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Journal of Organometallic Chemistry 524 (1996) 203–209

Journal of Organometallic Chemistry

# Fluorosilyl(pyrrolyl)silylamines as precursors for intra- and intermolecularly stabilized iminosilanes

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Received 14 March 1996

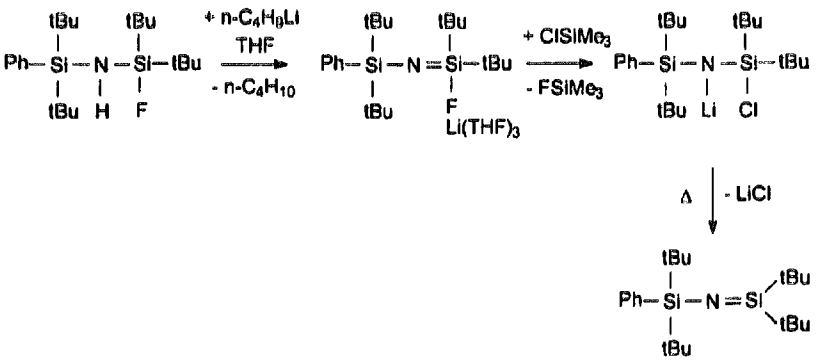
**Abstract**

Three indolyl- and pyrrolylsilylamines **1–3** were prepared from lithiated heterocyclics and fluorosilylamines. Further reaction with di-*tert*-butyldifluorosilane led to the fluorosilylpyrrolylsilylamines **4** and **5**. The fluorosilylpyrrolylsilylamine **6** was prepared by reaction of bis(fluorodiisopropylsilyl)amine and lithium pyrrolide. Lithiation with n-butyllithium of **4–6** solved in THF gave the iminosilane–LiF adducts **7–9**; in contrast, lithiation of **5** in n-hexane led to the lithium fluorosilylamid **10**. Heating of the iminosilane–LiF adduct **7** gave the bicyclic system **11**, an intramolecularly stabilized iminosilane. Addition of chlorotrimethylsilane to **9** led to fluorine–chlorine exchange and elimination of lithium chloride. The product is the intermolecular stabilization of the intermediate iminosilane as a four-membered ring **12**. The X-ray structures of **1**, **11** and **12** have been determined.

*Keywords:* Iminosilanes; Indolylsilanes; Pyrrolylsilanes; Bicyclic ring systems

## 1. Introduction

In 1986, five years after the syntheses of the first silaethene and disilene [1–6], two independent routes for the preparation of uncoordinated iminosilanes were published. Wiberg and coworkers [7,8] managed the synthesis of an iminosilane and two THF adducts of iminosilanes. All these Si=N compounds were characterized by NMR and some by X-ray. The synthesis is based on a complicated process of many steps, e.g. $N_2$/NaCl and LiCl elimination. Our group developed a different route based on fluorine–chlorine exchange on lithiated fluorosilylamines [9,10]:

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[1] Crystal structures.



*PII* S0022-328X(96)06429-7

Aminofluorosilanes have NH and SiF functional groups. Lithiation of the NH function makes either elimination of lithium fluoride or fluorine–chlorine exchange by chlorotrimethylsilane possible. The latter variant leads to thermally less drastic conditions for the elimination of lithium chloride [9,11–13].

Altogether, three free iminosilanes, one THF adduct of an iminosilane and all intermediate products, have been synthesized and characterized by NMR and some by X-ray [9,10,12–14], many cycloadditions were carried out [15].

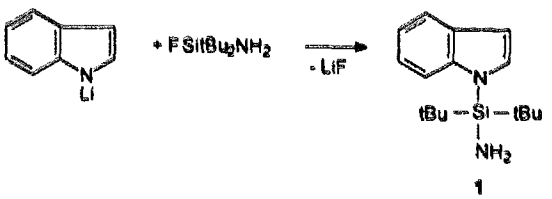
Iminosilanes like the di-*tert*-butylphenylsilyl-di-*tert*-butyliminosilane [13] with bulky substituents are stable in a monomeric state. In the case of less bulky alkyl groups, dimerisation via [2 + 2]-cycloaddition and formation of a four-membered $(SiN)_2$ ring is observed [16].

Here we discuss the synthesis of heteroaromatic substituted aminofluorosilanes and their role as precursors for intra- and intermolecularly stabilized iminosilanes.

## 2. Results and discussion

### 2.1. Synthesis of fluorosilyl(indol-1-yl) and -(pyrrol-1-yl)silylamines

In the reaction of di-*tert*-butylfluoro(indol-1-yl)silane and lithium amide the latter acts as the lithiation reagent for the more basic nitrogen atom of the heteroaromatic system. The products are lithium indolide and di-*tert*-butylfluorosilylamine. For this reason a reverse synthetic strategy is necessary to obtain the silylamine **1**:

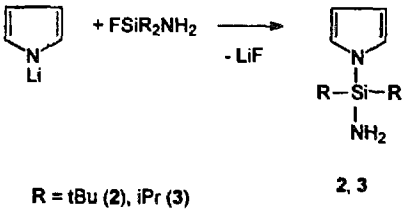



1

**1** crystallizes in n-hexane. Fig. 1 shows the crystal structure of **1**.

The Si(1)–N(1) distance (169.3 pm) is shorter than a typical single bond (175 pm) [17], while the Si(1)–N(2) bond length is elongated (178.9 pm).

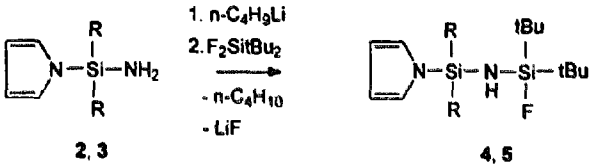
Because of the bulky indolyl substituent the smaller pyrrolyl substituent was chosen for the synthesis of heteroaromatic substituted fluorosilylamines. In the reaction of lithium pyrrolide [18] and di-*tert*-butylfluorosilylamine or fluorodiisopropylamine the pyrrol-1-ylsilylamines **2** and **3** are formed:




R = tBu (2), iPr (3)

2, 3

Lithiation of **2** and **3** and addition of di-*tert*-butylfluorosilane led to the desired fluorosilyl(pyrrol-1-yl)silylamines **4** and **5** in good yield:




2, 3 4, 5

R = tBu (2, 4), iPr (3, 5)

In contrast, the very basic NH function of **4** led to direct lithiation of **4** and formation of further products.

Another member of this class of substances can be synthesized via the reaction of lithium pyrrolide and bis(fluorodiisopropylsilyl)amine. The product of the monosubstitution **6** is formed:


6

### 2.2. Lithiation and reactions of the fluorosilyl(pyrrol-1-yl)silylamines 4–6

The fluorosilyl(pyrrol-1-yl)silylamines **4–6** dissolved in n-hexane/THF and added by n-butyllithium give the LiF adducts of iminosilanes **7–9**:

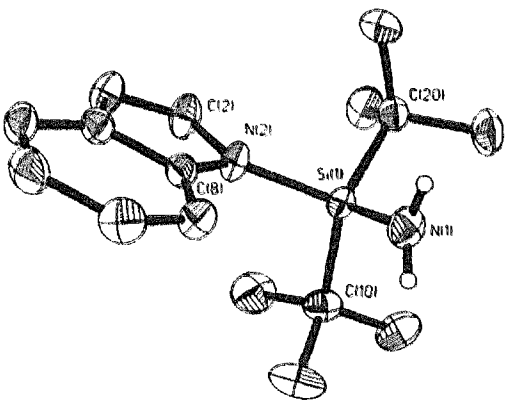
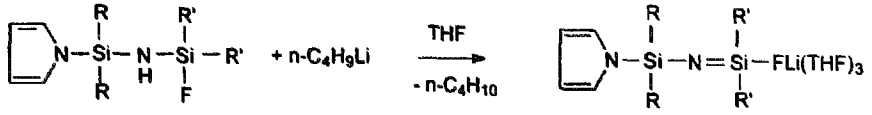


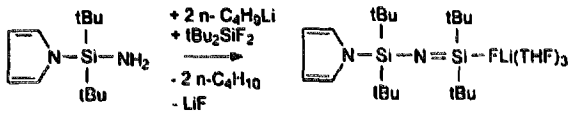

Fig. 1. Crystal structure of **1**, selected bond lengths (pm): Si(1)–N(1) 169.3(2), Si(1)–N(2) 178.9(2).



4 - 6 7 - 9

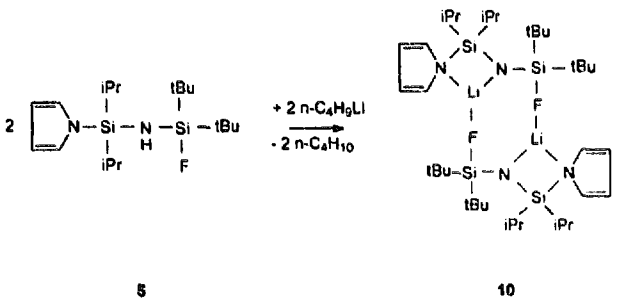
| | R | R' |
|---|---|---|
| 4, 7 | tBu | tBu |
| 5, 8 | iPr | tBu |
| 6, 9 | iPr | iPr |

7 is also formed in the reaction of the lithium derivative of 2 and di-*tert*-butyldifluorosilane. The lithium di-*tert*-butyl(pyrrol-1-yl)silylamide has the effect of a lithiation reagent on the bis(silyl)amine 4. The silylamine 2 is formed again. When two equivalents of n-butyllithium are added for the lithiation, 7 will be directly formed in a one-step synthesis:



2 7

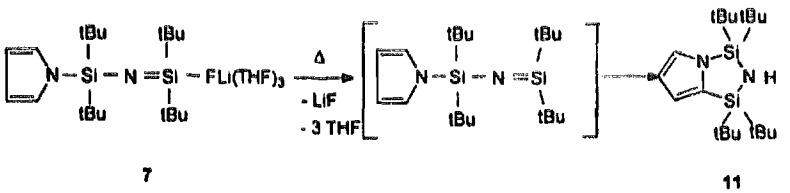
The fluorosilylamines 5 and 6 dissolved in THF react in quantitative yield to give the LiF adducts of iminosilanes 8 and 9. In contrast, lithiation of 5 with n-butyllithium in n-hexane gives the lithium fluorosilylamide 10, which was characterized in solution by NMR. In non-polar solvents like hexane, which do not react as a donor ligand, 10 probably has a dimeric structure [13,16]:



5 10

## 2.3. Crystal structure of the bicyclic system 11

The lithium derivatives of the fluorosilyl(pyrrol-1-yl)silylamines 7 and 9 make further, different reactions possible. Under drastic thermal conditions, 7 eliminates lithium fluoride. The intermediately formed iminosilane rearranges intramolecularly to the bicyclic system 11 [Eq. (9)], an example for an insertion reaction of an iminosilane into a polar C–H bond:



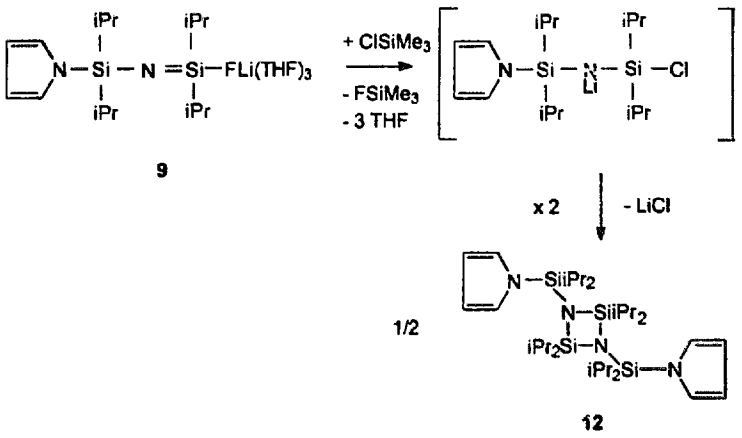
7 11

Single crystals of 11 were obtained in n-hexane and the X-ray structure was determined. Fig. 2 shows the crystal structure of 11.

11 is a bicyclic system. The pyrrolyl ring is disordered by exchanging N(1) and C(1). The two coupled five-membered rings lie almost in one plane (angle between the two planes 4.5° and 7.0° for the second position). The Si(1)–N(2) and Si(2)–N(2) distances are 172.7 and 173.1 pm.

## 2.4. Crystal structure of the cyclodisilazane 12

9 reacts with chlorotrimethylsilane under fluorine–chlorine exchange. Elimination of fluorosilane and lithium chloride are observed. The iminosilane stabilizes under [2 + 2]-cycloaddition and 12 is isolated:




9

12

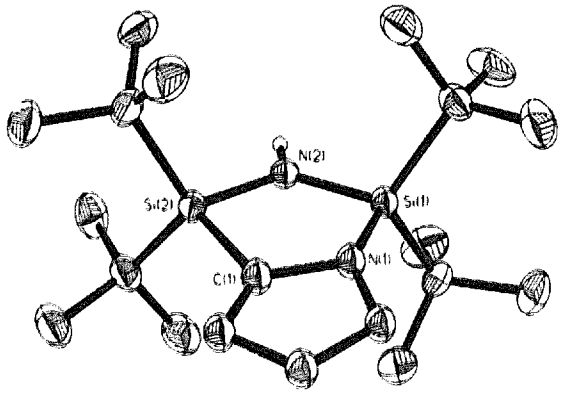



Fig. 2. Crystal structure of **11**, selected bond lengths (pm) and angles (°): Si(1)–N(2) 172.7(2), N(2)–Si(2) 173.1(2); Si(1)–N(2)–Si(2) 118.4(1).

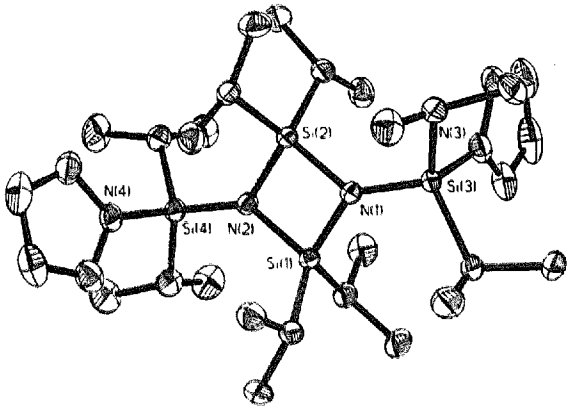



Fig. 3. Crystal structure of **12**, selected bond lengths (pm) and angles (°): Si(1)–N(1) 176.8(2), Si(1)–N(2) 177.0(2), N(1)–Si(3) 173.3(2), N(1)–Si(2) 177.3(2), Si(2)–N(2) 177.7(2), N(2)–Si(4) 173.6(2), Si(3)–N(3) 178.5(2), Si(4)–N(4) 178.5(2); N(1)–Si(1)–N(2) 89.3(1), Si(3)–N(1)–Si(1) 135.0(1), Si(3)–N(1)–Si(2) 133.0(1), Si(1)–N(1)–Si(2) 91.0(1), N(1)–Si(2)–N(2) 88.9(1), Si(4)–N(2)–Si(1) 136.1(1), Si(4)–N(2)–Si(2) 132.2(1), Si(1)–N(2)–Si(2) 90.8(1), N(1)–Si(3)–N(3) 110.1(1), N(2)–Si(4)–N(4) 110.8(1).

The formation of the lithium chloride derivative of **6** is proved by the reaction of the distillation residue with silver nitrate.

Single crystals of **12** were obtained in n-hexane. Fig. 3 shows the crystal structure of **12**.

The ring angles of the cyclodisilazane **12** are within the normal range of 90° for a symmetric four-membered ring. The angles at N(1) and N(2) are a little smaller than the angles at the silicon atoms. The sums of the angles at N(1) and N(2) are 359.0° and 359.1°, and represent the trigonal-planar structure. The silicon–nitrogen distances of the central four membered ring (about 177.2 pm) are a little longer than the silicon–nitrogen single bonds. The lengths of the exocyclic silicon–nitrogen bonds of Si(3) and Si(4) are 173.3 and 173.6 pm. The Si(1)–Si(2) distance is 252.6 pm.

## 3. Experimental section

All reactions were carried out under exclusion of water and under inert atmosphere ($N_2$, Ar). The degree of purity of the isolated compounds was checked by NMR spectroscopy and gas chromatography. Solvents were dried by the usual methods and stored over sodium where possible.

MS: Varian CH5 or Finnigan MAT 8200 or 9500 spectrometer, NMR: 30% solution in $CDCl_3$ or $C_6D_6$ (**7–10**); TMS int., $C_6F_6$, $CH_3NO_2$, LiCl ext., Bruker AM 250 or 400 spectrometer, MSL 400 spectrometer ($^{19}F$ NMR).

In the following, the abbreviation "pyr" is used for the pyrrolyl substituent.

### *3.1. Silylamines 1–3*

0.2 mol indole (**1**) or pyrrole (**2**, **3**) was solved in 50 ml n-hexane and 30 ml THF and added to the equimolar amount of n-butyllithium. The reaction mixture was refluxed for 1 h and added to 0.2 mol di-*tert*-butylfluorosilylamine (**1**, **2**) or 0.2 mol fluorodiisopropylsilylamine (**3**). After refluxing for 3 h more the lithium fluoride was separated. The crude product was purified by fractional distillation.

*3.1.1. Di-tert-butyl(indol-1-yl)silylamine (1)*

$C_{16}H_{26}N_2Si$ (274.47). Yield: 15.92 g (29%); b.p. 102°C (0.01 mbar). $^1$H NMR (400.13 MHz): δ = 1.13 (s, 18H, $C(CH_3)_3$), 1.32 (s, 2H, $NH_2$), 6.67 (dd, $^3J$(H,H) = 3.30 Hz, $^4J$(H,H) = 0.66 Hz, 1H, H-3), 7.13–8.17 (m, 5H, H-2, H-4–H-7). $^{13}$C NMR (100.6 MHz): δ = 21.16 (s, $^1J$(C,Si) = 68 Hz, $C(CH_3)_3$), 28.29 (s, $C(CH_3)_3$), 104.58 (s, C-3), 115.08 (s, C-7), 119.68/120.28/121.07 (s, C-4/C-5/C-6), 131.03 (s, C-2, C-9/C-8), 142.10 (s, C-8/C-9). $^{15}$N NMR (40.56 MHz): δ = −375.54 (br, $^1J$(N,H) = 75.5 Hz, $NH_2$. $^{29}$Si NMR (79.46 MHz): δ = −0.04 (s). MS (70 eV, EI) *m/z* (%): 274 (33) $M^+$, 217 (100) $[M-C_4H_9]^+$.

*3.1.2. Di-tert-butyl-(pyrrol-1-yl)silylamine (2)*

$C_{12}H_{24}N_2Si$ (224.42). Yield: 35.46 g (79%); b.p. 56°C (0.01 mbar). $^1$H NMR (250.13 MHz): δ = 1.01 (s, 18H, $C(CH_3)_3$), 6.28 (t *, $^3J$(H,H) = 1.98 Hz, 2H, CH–C), 6.96 (t *, $^3J$(H,H) = 1.98 Hz, 2H, CH–N). $^{13}$C NMR (62.89 MHz): δ = 20.02 (s, $C(CH_3)_3$), 27.70 (s, $C(CH_3)_3$), 109.60 (s, CH–C), 124.37 (s, CH–N). $^{29}$Si NMR (49.69 MHz): δ = −0.86 (s). MS (70 eV, EI) *m/z* (%): 224 (38) $M^+$, 150 (100) $[M-C_4H_{12}N]^+$.

*3.1.3. Diisopropyl(pyrrol-1-yl)silylamine (3)*

$C_{10}H_{20}N_2Si$ (196.37). Yield: 32.99 g (84%); b.p. 54°C (0.01 mbar). $^1$H NMR (200.13 MHz): δ = 0.92–1.03 (m, 12H, $CH(CH_3)_2$), 1.05–1.32 (m, 2H, $CH(CH_3)_2$), 6.30 (t *, $^3J$(H,H) = 1.99 Hz, 2H, CH–C), 6.87 (t *, $^3J$(H,H) = 1.99 Hz, 2H, CH–N). $^{13}$C NMR (62.89 MHz): δ = 11.92 (s, $CH(CH_3)_2$), 16.71 (s, $CH(CH_3)_2$), 110.05 (s, CH–C), 123.43 (s, CH–N). $^{29}$Si NMR (49.69 MHz): δ = 0.95 (s). MS (70 eV, EI) *m/z* (%): 196 (62) $M^+$, 153 (100) $[M-C_3H_7]^+$.

*3.2. Fluorosilyl(pyrrol-1-yl)silylamines (4) and (5)*

0.2 mol **2** (**4**) or **3** (**5**) were solved in 50 ml n-hexane and 20 ml THF and added to 0.2 mol n-butyllithium. The reaction mixture was refluxed for 2 h and 0.2 mol di-*tert*-butyldifluorosilane added. The reaction mixture was narrowed down and refluxed for 2 days. The lithium fluoride was separated and the crude product purified by fractional distillation.

*3.2.1. Di-tert-butylfluorosilyl-(di-tert-butyl(pyrrol-1-yl)silyl)amine (4)*

$C_{20}H_{41}FN_2Si_2$ (384.72). Yield: 16.16 g (21%); b.p. 117°C (0.01 mbar). $^1$H NMR (250.13 MHz): δ = 1.05 (d, $^4J$(H,F) = 0.94 Hz, 18H, $FSiC(CH_3)_3$), 1.11 (s, 18H, $pyrSiC(CH_3)_3$), 6.27 (t, $^3J$(H,H) = 2.02 Hz, 2H, CH–C), 7.01 (t *, $^3J$(H,H) = 2.02 Hz, 2H, CH–N). $^{13}$C NMR (62.89 MHz): δ = 20.88 (d, $^2J$(C,F) = 15.41 Hz, $FSiC(CH_3)_3$), 21.13 (s, $pyrSiC(CH_3)_3$), 27.57 (d, $^5J$(C,F) = 0.35 Hz, $pyrSiC(CH_3)_3$), 28.43 (d, $^3J$(C,F) = 1.95 Hz, $FSiC(CH_3)_3$), 109.70 (s, CH–C), 124.94 (d, $^5J$(C,F) = 1.16 Hz, CH–N). $^{19}$F NMR (235.32 MHz): δ = 3.28 (d, $^3J$(F,H) = 9.11 Hz. $^{29}$Si NMR (49.69 MHz): δ = −0.93 (d, $^3J$(Si,F) = 1.21 Hz, Sipyr), 2.89 (d, $^1J$(Si,F) = 305.70 Hz, SiF). MS (70 eV, EI) *m/z* (%): 384 (12) $M^+$, 327 (100) $[M-C_4H_9]^+$.

*3.2.2. Di-tert-butylfluorosilyl-(diisopropyl(pyrrol-1-yl)silyl)amine (5)*

$C_{18}H_{37}FN_2Si_2$ (356.67). Yield: 54.93 g (77%); b.p. 118°C (0.1 mbar). $^1$H NMR (400.13 MHz): δ = 0.99–1.41 (m, 32H, $CH(CH_3)_2$, $C(CH_3)_3$), 6.29 (t *, $^3J$(H,H) = 1.99 Hz, 2H, CH–C), 6.88 (t *, $^3J$(H,H) = 1.99 Hz, 2H, CH–N). $^{13}$C NMR (100.6 MHz): δ = 13.17 (s, $CH(CH_3)_2$), 17.23 (m, $CH(CH_3)_2$), 17.32 (m, $CH(CH_3)_2$), 20.59 (d, $^2J$(C,F) = 14.78 Hz, $C(CH_3)_3$), 20.60 (d, $^2J$(C,F) = 14.80 Hz, $C(CH_3)_3$), 27.36 (s, $C(CH_3)_3$), 110.29 (s, CH–C), 123.67 (s, CH–N). $^{19}$F NMR (376.50 MHz): δ = −2.48 (d, $^3J$(F,H) = 11.25 Hz). $^{29}$Si NMR (49.69 MHz): δ = 4.11 (d, $^1J$(Si,F) = 301.63 Hz, SiF), 0.63 (d, $^3J$(Si,F) = 0.75 Hz, Sipyr). MS (70 eV, EI) *m/z* (%): 356 (42) $M^+$, 313 (100) $[M-C_3H_7]^+$.

*3.3. Diisopropylfluorosilyl-(diisopropyl(pyrrol-1-yl)silyl)amine (6)*

0.1 mol bis(fluoro-diisopropylsilyl)amine in 40 ml n-hexane was added to 0.1 mol lithium pyrrolide in 50 ml n-hexane and 30 ml THF and refluxed for 5 h. The crude product was separated from the lithium fluoride and **6** purified by fractional distillation. $C_{16}H_{33}FN_2Si_2$ (328.62). Yield: 27.60 g (84%); b.p. 82°C (0.01 mbar). $^1$H NMR (400.13 MHz): δ = 1.01–1.40 (m, 28H, $CH(CH_3)_2$), 6.30 (t *, $^3J$(H,H) = 2.00 Hz, 2H, CH–C), 6.85 (t *, $^3J$(H,H) = 2.00 Hz, 2H, CH–N). $^{13}$C NMR (100.6 MHz): δ = 12.65 (d, $^4J$(C,F) = 0.60 Hz, $NSiCH(CH_3)_2$), 13.24 (d, $^2J$(C,F) = 16.27 Hz, $FSiCH(CH_3)_2$), 16.97 (d, $^3J$(C,F) = 1.15 Hz, $FSiCH(CH_3)_2$), 17.11 (d, $^5J$(C,F) = 0.65 Hz, $NSiCH(CH_3)_2$), 110.51 (s, CH–C), 123.70 (s, CH–N). $^{15}$N NMR (40.56 MHz): δ = −366.52 (d, $^2J$(N,F) = 5.90 Hz, NH). $^{19}$F NMR (376.50 MHz): δ = 7.60 (d, $^3J$(F,H) = 5.69 Hz). $^{29}$Si NMR (79.46 MHz): δ = 2.00 (s, Sipyr), 5.08 (d, $^1J$(Si,F) = 295.17 Hz, SiF). MS (70 eV, EI) *m/z* (%): 328 (28) $M^+$, 285 (100) $[M-C_3H_7]^+$.

*3.4. Iminosilane–LiF adducts 7–9 and lithium fluorosilylamide 10*

0.1 mol **4** (**7**), 0.1 mol **5** (**8**, **10**) or 0.1 mol **6** (**9**) was solved in 50 ml n-hexane and 20 ml THF (in the case of **10** in 50 ml n-hexane only) and added to an equimolar

* Pseudotriplet.

amount of n-butyllithium. The lithium derivatives **7–10** were stirred for 6 h at room temperature and characterized by NMR in solution.

*3.4.1. Di-tert-butyl-(di-tert-butyl(pyrrol-1-yl)silyl)iminosilane–LiF adduct (7)*

$C_{32}H_{64}FLiN_2O_3Si_2$ (606.92). Yield: 60.69 g (100%). $^7$Li NMR (97.21 MHz): δ = −0.04 (s). $^{19}$F NMR (235.32 MHz): δ = 9.86 (s). $^{29}$Si NMR (49.69 MHz): δ = −17.13 (s, Sipyr), −6.22 (d, $^1J$(Si,F) = 261.28 Hz, SiF).

*3.4.2. Di-tert-butyl-(diisopropyl(pyrrol-1-yl)silyl)iminosilane–LiF adduct (8)*

$C_{30}H_{60}FN_2O_3Si_2$ (571.97). Yield: 57.20 g (100%). $^7$Li NMR (97.21 MHz): δ = −0.28 (s). $^{19}$F NMR (188.32 MHz): δ = 8.79 (s). $^{29}$Si NMR (49.69 MHz): δ = −18.77 (d, $^3J$(Si,F) = 10.23 Hz, Sipyr), −5.59 (d, $^1J$(Si,F) = 260.31 Hz, SiF).

*3.4.3. Diisopropyl-(diisopropyl(pyrrol-1-yl)silyl)iminosilane–LiF adduct (9)*

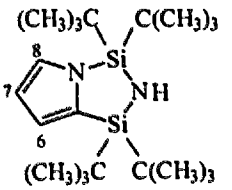
$C_{28}H_{56}FLiN_2O_3Si_2$ (550.81). Yield: 55.08 g (100%). $^7$Li NMR (155.45 MHz): δ = −0.20 (s). $^{19}$F NMR (376.50 MHz): δ = 7.63 (s). $^{29}$Si NMR (79.46 MHz): δ = −15.14 (d, $^3J$(Si,F) = 13.08 Hz, Sipyr), −2.22 (d, $^1J$(Si,F) = 250.91 Hz, SiF).

*3.4.4. N-lithium-(di-tert-butylfluorosilyl)(diisopropyl-(pyrrol-1-yl)silyl)amide (10)*

$(C_{18}H_{36}FLiN_2Si_2)_2$ (725.12). Yield: 72.51 g (100%). $^7$Li NMR (97.21 MHz): δ = 0.27 (s). $^{13}$C NMR (62.89 MHz): δ = 11.59–42.11 (m, $CH(CH_3)_2$, $C(CH_3)_3$), 111.35 (s, CH–C), 123.49 (s, CH–N). $^{19}$F NMR (376.50 MHz): δ = 5.11 (s). $^{29}$Si NMR (79.46 MHz): δ = −13.30 (s, Sipyr), −0.19 (d, $^1J$(Si,F) = 262.87 Hz, SiF).

*3.5. 2,2,4,4-Tetra-tert-butyl-1,3-diaza-2,4-disilabicyclo[3.3.0]octane (11)*

The lithium fluoride was thermally separated from 0.1 mol **7**. The crude product was purified by fractional distillation and recrystallization from n-hexane.




Structure 1.

Table 1
Crystal data for **1**, **11** and **12**

| Structure | 1 | 11 | 12 |
|---|---|---|---|
| Empirical formula | $C_{16}H_{26}N_2Si$ | $C_{20}H_{40}N_2Si_2$ | $C_{32}H_{64}N_4Si_4$ |
| Formula weight | 274.48 | 364.72 | 617.23 |
| Crystal system | orthorhombic | monoclinic | triclinic |
| Space group | $Pca2_1$ | $P2_1/c$ | $P\bar{1}$ |
| $a$ (pm) | 2058.3(6) | 1789.3(1) | 1001.1(2) |
| $b$ (pm) | 817.1(3) | 882.4(1) | 1195.2(2) |
| $c$ (pm) | 956.7(3) | 1438.8(1) | 1628.0(3) |
| α (°) | 90 | 90 | 103.21(1) |
| β (°) | 90 | 94.08(1) | 104.84(1) |
| γ (°) | 90 | 90 | 91.30(1) |
| $V$ (nm$^3$) | 1.6090(9) | 2.22659(3) | 1.8263(6) |
| $Z$ | 4 | 4 | 2 |
| $D_x$ (Mg m$^{-3}$) | 1.133 | 1.069 | 1.122 |
| μ (mm$^{-1}$) | 0.137 | 0.161 | 0.189 |
| $F$(000) | 600 | 808 | 680 |
| Crystal size (mm$^3$) | 0.4 × 0.4 × 0.8 | 0.3 × 0.4 × 0.5 | 0.4 × 0.4 × 0.5 |
| 2θ range (θ) | 7–50 | 7–50 | 7–50 |
| Reflections collected | 4531 | 5474 | 14463 |
| Independent reflections | 2839 | 4021 | 6353 |
| $R_{int}$ | 0.0254 | 0.0320 | 0.0429 |
| Data used | 2839 | 4021 | 6351 |
| Parameters | 186 | 279 | 377 |
| Restraints | 2 | 172 | 0 |
| $S$ | 1.034 | 1.048 | 1.052 |
| $R_1[I > 2\sigma(I)]$ | 0.0366 | 0.0468 | 0.0456 |
| $wR_2$ (all data) | 0.0816 | 0.1054 | 0.1298 |
| Extinction coefficient | 0.0033(7) | — | — |
| Absolute structure parameter [21] | −0.06(13) | — | — |
| Largest difference peak (e nm$^{-3}$) | 222 | 319 | 478 |
| Largest difference hole (e nm$^{-3}$) | −136 | −233 | −291 |

$C_{20}H_{40}N_2Si_2$ (364.71). Yield: 31.73 g (87%); b.p. 96°C (0.01 mbar); m.p. 107°C. $^1$H NMR (250.13 MHz): δ = 0.70 (s, 1H, NH), 1.06 (s, 18H, $C(CH_3)_3$), 1.07 (s, 18H, $C(CH_3)_3$), 6.45 (dt, $^3J$(H,H) = 2.65 Hz, $^6J$(H,H) = 0.65 Hz, 1H, H-7), 6.51 (dd, $^3J$(H,H) = 3.00 Hz, $^5J$(H,H) = 0.90 Hz, 1H, H-6), 7.04 (dd, $^3J$(H,H) = 2.35 Hz, $^5J$(H,H) = 0.90 Hz, 1H, H-8). $^{13}$C NMR (62.89 MHz): δ = 21.27 (s, $C(CH_3)_3$), 22.10 (s, $C(CH_3)_3$), 28.86 (s, $C(CH_3)_3$), 29.44 (s, $C(CH_3)_3$), 113.23 (s, C-6/C-7), 117.23 (s, C-7/C-6), 125.14 (s, C-8). $^{15}$N NMR (25.35 MHz): δ = −377.22 (br, NH). $^{29}$Si NMR (49.69 MHz): δ = 3.02 (s, N–Si–N), 7.92 (s, N–Si–C). MS (70 eV, EI) *m/z* (%): 364 (4) $M^+$, 307 (100) $[M-C_4H_9]^+$.

### 3.6. 1,3-Bis(diisopropyl(pyrrol-1-yl)silyl)-2,2,4,4-tetraisopropylcyclodisilazane (12)

0.1 mol **6** in 50 ml THF was added to an equimolar amount of chlorotrimethylsilane. To complete the fluorine–chlorine exchange the reaction mixture was stirred for 5 h at room temperature. The lithium chloride was separated and the crude product purified by fractional distillation and recrystallization from n-hexane. $C_{32}H_{64}N_4Si_4$ (617.22). Yield: 33.33 g (54%); m.p. 132°C. $^1$H NMR (400.13 MHz): δ = 0.87–1.46 (m, 56H, $CH(CH_3)_2$), 6.20 (t *, $^3J$(H,H) = 1.98 Hz, 4H, CH–C), 6.79 (t *, $^3J$(H,H) = 1.98 Hz, 4H, CH–N). $^{13}$C NMR (100.6 MHz): δ = 15.81/17.53/18.83/19.07/19.83 (s, pyrSi$CH(CH_3)_2$, Si$(CH(CH_3)_2)_2$), 109.70 (s, CH–C), 124.28 (s, CH–N). $^{29}$Si NMR (79.46 MHz): δ = −9.42 (s, Sipyr), 12.36 (s, NSiN). MS (70 eV, EI) *m/z* (%): 616 (3) $M^+$, 573 (100) $[M-C_3H_7]^+$.

### 3.7. X-ray structure determination for 1, 11 and 12

Crystal data are summarised in Table 1. Data for **1** and **11** were collected at −120°C on a Stoe-Siemens AED diffractometer and for **12** at −60°C on a Stoe-Siemens AED2 diffractometer, both with monochromated Mo Kα radiation (λ = 71.073 pm). The structures were solved by direct methods [19]. All non-hydrogen atoms were refined anisotropically [20]. For the hydrogen atoms bound to carbon atoms the riding model was used. The structures were refined against $F^2$ with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$. The $R$ values are defined as $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{0.5}$.

In structures **1** and **11** the hydrogens bound to nitrogen were refined with distance restraints. In structure **11** the ring N(1)C(1)C(2)C(3)C(4) is disordered. The positions of N(1) and C(1) are interchanged. The whole ring was refined with distance restraints and restraints for the anisotropic displacement parameters.

## 4. Supplementary material available

Further details of the crystal structure investigations are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on quoting the full journal citation.

## Acknowledgements

We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support.

## References

[1] A.G. Brook, S.C. Nyberg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. Kishna, M.R. Kallury, Y.C. Poon, Y.-M. Chang and W. Wong-Ng, *J. Am. Chem. Soc.*, *104* (1982) 5667–5672.
[2] N. Wiberg and G. Wagner, *Angew. Chem.*, *95* (1983) 1027–1028.
[3] N. Wiberg, G. Wagner, G. Müller and J. Riede, *J. Organomet. Chem.*, *271* (1984) 381–391.
[4] N. Wiberg, G. Wagner and G. Müller, *Angew. Chem.*, *97* (1985) 220–222.
[5] M.J. Fink, R. West and J. Michl, *Science*, *214* (1981) 1343–1344.
[6] M.J. Fink, M.J. Michalczyk, K.J. Haller, R. West and J. Michl, *J. Chem. Soc., Chem. Commun.*, (1983) 1010–1011.
[7] N. Wiberg, K. Schurz and G. Fischer, *Angew. Chem.*, *97* (1985) 1058–1059.
[8] N. Wiberg, K. Schurz, G. Reber and G. Müller, *J. Chem. Soc., Chem. Commun.*, (1986) 591–592.
[9] M. Hesse and U. Klingebiel, *Angew. Chem.*, *98* (1986) 638–639.
[10] S. Walter and U. Klingebiel, *Coord. Chem. Rev.*, *130* (1994) 481–508.
[11] I. Hemme and U. Klingebiel, *Adv. Organomet. Chem.*, *39* (1996) 159–192.
[12] S. Walter, U. Klingebiel and D. Schmidt-Bäse, *J. Organomet. Chem.*, *412* (1991) 319–326.
[13] D. Großkopf, L. Marcus, U. Klingebiel and M. Noltemeyer, *Phosphorus, Sulfur and Silicon*, *97* (1994) 113–123.
[14] R. Boese and U. Klingebiel, *J. Organomet. Chem.*, *315* (1986) C17–C21.
[15] J. Niesmann, U. Klingebiel, S. Rudolph and R. Herbst-Irmer, *J. Organomet. Chem.*, in press.
[16] S. Walter, U. Klingebiel and M. Noltemeyer, *Chem. Ber.*, *125* (1992) 783–788.
[17] W.S. Sheldrick, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, UK, 1989, Chap. 3.
[18] A. Frenzel, M. Gluth, R. Herbst-Irmer and U. Klingebiel, *J. Organomet. Chem.*, in press.
[19] G.M. Sheldrick, SHELXS-90, *Acta Crystallogr. A*, *46* (1990) 467–473.
[20] G.M. Sheldrick, SHELXL-93, University of Göttingen, 1993.
[21] H.D. Flack, *Acta Crystallogr. A*, *39* (1983) 876–881.