5376 *Organometallics* **2000,** *19,* 5376−5383

Asymmetric Tris- and Cyclic Silylhydroxylamines from Trimeric and Tetrameric Lithium *N,N*-Bis(silyl)hydroxylamides

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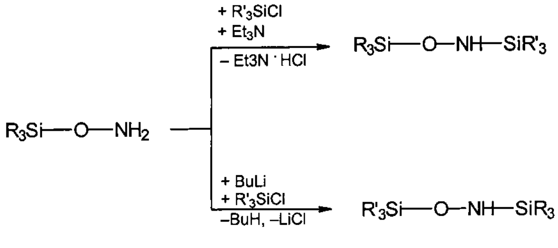
The fluorosilylhydroxylamine ^{t}BuSiF(Me)−ONH$_2$ (**2**) is obtained in the reaction of ^{t}BuSiF(Me)−NH^{t}Bu (**1**) and HONH$_2$·HCl. The reaction of ^{t}BuSiMe$_2$−ONH$_2$ with butyllithium leads to the formation of the bis(silyl)hydroxylamine ^{t}BuSiMe$_2$−NH−O−SiF(Me)^{t}Bu (**3**). Depending on the bulkiness of the substituents and the solvent, lithium salts of *N*,*O*-bis(silyl)-hydroxylamines crystallize as dimeric, trimeric, or tetrameric *O*-lithium-*N*,*N*-bis(silyl)-hydroxylamides, e.g., [(^{t}BuSiMe$_2$)$_2$N−OLi·THF]$_2$, [(^{t}BuSiMe$_2$)$_2$N−OLi]$_3$ (**4**), and [^{t}BuSiMe$_2$(Me$_3$-Si)N−OLi]$_4$ (**6**). Lithiation of ^{t}BuSiMe$_2$ONHSiMe$_2$^{t}Bu in the presence of TMEDA leads to a cleavage of the N−O bond. The hexameric lithium silanolate (^{t}BuSiMe$_2$O−Li)$_6$ (**5**) is obtained. Above 0 °C the lithium derivative of **3** (**3a**) reacts with LiF and the cyclic silylhydroxylamine (^{t}BuSiMe-O−N−SiMe$_2$^{t}Bu)$_2$ (**7**). In the reactions of **3a** and **6** with F$_2$SiMe$_2$ and F$_3$SiMe the first asymmetrical tris(silyl)hydroxylamines *N*,*N*-^{t}BuSiMe$_2$(FSi(Me)^{t}Bu)N−O−SiFMe$_2$ (**8**), *N*,*N*-^{t}BuSiMe$_2$(SiMe$_3$)N−O−SiFMe$_2$ (**9**), *N*,*N*-^{t}BuSiMe$_2$(SiMe$_3$)N−O−SiF$_2$Me (**10**), and the bis((bis)(silyl)hydroxylamino)silane [*N*,*N*-^{t}BuSiMe$_2$(SiMe$_3$)]$_2$−O−SiFMe (**11**) are isolated. Chlorodimethylalane reacts with the trimeric *O*-lithium-*N*,*N*-bis(*tert*-butyldimethylsilyl)hydroxylamide to give LiCl and the four-membered ring system 2,4-bis-*N*,*N*-bis(*tert*-butyldimethylsilylhydroxylamide)-1-dimethylalano-3-lithio-2,4-dioxocyclobutane (**12**). Crystal structures of **4**−**7** and **12** are reported.

Introduction

The first (organosilyl)hydroxylamines were prepared by Wannagat and Pump.[1] It was found that substitution by the first silyl group occurs at oxygen, whereas the opposite is true for organyl groups. It depends on the reaction pathway whether the second silyl group is attached to the oxygen again or to the nitrogen;[2,3] for example,



(1)

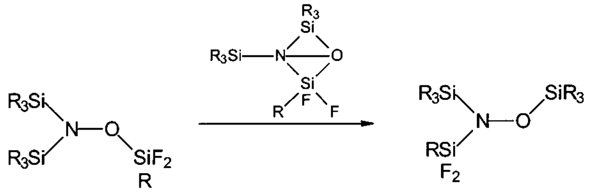
Isomeric *N*,*O*-bis(silyl)hydroxylamines are preparable. *N*,*N*,*O*-Tris(organylsilyl)hydroxylamines can be obtained from the *N*,*O*-bis(organylsilyl)hydroxylamines, butyllithium, and organohalosilanes.[2] Although lithium (silyl)hydroxylamides were successfully used in these reactions since the end of the 1960s, no crystal structures of these compounds are described until now.

$$\mathrm{R_3Si{-}O{-}NH{-}SiR_3} \xrightarrow[-\,\mathrm{BuH},\ -\,\mathrm{LiHal}]{+\,\mathrm{BuLi} \atop +\,\mathrm{HalSiR'_3}} \mathrm{(R_3Si)_2N{-}O{-}SiR'_3} \quad (2)$$

Derivatization with triorganohalosilanes gives, in every case, only the rearranged isomer, in which the new silyl group is attached to the oxygen.[2] This result implies a 1,2-anionic silyl group migration from oxygen to nitrogen.[3] Recently we could show that primarily

$$\mathrm{R_3Si{-}\overset{\ominus}{N}{-}O{-}SiR_3} \xrightarrow{0} \mathrm{(R_3Si)_2N{-}O^{\ominus}} \quad (3)$$

formed *O*-fluorosilyl-*N*,*N*-bis(organosilyl)hydroxylamines undergo an irreversible rearrangement with formation of the isomeric *N*-(fluorosilyl)-*N′*,*O*-bis(organosilyl)hydroxylamines.[4,5]



(4)

Mitzel and Losehand could show that *O*-silylhydroxylamines are able to form intramolecular donor acceptor

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(1) Wannagat, U.; Pump, J. *Monatsh. Chem.* **1963**, *94*, 141.
(2) West, R.; Boudjouk, P. *J. Am. Chem. Soc.* **1973**, *95*, 3987.
(3) Boudjouk, P.; West, R. *Intra-Sci., Chem. Rep.* **1973**, *7*, 65.
(4) Wolfgramm, R.; Klingebiel, U. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1031.
(5) Wolfgramm, R.; Müller, T.; Klingebiel, U. *Organometallics* **1998**, *17*, 3222.

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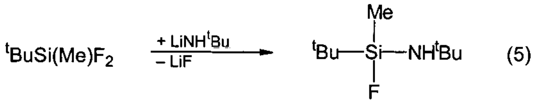
bonds between silicon and nitrogen centers, separated by one oxygen only.[6,7] These strong β-donor interactions help to explain the easy silyl group migrations in tris(silyl)hydroxylamines.

Knowing that the high Si−F bond energy allows the preparation of fluorofunctional compounds, we present in this paper the synthesis of a fluorosilylhydroxylamine, the first tri- and tetrameric *O*-lithium *N*,*N*-bis(silyl)hydroxylamides, a cyclic silylhydroxylamine, asymmetrically substituted tris(silyl)hydroxylamines, a bis[*N*,*N*-bis(silyl)hydroxylamino]silane, and a four-membered ring system 2,4-bis-*N*,*N*-bis(*tert*-butyldimethylsilylhydroxylamide)-1-dimethylalano-3-lithio-2,4-dioxocyclobutane.

Results and Discussion

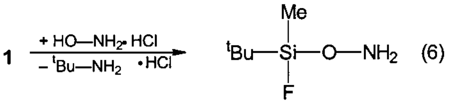
The synthesis of the monofluorosilylhydroxylamine (**2**) occurs in a base exchange reaction. For that reason we prepared the aminofluorosilane first (**1**).



$$^tBuSi(Me)F_2 \xrightarrow[-\,LiF]{+\,LiNH^tBu} {^tBu}-Si(Me)(F)-NH^tBu \quad (5)$$

1

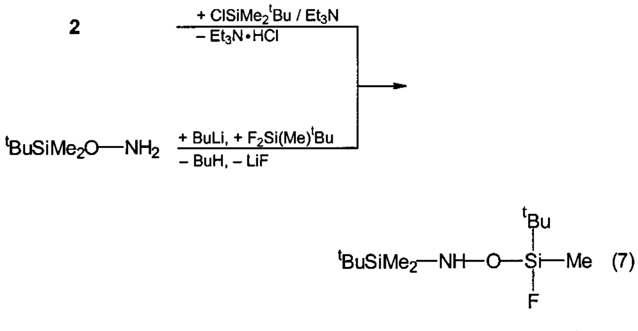
1 reacts with HO−NH$_2$•HCl to give **2**.



$$\mathbf{1} \xrightarrow[-\,^tBu-NH_2\,\cdot HCl]{+\,HO-NH_2\cdot HCl} {^tBu}-Si(Me)(F)-O-NH_2 \quad (6)$$

2

The classical method for the preparation of *N*,*O*-bis(silyl)hydroxylamines is the reaction of monosilylhydroxylamines, chlorosilanes, and a base. This reaction and the reaction of the lithium derivative of $^tBuSiMe_2$-ONH_2 with $F_2Si(Me)^tBu$ lead to the formation of $^tBuSiMe_2-NH-O-SiF(Me)^tBu$ (**3**).



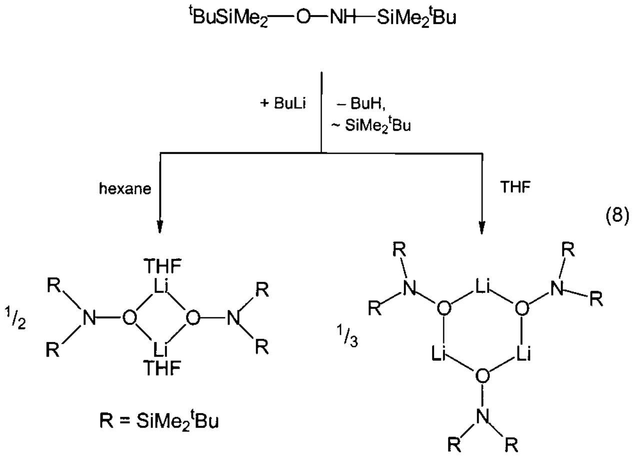
$$^tBuSiMe_2-NH-O-Si(^tBu)(F)-Me \quad (7)$$

3

In the second case a 1,2-silyl group migration occurred from the oxygen to the nitrogen atom at −78 °C. In contrast with the lithium derivatives of monosilylhydroxylamines, the lithium derivatives of *N*,*O*-bis(silyl)hydroxylamines are kinetically more stable. We lithiated the following bis(silyl)hydroxylamines: $^tBuSiMe_2-NH-O-SiMe_2{}^tBu$, $^tBuSiMe_2-NH-O-SiMe_3$, its structural isomer $^tBuSiMe_2-O-NH-SiMe_3$, and **3**. Colorless crystalline compounds were isolated. The lithium derivative of the bis-*N*,*O*-*tert*-butyldimethylsilylhydroxylamine forms a dimer via a Li_2O_2 four-membered ring in THF[8] and a trimer via a Li_3O_3 six-membered ring in hexane. In both reactions

$$(^tBuSiMe_2)_2N-\overline{\underline{O}}|^{\ominus}$$

units are formed. That means a silyl group migration from oxygen to the nitrogen occurred.



4

The solubility of **4** in hexane is low. To get single crystals, we recrystallized **4** from boiling toluene. The high temperature leads to a partial cleavage of the N−O bond and the formation of $(LiO-NSiMe_2{}^tBu)_3\cdot(LiOSiMe_2{}^tBu)_6$ (**4a**). The easy thermal cleavage of the N−O bond is known, for example, from the decomposition of *N*-boryl-*N*,*O*-bis(silyl)hydroxylamines.[9]

4a crystallizes as the first silylhydroxylamide−silanolate double salt in a ratio of 2:1 The crystal system is monoclinic and the space group *P*2(1)/*c*.

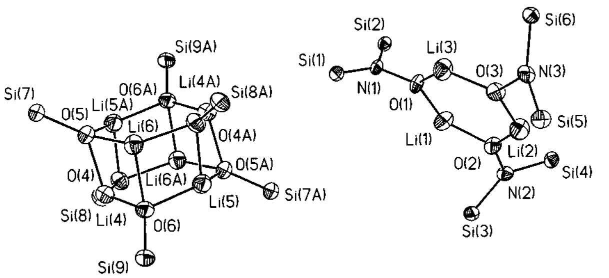


Figure 1. Crystal structure of **4a** in the crystal.

Crystal Structure of 4a. The bis(silyl)hydroxylamide is a trimer with a central nearly planar six-membered ring (Figure 1). In contrast with calculations with the $LiONH_2$ system[10] no Li−N contact is found in **4a**. The central ring consists of an alternating arrangement of Li and O atoms, where Li is only two-coordinated and O additionally bonds to the exocyclic functions. The Li−O−Li ring angles (114.1°, 115.5°, 119.7°) are smaller than the O−Li−O ring angles

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[6] Mitzel, N. W.; Losehand, U. *Angew. Chem.* **1997**, *109*, 2897; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2807.

[7] Mitzel, N. W.; Losehand, U. *J. Am. Chem. Soc.* **1998**, *120*, 7320.

[8] Diedrich, F.; Klingebiel, U.; Schäfer, M. *J. Organomet. Chem.* **1999**, *588*, 242.

[9] Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123.

[10] Armstrong, D. R.; Clegg, W.; Hodgson, S. M.; Snaith, R.; Wheatley, A. E. H. *J. Organomet. Chem.* **1998**, *550*, 233.

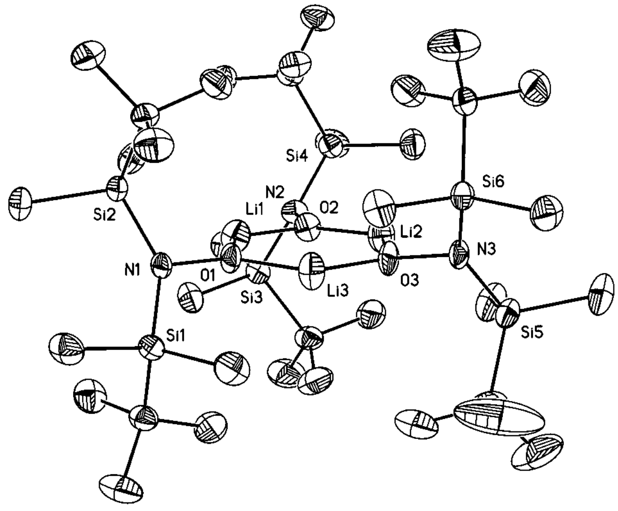


Figure 2. Structure of the lithium bis(silyl)hydroxylamide part of **4a**. Selected bond lengths [Å] and angles [deg]: O(1)–N(1) 1.491(5), O(1)–Li(3) 1.799(8), O(1)–Li(1) 1.820(6), N(1)–Si(2) 1.738(5), N(1)–Si(1) 1.742(7), Si(1)–C(12) 1.888(8), Si(1)–C(13) 1.910(7), Li(1)–O(2) 1.829(7); N(1)–O(1)–Li(3) 125.7(2), N(1)–O(1)–Li(1) 118.8(3), Li(3)–O(1)–Li(1) 115.5(2), O(1)–N(1)–Si(2) 109.7(3), O(1)–N(1)–Si(1) 110.7(3), Si(2)–N(1)–Si(1) 139.1(1), N(1)–Si(1)–C(12) 110.0(2), N(1)–Si(1)–C(11) 108.9(3), C(12)–Si(1)–C(11) 108.0(2), N(1)–Si(1)–C(13) 113.2(2), O(1)–Li(1)–O(2) 126.4(3).

(121.4°, 122.8°, 126.4°). The bond lengths show small but acceptable variations: Li–O 1.799–1.829 Å, Si–N 1.730–1.745 Å, and Si–C 1.884–1.920 Å. The N atoms (Σ: N1 = 359.49°, N2 = 358.99°, N3 = 359.62°) and the O atoms (Σ: O(1) = 360.0°, O(2) = 359.9°, O(3) = 359.1°) have a planar geometry. The Si–N–Si angles of 139.0°, 139.26°, and 141.3° are rather large (Figure 2).

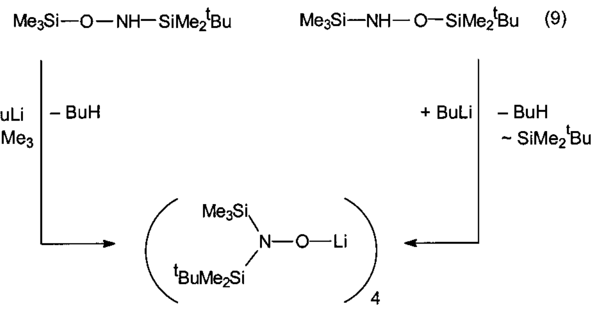
The lithium silanolate part of **4a** is arranged in a central distorted hexagonal prism, in which two six-membered Li–O ring systems are held together by six Li–O bonds. The individual six-membered Li–O rings have chair conformations (Figure 3).

The Si–O and Li–O bond lengths are found to be between 1.631–1.638 and 1.900–1.973 Å. Similar to the hydroxylamide part of **4a**, the O–Li–O angles of the six-membered ring are larger than 120° and the Li–O–Li angles are smaller than 120°, respectively; for example, O(6)–Li(4)–O(4) = 127.9°, O(5)–Li(6)–O(6) = 99.9°. The lithium atoms are three-coordinated. At 2.476–2.491 Å very short Li–Li distances to other members of the core are observed.

Crystal Structure of 5. The experiment to lithiate ^{t}BuSiMe$_2$–O–NHSiMe$_2$^{t}Bu in the presence of TMEDA leads to a total cleavage of the N–O bond, and only the hexameric lithium silanolate **5**, (^{t}BuSiMe$_2$–OLi)$_6$, could be isolated. After recrystallization from toluene the hexameric ^{t}BuSiMe$_2$OLi structure consists of a Li–O framework with Li–O bonds ranging from 1.865 to 1.953 Å with three-coordinate Li and four-coordinate O centers. This is comparable with other known lithium silanolates[11] and **4a**. Despite the different unit cell content, the core of this structure and the core of the silanolate part of **4a** are very similar. However, steric hindrance of the bulky groups causes small geometrical changes, at least regarding the bond angles.

The Li(1)–Li(3) distances (2.404 Å) are below the sum of the van de Waals radii. The Li–O–Li angles of the six-membered rings are smaller than 120°, and the O–Li–O angles are larger than 120° (Figure 4).

Starting with the *O*-trimethylsilyl- or *O*-*tert*-butyldimethylsilylhydroxylamine, we prepared the isomeric *N*,*O*-bis(silyl)hydroxylamines and found that they form the same lithium derivative, **6** (eq 9), upon reaction with butyllithium. We obtained useful crystals from toluene and are able to present the first crystal structure of a tetrameric lithium bis(silyl)hydroxylamide.



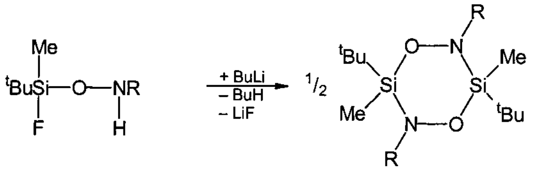
(9)

6

For $(H_2NOLi)_4$, calculations suggest the unsatisfactory nature of either a ladder structure or a planar ring. Of considerably higher stability are stacked dimer cubanes.[10]

Crystal Structure of 6. The crystal structure of **6**, which is depicted in Figure 5, shows that **6** forms a tetramer in the solid state. The crystals of **6** are tetragonal, space group $P\bar{4}$ with two molecules in the unit cell, corresponding to one monomer per asymmetric unit. The molecule is composed of a central eight-membered (Li–O) ring. As a result, each Li$^{\oplus}$ ion is bound to two oxygen atoms and one nitrogen atom, with N atoms attached to oxygen. The side-on bond lengths for the Li ions were determined to be Li(1A)–O(1) = 1.81 and Li(1A)–N(1) = 2.097 Å, respectively. The angles at O(1) and N(1) to Li(1A) deviate by 20°: (Li(1A)–N(1)–O(1A) = 57.6°, Li(1A)–O(1)–N(1A) = 78.0°. Without the coordinative N–Li bond the N atoms have an almost pyramidal environment, with the widest angle, 137.1°, between the silyl groups (sum of angles N(1) = 352.1°).

Although only three lithium salts have been characterized by X-ray diffraction until now, we found that the structural features depend on the solvent and the bulkiness of the substituents. Experiments to lithiate **3** and characterize its lithium derivative lead to LiF elimination below 0 °C and formation of the cyclic silylhydroxylamine **7**.



(10)

R = SiMe$_2$^{t}Bu

7

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[11] Pauer, F.; Power, P. P. In *Lithium Chemistry;* Sapse, A. M., Ragué Schleyer, P. v., Eds.; John Wiley & Sons: New York, 1995; p 295.

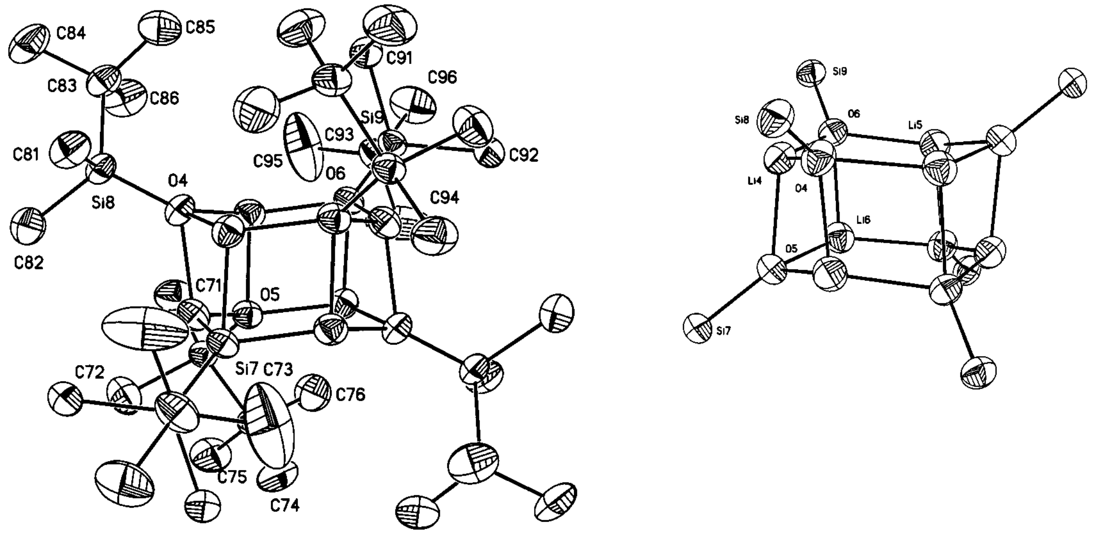


Figure 3. Lithium silanolate part of **4a** (left) and prismatic core (right). Selected bond lengths [Å] and angles [deg]: Si(7)–O(5) 1.638(6), Si(8)–O(4) 1.631(5), Si(9)–O(6) 1.636(5), O(4)–Li(4) 1.912(7), O(4)–Li(5)#1 1.947(8), O(4)–Li(6)#1 1.949(9), O(5)–Li(6) 1.900(7), O(5)–Li(5)#1 1.934(7), O(5)–Li(4) 1.973(8), O(6)–Li(5) 1.912(9), Li(6)–O(4)#1 1.949(9), Li(6)–Li(4) 2.484(8), Li(6)–Li(5) 2.491(11), Li(5)–O(5)#1 1.934(7), Li(5)–O(4)#1 1.947(8), Li(5)–Li(4)#1 2.476(9), Li(4)–Li(5)#1 2.476(9); Si(8)–O(4)–Li(4) 131.5(3), Si(8)–O(4)–Li(5)#1 125.2(2), Li(4)–O(4)–Li(5)#1 79.8(2), Si(8)–O(4)–Li(6)#1 115.5(2), Li(4)–O(4)–Li(6)#1 109.3(3), Li(5)#1–O(4)–Li(6)#1 79.5(3), O(4)–Li(4)–O(6) 127.9(3), O(4)–Li(4)–O(5) 99.7(2), O(6)–Li(4)–O(5) 99.0(2).

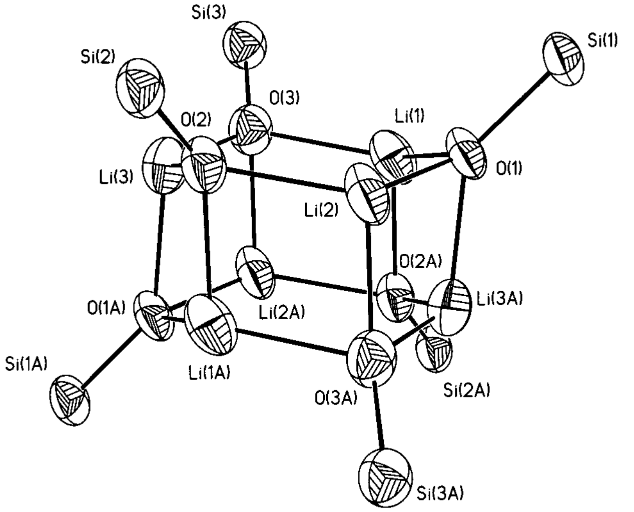


Figure 4. Structure of **5** in the crystal. Selected bond lengths [Å] and angles [deg]: Si(1′)–O(1′) 1.615(3), Si(1)–O(1) 1.621(3), O(1)–Li(1) 1.865(8), O(1)–Li(2) 1.884(7), O(1)–Li(3)#1 1.934(8), O(1′)–Li(1′) 1.909(8), O(1′)–Li(3′)#2 1.943(7), Li(1)–O(3)#1 1.920(8), Li(1)–O(2) 1.944(8), Li(1′)–O(3′) 1.895(8), Li(1′)–O(2′)#2 1.941(7), O(2)–Li(2)#1 1.906(8), O(2)–Li(3) 1.910(8), O(2′)–Li(3′) 1.881(8), O(2′)–Li(2′) 1.915(8), O(2′)–Li(1′)#2 1.941(7), Li(2′)–O(3′)#2 1.953(7), Li(2)–O(3) 1.905(8), Li(2)–O(2)#1 1.906(8), Li(3)–O(1)#1 1.934(8), Li(3′)–O(1′)#2 1.943(7); Si(1)–O(1)–Li(1) 121.6(3), Si(1)–O(1)–Li(2) 117.3(3), Li(1)–O(1)–Li(2) 110.3(3), Si(1)–O(1)–Li(3)#1 140.7(3), Li(1)–O(1)–Li(3)#1 78.5(3), Li(2)–O(1)–Li(3)#1 78.9(3), Si(1′)–O(1′)–Li(2′) 134.7(3), Si(1′)–O(1′)–Li(1′) 107.1(3), Li(2′)–O(1′)–Li(1′) 109.8(3), Si(1′)–O(1′)–Li(3′)#2 132.4(3), Li(2′)–O(1′)–Li(3′)#2 81.0(3), Li(1′)–O(1′)–Li(3′)#2 78.2(3), O(1)–Li(1)–O(3)#1 101.9(4), O(1)–Li(1)–O(2) 125.1(4), O(3)#1–Li(1)–O(2) 100.0(3).

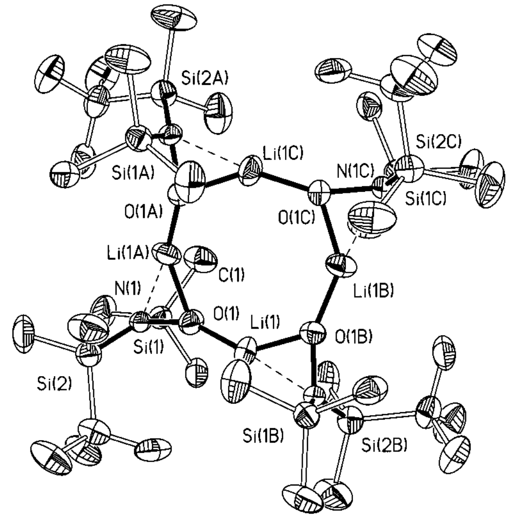


Figure 5. Molecular structure of **6**, diagram of the Li(1) molecule. Selected bond lengths [Å] and angles [deg]: Si(2)–N(1) 1.744(7), Si(1)–C(1) 1.875(7), N(1)–O(1) 1.500(6), N(1)–Si(2) 1.742(6), N(1)–Li(1A) 2.097(12), O(1)–Li(1) 1.763(11), Li(1A)–O(1) 1.810(12); O(1)–N(1)–Si(2) 109.3(4), O(1)–N(1)–Si(1) 105.7(4), Si(2)–N(1)–Si(1) 137.1(3), O(1)–N(1)–Li(1A) 57.6(4), N(1)–O(1)–Li(1) 155.8(5), N(1)–O(1)–Li(1A) 78.0(4), Li(1)–O(1)–Li(1A) 123.7(7), O(1)–Li(1)–N(1B) 172.2(8), O(1B)–Li(1)–N(1B) 44.4(3).

Compound **7** was characterized by nuclear magnetic resonance spectroscopy and X-ray crystallography. Five signals were found in the ^{1}H NMR spectra. The first three signals (δ = 0.1, δ = 0.1, and δ = 0.3 ppm) correspond to Si-bound methyl groups, indicating that the methyl groups of the *tert*-butyldimethylsilyl group are chemically not equivalent. This effect could be attributed to the endocyclic chiral silicon atoms. For the identification of the silyl groups the isotope coupling of the ^{29}Si NMR spectra was used. The $^{2}J_{29\mathrm{Si}29\mathrm{Si}}$ coupling via the nitrogen atom was found to be 5.4 Hz. The endo- and exocyclic silicon atom signals can be identified through the chemical shifts and the number of ^{29}Si–^{13}C sidebands (Figures 6, 7).

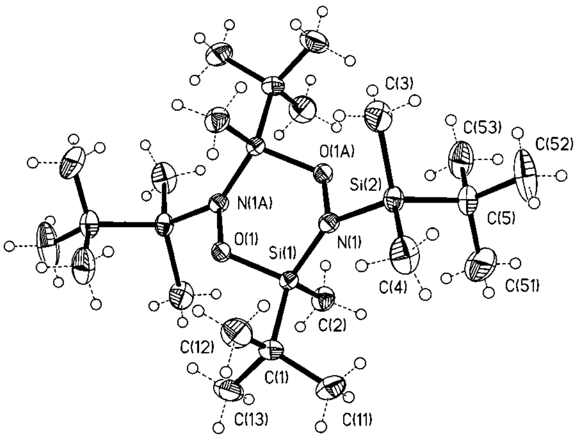


Figure 6. Crystal structure of **7**. Selected bond lengths [Å] and angles [deg]: O(1)−N(1A) 1.510(2), N(1)−O(1A) 1.510(2), N(1)−Si(2) 1.756(14), O(1)−Si(1) 1.678(12), N(1)−Si(1) 1.744(14); O(1A)−N(1)−Si(1) 101.1(1), O(1A)−N(1)−Si(2) 104.1(1), Si(1)−N(1)−Si(2) 148.7(1), O(1)−Si(1)−N(1) 104.8(1), N(1A)−O(1)−Si(1) 116.9(1).

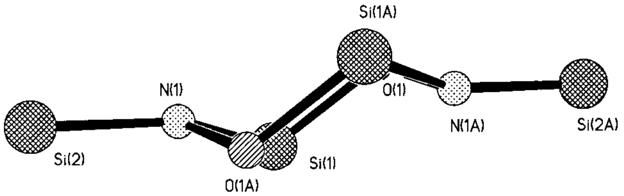
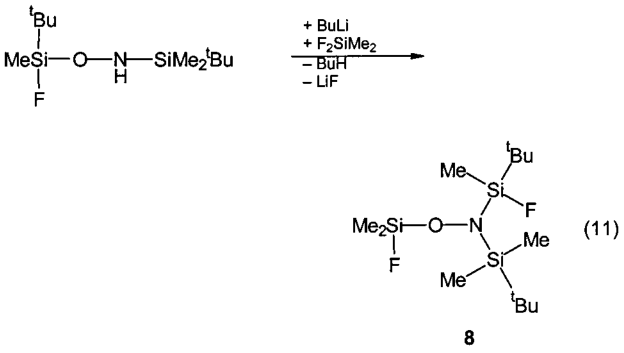


Figure 7. Side view of the structure of **7**.

Crystal Structure of 7. Compound **7** crystallizes from *n*-hexane in the orthorhombic space group *Pbca*. In contrast with the only known cyclic silylhydroxylamine[12,13] which crystallizes in a twist conformation, compound **7** has a chair conformation. Si(1) and Si(2) are related by an inversion center, which means that compound **7** is achiral. The nitrogen atom is 22 pm above the plane defined by the three atoms Si(1), Si(2), and O(1A). The sum of angles around the nitrogen atom is 353.9°, indicating a nonplanar environment. Both, the X-ray and NMR data prove the formation of the trans conformation.

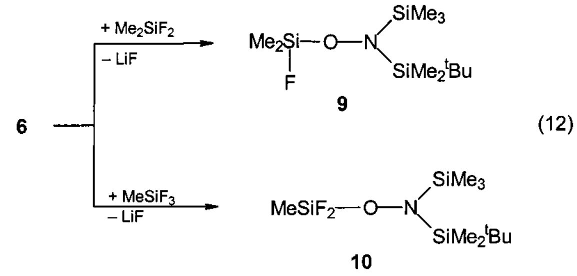
At −78 °C, lithiated **3** reacts with Me_2SiF_2 to give the asymmetrically substituted tris(silyl)hydroxylamine **8**.

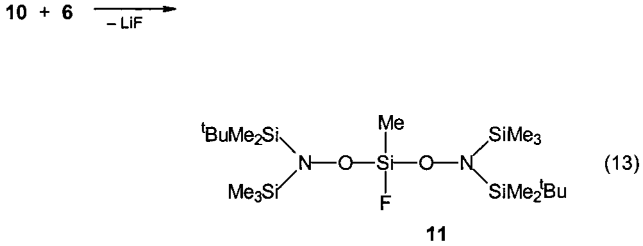


8

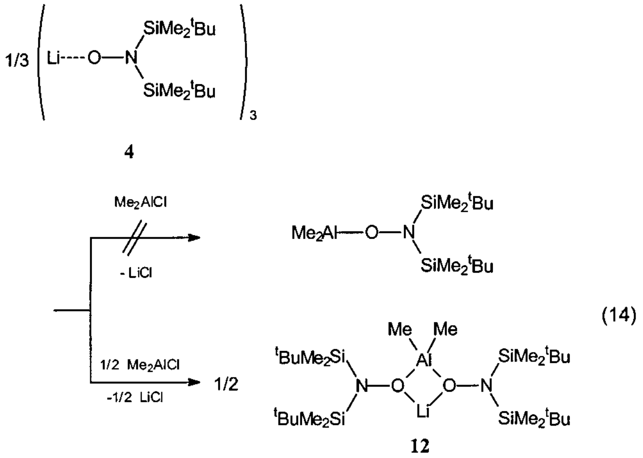
Again the new silyl group is attached to the oxygen atom. The silyl group migration occurred on the stage of the lithium derivative. To characterize **8**, both C−H 2D NMR spectra and isotopic coupling constants of the ^{29}Si NMR spectra were determined. Only two ^{29}Si NMR signals correspond to a $^2J_{SiSi}$ coupling of 5.59 Hz, proving that the respective Si atoms are bound to the nitrogen atom.

Other asymmetrically substituted tris(silyl)hydroxylamines were obtained in the reaction of **6** with Me_2SiF_2 and $^tBuSiF_3$. Fluorofunctional silylhydroxylamines allow the easy synthesis of unknown bis[bis(silyl)hydroxylamino]silanes. In the reaction of **6** and $MeSiF_3$ the byproduct is the bis[bis(silyl)hydroxylamino]silane **11**. **11** can be prepared in good yields from **10** and **6**.





Attempts to prepare a 2,4-bis-*N*,*N*-bis(*tert*-butyldimethylsilylhydroxylamide)-1-dimethylalano-3-lithio-2,4-dioxocyclobutane in the reaction of **4** and $ClAlMe_2$ in a molar ratio 1:1 stopped with the formation of the *O*-aluminum-*O*-lithium bis[*N*,*N*-(silyl)hydroxylamide] **12**. A few (AlO_2Li)-four-membered ring systems are known,[16] but **12** is the first case without additional coordination of solvent molecules or other Lewis bases.



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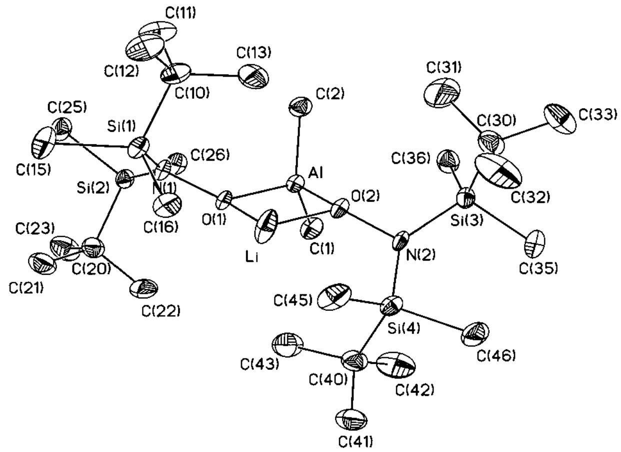

Figure 8. Crystal structure of **12**. Selected bond lengths [Å] and angles [deg]: Al−O(2) 1.830(17), Al−O(1) 1.831(17), Al−C(1) 1.968(3), Al−Li 2.702(5), Si(1)−N(1) 1.738(2), O(1)−N(1) 1.477(2), O(1)−Li 1.850(5), O(2)−N(2) 1.484(2), O(2)−Li 1.841(5); O(2)−Al−O(1) 85.8(1), O(2)−Al−C(1) 109.9(1), O(2)−Al−C(2) 116.8(1), N(1)−O(1)−Al 128.5(1), N(1)−O(1)−Li 125.0(2), Al−O(1)−Li 94.5(2), N(2)−O(2)−Al 127.8(1), N(2)−O(2)−Li 125.1(2), Al−O(2)−Li 94.8(2), O(1)−N(1)−Si(1) 109.7(1), O(1)−N(1)−Si(2) 113.5(1), Si(1)−N(1)−Si(2) 134.6(1), O(2)−N(2)−Si(3) 111.4(1), O(2)−N(2)−Si(4) 109.6(1), Si(3)−N(2)−Si(4) 134.3(1).

Crystal Structure of 12. The crystals of **12** are monoclinic, space group $P2(1)/n$ with $Z = 4$. **12** forms an (Al−O−Li−O) four-membered planar ring. Aluminum is tetracoordinated and lithium two-coordinated. Because of steric hindrance of the bulky silyl groups, neither the lithium nor the aluminum are bound side-on to a N−O unit. Only in the case of structure **6** with less bulky groups is a side-on bond possible.

The Si−N bond lengths are found from 1.738 to 1.746 Å. The O−N bonds are (O(1)−N(1): 1.477 Å, O(2)−N(2): 1.484 Å). The sum of the angles of the nitrogen atoms is measured with Σ N(1) = 357.75 ° and Σ N(2) = 355.19 °. The N atoms have nearly planar geometry (Figure 8).

Conclusion

Starting from *O*,*N*-bis(silyl)hydroxylamines, *O*-lithium-*N*,*N*-bis(silyl)hydroxylamides were prepared. Depending on the bulk of the silyl groups, the lithium salts crystallize as dimers, trimers, or tetramers. A cyclic silylhydroxylamine was obtained in the reaction of *N*-*tert*-butyldimethylsilyl-*O*-*tert*-butylfluoromethylsilylhydroxylamine with BuLi. *O*-Lithium-*N*,*N*-bis(silyl)-hydroxylamides react with halosilanes to give asymmetrical tris(silyl)hydroxylamines and a bis[bis(silyl)hydroxylamino]silane. A four-membered *O*-aluminum-*O*-lithium bis[*N*,*N*-(silyl)hydroxlamide] was obtained in the reaction of the trimeric *O*-lithium *N*,*N*-bis(*tert*-butyldimethylsilyl)hydroxylamide and $ClAlMe_2$.

Experimental Section

All experiments were performed in oven-dried glassware under purified nitrogen or argon using standard inert atmosphere and vacuum line techniques. The solvents were dried over Na and distilled under nitrogen prior to use. All NMR spectra were obtained on either a Bruker AM-250 or a MSL-400 spectrometer and were recorded in C_6D_6 or $CDCl_3$ with $SiMe_4$ as internal and C_6F_6 or LiCl as external references. Mass spectra were obtained on a Varian CH-5 and Finnigan MAT 8200 or 95 spectrometer. The data are reported in mass to charge units (*m*/*z*) with their relative intensities in parentheses. The progress of the reaction was checked by ^{19}F NMR spectroscopy. The purity of the compounds was measured by NMR spectroscopy.

***tert*-Butylamino-*tert*-butylfluormethylsilane (1).** To a solution of 7.3 g of *tert*-butylamine (0.1 mol) in 20 mL of *n*-hexane was slowly added *n*-butyllithium (0.1 mol, 15% in *n*-hexane). The reaction mixture was refluxed for 1 h and cooled to room temperature and then added to a solution of 13.8 g of *tert*-butyldifluoromethylsilane (0.1 mol) in 20 mL of THF. The mixture was heated under reflux for 3 h, and **1** was separated from LiF by condensing the product and the solvents into a cooled trap in vacuo. **1** (18.6 g, 97 mmol, 97% yield) was distilled (bp 157 °C) to give a pure sample. ^1H NMR ($CDCl_3$): δ 0.2 (d, $FSiCH_3$, $^3J_{HF} = 6.0$ Hz, 3H), 0.9 [d, $FSiC(CH_3)_3$, $^4J_{HF} = 0.8$ Hz, 9H], 1.2 [s, $NC(CH_3)_3$, 9H]. ^{13}C NMR ($CDCl_3$): δ −4.3 (d, $FSi\mathit{C}H_3$, $^2J_{CF} = 24.8$ Hz), 17.2 [d, $FSi\mathit{C}(CH_3)_3$, $^2J_{CF} = 15.0$ Hz], 24.9 [s, $N\mathit{C}(CH_3)_3$], 26.0 [s, $NC(\mathit{C}H_3)_3$], 33.5 [d, $FSiC(\mathit{C}H_3)_3$, $^3J_{CH} = 1.6$ Hz]. ^{19}F NMR ($CDCl_3$): δ 16.6 (d, FSi, $^1J_{SiF} = 295.0$ Hz). ^{29}Si NMR ($CDCl_3$): δ 1.1 (d, SiF, $^1J_{SiF} = 295.0$ Hz). MS (EI) *m*/*z* [%]: 176 (100) [$M^+ - CH_3$]. Anal. Calcd for C_9H_{22}-FNSi (191.37): C, 56.49; H, 11.59. Found: C, 56.71; H, 11.83.

***O*-*tert*-Butylfluormethylsilylhydroxylamine (2).** A solution of 9.6 g of **1** (0.05 mol) in 50 mL of THF was added to 3.5 g of hydroxylamine hydrochloride (0.05 mol), and the reaction mixture was stirred under reflux for 24 h. The product was isolated (5.3 g, 36 mmol, 71% yield) by distillation (bp 68 °C/39 Torr) after removing the resulting *tert*-butylammonium-chloride. ^1H NMR ($CDCl_3$): δ 0.2 (d, $FSiCH_3$, $^3J_{FH} = 6.2$ Hz, 3H), 0.9 [d, $FSiC(CH_3)_3$, $^4J_{FH} = 0.9$ Hz, 9H], 5.3 (s, ONH_2, 2H). ^{13}C NMR ($CDCl_3$): δ −8.6 (d, $FSi\mathit{C}H_3$, $^2J_{CF} = 0.3$ Hz), 18.0 [d, $FSi\mathit{C}(CH_3)_3$, $^2J_{CF} = 0.4$ Hz], 25.4 [s, $SiC(\mathit{C}H_3)_3$]. ^{19}F NMR ($CDCl_3$): δ 8.6 [qdec, $FSi(CH_3)C(CH_3)_3$, $^3J_{FH} = 6.2$ Hz, $^4J_{FH} = 0.9$ Hz]. ^{29}Si NMR ($CDCl_3$): δ 2.8 (d, FSi, $^1J_{SiF} = 304.9$ Hz). MS (EI) *m*/*z* [%]: 94 (67) [$M^+ - {}^tBu$]. Anal. Calcd for C_5H_{14}-FNOSi (151.26): C, 39.70; H, 9.33. Found: C, 39.88; H, 9.54.

***N*-*tert*-Butyldimethylsilyl-*O*-*tert*-butylfluoromethylsilylhydroxylamine (3).** A solution of 14.7 g of *tert*-butyldimethylsilylhydroxylamine (0.1 mol) in 20 mL of *n*-hexane was cooled to −78 °C and metalated with 1 equiv of *n*-butyllithium (0.1 mol, 15% in *n*-hexane). The reaction mixture was stirred for 1 h at −78 °C, and then a solution of 13.8 g of *tert*-butyldifluoromethylsilane (0.1 mol) in 20 mL of THF was slowly added. The mixture was allowed to warm overnight. The crude product was separated from LiF by condensing the product and the solvents into a cooled trap in vacuo. **3** (25.2 g, 95 mmol, 95% yield) was purified by distillation (bp 46 °C/0.1 Torr), $C_{11}H_{28}FNOSi_2$ (265.52). ^1H NMR ($CDCl_3$): δ 0.1 [s, $NSi(CH_3)_2$, 6H], 0.2 (d, $OSiFCH_3$, $^3J_{HF} = 6.2$ Hz, 3H), 0.9 [s, $NSiC(CH_3)_3$, 9H], 0.9 [d, $OSiFC(CH_3)_3$, $^4J_{HF} = 0.9$ Hz, 9H], 5.1 (s, ONH, 1H). ^{13}C NMR ($CDCl_3$): δ −8.4 (d, $OSiF\mathit{C}H_3$, $^2J_{CF} = 19.1$ Hz), −6.8 (d, $NSi\mathit{C}H_3$, $^5J_{CF} = 0.8$ Hz), −6.8 (d, $NSi\mathit{C}H_3$, $^5J_{CF} = 0.6$ Hz), 17.7 (s, $NSi\mathit{C}(CH_3)_3$), 17.8 (d, $OSiF\mathit{C}(CH_3)_3$, $^2J_{CF} = 14.5$ Hz), 25.6 (s, $OSiFC(\mathit{C}H_3)_3$), 26.5 (s, $NSiC(\mathit{C}H_3)_3$). ^{15}N NMR ($CDCl_3$): δ −255.0 (dd, ONH, $^1J_{NH} = 66.0$ Hz, $^4J_{NF} = 2.4$ Hz). ^{19}F NMR ($CDCl_3$): δ 9.6 (q, $SiFCH_3$, $^3J_{HF} = 6.2$ Hz, $^1J_{SiF} = 305.3$ Hz). ^{29}Si NMR ($CDCl_3$): δ 1.6 (d, OSiF, $^1J_{SiF} = 305.3$ Hz), 16.9 (s, NSi). MS (EI) *m*/*z* [%]: 265 (7) [M^+]. Anal. Calcd: C, 49.77; H, 10.63. Found: C, 49.53, H, 10.49.

Preparation of Compounds 4a, 5, and 6. For **4a** and **5** a 5.2 g amount of *N*,*O*-bis(*tert*-butyldimethylsilyl)hydroxylamine (0.02 mol) or for **6** 4.4 g of *O*-trimethylsilyl-*N*-*tert*-butyldimethylsilylhydroxylamine (0.02 mol) was solved in *n*-hexane (20 mL) and cooled to 0 °C. In the case of **5** there was also added 4.7 g of TMEDA (0.04 mol). Thereafter the corresponding bissilylhydroxylamine was metalated with 1 equiv of *n*-butyllithium (0.02 mol, 15% in *n*-hexane). The mixture was

Table 1. Crystallographic Data for Compounds 4, 5, 6, 7, and 12

	4	**5**	**6**	**7**	**12**
empirical formula	$C_{36}H_{90}Li_3N_3O_3Si_6 \cdot 0.5C_{36}H_{90}Li_6O_6Si_6$	$C_{36}H_{90}Li_6O_6Si_6$	$C_{36}H_{96}Li_4N_4O_4Si_8$	$C_{22}H_{54}N_2O_2Si_4$	$C_{26}H_{66}AlLiN_2O_2Si_4$
fw	802.46 + 0.5 × 829.26	829.26	901.65	491.03	585.09
color of crystal	colorless	colorless	colorless	colorless	yellow
temp (K)	133(2)	133(2)	150(2)	150(2)	133(2)
cryst size (mm)	0.8 × 0.8 × 0.8	0.8 × 0.8 × 0.4	1.0 × 1.0 × 0.4	1.0 × 0.4 × 0.2	0.7 × 0.7 × 0.4
cryst syst	monoclinic	monoclinic	tetragonal	Orthorhombic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{4}$	*Pbca*	$P2_1/n$
a (Å)	28.683(10)	21.674(4)	18.046(3)	11.344(2)	11.287(2)
b (Å)	12.691(5)	18.964(4)	18.046(3)	13.663(3)	23.893(5)
c (Å)	22.890(11)	13.195(3)	9.189(2)	19.862(4)	14.038(3)
α (deg)	90	90	90	90	90
β (deg)	99.83(20)	94.09(3)	90	90	99.44(3)
γ (deg)	90	90	90	90	90
cell vol (Å^3)	8210(60)	5410(2)	2992.4(8)	3078.5(11)	3734.5(13)
Z	4	4	2	4	4
ρ_c (mg mm^{-3})	0.985	1.018	1.001	1.059	1.041
μ (mm^{-1})	0.183	0.188	0.212	0.212	0.205
F(000)	2688	1824	992	1088	1296
2θ range (deg)	4.06−49.86	3.76−45.00	7.14−45.06	7.18−49.98	5.06−50.06
no. of data measd	97909, 13531	39579, 7035	2876, 2582	5218, 2704	48333, 6591
unique	($R_{int} = 0.0339$)	($R_{int} = 0.1134$)	($R_{int} = 0.0456$)	($R_{int} = 0.0284$)	($R_{int} = 0.0856$)
R,[a] wR2[b] ($I > 2\sigma(I)$)	0.0444, 0.0982	0.0724, 0.1813	0.0560, 0.1318	0.0343, 0.0892	0.0459, 0.1066
R, wR2 (all data)	0.0539, 0.1032	0.1036, 0.2002	0.0698, 0.1474	0.0434, 0.0987	0.0737, 0.1148
goodness of fit, S [c]	1.118	0.990	1.045	1.052	1.030
no. of refined params	748	517	269	145	348
largest diff peak/ hole (e Å^{-3})	0.562/−0.286	0.753/−0.338	0.342/−0.250	0.265/−0.275	0.652/−0.280

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [c] $S = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum(n - p)]\}^{1/2}$.

heated to reflux for 1 h. After removal of the solvents in vacuo (10^{-2} Torr) and recrystallization of the residue from toluene the crystalline compounds **4a** (2.5 g, 9.4 mmol, 47% yield), **5** (2.1 g, 16 mmol, 77% yield), and **6** (2.3 g, 10 mmol, 50% yield) were obtained.

***N*,*N*-Bis(*tert*-butyldimethylsilyl)-*O*-lithiumhydroxylamide (4a).** No NMR data are available.

Lithium-*tert*-Butyldimethylsilanolate (5). ^{1}H NMR (C_6D_6/THF): δ 0.04 [s, Si(CH_3)$_2$, 6H], 0.9 [s, SiC(CH_3)$_3$, 9H]. ^{7}Li NMR (C_6D_6/THF): δ 0.2 [s, SiOLi]. ^{13}C NMR (C_6D_6/THF): δ 3.4 [s, Si(CH$_3$)$_2$], 18.1 [s, SiC(CH$_3$)$_3$], 25.8 [s, SiC(CH$_3$)$_3$]. ^{29}Si NMR (C_6D_6/THF): δ 14.7 (s, SiO).

***N*-*tert*-Butyldimethylsilyl-*N*-trimethylsilyl-*O*-lithiumhydroxylamide (6).** $C_9H_{24}LiNOSi_2$ (225.41): ^{7}Li NMR (hexane/C_6D_6): δ −0.2. ^{29}Si NMR (hexane/C_6D_6): δ −0.7 [d, NSi(CH$_3$)$_3$, $^2J_{SiSi} = 7.4$ Hz], 7.4 [d, NSi(CH$_3$)$_2$C(CH$_3$)$_3$, $^2J_{SiSi} =$ 7.4 Hz).

Preparation of Compounds 7 and 8. A solution of 5.3 g of **3** (0.02 mol) in 50 mL of *n*-hexane was cooled to −78 °C, and 1 equiv of *n*-butyllithium (0.02 mol, 15% in *n*-hexane) was added slowly. For **8** 2.2 g of difluorodimethylsilane (0.022 mol) was also added slowly. The mixture was stirred and warmed to room temperature overnight. The formation of the products was monitored by ^{19}F NMR spectroscopy. **7** was isolated (4.4 g, 9.0 mmol, 90% yield) after removing the solvents in vacuo and recrystallization from *n*-hexane (mp 175 °C). **8** was isolated (6.6 g, 19 mmol, 96% yield) by distillation (bp 49 °C/0.1 Torr) after the crude product was separated from LiF by condensing the product and the solvents into a cooled trap in vacuo.

1,4-Bis(*tert*-butyldimethylsilyl)-3,6-di(*tert*-butyl)-3,6-dimethyl-1,4-diaza-2,5-dioxa-3,6-disilacyclohexane (7). $C_{22}H_{54}N_2O_2Si_4$ (491.03): ^{1}H NMR (CDCl$_3$): δ 0.1 (s, NSiCH$_3$, 3H), 0.1 (s, NSiCH$_3$, 3H), 0.3 (s, OSiCH$_3$, 3H), 0.9 [s, NSiC(CH$_3$)$_3$, 9H], 1.0 [s, OSiC(CH$_3$)$_3$, 9H]. ^{13}C NMR (CDCl$_3$): δ −6.5 (s, OSiCH$_3$), −3.9 (s, NSiCH$_3$), −3.1 (s, NSiCH$_3$), 19.0 [s, OSiC(CH$_3$)$_3$], 19.8 [s, NSiC(CH$_3$)$_3$], 26.7 [s, OSiC(CH$_3$)$_3$], 27.4 [s, NSiC(CH$_3$)$_3$]. ^{29}Si NMR (CDCl$_3$): δ 3.0 (d, OSiN, $^2J_{SiSi} =$ 5.4 Hz, 8.5 (d, NSi, $^2J_{SiSi} = 5.4$ Hz). MS (EI) *m/z* [%]: 491 (38) [M$^+$]. Anal. Calcd: C, 53.81; H, 11.08. Found: C, 53.71; H, 10.99.

***N*-*tert*-Butyldimethylsilyl-*N*-*tert*-butylfluoromethylsilyl-*O*-dimethylfluorosilylhydroxylamine (8).** $C_{13}H_{33}F_2NOSi_3$ (341.66): ^{1}H NMR (CDCl$_3$): δ 0.1 (d, NSiCH$_3$, $^5J_{HF} =$ 1.1 Hz, 3H), 0.1 (s, NSiCH$_3$, 3H), 0.2 (d, NSiFCH$_3$, $^3J_{HF} = 6.8$ Hz, 3H), 0.3 [dd, OSiF(CH$_3$)$_2$, $^3J_{HF} = 6.3$ Hz, $^5J_{HF} = 0.9$ Hz, 3H], 0.3 [dd, OSiF(CH$_3$)$_2$, $^3J_{HF} = 6.3$ Hz, $^6J_{HF} = 1.8$ Hz, 3H], 1.0 [s, NSiC(CH$_3$)$_3$, 9H], 1.0 [d, NSiFC(CH$_3$)$_3$, $^4J_{HF} = 1.1$ Hz, 9H]. ^{13}C NMR (CDCl$_3$): δ −5.0 (dd, NSiFCH$_3$, $^2J_{CF} = 13.8$ Hz, $^5J_{CF} = 1.1$ Hz), −4.5 (dd, NSiCH$_3$, $^4J_{CF} = 2.8$ Hz, $^5J_{CF} = 0.8$ Hz), −3.4 (dd, NSiCH$_3$, $^4J_{CF} = 1.9$ Hz, $^5J_{CF} = 0.5$ Hz), −2.8 (dd, OSiFCH$_3$, $^2J_{CF} = 18.7$ Hz, $^5J_{CF} = 4.1$ Hz), −2.6 (dd, OSiFCH$_3$, $^2J_{CF} = 19.9$ Hz, $^5J_{CF} = 2.2$ Hz), 19.5 [d, NSiC(CH$_3$)$_3$, $^4J_{CF} = 0.8$ Hz], 19.8 [d, NSiFC(CH$_3$)$_3$, $^2J_{CF} = 19.3$ Hz], 26.8 [dd, NSiFC(CH$_3$)$_3$, $^3J_{CF} = 1.1$ Hz, $^6J_{CF} = 0.5$ Hz], 27.5 [dd, NSiC(CH$_3$)$_3$, $^5J_{CF} = 1.0$ Hz, $^6J_{CF} = 0.5$ Hz]. ^{19}F NMR (CDCl$_3$): δ 10.0 (d, NSiF, $^5J_{FF} = 4.4$ Hz), 36.9 (d, OSiF, $^5J_{FF} = 4.4$ Hz). ^{29}Si NMR (CDCl$_3$): δ 6.7 (dd, NSiF, $^1J_{SiF} = 294.0$ Hz, $^4J_{SiF} =$ 0.9 Hz, $^2J_{SiSi} = 5.6$ Hz), 10.2 (dd, OSiF, $^1J_{SiF} = 292.2$ Hz, $^4J_{SiF}$ = 0.6 Hz), 12.2 (s, NSi, $^2J_{SiSi} = 5.6$ Hz]. MS (EI) *m/z* [%]: 299 (2) [M$^+$], 284 (2) [M$^+$ − Me]. Anal. Calcd: C, 45.70; H, 9.73. Found: C, 45.51; H, 9.52.

Preparation of 9, 10, and 11. A solution of 4.5 g of **6** (0.02 mol) in 30 mL of *n*-hexane and 50 of mL THF was cooled to −50 °C. After that the corresponding fluorosilanes were added slowly: for **9** 2.2 g of difluorodimethylsilane (0.022 mol) and for **10** and **11** methyltrifluorosilane (**10**: 0.02 mol, 2 g; **11**: 0.01 mol, 1 g). The mixture was warmed to room temperature within 6 h and heated to reflux for 0.5 h. The crude product was separated from LiF by condensing the product and the solvents into a cooled trap in vacuo. The products (**9**: 5.7 g, 19 mmol, 96% yield; **10**: 4.5 g, 15 mmol, 75% yield; **11**: 8.0 g, 16 mmol, 80% yield) were purified by distillation (**9**: bp 41 °C/0.075 Torr; **10**: bp 52 °C/0.03 Torr; **11**: bp 110 °C/0.03 Torr).

***N*-*tert*-Butyldimethylsilyl-*N*-trimethylsilyl-*O*-dimethylfluorsilylhydroxylamine (9).** $C_{11}H_{30}FNOSi_3$ (295.66): ^{1}H NMR (CDCl$_3$): δ 0.1 [d, NSiCH$_3$, $^6J_{HF} = 0.1$ Hz, 6H], 0.2 [d, NSiCH$_3$, $^6J_{HF} = 0.4$ Hz, 9H], 0.3 [d, OSiFCH$_3$, $^3J_{HF} = 6.2$ Hz, 6H], 0.9 [s, NSiC(CH$_3$)$_2$, 9H]. ^{13}C NMR (CDCl$_3$): δ −3.6 [d, NSiCH$_3$, $^5J_{CF} = 1.3$ Hz], −2.8 [d, OSiCH$_3$, $^2J_{CF} = 19.7$ Hz], −0.8 [d, NSiCH$_3$, $^5J_{CF} = 1.5$ Hz], 19.6 [s, NSiC(CH$_3$)$_3$], 27.5 [s,

$NSiC(CH_3)_3$]. ^{19}F NMR ($CDCl_3$): δ 38.7 [sept, OSiF, $^3J_{HF} = 6.2$ Hz]. ^{29}Si NMR ($CDCl_3$): δ 8.3 [s, $NSi(CH_3)_3$], 9.5 [d, OSiF, $^1J_{SiF} = 293.2$ Hz], 11.8 [d, $NSiC(CH_3)_3$, $^4J_{SiF} = 0.7$ Hz]. MS (EI) m/z [%]: 295 (5%) [M^+]. Anal. Calcd: C, 44.69; H, 10.23. Found: C, 44.48; H, 10.03.

***N*-*tert*-Butyldimethylsilyl-*N*-trimethylsilyl-*O*-methyldifluorsilylhydroxylamine (10).** $C_{10}H_{27}F_2NOSi_3$ (299.59): ^1H NMR ($CDCl_3$): δ 0.1 [s, $SiMe_2$,6H], 0.2 [s, $SiMe_3$, 9H], 0.4 (t, F_2SiMe, $^3J_{HF} = 2.2$ Hz, 9H], 0.9 [s, ^tBu, 9H]. ^{13}C NMR ($CDCl_3$): δ −8.3 [t, F_2SiC, $^2J_{CF} = 22.7$ Hz], −3.9 [t, SiC_2, $^5J_{CF} = 1.2$ Hz], 0.5 [t, SiC_3, $^5J_{CF} = 0.9$ Hz], 19.5 [s, $SiCC_3$], 27.3 [s, $SiCC_3$]. ^{19}F NMR ($CDCl_3$): δ 31.8 [s, F_2Si]. ^{29}Si NMR ($CDCl_3$): δ −45.9 [t, F_2Si, $J_{SiF} = 275.6$ Hz], 10.0 [s, $SiMe_3$], 13.7 [s, $SiMe_2$]. MS (EI) m/z [%]: 341 (2) [M^+]. Anal. Calcd: C, 40.09; H, 9.08; Found: C, 40.49; H, 9.31.

Bis(*N*-*tert*-butyldimethylsilyl-*N*-trimethylsilylhydroxylamine)-*O*,*O*-methylfluorosilane (11). $C_{19}H_{51}FN_2O_2Si_5$ (499.06): ^1H NMR ($CDCl_3$): δ 0.1 [s, $SiMe_2$, 6H], 0.1 [s, $SiMe_2$, 6H], 0.2 [s, $SiMe_3$, 18H], 0.4 [d, FSiMe, $^3J_{HF} = 4.4$ Hz, 9H], 0.9 [s, ^tBu, 18H]. ^{13}C NMR ($CDCl_3$): δ −5.7 [d, FSiC, $^2J_{CF} = 21.8$ Hz], −3.9 [d, SiC_2, $^5J_{CF} = 1.5$ Hz], − 3.8 [d, SiC_2, $^5J_{CF} = 0.7$ Hz], 0.6 [d, SiC_3, $^5J_{CF} = 0.9$ Hz], 19.6 [s, $SiCC_3$], 27.4 [s, $SiCC_3$]. ^{19}F NMR ($CDCl_3$): δ 33.8 [s, SiF]. ^{29}Si NMR ($CDCl_3$): δ −31.8 [d, SiF, $J_{SiF} = 281.6$ Hz], 8.0 [s, SiC_3], 13.0 [s, SiC_2]. MS (EI) m/z [%]: 499 (10) [M^+]. Anal. Calcd: C, 45.73; H, 10.30. Found: C, 46.01; H, 10.51.

2,4-Bis-*N*,*N*-bis(*tert*-butyldimethylsilylhydroxylamide)-1-dimethylalano-3-lithio-2,4-dioxocyclobutane (12). A 2.6 g amount of *N*,*O*-bis(*tert*-butyldimethylsilyl)hydroxylamine (0.01 mol) was solved in *n*-hexane (20 mL), cooled to 0 °C, and metalated with 1 equiv of *n*-butyllithium (0.01 mol, 15% in *n*-hexane). The mixture was heated to reflux for 1 h and after that cooled to −50 °C. Then a solution of 1.0 g of dimethylchloralane (0.01) in 20 mL of *n*-hexane was added slowly, and the reaction mixture was allowed to come to room temperature. After removal of the solvents in vacuo (10^{-2} Torr) and recrystallization of the residue from toluene the crystalline compound **12** (4.7 g, 8.0 mmol, 80% yield) was obtained. $C_{26}H_{66}AlLiN_2O_2Si_4$ (584.42): ^1H NMR (toluene/C_6D_6): δ −0.7 [s, $AlCH_3$, 6H], 0.1 [s, $SiCH_3$, 24H], 0.9 [s, $SiC(CH_3)_3$, 36H]. ^{13}C NMR ($CDCl_3$): δ −1.7 [br s, $AlCH_3$], −6.5 [s, $SiCH_3$], 21.4 [s, $SiC(CH_3)_3$], 26.2 [s, $SiC(CH_3)_3$]. ^{29}Si NMR (toluene/C_6D_6): δ 9.0 [s, Si_2NO]. MS (EI) m/z [%]: (3%) [M^+]; (FI) m/z [%] 584 (100%) [M^+].

Crystal Structure Solution and Refinement for 4, 5, 6, 7, and 12 (Table 1). Data for structures **4**, **5**, and **12** were collected on a Stoe-Siemens-Huber four-circle diffractometer with a Siemens CCD area detector by use of φ and ω scans. Data for structures **6** and **7** were collected on a STOE AED2 four-circle diffractometer with θ/ω-scan profile fitting. A semiempirical absorption correction was applied. All structures were solved by direct methods (SHELXS-96)[15] and refined against F^2 using SHELXL-97.[16] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed.

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Supporting Information Available: Tables of crystal data, complete fractional coordinates, bond lengths and angles, and anisotropic displacement parameters of the structures **4**−**7** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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