Review

From lithiumhalosilylamide to small and large ring compounds, iminosilenes and iminosilanes

Uwe Klingebiel *, Christoph Matthes

*University of Goettingen, Institute of Inorganic Chemistry, Tammannstr. 4, 37077 Goettingen, Germany*

Abstract

Structure investigations on lithiumhalosilylamides have repeatedly yielded astonishing results. Depending on the solvents and the substitution of the nitrogen, they are isolated as acyclic, three- to penta-, bi-, and spiro-cyclic compounds. The shortest Si–N bond (157.9 pm) of four-coordinated silicon is found in these salts. The different formation of silicon–nitrogen containing rings by elimination of alkaline halides from halosilylamides depends on the solvent and structural make-up of the halosilylamides. Four- to 14-membered rings are formed.

Four-membered SiN-rings with the smallest angles at the silicon (76°), and the cyclodisilazane dications are obtained. Stable iminosilenes and iminosilanes are isolated and unusual cycloaddition products are presented
.
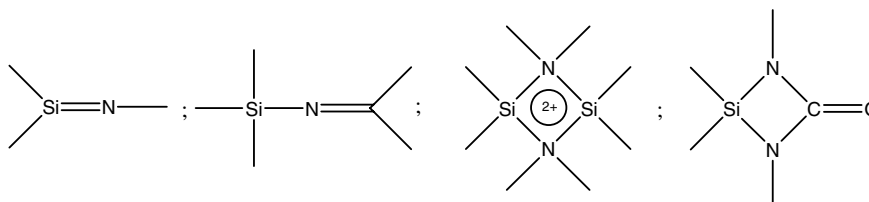
© 2006 Elsevier B.V. All rights reserved.

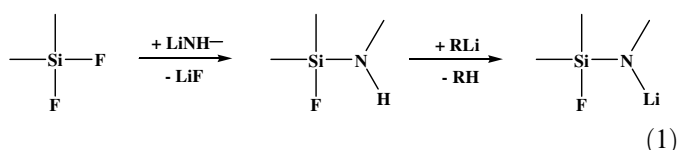*Keywords:* Lithiumhalosilylamide; Iminosilane; Iminosilene; Cyclosilazanes

Contents

* Corresponding author. Tel.: +49 551 393 052; fax: +49 551 393 373.
  E-mail address: uklinge@gwdg.de (U. Klingebiel).

1. Introduction

Normally aminofluorosilanes are stable, they do not condense with formation of amines, ammonia, or HF and they form stable lithium salts (Eq. (1)) which crystallize depending on the solvent as monomers, dimers, trimers, tetramers via the Li–N or Li–F bond (**I**) or form LiF-adducts of iminosilenes (**II**), and amides (**III**) [1]. (Difluoro-silyl)diamides were characterized as spirocyclic compounds (**IV**). Lithium salts of bis(fluorosilyl)amines form planar six-membered rings (**V**). Bis(difluorosilyl)amides crystallize as polymers (**VI**) (Scheme 1) [1]:

$$—\overset{|}{\underset{|}{Si}}—F \quad \xrightarrow[- \text{LiF}]{+ \text{LiNH}—} \quad —\overset{|}{\underset{|}{Si}}—\underset{H}{N}\diagup \quad \xrightarrow[- \text{RH}]{+ \text{RLi}} \quad —\overset{|}{\underset{|}{Si}}—\underset{Li}{N}\diagup$$

$$(1)$$

Here we present lithium salts with new and interesting results in their structure make-up and lithium salts which led to new and astonishing results in reactions.

2. Results and discussion

2.1. LiF-adduct of lithium-1,3-di-tert-butyl-2-(2,6-diisopropylphenyl)amide-2-fluoro-1,3-diaza-2-sila-cyclopentene (2)

The lithium salt of 2,6-diisopropylphenyl-amino-fluoro-1,3-diaza-2-silacyclopentene thermally loses LiF, and an

iminosilene **1** is obtained. However, it also adds LiF and forms a tetramer with a central eight-membered Li–F ring system having a chair conformation (Eq. (2)). In the six-membered rings, fluorine is two- and lithium with the π-system of the aryl group, two-plus six-coordinated (Fig. 1) [2]. One six-membered (SiFLiFLiN) ring has a boat- and the other one a twist-form. Compound **2** can be considered as an LiF cluster covered by organic groups:
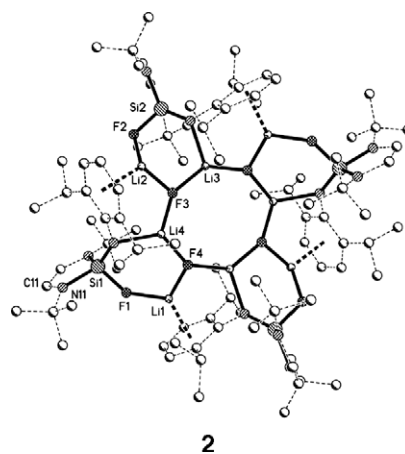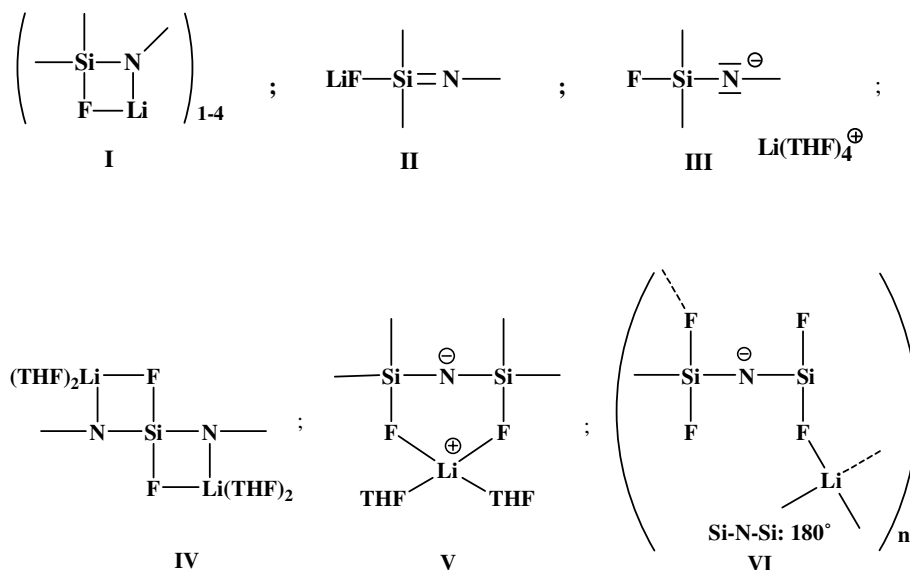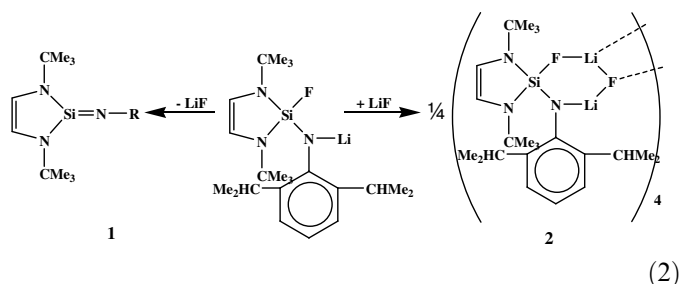

2

Fig. 1. Structure of **2**; selected bond lengths (pm) and angles (°): Si(1)–N(13) 163.7, F(4)–Li(4) 179.7, Si(1)–F(1) 166.3, Li(4)–N(13) 203.3, Si(1)–N(11) 174.2, F(1)–Li(1) 184.1, $\sum$(F) 360, Li(1)–F(4) 178.7, $\sum$(Li) 360.

Scheme 1. Structures of lithiated aminofluorosilanes.

$$(2)$$

2.2. Lithium salts of 1-amino-1,3-disiloxanes and -silylethers

1-Amino-2-fluoro-1,3-disiloxanes form a different type of lithium salts depending on the properties and bulkiness of the silyl groups, 1,3-disilylamino-1-olates or the less stable 1-amido-1,3-disiloxanes [3]. The second case includes a 1,3-silyl group migration from the oxygen to the nitrogen atom, as is well-known from silylhydroxylamine chemistry [4].

In fluorine containing compounds, lithium often is coordinated to the fluorine atom. The most stable isomer of the model compound MeSiF$_2$–NH–SiMe$_2$OLi generates a six-membered (Li–O–Si–N–Si–F)-ring system with Li–F contact (Fig. 3).

The 1,3-(O → N)silyl group migration can be suppressed by bulky groups, and 1-amido-1,3-disiloxanes are kinetically stabilized, e.g. the lithium salt of 1-amino-1,1-di-*tert*-butyl-3-fluoro-3,3-bis(isopropyltrimethylsilyl)amine crystallizes as amide **3** and forms an (F–Si–O–Si–N–Li)-six-membered ring as a dimer via the Li–N-bond (Fig. 2, [5]):
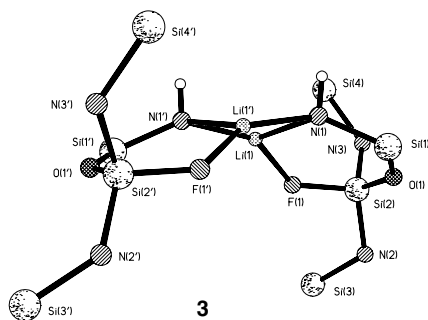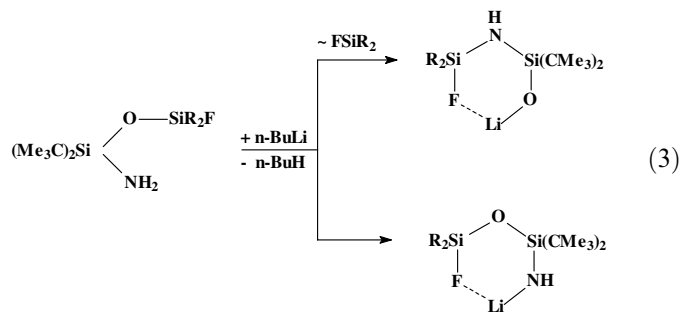

$$(3)$$

The hydrogen atoms at the nitrogen atoms are in *cis*-position.

Quantum chemical calculations of model compounds show that in this case the 1-lithium-silylamido-1,3-disiloxane is more stable than the possible olate isomer [3].

LiF-elimination of such lithium salts leads to the formation of planar eight-membered rings, which have a linear Si–O–Si-unit [3].

2.2.1. Lithium salts of 1-silylamino-3-silylethers and 1,3-disiloxanes

No silyl group migration is observed in reactions of 1-silylamino-3-silylether (**4**) or -disiloxanes (**4b**) with BuLi. These lithium salts often crystallize as tricyclic systems
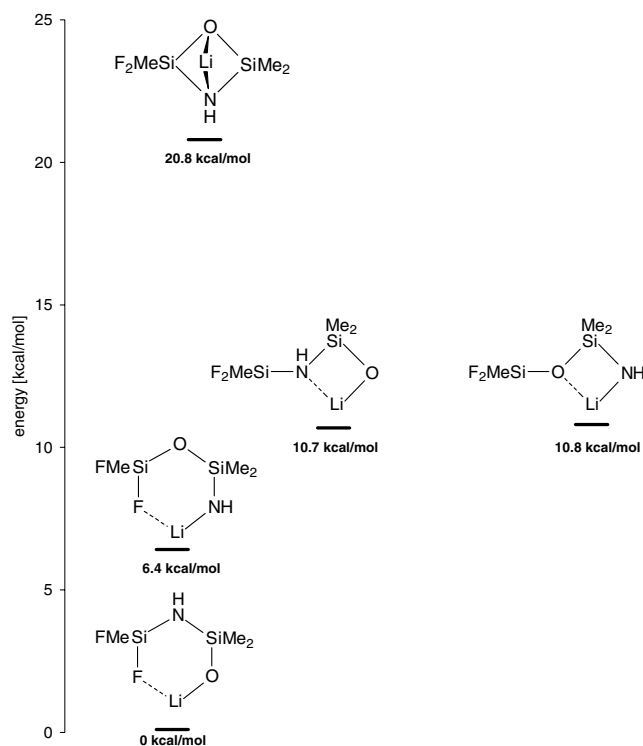

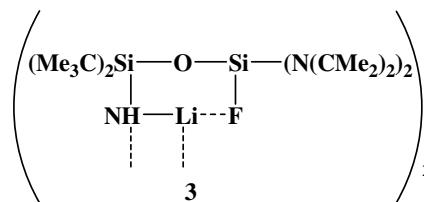
Fig. 3. Relative energies of isomeric lithium salts and the saddle point structure ("transition state") corresponding to isomerization [3].

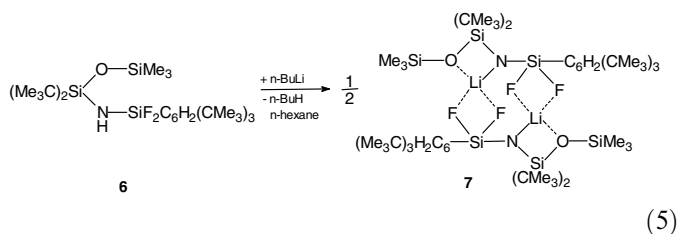Fig. 2. Structure of **3**; selected bond lengths (pm) and angles (°): Si(1)–O(1) 168.8(2), Si(2)–F(1) 163.13(11), Li(1)–F(1) 193.9(4), Si(1)–N(1) 168.8(2), Li(1)–Li(1′) 238.6(5), ∑Li(1) 355.6.

via an eight-membered $(Li–F–Si–N)_2$ ring with lithium in a planar environment. Normally, LiF elimination leads to the formation of cyclodisilazanes (Eq. (4)) [3] (Fig. 4):

$$\tag{4}$$

R = CMe_3
R' = SiMe_3
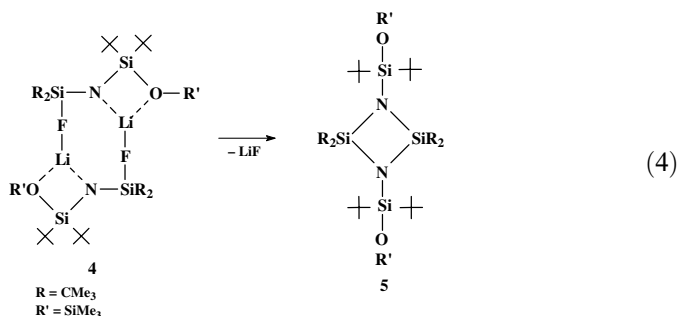
2.2.2. Lithium salts of 2,4,6-$(Me_3C)_3C_6H_2$-SiF_2NH-$Si(CMe_3)_2$-O-$SiMe_3$ (7)

By using very bulky groups like the 2,4,6-tri-*tert*-butyl-phenyl group, the lithiated 1-silylamino-1,3-disiloxane forms a dimer in the crystal (**7**) (Eq. (5)). Lithium has a tetrahedral coordination: two fluorine, one oxygen, and one amido contact. This coordination of the lithium ion was hitherto unknown. The dimer **7** consists of two four-membered rings, a (OSiNLi)- and a (SiF_2Li) ring. The two spirocyclic units are connected by an eight-membered $(NSiFLi)_2$ ring (Eq. (5)) (Fig. 5) [3]:

$$\tag{5}$$

The structure of the lithium salt depends very much on the solvents. Crystallization from THF (Eq. (6)) leads to a complete rupture of the Li–N contact (Fig. 6). Now lithium

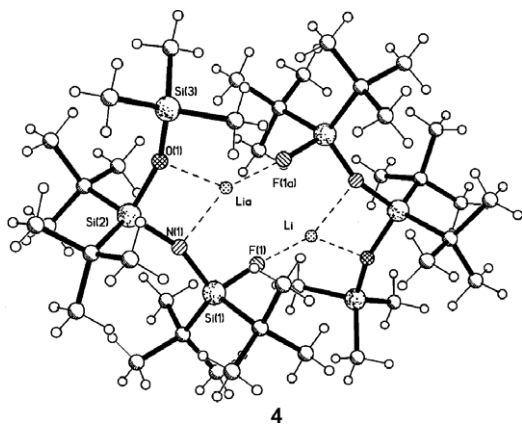Fig. 4. Crystal structure of **4**; selected bond lengths (pm) and angles (°): Si(1)–F 169.2, Si(1)–N–Si(2) 161.1, Si(1)–N 163.9, F(1)–Li–N(1a) 140.2, Si(2)–N 166.5, F(1)–Li–O(1a) 136.3, Li–F 182.9, N(1a)–Li–O(1a) 80.5, Li–O 205.6, $\sum$Li 357, Li–N 197.8, Si(2)–O 169.7, Si(3)–O 164.7.
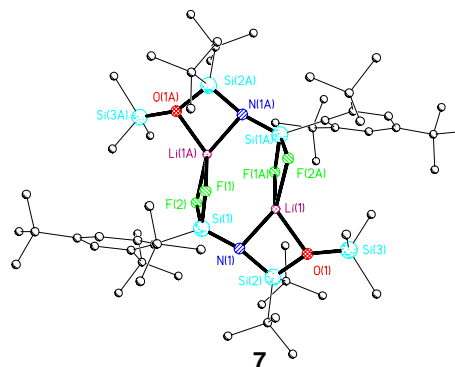
Fig. 5. Crystal structure of **7** [3]; selected bond lengths (pm) and angles (°): Si(1)–F(1) 164.8, Si(1)–N(1) 160.7, F(1)–Li(1A) 200.6, N(1)–Li(1) 204.5, Si(2)–O(1) 168.7, F(1A)–Li(1)–F(2A) 69.6, Si(1)–N(1)–Si(2) 167.6, $\sum$N(1) 359.7.

has migrated to the stronger Lewis base fluorine. The result is a short Li–F bond (186.6 pm) and a long Si–F bond (165.9 pm). The Si–N bond with 157.9 pm is a double length, as far as we know, the shortest Si–N bond with four-coordinated silicon. The Si–N–Si angle of 167.2° is typical of an imine. Therefore, the compound must be considered as a Li–F adduct of an iminosilene [3]:

$$\tag{6}$$
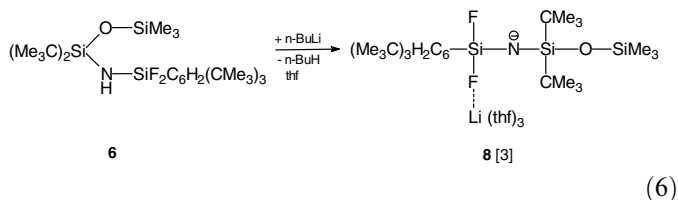
2.3. Syntheses of iminosilenes

Iminosilenes, which are excellent precursors for the synthesis of new and unusual ring systems are formed by LiF-elimination from lithiumfluorosilylamides, e.g. (Eq. (7), Fig. 7a and b) [1]:

$$\tag{7}$$
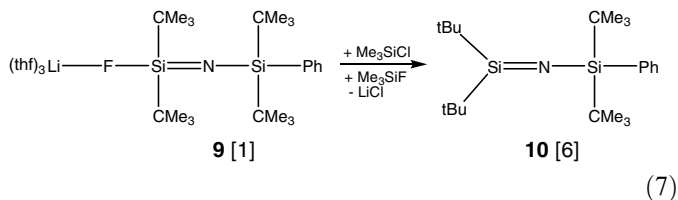
The crystal structure of **10** [6] shows a trigonal planar arrangement of the $C_2Si=N$ unit around the silicon atom. In solid state, the iminosilene is monomeric and the Si–N–Si skeleton is nearly linear (168.3°). The Si–N bond lengths are drastically different. The Si–N single bond is 169.6 pm, and the Si=N double bond is 156.9 pm. This is only 1 pm shorter than the Si–N bond in **8** [3].

2.3.1. Monomeric bis(silyl)amino-dimethylalane (11)

A surprising result is yielded in the reaction of iminosilenes and trimethylalane. First an adduct is formed which
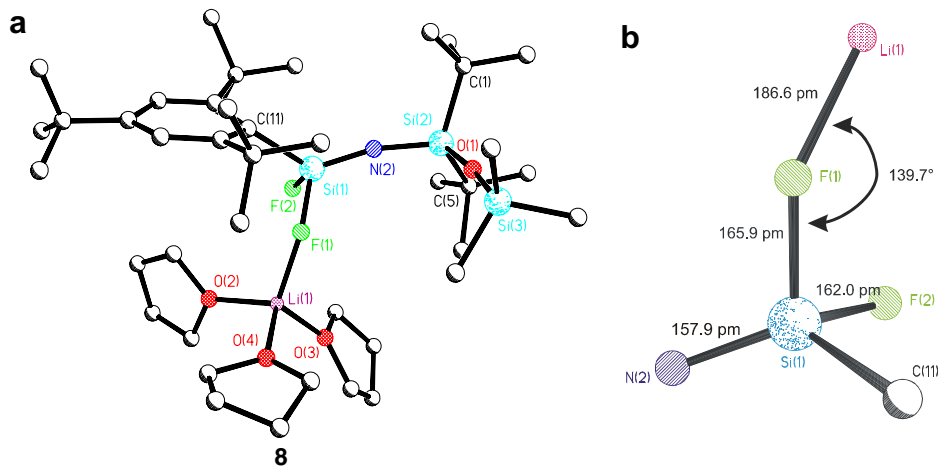
Fig. 6. (a, b) Crystal structure of **8** [3]; selected bond lengths (pm) and angles (°): Si(1)–N(2) 157.9, Si(3)–O(1) 159.6, Si(2)–N(2) 163.2, Si(2)–O(1) 165.3, Si(1)–N(2)–Si(2) 167.2.

9

δ ^{29}Si: 5.05 ppm (J_{SIF} = 126.9 Hz)

Si=N: 160.8 pm

Si-N-Si: 176.3 °

10

δ ^{29}Si: 80.4 ppm

Si=N: 156.9 pm
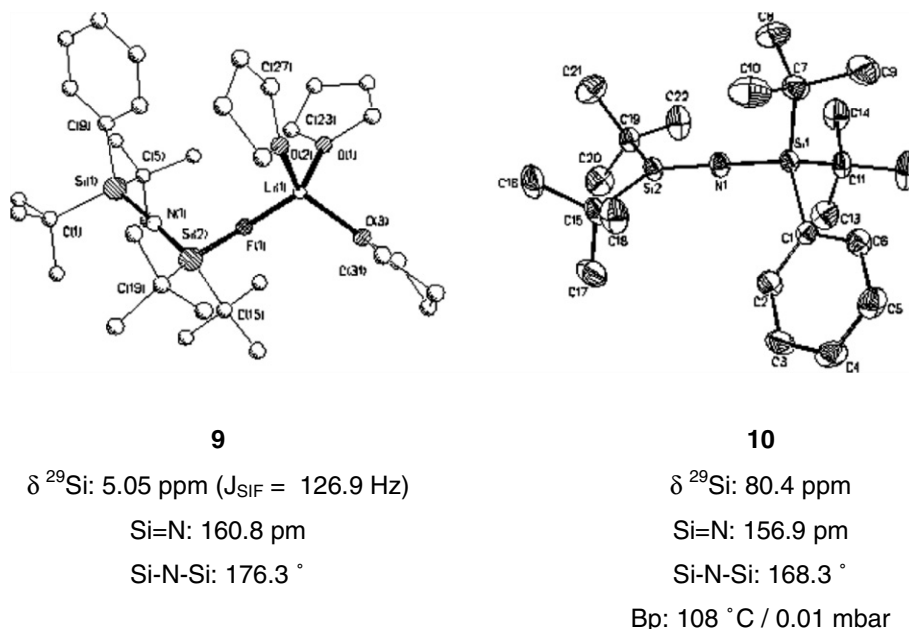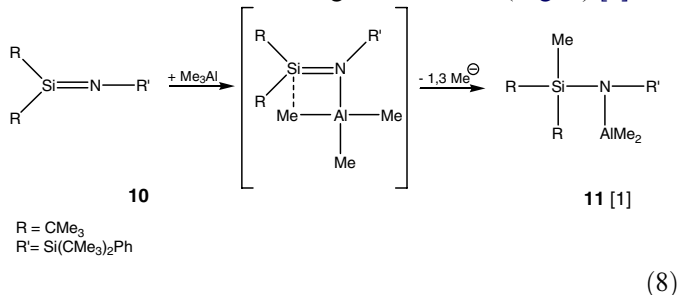
Si-N-Si: 168.3 °

Bp: 108 °C / 0.01 mbar

Fig. 7. (a, b) Crystal structures of **9** and **10** [3].

stabilizes itself in a 1,3-methanide ion migration from the aluminum atom to the silicon atom (Eq. (8)) [1]. Such isomerization reactions were unknown so far and prove that three-coordinated silicon is – compared to three-coordinated aluminum – the stronger Lewis acid (Fig. 8) [1].

10

R = CMe$_3$
R'= Si(CMe$_3$)$_2$Ph

11 [1]

(8)

Compound **11** is a monomer, the nitrogen and the aluminum atoms have planar environments [7].

2.3.2. Cycloaddition of phenylisocyanate and an iminosilene (12)

Iminosilenes are excellent precursors for the synthesis of new and unusual ring systems. For example, there is definitely no other way to prepare four-membered SiN$_2$-rings with an exocyclic C=O double bond as in the cycloaddition of an imine with isocyanates, e.g. phenylisocyanate (Eq. (9), Fig. 9) [8]:

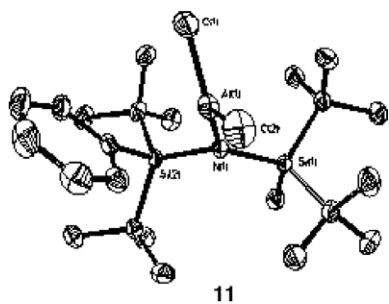**10**   **12**

(9)
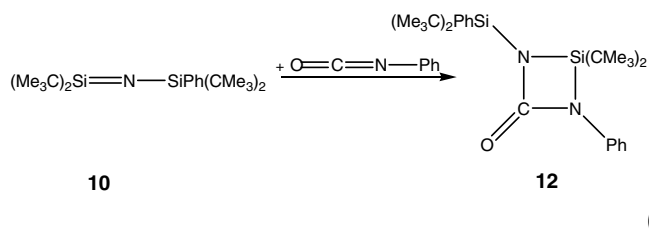
Fig. 8. Crystal structure of **11**; selected bond lengths (pm) and angles (°): Al(1)–N(1) 186.9, Al(1)–C(8) 256.4, Si(1)–N(1) 175.2, Si(2)–N(1) 175.0, Al(1)–N(1)–Si(2) 103.6, C(8)–Si(2)–N(1) 99.1, $\sum$N(1) 360, $\sum$Al(1) 357.8, C(2)–Al(1)–N(1)–Si(1) −57.5.
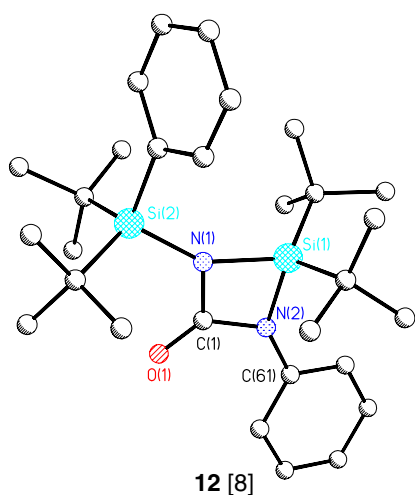

Fig. 9. Crystal structure of **12**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 177.94, Si(1)–N(2) 176.07, Si(2)–N(1) 177.55, C(1)–N(2) 139.4, C(1)–N(1) 140.9, C(61)–N(2) 141.1, C(1)–O(1) 120.9, N(1)–Si(1)–N(2) 76.24, N(1)–C(1)–N(2) 102.48, C(1)–N(1)–Si(1) 89.97, C(1)–N(2)–Si(1) 91.21.

Because of the long endocyclic bond lengths starting from the silicon atom, the endocyclic N–Si–N angle is very small (76.2°).

2.4. From lithiumfluorosilylamine to bicyclic system (14) and dipheno-silyliminoquinones (16)

The iminosilene prepared by LiF-elimination from lithiated di-*tert*-butylfluoro-2,6-dimethylaniline (**13**) stabilizes itself at room temperature forming the bicyclus (**14**) [9] (Scheme 2).

Two iminosilene molecules react with each other resulting in a C–Si bond of the *para*-C(4)-atom of one aryl group. The C(4)-proton migrates to the nitrogen of the iminosilene. The other Si=N bond undergoes an ene reaction with one of the *ortho* CH₃-groups of the aryl ring forming a bicyclic unit [9].

Addition reactions of H-acidic compounds and intramolecular ene-reactions of unsaturated systems occur when the substituents prevent a dimerization because of bulki-
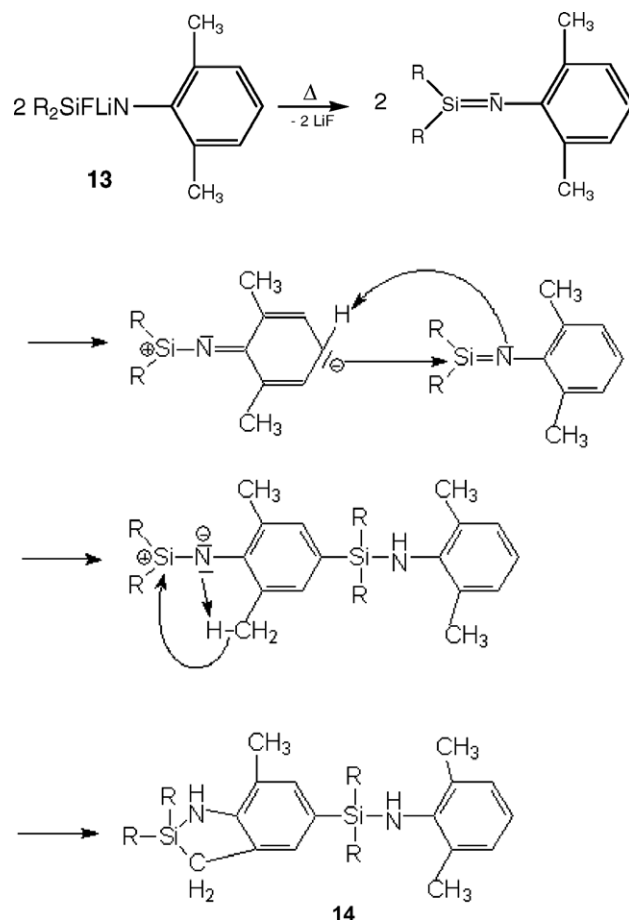
Scheme 2. Formation mechanism of **14** [9].

ness. The formation of **14** may be a borderline case between dimerization and ene-reaction.
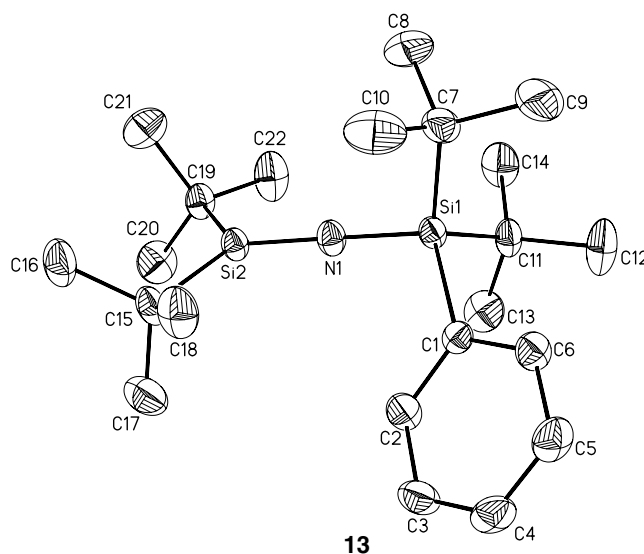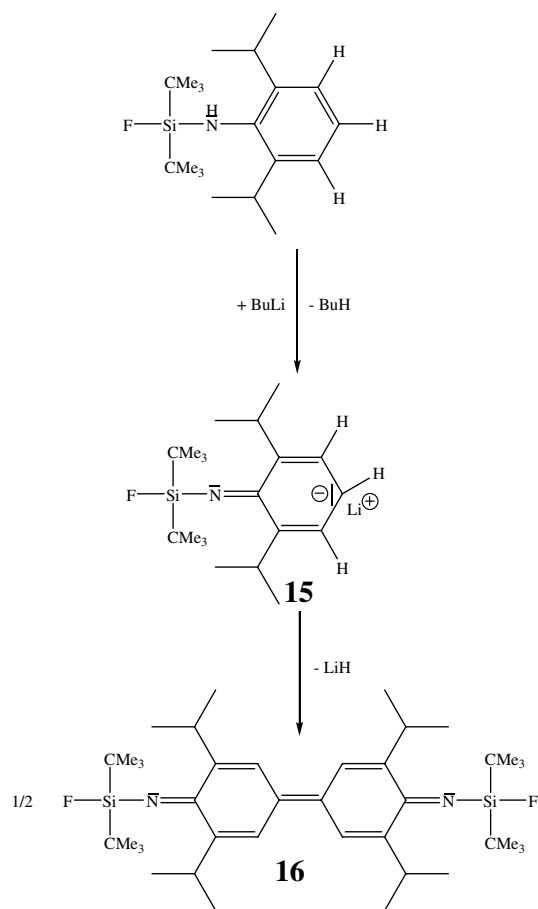

Fig. 10. Crystal structure of **13**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 164.44, Si(1)–F(1) 168.40, F(1)–Li(2) 187.1, F(2)–Li(1) 192.0, N(1)–C(11) 140.3, N(1)–Li(1) 200.4, N(2)–C(21) 140.5, N(2)–Li(2) 195.7, Li(1)–O(1) 189.9, N(1)–Si(1)–F(1) 106.18, Si(1)–F(1)–Li(2) 170.24, Si(1)–N(1)–Li(1) 109.56.

The lithium salt **13** crystallizes from THF as dimer forming an eight-membered (SiFLiN)$_2$ ring which has no symmetry. The long Li–N and Si–F as well as short Si–N and Li–F distances with large angles at the fluorine atoms are remarkable (Fig. 10).

The fluorine atoms are two, the lithium atoms are three coordinated. The coordination sphere of the lithium is made up of one fluorine atom, one nitrogen atom, and one THF molecule. The sum of the angles around Li(2) is measured 360° and around N(2) 356.9° [9] (Fig. 11).

In order to prevent this reaction (Scheme 2) of the intermediate iminosilene, the analogous reaction was carried out using the lithium salt of the bulkier amino-2,6-diisopropylbenzene-(di-*tert*-butyl)fluorosilane (**15**). In a strange reaction red crystals with the composition of compound **16** were isolated [9].

The formation of **16** occurs in a lithium hydride elimination which was proved in the hydrogenation of Me$_3$SiCl. Compound **16** presents a stable iminosilane with a 14π-system [9] (Fig. 12):
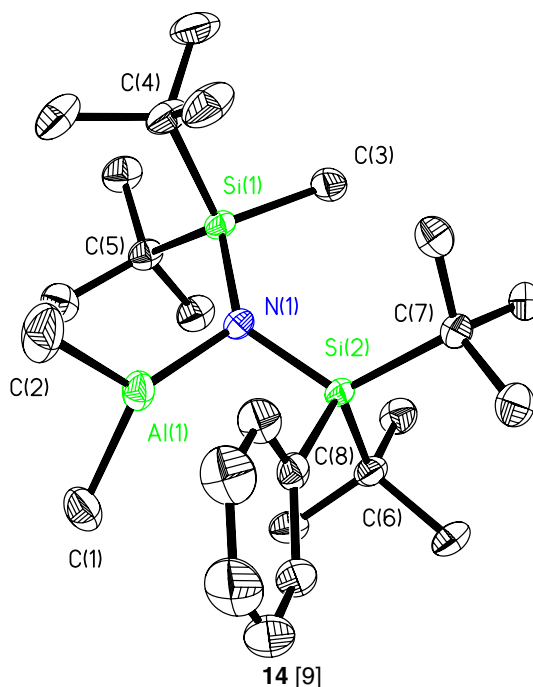

14 [9]

Fig. 11. Crystal structure of **14**; selected bond lengths (pm) and angles (°): Si(1)–N(1) 175.39, Si(1)–C(1) 188.6, Si(1)–N(2) 175.1, N(1)–C(11) 141.3, N(2)–C(4) 140.1, C(3)–C(4) 140.5, N(1)–Si(1)–C(1) 108.66, N(2)–Si(29)–C(8) 93.01.

e.g. the reaction of lithium-diisopropyl-fluorosilyl-*tert*-butylamide and trichloroalane leads quantitatively to the formation of a dimeric adduct of an iminosilene. Hydrolyses give a dicationic cyclodisilazane [10]. The counterion is bis(trichloro)aloxane, (Eq. (11)).

(11)
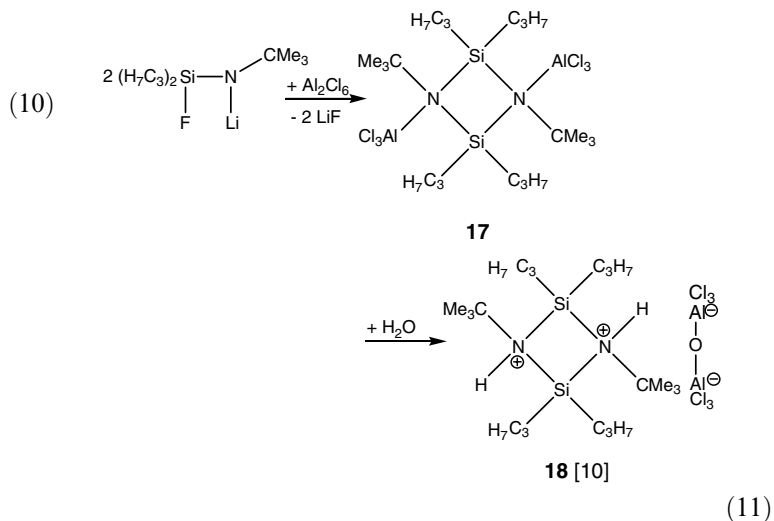
Selected bond lengths (pm) and angles (°): Al–Cl 209, Al–O 177, Al–O–Al 152.5, Si(1)/(2)–N(1)/(2) 179.2, Si(1)/(2)–N(2)/(1) 179.3, N(1)–Si(1)–N(2) 84.1, Si(1)–N(1)–Si(2) 95.9.

The Si–N-bond lengths are single bond lengths (179.2 pm).

Substituting the isopropyl by the bulkier *tert*-butyl groups, no dicationic cyclosilazane but a monomeric

(10)

2.5. Trichloroalane adducts of a cyclodisilazane (17) and an iminosilene (19)

In many cases, lithiated aminofluorosilanes have the same reaction behavior as the iminosilenes. Therefore it is not necessary to prepare in every case the iminosilene,
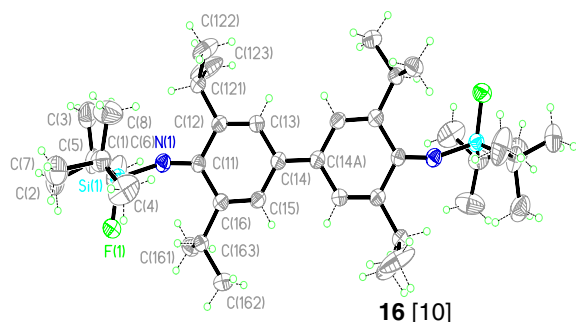
Fig. 12. Crystal structure of **16**; selected bond lengths (pm) and angles (°): Si(1)–F(1) 161.60, Si(1)–N(1) 167.91, N(1)–C(11) 127.9, C(11)–C(12) 148.7, C(12)–C(13) 135.2, C(12)–C(121) 151.9, C(13)–C(14) 144.7, C(5)–Si(1)–C(1) 120.96, C(11)–N(1)–Si(1) 159.74, N(1)–C(11)–C(12) 119.64.
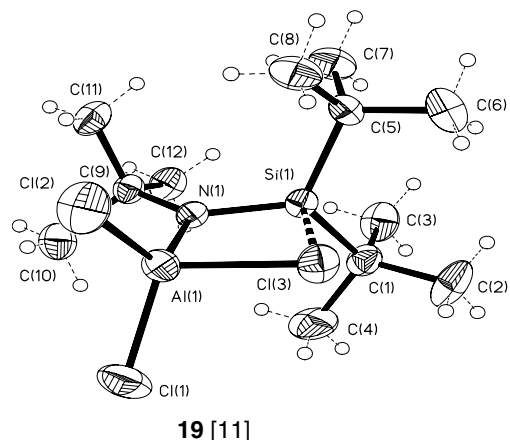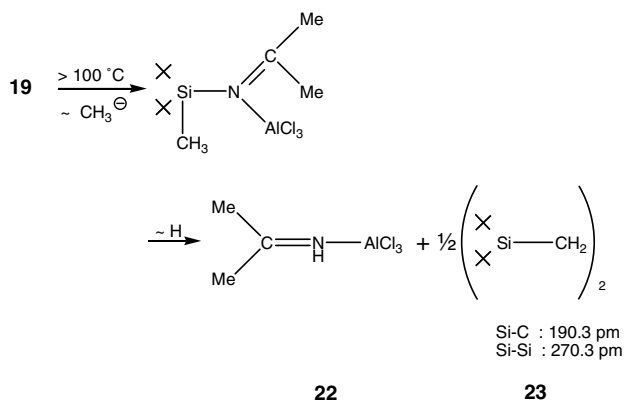
adduct of an iminosilene and trichloroalane is obtained (**19**) [1,11].

This compound forms a planar four-membered ring with two significantly long chlorine bridging bonds (Al–Cl: 231.8, Si–Cl: 233.2 pm). The Al–N bond is short (180.9 pm) in comparison to the sum of the aluminum and nitrogen covalent radii (200 pm). The nitrogen has a planar environment, the silicon and aluminum atoms have – without the bridging chlorine atom – an almost planar environment. Such adducts can be distilled without decomposition. Hydrolyses lead to a planar six-membered cyclosiloxane (**20**) [12] and the *tert*-butyl-amino-trichloroalane adduct (**21**) [11] (Eq. (12)):
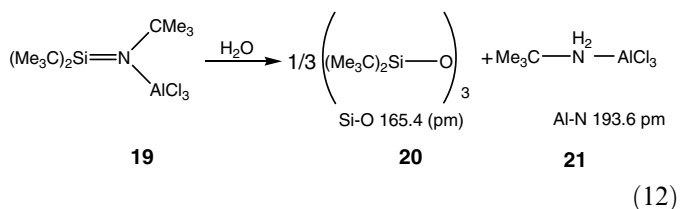
(12)

Thermally a methanide ion migration from the nitrogen *tert*-butyl group to the silicon occurs followed by potonation of the nitrogen by the SiCH₃ group leading to the dimethylazomethine-trichloroaluminum adduct (**22**) [11] and the 1,3-disilacyclobutane (**23**). The free dimethylazomethine is still unknown (Eq. (13)) (Figs. 13 and 14):
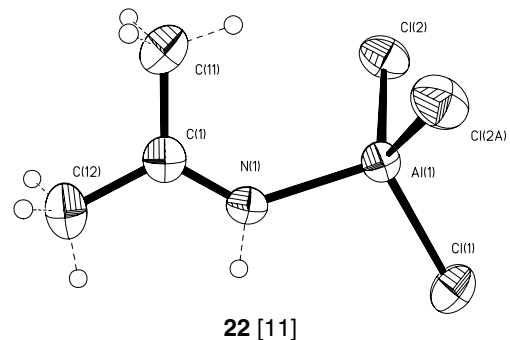

(13)

Fig. 13. Crystal structure of **19**; selected bond lengths (pm): Al–N 180.9, Al–Cl(1) 211.2, Al–Cl(3) 231.8, Si–N 170.6, Si–Cl 233.2.

Fig. 14. Crystal structure of **22**; selected bond lengths (pm) and angles (°): Al–N 189.8, Al–Cl 211.8, C=N 128.2, C–N–Al 131.7.

2.6. Formation of a (SiNC₄O)₂ heterocyclus (25)

LiCl-elimination of lithiated aminochlorosilanes depends very much on the solvent, e.g. in hexane (Scheme 3), LiCl elimination from lithium trichlorosilylamides leads to the formation of cyclodisilazanes (**24**). In THF, a new type of THF cleavage occurs [12]. At first the lithium ion coordinates the oxygen atom of the THF molecule. This leads to a cleavage of the H₂C–O bond and the formation of a H₂C–N bond. The formed lithium salt reacts intermolecularly to a 14-membered macrocycle (**25**) [12]. In general, THF-cleavage follows the formation of ethene and lithiumenolate [13] (Fig. 15).

3. Conclusion

Lithiumhalosilylamides are useful building blocks for acyclic and cyclic silicon–nitrogen containing compounds. Depending on the bulkiness of the substituents, LiHal-elimination leads to the formation of Si–N-rings, iminosilanes and iminosilenes. These compounds promise an interesting continuation in this chemistry.
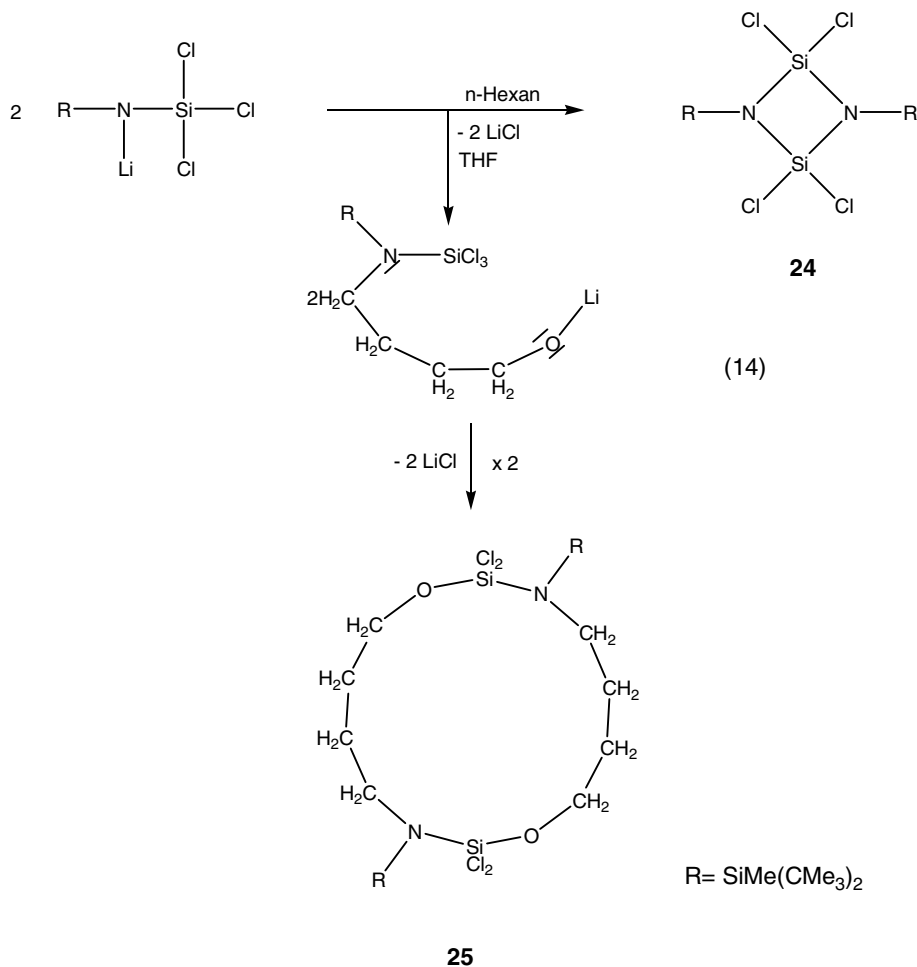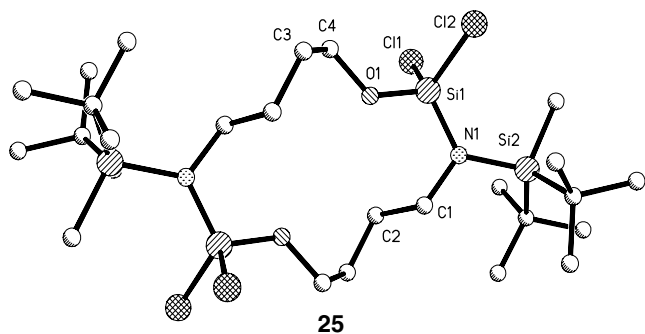
Scheme 3. Formation of the four- and 14-membered rings **24** and **25**.

25

Fig. 15. Crystal structure of **25**; selected bond lengths (pm): N(1)–Si(1) 168.8, N(1)–C(1) 149.8(2), N(1)–Si(2) 176.7, C(4)–O(1) 144.1(2), Si(1)–Cl(1) 205.4, Si(1)–O(1) 160.8(1).

References

[1] P. Neugebauer, B. Jaschke, U. Klingebiel, Recent developments in the chemistry of compounds with silicon–nitrogen bonds, in: Z. Rappoport, Y. Apeloig (Eds.), Supplement Si: The Chemistry of Organic Silicon Chemistry, vol. 3, Interscience Publishers, John Wiley & Sons, Ltd, 2001, p. 429.

[2] A. Fischer, N. Sievert, U. Klingebiel, M. Noltemeyer, in preparation.

[3] S. Kliem, U. Klingebiel, M. Noltemeyer, S. Schmatz, J. Organomet. Chem. 690 (2005) 1100.

[4] C. Ebker, F. Diedrich, S. Schmatz, U. Klingebiel, Silicon Chem. 2 (2003) 117.

[5] C. Reiche, S. Kliem, U. Klingebiel, M. Noltemeyer, C. Voit, R. Herbst-Irmer, S. Schmatz, J. Organomet. Chem. 667 (2003) 24.

[6] J. Niesmann, U. Klingebiel, M. Schäfer, R. Boese, Organometallics 17 (1998) 947.

[7] R. Wolfgramm, U. Klingebiel, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry, vol. 3, VCH, Weinheim, 1997, p. 348.

[8] J. Niesmann, U. Klingebiel, S. Rudolph, R. Herbst-Irmer, M. Noltemeyer, J. Organomet. Chem. 515 (1996) 43.

[9] U. Klingebiel, M. Noltemeyer, A. Wand, J. Organomet. Chem. 691 (2006) 2657.

[10] U. Klingebiel, N. Helmold, S. Schmatz, Adv. Organomet. Chem. (2006) 1.

[11] U. Klingebiel, M. Noltemeyer, H.-G. Schmidt, D. Schmidt-Bäse, Chem. Ber. 130 (1997) 753.

[12] W. Clegg, Acta Crystallogr., Sect. B 38 (1982) 1648.

[13] B. Jaschke, R. Herbst-Irmer, U. Klingebiel, P. Neugebauer, T. Pape, Z. Anorg. Allg. Chem. 625 (1999) 1035–1040.

Uwe Klingebiel was born in 1944 in Fraustadt, Germany. He studied chemistry at the Universities of Clausthal-Zellerfeld and Göttingen, where he received his Ph.D. in 1972. In 1978 he completed his habilitation in Inorganic Chemistry. In 1981 he received a professorship at the University of Göttingen. His main interests are in the field of synthetic chemistry, focusing on molecular compounds containing silicon.