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Synthesis of (SiNSiO) four-membered rings; crystal structure of $(Me_3C)_2\overline{SiOSi(CMe_3)_2N}SiMe_3$

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Abstract

Siloxanes (**1–3**), of the type $H_2N\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ are formed in the reaction of halogenosilanes with a lithiated aminosilanol. Lithium salts of **1–3** (**4–6**) react with halogenosilanes to yield **7–9** $(-\overset{|}{\underset{|}{Si}}-NH-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-)$; **8** and **9** are structural isomers. The silyl group introduced normally becomes bonded to the oxygen atom. The silyl group migration can be kinetically controlled, as shown by the formation of **7**. Compounds **7** and **8** form the thermally stable lithium compounds **10**, **11** $(-\overset{|}{\underset{|}{Si}}-NLi-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-F)$, which are direct precursors of four-membered 1-oxa-3-aza-2,4-disiletanes (**12**, **13**). The intramolecular cyclization is catalyzed by fluorosilanes present. The crystal structure of the four-membered (SiNSiO) ring species **12**, has been determined, and its features are compared with those of $(-\overset{|}{\underset{|}{Si}}-O-)_2$ ring species.

Introduction

The kinetic stabilization of halogeno- [1] and amino-silanoles [2] has made possible the stepwise synthesis of numerous aliphatic and cyclic organosilicon species [3–6].

After lithiation of di-t-butylaminosilanol, treatment with a silicon halide always results in attachment of the new organosilicon group, to the oxygen atom and so we were able to make (SiNSiO) chains. When we lithiated and silylated these products again we observed that sometimes the new organosilicon group again becomes bonded to the oxygen atom, depending on the nature of the ligand itself. This means

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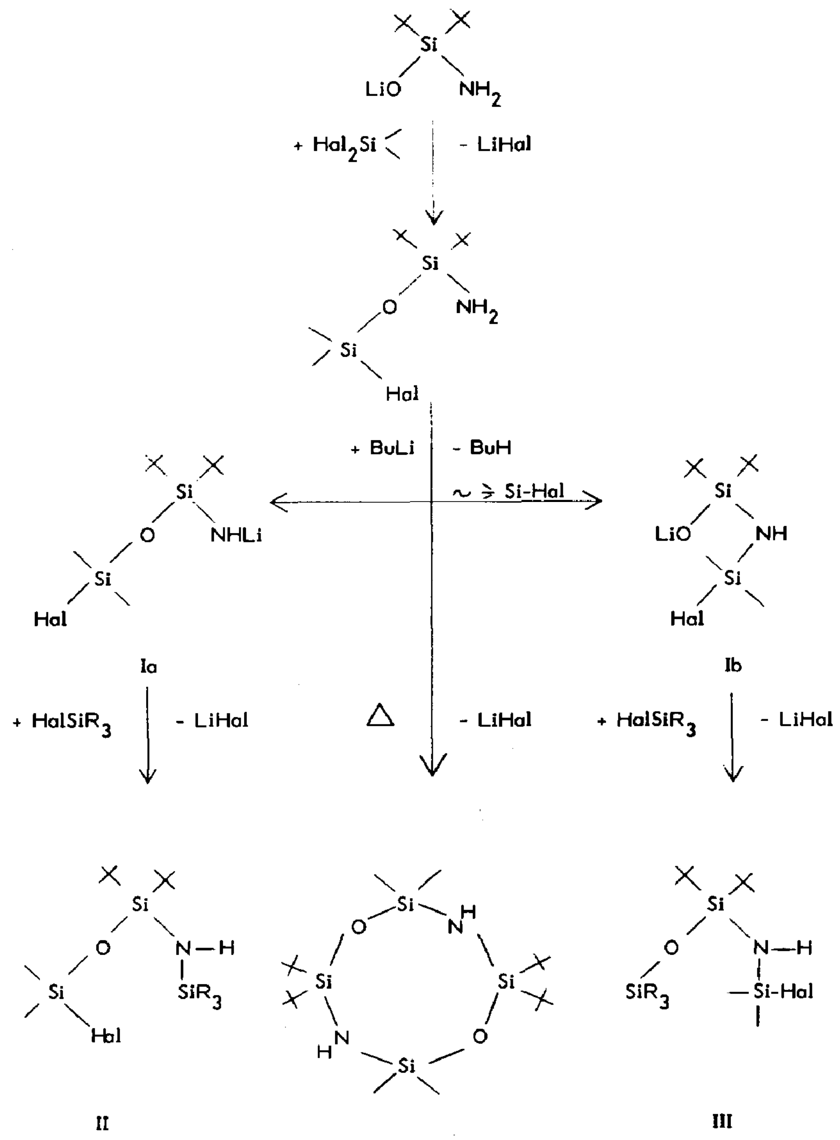
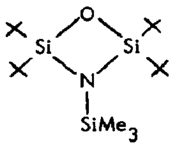


Scheme 1.

that in the lithiation reaction the silyl substituent on the oxygen atom is displaced by the more electropositive lithium atom, so that an O → N silyl group migration takes place (Scheme 1).

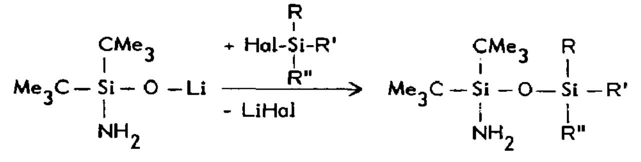
In attempting to obtain cyclic products by salt elimination from lithium compounds of type I we obtained eight-membered ring species [5,6]. We found that the silyl group migration can be kinetically controlled, and thus the formation of type III isomers can either be prevented or induced. Compounds of type II are direct precursors of 1-oxa-3-aza-2,4-disiletanes [4].

In order to compare the geometry of this new ring system with that of the very interesting four-membered $(\geqslant\text{Si-O-})_2$ ring system [7], we have determined the crystal structure of:



Results and discussion

The lithiated aminosilanol [2] reacts with halogenosilanes to yield the siloxanes **1–3** (eq. 1).

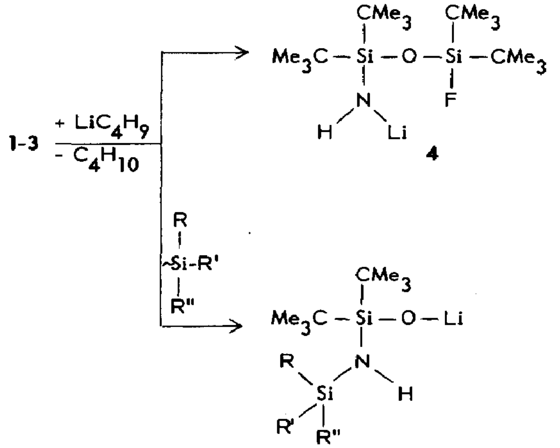


1 [4], **2**, **3**

(1)

On treatment with n-C_4H_9Li in n-hexane they form the lithium compounds **4–6** (eq. 2). In the case of **5** and **6** the silyl groups on the more electronegative oxygen atom are replaced by the lithium atom, the silyl groups moving to the nitrogen atom. In the case of **4**, however, such migration does not occur, because of the bulk of the $(CMe_3)_2$ SiF group, i.e., the silyl group migration is kinetically controlled.

The dissolved lithium derivatives **4–6** were again silylated, to yield the compounds **7–9** (eq. 3).

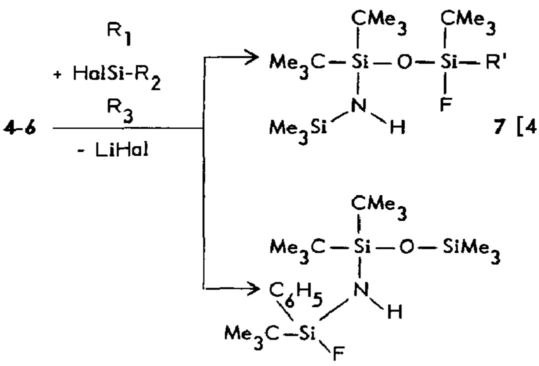


4

5, **6**

(2)

	1,4[4]	2, 5	3, 6
R	F	F	Me
R'	CMe_3	C_6H_5	Me
R"	CMe_3	CMe_3	Me

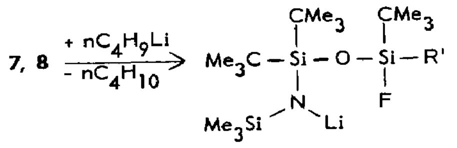


9

7 [4]: R'= CMe_3, 8: R'= C_6H_5 (3)

Products **8** and **9** are structural isomers. Because of the presence of the silyl group on the oxygen atom, **9** does not serve as a precursor for a four-membered (SiNSiO) ring species. By taking advantage of the 1,3-silyl group migration involved in going from species **3** to **6**, we were able to synthesize compound **8** directly. Since, as a rule, the silyl group that is added last becomes bonded to the oxygen atom, the Me_3Si group had to be introduced before the $FSi(C_6H_5)CMe_3$ group in order to make possible the synthesis of compound **8**.

Lithiation of **7** and **8** yields the stable lithium compounds **10** and **11**, which do show no tendency towards LiF elimination even in boiling toluene (eq. 4).



(4)

10: R'= CMe_3, 11: R'= C_6H_5

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)	5005(1)	2426(2)	6815(1)	51(1)
Si(2)	5000	−889(2)	7500	62(1)
O(1)	5000	3688(5)	7500	51(2)
N(1)	5000	1021(6)	7500	48(2)
C(1)	6032(4)	2604(7)	6276(4)	73(2)
C(11)	6341(5)	4226(8)	6317(5)	117(3)
C(12)	6756(5)	1572(11)	6549(6)	148(5)
C(13)	5866(6)	2263(11)	5429(5)	139(4)
C(2)	3976(5)	2689(7)	6180(3)	79(3)
C(21)	3166(6)	2543(11)	6618(6)	136(5)
C(22)	3953(7)	4269(8)	5890(6)	141(4)
C(23)	3812(7)	1573(11)	5558(5)	166(5)
C(4)	5113(19)	−1544(17)	8464(11)	174(12)
C(5)	3907(13)	−1622(18)	7148(14)	141(10)
C(6)	5736(13)	−1768(20)	6901(19)	149(12)

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

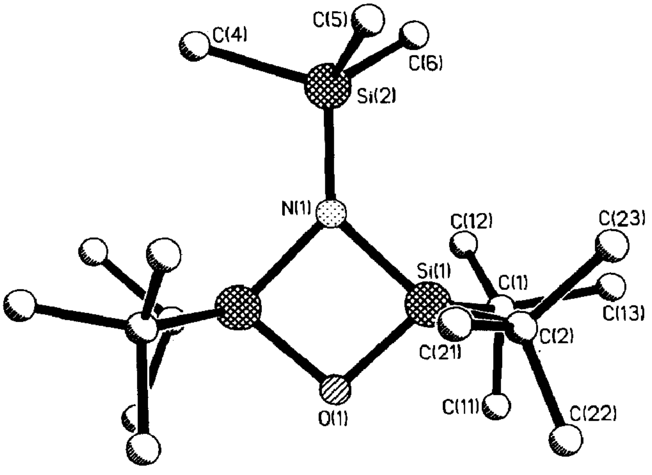


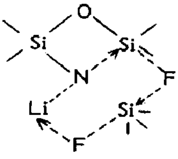
Fig. 1.

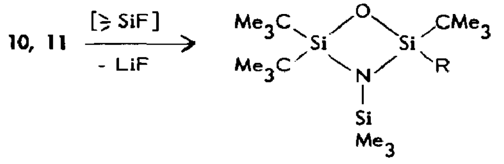
The ^{19}F NMR shifts of the NLi compounds **10** and **11** differ only slightly from those of the corresponding NH compounds **7** and **8**. This indicates that there is no contact between the lithium and the fluorine atoms in the products **10** and **11**, and thus salt elimination cannot occur. We have observed previously that contact between lithium and fluorine atoms leads to a strong low field shift of the ^{19}F NMR signals [8].

Formation of oxa-aza-disiletanes occurs at once, however, when catalytic amounts (1–5%) of fluorosilanes are added to a solution of compounds **10** or **11** in hexane/THF.

Since attachment of the silyl group to the nitrogen atom competes with the desired formation of a four-membered ring, the former has to be prevented by use of a catalyst of a fluorosilane bearing bulky organic substituents; i-Pr_2SiF_2 proved to be satisfactory in this respect.

We assume that the transition state of the catalysed process involves a bicyclic nature (**A**) which makes LiF elimination possible (eq. 5).





(5)

12: R = CMe_3 [4], **13**: R = C_6H_5

A crystal structure determination was carried out in the case of compound **12**.

Table 2

Bond lengths (pm)

Si(1)–O(1)	168.2(3)	Si(1)–N(1)	177.3(4)
Si(1)–C(1)	191.6(7)	Si(1)–C(2)	190.2(7)
Si(2)–N(1)	172.2(6)	Si(2)–C(4)	183.7(20)
Si(2)–C(5)	187.2(19)	Si(2)–C(6)	180.2(27)
Si(2)–C(4A)	183.7(20)	Si(2)–C(5A)	187.2(19)
Si(2)–C(6A)	180.2(27)	O(1)–Si(1A)	168.2(3)
N(1)–Si(1A)	177.3(4)	C(1)–C(11)	153.8(9)
C(1)–C(12)	150.5(11)	C(1)–C(13)	156.6(10)
C(2)–C(21)	152.6(12)	C(2)–C(22)	151.8(10)
C(2)–C(23)	151.7(11)		

Table 3

Bond angles (°)

O(1)–Si(1)–N(1)	88.2(2)	O(1)–Si(1)–C(1)	111.4(2)
N(1)–Si(1)–C(1)	117.3(2)	O(1)–Si(1)–C(2)	108.4(2)
N(1)–Si(1)–C(2)	117.9(2)	C(1)–Si(1)–C(2)	111.0(3)
N(1)–Si(2)–C(4)	108.7(5)	N(1)–Si(2)–C(5)	110.7(5)
C(4)–Si(2)–C(5)	103.5(11)	N(1)–Si(2)–C(6)	116.1(7)
C(4)–Si(2)–C(6)	114.0(12)	C(5)–Si(2)–C(6)	102.9(10)
N(1)–Si(2)–C(4A)	108.7(5)	N(1)–Si(2)–C(5A)	110.7(5)
C(4A)–Si(2)–C(5A)	103.5(11)	N(1)–Si(2)–C(6A)	116.1(7)
C(4A)–Si(2)–C(6A)	114.0(12)	C(5A)–Si(2)–C(6A)	102.9(10)
Si(1)–O(1)–Si(1A)	94.9(2)	Si(1)–N(1)–Si(2)	135.6(1)
Si(1)–N(1)–Si(1A)	88.7(3)	Si(2)–N(1)–Si(1A)	135.6(1)
Si(1)–C(1)–C(11)	108.4(5)	Si(1)–C(1)–C(12)	113.3(5)
C(11)–C(1)–C(12)	110.7(6)	Si(1)–C(1)–C(13)	113.5(5)
C(11)–C(1)–C(13)	105.2(6)	C(12)–C(1)–C(13)	105.4(7)
Si(1)–C(2)–C(21)	110.3(5)	Si(1)–C(2)–C(22)	108.9(5)
C(21)–C(2)–C(22)	105.1(7)	Si(1)–C(2)–C(23)	117.0(6)
C(21)–C(2)–C(23)	103.3(7)	C(22)–C(2)–C(23)	111.6(6)

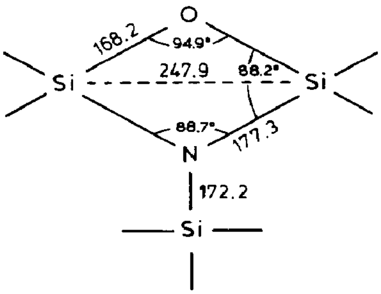
*Crystal structure of **12***

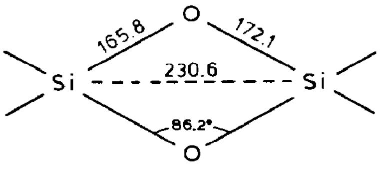
Final atomic coordinates and bond lengths and angles are shown in Tables 1–3.

The molecule possesses crystallographic twofold rotation symmetry with O(1), N(1) and Si(2) on this axis, and this results in a planar arrangement of the four-membered ring and the Si(2) atom bonded to it. This symmetry is made possible only by a corresponding disorder of the methyl groups of the Me_3Si substituent. The four-mememberd ring is almost a square, but there are some irregularities as follows. At the oxygen atom there is a slight opening of the Si(1)–O(1)–Si(1A) angle (94.9°), which is accompanied by a contraction of the angles at the other ring atoms (N(1)–Si(1)–O(1), 88.2°; Si(1)–N(1)–Si(1A), 88.7°). The Si–O (168.2 pm) and Si–N (177.3 pm) bond distances are lengthened. The Si · · · Si non-bonding distance in the ring is 247.9, corresponding N · · · O distance is 240.5 pm. These short distances illustrate that the ring atoms in a four-membered ring system as strained as this one are forced to approach each other to an extra-ordinary extent. The same applies to the bulky substituents; for example, there are short H–H distances between the trimethylsilyl- and the t-butyl groups, e.g.

H(6A)–H(12C) is 214.2 pm, and H(5C)–H(23C) 235.3 pm, and between the t-butyl groups facing each other above the ring, e.g. H(21B)–H(12AA) is 205.2 pm, and H(21A)–H(12AA) is 213.2 pm. By bending slightly, the t-butyl groups seek to make room for the trimethylsilyl groups (N1–Si1–C1, 117.3°; N1–Si1–C2, 117,9 °). The contraction of the angle at the nitrogen atom reflects the decrease in strain between these substituents, but this is limited because a further contraction of the angle would lead to an even stronger repulsion between the t-butyl groups facing each other. In order to counterbalance this, the ring angles at silicon also contract.

1,3-Dioxa-2,4-disiletanes [7], e.g. $(\text{-Mes}_2\text{Si-O-})_2$, have different characteristics:





In particular they have smaller angles at the oxygen atoms. The shorter Si–O bond length compared with the Si–N bond length in 1-oxa-3-aza-2,4-disiletane, together with this contraction of the angle at the oxygen atom, leads to a marked shortening of the Si · · · Si distance. The Si–N–Si angles in the 1,3-diaza-2,4-disiletanes are always larger than 90 °, in contrast to those in the the (SiOSiN) ring [9].

The large Si–O and Si–N bond lengths in the 1-oxa-3-aza-2,4-disiletane may account for the strong ^{29}Si NMR low field shifts of the silicon atoms of the ring compared with those for the compounds **7** and **8** and those for eight-membered (SiOSiN) ring species [5,6]. The short exocyclic Si–N bond causes the high field shift of the $SiMe_3$ group signals.

Crystal data

12: $C_{19}H_{45}NOSi_3$, $M = 387.8$, monoclinic, space group $C2/c$, a 1533.9(2), b 901.5(1), c 1808.8(3) pm, β 93.98(1)^3, U 2.495 nm^3, $Z = 4$, D_c 1.032 g cm^{-3}, $F(000) = 864$, $\lambda(\text{Mo-}K_\alpha)$ 71.069 pm, μ 0.19 mm^{-1}, crystal size $0.27 \times 0.35 \times 0.50$ mm^3, sealed in capillary; Stoe–Siemens AED diffractometer, 2237 reflections with $2\theta < 50°$, 1333 unique data with $F > 4\sigma(F)$.

Structure determinations

The structure was determined by multisolution direct methods and refined with anisotropic non-H atoms to a minimum of $\Sigma w\Delta^2(\Delta = |F_0| - |F_c|;\ w^{-1} = \sigma(F) + gF^2$ with $g = 0.001)$. Hydrogen atoms were allowed to ride on the carbon atoms at C–H distances of 96 pm and fixed $U_{eq}(H) = 0.15$ Å^2. Complex scattering factors were employed [10]. Final difference syntheses showed no significant features. 124 parameters, $R = 0.084$, $R_w(= (\Sigma w\Delta^2/\Sigma wF_0^2)^{1/2}) = 0.087$. Lists of structure factors, anisotropic thermal displacement parameters, and hydrogen coordinates may be obtained from the authors. Relevant bond lengths, bond angles, atomic coordinates and equivalent isotropic displacement factors are given in Tables 1–3.

Experimental

Mass spectra: CH 5-spectrometer, Varian. NMR spectra: 30% solution in $\mathrm{CH_2Cl_2/CDCl_3}$, TMS, $\mathrm{C_6F_6}$ int., Bruker Am-250.

Siloxanes 2 and 3

A solution of 50 mmole of $\mathrm{(CMe_3)_2Si(NH_2)OLi}$ in 100 ml THF was treated with 50 mmol of HalSiRR′R″ (**2**: Hal = F, R = F, R′ = $\mathrm{C_6H_5}$, R″ = $\mathrm{CMe_3}$; **3**: Hal = Cl, R = R′ = R″ = Me). The solution was boiled for 1 h. Products **2** and **3** were purified by distillation.

1-Amino-1,1,3-tri-t-butyl-3-fluoro-3-phenyl-disiloxan (2)

$\mathrm{C_{18}H_{34}FNOSi_2}$ (355.7), b.p. 110 °C/0.01 mbar, yield 1.1 g (59%). MS: m/e = 340(1) $[M-\mathrm{CH_3}]^+$, 298(100) $[M-\mathrm{C(CH_3)_3}]^+$. IR: 3410, 3490 $\mathrm{cm^{-1}}$ ($\mathrm{NH_2}$). ^{1}H NMR: δ 1.1 $\mathrm{CMe_3}$, 1.35 $\mathrm{NH_2}$, 7.5 $\mathrm{C_6H_5}$. ^{13}C NMR: 18.42 FSi*C*Me$_3$ (^2J(CF) 17.1 Hz), 19.76 Si(*C*Me$_3$)$_2$ (^4J(CF) 1.2 Hz), 25.59 FSiC*C*$_3$, 27.76 Si(C*C*$_3$)$_2$, 127.8, 130.3, 132.2 (^2J(CF) 19.9 Hz), 134.6 (^3J(CF) 2.7 Hz) $\mathrm{C_6}$. ^{19}F NMR: 10.8. ^{29}Si NMR: −27.6 SiF (J(SiF) 310.0 Hz), −9.1 $\mathrm{SiNH_2}$.

1-Amino-1,1-di-tert-butyl-3,3,3-trimethyl-disiloxan (3)

$\mathrm{C_{11}H_{29}NOSi_2}$ (247.6), b.p. 142 °C/40 mbar, yield 5.0 g (40%). MS: m/e = 247(22) M^+, 190(100) $[M-\mathrm{C_4H_9}]^+$. IR: 3400, 3480 $\mathrm{cm^{-1}}$ ($\mathrm{NH_2}$). ^{1}H NMR: 0.12 $\mathrm{SiCH_3}$, 0.97 $\mathrm{SiCMe_3}$. ^{13}C NMR: 2.12 $\mathrm{SiC_3}$, 19.65 *C*C$_3$, 27.77 C*C*$_3$. ^{29}Si NMR: −11.9 $\mathrm{SiNH_2}$, 5.4 $\mathrm{SiMe_3}$.

1-(Silylamino)disiloxanes 8 and 9

Compounds **2** or **3** (50 mmol) were lithiated with 50 mmole of $\mathrm{nC_4H_9Li}$ (15% in n-hexane) to give **5** and **6**. On treatment with $\mathrm{ClSiMe_3}$, **5** gave **9**, on treatment with $\mathrm{F_2Si\ (C_6H_5)CMe_3}$ **6** gave **8**. **8** and **9** were purified by distillation.

8: $\mathrm{C_{21}H_{42}FNOSi_3}$ (M = 427.9), b.p. 73 °C/0.01 mbar, yield 1.0 g (45%). MS: m/e 412(6) $[M-\mathrm{CH_3}]^+$, 370(100) $[M-\mathrm{C_4H_9}]^+$. ^{1}H NMR: −1.40 SiMe, 0.94 $\mathrm{FSiCMe_3}$, 0.97 $\mathrm{Si(CMe_3)_2}$, 7.5 $\mathrm{C_6H_5}$. ^{13}C NMR: 1.7 $\mathrm{SiCH_3}$, 18.27 FSi*C*C$_3$ (^2J(CF) 24.9 Hz), 20.78 NSi*C*C$_3$ (^4J(CF) 0.7 Hz), 20.85 NSi*C*C$_3$ (^4J(CF) 0.6 Hz), 25.96 FSiC*C*$_3$, 27.85, 28.00 NSiC*C*$_3$, 127.5, 129.9, 134.8 (^2J(CF) 24.1 Hz), 135.2 (^3J(CF) 2.5 Hz) $\mathrm{C_6}$. ^{19}F NMR: 5.25. ^{29}Si NMR: −10.35 NSiO, −9.3 SiF (J(SiF) 290.6 Hz), 6.13 $\mathrm{SiMe_3}$.

9: $\mathrm{C_{21}H_{42}FNOSi_3}$ (M = 427.9), b.p. 73 °C/0.01 mbar, yield 0.9 g (43%). MS: m/e = 412(10) $[M-\mathrm{CH_3}]$, 370(100) $[M-\mathrm{C_4H_9}]^+$. ^{1}H NMR: 0.26 SiMe, 0.90 $\mathrm{FSiCMe_3}$, 0.96 $\mathrm{Si(CMe_3)_2}$, 7.5 $\mathrm{C_6H_5}$. ^{13}C NMR: 2.34 $\mathrm{SiCH_3}$, 19.1 FSi*C*C$_3$, 20.2, 20.4 Si(*C*C$_3$)$_2$, 26.41 FSiC*C*$_3$, 27.45, 27.56 (SiC*C*$_3$)$_2$, 127.2, 129.2, 134.0, 135.0 $\mathrm{C_6}$. ^{19}F NMR: 0.66 (^3J(HF) 6.6 Hz). ^{29}Si NMR: −22.67 $\mathrm{SiMe_3}$, −2.76 FSi (J(SiF) 304.1 Hz), 6.98 NSiO.

Lithium salts 10 and 11

A solution of 50 mmole of **7** [4] or **8** in 50 ml n-hexane was treated with 50 mmole n-$\mathrm{C_4H_9Li}$ (15% in n-hexane). The reactions of the lithiated species were monitored by ^{19}F NMR spectroscopy and found to be complete at room temperature in 2 h.

10: $C_{19}H_{45}FLiNOSi_3$ ($M = 413.9$), yield 2.0 g (95%). ^{19}F NMR: 6.27. ^{29}Si NMR: −22.47 NSiO, −18.60 FSi (J(SiF) 339.8 Hz), −0.27 $SiMe_3$.

11: $C_{21}H_{41}FLiNOSi_3$ ($M = 433.8$), yield 1.8 g (85%). ^{19}F NMR: 9.78. ^{29}Si NMR: −22.30 NSiO, −17.38 FSi (J(SiF) 249.7 Hz), 1.02 $SiMe_3$.

1-Oxa-3-aza-2,4-disiletanes 12 and 13

A solution of 20 mmole of **10** or **11** in a mixture of 50 ml of n-hexane and 5 ml THF was treated with catalytic amounts of $F_2Si(CHMe_2)_2$. The cyclic species **12**, **13** and LiF were formed. Product **12** was isolated as crystals. The yield of **13** was only 5%.

13: $C_{21}H_{41}NOSi_3$ ($M = 407.9$). MS: $m/e = 407$, M^+. ^{29}Si NMR: −11.14 $SiMe_3$, −2.5 $SiCMe_3$, 6.31 $Si(CMe_3)_2$.

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