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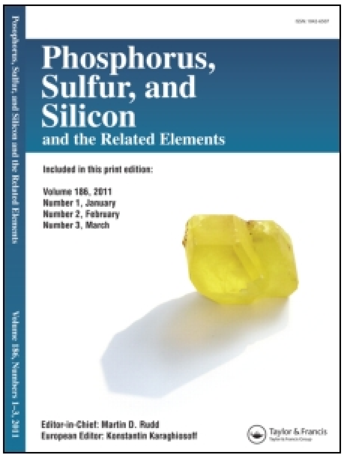

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STEPWISE SYNTHESIS OF S*i*OS*i*N-RINGS AND CAGES

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STEPWISE SYNTHESIS OF SiOSiN-RINGS AND CAGES

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Aminosilanols can be stabilized kinetically, e.g. $(Me_3C)_2Si(OH)NH_2$*, which crystallizes in ladder like chains via H-bridges. Its lithium salt was characterized as tetramer, forming a Li—O cubane, while the sodium and potassium salts are hexagonal prisms. The aminosilanol reacts with halosilanes to give amino-1,3-siloxanes. Lithium salts of amino-1,3-disiloxanes were isolated as amido-1,3-siloxanes or silylamino-silanolates. This includes a 1,3-silylgroup migration from the oxygen to nitrogen atom. Lithium salts of fluorofunctional amino-1,3-disiloxanes were characterized by X-ray. They crystallize as monomers or dimers and have unusual types of structures. LiF-elimination from such lithium salts leads to the formation of four- or eight-membered (SiNSiO)-ring systems. The chemical behavior of aminosilanols, the formation of structural isomers and of different ring systems are proved by experiments, crystal structures, and quantum chemical calculations.*

Keywords: Aminosiloxanes; lithium salts; (SiOSiN)-rings

In contrast to carbon chemistry, compounds with two or three H-acidic electronegative groups like NH_2 or OH at one silicon atom can be stabilized kinetically.[1–5] In the 1980s the first aminosilanol,[6] $(Me_3C)_2Si(NH_2)OH$, could be prepared. Its alkaline metal derivatives form an aminosilanolate-anion that is 15.9 kcal/mol more stable than the isoelectronic amidosilanol-anion. The lithium salt crystallizes as cubane, the sodium and potassium salts as prisms.[7]

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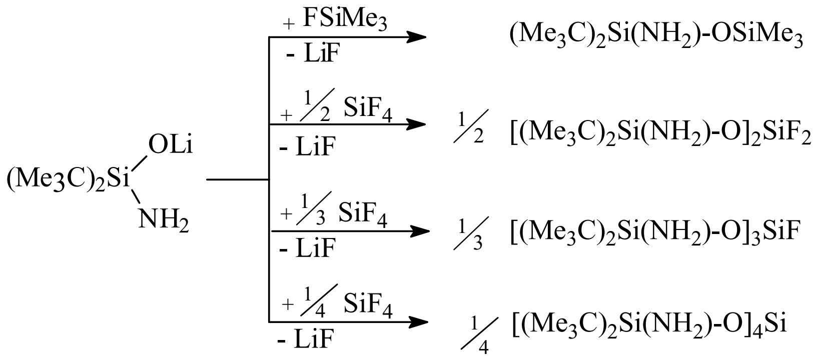
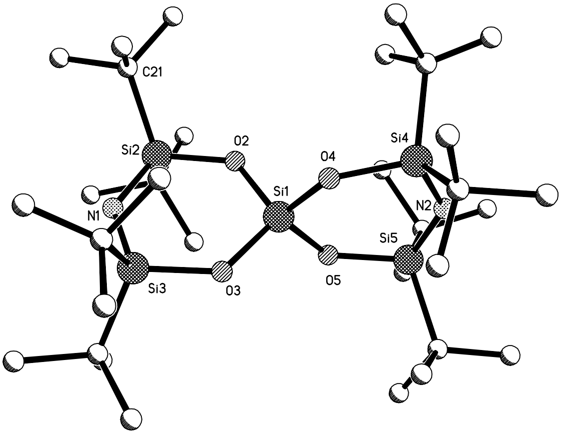


SCHEME 1

AMINOSILOXANES

The stability of the aminosilanolate salts explains the position of substituents, e.g., in reactions with halosilanes, numerous mono-, bis-, tris-, and tetrakis-aminosiloxanes are formed,[7–10] e.g., The tetrakis-aminosiloxane condenses thermally yielding a spirocyclic six-membered ring and NH_3.[11] One of the rings has a twist and the other a boat conformation. It is interesting that some Si—N-bonds are shorter than the Si—O-bonds (Figure 1).

Starting with the 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,

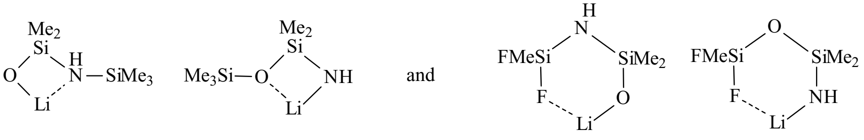


Si(1)-O(1):	166.9 pm
Si(3)-O(1):	169.6 pm
Si(3)-N(1):	166.2 pm

FIGURE 1 Molecular structure of a spinocyclic aminosiloxane.

1,3-disilazane-1-olates or the less stable 1-amido-1,3-disiloxanes. The first case includes a 1,3-silyl group migration from the oxygen to the nitrogen atom.

In order to understand the driving force of this isomerisation, we calculated the energies of the following isomeric lithium salts.

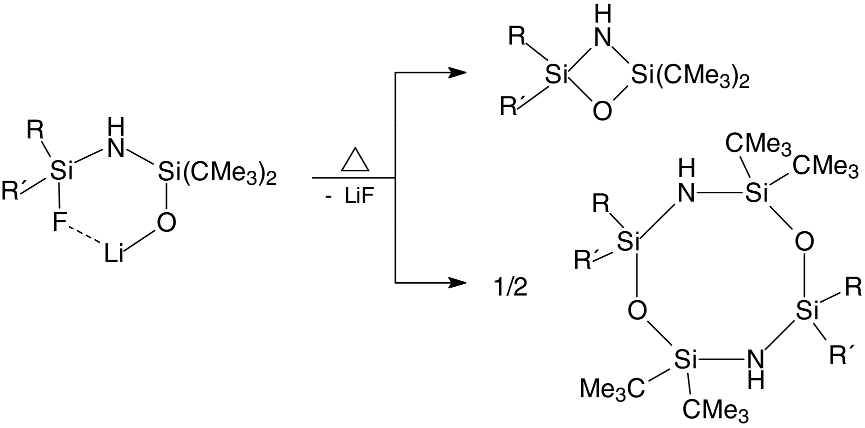


Silanolate **0 kcal/mol** | Silylamide **0.7 kcal/mol** | Silanolate **0 kcal/mol** | Silylamide **6.4 kcal/mol**

The silanolates are more stable the silylamides. Using fluorosilyl groups lithium is coordinated to the fluorine atom. In experiments isolated lithium salts normally crystallize as tetramers (cubanes) via the Li—O-bond and, if the silyl group migration is prevented sterically or thermodynamically as dimers (tricyclic compounds) via the Si—N-bond.

In reactions of the olate with halosilanes the new organosilicon group is bonded to the oxygen, in reaction of the amide to the nitrogen atom. LiF-elimination from the isomeric salts leads to the formation of four- or eight-membered (SiOSiN)-rings.

The lithium salt of the four-membered ring crystallizes as dimer via the Li· · ·N-bond. The transannular Si· · ·Si-distance is found to be only 237.2 pm.



SCHEME 2

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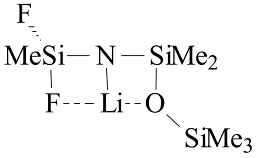
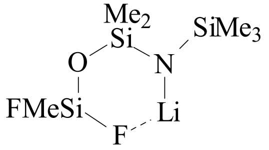
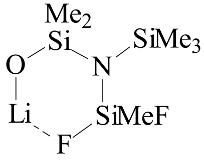
Chemical calculations and the experiments show that in contrast to lithium salts of 1-amino-1,3-siloxanes lithium salts of 1-silylamino-1,3-disiloxanes form stable amides and less stable olates, e.g.,



Silylamide
0 kcal/mol



Silylamide
6.0 kcal/mol



Silanolate
12.1 kcal/mol

We succeeded in the preparation of some lithium salts of 1-silylamino-1,3-disiloxanes. The lithium salts could be isolated as dimers. The first one forms a tricyclic compound existing as two (SiOSiN)-four-membered rings connected by an (LiFSiN)$_2$-eight-membered ring (Figure 2) and the second salt forms a spiro-pentacyclic compound existing as two (SiOSiN), two (SiF$_2$Li)-four-membered rings that are connected by an (LiNSiF$_2$)$_2$-eight-membered ring system (Figure 3).

The coordination of the lithium ion forming an LiF$_2$Si-ring was unknown so far. The structure of the lithium salt depends on the used solvents. Crystallization from thf leads to a complete rupture of the Li···N contact. Lithium now has migrated to the stronger Lewis base fluorine. The Si—N bond is with 157.9 pm a double bond length, as far as we know, the shortest Si—N bond with four coordinate silicons. The Si—N—Si angle of 167.2° is typical of an imine. The molecule must be considered as an Li—F adduct of an iminosilane (Figure 4).

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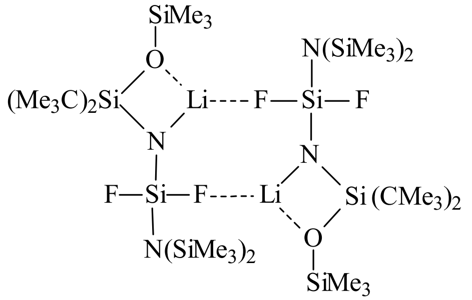
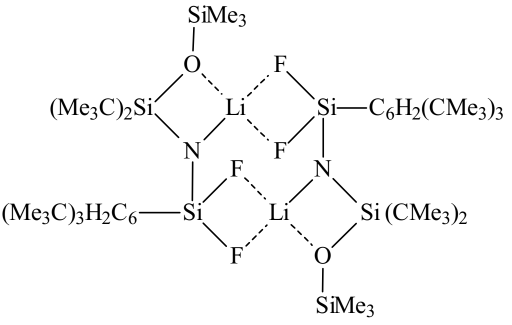


Si – F :	159.3 pm
Si – F(Li) :	164.7 pm
FSi – N(Li) :	160.9 pm
FSi – N(SiMe$_3$) :	171.1 pm

FIGURE 2 Lithioaminosiloxane cluster with two four membered rings connected by an eight membered ring.



Si – F :	164.8 pm
F_2Si – N :	160.7 pm
F – Li :	200.6 pm
N – Li :	204.5 pm
F - Li - F:	69.6°
Σ° N :	359.7°

FIGURE 3 Spinopentacyclic lithioaminosiloxane.

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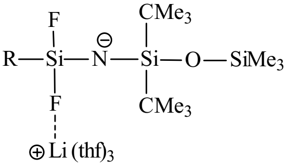

$$R{-}\overset{F}{\underset{F}{Si}}{-}\overset{\ominus}{N}{-}\overset{CMe_3}{\underset{CMe_3}{Si}}{-}O{-}SiMe_3 \quad \oplus Li(thf)_3$$

$R = 2.4.6\text{-}(Me_3C)_3C_6H_2$

Si(1) – N(2) :	157.9 pm
Si(3) – O(1) :	159.6 pm
Si(2) – N(2) :	163.2 pm
Si(2) – O(1) :	165.3 pm
Si(1) – N(2) – Si(2) :	167.2°

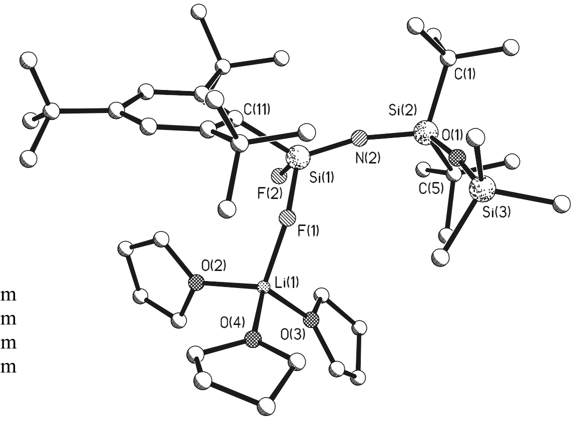

FIGURE 4 Molecular structure of $Li(thf)_3^+$ $RSiF_2NSi(CMe_3)_2OSiMe_3^-$.

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