

## Facile synthesis of bidentate boron Lewis acids by pentafluorobenzene elimination

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### Abstract

The obtained results reveal simple synthetic approach for bidentate boron Lewis acids with the  $-\text{OB}(\text{C}_6\text{F}_5)_2$  acid group and aliphatic or aromatic linkers. Computational results showed comparable FIA for the  $-\text{OB}(\text{C}_6\text{F}_5)_2$  site in boron bidentate Lewis acids relative to initial  $\text{B}(\text{C}_6\text{F}_5)_3$ . The relative Lewis acid strength of  $\text{R}[\text{OB}(\text{C}_6\text{F}_5)_2]_2$  ( $\text{R} = \text{C}_2\text{H}_4$ ,  $p\text{-C}_6\text{H}_4$ ,  $m\text{-C}_6\text{H}_4$ ) was characterized by Gutman-Becket tests. The elimination of pentafluorobenzene by the reaction of  $\text{R-OH}$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  can be used for the synthesis of  $\text{R-OB}(\text{C}_6\text{F}_5)_2$  derivatives and polydentate strong Lewis acids.

**Keywords:** boron Lewis acids, bidentate acids,  $\text{B}(\text{C}_6\text{F}_5)_3$ , structural study, DFT computations

### Introduction

The coordination of bidentate boron Lewis acids was first observed in compounds such as 1,2-bis(dichloroboryl)ethane [1] and 1,8-naphthalenediylbis(dichloroborane) [2]. Recently, bidentate Lewis acids, particularly those based on group 13 elements, have garnered significant interest as catalysts derived from p-block elements. While the catalytic activity of monodentate Lewis acids for organic substrate activation is well established, Maruoka and colleagues demonstrated the enhanced efficiency of a bidentate aluminum-based Lewis acid in the reduction of ketones with  $n\text{-Bu}_3\text{SnH}$ , contrasting with the lower activity of monodentate Lewis acids [3, 4].

Nowadays, bidentate Lewis acids are recognized for their roles in catalyzing inverse-electron-demand Diels-Alder (IEDDA) reactions involving 1,2-diazines and phthalazines [5-9]. Additionally, bi- and polydentate Lewis acids are of interest as chelating agents in host-guest chemistry [10-14]. In a significant breakthrough in 2006, Stephan and collaborators revealed that sterically hindered Lewis acid-base pairs could reversibly activate hydrogen, leading to the concept of Frustrated Lewis Pairs (FLPs) [15], which have attracted considerable attention for their catalytic applications in hydrogenation processes [16-20].

Notably, quantum chemical calculations indicate that bidentate Lewis acids possess an enhanced acidic character compared to their monodentate counterparts. For example, the fluoride ion affinity (FIA) of  $\text{F}_4\text{C}_6(1,2\text{-}(\text{B}(\text{C}_6\text{F}_5)_2)_2)$  ( $523 \text{ kJ mol}^{-1}$  [21] and  $487 \text{ kJ mol}^{-1}$  [22]) exceeds that of  $\text{B}(\text{C}_6\text{F}_5)_3$  ( $452 \text{ kJ mol}^{-1}$  [21] and  $448 \text{ kJ mol}^{-1}$  [22]).

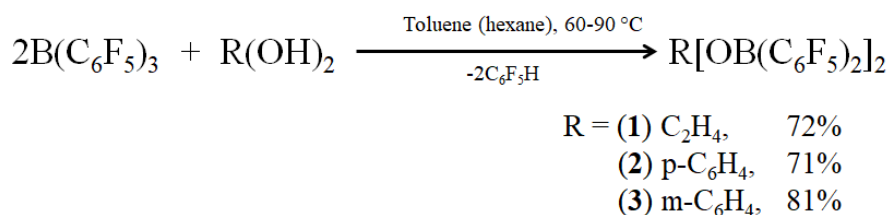
The synthesis of bi- and polydentate Lewis acids typically involves the modification of organic backbones. Various organic derivatives of mercury [2], tin [10, 14, 23] or silicon [5, 7, 8] are employed for the exchange of group 13 elements. The Piers' borane  $\text{HB}(\text{C}_6\text{F}_5)_2$  [24] has been utilized to modify alkenes or alkynes via hydroboration reactions [25, 26]. Notably, the reaction of 6-tert-butyl-2-pyridone with  $\text{HB}(\text{C}_6\text{F}_5)_2$  yields a pyridone-borane complex featuring an  $-\text{OB}(\text{C}_6\text{F}_5)_2$  moiety. Obtained FLP molecule is capable of hydrogen

activation under mild conditions [27]. A more versatile method for preparing bidentate acids involves the reaction of  $\text{AlMe}_3$  with diols [4] or alkynes [13]. Additionally,  $\text{B}(\text{C}_6\text{F}_5)_3$  can react with diols to form new Lewis acids. For instance, the reaction of 9,10-phenanthrenediol with  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene at 110 °C results in the formation of a boronic ester,  $(\text{C}_6\text{F}_5)\text{B}(\text{O}_2\text{C}_{14}\text{H}_8)$ , along with the elimination of  $\text{HC}_6\text{F}_5$  [28]. Similarly, the reaction of 1,4-dihydroxybenzoquinone with  $\text{B}(\text{C}_6\text{F}_5)_3$  in toluene yields a dioxoborocyclic molecule with two  $-\text{OB}(\text{C}_6\text{F}_5)_2$  sites [29]. The formation of the B-O bond in  $\text{B}(\text{C}_6\text{F}_5)_x(\text{OC}_6\text{F}_5)_{3-x}$  ( $x=1-2$ ) observed through the reaction of  $\text{B}(\text{C}_6\text{F}_5)_x(\text{Cl})_{3-x}$  ( $x=1-2$ ) with  $\text{C}_6\text{F}_5\text{OH}$  [30].

The growing interest in strong Lewis acids and FLPs underscores the need for new synthetic strategies. In this study, we report the synthesis of bidentate Lewis acids through the reactions of  $\text{B}(\text{C}_6\text{F}_5)_3$  with diols  $\text{R}(\text{OH})_2$  ( $\text{R} = \text{C}_2\text{H}_4$ ,  $p\text{-C}_6\text{H}_4$ ,  $m\text{-C}_6\text{H}_4$ ). The elimination of pentafluorobenzene presents a valuable synthetic approach for developing bi- and polydentate Lewis acids using readily available reagents.

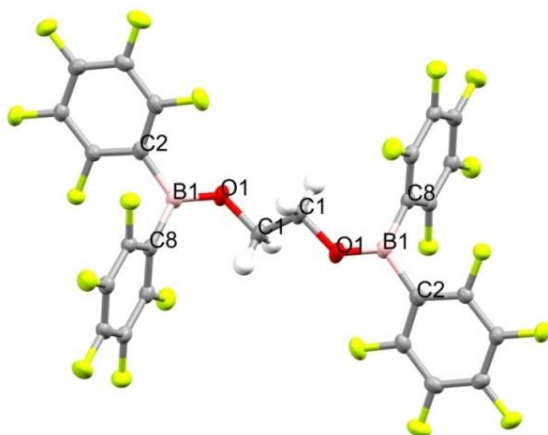
## Results and Discussion

Heating stoichiometric amounts of trispentafluorophenylborane  $\text{B}(\text{C}_6\text{F}_5)_3$  with  $\text{R}(\text{OH})_2$  ( $\text{R} = \text{C}_2\text{H}_4$ ,  $p\text{-C}_6\text{H}_4$ ,  $m\text{-C}_6\text{H}_4$ ) in hexane or toluene solutions leads to the elimination of pentafluorobenzene and the formation of bidentate Lewis acids,  $\text{R}[\text{OB}(\text{C}_6\text{F}_5)_2]_2$ , with good yields (Scheme 1). Reaction completeness is achieved within 5-7 days, as confirmed by  $^1\text{H}$  NMR spectroscopy, which shows a complete disappearance of the  $-\text{OH}$  group signal in the non-volatile residue of the reaction solution. Based on  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{11}\text{B}$  NMR spectroscopic data in  $\text{CDCl}_3$  solution, it is evident that the  $-\text{OH}$  group of diols is replaced by the  $-\text{OB}(\text{C}_6\text{F}_5)_2$  group, forming bidentate boron acids.

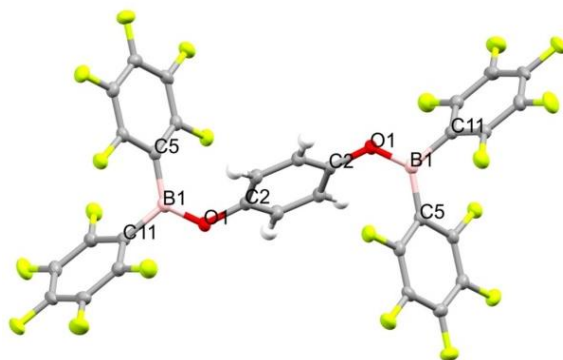


**Scheme 1.** Reaction of trispentafluorophenylborane  $\text{B}(\text{C}_6\text{F}_5)_3$  with  $\text{R}(\text{OH})_2$  ( $\text{R} = \text{C}_2\text{H}_4$ ,  $p\text{-C}_6\text{H}_4$ ,  $m\text{-C}_6\text{H}_4$ ).

Recrystallization of **1-3** from dichloromethane resulted in the formation of colorless needle crystals. Molecular structures for **1** and **2** were determined (Fig. 1-2; SI Table 1S). In both cases, two symmetrical uncoordinated  $-\text{OB}(\text{C}_6\text{F}_5)_2$  groups with distorted trigonal planar coordinated boron atoms were observed. The B-O distances measured 1.335(2) Å for **1** and 1.343(2) Å for **2**, which are smaller than 1.388(8) Å and 1.381(8) Å observed for three-coordinated boron in  $(\text{C}_6\text{F}_5)\text{B}(\text{O}_2\text{C}_{14}\text{H}_8)$  [28] and 1.358(6) Å for  $(\text{C}_6\text{F}_5)_2\text{BOC}_6\text{F}_5$  [30]. For **3**, multiple attempts to establish a crystal structure were unsuccessful due to low crystal quality.



**Figure 1.** Molecular structure of **1** in the crystal. Selected bond lengths /Å and angles /°: B1–O1 1.335(2), O1–C1 1.440(2), B1–C2 1.577(3), B1–C8 1.591(3), C1–C1' 1.509(4), O1–B1–C2 117.07(15), O1–B1–C8 124.73(16), C1–O1–B1 125.39(14), C2–B1–C8 118.15(15).



**Figure 2.** Molecular structure of **2** in the crystal. Selected bond lengths /Å and angles /°: B1–O1 1.343(2), O1–C2 1.3916(18), B1–C5 1.576(2), B1–C11 1.584(2), O1–B1–C5 125.52(14), O1–B1–C11 114.44(13), C2–O1–B1 127.73(12), C5–B1–C11 120.03(13).

The  $^{11}\text{B}$  chemical shifts increase in the order **1** (41.1 ppm) < **3** (41.3 ppm) < **2** (42.0 ppm), indicating a correlation with the relative electron density at the boron atom and suggesting an order of Lewis acidity. The computed fluoride ion affinity (FIA) serves as a valuable descriptor for assessing the Lewis acidity of a compound. FIA values were calculated for the gas phase using isodesmic reactions, referencing the reaction  $\text{COF}_2 + \text{F}^- = \text{COF}_3^-$  [31] for coordination of one or two  $\text{F}^-$  ions (Table 1).

The calculated FIA values for the coordination of one  $\text{F}^-$  increase in the order **1** < **3** < **2**, consistent with the  $^{11}\text{B}$  chemical shifts. The FIA value for **1** (463.2 kJ/mol) is higher than that for  $\text{B}(\text{C}_6\text{F}_5)_3$  (452 kJ/mol [21] and 448 kJ/mol [22]). In contrast, the FIA values for **2** (421.7 kJ/mol) and **3** (426.4 kJ/mol) indicate that the presence of an aromatic ring spacer reduces the FIA compared to  $\text{B}(\text{C}_6\text{F}_5)_3$ . Therefore, the organic backbone in  $\text{R}[\text{OB}(\text{C}_6\text{F}_5)_2]_2$  can be utilized for the modification and tuning of acidity in target bidentate Lewis acids.

It is known that the coordination of a second Lewis acid molecule to a bidentate Lewis base results in the weakening of the donor-acceptor bond. For instance, the donor-acceptor bond strength for pyrazine (pyz) complexes with  $\text{MX}_3$  (where  $\text{M} = \text{Al}, \text{Ga}$ ;  $\text{X} = \text{Cl}, \text{I}$ ) decreases by approximately 25 kJ/mol when comparing  $\text{MX}_3 \cdot \text{pyz} \cdot \text{MX}_3$  complexes to  $\text{MX}_3 \cdot \text{pyz}$ , due to competition for the transferred charge [32]. As bidentate Lewis acids can

accept two Lewis bases, the FIA values for complexes of **1-3** with F<sup>-</sup> were calculated, both in gas phase and taking into account solvation corrections in CH<sub>2</sub>Cl<sub>2</sub>. The use of two Lewis acid sites for **1-3** in a non-chelating mode for fluoride ion coordination results in a significant decrease in gas phase FIA values attributed to the coordination of the second F<sup>-</sup> (Table 1). Computed for CH<sub>2</sub>Cl<sub>2</sub> media, decrease in FIA<sub>2solv</sub> over FIA<sub>1solv</sub> are only 29.4 kJ/mol and 34.1 kJ/mol for **2** and **3** respectively. For the small aliphatic organic backbone of **1** the difference between FIA1 and FIA2 values is significantly higher, than for **2** and **3**. Increased FIA1 value for **1** with most flexible linker attributed to coordination of -OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> to the oxygen atom of the -OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>F<sup>-</sup> group.

To evaluate the relative Lewis acid strength of the acids **1-3**, we have chosen Gutman-Beckett test, as the change in <sup>31</sup>P{H} NMR chemical shift ( $\Delta\delta$ ) between Et<sub>3</sub>PO and its adduct [33]. In this test, a CDCl<sub>3</sub> was used as the solvent. As a reference, the  $\Delta\delta$  value obtained for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is 22.7 ppm. The mono-coordinated **1-3** showed higher  $\Delta\delta$  values, indicating a interaction with Et<sub>3</sub>PO than that observed for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Higher  $\Delta\delta$  values and stronger interaction with Et<sub>3</sub>PO were observed for BOC<sub>6</sub>F<sub>5</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> compared to B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> [30]. According to  $\Delta\delta$  values the complexes of mono-coordinated **1-3** exhibited higher Lewis acidity compared to bi-coordinated Lewis acids **1-3**. These observations are consistent with computational results.

**Table 1.** Lewis acidity of **1-3**. Calculated (M06-2X/def2-TZVP) fluoride ion affinity (FIA) values for **1-3** (FIA1) and for complexes (**1-3**)·F<sup>-</sup> (FIA2) both in gas phase and taking into account solvation corrections in CH<sub>2</sub>Cl<sub>2</sub>. Difference ( $\Delta\delta$ ) between <sup>31</sup>P{H} NMR of Et<sub>3</sub>PO (53.1 ppm) and Lewis acid - Et<sub>3</sub>PO adduct with composition 1:1 and 1:2 in CDCl<sub>3</sub> solution.

LA	Gas phase (M06-2X/def2-TZVP)		CH <sub>2</sub> Cl <sub>2</sub> (M06-2X/def2-TZVP)		<sup>31</sup> P{H} NMR of Et <sub>3</sub> PO (CDCl <sub>3</sub> ), $\Delta\delta$ ppm	
	FIA1	FIA2	FIA <sub>1solv</sub>	FIA <sub>2solv</sub>	1:1	1:2
<b>1</b>	463.2	95.9	329.8	195.4	26.1	22.6
<b>2</b>	421.7	213.9*	303.0	273.6*	26.2	24.4
<b>3</b>	426.4	205.1*	308.1	274.0*	26.1	25.1

\*Calculated values for trans-conformation of Lewis acid adduct

## Conclusion

The elimination of pentafluorobenzene in the reaction of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with diols provides a straightforward synthetic approach to bidentate Lewis acids, yielding favorable results. The described synthetic strategy can also be beneficial for the synthesis of other mono- and polydentate Lewis acids containing -OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> groups. As confirmed by FIA calculations and Gutman-Beckett tests, the -OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> Lewis acid site exhibits acidic properties comparable to those of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. However, the use of both acidic sites in R[OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub> leads to a weakening of the donor-acceptor bond. This was demonstrated by the calculated FIA for complexes of R[OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub>·F<sup>-</sup> (R = C<sub>2</sub>H<sub>4</sub>, p-C<sub>6</sub>H<sub>4</sub>, m-C<sub>6</sub>H<sub>4</sub>) and the comparison of changes in <sup>31</sup>P{H} NMR chemical shift of Et<sub>3</sub>PO for mono- and bi-coordinated Lewis acids **1-3**.

## Experimental

All synthetic procedures and manipulations were carried out in argon-filled glove box Inertlab 2GB or using standard Schlenk technique. Hexane (Vecton, pure) and toluene

(Vecton, pure) were dried over Na/benzophenone. CH<sub>2</sub>Cl<sub>2</sub> (Vecton, pure), CDCl<sub>3</sub> (Carl Roth, 99.8% D) was dried over CaH<sub>2</sub>. All solvents have been distilled, degassed by freezing/thawing under vacuum and stored over 3 Å molecular sieves. Tris(pentafluorophenyl)borane was synthesized by known procedure [34]. 1,2-ethanediol (Vecton, pure) was dried over small amount of sodium, distilled and stored over 3 Å molecular sieves. 1,4-benzenediol (Vecton, pure) and 1,3-benzenediol (Vecton, pure) were purified by vacuum sublimation.

NMR measurements were carried out on Bruker AVANCE 500 spectrometer. TMS, BF<sub>3</sub>·Et<sub>2</sub>O and CFCl<sub>3</sub> were used as external standards. The resonance frequency in <sup>1</sup>H NMR is 500 MHz, in <sup>11</sup>B NMR is 160.39 MHz, in <sup>13</sup>C NMR is 125.7 MHz, in <sup>19</sup>F{<sup>1</sup>H} NMR is 470.38 MHz. IR spectra were obtained on Shimadzu IRPrestige-21 in KBr pellets. X-ray powder diffraction was performed on Bruker D2 Phaser with CuKα irradiation. Samples were placed into the sealed camera in glove box under argon atmosphere.

For single crystal X-ray diffraction experiment, crystals of **1-2** were fixed on a micro mount and placed on a Rigaku «XtaLAB Synergy S» diffractometer using monochromatic radiation source (CuKα radiation, λ = 1.54184). The unit cell parameters were refined by least square techniques. The structure was solved using ShelXT [35] structure solution program by Intrinsic Phasing and refined with the ShelXL [36] incorporated in the Olex2 refinement package [37]. Empirical absorption correction was applied in CrysAlisPro [38] program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the ‘riding’ model approximation, with U<sub>iso</sub>(H) set to 1.2U<sub>eq</sub>(C) and C–H 0.95 Å for the CH groups. Deposition numbers 2288215 (for **1**) and 2288216 (for **2**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe <http://www.ccdc.cam.ac.uk/structures>.

All computations have been carried out using Gaussian 16 program package [39] on the High-Performance Computing cluster of St. Petersburg State University. The geometries of the compounds have been fully optimized in a gas phase using DFT methods with subsequent vibrational analysis: M06-2X method including high-nonlocality functional with double the amount of nonlocal exchange (2X) [40] with all electron def2-TZVP basic set [41]. FIA<sub>solv</sub> were computed for gas phase optimized geometries using SMD solvation model for CH<sub>2</sub>Cl<sub>2</sub> [42, 43].

Detailed experimental information and computation details can be found in the supporting information.

**Synthesis of C<sub>2</sub>H<sub>4</sub>[OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub> (**1**).** Compound **1** was obtained by reaction of tris(pentafluorophenyl)borane (177.4 mg, 0.3465 mmol) and 1,2-ethanediol (10.74 mg, 0.1732 mmol) in n-hexane (15 ml). Suspension was stirred and heated to 60 °C for 7 d in closed vessel. Colorless crystalline material was obtained by evaporation of volatiles in vacuum. Yield 267 mg (72%). Colorless crystals of **1**, suitable for the X-ray analysis, were obtained after recrystallization in CH<sub>2</sub>Cl<sub>2</sub>. NMR: <sup>1</sup>H (CDCl<sub>3</sub>) s 4.47 ppm (C<sub>2</sub>H<sub>4</sub>); <sup>19</sup>F{<sup>1</sup>H} (CDCl<sub>3</sub>) m -160.50 ppm (m-F, C<sub>6</sub>F<sub>5</sub>), t -147.97 ppm (p-F, C<sub>6</sub>F<sub>5</sub>, J=22 Hz), dd -131.59 ppm (o-F, C<sub>6</sub>F<sub>5</sub>, J<sub>1</sub>=10 Hz, J<sub>2</sub>=26 Hz); <sup>11</sup>B (CDCl<sub>3</sub>) br s 41.1 ppm; <sup>13</sup>C{<sup>1</sup>H} (CDCl<sub>3</sub>) s 69.6 ppm (C<sub>2</sub>H<sub>4</sub>); <sup>13</sup>C{<sup>1</sup>H, <sup>19</sup>F} (CDCl<sub>3</sub>) s 69.6 ppm (C<sub>2</sub>H<sub>4</sub>), s 137.6 (C<sub>6</sub>F<sub>5</sub>), s 143.5 (C<sub>6</sub>F<sub>5</sub>), s 147.9 (C<sub>6</sub>F<sub>5</sub>). IR (KBr, cm<sup>-1</sup>): w 552.5, w 577.2, w 635.8, w 657.7, w 683.7, m 703.1, m 744.5, w 761, w

790.1, w 813.1, w 847.4, w 882.5, s 975.5, m 1002, m 1103, w 1122, m 1162, m 1228, m 1293, m 1321, m 1400, s 1477, m 1522, m 1652.

**Synthesis of p-C<sub>6</sub>H<sub>4</sub>[OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub> (2).** Compound **2** was obtained by reaction of tris(pentafluorophenyl)borane (512.0 mg, 1.000 mmol) and 1,4-benzenediol (55.0 mg, 0.500 mmol) in toluene (10 ml). Solution was stirred and heated to 90 °C for 5 d in closed vessel. Colorless crystalline material was obtained by evaporation solution in vacuum. Crystals were washed with hexane and volatiles were removed in vacuum. Yield 284 mg (71%). Colorless crystals of **2**, suitable for the X-ray analysis, were obtained after recrystallization in CH<sub>2</sub>Cl<sub>2</sub>. NMR: <sup>1</sup>H (CDCl<sub>3</sub>) s 6.68 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>19</sup>F{<sup>1</sup>H} (CDCl<sub>3</sub>) m -160.40 ppm (m-F, C<sub>6</sub>F<sub>5</sub>), t -147.02 ppm (p-F, C<sub>6</sub>F<sub>5</sub>, J=17 Hz), dd -130.67 ppm (o-F, C<sub>6</sub>F<sub>5</sub>, J<sub>1</sub>=7 Hz, J<sub>2</sub>=24 Hz); <sup>11</sup>B (CDCl<sub>3</sub>) br s 42.0 ppm; <sup>13</sup>C{H} (CDCl<sub>3</sub>) s 120.5 ppm (C<sub>6</sub>H<sub>4</sub>), dm 137.5 (C<sub>6</sub>F<sub>5</sub>, J=256 Hz), dm 143.7 (C<sub>6</sub>F<sub>5</sub>, J=259 Hz), dm 147.9 (C<sub>6</sub>F<sub>5</sub>, J=247 Hz), s 151.4 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{H, F} (CDCl<sub>3</sub>) s 120.5 ppm (C<sub>6</sub>H<sub>4</sub>), s 137.5 (C<sub>6</sub>F<sub>5</sub>), s 143.7 (C<sub>6</sub>F<sub>5</sub>), s 147.9 (C<sub>6</sub>F<sub>5</sub>), s 151.4 ppm (C<sub>6</sub>H<sub>4</sub>). IR (KBr, cm<sup>-1</sup>): w 687, m 756, m 841, w 874, s 972, w 1016, m 1097, m 1166, m 1190, w 1297, m 1321, m 1369, m 1393, s 1477, w 1504, m 1525, w 1560, m 1653.

**Synthesis of m-C<sub>6</sub>H<sub>4</sub>[OB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sub>2</sub> (3).** Compound **3** was obtained by reaction of tris(pentafluorophenyl)borane (512.0 mg, 1.000 mmol) and 1,3-benzenediol (55.0 mg, 0.500 mmol) in toluene (10 ml). Solution was stirred and heated to 90 °C for 5 d in closed vessel. Colorless crystalline material was obtained by evaporation solution in vacuum. Crystals were washed with hexane and volatiles were removed in vacuum. Yield 324 mg (81%). According to NMR, sample contains minor impurities that can be assigned to partially reacted 1,3-benzenediol and unidentified species. See SI for details. NMR: <sup>1</sup>H (CDCl<sub>3</sub>) dd 6.69 ppm (2H, C<sub>6</sub>H<sub>4</sub>, J<sub>1</sub>=8 Hz, J<sub>2</sub>=2 Hz), t 6.75 ppm (1H, C<sub>6</sub>H<sub>4</sub>, J=2 Hz), t 7.15 ppm (1H, C<sub>6</sub>H<sub>4</sub>, J=8 Hz); <sup>19</sup>F{<sup>1</sup>H} (CDCl<sub>3</sub>) m -160.34 ppm (m-F, C<sub>6</sub>F<sub>5</sub>), t -146.85 ppm (p-F, C<sub>6</sub>F<sub>5</sub>, J=19 Hz), dd -130.83 ppm (o-F, C<sub>6</sub>F<sub>5</sub>, J<sub>1</sub>=7 Hz, J<sub>2</sub>=25 Hz); <sup>11</sup>B (CDCl<sub>3</sub>) br s 41.3 ppm; <sup>13</sup>C{H} (CDCl<sub>3</sub>) s 111.4 ppm (C<sub>6</sub>H<sub>4</sub>), s 116.2 ppm (C<sub>6</sub>H<sub>4</sub>), s 130.7 ppm (C<sub>6</sub>H<sub>4</sub>), dm 137.5 (C<sub>6</sub>F<sub>5</sub>, J=256 Hz), dm 143.8 (C<sub>6</sub>F<sub>5</sub>, J=252 Hz), dm 148.0 (C<sub>6</sub>F<sub>5</sub>, J=249 Hz), s 154.9 ppm (C<sub>6</sub>H<sub>4</sub>); <sup>13</sup>C{H, F} (CDCl<sub>3</sub>) s 111.4 ppm (C<sub>6</sub>H<sub>4</sub>), s 116.2 ppm (C<sub>6</sub>H<sub>4</sub>), s 130.7 ppm (C<sub>6</sub>H<sub>4</sub>), s 137.5 (C<sub>6</sub>F<sub>5</sub>), s 143.8 (C<sub>6</sub>F<sub>5</sub>), s 148.0 (C<sub>6</sub>F<sub>5</sub>), s 154.9 ppm (C<sub>6</sub>H<sub>4</sub>). IR (KBr, cm<sup>-1</sup>): w 683, w 750, w 788, w 858, s 977, m 1097, m 1168, w 1293, m 1320, m 1346, m 1398, s 1478, m 1525, w 1605, m 1652.

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