Addition and cycloaddition reactions of di-tert-butyl(di-tert-butylphenylsilylimino) silane [1]

Jörg Niesmann, Uwe Klingebiel *, Mathias Noltemeyer

Institut für Anorganische Chemie der Universität Göttingen, Tammannstr. 4, D-37077 Göttingen, Germany

Received 19 January 1996

Abstract

The di-tert-butyl(di-tert-butylphenylsilyl)iminosilane $R_2Si=NR'$ ($R = CMe_3$, $R' = Si(CMe_3)_2Ph$) (1) reacts with compounds having acidic protons to give insertion products. Treatment of 1 with ethanol leads to the silyl ether $(R_2SiOC_2H_5NHR)$ (2). In reaction with HCl the aminochlorosilane $(R_2SiClNHR')$ (3) is formed. Compound 3 is also obtained by hydrolysis of the corresponding lithium derivative. Compound 1 reacts with acetone (4) and 2,3-dimethyl-1,3-butadiene (5) in an ene reaction to give the isopropenyloxysilylamine $R_2SiOC(CH_2)Me-NHR'$ (4), and the 4,5-dimethylene-1-aza-2-silahexane $(R_2Si(C_6H_9)-NHR'$ (5). Compound 1 combines with 2,6-diethylphenylazide in a [2 + 3]-cycloaddition to give the tetraazasilacyclopentene $R_2SiNR'(NR'')N_2$ ($R'' = 2,6-C_6H_3(C_2H_5)_2$) (6). Treatment of 1 with THF leads to the THF adduct $R_2Si(THF)NR'$ (7). The latter reacts with 1,4-dihydroxybenzene by insertion into the O-H bonds to give the 1,4-bis(1-oxa-3-aza-2,4-disilabutyl)benzene $1,4-C_6H_4(OSiR_2-NHR')_2$ (8). With divinyloxyethane the bis(1-aza-2-silacyclobutyloxy)ethane $1,2-C_2H_4(OCHCH_2SiR2NR')_2$ (9) is formed in a [2 + 2]-cycloaddition. The crystal structures of 5 and 6 are described

*Keywords:* Silicon; Crystal structure; Iminosilanes

1. Introduction

Development of the chemistry of multiple bond systems involving heavier main group elements is one of the most fruitful recent innovations in inorganic chemistry, in spite of the fact that such compounds were formerly considered to be unstable and synthetically inaccessible.

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

The synthesis we developed is based on an intermolecular fluorine-chlorine exchange in lithiated aminofluorosilanes [4-7]. The investigations have shown that the high strength of the Si-F bond is responsible for the fact that many of those lithium derivatives of aminofluorosilanes with bulky substituents can be distilled or sublimed in vacuo without decomposition [5,7],

thermally enforced LiF elimination leads to dimerization or rearrangement of the free iminosilanes [5]. Thus a better leaving group than fluorine had to be used. One of the remarkable features of lithiated aminofluorosilanes with bulky substituents is that they do not undergo substitution on treatment with Me_3SiCl at the nitrogen atom but instead at the silicon atom, to give Me_3SiF [4-7]; that is, intermolecular fluorine-chlorine exchange takes place. A necessary condition for this is that a Lewis base, e.g. THF, must be present. The lithium-aminochlorosilanes are far less thermally stable than the analogous fluorine compounds, and LiCl-elimination give iminosilanes, which can be distilled in vacuo without decomposition:
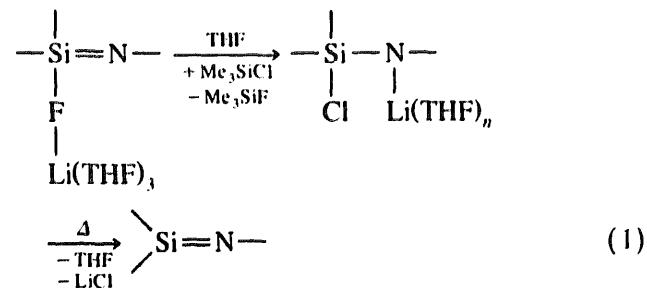
$$\underset{\underset{Li(THF)_3}{|}}{\overset{|}{\underset{F}{Si}}}\!\!=\!\!N\!-\xrightarrow[\substack{+\,Me_3SiCl \\ -\,Me_3SiF}]{THF} \underset{\underset{Cl}{|}\ \underset{Li(THF)_n}{|}}{\overset{|}{Si}}\!-\!\overset{|}{N}\!-$$

$$\xrightarrow[\substack{-THF \\ -LiCl}]{\Delta} \ \ \overset{\diagdown}{\underset{\diagup}{Si}}\!\!=\!\!N\!- \tag{1}$$

Although the Si=N double bond is sterically shielded, the high reactivity of iminosilanes allowed synthesis of a number of interesting compounds [8–10]. In this paper some characteristic insertion and cycloaddition reactions of di-*tert*-butyl(di-*tert*-butylphenylsilyl)iminosilane [7, 10] (1) are described.

2. Results and discussion

The iminosilane (1) [7] has been shown to react with protic compounds by insertion into the R′–H bond [9]. Thus, treatment of 1 with ethanol or HCl gives the silyl ether 2 and the aminochlorosilane 3 respectively:

$$\underset{X}{\overset{X}{\diagdown}}Si{=}N{-}R \xrightarrow{+R'-H} \overset{+}{+}Si{-}\overset{+}{N}{-}R \qquad (2)$$

$$1 \qquad\qquad\qquad \underset{R'}{\mid}\ \underset{H}{\mid}$$

$$2, 3$$

	R′
2	OEt
3	Cl

$$R = Si(CMe_3)_2C_6H_5$$
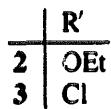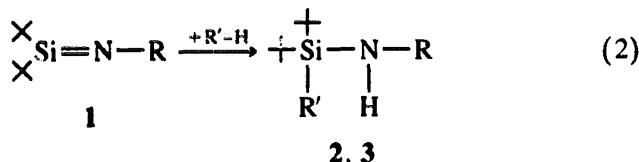
Compound 3 is also formed in the reaction of the lithiated aminochlorosilane with traces of water:

$$(THF)_3LiF{-}\overset{+}{\underset{+}{Si}}{=}N{=}\overset{+}{\underset{+}{Si}}{-}Ph$$

$$\delta\,^{29}Si = -17.60\ SiPh$$

$$= -5.05\ SiF$$

$$\xrightarrow[-Me_3SiF]{+Me_3SiCl}\ \overset{+}{+}Si{-}N{=}\overset{+}{Si}{-}Ph \xrightarrow[{-\,n\ THF}]{\underset{-\ LiOH}{H_2O}} 3 \qquad (3)$$

$$\underset{Cl}{\mid}\ \underset{\underset{(THF)_n}{Li}}{\mid}$$

$$\delta\,^{29}Si = -23.52\ SiPh$$

$$= -13.23\ SiCl$$
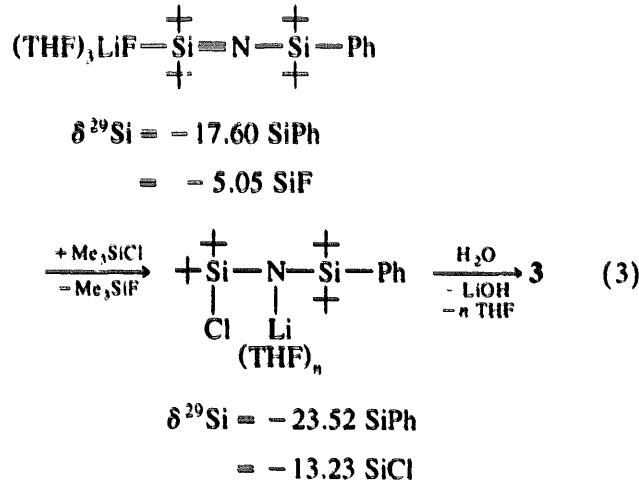
The lithiated aminochlorosilane was characterized in solution. In the ^{29}Si NMR spectrum there is an upfield shift of the signals with respect to those from the LiF-adduct [7]. Compound 3 is remarkably stable, and it could be separated from LiOH by distillation in vacuo. Comparison with the lithiated derivative shows a strong and significant downfield shift of the signals in the ^{29}Si NMR spectrum. Reaction of 1 with acetone gives the isopropenyloxysilylamine 4 (Eq. (4)). Even 2,3-di-

methyl-1,3-butadiene reacts like an enophile and not like a diene, giving 5:

$$\underset{X}{\overset{X}{\diagdown}}Si{=}N{-}R \longrightarrow \begin{array}{l} \overset{+}{+}Si{-}\overset{+}{N}{-}R \\ \quad\ \underset{O}{\mid}\ \underset{H}{\mid} \\ \\ 4 \end{array}$$

$$\overset{+}{+}Si{-}\overset{+}{N}{-}R \qquad (4)$$

$$1 \qquad\qquad\qquad \underset{H}{\mid}$$

$$5$$

$$R = Si(CMe_3)_2C_6H_5$$
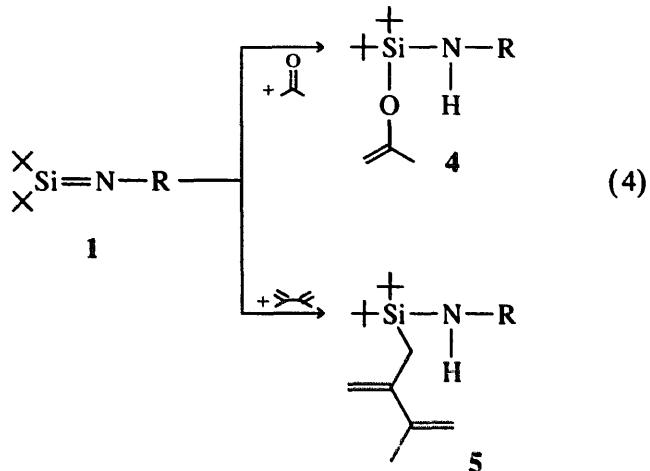
Compound 5 was characterized by a crystal structure determination.

3. Crystal structure of 5

The crystal structure study of 5 confirms the structure suggested on the basis of the NMR data. Crystals of 5 were obtained from n-hexane. The bulky silyl groups give rise to an enlarged angle at the nitrogen atom.

Reactions of iminosilanes with silylazides have already been described [8,9]. Because of the polarity of the azide

$$R{-}N{=}\overset{\oplus}{\underline{N}}{=}\underline{\underline{N}}^{\ominus} \longleftrightarrow R{-}\underline{\underline{N}}^{\ominus}{=}N{=}\overset{\oplus}{\underline{N}}|$$

$$\longleftrightarrow R{-}\overset{\oplus}{\underline{N}}{-}N{=}\underline{\underline{N}}^{\ominus}$$

the regioselectivity of the reaction cannot be easily predicted. On treating the iminosilane 1 with 2,6-dieth-


Fig. 1. Crystal structure of 5, selected bond lengths (pm) and angles (°): Si(1)–N(1) 174.9(2), N(1)–Si(2) 174.7(2), Si(1)–C(1) 192.7(3), Si(1)–C(6) 190.8(3), Si(2)–C(5) 189.6(3), Si(2)–C(3) 192.2(3), Si(2)–N(1)–Si(1) 147.15(13).
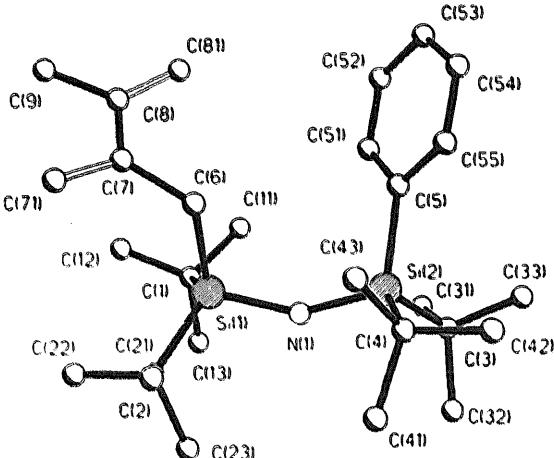
ylphenylazide, the tetraazasilacyclopentene **6** was formed by a [2 + 3]-cycloaddition:

1 +

(5)

6
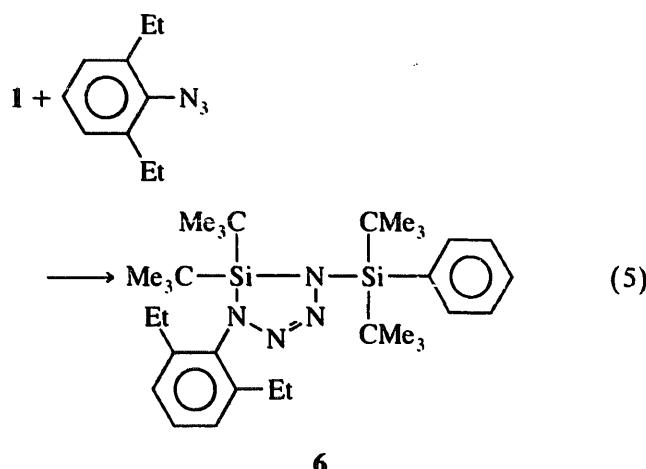
The tetraazasilacyclopentene **6** decomposes at elevated temperatures by [2 + 3]-cycloreversion into both possible azides and iminosilanes.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **5**

Atom	x	y	z	U_{eq}
Si(1)	600(1)	−350(1)	−1278(1)	49(1)
N(1)	−919(2)	−389(1)	−1483(1)	48(1)
Si(2)	−2182(1)	−511(1)	−1049(1)	46(1)
C(1)	1160(3)	−1173(2)	−1961(2)	60(1)
C(11)	602(3)	−1977(2)	−1807(2)	71(1)
C(12)	2489(3)	−1287(3)	−1729(2)	85(1)
C(13)	823(3)	−1003(3)	−2951(2)	82(1)
C(2)	1053(3)	698(2)	−1615(3)	77(1)
C(21)	880(4)	1311(2)	−907(3)	95(1)
C(22)	2328(4)	742(3)	−1744(4)	107(2)
C(23)	274(4)	966(3)	−2491(3)	99(1)
C(3)	−3352(2)	−909(2)	−1991(2)	63(1)
C(31)	−2886(3)	−1617(2)	−2435(2)	83(1)
C(32)	−3754(4)	−288(3)	−2700(3)	99(1)
C(33)	−4413(3)	−1222(3)	−1631(3)	102(1)
C(4)	−2593(3)	486(2)	−576(2)	64(1)
C(41)	−2497(4)	1172(2)	−1221(3)	87(1)
C(42)	−3845(3)	519(3)	−366(3)	90(1)
C(43)	−1723(3)	654(2)	284(2)	75(1)
C(5)	−1979(2)	−1310(2)	−166(2)	52(1)
C(51)	−1333(3)	−1991(2)	−250(2)	67(1)
C(52)	−1237(3)	−2621(2)	331(3)	82(1)
C(53)	−1791(3)	−2584(2)	1045(2)	83(1)
C(54)	−2444(4)	−1938(3)	1150(2)	88(1)
C(55)	−2534(3)	−1305(2)	563(2)	73(1)
C(6)	1057(2)	−506(2)	−38(2)	55(1)
C(7)	2338(4)	−633(3)	393(3)	91(1)
C(71)	3105(4)	15(3)	583(3)	110(2)
C(8)	2767(4)	−1392(3)	632(3)	103(1)
C(81)	1990(4)	−2006(2)	658(3)	92(1)
C(9)	4061(4)	−1512(4)	864(5)	145(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.
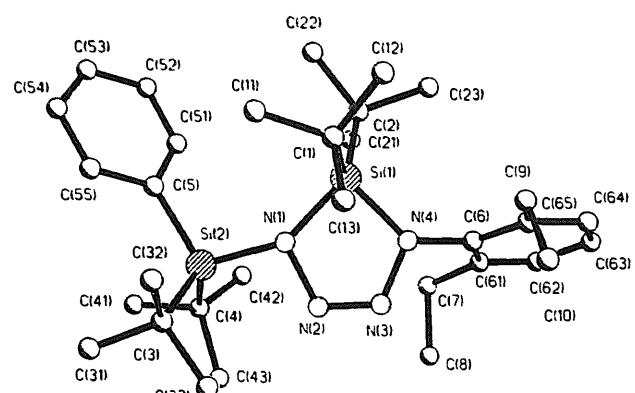
Fig. 2. Crystal structure of **6**, selected bond lengths (pm) and angles (°): N(1)-Si(1) 178.9(7), N(1)-Si(2) 179.8(6), N(2)-N(3) 124.8(8), N(1)-N(2) 145.2 (8), Si(1)-N(4) 177.0(7), N(3)-N(4) 139.0(8), Si(1)-N(1)-Si(2) 149.3(4), N(1)-Si(1)-N(4) 87.7(3).

$R = 2,6\text{-}Et_2C_6H_3$
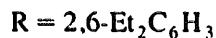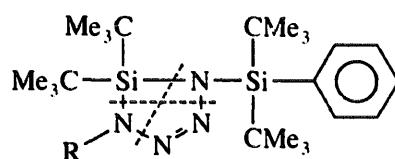
Because of this complication, azides do not serve in every case as precursors for iminosilanes [11]. The structure of **6** was established by an X-ray determination study.

4. Crystal structure of 6

Crystals of **6** were obtained by crystallization from n-hexane. The structure determination of **6** reveals a nearly planar five-membered ring system. Only the Si(1) atom is located below the plane. Because of the bulk of the silyl groups the Si-N distances are increased and the Si(1)-N(1)-Si(2) angle is enlarged. The sum of the bond angles at the nitrogen atoms N(1) and N(4) is 360°.

Upon addition of THF, the iminosilane **1** forms the THF adduct **7**:

$$\underset{X}{\overset{X}{\diagdown}}Si{=}N{-}R \ + \ THF \ \longrightarrow \ \overset{+}{\underset{THF}{\overset{|}{Si}}}{=}N{-}R \qquad (6)$$

1

7

$R = Si(CMe_3)_2C_6H_5$
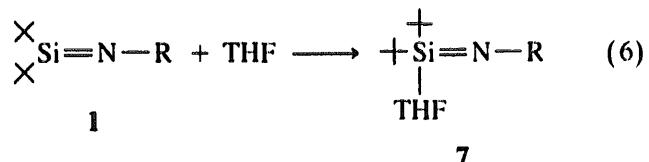
Compound **7** was characterized in solution. Characteristic of the adduct formation by complexation at the unsaturated Si atom is a remarkable ^{29}Si NMR upfield shift of the signal from the complexed Si atom in **7**

$(\delta^{29}Si\ THF = 0.97)$ relative to that from the free imi-nosilane **1** $(\delta^{29}Si=N = 80.43)$ [6].

Nevertheless, the THF-adduct **7** is extremely reactive; it combines with 1,4-dihydroxybenzene by inser-

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **6**

Atom	x	y	z	U_{eq}
Si(1)	2143(1)	2329(1)	2783(1)	57(1)
N(1)	2931(3)	2853(4)	2897(3)	52(2)
N(2)	2735(4)	3629(4)	2785(3)	56(2)
N(3)	2074(4)	3759(4)	2564(4)	57(2)
N(4)	1630(4)	3145(4)	2463(3)	54(2)
Si(2)	3883(1)	2882(1)	3107(1)	56(1)
C(1)	2285(5)	1988(5)	3726(5)	67(3)
C(11)	3004(5)	1554(6)	4038(5)	92(3)
C(12)	1696(6)	1510(6)	3806(6)	104(4)
C(13)	2392(5)	2685(5)	4210(5)	84(3)
C(2)	1753(5)	1554(5)	2081(5)	66(3)
C(21)	1812(5)	1750(5)	1365(5)	81(3)
C(22)	2113(5)	801(5)	2346(5)	86(3)
C(23)	942(5)	1480(5)	1904(5)	94(3)
C(3)	4412(5)	3407(5)	4001(4)	60(2)
C(31)	5217(4)	3503(6)	4113(5)	86(3)
C(32)	4397(5)	3007(5)	4661(4)	80(3)
C(33)	4110(5)	4187(5)	4009(5)	88(3)
C(4)	4013(4)	3305(5)	2306(5)	57(2)
C(41)	4754(5)	3075(6)	2317(6)	102(4)
C(42)	3425(5)	3028(5)	1586(5)	87(3)
C(43)	3977(5)	4157(5)	2268(5)	87(3)
C(5)	4196(5)	1895(5)	3178(5)	60(2)
C(51)	3839(5)	1415(6)	2626(6)	77(3)
C(52)	4027(6)	685(6)	2610(6)	86(3)
C(53)	4622(7)	414(6)	3175(8)	82(3)
C(54)	5006(6)	855(7)	3735(7)	87(3)
C(55)	4802(5)	1597(6)	3739(5)	78(3)
C(6)	885(5)	3306(5)	1982(5)	59(2)
C(61)	724(5)	3540(5)	1274(5)	63(3)
C(62)	12(7)	3689(5)	832(5)	82(3)
C(63)	=536(6)	3611(7)	1062(8)	101(4)
C(64)	=362(6)	3402(6)	1753(8)	91(3)
C(65)	338(6)	3259(5)	2224(6)	71(3)
C(7)	1297(5)	3659(5)	979(5)	77(3)
C(8)	1456(6)	4484(6)	929(5)	104(4)
C(9)	493(6)	3068(7)	2991(7)	112(4)
C(10)	529(9)	3719(9)	3431(7)	191(8)
Si(1')	6926(1)	1241(1)	1941(1)	55(1)
N(1')	7624(3)	1028(4)	2812(3)	52(2)
N(2')	8010(4)	405(4)	2765(4)	67(2)
N(3')	7851(4)	153(4)	2133(5)	67(2)
N(4')	7310(4)	569(4)	1582(4)	58(2)
Si(2')	8039(1)	1179(1)	3769(1)	62(1)
C(1')	6030(4)	1004(5)	1980(5)	66(3)
C(11')	6057(5)	177(6)	2171(5)	95(4)
C(12')	5320(5)	1141(6)	1323(5)	101(4)
C(13')	5984(4)	1430(5)	2607(5)	73(3)
C(2')	6857(5)	2153(5)	1445(5)	73(3)
C(21')	7614(5)	2474(5)	1596(6)	95(3)
C(22')	6416(5)	2768(5)	1600(5)	86(3)
C(23')	6470(6)	1985(6)	618(5)	99(4)
C(3')	9050(5)	1379(6)	4050(5)	79(3)
C(31')	9370(6)	1820(7)	4774(6)	123(4)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

tion into the O–H bonds to give **8**, and forms the [2 + 2]-cycloadduct **9** with divinyloxyethane:

$R = Si(CMe_3)_2C_6H_5$ **9**

(7)
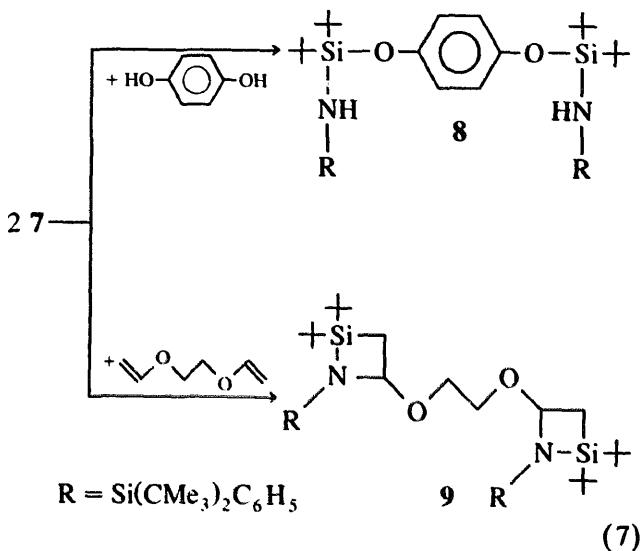
5. Experimental section

All experiments were performed in oven-dried glassware under purified nitrogen or argon using standard inert atmosphere and vacuum line techniques. The n-hexane and THF solvents were dried over Na and distilled under nitrogen prior to use. All NMR spectra were obtained on either a Bruker AM-250 or MSL-400 spectrometer and were recorded in C_6D_6/THF (**7**) and $CDCl_3$ with $SiMe_4$ as internal reference. The data are reported in mass to charge units (m/z) with their relative intensities in parentheses. The NMR spectra and CH analyses confirmed the purities of the isolated compounds.

5.1. Compounds 2 and 4

To a solution of 4.01 g **1** [6] (10.7 mmol) in 10 ml of n-hexane was slowly added at 0°C 5 ml of ethanol (**2**) or 5 ml of acetone (**4**). The mixture was stirred at room temperature for 1 h and the solvent then evaporated in vacuo to leave **2** and **4** respectively, which were purified by recrystallization from n-hexane/THF.

5.2. Di-tert-butyl-ethoxysilyl(di-tert-butylphenylsilyl)-amine (2)

$C_{24}H_{47}NOSi_2$ (421.82), yield 92%; m.p. 95°C. MS (EI): m/z (%) 364(100) $[M-C_4H_9]^+$. ^1H NMR: δ 0.22 NH, 1H, 1.04/1.08 $C(CMe_3)_2$, 36H, 1.29 OCH_2CH_3, 3H (t, $^3J_{HH} = 6.9$ Hz), 4.05, OCH_2CH_3, 2H (q, $^3J_{HH} = 6.9$ Hz), 7.28–7.93 (m, Ph, 5H). ^{13}C NMR: δ 18.41 OCH_2CH_3, 21.25/22.39 $SiCC_3$, 29.08/29.11 $SiCC_3$, 60.09 OCH_2CH_3, 126.42 Ph (C-2, C-6/C-3, C-5),

128.30 Ph (C-4), 136.18 Ph (C-2, C-6/C-3, C-5), 136.26 Ph (C-1). ^{29}Si NMR: δ −7.99 SiO, 0.60 SiPh.

5.3. Di-tert-butyl(isopropenyloxy)silyl(di-tert-butylphenylsilyl)amine (4)

$C_{25}H_{47}NOSi_2$ (433.83), yield 73%; m.p. 124°C. MS (EI): m/z (%) 376(100) [M−C_4H_9]$^+$. ^{1}H NMR: δ 0.39 NH, 1H, 1.08/1.10 C(CH$_3$)$_3$, 36H, 1.90 CH$_3$, 3H (d, $^4J_{HH}$ = 0.4 Hz), 4.15/4.31 =CH$_2$, 2H (m), 7.28–7.92 Ph, 5H (m). ^{13}C NMR: δ 21.31/22.62 SiCC_3, 23.20 OCCH$_3$, 28.91/29.11 SiCC_3, 92.50 CH$_2$, 126.59 Ph (C-2, C-6/C-3, C-5), 128.54 Ph (C-4), 135.18 Ph (C-1), 136.16 (C-2, C-6/C-3, C-5), 155.44 C=CH$_2$. ^{29}Si NMR: δ −8.39 SiO, 0.86 SiPh.

5.4. Di-tert-butylchlorosilyl(di-tert-butylphenylsilyl)amine (3)

(A) A solution of 4.35 g 1 [6] (11.6 mmol) in 15 ml of n-hexane was treated with 1.24 g of Me$_3$NHCl (13.0 mmol) and the mixture was stirred at room temperature for 1 h then filtered. The solvent was evaporated from the filtrate in vacuo, to leave 3 which was purified by distillation in vacuo.

(B) To a solution of 6.80 g of di-tert-butyl(di-tert-butylphenylsilyl)iminosilane–LiF-adduct (11.0 mmol) in 30 ml of n-hexane/THF was slowly added at room temperature 1.42 g of Me$_3$SiCl (13.0 mmol). The mixture was stirred for 3 days, during which the presence of traces of moisture led to the formation of 3, which was separated from LiOH by distillation in vacuo.

$C_{22}H_{42}ClNSi_2$ (412.21), yield 85%; b.p. 158°C (0.01 Torr). MS (EI): m/z (%) 354(100) [M−C_4H_9]$^+$. ^{1}H NMR: δ 1.06/1.10 C(CH$_3$)$_3$, 36H, 7.26–7.92 Ph (m). ^{13}C NMR: δ 21.26/23.50 SiCC_3, 28.36/29.08 SiCC_3, 126.80 Ph (C-2, C-6/C-3, C-5), 128.93 Ph (C-4), 135.86 Ph (C-1), 136.29 Ph (C-2, C-6/C-3, C-5). ^{29}Si NMR: δ 1.54 SiPh, 16.43 SiCl.

5.5. 2,2-Di-tert-butyl-4,5-dimethylene-1-(di-tert-butylphenylsilyl)-1-aza-2-silahexane (5)

A solution of 2.66 g of 1 [6] (7.10 mmol) in 10 ml of n-hexane was treated at room temperature with 0.66 g 2,3-dimethyl-2,3-butadiene (8.00 mmol). The mixture was stirred for 3 h and the solvent then evaporated in vacuo to leave 5, which was purified by crystallization from n-hexane/THF.

$C_{28}H_{51}NSi_2$ (457.88), yield 79%; m.p. 126°C. MS (EI): m/z (%) 400(100) [M−C_4H_9]$^+$. ^{1}H NMR: δ 0.05 NH, 1H, 1.21/1.24 C(CH$_3$)$_3$, 36H, 1.81 CCH$_3$, 3H (d, $^4J_{HH}$ = 0.86 Hz), 2.19 SiCH$_2$, 2H (d, $^4J_{HH}$ = 0.74 Hz), 4.94–5.11 CH$_2$, 4H (m), 7.28–7.93 Ph, 5H (m). ^{13}C

NMR: δ 18.79 SiCH$_2$, 21.58/22.93 SiCC_3, 21.69 CCH$_3$, 29.60/29.75 SiCC_3, 112.29/113.79 C=CH$_2$, 126.85 Ph (C-2, C-6/C-3, C-5), 128.78 Ph (C-4), 136.15 Ph (C-2, C-6/C-3, C-5), 136.21 Ph (C-1), 144.50/146.49 CC_2. ^{29}Si NMR: δ −0.78 SiPh, 5.47 SiCH$_2$.

5.6. 5,5-Di-tert-butyl-1-(2',6'-diethylphenyl)-4-di-tert-butylphenylsilyl-1,2,3,4-tetraaza-5-sila-2-cyclopentene (6)

To a solution of 5.00 g 1 [6] (13.3 mmol) in 15 ml of n-hexane was added 2.63 g of 2,6-diethylphenylazide (15.0 mmol). The mixture was stirred at room temperature for 1 h, and then cooled to 0°C to give crystals of 6.

$C_{32}H_{54}N_4Si_2$ (550.97), yield 67%; m.p. 138°C. MS (EI): m/z (%) 550(8) [M]$^+$, 493(18) [M−C_4H_9]$^+$. ^{1}H NMR: δ 0.95/1.26 C(CH$_3$)$_3$, 36H, 1.20 CH$_2$CH_3, 6H (t, $^3J_{HH}$ = 7.4 Hz), 2.46/2.77 CH_2CH$_3$, 4H (dq/dq, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 7.4 Hz), 7.05–7.96 Ar–H, 8H (m). ^{13}C NMR: δ 15.88 CH$_2$CH$_3$, 23.43 CH$_2$CH$_3$, 23.54/26.29 SiCC_3, 28.83/30.82 SiCC_3, 127.05 Ph (C-4'), 127.12 Ph (C-2', C-6'/C-3', C-5'), 127.47 Ph (C-2, C-6/C-3, C-5), 129.56 Ph (C-4), 134.81 Ph (C-1), 135.92 Ph (C-2, C-6/C-3, C-5), 140.40 Ph (C-1'), 142.72 Ph (C-2', C-6'/C-3', C-5'). ^{29}Si NMR: δ −0.42, 1.80.

5.7. Compounds 7–9

THF (15 ml) was slowly added to 5.7 g of 1 [6] (15.2 mmol) at 0°C. The mixture was then stirred for 1 h and 7 was shown to be present in solution. A solution of 0.84 g of 1,4-dihydroxybenzene (7.60 mmol) in 10 ml of THF [0.87 g of divinyloxyethane (7.60 mmol) in 15 ml of THF] was slowly added at room temperature and the mixture stirred for 2 h. The solvent was evaporated in vacuo to give 8 or 9 respectively. Compound 8 was recrystallized from n-hexane/THF and compound 9 from CH$_2$Cl$_2$.

5.8. Di-tert-butyl(di-tert-butylphenylsilyl)iminosilane–THF-adduct (7)

^{29}Si NMR: δ −21.02 SiPh, 0.97 SiO.

5.9. 1,4-Bis[2,2,4,4-tetra-tert-butyl-4-phenyl-3-aza-1-oxa-2,4-disilabutyl]benzene (8)

$C_{50}H_{88}N_2O_2Si_4$ (861.6), yield 62%; m.p. 159°C. MS (EI): m/z (%) 803(100) [M−C_4H_9]$^+$. ^{1}H NMR: δ 0.48 NH, 2H, 1.08/1.13 C(CH$_3$)$_3$, 72H, 6.93 Ar–H, 4H, 7.21–7.95 Ph, 10H (m). ^{13}C NMR: δ 21.35/22.52

SiCC_3, 29.03/29.?! SiCC_3, 120.57 SiOCC_2, 126.73 Ph (C-2, C-6/C-3, C-5), 128.58 Ph (C-4), 135.57 Ph (C-1), 136.12 Ph (C-2, C-6/C-3, C-5), 149.57 SiOCC_2. ^{29}Si NMR: δ −8.00 SiO, 0.97 SiPh.

5.10. Bis[2,2-di-tert-butyl-1-di-tert-butylphenylsilyl-1-aza-2-silacyclobutyloxy]ethane (9)

$C_{50}H_{92}N_2O_2Si_4$ (865.6), yield 64%; m.p. 174°C. MS (EI): m/z (%) 807(66) $[M-C_4H_9]^+$. ^{1}H NMR: δ 0.76/1.04/1.18/1.26 C$(CH_3)_3$, 72H, 1.40–1.59 SiCH_2, 4H (m), 3.24–3.63 OCH_2, 4H (m), 5.10–5.19 CH, 2H (m), 7.27–7.94 Ph, 10H (m). ^{13}C NMR: δ 17.03 SiCH_2, 22.12/22.49/22.81/23.38 SiCC_3, 29.07/30.09/31.22/31.28 SiCC_3, 63.77 OCH_2, 88.99 CH, 127.09 Ph (C-2, C-6/C-3, C-5), 128.38 Ph (C-4), 135.46 Ph (C-2, C-6/C-3, C-5), 138.01 Ph (C-1). ^{29}Si NMR: δ −3.84 SiPh, 25.04 SiC.

6. X-ray structure determination of 5 and 6

The crystal data and details of the refinement are summarized in Table 3.

Acknowledgements

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Table 3
Crystal data and details of structure refinement for 5 and 6

	5	6
Empirical formula	$C_{28}H_{51}NSi_2$	$C_{32}H_{54}N_4Si_2$
Formula weight	457.88	550.97
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	Cc	P2(1)/n
Unit cell dimensions	$a = 11.708(2)$ Å $\alpha = 90°$	$a = 20.286(4)$ Å $\alpha = 90°$
	$b = 16.797(3)$ Å $\beta = 100.760(10)°$	$b = 18.115(4)$ Å $\beta = 114.52(3)°$
	$c = 15.453(3)$ Å $\alpha = 90°$	$c = 20.396(4)$ Å $\alpha = 90°$
Volume	2985.5(9) Å^3	6819(2) Å^3
Z	4	8
Density (calc.)	1.019 Mg m^{-3}	1.073 Mg m^{-3}
Absorption coefficient	0.133 mm^{-1}	0.129 mm^{-1}
F(000)	1016	2416
Crystal size	0.80 × 0.70 × 0.40 mm^3	0.70 × 0.40 × 0.30 mm^3
Theta range for data collection	3.54 to 22.51°	3.55 to 20.00°
Index ranges	$-12 \leqslant h \leqslant 12$, $-18 \leqslant k \leqslant 18$, $-16 \leqslant l \leqslant 16$	$-19 \leqslant h \leqslant 17$, $0 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 19$
Reflections collected	7710	6335
Independent reflections	3868 [R(int) = 0.0118]	6335 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3868/2/293	6317/0/713
Goodness-of-fit on F^2	0.932	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0382$, $wR_2 = 0.1092$ (3767 reflections)	$R_1 = 0.0801$, $wR_2 = 0.1750$ (3504 reflections)
R indices (all data)	$R_1 = 0.0393$, $wR_2 = 0.1114$	$R_1 = 0.1546$, $wR_2 = 0.2466$
Absolute structure parameter	0.04(11)	
Largest difference peak and hole	0.443 and −0.172 e A^{-3}	0.285 and −0.274 e A^{-3}

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