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A facile synthesis of iminosilanes. Crystal structure of $(Me_3C)_2(THF)Si{=}N{-}SiMe(CMe_3)_2$

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Abstract

The aminofluorosilane 1 $(Me_3C)_2SiFNHSiMe(CMe_3)_2$ is formed by treatment of $(Me_3C)_2SiF_2$ with $(Me_3C)_2MeSiNHLi$. The lithium derivative of 1, $(Me_3C)_2SiFLi(THF)_2NSiMe(CMe_3)_2$, 3, is formed by treatment with n-C_4H_9Li. Treatment of 3 with Me_3SiCl gives Me_3SiF, LiCl and the iminosilane $(Me_3C)_2(THF)Si{=}N{-}SiMe(CMe_3)_2$, 4. Compound 4 can be distilled and recrystallized from benzene. Its crystal structure has been determined.

Introduction

The first unsaturated silicon compounds, disilenes [1], and silaethenes [2], were prepared in 1981. In the mid-1980's the first iminosilanes were synthesized independently and by different in our laboratory [3,4] and in Wiberg's [5].

The synthesis we developed is based on an intermolecular fluorine–chlorine exchange at lithiated aryl-aminofluorosilanes (Scheme 1).

Because of their high stability aminofluorosilanes [4,6] and their mainly-covalent character the lithium derivatives, many of them containing bulky substituents can be distilled or sublimed *in vacuo* without decomposition, and so thermally-induced LiF-elimination leads to dimerization or rearrangement of the free iminosilanes [7]. Thus a 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 on treatment with Me_3SiCl but instead give Me_3SiF; that is, an intermolecular fluorine–chlorine exchange takes place [3,6,7] (Scheme 1). A necessary condition for this is that a Lewis base, e.g. THF, must be present.

We showed by structure determinations that the coordination of the lithium to Lewis bases has the following effects [7]: (a) elongation of the Li–N bond; (b) movement of the lithium toward fluorine; and (c) lengthening of the Si–F bond. Thus formation of the Si–F bond on going to Me_3SiF is favoured energetically.

The lithium-aminochlorosilanes are far less thermally stable than the analogous fluorine compounds [3,6], but evenso the aryl-substituted lithium-aminochlorosi-

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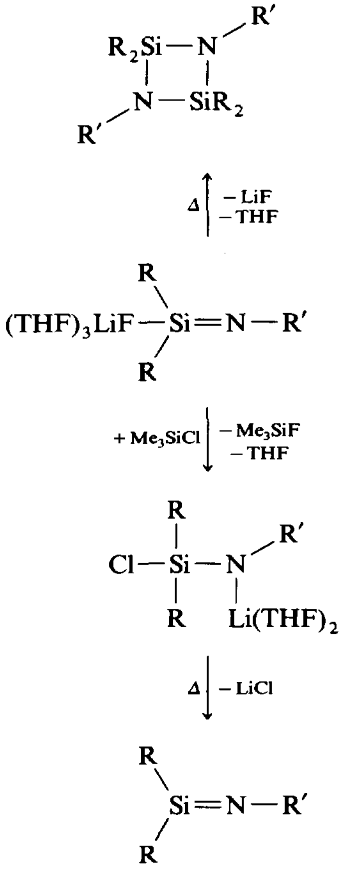


(R′ = Ar)

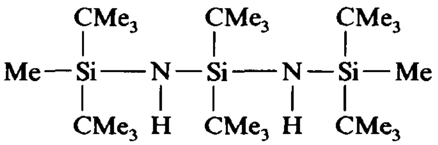
Scheme 1

lanes can be isolated [6]. The silyl-substituted compounds, however, form iminosilanes by LiCl elimination at room temperature.

Results and discussion

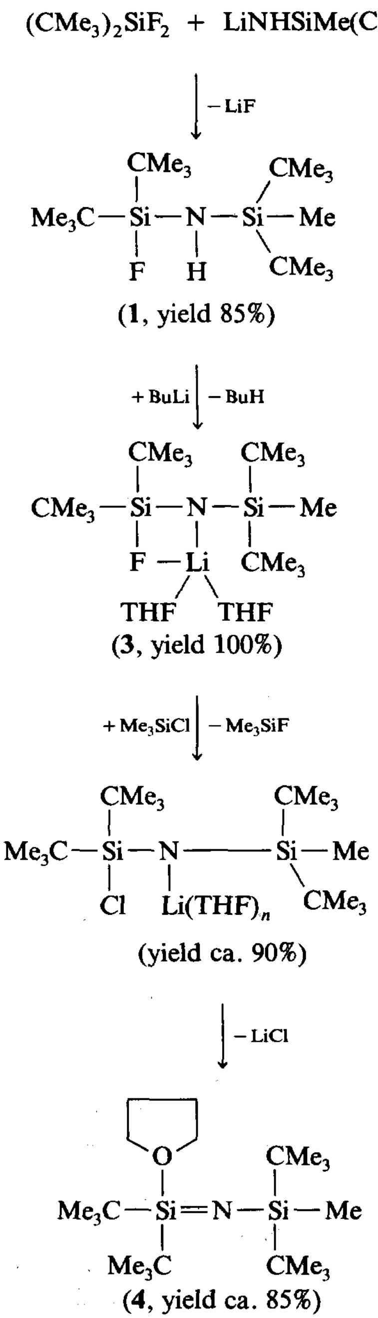
Scheme 2 shows the stepwise synthesis of the iminosilane **4**.

Di-tert-butyldifluorosilane was found to react with lithiated di-tert-butylmethylaminosilane to give the aminofluorosilane **1**, along with trisilazane **2** as a by-product.



$$\mathrm{Me{-}Si(CMe_3)_2{-}N(H){-}Si(CMe_3)_2{-}N(H){-}Si(CMe_3)_2{-}Me}$$

(**2**)



Scheme 2

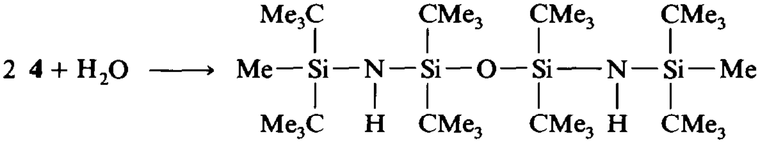
With butyllithium **1** formed the derivative **3**, which yielded colourless crystals from hexane/THF. The crystals were taken up in C_6D_6 and their NMR spectra revealed the presence of two molecules of THF coordinated to the lithium atom. There was also a significant downfield shift of the fluorine signal in the ^{19}F-NMR spectrum compared with that for **1** (a difference of nearly 13 ppm) and a strong upfield shift of the signals in the ^{29}Si-NMR spectrum.

Comparison with analogous lithium derivatives [7], the structures of which we determined, allowed us to suggest the structure shown in Scheme 2. To confirm this we carried out a single crystal X-ray study. As mentioned above, addition of Me_3SiCl to **3** immediately gives Me_3SiF, as revealed by ^{19}F-NMR spectroscopic monitoring. After some of the solvent had been evaporated off the iminosilane **4** crystallized from the mixture. It was found to be remarkably stable; it could be separated from LiCl by distillation *in vacuo* without decomposition and without loss of THF. During the distillation it crystallized again.

In the ^{13}C-NMR spectrum of **4** the C_2O-signal of the THF molecule appears at 73.78 ppm—a downfield shift of nearly 6 ppm compared with that for free THF. This reflects the strong Lewis-acid character of the three-coordinate silicon atom in the intermediate.

The comparison with the ^{29}Si-NMR shifts for the free iminosilanes known so far shows that the unsaturated silicon atom is a stronger Lewis-acid centre in the silyl-substituted compounds [$\delta(^{29}\text{Si}) \approx 78$ ppm] [5] than in the aryl substituted ones [$\delta(^{29}\text{Si}) \approx 60$ ppm] [3,4]. This explains why the same synthetic approach results in addition of the Lewis base THF in the case of **4** whereas the aryl substituted free iminosilane is left unattacked.

Traces of moisture lead to formation of the siloxane **5** (eq. 1):



$$2\ \mathbf{4} + H_2O \longrightarrow \begin{array}{ccccccccccccc} & & Me_3C & & & & CMe_3 & & CMe_3 & & & & CMe_3 & \\ & & | & & & & | & & | & & & & | & \\ Me & - & Si & - & N & - & Si & -O- & Si & - & N & - & Si & - Me \\ & & | & & | & & | & & | & & | & & | & \\ & & Me_3C & & H & & CMe_3 & & CMe_3 & & H & & CMe_3 & \end{array} \qquad (1)$$

(5)

An X-ray structural analysis was carried out on single crystals of **4**, recrystallized from benzene.

Crystal structure of 4

The structure determination of **4** confirms the structure suggested on the basis of the NMR data. This THF – adduct (Si(1)–O(1) 190.2(2) pm) of an iminosilane has a nearly linearly coordinated nitrogen atom (174.3(1)°), with two significantly different Si–N bond lengths. These bond lengths (Si(1)–N(1) 159.6(2) pm, Si(2)–N(1) 166.1(2) pm) reflect the difference between a double and a single Si–N bond [5,8], although the THF-adduct-formation has resulted in a slight elongation of the double bond and a shortening of the single bond. The unsaturated Si(1) atom has a distorted tetrahedral geometry; the two tert-butyl-groups and the nitrogen atom tend towards forming a trigonal planar environment around Si(1) (bond angle sum 347.7°). The tert-butyl-groups are in a synclinal conformation with respect to each other. Compound **4** shows the same general structural features as the only other known compound of this type, THF · $Me_2Si{=}N{-}Si(CMe_3)_3$ [5]. The only noteworthy difference between THF · $Me_2Si{=}N{-}Si(CMe_3)_3$ and **4** lies in the Si–N–Si bond angles of 161.0 and 174.4°, respectively, which shows the sensitivity of the valence angle at the nitrogen atom to the variation in the substituents and hence in the intramolecular strain.

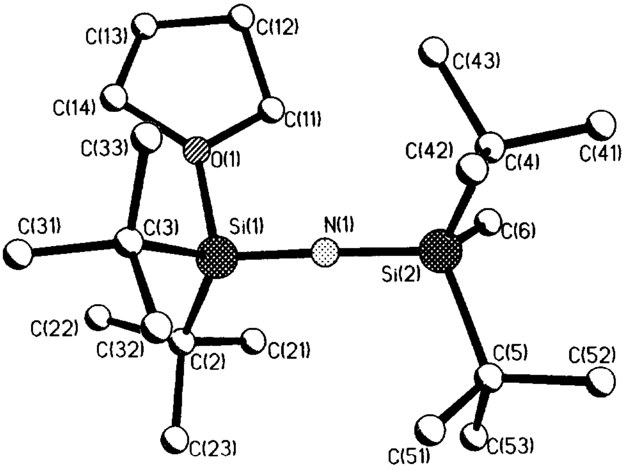


Fig. 1

Crystal data

4: $C_{21}H_{47}NOSi_2$, $M = 385.8$, monoclinic, space group $P2_1/c$, a 1115.6(1), b 1143.9(2), c 2005.6(2) pm, β 101.55(1)°, U 2.508 nm^3, $Z = 4$, $D_c = 1.022$ M g cm^{-3},

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2 \times 10^{-1}$)

	x	y	z	U_{eq} [a]
Si(1)	2006(1)	5629(1)	1784(1)	24(1)
Si(2)	2561(1)	7619(1)	727(1)	24(1)
N(1)	2291(2)	6652(2)	1297(1)	26(1)
O(1)	269(2)	5583(2)	1633(1)	37(1)
C(11)	−459(2)	6050(3)	993(1)	42(1)
C(12)	−1671(3)	6296(3)	1154(2)	60(1)
C(13)	−1812(3)	5419(3)	1688(2)	62(1)
C(14)	−574(3)	5181(3)	2070(2)	68(1)
C(2)	2311(3)	4065(2)	1533(1)	37(1)
C(21)	1958(3)	3966(2)	756(1)	43(1)
C(22)	1588(4)	3103(2)	1825(2)	75(2)
C(23)	3675(3)	3817(3)	1744(2)	66(1)
C(3)	2437(2)	5961(2)	2736(1)	33(1)
C(31)	2270(3)	4987(3)	3236(1)	44(1)
C(32)	3807(3)	6281(3)	2871(1)	57(1)
C(33)	1753(3)	7057(3)	2891(1)	59(1)
C(4)	2149(2)	9176(2)	972(1)	33(1)
C(41)	2083(3)	10072(2)	390(2)	50(1)
C(42)	3050(3)	9620(2)	1598(1)	47(1)
C(43)	877(3)	9134(2)	1151(2)	44(1)
C(5)	4224(2)	7496(2)	611(1)	35(1)
C(51)	5095(3)	7376(3)	1305(2)	50(1)
C(52)	4663(3)	8519(3)	229(2)	53(1)
C(53)	4354(3)	6381(3)	207(2)	56(1)
C(6)	1561(3)	7365(2)	−143(1)	40(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2

Bond lengths (pm)

Si(1)–N(1)	159.6(2)	Si(1)–O(1)	190.2(2)
Si(1)–C(2)	190.7(3)	Si(1)–C(3)	191.1(2)
Si(2)–N(1)	166.1(2)	Si(2)–C(4)	192.7(3)
Si(2)–C(5)	192.1(3)	Si(2)–C(6)	189.7(2)
O(1)–C(11)	147.4(3)	O(1)–C(14)	148.2(4)
C(11)–C(12)	147.7(4)	C(12)–C(13)	149.9(5)
C(13)–C(14)	146.5(4)	C(2)–C(21)	153.4(4)
C(2)–C(22)	154.7(5)	C(2)–C(23)	152.2(4)
C(3)–C(31)	153.6(4)	C(3)–C(32)	154.2(4)
C(3)–C(33)	153.1(4)	C(4)–C(41)	154.4(4)
C(4)–C(42)	152.9(4)	C(4)–C(43)	153.2(4)
C(5)–C(51)	153.6(4)	C(5)–C(52)	153.2(4)
C(5)–C(53)	153.3(4)		

$F(000) = 864$, $\lambda(\text{Mo-}K_\alpha)$ 71.073 pm, μ 0.15 mm^{-1}, crystal size $0.7 \times 0.8 \times 0.9$ mm^3, data-collection on a Stoe-Siemens AED diffractometer at $-120\,^\circ\text{C}$, 5036 reflections with $2\theta < 45^\circ$, 2810 unique data with $F > 4\sigma(F)$.

Structure determination

The structure was solved by multisolution direct methods [9] and refined, with all non H-atoms anisotropic, to a minimum $\Sigma w\Delta^2$ ($\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F) + gF^2$ with $g = 0.0001$). Hydrogen atoms were allowed to ride on the carbon atoms at a C–H distance of 100 pm. U_{eq} for groups of equivalent hydrogen atoms were

Table 3

Bond angles (°)

N(1)–Si(1)–O(1)	104.2(1)	N(1)–Si(1)–C(2)	117.3(1)
O(1)–Si(1)–C(2)	99.3(1)	N(1)–Si(1)–C(3)	115.1(1)
O(1)–Si(1)–C(3)	102.0(1)	C(2)–Si(1)–C(3)	115.3(1)
N(1)–Si(2)–C(4)	110.8(1)	N(1)–Si(2)–C(5)	110.3(1)
C(4)–Si(2)–C(5)	112.6(1)	N(1)–Si(2)–C(6)	112.1(1)
C(4)–Si(2)–C(6)	104.5(1)	C(5)–Si(2)–C(6)	106.3(1)
Si(1)–N(1)–Si(2)	174.3(1)	Si(1)–O(1)–C(11)	119.7(2)
Si(1)–O(1)–C(14)	131.4(2)	C(11)–O(1)–C(14)	108.9(2)
O(1)–C(11)–C(12)	104.4(2)	C(11)–C(12)–C(13)	105.1(3)
C(12)–C(13)–C(14)	106.0(3)	O(1)–C(14)–C(13)	106.0(3)
Si(1)–C(2)–C(21)	108.3(2)	Si(1)–C(2)–C(22)	115.7(2)
C(21)–C(2)–C(22)	106.5(2)	Si(1)–C(2)–C(23)	108.8(2)
C(21)–C(2)–C(23)	107.9(2)	C(22)–C(2)–C(23)	109.3(2)
Si(1)–C(3)–C(31)	118.0(2)	Si(1)–C(3)–C(32)	105.4(2)
C(31)–C(3)–C(32)	107.6(2)	Si(1)–C(3)–C(33)	109.2(2)
C(31)–C(3)–C(33)	109.3(2)	C(32)–C(3)–C(33)	106.7(2)
Si(2)–C(4)–C(41)	113.5(2)	Si(2)–C(4)–C(42)	111.4(2)
C(41)–C(4)–C(42)	108.9(2)	Si(2)–C(4)–C(43)	108.1(2)
C(41)–C(4)–C(43)	107.0(2)	C(42)–C(4)–C(43)	107.8(2)
Si(2)–C(5)–C(51)	110.3(2)	Si(2)–C(5)–C(52)	114.7(2)
C(51)–C(5)–C(52)	108.3(2)	Si(2)–C(5)–C(53)	108.8(2)
C(51)–C(5)–C(53)	107.1(2)	C(52)–C(5)–C(53)	107.3(2)

refined isotropically. Complex scattering factors were employed [10]. Final difference synthese shows no significant features. 241 parameters, $R = 0.041$, R_w $(= (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}) = 0.042$. Lists of H-atom coordinates and calculated and observed structure factors are available from the authors.

Summary

The synthesis of iminosilanes based on fluorine–chlorine exchange at lithium-aminofluorosilanes followed by elimination of lithiumchloride shows the following features: (a) the method is a general one in the sense that it can be applied to differently-substituted aminosilanes; (b) the iminosilanes obtained, whether as THF adducts or free imines are formed, in good yield; (c) the tedious and sometimes complicated synthesis of aminochlorosilanes as precursors is avoided since the fluorine–chlorine exchange takes place in one step in the lithium derivative.

Experimental

Silylamines 1 and 2

A solution of 0.1 mole of $(\mathrm{Me_3C})_2\mathrm{MeSiNHLi}$ in 50 ml THF was treated with 0.1 mole of $(\mathrm{Me_3C})_2\mathrm{SiF_2}$. The solution was boiled under reflux for 40 h. The products **1** and **2** were isolated by distillation.

Di-tert-butylfluorosilyl(di-tert-butylmethylsilyl)amine (1)

$\mathrm{C_{17}H_{40}FNSi_2}$ (333.7), b.p. 78 °C/0.01 mbar, yield 25.0 g (75%). MS: (F.J.) *m/z* (%) = 333 (22) $[M]^+$. IR: $\tilde{\nu} = 3359$ (NH). NMR: ($\mathrm{CDCl_3}$/TMS). ^{1}H: $\delta = 0.14$ (D, $^5J(\mathrm{HF}) = 0.9$ Hz, SiMe, 3H); 1.0 ($\mathrm{SiCMe_3}$, 18H); 1.05 (D, $^4J(\mathrm{HF}) = 1.0$ Hz, ($\mathrm{FSiCMe_3}$, 18H); ^{13}C: $\delta = -6.91$ (D, $^4J(\mathrm{CF}) = 2.67$ Hz, SiC, 1C); 20.66 (D, $^4J(\mathrm{CF}) = 0.46$ Hz, $\mathrm{Si}\mathit{C}\mathrm{C_3}$, 2C); 20.84 (D, $^2J(\mathrm{CF}) = 15.30$ Hz, $\mathrm{FSi}\mathit{C}\mathrm{C_3}$, 2C); 27.94 (D, $^3J(\mathrm{CF}) = 0.66$ Hz, $\mathrm{FSiC}\mathit{C}_3$, 6C); 28.30 (D, $^5J(\mathrm{CF}) = 0.60$ Hz, $\mathrm{SiC}\mathit{C}_3$, 6C). ^{15}N: $\delta = -371.56$ (D, $^2J(\mathrm{NF}) = 6.06$ Hz). ^{19}F: $\delta = -2.69$ (D, $^3J(\mathrm{HF}) = 11.5$ Hz). ^{29}Si: $\delta = 3.42$ (D, $^1J(\mathrm{SiF}) = 299.67$ Hz, SiF, 1Si); 9.84 (D, $^3J(\mathrm{SiF}) = 0.96$ Hz, SiMe, 1Si).

1,1,3,3,5,5-Hexa-tert-butyl-1,5-dimethyl-1,3,5-trisilazane (2)

$\mathrm{C_{26}H_{62}N_2Si_3}$ (487,1), b.p. 135 °C/0.01 mbar, yield 0.7 g (15%) MS: (F.J.) *m/z* (%) = 429 (79) $[M - \mathrm{CMe_3}]^+$. NMR: ($\mathrm{CDCl_3}$/TMS). ^{1}H: $\delta = 0.16$ (SiMe, 6H); 1.00 ($\mathrm{SiCMe_3}$, 36H); 1.06 ($\mathrm{SiCMe_3}$, 18H). ^{13}C: $\delta = -5.32$ (SiC, 2C); 21.37 ($\mathrm{Si}\mathit{C}\mathrm{C_3}$, 4C); 22.65 ($\mathrm{Si}\mathit{C}\mathrm{C_3}$, 2C); 29.10 ($\mathrm{SiC}\mathit{C}_3$, 12C); 29.78 ($\mathrm{SiC}\mathit{C}_3$, 6C). ^{29}Si: $\delta = -0.73$ ($\mathrm{SiCC_3}$, 1Si); 7.69 ($\mathrm{SiCC_3}$ 2Si).

Lithium-di-tert-butylfluorosilyl(di-tert-butyl-methylsilyl)amide-THF adduct (3)

0.05 mole of compound **1** was treated with 0.05 mole of n-$\mathrm{C_4H_9Li}$ (15% in hexane) to give **3**, which was purified by crystallization from hexane/THF. $\mathrm{C_{25}H_{55}FLiNO_2Si_2}$ (483.9), yield 20.6 g (85%). NMR: ($\mathrm{C_6D_6}$). ^{1}H: $\delta = 0.24$ (SiMe, 3H); 1.23 ($\mathrm{SiCMe_3}$, 18H); 1.31 (D, $^4J(\mathrm{HF}) = 1.02$ Hz, ($\mathrm{FSiCMe_3}$, 18H); 1.35 ($\mathrm{O(CH_2}\mathit{H}_2)_2$, 8H); 3.46 ($\mathrm{O(C}\mathit{H}_2\mathrm{CH_2)_2}$, 8H). ^{7}Li: $\delta = -0.16$. ^{13}C: $\delta = -0.95$ (D, $^4J(\mathrm{CF}) = 1.89$ Hz, SiC, 1C); 22.34 (D, $^4J(\mathrm{CF}) = 0.58$ Hz, $\mathrm{Si}\mathit{C}\mathit{C}_3$, 2C); 22.80 (D, $^2J(\mathrm{CF}) = 20.62$ Hz, $\mathrm{FSi}\mathit{C}\mathrm{C_3}$, 2C); 25.36 ($\mathrm{O(C_2C_2)}$, 4C); 29.83 ($\mathrm{FSiC}\mathit{C}_3$, 6C); 30.56 ($\mathrm{SiC}\mathit{C}_3$, 6C; 68.32 ($\mathrm{O(}\mathit{C}_2\mathrm{C_2)}$, 4C). ^{19}F: $\delta = 9.88$. ^{29}Si: $\delta = 11.14$ (D, $^3J(\mathrm{SiF}) = 11.35$ Hz, SiMe, 1Si); -4.21 (D, $^1J(\mathrm{SiF}) = 225.65$ Hz, SiF, 1Si).

*Di-tert-butyl(di-tert-butylmethylsilyl)iminosilane-THF adduct (**4**)*

A solution of 0.02 mole of **3** in 50 ml hexane/THF was treated with 0.02 mole of Me_3SiCl and the mixture stirred for 8 h. The formation of Me_3SiF was monitored by ^{19}F-NMR spectroscopy. **4** was separated from LiCl by distillation *in vacuo* and purified by recrystallization from benzene. $C_{21}H_{47}NOSi_2$ (385.8), b.p. 60–70 °C/0.01 mbar. NMR: (C_6D_6). ^1H: $\delta = 0.05$ (SiMe, 3H); 1.08 ($SiCMe_3$, 18H); 1.15 ($SiCMe_3$, 18H); 1.37 ($O(CH_2C\mathit{H}_2)_2$, 4H); 3.95 ($O(C\mathit{H}_2CH_2)_2$, 4H). ^{13}C: $\delta = -2.59$ (SiC, 1C); 22.31 ($CSiC\mathit{C}_3$, 2C); 24.50 ($OSiC\mathit{C}_3$, 2C); 24.55 ($O(C_2\mathit{C}_2)$, 2C); 29.79 ($CSiC\mathit{C}_3$, 6C); 30.37 ($OSiC\mathit{C}_3$, 6C); 73.78 ($O(\mathit{C}_2C_2)$, 2C). ^{14}N: $\delta = -329.08$. ^{29}Si: $\delta = -14.57$ ($CSiCC_3$, 1 Si); 3.60 ($OSiCC_3$, 1Si).

*1,1,3,3,5,5,7,7-Octa-tert-butyl-1,7-dimethyl-1,3,5,7-tetra-sila-2,6,-diaza-4-oxane (**5**)*

The presence of traces of moisture led to formation of some **5** during the synthesis of **4**. **5** was purified by recrystallization from THF. $C_{34}H_{80}N_2OSi_4$ (645.4) Sublimation: ≈ 110 °C/0.01 mbar. MS: (EI) m/z (%) = 587 (100) $[M - CMe_3]^+$. IR: $\tilde{\nu} = 3314$ (NH) (in $CDCl_3$). NMR: ^1H: $\delta = 0.18$ (SiMe, 6H); 1.01 ($SiCMe_3$, 36H); 1.13 ($SiCMe_3$, 36H). ^{13}C: $\delta = -4.41$ (C, 2C); 21.62 ($\mathit{C}C_3$, 4C); 21.99 ($\mathit{C}C_3$, 4C); 29.33 ($C\mathit{C}_3$, 12C); 29.73 ($C\mathit{C}_3$, 12C). ^{29}Si: $\delta = -9.32$ (SiO, 1Si); 7.07 (SiMe, 1Si).

Acknowledgements

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References

1 R. West, M.J. Fink and J. Michl, Science, 214 (1981) 1343.
2 See references in A.G. Brook and K.M. Baines, Adv. Organomet. Chem., 25 (1986) 1.
3 M. Hesse and U. Klingebiel, Angew. Chem., 98 (1986) 638.
4 D. Stalke, N. Keweloh, U. Klingebiel, M. Noltemeyer and G.M. Sheldrick, Z. Naturforsch. B, 42 (1987) 1237.
5 N. Wiberg, K. Schurz, G. Reber and G. Müller, J. Chem. Soc., Chem. Commun., 591 (1986).
6 R. Boese and U. Klingebiel, J. Organomet. Chem., 315 (1986) C17.
7 U. Klingebiel in Silicon and Bioorganosilicon Chemistry, Ellis Horwood, Chicester, 1988, Chap. 31, p. 337.
8 P.v.R. Schleyer and P.D. Stout, J. Chem. Soc., Chem. Commun., 1373 (1986).
9 G.M. Sheldrick, Acta Crystallogr., Sect. A, 46 (1990) 467.
10 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, UK, p. 99 and 149.