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Bifunctional Perfluoroaryl Boranes: Synthesis and Coordination Chemistry with Neutral Lewis Base Donors

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A practical synthetic route for the preparation of the known bifunctional perfluoroaryldiborane C_6F_4-1,2-$[B(C_6F_5)_2]_2$, **1**, and the new diborane C_6F_4-1,2-$[B(C_{12}F_8)]_2$, **2**, that circumvents the use of toxic mercury reagents has been developed. Key intermediates and **2** have been fully characterized in solution and the solid state. Solution and structural investigations of their MeCN and THF adducts have shown that **2** is a superior Lewis acid to **1**, primarily owing to the reduction in steric pressure afforded by the planar 9-borafluorene rings in **2** versus the freely rotating set of pentafluorophenyl rings in **1**. The two compounds bind Lewis bases via differing coordination modes, as demonstrated by the solid-state structures of the Lewis base adducts **1·MeCN**, **2·THF**, and **2·MeCN**. Solution studies suggest that bis Lewis base adducts are also accessible; the structures of two examples (**1·(MeCN)$_2$** and **2·(THF)$_2$**) have been determined, and their role in the dynamic solution behavior of these systems is discussed.

Introduction

Perfluoroaryl boranes are an important class of Lewis acids[1] with a variety of applications as catalysts for organic transformations[1,2] polymer synthesis[3] and cocatalysts in olefin polymerization processes.[4] They are generally comparable in terms of Lewis acid strength to the prototypical haloborane Lewis acids, but exhibit a high degree of tolerance toward protic Lewis bases such as alcohols and water. The perfluorination also results in extensive charge delocalization in borate anions formed from these Lewis acids, such that perfluoroarylborate anions are among the most weakly coordinating anions available to synthetic chemists.[5]

To extend the chemistry of this class of Lewis acids and explore the effect of having multiple perfluoroaryl Lewis acid centers in a molecular framework, we and others[6] have prepared bi- and multifunctional[7] perfluoroaryl boranes where the borane centers are aligned in both chelating and nonchelating arrays.[1,8] Our interest has focused mainly on chelating diboranes bridged by the *ortho*-C_6F_4 moiety, and in particular the simplest chelating diborane based on $B(C_6F_5)_3$, C_6F_4-1,2-$[B(C_6F_5)_2]_2$, **1**.[9] This compound is able to activate simple group 4 metallocene dialkyls,[10] chelate a variety of anions to form new classes of weakly coordinating anions,[11] and initiate cationic polymerization of isobutylene in hydrocarbon[12] and aqueous suspension media.[13] In the latter application in particular, the chelating array of two Lewis acid centers appears to be crucial for the observed efficacy of this chemistry, since nonchelating diboranes or monofunctional boranes do not serve as effective polymerization initiators under these unusual conditions.

Given the several potential applications for **1**, we became interested in both improved synthetic routes to the compound and modifications to **1** so as to explore structure−activity relationships for various chelating perfluoroaryl diboranes. Our original synthesis of **1** utilized the known mercury trimer $[1,2\text{-}Hg(C_6F_4)]_3$[14] as a *o*-$C_6F_4$ synthon for installing the borane centers, and while effective, for larger scale syntheses use of this reagent is not convenient nor desirable from an environmental perspective. We have therefore developed a “mercury-free” route to **1**,[15] which can also be used to prepare a new member of this family of diboranes, **2**, which is based on a bis-9-borafluorene framework. Constraining the boron centers into a 9-borafluorene heterocycle renders them more sterically

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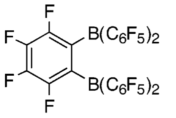
accessible, while sacrificing little in terms of the inherent Lewis acid strength of the boron.[16] In addition to the synthetic chemistry described, we compare the coordination chemistry of **1** and **2** with the neutral Lewis bases acetonitrile and THF.



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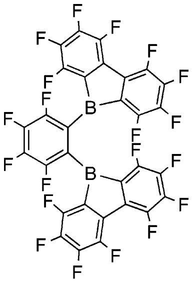

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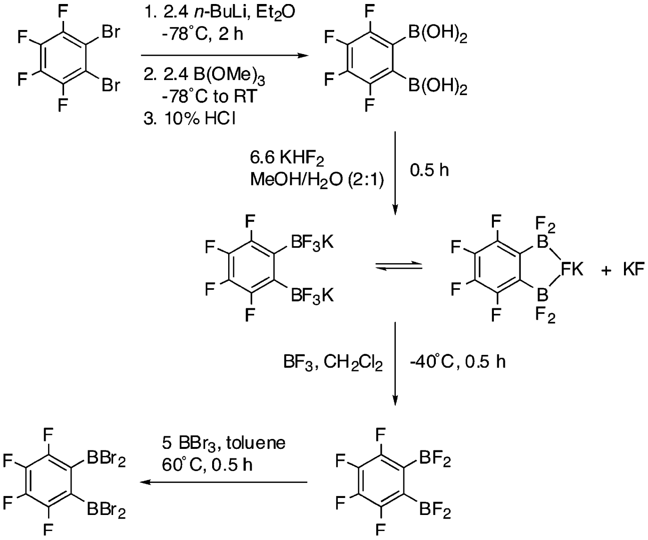
Results and Discussion

Synthesis. The syntheses of both **1** and **2** rely on the key bis-dibromoboryl intermediate C_6F_4-1,2-$(BBr_2)_2$, which was originally prepared in 51% yield via reaction of [1,2-Hg(C_6F_4)]$_3$ with BBr_3.[8] Given that the preparation of the mercury trimer via thermal decarboxylation of [1,2-Hg($O_2CC_6F_4$)]$_3$ occurs in modest yields, and the fact that organomercury compounds are toxic,[17] we sought an alternative route to this compound. The protocol that has been developed is outlined in Scheme 1 and starts from commercially available 1,2-dibromotetrafluorobenzene; installation of the dihalo boryl groups takes advantage of some boron functional group manipulations recently reported by Vedejs[18] and Fröhn.[19] While the route contains a few more steps, each step is convenient and high yielding, resulting in a protocol that, in terms of overall yield, is superior to the mercury trimer route and avoids the use of organomercurials.

Scheme 1



Dilithiation of 1,2-$Br_2C_6F_4$ is accomplished with 2.4 equiv of ^nBuLi at −78 °C in Et_2O or THF. *WARNING: this solution should not be warmed above this temperature in the absence of an electrophile*. Once formed, the dilithio derivative may be quenched with $B(OMe)_3$, and hydrolytic workup leads to the crude bis-boronic acid product. Subsequent fractional recrystallization from hot water afforded C_6F_4-1,2-[B(OH)$_2$]$_2$ as an off-white powder in greater than 85% yield. Both ^{19}F and ^{11}B NMR spectroscopy indicated that this material was >95% pure,[20] so it was used without further purification.

A methanol solution of the bis-boronic acid was treated with an aqueous solution of KHF_2 to give a solid comprised of a mixture of $[K]_2^+[C_6F_4\text{-}1,2\text{-}(BF_3)_2]^{2-}$, monoanionic $[K]^+\{C_6F_4\text{-}1,2\text{-}[(BF_2)_2(\mu\text{-}F)]\}^-$, and KF in 65% overall yield based on mass balance. As shown in Scheme 1, the two fluoroborate species are in equilibrium and the position of the equilibrium is dependent to some degree on the amount of water present. In solution, both species are observable and each has a diagnostic ^{19}F NMR spectrum in CD_3CN/D_2O. $[K]_2^+[C_6F_4\text{-}1,2\text{-}(BF_3)_2]^{2-}$ exhibits three signals at −141.2, −162.9, and −146.2 ppm in a 1:1:3 ratio, while $[K]^+\{C_6F_4\text{-}1,2\text{-}[(BF_2)_2(\mu\text{-}F)]\}^-$ shows slightly shifted signals for the C_6F_4 fluorines, and two other signals at −143.4 and −139.7 ppm in a 4:1 ratio for the terminal and bridging fluorines, respectively. Although $C_6F_5BF_3K$ has been observed to condense in an intermolecular sense to give observable amounts of $(C_6F_5)_2BF_2K$ and KF,[19] only intramolecular condensation is observed for $[K]_2^+[C_6F_4\text{-}1,2\text{-}(BF_3)_2]^{2-}$.

Pure samples of $[K]_2^+[C_6F_4\text{-}1,2\text{-}(BF_3)_2]^{2-}$ may be obtained by crystallization from concentrated solutions of CH_3CN, while crystals of the μ-fluoride were obtained from CH_3CN/H_2O solutions. The molecular structures of both compounds have been determined by X-ray crystallography and are shown in Figure 1 along with selected metrical parameters.[21] While both compounds exhibit extensive intermolecular contacts in the extended structure, with many K···F contacts under 3.25 Å, from a synthetic perspective, the structures illustrate conclusively that the *ortho*-diboryl groups have been installed successfully. For $[K]_2^+[C_6F_4\text{-}1,2\text{-}(BF_3)_2]^{2-}$, Figure 1a, the network of K···F contacts distorts the metrical parameters within the molecule somewhat, while in the condensed compound $[K]^+\{C_6F_4\text{-}1,2\text{-}[(BF_2)_2(\mu\text{-}F)]\}^-$, Figure 1b, the molecular structure is symmetrical since the potassium ions link adjacent molecules in the extended structure.

Both of these air- and moisture-stable potassium perfluoroaryltrifluoroborate salts can be readily converted to the bis-difluoroborane, C_6F_4-1,2-$(BF_2)_2$, in 84% yield by treatment of a CH_2Cl_2 solution with a BF_3(g) atmosphere at −40 °C for 30 min. This compound may be isolated as an air- and moisture-sensitive oil after removal of the KBF_4 byproduct and the solvent volatiles, taking care not to pump away the product. This compound, which is an interesting bifunctional diborane in its own right, unfortunately cannot be converted into compound **1** conveniently using copper,[22] zinc,[23] or tin[24] $-C_6F_5$ transfer agents. However, halogen exchange by reaction with a 5-fold excess of BBr_3 with the bis-difluoroborane at 50 °C for 30 min cleanly afforded the known dibromo analogue C_6F_4-1,2-$(BBr_2)_2$.

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(21) Molecular structures are depicted using Crystalmaker; ORTEP diagrams of crystallographically characterized molecules can be found in the Supporting Information.

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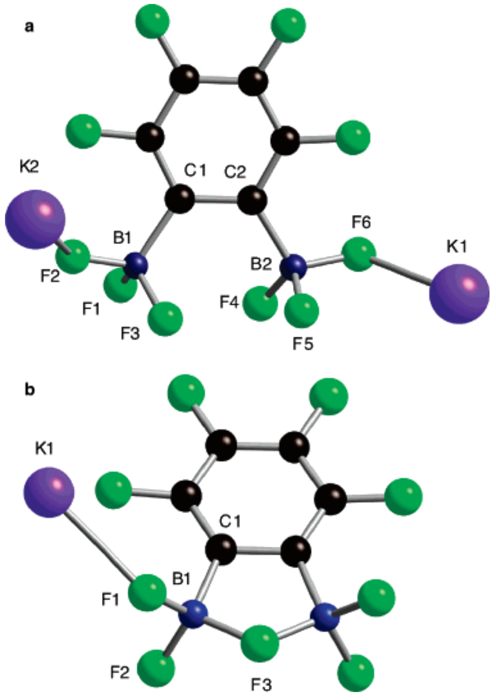


Figure 1. (a) Crystalmaker depiction of the molecular structure of a monomeric unit of $[K]^+_2[C_6F_5\text{-}1,2\text{-}(BF_3)_2]^{2-}$. Selected bond lengths (Å): K(1)···F(6), 2.963(14); K(1)···F(4), 3.017(17); K(2)···F(4), 3.170(29); K(2)···F(1), 2.607(20); C(1)−B(1), 1.631(6); C(2)−B(2), 1.634(7); B(1)−F(1), 1.415(3); B(1)−F(2), 1.419(8); B(1)−F(3), 1.406(14); B(2)−F(4), 1.419(4); B(2)−F(5), 1.413(18); B(2)−F(6), 1.417(4); B(1)···B(2), 3.201(11); K(1)···K(2), 4.550(9). Selected bond angles (deg): B(2)−C(2)−C(1), 122.1(2); B(1)−C(1)−C(2), 122.7(2). Selected dihedral angle (deg): B(2)−C(2)−C(1)−B(1), 11.07(37). (b) Crystalmaker depiction of the molecular structure of a monomeric unit of $[K]^+\{C_6F_4\text{-}1,2\text{-}[(BF_2)_2(\mu\text{-}F)]\}^-$. Selected bond lengths (Å): K(1)···F(1), 2.660(2); B(1)−F(1), 1.427(4); B(1)−F(2), 1.405(4); B(1)−F(3), 1.487(4); B(1)−C(1), 1.610(4); C(1)−C(1′), 1.409(5). Selected bond angles (deg): B(1)−F(3)−B(1′), 113.2(3); B(1)−C(1)−C(1′), 109.5(2). Selected dihedral angles (deg): B(1)−C(1)−C(1′)−B(1′), 0.0; B(1)−F(3)−B(1′)−C(1′), −14.1(4).

(Unfortunately, conversion of $[K]_2^+[C_6F_4\text{-}1,2\text{-}(BF_3)_2]^{2-}$ directly into $C_6F_4\text{-}1,2\text{-}(BBr_2)_2$ by treatment with BBr_3 was not successful.) Given the relatively mild reaction conditions employed, condensation to the 9,10-diboraanthracene $C_{12}F_8\text{-}9,10\text{-}(\mu\text{-}BBr)_2$, which is a complication in the conversion of the mercury trimer to $C_6F_4\text{-}1,2\text{-}(BBr_2)_2$ using BBr_3, is not observed. Thus, this key bis-dibromoboryl compound is obtained in 41% overall yield from $1,2\text{-}Br_2C_6F_4$ in four convenient steps.

Perfluoroaryl diboranes **1** and **2** are readily prepared as shown in Scheme 2. The synthesis of **1** from $C_6F_4\text{-}1,2\text{-}(BBr_2)_2$ and $Zn(C_6F_5)_2$ has been reported previously.[9] The preparation of **2**, a new diborane Lewis acid, utilizes the organotin reagent $Me_2SnC_{12}F_8$[24] to install the $C_{12}F_8$ unit via tin−boron exchange.[16] Although relatively forcing conditions are required, the reaction is clean and high yielding. The ^{19}F NMR spectrum of **2** shows a six-line pattern consistent with a molecule having C_{2v} symmetry. Like its monofunctional counterpart,[16] **2** is deep orange in the solid and in dry, noncoordinating solvents due to the presence of a low-energy $\pi-\pi$ transition. The UV−vis spectrum (λ_{max} (hexanes) = 425 nm, $\epsilon = 5.9 \times 10^2$ L mol^{-1} cm^{-1}) is essentially identical to that of $(F_5C_6)B(C_{12}F_8)$, indicating the two chromophores are not coupled and offer similar electronic environments. The UV−vis properties of boroles have been used as the basis for sensing fluoride ions.[25]

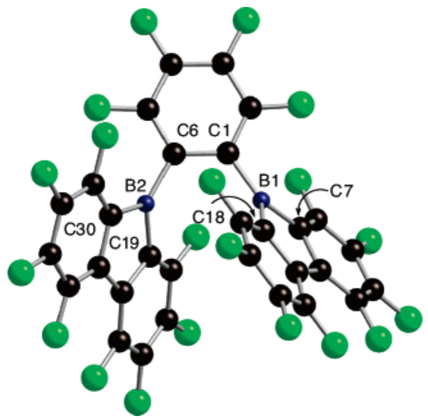
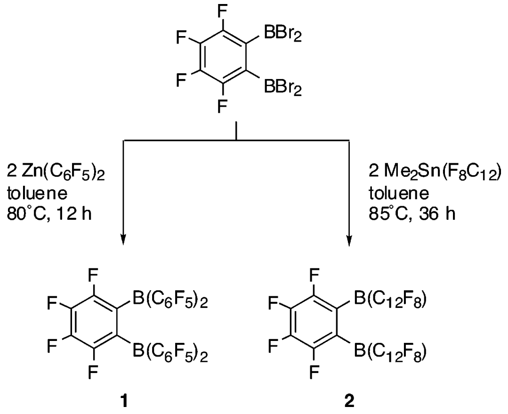


Figure 2. Crystalmaker depiction of the molecular structure of **2**. Selected bond distances (Å): B(1)−C(1), 1.563(4); B(1)−C(7), 1.558(4); B(1)−C(18), 1.557(4); B(2)−C(6), 1.567(4); B(2)−C(19), 1.564(4); B(2)−C(30), 1.557(4). Selected bond angles (deg): C(1)−B(1)−C(7), 129.7(2); C(1)−B(1)−C(18), 126.7(2); C(7)−B(1)−C(18), 103.6(2); C(6)−B(2)−C(19), 127.5(2); C(6)−B(2)−C(30), 129.1(2); C(19)−B(2)−C(30). Selected dihedral angles (deg): B(1)−C(1)−C(6)−B(2) 6.48(2).

Scheme 2



X-ray quality crystals of **2** were obtained from cold toluene solutions, and a view of the molecular structure is shown in Figure 2. The metrical parameters of the two 9-borafluorene groups are essentially identical to those observed in $(F_5C_6)B(C_{12}F_8)$.[16] The bond lengths between the *ortho*-phenylene linker and the boron atoms (B(1)−C(1) = 1.563(2) Å, B(2)−C(6) = 1.567(2) Å) are comparable with those in **1**.[9] As in **1**, the C(1)−C(6) distance of 1.425(1) Å is elongated to a small degree over the remaining C−C linkages (average C−C = 1.379(2) Å).[6b] There are, however, some striking differences in the structures of **1** and **2**, due to the planarity enforced by the 9-borafluorene framework. For example, the B(1)−C(1)−C(6)−B(2) torsion angle in **2** (6.78(1)°) is significantly lower than observed for **1** (19.9(2)°). As a result, the B···B distance in **2** is smaller (3.056 Å) than that observed in **1** (3.138 Å).[9] Although all boron centers in both of these systems are essentially planar ($\Sigma_{C-B-C} = 360°$), the angle between the trigonal planes of the individual boron atoms of **2** is ∼14° (cf. ∼39° for **1**). The borafluorene groups form a dihedral angle of ∼57−61° with respect to the backbone C_6F_4 plane. The reduced distortions in **2** as opposed to **1** reflect the greater steric pressures in **1** since the C_6F_5 rings are free to rotate and occupy more volumetric space in the B···B region; the aryl substituents in **2** are constrained into planes that coexist

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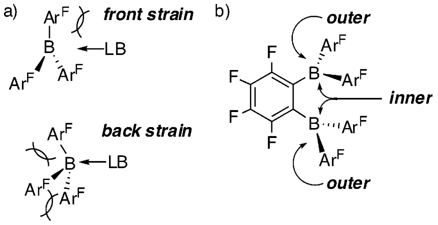

Figure 3. (a) Front and back strain in Lewis base/perfluoroarylborane adducts. (b) Inner and outer coordination to bifunctional Lewis acids **1** and **2**.

in the *ortho* positions more easily. As discussed below, this effect has a significant impact on the relative Lewis acidity of **2** versus **1**.

Factors Affecting Lewis Acidity. The Lewis acid strength of monofunctional perfluoroaryl boranes is influenced by several factors.[1] The fluorination of the aryl groups is a key electronic influence that serves to increase the Lewis acidity of the boron center by lowering the energy of the boron-based LUMO as the extent of fluorination increases.[26] The lower degree of fluorination in the borole function, as opposed to the $B(C_6F_5)_2$ analogue, is compensated by the antiaromatic nature[27] of the five-membered BC_4 ring, resulting in comparable Lewis acid strength despite the fewer number of electron-withdrawing fluorines present. Steric factors, which include front strain and back strain[28] engendered upon complexation of a Lewis base with the boron center, are illustrated in Figure 3a. Both of these effects are likely alleviated in the 9-borafluorene Lewis acid $(F_5C_6)B(C_{12}F_8)$ relative to $B(C_6F_5)_3$ due to the planar nature of the $-B(C_{12}F_8)$ moiety. Back strain is also related to the preorganization energy required to pyramidalize the boron center from trigonal planar to pyramidal geometry, a process that requires less energy in the borole Lewis acids since the C$-$B$-$C angle of the five-membered ring is closer to the ideal tetrahedral value than the trigonal planar value.

For the bifunctional Lewis acids **1** and **2**, consideration of these factors must take into account the presence of the two Lewis acid centers, which serves to delineate the two faces of each borane center, which are likely unable to interconvert via rotation about the C$-$B bonds, as shown in Figure 3b. Coordination of a single Lewis base thus can occur on the outer face of one of the borons, or by approach on a vector into the chelation pocket, resulting in coordination to the inner face. Coordination of one Lewis base molecule, whether to the outer or inner face, results in a Lewis acid of different structure; so the ability to coordinate a second Lewis base will be dependent upon the properties of the monoadducts. It can be appreciated that, relative to their monofunctional counterparts, these bifunctional Lewis acids experience increased front strain forces for approach of a Lewis base to the inner face and more severe back strain for approach from the outer face. Thus, while electronically they should be comparable (or even more electron deficient) to monofunctional systems, they are sterically more constrained and, in the absence of chelation, are not expected to be competitive with the monofunctional systems for simple, nonchelatable Lewis bases. With this discussion as a backdrop, the following compares the Lewis acid properties of **1** and **2** using the Lewis bases THF and MeCN, both of which are known to form stable adducts with the monofunctional analogues. These bases are of similar strength (as judged by their proton affinities[29]) but are sterically somewhat differentiated.

Reactions with MeCN and THF. Methylene chloride solutions of diborane **1** (~0.03 M) were treated with 1 equiv of either THF or MeCN and studied by multinuclear NMR spectroscopy. In the case of THF, minimal interaction between **1** and THF was observed, as judged by the minor perturbations to the room-temperature ^{19}F NMR spectrum of **1·THF** versus **1** in the absence of THF. Cooling the sample resulted in some broadening of the spectrum and shifting of the positions of the resonances, indicative of reversible formation of a labile adduct. Dissolution of **1** in THF, followed by removal of the solvent in vacuo, gave ^{19}F NMR spectra of unligated **1**, demonstrating that the adduct, if present, is quite weak. Using 1 equiv of the more rod-like Lewis base MeCN did, however, result in an observable, isolable adduct. The signal for the CH_3CN protons shifted to 2.47 from 2.10 ppm, while in the ^{19}F NMR spectrum, all the signals shift upfield of those seen for free **1**. At room temperature, rapid exchange of MeCN between boron centers in **1** is implied by the retention of the five-line pattern in these spectra; cooling the sample results in coalescence behavior, and at -40 °C, the number of signals is reflective of the disruption of C_{2v} symmetry expected upon ligation of MeCN to one boron center. As the number of equivalents of acetonitrile is raised to 3, the resonance for the *para*-fluorines of the C_6F_5 groups in the room-temperature spectra gradually shifts upfield from -149 to -152 ppm, indicating a shift in this dynamic system toward the adduct.[30] Two signals, one for neutral, four-coordinate boron at -7.6 ppm and one for three-coordinate boron at 41.7 ppm, were observed in the ^{11}B NMR spectrum at -40 °C, consistent with this picture. Removal of solvent from solutions of **1·MeCN** and redissolution indicated that the acetonitrile is retained in the solid state (see below).

The behavior of diborole **2** under similar treatment indicates it is a significantly stronger Lewis acid than **1** toward these two Lewis bases. Treatment of **2** with *exactly* 1 equiv (or a slight deficiency) of either THF or MeCN results in a lowering of symmetry from C_{2v} to C_s as demonstrated by the presence of two sets of four signals for the complexed and uncomplexed $-B(C_{12}F_8)$ rings and four separate signals for the inequivalent C_6F_4 backbone fluorines in the room-temperature ^{19}F NMR spectra. The ^{11}B NMR spectra are also consistent with formation of **2·THF** and **2·MeCN**; furthermore, solutions of these adducts retain a light green color, indicative of a base-free 9-borafluorene function. These observations indicate that, unlike the situation in **1·MeCN**, exchange of the coordinated Lewis base from one center to the other (by whatever mechanism) is slow in the monoadducts involving **2**. However, addition of even a slight (10%) excess of Lewis base to solutions of **2·LB** results in symmetrization of the ^{19}F NMR spectrum to one reflective of rapid exchange between two C_s symmetric structures. Thus, while **2·LB** compounds are nonlabile at room temperature, exchange of LB from one borole center to the other is catalyzed by free Lewis base. As the equivalency of Lewis base is

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[26] (a) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841. (b) Rauk, A. *Orbital Interaction Theory of Organic Chemistry*, 2nd ed.; Wiley: New York, 2001.

[27] Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379.

[28] Brown, H. C. *J. Chem. Soc.* **1956**, 1248.

[29] They have similar proton affinities: http://webbook.nist.gov/chemistry/pa-ser.html.

[30] (a) The $\Delta_{m,p}$ value has been used as an indication of the coordination environment at boron in C_6F_5-substituted boranes.[1] With 1 equiv of MeCN, the value is 13.1 ppm, which reaches a minimum of ~10.5 ppm, which is substantially lower than the values of ~18 ppm observed for base-free, three-coordinate boron centers, but not as low as those observed for fully ligated systems such as $MeCN{\cdot}B(C_6F_5)_3$ ($\Delta_{m,p} = 8.4$ ppm).[32b] Thus, these observations point toward a solution equilibrium between **1** and **1·MeCN** at equimolar amounts, with formation of low amounts of **1·(MeCN)₂** at higher equivalencies of base.

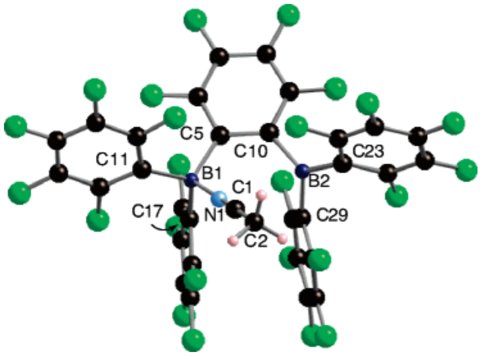

Figure 4. Crystalmaker depiction of the molecular structure of **1·MeCN**.

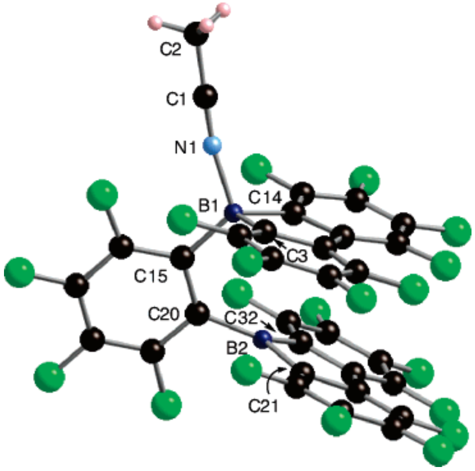

Figure 5. Crystalmaker depiction of the molecular structure of **2·MeCN**.

increased to 3.0 equiv, the ^{19}F NMR spectrum sharpens somewhat, but remains averaged with little change in the positions of the signals.

Although **2** is clearly a more powerful Lewis acid toward THF, the greater affinity of **2** for MeCN in comparison to **1** was demonstrated semiquantitatively by a competition experiment. Mixtures of **1**, **2**, and MeCN (1:1:1) or isolated **1·MeCN** and **2** (1:1) resulted in solutions that were, within the detection limits of ^{19}F NMR spectroscopy, exclusively free **1** and **2·MeCN**, placing a lower limit on the K_{eq} for the equilibrium shown in eq 1 at ~2500. In the monofunctional analogues of **1**

$$\mathbf{1\cdot MeCN} + \mathbf{2} \rightleftharpoons \mathbf{1} + \mathbf{2\cdot MeCN} \qquad (1)$$

and **2** ($B(C_6F_5)_3$ and $(F_5C_6)B(C_{12}F_8)$, respectively) a competition experiment with MeCN had a $K_{eq} = 1.30(3)$ at 25 °C in favor of the 9-borafluorene adduct.[16]

A rationale for the greater LA strength of **2** toward THF and MeCN is afforded by the molecular structures of the monoadducts **1·MeCN** and **2·MeCN**,[31] shown in Figures 4 and 5, respectively; comparative selected metrical data are given in Table 1. Metrical parameters associated with the coordinated nitrile moiety are in general agreement with data for monofunctional $B(C_6F_5)_3$[32] and $(C_6F_5)BC_{12}F_8$[33] adducts of nitriles and will not be discussed in detail here. That **2** coordinates MeCN more strongly than **1** is indicated by the shorter B(1)−N(1) distance in **2·MeCN** and the greater degree of pyramidalization

Table 1. Selected Metrical Data for 1·MeCN and 2·MeCN

1·MeCN		**2·MeCN**	
Selected Bond Lengths (Å)			
B(1)−C(5)	1.658(7)	B(1)−C(15)	1.603(9)
B(1)−C(11)	1.647(8)	B(1)−C(3)	1.626(8)
B(1)−C(17)	1.656(8)	B(1)−C(14)	1.619(9)
B(1)−N(1)	1.607(6)	B(1)−N(1)	1.592(8)
B(2)−C(10)	1.571(6)	B(2)−C(20)	1.567(9)
B(2)−C(23)	1.583(8)	B(2)−C(21)	1.573(9)
B(2)−C(29)	1.602(7)	B(2)−C(32)	1.578(9)
C(5)−C(10)	1.451(7)	C(15)−C(20)	1.425(8)
N(1)−C(1)	1.155(5)	N(1)−C(1)	1.138(7)
C(1)−C(2)	1.442(7)	C(1)−C(2)	1.441(9)
B(1)···B(2)	3.321	B(1)···B(2)	3.174
Selected Bond Angles (deg)			
B(1)−N(1)−C(1)	170.6(4)	B(1)−N(1)−C(1)	170.1(6)
N(1)−C(1)−C(2)	179.2(5)	N(1)−C(1)−C(2)	177.2(6)
C(11)−B(1)−C(5)[a]	114.3(4)	C(3)−B(1)−C(14)[c]	97.9(5)
C(17)−B(1)−C(5)	112.9(4)	C(14)−B(1)−C(15)	115.0(5)
C(11)−B(1)−C(17)	113.6(4)	C(3)−B(1)−C(15)	113.9(5)
C(10)−B(2)−C(23)[b]	118.4(4)	C(21)−B(2)−C(32)[d]	102.2(5)
C(10)−B(2)−C(29)	121.9(4)	C(20)−B(2)−C(32)	129.3(5)
C(23)−B(2)−C(29)	119.2(4)	C(20)−B(2)−C(21)	128.2(5)
B(1)−C(5)−C(10)	123.9(4)	B(1)−C(15)−C(20)	120.0(5)
B(2)−C(10)−C(5)	126.7(4)	B(2)−C(20)−C(15)	127.1(5)
Selected Dihedral Angles (deg)			
B(1)−C(5)−C(10)−B(2)	7.0(1)	B(1)−C(15)−C(20)−B(2)	0.9(1)

[a] Sum of C−B−C angles about B(1) for **1·MeCN**: 340.7°. [b] Sum of C−B−C angles about B(2) for **1·MeCN**: 359.5°. [c] Sum of C−B−C angles about B(1) for **2·MeCN**: 326.8°. [d] Sum of C−B−C angles about B(2) for **2·MeCN**: 359.7°.

of B(1) as measured by the lower $\sum_{C-B-C}$ value in **2·MeCN**. The other obvious difference in these structures is that, in **1·MeCN**, the acetonitrile coordinates to the inner face of B(1), while in **2·MeCN**, coordination occurs on one of the outer faces. This is likely due to the significantly lower degree of back strain encountered upon pyramidalization of the borole boron upon outer face coordination in **2**; it is also likely that, in the event of coordination of the rod-like MeCN to an inner face of **2**, strong steric interactions with the (more rigid) adjacent borafluorene ring would result. The flat 9-borafluorene rings are able to stack and are essentially parallel in **2·MeCN**, spaced by about 3.2−3.3 Å. In **1·MeCN**, this mode of coordination would push two C_6F_5 rings into the crowded B−B pocket, and so the base opts to coordinate to the more sterically challenging inner face. To accommodate the coordination of MeCN to the inner boron face, the (B(1)−C(5)−C(10) (123.9(4)°) and B(2)−C(10)−C(5) (126.7(4)°) angles have increased relative to the analogous angles in **1** (122.8(3)° and 121.8(3)°). Although the face of the planar, noncoordinated boron center B(2) is oriented toward the coordinated nitrile, there is no indication of any interaction of this center with the nitrile (B(2)−N(1) = 2.949 Å, $\sum_{C-B(2)-C} = 359.7°$).

The presence of a second, unligated borane center in these adducts raises the possibility of coordination of a second Lewis base.[34] Indeed, the dynamic character of the ^{19}F NMR spectra for these adducts as discussed above implies that bis-Lewis base adducts might be accessible, particularly in the case of **2**

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(31) The molecular structure of **2·THF** has also been determined and is comparable to **2·MeCN** in terms of overall geometry and the metrical parameters. Full details of this structure are included in the Supporting Information.

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(33) Chase, P. A.; Romero, P. E.; Piers, W. E.; Parvez, M.; Patrick, B. O. *Can. J. Chem.*, submitted.

(34) Perfluoro-9,10-diboraanthracene readily coordinates 2 equiv of MeCN.[6b]

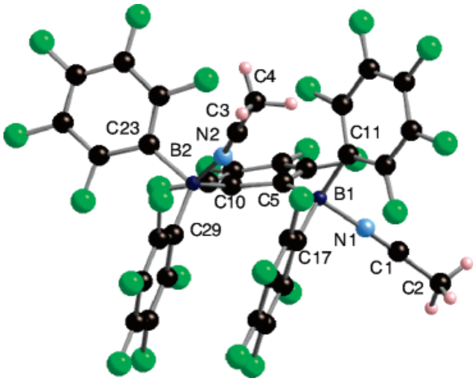


Figure 6. Crystalmaker depiction of the molecular structure of **1·(MeCN)$_2$**.

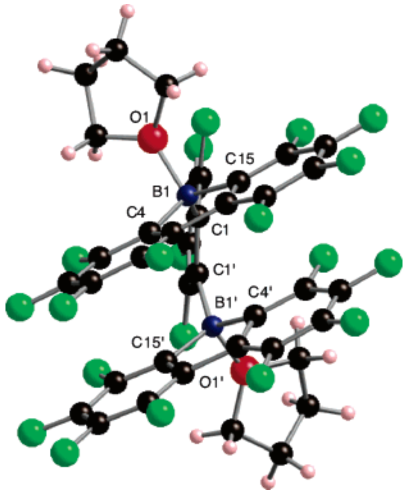
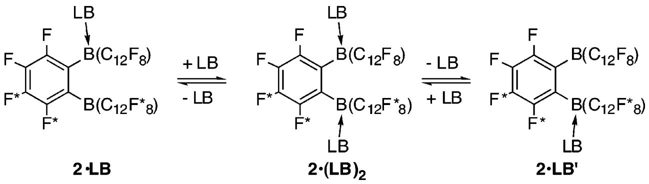


Figure 7. Crystalmaker depiction of the molecular structure of **2·(THF)$_2$**.

Scheme 3



(Scheme 3). Although their viability in solution is based on indirect evidence, crystals grown from solutions of **1**/excess MeCN and **2**/excess THF demonstrate that bis-adducts are accessible. Figure 6 shows the molecular structure of **1·(MeCN)$_2$**, Figure 7 shows the structure of **2·(THF)$_2$**, while Table 2 gives comparative metrical data.

In the structure of **2·(THF)$_2$**, the two THF bases coordinate to the outer faces of the Lewis acid centers, giving a structure with crystallographic 2-fold symmetry. The B(1)−O(1) distance of 1.611(3) Å is somewhat longer that typical B−O distances in adducts of B(C$_6$F$_5$)$_3$ with oxygen-based donors;[1] the B−O distance in **2·THF** is 1.581(3) Å.[31] The flat borafluorene rings are essentially parallel and slightly closer together than the rings in **2·MeCN**, and the B(1)−C(1)−C(1′)−B(1′) dihedral angle is quite large at 27.7°, indicating a fair degree of steric tension in this structure. Nonetheless, it lends credence to the involvement of such a species in the rapid symmetrization observed in adducts **2·LB** in the presence of slight excesses of base via the process given in Scheme 3.

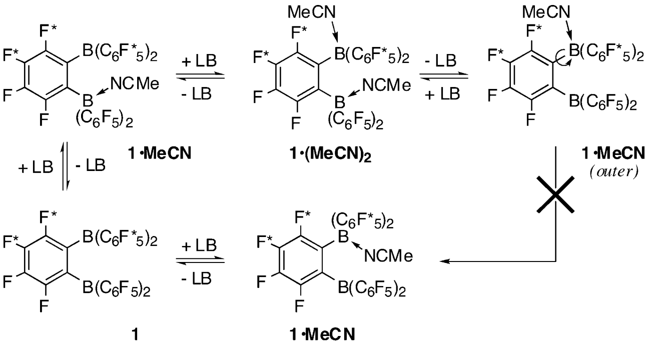
The isolation of crystals of **1·(MeCN)$_2$** is perhaps more surprising given the higher steric congestion present in this system. Here, the first Lewis base coordinates to the inner face (see above), but the second acetonitrile donor approaches the other boron center from the outer face. The metrical parameters associated with the inner coordinated MeCN (the boron labeled B(2) in Figure 6) differ only slightly from that observed in **1·MeCN**, but indications are that the outer coordinated acetonitrile is more weakly bound. The B(1)−N(1) distance is longer, and the extent of pyramidalization at B(1) ($\Sigma_{\mathrm{C-B-C}} = 346.2°$) is less than that at B(2) ($\Sigma_{\mathrm{C-B-C}} = 340.8°$). Given that the second acetonitrile coordinates in this fashion, it is unlikely that this bis-acetonitrile adduct is involved in the mechanism of process responsible for symmetrization of the ^{19}F atoms in **1·MeCN** (Scheme 4). Dissociation of the inner coordinated acetonitrile in **1·(MeCN)$_2$** would lead to an outer coordinated isomer of **1·MeCN**, which could not revert to the inner coordinated species observed via simple rotation about the appropriate B−C bond based on steric arguments. Thus the symmetrization observed in the ^{19}F NMR spectra of **1·MeCN**

Table 2. Selected Metrical Data for 1·(MeCN)$_2$ and 2·(THF)$_2$

1·(MeCN)$_2$		2·(THF)$_2$	
Selected Bond Lengths (Å)			
B(1)−C(5)	1.645(3)	B(1)−C(1)	1.631(3)
B(1)−C(11)	1.636(4)	B(1)−C(4)	1.619(3)
B(1)−C(17)	1.641(4)	B(1)−C(15)	1.614(3)
B(1)−N(1)	1.630(4)	B(1)−O(1)	1.611(3)
B(2)−C(10)	1.647(4)		
B(2)−C(23)	1.655(4)		
B(2)−C(29)	1.639(4)		
B(2)−N(2)	1.607(3)		
C(5)−C(10)	1.434(3)	C(1)−C(1′)	1.440(4)
N(1)−C(1)	1.135(3)		
C(1)−C(2)	1.450(7)		
N(2)−C(3)	1.134(3)		
C(3)−C(4)	1.455(4)		
B(1)···B(2)	3.468	B(1)···B(1′)	3.344
Selected Bond Angles (deg)			
B(1)−N(1)−C(1)	167.8(2)		
N(1)−C(1)−C(2)	177.5(3)		
C(11)−B(1)−C(5)^{a}	117.3(2)	C(1)−B(1)−C(4)^{c}	118.7(2)
C(17)−B(1)−C(5)	112.8(2)	C(1)−B(1)−C(15)	122.7(2)
C(11)−B(1)−C(17)	116.1(2)	C(4)−B(1)−C(15)	98.6(2)
B(2)−N(2)−C(3)	169.7(2)		
N(2)−C(3)−C(4)	179.1(3)		
C(10)−B(2)−C(23)^{b}	109.7(2)		
C(10)−B(2)−C(29)	118.7(2)		
C(23)−B(2)−C(29)	112.4(2)		
B(1)−C(5)−C(10)	127.0(2)	B(1)−C(1)−C(1′)	124.4(1)
B(2)−C(10)−C(5)	126.8(2)		
Selected Dihedral Angles (deg)			
B(1)−C(5)−C(10)−B(2)	28.1(1)	B(1)−C(1)−C(1′)−B(1′)	27.7(1)

[a] Sum of C−B−C angles about B(1) for **1·(MeCN)$_2$**: 346.2°. [b] Sum of C−B−C angles about B(2) for **1·(MeCN)$_2$**: 340.8°. [c] Sum of C−B−C angles about B(1) for **2·(THF)$_2$**: 340.0°.

Scheme 4



is likely due simply to a labile acetonitrile that dissociates from one borane and recoordinates to the other. While it may be tempting to invoke a transition state in which the acetonitrile is simultaneously engaging both borane centers, there is no direct evidence for chelation of acetonitrile in this instance.

Conclusions. In summary, a new, mercury-free route to the synthon C_6F_4-1,2-$(BBr_2)_2$ has been developed from 1,2-$Br_2C_6F_4$ in a four-step synthesis with an overall yield of $\sim$47%, on par with the previously reported procedure employing mercury reagents. This was used to generate the new bifunctional 9-borafluorene Lewis acid C_6F_4-1,2-$[B(C_{12}F_8)]_2$ (**2**) by reaction with 2 equiv of $Me_2SnC_{12}F_8$ in 81% yield and generate C_6F_4-1,2-$[B(C_6F_5)_2]_2$ (**1**) via existing methodology. Compound **2** is deep orange, due to the presence of a low-energy $\pi-\pi$ transition in the 9-borafluorene chromophores.

Fundamental aspects of the Lewis acid/base chemistry of these two diboranes were also investigated. Spectroscopic, structural, and solution competition studies have shown **2** to be a significantly stronger Lewis acid than **1** for neutral Lewis bases MeCN and THF. For **2**, strong stable adducts are generated, whereas a relatively weak MeCN adduct of **1** is formed and virtually no interaction is observed with THF. This is primarily ascribed to steric effects due the significant reduction in front- and back-strain engendered by the planar 9-borafluorene groups.

Structural studies also show significant differences in the coordination mode of the Lewis bases, especially in terms of facial discrimination. Exclusive coordination to the sterically more accessible outer face is observed with **2**. However, the seemingly more congested Lewis acid **1** exhibits MeCN coordination inside the B−B pocket to the hindered inner face. Also, the differences in facial coordination gave rise to distinct pathways for Lewis base exchange between Lewis acid sites. This difference in facial reactivity could have potential impact on the use of these systems in catalysis, especially for **2**, where potential chelation of a substrate by both acidic centers is precluded by preferential outer coordination.

Experimental Section

General Procedures. All manipulations of air- and moisture-sensitive materials were performed on a double-manifold high-vacuum line using modified Schlenck techniques or in a glovebox under an atmosphere of nitrogen.[35] Residual oxygen and moisture were removed from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products. All solvents were dried and purified by passing through suitable drying agents (toluene, hexanes, and tetrahydrofuran, Grubbs/Dow purification system;[36] benzene, d_6-benzene, and d_8-toluene, sodium/benzophenone ketal; diethyl ether, $LiAlH_4$; methylene chloride and d_2-methylene chloride, CaH_2), with the exception of d_3-chloroform, d_3-acetonitrile, and D_2O, which were used as received. Nuclear magnetic resonance spectroscopy was performed on a AMX-300 MHz (^1H, 300.138 MHz; $^{11}B\{^1H\}$, 96.293 MHz, ^{19}F, 282.371 MHz) or Bruker Avance DRX-400 (^1H, 400.134 MHz; $^{11}B\{^1H\}$, 128.375 MHz) spectrometers. Data are given in ppm relative to the solvent signals for ^1H spectra or relative to external standards for ^{11}B ($BF_3{\cdot}OEt_2$, 0 ppm) and ^{19}F (C_6F_6, −163.0 ppm). Temperature calibration for NMR experiments was achieved by monitoring the ^1H NMR spectrum of pure methanol (below room temperature) and pure ethylene glycol (above room temperature).[37] Elemental analyses were performed on a Control Equipment Corporation 440 elemental analyzer by Mrs. Dorothy Fox, Mrs. Roxanna Smith, and Mrs. Olivera Blagojevic of this department. GC-MS experiments were run on a Varian Saturn 2000 GC-MS. Column and injector temperature were initially 50 °C, and the column temperature was ramped to 250 °C over 20 min and held at that temperature for an additional 20 min.

The compounds $Zn(C_6F_5)_2$[20,38] and $C_{12}F_8SnMe_2$[24] were synthesized via literature procedures. Bifunctional Lewis acid **1** was prepared from C_6F_4-1,2-$(BBr_2)_2$ using the previously described procedure.[9] Reagent quantities of MeOH and $B(OMe)_3$ were dried over Na, while MeCN was dried over CaH_2; all reagents were freshly distilled prior to use. BBr_3 was dried over Cu wire and vacuum transferred directly into reaction flasks. All other reagents were purchased from Aldrich Chemicals or Boulder Scientific and used as received.

Synthesis of C_6F_4-1,2-$[B(OH)_2]_2$. Butyllithium (12.6 mL, 1.6 M in hexanes, 20.16 mmol) was added dropwise to a stirred solution of 1,2-$Br_2C_6F_4$ (2.6 g, 8.44 mmol) in ether (50 mL) at −78 °C. After 2 h this solution was slowly added to a precooled solution (−78 °C) of $B(OMe)_3$ (2.3 mL, 20.52 mmol) in ether (25 mL) via cannula. The fluoroaryllithium reagent was kept cool during this transfer by constantly rubbing the cannula with a cotton swab cooled in a dry ice/acetone bath. The resulting suspension was stirred at −78 °C for 2 h, then gradually warmed to room temperature and hydrolyzed with 20 mL of 10% HCl. Volatiles were removed from the sample, leaving an oily residue, which was extracted with hot water (3 × 25 mL). The solution was concentrated (ca. 50 mL) and left to recrystallize at 5 °C overnight. The resulting solid (predominantly borate salts) was filtered, and the remaining water layer was evaporated to dryness, affording a white solid (1.76 g, 88%). ^{19}F NMR (D_2O/HCl): δ −136.6 (2F, $-C_6F_4$), −156.5 (2F, $-C_6F_4$). $^{11}B\{^1H\}$ NMR (D_2O/HCl): δ 20.7. Anal. Calcd for $C_6H_4B_2F_4O_4$: C, 30.31; H, 1.70. Found: C, 30.55; H, 1.57. **CAUTION:** The isolation or warming of solutions containing fluoroaryllithium compounds has been known to cause explosions.[39]

Synthesis of $[K]^+_2[C_6F_4\text{-1,2-}(BF_3)_2]^{2-}$. A solution of C_6F_4-1,2-$\{B(OH)_2\}_2$ (2.75 g, 11.56 mmol) in methanol (40 mL) was added to a stirred solution of KHF_2 (5.92 g, 75.79 mmol) in water (20 mL) and stirred for 3.5 h. The solution was filtered, and the solid was washed with a 25% water solution in ether (3 × 10 mL), then ether (3 × 10 mL), and dried under reduced pressure, affording an off-white solid (2.51 g, 60%). ^{19}F NMR (CD_3CN/D_2O): δ −141.2 (2F, $-C_6F_4$), −146.2 (q, J_{F-B} = 56 Hz, 6F, $-BF_3$), −162.9 (2F, $-C_6F_4$). $^{11}B\{^1H\}$ NMR (CD_3CN/D_2O): δ 3.9. X-ray quality crystals were grown from a concentrated acetonitrile solution of the product. $[K]^+[C_6F_4\text{-1,2-}(BF_2)_2(\mu\text{-}F)]^-$: ^{19}F NMR (CD_3CN/D_2O): δ −138.4 (2F, $-C_6F_4$), −139.7 (br s, 1F, μ-F), −143.4 (4F, $-BF_2$), −159.8 (2F, $-C_6F_4$). X-ray quality crystals were grown from a concentrated solution of $[K]^+_2[C_6F_4\text{-1,2-}(BF_3)_2]^{2-}$ containing $\sim$10% water.

Synthesis of C_6F_4-1,2-$(BF_2)_2$. An excess of boron trifluoride gas was introduced to a stirred suspension of $[K]^+_2[C_6F_4\text{-1,2-}(BF_3)_2]^{2-}$ (1.0 g, 2.76 mmol) in dichloromethane (10 mL) in a thick walled pressure vessel at −40 °C. After 30 min the solution was degassed under vacuum at −78 °C. The faint red colored solution was filtered, and the remaining solid (KBF_4) was washed with dichloromethane (2 × 5 mL). A red liquid was obtained after solvent was distilled from the product under reduced pressure (0.57 g, 84%). ^{19}F NMR (CD_2Cl_2): δ −72.0 (4F, $-BF_2$), −126.9 (2F, $-C_6F_4$), −146.5 (2F, $-C_6F_4$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ 22.6. **NOTE:** The product is relatively volatile and will be removed under full vacuum.

Synthesis of C_6F_4-1,2-$(BBr_2)_2$. Boron tribromide (0.76 g, 3.05 mmol) was introduced to a solution of 1,2-$(BF_2)_2C_6F_4$, (0.15 g, 0.61 mmol) in toluene (5 mL) in a thick walled bomb at −78 °C. The

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Table 3. Summary of Data Collection and Structure Refinement Details for $[K]_2^+[C_6F_4\text{-1,2-}(BF_3)_2]^{2-}$, $[K]^+\{C_6F_4\text{-1,2-}[(BF_2)_2(\mu\text{-F})]\}^-$, 2, 1·MeCN, 2·MeCN, 1·(MeCN)$_2$, and 2·(THF)$_2$

	$[K]_2^+[C_6F_4\text{-1,2-}(BF_3)_2]^-$	$[K]^+\{C_6F_4\text{-1,2-}[(BF_2)_2(\mu\text{-F})]\}^-$	**2**	**1·MeCN**
formula	$C_6B_2F_{10}K_2$	$C_8H_5B_2F_9KNO$	$C_{30}B_2F_{20}\cdot1.5C_7H_8$	$C_{32}H_3B_2F_{24}N$
fw	361.88	362.85	900.12	878.97
temp, K	173(2)	173(2)	160(2)	173(2)
cryst syst	monoclinic	orthorhombic	triclinic	triclinic
space group	$P2_1/n$	*Cmcm*	$P\bar{1}$	$P\bar{1}$
a, Å	7.046(2)	8.111(5)	9.9667(7)	9.5370(15)
b, Å	15.853(6)	26.229(5)	11.3162(7)	10.7220(7)
c, Å	9.341(4)	11.966(5)	16.8523(11)	17.0989(12)
α, deg	90	90	83.699(2)	73.417(5)
β, deg	104.46(2)	90	89.897(2)	82.369(3)
γ, deg	90	90	71.640(2)	71.803(2)
V, Å^3	1010.3(6)	2546(3)	1792.0(2)	1591.1(3)
Z	4	8	2	2
d_{calc}, Mg m^{-3}	2.379	1.893	1.668	1.836
μ, mm^{-1}	1.068	0.526	0.169	0.206
cryst size, mm	0.012 × 0.08 × 0.08	0.14 × 0.12 × 0.10	0.75 × 0.50 × 0.50	0.30 × 0.25 × 0.08
no. of rflns measd	4494	4973	14 384	33 552
no. of unique rflns	2310	1609	7982	7211
R_1/wR_2	0.031/0.090	0.0508/0.1365	0.0643/0.2118	0.0736/0.2472
gof	0.97	1.067	1.076	1.001
res density, e/ Å^3	0.33 / −0.43		0.85 / −0.50	0.29 / −0.38

	2·MeCN	**1·(MeCN)$_2$**	**2·(THF)$_2$**
formula	$C_{32}H_3B_2F_{20}N\cdot C_7H_8$	$C_{34}H_6B_2F_{24}N_2\cdot CH_2Cl_2$	$(C_{19}H_8BF_{10}O)_2\cdot0.5CH_2Cl_2$
fw	895.11	1004.95	991.05
temp, K	160(2)	173(2)	173(1)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2/c$
a, Å	9.8508(6)	13.8512(10)	9.0312(3)
b, Å	12.5539(7)	13.3129(8)	12.3044(4)
c, Å	26.6988(15)	20.046(2)	16.8288(6)
α, deg	90		90
β, deg	95.590(2)	105.369(8)	99.018(2)
γ, deg	90		90
V, Å^3	3286.0(3)	3564.3(5)	1846.96(11)
Z	4	4	2
d_{calc}, Mg m^{-3}	1.809	1.873	1.782
μ, mm^{-1}	0.185	0.342	0.317
cryst size, mm	0.52 × 0.10 × 0.03	0.30 × 0.15 × 0.10	0.35 × 0.20 × 0.05
no. of rflns measd	16 280	41 462	12 594
no. of unique rflns	4297	8008	4152
R_1/wR_2	0.0730/0.01741	0.0466/0.1156	0.052/0.149
gof	1.168	1.068	1.03
res density, e/ Å^3	0.56/−0.46	0.44/−0.59	0.33/−0.54

bomb was sealed and heated at 60 °C for 30 min. Volatiles were removed under reduced pressure to afford a yellow-green oil with the same spectroscopic properties as those previously reported[9] (0.25 g, 85%). ^{19}F NMR (C_6D_6): δ −125.7 (2F, $-C_6F_4$), −147.3 (2F, $-C_6F_4$). ^{11}B{^{1}H} NMR (C_6D_6): δ 54.0.

Synthesis of C_6F_4-1,2-[B($C_{12}F_8$)]$_2$ (2). $Me_2Sn(C_{12}F_8)$ (0.786 g, 1.77 mmol) and $C_6F_4(BBr_2)_2$ (0.435 g, 0.84 mmol) were dissolved in toluene (20 mL), sealed in a glass bomb equipped with a Kontes valve, and heated to 85 °C for 36 h. The solvent was removed in vacuo, and the Me_2SnBr_2 byproduct was removed via sublimation (30 °C, 0.01 mmHg). The sublimation residues were placed in a frit assembly, and hexanes (30 mL) was condensed into the flask. The solution was cooled to −78 °C and stirred for 1 h. The solution was cold filtered, and a light yellow solid was obtained and dried in vacuo (0.520 g, 81%). ^{19}F NMR (C_6D_6): δ −121.1 (4F, $C_{12}F_8$), −123.6 (2F, C_6F_4), −128.9 (4F, $C_{12}F_8$), −138.6 (4F, $C_{12}F_8$), −148.6 (2F, C_6F_4), −151.9 (4F, $C_{12}F_8$). λ_{max} (hexanes): 425 nm $\epsilon = 5.9 \times 10^2$ L mol^{-1} cm^{-1}. Anal. Calcd for $C_{30}B_2F_{20}$: C 47.29. Found: C 47.78. X-ray quality crystals were grown from a concentrated toluene solution cooled to −40 °C.

Synthesis of C_6F_4-1,2-[B(C_6F_5)$_2$]$_2$·MeCN (1·MeCN). Solid C_6F_4-1,2-[B(C_6F_5)$_2$]$_2$, **1** (50 mg, 0.060 mmol), was dissolved in CH_2Cl_2 (3 mL) and stirred while an excess of MeCN (ca. 2 mL) was added. The reaction mixture was stirred for 1 h before volatiles were removed under reduced pressure, affording the product as a white solid (36 mg, 69% yield). ^{1}H NMR (CD_2Cl_2): δ 2.47 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2): δ −128.7 (2F, $-C_6F_4$), −130.0 (8F, *o*-B(C_6F_5)$_2$), −149.7 (4F, *p*- B(C_6F_5)$_2$), −156.4 (2F, $-C_6F_4$), −162.1 (8F, *m*-B(C_6F_5)$_2$). ^{11}B{^{1}H} NMR (CD_2Cl_2, 228 K): δ 41.7, −7.6. ^{13}C{^{1}H} (CD_2Cl_2): δ 2.95 (*Me*CN). ^{1}H NMR (CD_2Cl_2, 228 K): δ 2.50 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2, 228 K): δ −126.3 (4F, *o*-B(C_6F_5)$_2$), −126.9 (1F, $-C_6F_4$), −130.9 (1F, $-C_6F_4$), −132.9 (4F, *o*-B(C_6F_5)$_2$), −141.9 (2F, *p*-B(C_6F_5)$_2$, −154.0 (1F, $-C_6F_4$), −154.6 (2F, *p*-B(C_6F_5)$_2$), −157.8 (1F, $-C_6F_4$), −160.0 (4F, *m*-B(C_6F_5)$_2$), −163.1 (4F, *m*-B(C_6F_5)$_2$). X-ray quality crystals of **1·MeCN** were obtained by layering 1 equiv of MeCN (0.320 mL, 0.0487 M in hexanes, 0.016 mmol) on a solution of C_6F_4-1,2-[B(C_6F_5)$_2$]$_2$, **1** (13 mg, 0.016 mmol), in CH_2Cl_2 (0.3 mL), which was allowed to stand at −40 °C. X-ray quality crystals of **1·(MeCN)$_2$** were obtained by layering excess equivalents of MeCN (1.274 mL, 0.0487 M solution in hexanes, 0.062 mmol) over a solution of C_6F_4-1,2-[B(C_6F_5)$_2$]$_2$ (13 mg, 0.016 mmol) in CH_2Cl_2 (0.3 mL), which was allowed to stand at −40 °C.

Synthesis of C_6F_4-1,2-[B($C_{12}F_8$)]$_2$·MeCN (2·MeCN). In the glovebox, C_6F_4-1,2-[B($C_{12}F_8$)]$_2$, **2** (0.100 g, 0.13 mmol), was weighed into a vial and dissolved in CH_2Cl_2 (8 mL). MeCN (0.006 g, 0.14 mmol) was also weighed into a vial and diluted with CH_2Cl_2 (2 mL). The solutions were combined, stirred for 10 min, and place in the freezer (−40 °C) overnight. The solution was decanted and the solid product was dried in vacuo (0.090 g, 86%). ^{1}H NMR

(CD_2Cl_2): δ 2.65 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2): δ −124.5 (2F, $C_{12}F_8$), −130.7 (1F, C_6F_4), −131.4 (2F, $C_{12}F_8$), −131.8 (2F, $C_{12}F_8$), −132.6 (1F, C_6F_4), −133.5 (2F, $C_{12}F_8$), −142.2 (2F, $C_{12}F_8$), −153.5 (4F, 2 overlapping signals, $C_{12}F_8$), −155.1 (2F, $C_{12}F_8$), −155.3 (1F, C_6F_4), −158.0 (1F, C_6F_4). ^{11}B{^{1}H} (CD_2Cl_2): 49.2 (br), −5.6 (br). X-ray quality crystals of **2·MeCN** were obtained by layering hexanes onto a CH_2Cl_2 solution of **2·MeCN** and cooling to −40 °C.

Synthesis of C_6F_4-1,2-[B($C_{12}F_8$)$_2$]·THF (2·THF). In the glovebox, C_6F_4-1,2-[B($C_{12}F_8$)]$_2$, **2** (0.100 g, 0.13 mmol), was weighed into a vial and dissolved in CH_2Cl_2 (8 mL). THF (0.010 g, 0.14 mmol) was also weighed into a vial and diluted with CH_2Cl_2 (2 mL). The solutions were combined, stirred for 10 min, and place in the freezer (−40 °C) overnight. The solution was decanted, and the solid product was dried in vacuo (0.103 g, 94%). ^{1}H NMR (CD_2Cl_2): δ 4.24 (m, 4H, *THF*)), 2.13 (m, 4H, *THF*). ^{19}F NMR (CD_2Cl_2): δ −124.6 (2F, $C_{12}F_8$), −130.7 (2F, $C_{12}F_8$), −131.5 (2F, $C_{12}F_8$), −132.2 (3F, 2 overlapping signals, $C_{12}F_8$ and C_6F_4), −132.5 (1F, C_6F_4), −142.2 (2F, $C_{12}F_8$), −152.4 (2F, $C_{12}F_8$), −153.5 (2F, $C_{12}F_8$), −154.2 (2F, $C_{12}F_8$), −154.9 (1F, C_6F_4), −157.2 (1F, C_6F_4). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ 39.9, 6.3. X-ray quality crystals of **2·THF** were obtained by layering hexanes onto a CH_2Cl_2 solution of **2·THF** and cooling to −40 °C. X-ray quality crystals of **2·(THF)$_2$** were obtained by layering excess equivalents of THF (1.0 mL, 0.05 M solution in hexanes, 0.062 mmol) over a solution of **2** (10 mg, 0.013 mmol) in CH_2Cl_2 (0.3 mL), which was allowed to stand at −40 °C.

Spectroscopic Studies of the Addition of LB to 1 and 2. In a glovebox a 5 mm NMR tube was charged with a known amount of **1** or **2** (∼0.012 mmol), and CD_2Cl_2 (0.4 mL) was added. The sample was capped with a rubber septum and removed from the glovebox. Varying equivalents of dry and degassed LB (LB = MeCN, 0.464 M in CD_2Cl_2; LB = THF, 0.500 M in CD_2Cl_2) was added via gastight syringe, and the NMR tube was placed in the spectrometer.

1 + 1.0 MeCN. ^{1}H NMR (CD_2Cl_2, 298 K): δ 2.51 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2, 298 K): δ −127.5 (10F, −C_6F_4 and *o*-B(C_6F_5)$_2$), −143.2 (br, 4F, *o*-B(C_6F_5)$_2$), −148.7 (br, 2F, −C_6F_4), −161.0 (8F, *m*-B(C_6F_5)$_2$). ^{11}B{^{1}H} NMR (CD_2Cl_2. 228 K): δ 41.7, −8.6. **1** + 2.0 MeCN (**1·(MeCN)$_2$**): ^{1}H NMR (CD_2Cl_2, 298 K): δ 2.27 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2, 298 K): δ −128.2 (2F, −C_6F_4), −130.6 (8F, *o*-B(C_6F_5)$_2$), −151.0 (4F, *p*-B(C_6F_5)$_2$), −157.1 (2F, −C_6F_4), −162.3 (8F, *m*-B(C_6F_5)$_2$). **1** + 3.0 MeCN: ^{1}H NMR (CD_2Cl_2, 298 K): δ 2.15 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2, 298 K): δ −127.8 (2F, −C_6F_4), −130.9 (8F, *o*-B(C_6F_5)$_2$), −152.0 (4F, *p*-B(C_6F_5)$_2$), −157.6 (2F, −C_6F_4), −162.5 (8F, *m*-B(C_6F_5)$_2$). ^{11}B{^{1}H} NMR (CD_2Cl_2): δ −7.0.

2 + 0.8 equiv MeCN. ^{1}H NMR (CD_2Cl_2, 301 K): δ 2.65 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2, 301 K): δ −124.5 (2F, $C_{12}F_8$), −130.7 (1F, C_6F_4), −131.4 (2F, $C_{12}F_8$), −131.8 (2F, $C_{12}F_8$), −132.6 (1F, C_6F_4), −133.5 (2F, $C_{12}F_8$), −142.2 (2F, $C_{12}F_8$), −153.5 (4F, 2 overlapping signals, $C_{12}F_8$), −155.1 (2F, $C_{12}F_8$), −155.3 (1F, C_6F_4), −158.0 (1F, C_6F_4). ^{11}B{^{1}H} (CD_2Cl_2): 49.2 (br), −5.6 (br). **2** + 2.0 equiv MeCN (**2·(MeCN)$_2$**): ^{1}H NMR (CD_2Cl_2, 301 K): 2.40 (s, 3H, *Me*CN). ^{19}F NMR (CD_2Cl_2, 301 K): −128.0 (4F, $C_{12}F_8$), −131.6 (2F, C_6F_4), −132.6 (4F, $C_{12}F_8$), −147.9 (4F, $C_{12}F_8$), −154.3 (4F, $C_{12}F_8$), −156.7 (2F, C_6F_4).

2 + 0.9 equiv THF. ^{1}H NMR (CD_2Cl_2, 301 K): δ 3.77 (m, 4H, *THF*), 1.87 (m, 4H, *THF*). ^{19}F NMR (CD_2Cl_2, 301 K): δ −126.5 (4F, $C_{12}F_8$), −131.9 (4F, $C_{12}F_8$), −132.3 (2F, C_6F_4), −147.5 (4F, $C_{12}F_8$), −153.9 (4F, $C_{12}F_8$), −156.1 (2F, C_6F_4). ^{1}H NMR (CD_2Cl_2, 193 K): δ 3.62 (br, 4H, *THF*), 1.76 (br, 4H, *THF*). ^{19}F NMR (CD_2Cl_2, 193 K): δ −131.2 (2F, C_6F_4), −131.5 (4F, $C_{12}F_8$), −134.2 (4F, $C_{12}F_8$), −154.8 (4F, $C_{12}F_8$), −155.2 (4F, $C_{12}F_8$), −158.3 (2F, C_6F_4). ^{11}B {^{1}H} NMR: 39.9 (br s), 6.3 (br s). **2** + 2.0 equiv THF (**2·(THF)$_2$**): ^{1}H NMR (CD_2Cl_2, 301 K): δ 3.94 (m, 4H, *THF*), −1.97 (m, 4H, *THF*). ^{19}F NMR (CD_2Cl_2, 301 K): −126.4 (4F, $C_{12}F_8$), −131.9 (4F, $C_{12}F_8$), −132.3 (2F, C_6F_4), −147.4 (4F, $C_{12}F_8$), −153.9 (4F, $C_{12}F_8$), −156.1 (2F, C_6F_4).

X-ray Crystallography. Measurements were made on either a Nonius Kappa CCD or Bruker SMART 1K CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The structures were solved by direct methods and refined on F^2 values by full-matrix least squares for all unique data. Table 3 gives further details, and the crystallographic information files are available as Supporting Information. The CCDC contains the supplementary crystallographic data for the crystal structures reported in this paper (CCDC 278193, $[K]^+_2[C_6F_5\text{-}1,2\text{-}(BF_3)_2]^{2-}$; CCDC 278389, $[K]^+\{C_6F_4\text{-}1,2\text{-}[(BF_2)_2(\mu\text{-}F)]\}^-$; CCDC 278192, **2**; CCDC 279195, **1·MeCN**; CCDC 281017, **2·MeCN**; CCDC 278194, **1·(MeCN)$_2$**; CCDC 278196, **2·(THF)$_2$**; CCDC 278197, **2·THF**, Supporting Information only). These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

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Supporting Information Available: Crystallographic information files for $[K]_2^+[C_6F_4\text{-}1,2\text{-}(BF_3)_2]^{2-}$, $[K]^+\{C_6F_4\text{-}1,2\text{-}[(BF_2)_2(\mu\text{-}F)]\}^-$, **2**, **1·MeCN**, **2·MeCN**, **2·THF**, **1·(MeCN)$_2$**, and **2·(THF)$_2$**, as well as ORTEP diagrams for each structure and selected ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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