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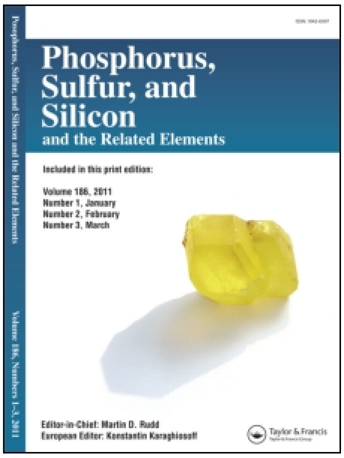

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Uwe Klingebiel; Joerg Niesmann

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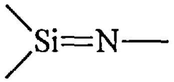
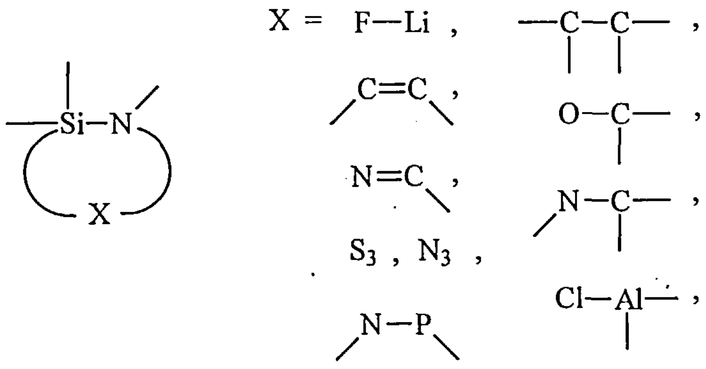
IMINOSILANES AS PRECURSORS OF NEW RINGS AND UNKNOWN RING SYSTEMS

UWE KLINGEBIEL, and JOERG NIESMANN
Institute of Inorganic Chemistry, University of Goettingen,
Tammannstrasse 4, D-37077 Goettingen, Germany

Lithium derivatives of aminochlorosilanes are obtained in the reaction of LiF-adducts of iminosilanes. LiCl-elimination leads to the formation of iminosilanes.



Intramolecular cyclisation reactions of iminosilanes occur with silyl group-, methanid ion-, or siloxy group-migration. Cycloaddition reactions of iminosilanes with organic and inorganic molecules lead to the formation of new rings and unknown ring systems.

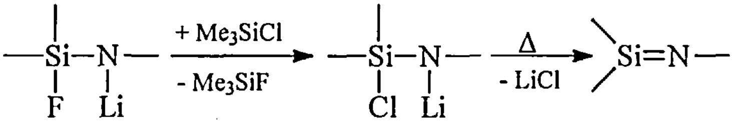


Keywords: Iminosilanes; Rearrangements; Cycloadditions

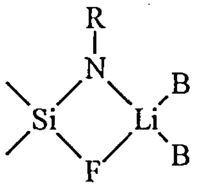
INTRODUCTION

Compounds of multiple bond systems involving heavier main group elements were long considered to be unstable and synthetically inaccessible. In particular, the so-called double bond rule forbade the formation of (pπ-pπ) multiple bonds between heavier main group elements. The first silaethenes and disilenes were synthesized at the beginning of the 1980s and the first iminosilanes were reported in the mid-1980s[1].

Our preparation for a free iminosilane is based on a fluorine/chlorine exchange of lithiated aminofluorosilanes with subsequent thermal LiCl elimination.



In order to understand these reactions, we isolated lithium derivatives and carried out crystal structure investigations.



B: thf, tmeda

R	effect
alkyl	+ I
silyl	+ I, -M
aryl	- M

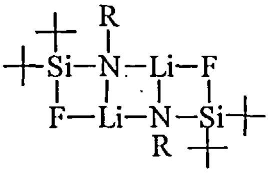
Essentially three factors determine the structural make of the lithium derivatives:

1. A common feature is that the Lewis acid lithium prefers to bind the Lewis base fluorine.
2. The structure is influenced by the presence or absence of solvent bases which can coordinate lithium
3. The decreasing basicity of the nitrogen in the series of lithium derivatives with R = alkyl, silyl, aryl finally leads to rupture of the Li-N bond.

In general, the lithium derivatives show long Li-N and Si-F and short Si-N and Li-F distances with large angles at the nitrogen atom.

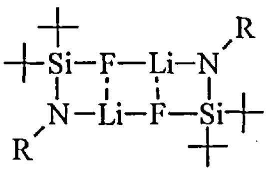
Some examples:

a)



R = CMe_3

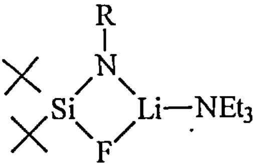
b)



R = $Si(CMe_3)_2Me$

We found dimers via the Li-N bond with R = alkyl and dimers via the Li-F bond with R = silyl. The silyl group bound to nitrogen decreases the basicity of the nitrogen centre and leads to the formation of a dimer via the Li-F bond. Most remarkable is the shortness of the Li-F bond, which is only 177.1 pm, the shortest observed so far in a lithium-fluorine compound. The shortness of the Li-F bond may account for the fact that lithium is only three or even only two and a half coordinate. The eight membered (FSiNLi) ring is nearly planar, the Si-N bond length is in the range of a double bond, and the Li-F-Si angle is wide. Therefore, we interpret this molecule as a dimer of an iminosilane Li-F adduct[1].

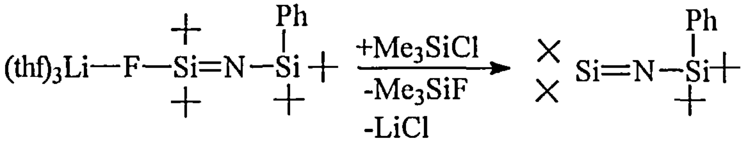
Solvent bases, for example thf or NEt_3, allow the formation of monomers. Sometimes (SiFLiN) four membered rings are formed with the lithium coordination sphere satisfied by two thf molecules or one NEt_3 molecule.



, $R = Si(CMe_3)_2Me$,
Σ Li = 356.3 °

Lithium is often three coordinated and has a planar environment in these molecules.

Further decrease in the basicity of the nitrogen atom leads to a complete rupture of the Li-N contact.



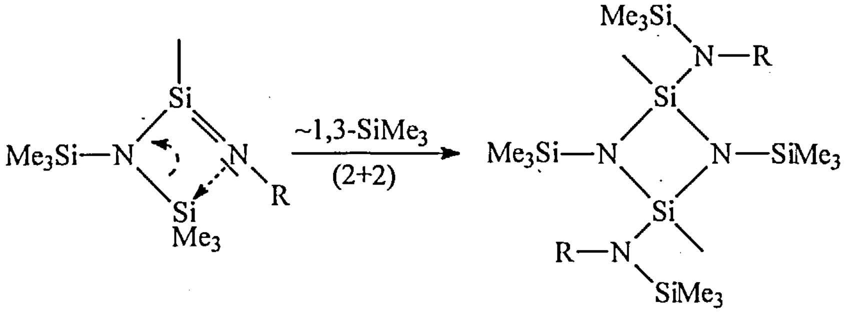
$\delta^{29}Si$: -5.05 ppm (J_{SiF}= 126.9 Hz)	$\delta^{29}Si$: 80.4 ppm
Si=N: 160.8 pm	Si=N: 156.9 pm
Si-N-Si: 176.3°	Si-N-Si: 168.3°
	Kp.: 108°C/0.01 mbar

Now lithium has migrated completely to the stronger Lewis base fluorine. The result is a short Li-F bond and a long Si-F bond. The Si=N double bond length is 160.8 pm and the Si-N-Si angle of 176.3° is typical of an imine. Therefore, these molecules must be considered as LiF adducts of iminosilanes[1]. When the lithiated aminofluorosilane is converted into the lithiated aminochlorosilane LiCl elimination leads to the formation of iminosilanes[2].

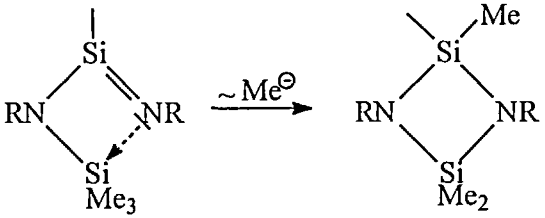
REARRANGEMENTS OF IMINOSILANES

Kinetically unstable iminosilanes react in the same way as stable iminosilanes do. However, some new reaction mechanisms are found in the silicon-nitrogen chemistry.

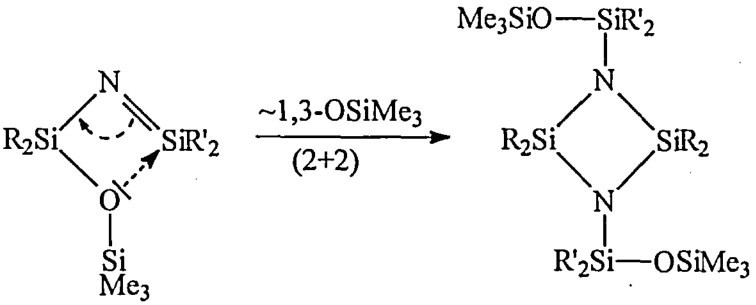
Bis(silyl)amino-organyliminosilanes cyclize with an electrophilic 1,3-migration of a silyl group from one nitrogen atom to the other. The silyl group migration can be explained by the propensity of silyl groups to be bonded to the more negatively charged nitrogen atom. The kinetically unstable trimethylsilyl-iminosilanes dimerize[1].



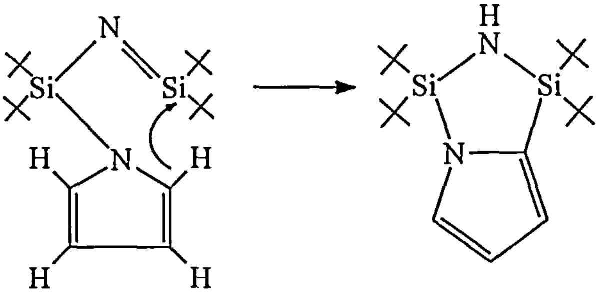
A nucleophilic 1,3-methanid ion migration with formation of an Si_2N_2 ring occurs in the intramolecularly cyclisation of organyl-trimethylsilylamino-organyliminosilanes[1].



Differently substituted siloxyiminosilanes stabilize themselves in a nucleophilic 1,3-siloxy group migration to the three coordinated Lewis acid silicon.

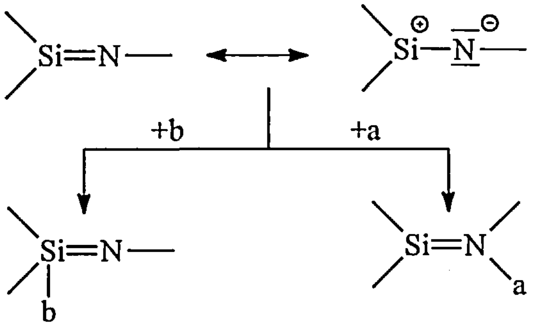


Bulky substituted pyrrolsilyliminosilanes stabilize themselves in an insertion reaction of the iminosilane into a polar C-H bond of the pyrrol substituent[3].



REACTIONS OF IMINOSILANES

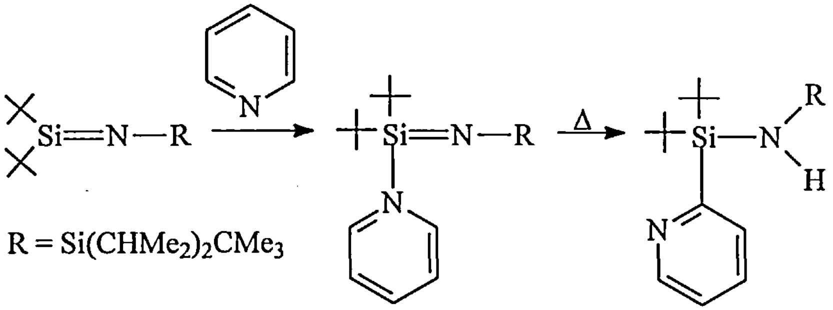
Iminosilanes form adducts with Lewis bases at the silicon and with Lewis acids at the nitrogen atom.



a = $AlMe_3$, $AlCl_3$
b = thf, py, NR_3, LiF

1. Iminosilane Adducts, Reactions with Lewis Bases

In the reaction with Lewis bases the unsaturated silicon atoms form five bonds because of the donor. They have a tetrahedral environment and are four-coordinated. For example: This pyridine adduct has a Si=N double bond length (160.2 pm) and a nearly linear coordinated nitrogen atom.

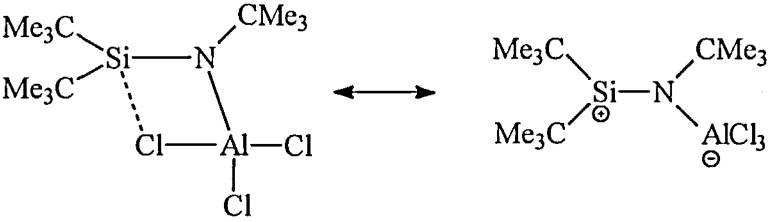


R = $Si(CHMe_2)_2CMe_3$

Above 50 °C the unsaturated nitrogen of the iminosilane adds one proton of the pyridine and a silicon-carbon bond is formed in a Stevens migration.

2. Reactions with Lewis Acids

Iminosilanes react with Lewis acids at the nitrogen atoms, e.g. the *tert*-butylimino-di-*tert*-butylsilane reacts with aluminiumtrichloride with formation of an adduct[4].



Si-N: 170.6 pm
Al-N: 180.9 pm
Si-Cl: 223.2 pm

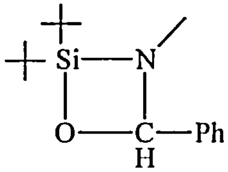
Al-Cl(1): 211.2 pm
Al-Cl(3): 231.8 pm
Σ N: 359.9°
Σ C_2SiN: 354.0°

These compounds may be considered as $AlCl_3$ adducts of silicenium ylides or four-membered rings with bridging chlorine atoms[4]. Although these were the first unsaturated Si-N compounds to be reported in the literature in 1983, they were not noticed, perhaps because the crystal structure data were missing. The X-ray determination was carried out recently[4].

3. Cycloaddition Reactions

(2+2) and (2+3) cycloaddition reactions of iminosilanes with organic and inorganic molecules lead to the formation of new rings and unknown ring systems, e.g.

a)



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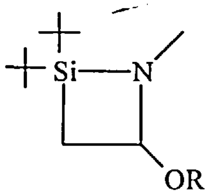
b)



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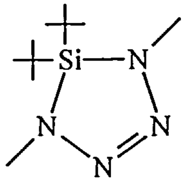
c)

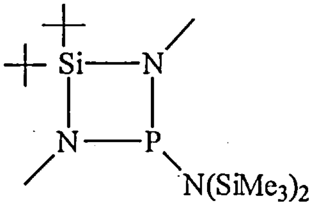


a) Oxaazasilacyclobutanes (SiNCO) rings are obtained in the reaction of the iminosilane with benzaldehyd. The ring is not planar, because of the steric hindrance. The angle between the planes C-N-O and Si-N-O is found to be 17 °[1].

b) Using vinylethers $SiNC_2$-four-membered rings are formed[1]. The two long endocyclic bonds start from the silicon. Therefore the C-Si-N angle is found to be very small in this ring (79.5°).

c) A (2+3) cycloaddition occurs in the reaction with azides. Tetrazoles are obtained quantitatively[1].

d)



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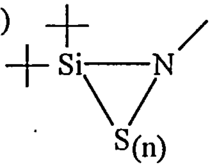
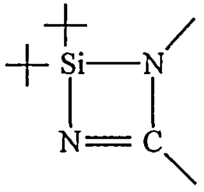
e)



d) In the reaction of an iminosilane and an iminophosphane, a 1.3-diaza-2-sila-4-phosphacyclobutane is formed in a head-to-tail dimerisation. Because of the bulkiness of the substituents, the Si-N and P-N ring bonds are remarkably elongated. At ambient temperature, this compound shows hindered rotation via the P-N $(SiMe_3)_2$ bond. The ring is not planar[1].

e) Methylthiirane reacts with iminosilanes with formation of silicon-nitrogen-sulfur rings. The five-membered ring (n = 3) was characterized by X-ray analysis[5].

f)



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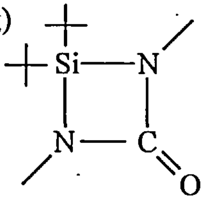
g)



f) The (2+2) cycloadditions occur in the reaction of silylcyanides or ethines with iminosilanes, too[5].

g) With tert-butylisocyanate or silylisocyanates the usual (SiNCO) four-membered ring system is formed, however the (SiNCN) ring with phenylisocyanat[1].

Conclusion

Unsaturated silicon-nitrogen compounds can easily be prepared and they are useful precursors for unknown silicon containing compounds in addition reactions.

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