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Formation of a Unique Fluorosilene–KF Complex Bearing Bulky Substituents

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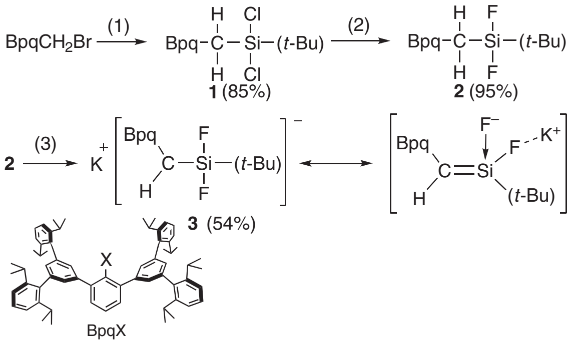
We report here the attempted synthesis of a stable 1-fluoro-2-hydrosilene bearing a Bpq group, which is a bulky aryl group bearing a cavity-shaped framework. We have successfully synthesized an overcrowded benzyldifluorosilane as a precursor. Treatment of the benzyldifluorosilane with 2 equiv of *t*-BuOK in THF afforded the corresponding benzyl anion, the structure of which showed a unique feature as a fluorosilene–KF complex.

Multiply bonded silicon species have been studied over a long period and continue to be of substantial interest.[1] Generally, such species are too reactive to be synthesized and isolated as stable compounds, but they can be isolated as stable species when they are well kinetically stabilized by using bulky substituents. Especially, a disilene (Si=Si) or a silene (Si=C) bearing an Si–X (X = halogen) bond is a fascinating species as a simple-disilene or silene and as a building block of a low-coodinated Si moiety. The first stable disilene bearing Si–Cl bonds, $R_{Si}(Cl)Si{=}Si(Cl)R_{Si}$ [$R_{Si} = SiMe(Si\textit{t}\text{-}Bu_3)_2$], was reported by Wiberg et al., but it was inert toward water, methanol, or hydrogen fluoride probably due to the extremely bulky substituents.[2] On the other hand, we[3] and Tamao's group[4] independently reported the synthesis of stable 1,2-dibromodisilenes bearing two =Si–Br bonds by taking advantage of bulky aryl groups, Bbt[5] and Eind,[6] respectively. In particular, our stable dibromodisilene, Bbt(Br)Si=Si(Br)Bbt, was found to undergo unique substitution reactions with organometallic reagents such as MeMgBr on the Si=Si moiety to give the corresponding disilene, Bbt(R)Si=Si(Br)Bbt (R = Me, Bu, or Ph), showing its potential as a good precursor for several types of disilenes.[3] In the case of a silene, a stable difluoro-substituted silene on the central carbon atom was synthesized by Sekiguchi et al., which was characterized by NMR spectra.[7] However, there is no example of a halogen-substituted silene on a doubly bonded silicon atom. We report here the attempted synthesis of a stable 1-fluorosilene bearing bulky substituents. During the course of our studies of the synthesis of a 1-fluorosilene bearing Bpq and *t*-Bu groups (Scheme 1) on the C and Si atoms, respectively, unique benzyl anion species, $K^+[BpqCHSiF_2(\textit{t}\text{-}Bu)]^-$ (**3**), was obtained as a stable compound. Compound **3** was found to feature a silene–KF complex character.

A primary alkyl bromide with a cavity-shaped framework, $BpqCH_2Br$, was synthesized according to literature procedure.[8] The reaction of $BpqCH_2Br$ with 3 equiv of Mg metal and *t*-$BuSiCl_3$ in THF under reflux afforded $BpqCH_2SiCl_2(\textit{t}\text{-}Bu)$ (**1**) in 85% yield (Scheme 1).



Scheme 1. Reagents and conditions: (1) *t*-$BuSiCl_3$, THF, reflux; (2) $AgBF_4$, toluene, reflux; (3) *t*-BuOK, THF, rt.

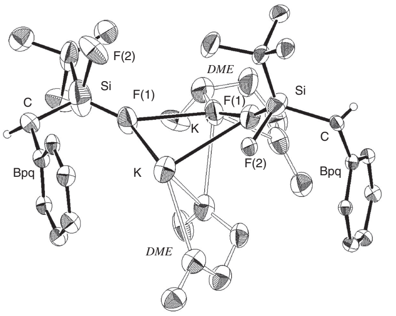


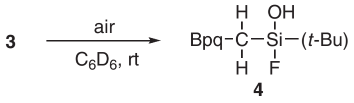
Figure 1. Molecular structure of the core moiety of $[\mathbf{3}_2{\cdot}(dme)_{1.5}]_2$ (30% probability). The hydrogen atoms other than those on the benzyl position, substituents of the Bpq groups, and one of the DME molecule were omitted for clarity.

Dichlorosilane **1** was treated with an excess amount of $AgBF_4$ in toluene under reflux to give $BpqCH_2SiF_2(\textit{t}\text{-}Bu)$ (**2**) in 95% yield. The ^{19}F NMR spectrum of **2** (C_6D_6) showed a signal at −147.0 ppm as a pseudo-triplet ($^{3}J_{FH} = 4.2$ Hz). The ^{29}Si NMR signal of **2** (C_6D_6) was observed at −9.2 ppm as a triplet with $^{1}J_{FSi} = 320$ Hz. When **2** was treated with 2 equiv of *t*-BuOK at rt in THF, it was completely converted to a new product as judged by ^{1}H and ^{19}F NMR spectra. Recrystallization of the crude mixture from DME gave benzyl anion **3** as colorless crystals. X-ray crystallographic analysis of **3** revealed its unique dimeric structure with two potassium cations intermolecularly bridging two fluorine atoms as shown in Figure 1, where the two K^+ ions are coordinated by the two DME molecules. Interestingly, the two Si–F bonds are not identical, where one fluorine atom [F(1)] is coordinated by the potassium atom and the other one [F(2)] is bonded with the silicon atom without any coordination. The Si–F(2) bond [1.805(19) and 1.86(2) Å] is apparently longer than the Si–F(1) bond [1.602(18) and 1.527(15) Å]. Compared with the Si–F bond lengths of compound **2** [1.5851(11) and 1.5868(12) Å], it was suggested that the Si–F(1) bond is fastened and the Si–F(2) bond is weakened by the coordination of K^+ atom toward F(1) atom.[9] In addition, the Si–C(benzyl) bond lengths are 1.832(15) and 1.827(16) Å, which are slightly shorter than those of **2** [1.856(6) Å]. Accordingly, it was suggested that compound **3** should have structural features as a fluorosilene–KF complex rather than a silyl-substituted benzyl anion as in the case of $[Li(12\text{-crown-}4)_2]^+\{FMe_2Si–C(SiMe_3)[SiMe(t\text{-Bu})_2]\}^-$ showing F^--coordinated silene character.[10]

In C_6D_6 solution, the ^{29}Si NMR spectrum of **3** showed a doublet signal at −21.7 ppm with $^1J_{SiF} = 293.5$ Hz, that is, the central Si nuclei was found to be coupled with only one fluorine atom. In the ^{19}F NMR spectrum of **3** in C_6D_6, two independent signals were observed at −134.73 (d, $^3J_{FH} = 11.2$ Hz) and −134.97 (d, $^3J_{FH} = 11.2$ Hz) ppm with negligible F–F *J*-coupling.[11] Thus, one of the Si–F bonds of compound **3** is apparently weakened in solution as in the case of the crystalline state. On the basis of these structural and spectral features of compound **3**, it can be concluded that compound **3** exhibits unique character as a 1-fluorosilene–KF complex, that is, a 1-fluorosilene weakly coordinated by a fluoride anion at the silicon center.

Unfortunately, ^{1}H and ^{13}C NMR spectra of **3** are very broadened and/or complicated probably due to the restricted rotation of the bulky aryl groups of the Bpq group and several types of coupling with ^{19}F and ^{1}H nuclei. Such complexity of the spectra could not be solved by variable temperature NMR spectra (−100 – +60 °C in toluene-d_8 or C_6D_6). In order to assign the ^{13}C NMR chemical shift of the benzyl carbon of **3**, ^{13}C-labeled benzyl anion **3** (**3-^{13}C**) was prepared according to a similar procedure for **3** with using ^{13}C-labeled methyl acetate. In the ^{13}C NMR spectrum of **3-^{13}C** in C_6D_6, a characteristic doublet signal was observed at 18.9 ppm with $^2J_{CF} = 21$ Hz, where the *J*-coupling with only one fluorine nucleus was observed. The Si–C coupling constant, $^1J_{SiC}$, of **3** is 58.2 Hz, which is slightly larger than those of typical Si–C single-bond compounds (ca, 50 Hz)[12] but smaller than that of **2-^{13}C** ($^1J_{SiC} = 68$ Hz).[13] Interestingly, ^{19}F NMR spectrum of **3-^{13}C** showed two double-doublet signals, both of which were found to be coupled with the ^{13}C nucleus to similar extent ($^2J_{CF} = 19.6$ and 19.4 Hz). The ^{19}F NMR spectrum of compound **3-^{13}C** seems to be inconsistent with that of the ^{13}C NMR spectra showing not a triplet signal but a doublet signal coupled with one ^{19}F nucleus. Although we have no clear explanation for the observed NMR spectra at present, it can be thought that the two fluorine atoms (F1 and F2) would rapidly exchange with each other in solution. Indeed, ^{19}F, ^{13}C, and ^{29}Si NMR spectra of **3-^{13}C** at low temperature in toluene (−60 °C to rt) showed dynamic behavior. For example, the two signals of ^{19}F NMR spectra ($\delta_F = -134.41$ and −134.60) were shifted to $\delta_F = -138.41$ and −146.77 at −60 °C.[14] Thus, there would be some dynamic change of the structure in solution, though the geometry around C–Si–F moiety is not clear at present.

Compound **3** was found to be thermally stable at 80 °C in C_6D_6 solution and up to 156.5 °C in the crystalline state (decomp). Interestingly, exposure of **3** toward air and moisture in C_6D_6 solution afforded not the protonated compound **2** but the corresponding fluorohydroxysilane **4**, $BpqCH_2SiF(OH)(t\text{-Bu})$, quantitatively as judged by the NMR spectra, suggesting that one Si–F bond would be weakened to undergo facile hydrolysis (Scheme 2). Thus, compound **3** was found to show the reactivity as a 1-fluorosilene.[15]



Scheme 2. Hydrolysis of **3**.

In summary, we have succeeded in the synthesis of 1-fluorosilene–KF complex **3** as a stable crystalline compound. Its unique structure was characterized by the X-ray crystallographic and spectroscopic analyses, showing F^-coordinating silene character of **3**.[16] Further investigation of the elimination of KF from **3** leading to the formation of the corresponding 1-fluorosilene, Bpq(H)C=SiF(*t*-Bu), and reactivity of **3** are currently in progress.

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14 Unfortunately, the coupling constants of the ^{19}F signals could not be determined due to broadening of the signals. In the ^{29}Si spectrum of **3-^{13}C**, the coupling constants could not be found probably due to the low solubility and broadening under these conditions. The ^{13}C NMR signals were broadened at −60 °C probably due to the slow dynamic process and the coupling with ^{19}F atoms.

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