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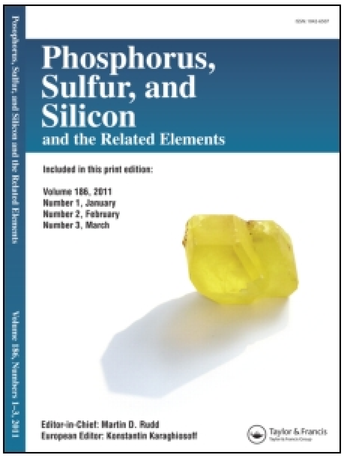

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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Cyclosilazanes Reactions and Interconversions

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To cite this Article Klingebiel, Uwe(1989) 'Cyclosilazanes Reactions and Interconversions', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 3, 361 — 366

To link to this Article: DOI: 10.1080/10426508908039726

URL: http://dx.doi.org/10.1080/10426508908039726

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Phosphorus, Sulfur and Silica, Vol. 41, pp. 361–366
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CYCLOSILAZANES
REACTIONS AND INTERCONVERSIONS

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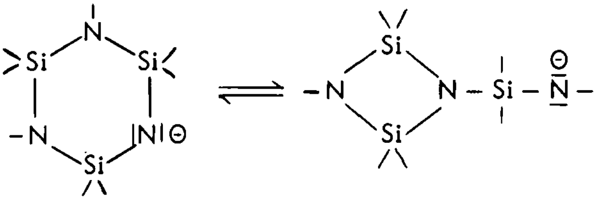
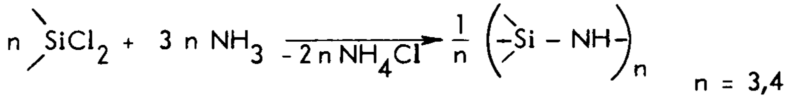
Abstract Anionic rearrangements occur very frequently in reactions of cyclosilazanes. For example, there is an equilibrium between the six- and four-membered ring anions.



The mechanism of the isomerization of cyclosilazanes is studied by the reaction of lithiated rings with halogenosilanes. The first derivatives of the octamethylcyclotetrasilazanes are prepared.

SYNTHESIS

Forty years ago in 1948 Brewer and Haber synthesized the first Si-N-rings[1] by ammonolysis of dichlorodimethylsilane.

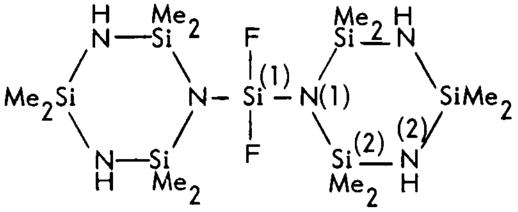


$$n\ {>}SiCl_2 + 3\,n\,NH_3 \xrightarrow[-2n\,NH_4Cl]{} \frac{1}{n}\left(-\overset{|}{\underset{|}{Si}} - NH-\right)_n \qquad n = 3,4$$

The six-membered hexamethylcyclotri- and the eight-membered octamethylcyclotetrasilazanes were formed.[1] In the meantime many other preparation methods of four- to eight-membered cyclosilazanes are known.[2-4]

REACTIONS

Because of the weakness of the Si-N-bond the ring of cyclosilazanes is cleaved upon treatment with halides of main group elements. For more than twenty years only substitution reactions with Me_3SiCl and Me_3SnCl had been known. However, as we could show mono-, di-, and trisubstitution of the sixring is possible in reactions with fluorosilanes and -boranes. Starting with SiF-substituted rings we succeeded in coupling four-four-, four-six-, four-eight-, and six-sixrings, for example:



$Si^{(1)}$- $N^{(1)}$: 169 pm
$Si^{(2)}$- $N^{(1)}$: 176 pm
$Si^{(2)}$- $N^{(2)}$: 171 pm

The rings are far from being planar.

The electron withdrawing fluoroatoms have a considerable effect on the geometry of the silicon nitrogen molecular skeleton, causing shortening of the exocyclic Si-N-bonds and cocomitant lengthening the nearest ring bonds, compared with the other ring bonds. The weakening of these Si-N-bonds is important for interconversion reactions.

INTERCONVERSIONS

Silylgroups always have the propensity to be bonded to the most negatively charged atom in the molecule. This led to the formation of the first phospha- and silaethenes. A comparable charge transfer silylgroup migration leads to interconversions in cyclic systems.

In 1969 Fink recognized that a bis(silyl)-substituted sixring was an isomeric cyclodisilazane.[3,5]

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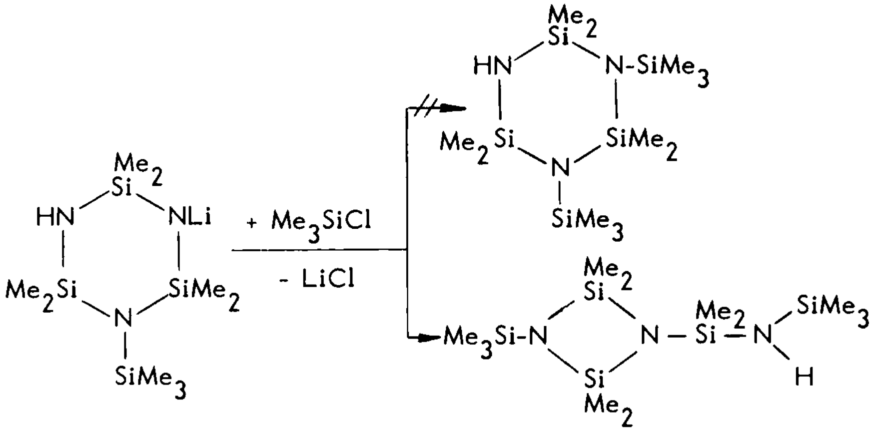
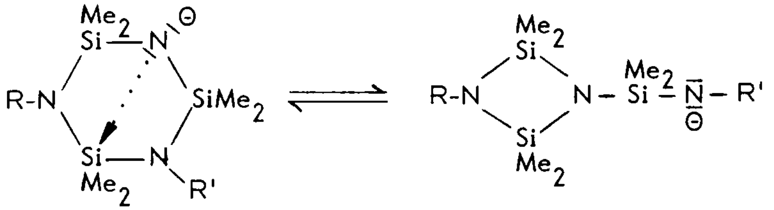


He found an equilibrium between the six- and four-membered ring anion, which depends very strongly on the temperature of the reaction.[5]



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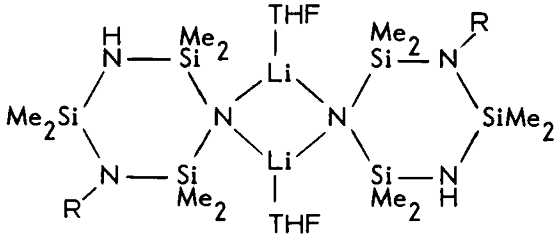
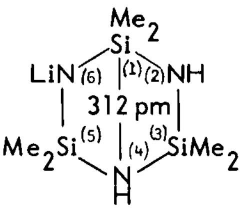
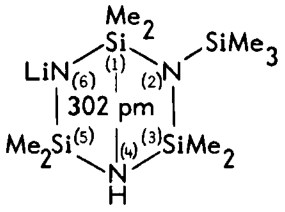
We studied the anionic rearrangements with our systems and found that there are four reasons for interconversions altogether.

1. Thermic effects:[5] Higher temperatures lead to a better N-Si contact. Ring contraction is possible.
2. Effects of substituents:[3] Substituents which increase the basic character of the nitrogen raise the tendency to ring contraction and the other way round. This explains that we succeeded in di- and trisubstitution of the six- and eight-membered rings with fluoroboranes and -silanes. These groups decrease the basic character of the ring and the tendency to ring contraction.
3. Kinetic effects:[3] Bulky groups increase the tendency of the ring contraction. Lithiated cyclotrisilazanes crystallize with THF as dimers in boat confirmation, for example:





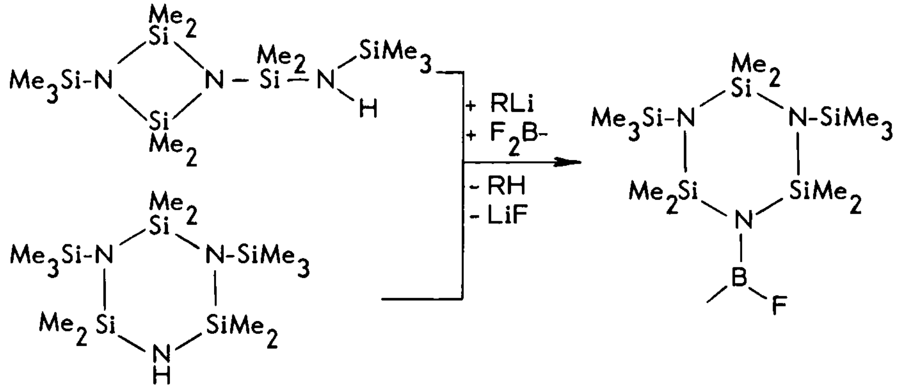


Si(1) - N(2)H - Si(2) = 125 °

Si(1) - N(2)SiMe$_3$- Si(3) = 116 °

Because of the SiMe$_3$-group the Si(1) - N(2) - Si(3) angle gets smaller and a contraction of the Si(1) - N(4)-distance occurs above the ring.

4. Properties of the attacting ligand:[3] If the attacting ligand is a Lewis acid, the basic character of the ring nitrogen is decreased and retention of the ring size of the sixring occurs. Starting with the isomeric four-membered ring ring expansion is observed, for example:



These four reasons for interconversions are effective in the eight-six-four-system, too.

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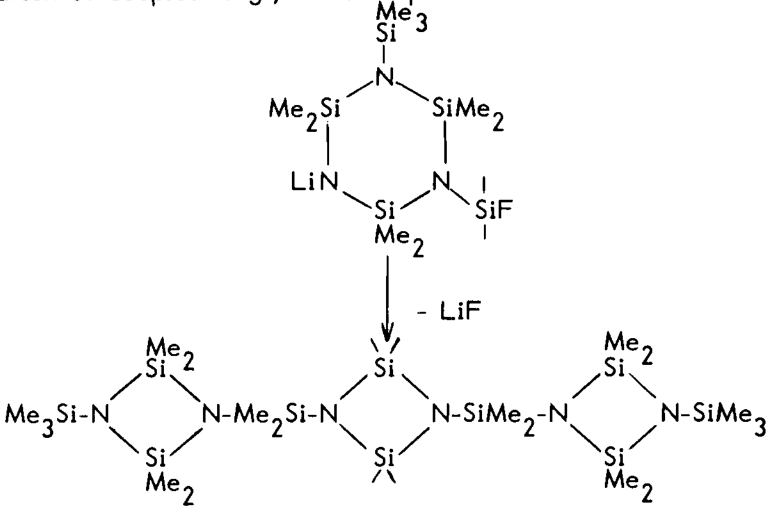
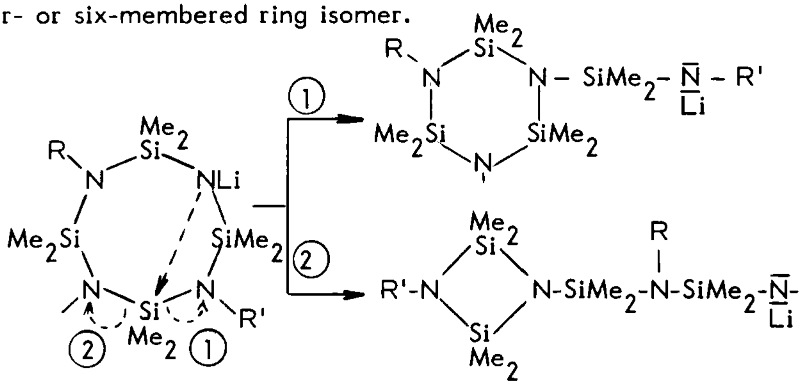
PREPARATIVE APPLICATIONS

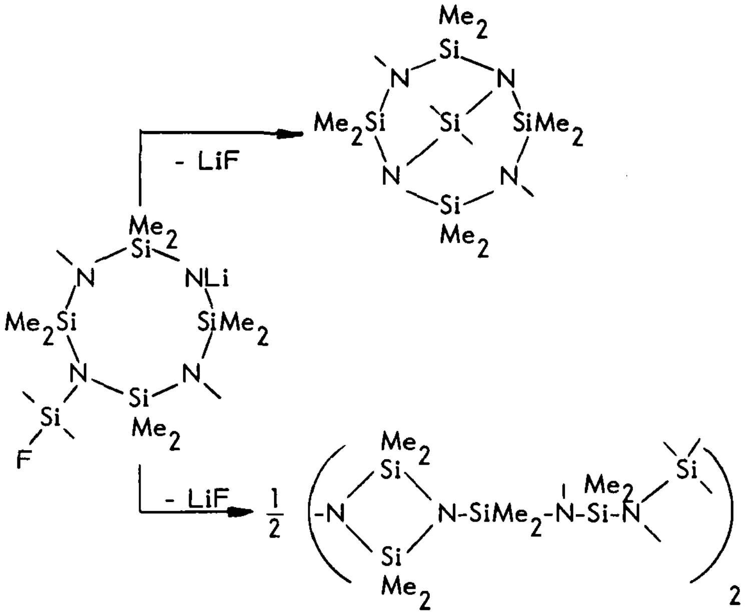
Ring contraction reactions are used for the preparation of silyl-bridged cyclotri- and cyclodisilazanes. The cleavage of the Si-N-bond of the ring depends on the substituted groups.[3] The Si-N-bond in neighborhood of a SiF-group is longer and therefore weaker than in neighborhood of a $SiMe_3$-group. The weakest bond cleaves. LiF-elimination of the isomer leads to formation of coupled rings, for example:



Depending on the substituents the lithiated eight-membered ring contracts to a four- or six-membered ring isomer.



Way ① is prefered for SiF-disubstituted eight-membered rings because of the weakening of the exocyclic Si-N-bond.[6] Four-membered rings are formed in reactions of the eightring with $ClSiMe_3$. Depending on the SiF-group and the reaction conditions LiF-elimination from SiF-monosubstituted, lithiated eightrings leads to the formation of silyl-bridged eight-membered rings or SiNSi-coupled four-membered rings.[6]



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OUTLOOK

The knowledge of the interconversion-conditions will surely lead to further interesting results in the Si-N-ring chemistry.

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