

## Anion complexation by bidentate Lewis acidic hosts, *ortho*-bis(fluorosilyl) benzenes <sup>☆</sup>

Kohei Tamao <sup>a,\*</sup>, Takashi Hayashi <sup>b</sup>, Yoshihiko Ito <sup>b</sup>

<sup>a</sup> Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

<sup>b</sup> Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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### Abstract

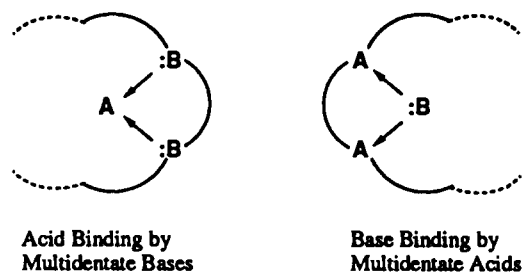
*Ortho*-bis(fluorosilyl)benzenes, precursors for bis-siliconates, *o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub> (**1**), *o*-C<sub>6</sub>H<sub>4</sub>(SiF<sub>3</sub>)(SiPh<sub>2</sub>F) (**2**) and *o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)(SiPh<sub>2</sub>F) (**3**), possess anion binding properties as bidentate Lewis acidic hosts in organic solvents. Compound **1** quantitatively binds a fluoride ion from KF suspended in acetone or tetrahydrofuran without support of 18-crown-6 to form the corresponding soluble bis-siliconate [*o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub>F]<sup>-</sup>K<sup>+</sup> (**4**). The binding constants of a series of fluorosilanes for a fluoride ion are measured by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopies. The affinity of fluorosilanes towards a fluoride ion increases in the order PhMeSiF<sub>2</sub> (**7**) < Ph<sub>2</sub>SiF<sub>2</sub> (**9**) < **3** < **1** < **2**. The fluoride ion binding constant of **2** is estimated to be  $K > 1.1 \times 10^9 \text{ M}^{-1}$  at 193 K. These bidentate Lewis acids **1–3** are among the strongest organic hosts for a fluoride ion in organic solvents ever reported.

**Keywords:** Fluorine; Silicon; Silane; Pentacoordinate siliconate; Bidentate Lewis acid; Fluoride binding constant

### 1. Introduction

In comparison with cation complexation by multidentate bases [1], the binding of anionic species by multidentate acids has been much less extensively studied (Scheme 1). However, the anion complexation by multidentate acids is of increasing interest recently in the whole field of chemistry.

There are two types of host molecule for anion species so far reported: one is positively charged molecules and the other is the Lewis acidic multidentate molecules. The former type includes the encapsulation of halide anions by macrocyclic ammonium ions in aqueous media [2]. The latter type, the anion complexation by bidentate or multidentate Lewis acid in organic media, had been studied only by a few groups but has recently begun to receive much attention. The pioneering work relating to anion complexation, the chelation



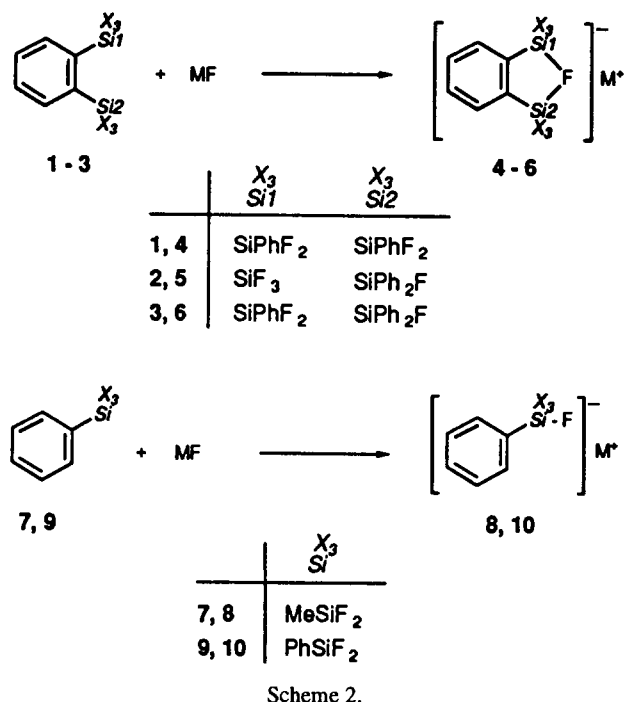
Scheme 1.

of MeO<sup>-</sup> with a bidentate Lewis acid F<sub>2</sub>BCH<sub>2</sub>CH<sub>2</sub>BF<sub>2</sub>, was reported by Shriver and Biallas [3] in 1967. In the last few years, various types of multidentate Lewis acid have been reported, which contain B [4], Al [5], Si [6], Ge [7], Sn [8], Ti [9], Fe [10], Co [11], Cu [12], Zn [13], Hg [14] and S [15]. They behave as host molecules not only for halides anions but also for neutral Lewis bases such as amines [4e,4f,13,14g] and carbonyl compounds [5,9,10,14b,14e].

We have recently reported the synthesis and structural aspects of the novel pentacoordinate anionic bis-siliconates **4–6** (M<sup>+</sup> = K<sup>+</sup> · 18-crown-6) which contain a fluoride ion chelated by two silyl groups, as evidenced by the X-ray structural analysis (Scheme 2) [16,17].

<sup>☆</sup> Dedicated to Professor Hideki Sakurai for his outstanding achievements in the field of organosilicon chemistry on the occasion of his retirement from Tohoku University.

\* Corresponding author.

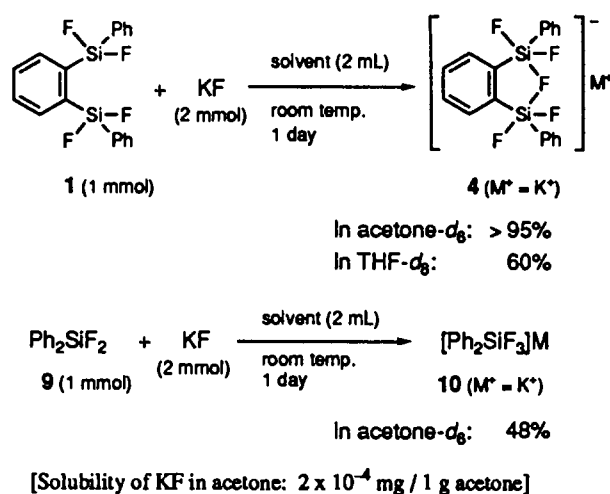
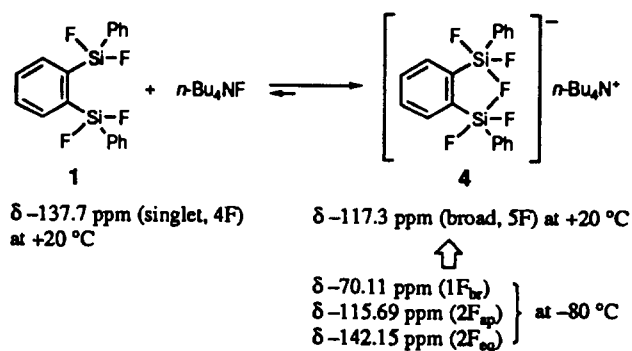


Thus the precursors of bis-silicates, *ortho*-bis(fluorosilyl)benzenes 1–3, behave as bidentate Lewis acidic host molecules for a fluoride anion. This paper reports the details of the study on the anion binding properties of *ortho*-bis(fluorosilyl)benzenes (1–3). In this study, we have determined the equilibrium constants for the fluoride ion binding by *ortho*-bis(fluorosilyl)benzenes. Their Lewis acidities are compared with those of fluoromonosilanes PhMeSiF<sub>2</sub> (7) and Ph<sub>2</sub>SiF<sub>2</sub> (9) (Scheme 2).

## 2. Results and discussion

### 2.1. Anion binding

Scheme 3 outlines the binding of a fluoride ion by *ortho*-bis(difluorophenylsilyl)benzene (1) when mixed with *n*-Bu<sub>4</sub>NF in tetrahydrofuran (THF). The formation



of 4 ( $M^+ = n\text{-Bu}_4\text{N}^+$ ) is readily detected by the <sup>19</sup>F NMR spectroscopy at ambient temperatures and/or low temperatures as shown in Scheme 3. At ambient temperature, five fluorine atoms appear as one signal owing to the intramolecular exchange possesses [16]. The fluoride complex 4 shows no intermolecular fluoride exchange with excess fluorosilane 1 on NMR time scale even at +45°C; the fluorine signals of 1 and 4 are observed separately. This is a sharp contrast with the fast equilibrium between [PhMeSiF<sub>3</sub>]<sup>-</sup>, K<sup>+</sup> · 18-crown-6 (8) and excess PhMeSiF<sub>2</sub> (7) detectable even at -78°C by the <sup>19</sup>F NMR measurement. Thus the bidentate Lewis acidic host 1 binds the fluoride ion: much more tightly than fluoromonosilanes.

*o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub> (1) quantitatively captures a fluoride ion from potassium fluoride suspended in acetone-*d*<sub>6</sub> without support of 18-crown-6 to form 4 ( $M^+ = K^+$ ), while fluoromonosilane Ph<sub>2</sub>SiF<sub>2</sub> (9) forms the silicate [Ph<sub>2</sub>SiF<sub>3</sub>]K (10) with less than 50% yield, as shown in Scheme 4. Thus host 1 appears to be a stronger Lewis acid than 9 for the capture of a fluoride ion in organic media. The result demonstrates that, since the concentration of the resulting 4 ( $M^+ = K^+$ ) in acetone is  $5 \times 10^{-1}$  mol L<sup>-1</sup>, the host 1 solubilizes the sparingly soluble KF in acetone (solubility,  $2 \times 10^{-4}$  mg L<sup>-1</sup> acetone =  $4.3 \times 10^{-6}$  mol L<sup>-1</sup> at 18°C) [18] by higher than 10<sup>4</sup> times.

### 2.2. Fluoride binding constants

The binding constants for a fluoride ion by bidentate fluorosilanes 1–3 in solution have been determined as a function of the number of fluorine atoms on silicon atoms by means of <sup>1</sup>H and <sup>19</sup>F NMR spectroscopies. Since these binding constants were, however, too large to measure directly by NMR measurements, the binding constant of fluoromonosilane 7 was determined first and

then other binding constants were estimated by competition experiments. Five experimental data are summarized in Scheme 5.

### 2.2.1. Determination of the fluoride binding constant for *PhMeSiF<sub>2</sub>* (7) (Scheme 5(a))

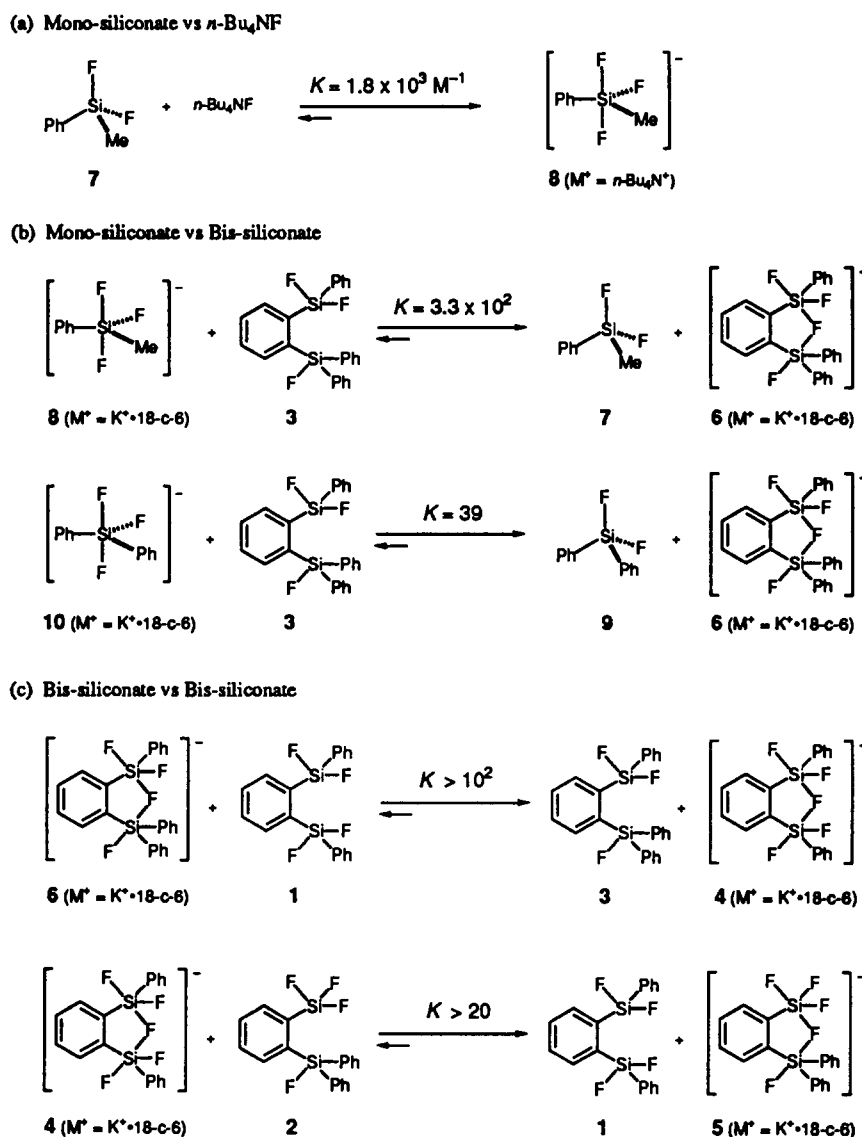
An acetone-*d*<sub>6</sub> solution of 7 was titrated with a dry 1 M solution of *n*-Bu<sub>4</sub>NF in THF at 18°C. The chemical shifts of Si-CH<sub>3</sub> protons moved steadily from  $\delta = +0.533$  ppm for the tetracoordinated PhMeSiF<sub>2</sub> (7) to  $\delta = -0.058$  ppm for the pentacoordinated [PhMeSiF<sub>3</sub>]<sup>-</sup> (8) (M<sup>+</sup> = *n*-Bu<sub>4</sub>N<sup>+</sup>) owing to a rapid intermolecular fluoride exchange between these two species. The chemical shifts were plotted against the molar equivalent of *n*-Bu<sub>4</sub>NF, as shown in Fig. 1. The binding constant of 7 for a fluoride ion could be calculated by the Benesi-Hildebrand [19] treatment to be  $K = 1.8 \times 10^3$  M<sup>-1</sup> at 291 K in acetone-*d*<sub>6</sub>.

### 2.2.2. Determination of the fluoride binding constant for *o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub>(SiPh<sub>2</sub>F) (3) (Scheme 5(b))

The equilibrium constant between [PhMeSiF<sub>3</sub>]<sup>-</sup> (8) (M<sup>+</sup> = K<sup>+</sup> · 18-crown-6) and host 3 was measured by following the chemical shifts of Si-CH<sub>3</sub> protons in 8 upon titration with 3 in an acetone-*d*<sub>6</sub> solution at +18°C, to be  $3.3 \times 10^2$ . The binding constant for complexation of a fluoride ion by host 3 is therefore calculated to be  $K = 5.9 \times 10^5$  M<sup>-1</sup>.

### 2.2.3. Determination of the fluoride binding constants for *o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub> (1) (Scheme 5(c)), *o*-C<sub>6</sub>H<sub>4</sub>(SiF<sub>3</sub>)(SiPh<sub>2</sub>F) (2) (Scheme 5(c)) and Ph<sub>2</sub>SiF<sub>2</sub> (9) (Scheme 5(b)) by the <sup>19</sup>F NMR spectroscopy at -80°C to -90°C

The fluoride binding constant for 1 was determined by <sup>19</sup>F NMR spectroscopy by titration of a solution of bis-siliconate [*o*-C<sub>6</sub>H<sub>4</sub>(SiPhF<sub>2</sub>)<sub>2</sub>(SiPh<sub>2</sub>F)F]<sup>-</sup> (6) (M<sup>+</sup> =



Scheme 5. (18-c-6 = 18-crown-6).

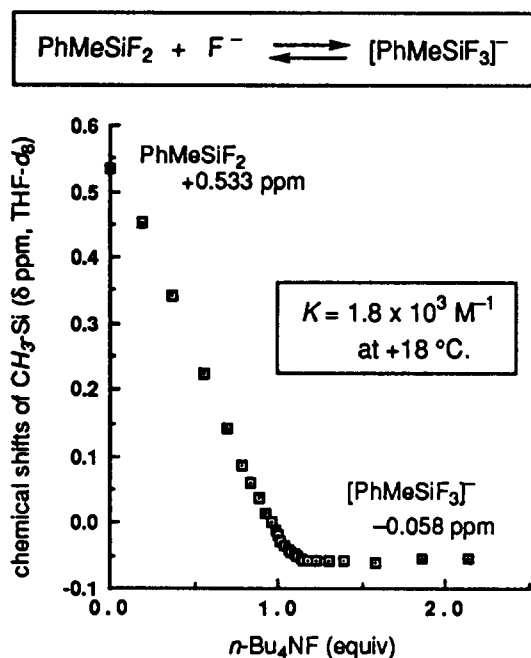


Fig. 1. The change in  $^1\text{H}$  NMR chemical shifts of the methyl protons in  $\text{PhMeSiF}_2$  (7) upon titration with  $n\text{-Bu}_4\text{NF}$  in  $\text{THF-d}_6$ .

$\text{K}^+ \cdot 18\text{-crown-6}$ ) in acetone- $d_6$  with host 1, to give an equilibrium mixture with host 3 and bis-silicate  $[\text{o-C}_6\text{H}_4(\text{SiPhF}_2)_2\text{F}]^-$  (4) ( $\text{M}^+ = \text{K}^+ \cdot 18\text{-crown-6}$ ); the NMR spectra in several stages are reproduced in Fig. 2.

Upon addition of one equivalent of host 1, only the fluorine signals due to host 3 and bis-silicate 4 were observed without residual 1 and 6 at  $-90^\circ\text{C}$ . Thus the fluoride ion is transferred completely from bis-silicate 6 to host 1. We can therefore estimate the equilibrium constant between 1 and 3 to be greater than  $10^2$ , and in turn the fluoride binding constant by host 1 is calculated to be about  $K > 5.9 \times 10^7 \text{ M}^{-1}$  (at 183 K). In a similar manner, the fluoride binding constant for host 2 was determined by titration of an acetone- $d_6$  solution of bis-silicate 4 with host 2 in equilibration with host 1 and bis-silicate 4 with host 2 in equilibration with host 1 and bis-silicate 4 [ $\text{o-C}_6\text{H}_4(\text{SiF}_3)(\text{SiPh}_2\text{F})\text{F}]^-$  (5) ( $\text{M}^+ = \text{K}^+ \cdot 18\text{-crown-6}$ ). According to  $^{19}\text{F}$  NMR at  $-80^\circ\text{C}$ , the equilibrium constant between 2 and 1 is about 20 based on the relative ratios of the species present upon addition of one equivalent of host 2 (the spectra not shown here). Thus the binding constant of host 2 is larger than that of 1 and is estimated to be  $K > 1.1 \times 10^9 \text{ M}^{-1}$  (at 193 K). The binding constant of  $\text{Ph}_2\text{SiF}_2$  (9) was also determined to be  $K = 1.5 \times 10^4 \text{ M}^{-1}$  similarly by measurement of the equilibrium constant between host 3 and  $[\text{Ph}_2\text{SiF}_3]^-$  (10) ( $\text{M}^+ \text{K}^+ \cdot 18\text{-crown-6}$ ) at  $-85^\circ\text{C}$ .

In contrast, no reaction occurred when a solution of host 1 in acetone- $d_6$  was treated with an excess amount of  $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$ , as observed by the  $^{19}\text{F}$  NMR measurement at  $-80^\circ\text{C}$ . Thus the host 1 cannot take a fluoride ion from  $\text{BF}_4^-$ , indicating that  $\text{BF}_3$  possesses

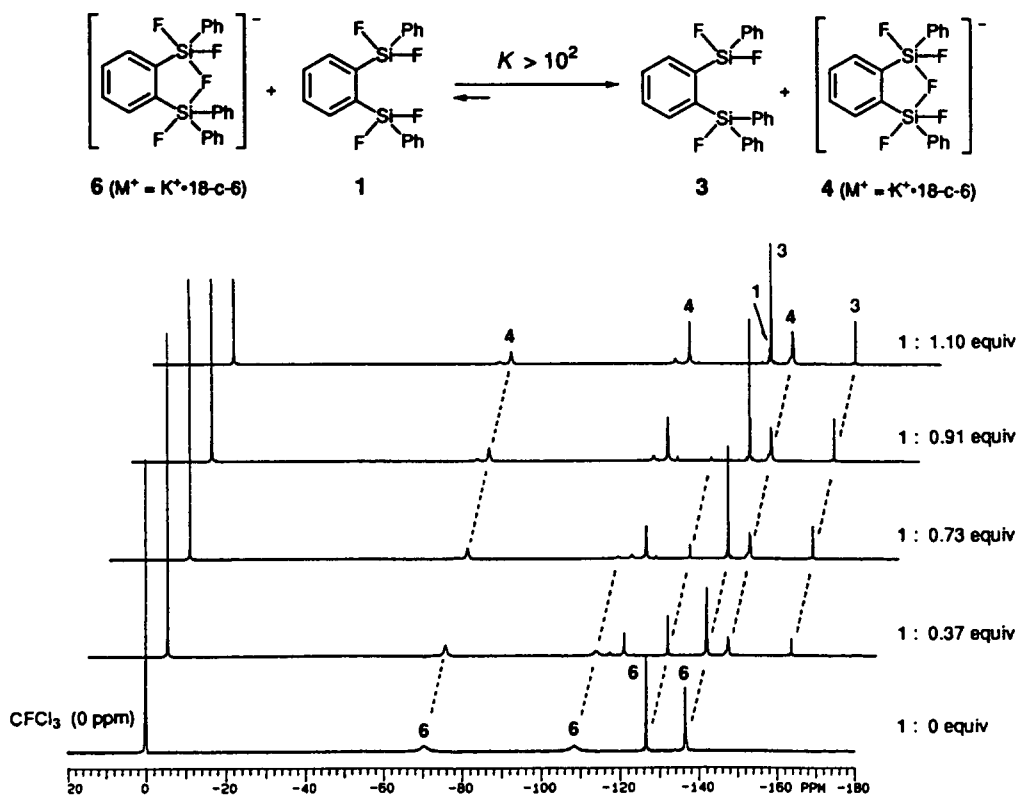
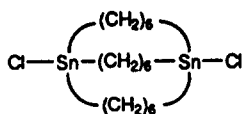


Fig. 2.  $^{19}\text{F}$  NMR spectral change of bis-silicate 6 at  $-85^\circ\text{C}$  upon addition of 0, 0.37, 0.73, 0.91 and 1.10 equivalents of host 1.



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For F<sup>-</sup>,  $K = 1.2 \times 10^4 \text{ M}^{-1}$  (ref 21).

much stronger Lewis acidity for a fluoride ion than host **1** by more than  $10^2$  times.

The results are summarized in Table 1, which contains the binding constants and the free-energy differences. It should be noted that while data for **7** correspond to the direct binding with a “free” fluoride ion, the other data have been obtained indirectly by the competition experiments between the “complexed” fluoride ions and free hosts. Thus data other than **7** should be regarded as the lowest limits for the binding of a “free” fluoride ion. In particular, the free energy differences  $-\Delta G$  for **7** and **9** cannot be compared directly with each other, since the fluoride ion binding order  $7 < 9$  is apparent from the two competition experiments in Scheme 5(b). As a whole, the fluoride binding ability thus increases in the order  $7 < 9 < 3 < 1 < 2 < \text{BF}_3$ . The following three general tendencies may be deduced: (1) the bidentate Lewis acid silanes bind anionic species more tightly than monosilanes; (2) the anion binding ability of the bidentate silanes increases with an increase in the total number of fluorine atoms on silicon atoms; and (3) if the total numbers are same, the asymmetrically substituted compound is a stronger Lewis acid than the other as shown by the order  $1 < 2$ . This tendency is consistent with the gas-phase Lewis acidities of fluorosilanes in the order  $\text{Me}_3\text{SiF} < \text{Me}_2\text{SiF}_2 < \text{MeSiF}_3 < \text{SiF}_4 < \text{BF}_3$  determined by ion cyclotron resonance spectroscopy, as reported by Murphy and Beauchamp [20a] and Larson and McMahon [20b].

Our bidentate silicon host **2** is more efficient than the known macrocyclic tin host molecule **11** whose binding constant is  $1\text{--}2 \times 10^4 \text{ M}^{-1}$  between  $-50$  and  $30^\circ\text{C}$  and thus seems to have the highest binding ability for a fluoride ion in organic solvents among organic host molecules ever reported [21].

Finally, these *ortho*-bis(fluorosilyl)benzenes having the strong affinity for anion species such as a fluoride ion would be applicable to a wide range of anion complex systems. As one possibility, we have applied the host molecules **1–3** as the titration agent for determination of the concentration of a fluoride ion in organic media, i.e. the concentration of the commercially available THF solution of *n*-Bu<sub>4</sub>NF (see Section 3).

### 3. Experimental details

#### 3.1. General remarks

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Varian VXR-200 spectrometer, operating at 200 MHz and 185.15 MHz respectively. <sup>1</sup>H chemical shifts are reported relative to Me<sub>4</sub>Si. <sup>19</sup>F chemical shifts refer to CFC1<sub>3</sub> ( $\delta(^{19}\text{F}) = 0$  ppm) as an internal standard. Temperature calibration was accomplished by using a standard methanol sample with a calibration error of  $\pm 1.0^\circ\text{C}$ .

THF-*d*<sub>8</sub> and acetone-*d*<sub>6</sub> were purchased from CEA and Wako Pure Chemical Ind. Ltd. respectively. A solution of *n*-Bu<sub>4</sub>NF (1.0 M) in THF was purchased from Aldrich Chemical Co. and allowed to stand over 4 Å molecular sieves activated by heating to  $250^\circ\text{C}$  for 5 h and cooled in vacuo. The preparation of *ortho*-bis(fluorosilyl)benzenes **1–3** and the corresponding bis-siliconates **4–6** have been reported in our previous paper [16]. Mono-siliconates **8** and **10** were prepared by the Damrauer–Darahey [22] method [23].

#### 3.2. Determination of concentration of *n*-Bu<sub>4</sub>NF in tetrahydrofuran

A solution of 0.105 mmol of **1** in 0.6 ml of acetone-*d*<sub>6</sub> and 50 μl of commercially available *n*-Bu<sub>4</sub>NF solution in THF were mixed. The <sup>19</sup>F NMR spectrum at  $-80^\circ\text{C}$  was recorded and the quantity of *n*-Bu<sub>4</sub>NF was determined by the ratio of free host **1** to bis-siliconate **4** determined by direct integration of both fluorine signals (free host **1**,  $\delta = -136.1$  ppm (4F); bis-siliconate **4**,  $\delta = -142.2$  ppm (2F<sub>eq</sub>)). The transmitter was located at

Table 1  
Order of the fluoride ion binding constants and free energy differences

	PhMeSiF <sub>2</sub> <b>7</b>	<	Ph <sub>2</sub> SiF <sub>2</sub> <b>9</b>	<	 <b>3</b>	<	 <b>1</b>	<	 <b>2</b>
log <i>K</i>	3.3 (291 K)		4.2 <sup>a</sup> (188 K)		5.8 <sup>a</sup> (183 K)		> 7.8 <sup>a</sup> (183 K)		> 9.0 <sup>a</sup> (193 K)
$-\Delta G$ (kcal mol <sup>-1</sup> )	4.4		3.6 <sup>a</sup>		5.0 <sup>a</sup>		> 6.5 <sup>a</sup>		> 6.7 <sup>a</sup>

<sup>a</sup> The lowest limit data (see text).

the midpoint of the two fluorine signals to guarantee that each signal received equal power.

### 3.3. Measurement of equilibrium binding constants of fluoride ion for 1–3, 7 and 9

#### 3.3.1. $\text{PhMeSiF}_2$ (7)

In an NMR tube, fluorosilane 7 (0.112 mmol) was dissolved in 0.7 ml of THF- $d_8$  containing 0.1% tetramethylsilane (TMS). After measurement of the initial chemical shift of the methyl protons,  $\delta = 0.553$  ppm, aliquots of a 1.04 M THF solution of  $n\text{-Bu}_4\text{NF}$ , the concentration of which was determined by the above method, were successively added via a microsyringe, and the NMR spectrum of each resulting solution was recorded. In all cases the methyl proton signal was observed at 18–20°C and the binding constant was determined by a Benesi–Hildebrand plot (Fig. 1).

#### 3.3.2. $o\text{-C}_6\text{H}_4(\text{SiPhF}_2)(\text{SiPh}_2\text{F})$ (3)

Silicate  $[\text{PhMeSiF}_3]^- \cdot \text{K}^+ \cdot 18\text{-crown-6}$  (8) (0.0315 mmol) was dissolved in 0.6 ml of acetone- $d_6$  containing 0.1% TMS. After measurement of the initial chemical shift of the methyl protons,  $\delta = 0.058$  ppm, aliquots of a 0.740 M solution of host 3 in acetone- $d_6$  were successively added via a microsyringe, and the equilibrium constant between host 3 and silicate 8 was determined in a similar manner as above. The binding constant for host 3 was calculated by multiplication of the equilibrium constant by the binding constant of  $\text{PhMeSiF}_2$  (7).

#### 3.3.3. $o\text{-C}_6\text{H}_4(\text{SiPhF}_2)_2$ (1), $o\text{-C}_6\text{H}_4(\text{SiF}_3)(\text{SiPh}_2\text{F})$ (2) and $\text{Ph}_2\text{SiF}_2$ (9)

The binding constant for host 1 was determined as follows. Bis-siliconate 3 (0.168 mmol) was dissolved in 0.6 ml of acetone- $d_6$  containing 0.3%  $\text{CFCl}_3$ . After measurement of the initial fluorine signals of bis-siliconate 3 ( $\delta = -126.6$  ppm), aliquots of 0.626 M solution of host 1 in acetone- $d_6$  were successively added.  $^{19}\text{F}$  NMR spectra were recorded at  $-85^\circ\text{C}$  (Fig. 2) and the equilibrium constants were calculated by the integration ratio of fluorine signals [16]. The binding constant for host 2 was determined by the measurement of the equilibrium constant between bis-siliconate 1 and host 2 in a similar manner to the above. The binding constant for fluorosilane 9 was determined by the measurement of the equilibrium constant between siliconate 10 and host 3.

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