Synchronized Fluorine Exchange with Ring Inversion of Pentafluoro-1,4-disilacyclohexane Anion

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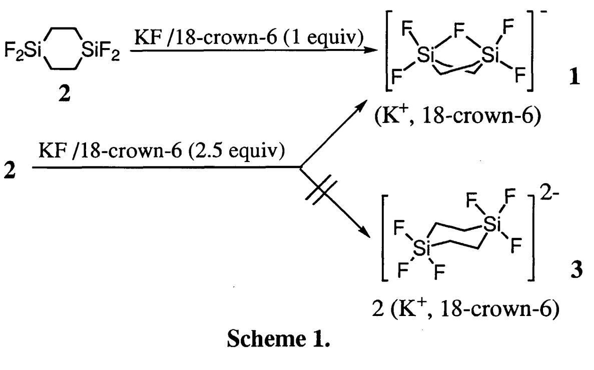
(Received May 2, 1996)

A new intramolecular fluoride-ion donor-acceptor system, pentafluoro-1,4-disilacyclohexane anion showed an unusually rapid intramolecular intersilicon fluoride-ion exchange *synchronized with ring inversion.*

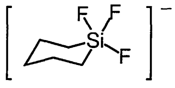
There is rapidly growing interest in the unique behavior of fluoride ions bonded to silicon atoms.[1] Since a tetracoordinate silicon atom and a fluorinated pentacoordinate silicon atom serve as a fluoride-ion acceptor and a fluoride-ion donor, respectively, the fluoride-ion can rapidly exchange and even bridge between two or more silicon atoms. Following the finding of a stable fluorine-bridged complex, $[(AcO)F_3Si\text{-}F\text{-}SiF_3(OAc)]^-$, in solution by Brownstein,[1a] Tamao et al. have first isolated a salt of $[o\text{-}C_6H_4(SiPhF_2)_2F]^-$ (K^+•18-crown-6) having a fluoride-ion cheleted by two silyl groups.[1b,c] Unique merry-go-round degenerate fluorine migration of hexakis(fluorodimethylsilyl)benzene has been reported by Ebata, Inada, and Sakurai.[1d] We have recently found a concerted bimolecular fluoride-ion exchange reaction through a fluorine-bridged cyclophane-like transition state in an intramolecular fluoride-ion donor-acceptor system such as [*p*- and *m*-(difluorophenylsilyl)]trifluorophenylsilicates.[1e] We wish herein to report on the synthesis, structure, and dynamic behavior of pentafluoro-1,4-disilacyclohexane anion (**1**), which shows an unusually rapid intramolecular intersilicon fluoride-ion exchange *synchronized with ring inversion.* After completion of our present work, we were aware of a closely related study of heptafluoro-1,3,5-trisilacyclohexane anion, which exhibits a similar intramolecular fluoride-ion exchange in solution and in the solid state.[1f]

A potassium•18-crown-6 salt of **1** was prepared by a reaction of **2**[2] with KF (1 equiv) in the presence of 18-crown-6 (1 equiv) in toluene (Scheme 1).[3] Recrystallization from a 1:1 mixture of THF/Et_2O at -20 °C afforded **1** as colorless crystals in 61% yield.[4] Interestingly, the hexafluoro-1,4-disilacyclohexane dianion **3** was not produced even when **2** was treated with large excess KF and 18-crown-6 in toluene (Scheme 1), indicating that only one fluoride ion can be incorporated in **2**.



Scheme 1.

The ^1H NMR spectrum of **1** in acetone-d_6 shows a singlet due to ring methylene protons over the temperature range between 183 and 293 K. The ^{29}Si NMR signal of **1** appears at δ -39.2 as a broad singlet in acetone-d_6 in the above temperature range. The chemical shift is intermediate between those of **2** (δ -2.0) and a related pentacoordinate silicon compound, trifluoro-1-silacyclohexane anion **4** (δ -77.0),[5b] suggesting that the two silicons of **1** are equivalent and their coordination character is in the middle between tetra- and pentacoordinate silicons.[6] The ^{19}F NMR spectrum of **1** in acetone-d_6 shows a sharp singlet at δ 119.4 in the temperature range between 183 – 293 K. In THF-d_6, the signal is kept to be a sharp singlet over the 163 – 293 K temperature range. The apparent equivalence of the five fluorine atoms is indicative of the very rapid intersilicon fluoride-ion exchange reaction of **1** even at 168 K. The activation free energy ($\Delta G^{\ddagger}$) for the exchange is estimated to be lower than 25 kJ/mol at 168 K, on the basis of the chemical shift difference between fluorines on the pentacoordinate (δ –140 for an equatorial fluorine of the trigonal bipyramidal structure) and the bridged silicons (δ –70) by 282.4 MHz ^{19}F NMR spectroscopy.[1c]



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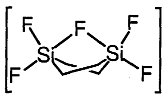
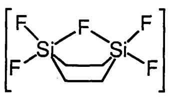
In order to elucidate the structure of **1**, we have carried out ab initio MO calculations at the Hartree-Fock level using 3-21G* basis set.[7] Three different conformations, a twist-boat (**1a**), a boat (**1b**) and a chair (**1c**) conformations, were found to be minima. The optimized structure of **1a** is shown in Figure 1 with the selected bond lengths and angles. The geometry around the pentacoordinate silicon atoms of **1a** is distorted trigonal bipyramidal (TBP) with the bridging and non-bridging fluorines at the apical positions. There is symmetrical fluorine bridging for **1a** with the same distance of Si1–F5 to Si2–F5 (1.879 Å), while $[o\text{-}C_6H_4(SiPhF_2)_2F]^-$ has an unsymmetrical fluorine bridge (two Si-F distances are 1.898 and 2.065 Å) in the solid-state.[1b,c] Similar symmetrical fluorine bridging is found in **1b**. The optimized chair conformation **1c** contains a pentacoordinate silicon atom and a tetracoordinate silicon atom, where no fluorine-bridge exists. The geometry around the pentacoordinate silicon is TBP with a fluorine atom and a ring carbon atom at the apical positions. Among these three structures, the twist-boat **1a** is the lowest energy conformation; **1b** and **1c** are less stable than **1a** by 4.56 and 13.27 kJ/mol at the 6-31+G*//3-21G* level. However, the energy difference among the three structures are so small that the order will be changed by solvation in solution.

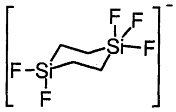
It should be noted that the intramolecular fluorine exchange of **1** is much faster than that of $[o\text{-}C_6H_4(SiPhF_2)_2F]^-$, where the exchange is reported to be frozen at 193 K.[1b,c] The $\Delta G^{\ddagger}$ value for the latter exchange is estimated to be as large as 40 kJ/mol,



1a



1b



1c

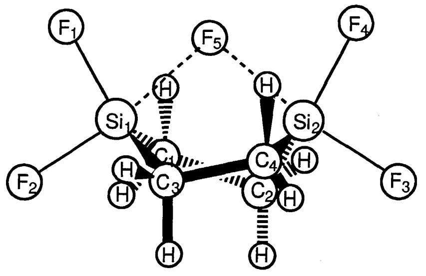
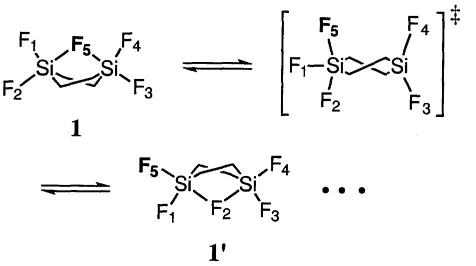


Figure 1. Ab initio optimized structure of **1a**. Selected bond lengths (Å): Si1–F5 = 1.879; Si2–F5 = 1.879; Si1–F1 = 1.614; Si1–F2 = 1.640; Si1–C1 = 1.878; C1–C2 = 1.572. Selected bond angles (deg): Si1–F5–Si2 = 106.8; F5–Si1–F2 = 177.6; F5–Si1–F1 = 84.7; F1–Si1–C1 = 120.9; C1–Si1–C3 = 115.5.

since the exchange requires the Berry pseudorotation to allow the equivalence of all the fluorines in the molecule.[8] The exchange of **1** should proceed via a novel mechanism without involving the Berry pseudorotation, since the $\Delta G^{\ddagger}$ value is lower than 25 kJ/mol. The synchronized fluorine exchange with ring inversion mechanism is proposed as the most plausible mechanism for the facile exchange among the five fluorine atoms, where during the ring inversion from a twist boat to another twist-boat, fluorine atoms exchange the positions as shown in Scheme 2. The small energy differences among **1a**, **1b**, and **1c**, as shown by the above MO calculations, may imply the energy barrier for the ring inversion small enough to support the mechanism. Since in Scheme 2, the five fluorine atoms rotate almost in a plane, *the dynamics looks like the fluorine wheel driven by the ring-inversion.*



Scheme 2. The synchronized fluorine exchange with ring inversion of 1.

The ^{19}F NMR spectrum of a 1:3 mixture of **1** and 1,1-difluorosilacyclohexane showed only two signals due to **1** and 1,1-difluorosilacyclohexane at 193 K; no signals due to **2** and **4** were observed. The equilibrium constant was estimated to be over 3000 by ^{19}F NMR spectroscopy. The high ability of **2** as a bidentate fluoride-ion host is comparable to Tamao's *o*-$C_6H_4(SiPhF_2)_2$.[1b,c]

We are grateful to the Ministry of Education, Science, and Culture of Japan for financial support (Grand-in Aids for Scientific Research No. 05640587).

References and Notes

1 a) S. Brownstein, *Can. J. Chem.*, **58**, 1407 (1980). b) K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *J. Am. Chem. Soc.*, **112**, 2422 (1990). c) K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *Organometallics*, **11**, 2099 (1992). d) K. Ebata, T. Inada, C. Kabuto, and H. Sakurai, *J. Am. Chem. Soc.*, **116**, 3595 (1994). e) M. Kira, T. Hoshi, and H. Sakurai, *Chem. Lett.*, **1995**, 807. f) D. Brondani, F. H. Carré, R. J. P. Corriu, J. J. E. Moreau, and M. W. C. Man, *Angew. Chem., Int. Ed. Engl.*, **35**, 324 (1996).

2 The compound **2** was prepared by a reaction of antimony trifluoride with 1,1,4,4-tetrachloro-1,4-disilacyclohexane, which was obtained by hydrosilylation of diphenyldivinylsilane with diphenylsilane in the presence of a catalytic amount of chloroplatinic acid in toluene at 90 °C followed by chlorodephenylation with $HCl/AlCl_3$. **2**: mp 53 °C; ^{1}H NMR (CD_2Cl_2, δ) 1.16 (s, 8H); ^{13}C NMR (CD_2Cl_2, δ) 4.7 (J = 13.4 Hz); ^{19}F NMR (CD_2Cl_2, δ) -142.3 (J = 304.4 Hz); ^{29}Si NMR (CD_2Cl_2, δ) -20 (t, J = 304.4 Hz); MS, *m/z* 188 (M^+, 48), 160 (100); HRMS Found: 188.0100, Calcd for $C_4H_8F_4Si_2$: 188.0101.

3 R. Damrauer and S. E. Danahey, *Organometallics*, **5**, 1490 (1986).

4 **1**: mp 150 °C (dec.): ^{1}H NMR (acetone-d_6, δ) 0.81 (s, 8H), 3.65 (s, 24H); ^{13}C NMR (acetone-d_6, δ) 9.9; ^{19}F NMR (acetone-d_6, δ) -119 (s, 5F); ^{19}F NMR (CD_2Cl_2, 233 K, δ) -119.4 (s, $^1J_{SiF}$ = 134.2 Hz, 5F); ^{29}Si NMR (acetone-d_6, δ) -39.2; Calcd for $C_{16}H_{32}F_5KO_6Si_2$: C, 37.63; H, 6.32%. Found: C, 37.08; H, 6.32%.

5 a) K. Tamao, T. Hayashi, Y. Ito, and M. Shiro, *Organometallics*, **11**, 182 (1992). b) S. E. Johnson, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, **28**, 3182 (1989). c) S. E. Johnson, J. S. Payne, R. O. Day, J. M. Holmes, and R. R. Holmes, *Inorg. Chem.*, **28**, 3190 (1989).

6 A set of satellites due to $^1J_{SiF}$ was observed only in CD_2Cl_2 at low temperatures.[4] A much smaller $^1J_{SiF}$ value of **1** than those of known diaryl- or dialkyltrifluorosilicates ($^1J_{SiF}$ = ca. 240 Hz) may be another indication of the fluorine bridging in **1**.

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8 The activation energies for the Berry pseudorotation for various diaryl- or dialkyltrifluorosilicates have been estimated to be about 40 kJ/mol;[9] typically, the activation energy for **4** is 38.1 kJ/mol.[5c]

9 C. Chuit, R. J. P. Corriu, C. Reye, and C. Young, *Chem. Rev.*, **93**, 1371 (1993).