# Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 11758

## PAPER

### A highly Lewis acidic triarylborane bearing peripheral o-carborane cages†

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Received 7th June 2011, Accepted 16th August 2011 DOI: 10.1039/c1dt11064k

A triarylborane (2) bearing three *o*-carborane cages at peripheral positions on the aryl groups was prepared and its crystal structure was determined from X-ray diffraction study. Treatment of **2** with KF in the presence of 18-crown-6 led to the potassium salt,  $[2F]^-$ . A UV-vis titration experiment carried out in THF/H<sub>2</sub>O (9/1 v/v) showed that **2** binds fluoride ions with a binding constant (*K*) of  $4.8 \times 10^4$  M<sup>-1</sup>, which is an order-of-magnitude greater than *K* for the mono-carborane substituted triarylborane. The enhanced fluoride ion affinity of **2** indicates an apparent additive effect of multiple carborane substitutions on the Lewis acidity enhancement of the triarylborane. The highly Lewis acidic nature of **2** was further utilized in evaluating the fluoride ion affinity of tris(pentafluorophenyl)borane (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). A fluoride exchange reaction between [**2**F]<sup>-</sup> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> resulted in 15 times higher fluorophilicity for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> than for **2**. The lower Lewis acidity of **2** compared with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was confirmed from its greater cathodic reduction potential.

#### Introduction

Triarylboranes have attracted great interest for applications in various chemical fields due to their high Lewis acidity. For example, they have been utilized as effective cocatalysts in transition metal-catalyzed olefin polymerizations.<sup>1-3</sup> Recently, Stephan and co-workers demonstrated that highly Lewis acidic triarylboranes constitute a key component in frustrated Lewis pairs that promote dihydrogen activation.<sup>4,5</sup> It is also well established that triarylboranes function as selective anion sensors for the detection of harmful anions such as fluoride and cyanide.<sup>6-11</sup> Thus, much effort has been devoted to enhancing the Lewis acidity of triarylboranes for such applications.

To this end, the introduction of electron-withdrawing groups into triarylboranes has been widely exploited. This approach has included the use of perfluorinated arenes,<sup>5,11-13</sup> metal chelation,<sup>9,14</sup> and cationic substituents,<sup>6,8,15-19</sup> all of which were found to be effective in increasing the Lewis acidity of the tri-coordinate boron atom (Chart 1). While perfluorinated boranes are highly Lewis acidic, they lack protecting groups around the boron atom that may greatly limit their use under ambient atmosphere conditions and in Lewis basic media. In contrast, the attachment of electron-withdrawing substituents at the peripheral positions of aryl moieties has been shown to increase Lewis acidity as well as to retain high stability when the boron center has steric protection from *ortho*-methyl groups. This approach has enabled

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<sup>†</sup> CCDC reference numbers 837136 and 837137. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11064k



such boranes to be compatible with Lewis basic media even under aqueous conditions adequate for anion sensing purposes.<sup>6,16–19</sup>

As a new approach to enhance the Lewis acidity of triarylborane, our group recently demonstrated that the introduction of closo-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, so called *o*-carborane<sup>20</sup> into triarylboranes greatly increase their Lewis acidity (I in Chart 1).<sup>21</sup> It was revealed that both the inductive electron withdrawing effect of *o*carborane and the contribution of the carborane cage to LUMO (lowest unoccupied molecular orbital) delocalization give rise to substantial stabilization of the LUMO of boranes. In particular, the increased Lewis acidity resulted in an increase in fluoride ion affinity by two orders of magnitude compared with the fluorinesubstituted borane. This property of enhanced Lewis acidity by the carborane cage led us to consider whether the Lewis acidity of triarylborane could be further increased by the introduction of multiple carboranyl groups. Since we note that the introduction of multiple pentafluorophenyl<sup>12</sup> or cationic aryl groups<sup>16</sup> exhibits

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Scheme 1 The synthesis of triarylborane bearing three o-carborane cages (2) and its fluoride adduct ([2F]-).

apparent additive effects on Lewis acidity enhancement, it was anticipated that multi-carborane substitution might also greatly enhance the Lewis acidity of triarylboranes.

In this report, we synthesized a triarylborane bearing three *o*-carborane cages at peripheral positions of the aryl groups (2) and investigated its fluoride binding properties as a measure of enhanced Lewis acidity. It is also shown for the first time that the highly Lewis acidic nature of 2 could be used to evaluate the fluoride ion affinity of tris(pentafluorophenyl)borane (B( $C_6F_5$ )<sub>3</sub>).

#### **Results and discussion**

#### Synthesis and characterization

The *o*-carborane substituted aryl starting compound, 1-bromo-4-(2-phenyl-*o*-carboran-1-yl)-2,6-dimethylbenzene (1) was obtained from the cage forming reaction between diarylalkyne,  $1a^{22}$  and decaborane (B<sub>10</sub>H<sub>14</sub>) in high yield (85%) (Scheme 1).

spectroscopy and elemental analysis. While <sup>1</sup>H and <sup>13</sup>C NMR spectra show the expected resonances corresponding to the Ar<sup>*CB*</sup> (Ar<sup>*CB*</sup> = 4-(2-Ph-*o*-C<sub>2</sub>B<sub>10</sub>-1-yl)-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>) moiety, <sup>11</sup>B NMR signals detected in the region of  $\delta$  –2 ~ –11 ppm in a 2:4:2:2 ratio confirmed the presence of the *closo*-carborane cage. Furthermore an X-ray diffraction study revealed the molecular structure of **1** (Fig. 1 and Table 1).† From the crystal structure, it can be seen that both aryl ring planes are oriented roughly perpendicular to the plane defined by C6–C1–C2–C11 (81.1° for C<sub>6</sub>H<sub>2</sub>Me<sub>2</sub>Br and 84.5° for C<sub>6</sub>H<sub>5</sub>) as has been similarly observed in other mono- and diarylcarborane compounds, indicating the existence of interactions between the aryl  $\pi$ -systems and the tangential p-orbital on the cage carbon atom.<sup>23,24</sup>

The formation of 1 was characterized by multinuclear NMR

Lithiation of **1** with *n*-BuLi followed by reaction with one third equiv of  $BF_3 \cdot OEt_2$  in ether afforded the triarylborane (2) bearing *o*-carborane moieties at the peripheral positions of each aryl group (45%). The identity of the white crystalline solid

 Table 1
 Crystallographic data and parameters for 1 and 2

Compound	1	$2 \cdot CH_2 Cl_2$
Formula	$C_{16}H_{23}B_{10}Br$	$C_{49}H_{71}B_{31}Cl_2$
Formula weight	403.37	1066.07
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	12.9548(7)	19.882(2)
b/Å	11.2634(6)	14.743 (2)
c/Å	14.4557(7)	23.618(3)
α (°)	90.00	90.00
β (°)	100.072(3)	111.808(6)
γ (°)	90.00	90.00
$V/Å^3$	2076.80(19)	6427.3(12)
Ζ	4	4
$\rho_{\rm c}/{\rm g~cm^{-3}}$	1.290	1.102
$\mu/\text{mm}^{-1}$	1.977	0.135
F(000)	816	2216
T/K	296(2)	296(2)
scan mode	$\phi, \overline{\omega}$	$\phi, \sigma$
hkl range	$-14 \rightarrow +14, -12 \rightarrow +12, -16 \rightarrow +16$	$-18 \rightarrow +20, -15 \rightarrow +15, -24 \rightarrow +24$
measd reflns	18512	36715
unique reflns $[R_{int}]$	3293 [0.0286]	7878 [0.0514]
reflns used for refinement	3293	7878
refined parameters	286	865
$R_1^{a} (I > 2\sigma(I))$	0.0325	0.0794
$wR_2^b$ all data	0.1002	0.2606
GOF on $F^2$	1.001	1.042
$\rho_{\text{fin}} (\text{max/min})/\text{e} \text{\AA}^{-3}$	0.356, -0.333	0.899, -0.565



Fig. 1 The crystal structure of 1 (40% ellipsoid). H atoms are omitted for clarity. Selected bond lengths (Å): C(1)-C(2) 1.738(3), C(1)-C(6) 1.504(3), C(2)-C(11) 1.503(3).

**2** was fully characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray diffraction study. The <sup>1</sup>H NMR spectrum exhibits one methyl and one aromatic CH proton resonance indicating that the three  $Ar^{CB}$  moieties are in the same chemical environment in solution. Similarly, the <sup>13</sup>C NMR spectrum also shows resonances corresponding to a single type of  $Ar^{CB}$ , suggesting that all three  $Ar^{CB}$  moieties are freely rotating in solution. Although the <sup>11</sup>B NMR signal attributable to the trigonal boron atom was not observed despite a prolonged acquisition time, the two broad <sup>11</sup>B NMR signals detected in the region of  $\delta - 2 \sim -10$  ppm confirm the presence of *o*-carboranyl boron atoms. The crystal structure of **2** belonging to the monoclinic space group  $P2_1/c$  (Fig. 2 and Table 1) was unequivocally determined by the X-ray diffraction method.<sup>†</sup>



Fig. 2 The crystal structure of 2 (40% ellipsoid). H atoms and one  $CH_2Cl_2$  molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): B(1)–C(3) 1.573(6), B(1)–C(19) 1.585(6), B(1)–C(35) 1.588(6), C(1)–C(2) 1.736(5), C(17)–C(18) 1.751(5), C(33)–C(34) 1.735(6); C(3)–B(1)–C(19) 120.3(4), C(3)–B(1)–C(35) 119.6(4), C(19)–B(1)–C(35) 120.1(4).

The B(1) boron atom adopts a trigonal planar geometry as judged from summation of the three C–B–C angles ( $\Sigma_{(C-B-C)} = 360^{\circ}$ ). The three *o*-carborane cages are attached at the *para*-positions of the aryl groups, and the six *ortho*-methyl groups surround the central tri-coordinate boron atom. As similarly noted in the structure of **1**, the two aryl rings on the carboranyl

carbon atoms (Ccage) are oriented almost perpendicular to the  $C_{Ar}-C_{cage}-C_{cage}-C_{Ph}$  plane (72.7°/88.6°, 82.4°/88.0°, 87.3°/88.4° for each  $Ar^{CB}$  moiety;  $Ar = 2,6-Me_2-Ph$ ). Although the angles for the Ar ring planes deviate to a certain extent from an ideal 90°, probably due to steric congestion around the B(1)boron center, the deviation for the Ph rings is very small ( $<2^{\circ}$ ) and is even smaller than that observed for  $1 (5.5^{\circ})$ . It was previously shown from molecular orbital calculations for the mono-carborane substituted I that the higher-lying unoccupied orbital (LUMO<sub>+1</sub>) is dominated by the appended Ph group and the cage carbon atoms.<sup>21</sup> Thus, the perpendicular orientation of the Ph rings could reflect an appreciable  $\pi$ -interaction between the Ph group and the cage carbon atom, although the cage carbon atoms contribute to LUMO delocalization at the same time. Similar to other triarylboranes possessing ortho-methyl groups, 2 is air and moisture stable.

Compound 2 was further converted into its fluoride adduct [2F]<sup>-</sup> by reaction with KF in the presence of 18-crown-6 in toluene (Scheme 1). Although a crystal structure of this adduct could not be obtained, the formation of [2F]<sup>-</sup> was fully confirmed by multinuclear NMR spectroscopy. Unlike the neutral compound 2, the <sup>1</sup>H NMR spectrum of [2F]<sup>-</sup> shows two distinct methyl proton resonances as well as two aromatic CH proton resonances for the Ar<sup>CB</sup> moieties, which indicates steric congestion around the boron center. The <sup>11</sup>B NMR spectrum features two broad signals in the region of  $\delta - 5 \sim -13$  ppm indicative of the *o*-carborane cage and also shows a weak peak at around  $\delta + 1.3$  ppm attributable to a tetra-coordinate boron atom. The <sup>19</sup>F NMR signal detected at  $\delta$  -173 ppm is consistent with the formation of a four-coordinate triarylfluoroborate, thus indicating the binding of fluoride to the trigonal boron atom of **2**.

#### Fluoride ion binding properties

To investigate the fluoride ion binding properties of **2**, UV-vis titrations were carried out. The experiment was conducted in a THF/H<sub>2</sub>O (9/1 v/v) medium to compare the binding ability of **2** with that of the previously reported mono-carborane substituted  $\mathbf{L}^{21}$  Compound **2** features a low-energy absorption band at 324 nm (log  $\varepsilon = 4.30$ ) assignable to the dominant  $\pi$ (Mes)–p<sub> $\pi$ </sub>(B) transition in the borane moiety (Fig. 3).<sup>10,13,18,25</sup>

Upon addition of incremental amounts of fluoride, the intensity of the absorption band gradually decreases as a result of fluoride binding to the tri-coordinated boron atom of 2. An estimation from the 1:1 binding isotherm gives a binding constant (K) of  $4.8 \times 10^4$  M<sup>-1</sup> in THF/H<sub>2</sub>O (9/1 v/v). Comparison of this K value with that of I ( $K = 5.0 \times 10^3 \text{ M}^{-1}$ ) under the same conditions reveals that 2 has a 10-fold increase in fluorophilicity. Considering that the binding constant of  $Mes_2B(C_6H_5)$  ( $K = 5.0 \times 10^6 M^{-1}$  in THF) which lacks the two ortho-methyl groups is 10 times larger than that of Mes<sub>3</sub>B ( $K = 3.3 \times 10^5$  M<sup>-1</sup> in THF),<sup>21</sup> this result implies that the introduction of three o-carborane cages into the triarylborane intrinsically enhances the fluorophilicity of the boron atom by more than one order-of-magnitude when compared to the monosubstituted triarylborane. The high fluoride ion affinity of 2 also reflects the increased Lewis acidity of the boron atom, and thus it can be suggested that the multiple carborane substitution has an apparent additive effect on the Lewis acidity enhancement of the triarylborane.



**Fig. 3** Spectral changes in the UV-vis absorption of **2** in THF/H<sub>2</sub>O (9 : 1 v/v) (2.45 × 10<sup>-5</sup> M) upon addition of Bu<sub>4</sub>NF (0 – 2.34 × 10<sup>-4</sup> M). The inset shows the absorbance at 324 nm as a function of [F<sup>-</sup>]. The line corresponds to the binding isotherm calculated with  $K = 4.8 \times 10^4$  M<sup>-1</sup>.

#### Comparison of fluorophilicity of 2 with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

 $B(C_6F_5)_3$  has been regarded as one of the strongest Lewis acidic compounds known.<sup>3,26</sup> Despite its facile conversion into the wellcharacterized  $[FB(C_6F_5)_3]^{-,27,28}$  evaluation of the fluorophilicity of  $B(C_6F_5)_3$  using common fluoride sources has not yet been reported, probably due to its high air and moisture sensitivity. As the Lewis acid 2 was shown to be highly Lewis acidic, we decided to determine the fluorophilicity of  $B(C_6F_5)_3$  by the fluoride exchange reaction with readily accessible  $[2F]^-$ . This experiment may also serve as an estimation of the Lewis acidity of 2 in comparison to the family of highly Lewis acidic fluorinated triarylboranes.<sup>2,3,29</sup> Because of the limited choice of reaction solvent for  $B(C_6F_5)_3$ , which excludes any use of coordinating solvents, the fluoride exchange reaction was carried out in toluene- $d_8$ , a solvent that all of the reaction species were soluble in. After dissolving the prescribed amounts of  $[2F]^-$  and  $B(C_6F_5)_3$  (initial concentration ratio = 1: 0.890), the reaction mixture was monitored by <sup>19</sup>F NMR spectroscopy. As shown in Fig. 4, fluorine signals could be assigned

for all of the species in equilibrium. The fluorine signal at  $\delta$  – 188 ppm was newly observed and it could be assigned to the B– F fluorine of  $[FB(C_6F_5)_3]^{-,27}$  indicating that  $B(C_6F_5)_3$  abstracts a fluoride ion from  $[2F]^-$ .

Most interestingly, even though the intensity of the fluorine signal at  $\delta$  –169 ppm, ascribable to [2F]<sup>-</sup>, was largely reduced, it was greater than the expected intensity that would have remained after complete abstraction by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. This indicates that 2 competes with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> for fluoride ion binding.

From the integral ratio of the two fluorine signals and the equations below (eqns (1) and (2)), the relative fluorophilicity (*K*) of the two compounds was calculated to be 15.0, which indicates that B( $C_6F_5$ )<sub>3</sub> ( $K_{B(C_6F_5)_3}$ ) is 15 times more fluorophilic than **2** ( $K_2$ ).

$$[\mathbf{2}F]^{-} + B(C_6F_5)_3 \xrightarrow{K} \mathbf{2} + [FB(C_6F_5)_3]^{-}$$
(1)

$$K = \frac{[\mathbf{2}][FB(C_6F_5)_3]}{[\mathbf{2}F][B(C_6F_5)_3]} = \frac{K_{B(C_6F_5)_3}}{K_2}$$
(2)

To further elucidate this result, we compared the reduction potentials of **2** and  $B(C_6F_5)_3$ . From the cyclic voltammogram shown in Fig. 5, it can be seen that **2** undergoes two sequential



Fig. 5 Cyclic voltammograms of 2 (1 mM) in DMSO (3 cycles, scan rate =  $50 \text{ mV s}^{-1}$ ).



Fig. 4 A <sup>19</sup>F NMR spectrum for the reaction between  $[2F]^-$  and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene-d<sub>8</sub> (initial concentration ratio = 1:0.890).

reductions, although the second reduction is observed as a weak shoulder at around -1.6 V. Three consecutive measurements reveal that the reduction processes are chemically reversible but electrochemically quasi-reversible.

Since it was previously shown that the LUMO of monosubstituted I mainly resides on the central borane moiety with a contribution from the carborane cage,<sup>21</sup> the first reduction observed for 2 could be ascribed to the reduction at the boron atom of the borane moiety. The second reduction, whose potential value is similar to the reduction range observed for 1-Ar-2-Ph-ocarboranes,<sup>23,30</sup> could be assigned to reduction at the carborane cage of 2. In particular, the first reduction appears at an  $E_{1/2}$  of -1.35 V indicating that 2 is highly Lewis acidic, in accordance with its high fluoride affinity. Although it is known that the reduction potential of  $B(C_6F_5)_3$  cannot be determined experimentally due to the instability of its radical anion, an estimated reduction potential of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was reported to be *ca.* -1.17 V vs. Fc<sup>0/+</sup>.<sup>12</sup> Therefore, comparison of the reduction potential of 2 with that of  $B(C_6F_5)_3$ is consistent with the lower Lewis acidity of 2 demonstrated in the fluoride ion exchange experiment.

#### Conclusions

We prepared and characterized a highly Lewis acidic triarylborane (2) that bears three *o*-carborane cages at the peripheral positions of the aryl groups. It was demonstrated by fluoride ion binding experiment that the introduction of multiple carborane moieties into the triarylborane has an apparent additive effect on the Lewis acidity enhancement of the triarylborane. The highly Lewis acidic nature of **2** was successfully utilized in evaluating the fluoride ion affinity of  $B(C_6F_5)_3$ , and the result was corroborated by comparing the reduction potentials of **2** and  $B(C_6F_5)_3$ . Although less Lewis acidic than  $B(C_6F_5)_3$ , compound **2** constitutes a novel type of highly Lewis acidic triarylborane that also possesses high chemical stability.

#### **Experimental section**

#### **General considerations**

All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous grade solvents (Aldrich) were dried by passing through an activated alumina column and stored over activated molecular sieves (5 Å). Spectrophotometric grade THF (Aldrich) was used for absorption measurements. Commercial reagents were used as obtained without any further purification from Aldrich (BF<sub>3</sub>·OEt<sub>2</sub>, n-BuLi (2.5 M solution in n-hexanes), 18-crown-6, diethyl sulfide, KF, tetra-n-butylammonium fluoride (TBAF)) and Katchem (Decaborane, B10H14). B(C6F5)3 (Strem) was used after recrystallization from hexane. 1a was synthesized in a manner analogous to reported procedures.<sup>22</sup> Deuterated solvents from Cambridge Isotope Laboratories were used. NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for <sup>1</sup>H, 100.62 MHz for <sup>13</sup>C), a Bruker AM 300 spectrometer (96.29 MHz for <sup>11</sup>B) and a Bruker DRX300 spectrometer (282.38 MHz for <sup>19</sup>F) at ambient temperature. Chemical shifts are given in ppm, and are referenced against external Me<sub>4</sub>Si (<sup>1</sup>H, <sup>13</sup>C), BF<sub>3</sub>·OEt<sub>2</sub>  $(^{11}B)$ , and CFCl<sub>3</sub>  $(^{19}F)$ . Elemental analyses were performed on an

EA1110 (FISONS Instruments) by the Environmental Analysis Laboratory at KAIST. UV-vis spectra were recorded on a Jasco V-530 spectrophotometer. Cyclic voltammetry experiments were performed using an AUTOLAB/PGSTAT12 system.

#### Synthesis of 1

To a toluene solution (50 mL) of decaborane ( $B_{10}H_{14}$ , 0.29 g, 2.4 mmol) and 1a (0.57 g, 2.0 mmol) was added an excess of  $Et_2S$  (5 equiv) at room temperature. After heating to reflux, the reaction mixture was stirred for 3 days. The solvent was removed under vacuum and the resulting solid was purified by column chromatography on alumina using toluene as eluent, affording 1 as a white solid (0.69 g, 85%). Recrystallization from EtOAc/MeOH gave single crystals suitable for X-ray structure determination. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.24 (s, 6H, Ar<sup>CB</sup>-CH<sub>3</sub>), 7.07 (s, 2H, Ar<sup>CB</sup>-CH), 7.16 (t, J = 8.0 Hz, 2H, Ph-CH), 7.25 (t, J = 8.0 Hz, 1H, Ph-CH), 7.43 (d, J = 8.0 Hz, 2H, Ph-CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  23.80 (Ar<sup>CB</sup>-CH<sub>3</sub>), 84.33 (CB-C), 85.18 (CB-C), 128.33, 129.12, 129.93, 130.02, 130.26, 130.59, 130.63, 138.32. <sup>11</sup>B NMR (CDCl<sub>3</sub>): δ –2.5 (br s, 2B), -9.2 (br s, 4B), -10.4 (br s, 2B), -11.4 (br s, 2B). Anal. Calcd for C<sub>16</sub>H<sub>23</sub>B<sub>10</sub>Br: C, 47.64; H, 5.75. Found: C, 47.82; H, 5.47.

#### Synthesis of 2

A hexane solution of n-BuLi (2.5 M, 0.55 mL, 1.37 mmol) was added to a solution of 1 (0.50 g, 1.24 mmol) in Et<sub>2</sub>O (20 mL) at -78 °C. After stirring for 30 min, the reaction mixture was allowed to warm to 0 °C and was stirred for another 20 min. The mixture was then recooled to -78 °C, and BF<sub>3</sub>·OEt<sub>2</sub> (0.05 mL, 0.4 mmol) was added via syringe. After stirring for 1 h, the reaction mixture was allowed to warm to room temperature and then stirred overnight. After quenching with saturated aqueous NH<sub>4</sub>Cl (30 mL), the organic layer was separated, and the aqueous layer was extracted with Et<sub>2</sub>O (20 mL). The combined organic layers were dried over MgSO4 and concentrated under reduced pressure. The yellow residue was dissolved in a THF/MeOH mixed solvent. Cooling of the solution afforded 2 as a white crystalline solid (0.18 g, 45%). Single crystals suitable for X-ray diffraction study were grown through cooling a CH<sub>2</sub>Cl<sub>2</sub> solution of **2**. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.44 (s, 18H, Ar<sup>CB</sup>-CH<sub>3</sub>), 6.83 (s, 6H, Ar<sup>CB</sup>-CH), 7.11 (t, J = 8.0 Hz, 6H, Ph-CH), 7.24 (t, J = 8.0 Hz, 3H, Ph-CH), 7.38 (d, J = 8.0 Hz, 6H, Ph-CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  22.61 (Ar<sup>CB</sup>-CH<sub>3</sub>), 84.65 (CB-C), 85.03 (CB-C), 128.05, 129.89, 129.93, 130.65, 130.68, 131.92, 140.18, 146.89 (B-CAr<sup>CB</sup>). <sup>11</sup>B NMR (CDCl<sub>3</sub>):  $\delta$ -2.6 (br s, 6B, CB-B), -10.5 (br s, 24B, CB-B). Anal. Calcd for C<sub>48</sub>H<sub>69</sub>B<sub>31</sub>: C, 58.76; H, 7.09. Found: C, 58.48; H, 7.48.

#### Synthesis of [K·(18-crown-6)][2F]

Toluene (2.0 mL) was added to a mixture of the solids **2** (30 mg, 0.031 mmol), 18-crown-6 (16 mg, 0.061 mmol), and KF (18 mg, 0.031 mmol), and the reaction mixture was stirred at room temperature for 2 h. After removal of excess KF by filtration, the filtrate was dried *in vacuo*. The resulting white solid was recrystallized from THF/*n*-hexane at -20 °C, affording [K·(18-crown-6)][**2**F] (28 mg, 69%) as colorless microcrystals. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>):  $\delta$  1.11 (s, 9H, Ar<sup>CB</sup>-CH<sub>3</sub>), 1.73 (s, 9H, Ar<sup>CB</sup>-CH<sub>3</sub>), 3.60 (s, 24H, *crown*), 6.48 (s, 3H, Ar<sup>CB</sup>-CH), 6.70 (s, 3H, Ar<sup>CB</sup>-CH),

7.13 (t, J = 8.0 Hz, 6H, Ph-C*H*), 7.24 (t, J = 8.0 Hz, 3H, Ph-C*H*), 7.40 (d, J = 8.0 Hz, 6H, Ph-C*H*). <sup>13</sup>C NMR (acetone- $d_6$ ):  $\delta$  20.93 (Ar<sup>CB</sup>-CH<sub>3</sub>), 25.37 (Ar<sup>CB</sup>-CH<sub>3</sub>), 70.86 (crown), 86.63 (CB-C), 89.47 (CB-C), 125.39, 129.00, 129.28, 129.61, 130.08, 130.81, 131.44, 131.63, 141.83, 145.14 (B-C<sub>Mes</sub>). <sup>11</sup>B NMR (THF- $d_8$ ):  $\delta$  +1.3 (br s, *B*-F), -5.0 (br s, 6B, CB-*B*), -12.8 (br s, 24B, CB-*B*). <sup>19</sup>F NMR (THF- $d_8$ ):  $\delta$  -173. Anal. Calcd for C<sub>60</sub>H<sub>93</sub>B<sub>31</sub>FKO<sub>6</sub>: C, 55.28; H, 7.19. Found: C, 55.26; H, 7.35.

#### X-ray structure determination

A specimen of suitable size and quality was coated with Paratone oil and mounted onto a glass capillary. The crystallographic measurements were performed on a Bruker SMART Apex II CCD area detector diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and all nonhydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  using the SHELXTL/PC package. Hydrogen atoms were placed at their geometrically calculated positions and were refined riding on the corresponding carbon atoms with isotropic thermal parameters. The detailed crystallographic data are given in Table 1.

#### UV-vis titration experiments

A solution of **2** (3.0 mL,  $2.45 \times 10^{-5}$  M, THF/H<sub>2</sub>O 9/1 v/v) was titrated with incremental amounts of fluoride anion by the addition of TBAF solution ( $1.58 \times 10^{-2}$  M in THF). The absorption was monitored at  $\lambda_{max} = 324$  nm. In fitting the experimental points, a correction was applied to account for the absorption of [**2**F]<sup>-</sup> at 324 nm. The experimental data obtained were fitted to a 1:1 binding isotherm (Fig. 3).

#### Cyclic voltammetry

Cyclic voltammetry measurements were carried out in DMSO with a three-electrode cell configuration consisting of platinum working and counter electrodes and a Ag/AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN) reference electrode at room temperature. Tetra-*n*-butylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. The reduction potentials were recorded at a scan rate of 50 mV s<sup>-1</sup> and are reported with reference to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple.

#### Acknowledgements

Financial supports from the National Research Foundation of Korea (No. 2010-0008264 for Y. Do and No. 2010-0007796 for M.H. Lee) and the Priority Research Centers Program of the NRF (No. 2009-0093818 for M.H. Lee) funded by the Korea Ministry of Education, Science and Technology are gratefully acknowledged.

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