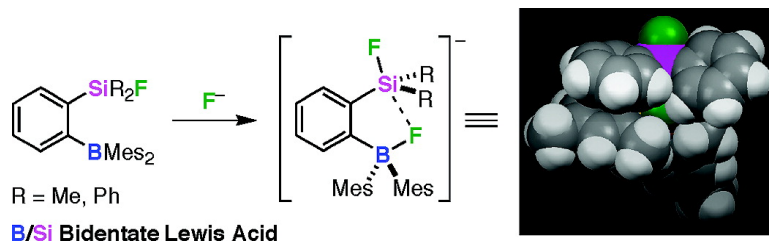


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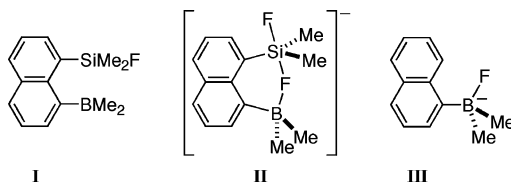
Synthesis of B/Si Bidentate Lewis Acids, *o*-(Fluorosilyl)(dimesitylboryl)benzenes, and Their Fluoride Ion Affinity

Atsushi Kawachi,* Atsushi Tani, Junpei Shimada, and Yohsuke Yamamoto

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

Received November 26, 2007; E-mail: kawachi@sci.hiroshima-u.ac.jp

Homocyclic bidentate Lewis acids¹ consisting of two identical Lewis acidic sites have received much attention in the fields of organic synthesis and molecular recognition because they can efficiently accept Lewis bases compared to corresponding monodentate Lewis acids. Since the Lewis acidity of tricoordinate boranes and tetracoordinate silanes is well recognized and commonly used in organic synthesis, it is natural that the chemistry of bidentate Lewis acids having two boron centers² or two silicon centers³ is pursued with much interest. However, there are few examples of bidentate Lewis acids having boron and silicon centers.^{4,5} Katz prepared 1-dimethylboryl-8-fluorodimethylsilylnaphthalene (**I**) but found that its fluoride complex **II** was less stable than its non-silylated counterpart **III**.^{4a} This may be due to the unsuitable geometry of the 1,8-naphthylene backbone for the formation of the Si(V)–F–B(IV) bridge.

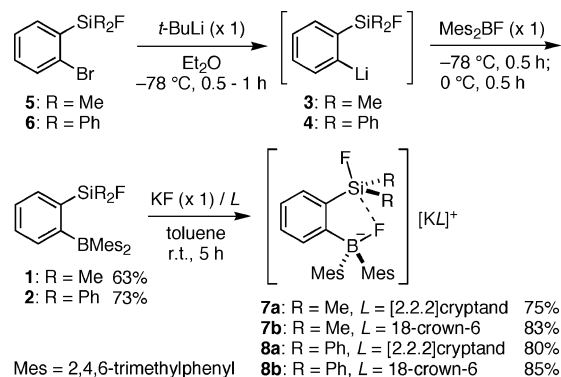


In this context, we have focused our attention on the *o*-phenylene backbone,^{2d,e,3a,c} which affords a suitable scaffold to boron and silicon to chelate fluoride ion. Here we report the facile preparation of new B/Si bidentate Lewis acids, *o*-(fluorosilyl)(dimesitylboryl)benzenes⁶ **1** and **2**, and disclose their ability to bind fluoride ion by forming a μ -fluoro bridge.

Compounds **1** and **2** were readily prepared by reacting fluorodimesitylborene with *o*-(fluorosilyl)phenyllithiums **3**⁷ and **4**,⁸ respectively, as shown in Scheme 1. In the presence of [2.2.2]cryptand or 18-crown-6 **1** and **2** efficiently capture fluoride ion from KF in toluene, giving μ -fluoro bridged **7a** (75%), **7b** (83%), **8a** (80%), and **8b** (85%) as colorless crystals after recrystallization from THF-hexane.⁹

The binding modes of the fluoride ion in **7** and **8** were revealed by X-ray crystallographic analysis. A summary of the bond lengths and the bond angles of **7** and **8** is provided in the Supporting Information (Table S-1), and the crystal structure of **8b** is shown in Figure 1 as a representative. Whereas **7a**, **8a**, and **8b** exist as solvent-separated ion pairs with K⁺ fully coordinated by the cryptand or THF molecules, **7b** shows anion–cation contact (Si–F1⋯K⁺(18-crown-6)(thf) = 2.808(3) Å). While fluoride F2 is tightly bonded to the boron atom (B–F2 = 1.491(2) (7a); 1.492(4) (7b); 1.508(2) (8a); 1.514(3) (8b) Å)¹⁰ to form a fluoroborate moiety, it simultaneously coordinates to silicon with the following Si–F2 distances (2.5309(13) (7a); 2.4385(23) (7b); 2.2655(14) (8a); 2.2481(13) (8b) Å) and linear F1–Si–F2 arrangement (175°–176°), forming a pseudopentacoordinate geometry at the silicon atom. The Si–F2 distances are shorter than the

Scheme 1. Preparation and Fluoride Binding of **1** and **2**



distance (2.63 Å) of the minimal nonbonded approach between Si and F,¹¹ and those in **8** are comparable to the bridging Si–F bonds in μ -fluoro-bis(silicates) (1.700(3)–2.369(3) Å)^{3a} and in hexakis-(fluorodimethylsilyl)benzene (av 2.39 Å).^{3b} As the Si–F2 distance shortens in the order of **7a** > **7b** > **8a** > **8b**, the sum of the three C–Si–C angles increases in the order of **7a** (349°) < **7b** (352°) < **8a**, **8b** (354°), indicating the increase of the pentacoordination character at the silicon atom. AIM analysis of **7a** and **8b** exhibited the bond path and the bond critical point between Si and F2 in each compound:¹² electron density $\rho(r) = 0.0212 \text{ e/a}_0^3$ (**7a**) and 0.0346 e/a_0^3 (**8b**); Laplacian value $\nabla^2\rho(r) = 0.0506 \text{ e/a}_0^5$ (**7a**) and 0.0604 e/a_0^5 (**8b**). As far as we know, this work is the first to accomplish the solid-state characterization of the intramolecular Si(V)–F–B(IV) bridge.

The structures of **7** and **8** in the THF solution are revealed by multinuclear NMR analysis (Table S-1). Cryptand complex **7a** and crown ether complex **7b** exhibit almost the same spectra, which indicates that **7b** also exists as a solvent-separated ion pair in THF. ¹¹B chemical shifts ($\delta = 6$ (**7**); 7 (**8**)) fall in the region typical for tetracoordinate borates. In ¹⁹F NMR spectra the terminal fluorine (F1) signal resonates in the low field region ($\delta = -147$ (**7**); -145 (**8**)) and is accompanied by ²J_{F–F} coupling (9 Hz (**7**); 18 Hz (**8**)), whereas the bridging fluorine (F2) exhibits a broad signal in the high field region ($\delta = -152$ (**7**); -148 (**8**)). The coordination of F2 to silicon is also reflected in the ²⁹Si NMR spectra: (i) ²⁹Si signals ($\delta = 6.5$ (**7**); -32.6 (**8**)) were shifted upfield by 14 ppm in **7** and by 29 ppm in **8** relative to those in **1** and **2**, respectively; (ii) Si–F1 coupling constants in **7** and **8** (260–266 Hz) were reduced relative to those of **1** (278 Hz) and **2** (284 Hz), suggesting axial elongation of the Si–F1 bonds in the pentacoordinate geometry; and (iii) Si–F2 coupling constants increase from 7 Hz in **7** to 17 Hz in **8** with reduced Si–F2 distances. These trends are consistent with the general tendency that aryl substitution increases the Lewis acidity of the silicon to stabilize pentacoordinate silicates.⁹

Exchange of the two fluorines in **8** was observed by variable-temperature ¹⁹F NMR analysis. The two fluorine signals in both

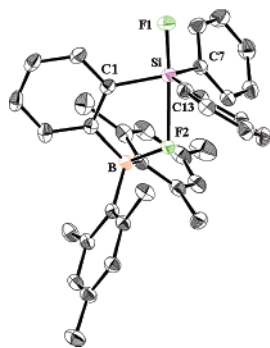
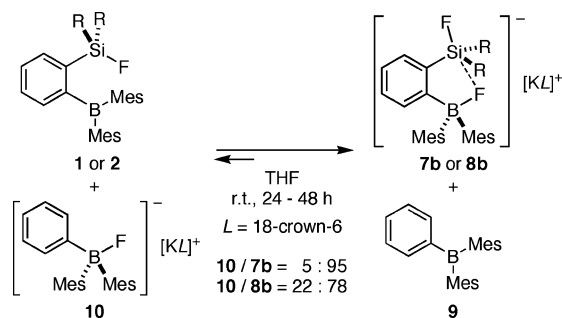


Figure 1. Crystal structure of **8b** (30% thermal ellipsoids). $K^+(18\text{-crown-6})(\text{thf})_2$ and hydrogen atoms are omitted for clarity.

Scheme 2. Competition Reactions of Fluoride Ion Affinity



8a and **8b** underwent coalescence at 361 K in $\text{DMSO-}d_6$ ($k_{361} = 4.3 \times 10^3 \text{ s}^{-1}$, $\Delta G_{361}^\ddagger = 15 \text{ kcal/mol}$). In contrast, **7** exhibited no coalescence up to 383 K.

Fluoride ion affinities of **1** and **2** were investigated by competition experiments with non-silylated triarylborane¹³ **9** and its fluoroborate **10**, as shown in Scheme 2. Mixing equimolar amounts of **1** and **10** in THF at room-temperature gave **7b** and **9** ($10/7b = 5:95$; $K_{298} = 3.6 \times 10^2$, $\Delta G_{298} = -3.5 \text{ kcal/mol}$).^{14,15} Phenyl derivative **2** also captured fluoride ion from **10** to give **8b** and **9** ($10/8b = 22:78$; $K_{298} = 13$, $\Delta G_{298} = -1.5 \text{ kcal/mol}$).^{14,15} Thus, the presence of *o*-fluorosilyl groups tended to increase fluoride ion affinity of the triarylboranes.¹⁶ These results also suggested that fluoride ion affinity of **1** is higher than that in **2**. Actually competition reactions between **1** and **8b** as well as **7b** and **2** in THF displayed preferential formation of **7b** ($7b/8b = 82:18$; $K_{298} = 21$, $\Delta G_{298} = -1.8 \text{ kcal/mol}$).¹⁴

Fluoride ion affinities of **1** and **2** were calculated from the energy of **1**, **2**, the anion part of **7** ($[1-F]^-$), and the anion part of **8** ($[2-F]^-$): their structures were optimized at the B3LYP/6-31G(d) level, and their energies were obtained at the MP2/6-31+G(d,p) level.¹⁷ ΔG calculated for $\{1 + [2-F]^- \rightarrow [1-F]^- + 2\}$ (-1.68 kcal/mol) is consistent with ΔG estimated from the equilibrium ratio of **7b/8b** (-1.8 kcal/mol). We noticed that the Si–F2 distance in $[2-F]^-$ (2.405 Å) is longer than that in the crystal structures of **8a** and **8b**, whereas the Si–F2 distance in $[1-F]^-$ (2.533 Å) is equal to that in the crystal structure of **7a**. It is plausible that elongation of the Si–F2 bond in $[2-F]^-$ is due to steric repulsion between phenyl groups and mesityl groups, and this is the case of **8** in THF.¹⁷ Total stability of **8** may be determined by balance between attractive interaction between Si and F2 and steric repulsion between the aryl groups, which destabilizes **8** in THF and lowers fluoride ion affinity of **2** relative to **1**.

In conclusion, *o*-(fluorosilyl)borylbenzenes **1** and **2** have high fluoride ion affinity compared to the triarylborane **9**, which is in clear contrast to 1-boryl-8-silylnaphthalene **I**.^{4a} Changing the substituents on the boron and silicon centers may lead to diversity of the B/Si bidentate Lewis acids for selective binding of a particular Lewis base, such as detection of a specified halide ion.

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Supporting Information Available: Summary of structural data; experimental details; tables of crystallographic data for **7a**, **7b**, **8a**, and **8b** (PDF/CIF); and computational works. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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