Effect of Solvent in the Reaction of $Cp_2ZrH\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8, C_8H_{14}$) with $B(C_6F_5)_3$: Formation of $[HB(C_6F_5)_3]^-$ Salts of the Unsupported Hydrogen-Bridged Cations $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BR_2\}_2]^+$ ($R_2 = C_4H_8, C_8H_{14}$) and $[Cp_2Zr(OEt_2)X]^+$ ($X = OEt, \{(\mu\text{-}H)_2BC_8H_{14}\}$)

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Hydride abstraction reactions of the zirconocene cyclic organohydroborate complexes $Cp_2ZrH\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, **1**; C_8H_{14}, **2**) with $B(C_6F_5)_3$ were observed as a function of solvent. The reaction in poorly coordinating solvents, benzene and toluene, forms $[HB(C_6F_5)_3]^-$ salts of Zr−H−Zr hydrogen-bridged cations $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BR_2\}_2]^+$ ($R_2 = C_4H_8$, **3**; C_8H_{14}, **4**), in which there is no direct metal−metal bonding between the bridged metals. The unsupported hydrogen-bridged bond in complex **4** was cleaved when it was dissolved in the coordinating solvent THF to produce the neutral complex **2** and the ionic complex $[Cp_2Zr(THF)\{(\mu\text{-}H)_2BC_8H_{14}\}][HB(C_6F_5)_3]$. In the coordinating solvent, diethyl ether, the salts of $[Cp_2Zr(OEt_2)X]^+[HB(C_6F_5)_3]^-$ (X = OEt, **5**; $\{(\mu\text{-}H)_2BC_8H_{14}\}$, **6**) consisting of zirconocene cations with coordinated solvent ligands were isolated. The formation of **5** involves hydride insertion from zirconium into the carbon oxygen bond of one the coordinated ethers, resulting in the liberation of ethane and the formation of an ethoxyl group coordinated to zirconium. The diethyl ether molecules in the cations **5** and **6** are weakly coordinated to Zr and are displaced in THF solution. Single-crystal X-ray structures of **3**, **4**, and **5** were determined.

Introduction

Recently, group IV and V transition metal metallocene complexes of the cyclic organohydroborate anions $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ (a transannular hydrogen-bridged 10-membered ring anion), $[H_2BC_5H_{10}]^-$, and $[H_2BC_8H_{14}]^-$ (the hydroborate anion of the 9-BBN dimer) were investigated.[1] A common structural feature of all those complexes is the M−H−B (3c-2e) bond, like that observed in transition metal tetrahydroborate complexes, but the reactivity and fluxional behavior of cyclic organohydroborate complexes are unlike those of the tetrahydroborate analogues.[2] Without the contribution of hydrogen exchange between M−H−B and B−H bonds that occurs in tetrahydroborate derivatives, it is possible to isolate and investigate the reactivity and interchange of bridging hydrogens (M−H−B) and terminal hydrogen (M−H) of the cyclic organohydroborate. A recent report from this laboratory shows that terminal metal hydride assumes a required role in the process of intramolecular hydrogen exchange between Cp and Zr−H−B hydrogens.[2b,3] Exchange between bridging and Cp-hydrogens in zirconocene cyclic organohydroborates does not occur when there is no terminal M−H bond. However, a terminal hydrogen on zirconium in the complexes $Cp_2ZrH\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8, C_5H_{10}, C_8H_{14}$) participates in intramolecular exchange with bridging and Cp-hydrogens. The order of exchange as a function of increasing temperature is as follows: bridging hydrogens interchange; then bridging hydrogens and terminal Zr-hydrogen exchange; then terminal Zr-hydrogen, bridging hydrogens, and Cp-hydrogens exchange.

Another point of interest with respect to the reactivity of the hydrogen bridge systems of the cyclic organohydroborates of the group IV and V metals is their reactions with a hydride abstraction reagent such as $B(C_6F_5)_3$.[4] The question of interest is whether the

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bridging hydrogen in the M−H−B (3c-2e) bond is sufficiently basic for it to be abstracted to generate a metallocene cation. The reagent $B(C_6F_5)_3$ has been widely employed as an alkyl carbanion abstracting reagent to produce metallocene cations for olefin polymerization,[5] and weakly coordinating anions containing boron and aluminum can greatly improve the activity of metallocene catalysts used in industrial olefin polymerization.[6] We found that the bridging hydrogens are sufficiently basic for abstraction to produce ionic complexes in the reaction of $B(C_6F_5)_3$ with the complexes $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$and $Cp_2Nb\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, C_5H_{10}, C_8H_{14}), which possess only bridging hydrogens but no terminal M−H hydrogens.[4b,c] Furthermore, it was observed that the abstraction product is a function of the coordinating ability of the solvent. The reaction of titanocene cyclic organohydroborates $Cp_2Ti\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, C_5H_{10}, C_8H_{14}) with $B(C_6F_5)_3$ in the poorly coordinating solvent toluene produces the covalent metathesis product $Cp_2Ti\{(\mu\text{-}H)_2B(C_6F_5)\}$, while in the coordinating solvent diethyl ether, the $[HB(C_6F_5)_3]^-$ salt of the titanocene cation, $[Cp_2Ti(OEt_2)_2]^+$, is formed.[4c] On the other hand, the reaction of niobocene cyclic organohydroborates $Cp_2Nb\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, C_5H_{10}, C_8H_{14}) with $B(C_6F_5)_3$ is much more complicated. In the poorly coordinating solvent toluene, the product is the $[HB(C_6F_5)_3]^-$ salt of the triniobocene cation $[Cp_2Nb(\mu\text{-}H)(\eta^5\text{-}\eta^1\text{-}C_5H_4)Nb(\eta^5\text{-}\eta^1\text{-}C_5H_4)_2Nb\{(\mu\text{-}H)(\eta^5\text{-}C_5H_4B(C_6F_5)_2)\}]^+$, but the neutral complex $CpNb(C_6F_5)\{(\mu\text{-}H)(\eta^5\text{-}C_5H_4B(C_6F_5)_2)\}$ is obtained in the coordinating solvent diethyl ether.[4b]

For the zirconocene complex $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**, although both terminal and bridging hydrogens are present, the terminal hydrogen is more hydridic and is preferentially abstracted by $B(C_6F_5)_3$ in the poorly coordinating solvent benzene to form the $[HB(C_6F_5)_3]^-$ salt of the unsupported hydrogen-bridged cation $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BC_4H_8\}_2]^+$. However, in the coordinating solvent diethyl ether the $[HB(C_6F_5)_3]^-$ salt of the mononuclear cation $[Cp_2Zr(OEt_2)(OEt)]^+$ is produced.[4d] In this paper we provide new examples of hydride abstraction reactions from the zirconocene complex $Cp_2ZrH\{(\mu\text{-}H)_2BC_8H_{14}\}$, **2**, and provide additional details of hydride abstractions from **1**.

Results and Discussion

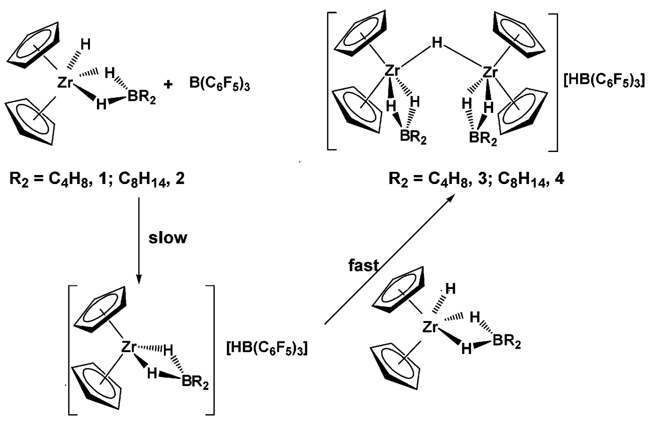
Formation of $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BR_2\}_2]$ $[HB(C_6F_5)_3]$ ($R_2 = C_4H_8$, 3; C_8H_{14}, 4). In reactions of **1** and **2** with $B(C_6F_5)_3$ in the poorly coordinating solvents benzene and toluene, the complexes $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BC_4H_8\}_2][HB(C_6F_5)_3]$, **3**, and $[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BC_8H_{14}\}_2][HB(C_6F_5)_3]$, **4**, are produced (reaction 1). Each complex

$$2\ Cp_2ZrH\{(\mu\text{-}H)_2BR_2\} + B(C_6F_5)_3 \rightarrow \atop (R_2 = C_4H_8,\ \mathbf{1};\ C_8H_{14},\ \mathbf{2})$$

$$[(\mu\text{-}H)\{Cp_2Zr(\mu\text{-}H)_2BR_2\}_2][HB(C_6F_5)_3] \atop (R_2 = C_4H_8,\ \mathbf{3};\ C_8H_{14},\ \mathbf{4}) \quad (1)$$

contains a Zr−H−Zr hydrogen-bridged cation. These cations are unusual since unsupported hydrogen-bridged systems are usually either neutral or anionic.[7] Marks and co-workers showed that the reaction of Cp^*ZrH_2 with $B(C_6F_5)_3$ generates the ionic complex $[(Cp^*_2\ ZrH][HB(C_6F_5)_3]$ in the solid state.[8] A dinuclear unsupported Zr−H−B bridge was not observed in the solid state. In the formation of **3** and **4** the reactants react in a 2:1 ratio, irrespective of their initial ratio. When the initial reactant ratio is 1:1, the excess $B(C_6F_5)_3$ does not react with either **3** or **4**. It should be noted that the reaction of L_2ZrMe_2 ($L = C_5H_5$, 1,2-$Me_2C_5H_3$, Me_5C_5) with $B(C_6F_5)_3$ in a 1:1 ratio always produces ion-paired complexes $L_2ZrMe^+MeB(C_6F_5)_3^-$. Even when the $B(C_6F_5)_3$ is in excess, the second methyl group is still not removed.[8] In contrast, the reaction of L_2ZrMe_2 ($L = C_5H_5$, 1,2-$Me_2C_5H_3$, Me_5C_5) with PBB (tris(2,2′,2″-perfluorobiphenyl)borane) in 2:1 ratios gives the methyl-bridged complexes $[L_2Zr(Me)(\mu\text{-}Me)MeZrL_2][MePBB]^-$.[9]

Scheme 1



A possible pathway for the formation of **3** and **4** is shown in Scheme 1. The terminal Zr−H hydrogen in complexes **1** and **2** is abstracted by $B(C_6F_5)_3$ to first produce a 16-electron Zr cation $[Cp_2Zr\{(\mu\text{-}H)_2BR_2\}]^+$. Then the terminal hydrogen of the second molecule $Cp_2ZrH\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, C_8H_{14}) adds to the vacant site on the cation to form the unsupported hydrogen-bridged cation of **3** and **4**. On the basis of the fact that the product is not influenced by the reactant ratio, it is believed that the first step of the reaction, hydride abstraction by $B(C_6F_5)_3$, is slower than the second step, hydride addition by $Cp_2ZrH\{(\mu\text{-}H)_2BR_2\}$. Moreover, the

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Table 1. Comparison of Proton Chemical Shifts of 2, 3, 4, and 6 in Different Solvents

	H(Cp)	Zr−H	H(anion)	Zr−H−B	Zr−H−Zr
3 in toluene	5.70		4.09	−2.03; −3.86	−5.55
4 in toluene	5.85		4.38	−1.64; −3.60	−5.20
4 in THF	6.65; 6.02	3.85	3.73	0.30; −2.21; −3.34; −4.20	
6 in THF	6.64		3.74	0.32; −2.19	
2 in THF	6.02	3.85		−3.34; −4.07	

Table 2. Crystallographic Data for 4[a]

formula	$C_{54}H_{54}B_3F_{15}Zr_2$
mol wt	1202.84
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	21.6948(2)
b (Å)	10.2050(1)
c (Å)	24.4983(2)
β (deg)	114.05
volume (Å^3)	4952.97(8)
Z	4
D_c (g/cm^3)	1.613
F(000)	2432
θ range (deg)	2.12−27.48
$h\ k\ l$ ranges	−28 28,−13 13,−31 31
cryst size (mm)	0.27 × 0.23 × 0.12
μ(Mo Kα) (mm^{-1})	0.516
transmission: max., min.	0.9407, 0.8733
no. of reflns collected	22 011
no. of indep reflns	11 341
R_{int}	0.0309
completeness to θ	99.9%
no. of data/restraints/params	11 341/0/707
final R indices [$I \geq 2\sigma(I)$][b]	$R_1 = 0.0387$; $wR_2 = 0.1025$
R indices (all)	$R_1 = 0.0642$; $wR_2 = 0.1438$
GOF	1.106
largest diff peak, e/Å^3	1.040/−0.911

[a] Features common to all determinations: λ(Mo Kα) = 0.71073 Å. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma||F_o|$; $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

Table 3. Selected Bond Distances and Angles for 4[a]

Bond Distances (Å)

Zr1−Zr2	3.9755(4)	Zr2−H(2A)	1.95(3)
Zr1−H	2.00(4)	Zr2−H(2B)	1.99(3)
Zr2−H	2.01(4)	Zr1−$Cp_{centroid(C1-C5)}$	2.185(2)
Zr1−B1	2.578(4)	Zr1−$Cp_{centroid(C6-C10)}$	2.190(2)
Zr2−B2	2.580(4)	Zr2−$Cp_{centroid(C11-C15)}$	2.194(2)
Zr1−H(1A)	1.95(3)	Zr2−$Cp_{centroid(C16-C20)}$	2.190(2)
Zr1−H(1B)	1.90(3)	B3−H(3A)	1.21(3)

Bond Angles (deg)

Zr1−H−Zr2	164(2)
$Cp_{centroid(C1-C5)}$−Zr1−$Cp_{centroid(C6-C10)}$	130.86(7)
H−Zr1−$Cp_{centroid(C1-C5)}$	105(1)
H−Zr1−$Cp_{centroid(C6-C10)}$	99(1)
H−Zr1−B1	100(1)
B1−Zr1−$Cp_{centroid(C1-C5)}$	108.45(9)
B1−Zr1−$Cp_{centroid(C6-C10)}$	108.6(1)
$Cp_{centroid(C11-C15)}$−Zr2−$Cp_{centroid(C16-C20)}$	131.39(6)
H−Zr2−$Cp_{centroid(C11-C15)}$	103(1)
H−Zr2−$Cp_{centroid(C16-C20)}$	100(1)
H−Zr2−B2	103(1)
B2−Zr2−$Cp_{centroid(C11-C15)}$	108.39(9)
B2−Zr2−$Cp_{centroid(C16-C20)}$	107.52(9)

[a] Centroid, Cp, parameters were calculated as unweighted averages, $\langle p\rangle$, of the corresponding cyclopentadiene carbon parameters. Their standard deviations, $S_{\langle p\rangle}$, for the Cp centroids were estimated from the individual carbon standard deviations: $S_{\langle p\rangle} = (\Sigma Si^2)^{1/2}/N$, $N = 5$. The geometric relations involving Cp were then obtained with PARST (Nardelli, M. J. *J. Appl. Crystallogr.* **1995**, *28*, 659) in its implementation in WINGX (Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837).

precipitation of products **3** and **4** from benzene or toluene prevents reversal of the reaction. The ability of the Zr−H bond to act as an electron donor in the formation of a three-center hydrogen bridge was demonstrated in the formation of $Cp_2Zr\{(\mu\text{-}H)BC_4H_8(CH_2Ph)\}\{\mu\text{-}H)_2BC_4H_8\}$.[1d]

Complexes **3** and **4** are white solids that are stable at room temperature under nitrogen. Their ^1H NMR spectra in d_8-toluene indicate bridge hydrogen resonances of Zr−H−Zr at δ −5.55 and −5.20 ppm and bridge hydrogen resonances of Zr−H−B at δ −2.03, −3.86 and −1.64, −3.60 ppm, respectively. The $^1H\{^{11}B\}$ NMR spectra of **3** and **4** show that the proton in the anion $[HB(C_6F_5)_3]^-$ resonates at δ 4.09 and 4.38 ppm, respectively. The ^{11}B NMR spectrum of complex **3** in d_8-toluene displays one broad signal from Zr−H−B at δ 36.59 ppm and one broad doublet from $[HB(C_6F_5)_3]^-$ at δ −25.27 ppm. The ^{11}B NMR spectrum of complex **4** in d_8-toluene contains one broad doublet at δ −23.44 ppm produced by $[HB(C_6F_5)_3]^-$. The ^{11}B signal from the cation was not observed, consistent with a report by Choukroun and co-workers.[6b] However, in d_2-methylene chloride, in which complex **4** is significantly more soluble, the ^{11}B NMR spectrum clearly displays two signals, a broad signal at δ 38.62 ppm (B−H−Zr) and a doublet at −25.48 ppm ($[HB(C_6F_5)_3]^-$). Its proton NMR spectrum is consistent with that of **4** in d_8-toluene. When **4** is dissolved in THF, on the basis of ^{11}B and ^1H NMR spectra, the Zr−H−Zr hydrogen bridge is cleaved to produce the previously reported neutral complex $Cp_2ZrH\{(\mu\text{-}H)_2BC_8H_{14}\}$, **2**,[2b] and the ionic complex $[Cp_2Zr(THF)\{(\mu\text{-}H)_2BC_8H_{14}\}][HB(C_6F_5)_3]$, which also forms when **6** is dissolved in THF. Comparisons of the proton chemical shifts of **2**, **3**, **4**, and **6** are given in Table 1.

Molecular Structures of 3 and 4. The molecular structures of **3** and **4** were determined by single-crystal X-ray diffraction analysis. The structure of **3** is very similar to **4** and has been reported simply as a communication, and Supporting Information is available.[4d] Crystallographic data for **4** are given in Table 2, and selected bond distances and bond angles for **4** are given in Table 3. The structure of the cation of **4** is depicted in Figure 1. Two structural units of $Cp_2Zr\{(\mu\text{-}H)_2B(C_8H_{14})\}$ are connected by a single bridged hydrogen. Four Cp and two $\{(\mu\text{-}H)_2B(C_8H_{14})\}$ groups are in a staggered conformation, Figure 2, with respect to the Zr−H−Zr axis. The coordination geometry of each zirconium atom can be described as a distorted tetrahedron, consisting of B, H, and the centroids of two Cp rings at the corners of the tetrahedron.

To our knowledge these are the first examples of unsupported M−H−M hydrogen-bridged bonds of group IV[10−15] even though numerous complexes containing three-center two-electron M−H−M bonds of groups V,[11] VI,[12] VII,[13] and VIII[14] are well known. The Zr−H−Zr bond is bent, consistent with previously reported M−H−M bonds, with the exception of the Ru−H−Ru bond in $\{Ru_2H(\mu\text{-}H)Cl(syn\text{-}Me_4[14]aneS_4)_2\}Cl$.[14b,d] The angle of Zr−H−Zr is 163(2)° for **3** and 164(2)° for **4**, and the Zr···Zr distance is 3.8983(9) Å for **3** and 3.9755(4) Å for **4**. A noteworthy feature of both structures is that the Zr···Zr distance is 0.2−0.3 Å longer than the sum [2radii Zr(cov) + 2radii H(cov)] = 3.70 Å for a bond angle of about 164°.[16] These results suggest that the Zr−H−

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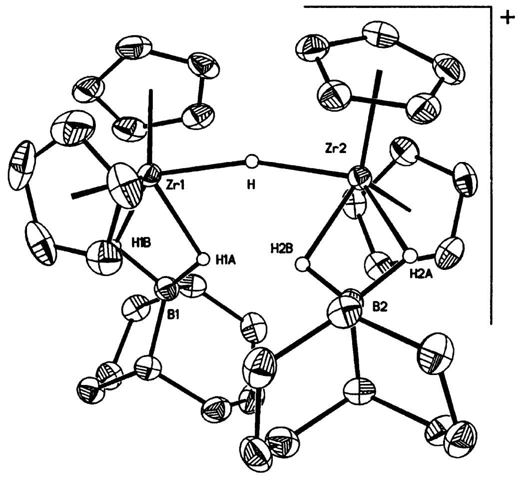

Figure 1. Molecular structure of the cation of **4**, showing 50% probability thermal ellipsoids. Bridging hydrogens are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms are omitted for clarity.

Zr bond is an open three-center bond in which there is no significant overlap of metal orbitals.[10,12]

As indicated above, the Zr−H−Zr bond in complexes **3** and **4** represents the second type of hydrogen-bridged bond in which a terminal Zr−H functions as an electron pair donor in the formation of the bond. In earlier work from this laboratory it was shown that a Zr−H−B bond is formed in the reaction of **1** with $B(C_4H_8)CH_2Ph$ to form $Cp_2Zr\{(\mu\text{-}H)BC_4H_8(CH_2Ph)\}\{\mu\text{-}H)_2BC_4H_8\}$. The Zr−H−B bond in this complex is weaker than that of **3** and **4**. NMR spectra in benzene indicate that it is dissociated into **1** and $B(C_4H_8)CH_2Ph$ at room temperature but exists in solution at −60 °C. It crystallizes as the hydrogen-bridged species, and its molecular structure was determined from data obtained at −60 °C. It is of interest to compare the structural parameters of the Zr−H−Zr bond with those of the Zr−H−B bond. The bond angle of the Zr−H−B bond is 159.9(2)°. As in the case of the Zr−H−Zr bond, the Zr···B distance is longer, 3.263 (4) Å, than the calculated Zr···B distance, [radius Zr(cov) + radius B(cov) + 2radii H(cov)] = 3.09 Å, for an angle of 159.9(2)°.[16]

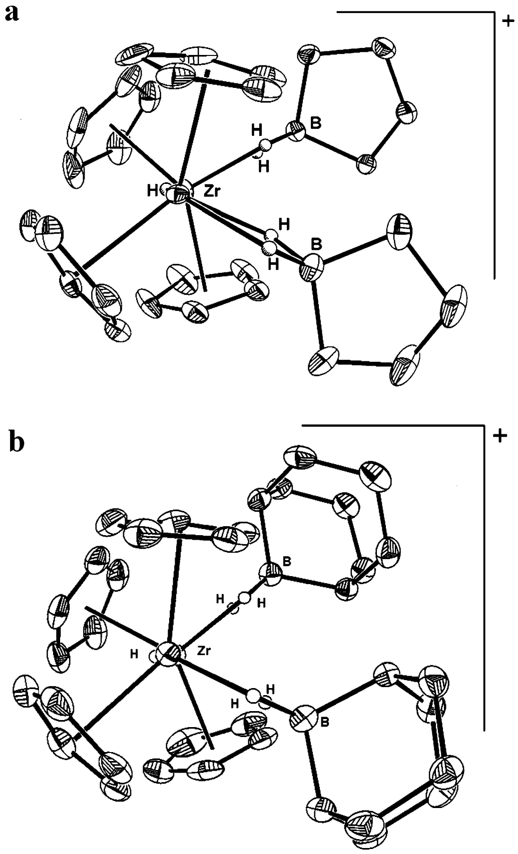

Figure 2. Staggered configuration of the cation viewed through the Zr−H−Zr axis in complexes **3** and **4**.

Formation of [$Cp_2Zr(OEt_2)X$] [HB(C_6F_5)$_3$] (X = OEt, 5; X = {(μ-H)$_2$BC_8H_{14}}, 6). Reactions of **1** and **2** with $B(C_6F_5)_3$ in diethyl ether produce ionic complexes: $[Cp_2Zr(OEt_2)(OEt)]\,[HB(C_6F_5)_3]$, **5**, and $[Cp_2Zr(OEt_2)\{(\mu\text{-}H)_2BC_8H_{14}\}][HB(C_6F_5)_3]$, **6**, respectively. Note that in complex **5** the unit $\{(\mu\text{-}H)_2BC_4H_8\}$ has been eliminated as the organodiborane $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$, but this unit is retained in complex **6**. Products are formed rapidly in these reactions; observation of intermediates is precluded. Reasonable pathways for the formation of **5** and **6** are shown in Scheme 2.

The first step, like in the situation of poorly coordinating solvent benzene or toluene, is the abstraction of the terminal Zr−H hydrogen by $B(C_6F_5)_3$ to produce a 16-electron cation $[Cp_2Zr\{(\mu\text{-}H)_2BR_2\}]^+$ and $[HB(C_6F_5)_3]^-$. A solvent molecule of diethyl ether then adds to the vacant site on zirconium to form the cation $[Cp_2Zr(OEt_2)\{(\mu\text{-}H)_2BR_2\}]^+$. For the reaction of **2** with $B(C_6F_5)_3$, the reaction is complete and the final product is $[Cp_2Zr(OEt_2)\{(\mu\text{-}H)_2BC_8H_{14}\}][HB(C_6F_5)_3]$, **6**. However, the cation produced in the reaction of **1** with $B(C_6F_5)_3$ undergoes symmetrical cleavage of the hydrogen bridge bond by the attack of diethyl ether solvent, resulting in the formation of a terminal Zr−H hydrogen and addition of a second molecule of diethyl ether to the zirconium. The organodiborane $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$[17] is also formed in this reaction. With time it is converted to a trialkyl borane, based on ^{11}B NMR spectroscopy. The terminal

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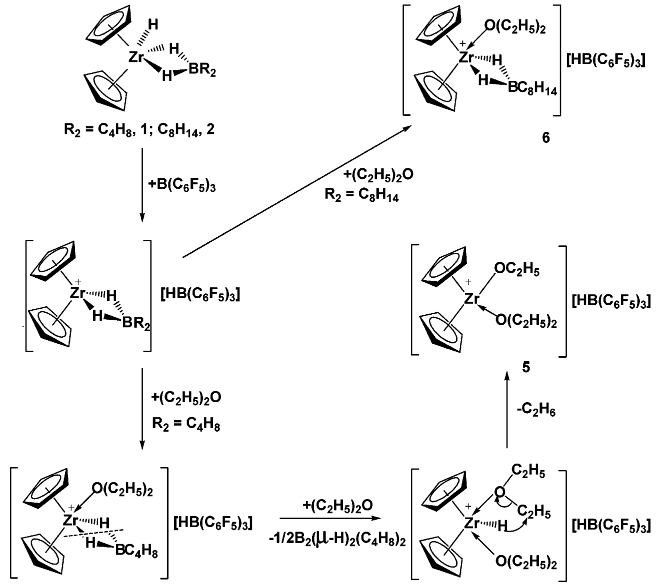
Scheme 2



Zr−H hydrogen of the cation inserts into a carbon−oxygen bond of a coordinated ether to liberate ethane and form a coordinated ethoxyl group, resulting in the ionic product $[Cp_2Zr(OEt_2)(OEt)][HB(C_6F_5)_3]$, **5**. The ethane liberated was identified by GS-mass spectrometry. The insertion of a terminal metal hydride into the carbon−oxygen bond of a coordinated ether has been established in earlier work,[4d] with results most relevant to this study being the conversion of coordinated THF to a butoxyl group in the formation of $[(C_5H_4Me)_2Zr(O\text{-}n\text{-}Bu)(THF)]^+$.[18]

Both of **5** and **6** are white solids in which the diethyl ether coordinated to Zr is partially removed by pumping under vacuum. There is no apparent sign of decomposition in diethyl ether. In THF solvent, the diethyl ether in both of **5** and **6** is displaced by THF to give free diethyl ether. The ^{11}B NMR spectrum of **5** in d_8-THF displays only one boron doublet signal at δ −26.43 ppm ($J_{B-H} = 93$ Hz). The ^1H NMR spectrum of **5** consists of the signal of the Cp hydrogens at δ 6.59, two signals of the ethoxyl group at δ 4.30 (q, $J = 7$ Hz) and 1.21 (t, $J = 7$ Hz), and two signals of free diethyl ether, which is displaced from the cation of **5** by d_8-THF in the NMR tube, at δ 3.38 (q, $J = 7$ Hz) and 1.11 (t, $J = 7$ Hz). The $^1H\{^{11}B\}$ NMR spectrum of **5** in d_8-THF shows the proton signal of $[HB(C_6F_5)_3]^-$ at δ 3.80 ppm. The ^{11}B NMR spectrum of **6** in d_8-THF consists of two boron signals at δ 27.60 (br) assigned to boron in the cation (B−H−Zr) and −26.50 (d, $J_{B-H} = 88$ Hz) assigned to boron in $[HB(C_6F_5)_3]^-$. In the ^1H NMR spectrum of **6**, the signal of the Cp hydrogens appears at δ 6.64 (s), and two signals at δ 3.38 (q, $J = 7$ Hz) and 1.11 (t, $J = 7$ Hz) are consistent with free diethyl ether. The multiple resonances at δ 1.90−1.43 are assigned to the α-, β-, and γ-hydrogens in a group of BC_8H_{14}. The hydrogen resonance in $[HB(C_6F_5)_3]^-$ appears at δ 3.74 ppm, and the signal of two bridged hydrogens appears at δ 0.32 and −2.19 in the $^1H\{^{11}B\}$ spectrum of **6**.

Molecular Structure of 5. While suitable crystals of **6** could not be obtained for an X-ray structure determination, the single-crystal X-ray structure of **5** was determined.[4d] Because of the limited amount of data that could be obtained and because of severe disorder with respect to rotation of the Cp rings and the angle between the rings, a number of restraints were applied in the solution of the structure. Details are given in the Experimental Section, and the RES file is in Supporting Information. Despite the difficulties, the structure of the molecule is clear.

The coordination geometry about the zirconium center in **5** is best described as a distorted tetrahedron. Occupying the corners of the tetrahedron are the centers of two cyclopentadienyl rings and the two oxygen atoms of the diethyl ether molecule and the ethoxyl group. The zirconium−oxygen distance in the $Zr-OEt_2$ linkage, 2.209(8) Å, is consistent with the sum of the covalent radii, 2.16 Å.[16] On the other hand the zirconium−oxygen distance in the Zr−OEt linkage is significantly shorter, 1.884(8) Å. It is intermediate between a single and double bond of Zr−O. In the complex $Cp^{Et*}{}_2Zr(O)(NC_5H_5)$, which has a zirconium−oxygen double bond, the Zr−O distance is 1.804(4) Å, the shortest Zr−O distance reported[16a,b] to date.

Possibly, the short distance in the Zr−O bond in the Zr−OEt linkage of **5** can be attributed to two contributions to the bonding in addition to σ character: $p\pi-d\pi$ bonding and partial ionic bonding ($Zr^{\delta+}-O^{\delta-}$) between Zr and O. On the basis of the angles around the oxygen of the diethyl ether, Zr1−O1−C12, Zr1−O1−C14, and C12−O1−C14 of 120.3(9)°, 123.0(9)°, and 111.2(11)°, and the angle around the oxygen of the ethoxyl group, Zr1−O2−C16 of 153.4(9)°, $p\pi-d\pi$ bonding between Zr and O2 of the ethoxyl group can be considered to be a factor because the large angle of Zr1−O2−C16 implies more sp character for oxygen.

However, after comparing the distance of Zr−O in different zirconocene complexes, it is concluded that partial ionic contribution to the bonding ($Zr^{\delta+}-O^{\delta-}$) is a persuasive factor for short Zr−O distances in the Zr−OEt linkage.[15,16a,b,19−21] When a neutral ligand, like THF or diethyl ether, coordinates to zirconium, the Zr−O distance is always longer than the Zr−O distance when the ligand is an anion (see Table 4).[19,20] Undoubtedly, the electrostatic contribution to bonding is larger when the anionic ligand is employed. Thus the length of the Zr−O2 bond (oxygen in the anion of the ethoxyl group) is significantly shorter than that of the Zr−O1 bond distance (oxygen in the neutral molecule diethyl ether). When the anionic ligand is involved, the Zr−O−C angle is observed to vary from 125.2(3)° [20c] to 177(2)° [20q] even though the Zr−O distance is relatively unchanged in zirconocene complexes.[20] This variability of angle, lack of a directional effect, is consistent with an ionic contribution to the bonding.

A thorough study by Parkin and co-workers[16a,b,20c,d] indicates that both the Zr−O single and double bond lengths in two series of chalcogenido and hydrochalcogenido complexes are anomalously short on the basis of the sum of the covalent radii of Zr and O with respect

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Table 4. Distances of Zr−O and Angles of Zr−O−C in Zirconocene Derivatives and Monocyclopentadienyl Zirconium Derivatives*

	d(Zr−O)/Å	Zr−O−C/deg	ref
Zr═O (double bond)			
$Cp^{Et*}_2Zr(O)(NC_5H_5)$	1.804(4)		18a,b
Zr−O (neutral ligand)			
$[\{Cp_2Zr(OEt_2)(OEt)][HB(C_6F_5)_3]$	2.209(8)	123.0(9); 120.3(9)	19a
$[(Cp')_2Zr(Me)CC(Me)(^nPr)(THF)]^+$	2.289(6)		19b
$[Cp_2ZrMe(THF)][BPh_4]$	2.122(14)		19c
$Cp_2Zr(THF)(Me_3SiC/CSiMe_3)$	2.390(5)		19d
Zr−O (anion ligand)			
$[\{Cp_2Zr(OEt_2)(OEt)][HB(C_6F_5)_3]$	1.884(8)	153.4(9)	20a
$Cp^*Zr\{2,6\text{-}OC_6H_3(CH_3)_2\}_3$	1.940(4); 1.947(4); 1.950(4)	167.5(4); 155.3(4); 166.1(5)	20b
$Cp^*_2Zr[\eta^2\text{-}OCH(Bu^t)OCH(Bu^t)O]$	2.011(4); 2.007(3)	126.4(3); 125.2(3)	20c
$Cp^*_2Zr(OH)[\eta^1\text{-}OC(Bu^t){=}CH_2]$	2.001(6); 2.006(5)	169.9(6)	20c
$Cp^*_2Zr(OH)(NHPh)$	2.061(7)		20c
$Cp^*_2Zr(\eta^2\text{-}O_2CMe)(\eta^1\text{-}OCOMe)$	2.067(2)	161.8(2)	20c
$Cp^*_2Zr(OH)[\eta^1\text{-}OC(Ph){=}CH_2]$	2.010(2); 1.993(2)	174.6(2)	20d
$Cp^*_2Zr(SH)[\eta^1\text{-}OC(Ph){=}CH_2]$	1.987(3)	168.8(3)	20d
$Cp^*_2Zr(SeH)[\eta^1\text{-}OC(Ph){=}CH_2]$	2.012(5)	168.5(4)	20d
$Cp_2Zr(OPh)(\eta^2\text{-}S_2CNMe_2)$	2.023(8)	159.7(8)	20h

[a] The data for aryloxy and alkoxy zirconocene derivatives have been summarized by G. Parkin in ref 20d.

to the other chalcogens (S, Se, and Te). They compare the Zr−O distance and the Zr−O−C angle in a number of alkoxy and aryloxy zirconocene complexes and provide evidence that short Zr−O bond lengths and linear Zr−O−C units are not necessarily a consequence of a strong pπ−dπ lone pair donation from oxygen to the zirconium.[20d] Furthermore, Parkin and co-workers point out that such a shortening of the Zr−O single and double bonds is believed to be a consequence of partial ionic character in the zirconium oxygen bond ($Zr^{\delta+}{-}O^{\delta-}$) mainly due to the greater electronegativity of oxygen with respect to the other chalcogens and the smaller size of oxygen, both of which serve to increase the Coulombic stabilization associated with the dipolar moiety $Zr^{\delta+}{-}O^{\delta-}$.[20d] The fact that the Zr−O distances in neutral ligand complexes are significantly longer than the Zr−O distance in anion ligand complexes (Table 4) and the sum of the covalent radii of zirconium and oxygen is in accord with the Zr−O distance in neutral ligand complexes are consistent with substantial ionic contribution to the short Zr−O bonding.

Experimental Section

General Comments. All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of nitrogen or argon. Tetrahydrofuran, diethyl ether, toluene, and benzene were dried over sodium/benzophenone and freshly distilled prior to use. Methylene chloride was stirred over P_2O_5 for 10 days before being distilled for use. Hexane was stirred over concentrated sulfuric acid for 2 days and then decanted and washed with water. Next the hexane was stirred over sodium/benzophenone for 1 week, followed by distillation into a storage bulb containing sodium/benzophenone. Celite was dried by heating at 150 °C under dynamic vacuum for 5 h. $B(C_6F_5)_3$ was purchased from Aldrich and used as received. The zirconocene organohydroborates $Cp_2ZrH\{(\mu\text{-}H)_2BR_2\}$ ($R_2 = C_4H_8$, **1**; C_8H_{14}, **2**) were prepared by literature procedures.[1c,2b] Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN. NMR spectra were recorded on a Bruker AM-250 spectrometer. ^1H NMR spectra were obtained at 250.1 MHz and referenced to residual solvent protons. ^{11}B NMR spectra were obtained at 80.3 MHz and externally referenced to $BF_3{\cdot}OEt_2$ in C_6D_6 ($\delta = 0.00$ ppm). Infrared spectra were recorded on a Mattson-Polaris FT-IR spectrometer with 2 cm^{-1} resolution.

X-ray Structure Determination. Single-crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffraction system, which employs graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$). A single crystal of **3**, **4**, and **5** was mounted on the tip of a glass fiber coated with Fomblin oil (a pentafluoropolyether). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the DENZO-SMN package (Nonius BV, 1999).[22] The empirical absorption correction was applied with the SORTAV program[23] provided by MaXus software.[24] The positions of the heavy atoms were revealed by the Patterson method. The structures were refined using the SHELXTL-97 (difference electron density calculations and full-matrix least-squares refinements) structure solution package.[25] Data merging was performed using the data preparation program supplied by SHELXTL-97.

For molecular structures **3** and **4**, after all non-hydrogen atoms were located and refined anisotropically, hydrogen atom positions were calculated assuming standard geometries. Bridge hydrogens and the terminal B−H hydrogens of the anions were located and refined isotropically. The molecular structure of the cation $[Cp_2Zr(OEt_2)(OEt)]^+$ in **5** was highly disordered. Two sets of coordinates for carbon and oxygen atoms were located. The SADI and SAME instructions were used to restrain the bond distances between the carbon atoms and carbon−oxygen atoms such that all carbon−carbon distances are equal and carbon−oxygen distances are equal within effective standard deviations. Extra constraints for common site occupation factors were also applied. The carbon and oxygen in OEt_2 and OEt groups were refined isotopically,

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and all other non-hydrogen atoms were refined anisotopically. The hydride atom on boron in the anion was located and refined isotopically, and other hydrogen atoms were calculated.

Preparation of [(μ-H){$Cp_2Zr(\mu\text{-}H)_2BC_4H_8$}$_2$][$HB(C_6F_5)_3$], 3. In a drybox 147 mg (0.50 mmol) of **1** 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 precipitate, which was washed with hexane twice, and a 215 mg (mmol), 78% yield of white product was isolated. ^{11}B NMR (d_8-toluene): δ 36.59 (br, (B−H−Zr)), −25.27 (d, $[HB(C_6F_5)_3]^-$) ppm. ^{1}H NMR (d_8-toluene): δ 5.70 (s, Cp), 1.62 (br, 8H, β-H), 0.89 (br, 8H, α-H), −2.03 (br, 2 μ-H), −3.86 (br, 2 μ-H), and −5.55 (br, 1 μ-H) ppm. ^{1}H{^{11}B} NMR (d_8-toluene): δ 4.09 (br, HB). Anal. Calcd: C, 50.47; H, 3.87. Found: C, 50.36; H, 4.01. IR (KBr): 3114(s), 3099(sh), 2912(s), 2845(s), 2809(m), 2659(w), 2649(w), 2367(s), 1898(sh), 1873(s), 1850(s), 1822(m), 1708(m), 1640(s), 1604(w), 1548(w), 1510(vs), 1465(vs), 1427(vs), 1416(vs), 1373(s), 1343(s), 1327(m), 1275(s), 1224(s), 1203(m), 1167(w), 1099(vs), 1075(s), 1039(w), 1924(s), 1017(s), 995(w), 970(vs), 910(m), 897(w), 841(s), 811(vs), 759(m), 731(w), 696(w), 659(m), 649(m), 603(m), 587(w), 568(m).

Preparation of [(μ-H){$Cp_2Zr(\mu\text{-}H)_2BC_8H_{14}$}$_2$][$HB(C_6F_5)_3$], 4. In a drybox 173 mg (0.50 mmol) of **2** and 128 mg (0.25 mmol) of $B(C_6F_5)_3$ were put in a flask. After degassing, 5 mL of toluene was transferred to the flask and stirred for 10 min, and hexane was transferred to the system to produce a white precipitate, which was washed with hexane twice, producing a 220 mg (mmol), 73% yield of white product. ^{11}B NMR (d_8-toluene): δ −23.44 ($[HB(C_6F_5)_3]^-$, br) ppm. ^{1}H NMR (d_8-toluene): δ 5.85 (s, Cp), 2.05−1.20 (m, 28H, α-,β-, and γ-H in C_8H_{14} group), −1.64 (br, 2 μ-H), −3.60 (br, 2 μ-H), and −5.20 (br, 1 μ-H) ppm. ^{1}H{^{11}B} NMR (d_8-toluene): δ 4.38 (br, HB). ^{11}B NMR (d_2-methylene chloride): δ 38.62 ((B−H−Zr), br), −25.48 ($[HB(C_6F_5)_3]^-$, d, J_{B-H} = 80 Hz) ppm. ^{1}H NMR (d_2-methylene chloride): δ 6.33 (s, Cp), 2.34−1.48 (m, 28H, α-,β-, and γ-H in C_8H_{14} group), −1.36 (br, μ-H), −3.14 (br, 2 μ-H), and −4.90 (br, 1 μ-H) ppm. ^{1}H{^{11}B} NMR (d_2-methylene chloride): δ 3.72 (br, HB). ^{11}B NMR (d_8-THF): δ 31.82 ((B−H−Zr), s, in neutral complex), 29.20 ((B−H−Zr), br, in ionic complex), and −25.46 ($[HB(C_6F_5)_3]^-$, d, J_{B-H} = 90 Hz) ppm. ^{1}H{^{11}B}NMR (d_8-THF): δ 6.65 (s, Cp), 6.02 (s, Cp), 3.85 (m, $HB(C_6F_5)_3]^-$), 3.73 (br, Zr−H), 2.04−1.23 (m, 28H, α-,β-, and γ-H in C_8H_{14} group), 0.30 (br, μ-H), −2.21 (br, μ-H), −3.34 (br, μ-H), and −4.20 (br, μ-H) ppm. Anal. Calcd: C, 53.92; H, 4.53. Found: C, 53.39; H, 4.45. IR (KBr): 3108(m), 2984(sh), 2919(s), 2888(s), 2836(m), 2689(w), 2665(w), 2365(s), 1869(m), 1845(s), 1652(sh), 1644(s), 1510(vs), 1464(vs), 1437(sh), 1420(sh), 1374(sh), 1350(w), 1331(w), 1314(w), 1277(m), 1210(m), 1173(w), 1114(m), 1093(s), 1069(sh), 1924(m), 969(vs), 925(m), 912(m), 889(w), 809(vs), 768(w), 754(w), 680(w), 632(w), 568(w).

Preparation of [$Cp_2Zr(OEt_2)(OEt)$][$HB(C_6F_5)_3$], 5. In a drybox 294 mg (1 mmol) of **1**, 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 ^{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 less than 5 min. But with increasing time $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$ 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 **5** has limited solubility in Et_2O. For the NMR spectra in THF the Et_2O in **5** is replaced by THF solvent. ^{11}B NMR (d_8-THF): δ −26.43 (d, J_{B-H} = 93 Hz) ppm. ^{1}H NMR (d_8-THF): δ 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 (6H, t, J = 7 Hz) ppm. ^{1}H{^{11}B} NMR (d_8-THF): δ 3.80 (m, HB, J_{H-B} = 4.6 Hz). Anal. Calcd: C, 47.84; H, 3.07. Found: C, 47.01; H, 3.09. IR (KBr): 3123(m), 2982(s), 2940(m), 2884(m), 2734(w), 2373(s), 1643(s), 1606(w), 1551(w), 1511(vs), 1466(vs), 1412(w), 1384(s), 1328(w), 1274(s), 1185(w), 1108(vs), 1078(vs), 1020(s), 968(vs), 930(m), 914(m), 893(w), 881(w), 866(m), 840(sh), 825(s), 787(w), 765(m), 757(m), 733(w), 688(w), 664(m), 637(m), 605(m), 569(m), 542(m), 524(w).

Preparation of [$Cp_2Zr(OEt_2)${(μ-H)$_2BC_8H_{14}$}][$HB(C_6F_5)_3$], 6. In a drybox 345 mg (1 mmol) of **2**, 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 ^{11}B NMR. The anion $[HB(C_6F_5)_3]^-$ (−27.0 ppm, d, J_{B-H} = 88 Hz) and 9-BBN dimer $(\mu\text{-}H)_2(BC_8H_{14})_2$ (27.3 ppm) were formed in less than 5 min. But with increasing time $(\mu\text{-}H)_2(BC_8H_{14})_2$ diminished in concentration, while a new signal at 59.4 ppm (singlet) appeared, indicative of a trialkyl borane. After stirring this system for 1 h, the ether solution was removed by filtration, and 610 mg (70.5% yield) of white solid was isolated. Complex **6** has limited solubility in Et_2O. For the NMR spectra in THF the Et_2O in **6** is replaced by THF solvent. ^{11}B NMR (d_8-THF): δ 27.60 ((B−H−Zr)$_2$, br), −26.50 ($[HB(C_6F_5)_3]^-$, d, J_{B-H} = 88 Hz) ppm. ^{1}H NMR (d_8-THF): δ 6.64 (s, Cp), 3.38 (4H, q, J = 7 Hz), 1.90−1.43 (14H, m), and 1.11 (6H, t, J = 7 Hz) ppm. ^{1}H{^{11}B} NMR (d_8-THF): δ 3.74 (m, HB), 0.32 (br, 1 μ-H), and −2.19 (br, 1 μ-H). Complex **2** was dried under vacuum overnight, and part of the ether ligand was lost. Anal. Calcd: C, 50.55; H, 3.26 for [$Cp_2Zr(OEt_2)_{0.1}${(μ-H)$_2BC_8H_{14}$}][$HB(C_6F_5)_3$]. Found: C, 50.08; H, 3.68. IR (KBr): 3117(m), 2984(s), 2890(s), 2836(s), 2373(m), 1982(w), 1965(w), 1941(w), 1642(s), 1511(vs), 1463(vs), 1390(s), 1312(w), 1276(s), 1209(w), 1097(s), 1016(s), 969(vs), 924(w), 817(s), 760(m), 678(w), 600(w), 566(m), 524(w).

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Supporting Information Available: Molecular structure of the anion in **3**, **4**, and **5**; the second set of structures of the cation $[Cp_2Zr(OEt_2)(OEt)]^+$ and disordered $[Cp_2Zr(OEt_2)(OEt)]^+$ in **5**; tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **3**, **4**, and **5**; relevant additional ^{1}H, ^{11}B NMR spectra for **3**, **4**, **5**, and **6**. Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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