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Reactions of Zinc Dialkyls with (Perfluorophenyl)boron Compounds: Alkylzinc Cation Formation vs C_6F_5 Transfer

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Reaction between ZnR_2 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 ZnR_2 (R = Me, Et) and $B(C_6F_5)_3$ in toluene-d_8 undergo facile alkyl/C_6F_5 group exchange to give $Zn(C_6F_5)_2$·(toluene). Mixtures of ZnR_2 and $B(C_6F_5)_3$ 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 $ZnEt_2$ with $[Ph_3C][B(C_6F_5)_4]$ in toluene-d_8 proceeds with β-H abstraction to give ethene and Ph_3CH, with the subsequent rapid formation of $Zn(C_6F_5)_2$.

Introduction

As has recently been shown, aluminum trialkyls react with $B(C_6F_5)_3$ in hydrocarbon solvents under ligand exchange; for example, the reaction of $AlMe_3$ 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 AlR_3 with $[Ph_3C][B(C_6F_5)_4]$.[3] Some, such as $AlEt_3/B(C_6F_5)_3$ 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 Cp_2ZrMe_2, which lead to alkyl abstraction and ionic or zwitterionic products.[5] On the other hand, in coordinating solvents the reaction between aluminum trialkyls and $B(C_6F_5)_3$ gives solvent-stabilized ion pairs, $[R_2Al(OEt_2)_2]^+[RB(C_6F_5)_3]^-$, 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 AlR_3 or tetraphenylcyclopentadiene, to give $[RZn(crown)]^+X^-$ ($X = AlR_4$, C_5HPh_4).[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

$$[H(OEt_2)_2][B(C_6F_5)_4] + ZnR_2 \xrightarrow{Et_2O} [RZn(OEt_2)_3]^+[B(C_6F_5)_4]^- \quad (1)$$
$$R = Me\ (\mathbf{1}),\ Et\ (\mathbf{2}),\ {}^tBu\ (\mathbf{3})$$

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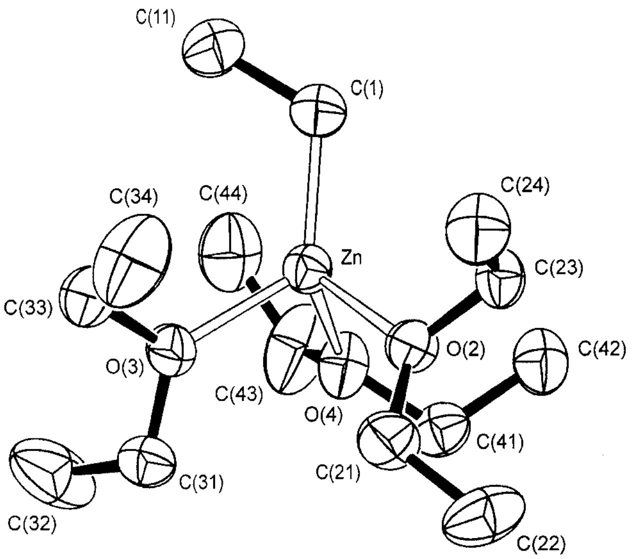

Figure 1. Structure of the $[EtZn(OEt_2)_3]^+$ cation in **2**, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity.

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 ^{11}B 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 $[EtZn(OEt_2)_3]^+$ 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 $[Et_2Zn(\mu\text{-}OBu^t)_2ZnEt_2]^{2-}$.[10] In crystalline $[Bu^tZn(OEt_2)_3][B(C_6F_5)_4]$ the Me_3C-ZnO_3 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.

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

The main products are BMe_3 and $Zn(C_6F_5)_2$ together with a small amount of $BMe_2(C_6F_5)$, as shown by ^1H, ^{19}F, and ^{11}B NMR spectroscopy. In particular, the presence of BMe_3 is very distinctive, with a singlet in the ^1H NMR spectrum at δ 0.78 and a broad ^{11}B NMR peak at δ 89.5. In a similar fashion the reaction of $ZnEt_2$ with $B(C_6F_5)_3$ affords a mixture of $Zn(C_6F_5)_2$, BEt_3, $BEt_2(C_6F_5)$, and $BEt(C_6F_5)_2$. In contrast to the analogous reactions of aluminum trialkyls with $B(C_6F_5)_3$, where an equilibrium between various dimeric aluminum species is established which is shifted toward the formation of $Al(C_6F_5)_3$ only upon removal of BMe_3 in vacuo,[3] the conversion of ZnR_2 to $Zn(C_6F_5)_2$ 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 $ZnR(C_6F_5)$ intermediates. A similar reaction of $ZnMe_2$ with $B(C_6F_5)_3$ 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 $Zn(C_6F_5)_2\cdot$(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 $Al(C_6F_5)_3\cdot$(toluene).[11] Previously, $Zn(C_6F_5)_2$ has been prepared from $ZnCl_2$ and C_6F_5MgX,[12] from AgC_6F_5 and ZnI_2,[13] or by decarboxylation of $Zn(O_2CC_6F_5)_2$.[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

$$B(C_6F_5)_3 + ZnR_2 \xrightarrow{\text{toluene-}d_8/Et_2O} [RZn(OEt_2)_3]^+[RB(C_6F_5)_3]^- \quad (3)$$
$$R = Me\ (\mathbf{6}),\ Et\ (\mathbf{7})$$

$[MeB(C_6F_5)_3]^-$ 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 $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$,[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 $[MeB(C_6F_5)_3]^-$ anion is further confirmed by the small chemical shift difference ($\Delta\delta$ 2.5 ppm) between the *m*- and *p*-fluorine ^{19}F NMR resonances.[16] Diethyl ether solutions of $ZnEt_2$ react similarly, to give $[EtZn(OEt_2)_3]^+[EtB(C_6F_5)_3]^-$ (**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 BMe_3 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_2Cl_2 showed the presence of BMe_3, $BMe_2(C_6F_5)$, and **6** in the ratio 4.3:1:7.8. Evidently BMe_3, $Zn(C_6F_5)_2$, and **6** are in equilibrium in solution, and removal of BMe_3 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 $[Ph_3C][B(C_6F_5)_4]$ in toluene-d_8 takes a different course and proceeds with β-H abstraction and ethene elimination (Scheme 1).[17]The reaction is swift, with the loss of the orange color of CPh_3^+ within ca. 2 s. The NMR spectra show the presence of $Zn(C_6F_5)_2$ and BEt_3. Clearly 1 equiv of $ZnEt_2$ requires only two aryl groups to generate $Zn(C_6F_5)_2$, and consequently further exchange between $BEt_x(C_6F_5)_{3-x}$ for $x = 0-2$ and $ZnEt_2$, as already described above, results in total $[B(C_6F_5)_4]^-$ consumption.

Scheme 1

$$[CPh_3][B(C_6H_5)_4] + ZnEt_2 \rightarrow Ph_3CH + \text{“}[ZnEt][B(C_6F_5)_4]\text{”} + C_2H_4$$

$$\text{“}[ZnEt][B(C_6F_5)_4]\text{”} \rightarrow ZnEt(C_6F_5) + B(C_6F_5)_3$$

$$ZnEt(C_6F_5) + B(C_6F_5)_3 \rightleftharpoons Zn(C_6F_5)_2 + BEt(C_6F_5)_2$$

$$ZnEt_2 + BEt(C_6F_5)_2 \rightleftharpoons ZnEt(C_6F_5) + BEt_2(C_6F_5)$$

$$ZnEt(C_6F_5) + BEt_2(C_6F_5) \rightleftharpoons Zn(C_6F_5)_2 + BEt_3$$

Although the alkyl/C_6F_5 exchange observed in the above reactions presumably involves alkyl-bridged intermediates $RZn(\mu\text{-}R)B(C_6F_5)_3$, 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 $[Ph_3C][B(C_6F_5)_4]$ 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)$B(C_6F_5)_3$, with sharp ^{1}H 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 $[MeB(C_6F_5)_3]^-$ (δ 0.37) and a broad signal at δ −0.97 for a $[ZnMe(TMEDA)]^+$ cation in rapid exchange with the excess $ZnMe_2$(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 $ZnMe_2$(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 CaH_2 (dichloromethane). Deuterated solvents were stored over 4 Å molecular sieves and degassed by several freeze−thaw cycles. $ZnMe_2$ (2.0 M solution in toluene) and $ZnEt_2$ (1.1 M solution in toluene) were used as purchased. The compounds $ZnBu^t{}_2$,[19] $[H(OEt_2)_2][B(C_6F_5)_4]$,[8] $B(C_6F_5)_3$,[20] and $[Ph_3C][B(C_6F_5)_4]$[21] were prepared by literature methods. NMR spectra were recorded on a Bruker DPX300 spectrometer. ^{1}H and ^{13}C NMR spectra are referenced to residual solvent peaks relative to TMS, ^{19}F NMR spectra (282.2 MHz) are relative to external $CFCl_3$, and ^{11}B NMR spectra (96.2 MHz) are relative to $BF_3 \cdot OEt_2$.

$[MeZn(OEt_2)_3][B(C_6F_5)_4]$ (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 $C_{37}H_{33}BF_{20}O_3Zn$: C, 45.26; H, 3.39. Found: C, 45.21; H, 3.34. ^{1}H NMR (300 MHz, 27 °C, CD_2Cl_2): δ 3.80 (q, 12 H, J_{HH} = 7.1 Hz, CH_3CH_2O), 1.25 (t, 18 H, J_{HH} = 7.1 Hz, CH_3CH_2O), −0.56 (s, 3 H, MeZn). $^{13}C\{^1H\}$ NMR (75.5 MHz, 27 °C, CD_2Cl_2): 68.0 (CH_3CH_2O), 14.5 (CH_3CH_2O), −14.4 (MeZn). ^{19}F NMR (282.4 MHz, 27 °C, CD_2Cl_2): δ −133.6 (br, 8 F, *o*-F), −164.1 (t, 4 F, J_{FF} = 22.6 Hz, *p*-F), −168.0 (br, 8 F, *m*-F). ^{11}B NMR (96.3 MHz, 27 °C, CD_2Cl_2): δ −13.6.

$[EtZn(OEt_2)_3][B(C_6F_5)_4]$ (2). $[H(OEt_2)_2][B(C_6F_5)_4]$ (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 $C_{38}H_{35}BF_{20}O_3Zn$: C, 45.83; H, 3.54. Found: C, 45.64; H, 3.57. ^{1}H NMR (300 MHz, 25 °C, CD_2Cl_2): δ 3.91 (q, 12 H, J_{HH} = 7.2 Hz, CH_3CH_2O), 1.35 (t, 18 H, J_{HH} = 7.2 Hz, CH_3CH_2O), 1.21 (t, 3 H, J_{HH} = 8.1 Hz, CH_3CH_2Zn), 0.49 (q, 2 H, J_{HH} = 8.1 Hz, CH_3CH_2Zn). $^{13}C\{^1H\}$ NMR (75.5 MHz, 27 °C, CD_2Cl_2): δ 67.0 (CH_3CH_2O), 14.5 (CH_3CH_2O), 11.5 (CH_3CH_2Zn), 0.8 (CH_3CH_2Zn). ^{19}F NMR (282.4 MHz, 27 °C, CD_2Cl_2): δ −133.6 (br, 8 F, *o*-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). ^{11}B NMR (96.3 MHz, 27 °C, CD_2Cl_2) δ −13.6.

$[Bu^tZn(OEt_2)_3][B(C_6F_5)_4]$ (3). A suspension of $[H(OEt_2)_2][B(C_6F_5)_4]$ (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 $C_{40}H_{39}BF_{20}O_3Zn$: C, 46.92; H, 3.84. Found: C, 46.83; H, 3.55. ^{1}H NMR (300 MHz, 27 °C, CD_2Cl_2): δ 3.79 (q, 12 H, J_{HH} = 7.2 Hz, CH_3CH_2O), 1.31 (t, 18 H, J_{HH} = 7.2 Hz, CH_3CH_2O), 1.17 (s, 9 H, CMe_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, 25 °C, C_6D_6): δ 14.76 (CH_3CH_2O), 25.20 (CMe_3), 32.27 (CMe_3), 67.08 (CH_3CH_2O). ^{19}F NMR (282.4 MHz, 27 °C, CD_2Cl_2): 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). ^{11}B NMR (96.3 MHz, 27 °C, CD_2Cl_2): δ −13.6.

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Reaction of $ZnMe_2$ with $B(C_6F_5)_3$ in Toluene-d_8. A solution of $B(C_6F_5)_3$ (30 mg, 59 μmol) in toluene-d_8 (4 mL) was treated with a solution of $ZnMe_2$ (0.04 mL, 80 μmol, 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 BMe_3, $BMe_2(C_6F_5)$, and $Zn(C_6F_5)_2$. BMe_3: ^{1}H NMR (300 MHz, 25 °C, toluene-d_8) δ 0.78 (s); ^{11}B NMR (96.3 MHz, 25 °C, toluene-d_8) δ 89.5. $BMe_2(C_6F_5)$: ^{1}H NMR (toluene-d_8) δ 1.07 (t, 6 H, $J = 1.9$ Hz, Me); ^{11}B NMR (toluene-d_8) δ 83.8; ^{19}F 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). $Zn(C_6F_5)_2$: ^{19}F 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 $ZnMe_2$ with $B(C_6F_5)_3$ in Toluene-d_8/1,2-Difluorobenzene. A solution of $B(C_6F_5)_3$ (30 mg, 59 μmol) in a mixture of toluene-d_8 (4 mL) and 1,2-difluorobenzene (1 mL) was treated with a solution of $ZnMe_2$ (0.04 mL, 80 μmol, 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 BMe_3, $BMe_2(C_6F_5)$, $BMe(C_6F_5)_2$, and $Zn(C_6F_5)_2$. $BMe(C_6F_5)_2$: ^{1}H NMR (300 MHz, 25 °C, toluene-d_8/1,2-difluorobenzene) δ 1.48 (q, 3 H, $J = 1.78$ Hz, Me); ^{11}B NMR (96.3 MHz, 25 °C, toluene-d_8/1,2-difluorobenzene) δ 75.2; ^{19}F NMR (282.4 MHz, 25 °C, toluene-d_8) δ −130.55 (m, 2 F), −147.92 (m, 1 F), −162.17 (m, 2 F).

Reaction of $ZnEt_2$ with $B(C_6F_5)_3$ in Toluene-d_8. A solution of $B(C_6F_5)_3$ (30 mg, 59 μmol) in toluene-d_8 (4 mL) was treated with a solution of $ZnEt_2$ (0.07 mL, 77 μmol, 1.1 M) in toluene. The reaction was complete in the time taken to place the sample in the NMR spectrometer. The solution contained BEt_3, $BEt_2(C_6F_5)$, $BEt(C_6F_5)_2$, and $Zn(C_6F_5)_2$. BEt_3: ^{1}H NMR (300 MHz, 25 °C, toluene-d_8) δ 1.16 (q, 6 H, $J = 7.7$ Hz, $\mathrm{CH_3C}\mathit{H}_2\mathrm{-B}$), 1.01 (t, 9 H, $J = 7.7$ Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2-B}$); ^{11}B NMR (96.3 MHz, 25 °C, toluene-d_8) δ 89.7. $BEt_2(C_6F_5)$: ^{1}H NMR (300 MHz, 25 °C, toluene-d_8) δ 1.42 (q, 4 H, $J = 7.6$ Hz, $\mathrm{CH_3C}\mathit{H}_2\mathrm{-B}$), 0.92 (t, 6 H, $J = 7.6$ Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2-B}$); ^{11}B NMR (96.3 MHz, 25 °C, toluene-d_8) δ 87.8; ^{19}F 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). $BEt(C_6F_5)_2$: ^{1}H NMR (toluene-d_8) δ 1.87 (q, 2 H, $J = 7.6$ Hz, $\mathrm{CH_3C}\mathit{H}_2\mathrm{-B}$), 0.98 (t, 3 H, $J = 7.6$ Hz, $\mathrm{C}\mathit{H}_3\mathrm{CH_2-B}$); ^{11}B NMR (toluene-$d_8$) δ 77.3; ^{19}F NMR (toluene-d_8) δ −134.85 (m, 2 F), −148.14 (m, 1 F), −162.51 (m, 2 F).

$Zn(C_6F_5)_2\cdot$(toluene) (4). A solution of $B(C_6F_5)_3$ (3.01 g, 5.88 mmol) in toluene (50 mL) was treated with a solution of $ZnMe_2$ 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 $Zn(C_6F_5)_2\cdot$(toluene) as needlelike crystals, yield 3.33 g (76.6%). Anal. Calcd for $C_{12}F_{10}Zn\cdot C_7H_8$: C, 46.42; H, 1.64. Found: C, 45.93; H, 1.46. ^{1}H NMR (300 MHz, 25 °C, C_6D_6): δ 6.98−7.13 (m, 5 H, Ph), 2.10 (s, 3 H, Me). ^{19}F NMR (C_6D_6): 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).

$Zn(C_6F_5)_2\cdot C_6Me_6$ (5). A solution of $Zn(C_6F_5)_2\cdot$(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 $C_{12}F_{10}Zn\cdot C_{12}H_{18}$: C, 51.31; H, 3.23. Found: C, 51.95; H, 3.49. ^{1}H NMR (300 MHz, 25 °C, C_6D_6): δ 2.03 (s, 18 H, Me). ^{13}C NMR (75.5 MHz, 25 °C, C_6D_6): δ 16.79 (Me), 132.48 (C_6). ^{19}F NMR (282.4 MHz, 25 °C, C_6D_6): δ −118.1 (m, 4 F, *o*-F), −153.2 (t, 2 F, $J_{FF} = 19.8$ Hz, *p*-F), −160.9 (m, 4 F, *m*-F).

Generation of $[MeZn(OEt_2)_3][MeB(C_6F_5)_3]$ (6). A solution of $B(C_6F_5)_3$ (40 mg, 79 μmol) in toluene-d_8 (4 mL) and ether (0.5 mL) was treated with a solution of $ZnMe_2$ (0.04 mL, 80 μmol, 2 M) in toluene. The reaction was instantaneous. ^{1}H NMR (300 MHz, 25 °C, C_7D_8/ether): δ 3.34 (q, 12 H, $J = 7.2$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 1.02 (br s, 3 H, BMe), 0.88 (t, 18 H, $J = 7.2$ Hz, $\mathrm{OCH_2C}\mathit{H}_3$), −0.73 (s, 3 H, ZnMe). ^{13}C{^{1}H} NMR (75.5 MHz, 25 °C, C_7D_8, ether): δ 67.62 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 14.42 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 11.15 (br, BMe), −14.93 (ZnMe). ^{19}F NMR (282.4 MHz, 25 °C, C_7D_8/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). ^{11}B NMR (96.3 MHz, 27 °C, C_7D_8/ether): δ −11.4.

Generation of $[EtZn(OEt_2)_3][EtB(C_6F_5)_3]$ (7). A solution of $B(C_6F_5)_3$ (30 mg, 59 μmol) in toluene-d_8 (4 mL) and ether (0.5 mL) was treated with a solution of $ZnEt_2$ (0.05 mL, 55 μmol, 1.1 M) in toluene. ^{1}H NMR (300 MHz, 25 °C, C_7D_8/ether): δ 3.38 (q, 12 H, $J = 7.1$ Hz, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 1.63 (br q, 2 H, $J = 7.1$ Hz, $\mathrm{BC}\mathit{H}_2\mathrm{CH_3}$), 1.06 (t, 3 H, $J = 8.1$ Hz, $\mathrm{ZnCH_2C}\mathit{H}_3$), 1.03 (br t, 3 H, $J = 7.0$ Hz, $\mathrm{BCH_2C}\mathit{H}_3$), 0.91 (q, 18 H, $J = 7.1$ Hz, $\mathrm{OCH_2C}\mathit{H}_3$), 0.13 (q, 2 H, $J = 8.1$ Hz, $\mathrm{ZnC}\mathit{H}_2\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (75.5 MHz, 25 °C, C_7D_8/ether): δ 67.49 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 15.18 (vbr, $\mathrm{B}\mathit{C}\mathrm{H_2CH_3}$), 13.50 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 12.51 ($\mathrm{BCH_2}\mathit{C}\mathrm{H_3}$), 11.40 ($\mathrm{ZnCH_2}\mathit{C}\mathrm{H_3}$), −0.47 ($\mathrm{Zn}\mathit{C}\mathrm{H_2CH_3}$). ^{19}F NMR (282.4 MHz, 25 °C, C_7D_8/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). ^{11}B NMR (96.3 MHz, 27 °C, C_7D_8/ether): δ −9.1.

Reaction of $ZnEt_2$ with $[Ph_3C][B(C_6F_5)_4]$ in Toluene-d_8. A solution of $[Ph_3C][B(C_6F_5)_4]$ (0.020 g, 21 μmol) in toluene-d_8 (0.4 mL) was treated with a solution of $ZnEt_2$ (0.09 mL, 1.1 M, 99 μmol) 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 $ZnEt_2$, there were also signals for BEt_3 and $[B(C_6F_5)_4]^-$.

Reaction of $ZnMe_2$(TMEDA) with $B(C_6F_5)_3$ in Dichloromethane-d_2. A solution of $ZnMe_2$(TMEDA) (TMEDA = 1,2-$C_2H_4(NMe_2)_2$; 7 mg, 33 μmol) in dichloromethane-d_2 (3 mL) was treated with a solution of $B(C_6F_5)_3$ (10 mg, 20 μmol) also in dichloromethane-d_2 (3 mL) at −70 °C. The products were characterized by NMR. Besides signals for $[MeB(C_6F_5)_3]^-$ and the resonances of coordinated TMEDA, the solution contained signals for (TMEDA)ZnMe(μ-Me)$B(C_6F_5)_3$ 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(μ-Me)$B(C_6F_5)_3$: ^{1}H NMR (300 MHz, −70 °C, CCl_2D_2): δ −0.41 (s, 3 H, μ-Me), −0.83 (s, 3 H, ZnMe). ^{11}B 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(μ-Me)$B(C_6F_5)_3$ broadened and merged with the signals for $[MeB(C_6F_5)_3]^-$ and $[ZnMe(TMEDA)]^+$/$ZnMe_2$(TMEDA).

X-ray Crystallography. Crystals are clear, colorless plates. A crystal of dimensions ca. 0.4 × 0.3 × 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 Kα 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/SCALEPACK[22] programs. The structure was determined by the automated Patterson routines in the SHELXS program[23] 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 $w = [\sigma^2(F_o^2) + (0.0416P)^2 + 1.53P]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$; 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; $P2_1/c$, $a = 14.824(1)$ Å, $b = 15.947(1)$ Å, $c = 18.037(1)$ Å; $\beta = 108.25(1)°$; $V = 4049.4(4)$ Å^3; $Z = 4$; $D_{calcd} = 1.633$ g/cm^3; $\mu = 0.736$ mm^{-1}; $F(000) = 2008$; $1.7 \leq \theta \leq 25.4°$; $-17 \leq h \leq 17$, $-19 \leq k \leq 19$, $-21 \leq l \leq 21$; 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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