

Intramolecular rearrangement of organosilyl groups between oxygen and nitrogen in aminosiloxanes: A joint experimental–theoretical study

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Abstract

Lithium amino-di-*tert*-butysilanolate reacts with halosilanes to give 1-silylamino-1,3-siloxanes (**1–4**). The tetrakis(1-silylamino)siloxane **4** thermally condenses yielding a spirocyclic six-membered ring (**5**) and NH₃. Lithium salts of amino-disiloxanes form silylamino-silanolates or amido-disiloxanes. The first includes a 1,3-silyl group migration from the oxygen to the nitrogen atom. The energies of the isomeric lithium salts of model compounds are calculated. Exemplary crystal structures are presented.

(SiOSiN)-four- or eight-membered rings (**6,7**) are thermally obtained by LiF-elimination from fluoro containing salts. In further reactions of lithiated amino-disiloxanes with halosilanes isomeric 1-silylamino-1,3-disiloxanes can be obtained (**15,16**). The 1,3-silyl group migration can sterically (**9**) or electronically (**10–14**) be prevented.

The most stable lithium salts of 1-silylamino-1,3-disiloxanes form amides. This explains that in further reactions with halosilanes, the new ligand is bonded to the nitrogen atom (**23–25**). In results of crystal structure determinations new lithium-1-fluorosilylamino-1,3-disiloxanes (**19–21**) are presented. **19** crystallizes as tricyclic, **20** as an unknown pentacyclic, and **21** as monomeric compound. In **21**, the shortest Si–N bond length (157.9 pm) with four coordinate silicon is found.

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1. Introduction

In contrast to carbon chemistry, compounds with two or three H-acidic electronegative groups like NH₂ or OH at one silicon atom can be stabilized kinetically [1–5]. In the 1980s, the first aminosilanol, (Me₃C)₂Si(NH₂)OH [6], that crystallizes in ladder-like chains via H-bridges could be prepared [7]. Its alkaline metal derivatives form an aminosilanolate anion that is 15.9 kcal mol⁻¹ more stable than the isoelectronic amidosilanol anion.



The lithium salt was characterized as tetramer,

forming a Li–O cubane [6], while the sodium and potassium salts are described as hexagonal prisms [7]. These structural elements are stable even in the gas phase [6,7].

In the present work, we report on recent experimental results and rationalize them by means of quantum chemical calculations. All theoretical results given in this work were obtained from density-functional calculations employing the variant B3LYP and the large 6-311+G(2d,p) basis set.

2. Results and discussion

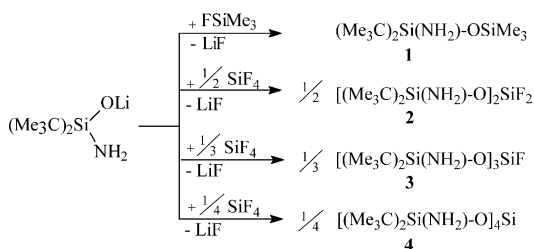
2.1. 1-Aminosiloxanes

The stability of the aminosilanolate salts explains the position of substituents, e.g. in reactions with halosi-

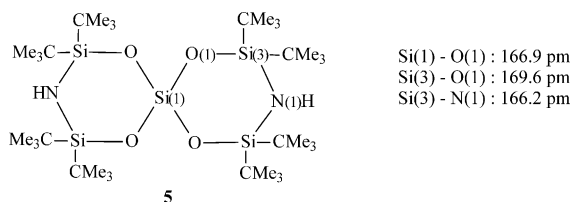
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lanes, numerous mono-, bis-, tris- and tetrakis-1-amino-siloxanes are formed [7–10]. For example:



The tetrakis-(1-amino-siloxane) (**4**) condenses ther-

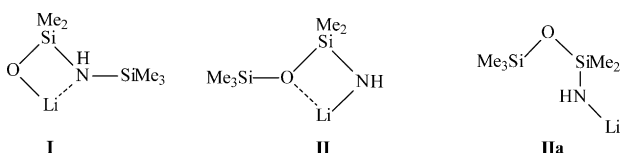


mally yielding a spirocyclic six-membered ring and NH_3 [11].

2.2. Lithium-1-amido-1,3-disiloxanes and 1,3-disilylamino-1-olates

Starting with 1-amino-siloxanes, further substitutions turn out to be more complicated. Lithium salts of these compounds form, depending on the properties and bulkiness of the silyl groups, 1,3-disilylamino-1-olates or the less stable 1-amido-1,3-disiloxanes [7–11]. The second case includes a 1,3-silyl group migration from the oxygen to the nitrogen atom, as is well-known from silylhydroxylamine chemistry [12].

In order to understand the driving force of this isomerization, we calculated the energies of the isomeric lithium salts of the model compounds **I** and **II** and found that **I** is $0.7 \text{ kcal mol}^{-1}$ more stable than **II** (Fig. 1).



Without an $\text{O} \rightarrow \text{Li}$ donor bond (**IIa**) is even $9.0 \text{ kcal mol}^{-1}$ less stable than **I**. The $\text{Li}-\text{O}$ contact in **I** shortens the $\text{Me}_2\text{Si}-\text{O}$ bond (**I**: $\text{Me}_2\text{Si}-\text{O} = 159.5 \text{ pm}$; **II**: $\text{Me}_2\text{Si}-\text{O} = 192.8 \text{ pm}$) and lengthens the $\text{Me}_2\text{Si}-\text{N}$ bond (**I**: $\text{Me}_2\text{Si}-\text{N} = 184.1 \text{ pm}$; **II**: $\text{Me}_2\text{Si}-\text{N} = 179.8 \text{ pm}$).

The small energetic difference between **I** and **II** explains the formation of structural isomers in reactions with halosilanes.

In fluorine-containing compounds, lithium often is coordinated to the fluorine atom. The most stable isomer of the model compound $\text{MeSiF}_2\text{-NH-Si-Me}_2\text{OLi}$ forms a six-membered ($\text{Li}-\text{O}-\text{Si}-\text{N}-\text{Si}-\text{F}$) ring system with $\text{Li} \cdots \text{F}$ contact (**III**).

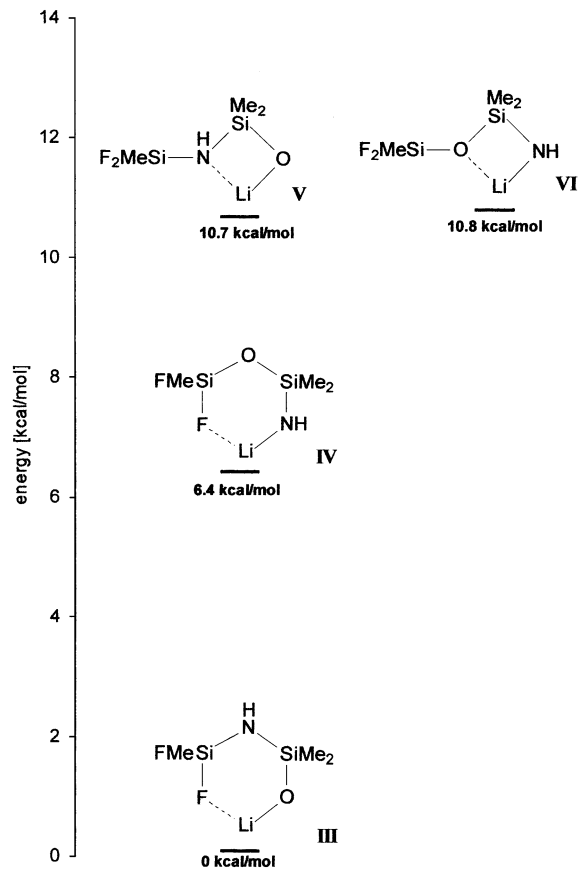
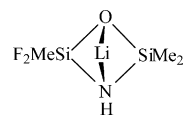


Diagram 1. Relative energies [kcal/mol] of isomeric lithium salts **III**–**VI**.

Regarding to Diagram (1) lithium salts of aminodisiloxanes are usually isolated as 1,3-disilylamino-1-olates (**III**). The isomeric 1-amido-1,3-disiloxane (**IV**) can be formed via the following transition state,



which affords $20.8 \text{ kcal mol}^{-1}$.

The 1,3-($\text{O} \rightarrow \text{N}$)-silyl group migration can be suppressed by bulky groups and 1-amido-1,3-disiloxanes (**IV**) are stabilized kinetically, e.g. the lithium salt of 1-amino-1,1-di-*tert*-butyl-3-fluoro-3,3-bis(isopropyltrimethylsilyl)amine crystallizes as type **IV** and forms the hitherto unknown six-membered ($\text{F}-\text{Si}-\text{O}-\text{Si}-\text{N}-\text{Li}$) ring as a dimer via the $\text{Li}-\text{N}$ bond (Fig. 2) [7].

Lithium salts of types **V** and **IV** could not be detected so far.

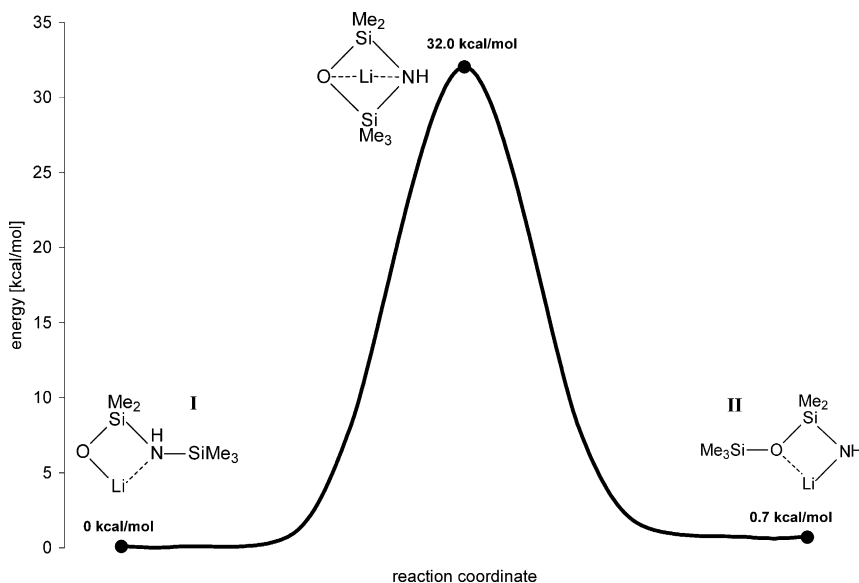


Fig. 1. Relative energies (kcal mol^{-1}) of isomeric lithium salts I–II.

3. (SiOSiNH)-eight-and-four-membered rings

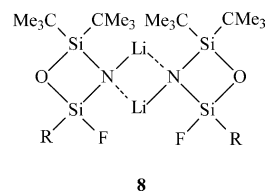
3.1. 1,5-Diaza-3,7-dioxa-2,4,6,8-tetrasilacyclo-octanes

Experimental results show that LiF elimination from lithiated 1-fluoro-1,3-disilazane-1-olates (type **III**) leads to the formation of eight-membered (SiOSiN)₂ rings [9,11], e.g.

The structure determinations of known eight-membered (Si–O–Si–NH)₂ rings and also of **6** show mostly effectively planar rings. Such backbones in molecular structures are rare. Particularly unusual features of these compounds are the virtually linear Si–O–Si units in the ring (Fig. 3).

3.2. 1-Aza-3-oxa-2,4-disilacyclobutanes

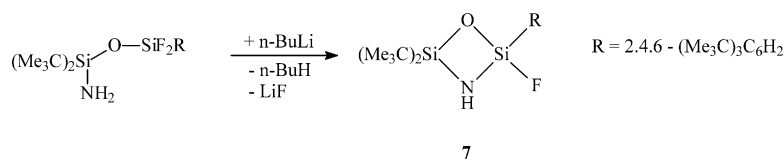
Lithium salts of type **IV** are kinetically stabilized. LiF elimination of these salts leads to the formation of four-membered (Si–O–Si–NH) rings, e.g.



With halosilanes it is possible to substitute the ring by silyl groups at the nitrogen atom.

4. 1-Silylamino-1,3-disiloxanes

X-ray structures and calculations of lithium salts of amino-1,3-disiloxanes, types **I** and **II** or types **III** and **IV** explain that in further reactions of these compounds with halosilanes isomeric 1-silylamino-1,3-disiloxanes can be obtained [8,9,11]. In reactions of **I** or **III** with halosilanes, the new organosilicon group is bonded to the oxygen, and in the reactions of **II** and **IV** to the nitrogen atom.

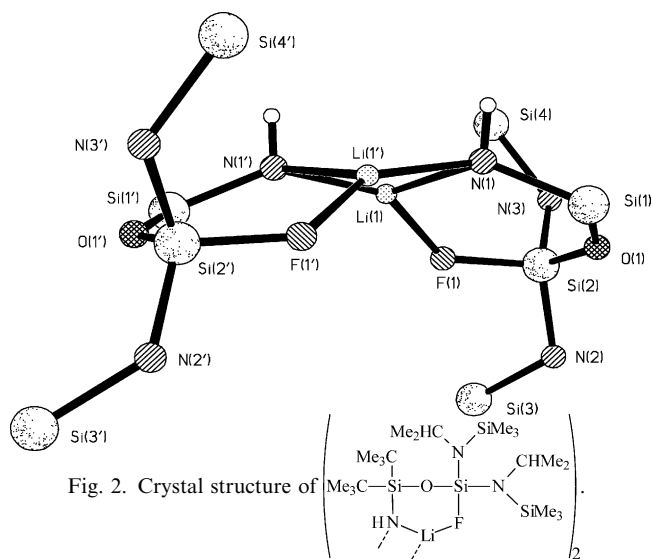


The lithium salt of **7** (**8**) crystallizes as a dimer forming a four-membered (Li–N)₂ ring system [10]. The Si···Si nonbonding distance in the (Si–O–Si–N) ring amounts to only 237.2 pm, which is in the range of a typical Si–Si single bond.

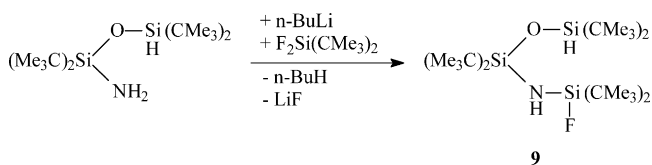
4.1. Retention of the siloxane unit

4.1.1. Kinetically prevented rearrangement

Bulky groups kinetically prevent the silyl group migration from the oxygen to the nitrogen atom and

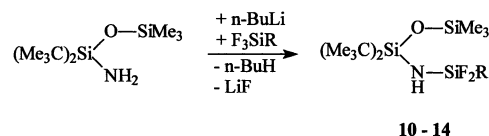
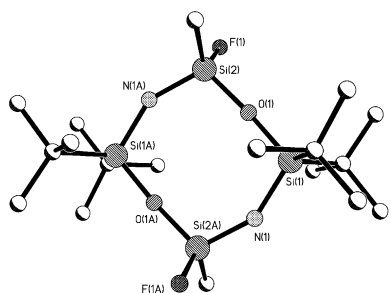
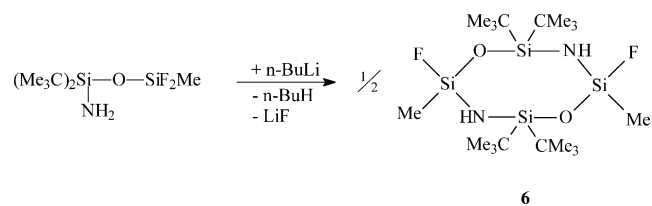


hence the isomerization in the lithiation reaction (type **II**), e.g.



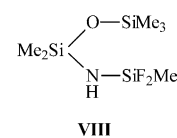
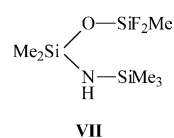
4.1.2. Thermodynamically prevented rearrangement

Starting with lithium salts of 1-amino-1,1,3,3,3-pentaorganyl-1,3-disiloxanes (type **I**), reactions with trifluorosilanes lead only to 1-difluorosilylamino-1,3-disiloxanes with retention of the siloxane unit.



R	10	11	12	13	14
	Me	CMe ₃	Ph	N(SiMe ₃) ₂	2.4.6-(Me ₃ C) ₃ C ₆ H ₂

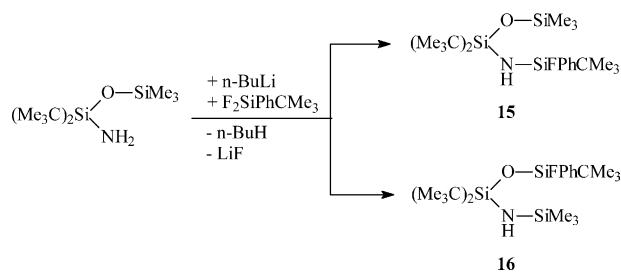
The easy formation of *N*-difluorosilylamino-1,3-disiloxanes with retention of the siloxane unit promoted us to study the relative energies of model compounds **VII** and **VIII**.



We found that **VIII** is 0.8 kcal mol⁻¹ more stable than **VII**. Though this is not very much, we could not isolate isomeric compounds of **10–14**.

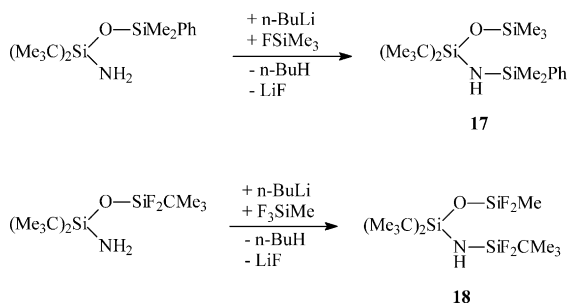
4.2. Formation of isomeric silylamino-1,3-disiloxanes

In the absence of strong steric or electronic restraints, the lithium salts of 1-amino-1,3-pentaorganyl disiloxanes (types **I** and **II**) react with halosilanes, e.g. F₂SiPhCMe₃ to give both isomeric silylamino-1,3-disiloxanes [8], e.g.



4.3. 1,3-O → N-silyl group migration—formation of the isomeric 1-silylamino-1,3-disiloxane

Only the rearranged isomer of 1-silylamino-1,3-disiloxane could be detected and obtained in reactions of halotriorganylsilanes with trifluoro(organyl)silanes with lithiated 1-amino-1,3-disiloxanes. Trifluoro(organyl)silanes react with the lithium salt of 1-amino-1,1-di-*tert*-butyl-3,3-difluoro-3-*tert*-butyl-1,3-disiloxane, e.g.



5. Crystal structure determinations of 1-difluorosilylamino-1,3-disiloxanes (**13**, **14**)

The retention of the siloxane unit in the reaction of 1-amino-1,3-disiloxanes with BuLi and trifluorosilanes could be proved by X-ray crystallography of compounds **13** and **14**. Compounds **13** and **14** crystallize from *n*-hexane as monomers in the monoclinic crystal system space groups $P2_1/c$ and $P2_1/n$, respectively. In both compounds, N···H- or F···H-donor bonds do not exist (Figs. 4 and 5).

Steric effects may be the reason for the wide angle at the oxygen atom.

Because of the electron-withdrawing effect of the fluorine atoms, the Si–N bond lengths in neighborhood to SiF₂ group are shorter than the others. The N atoms have a planar environment. The bulky groups at the siloxane unit are the reason for the large Si–O–Si angle (**13**: 172.37°, **14**: 177.17°).

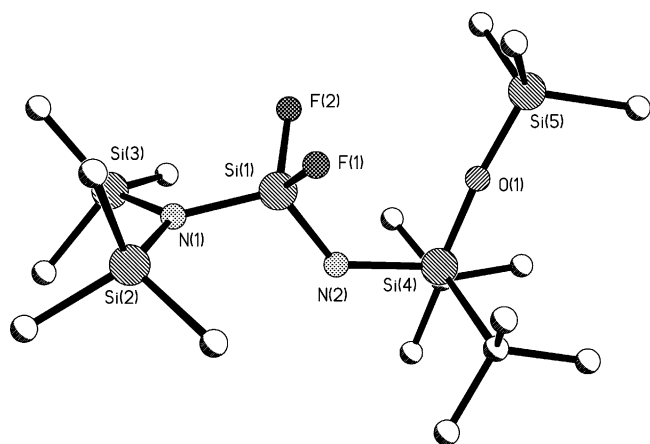


Fig. 4. Structure of **13**; selected bond lengths (pm) and angles (°): Si(1)–F(1), 156.26; Si(1)–N(1), 169.16; Si(1)–N(2), 166.62; N(1)–Si(2), 174.99; N(2)–Si(4), 174.00; Si(4)–O(1), 159.59; O(1)–Si(5), 161.56. Si(1)–N(2)–Si(4), 130.78; Si(4)–O(1)–Si(5), 172.37.

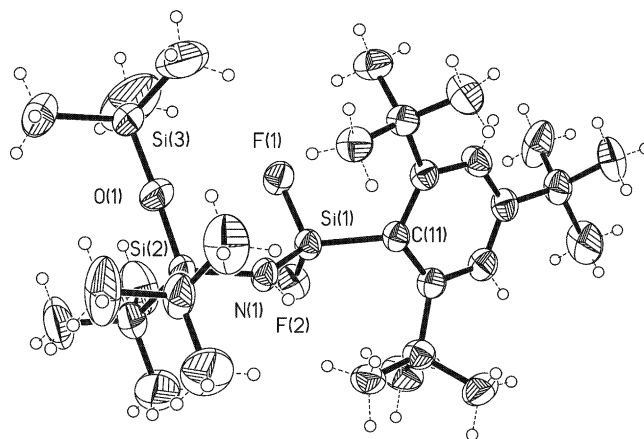


Fig. 5. Structure of **14**; selected bond lengths (pm) and angles (°): Si(1)–F(1), 158.6; Si(1)–N(1), 168.5; Si(2)–O(1), 160.6; Si(2)–N(1), 173.4. Si(1)–N(1)–Si(2), 135.8; Si(2)–O(1)–Si(3), 177.2.

6. Lithium-1-silylamido-1,3-disiloxanes

No silyl group migration is observed in reactions of lithiated 1-silylamino-1,3-disiloxanes.

Quantum chemical calculations of model compounds show that in this case the most stable lithium salt is 1-lithium-silylamido-1,3-disiloxane (**IX**), which is 19.2 kcal mol^{−1} more stable than the possible olate isomer **X**.

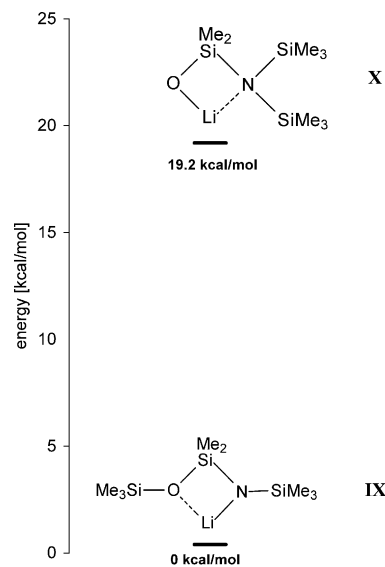


Diagram 2. Relative energies [kcal/mol] of isomeric lithium salts **IX**–**X**.

The N atom in **X** has an almost planar environment with a Li···N contact of 216.5 pm. The Li···N contact in **IX** is only 184.1 pm.

In lithium salts of fluoro-containing 1-silylamino-1,3-disiloxane, the hard Lewis acid lithium additionally binds the hard Lewis base fluorine (Diagram (4)). Again, the silyl group migration affords too much

energy, so that the new ligand will be bonded at the nitrogen atom.

The most stable lithium salt of the isomers **VII** and **VIII** forms the bicyclic compound **XI** of two four-membered rings connected by the Li–N unit.

Lithium is coordinated to the nitrogen, fluorine and oxygen atoms. The SiF₂Me group is bonded to the nitrogen atom and consequently the SiMe₃ group to the oxygen atom.

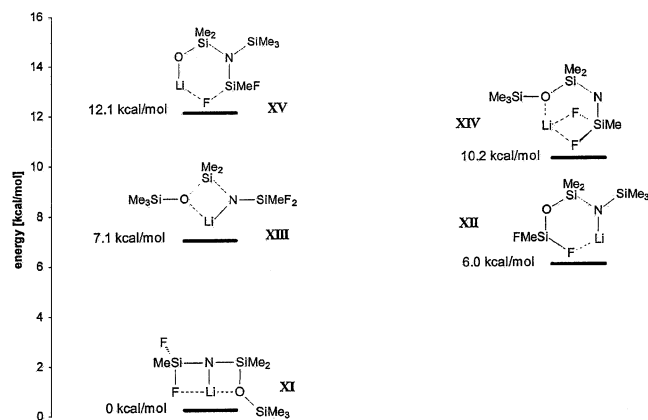


Diagram 3. Relative energies [kcal/mol] of isomeric lithium salts **XI–XV**.

The other four lithium salts form isomeric amides as six-membered rings (**XII**, **XIV**, **XV**) with Li···F contact or a four-membered ring (**XIII**) with Li···O contact. The two most unstable isomers are bis(silylamino)silanolates with O–Li···F₂ (**XIV**) and O–Li···F (**XV**) contacts, respectively. The stability of the lithium-silylamides (**XI–XV**) explains that in further reactions with halosilanes the new ligand will be bonded at the nitrogen atom.

7. Crystal structure determinations of lithium-1-silylamido-1,3-disiloxanes

In chemical experiments, lithium salts of types **XIII** and **XIV** could be isolated as dimers forming a tricyclic compound existing as two (SiOSiN) four-membered rings connected by (LiFSiN)₂ eight-membered ring **19** and a spiro-pentacyclic compound **20** existing as two (SiOSiN), two (SiF₂Li) four-membered rings which are connected by (LiNSiF₂)₂ eight-membered ring system.

7.1. Crystal structure of (Me₃Si)₂N–SiF₂–N–Li–Si(CMe₃)₂–O–SiMe₃ (**19**)

The lithium compound **19** is obtained in high yields from the reaction of **13** with *n*-BuLi, thus confirming the structure of **19**.

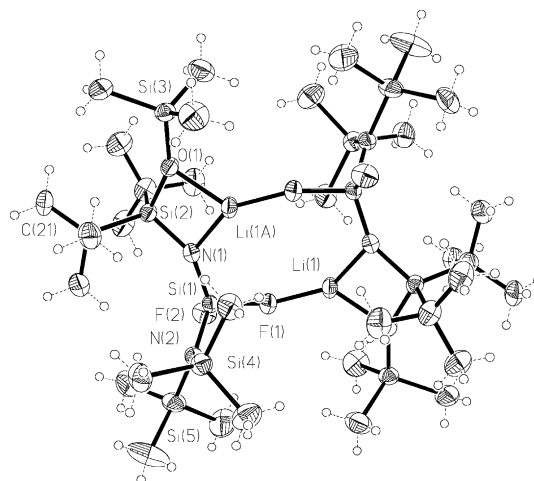
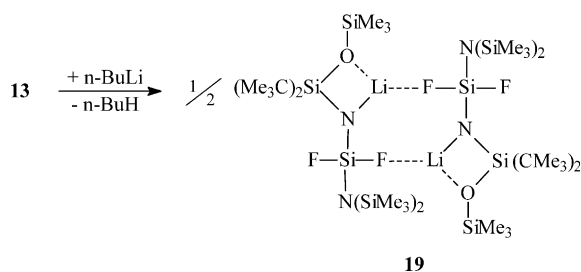


Fig. 6. Crystal structure of **19**; selected bond lengths (pm) and angles (°): Si(1)–F(2), 159.3; Si(1)–F(1), 164.7; Si(1)–N(1), 160.9; Si(1)–N(2), 171.1; Si(2)–N(2), 167.2; Si(2)–O(1), 168.7; Si(3)–O(1), 164.3; Li(1)–F(1), 181.8; Li(1)–N(1'), 193.2; Li(1)–O(1'), 200.7. Si(3)–O(1)–Si(2), 152.8; Si(1)–N(1)–Si(2), 145.8; Si(1)–F(1)–Li(1), 165.6.



The crystal structure of **19** (Fig. 6) shows some irregularities: one Si–F bond length is, because of the Li···F contact, 5.3 pm longer than the other. The Si(1)–N(1) bond length is in the range of a double bond length. The Li···O contact lengthens the Si(2)–O(1) bond. The Li–F contact is unusually short and even shorter than the Si–N bond. Lithium is only three-fold coordinated ($\Sigma^\circ\text{Li} = 349.7^\circ$).

7.2. Crystal structures of lithiated 2,4,6-(Me₃C)₃C₆H₂-SiF₂NHSi(CMe₃)₂-O-SiMe₃ (**20**, **21**)

Compound **20** (Fig. 7) crystallizes from *n*-hexane as a dimer in the space group $P\bar{1}$.

Lithium has a tetrahedral coordination: two fluorine, one oxygen and one amido contact.

This coordination of the lithium ion was unknown so far. The Si–F bonds are equal in length (164.7 pm).

Depending on the used solvents, **14** reacts with *n*-BuLi to give **20** or **21**. **20** is formed in *n*-hexane and **21** in thf.

The lithium salt of **14**, which is crystallized from thf (**21**) (Fig. 8), is monomeric.

Crystallization of **20** from thf (**21**) leads to a complete rupture of the Li···N contact. Lithium now has migrated to the stronger Lewis base fluorine. The result

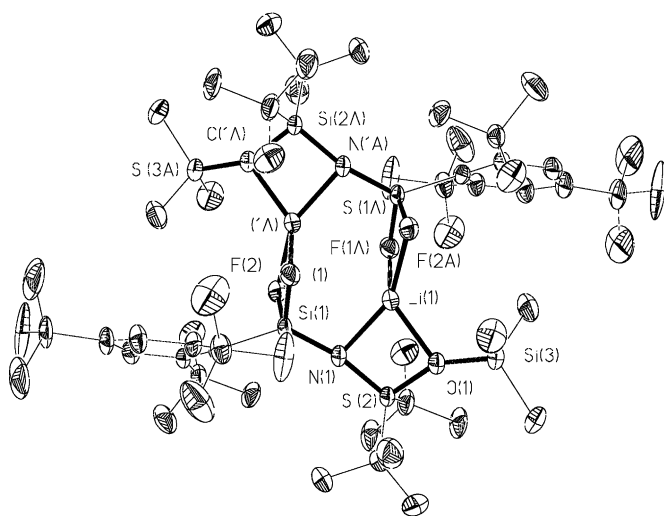
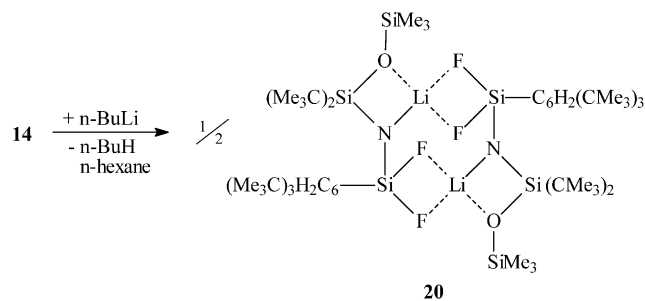


Fig. 7. Structure of **20**; selected bond lengths (pm) and angles ($^{\circ}$): Si(1)–N(1), 160.7; O(1)–Si(3), 164.2. F(1)–Li(1a)–F(2), 69.6.

is a short Li \cdots F bond (186.6 pm) and a long Si–F bond (165.9 pm). The Si–N bond is with 157.9 pm, a double

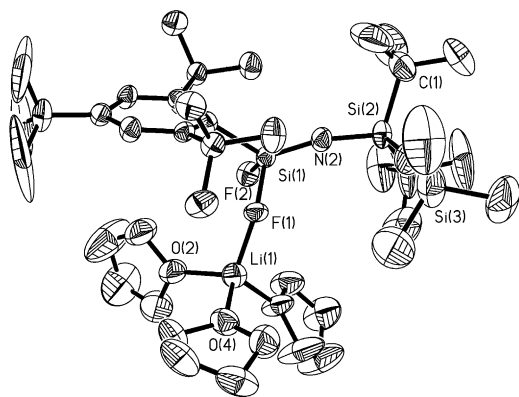
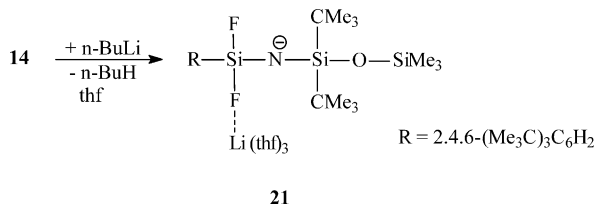


Fig. 8. Crystal structure of **21**; selected bond lengths (pm) and angles ($^{\circ}$): Si(1)–N(2), 157.9; Si(2)–N(2), 163.2; Si(1)–F(1), 165.9; Si(1)–F(2), 162.0. Li(1)–F(1), 186.6.

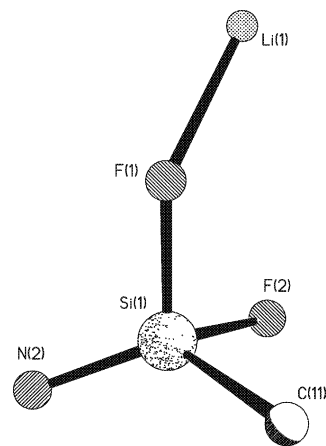


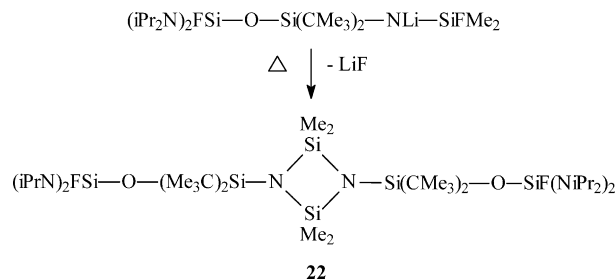
Fig. 9. Part of structure of **21**.

bond length, and the shortest Si–N bond with four coordinate silicons, as far as we know. The Si–N–Si angle of 167.2° is typical of an imine. Therefore, the molecule must be considered as Li–F adduct of an iminosilane, as shown in Fig. 9.

8. Reactions of lithium-1-fluorosilylamido-1,3-disiloxanes

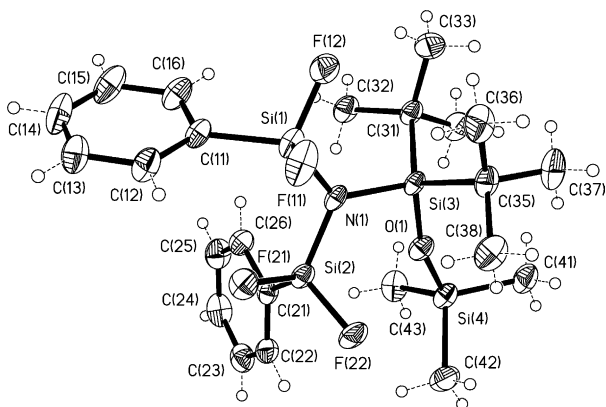
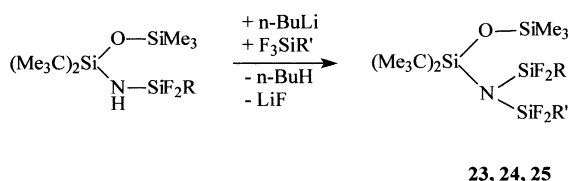
8.1. Formation of cyclodisilazanes

Lithium salts of 1-fluorosilylamido-1,3-disiloxanes (**XI**) thermally lose LiF with formation of siloxane-substituted cyclodisilazanes, e.g.



8.2. Synthesis of 1,1-bis(silylamino)-1,3-disiloxanes

Regarding these quantum chemical calculations and the experiments, it was to be expected that lithium salts of 1-silylamino-1,3-disiloxanes react with further fluorosilanes under retention of the configuration to give 1,1-bis(silylamino)-1,3-disiloxanes.

Fig. 10. Structure of **25**.

	23	24	25
R	Me	CMe ₃	Ph
R'	Me	Me	Ph

8.3. Crystal structure of 1,1-bis(difluorophenylsilyl)amino-1,3-disiloxane (**25**)

25 (Fig. 10) was characterized by X-ray crystallography. It crystallizes in the triclinic crystal system, space group $P\bar{1}$.

Because of the electron-withdrawing effect of the SiF₂ unit, there are two short Si–N bond lengths (170.4, 171.0 pm) and one stretched Si–N bond (179.2 pm). The nitrogen atom has a planar environment.

9. Summary

That aminosilanol and their alkaline salts react with halosilanes to aminosiloxanes has been proven by experiments and rationalized by quantum chemical calculations. In further reactions, the second silyl group may be bonded to the nitrogen or oxygen atoms. Normally, the aminosiloxanes form alkaline ions, silylamino-silanolates. This includes a 1,3-silyl group migration from the oxygen to the nitrogen atom. The

isomerization reaction can be sterically prevented by bulky groups and electronically by difluorosilyl groups as second substituent. LiF elimination from lithium salts of fluorofunctional amino-1,3-disiloxanes leads to four- or eight-membered (SiNSiO) ring systems. No silyl group migration occurs in reactions of 1-silylamino-1,3-disiloxanes with lithium organyls. Always the lithium-1-silylamido-1,3-disiloxane is formed. No isomerization occurs for that reason and a third silyl group will be bonded at the nitrogen atom.

The chemical behavior of aminosilanol is proved by experiments, crystal structure determinations and quantum chemical calculations.

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