Dilithium Derivatives of Bis(*tert*-butyldimethylsilylamino)silanes as Building Units for Inorganic Ring Compounds

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The bis[(*tert*-butyldimethylsilyl)amino]silanes **1**–**3** are converted into their lithium derivatives **4**–**7** with BuLi. Depending on the bulkiness of the substituents, the dilithium derivatives **4** and **5** crystallize in *cis* or *trans* conformation. Monolithiated **3** (**6**) forms a four-membered (SiFLiN) ring system, while its dilithium salt is characterized as a lithium silyldiamide (**7**). Although **4**, **5**, and **7** have different structures, they react with PF_3 (**8**, **9**), SiF_4 (**10**, **11**), and CMe_3SiF_3 (**12**) as diamides to give the corresponding four-membered ring systems **8**–**12**. The crystal structures of **4** and **5** are reported.

Dilithium derivatives of bis(amino)silanes had already been used in the synthesis of cyclodisilazanes[1–3], diazasilaphosphetidines[4,5], or siladiazametallacycles[6,7] before they were characterized by spectroscopy and structure analysis. The first crystal structure analysis of dilithiated bis(*tert*-butylamino)dimethylsilane[8] was published in 1986. Meanwhile, further dilithiated bis(amino)silanes were studied[6,7,9,11]. The crystal structures reveal that both the type of the substituents at nitrogen and the solvent used exert a decisive influence on the structure of the lithium derivatives. The electron-donating power of the nitrogen atom as a bonding partner for the lithium atom depends on its basicity. Thus, electronic effects of the substituents decreasing the basicity may give rise to clearvage of the Li–N bond[11,14]. The use of solvents coordinating to the lithium atom may result in a decrease of the degree of oligomerization of the lithium derivatives[12–14].

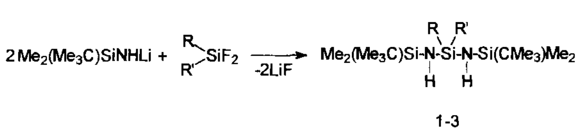
The following structural types of silylamides have mainly been found: a) dimeric dithiated bis(amino)diorganylsilanes[6–9]; b) a monomeric, dilithiated spirocyclic bis(silylamino)difluorosilane[10,12]; c) monomeric and dimeric lithiated silaamidides[13–15]; d) monomeric lithium diorganylsilyldiamides[10–15].

In the reaction of a lithiated fluorosilylhydrazine with an excess of BuLi the dilithium derivative of a bis(silylamino)silane of an unknown structure was accidentally obtained[16]. This induced us to systematically prepare such compounds. In this paper we describe the dilithium derivatives of bis(silylamino)silanes crystallizing in *cis* and *trans* conformation and utilize them for the synthesis of inorganic four-ring systems.

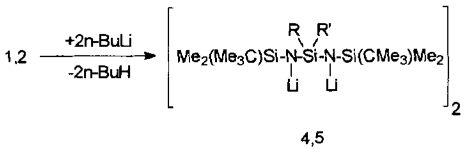
Results and Discussion

Di- and trifluorosilanes react with *tert*-butylsilylamide in a molar ratio of 2:1 to afford bis(amino)silanes **1**–**3**.

The reaction of **1** and **2** with two equivalents of *n*-BuLi in hexane/THF yields lithium derivatives **4** and **5** as colorless crystals.



$$2\,Me_2(Me_3C)SiNHLi + RR'SiF_2 \xrightarrow[-2LiF]{} Me_2(Me_3C)Si\text{-}NH\text{-}SiRR'\text{-}NH\text{-}Si(CMe_3)Me_2 \quad (1)$$



$$\mathbf{1,2} \xrightarrow[-2n\text{-}BuH]{+2n\text{-}BuLi} \left[Me_2(Me_3C)Si\text{-}N(Li)\text{-}SiRR'\text{-}N(Li)\text{-}Si(CMe_3)Me_2\right]_2 \quad (2)$$

	1, 4	2, 5	3
R	Me	$CHMe_2$	F
R'	Me	$CHMe_2$	CMe_3

Crystal Structure of Compound 4

Compound **4** crystallizes as a dimer being composed of four-membered ring systems. Three of these ring systems are built up from Li_2N_2 units and two by SiNLiN units. The latter ring systems may be regarded as planar [(ΣLi(2)–N(3)–Si(5)–N(4) 358.9°, ΣLi(1)–N(1)–Si(2)–N(2) 359°]. The Li_2N_2 systems exhibit larger deviations from planarity [ΣLi(1)–N(2)–Li(3)–N(3) 357.1°, ΣLi(2)–Li(1)–N(4) 357°], the central Li(1)–N(1)–Li(2)–N(3) four-membered ring deviating most significantly from planarity (Σ 348.4°). The lithium atoms are both dicoordinated [Li(3), Li(4)] and tricoordinated [Li(1), Li(2)]. The dicoordinated Li atoms are additionally saturated by extremely short Li–CH contacts, e.g. Li(4)–C(22)=Li(3)–C(51) 233.6 pm. The distances between these C atoms and the Li atoms are in a range as discussed for bonding interactions[17,18]. The N atoms N(2) and N(4) are tetracoordinated, whereas N(1) and N(3) are pentacoordinated[6,8,9,19,20]. The Li-to-N distance of the pentacoordinated N atoms is extended 10 pm compared with that of the tetracoordinated H atoms.

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The Si–N bond lengths are, as expected in the range from 169.8 to 173.6 pm. A look at the side view of the structure along the N(1)–N(3) line indicates a *cis* arrangement of Li(3)–Li(4) atoms. In $[Me_2Si(NLiSiMe_3)_2]_2$ the same structure type as in **4** occurs[21,22].

Figure 1. Structure of **4** in the crystal

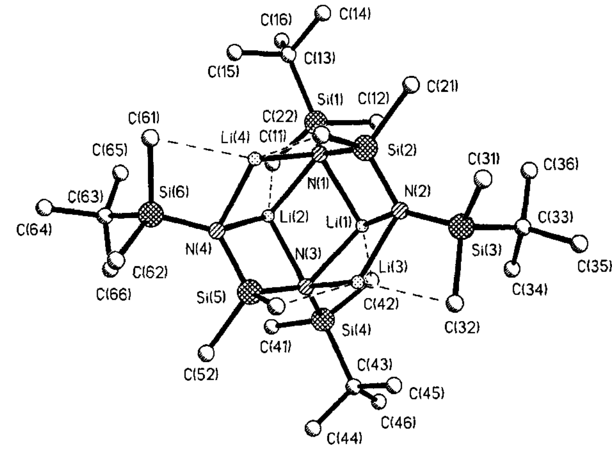


Table 1. Selected bond lengths [pm] and bond angles [°] in compound **4**

Si(1)–N(3)	170.3(3)	N(1)–Si(2)	173.4(3)
Si(2)–N(2)	171.1(3)	C(22)–Li(4)	233.6(8)
N(2)–Si(3)	169.8(3)	C(32)–Li(3)	265.3(8)
Si(4)–N(3)	170.3(3)	N(3)–Si(5)	173.6(3)
Si(5)–N(4)	170.5(3)	C(51)–Li(3)	233.6(8)
N(4)–Si(6)	169.8(3)	C(61)–Li(4)	260.1(8)
Li(2)–Li(4)	235.3(8)		
Li(4)–N(1)–Li(2)	68.8(2)	Si(2)–N(1)–Li(1)	80.9(2)
Li(2)–N(1)–Li(1)	70.5(2)	N(2)–Si(2)–N(1)	107.47(14)
N(4)–Li(2)–N(3)	85,8(2)	N(4)–Li(2)–N(1)	107.6(3)
N(3)–Li(2)–N(1)	103.7(3)	N(2)–Li(3)–N(3)	108.6(3)
N(4)–Li(4)–N(1)	107.8(3)	Si(2)–N(2)–Li(1)	85.4(2)
Li(1)–N(2)–Li(3)	72.2(3)	Li(3)–N(3)–Li(1)	68.6(3)
Si(5)–N(3)–Li(2)	80.7(2)	Li(1)–N(3)–Li(2)	71.0(2)
N(4)–Si(5)–N(3)	107.0(14)	Si(5)–N(4)–Li(2)	85.4(2)
Li(2)–N(4)–Li(4)	72.8(3)	N(2)–Li(1)–N(3)	107.7(3)
N(2)–Li(1)–N(1)	85.2(2)	N(3)–Li(1)–N(1)	103.2(3)

Crystal Structure of 5

In the crystal, molecule **5** exists like **4** as a dimer but here the two halves of the dimer are bridged by two Li atoms [Li(2), Li(2a)]. The Li–N bond lengths are Li(2)–N(2a)=Li(2a)–N(2) 198.8 pm and Li(2)–N(1)=Li(2-a)–N(1c) 199.6 pm. These bridged formally dicoordinated Li atoms project by 3.6 pm out of the plane formed by the four N atoms of the dimer. Also in this case the two Li atoms are saturated by short Li–C contacts with one methyl group each of the *tert*-butyldimethylsilyl ligands [Li(2)–C(31) 287.7 pm]. A comparison with other dilithium derivatives of bis(amino)silanes reveals that this molecule lacks a further saturation by a second Li–C contact. This is attributed to the higher sterical demand of the isobutyl substituents at the central Si atom.

The atom Li(1) and Li(1a) are coordinated by only the two N atoms of one dimer half, leading to the formation of two SiNLiN four-membered ring systems with a sum of the angles of 357.5°. In **5** the N atoms are, in contrast to those in **4**, tetracoordinated. The Si–N bond length values range from 170 to 173.4 pm and are thus in the expected range, the Si–N distances within a SiNLiN four-membered ring being longer than the exocyclic N–Si distances.

A side view of the structure along the plane formed by the six atoms reveals that the two atoms Li(1) or Li(1a) of the dimer halves are *trans*-oriented. The angle of the Li atoms with respect to the plane of six atoms amounts to 89.7°, the angle of the Si atoms to 72.5°. The *trans* position is attributed to the high sterical demand of the two Si(1) and Si(1a) atoms, each bearing two isopropyl groups[16]. The structure of two silyl-substituted compounds **4** and **5** clearly differs from those of the systems bearing organic residues which have been synthesized so far.

Figure 2a. Structure of **5** in the crystal

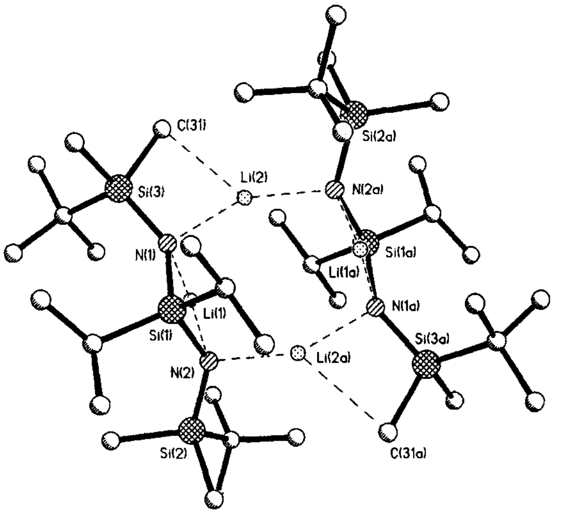


Figure 2b. Side view of structure **5** in the crystal

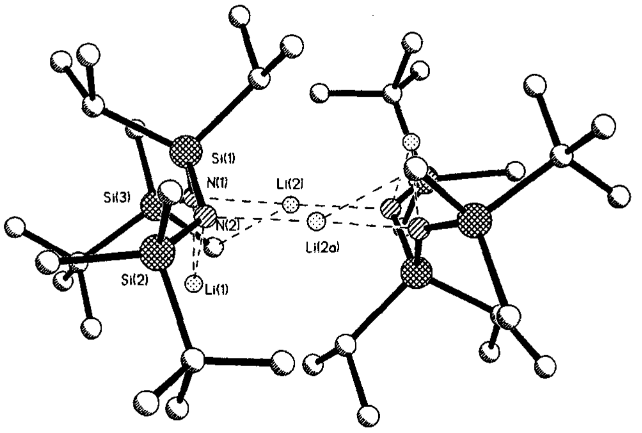
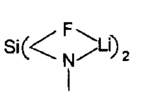


Table 2. Selected bond lengths [pm] and bond angles [°] in compound **5**

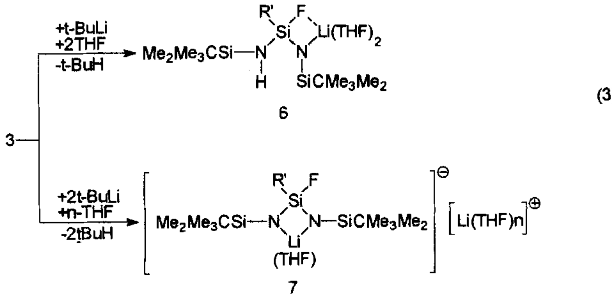
Si(1)–N(1)	172.8(2)	Si(1)–N(2)	173.4(4)
Si(2)–N(2)	170.6(2)	Si(3)–N(1)	170.0(2)
N(1)–Li(1)	198.2(5)	N(1)–Li(2)	199.6(5)
N(2)–Li(2a)	198.8(5)	N(2)–Li(1)	201.0(5)
Li(2)–C(31)	278.7	Li(2a)–C(31a)	278.7
Li(2)–N(1)	198.8		
N(1)–Si(1)–N(2)	104.18(10)	Si(3)–N(1)–Si(1)	141.09(13)
Si(3)–N(1)–Li(1)	115.7(2)	Si(1)–N(1)–Li(1)	84.0(2)
Si(3)–N(1)–Li(2)	100.9(2)	Si(1)–N(1)–Li(2)	110.6(2)
Li(1)–N(1)–Li(2)	95.6(2)	Si(2)–N(2)–Si(1)	133.86(13)
Si(2)–N(2)–Li(2a)	109.2(2)	Si(1)–N(2)–Li(2a)	110.6(2)
Si(2)–N(2)–Li(1)	110.3(2)	Si(1)–N(2)–Li(1)	83.00(14)
N(1)–Li(1)–N(2)	86.3(2)	N(2a)–Li(2)–N(1)	154.3(3)
N(1)–Li(2)–C(31)	73.4		

Mono- and Dilithium Derivative of 3

As already mentioned at the beginning of this paper spirocyclic structures occur if the central Si atom bears two F atoms[10,12].



The presence of an organic residue and a Cl atom at the central Si atom gives rise to elimination of LiCl which formation of monomeric silaamidides[13,14]. In contrast, thermal LiF elimination from analogous organyl-SiF compounds affords dimeric silaamides[15]. Since mono- and dilithium compounds of bis(silylamino)fluoro-organylsilanes of type **3** have previously not been studied we also synthesized and characterized NMR spectroscopically the mono- and dilithium derivatives **6** and **7** of **3**.

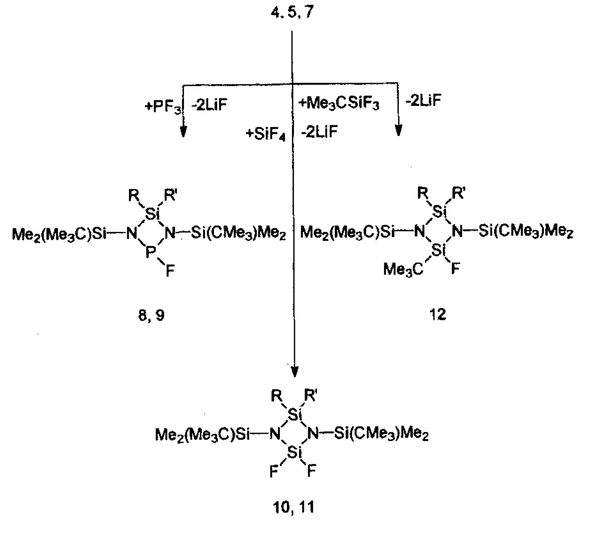


(3)

While the monolithium salt contains an SiFNLi four-membered ring the structure of the dilithium salt is characterized by an $(SiN_2Li)^-$ anion with a Li^+ counterion coordinated by THF[10,15].

Synthesis of Inorganic Four-membered Ring Systems

In spite of their different structures dilithium compounds **4**, **5** and **7** react with PF_3 and fluorosilanes (SiF_4, Me_3CSiF_3) to afford four-membered ring compounds **8**–**12**.



(4)

	8, 10	9	11, 12
R	Me	CHMe₂	F
R'	Me	CHMe₂	CMe₃

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Experimental

All experiments were carried out with the exclusion of moisture under dry N_2 or Ar. – MS: CH-5 spectrometer, Varian. – NMR: 25% solutions in $CDCl_3$; C_6D_6; TMS, C_6F_6; int.: Brucker-WP-80 or AM-250 NMR spectrometer. ^{31}P-NMR: 25% solutions in C_6D_6, H_3PO_4, ext: Bruker-AM-250 NMR spectrometer. The purity of the isolated compounds was determined by NMR spectroscopy.

Bis[(tert-butyldimethylsilyl)amino]dimethylsilane (**1**): To a solution of 26.26 g (0.2 mol) of $Me_2(Me_3C)SiNH_2$ in 75 ml of *n*-hexane was added 0.2 mol of *n*-BuLi (23% in *n*-hexane) and the mixture was heated at reflux for 2 h. A solution of Me_2SiCl_2 in 100 ml of *n*-hexane was cooled to 0°C and the mixture containing $Me_2(Me_3C)SiNHLi$ was added dropwise to this solution. After removal of the cooling the mixture was stirred for 2 h with slow warming, then heated at reflux for 5 h. The raw product was separated from LiCl at 0.01 mbar and purified by distillation. Yield: 25.76 g (81%), b.p. 79°C/0.01 mbar.

Bis[(tert-butyldimethylsilyl)amino]diisopropylsilane (**2**): To a solution of 15.76 g (0.12 mol) of $Me_2(Me_3C)SiNH_2$ in 80 ml of *n*-hexane was added 0.12 mol of *n*-BuLi (23% in *n*-hexane) and the mixture was heated at reflux for 1.5 h. After the mixture had been cooled to 0°C 9.14 g (0.06 mol) of $(Me_2CH)_2SiF_2$ was added dropwise. The solvent was removed by distillation and the residue was heated for 20 h. The product was condensed at 0.01 mbar into a cooling trap and purified by distillation. Yield: 19.57 g (87%), b.p. 111°C/0.01 mbar.

tert-Butyl-bis[(tert-butyldimethylsilyl)amino]fluorosilane (**3**): To a solution of 65.65 g (0.5 mol) of $Me_2(Me_3C)SiNH_2$ in 120 ml of *n*-hexane was added 0.5 mol of *n*-BuLi (23%) in *n*-hexane and the mixture was heated at reflux for 2 h. To a solution of 35.50 g (0.25 mol) of Me_3CSiF_3 in 50 ml of *n*-hexane/25 ml of THF cooled to 0°C was added the cooled lithiated amine. The reaction mixture was subsequently heated at reflux for 3 h and then the solvent was removed by distillation. The reaction products were separated from LiF and purified by fractional distillation over a 30-cm Vigreux column. Yield: 31.88 g (35%), b.p. 81°C/0.01 mbar.

Bis[bis(tert-butyldimethylsilyl-N-lithioamide)dimethylsilane] (**4**) *and Bis[bis(tert-butyldimethylsilyl-N-lithioamide)diisopropylsilane]* (**5**): To a solution of 3.19 g (0.01 mol) of **1** and 3.75 g (0.01 mol) of **2** respectively in 20 ml each of *n*-hexane was added 0.02 mol of *n*-BuLi (23% in *n*-hexane) and the corresponding mixture was refluxed for 1 h. The dilithium derivatives formed were dissolved in boiling THF. Compound **4** crystallized after 1 day at 2°C, compound **5** after 10 h at room temp. Yield: 2.84 g (86%) of **4**, 3.52 g (91%) of **5**.

N-Lithio-tert-butyl-bis[(tert-butyldimethylsilyl)amino]fluorosilane–bis(tetrahydrofuranate) (**6**) *and Lithium 2-tert-Butyl-1,3-bis(tert-butyldimethylsilyl)-2-fluoro-4-tetrahydrofuran-1,3-aza-2-sila-4-lithiocyclobutanide–tetrahydrofuranate* (**7**): Into a 100-ml Schlenk flask was placed 3.64 g (0.01 mol) of each compound in 10 ml of *n*-hexane and the solution was cooled to 0°C. Under argon in the case of **6** 0.01 mol of *t*BuLi (15% in *n*-hexane) and in the case of **7** 0.02 mol of *t*BuLi (15% in *n*-hexane) was added. The resulting mixture was stirred at 0°C for 0.5 h and slowly warmed to 20°C. After 1 h **6** and **7** precipitated as amorphous solids to which THF was added until they had dissolved; **6** reprecipitated as an amorphous product. Yield: 4.12 g (80%) of **6**; 4.42 g (60%) of **7** containing THF.

1,3-Bis(tert-butyldimethylsilyl)-2-fluoro-4,4-dimethyl-1,3-diaza-2-phospha-4-silacyclobutane (**8**) *and 1,3-Bis(tert-butyldimethyl)2-fluoro-4,4-diisopropyl-1,3-diaza-2-phospha-4-silacyclobutane* (**9**): To 3.31 g (0.01 mol) of **4** and 3.87 g (0.01 mol) of **5** respectively, cooled to −78°C, was added 0.88 g (0.01 mol) of PF$_3$ each. The reaction mixture was thawed within 48 h, then heated at reflux for 3 h and separated from LiF. Compounds **8** and **9** were purified by fractional distillation at 0.01 mbar. Yield: 1.80 g (49%) of **8**, 1.56 g (37%) of **9**.

1,3-Bis(tert-butyldimethylsilyl)-2,2-dimethyl-4,4-difluorocyclodisilazane (**10**): To 3.31 g (0.01 mol) of **4** was added at −78°C 1.04 (0.01 mol) of SiF$_4$. The mixture was thawed within 14 h, the raw product separated from LiF and purified by fractional distillation at 0.01 mbar. Yield: 2.72 g (71%) of **10**.

2-tert-Butyl-1,3-bis(tert-butyldimethylsilyl)-2,4,4-trifluorocyclodisilazane (**11**) *and 2,4-Di-tert-butyl-1,3-bis(tert-butyldimethylsilyl)-2,4-difluorocyclodisilazane* (**12**): Two separate solutions of 7.37 g each of **7** in 30 ml of *n*-hexane were prepared. One was cooled to −78°C (used for the synthesis of **11**), the other one to 0°C (used for the synthesis of **12**). For the preparation of **11** 1.04 g (0.01 mol) of SiF$_4$ was passed into the corresponding hexane solution and the mixture was stirred at −78°C for 0.5 h. For the preparation of **12** 1.42 g (0.01 mol) of Me$_3$CSiF$_3$ was dissolved in 10 ml of *n*-hexane and this solution was dropped to the corresponding previously prepared hexane solution. The reaction mixtures (for **11** and **12**) were refluxed for 2.5 h, the raw products were separated from LiF and purified by fractional distillation. Yield: 3.00 g (70%) of **11**, 3.73 g (80%) of **12**.

Crystal Data of **4**[23]: Space group $P2_1/n$, monoclinic, a = 1341.2(10), b = 2026.6(2), c = 1630.2(2) pm, α = 90, β = 101.71(1), γ = 90°, V = 4.3388(8) nm^3, Z = 4, $\rho_{\mathrm{calc.}}$ = 1.012 Mg/m^3, crystal size 0.7 × 0.5 × 0.4 nm, μ(Mo-K_α) = 0.213 mm^{-1}, 10336 reflections between $2\Theta < 45°$ measured, of which 5584 independent were used for refinement on R^2. Refinement with 379 parameters to $wR2$ = 0.1606 (all data) and $R1$ = 0.0565 [for $F > 4\sigma(F)$]. Maximal and minimal residual electron density: 476 and −437 e nm^{-3} respectively. Selected bond lengths and angles are compiled in Table 1.

Crystal Data of **5**[23]: Space group $Pbca$, orthorhombic, a = 1021.1(2), b = 2142.5(4), c = 2235.9(5) pm, $\alpha = \beta = \gamma$ = 90°, V = 4.892(2) nm^3, Z = 4, $\rho_{\mathrm{calc.}}$ = 1.050 Mg/m^3, crystal size 1 × 0.7 × 0.4 mm, μ(Mo-K_α) = 0.198 mm^{-1}, 7463 reflections between $2\Theta <$ 45° measured, of which 3182 independent were used for refinement of R^2. Refinement with 240 parameters to $wR2$ = 0.1207 (all data) and $R1$ = 0.0413 [for $F > 4\sigma(F)$]. Maximal and minimal residual density: 313 and −399 e nm^{-3} respectively. Selected bond lengths and angles are compiled in Table 2.

1: B.p. 79°C/0.01 mbar. − MS (EI), *m/z* (%): 303 (6) [M − CH$_3$]$^+$, 261 (100) [M − CMe$_3$]$^+$. − NMR (CDCl$_3$/TMS): ^{1}H: δ = 0.06 (s, SiCH$_3$, 12H), 0.12 (s, SiCH$_3$, 6H), 0.89 (s, SiCMe$_3$, 18H). − ^{13}C: δ = −2.45 (s, CH$_3$), 4.21 (s, CH$_3$), 17.99 (s, *C*C$_3$), 26.31 (s, C*C*$_3$). − ^{29}Si: δ = −6.15 (s, SiMe$_2$), 6.78 (s, SiCMe$_3$).

2: B.p. 111°C/0.01 mbar. − MS (EI), *m/z* (%): 359 (3) [M − CH$_3$]$^+$, 331 (100) [M − CHMe$_2$]$^+$, NMR (CDCl$_3$/TMS): ^{1}H: δ = −0.12 (s, NH, 2H), 0.07 (s, SiCH$_3$, 12H), 0.84 (sept., $^3J_{\mathrm{HH}}$ = 7.0 Hz, SiCHMe$_2$, 2H), 0.88 (s, SiCMe$_3$, 18H), 0.97 (d, $^3J_{\mathrm{HH}}$ = 7.0 Hz, SiCHMe$_2$, 12H). − ^{13}C: δ = −2.25 (s, CH$_3$), 14.41 (s, CHC$_2$), 17.81 (s, CHC$_2$), 17.93 (s, *C*C$_3$), 26.20 (s, C*C*$_3$). − ^{29}Si: δ = 0.50 [s, Si(CHMe$_2$)$_2$], 6.84 (s, SiCMe$_3$).

3: B.p. 81°C/0.01 mbar. − MS (EI), *m/z* (%): 349 (5) [M − Me]$^+$, 307 (100) [M − CMe$_3$]$^+$. − NMR (CH$_2$Cl$_2$/C$_6$D$_6$): ^{1}H: δ = −0.02 (s, SiCH$_3$, 12H), 0.78 (s, SiCMe$_3$, 18H), 0.84 (d, $^3J_{\mathrm{HF}}$ = 0.9 Hz, SiCMe$_3$, 9H). − ^{13}C: δ = −2.68 (d, $^4J_{\mathrm{CF}}$ = 1.6 Hz, CH$_3$), −2.38 (d, $^4J_{\mathrm{CF}}$ = 1.2 Hz, CH$_3$), 18.00 (d, $^4J_{\mathrm{CF}}$ = 0.3 Hz, *C*C$_3$), 18.72 (d, $^2J_{\mathrm{CF}}$ = 22.4 Hz, *C*C$_3$), 26.32 (s, C*C*$_3$), 26.84 (s, C*C*$_3$). − ^{19}F: δ = 20.62 (t, $^3J_{\mathrm{HF}}$ = 7.5 Hz). − ^{29}Si: δ = −19.08 (d, $^1J_{\mathrm{SiF}}$ = 274.4 Hz, SiCMe$_3$F), 9.02 (s, SiCMe$_3$).

4: M.p. 226°C. − NMR (C$_6$D$_6$/TMS): ^{1}H: δ = 0.10 (s, SiCH$_3$, 24H), 0.29 (s, SiCH$_3$, 12H), 0.99 (s, SiCH$_3$, 36H). − ^{13}C: δ = 0.29 (s, CH$_3$), 8.38 (s, CH$_3$), 19.63 (s, *C*C$_3$), 28.33 (s, C*C*$_3$). − ^{7}Li: δ = 1.66 (s, Li), 2.24 (s, Li). − ^{29}Si: δ = −21.67 (s, SiMe$_2$), −6.44 (s, SiCMe$_3$).

5: M.p. 245°C. NMR (C$_6$D$_6$/TMS/THF): ^{1}H: δ = −0.21 (s, SiCH$_3$, 24H), 0.81 (s, SiCMe$_3$, 36H), 0.96 (d, $^3J_{\mathrm{HH}}$ = 7.3 Hz, SiCHMe$_2$, 24H). − ^{13}C: δ = 1.70 (s, CH$_3$), 17.75 (s, *C*C$_2$), 19.60 (s, C*C*$_2$), 20.34 (s, *C*C$_3$), 28.59 (s, C*C*$_3$). − ^{7}Li: δ = 0.68 (s, Li). − ^{29}Si: δ = −14.42 (s, SiCHMe$_2$), 4.75 (s, SiCMe$_3$).

6: NMR (C$_6$D$_6$): ^{19}F: δ = 22.90 (d, $^3J_{\mathrm{HF}}$ = 6.8 Hz). − ^{29}Si: δ = −24.75 (d, $^1J_{\mathrm{SiF}}$ = 242.2 Hz, SiCMe$_3$F), −12.69 (d, $^3J_{\mathrm{SiF}}$ = 13.9 Hz, SiNLi), 5.43 (d, $^3J_{\mathrm{SiF}}$ = 0.9 Hz, SiNH).

7: NMR (C$_6$D$_6$): ^{13}C: δ = 2.37 (s, CH$_3$), 19.77 (s, *C*C$_3$), 20.87 (d, $^2J_{\mathrm{CF}}$ = 28.4 Hz, *C*C$_3$), 25.49 (OC$_2$*C*$_2$), 27.94 (C*C*$_3$), 28.43 (C*C*$_3$), 68.28 (O*C*$_2$C$_2$). − ^{7}Li: δ = 0.07 (LiN$_2$), 0.74 [Li(THF)$_4$]. − ^{19}F: δ = 31.24. − ^{29}Si: δ = −43.30 (d, $^1J_{\mathrm{SiF}}$ = 242.4 Hz, SiCMe$_3$F), −12.64 (d, $^3J_{\mathrm{SiF}}$ = 13.7 Hz, SiCMe$_3$).

8: B.p. 118°C/0.01 mbar. − MS (EI), *m/z* (%): 336 (15) [M]$^+$, 351 (5) [M − CH$_3$]$^+$, 309 (100) [M − CMe$_3$]$^+$. − NMR (C$_6$D$_6$): ^{1}H: δ = 0.06 (s, SiCH$_3$, 12H), 0.32 (s, SiCH$_3$, 3H), 0.39 (s, SiCH$_3$, 3H), 0.93 (s, SiCMe$_3$, 18H). − ^{13}C: δ = −3.59 8d, $^3J_{\mathrm{CP}}$ = 5.8 Hz, CH$_3$), −3.19 (d, $^3J_{\mathrm{CP}}$ = 5.0 Hz, CH$_3$), 5.72 (d, $^3J_{\mathrm{CP}}$ = 4.8 Hz, CH$_3$), 7.68 (dd, $^3J_{\mathrm{CP}}$ = 4.0 Hz, $^4J_{\mathrm{CF}}$ = 2.1 Hz, CH$_3$), 18.24 (d, $^3J_{\mathrm{CP}}$ = 1.9 Hz, *C*C$_3$), 26.39 (dd, $^4J_{\mathrm{CP}}$ = 2.5 Hz, $^5J_{\mathrm{CF}}$ = 0.5 Hz, C*C*$_3$). − ^{19}F: δ = 138.60 (d, $^1J_{\mathrm{FP}}$ = 1133.0 Hz). − ^{31}P: δ = 179.00 (d, $^1J_{\mathrm{PF}}$ = 1133.0 Hz). − ^{29}Si: δ = 6.91 (dd, $^2J_{\mathrm{SiP}}$ = 9.2 Hz, $^3J_{\mathrm{SiF}}$ = 2.0 Hz, SiCMe$_3$Me$_2$), 29.80 (dd, $^2J_{\mathrm{SiP}}$ = 8.5 Hz, $^3J_{\mathrm{SiF}}$ = 5.6 Hz, SiMe$_2$).

9: B.p. 147°C/0.01 mbar. − MS (EI), *m/z* (%): 422 (16) [M]$^+$, 365 (100) [M − CMe$_3$]$^+$. − NMR (C$_6$D$_6$): ^{13}C: δ = −2.97 (d, $^3J_{\mathrm{CP}}$ = 5.3 Hz, CH$_3$), −2.42 (d, $^3J_{\mathrm{CP}}$ = 3.6 Hz, CH$_3$), 14.47 (d, $^3J_{\mathrm{CP}}$ = 4.8 Hz, *C*HC$_2$), 16.40 (dd, $^3J_{\mathrm{CP}}$ = 5.7 Hz, $^4J_{\mathrm{CF}}$ = 0.6 Hz, CH*C*$_2$), 16.60 (d, $^4J_{\mathrm{CP}}$ = 2.5 Hz, CH$_2$*C*$_2$), 18.72 (d, $^3J_{\mathrm{CP}}$ = 0.6 Hz, *C*C$_3$), 26.60 (dd, $^4J_{\mathrm{CP}}$ = 4.1 Hz, $^5J_{\mathrm{CF}}$ = 0.6 Hz, C*C*$_3$). − ^{19}F: δ = 140.22 (d, $^1J_{\mathrm{FP}}$ = 1143.0 Hz). − ^{31}P: δ = 180.70 (d, $^1J_{\mathrm{PF}}$ = 1143.0 Hz). − ^{29}Si: δ = 6.23 (dd, $^2J_{\mathrm{SiP}}$ = 9.0 Hz, $^3J_{\mathrm{SiF}}$ = 1.9 Hz, SiCMe$_3$), 35.04 [dd, $^2J_{\mathrm{SiP}}$ = 0.1 Hz, $^3J_{\mathrm{SiF}}$ = 0.1 Hz, Si(CHMe$_2$)$_2$].

10: M.p. 90°C/0.01 mbar. − MS (EI), *m/z* (%): 382 (3) [M]$^+$, 367 (3) [M − CH$_3$]$^+$, 325 (58) [M − CMe$_3$]$^+$. MS (FI), *m/z* (%): 382 (100) [M]$^+$. − NMR (CDCl$_3$/TMS): ^{1}H: δ = 0.06 (s, SiCH$_3$, 12H), 0.38 (s, SiCH$_3$, 6H), 0.89 (s, SiCMe$_3$, 18H). − ^{13}C: δ = −2.96 (s, CH$_3$), 4.00 (t, $^3J_{\mathrm{CF}}$ = 2.3 Hz, CH$_3$), 17.86 (s, *C*C$_3$), 25.93 (t, $^5J_{\mathrm{CF}}$ = 0.7 Hz, C*C*$_3$). − ^{19}F: δ = 33.95. − ^{29}Si: δ = −77.07 (t, $^1J_{\mathrm{SiF}}$ = 259.8 Hz, SiF$_2$), 0.64 (s, SiMe$_2$), 5.33 (t, $^3J_{\mathrm{SiF}}$ = 1.4 Hz, SiCMe$_3$).

11: B.p. 82°C/0.01 mbar. − MS (EI), *m/z* (%): 371 (44) [M − CMe$_3$]$^+$. − NMR (C$_6$D$_6$): ^{1}H: δ = 0.10 (s, SiCH$_3$, 6H), 0.14 (s, SiCH$_3$, 6H), 0.93 (s, SiCHMe$_3$, 18H), 1.06 (d, $^4J_{\mathrm{HF}}$ = 1.0 Hz, SiCMe$_3$, 9H). − ^{13}C: δ = −2.86 (dt, $^4J_{\mathrm{CF}}$ = 0.5 Hz, CH$_3$). − 1.42 (d, $^4J_{\mathrm{CF}}$ = 0.9 Hz, CH$_3$), 18.28 (t, $^4J_{\mathrm{CF}}$ = 0.4 Hz, *C*C$_3$), 18.64 (dd, $^2J_{\mathrm{CF}}$ = 22.8 Hz, $^4J_{\mathrm{CF}}$ = 4.1 Hz, *C*C$_3$), 25.99 (dt, $^5J_{\mathrm{CF}}$ = 1.0 Hz, $^5J_{\mathrm{CF}}$ = 0.5 Hz, C*C*$_3$), 26.36 (d, $^3J_{\mathrm{CF}}$ = 0.2 Hz, C*C*$_3$). − ^{19}F: δ = 25.90 (dd, $^2J_{\mathrm{FF}}$ = 88.4 Hz, $^4J_{\mathrm{FF}}$ = 8.5 Hz), 29.50 (dd, $^4J_{\mathrm{FF}}$ = 8.5 Hz, $^4J_{\mathrm{FF}}$ = 1.7 Hz), 34.96 (dd, $^2J_{\mathrm{FF}}$ = 88.4 Hz, $^4J_{\mathrm{FF}}$ = 1.7 Hz). − ^{29}Si: δ = −72.00 (dd, $^1J_{\mathrm{SiF}}$ = 262.2 Hz, $^1J_{\mathrm{SiF}}$ = 255.0 Hz, SiF$_2$), −29.30 (dd, $^1J_{\mathrm{SiF}}$ = 342.2 Hz, $^3J_{\mathrm{SiF}}$ = 6.4 Hz, SiCMe$_3$F), 6.89 (t, $^3J_{\mathrm{SiF}}$ = 1.3 Hz, SiCMe$_3$).

12: B.p. 124°C/0.01 mbar. − MS (EI), *m/z* (%): 409 (100) [M − CMe$_3$]$^+$. − NMR (C$_6$D$_6$): ^{1}H: δ = 0.18 (d, $^5J_{\mathrm{HF}}$ = 0.8 Hz, SiCH$_3$, 12H), 1.00 (SiCMe$_3$, 18H), 1.10 (d, $^{4}J_{\mathrm{HF}} = 1.4$ Hz, SiCMe$_3$, 18H). – ^{13}C: $\delta = -1.35$ (t, $^{4}J_{\mathrm{CF}} = 0.8$ Hz, CH$_3$), 19.02 (s, *C*C$_3$), 19.45 (dd, $^{2}J_{\mathrm{CF}} = 23.9$ Hz, $^{4}J_{\mathrm{CF}} = 3.7$ Hz, *C*C$_3$), 26.60 (t, $^{5}J_{\mathrm{CF}} = 1.7$ Hz, C*C*$_3$), 28.70 (s, C*C*$_3$). – ^{19}F: $\delta = 48.24$. – ^{29}Si: $\delta = -26.20$ (dd, $^{1}J_{\mathrm{SiF}} = 344.4$ Hz, $^{3}J_{\mathrm{SiF}} = 3.2$ Hz, SiCMe$_3$F), 4.70 (t, $^{3}J_{\mathrm{SiF}} = 1.3$ Hz, SiCMe$_3$Me$_2$).

☆ Dedicated to Professor *Gerhard Fritz* on the occasion of his 75th birthday.

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