Reactions of Zinc Dialkyls with (Perfluorophenyl)boron Compounds: Alkylzinc Cation Formation vs C₆F₅ Transfer

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Reaction between ZnR₂ and $[H(OEt_2)_2][B(C_6F_5)_4]$ in ether leads to the salts $[RZn(OEt_2)_3]$ - $[B(C_6F_5)_4]$, while mixtures of ZnR₂ (R = Me, Et) and $B(C_6F_5)_3$ in toluene- d_8 undergo facile alkyl/C₆F₅ group exchange to give Zn(C₆F₅)₂·(toluene). Mixtures of ZnR₂ and B(C₆F₅)₃ in hydrocarbon/diethyl ether solvent mixtures react with alkyl transfer to afford the ion pairs $[RZn(OEt_2)_3][RB(C_6F_5)_3]$, whereas the reaction of ZnEt₂ with $[Ph_3C][B(C_6F_5)_4]$ in toluene- d_8 proceeds with β -H abstraction to give ethene and Ph₃CH, with the subsequent rapid formation of Zn(C₆F₅)₂.

Introduction

As has recently been shown, aluminum trialkyls react with B(C₆F₅)₃ in hydrocarbon solvents under ligand exchange; for example, the reaction of AlMe₃ with $B(C_6F_5)_3$ provides a convenient route for the preparation of $Al(C_6F_5)_3$.¹ Similar exchange reactions have been observed between $M(C_6F_5)_3$ (M = Al, B) and MAO (or MMAO)² and in the reaction of AlR₃ with [Ph₃C]- $[B(C_6F_5)_4]$.³ Some, such as AlEt₃/B(C₆F₅)₃ mixtures, show modest ethene polymerization activity.⁴ This propensity to ligand redistribution in main-group alkyls is in contrast to the reactions of (perfluoroaryl)boron compounds with early-transition-metal alkyls, notably Cp₂ZrMe₂, which lead to alkyl abstraction and ionic or zwitterionic products.⁵ On the other hand, in coordinating solvents the reaction between aluminum trialkyls and B(C₆F₅)₃ gives solvent-stabilized ion pairs, [R₂Al-

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 $(OEt_2)_2]^+[RB(C_6F_5)_3]^-$, which have been used as activators in high-temperature alkene polymerizations.⁶

The behavior of zinc alkyls under similar conditions has not been studied so far. Some cationic zinc alkyl complexes have been generated by adding nitrogen macrocycles or crown ethers to zinc alkyls in the presence of AlR₃ or tetraphenylcyclopentadiene, to give [RZn(crown)]⁺X⁻ (X = AlR₄, C₅HPh₄).⁷ We were therefore interested in exploring the possibility of stabilizing cationic zinc alkyls with weakly coordinating perfluoroarylborate anions.

Results and Discussion

The reaction of ZnR_2 with an equimolar amount of "Jutzi's acid",⁸ $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$, in diethyl ether proceeds quantitatively under alkane elimination to give the salts $[RZn(OEt_2)_3]^+[B(C_6F_5)_4]^-$ (1, R = Me; 2, R = Et; 3, $R = Bu^t$) (eq 1). These compounds are obtained

$$[H(OEt_{2})_{2}][B(C_{6}F_{5})_{4}] + ZnR_{2} \xrightarrow{Et_{2}O} [RZn(OEt_{2})_{3}]^{+}[B(C_{6}F_{5})_{4}]^{-} (1)$$

$$R = Me (1), Et (2), {}^{t}Bu (3)$$

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Figure 1. Structure of the $[EtZn(OEt_2)_3]^+$ cation in **2**, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

as colorless crystalline solids which show good solubility in diethyl ether and dichloromethane but are sparingly soluble in light petroleum. The borate anion shows a sharp signal in the ¹¹B NMR spectrum at around δ –13.6, while the identity of the [MeZn(OEt_2)_3]⁺ cation is confirmed by a singlet at δ –0.56 in the ¹H NMR spectrum. The ¹H NMR spectra and elemental analyses of all three compounds confirm the presence of three coordinated ether molecules per zinc cation.

Crystals of **2** suitable for single-crystal X-ray diffraction were grown from diethyl ether solution at -20 °C. The structure of the cation is shown in Figure 1. The [EtZn(OEt₂)₃]⁺ cation displays a slightly distorted tetrahedral arrangement, with C–Zn–O angles ranging from 115.37(10) to 123.60(9)°. The Zn–C bond length of 1.964(3) Å is similar to that observed in the neutral zinc complex [MeZnOBu^t]₄ (1.955 Å),⁹ though slightly shorter than the corresponding bond distance of 2.058. (7) Å in the anionic complex [Et₂Zn(μ -OBu^t)₂ZnEt₂]^{2–,10} In crystalline [Bu^tZn(OEt₂)₃][B(C₆F₅)₄] the Me₃C–ZnO₃ core adopts a staggered conformation; however, the crystals deteriorated during data collection, and the bonding parameters will not be discussed in detail.

The reactions of ZnR_2 (for R = Me, Et) with $B(C_6F_5)_3$ were explored as in situ NMR experiments. Mixing equimolar amounts of $ZnMe_2$ with $B(C_6F_5)_3$ in toluene d_8 produces a mixture of species following rapid alkyl/ C_6F_5 exchange (eq 2). No ion pairs could be detected.

$$3B(C_6F_5)_3 + 4ZnMe_2 \xrightarrow{\text{toluene-}d_8} 2BMe_3 + BMe_2(C_6F_5) + 4Zn(C_6F_5)_2 (2)$$

The main products are BMe₃ and $Zn(C_6F_5)_2$ together with a small amount of BMe₂(C_6F_5), as shown by ¹H, ¹⁹F, and ¹¹B NMR spectroscopy. In particular, the presence of BMe₃ is very distinctive, with a singlet in the ¹H NMR spectrum at δ 0.78 and a broad ¹¹B NMR peak at δ 89.5. In a similar fashion the reaction of ZnEt₂ with B(C₆F₅)₃ affords a mixture of Zn(C₆F₅)₂, BEt₃, BEt₂-(C₆F₅), and BEt(C₆F₅)₂. In contrast to the analogous reactions of aluminum trialkyls with B(C₆F₅)₃, where an equilibrium between various dimeric aluminum species is established which is shifted toward the formation of Al(C₆F₅)₃ only upon removal of BMe₃ in vacuo,³ the conversion of ZnR₂ to Zn(C₆F₅)₂ is essentially complete within ca. 3 min, which is the minimum amount of time required to obtain the NMR spectra. There was no evidence for ZnR(C₆F₅) intermediates. A similar reaction of ZnMe₂ with B(C₆F₅)₃ in toluene-*d*₈ containing 20 vol % 1,2-difluorobenzene as polar ionizing solvent proceeds in essentially the same fashion.

The reaction of $ZnMe_2$ with $B(C_6F_5)_3$ in toluene on a preparative scale proved to be a convenient route to Zn- $(C_6F_5)_2$ (toluene) (4), which was isolated as a colorless, hydrocarbon-soluble crystalline solid. All attempts to remove the toluene by heating to 50 °C in vacuo failed, and it is thought likely that the toluene is coordinated to the electrophilic metal center in a manner similar to that seen in Al(C_6F_5)₃·(toluene).¹¹ Previously, Zn(C_6F_5)₂ has been prepared from ZnCl₂ and C₆F₅MgX,¹² from AgC₆F₅ and ZnI₂,¹³ or by decarboxylation of Zn(O₂- $CC_6F_5)_2$.¹⁴ Treatment of a light petroleum solution of **4** with hexamethylbenzene displaces the toluene in favor of the more electron rich arene, to give microcrystalline $Zn(C_6F_5)_2 \cdot C_6Me_6$ (5). In contrast, crystallization of Zn- $(C_6F_5)_2$ from benzene has been reported to give a benzene-free product.¹⁵ Cooling samples of 5 to -80 °C did lead to broadening of the methyl signal, but the slow exchange limit could not be reached.

When the reaction between $ZnMe_2$ and $B(C_6F_5)_3$ is repeated in toluene- d_8 in the presence of diethyl ether, the ligand exchange chemistry described above is almost totally suppressed. Instead, alkyl abstraction by $B(C_6F_5)_3$ occurs, leading to the borate salt $[MeZn(OEt_2)_3]^+[MeB-(C_6F_5)_3]^-$ (6) (eq 3). The degree of ion pairing of the

$$B(C_{6}F_{5})_{3} + ZnR_{2} \xrightarrow{\text{toluene-}d_{8}/\text{Et}_{2}\text{O}} [RZn(OEt_{2})_{3}]^{+}[RB(C_{6}F_{5})_{3}]^{-} (3)$$
$$R = Me (6), Et (7)$$

[MeB(C₆F₅)₃]⁻ anion can be deduced from its ¹H NMR chemical shift; tight ion pairs with methyl bridges show signals at ca. δ 0.1, as in Cp₂ZrMe(μ -Me)B(C₆F₅)₃,^{5b} whereas the free anion shows chemical shifts around δ 1.3. The value for **5** is δ 1.02. The noncoordinating nature of the [MeB(C₆F₅)₃]⁻ anion is further confirmed by the small chemical shift difference ($\Delta\delta$ 2.5 ppm) between the *m*- and *p*-fluorine ¹⁹F NMR resonances.¹⁶ Diethyl ether solutions of ZnEt₂ react similarly, to give [EtZn(OEt₂)₃]⁺[EtB(C₆F₅)₃]⁻ (**7**).

Attempts to isolate **6** by solvent removal afforded a colorless oil. Multinuclear NMR analysis showed that

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this oil contained large amounts of $MeB(C_6F_5)_2$, $Me_2B-(C_6F_5)$, and $Zn(C_6F_5)_2$, as well as the expected product, **6**. A repeat of the NMR experiment revealed the presence of BMe₃ alongside $[MeZn(OEt_2)_3]^+[MeB(C_6F_5)_3]^-$, in the ratio 1:15. Removing the solvents from this NMR reaction in vacuo and redissolving the residue in CD_2 - Cl_2 showed the presence of BMe₃, $BMe_2(C_6F_5)$, and **6** in the ratio 4.3:1:7.8. Evidently BMe₃, $Zn(C_6F_5)_2$, and **6** are in equilibrium in solution, and removal of BMe₃ in vacuo shifts the equilibrium toward the formation of $Zn(C_6F_5)_2$, thus preventing the isolation of pure **6**. Compound **7** shows a very similar chemistry.

In contrast, the reaction of an excess of ZnEt_2 with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in toluene- d_8 takes a different course and proceeds with β -H abstraction and ethene elimination (Scheme 1).¹⁷The reaction is swift, with the loss of the orange color of CPh_3^+ within ca. 2 s. The NMR spectra show the presence of $\text{Zn}(\text{C}_6\text{F}_5)_2$ and BEt₃. Clearly 1 equiv of ZnEt_2 requires only two aryl groups to generate $\text{Zn}(\text{C}_6\text{F}_5)_2$, and consequently further exchange between $\text{BEt}_x(\text{C}_6\text{F}_5)_{3-x}$ for x = 0-2 and ZnEt_2 , as already described above, results in total $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ consumption.

Scheme 1

$$\begin{split} & [\text{CPh}_3][\text{B}(\text{C}_6\text{H}_5)_4] + \text{ZnEt}_2 \rightarrow \\ & \text{Ph}_3\text{CH} + \text{``}[\text{ZnEt}][\text{B}(\text{C}_6\text{F}_5)_4]\text{''} + \text{C}_2\text{H}_4 \\ & \text{``}[\text{ZnEt}][\text{B}(\text{C}_6\text{F}_5)_4]\text{''} \rightarrow \text{ZnEt}(\text{C}_6\text{F}_5) + \text{B}(\text{C}_6\text{F}_5)_3 \\ & \text{ZnEt}(\text{C}_6\text{F}_5) + \text{B}(\text{C}_6\text{F}_5)_3 \rightleftharpoons \text{Zn}(\text{C}_6\text{F}_5)_2 + \text{BEt}(\text{C}_6\text{F}_5)_2 \\ & \text{ZnEt}_2 + \text{BEt}(\text{C}_6\text{F}_5)_2 \rightleftharpoons \text{ZnEt}(\text{C}_6\text{F}_5) + \text{BEt}_2(\text{C}_6\text{F}_5) \\ & \text{ZnEt}(\text{C}_6\text{F}_5) + \text{BEt}_2(\text{C}_6\text{F}_5) \rightleftharpoons \text{Zn}(\text{C}_6\text{F}_5)_2 + \text{BEt}_3 \end{split}$$

Although the alkyl/C₆F₅ exchange observed in the above reactions presumably involves alkyl-bridged intermediates $RZn(\mu-R)B(C_6F_5)_3$, no evidence for such species was found. In an effort to further understand the chemistry of these systems, reactions were undertaken with the tetramethylethylenediamine adducts ZnR_2 (TMEDA) (8, R = Me; 9, R = Et). Reactions of equimolar amounts of either 8 or 9 with [Ph₃C]- $[B(C_6F_5)_4]$ or $B(C_6F_5)_3$ in toluene- d_8 provided complex mixtures which were not analyzed further. However, the reaction between $ZnMe_2(TMEDA)$ and $B(C_6F_5)_3$ in a 1.5:1 molar ratio in dichloromethane- d_2 at -70 °C indicated the formation of the zwitterionic species (TMEDA)ZnMe(μ -Me)B(C₆F₅)₃, with sharp ¹H NMR signals at δ –0.41 and –0.83 assigned as the terminal and bridging Zn-methyl groups, respectively. There are also signals for the solvent-separated ions [MeB(C₆F₅)₃]⁻ (δ 0.37) and a broad signal at δ -0.97 for a [ZnMe-(TMEDA)]⁺ cation in rapid exchange with the excess ZnMe₂(TMEDA).¹⁸ When the system is warmed to room temperature, the signals for (TMEDA)ZnMe(µ-Me)B- $(C_6F_5)_3$ broaden and merge with the signals for the $[MeB(C_6F_5)_3]^-$ anion and the $[ZnMe(TMEDA)]^+$ cation and excess ZnMe₂(TMEDA).

Experimental Section

General Procedures. All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium (toluene), sodium benzophenone (diethyl ether), sodium–potassium alloy (light petroleum, bp 40–60 °C), and CaH₂ (dichloromethane). Deuterated solvents were stored over 4 Å molecular sieves and degassed by several freeze–thaw cycles. ZnMe₂ (2.0 M solution in toluene) and ZnEt₂ (1.1 M solution in toluene) were used as purchased. The compounds ZnBut₂,¹⁹ [H(OEt₂)₂][B(C₆F₅)₄],⁸ B(C₆F₅)₃,²⁰ and [Ph₃C][B(C₆F₅)₄]²¹ were prepared by literature methods. NMR spectra were recorded on a Bruker DPX300 spectrometer. ¹H and ¹³C NMR spectra are referenced to residual solvent peaks relative to TMS, ¹⁹F NMR spectra (282.2 MHz) are relative to external CFCl₃, and ¹¹B NMR spectra (96.2 MHz) are relative to BF₃·OEt₂.

[MeZn(OEt₂)₃][B(C₆F₅)₄] (1). A solution of dimethylzinc (0.13 mL, 2.0 M, 0.26 mmol) in toluene was added dropwise to a suspension of $[H(OEt_2)_2][B(C_6F_5)_4]$ (0.24 g, 0.29 mmol) in diethyl ether (20 mL) at room temperature. The mixture was stirred for 1 h to allow the gas formation to subside. Removal of volatiles in vacuo left a white powder which was recrystallized from a diethyl ether/light petroleum mixture at -20 °C to afford 1 as colorless crystals, yield 0.19 g (80.0%). Anal. Calcd for C₃₇H₃₃BF₂₀O₃Zn: C, 45.26; H, 3.39. Found: C, 45.21; H, 3.34. ¹H NMR (300 MHz, 27 °C, CD₂Cl₂): δ 3.80 (q, 12 H, $J_{\rm HH} = 7.1$ Hz, CH₃CH₂O), 1.25 (t, 18 H, $J_{\rm HH} = 7.1$ Hz, CH₃-CH₂O), -0.56 (s, 3 H, MeZn). ¹³C{¹H} NMR (75.5 MHz, 27 °C, CD₂Cl₂): 68.0 (CH₃CH₂O), 14.5 (CH₃CH₂O), -14.4 (MeZn). ¹⁹F NMR (282.4 MHz, 27 °C, CD₂Cl₂): δ -133.6 (br, 8 F, o-F), -164.1 (t, 4 F, $J_{\text{FF}} = 22.6$ Hz, p-F), -168.0 (br, 8 F, m-F). ¹¹B NMR (96.3 MHz, 27 °C, CD₂Cl₂): δ –13.6.

[EtZn(OEt₂)₃][B(C₆F₅)₄] (2). [H(OEt₂)₂][B(C₆F₅)₄] (0.92 g, 1.1 mmol) and diethylzinc (1.1 mL, 1.0 M, 1.1 mmol) in hexane were reacted as described for **1**. Recrystallization from a diethyl ether/light petroleum mixture at -20 °C provided colorless crystals, yield 0.83 g (79.1%). Anal. Calcd for C₃₈H₃₅-BF₂₀O₃Zn: C, 45.83; H, 3.54. Found: C, 45.64; H, 3.57. ¹H NMR (300 MHz, 25 °C, CD₂Cl₂): δ 3.91 (q, 12 H, *J*_{HH} = 7.2 Hz, CH₃C*H*₂O), 1.35 (t, 18 H, *J*_{HH} = 7.2 Hz, C*H*₃CH₂O), 1.21 (t, 3 H, *J*_{HH} = 8.1 Hz, C*H*₃CH₂Zn), 0.49 (q, 2 H, *J*_{HH} = 8.1 Hz, CH₃C*H*₂O), 1.45 (*C*H₃CH₂O), 11.5 (*C*H₃CH₂Zn), 0.8 (CH₃*C*H₂-Zn). ¹⁹F NMR (282.4 MHz, 27 °C, CD₂Cl₂): δ -133.6 (br, 8 F, *ο*-F), -164.3 (t, 4 F, *J*_{FF} = 19.8 Hz, *p*-F), -168.1 (t, 8 F, *J*_{FF} = 19.8 Hz, *m*-F). ¹¹B NMR (96.3 MHz, 27 °C, CD₂Cl₂) δ -13.6.

[Bu^tZn(OEt₂)₃][B(C₆F₅)₄] (3). A suspension of [H(OEt₂)₂]- $[B(C_6F_5)_4]$ (0.74 g, 0.95 mmol) in diethyl ether (10 mL) at 0 °C was treated with a solution of di-tert-butylzinc (0.17 g, 0.95 mmol) in diethyl ether (10 mL). The reaction mixture was stirred at 0 °C for 3 h. Removal of volatiles in vacuo left a white powder, which was recrystallized from a diethyl ether/ light petroleum mixture at -20 °C to give colorless crystals of **3**, yield 0.67 g (72.3%). Anal. Calcd for C₄₀H₃₉BF₂₀O₃Zn: C, 46.92; H, 3.84. Found: C, 46.83; H, 3.55. ¹H NMR (300 MHz, 27 °C, CD₂Cl₂): δ 3.79 (q, 12 H, J_{HH} = 7.2 Hz, CH₃CH₂O), 1.31 (t, 18 H, $J_{\rm HH} = 7.2$ Hz, CH_3CH_2O), 1.17 (s, 9 H, CMe_3). ¹³C-{¹H} NMR (75.5 MHz, 25 °C, C₆D₆): δ 14.76 (*C*H₃CH₂O), 25.20 (CMe₃), 32.27 (CMe₃), 67.08 (CH₃CH₂O). ¹⁹F NMR (282.4 MHz, 27 °C, CD₂Cl₂): δ -133.6 (br, 8 F, o-F), -164.1 (t, 4 F, J_{FF} = 19.8 Hz, *p*-F), -168.0 (t, 8 F, $J_{FF} = 19.8$ Hz, *m*-F). ¹¹B NMR (96.3 MHz, 27 °C, CD_2Cl_2): δ -13.6.

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Reaction of ZnMe₂ with B(C₆F₅)₃ in Toluene-*d*₈. A solution of B(C₆F₅)₃ (30 mg, 59 μ mol) in toluene-*d*₈ (4 mL) was treated with a solution of ZnMe₂ (0.04 mL, 80 μ mol, 2 M) in toluene. The reaction was complete in the time taken to place the sample in the NMR spectrometer (ca. 3 min). The solution contained BMe₃, BMe₂(C₆F₅), and Zn(C₆F₅)₂. BMe₃: ¹H NMR (300 MHz, 25 °C, toluene-*d*₈) δ 0.78 (s); ¹¹B NMR (96.3 MHz, 25 °C, toluene-*d*₈) δ 89.5. BMe₂(C₆F₅): ¹H NMR (toluene-*d*₈) δ 1.07 (t, 6 H, *J* = 1.9 Hz, Me); ¹¹B NMR (toluene-*d*₈) δ 83.8; ¹⁹F NMR (282.4 MHz, 25 °C, toluene-*d*₈) δ -131.23 (m, 2 F), -151.83 (m, 1 F), -163.15 (m, 2 F). Zn(C₆F₅)₂: ¹⁹F NMR (282.4 MHz, 25 °C, toluene-*d*₈) δ -118.46 (m, 2 F), -153.74 (t, 1 F, *J*_{FF} = 19.8 Hz), -161.33 (m, 2 F).

Reaction of ZnMe₂ with B(C₆F₅)₃ in Toluene-*d***₈/1,2-Difluorobenzene. A solution of B(C₆F₅)₃ (30 mg, 59 \mumol) in a mixture of toluene-***d***₈ (4 mL) and 1,2-difluorobenzene (1 mL) was treated with a solution of ZnMe₂ (0.04 mL, 80 \mumol, 2 M) in toluene-***d***₈. The reaction was completed in the time taken to place the sample in the NMR spectrometer (ca. 3 min). The solution contained BMe₃, BMe₂(C₆F₅), BMe(C₆F₅)₂, and Zn-(C₆F₅)₂. BMe(C₆F₅)₂: ¹H NMR (300 MHz, 25 °C, toluene-***d***₈/ 1,2-difluorobenzene) \delta 1.48 (q, 3 H,** *J* **= 1.78 Hz, Me); ¹¹B NMR (96.3 MHz, 25 °C, toluene-***d***₈/1,2-difluorobenzene) \delta 75.2; ¹⁹F NMR (282.4 MHz, 25 °C, toluene-***d***₈) \delta –130.55 (m, 2 F), -147.92 (m, 1 F), -162.17 (m, 2 F).**

Reaction of ZnEt₂ with B(C₆F₅)₃ in Toluene-d₈. A solution of B(C₆F₅)₃ (30 mg, 59 μ mol) in toluene- d_8 (4 mL) was treated with a solution of $ZnEt_2$ (0.07 mL, 77 μ mol, 1.1 M) in toluene. The reaction was complete in the time taken to place the sample in the NMR spectrometer. The solution contained BEt₃, BEt₂(C₆F₅), BEt(C₆F₅)₂, and Zn(C₆F₅)₂. BEt₃: ¹H NMR (300 MHz, 25 °C, toluene- d_8) δ 1.16 (q, 6 H, J = 7.7 Hz, CH₃CH₂-B), 1.01 (t, 9 H, J = 7.7 Hz, CH_3 CH₂-B); ¹¹B NMR (96.3 MHz, 25 °C, toluene- d_8) δ 89.7. BEt₂(C₆F₅): ¹H NMR (300 MHz, 25 °C, toluene- d_8) δ 1.42 (q, 4 H, J = 7.6 Hz, CH₃CH₂-B), 0.92 (t, 6 H, J = 7.6 Hz, CH_3CH_2-B); ¹¹B NMR (96.3 MHz, 25 °C, toluene- d_8) δ 87.8; ¹⁹F NMR (282.4 MHz, 25 °C, toluene- d_8) δ -131.08 (m, 2 F), -154.24 (m, 1 F), -161.70 (m, 2 F). BEt(C₆F₅)₂: ¹H NMR (toluene- d_8) δ 1.87 (q, 2 H, J = 7.6 Hz, CH₃CH₂-B), 0.98 (t, 3 H, J = 7.6 Hz, CH₃CH₂-B); ¹¹B NMR (toluene- d_8) δ 77.3; ¹⁹F NMR (toluene- d_8) δ –134.85 (m, 2 F), -148.14 (m, 1 F), -162.51 (m, 2 F).

Zn(C₆F₅)₂·(toluene) (4). A solution of B(C₆F₅)₃ (3.01 g, 5.88 mmol) in toluene (50 mL) was treated with a solution of ZnMe₂ in toluene (4.41 mL, 8.82 mmol, 2 M) at room temperature. The mixture was stirred for 30 min. Removal of volatiles left a white solid, which was recrystallized from light petroleum (60 mL) at -20 °C overnight to give Zn(C₆F₅)₂·(toluene) as needlelike crystals, yield 3.33 g (76.6%). Anal. Calcd for C₁₂F₁₀-Zn·C₇H₈: C, 46.42; H, 1.64. Found: C, 45.93; H, 1.46. ¹H NMR (300 MHz, 25 °C, C₆D₆): δ 6.98–7.13 (m, 5 H, Ph), 2.10 (s, 3 H, Me). ¹⁹F NMR (C₆D₆): δ -118.3 (m, 4 F, *o*-F), -152.9 (t, 2 F, *J*_{FF} = 19.8 Hz, *p*-F), -160.9 (m, 4 F, *m*-F).

Zn(C₆F₅)₂·C₆Me₆ (5). A solution of Zn(C₆F₅)₂·(toluene) (1.02 g, 2.07 mmol) in toluene (20 mL) was treated with hexamethylbenzene (0.334 g, 2.06 mmol). After the mixture was stirred for 1 h, the solvent was removed and the colorless residue recystallized from light petroleum at -20 °C to give **5** as a white microcrystalline solid, yield 0.96 g (82.3%). Anal. Calcd for C₁₂F₁₀Zn·C₁₂H₁₈: C, 51.31; H, 3.23. Found: C, 51.95; H, 3.49. ¹H NMR (300 MHz, 25 °C, C₆D₆): δ 2.03 (s, 18 H, Me). ¹³C NMR (75.5 MHz, 25 °C, C₆D₆): δ 16.79 (Me), 132.48 (C₆). ¹⁹F NMR (282.4 MHz, 25 °C, C₆D₆): δ -118.1 (m, 4 F, σ -F), -153.2 (t, 2 F, $J_{\text{FF}} = 19.8$ Hz, p-F), -160.9 (m, 4 F, m-F).

Generation of [MeZn(OEt₂)₃][MeB(C₆F₅)₃] (6). A solution of B(C₆F₅)₃ (40 mg, 79 μ mol) in toluene-*d*₈ (4 mL) and ether (0.5 mL) was treated with a solution of ZnMe₂ (0.04 mL, 80 μ mol, 2 M) in toluene. The reaction was instantaneous. ¹H NMR (300 MHz, 25 °C, C₇D₈/ether): δ 3.34 (q, 12 H, *J* = 7.2 Hz, OCH₂CH₃), 1.02 (br s, 3 H, BMe), 0.88 (t, 18 H, *J* = 7.2 Hz, OCH₂CH₃), -0.73 (s, 3 H, ZnMe). ¹³C{¹H} NMR (75.5 MHz, 25 °C, C₇D₈, ether): δ 67.62 (O*C*H₂CH₃), 14.42 (OCH₂*C*H₃), 11.15 (br, BMe), -14.93 (ZnMe). ¹⁹F NMR (282.4 MHz, 25 °C, C₇D₈/ether): δ -132.7 (d, 6 F, *J*_{FF} = 19.8 Hz, *o*-F), -165.6 (t, 3 F, *J*_{FF} = 19.8 Hz, *p*-F), -168.1 (m, 6 F, *m*-F). ¹¹B NMR (96.3 MHz, 27 °C, C₇D₈/ether): δ -11.4.

Generation of [EtZn(OEt₂)₃][EtB(C₆F₅)₃] (7). A solution of B(C₆F₅)₃ (30 mg, 59 μ mol) in toluene-*d*₈ (4 mL) and ether (0.5 mL) was treated with a solution of ZnEt₂ (0.05 mL, 55 μ mol, 1.1 M) in toluene. ¹H NMR (300 MHz, 25 °C, C₇D₈/ ether): δ 3.38 (q, 12 H, *J* = 7.1 Hz, OC*H*₂CH₃), 1.63 (br q, 2 H, *J* = 7.1 Hz, BC*H*₂CH₃), 1.06 (t, 3 H, *J* = 8.1 Hz, ZnCH₂C*H*₃), 1.03 (br t, 3 H, *J* = 7.0 Hz, BCH₂C*H*₃), 0.91 (q, 18 H, *J* = 7.1 Hz, OCH₂C*H*₃), 0.13 (q, 2 H, *J* = 8.1 Hz, ZnC*H*₂CH₃). ¹³C{¹H} NMR (75.5 MHz, 25 °C, C₇D₈/ether): δ 67.49 (O*C*H₂CH₃), 15.18 (vbr, B*C*H₂CH₃), 13.50 (OCH₂*C*H₃), 12.51 (BCH₂*C*H₃), 11.40 (ZnCH₂*C*H₃), -0.47 (Zn*C*H₂CH₃). ¹⁹F NMR (282.4 MHz, 25 °C, C₇D₈/ether): δ -132.2 (d, 6 F, *J*_{FF} = 22.6 Hz, *o*-F), -165.5 (t, 3 F, *J*_{FF} = 19.8 Hz, *p*-F), -168.1 (m, 6 F, *m*-F). ¹¹B NMR (96.3 MHz, 27 °C, C₇D₈/ether): δ -9.1.

Reaction of ZnEt₂ with [Ph₃C][B(C₆F₅)₄] in Toluened₈. A solution of [Ph₃C][B(C₆F₅)₄] (0.020 g, 21 \mumol) in toluened₈ (0.4 mL) was treated with a solution of ZnEt₂ (0.09 mL, 1.1 M, 99 \mumol) in toluene. The orange color faded to colorless immediately. The products of the reaction were characterized by NMR. Apart from the reaction products ethene and triphenylmethane, and some excess ZnEt₂, there were also signals for BEt₃ and [B(C₆F₅)₄]⁻.

Reaction of ZnMe₂(TMEDA) with B(C₆F₅)₃ in Dichloromethane- d_2 . A solution of ZnMe₂(TMEDA) (TMEDA = 1,2- $C_2H_4(NMe_2)_2$; 7 mg, 33 μ mol) in dichloromethane- d_2 (3 mL) was treated with a solution of $B(C_6F_5)_3$ (10 mg, 20 μ mol) also in dichloromethane- d_2 (3 mL) at -70 °C. The products were characterized by NMR. Besides signals for [MeB(C₆F₅)₃]⁻ and the resonances of coordinated TMEDA, the solution contained signals for (TMEDA)ZnMe(u-Me)B(C₆F₅)₃ and a broad peak for the Me signals of rapidly interchanging [ZnMe(TMEDA)]+/ $ZnMe_2$ (TMEDA), which could not be resolved on cooling to -80°C. (TMEDA)ZnMe(*u*-Me)B(C₆F₅)₃: ¹H NMR (300 MHz, -70 °C, CCl₂D₂): δ –0.41 (s, 3 H, μ -Me), –0.83 (s, 3 H, ZnMe). ¹¹B NMR (96.3 MHz, -70 °C, CCl_2D_2): δ -12.0 (br). When the system was warmed to room temperature, the signals for $(TMEDA)ZnMe(\mu-Me)B(C_6F_5)_3$ broadened and merged with the signals for [MeB(C₆F₅)₃]⁻ and [ZnMe(TMEDA)]⁺/ZnMe₂-(TMEDA).

X-ray Crystallography. Crystals are clear, colorless plates. A crystal of dimensions ca. $0.4 \times 0.3 \times 0.1$ mm coated with dry Nujol was mounted on a glass fiber under a cold nitrogen stream. Data were collected at 140 K on a Rigaku R-Axis IIc image plate diffractometer equipped with a rotating-anode X-ray source (Mo K α radiation, $\lambda = 0.710$ 69 Å) and graphite monochromator. Using 4° oscillations, 46 exposures of 15 min were made. Data were processed using the DENZO/SCALE-PACK²² programs. The structure was determined by the automated Patterson routines in the SHELXS program²³ and refined by full-matrix least-squares methods, on F^2 values, in SHELXL.²⁴ The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms in the cation were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. At the conclusion of the refinement, wR2 = 0.095 and $R1 = 0.047^{26}$ for all 7018 reflections weighted $w = [\sigma^2(F_0^2) + (0.0416P)^2 +$ 1.53P]⁻¹ with $P = (F_0^2 + 2F_c^2)/3$; for the "observed" data only,

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R1=0.036. In the final difference map, the highest peaks (to ca. 0.34 e Å^-3) were in the ether ligands. Scattering factors for neutral atoms were taken from ref 25. Computer programs used were as noted above or in Table 4 of ref 26.

Crystal Data for **2**: $C_{14}H_{35}O_3Zn \cdot C_{24}BF_{20}$, fw 995.8; monoclinic; $P_{2_1/c}$, a = 14.824(1) Å, b = 15.947(1) Å, c = 18.037(1) Å; $\beta = 108.25(1)^\circ$; V = 4049.4(4) Å³; Z = 4; $D_{calcd} = 1.633$ g/cm³; $\mu = 0.736$ mm⁻¹; F(000) = 2008; $1.7 \le \theta \le 25.4^\circ$; $-17 \le h \le 17$, $-19 \le k \le 19$, $-21 \le l \le 21$; 22 855 reflections collected, of which 7018 were independent ($R_{int} = 0.079$) and 5735

observed ($I > 2\sigma(I)$); no. of data/restraints/parameters 7018/ 0/568; goodness of fit, S = 1.031.

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Supporting Information Available: Full listings of crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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