Anion Stability in Stannylium, Oxonium, and Silylium Salts of the Weakly Coordinating Anion [C6F4-1,2-{B(C6F5)2}2(μ-OCH3)]−

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Reaction of [Ph3C]+[C6F4-1,2-{B(C6F5)2}2(μ-OCH3)]−, **1**, with Bu3SnH gives the solvated stannylium ion [Bu3Sn(arene)]+[C6F4-1,2-{B(C6F5)2}2(μ-OCH3)]−, **2**, as a light brown oil (δ ^{119}Sn = 434 ppm). This material is thermodynamically stable toward transfer of the chelated OMe− anion to "Bu3Sn+" as evidenced by the reaction of free diborane C6F4-1,2-[B(C6F5)2]2 with 2 equiv of Bu3SnOMe. This reaction produces the stannyloxonium complex [(Bu3Sn)2OCH3]+[C6F4-1,2-{B(C6F5)2}2(μ-OCH3)]−, **3** (δ ^{119}Sn = 277 ppm), which is stable at −60 °C. Upon warming, the cation in **3** undergoes decomposition to unidentified products, while the anion remains intact. Ion pair **2** reacts rapidly with ethereal HCl in CH2Cl2 to generate Bu3SnCl and the oxonium acid [(Et2O)2H]+[C6F4-1,2-{B(C6F5)2}2(μ-OCH3)]−, **4**, isolated in 76% yield as a white, crystalline solid. Acid **4** is thermally stable in solution and was characterized crystallographically. The C2B2OMe core of the anion in **4** deviates from planarity due to intermolecular interactions in the crystal, in contrast to the structures found in other ion pairs with this anion. Reaction of **2** with anhydrous HCl gives the unsymmetrical MeOH adduct of C6F4-1,2-[B(C6F5)2]2, **5**, which was separately synthesized by direct reaction of methanol with the free diborane. The anion [C6F4-1,2-{B(C6F5)2}2(μ-OCH3)]− is not stable in the presence of the triethylsilylium ion, generated from **1** and Et3SiH.

Introduction

Previously, we have reported the synthesis of the weakly coordinating anions [C6F4-1,2-{B(C6F5)2}2(μ-OR)]− (R = CH3, C6F5) as their trityl salts and a preliminary account of their behavior as counteranions for zirconocenium cations.[2] We found them to be both kinetically and thermodynamically stable toward transfer of the μ-OR group to zirconium, suggesting that these anions might find application in the stabilization of other highly electrophilic species. Herein we report the generation of stannylium, oxonium, and silylium ions in the presence of the [C6F4-1,2-{B(C6F5)2}2(μ-OCH3)]− anion. We chose the μ-methoxide anion for two reasons. First, its trityl salt crystallizes beautifully and is more easily isolated analytically pure than other OR derivatives, and second, the methoxide group provides a convenient ^{1}H NMR handle, allowing for easy spectroscopic monitoring of the chemistry described.

Results and Discussion

The trityl salt of the μ-methoxy anion [C6F4-1,2-{B-(C6F5)2}2(μ-OCH3)]− (**1**) is readily prepared via reaction

of the chelating diborane C6F4-1,2-[B(C6F5)2]2[3] with trityl methoxy ether as shown in Scheme 1. Compound **1** is a highly crystalline, convenient reagent for generating a number of ion pairs via hydride abstraction protocols.[4] For example, reaction of **1** with Bu3SnH occurs rapidly with loss of Ph3CH to provide the solvated stannylium ion pair [Bu3Sn(arene)]+[C6F4-1,2-{B(C6F5)2}2-(μ-OCH3)]−, **2**, quantitatively as a light brown liquid clathrate-like oil[5] when the reaction is done in benzene or toluene. Attempts to purify this species via removal of solvent in vacuo or via recrystallization procedures using more polar solvents (CD2Cl2 in particular) failed to generate conveniently workable solid samples of **2**. However, when generated in deuterated arene solvents, the oil is separable and can be studied directly using multinuclear NMR spectroscopy.

Samples were prepared by placing an insert filled with the oil into a 5 mm NMR tube containing either d_6-benzene or d_8-toluene as a lock solvent. ^{19}F NMR spectroscopy at room temperature showed only the five signals characteristic of the symmetrical μ-methoxy anion for **2**, indicating that the oil is at least 95% pure as generated in this fashion (aside from any occluded

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(4) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237.
(5) The oils formed in these and related reactions are of uncertain stoichiometry and structure but behave as though they were liquid clathrates. For a more detailed discussion on this topic, see: Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001.

Scheme 1
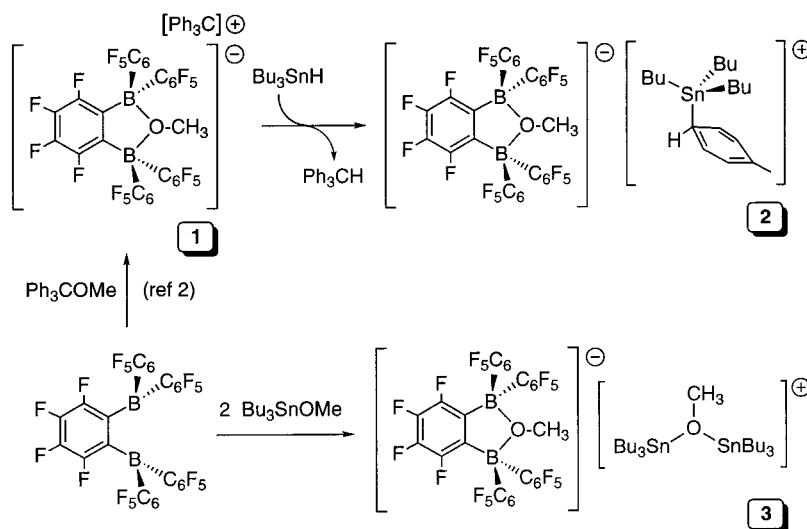
solvent and Ph$_3$CH byproduct). ^{11}B NMR spectroscopy was less informative in this regard, exhibiting a broad signal at 4.8 ppm. The ^{119}Sn NMR spectrum of oil **2** was recorded at −60 °C using samples generated at room temperature in d_8-toluene. A sharp signal at 434 ppm was observed and is attributed to the [R$_3$Sn(arene)]$^+$ cation, ligated by toluene in an undefined mode of bonding.[6] This chemical shift is almost exactly the same as what we observe for the related species [Bu$_3$Sn-(arene)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ when the spectrum is recorded under the same conditions.[7] A signal of lower intensity, representing no more than 10% of the tin in the sample, is also observed at 262 ppm under these conditions for both anions. Previously, Lambert and co-workers have reported a chemical shift of 263 ppm for this stannylium moiety,[8] but their spectrum was recorded at room temperature. When samples of **2** or [Bu$_3$Sn(arene)]$^+$[B-(C$_6$F$_5$)$_4$]$^-$ are allowed to warm to room temperature, the signal at 434 is broadened almost into the baseline, while the signal of lesser overall intensity at 262 remains. As the sample is cooled again, the broad signal centered around 434 ppm sharpens, probably as exchange between free and bound toluene slows. The peak at 262 remains sharp throughout these changes, but is a minor component of the sample. We are unsure as to what gives rise to this signal, but it appears in the range expected for some species [Bu$_3$Sn(L)]$^+$[A]$^-$.[9] Since the appearance of the signal for this species is temperature independent, it is not likely to be in equilibrium with complex **2** or [Bu$_3$Sn(arene)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and likely arises due to an impurity in the solvent.[7,10] Furthermore, the chemical shift of 434 for toluene-stabilized

[Bu$_3$Sn(arene)]$^+$ is more in line with observed chemical shifts for the ions [Bu$_3$Sn(arene)]$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$ (356 ppm at −20 °C in CD$_2$Cl$_2$),[11] [Bu$_3$Sn(arene)]$^+$[HB-(C$_6$F$_5$)$_3$]$^-$ (360 ppm),[12] and [Bu$_3$Sn]$^+$[CB$_{11}$Me$_{12}$]$^-$ (454.3 ppm, cyclohexane).[13]

Stannylium ion pair **2** is thermally stable as a liquid clathrate-like oil in arene media or in CD$_2$Cl$_2$ solution for long periods of time at room temperature and for at least 2 h at temperatures as high as 60 °C. This stability appears to be thermodynamic in nature, since the diborane C$_6$F$_4$-1,2-[B(C$_6$F$_5$)$_2$]$_2$ is capable of abstracting a methoxide group from Bu$_3$SnOMe,[14] resulting in clean formation of the [C$_6$F$_4$-1,2-{B(C$_6$F$_5$)$_2$}$_2$(μ-OCH$_3$)]$^-$ anion as judged by ^{19}F NMR spectroscopy (Scheme 1). The stannyl ether reagent effectively competes for the stannylium cation generated, and so clean overall reactions require the use of 2 equiv of Bu$_3$SnOMe to generate the ion pair we have assigned as the stannyloxonium ion **3**. Moderately stable oils of **3** can thus be generated by treating C$_6$F$_4$-1,2-[B(C$_6$F$_5$)$_2$]$_2$ with 2 equiv of Bu$_3$SnOMe in toluene at −78 °C. This species exhibits a ^{119}Sn NMR chemical shift of 277.0 ppm at −60 °C. To our knowledge, stannyloxonium ions of this type have not been studied in detail; however, related silyloxonium cations of general formula [(R$_3$Si)$_n$OR′$_{3-n}$]$^+$[B(Ar$_F$)$_4$]$^-$ ($n = 1-3$, Ar$_F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$,[15] C$_6$F$_5$^{15b}) have been generated and studied in solution by ^{29}Si and ^{13}C NMR spectroscopy. The closest silicon analogue of **3** is the silyloxonium ion pair [(Me$_3$Si)$_2$OEt]$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$, which exhibits a ^{29}Si chemical shift of 59.0 ppm in CD$_2$Cl$_2$ at −70 °C.^{15a} Using an empirically derived correlation between ^{29}Si and ^{119}Sn chemical shifts,[16] a ^{119}Sn resonance at ≈261 ppm would be predicted for the analogous

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(9) (a) To our knowledge, no systematic study of the chemical shift trends in solvated stannylium ions has been published. However, we have observed that stannylium ions of general formula [Bu$_3$Sn-(aldehyde)]$^+$[A]$^-$ give rise to ^{119}Sn signals in the 280−310 range, with more basic aldehydes giving more upfield-shifted resonances. Shifts to higher field for higher coordination numbers has been noted in neutral organotin compounds,^{9b} and a detailed study on the ^{29}Si NMR chemical shifts of solvated silylium ions has indicated a similar trend.^{9c} (b) Nadvornik, M.; Holecek, J.; Handlir, K. *J. Organomet. Chem.* **1984**, *275*, 43. (c) Arshadi, M.; Johnels, D.; Edlund, U.; Ottosson C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1996**, *118*, 5120.

(10) Separate experiments show that it is not the water adduct of [Bu$_3$Sn]$^+$.[7]

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tin compound, i.e., $[(Me_3Sn)_2OEt]^+[B(3,5-(CF_3)_2C_6H_3)_4]^-$, in good agreement with what we observe for the closely related stannyloxonium ion pair **3**.

While stable at −60 °C for long periods, upon warming samples of **3**, signals for other, unidentified tin-containing species begin to appear over the course of a few hours. However, these transformations are exclusively associated with the cationic portion of **3**; by ^{19}F NMR spectroscopy, the integrity of the anion is retained. The related silyloxonium species discussed above were also found to be quite thermally unstable.[15] Despite the complications encountered in the reactions of diborane C_6F_4-1,2-$[B(C_6F_5)_2]_2$ and Bu_3SnOMe, it is clear that ion pair formation to the μ-methoxide stannylium species is thermodynamically preferred over back-transfer of OMe$^-$ to the cationic tin center, making the $[C_6F_4$-1,2-$\{B(C_6F_5)_2\}_2(\mu$-$OCH_3)]^-$ anion suitable for the stabilization of stannylium ions.

The μ-OMe anion is also appropriate for use with oxonium acids. Ether-solvated proton salts of weakly coordinating fluorinated aryl borate anions have proven to be effective reagents for the generation of electrophilic transition metal cations.[17] A complementary reagent incorporating the $[C_6F_4$-1,2-$\{B(C_6F_5)_2\}_2(\mu$-$OCH_3)]^-$ anion can be obtained in high yield by treating the solvated stannylium salt **2** with an ether solution of HCl.[18] Loss of Bu_3SnCl is accompanied by production of $[(Et_2O)_2H]^+$-$[C_6F_4$-1,2-$\{B(C_6F_5)_2\}_2(\mu$-$OCH_3)]^-$, **4**, as an isolable white solid in 76% yield. Again, ^{19}F NMR spectroscopy was informative for showing that the anion remains intact, giving the five sharp signals characteristic of the symmetrical μ-methoxide anion. In the ^{1}H NMR spectrum, signals for the coordinating ether molecules are observed, along with a downfield-shifted signal at 16.4 ppm for the solvated proton. Similar shifts are observed for Brookhart's acid ($[(Et_2O)_2H]^+[B(3,5-(CF_3)_2C_6H_3)_4]^-$, 16.7 ppm, CD_2Cl_2[19]) and Jutzi's acid ($[(Et_2O)_2H]^+[B-(C_6F_5)_4]^-$, 15.50 ppm, CD_2Cl_2[17b]). Interestingly, the oxonium ion in **4** exhibits no tendency to protonate the anion, an observation probably reflecting the kinetic stability of ether-solvated protons (vide infra). Extended heating of solutions of **4** results eventually in production of detectable amounts of C_6F_5H, but, in contrast to Brookhart's acid, this species is quite thermally robust in solution and the solid state.

The solid state structure of **4** was determined, confirming its formulation. ORTEP diagrams of the cation and anion are shown in Figure 1A and B, respectively, along with selected metrical data. Further details can be found in the Supporting Information. In the cation, the structural parameters are unremarkable and similar to other determinations of this cation. The anion, however, differs in structure from other $[C_6F_4$-1,2-$\{B-(C_6F_5)_2\}_2(\mu$-$OR)]^-$ anions we have structurally characterized, which invariably contain essentially planar C_2B_2OR molecular cores. In **4**, the μ-methoxide anion adopts a structure in which the dihedral angle between the planes defined by C(11)−C(12)−B(1)−B(2) and
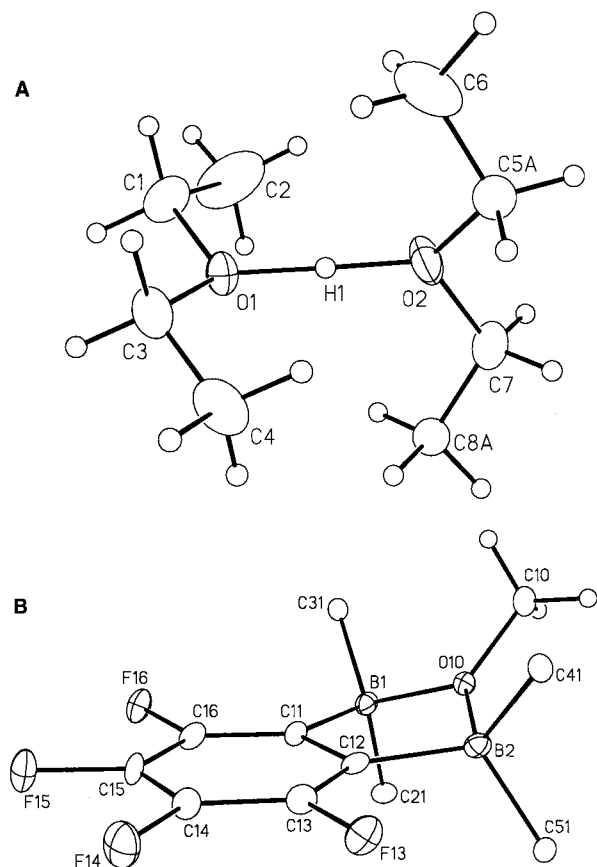
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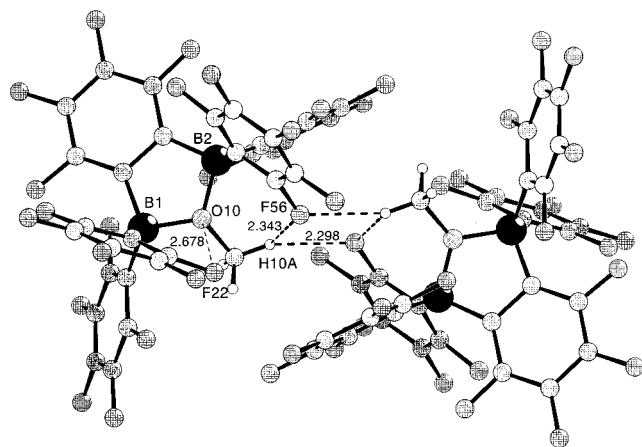

Figure 1. ORTEP diagram of **4**: (A) the $[(Et_2O)_2H]^+$ cation; (B) the $[C_6F_4$-1,2-$\{B(C_6F_5)_2\}_2(\mu$-$OCH_3)]^-$ anion. Only the *ipso* carbons of the −C_6F_5 rings are shown for clarity. Selected bond distances (Å): O(1)−H(1), 1.21(7); O(2)−H(1), 1.18(7); B(1)−C(11), 1.605(7); B(2)−C(12), 1.579(7); B(1)−O(10), 1.541(6); B(2)−O(10), 1.563(5); O(1)−C(10), 1.455-(5); C(11)−C(12), 1.398(6). Selected bond angles (deg): O(1)−H(1)−O(2), 178.3; B(1)−O(10)−B(2), 112.7(3); B(1)−O(10)−C(10), 121.1(3); B(2)−O(10)−C(10), 124.2(3); B(1)−C(11)−C(12), 110.3(4); B(2)−C(12)−C(11), 113.3(4); C(11)−B(1)−O(10), 98.7(3); C(12)−B(2)−O(10), 98.4(3).

O(10)−C(10)−B(1)−B(2) is 35.0(3)°. Thus, while O(10) is only slightly pyramidalized (the sum of the angles about O(10) is 358.0(5)°), the methoxide is tilted out of the chelating pocket of the diborane significantly. This results in a closing of the B(1)−O(1)−B(2) angle to 112.7(2)° from the 117.72(12)° observed in the structure of the trityl salt of this anion,[2] in which the six atoms in question are coplanar. The reasons for this distortion from planarity are likely packing forces in the crystal. Inspection of a packing diagram reveals that the anions appear to pair up in the crystal via interactions between an *ortho* fluorine and a μ-methoxide C−H bond (Figure 2). No such motif is found in the trityl salt of this anion, suggesting that these close contacts are responsible for the methoxide's deviation from the chelation plane. Another result of this is that the two C_6F_5 rings pointing away from the μ-OMe group (beginning with C(21) and C(51)) are roughly parallel to one another, while the other two are splayed out to the sides, a distinctly different arrangement from that found in the structure of **1** and the related μ-OC_6F_5 derivative.[2]

As mentioned, the isolability of **4** reflects the kinetic stability of the diethyl ether solvated proton. When
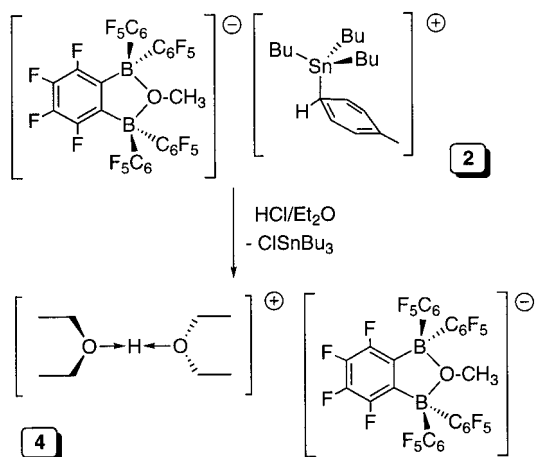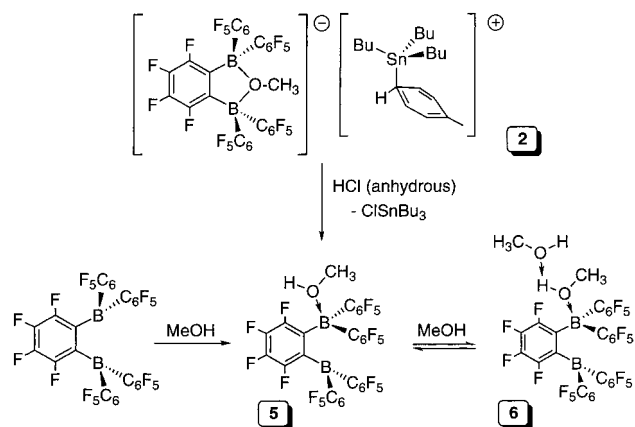
Figure 2. Partial packing diagram of **4**, illustrating the ion–ion contacts responsible for the deviation of the μ-methoxide from the C(11)–C(12)–B(1)–B(2) plane.

Scheme 2

Scheme 3

protonation of **2** is carried out in the absence of ether with anhydrous HCl gas, the resulting product, in addition to Bu_3SnCl, is the methanol adduct of the diborane, **5** (Scheme 3). Thus, when there are no stronger bases present, the $[C_6F_4\text{-}1,2\text{-}\{B(C_6F_5)_2\}_2(\mu\text{-}OCH_3)]^-$ anion is basic enough to be protonated. Even when **2** is treated with HCl (anhydrous) in the presence of mesitylene, formation of adduct **5** is preferred over protonation of the relatively electron-rich arene. This contrasts with the behavior of the $[B(C_6F_5)_4]^-$ anion.[17] The identity of the adduct **5** was further confirmed

$C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2 + CH_3OH$

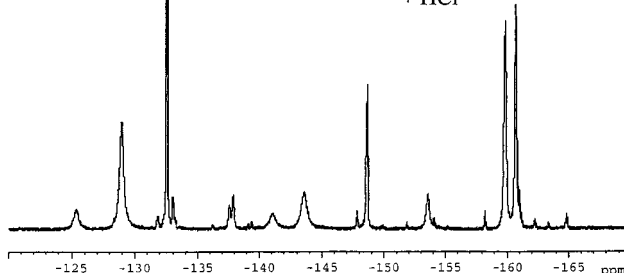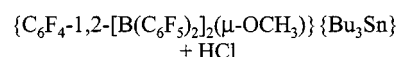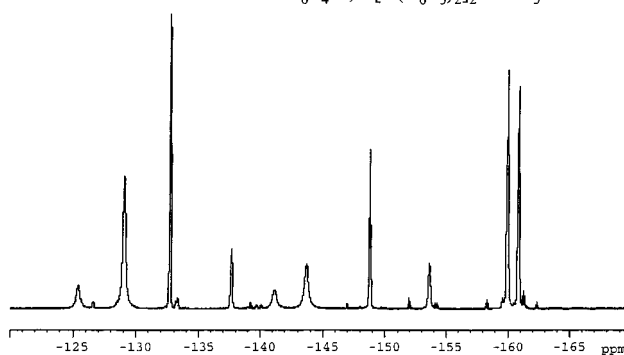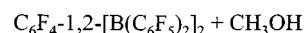$\{C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2(\mu\text{-}OCH_3)\} \{Bu_3Sn\}$
$+ HCl$

Figure 3. ^{19}F NMR spectra of methanol adduct **5** derived from reaction of $C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2$ with 1 equiv of MeOH (top) and the reaction of **2** with anhydrous HCl (bottom).

through its separate synthesis from $C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2$ and 1 equiv of MeOH. In the ^{19}F NMR spectrum, 10 separate resonances are observed for **5**, suggesting an unsymmetrical structure where the methanol interacts only with one of the two boron centers. The OH proton for the bound methanol appears at 6.52 ppm, shifted downfield from that of free methanol in C_6D_6. Attempts to isolate this species revealed it to be a viscous oil which did not readily solidify, so characterization was limited to solution spectroscopy.

As can be seen in Figure 3, the ^{19}F NMR spectra of **5** generated via these two methods are almost identical. The broadness of some of the signals and the impurities present in the baseline of the spectra are due to the presence of small amounts of a bis-methanol adduct, **6**, where the second equivalent of MeOH is bound via hydrogen bonding to the first methanol molecule. Addition of 2 equiv of MeOH to $C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2$ gives this bis-methanol adduct directly (Scheme 3). This type of second sphere adduct has precedent in the alcohol[20] and water[21] binding chemistry of the monofunctional analogue of $C_6F_4\text{-}1,2\text{-}[B(C_6F_5)_2]_2$, i.e., $B(C_6F_5)_3$, but is somewhat surprising in light of the presence of a second highly electrophilic boron center. Nonetheless, the ^{19}F spectroscopic data for **6**, where a different set of 10 resonances is observed, conclusively show that the asymmetry is retained in the bis-adduct. A $^{19}F-^{19}F$ COSY experiment allows for assignment of the *ortho*, *meta*, and *para* fluorines of each $B(C_6F_5)_2$ moiety. The

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$\Delta_{m,p}$ values found are 12.0 and 8.0 ppm, consistent with the presence of a neutral three-coordinate and a neutral four-coordinate boron center;[22] furthermore, the chemical shifts of 40 and 4.6 ppm for the two [11]B nuclei support this assignment.[23] Two methyl and two OH resonances are observed in the ^{1}H NMR spectrum for the inner and outer bound MeOH ligands. This material also failed to solidify upon attempted workup, and loss of varying amounts of the coordinated alcohol is observed upon exposure to vacuum. The fact that the second equivalent of MeOH binds in this fashion, as opposed to forming a symmetrical bis-adduct via bonding to the second borane center, attests to the steric blocking of this second boron upon pyramidalization of the first borane with adduct formation.

Attempts to generate arene-stabilized silylium ions[24] using this counteranion were less successful. For example, reaction of **1** with 1 equiv of Et₃SiH resulted in production of Ph₃CH, but did not completely consume the full equivalent of **1**. In addition at least three methyl-containing products resulted, including a major species with a 10-resonance ^{19}F NMR spectral pattern reminiscent of that observed for adduct **5**. Addition of a further 0.5 equiv of Et₃SiH resulted in consumption of the remaining amount of **1** and production of detectable amounts of the free diborane. We speculate that back-transfer of OMe⁻ to the silylium ion produces Et₃SiOMe, which then forms unstable silyloxonium ions, which degenerate into a mixture of products. Given the complex nature of these reactions and the apparent unsuitability of this weakly coordinating anion for use with "R₃Si⁺", we abandoned further investigations.

In summary, we have prepared and characterized the stannylium ion pair **2**, incorporating the weakly coordinating [C₆F₄-1,2-{B(C₆F₅)₂}₂(μ-OCH₃)]⁻ anion, as a liquid clathrate-like oil. This species may be protonated with ethereal HCl to give the oxonium acid **4** as a stable, usable Bronsted acid reagent for organometallic synthesis. Protonation of **2** in the absence of diethyl ether results in protonation of the anion, to give the unsymmetrical methanol adduct **5**, itself a potential Bronsted acid activator for use in protonolysis reactions.[20b]

Experimental Section

General Procedures. All manipulations of air- and moisture-sensitive materials were undertaken using standard vacuum and Schlenk techniques or in a glovebox under an atmosphere of nitrogen. All solvents were dried and purified by passing through suitable drying agents (alumina and Q5).[25] NMR spectra were recorded in C₇D₈ unless otherwise noted. Data are given in ppm relative to solvent signals for ^{1}H and ^{13}C spectra or relative to external standards for [119]Sn (SnMe₄, 0.0 ppm), ^{11}B NMR (BF₃·OEt₂, 0.0 ppm), and ^{19}F NMR (CFCl₃ at 0.0 ppm) experiments. Elemental analyses were performed by Mrs. Dorothy Fox in the microanalytical laboratory of the Department of Chemistry at the University of Calgary. The compounds C₆F₄-1,2-[B(C₆F₅)₂]₂,[3] **1**,[2] and Bu₃SnOMe[14] were all prepared via literature procedures; other materials were

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purchased from Sigma-Aldrich and used as received or purified according to standard procedures.

Preparation of [Bu₃Sn]⁺[C₆F₄-1,2-{B(C₆F₅)₂}₂(μ-OCH₃)]⁻, 2. To an orange suspension of trityl salt **1** (30 mg, 0.027 mmol) in d₈-toluene (0.4 mL) was added Bu₃SnH (8.0 μL, 0.030 mmol), generating a light brown colored liquid oil that settled to the bottom of the reaction vial. This material was placed into a 3 mm glass tube which was inserted into a 5 mm NMR tube containing d₈-toluene as a reference and locking solvent. ^{1}H NMR: 3.54 (s, 3H, μ-OC*H*₃); 1.96 (m, 12H, *Bu₃*Sn); 1.08 (m, 6H, *Bu₃*Sn); 0.72 (m, 9H, *Bu₃*Sn). ^{19}F NMR: −131.3 (8F, *o*-C₆F₅); −136.2 (2F, −C₆*F₄*); −159.2 (4F, *p*-C₆F₅); −162.9 (2F, −C₆*F₄*); −165.2 (8F, *m*-C₆F₅). ^{13}C{^{1}H} NMR: 60.4 (μ-O*C*H₃), 29.2, 27.4, 13.5, 11.8 (*Bu₃*Sn). ^{11}B NMR: 4.8 (br s). ^{119}Sn NMR (−60 °C): 434.9 ppm.

Preparation of [(Bu₃Sn)₂OMe]⁺[C₆F₄-1,2-{B(C₆F₅)₂}₂(μ-OCH₃)]⁻, 3. Diborane C₆F₄-1,2-[B(C₆F₅)₂]₂ (47 mg, 0.056 mmol) was dissolved in d₈-toluene (0.4 mL) and placed in a 5 mm NMR tube. The solution was cooled to −78 °C, and a solution of Bu₃SnOMe (36 mg, 0.112 mmol) in d₈-toluene (0.2 mL) was added via syringe. The resulting liquid oil settled to the bottom of the NMR tube, and the sample was subjected to NMR spectroscopic analysis. ^{1}H NMR: 3.88 (s, 3H, μ-OC*H*₃); 3.10 (s, 3H, Sn₂OC*H*₃); 1.38 (m, 12H, *Bu₃*Sn−); 1.16 (m, 24H, *Bu₃*Sn−); 0.85 (m, 18H, *Bu₃*Sn−). ^{19}F NMR: −131.1 (8F, *o*-C₆F₅); −136.0 (2F, −C₆*F₄*); −159.2 (4F, *p*-C₆F₅); −162.9 (2F, −C₆*F₄*); −165.1 (8F, *m*-C₆F₅). ^{13}C{^{1}H} NMR: 56.8 (μ-O*C*H₃), 28.3, 27.7, 20.2, 13.8 (*Bu₃*Sn). [119]Sn (−60 °C): 277.0.

Preparation of [(Et₂O)₂H]⁺[C₆F₄-1,2-{B(C₆F₅)₂}₂(μ-OCH₃)]⁻, 4. Stannylium ion pair **2** was generated in situ by loading **1** (50 mg, 0.045 mmol) into a two-necked 25 mL flask equipped with frit assembly, dissolving in CH₂Cl₂ (5 mL), and treating with ⁿBu₃SnH (12.1 μL, 0.045 mmol). After stirring for 20 min, HCl/Et₂O (22.5 μL of a 2 M solution, 0.045 mmol) was added to the pale yellow solution and the reaction stirred for 8 h. The solvent was removed in vacuo, leaving an oily product, which was washed with hexanes (3 × 5 mL) to remove byproducts. The resulting beige solid was recrystallized from CH₂Cl₂ (2 mL) layered with hexanes (4 mL) at −40 °C to afford a beige crystalline product (35 mg, 76.1%). ^{1}H NMR (CD₂Cl₂): 16.44 (br s, 1H, *H*(OEt₂)₂); 4.08 (q, 8H, $J_{H-H} = 6.80$ Hz, OC*H*₂); 3.65 (s, 3H, −μ-OC*H*₃); 1.43 (t, 12H, OCH₂C*H*₃). ^{19}F NMR (CD₂Cl₂): −132.3 (8F, *o*-C₆F₅), −137.6 (2F, −C₆*F₄*), −160.1 (4F, *p*-C₆F₅), −163.6 (2F, −C₆*F₄*), −166.0 (8F, *p*-C₆F₅). ^{13}C{^{1}H} NMR (CD₂Cl₂): 69.0 (−O*C*H₃), *57*.3 (−O*C*H₂CH₃), 14.5 (−OCH₂*C*H₃). ^{11}B NMR (CD₂Cl₂): δ 5.8 (br s). Anal. Calcd for C₃₉H₂₄B₂F₂₄O₃: C, 46.0; H, 2.4. Found: C, 45.43; H, 2.57.

Generation of 5 via Reaction of 2 with Anhydrous HCl. Stannylium ion pair **2** was generated in situ by loading **1** (12 mg, 0.011 mmol) into a flame-sealable NMR tube, suspending in d₈-toluene (0.8 mL), and treating with Bu₃SnH (3 μL, 0.011 mmol). The resulting sample was cooled to −78 °C, and a 10-fold excess of anhydrous HCl gas (0.110 mmol) was condensed into the tube. The NMR tube was flame sealed and allowed to warm to room temperature. Stannylium ion pair **2** was consumed immediately, generating the methanol adduct **5** and Bu₃SnCl as a byproduct. ^{1}H NMR: 6.52 (br s, 1H, MeO*H*); 3.29 (s, 3H, C*H*₃OH); additional resonances for the Ph₃CH and Bu₃SnCl byproducts also present. ^{19}F NMR: −125.4 (1F, −C₆*F₄*); −128.9 (4F, *o*-C₆F₅); −132.6 (4F, *o*-C₆F₅); −137.6 (1F, −C₆*F₄*); −141.0 (1F, −C₆*F₄*); −143.6 (2F, *p*-C₆F₅); −148.7 (2F, *p*-C₆F₅); −153.6 (1F, −C₆*F₄*); −159.9 (4F, *m*-C₆F₅); −160.9 (4F, *m*-C₆F₅).

Generation of 5 via Reaction of C₆F₄-1,2-[B(C₆F₅)₂]₂ with Methanol. Diborane C₆F₄-1,2-[B(C₆F₅)₂]₂ (10 mg, 0.012 mmol) was loaded into a 5 mm NMR tube and dissolved in d₆-benzene (0.6 mL). Dry and degassed methanol (0.5 μL, 0.012 mmol) was injected into this solution via a gastight syringe, affording the methanol adduct **5** in a quantitative yield by NMR spectroscopy. ^{1}H and ^{19}F NMR spectra were essentially

identical to those found for **5** generated as described above (see also Figure 3). $^{13}C\{^1H\}$ NMR: 57.2 (*C*H$_3$OH). ^{11}B NMR: 40.3.

Generation of Bis-methanol Adduct 6. Diborane C_6F_4-1,2-[B(C$_6$F$_5$)$_2$]$_2$ (10 mg, 0.012 mmol) was loaded into a 5 mm NMR tube and dissolved in d_6-benzene (0.6 mL). Dry and degassed methanol (1.0 μL, 0.024 mmol) was injected into this solution via a gastight syringe to afford the bis-methanol adduct **6** in quantitative yield by NMR. ^1H NMR: 6.49 (br s, 1H, inner MeO*H*); 4.70 (br s, 1H, outer MeO*H*); 3.26 (s, 3H, inner C*H*$_3$OH); 2.25 (s, 3H, outer C*H*$_3$OH). ^{19}F NMR: −132.7 (4F, *o*-C$_6$*F*$_5$); −133.7 (1F, −C$_6$*F*$_4$); −133.9 (4F, *o*-C$_6$*F*$_5$); −139.7 (1F, −C$_6$*F*$_4$); −148.8 (2F, *p*-C$_6$*F*$_5$); −154.0 (2F, *p*-C$_6$*F*$_5$); −155.2 (1F, C$_6$*F*$_4$); −156.9 (1F, −C$_6$*F*$_4$); −160.9 (4F, *m*-C$_6$*F*$_5$); −161.9 (4F, *m*-C$_6$*F*$_5$). $^{13}C\{^1H\}$ NMR: 57.2 (inner *C*H$_3$OH), 53.0 (outer *C*H$_3$OH). ^{11}B NMR: δ 39.8 (s); 4.6 (br).

X-ray Crystallography for [(Et$_2$O)$_2$H]$^+$[C$_6$F$_4$-1,2-{B-(C$_6$F$_5$)$_2$}$_2$(μ-OCH$_3$)]$^-$, 4. Colorless crystals of **4** were obtained from layering of hexanes onto a dichloromethane solution of the compound. Data were collected on a Bruker PLATFORM/SMART 1000 CCD diffractometer[26] using Mo Kα radiation at −80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 2984 reflections from the data collection. The space group was determined to be $P\bar{1}$ (No. 2). The data were corrected for absorption through use of Gaussian integration (indexing of crystal faces). See Table 1 for a summary of crystal data and X-ray data collection information. The structure of **4** was solved using direct methods (*SHELXS-86*[27]), and refinement was completed using the program *SHELXL-93*.[28] Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons except for H1, which was located from a difference Fourier map; its positional and thermal parameters were allowed to refine freely. Within one of the diethyl ether molecules of the [(Et$_2$O)$_2$H]$^+$ ion, severely elongated thermal ellipsoids indicated that one of the methylene carbons and both carbons of the other ethyl group were positionally disordered; these atoms were split into two positions each (C5A, C5B for the methylene, C7A, C8A and C7B,

Table 1. Summary of Data Collection and Refinement Details for 4

formula	C$_{39}$H$_{24}$B$_2$F$_{24}$O$_3$
fw	1018.20
cryst syst	triclinic
space group	$P\bar{1}$ (#2)
a, Å	11.8694(17)
b, Å	12.8153(18)
c, Å	13.527(2)
α, deg	76.633(3)
β, deg	82.751(3)
γ, deg	78.299(3)
V, Å^3	1953.5(5)
Z	2
d_{calc}, mg m^{-3}	1.731
μ, mm^{-1}	0.185
T, °C	−80
cryst dimens, mm^3	0.46 × 0.29 × 0.04
rel transmn factors	0.9918−0.9936
scan type	ω scans (0.2°)
2θ (max), deg	52.82
no. of unique reflns	7283
no. of reflns with $I > 2\sigma I$	3099
no. of variables	615
R_1	0.0653
wR_2	0.1373
gof	0.932
residual density, e/Å^3	−0.273−0.382

C8B for the ethyl) that were refined with equal occupancy factors (50% each). The final model for **4** refined to values of $R_1(F) = 0.0653$ (for 3099 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1373$ (for all 7283 independent data).

Supporting Information Available: Full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, and complete bond distances, angles, and torsion angles for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010750X

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