X-Ray Crystal Structure and Dynamic Behavior of Pentafluoro-9,10-disila-9,10-dihydroanthracene Anion Salts Having Transannular 1,4-Fluorine Bridge

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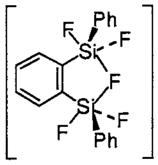
(Received July 28, 1999; CL-990662)

Potasium-18-crown-6 and tetraethylammonium ion salts of pentafluoro-9,10-disila-9,10-dihydroanthracene anion (**5a** and **5b**) have an unsymmetrical transannular 1,4-fluorine bridge in the solid states. In solution, **5a** and **5b** show a facile intramolecular fluorine exchange.

Much attention has been focused on the compounds with fluorine bridges between silicon atoms.[1] Since the first finding of such a complex in solution by Brownstein,[1a] anionic and neutral silicon compounds such as **1** – **3** have been isolated and their structural characteristics have been revealed both in the solid states and in solution. Tamao et al. have first isolated salts of **1** and related bissilicates,[1b,c] which show facile intramolecular fluorine exchange due to the Berry pseudo-rotation[2] in solution. Sakurai et al. have found unique merry-go-round degenerate fluorine migration of **2**.[1d] More recently, Corriu et al. have investigated the solid-state structure and the dynamic behavior in solution of **3**.[1e] At almost the same time, we have reported that pentafluoro-1,4-disilacyclohexane anion (**4**) shows a similar rapid intramolecular intersilicon fluoride-ion exchange, while the solid state structure was not determined by X-ray crystallography.[1f] We report herein the isolation and characterization of the salts of pentafluoro-9,10-disila-9,10-dihydroanthracene anion **5**, which constitute the first bissilicates having transannular 1,4-fluorine bridge in the solid states. An intramolecular fluorine exchange in **5** is observed in solution but slower than that in **4**, probably due to the slow fluttering of the dibenzo-1,4-disilacyclohexadiene ring.



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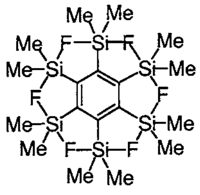

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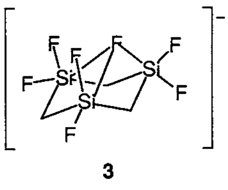

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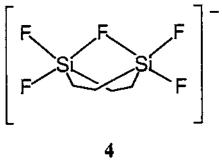

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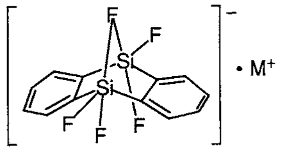
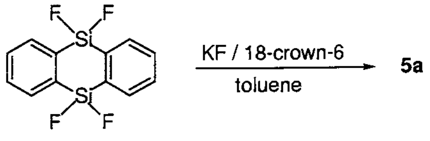


5a ($M^+ = K^+ \cdot$ 18-crown-6)
5b ($M^+ = Et_4N^+$)

A potassium•18-crown-6 salt of pentafluoro-9,10-disila-9,10-dihydroanthracene anion (**5a**) was prepared using reaction of **6**[3] with KF (1 equiv) in the presence of 18-crown-6 (1 equiv) in toluene (Eq. 1).[5] Recrystallization from THF afforded **5a** as colorless crystals in 96% yield.[6] Similarly, the reaction of **6** with tetraethylammonium fluoride gave **5b** in 94% yield (Eq. 2).[7] No hexafluorinated derivative was obtained even when **6** was treated with excess fluoride ion.



6 (1)

$$6 \xrightarrow[\text{THF}]{Et_4NF} 5b \qquad (2)$$

Figure 1 shows an ORTEP drawing of **5a**.[8] Compound **5a** has a boat 1,4-disilacyclohexadiene structure with unsymmetrical fluorine-bridge between two silicon atoms. The dihedral angles of Si1-C12-C1-C7 and Si2-C7-C6-C1 are 138° and 144°, respectively. The distances between the bridging fluorine atom (F1) and the two silicon atoms (Si1 and Si2) are 1.847 (3) Å and 2.020 (2) Å, respectively, which are comparable with those in $1 \cdot K^+$(18-crown-6) reported by Tamao et al. (1.898 (4) and 2.065 (4) Å).[1b] The unsymmetrical nature of the fluorine bridge

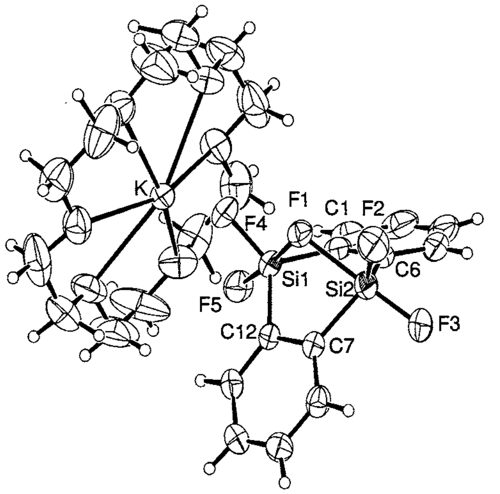
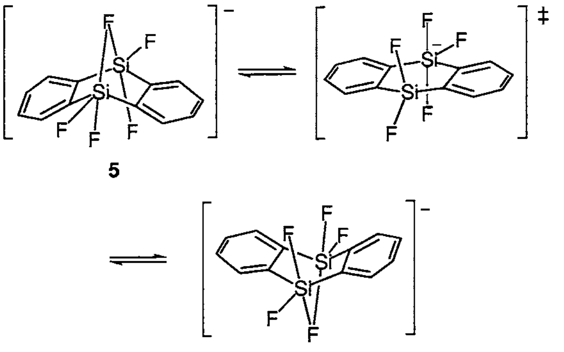


Figure 1. ORTEP drawing of **5a**. Selected bond lengths(Å) and bond angles(deg.): Si1–F1 = 1.847(3), Si1–F4 = 1.621(3), Si1–F5 = 1.657(3), Si2–F1 = 2.020(2), Si2–F2 = 1.595(3), Si2–F3 = 1.632(3), F4···K = 2.735(3), F5···K = 2.824(2); Si1–F1–Si2 = 103.1(1), C7–Si2–C6 = 112.8(2), C12–Si1–C1 = 111.4(2), F2–Si2–F3 = 94.2(1), F4–Si1–F5 = 90.1(1), F1–Si1–F5 = 174.4(1), F1–Si2–F3 = 177.0(1).

is reflected on the trigonal bipyramidal character of silicon atoms in **5a** as estimated by the %TBP value defined by Bürgi et al.;[9] the %TBP values for Si1 and Si2 in **5a** are 92% and 82%, respectively. Five fluorine and two silicon atoms of **5a** are almost in a plane bisecting the dibenzo-1,4-disilacyclohexadiene skeleton; the deviation from the least-square plane is within 0.022 Å. The significant contact of potassium ion with both an apical and an equatorial fluorine atoms is suggested by the distances of K•••F4 and K•••F5 in **5a** (2.735 and 2.824 Å, respectively); these values are almost the same with the sum of potassium and fluoride ion radii (2.66 - 2.71 Å). The origin of the unsymmetrical fluorine bridge is not ascribed to the significant K•••F contacts, because the molecular structure of **5b**[10] shows a similar unsymmetrical bridging, although **5b** has no significant interaction between the anion and the counter cation; the Si1-F1 and Si2-F1 distances are 1.867 Å and 2.124 Å, respectively, while the shortest distance between fluorine atoms and hydrogens of tetraethylammonium ions is 2.696 Å, which is larger than the sum of van der Waals radii of fluorine and hydrogen atoms (2.65 Å). The %TBP values for Si1 and Si2 are 90% and 76%, respectively.

The NMR spectral characteristics of **5a** in acetone-d_6 at 298 K are as follows: The ^1H NMR spectrum shows two kinds of signals due to ortho and meta protons on aromatic rings. In the ^{13}C NMR spectrum, four carbons bonded to two silicons are observed equivalently at δ 155.8 as a sextet due to the coupling with five equivalent fluorine atoms ($^2J_{C\text{-}F}$ = 18 Hz). The ^{29}Si NMR signal appears at δ –83.6 as a sextet due to the coupling with the five equivalent fluorine atoms. The ^{19}F NMR spectrum shows a sharp singlet at δ –115.4 with satellite signals due to ^{29}Si nuclei ($^1J_{Si\text{-}F}$ = 130 Hz). The ^{19}F chemical shift is intermediate between those of Ph_2SiF_2 (δ -143.2)[1c] and a related pentacoordinate silicon compound, $[Ph_2SiF_3]^-$ (δ –111.2).[5] These NMR results indicate that a rapid intramolecular exchange involving all five-fluorine nuclei takes place in **5**.

Previously, we have reported a rapid intramolecular intersilicon fluoride-ion exchange in pentafluoro-1,4-disilacyclohexane anion **4** and proposed a mechanism involving the fluorine exchange synchronized with the ring inversion as the most plausible mechanism.[1f] A similar mechanism is suggested for the rapid fluorine exchange in **5** (Scheme 1).



5

Scheme 1.

However, at a low temperature (203 K), the singlet ^{19}F NMR signal of **5a** is significantly broadened (the half band width is about 6 Hz at 298 K and 266 Hz at 203 K), suggesting that the exchange rate and the activation free energy at the same temperature are significantly smaller than those for **4**.[11] The slower exchange in **5** is probably due to the slow fluttering of the dibenzo-1,4-disilacyclohexadiene ring.

This work was supported by the Ministry of Education, Science, Sports, and Culture of Japan (Grand-in-Aid for Scientific Research (A) No.08404042).

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) D. Brondani, F. H. Carré, R. J. P. Corriu, J. J. E. Moreau, and M. Wong Chi Man, *Angew. Chem., Int. Ed. Engl.*, **35**, 324 (1996). f) T. Hoshi, M. Takahashi, and M. Kira, *Chem. Lett.*, **1996**, 608.

2 S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

3 The compound **6** was prepared according to the procedure reported by Chernyshev et al.[4] **6**: mp 163 °C; ^1H NMR (acetone-d_6, 298 K, δ) 7.85 (m, 4 H), 8.03 (m, 4 H); ^{13}C NMR (acetone-d_6, 298 K, δ) 137.9, 139.3, 141.5 (tt, $^2J_{C\text{-}F}$ = 18 Hz, $^3J_{C\text{-}F}$ = 4.2 Hz); ^{29}Si NMR (acetone-d_6, 298 K, δ) –39.23 (t, $^1J_{Si\text{-}F}$ = 287 Hz); ^{19}F NMR (acetone-d_6, 298 K, ppm) –136.3 (s, $^1J_{Si\text{-}F}$ = 287 Hz); MS (70 eV) *m/z* (%) 284 (M^+, 71), 218 (100), 199 (21), 152 (45); Anal. Calcd for $C_{12}H_8Si_2F_4$; C, 50.67; H, 2.84%. Found: C, 51.05; H, 3.01%.

4 E. A. Chernyshev, N. V. Komalenkova, L. N. Shamshin, and S. A. Shchepinov, *Zh. Obshch. Khim.*, **41**, 843 (1971).

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

6 **5a**: mp 151-152 °C (dec.); ^1H NMR (acetone-d_6, 298 K, δ) 3.60 (s, 24 H), 7.20 (m, 4 H), 7.67 (m, 4 H); ^{13}C NMR (acetone-d_6, 298 K, δ) 75.6, 132.7, 137.6, 155.8 (sextet, $^2J_{C\text{-}F}$ = 18 Hz); ^{29}Si NMR (THF-d_8, 298 K, δ) –83.6 (sextet, $^1J_{Si\text{-}F}$ = 130 Hz); ^{19}F NMR (acetone-d_6, 298 K, ppm) –115.4 (s, $^1J_{Si\text{-}F}$ = 130 Hz, 5F); negative-ion HRMS calcd for $C_{12}H_8F_5Si_2$ 303.0085, Found 303.0074.

7 A mixture of **6** (0.33 g, 1.16 mmol) and vacuum-dried tetraethylammonium fluoride (0.17 g, 1.16 mmol) were stirred vigorously in THF (1.5 ml) at room temperature for 9 h under argon. Filitration followed by evaporation of solvents gave **5b**. Recrystallization from THF gave pure **5b** (0.47 g, 94% yield) as colorless crystals. **5b**: mp 148-149 °C (dec.); ^1H NMR (THF-d_8, 298 K, δ) 0.95-1.01 (m, 12 H), 2.89-2.96 (m, 8 H), 7.16 (m, 4 H), 7.67 (m, 4 H); ^{13}C NMR (THF-d_8, 298 K, δ) 7.1, 52.5, 127.7, 132.8, 151.1 (sextet, $^2J_{C\text{-}F}$ = 18 Hz); ^{29}Si NMR (THF-d_8, 298 K, δ) –85.6 (sextet, $^1J_{Si\text{-}F}$ = 130 Hz); ^{19}F NMR (acetone-d_6, 298 K, ppm) –115.8 (s, $^1J_{Si\text{-}F}$ = 130 Hz, 5 F); negative-ion HRMS calcd for $C_{12}H_8F_5Si_2$ 303.0085, Found 303.0071.

8 Crystal data for **5a**: $C_{24}H_{32}F_5O_6KSi_2$, FW = 606.77, monoclinic, space group $P2_1/n$, a = 8.856(2) Å, b = 20.242(2) Å, c = 16.654(2) Å, β = 102.17(2)°, V = 2918.2(8) Å^3, Z = 4, d_{calc} = 1.381 g/cm^3, temperature 283 K. The structure was solved by direct method using SAPI91. Full matrix least-squares refinement yielded the final R value of 0.046 (R_w = 0.042) for 3207 independent reflections [$2\theta \leq 125.4°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC5R diffractometer using Cu-Kα radiation (λ = 1.54178 Å) and ω-2θ scan.

9 H.–B. Bürgi, J. Dunitz, *Acc. Chem. Res.*, **16**, 153 (1983).

10 Crystal data for **5b**: $C_{20}H_{28}F_5NSi_2$, FW = 433.61, monoclinic, space group $P2_1P2_1P2_1$, a = 15.987(2) Å, b = 16.728(4) Å, c = 8.204(2) Å, V = 2193.8(6) Å^3, Z = 4, d_{calc} = 1.313 g/cm3, temperature 200 K. The structure was solved by direct method using SIR92. Full matrix least-squares refinement yielded the final R value of 0.033 (R_w = 0.031) for 1726 independent reflections [$2\theta \leq 128.0°$, $I > 3.00\sigma(I)$] measured on a Rigaku AFC5R diffractometer using Cu-Kα radiation (λ = 1.54178 Å) and ω-2θ scan. Selected bond lengths(Å) and bond angles(deg.): Si1–F1 = 1.867(3), Si1–F4 = 1.602(3), Si1–F5 = 1.650(2), Si2–F1 = 2.124(3), Si2–F2 = 1.587(3), Si2–F3 = 1.630(3), F5–H12 = 2.969, F3–H21 = 2.957; Si1–F1–Si2 = 101.1(1), C1–Si1–C12 = 112.9(2), C6–Si2–C7 = 113.7(2), F1–Si1–F4 = 85.3(1), F1–Si2 –F2 = 82.2(1), F1–Si1–F5 = 177.8(1), F1–Si2–F3 = 177.9(1).

11 In the ^{19}F NMR spectrum of a potassium 18-crown-6 salt of **4** in acetone-d_6, a sharp singlet signal is observed in the temperature range of 183 – 293 K. The activation free energy ($\Delta G^{\ddagger}$) for the exchange is estimated to be less than 25 kJ/mol, which is much smaller than the $\Delta G^{\ddagger}$ value for the Berry pseudorotation.[2]