

The First Stable β -Fluorosilylanion

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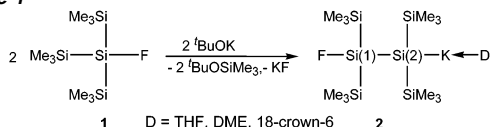
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The generation of molecules with seemingly incompatible functional groups such as functional carbanions can be considered as a major achievement of synthetic chemistry.² Recently, first examples of defined functional silylanions have also been prepared.^{3,4} Tamao and Kawachi have explored the chemistry of α -alkoxysilyllithium compounds which exhibit silylenoid character because they can serve both as nucleophiles as well as electrophiles.^{3a} This explains the condensation process of the silylenoid compounds to β -alkoxydisilanyl lithium species. It is very likely that similar compounds, where the alkoxy group is replaced by a halide, play a key role in the synthesis of polysilanes by Wurtz-type coupling of diorganodihalosilanes.⁵ A first example of a stable α -halosilylanion compound⁴ and some intermediate β -halosilylanions⁶ have been described recently by Wiberg.

Our studies on oligosilylanions have led to the development of a method for the generation of silyl potassium compounds by reaction of oligosilanes with potassium alkoxides.⁷ In due course, we have investigated this reaction for a number of functionalized silanes. Tris(trimethylsilyl)silyl halides were among the compounds studied. While the reactions of the respective chloro and bromo compounds with potassium *tert*-butoxide lead to complex product distributions, the conversion of the fluoride⁸ (**1**) in ethereal solvents such as THF or DME leads to the formation of a single product.⁹ ²⁹Si and ¹⁹F NMR spectroscopic investigations indicated the structures of solvent adducts of a dimerized product containing both a potassium and a fluorine atom (**2**) (Scheme 1).

Scheme 1



Structural proof for **2** was obtained by means of multinuclear NMR spectroscopy (Figures 1 and 2). In the ¹⁹F NMR spectrum, coupling to four different silicon groups can be observed. The ²⁹Si NMR spectrum exhibits four doublets due to ¹⁹F–²⁹Si coupling. Taking into account the coupling pattern and the ²⁹Si NMR shift values, we assigned structure **2**. While the ¹J coupling constant of 308 Hz is not very unusual, the value of the ²J coupling to the anionic silicon atom of about 78 Hz is remarkably high as compared to the other ²J coupling to the trimethylsilyl groups (27.5 Hz). This can be explained by the use of Bent's rule.¹⁰ The strongly electronegative fluorine substituent on Si(1) should cause a higher p-character of the bond between Si(1) and F. This effect is amplified by the electropositive character of the negatively charged silicon atom. In summary, a very high s-character of the bond between the two central silicon atoms, which is a prerequisite for a high coupling constant, can be assumed. Comparison with compound **3**, where potassium is exchanged for a trimethylsilyl group, seems to indicate that the influence of the negatively charged silicon atom is more important, because we observe a much smaller ²J coupling along the central silicon silicon bond.

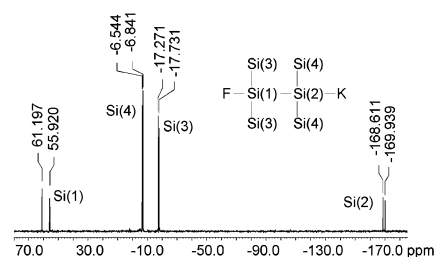


Figure 1. ²⁹Si NMR spectrum of **2**.

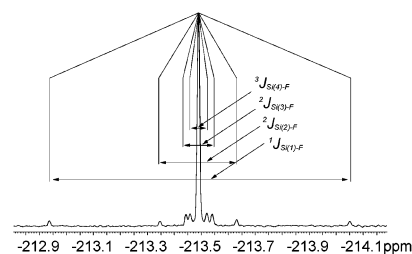


Figure 2. ¹⁹F NMR spectrum of **2**.

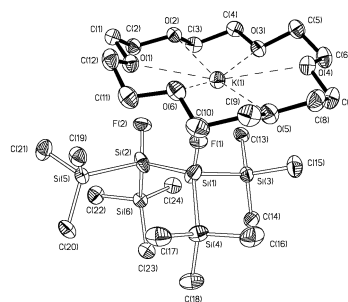
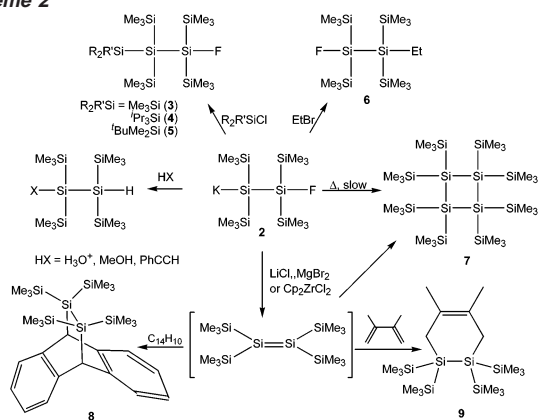


Figure 3. Thermal ellipsoid plot of **2** drawn at the 50% probability level.

A crown ether adduct of **2** was studied by X-ray diffraction analysis.¹¹ The result (Figure 3) confirms the expected hexasilane framework. However, the molecule is disordered in a way, that we find the fluorine atom with occupation factors of 0.5 bonding to the two central silicon atoms Si(1) and Si(2).¹² This implies that the steric demand of the two halves of the molecule must be approximately equal. It also seems to indicate that, besides the interaction between the anionic silicon and the potassium atom, there is also some kind of interaction between the fluorine and the potassium atom. This is at least true for the situation in the crystal. The bond lengths found for **2** exhibit some rather unusual features. First, the central silicon silicon bond is unusually short: (Si(1)–Si(2) = 2.293(2) Å). This must be attributed to the presence of the fluoride. Comparison with the recently prepared (Me₃Si)₅Si₂K (Si(1)–Si(2) = 2.3745(11) Å) and Ph(Me₃Si)₂SiSi(SiMe₃)₂K (Si(1)–Si(2) = 2.3677(17) Å)^{7b} reveals a shortening of approximately 0.07 Å. The length of the silicon fluoride bond is even more extreme. The values of 1.437(4) and 1.411(4) Å are smaller than in any entry of the Cambridge Crystallographic Database. The

Scheme 2



fact that one-half of the fluorine atoms are located between the formally negatively charged silicon atom and the potassium atom in the crown ether explains the elongated distance between the potassium atom and the anionic silicon of about 3.94 Å.

Compound **2** is formed in a very fast reaction. As the first step, alkoxide attack at **1** is assumed to cause elimination of *tert*-BuOSiMe₃ and formation of the silylenoid (Me₃Si)₂SiKF. We assume that this compound undergoes self-condensation similarly, as described by Tamao for the respective alkoxy compound.^{3a} While **2** could not be derivatized with any protonating agent without subsequent substitution of the fluoro group, reactions with other electrophiles such as chlorosilanes and ethylbromide yielded compounds **3**, **4**, **5**, and **6** in very clean reactions (Scheme 2). Attempts to transmetalate **2** with LiCl, MgBr₂, or Cp₂ZrCl₂ trigger a salt elimination accompanied by the formation of tetrakis-(trimethylsilyl)disilene.^{13,14} Without the presence of trapping agents, the persilylated four-membered ring **7**¹⁴ turns out to be the only isolated product. **2** is stable at room temperature, and even at 80 °C the potassium fluoride elimination is very slow as indicated by the formation of **7**.

That **2** functions as a very convenient disilene precursor can also be shown with various trapping reagents. Reaction with magnesium bromide in the presence of anthracene gives the 4 + 2 cycloaddition product (**8**)^{15,16} which was characterized by X-ray diffraction analysis¹⁷ (Figure 4). An analogous reaction was carried out with 2,3-dimethylbutadiene, which also gives rise to the formation of a cycloaddition product (**9**) (Scheme 2).

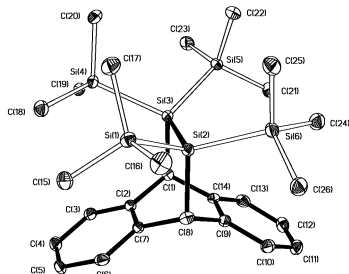


Figure 4. Thermal ellipsoid plot of **8** drawn at the 50% probability level.

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Supporting Information Available: CIF files of the structures of compounds **2** and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Synthesis of the 18-crown-6 adduct of **2**: At room temperature, potassium-*tert*-butoxide (200 mg, 1.78 mmol) and 18-crown-6 (470 mg, 1.78 mmol) are dissolved in a minimum amount of toluene. Upon addition of tris-(trimethylsilyl)silyl fluoride **1** (500 mg, 1.88 mmol), the reaction mixture immediately turns yellow, and within 15 min KF·18-crown-6 precipitates out. After filtration pentane is added. **2** is obtained as yellow crystals (483 mg, 81%) upon cooling to -35 °C. mp: 170 °C (decomp.). NMR data (δ in ppm): ¹H (C₆D₆) 3.37 (s, 24H, CH₂O), 0.71 (s, 18H, (CH₃)₃-Si), 0.56 (s, 18H, (CH₃)₃Si); ¹³C (C₆D₆) 70.50 (CH₂O), 8.11 ((CH₃)₃Si), 1.43 ((CH₃)₃Si); ²⁹Si (C₆D₆) 58.6 (d, Si-F ¹J_{Si-F} = 314 Hz), 6.5 (d, Me₃Si-SiK ³J_{Si-F} = 17.7 Hz), -17.5 (d, Me₃Si-SiF ²J_{Si-F} = 27.4 Hz), -169.3 (d, SiK ²J_{Si-F} = 79.1 Hz), ¹⁹F (C₆D₆) -213.5.
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- (11) Crystallographic data for **2**: C₂₄H₆₀FKO₆Si₆, monoclinic space group *P2*-(1)/*c*, *a* = 11.419(2) Å, *b* = 16.813(3) Å, *c* = 21.128(4) Å, β = 101.13(3)°, *V* = 3979.9(14) Å³, *Z* = 4, ρ_{calcd} = 1.120 Mg/m³, *R*1 = 0.0588, *wR*2 = 0.1440, *GOF* = 1.028 (CCDC 196311).
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- (15) Synthesis of **8**: A solution of **2** (315 mg, 0.47 mmol) in toluene is added to a stirred solution of anthracene (112 mg, 0.940 mmol) and MgBr₂·Et₂O (122 mg, 0.705 mmol) in THF to yield a brownish solution. After 1 h, the reaction mixture is subjected to an aqueous workup followed by removal of the solvent and excess anthracene in a vacuum and recrystallization from acetone to obtain 138 mg (56%) **8** as colorless crystals. mp: 278 °C. NMR data (δ in ppm): ¹H (C₆D₆) 7.05 (m, 4H, Ar), 6.94 (m, 4H, Ar), 4.39 (s, 2H, ArCH), 0.14 (s, 36H, (CH₃)₃Si); ¹³C (C₆D₆) 141.8 (Ar), 125.7 (Ar), 124.9 (Ar), 37.9 (ArCH), 2.4 ((CH₃)₃Si); ²⁹Si (C₆D₆) -11.9 ((CH₃)₃Si), -69.5 (((CH₃)₃Si)₂Si).
- (16) **8** was prepared previously by the thermolysis of (Me₃Si)₃SiOMe in the presence of anthracene: Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *J. Am. Chem. Soc.* **1979**, *101*, 486.
- (17) Crystallographic data for **8**: C₂₆H₄₆Si₆, orthorhombic space group *Pca*2-(1), *a* = 16.624(3) Å, *b* = 10.239(2) Å, *c* = 18.645(4) Å, *V* = 3173.7(11) Å³, *Z* = 4, ρ_{calcd} = 1.103 Mg/m³, *R*1 = 0.0532, *wR*2 = 0.1212, *GOF* = 1.037 (CCDC 201304).

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