl)amino]-1-aza-3-oxa-2,4-disilacyclobutane (**17**)

B.p. 155 °C/0.01 mbar. Yield 14%. NMR ($CDCl_3$): ^1H δ 0.13 ($(NSiMe_3)_2$, 18H), 0.27 (t, $NSiMe_2$, $^5J_{HF} = 1.3$ Hz, 9H), 1.28 ($SiCMe_3$, 18H), 1.41 ($NCMe_3$, 12H), 2.57 (NMe, 3H); ^{13}C δ 0.20 ($(NSiMe_3)_2$), 5.47 (t, $NSiMe_3$, $^4J_{CF} = 2.8$ Hz), 22.60 ($Si\mathit{C}Me_3$), 28.22 ($SiC\mathit{Me}_3$), 31.45 (t, NMe, $^5J_{CF} = 1.7$ Hz), 33.84 (t, $NC\mathit{Me}_3$, $^4J_{CF} = 2.3$ Hz), 54.28 ($N\mathit{C}Me_3$); ^{19}F δ 47.53); ^{29}Si δ −65.56 (t, SiF, $^1J_{SiF} = 291.9$ Hz), −43.05 ($OSiN_3$), 5.05 (t, $NSiMe_3$, $^3J_{SiF} = 1.5$ Hz), 6.32 $(NSiMe_3)_2$, 8.79 (t, $SiCMe_3$, $^3J_{SiF} = 1.5$ Hz); MS [EI, *m/z* (%)] 614 [8, M^+], 599 [19, $M-Me^+$], 557 [100, $M-CMe_3^+$].

3.7. X-ray crystal structure determinations of **1**, **2**, **3**, **9** and **12**

X-ray Data Collection and Refinement. Crystal data are summarized in Table 3.

Data were collected on a Stoe AED2 four-circle diffractometer (**1**, **2**, **9**, and **12**) or on a Stoe–Siemens–Huber four-circle diffractometer (**3**) equipped with a Siemens SMART area detector. Monochromated Mo–K_α radiation ($\lambda = 71.073$ pm) was used. The structures were solved by direct methods [14]. All non-hydrogen atoms were refined anisotropically [15]. The structures were refined against F^2. For the hydrogen atoms bonded to carbon the riding model was used. The hydrogen atoms bonded to nitrogen or oxygen were refined with distance restraints. In structure **2** the THF group and one *tert*-butyl group and in **3** the THF and one $OSi(C_4H_9)_2NH_2$ group were disordered. They were refined with distance restraints and restraints for the anisotropic displacement parameters.

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