Communications to the Editor

The Effect of Solvent in the Reaction of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ with $B(C_6F_5)_3$: Formation of $[HB(C_6F_5)_3]^-$ Salts of the Unsupported Hydrogen-Bridged Cation $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BC_4H_8\}_2]^+$ and the Cation $[Cp_2Zr(OEt_2)(OEt)]^+$

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Received March 27, 2000

Boron Lewis acids BF_3, BCl_3, and $B(C_6F_5)_3$ can serve as hydride ion abstracting agents.[1,2] A seminal contribution[2] on cationic zirconocene polymerization catalysts reported hydride ion abstraction from $(C_5Me_5)_2ZrH_2$ by $B(C_6F_5)_3$ in benzene and in toluene to produce the salt $[(C_5Me_5)_2ZrH][HB(C_6F_5)_3]$. While there is significant interest in generating metallocene cations,[3] with particular interest in alkyl carbanion abstraction,[4] relatively little effort to produce them through hydride ion abstraction by $B(C_6F_5)_3$ has been reported. Described here are hydride ion abstraction reactions by $B(C_6F_5)_3$ that are influenced by the nature of the solvent to produce new zirconocene cations, one of which is possibly the first example of a bimetallic hydrogen-bridged cation in which there is no metal−metal bonding between the bridged metals.[5] The common unsupported hydrogen-bridged systems are either neutral or anionic.

Reactions of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**,[6] with $B(C_6F_5)_3$ in benzene and in diethyl ether were investigated. Complex **1** contains a terminal Zr−H bond and two Zr−H−B bonds. Since bridge hydrogens tend to be abstracted as protons rather than hydride ion,[7] it was of interest to determine if the reaction with $B(C_6F_5)_3$ would remove only H^- from the Zr−H bond and generate a zirconocene cation that has retained the $\{(\mu\text{-}H)_2BC_4H_8\}$ moiety. It was observed that solvent plays a key role in determining the course of this reaction. In benzene, a poorly coordinating solvent, the unusual unsupported single hydrogen-bridged cation $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BC_4H_8\}_2]^+$, **2** (Figure 1a), was isolated as the $[HB(C_6F_5)_3]^-$ salt (78% yield). However, from the coordinating solvent, diethyl ether, the cation $[Cp_2Zr(OEt_2)(OEt)]^+$, **3** (Figure 1b), was isolated as the $[HB(C_6F_5)_3]^-$ salt (68% yield).[8−10]

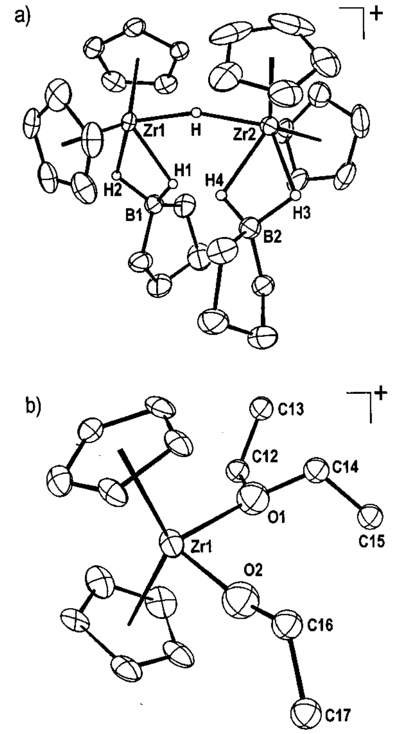
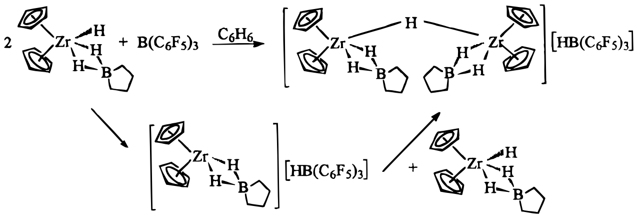


Figure 1. (a) Molecular structure of $[(\mu\text{-}H)(Cp_2Zr(\mu\text{-}H)_2BC_4H_8)_2]^+$ and the selected bond distances (Å) and angle (deg), Zr(1)−B(1): 2.567(5); Zr(2)−B(2): 2.561(5); Zr(1)−H: 1.99(4); Zr(2)−H: 1.94(4); Zr(1)−H(1): 1.97(4); Zr(1)−H(2): 1.96(4); Zr(2)−H(3): 1.97(4); Zr(2)−H(4): 2.00(4); B(1)−H(1): 1.19(4); B(1)−H(2): 1.27(4); B(2)−H(3): 1.26(4); B(2)−H(4): 1.15(4); Zr(1)−H−Zr(2): 163.3; Zr(1)- - -Zr(2) 3.898(4). (b) Molecular structure of $[(Cp_2Zr(OEt)(OEt_2)]^+$ and the selected bond distances (Å) and angle (deg), Zr(1)−O(1): 2.209(8); Zr−O(2): 1.884(8). O(1)−Zr(1)−O(2): 91.9(3); Zr(1)−O(2)−C(16): 159.6(9).

Scheme 1



The double hydrogen bridged unit $\{(\mu\text{-}H)_2BC_4H_8\}$ from reactant **1** is retained in the unsupported hydrogen bridge cation **2**, thereby suggesting that hydride ion is abstracted from the Zr−H bond in the initial phase of the reaction. Proton and ^{11}B NMR spectra are in accord with the solid-state structure.[8] The reaction between complex **1** and $B(C_6F_5)_3$ occurs in a 2:1 molar ratio even when the reactants are employed in a 1:1 molar ratio. In the earlier reported reaction[2] between $B(C_6F_5)_3$ and $(C_5Me_5)_2ZrH_2$ to produce $[(C_5Me_5)_2ZrH][HB(C_6F_5)_3]$ the formation of a dinuclear unsupported hydrogen bridged cation analogous to complex **2** was not

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(8) Preparation of $[(\mu\text{-}H)(Cp_2Zr(\mu\text{-}H)_2BC_4H_8)_2][HB(C_6F_5)_3]$: In the drybox a 147 mg (0.50 mmol) of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ and 128 mg (0.25 mmol) of $B(C_6F_5)_3$ were put in a flask. After degassing, 5 mL of benzene was transferred to the flask. After stirring for 10 min, hexane was transferred to the system to produce a white ppt that was washed with hexane twice and a 215 mg (mmol), 78% yield of white product was isolated. ^{11}B NMR (d_8-toluene) $\delta = -13.12$ ((B−H−Zr)$_2$, t, $J_{B-H} = 69$ Hz), −24.85 ppm ($[HB(C_6,F_5]^-$, d, $J_{B-H} = 72$ Hz). ^1H NMR (d_8-toluene) $\delta = 5.68$ (s, Cp), 1.66 (br, 8H, β-H), 0.88 (br, 8H, α-H), −2.02 (br, 2 μ-H), −3.89 (br, 2 μ-H), and −5.56 ppm (br, 1 μ-H). $^1H\{^{11}B\}$ NMR (d_8-toluene) 4.27 (br, HB). Calcd C, 50.47; H, 3.87. Found. C, 50.36; H, 4.01.

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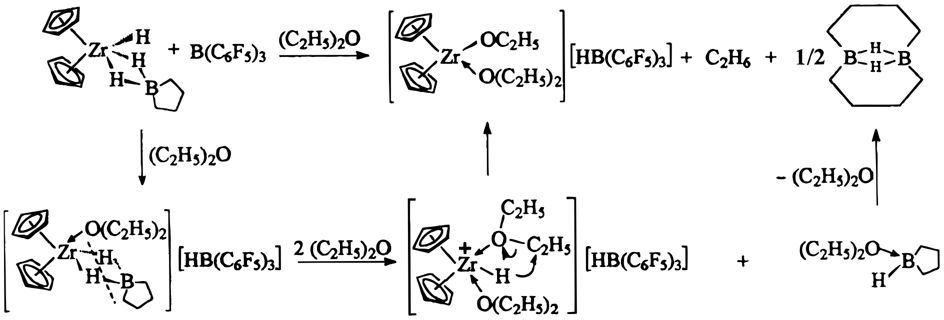
Scheme 2



observed. Interestingly, the reaction of $(1,2\text{-}Me_2Cp)_2ZrMe_2$ with $B(C_6F_5)_3$ requires a 2:1 molar ratio of reactants to produce the related methyl-bridged cation $[(1,2\text{-}Me_2Cp)_2ZrMe]_2(\mu\text{-}Me)^+$.[11] When the reactants are employed in a 1:1 molar ratio, the ion-paired complex $[(1,2\text{-}Me_2Cp)_2(Me)Zr]^+$- - -$[MeB(C_6F_5)_3]^-$ is produced.[12]

Scheme 1 suggests a pathway for the formation of **2**. Hydride ion abstraction from **1** produces a 16-electron Zr cation which reacts with a second molecule of **1** to form **2**. A recent report showed that **1** can function as a hydride donor to form an unsupported hydrogen bridge in the compound $\{Cp_2Zr\{(\mu\text{-}H)B(C_4H_8)CH_2Ph\}\}\{(\mu\text{-}H)_2BC_4H_8\}$.[13]

In diethyl ether, the overall reaction of **1** with $B(C_6F_5)_3$ (Scheme 2) was established from single crystal and NMR analysis of the crystalline product, $[Cp_2Zr(OEt_2)(OEt)][HB(C_6F_5)_3]$, by NMR spectra of the known organodiborane $(B_2(\mu\text{-}H)_2(C_4H_8)_2)$[14] formed, and the GC−MS spectrum of the ethane evolved. This is a rapid reaction that precluded observation of intermediates. However, it is reasonable to assume that ethane is formed through the intermediate species shown in this Scheme 2. The formation of the ethoxyl group on the cation is reminiscent of the conversion of coordinated THF to a butoxyl group in the formation of $[(C_5H_4Me)_2Zr(O{-}n\text{-}Bu)(THF)]^+$.[15]

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE 99-01115. NMR spectra and GC−MS were obtained at The Ohio State University Campus Chemical Instrumentation Center.

Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and bond distances and angles for $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BC_4H_8\}_2][HB(C_6F_5)_3]$ and $[Cp_2Zr(OEt_2)(OEt)][HB(C_6F_5)_3]$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] Preparation of $[Cp_2Zr(OEt)(OEt_2)][HB(C_6F_5)_3]$: In the drybox, 294 mg (1 mmol) of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$, 512 mg (1 mmol) of $B(C_6F_5)_3$, and 15 mL of ether were put in a flask. The reaction was monitored by the ^{11}B NMR. The anion $[HB(C_6F_5)_3]^-$ (−26.9 ppm, d, $J_{B-H} = 88$ Hz) and organodiborane $B_2(\mu\text{-}H)_2(C_4H_8)_2$ (28.5 ppm) were formed in <5 min. But with increasing time $B_2(\mu\text{-}H)_2(C_4H_8)_2$ diminished in concentration while a new signal at 58.0 ppm (singlet) appeared, indicative of a trialkyl borane. After stirring this system for 1 h, the ether solution was removed by filtration, and 583 mg (68.3% yield) of white solid was isolated. Complex **3** has limited solubility in Et_2O. For the NMR spectra in THF the Et_2O in **3** is displaced by THF solvent. ^{11}B NMR (THF): $\delta = -26.43$ ppm (d, $J_{B-H} = 93$ Hz). ^1H NMR (d_8-THF): $\delta = 6.59$ (s, Cp), 4.30 (2H, q, $J = 7$ Hz), 3.38 (4H, q, $J = 7$ Hz), 1.21 (3H, t, $J = 7$ Hz), and 1.11 ppm (6H, $J = 7$ Hz). $^1H\{^{11}B\}$ NMR (d_8-THF): 3.80 (m, HB, $J_{H-B} = 4.6$ Hz). Calcd C, 47.84; H, 3.07. Found: C, 47.01; H, 3.09.

[10] Crystal data for $[(\mu\text{-}H)(Cp_2Zr(\mu\text{-}H)_2BC_4H_8)_2][HB(C_6F_5)_3]$, **2**: monoclinic, space group $P2_1/n$, $a = 11.924(2)$ Å, $b = 17.218(3)$ Å, $c = 21.714(4)$ Å, $\beta = 94.79(3)°$, $V = 4442.6(15)$ Å^3, $Z = 4$, ρ(calcd) = 1.637 mg/m^3, fw = 1094.67, $\mu = 0.566$ mm^{-1}. R_1 (6293 independent reflections with $I > 2\sigma(I)$ and 675 parameters) = 0.0479 and wR_2 (29957 reflections measured) = 0.1242. Crystal data for $[Cp_2Zr(OEt_2)(OEt)][HB(C_6F_5)_3]$, **3**: monoclinic, space group $C2/c$, $a = 20.028(1)$ Å, $b = 15.467(1)$ Å, $c = 22.608(1)$ Å, $\beta = 107.26(1)°$, $V = 6687.5(7)$ Å^3, $Z = 8$, ρ(calcd) = 1.696 mg/m^3, fw = 853.58, $\mu = 0.445$ mm^{-1}. R_1 (3018 independent reflections with $I > 2\sigma(I)$ and 526 parameters) = 0.0775 and wR_2 (12937 reflections measured) = 0.2114.

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