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Synthesis, Characterization, and Properties of Weakly Coordinating Anions Based on *tris*-Perfluoro-*tert*-Butoxyborane.

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ABSTRACT: A convenient method for the preparation of strongly Lewis acidic *tris*-perfluoro-*tert*-butoxyborane $B(OR^F)_3$ (**1**), ($OR^F = OC(CF_3)_3$) was developed, and its X-ray structure determined. **1** was used as a precursor, guided by density functional theory (DFT) calculations and volume based thermodynamics, for the synthesis of $[NEt_4][NCB(OR^F)_3]$ (**3**) and $[NMe_4][FB(OR^F)_3]$ (**5**) and the novel large and weakly coordinating anion salts $[Li\ 15\text{-Crown-5}][B(OR^F)_4]$ (**2**) and $[NEt_4][CN\{B(OR^F)_3\}_2]$ (**4**). The stability of $[B(OR^F)_4]^-$ was compared with that of some related known weakly coordinating anions by appropriate DFT calculations.

INTRODUCTION

Weakly coordinated ion pairs are of fundamental importance to a wide variety of applied chemistries including olefin polymerization,¹ electrochemistry² and ionic liquids among others.³⁻⁵ In such systems a suitable unreactive non-basic, non-nucleophilic counter anion is required to balance formal charge, while behaving as a passive spectator to the desired processes. The observation that the activity of certain cationic catalyst systems can be improved substantially by reducing the coordinating ability of the counter anion has been an important motivator for the discovery of novel and ever more weakly coordinating anions (WCAs),⁶⁻⁹ some of which are included in Table 2 (given later in this work). These anions have been used to stabilize salts of homopolyatomic cations of the elements of Groups 14–18,⁹⁻¹³ as well as other reactive p-block cations, that have been the subject of an extensive recent review.⁹

One class of WCAs that have proven particularly effective for the stabilization of a variety of unique cations are the fluorinated alkoxyaluminates of the type $[Al(OR)_4]^-$ ($R = C(CF_3)_3$, $C(CCl_3)$, $C(CF_3)_2H$, $C(CF_3)_2(CH_3)$, and $C(CCl_3)(CF_3)_2$ ^{14,15} and, most notably, the perfluorinated derivative $[Al(OC(CF_3)_3)_4]^-$.¹⁶ This complex can be synthesized conveniently and on a large scale via the reaction of $LiAlH_4$ with $HOC(CF_3)_3$.¹⁶ It can then be converted to the corresponding silver salt via reaction with $Ag[SbF_6]$ ¹⁷ or AgF ,¹⁶ which facilitates subsequent incorporation of the supporting anion through salt metathesis reactions. The parent “super acid” $Al(OC(CF_3)_3)_3$ was only recently isolated via the reaction of $HOC(CF_3)_3$ with $Al(CH_2CH_3)_3$, provided that the temperature is kept below -20 °C.^{18,19} It is unstable above this temperature without donor solvent stabilization, likely decomposing via intramolecular C–F bond activa-

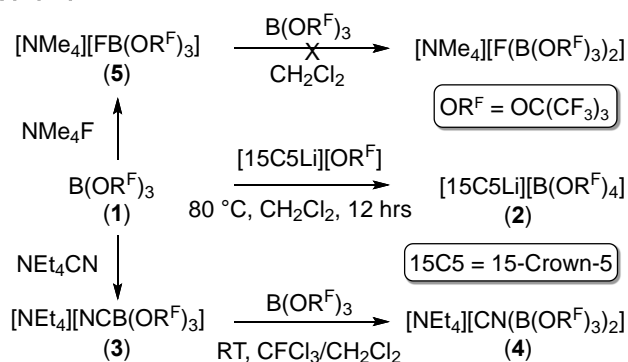
tion, following coordination to the highly Lewis acidic and, comparatively, sterically accessible aluminum center. Because of this instability, the related very large “least coordinating” anion,²⁰ $[Al(OC(CF_3)_3)_2(\mu-F)]^-$ is currently accessed via a high yielding but non-atom-economic route, starting from $Ag[(OC(CF_3)_3)_4]$,^{20,21} rather than via direct preparation from the parent Lewis acid.

Our interest in studying the analogous boron-based species sprang from the fortuitous isolation of crystals of $B(OC(CF_3)_3)_3$, (**1**), which were recovered from the cold traps of a vacuum line used in an unrelated preparation involving $HOC(CF_3)_3$ and $NaBF_4$. While the route by which these crystals were formed was uncertain, they were of sufficient quality for a successful X-Ray structure determination. This compound was one amongst a trio of the first isolated fluorinated borate compounds, originally reported in a paper by D. E. Young some decades ago.^{22,23} It was prepared according to a two-step synthesis involving (i) chlorofluorination of $HOC(CF_3)_3$ with ClF and (ii) subsequent reaction of the resulting hypochlorite with BCl_3 . These reactions were conducted in high-pressure stainless steel reactors, giving HF and Cl_2 gas as by-products, and unreported yields of the borate. Perhaps unsurprisingly given these reaction conditions, the compound has remained largely absent from the chemical literature, following the initial report. An alternate synthetic route was suggested in 1998, based on the reaction of borane methyl-sulfide complex $BH_3S(CH_3)_2$ with $HOC(CF_3)_3$.²⁴ Unfortunately, only sparse experimental details were provided, no yields were given, and the product was characterized exclusively by a previously unreported boiling point. The compound has been subsequently mentioned in papers describing the potential use of various fluorinated borates as additives in elec-

trolyte mixtures for battery applications,²⁵ and several times in the patent literature for the same purpose.²⁶

We were interested in developing a straightforward preparation of **1** to facilitate an investigation of its Lewis acid properties, and its potential as a conveniently handled direct precursor to novel weakly coordinating anions analogous to the perfluorinated alkoxyaluminates. Herein, we report a novel synthesis and complete characterization of **1**, and its use as a precursor to several hitherto unknown weakly coordinating anion salts, as depicted in Scheme 1. Volume based thermodynamic (VBT)/gas-phase DFT [BP86/SV(P)]/Born-Haber-Fajans calculations were used to guide the selection of a suitable counteranion for the synthesis of [Li 15-Crown-5][B(OC(CF₃)₃)₄] (**2**), and the thermodynamic properties of this anion relevant to its effectiveness as a supporting WCA were evaluated. Compound **1** was also used to form the novel fluoride and cyanide salts [N(CH₃)₄][F(B(OC(CF₃)₃)₃)] (**5**) and [N(CH₂CH₃)₄][NCB(OC(CF₃)₃)₃] (**3**), the latter of which was used to isolate the tenuously stable cyanide bridged adduct [N(CH₂CH₃)₄][CN{B(OC(CF₃)₃)₃}₂] (**4**).

Scheme 1



RESULTS AND DISCUSSION

Synthesis and properties of B(OC(CF₃)₃)₃ (1**).** Compound **1** can be prepared conveniently by salt metathesis of LiOR^F (OR^F = OC(CF₃)₃)²⁷ with a slight excess of BCl₃ in diethyl ether. The reaction is complete within a few hours of stirring at room temperature, and spectroscopically pure product can be isolated by vacuum transfer into a cold trap, followed by evacuation of volatiles at 0 °C. This high yield preparation (80–85%), avoids the corrosive by-products of the original preparation (HF, Cl₂, HCl)²² and hence can be done on a large scale in conventional glassware. We have found that acceptable yields of **1** can be also be produced by reaction of boron trichloride with three equivalents of perfluoro-*tert*-butanol in the absence of solvent. However, this method has a tendency to produce material containing residual amounts of alcohol, which is difficult to remove completely. Small amounts of this impurity decrease the already low melting point (35 °C),²² making it difficult to manipulate at room temperature. The compound was observed to sublime in sealed containers at low temperature, which is consistent with previous reports that it has a measurable vapor pressure at room temperature.²² Thus, if possible, even high purity samples should be manipulated while cold. The compound is also highly moisture sensitive, hydrolyzing rapidly in air to give B(OH)₃ and HOR^F.

The compound is sparingly soluble in CDCl₃, CD₂Cl₂ and SO₂, and it undergoes a phase change when suspended in these solvents, forming two immiscible liquid layers. It has better solubility in tetrahydrofuran (THF) (~1 g/100 g) and diethyl ether (~5 g/100 g) and good solubility in CFCl₃ (>100 g/100 g). The relatively low solubility in coordinating solvents is perhaps surprising, given the possibility of forming Lewis acid-base adducts. To test for adduct formation, the NMR signals of **1** in a 1:3 mixture of the nondonating solvents CFCl₃ and CD₂Cl₂ were compared to solutions in THF, diethyl ether and SO₂ (See Section S1 in the Supporting Information for nuclear magnetic resonance (NMR) details and Fourier transform infrared (FT-IR) and Fourier transform (FT)-Raman spectral details, along with calculated frequencies, intensities, and vibrational assignments. FT-IR for both liquid and gas samples are provided). The changes in the ¹⁹F chemical shifts were -2.13, -0.45, and +0.14 ppm respectively for the three solvents, while the changes in ¹¹B NMR signals were +1.92, -0.03, and -0.86 ppm. The small changes in chemical shift imply that adducts are indeed precluded, likely for steric reasons. In comparison, the ¹¹B NMR shift of B(OC₆F₅)₃²⁸ moves upfield by 11.9 ppm upon coordination of THF,²⁹ while the ¹⁹F NMR signals move by 11.1 ppm averaged over the ortho, meta, and para positions. This result was further supported by DFT calculations [BP86/SV(P)], which show negligible solvent coordination enthalpies (~2 kJ mol⁻¹) for both SO₂ and Et₂O complexes of **1** [c.f. ~10 kJ mol⁻¹ for SO₂ adduct of B(OC₆F₅)₃].

Subsequently, X-ray quality crystals of **1** were grown by slow sublimation at room temperature over several days, and the structure is shown in Figure 1 and is similar to that of the related B(OCH(CF₃)₂)₃.³⁰ Crystal refinement (Cambridge Crystallographic Data Centre (CCDC) No. 1448944) data are provided in Section S3.1 in the Supporting Information. The molecule has a C_{3h} symmetric core, with crystallographically equivalent B–O and O–C bond distances, as well as equivalent O–B–O and B–O–C angles (see Table 1). This symmetry is broken at the CF₃ groups, where one arm is rotationally offset, with respect to the other two, leading to overall C₁ symmetry (torsion angles, ∠B–O1–C1–C3, 76.7(4)°; ∠B–O2–C5–C7, 80.0(4)°; ∠B–O3–C9–C11, 45.3(5)°). DFT structure optimization starting from crystal structure coordinates found a local minimum very similar to the solid-state structure (Table 1). A C₃ symmetric global minimum was subsequently found, which was only 2.1 kJ mol⁻¹ lower in energy, indicating that rotation about the C–CF₃ bond is fairly unrestricted.

The B–O bond distance range of 1.357(4)–1.363(4) Å is typical for three coordinate alkyl borates (Table 1), and results in O...O nonbonded intramolecular contacts averaging ~2.357 Å, which is consistent with a ligand close packing (LCP) description of the oxygen atoms around boron.³¹ Nine F...F nonbonded contacts between adjacent OC(CF₃)₃ groups were found to be shorter than the sum of the van der Waals radii (2.94 Å), which we interpret to be indicative of steric strain in the molecule. It is noteworthy that this strain does not cause either the B–O or O–C bonds in **1** to lengthen relative to those of the comparatively unhindered alkyl borates such as B(OCH₃)₃ (1.359(6) Å).³² Rather, the only apparent geometric distortion in the structure is an increase in the B–O–

C angles, (Table 1) which would serve to increase the separation between the $C(CF_3)_3$ groups.

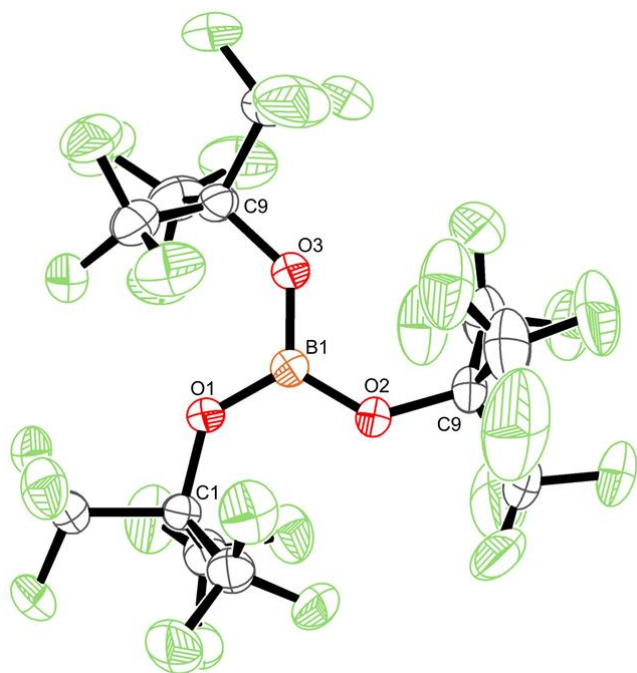


Figure 1. Crystal structure of **1** showing thermal ellipsoids at 50% probability. Selected bond lengths (Å): B1–O1 1.357(4), B1–O2 1.363(4), B1–O3 1.363(4), O1–C1 1.401(3), O2–C5 1.401(4), and O3–C9 1.403(3). Selected bond angles (°): $\angle O1-B1-O2$ 120.1(3), $\angle O1-B1-O3$ 119.9(3), and $\angle O2-B1-O3$ 120.0(3).

The B–O bond distance range of 1.357(4)–1.363(4) Å is typical for three coordinate alkyl borates (Table 1), and results in O···O nonbonded intramolecular contacts averaging ~ 2.357 Å, which is consistent with a ligand close packing (LCP) description of the oxygen atoms around boron.³¹ Nine F···F nonbonded contacts between adjacent $OC(CF_3)_3$ groups were found to be shorter than the sum of the van der Waals radii (2.94 Å), which we interpret to be indicative of steric strain in the molecule. It is noteworthy that this strain does not cause either the B–O or O–C bonds in **1** to lengthen relative to those of the comparatively unhindered alkyl borates such as $B(OCH_3)_3$ (1.359(6) Å).³² Rather, the only apparent geometric distortion in the structure is an increase in the B–O–C angles, (Table 1) which would serve to increase the separation between the $C(CF_3)_3$ groups.

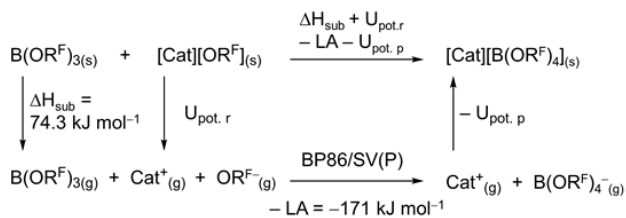
Predictive Thermodynamics and WCA syntheses. We began investigations into the use of **1** as a precursor for large, weakly coordinating anions by attempting to prepare the lithium salt $Li[B(OC(CF_3)_3)_4]$ using the straightforward reaction of **1** with $Li(OC(CF_3)_3)$. Initial attempts using a variety of different solvents, with or without heating were unsuccessful, yielding unreacted starting materials. This result and our previous successes^{11,17,38} in guiding syntheses using a combination of DFT calculations and “volume-based” thermodynamics (VBT)^{39–41} prompted an analysis of the energetics involved in the reaction. The Born-Haber-Fajans cycle incorporating the energy terms relevant to the synthesis of the target anion salt is shown in Scheme 2.

Table 1. Comparison of Selected Crystallographic and Calculated [BP86/SV(P)] Parameters for $M(OR^F)_3$ ($M = B, Al$; $OR^F = OC(CF_3)_3$) and Related Species.

| Compound | M–O (Å) | O–C (Å) | O–O (Å) | $\angle M-O-C$ (°) |
|--|---|---|---|---|
| $B(OR^F)_3$ (1) | 1.363(4), 1.363(4), 1.357(4) | 1.401(3), 1.401(4), 1.403(3) | 2.355(3), 2.361(3), 2.356(3) | 133.3(2), 133.4(2), 132.4(2) |
| $B(OR^F)_3$ (calc.) | 1.375 | 1.398 | 2.381 | 134.6 |
| $[NEt_4][NCB(OR^F)_3]$ (3) | 1.458(3), 1.466(4), 1.463(4) | 1.371(3), 1.365(3), 1.370(3) | 2.380(3), 2.368(3), 2.374(3) | 135.2(2), 135.0(2), 136.3(2) |
| $[Li15CS][B(OR^F)_4]$ (2) | 1.478(8), 1.463(8), 1.483(6), 1.482(8) | 1.388(8), 1.383(6), 1.348(7), 1.379(7) | 2.381(5), 2.484(6), 2.374(6), 2.490(5), 2.371(5), 2.363(4) | 137.0(4), 137.8(4), 138.7(5), 138.8(5) |
| $[B(OR^F)_4]^-$ (calc.) | 1.488 | 1.368 | 4 x 2.389, 2 x 2.509 | 140.4 |
| $B(OCH(CF_3)_2)_3$ ^a | 1.359(4), 1.358(4), 1.360(4) | 1.411(3), 1.416(3), 1.416(3) | 2.350(3), 2.352(3), 2.360(3) | 122.3(2), 122.3(2), 121.7(2) |
| $[Na(THF)_2][B(OCH(CF_3)_2)_4]$ ^b | 1.487(2), 1.450(2), 1.467(2), 1.472(2) | 1.390(2), 1.388(3), 1.390(2), 1.388(2) | 2.297(2), 2.455(2), 2.407(2), 2.399(2), 2.428(2), 2.396(2) | 120.8(1), 122.7(1) 123.5(1), 124.2(1) |
| $B(OCH_3)_3$ ^c | 1.367(4) | 1.424(5) | 2.366(7) | 121.4(5) |
| $NC_5H_{12}[B(OCH_3)_4]$ ^d | 1.454(5), 1.475(3), 1.451(2), 1.451(2) | 1.403(3), 1.412(5), 1.391(2), 1.391(2) | 2.276(1), 2.438(1), 2.438(1), 2.438(1), 2.438(1), 2.245(1) | 116.0(0), 117.3(1), 116.4(1), 116.4(1) |
| $B(OC_6H_5)_3$ ^e | 1.361(2), 1.365(2), 1.357(3) | 1.387(3), 1.386(2), 1.397(2) | 2.355(2), 2.363(2), 2.354(2) | 121.6(1), 122.4(2), 121.2(2) |
| $[Na(THF)_3][B(OC_6H_5)_4]$ ^e | 1.476(2), 1.495(2), 1.457(3), 1.451(2) | 1.365(2), 1.356(2), 1.353(2), 1.369(2) | 2.251(2), 2.475(2), 2.467(2), 2.443(2), 2.484(2), 2.260(2) | 123.9(1), 125.2(1), 126.4(1), 123.5(1) |
| $Al(OR^F)_3(THF)^f$ | 1.699(2), 1.708(2), 1.709(2) | 1.374(4), 1.363(4), 1.352(4) | 2.886(3), 2.814(3), 2.899(3) | 149.9(2), 152.1(2) 149.9(2) |
| $Al(OR^F)_3$ (calc.) ^g | 1.745 | 1.370 | 3.020 | 133.7 |

See ^a ref. 30. ^b ref. 33. ^c ref. 34. ^d ref. 35. ^e ref. 36. ^f ref. 20. ^g ref. 37.

Scheme 2. Born-Haber-Fajans Cycle Used To Predict the Minimum Cation Volume Required for Preparation of a Thermodynamically Feasible Salt of $[B(OC(CF_3)_3)_4]^{-a}$



^a $OR^F = OC(CF_3)_3$, Cat = generic cation, LA = ligand affinity of $B(OR^F)_3$, U_{pot} = lattice potential energy, H_{sub} = sublimation energy. Calculations at the BP86/SV(P) level of theory.

The energy terms used to complete the cycle were determined as follows. The energy of binding an $[OC(CF_3)_3]^-$ fragment to **1** in the gas-phase (ligand affinity, $-LA$) was determined computationally, at the BP86/SV(P) level of theory (c.f. MP2/TZVPP -217 kJ mol^{-1}). The enthalpy of sublimation was taken as the sum of the enthalpies of fusion (determined by differential scanning calorimetry) and of vaporization. The enthalpy of vaporization was estimated according to Trouton's rule,⁴² by substituting a calculated boiling point value (COSMO-RS) into the least squares fit of a previously reported experimental correlation of boiling points and vaporization enthalpies for an extensive series of organic and inorganic compounds.⁴³ For comparison, the same calculation was performed for three compounds with known enthalpies of vaporization, thus providing validation for the method, as well as an estimate of the associated error.⁴⁴ Finally, the lattice enthalpy terms ($U_{\text{pot. r}}$, $U_{\text{pot. p}}$) were estimated using "volume-based" thermodynamics (VBT) with ion volume data obtained from the relevant crystal structures (see Section S2 in the Supporting Information for complete details).

The results of the thermodynamics calculations are represented graphically in Figure 2, by plotting the overall reaction enthalpy against the volume of the counter cation used in the lattice energy estimations. The entropy differences between salts are negligible and therefore reaction enthalpy changes are essentially equal to the energy change.⁴⁵ As the volume of the cation increases, the unfavorable lattice energy difference between the products and the reactants decreases. Therefore, the x-intercept at $\sim 0.145 \text{ nm}^3$ represents the minimum cation volume required for a generalized perfluorinated *tert*-butoxide salt to give an overall enthalpically favorable reaction with **1**.³⁸ This result suggests the attempted reaction of $LiOC(CF_3)_3$ with **1** failed on thermodynamic grounds, given that the small volume of the Li^+ cation (0.00199 nm^3) falls far below the required threshold.³⁹ Furthermore, it predicts that employing a salt with a countercation volume of $>0.15 \text{ nm}^3$ should produce the target WCA, given that the entropic difference between reactants and products is negligible for these salts, and that solvent effects appear to be similarly negligible, as discussed above.^{38,45}

Therefore, based on this prediction, the volume of the counter-cation was conveniently expanded by encapsulating the Li atom of $LiOC(CF_3)_3$ in 15-Crown-5 ether. This increased the cation volume to $\sim 0.267 \text{ nm}^3$,⁴⁶ which is well above the required thermodynamic threshold. Using a straightforward preparation with the larg-

er-volume crown complex salt, instead of the simple Li^+ salt successfully produced the target WCA $[Li\ 15C5][B(OR^F)_4]$ (**2**) (where 15C5 = 15-Crown-5) in high yield (Scheme 3).

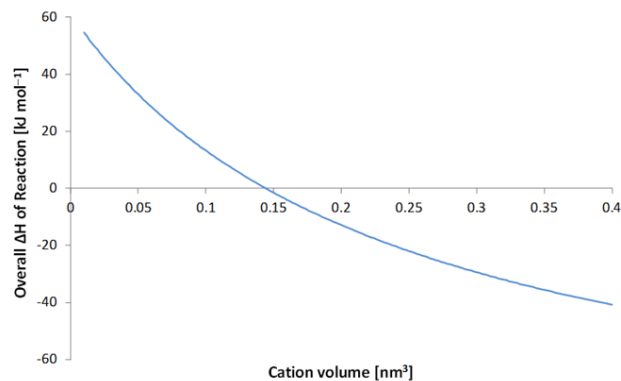
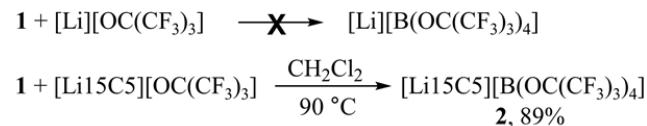


Figure 2. Plot showing the results of predictive thermodynamics used to estimate the minimum required cation volume for reactions of a general MOR^F salt ($M = +1$ cation) with $B(OR^F)_3$ that are favored by enthalpy (The data for this plot is supplied in Section S2 in the Supporting Information).

Scheme 3



Compound **1** and anion in **2** exhibit very similar spectra (via IR spectroscopy, as well as 1H , ^{13}C , and ^{19}F NMR; see Section S1 in the Supporting Information), but are readily distinguishable in solution by a diagnostic change in the ^{11}B NMR signal from 13.5 to -0.9 ppm, indicative of the increase in coordination number at the boron center. The connectivity in **2** is further confirmed by X-ray crystal structure analysis (CCDC No. 1510717; see Section S3.2 in the Supporting Information). Crystals were grown via slow solvent evaporation from a CH_2Cl_2 solution. Unfortunately, the quality of the structure solution was diminished by disorder in the $C(CF_3)_3$ groups. This precludes definitive structural comparisons; however, a discussion of the observed structural parameters and tentative conclusions can be found in Section S3.2 in the Supporting Information.

Comparison with Other Weakly Coordinating Anions.

Krossing et al.³⁷ derived a set of theoretical estimates to assess the stabilities of different weakly coordinating anion candidates and determine their suitability to be used as such. The calculated properties include the fluoride ion affinity (FIA), ligand affinity (LA), proton decomposition energy (PD), copper decomposition energy (CuD), and the energy of the HOMO and the HOMO – LUMO gap. FIA is the energy of binding a fluoride ion to the neutral parent Lewis acid of an anion, while LA is defined as the energy required to remove a ligand L from an anion to give its neutral parent Lewis acid. The PD and CuD represent attacks on the anion by hard (H^+) and soft (Cu^+) electrophiles, respectively, leading to elimination of HL and CuL. These four properties provide a reasonable approximation to the common experimentally observed WCA decomposition pathways. The HOMO energy and HOMO – LUMO gap give

means of gauging how susceptible the anion is to oxidation and reduction, respectively. Recently Krossing et al.³⁰ amended their original estimates for FIA, PD, and CuD. Their new estimates use enthalpies of reaction $\Delta_r H$ for FIA and Gibbs energies $\Delta_r G^\circ$ for PD and CuD instead of the $\Delta_r U$ values used in the original paper.³⁷ They determined the updated FIA values from isodesmic reactions referenced to FIA of Me_3Si^+ calculated at the G3 level. We have used the updated FIA, PD, and CuD values in our comparison of the properties of $[\text{B}(\text{OR}^{\text{F}})_4]^-$ with other weakly coordinating anions that is presented in Table 2.

Table 1. Literature Calculated Properties of WCAs and Comparison with $[\text{B}(\text{OR}^{\text{F}})_4]^-$ [BP86/SV(P)].

| Anion | symmetry | FIA ($\Delta_r H$) [kJ mol ⁻¹] | LA ($\Delta_r U$) [kJ mol ⁻¹] | PD ($\Delta_r G$) [kJ mol ⁻¹] | CuD ($\Delta_r G$) [kJ mol ⁻¹] | HOMO [eV] | HOMO-LUMO gap [eV] |
|---|----------|---|--|--|---|--------------------|-----------------------|
| $[\text{B}(\text{OR}^{\text{F}})_4]^-$ | S_4 | 420 | 171 | -1268 | -584 | -3.85 | 6.85 |
| $[\text{B}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$ ^a | S_4 | 403 | 285 | -1194 | -504 | -3.38 | 7.05 |
| $[\text{B}(\text{OC}_6\text{F}_5)_4]^-$ | D_2 | 431 | 202 | -1209 | -531 | -2.89 | 3.96 |
| $[\text{BF}_4]^-$ | T_d | 342 ^b | 338 ^c | -1212 ^b | -540 ^b | -1.80 ^b | 10.82 ^b |
| $[\text{B}(\text{CF}_3)_4]^-$ | T | 556 ^b | 520 ^d | -1143 ^b | -411 ^b | -3.53 ^b | 9.07 ^b |
| $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | S_4 | 452 ^b | 296 ^c | -1263 ^b | -567 ^b | -3.12 ^b | 4.21 ^b |
| $[\text{B}(\text{OTeF}_5)_4]^-$ | C_i | 552 ^b | 274 ^c | -1098 ^b | -496 ^b | -5.55 ^b | 2.13 ^b |
| $[\text{AsF}_6]^-$ | O_h | 430 ^b | 426 ^c | -1129 ^b | -457 ^b | -3.15 ^b | 6.28 ^b |
| $[\text{SbF}_6]^-$ | O_h | 493 ^b | 489 ^c | -1065 ^b | -393 ^b | -3.91 ^b | 5.13 ^b |
| $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ | S_4 | 543 ^b | 342 ^c | -1077 ^b | -413 ^b | -4.10 ^b | 6.74 ^b |
| $[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$ | S_4 | 551 | 426 | -1052 | -364 | -3.77 | 6.70 |

^a Note that our calculated differ from those given in ref. 30 mainly because of the lower DFT energy that we calculated. See ^b ref. 30, ^c ref. 37, ^d ref. 47.

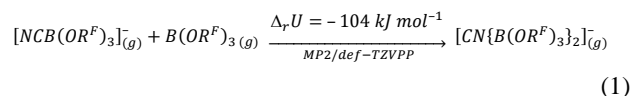
The LA of $[\text{B}(\text{OR}^{\text{F}})_4]^-$ is the lowest of all the species listed in Table 2. This is likely a reflection of the intramolecular strain imposed by close packing of the bulky OR^{F} groups, as exemplified by the substantial increase in LA found for the less hindered $[\text{B}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$. This can be compared to the smaller increase in LA observed in going from $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ to $[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$. Alongside the notably lower LA of $[\text{B}(\text{OR}^{\text{F}})_4]^-$ compared to others, it was found to be relatively unstable towards attack by both hard and soft electrophiles having PD and CuD values similar to $[\text{B}(\text{C}_6\text{F}_5)_4]^-$. Finally, the affinity towards oxidation or reduction reactions is close to that observed for $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ and less than that observed for $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $[\text{B}(\text{OC}_6\text{F}_5)_4]^-$. Viewed as a whole, these values suggest that $[\text{B}(\text{OR}^{\text{F}})_4]^-$ is relatively unstable in comparison to the other known WCAs and that the source of this instability appears to be primarily due to the ease with which the OR^{F} ligand can be abstracted.

Synthesis of CN^- and F^- Functionalized $\text{B}(\text{OR}^{\text{F}})_3$ Anions. Given, the detrimentally low ligand affinity of **1**, the incorporation of a bridging group between two molecules of **1** should act to alleviate some of the strain around each boron center, increasing the stability of the anion. Cyanide and fluoride were chosen as feasible bridging groups. This choice was supported by prior reports of the use of cyanide bridges to stabilize the formation of boron-based anions having a variety of bulky ligands,⁴⁸ and on

1 is a strong Lewis acid, with a FIA value just 73 kJ mol⁻¹ less than that needed for designation as a “Lewis superacid” (defined as any acid stronger than SbF_5).¹⁹ The FIA of **1** is greater than that of BF_3 , and is comparable to that of AsF_5 . It is notably less than those of $\text{B}(\text{CF}_3)_3$, $\text{B}(\text{OTeF}_5)_3$, and $\text{Al}(\text{OR}^{\text{F}})_3$. Of the calculated fluorinated oxyboranes, **1** has lower FIA than the perfluorinated $\text{B}(\text{OC}_6\text{F}_5)_3$ but higher than that of $[\text{B}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$.

fluorine’s analogous role in the aluminum-based “least coordinating anion” $[\{\text{Al}(\text{OC}(\text{CF}_3)_3)_2(\mu\text{-F})\}]^-$.²⁰

Following our successful preparation of **2**, we carried out volume-based thermodynamics (VBT) calculations for the formation of cyanide bridged $[\text{M}][\text{CN}\{\text{B}(\text{OR}^{\text{F}})_3\}_2]$ (eq. 1) to estimate the required cation M^+ size needed to stabilize the $[\text{CN}\{\text{B}(\text{OR}^{\text{F}})_3\}_2]^-$ anion in the solid state. Given the ambident nature of cyanide anion,⁴⁹ both $[\text{NCB}(\text{OR}^{\text{F}})_3]^-$ and $[\text{CNB}(\text{OR}^{\text{F}})_3]^-$ structures were considered initially in BP86/SV(P) calculations. $[\text{NCB}(\text{OR}^{\text{F}})_3]^-$ was calculated 16 kJ mol⁻¹ lower in energy (ΔG) than $[\text{CNB}(\text{OR}^{\text{F}})_3]^-$; it was used in subsequent calculations as the reference structure. A gas-phase reaction $\Delta_r U$ of -54 kJ mol⁻¹ for eq. 1 was calculated at the BP86/SV(P) level. This result implied, together with reports showing that increasing cation volume has a limited ability to change the energetics in the solid state,⁵⁰ that the CN-bridged anion should not be stable in the solid state. However, higher level MP2 calculations produced a significantly more exothermic gas-phase reaction ($\Delta_r U = -104$ kJ mol⁻¹).



Using the *ab initio* MP2 result and lattice energies from VBT calculations, we predicted that a minimum cation volume of 0.47 nm³ is required to enthalpically stabilize $[\text{CN}\{\text{B}(\text{OR}^{\text{F}})_3\}_2]^-$ in the solid-state as shown in Figure 3. The required volume is quite large;

however, given the expected error associated with estimations of the sublimation enthalpy of **1**, the calculated gas-phase energies, and the ion volumes we estimate the error in the solid-state reaction enthalpy to be of the order ± 10 kJ mol⁻¹. Assuming the most favorable case for the formation of $[\text{CN}\{\text{B}(\text{OR}^{\text{F}})_3\}_2]^-$ would reduce the minimum cation volume to 0.20 nm³, which corresponds to the volume of the tetraethylammonium cation.

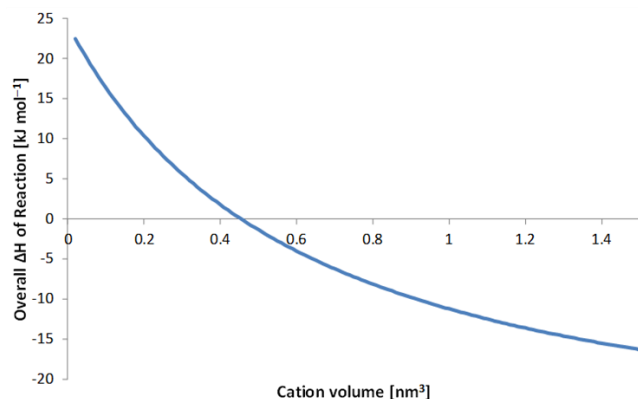


Figure 3. Plot showing the results of predictive thermodynamics used to estimate the minimum required cation volume for an enthalpically favorable reaction between a general $[\text{M}][\text{NCB}(\text{OR}^{\text{F}})_3]$ salt and $\text{B}(\text{OR}^{\text{F}})_3$. (The data used in the plot is given in Section S2 in the Supporting Information).

We attempted the synthesis of the NEt_4^+ salt of $[\text{CN}\{\text{B}(\text{OR}^{\text{F}})_3\}_2]^-$. First, the terminal cyano complex $[\text{NEt}_4][\text{NCB}(\text{OR}^{\text{F}})_3]$ (**3**) was synthesized via the reaction of equimolar amounts of **1** and NEt_4CN in sulfur dioxide. The compound is identifiable by a sharp singlet in the ¹¹B NMR spectrum at -4.6 ppm, as well as by a diagnostic cyanide stretch in the Raman spectrum at 2209 cm⁻¹ (see Section S1.3 in the Supporting Information). Crystals suitable for X-ray crystallographic analysis were grown via slow solvent evaporation from a diethyl ether solution. The crystal data (CCDC No. 1510754) provides further support for our proposed structure of cyano complex and not the higher energy isocyanide isomer (Figure S17 in the Supporting Information). The crystal refinement data, thermal ellipsoid diagram, and corresponding parameters are reported in Section S3.3 in the Supporting Information.

In agreement with the predicted thermodynamics, synthesis of the cyanide-bridged diadduct proved challenging; initial attempts made by stirring two equivalents of **1** with anhydrous NEt_4CN at room temperature in diethyl ether led to mixtures containing mainly **1** and **3**, alongside small amounts of a new product containing a diagnostic CN stretch in the Raman spectrum at 2264 cm⁻¹. A CH_2Cl_2 solution stirred at 90 °C for an extended period of time (10 days) gave a similar product distribution.

Donating solvents were presumed to inhibit formation of the diadduct, and heating the reaction mixtures could conceivably negate the small enthalpic benefit to adduct formation, because of the unfavorable entropy of reaction (c.f. $\Delta G(298 \text{ K})$ calculated at MP2/def-TZVPP level in the gas-phase (-36 kJ mol⁻¹) and using COSMO model in Et₂O (-6 kJ mol⁻¹)). To circumvent these prob-

lems, the reaction was repeated at room temperature using a non-donating solvent mixture consisting of CH_2Cl_2 and CFCl_3 . The addition of a CFCl_3 solution of **1** to a CH_2Cl_2 solution containing 0.5 equivalents of NEt_4CN led to the precipitation of a crystalline solid upon mixing. Evaporating the solvent at room temperature in the glovebox followed by washing with fresh CFCl_3 and CH_2Cl_2 , gave the desired CN bridged species: $[\text{NEt}_4][\text{CN}\{\text{B}(\text{OC}(\text{CF}_3)_3)_3\}_2]$ (**4**). The structure was supported by the appearance of a single new CN stretch in the Raman spectrum at 2264 cm⁻¹ (up from at 2209 cm⁻¹ in **3**), as well by a low-quality crystal structure that successfully established connectivity (see Sections S1.4 and S3.4 in the Supporting Information, respectively).

Poor solubility required that NMR characterization of **4** was attempted in polar solvents, and data was collected in THF-*d*₆. There was no indication by ¹¹B NMR experiments that dissociation had occurred under these conditions, which would regenerate the borate adduct (**1**) and the cyanide adduct **3**. However, the following evidence suggests that, as of yet, ill-defined equilibria are present in solution. The ¹⁹F NMR shift at -73.8 ppm appeared slightly downfield relative to **1** in CD_2Cl_2 , and was broadened substantially from 4 Hz to 83 Hz at peak half height. Similarly, two broad peaks appeared in the ¹¹B NMR at -1.6 and -5.7 ppm (164 Hz and 77 Hz at peak half height), which were assigned to N-bound and C-bound boron atoms, respectively, by comparison to the NMR data of **3**. In addition to broadened NMR signals, it was found that the addition of a further half-equivalent of **1** to a THF-*d*₆ solution of **4** produced a slight downfield shift of the ¹¹B NMR signal for the N-bound **1**, while no signal attributable to free borate appeared in the spectrum.

Crystals of **4** isolated by slow evaporation of the starting solvent mixture proved suitable for analysis by X-ray diffraction and yielded the structure depicted in Figure S18 in the Supporting Information. While this allowed connectivity to be established, the structure was severely disordered at multiple positions, including the cyanide group. Differentiation of the C and N atoms and further comment on specific bond distances and angles was not possible. The data did not permit definitive assignment of the bridging C and N atoms. The connectivity diagram showing 30% thermal ellipsoids and illustrating aspects of the disorder is provided in Figure S18.

When **4** was placed under dynamic vacuum in a resealable NMR tube, intermittent redissolution in CD_2Cl_2 and collection of the ¹¹B NMR spectrum revealed a gradual loss of the signals for the N-bound borate over a period of hours, until only a signal consistent with compound **3** remained. A sample stored in the glovebox at room temperature decomposed in similar fashion over a period of weeks. The tendency of the second borate to dissociate from the solid state, even at room temperature, is consistent with the weak binding predicted by the VBT calculations.

Prior to trying the synthesis of fluorine-bridged $[\text{F}\{\text{B}(\text{OR}^{\text{F}})_3\}_2]^-$, we attempted to optimize its structure at the BP86/def-SV(P) level of theory, but the calculations gave only discrete $[\text{FB}(\text{OR}^{\text{F}})_3]^-$ and $\text{B}(\text{OR}^{\text{F}})_3$ fragments. The calculation results suggested that even though **1** has a large fluoride ion affinity (see Table 2), the steric hindrance between two $\text{B}(\text{OR}^{\text{F}})_3$ fragments prevents the second borate from forming a bond with fluoride. Consistent with the calculation results a test reaction of two equivalents of **1** with anhy-

drous tetramethylammonium fluoride yielded only unreacted **1** and the fluoride adduct $[\text{NMe}_4][\text{B}(\text{OR}^{\text{F}})_3]$ (**5**). Compound **5** was subsequently prepared independently via the reaction of equimolar amounts of **1** and tetramethylammonium fluoride in sulfur dioxide, and was characterized by NMR spectroscopy and elemental analysis. Crystals of the material can be grown readily by slow evaporation from CH_2Cl_2 solutions, but single crystal X-ray analysis consistently gave structures with a high degree of rotational disorder about the $\text{C}(\text{CF}_3)_3$ groups.

CONCLUSIONS

A convenient and high yielding synthetic route to the strongly Lewis acidic borate $\text{B}(\text{OC}(\text{CF}_3)_3)_3$ has facilitated the preparation of novel weakly coordinating anions analogous to the highly acidic aluminum perfluoroalkoxy anions. In contrast to $\text{Al}(\text{OC}(\text{CF}_3)_3)_3$, the preparation of $\text{B}(\text{OC}(\text{CF}_3)_3)_3$ is facile and the potentially strong Lewis acid is stable under ambient conditions in an inert atmosphere. The calculated [BP86/SV(P)] and X-ray structure were in agreement, with the molecule displaying a C_{3h} symmetric core having crystallographically equivalent B–O and O–C bond distances and O–B–O and B–O–C angles. The C_{3h} symmetry is broken at the CF_3 groups, where one arm is rotationally offset with respect to the other two, reducing the overall anion symmetry to C_1 . The presence of nine nonbonded F–F contacts with distances less than the sum of the van der Waals radii was indicative of steric strain within the molecule. This led to an increase in the B–O–C angles which allowed an increase in separation between the bulky $\text{OC}(\text{CF}_3)_3$ groups.

Using a combination of Born-Haber-Fajans cycles, density functional theory (DFT) calculations for reactions in the gas phase, experimental enthalpy of fusion values, enthalpy of vaporization estimated from Trouton’s rule and volume-based thermodynamics (VBT) calculations for the condensed state, we explored the potential for preparing salts of $\text{B}(\text{OC}(\text{CF}_3)_3)_3$. The calculated gas-phase ligand affinity of $\text{B}(\text{OC}(\text{CF}_3)_3)_3$ for $[\text{OC}(\text{CF}_3)_3]^-$ was approximately half that of $\text{Al}(\text{OC}(\text{CF}_3)_3)_3$, which partially accounted for our failure to prepare $\text{Li}[\text{B}(\text{OC}(\text{CF}_3)_3)_4]$, the boron analogue of the synthetically useful $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$, from $\text{LiOC}(\text{CF}_3)_3$ and $\text{B}(\text{OC}(\text{CF}_3)_3)_3$. However, we estimated that the energetics of the reactions for $[\text{B}(\text{OC}(\text{CF}_3)_3)_4]^-$ salts of much larger cations were favorable and we prepared $[\text{Li 15-Crown-5}][\text{B}(\text{OC}(\text{CF}_3)_3)_4]$ (**2**), from $[\text{Li 15-Crown-5}][\text{OC}(\text{CF}_3)_3]$ and $\text{B}(\text{OC}(\text{CF}_3)_3)_3$, in high yield. A range of properties of $[\text{B}(\text{OR}^{\text{F}})_4]^-$ anions were compared with those of various known WCA using DFT calculations, either carried out in this work or reported in the literature. The results of our calculations show the $[\text{B}(\text{OC}(\text{CF}_3)_3)_4]^-$ anion to be relatively unstable, primarily because of the ease with which the $\text{OC}(\text{CF}_3)_3$ ligand can be abstracted.

Steric considerations play a very important role in the acid base chemistry of $\text{B}(\text{OC}(\text{CF}_3)_3)_3$. The calculated fluoride ion affinity of $\text{B}(\text{OC}(\text{CF}_3)_3)_3$ was very similar to that of AsF_5 ; the estimated energetics of the reaction between $\text{B}(\text{OC}(\text{CF}_3)_3)_3$ and NMe_4F were favorable and $[\text{NMe}_4][\text{B}(\text{OC}(\text{CF}_3)_3)_3]$ was prepared. However, the corresponding boron analogue of the “least coordinating anion” $[\{\text{Al}(\text{OC}(\text{CF}_3)_3)_2(\mu\text{-F})\}]^{2-}$ was not a minimum structure in the gas phase calculations due to steric repulsion, and therefore the boron

analogue of this anion is likely not accessible, even as a salt of a very large cation. Replacement of F by CN decreases the steric repulsion, and we estimated that the formation of $[\text{NEt}_4][\text{CN}\{\text{B}(\text{OC}(\text{CF}_3)_3)_3\}_2]$ from the corresponding components was marginally favorable. We subsequently prepared $[\text{NEt}_4][\text{NCB}(\text{OC}(\text{CF}_3)_3)_3]$ and $[\text{NEt}_4][\text{CN}\{\text{B}(\text{OC}(\text{CF}_3)_3)_3\}_2]$; both were characterized spectroscopically and by preliminary X-ray structures, although the latter readily dissociate to the starting reagents. Using the predictive and synthetic methods given above, a variety of salts of $[\text{Cat}][\text{X}\{\text{B}(\text{OC}(\text{CF}_3)_3)_3\}]$ [where Cat represents a cation that is large enough for the preparation to be thermodynamically favorable, and X is a basic anion] can be envisaged.

EXPERIMENTAL SECTION

General considerations. Unless otherwise specified reactions were performed in two-bulb glass vessels equipped with Teflon-in-glass Rotoflo valves and a medium sintered glass frit. All solids were manipulated in an MBraun Unilab glovebox under an N_2 atmosphere (O_2 and $\text{H}_2\text{O} < 1$ ppm). The techniques and apparatus used to perform reactions in SO_2 via a closed, greaseless Monel vacuum line have been described elsewhere.⁵¹ Elemental analyses were obtained from Galbraith Laboratories Inc., or through the use of an in-house analyzer (LECO, Model CHNS 932).

15-Crown-5 (98%, Alfa Aesar), LiH (95%, Aldrich) and NEt_4CN (Fluka, 95%) were used as received. $\text{HOC}(\text{CF}_3)_3$ (P&M-Invest, Russia) was vacuum-distilled and stored over 5 Å molecular sieves. BCl_3 (Matheson) was vacuum-distilled and evacuated for 30 min in an ethanol slush bath (-78 °C) to remove HCl and Phosgene impurities prior to use. $\text{LiOC}(\text{CF}_3)_3$ was synthesized according to a literature procedure.²⁷ Anhydrous NMe_4F was prepared by drying $\text{NMe}_4\text{F}\cdot 4\text{H}_2\text{O}$ (98%, Aldrich) according to a literature procedure.⁵² Diethyl ether and *n*-hexane were passed through a Grubbs apparatus style solvent purification system,⁵³ vacuum-distilled and stored over CaH_2 .

FT-IR spectra were recorded on a Thermo Nicolet Nexus 470. Solids were collected as mineral oil mulls between KBr plates or as neat samples on a ZnSe crystal, using a Smart Performer ATR accessory.

Raman spectra were recorded on a Thermo Nicolet 6700 FT-IR that was equipped with a Thermo Nicolet NXR FT-Raman accessory at 298 K, using a Nd:YVO₄ laser (emission wavelength 1064 nm; Ge detector; resolution of 4 cm^{-1}).

Experimental enthalpy of fusion values were determined from DSC measurements obtained with a differential scanning calorimeter (TA instruments, Model Q200) with Tzero hermetic pans, using TA Instruments Universal Analysis software 4.4A for data analysis.

NMR spectra were collected on a Varian 400 or Bruker Avance III RDQ 400 MHz spectrometer. Samples were prepared in 5 mm resealable J-young style NMR tubes, or standard tubes sealed with rubber septa and parafilm. Chemical shifts are reported based on residual solvents relative to TMS ($^1\text{H}/^{13}\text{C}$), internal CFCl_3 or external CFCl_3 5% (v/v) in CD_2Cl_2 (^{19}F), $\text{BF}_3\cdot\text{OEt}_2$ 5% (v/v) in CD_2Cl_2 (^{11}B) and 0.1M LiCl in D_2O (^7Li).

Computational details. Structure optimizations, energy calculations, and calculation of vibrational spectra were performed using

the Turbomole 6.3 program.⁵⁴ Structures were optimized with BP86⁵⁵ DFT functional using RI approximation,⁵⁶ and Ahlrich's def-SV(P) basis set.⁵⁷ For calculation of the relative Raman intensities⁵⁸ an excitation wavelength of 9398.5 cm⁻¹ and temperature of 298 K were used. Energies for some of the reactions were calculated using RI-MP2⁵⁹ method and def-TZVPP basis set.⁵⁶ Theoretical boiling points were estimated using COSMO-RS module of ADF program.⁶⁰

Synthesis of $B(OC(CF_3)_3)_3$ (1). Diethyl ether (20 mL) was condensed onto LiOC(CF₃)₃ (1.000 g, 4.133 mmol) in a two-bulb flask to give a clear colorless solution. BCl₃ (725 mmHg, 4.13 mmol) was deposited into the vessel at -196 °C in two aliquots, using a mercury manometer and a 35.3 mL transfer bulb, and the mixture was stirred overnight. This gave a clear liquid layer with a supernatant second liquid layer containing a suspension of LiCl. All volatiles were transferred to the second bulb of the vessel, and then removed under vacuum at 0 °C for 45 min to give a white solid (0.859 g, 87.1 %). ¹⁹F NMR (CFCl₃/CD₂Cl₂, 376.5 MHz) δ: -72.3 (s). ¹¹B NMR (128.3 MHz) δ: 13.5 (s). ¹³C NMR (100.62 MHz) δ: 120.9 (q, ¹J_{CF} = 292 Hz), 81.5 (m, ²J_{CF} = 34 Hz). The details for the calculated and observed vibrational frequencies and intensities (FT-IR and Raman) along with spectral assignments are provided in Section S1.1 in the Supporting Information.

X-Ray crystallography. Crystals of **1** were grown by spontaneous sublimation at 25 °C in a sealed reaction vessel. Single crystals were coated with Paratone-N oil, mounted using a polyimide Micro-Mount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3 ° and 10 s exposure times. The detector distance was 5 cm. The data were reduced (SAINT)⁶¹ and corrected for absorption (SADABS).⁶² The structure was solved by direct methods and refined by full-matrix least squares on F² (SHELXTL).⁶³ X-ray data collection and structure solution for **3** were as reported for **1**. Data collection for **2** and **4** used a Rigaku RAXIS RAPID diffractometer to a maximum 2θ of 60°, using a scan angle of 5°. The data were processed and the structures solved with the CrystalStructure crystallographic software package⁶⁴ and finally refined by full-matrix least squares on F² (SHELXTL).⁶³ All non-hydrogen atoms were refined using anisotropic displacement parameters.

Synthesis of [Li 15-Crown-5][OC(CF₃)₃]. Diethyl ether (10 mL) was condensed onto LiOC(CF₃)₃ (3.157 g, 13.0 mmol) in the first bulb of a standard vessel, producing a clear, colorless solution. The solution was filtered into the second bulb containing 15-Crown-5 (2.858 g, 12.9 mmol) and the mixture was stirred for 12 h. The resulting clear colorless solution was concentrated and stored at 5 °C to give large colorless crystals, which were isolated by filtration (5.533 g, 92 %). ¹H NMR (CDCl₃, 399.9 MHz) δ: 3.71. ¹³C NMR (CDCl₃, 100.6 MHz) δ: 123.9 (q, ¹J_{CF} = 298.2 Hz), 84.1 (m, ²J_{CF} = 27.2 Hz), 68.4 (t, ¹J_{CH} = 142.7) ¹⁹F NMR (CDCl₃, 376.3 MHz) δ: -76.9 (s). ⁷Li (CDCl₃, 155.4 MHz) δ: -0.7 (s). FT-IR (KBr, mineral oil mull), cm⁻¹: 530 (w), 721(s), 841(w), 946(s), 1102(s), 1118(s), 1216(s), 1245(s), 1320(m), 1356(m), 1378(s).

Elemental Analysis for C₁₄H₂₀F₉LiO₆: Calcd. C, 36.38; H, 4.36. Found: C, 36.44; H, 4.46.

Synthesis of [Li 15-Crown-5][B(OC(CF₃)₃)₄] (2). Dichloromethane (20 mL) was condensed onto a mixture of **1** (0.911 g, 1.272 mmol) and [Li 15-Crown-5][OC(CF₃)₃] (0.535 g, 1.157 mmol) in a 50 mL thick-walled glass bomb, giving two colorless immiscible liquid layers upon warming. The bomb was degassed by evacuating at -78 °C, and stirred at 80 °C for 12 h to give a single colorless liquid layer. The liquid layer was transferred via cannula to a two-necked round-bottomed flask, and volatiles were removed under vacuum to give a white solid, which was recrystallized from cold CH₂Cl₂ (1.218 g, 89.3 %). ¹H NMR (CDCl₃, 399.9 MHz) δ: 3.75. ¹³C NMR (CDCl₃, 100.6 MHz) δ: 121.5 (q, ¹J_{CF} = 294 Hz), 81.1 (broad, BOC), 68.5 (OCCO). ¹⁹F NMR (CFCl₃, 376.3 MHz) δ: -71.4. ¹¹B NMR (CFCl₃, 128.3 MHz) δ: -0.9. The details for the calculated and observed vibrational frequencies and intensities (FT-IR and Raman), along with spectral assignments, are provided in Section S1.2 in the Supporting Information. Elemental Analysis for C₂₆H₂₀BF₃₆LiO₉: Calcd. C, 26.51; H, 1.71. Found: C, 26.58; H, 1.93.

Synthesis of [NEt₄][NCB(OC(CF₃)₃)₃] (3). Diethyl ether (15 mL) was condensed onto a mixture of **1** (0.832g, 11.6 mmol) and NEt₄CN (0.174 g, 11.1 mmol) in a standard two-bulbed reaction vessel with an incorporated condenser, to give a clear colorless solution. The solution was refluxed at 80 °C for 15 h and the solvent was removed under vacuum to give a colorless solid (0.901g, 92%). ¹H NMR (CD₂Cl₂, 399.9 MHz) δ: 3.18 (q, ²J_{HH} = 7.3 Hz), 1.3 (tt, ²J_{HH} = 7.3 Hz, ³J_{NH} = 1.9 Hz). ¹³C NMR (CD₂Cl₂, 100.6 MHz) δ: 121.4 (q, ¹J_{CF} = 293 Hz), 79.8 (m, ²J_{CF} = 34 Hz), 53.2 (t, ¹J_{CN} = 3 Hz, NCH₂), 7.7 (CH₃). ¹⁹F NMR (CFCl₃, 376.3 MHz) δ: -71.3 (s). ¹¹B NMR (CFCl₃, 128.3 MHz) δ: -4.6 (s). The vibrational spectra (FT-IR and Raman) are provided in Section S1.3 in the Supporting Information. Elemental Analysis for C₂₁H₂₀BF₂₇N₂O₃: Calcd. C, 28.92; H, 2.31; N, 3.21. Found: C, 28.98; H, 2.53; N, 3.19.

Synthesis of [NEt₄][CN{B(OC(CF₃)₃)₃}₂] (4). A solution of **1** (0.920 g, 1.285 mmol) in CFCl₃ (1.5 g) was prepared in a 10 mL vial in the glovebox and added to a second vial containing solution of NEt₄CN (0.100 g, 0.640 mmol) in CH₂Cl₂ (0.5 g). The vial was sealed and shaken periodically over 15 min to produce a gelatinous precipitate, and then the solvent was evaporated to dryness in the glovebox. The resulting white powder was dissolved in 5 mL of THF and filtered, then transferred to a Schlenk flask. The solution was concentrated to ~2 mL, CH₂Cl₂ was condensed into the vessel (~5 mL), which was immersed in a -78 °C cold bath to promote crystallization. The solid was filtered cold, then washed twice with cold CFCl₃ to give a fine white powder (0.405 g, 39.7%). ¹H NMR (THF-*d*₆, 400 MHz) δ: 3.18 (q, 8H, ³J_{HH} = 7.2 Hz), 1.31 (tt, 12H, ³J_{HH} = 7.3 Hz, ³J_{NH} = 1.9 Hz). ¹³C NMR (THF-*d*₆, 100.6 MHz) δ: 121.5 (q, ¹J_{CF} = 293 Hz), 80.6 (m), 53.1 (t, ¹J_{CN} = 4.4 Hz, NCH₂), 7.4 (CH₃). ¹⁹F NMR (THF-*d*₆, 376.3 MHz) δ: -73.8. ¹¹B NMR (THF-*d*₆, 128.3 MHz) δ: -1.6, -5.7. The vibrational spectra (FT-IR and Raman) are provided in Section S1.4 in the Supporting Information.

Synthesis of [NMe₄][FB(OC(CF₃)₃)₃] (5). Sulfur dioxide (10 mL) was condensed onto a mixture of anhydrous NMe₄F (0.097g,

1.04 mmol) and **1** (0.759g, 1.06 mmol) in the first bulb of a standard vessel, giving two distinct liquid layers upon warming. The solution was stirred for 3 h to give a clear colorless solution and the product was crystallized by slow solvent transfer across a 5 °C temperature gradient. The remaining solution was decanted into the second bulb, and removed under vacuum to give 0.177 g of colorless crystals and 0.526 g of slightly off-white powder (82 %). ¹³C NMR (THF-*d*₆, 100.6 MHz) δ: 122.4 (q, ¹J_{CF} = 293 Hz), 55.8. ¹⁹F NMR (SO₂, 376.3 MHz) δ: -71.4 (s, CF₃), -135.9 (s, BF). ¹¹B -2.2 (d, ¹J_{BF} = 27 Hz). FTIR (KBr, Nujol mull) cm⁻¹: 669(m), 729(s), 756 (w), 769(m), 949(s), 964(s), 984(s), 1151(s), 1172(s), 1263(s, br), 1490(ms). Elemental Analysis for C₁₆H₁₂BF₂₈NO₃: Calcd. C, 23.75; H, 1.50; N, 1.73. Found: C, 23.46; H, 1.65; N, 1.80.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02670.

Details of thermodynamic and DFT calculations, NMR and vibrational spectra and tables with assignments for vibrational spectroscopy, X-ray structure comparisons of **1**, **2**, **3**, and **4** (PDF).

Crystallographic data (CCDC Nos. 1448944, 1510717, and 1510754) for this paper (CIF).

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Notes

The authors declare no competing financial interest.

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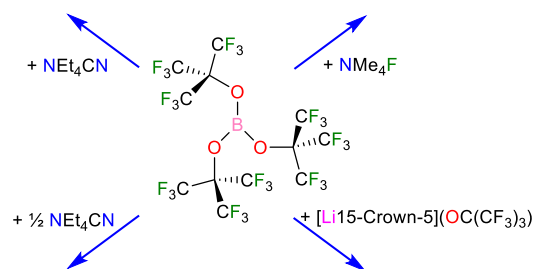
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TABLE OF CONTENTS FIGURE AND SYNOPSIS



A convenient synthesis and characterization for strong Lewis acid perfluoro-*tert*-butoxy borane (**1**) is reported and use of **1** as a precursor for weakly coordinating anions e.g. the analog of well-known $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ demonstrated.