

# From aminosilane to iminosilane

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## ABSTRACT

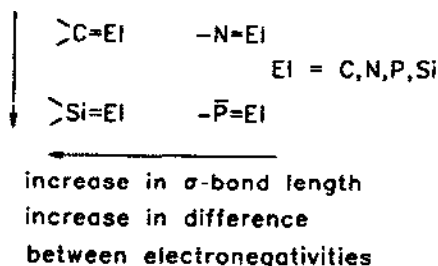
Lithium derivatives of amino-fluorosilanes are stable at room temperature and thus can be fully characterized by NMR spectroscopy, crystal structure analysis, etc. Crystal structure determinations prove that lithiated aminosilanes can, depending on the solvent and the substituent, be regarded as LiF adducts of iminosilanes. LiF elimination leads to dimerizations and interconversions of the iminosilanes formed. Lithiated aminosilanes react like silylamides as well as like iminosilanes. They are suitable precursors to iminosilanes after fluorine-chlorine exchange.

## A. INTRODUCTION

Development of the molecular chemistry of multiple bond systems involving heavier main group elements has to be regarded as one of the most fruitful recent innovations in inorganic chemistry, in spite of the fact that such compounds were considered to be unstable and synthetically inaccessible (Scheme 1).

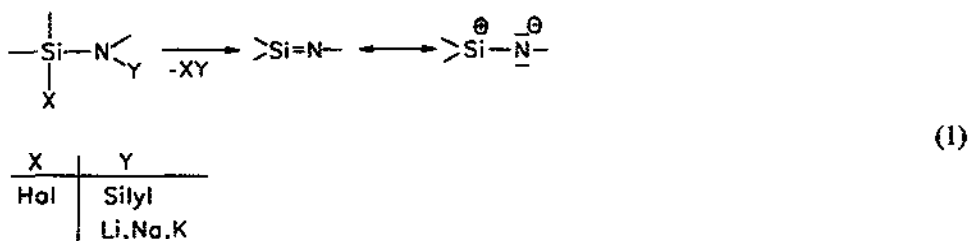
The multiply bonded systems of phosphorus, first prepared in the 1970s, are more stable than those of silicon. Nevertheless, the first silaethenes [1] and disilenes [2] were synthesized at the beginning of the 1980s and the first iminosilanes [3,4] were reported in

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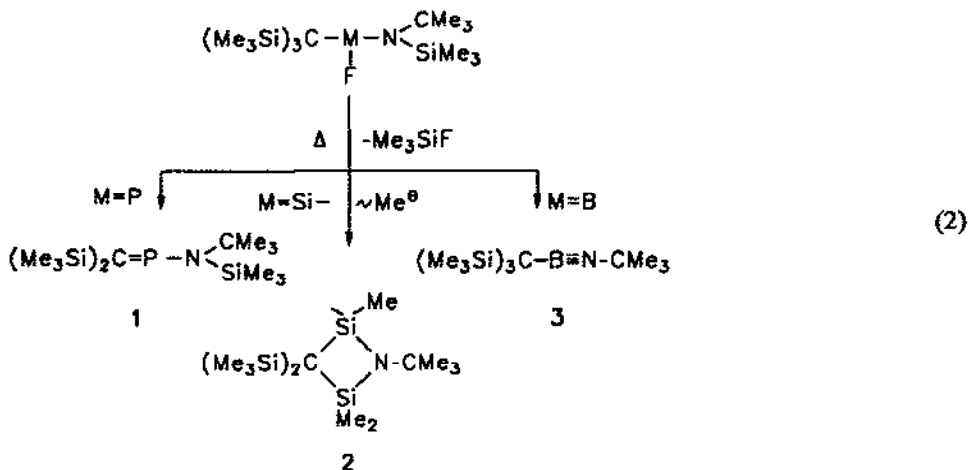
Scheme 1.

the mid-1980s. The difference in electronegativity of Si (1.8) and N (3.0) gives the iminosilanes an ylidic nature which makes them susceptible to oligomerization and dimerization. However, monomers can be kinetically stabilized by the presence of bulky substituents (eqn. (1)). In this review, we examine the methods of preparation for the iminosilanes, their structural features and some of their chemistry.



## B. FLUOROSILANE ELIMINATION

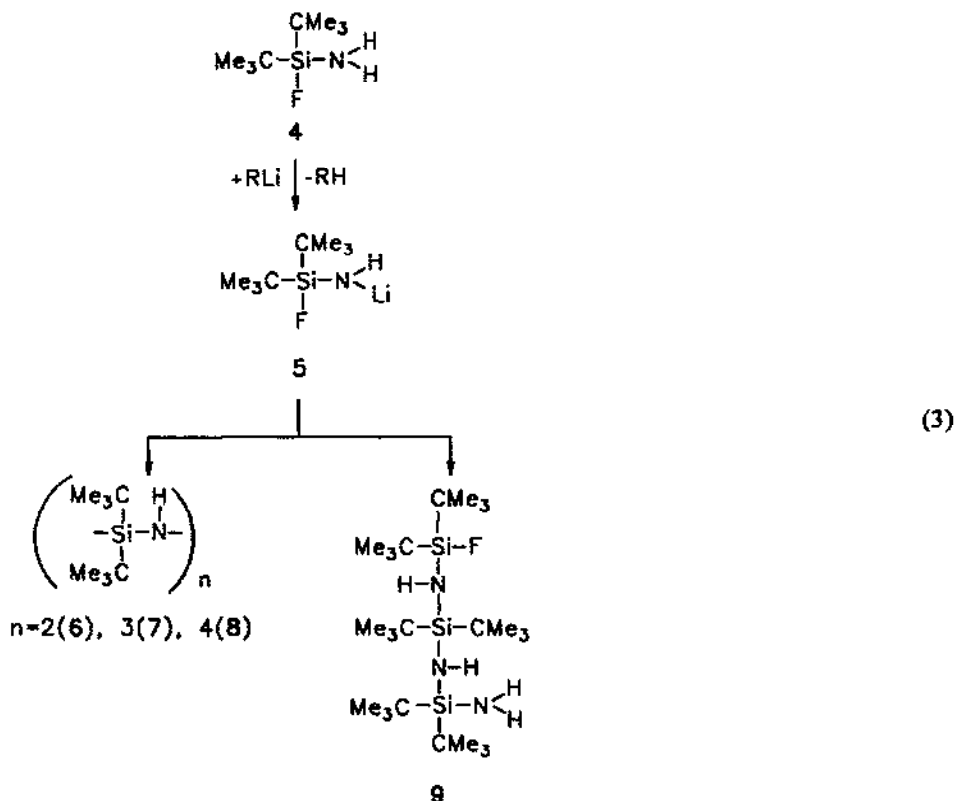
Since the first stable iminophosphanes were prepared by the elimination of fluorotrimethylsilane [5], we have attempted to isolate an iminosilane using an analogous method. To begin, we synthesized aminofluorosilanes with bulky substituents, for example with  $(\text{Me}_3\text{Si})_3\text{C-}$  and  $\text{Me}_3\text{Si}(\text{CMe}_3)\text{N-}$  groups at the silicon atom (eqn. (2)).



The fluorosilane-elimination occurred smoothly, but the unsaturated intermediate, which may be an iminosilane or a silaethene, rearranges by a nucleophilic 1,3-methanide ion migration [6]. A four-membered (SiCSiN) ring is formed in contrast to the analogous reactions with fluoroboranes or phosphanes, which lead to the formation of iminoboranes and phosphathenes [6].

### C. AMINOFLUOROSILANES

Salts are thermodynamically better leaving groups than halogenosilanes. For that purpose, we have prepared aminohalogenosilanes and their alkali derivatives. We used fluorine compounds because SiF–NH groups do not condense as easily as the chlorine compounds. NH<sub>2</sub>-functional aminochlorosilanes of the type >SiClNH<sub>2</sub> are still unknown today [7] (eqn. (3)).



The aminofluorosilane (CMe<sub>3</sub>)<sub>2</sub>SiFNH<sub>2</sub> (4) shows no tendency to condense either with HF- or with NH<sub>3</sub>-elimination, and forms stable alkali derivatives. At temperatures higher than 70°C the lithium salt (5) forms four- (6), six- (7), and eight-membered rings (8) via Li–F elimination. Their size can be influenced by the reaction conditions. The chain compound 9 is the direct precursor of the six-membered ring 7 [8].

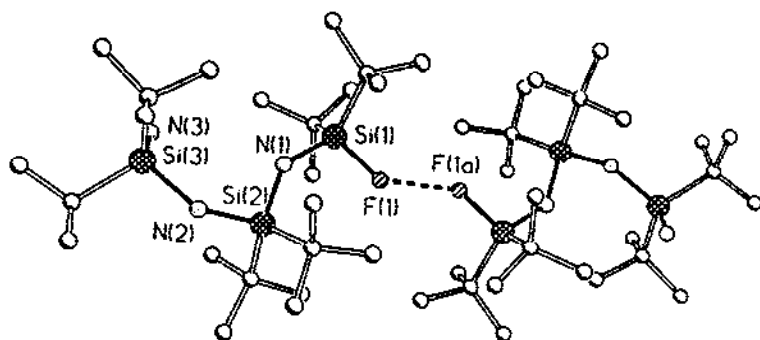


Fig. 1. Crystal structure of 9.

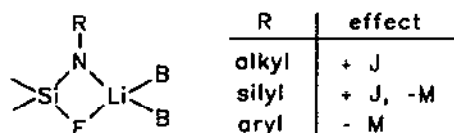
The  $^{19}\text{F}$  NMR spectrum of 9 shows an unusually large coupling ( $^3J(\text{FSiNH}) = 15.5 \text{ Hz}$ ). Therefore, we expected the molecule to form a cyclic structure with an intramolecular  $\alpha\text{-}\omega$  H–F-bridge. Instead, van der Waals F–F distances of 313.9 pm were found for the first time in an NSiF compound (Fig. 1). The six-membered  $(\text{SiN})_3$ -ring (7) is planar while the eight-membered  $(\text{SiN})_4$ -ring (8) shows a maximum deviation from the plane of 26 pm but is the most planar eight-membered  $(\text{SiN})_4$  ring [7] known so far.

#### D. LITHIUM DERIVATIVES OF AMINOFLUOROSILANES

The high reactivity of the lithiated aminofluorosilane 5 allows the step-by-step synthesis of numerous bis and tris-fluorosilylamines and chain compounds [9]. With an aim towards salt eliminations, we were especially interested in NH-functional bis(silyl)amines. In order to understand their reactions, we isolated their lithium derivatives and carried out extensive crystal structure investigations (Scheme 2).

Essentially three factors determine the structural make up 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.



B: thf, tmeda, 12-crown 4

Scheme 2.

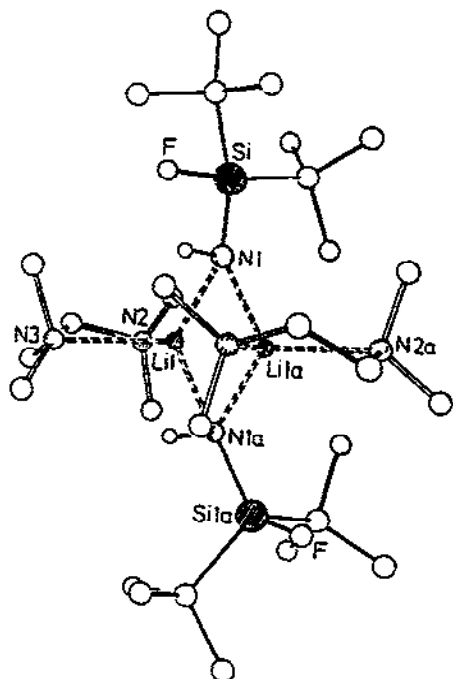


Fig. 2. Crystal structure of  $[(\text{CMe}_3)_2\text{SiFNHLi}(\text{tmeda})]_2$  (5). Si-F 164.3 pm, Si-N 167.2 pm, N-H 82.2 pm.

- (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 distances with large angles at the nitrogen atom. A selection of structure determinations illustrates these features. Figure 2 shows the crystal structure of the only lithium derivative of a  $\text{NH}_2\text{-SiF}$  compound characterized so far [7]. The compound crystallizes from tmeda as a dimer containing an  $(\text{LiN})_2$  four-membered ring. Lithium is bonded exclusively to the nitrogen atoms of the amino-fluorosilane and of the Lewis base tmeda. This is the only example in this class of compounds in which lithium is neither intramolecularly nor intermolecularly bound to fluorine. Since the dimer contains a twofold axis of symmetry rather than an inversion centre, both nitrogen bound hydrogen atoms are located on the same side of the  $(\text{LiN})_2$  four-membered ring.

In the next example, hydrogen is replaced by a tert-butyl group (Fig. 3). No donor solvent was used. The basicity of the nitrogen is still strong enough for the molecule to dimerize across a four-membered  $(\text{LiN})_2$ -ring, but lithium is also bound to fluorine to give a tricyclic compound. The result is a longer Si-F bond (166.0 pm) and a shorter Si-N bond (165.7 pm) than in the previous molecule. In this compound, the lithium atom seems to be only three coordinate, but according to the X-ray structural analysis, there are short

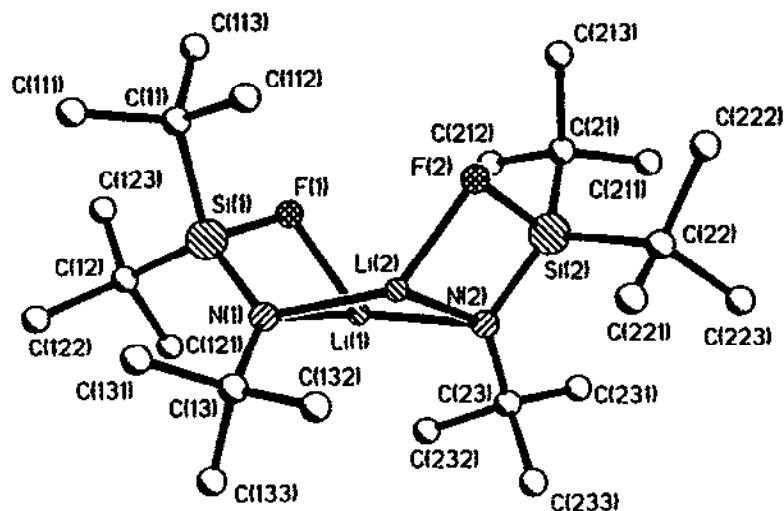


Fig. 3. Crystal structure of  $[(\text{CMe}_3)_2\text{SiFLiNCMe}_3]_2$  (10).

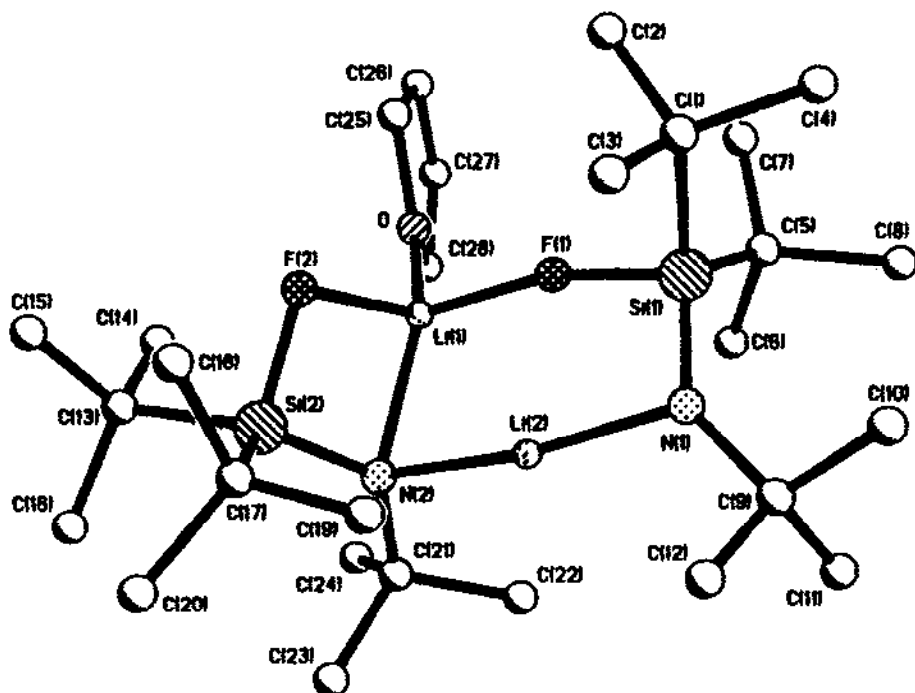
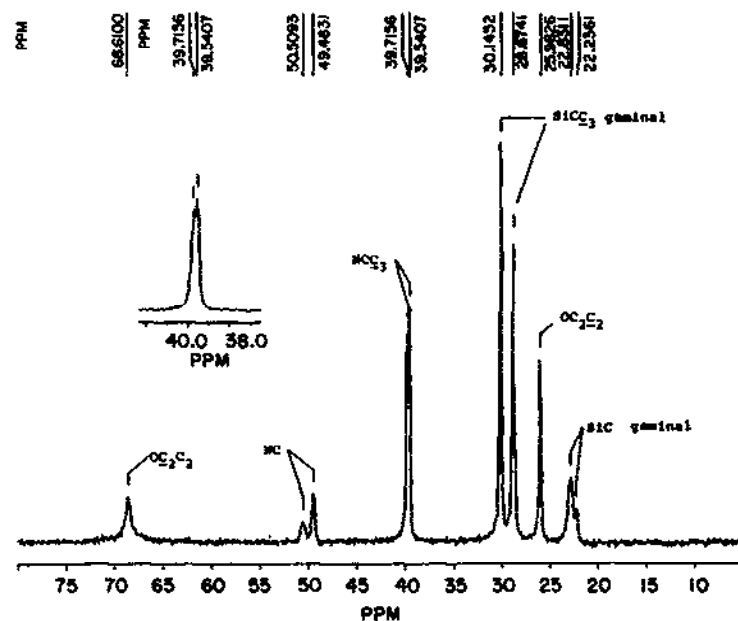


Fig. 4. Crystal structure of  $[(\text{CMe}_3)_2\text{SiFLiNCMe}_3]_2 \cdot \text{thf}$  (11).

Fig. 5. Solid state  $^{13}\text{C}$  NMR spectra of 11.

lithium–methyl distances of only 212 pm [11]. This compound adds one molecule of thf per dimer when crystallized from thf. A bicyclic compound is obtained with fourfold  $[\text{F}_2\text{Li}(\text{thf})\text{N}]$  and twofold  $[\text{NLiN}]$  coordinated lithium [12] (Fig. 4). In the solid state, the

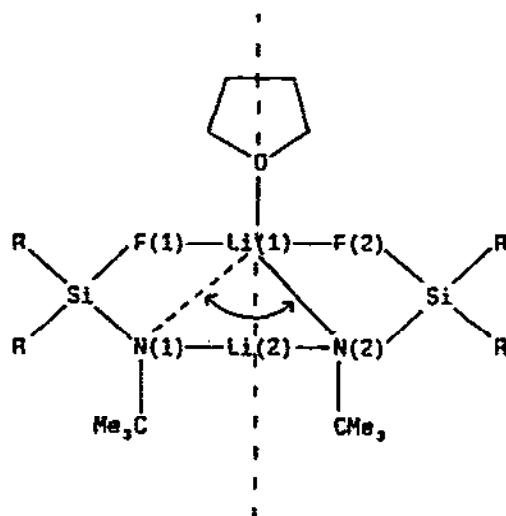


Fig. 6. Structure of 11 in solution.

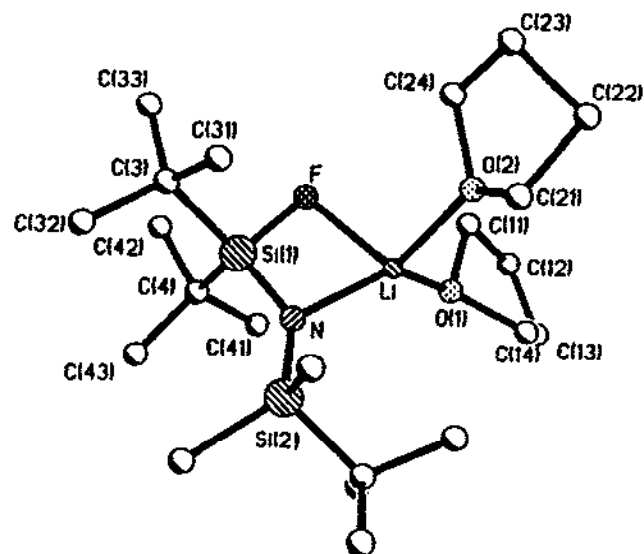


Fig. 7. Crystal structure of  $[(\text{CMe}_3)_2\text{SiFLi}(\text{thf})_2\text{NSiMe}_2\text{CMe}_3]$  (12).

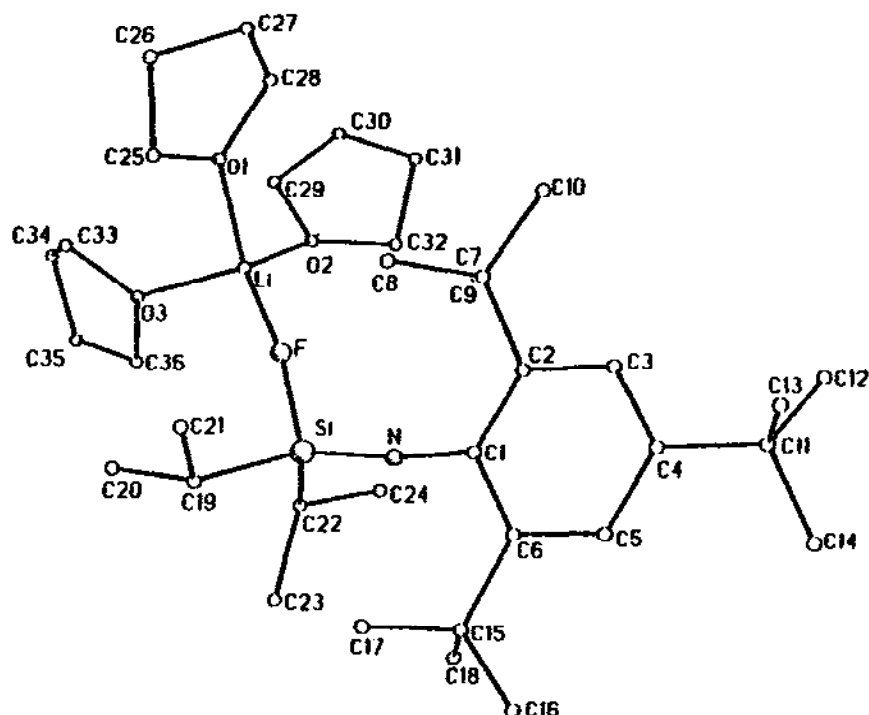


Fig. 8. Crystal structure of  $(\text{Me}_2\text{CH})_2\text{SiFLi}(\text{thf})_3\text{NC}_6\text{H}_2(\text{CMe}_3)_3$  (13).



molecules are made up of two different moieties. The Si(1)–N(1) bond length (162.7 pm) in the six-membered ring is typical of an Si=N– double bond. This part of the molecule can be interpreted as an iminosilane. The Si(2)–N(2) bond (168.1 pm) of the four-membered ring is 5.4 pm longer and is viewed as an aminosilane. The  $^7\text{Li}$  and solid state  $^{13}\text{C}$  NMR spectra confirm the asymmetry of 11 (Fig. 5). NMR spectra in solution show an equilibration of the H, C, F and Si atoms, consistent with fluctuation of the Li(1)–N(1) and Li(1)–N(2) bonds [12] (Fig. 6).

In molecule 12 (Fig. 7), the substituent bound to nitrogen is a silyl group and decrease in the basicity of the nitrogen centre allows for the formation of a monomer. The crystal structural analysis shows a four-membered (SiNLiF)-ring with the lithium coordination sphere satisfied by two thf molecules [13].

When the substituent attached to nitrogen is aromatic, as in 13 (Fig. 8), the further decrease in the basicity of the nitrogen atom leads to a complete rupture of the Li–N contact. Lithium now has migrated completely to the stronger Lewis base fluorine. The result is a short Li–F bond (182.2 pm) and a long Si–F bond (168.6 pm). The Si=N– double bond length is 161.9 pm and the Si–N–C angle of  $172.1^\circ$  is typical of an imine [14]. Therefore, this molecule must be considered as an LiF-adduct of an iminosilane.

The examples show that the strong Lewis acid lithium strives to bind the strong Lewis base fluorine, consistent with the Pearson concept. Weaker Lewis acids such as sodium in compound 14, favours a weaker Lewis basic nitrogen [15] (Fig. 9). When 13 is

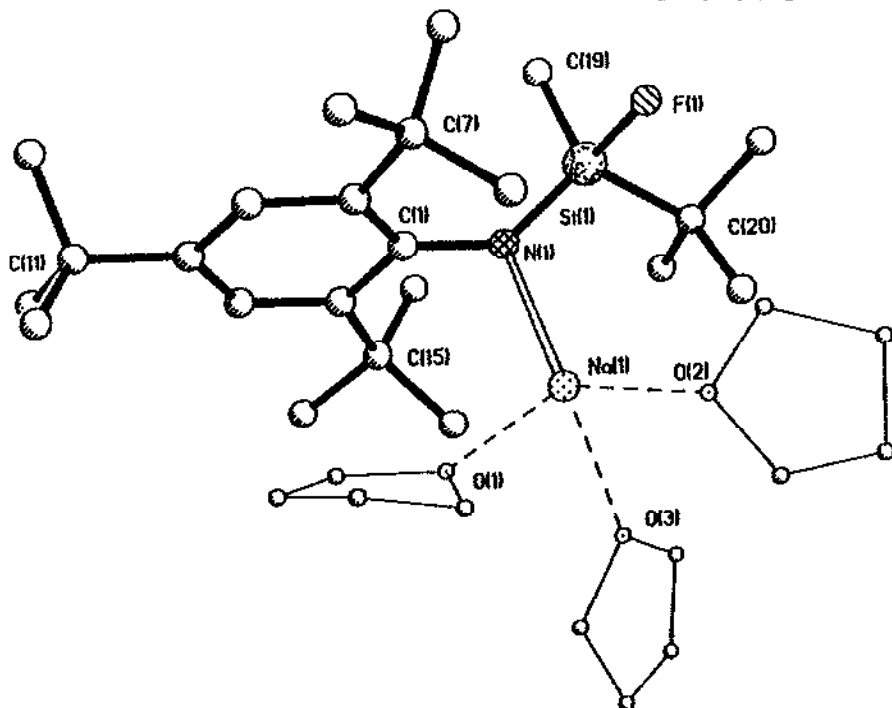


Fig. 9. Crystal structure of  $\text{CMe}_3\text{Si}(\text{Me})\text{FNa}(\text{thf})_3\text{NC}_6\text{H}_2(\text{CMe}_3)_3$  (14).

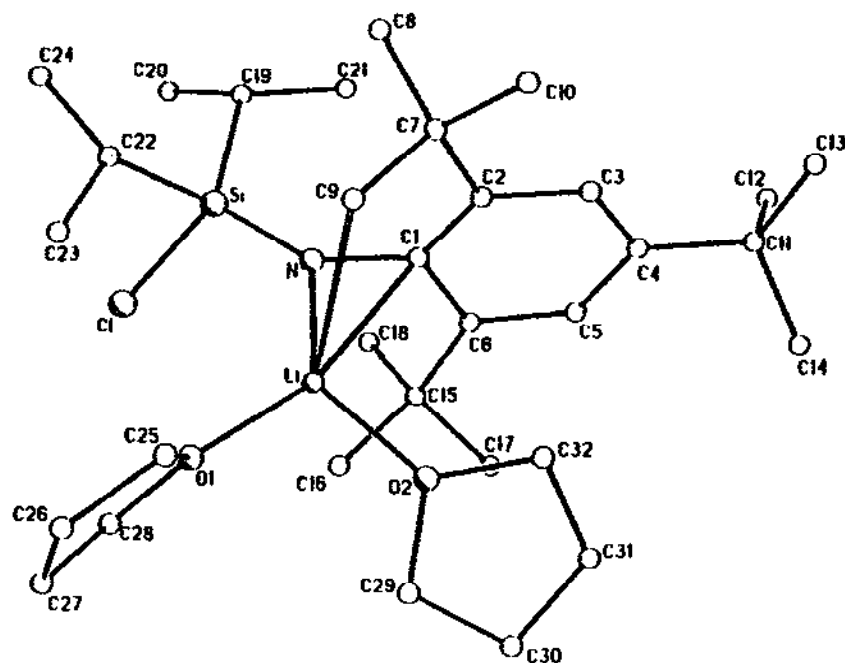


Fig. 10. Crystal structure of  $(\text{Me}_2\text{CH})_2\text{SiClNLi}(\text{thf})_2\text{C}_6\text{H}_2(\text{CMe}_3)_3$  (**15**).

converted into the lithiated aminochlorosilane **15** (Fig. 10), lithium is bound to nitrogen, which is now the strongest and therefore most attractive Lewis base in the molecule [14].

The following compounds were selected to illustrate the influence of further Lewis bases in the molecule on the structure. Figure 11 shows the lithium derivative of the bis(fluorosilyl)amine **16** recrystallized from thf. The coordination sphere of the lithium is made up of the two fluorine atoms and two thf molecules. Thus, the lithium atom brackets the skeleton of the molecule to form a planar six-membered ring. This geometry forces the tert-butyl groups into eclipsed positions. But despite this steric compression, the nitrogen atom is shifted towards the lithium atom due to electrostatic interaction. The result is an almost linear Si–N–Si unit in the ring with nitrogen  $\text{sp}$  hybridized. Again there are Si–N distances (163.6 pm) which lie in the range of double bonds [10]. Another interesting feature is that the  $^7\text{Li}$  NMR spectrum shows a triplet at room temperature with an LiF-coupling of 15 Hz indicating lithium is coordinated to fluorine even in solution. The influence of the donor solvent is illustrated when compound **16** is recrystallized in the presence of 12-crown-4 [10]. The crystal structure shows a free amid (**17**, Fig. 12) and the lithium centre is coordinated by two crown ether molecules and is formally eight-coordinate. There are no other contacts between the ions. Since the lithium atom no longer brackets the fluorine atoms, the tert-butyl groups become staggered and steric compression is minimized.

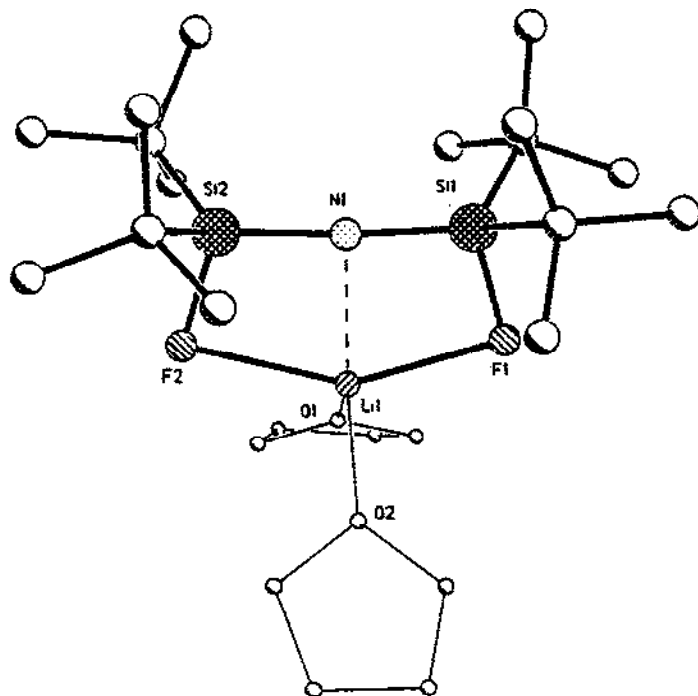


Fig. 11. Crystal structure of  $[(\text{CMe}_3)_2\text{SiF}]_2\text{NLi}(\text{thf})_2$  (16).

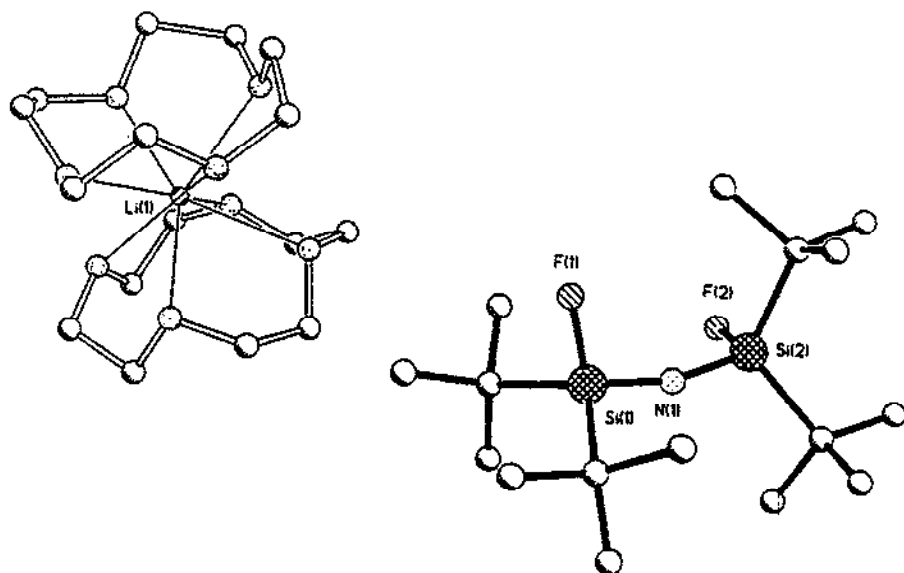


Fig. 12. Crystal structure of  $[(\text{CMe}_3)_2\text{SiF}]_2\text{N}^-\text{Li}^+(\text{12 crown-4})_2$  (17).

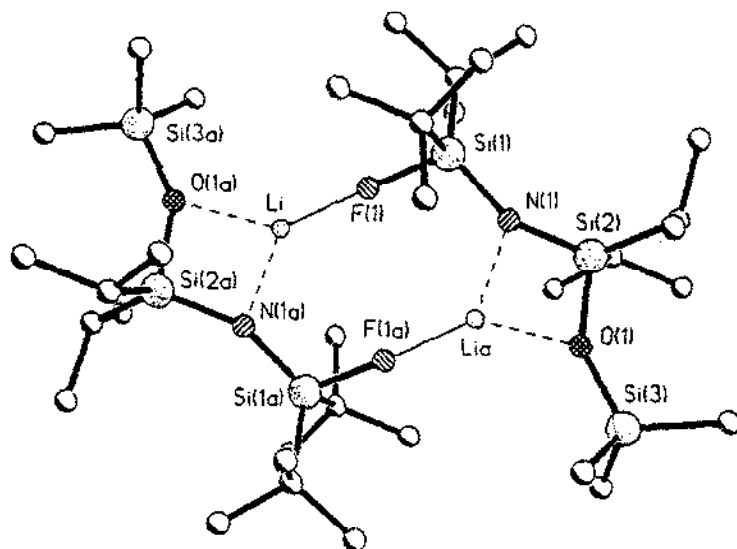


Fig. 13. Crystal structure of  $[(\text{CMe}_3)_2\text{SiFLi}(\text{CHMe}_2)_2\text{OSiMe}_3]_2$  (18).

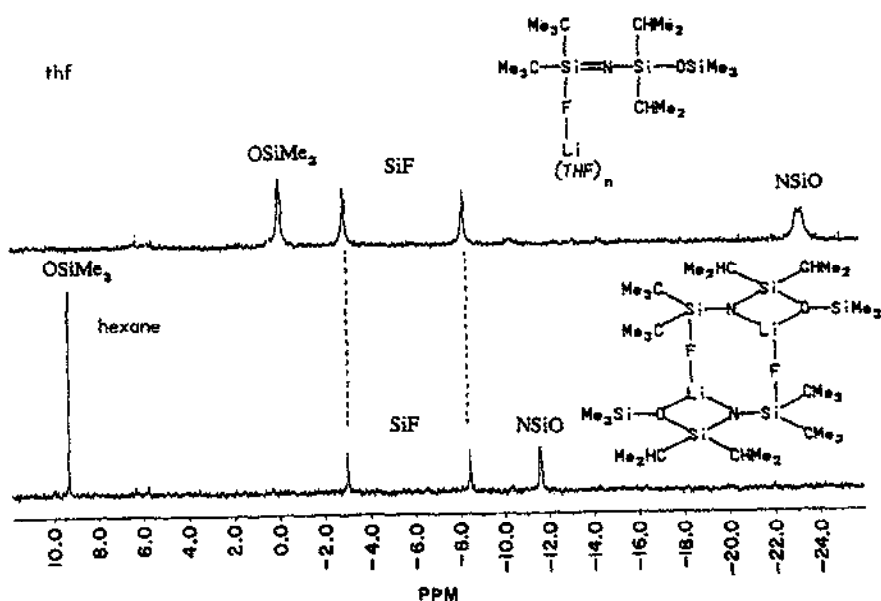


Fig. 14.  $^{29}\text{Si}$  NMR spectrum of 18 in hexane and thf.

The last example is the lithium derivative of an aminofluorosilane containing three different Lewis bases, fluorine, nitrogen and oxygen (**18**, Fig. 13) all of which are bound to lithium [16]. Most remarkable is the shortness of the Li–F bond, which is only 179.6 pm, the shortest observed so far in a covalent lithium compound. The strong Li–F interaction even exists in solution if the solvent is not polar. The  $^{19}\text{F}$  NMR spectrum shows a quartet and the lithium spectrum a doublet with a coupling constant as high as 95 Hz (compare **16**), the largest LiF coupling reported to date. The shortness of the Li–F bond may account for the fact that lithium is only three coordinate. The sum of the angles is  $357^\circ$  indicating lithium is  $\text{sp}^2$  hybridized. The Si(1)–N bond (163.6 pm) is again in the range of a double bond, the SiNSi angle is wide ( $155.6^\circ$ ) and the Si–F bond is long (168.0 pm). Therefore, we interpret this molecule as a dimer of an iminosilane Li–F adduct. The crystals for this structural analysis were obtained from hexane and it is interesting that crystals obtained from thf yielded an identical structure. Obviously lithium does not require saturation of its coordination sphere in the solid state even if there is a Lewis base available. This was a surprising result to us because the NMR spectra of the compound in thf was significantly different to that observed in hexane [16].

Figure 14 shows a comparison between the  $^{29}\text{Si}$  NMR spectrum of **18** in hexane and in thf. Most remarkable is the fact that the chemical shift and the coupling constant of the SiF group are unaffected by the solvent. However, in thf, the other two signals are shifted considerably upfield: the (NSiO) group from  $\delta -11.7$  to  $-24.3$  ppm and the siloxy group from  $\delta 9.3$  to  $-1$  ppm. This shows that the coordination of the lithium atom by oxygen and nitrogen is replaced by thf, but not the coordination by fluorine. So this Li–F adduct of an iminosilane must be a monomer when dissolved in a Lewis base. The crystal structure determinations prove that lithiated aminofluorosilanes can be regarded as LiF adducts of iminosilane depending on the solvent and the substituent. Therefore, these molecules should be suitable precursors for free iminosilanes.

## E. REACTIONS

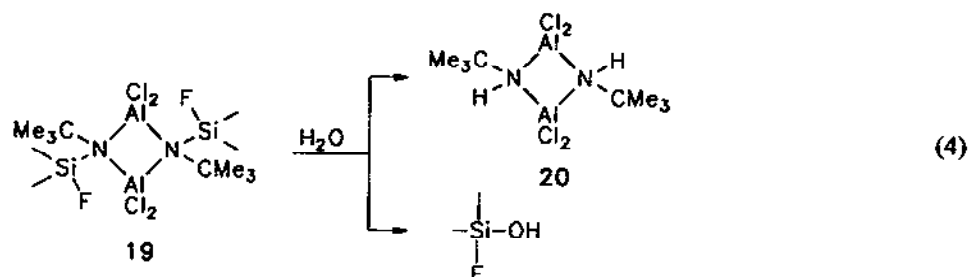
The high reactivity of lithiated aminofluorosilanes has lead to the synthesis of a number of interesting compounds. Some characteristic reactions are presented below with elements or compounds of Groups IIIa to VIa.

### (i) Characteristic reactions with compounds of Groups IIIa to VIa

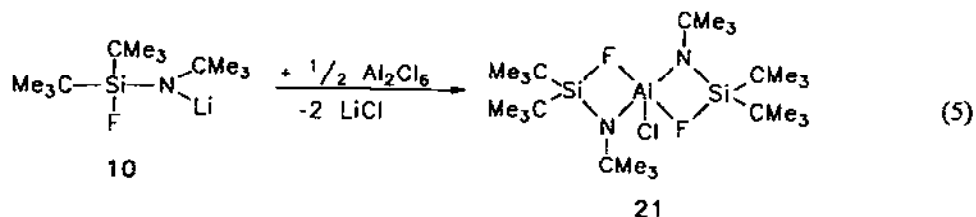
#### (a) Group IIIa

The products of the reaction of aluminium halides with lithiated aminofluorosilanes depend on the reaction conditions:

- (1) a dimeric  $\text{AlCl}_2$  compound is obtained if  $\text{AlCl}_3$  is added to a lithium salt of an aminofluorosilane in non-polar solvents (eqn. (4)). Hydrolysis of **20** leads to the formation of a dimeric iminoalane and a fluorosilanol [17].

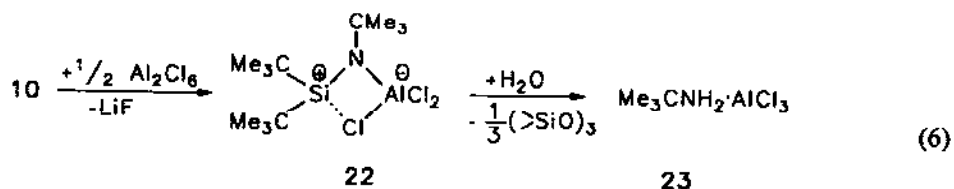


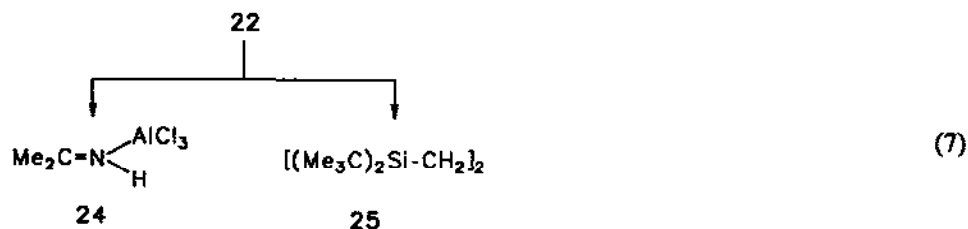
- (2) If the two agents are mixed in the reverse order, a monomeric disubstituted product is obtained (eqn. (5)) [18].



The molecular structure of 21 with bridging fluorine atoms, allows the interpretation of the molecule as an  $\text{AlClF}_2$  1:2 adduct of an iminosilane. Aluminium is five coordinate on account of its Lewis acid character, and the geometry of the nitrogen atoms is planar (sum of the bond angles around N(1) and N(2)  $359.4$  and  $359.0^\circ$ , respectively).

- (3) The reaction of 10 with  $\text{Al}_2\text{Cl}_6$  in ether leads to the elimination of  $\text{LiF}$  and formation of a 1:1 adduct of the iminosilane with  $\text{AlCl}_3$  (eqn. (6)). The partial zwitterionic character is supported by the low-field  $^{29}\text{Si}$  NMR chemical shift ( $\delta$  50.4 ppm). The  $^{27}\text{Al}$  NMR shift ( $\delta$  107 ppm) is typical of a four coordinate aluminium centre. Hydrolysis of 22 produces the aminoalane 23 (eqn. (6)), a compound in which an  $\text{AlCl}_3$  unit is preserved, and the cyclic siloxane  $[(\text{CMe}_3)_2\text{SiO}]_3$  [18]. Formation of 23 supports the interpretation of 22 as an iminosilane adduct. Compound 22 is thermally unstable and decomposes to an adduct of the azomethine 24 with  $\text{AlCl}_3$  and the four-membered  $(\text{SiC})_2$ -ring 25 [19].





Experiments to synthesize iminosilane adducts (like 22) by cleavage of Si–N-rings such as 26 gave the adduct 27. Hydrolysis of this compound gave the first cationic Si–N-rings with protonated nitrogen and correspondingly very long Si–N single bonds (eqn. (8)). The Si–N bonds in 28 (179.2 pm) are significantly longer than in 26 (174.7 pm), i.e. they are weakened due to the  $\text{sp}^3$  hybridization of the nitrogen centre [20] (Fig. 15).

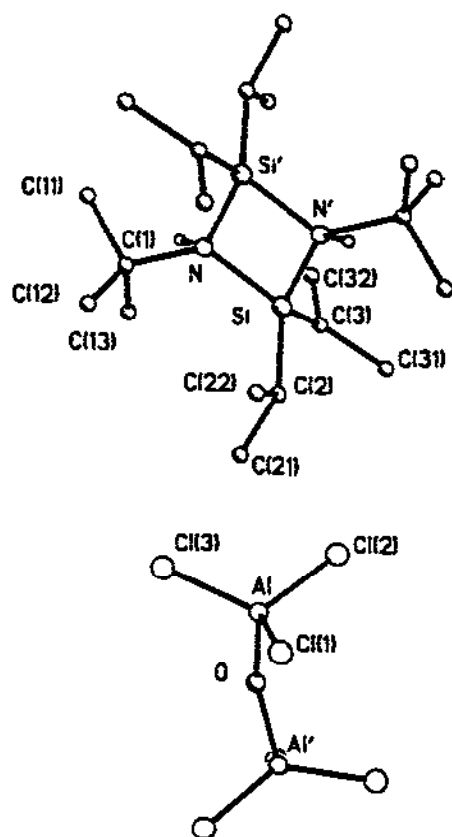
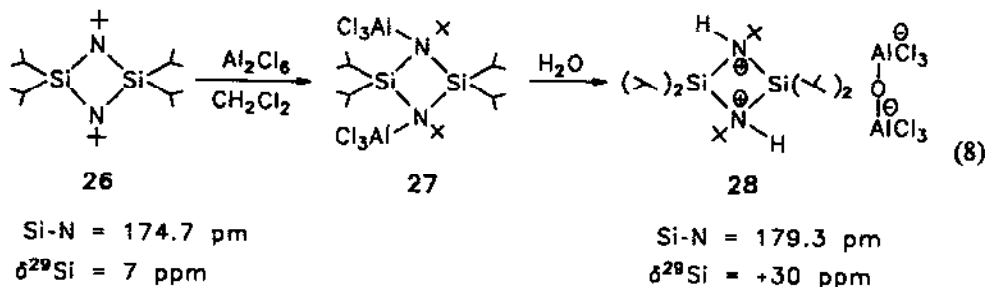
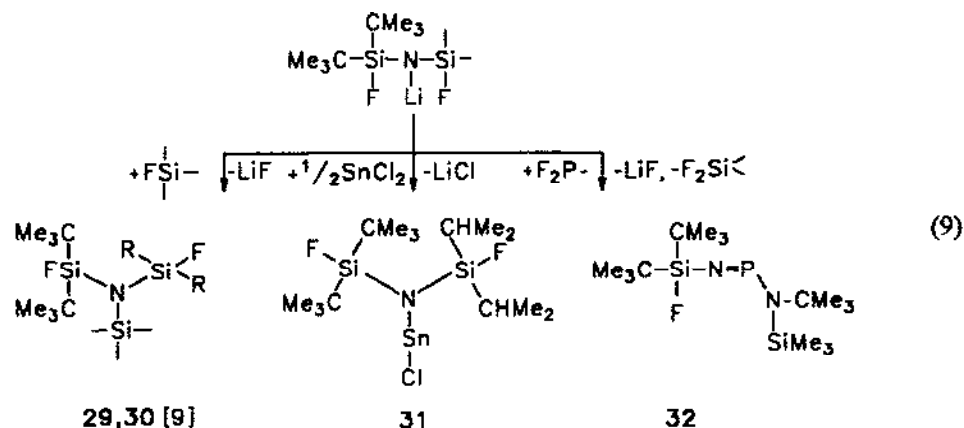


Fig. 15. Crystal structure of 28.



(b) Group IVa

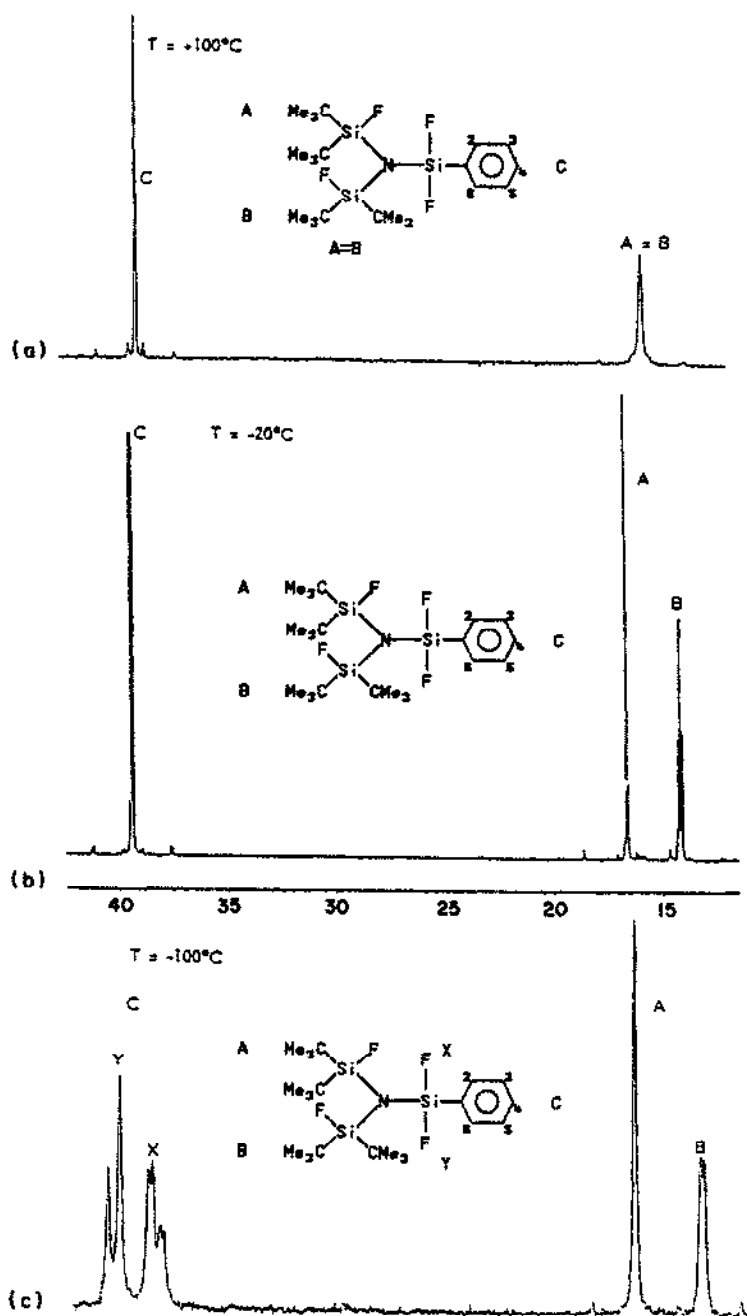
Equation (9) shows selected reactions of lithiated aminofluorosilanes with compounds of Groups IVa and V. In reactions with fluorosilanes, the high reactivity of the lithium salts allows the synthesis of very bulky molecules with a frozen Si-N bond at room temperature.



Tris(fluorosilyl)amines with three different silyl groups were synthesized in stepwise reactions [9]. In these compounds, the nitrogen atom is so often voluminously substituted, that a rotational barrier is observed by NMR spectroscopy at room temperature and even above. The influence of temperature on the Si-N bond rotation is illustrated by the  $^{19}\text{F}$  NMR spectrum of 29 [9].

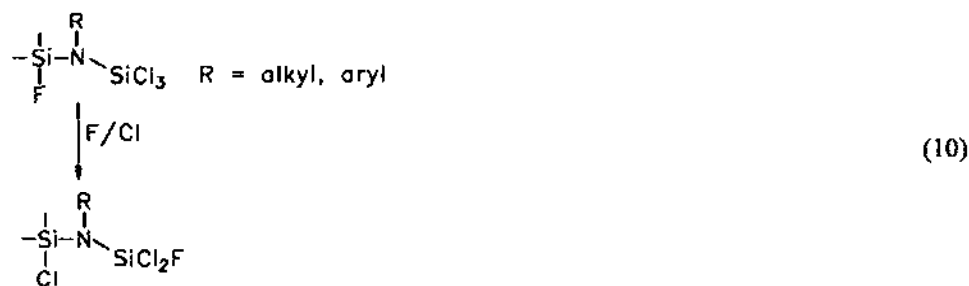
Above  $63^\circ\text{C}$ , the SiF groups are equivalent see (Fig. 16(a)), and the spectrum is first order. Below that temperature (Fig. 16(b)), two of the three Si-N bonds are frozen. At  $-20^\circ\text{C}$ , the fluorine atoms of the SiF<sub>2</sub> groups are still equivalent, implying that there still must be a rotation of the N-SiF<sub>2</sub> bond. However, at  $-100^\circ\text{C}$  (Fig. 16(c)), the fluorine atoms of the SiF<sub>2</sub> group show two chemical shifts with a coupling constant of  $^2J(\text{FF}) = 42 \text{ Hz}$ . Only the fluorine atom of the SiF group B couples with one fluorine atom (X) of the SiF<sub>2</sub> group C. The  $^4J(\text{FF})$  coupling is very large indicating a strong interaction between these two fluorine atoms, which was confirmed by the crystal structure analysis of 29 (Fig. 17) [9]. The non-bonding F(2)-F(3) distance (in the spectra F(B) and F(X)) is



Fig. 16.  $^{19}\text{F}$  NMR spectrum of  $[(\text{CMe}_3)_2\text{SiF}]_2\text{NSiF}_2\text{C}_6\text{H}_5$  (29).

very short (289 pm) and the Si(1)F group is in a *trans*-position, while the Si(2)F group is in a *cis*-position to the SiF<sub>2</sub> group. Compound **29** shows only one conformer, whereas the compound [(CMe<sub>3</sub>)<sub>2</sub>SiF]<sub>2</sub>NSiF<sub>3</sub> **30** [9] shows two in the <sup>29</sup>Si NMR spectrum, with two quartets for the SiF<sub>3</sub> group (Fig. 18). We concluded that the molecule forms a symmetrical (I) and a non-symmetrical (II) isomer. In the symmetrical molecule (I), the SiF<sub>3</sub> group couples with both fluorine atoms of the SiF groups. Therefore, a quartet of triplets is observed. In the non-symmetrical molecule (II), the SiF<sub>3</sub> group couples with only one SiF group, which leads to a quartet of doublets.

Lithiated aminofluorosilanes react with MCl<sub>4</sub> (M = Si, Ge, Sn) to give compounds of the type >SiF–NR–MCl<sub>3</sub> (R = alkyl, aryl, silyl) [21, 22]. An intermolecular F/Cl exchange occurs with alkyl- and arylamino compounds (eqn. (10)).



The halogeno exchange depends on the substituents, the solvents and the temperature and is proved by crystal structure determinations [22]. Bulky aminofluorosilyl ligands stabi-

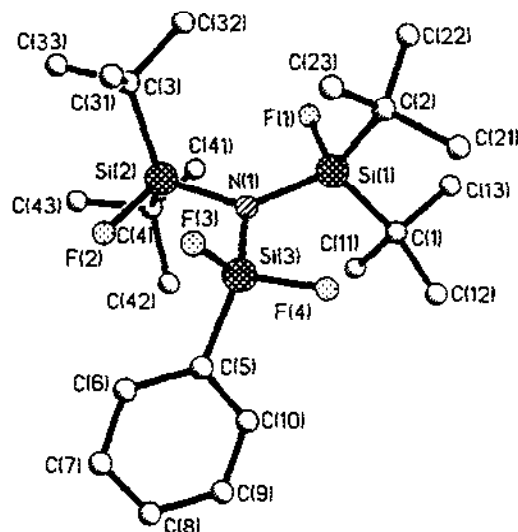


Fig. 17. Crystal structure of **29**.

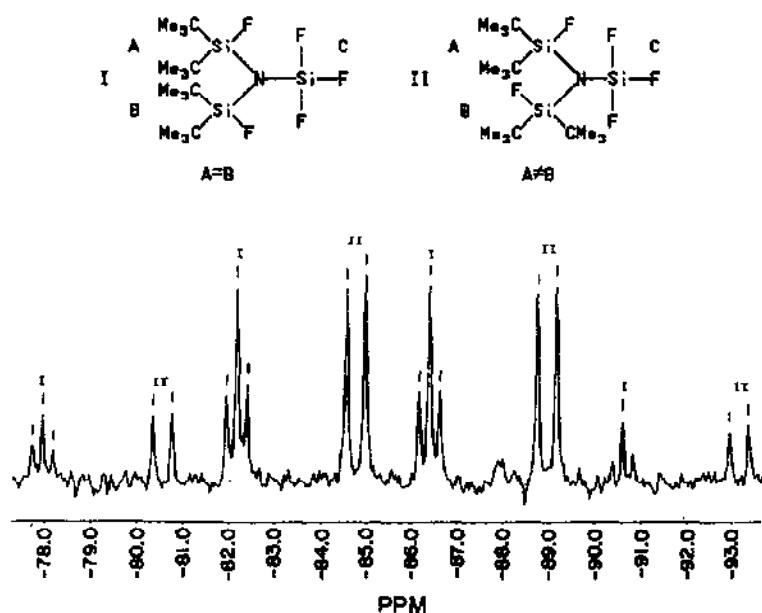
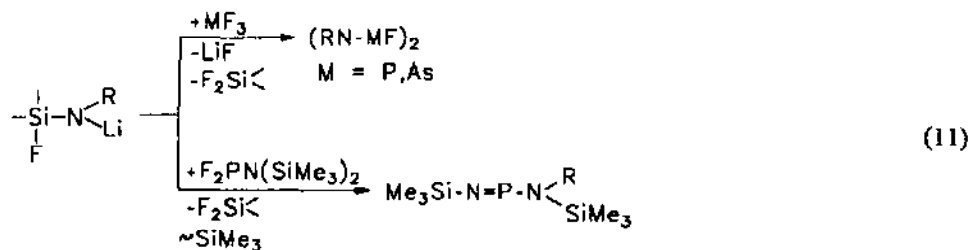


Fig. 18.  $^{29}\text{Si}$  NMR spectrum of 30 ( $\text{SiF}_3$  group).

lize elements in low coordination. So the lithium derivative of the bis(fluorosilyl)amine **16** reacts with  $\text{SnCl}_2$  to give the first bis(fluorosilyl)amino-chlorostannylene **31** (eqn. (9)), a compound with a covalent  $\text{Sn}^{\text{II}}\text{-Cl}$  bond [23] (eqn. (9)).

### (c) Group Va

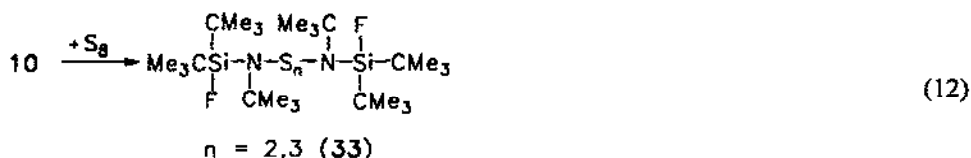
Halides of phosphorus and arsenic react with lithiated aminofluorosilanes to give substituted fluorosilylamines [23] (eqns. (9),(11)). Depending on the bulkiness of the ligands, halosilanes are cleaved off and four-membered rings or aminoiminophosphanes are formed. Compound **32** (eqn. (9)) is the first  $\text{SiF}$ -functionalized iminophosphane.



In the case of  $\text{R} = \text{aryl}$  a 1,3-migration of a silyl group from the silyl- to the arylamino-nitrogen is observed in these reactions [23].

## (d) Group VIa

Lithium derivatives of aminofluorosilanes, for example **10**, react with sulfur or selenium to give bis(fluorosilyl)aminosulfanes and selenanes, respectively (eqn. (12)). The trisulfane **33** crystallizes from *n*-hexane and exhibits a helical structure (Fig. 19) [24].



## (ii) Addition reactions

Products of many reactions prove that lithiated aminofluorosilanes indeed react like iminosilanes [11,16,25,26] (Scheme 3). For example, insertion products are obtained in reactions with H-acid compounds and silanols, silylethers, thioethers and acetylenes are formed [25]. (2+2)-Additions occur in reactions with iminophosphanes and SiN<sub>2</sub>P-rings are formed. Carbodiimides, sulfur diimides and azomethines are obtained with isocyanates, thionylamides and aldehydes [11,16,25]. These reactions are analogous to Wittig reactions. In the reaction of  $\alpha,\beta$ -unsaturated ketones with lithiated aminofluorosil-

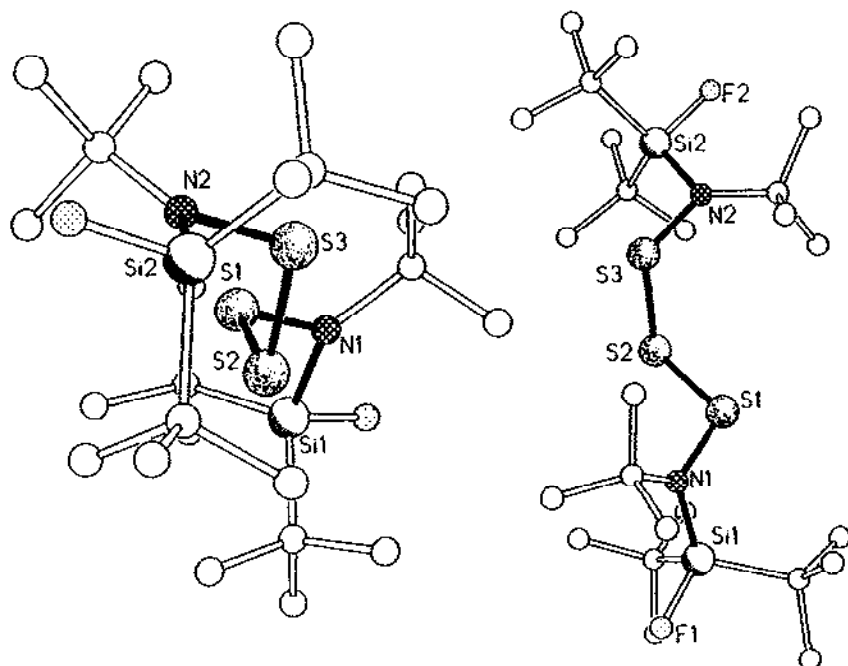
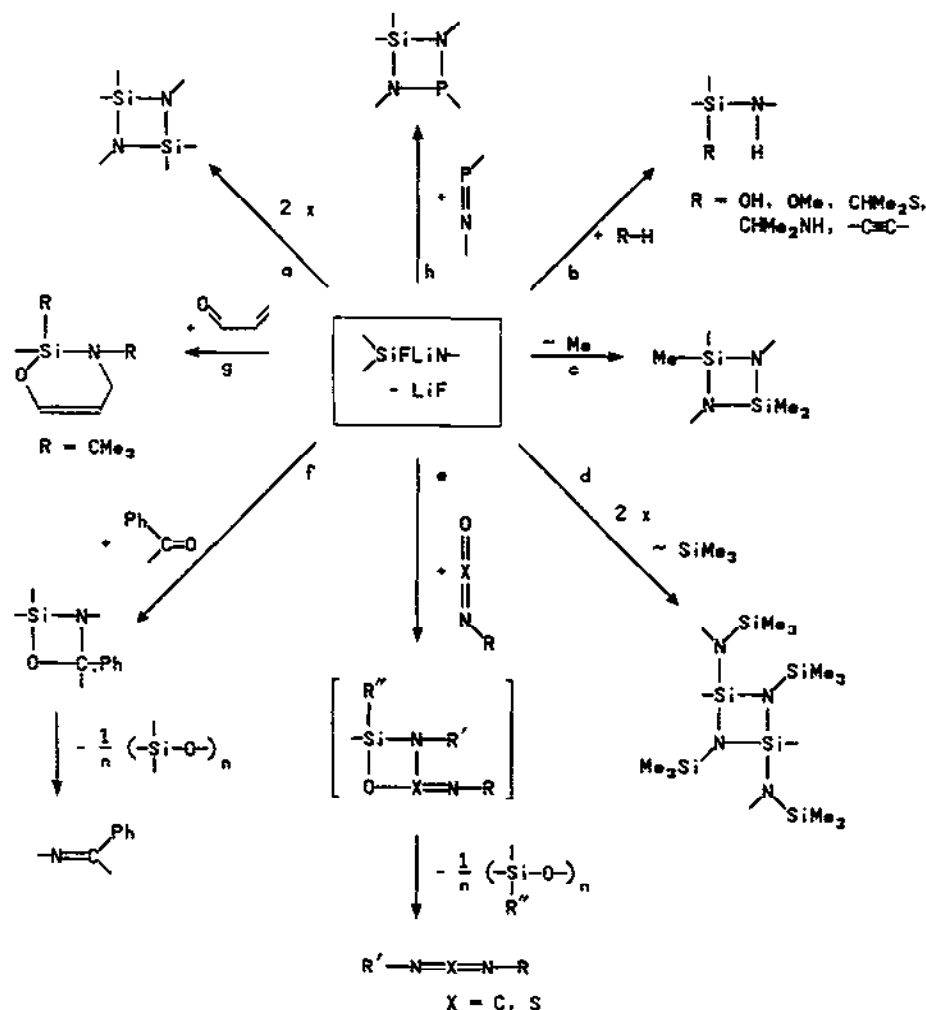
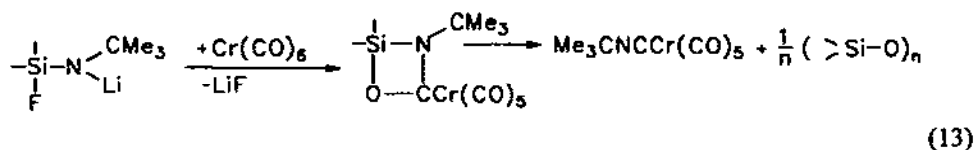


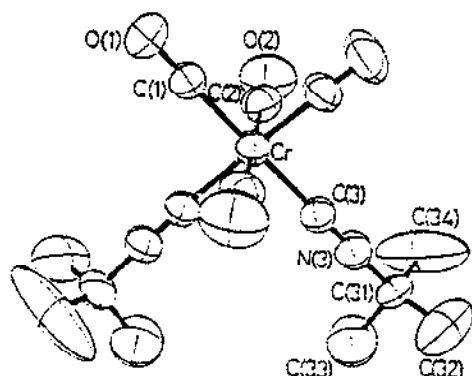
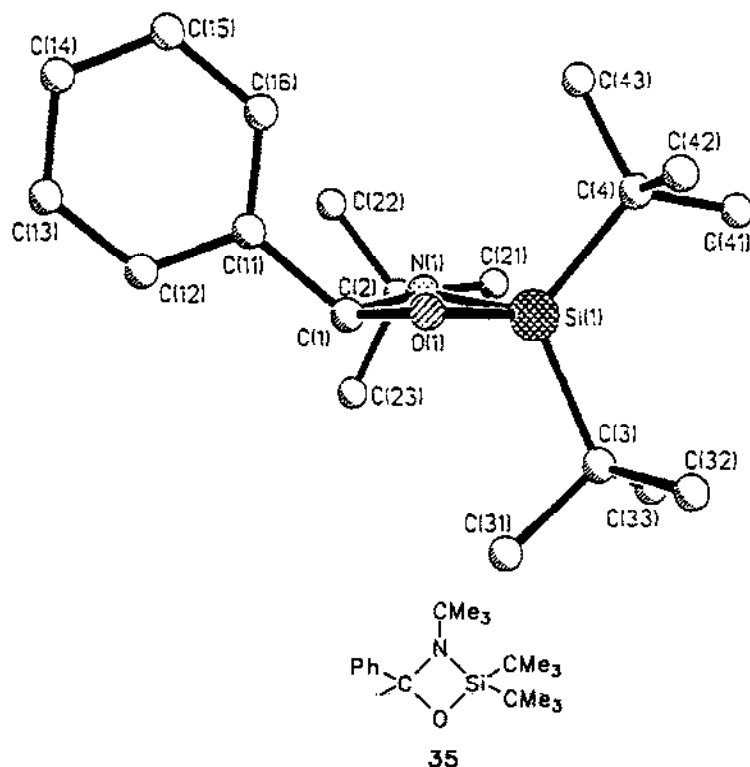
Fig. 19. Crystal structure of **33**.



Scheme 3.

anes, LiF is eliminated and (2+4)-cycloaddition to the intermediate iminosilane is observed [25]. The photochemical reaction of a lithiated aminofluorosilane with  $\text{Cr}(\text{CO})_6$  leads to substitution of one or two carbonyl oxygen atoms and formation of isonitrile complexes. The crystal structure of the disubstituted product *cis*-di(tert-butylisonitrile)tetracarbonylchromium (34) has been determined (Fig. 20) [26].



Fig. 20. Crystal structure of  $(\text{Me}_3\text{CNC})_2\text{Cr}(\text{CO})_4$  (34).

$\text{Si}(1)-\text{O}(1)=168.6 \text{ pm}$      $\text{O}(1)-\text{Si}(1)-\text{N}(1): 80.0^\circ$   
 $\text{N}(1)-\text{C}(1)=147.0 \text{ pm}$   
 $\text{Si}(1)-\text{N}(1)=172.3 \text{ pm}$   
 $\text{C}(1)-\text{O}(1)=145.6 \text{ pm}$

Fig. 21. Crystal structure of  $\text{C}_6\text{H}_5\text{CH}(\text{NCMe}_3)\text{OSi}(\text{CMe}_3)_2$  (35).

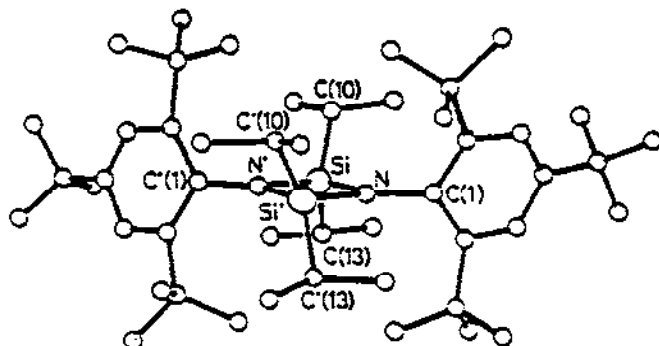


Fig. 22. Crystal structure of  $[(\text{Me}_2\text{CH})_2\text{Si}-\text{NC}_6\text{H}_2(\text{CMe}_3)_3]_2$  (36).

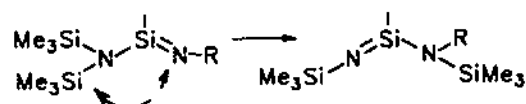
In the reaction of **10** with phenylaldehyde, a stable (SiNCO) four-membered ring (Fig. 21) is formed [27].

### (iii) Elimination of LiF

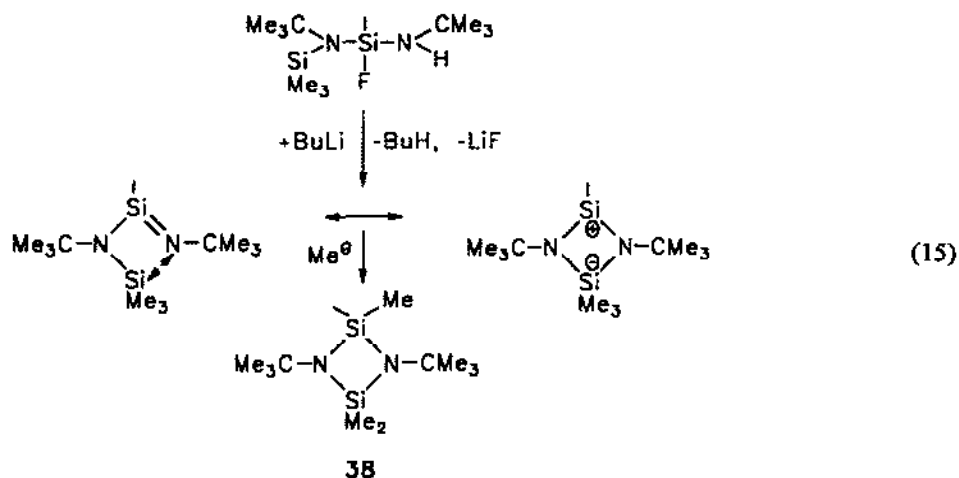
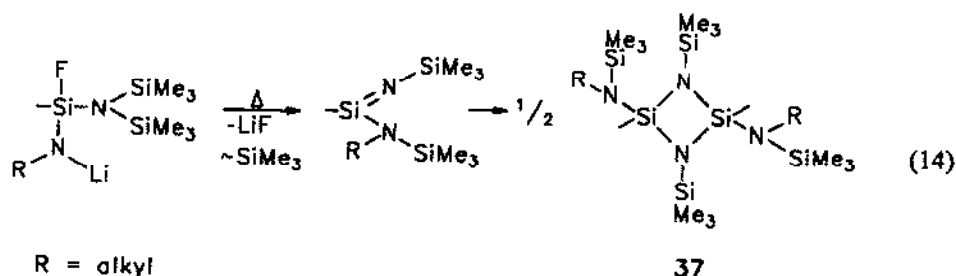
Is LiF a good thermodynamic leaving group? Because of the strong Si–F bond, lithiated aminofluorosilanes are often very stable and can be purified by distillation. Therefore, attempts to eliminate LiF lead to dimerization or rearrangement of the formed polar iminosilane. Let us focus on some reactions starting with the lithiated arylamino-fluorosilane **13**. After LiF elimination, the resulting dimer is an asymmetric stretched four-membered ring (Fig. 22) with the longest Si–N bonds observed in a ring so far [11]. The  $\text{CC}_2$ -isopropyl groups are twisted. These features indicate that the limits of dimerization have been reached. Silylamino groups stabilize elements in low coordination. They should reduce the polarity of the system  $>\text{Si}^\oplus\text{--N}^\ominus$  and because of the bulkiness of the substituents, dimerization of the iminosilane should not occur easily. However, bis(silyl)amino-organyliminosilanes cyclize with 1,3-migration of a silyl group from one nitrogen atom to the other (Scheme 4).

The silyl group migration can be explained by the propensity of silyl groups to be bonded to the more negatively charged atom.  $^{15}\text{N}$  NMR measurements prove that the electron density at the nitrogen centre is smaller in the silylimine than in the organylimine. The isomeric silyliminosilanes dimerize (eqn. (14)), and the 1,3-silyl group migration in such systems is proved by a crystal structure determination of **37** ( $\text{R} = ^i\text{Pr}$ ) [28].

If the size of the substituents is increased even further, another surprising ring closure occurs (eqn. (15)).



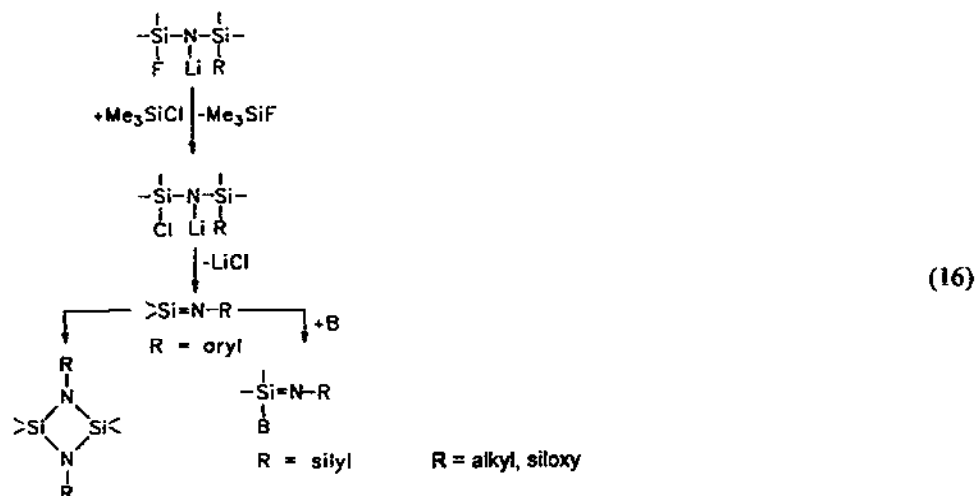
Scheme 4.



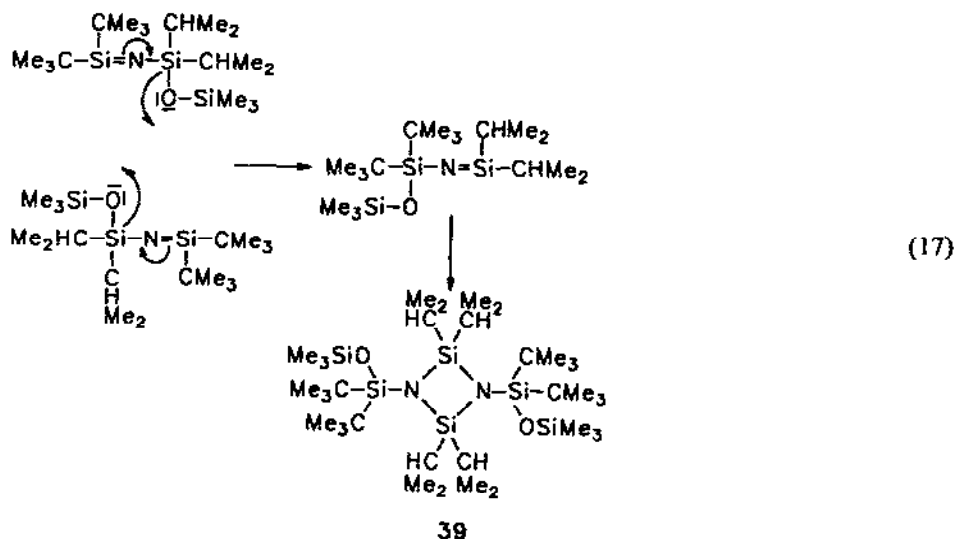
The product is an  $\text{Si}_2\text{N}_2$ -ring [29,30], the formation of which can be explained by a nucleophilic 1,3-rearrangement of a methanide-ion at silicon. The cyclic ylide is formed because the two nitrogen atoms are identically substituted and a silyl group migration would be without energy profit in such a molecule. The investigations show that the high stability of the lithium derivatives of aminofluorosilanes and their mostly covalent character are responsible for the fact that many of those with bulky substituents can be distilled or sublimed in vacuo without decomposition. Therefore thermally enforced LiF elimination leads to dimerization or rearrangement of the free iminosilanes. A thermodynamically better leaving group had to be found.

One of the remarkable features of lithiated aminofluorosilanes with bulky substituents is that they do not undergo substitution with  $\text{Me}_3\text{SiCl}$  but with formation of  $\text{Me}_3\text{SiF}$ . That is, an intermolecular fluorine-chlorine exchange takes place [4,14,31] (eqn. (16)). A Lewis base, such as thf, is required. As was proved by structural analyses, the coordination of the lithium to Lewis bases has the following effects [11,13,14]: (1) elongation of the Li–N bond; (2) shifting of the lithium towards fluorine; (3) lengthening of the Si–F bond. Therefore, the formation of the Si–F bond in  $\text{Me}_3\text{SiF}$  is favoured energetically.





The lithium-aminochlorosilanes are thermally far less stable than the analogous fluorine compounds [4,31]. LiCl-elimination leads to the formation of iminosilanes. Stable and uncoordinated iminosilanes are formed with a 2,4,6(CMe<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> group bonded at the nitrogen atom [4,11]. Two examples show how differently substituted iminosilanes stabilize themselves. Iminosilanes with siloxy groups [16] bonded at the nitrogen centre form rings (eqn. (17)).



According to the crystal structure determination of 39 (Fig. 23), the formation of this compound involves an intermolecular isomerization of the intermediate iminosilane followed by dimerization [16], which can be regarded as a Lewis acid-base reaction.

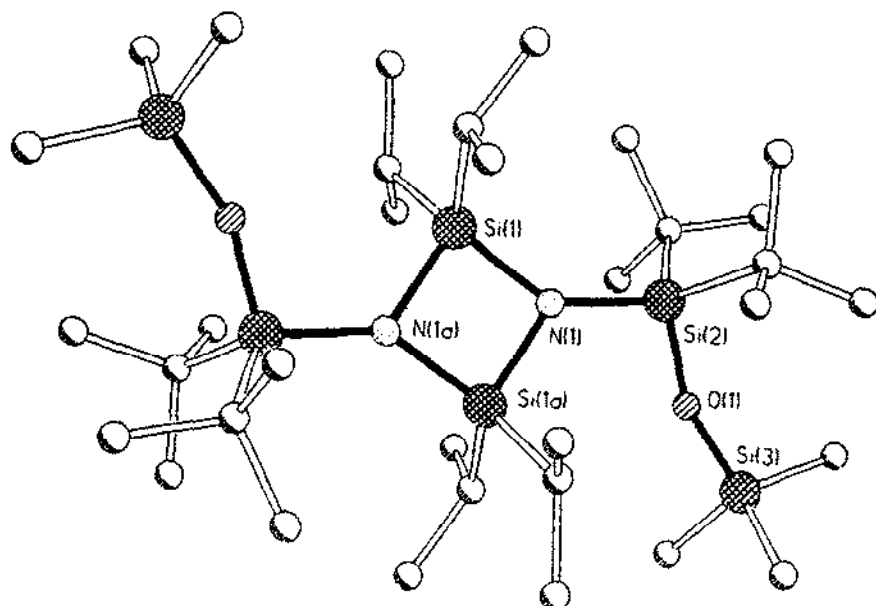


Fig. 23. Crystal structure of **39**.

However, if the isopropyl groups in **39** are replaced by *tert*-butyl groups and the siloxy groups replaced by methyl groups, the unsaturated silicon atom adds the solvent base (e.g. *thf*) which had previously been coordinated to the lithium atom, to give a silyliminosilane **40** (Fig. 24, Scheme 5). This remarkably stable compound could be separated from  $\text{LiCl}$

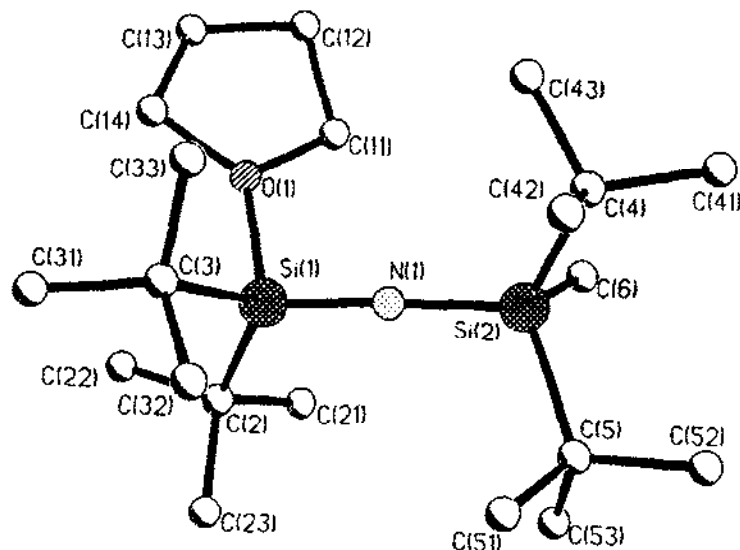
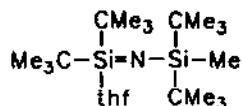


Fig. 24. Crystal structure of **40**.



Scheme 5.

by distillation in vacuo without decomposition and without losing thf. In the course of the distillation, it crystallized again. In the  $^{13}\text{C}$  NMR spectrum of **40**, the  $\text{C}_2\text{O}$  signal of the thf molecule appears at 73.78 ppm, a downfield shift of nearly 6 ppm compared with the non-bonded thf. This reflects the strong Lewis acid character of the intermediate tri-coordinated silicon atom. Comparison of the  $^{29}\text{Si}$  NMR shifts of the free iminosilanes known so far shows that the unsaturated silicon atom is a stronger Lewis acid in the silyl substituted compounds [ $\delta(^{29}\text{Si}) \sim 78$  ppm] [3] than in the aryl substituted derivatives [ $\delta(^{29}\text{Si}) \sim 60$  ppm] [4,11].

This explains why the same method of synthesis leads to addition of the Lewis base thf in the case of **40** while the aryl substituted free iminosilane is unaffected.

#### F. SUMMARY

Lithiated aminofluorosilanes can often be regarded as  $\text{LiF}$ -adducts of iminosilanes on the basis of their structures. They react like silylamides as well as iminosilanes. They are suitable precursors to iminosilanes after fluorine-chlorine exchange, but it is not always necessary to isolate the iminosilane because the lithium derivative often reacts in the same way.

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