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# Comparative Lewis Acidity in Fluoroarylboranes: $B(o\text{-}HC_6F_4)_3$, $B(p\text{-}HC_6F_4)_3$, and $B(C_6F_5)_3$

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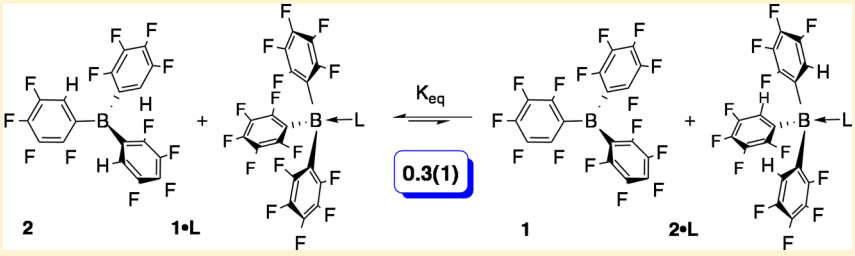
Supporting Information

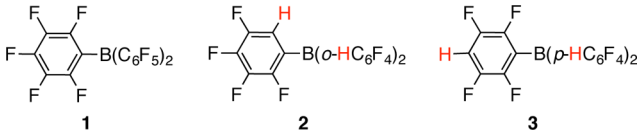



**ABSTRACT:** The Lewis acidic fluoroarylborane $B(o\text{-}HC_6F_4)_3$ (**2**) was prepared and its Lewis acid strength assessed in comparison to the known, related boranes $B(C_6F_5)_3$ (**1**) and $B(p\text{-}HC_6F_4)_3$ (**3**). Experimental methods based on spectroscopic probes and equilibrium measurements were used to show that $B(C_6F_5)_3$ is the strongest Lewis acid of the three; while the Lewis acidities of **2** and **3** are comparable, the *p*-H-substituted isomer is slightly stronger in the tests employed. This contrasts with predictions made on the basis of computed bond formation energies, as recently reported by Durfey and Gilbert.

The concept of Lewis acidity is one of the most enduring and useful in the discipline of chemistry.[1] However, unlike the more specific concept of Brønsted acidity, which can be straightforwardly quantified through $pK_a$ measurements, placing various Lewis acids on a relative scale of Lewis acid strength is nontrivial and indeed likely not possible in an absolute sense. Various spectroscopic[2−4] and computational[5−8] methods have been put forward that provide useful semiquantitative information, but the many steric and electronic factors that go into determining the strength of a given Lewis acid−Lewis base interaction mean that Lewis acid strength is situation dependent and cannot necessarily be placed on an absolute scale.

Fluoroaryl boranes[9,10] are an important class of Lewis acids with a wide variety of applications,[11−17] largely as a function of their strong Lewis acidity and hydrolytic stability.[18,19] These properties stem not only from the fact that the three-coordinate boron center is electron deficient but also from the strongly electron withdrawing nature of the fluoroaryl groups. Thus, it is not surprising that for boranes $B(C_6H_{5-n}F_n)_3$, the measured or calculated Lewis acid strength tends to correlate with the number of F substituents present in the molecule.[20] Use of larger fluoroaryl groups can also boost acidity, but only to a point; as these groups become sterically larger, the energy required to pyramidalize the boron center upon interaction with a Lewis base overwhelms the electron-withdrawing effects of high fluorine content.[21]

In the $B(C_6H_{5-n}F_n)_3$ series, the parent borane $B(C_6F_5)_3$ (**1**)[22,23] was thus considered to be the strongest Lewis acid in the family. However, recently Durfey and Gilbert reported a computational study[24] in which they assessed the Lewis acid strength of all possible members of this series by calculating the bond strengths between the acids and some standard Lewis bases. They found, not surprisingly, an additive relationship between Lewis acidity and both the number and position of the F atom substitution on the aryl rings. However, they did not find that **1** was the strongest Lewis acid in the family; rather, the borane in which one *o*-F on each aryl ring was replaced by H, **2**, was predicted to be the most potent Lewis acid on the basis of computed bond formation energies with $EMe_3$ (E = N, P) bases. The rationale for this finding was that, because H is smaller than F, the steric penalty for pyramidalization was less than in the slightly more sterically demanding $C_6F_5$ rings of **1**. Since the performance of these boranes in a variety of applications is directly related to their Lewis acid strength,[20,25] we set out to prepare **2**, which to our knowledge has not been studied experimentally, to test its efficacy as a Lewis acid in comparison to fully fluorinated **1**. We also utilized the known borane in which one *p*-F of each ring is replaced with H, **3**,[26] in these studies as a comparison; it has been shown both experimentally[26] and computationally[24] that **3** is slightly less Lewis acidic than **1**. In this case, the difference is due only to electronic effects, since para substitution has no steric impact on pyramidalization at boron.

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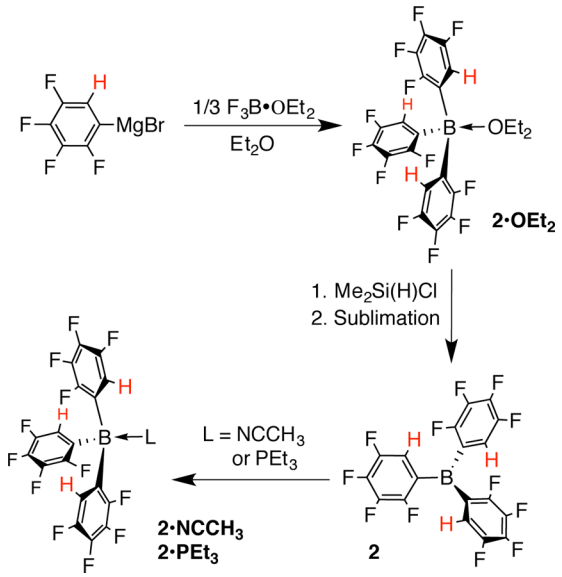
## RESULTS AND DISCUSSION

The new fluoroarylborane **2** was synthesized via a route analogous to that reported for the *p*-H-substituted borane **3**.[26] Thus, the necessary 2,3,4,5-tetrafluorophenyl Grignard reagent was generated in situ from the corresponding bromide and $^{i}$PrMgCl in diethyl ether[27] and quenched with $^{1}/_{3}$ equiv of $BF_3{\cdot}OEt_2$ (Scheme 1); careful control of stoichiometry is important to avoid excessive production of tetraarylborate salts. The diethyl ether adduct of **2** was isolated in 59% yield from this reaction upon workup. This crude product was carried on without further purification and treated with an excess of $Me_2Si(H)Cl$, which removes the coordinated ether via borane-catalyzed silation of the C−O ether bonds.[28−30] Removal of all volatiles gave an off-white solid that sublimed under high vacuum at 120 °C to afford the free borane in 53% yield as a white microcrystalline solid. The $^{19}$F NMR spectrum shows the expected four resonances in a 1:1:1:1 ratio, while the $^{11}$B NMR spectrum in $CD_2Cl_2$ is comprised of a broad resonance at 62.3 ppm, comparable to the value found for **3** (58.5 ppm).[26]

**Scheme 1**




We were unable to obtain X-ray-quality crystals of **2** in its unligated state, but adducts of **2** with the Lewis bases acetonitrile and triethylphosphine were straightforwardly prepared by reacting the two components in a nondonor solvent. These bases were chosen on the basis of their differing steric properties and donor strength. The adducts **2**·$NCCH_3$ and **2**·$PEt_3$ were both characterized by X-ray crystallography, and ORTEP depictions of each compound are shown in Figure 1, while selected metrical parameters are given in Table 1. The structures of the adducts for both of these Lewis bases with $B(C_6F_5)_3$ (**1**) have been reported previously ($NCCH_3$;[31] $PEt_3$[32]), but only that of **3**·$PEt_3$ has been disclosed.[26] Therefore, we also prepared and crystallized the acetonitrile adduct of **3** (the ORTEP drawing is also shown in Figure 1) in order to have all six structures for comparative analysis.

**Table 1. Selected Metrical Parameters for Lewis Base Adducts of $B(C_6F_5)_3$, $B(o\text{-}HC_6F_4)_3$, and $B(p\text{-}HC_6F_4)_3$ with Acetonitrile and Triethylphosphine[a]**

| L | param | $B(C_6F_5)_3$ | $B(o\text{-}HC_6F_4)_3$ | $B(p\text{-}HC_6F_4)_3$ |
|---|---|---|---|---|
| $NCCH_3$ | $\sum_{C-B-C}$ (deg) | 342.9 | 339.37 | *337.8* |
| | B−N (Å) | 1.616(3) | 1.604(4) | *1.589(3)* |
| | N−C (Å) | *1.124(3)* | 1.130(4) | 1.132(3) |
| $PEt_3$ | $\sum_{C-B-C}$ (deg) | 337.9 | *331.74* | 334.5 |
| | B−P (Å) | 2.081(4) | *2.057(2)* | 2.078(2) |

[a]For an explanation of the values in italics, see text.

For the acetonitrile adducts of **1**−**3**, three particular metrical parameters might be expected to correlate with relative Lewis acid strength toward this base: the B−N bond length, the C−N bond length, which is expected to get shorter upon complexation with at Lewis acid,[31] and the extent of pyramidalization of the boron center, as measured by the sum of the C−B−C angles. In the case of the $PEt_3$ adducts, only the B−P distance and the sum of the C−B−C angles are relevant. For the acetonitrile adducts, the values in italics in Table 1 indicate that the boron center is most pyramidalized and the B−N distance is shortest in the adduct with the *p*-H-substituted borane **3**, suggesting acetonitrile is most tightly bound to this LA. Conversely, it is the fully fluorinated borane that shortens the C−N triple bond the most in this series; in free $NCCH_3$, the C−N bond is 1.141(2) Å.[33] Thus, no clear trend emerges from these data, and indeed, the spread in the bond distance data is rather narrow and differences may be due to packing factors. In the $PEt_3$ adducts, the extent of pyramidalization at boron is greater than in the corresponding acetonitrile adducts, reflecting the greater steric bulk and donor strength of this base; the B−P bond distances are typical for such compounds.[32,34] Here, the data for the adduct **2**·$PEt_3$ imply that the strongest interaction is with this Lewis acid, although

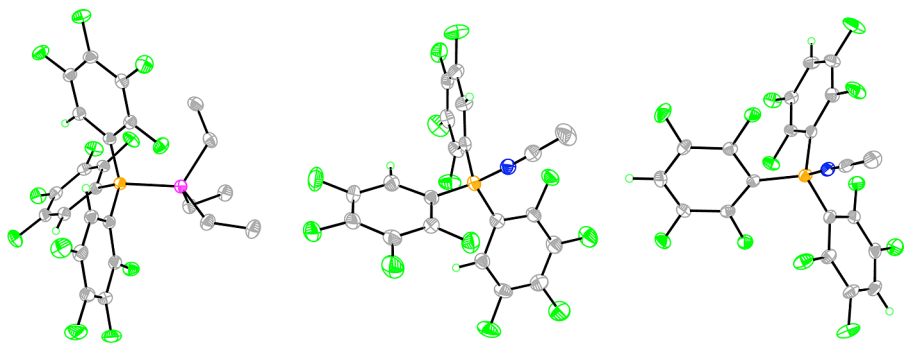


**Figure 1.** Thermal ellipsoid diagrams (35% probability level) of **2**·$PEt_3$ (left), **2**·$NCCH_3$ (middle), and **3**·$NCCH_3$ (right). Ligand hydrogen atoms are omitted for clarity. Color scheme: B, orange; C, gray; N, blue; F, green; P, pink; aryl H, small green spheres.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again the data for all three adducts are similar enough that firm conclusions regarding Lewis acid strength are not possible.

Given the inconclusive nature of the structural data, we assessed the Lewis acidity of each compound in solution using the Childs[2] and Gutmann–Beckett[3,4] methods. Both of these methods measure the perturbation in an NMR chemical shift of a probe Lewis base upon coordination to a given Lewis acid. In the Child method, the base is crotonaldehyde and the resonance probed is that of the $\gamma$ proton; in the Gutmann–Beckett method, the base is $Et_3P{=}O$, and the shift in the position of the $^{31}P$ NMR resonance is monitored. The results of both of these tests are summarized in Table 2. At the outset, it

**Table 2. Lewis Acidities of Boranes 1–3 in $CD_2Cl_2$ As Measured by the Childs and Gutmann–Beckett Methods**

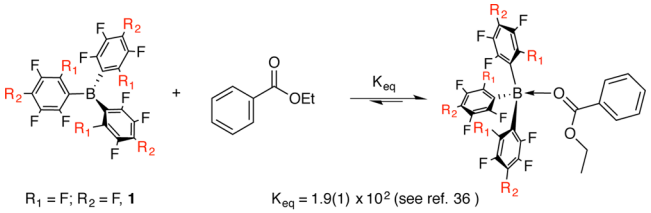
| Lewis Acid |  (ppm) | Lewis Acid Strength (Childs) |  (ppm) | Lewis Acid Strength (G-B) |
|---|---|---|---|---|
| Free | 6.89 | -- | 51.2 | -- |
| **1** | 7.89 | 100% | 77.8 | 100% |
| **2** | 7.85 | 96% | 76.7 | 97% |
| **3**[a] | 7.86 | 97% | 77.4 | 98% |

[a]Data taken from ref 21.

should be noted that the differences in LA strength for these three boranes are quite small; however, both methods show that the fully fluorinated borane **1** is the strongest Lewis acid in the series. Perhaps more surprising is the finding that the *o*-H substituted borane **2** is the weakest of the three, in contrast to the findings of Durfey and Gilbert.[24] Again, although the differences are small, the trend is reproducible over several measurements.

This relative ordering in LA strength was confirmed by measuring the equilibrium constants for coordination of one equivalent of ethyl benzoate (Scheme 2).[35] This has been done

**Scheme 2**




previously for the parent borane **1**[36] and was accomplished using established $^1H$ NMR spectroscopic methods.[37] The data shows that the equilibrium constant is largest for **1**[30,36] followed closely by that measured for the *p*-H-substituted borane **3**. Interestingly, the $K_{eq}$ value measured for **2** was only $[0.3(1)] \times 10^2$, 3–6 times smaller than those found for **1** and **3**. Consistent with this low equilibrium constant, the $^{11}B$ NMR spectrum of a 1:1 mixture of ethyl benzoate and **2** showed a signal at 60 ppm, not far perturbed from the shift of the free borane at 62.3 ppm; by comparison, the $^{11}B$ chemical shifts for the averaged signals in the **1**·OC(OEt)Ph and **3**·OC(OEt)Ph equilibria are 19.2[35] and 42 ppm, respectively, shifted more toward that expected for a neutral, four-coordinate borane adduct.

A final evaluation of the relative Lewis acidities of these boranes was performed by allowing pairs of Lewis acids to compete for 1 equiv of acetonitrile. The lability of this base allows for rapid establishment of the equilibria shown in Scheme 3, and measurement of the equilibrium constants was accomplished by integration of the $^{19}F$ NMR spectra obtained. Although complex, the spectra of all four species in each equilibrium are known and thus easily distinguished in the spectra of the mixtures (see the Supporting Information). The samples were prepared by weighing 1 equiv each of an isolated acetonitrile adduct and a free borane and dissolving in a measured amount of $C_6D_6$; each equilibrium was approached from both the left-hand and right-hand sides, providing consistent results as summarized in Scheme 3, in which the favored side of the equilibrium is on the left.

In each case, all four species are present in easily measurable quantities, underscoring the small differences in overall Lewis acidity between these closely related Lewis acids toward acetonitrile. However, the results in Scheme 3 clearly show that the *o*-H-substituted variant **2** is again the weakest of the series, at least when in competition for a rodlike Lewis base of minimal steric demand. Most interesting is the equation in Scheme 3c, in which the *p*-H-substituted borane **3** competes more effectively for the Lewis base than Lewis acid **2**, which is predicted to be the stronger Lewis acid.[24]

In conclusion, we have prepared the (fluoroaryl)borane $B(o\text{-}HC_6F_4)_3$ (**2**) and fully characterized its adducts with acetonitrile and triethylphosphine. By a variety of experimental spectroscopic and thermodynamic measurements we find that, contrary to predictions on the basis of computed bond formation energies,[24] compound **2** is *not* more Lewis acidic than the parent borane $B(C_6F_5)_3$ (**1**). Indeed, it is a slightly weaker Lewis acid than the related compound $B(p\text{-}HC_6F_4)_3$ (**3**), as measured by the methods described above. Thus, it seems that electronic effects dominate the Lewis acid properties of these boranes and that the cumulative steric effects of substituting three *o*-fluorines with slightly smaller hydrogen atoms are minimal, at least as far as the Lewis bases utilized herein are concerned. It is possible that, for larger Lewis bases, the steric advantage found in **2** may become important. Ultimately, the differences in Lewis acid strength among these three boranes, while measurable, is quite small and the relative acidities might change when other bases are employed.

## EXPERIMENTAL SECTION

All manipulations were performed under a purified argon atmosphere using vacuum line techniques or in an argon-atmosphere glovebox unless otherwise specified. Toluene and hexane were dried and purified using the Grubbs/Dow purification system[38] and stored in evacuated glass vessels over sodium/benzophenone ketal. All other solvents were dried over the appropriate drying agents ($CaH_2$, Na/benzophenone) and vacuum-distilled prior to use. 1-Bromo-2,3,4,5-tetrafluorobenzene, $BF_3{\cdot}Et_2O$, and triethylphosphine oxide were used as received from Aldrich. Crotonaldehyde, acetonitrile, and triethylphosphine were distilled prior to use. All NMR spectra were recorded from solution in dry, oxygen-free $C_6D_6$ or $CD_2Cl_2$ on a Bruker UGI-400 MHz or Bruker RDQ-400 MHz spectrometer operating at 400 MHz ($^1H$), 376 MHz ($^{19}F$), 100 MHz ($^{13}C$), or 128 MHz ($^{11}B$). Details on the X-ray analyses can be found in the deposited .cif files in the Supporting Information or via the Cambridge Crystallographic Data Centre (CCDC 911794–911796).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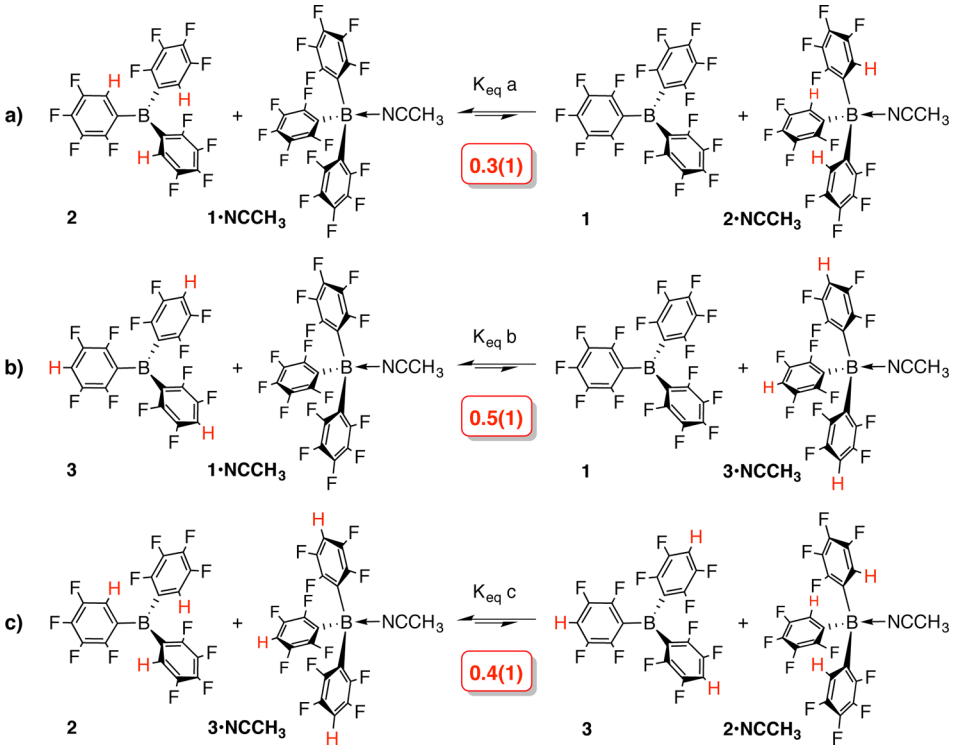
Scheme 3




**Sythesis of B(*o*-HC$_6$F$_4$)$_3$ (2).** The procedure below is modified from a literature report for B(*p*-HC$_6$F$_4$)$_3$.[26] $^{i}$PrMgCl (2.0 M in Et$_2$O, 1.05 mL, 2.1 mmol) was added to a stirred solution of 1-bromo-2,3,4,5-tetrafluorobenzene (500 mg, 2.2 mmol) in diethyl ether (20 mL) at room temperature. After 6 h of stirring, an aliquot of the reaction mixture was quenched with H$_2$O and the full conversion to Grignard reagent confirmed by $^{19}$F NMR spectroscopy. Trifluoroborane etherate was then added quickly (94 mg, 0.66 mmol), which caused heating of the reaction vessel momentarily. This mixture was stirred overnight; the mixture was then concentrated in vacuo to approximately $^{1}/_{4}$ of its initial volume. Addition of hexanes (20 mL) resulted in the formation of a sticky white precipitate. The slightly yellow supernatant was transferred to another flask, and the white precipitate was washed three more times by dissolution in benzene (30 mL) and precipitation of the residue with hexanes (20 mL). The combined filtrates were evaporated to dryness in vacuo to leave a dark yellow oil. This oil was dissolved in benzene and transferred into a sublimator, from which the benzene was sublimed away at 0 °C to give a brown powder. The brown powder was then sublimed in vacuo at 120 °C to give a fluffy white product (180 mg, 0.39 mmol, crude, 59%). The crude product was then slurried in hexanes and treated with Me$_2$SiHCl (4 mL), and this mixture was stirred for 3 h. All volatiles were removed in vacuo to leave a white solid, which was sublimed two additional times in vacuo at 120 °C to give the final product (160 mg, 0.35 mmol, 53%) free of any ether. $^{1}$H NMR (CD$_2$Cl$_2$): $\delta$ 6.97 (broad multiplet). $^{19}$F NMR (CD$_2$Cl$_2$): −125.5, −138.7, −146.8, −155.1. $^{11}$B NMR (CD$_2$Cl$_2$): 62.3. $^{13}$C{$^{1}$H} NMR (CD$_2$Cl$_2$): $\delta$ 151.66 (dd $^{1}J_{CF}$ = 252 Hz, $^{2}J_{CF}$ = 10 Hz, 3 × *o*-CF), 147.87 (dd $^{1}J_{CF}$ = 251 Hz, $^{2}J_{CF}$ = 10 Hz, 3 × *m*-CF), 144.58 (dm $^{1}J_{CF}$ = 262 Hz, 3 × *m*-CF), 141.37 (dm $^{1}J_{CF}$ = 278 Hz, 3 × *p*-CF), 123.70 (nonresolved, broad), 118.79 (d, $^{2}J_{CF}$ = 16 Hz, *o*-CH).

**Synthesis of 2·NCCH$_3$.** In the glovebox, borane **2** (20 mg) was taken up in acetonitrile (2 mL) and the mixture stirred for 10 min. The solvent was then removed in vacuo, and the white solid was redissolved into dry dichloromethane. Crystals of **2**·NCCH$_3$ were obtained via the slow evaporation of a CH$_2$Cl$_2$ solution of **2**·NCCH$_3$ (22 mg, 100%). $^{1}$H NMR (CD$_2$Cl$_2$): 6.33 (m, *o*-H), 2.66 (s, CH$_3$). $^{19}$F NMR (CD$_2$Cl$_2$): −132.51 (m), −141.14 (m), −157.73 (m), −158.21 (m). $^{11}$B NMR (CD$_2$Cl$_2$): −6.5 (br s).

**Synthesis of 2·PEt$_3$.** In the glovebox, borane **2** (30 mg, 0.06 mmol) was taken up in hexanes (3 mL). Et$_3$P (~5 equiv) was then added, and the solution was stirred for 10 min. The solvent was then removed in vacuo and the white solid redissolved in hexanes. The hexanes were allowed to slowly evaporate in the glovebox until clear crystals (34 mg, 100%) suitable for an X-ray structure determination formed. $^{1}$H NMR (CD$_2$Cl$_2$): $\delta$ 6.252 (br mult, 1 × *o*-H borane), 1.829 (t, 2 × CH$_2$), 1.101 (q, 3 × CH$_3$). $^{19}$F NMR (CD$_2$Cl$_2$): $\delta$ −124.78 (3 × *o*-F, t $^{3}J_{FF}$ = 23 Hz), −140.34 (nonresolved multiplet), −157.50 (t, $^{3}J_{FF}$ = 23 Hz) −158.37 (nonresolved multiplet). $^{31}$P NMR (CD$_2$Cl$_2$): $\delta$ 1.89 (d of m). $^{11}$B NMR (CD$_2$Cl$_2$): −10.4 (d, $^{1}J_{BP}$ = 70 Hz).

**Synthesis of 3·NCCH$_3$.** In the glovebox, borane **3** (20 mg) was taken up in acetonitrile (2 mL) and the mixture stirred for 10 min. The solvent was then removed in vacuo, and the white solid was redissolved in dry dichloromethane. Through slow evaporation of the DCM into toluene crystals suitable for an X-ray structural determination (22 mg, 100%) were recovered from the bottom of the vial. $^{1}$H NMR: $\delta$ 7.01 (br m, 3 × *p*-H), 2.66 (br s, 3 × NCCH$_3$). $^{19}$F NMR: $\delta$ −135.19 (m, 6 × *o*-F), −141.63 (m, 6 × *m*-F). $^{11}$B NMR: −10.1 (br s).

**Childs Lewis Acidity Tests in CD$_2$Cl$_2$.** In a sealable NMR tube, crotonaldehyde (1.6 uL) was added to CD$_2$Cl$_2$. The $^{1}$H NMR spectrum was then recorded at both 253 and 298 K. One equivalent of B(*o*-HC$_6$F$_4$)$_3$ or B(C$_6$F$_5$) was then added, and again the spectra were recorded at 253 and 298 K. An excess of borane was then added to ensure that all crotonaldehyde was coordinated, and the spectra were again recorded. $^{1}$H NMR (253 K): H$_3$CCH═CHCHO reference $\delta$ 6.89 (m, 1H); H$_3$CCH═CHCHO·B(C$_6$F$_5$)$_3$ adduct $\delta$ 7.89 (m, 1H), reference shift $\Delta\delta$ = 1.00; H$_3$CCH═CHCHO·B(*o*-HC$_6$F$_4$)$_3$ adduct $\delta$ 7.85, reference shift $\Delta\delta$ = 0.96; Lewis acidity relative to B(C$_6$F$_5$)$_3$ 96.0%. $^{1}$H NMR (298 K): H$_3$CCH═CHCHO reference $\delta$ 6.87 (m, 1H); H$_3$CCH═CHCHO·B(C$_6$F$_5$)$_3$ adduct $\delta$ 7.84 (m, 1H), reference shift $\Delta\delta$ = 0.97; H$_3$CCH═CHCHO·B(*o*-HC$_6$F$_4$)$_3$, adduct $\delta$ 7.83; reference shift $\Delta\delta$ = 0.96; Lewis acidity relative to B(C$_6$F$_5$)$_3$ 98.9%.

**Gutmann−Beckett Lewis Acidity Test.** In a sealable NMR tube, triethylphosphine oxide (1 mg) was dissolved in CD$_2$Cl$_2$. To this was added 3 equiv of borane. The $^{31}$P NMR spectra of initial and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coordinated triethylphosphine oxide was recorded at 25 °C for $B(C_6F_5)_3$, $B(o\text{-}HC_6F_4)_3$, and $B(p\text{-}HC_6F_4)_3$. $^{31}P\{^1H\}$ NMR: $Et_3P{=}O$ reference $\delta$ 51.2; $Et_3P{=}O{\cdot}B(C_6F_5)_3$ reference adduct $\delta$ 77.8, reference shift $\Delta\delta$ = 26.6; $Et_3P{=}O{\cdot}B(o\text{-}HC_6F_4)_3$ $\delta$ 76.7, reference shift $\Delta\delta$ = 25.5; Lewis acidity strength relative to $B(C_6F_5)_3$ 97.3%; $Et_3P{=}O{\cdot}B(p\text{-}HC_6F_4)_3$ $\delta$ 77.4, $\Delta\delta$ = 26.2; Lewis acidity strength relative to $B(C_6F_5)_3$ 98.5%.

**Acetonitrile Competition Reactions General Procedure.** A 1:1 mixture of borane−acetonitrile adduct and free borane was loaded into a sealable J. Young NMR tube and dissolved in $CD_2Cl_2$ (0.7 mL). The $^{19}F$ NMR spectra of each reaction mixture were then recorded. For complete fluorine spectra and assignment of peaks, see the Supporting Information (Figures S20−S22).

**Synthesis and Equilibrium Study of 2−Ethyl Benzoate.** To a solution of **2** (85 mg, 0.17 mmol) in toluene was added ethyl benzoate (24.32 uL, 0.17 mmol), and the mixture was stirred for 10 min. The solvent was then removed, the white product was washed three times with hexanes (10 mL), and the final product was isolated as a fluffy white powder (91 mg, 0.14 mmol, 82%). $^1H$ NMR ($CD_2Cl_2$): $\delta$ 8.00 (dd, $^3J_{HH}$ = 7.1 Hz, 2 × *o*-H), 7.568 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, 1 × *p*-H), 7.437 (t, *J* = 8 Hz, 2 × *m*-H), 6.955 (broad multiplet, 3 × *o*-*H* borane), 4.374 (q, 7.2 Hz, $CH_2O$), 1.387 (t, 7.2 Hz, $CH_3$). $^{19}F$ NMR: $\delta$ −125.88 (s), −138.82 (m), −147.54 (br s), −155.29 (t). $^{11}B$ NMR: $\delta$ 60.0 (broad). Equilibrium measurements were performed in $C_6D_6$, with the $CH_3$ group being the signal monitored: with 10 equiv of borane $^1H$ $\delta$ 0.918, free ethyl benzoate $^1H$ $\delta$ 1.004, and adduct $^1H$ $\delta$ 0.965.

**Synthesis and Equilibrium Study of 3−Ethyl Benzoate.** To a solution of **3** (85 mg, 0.17 mmol) in toluene was added ethyl benzoate (24.32 uL, 0.17 mmol), and the mixture was stirred for 10 minutes. The solvent was then removed, the white product was washed three times with hexanes (10 mL), and the final product was isolated as a fluffy white powder (21 mg, 0.03 mmol, 18%). $^1H$ NMR ($CD_2Cl_2$): $\delta$ 7.913 (m, 2 × *o*-H), 7.57 (m, 1 × *p*-H), 7.41(m, 2 × *m*-H), 7.18 (br s, 3 × *p*-H borane), 4.49 (q, *J* = 7.1 Hz, 2 × $CH_2$), 1.42 (t, *J* = 7.1 Hz, 3 × $CH_3$). $^{19}F$ NMR: $\delta$ −131.64 (br s), −139.88 (br s). $^{11}B$ NMR: $\delta$ 41.70 (br s). Equilibrium measurements were performed in $C_6D_6$, with the $CH_3$ group being the signal of interest: with 10 equiv of borane $^1H$ $\delta$ 0.816, free ethyl benzoate $^1H$ $\delta$ 1.004, adduct $^1H$ $\delta$ 0.874.

**X-ray Crystallography.** Colorless prismatic crystals of **2**·$PEt_3$, **2**·$NCCH_3$, and **3**·$NCCH_3$ were used for data collection. The crystals were coated with Paratone 8277 oil (Exxon) and mounted on glass fibers. All measurements were made on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo K$\alpha$ radiation. The data were collected using $\omega$ and $\varphi$ scans and corrected for Lorentz and polarization effects and for absorption using the multiscan method. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. An *o*-F atom in **2**·$NCCH_3$ was disordered over sites F1 and F5 in a 0.586(5):0.414(5) ratio with H2 and H6 occupying 0.414(5) and 0.586(5) site occupancy factors, respectively. In the final cycles of full-matrix least-squares refinement using SHELXL97 the weighting schemes were based on counting statistics and the final difference Fourier maps were essentially featureless. The figures were plotted with the aid of ORTEP-3.

## ■ ASSOCIATED CONTENT

### Supporting Information

Relevant $^1H$, $^{11}B$ and $^{19}F$ NMR spectra and crystallographic information for compounds **1**·$PEt_3$, **1**·$NCCH_3$, and **2**·$NCCH_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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