Cyclic Hydroborate Complexes of Metallocenes. V. Syntheses and Structures of Zirconocene Organoborate Derivatives: $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$, and $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$

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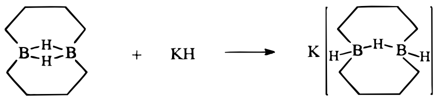
Three procedures were developed for the preparation of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**. It can be prepared from the reaction of Cp_2ZrCl_2 with $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ in a 1:2 molar ratio; the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ in a 1:1 molar ratio; and the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with LiH in a 1:1 molar ratio. Although the first and second procedures imply the possible synthesis of $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$, this compound is not formed. The preferential formation of **1** instead of $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$ is probably due to greater thermal stability of **1**. The benzyl-substituted compounds, $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$, **2**, and $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$, **3**, were prepared from the reactions of $Cp_2ZrCl(CH_2Ph)$ with $[H_2BC_4H_8]^-$ and $[H_2BC_5H_{10}]^-$, respectively. This preparative route eliminates the side reaction observed in the direct alkylation of zirconocene organohydroborate complexes. The structures of **1**−**3** are also reported. Crystal data for **1**: space group *Pnam*, $a = 9.836(2)$ Å, $b = 10.186(2)$ Å, $c = 13.393(3)$ Å, $Z = 4$. Crystal data for **2**: space group *Pbca*, $a = 8.3882(10)$ Å, $b = 16.6669(10)$ Å, $c = 27.0063(10)$ Å, $Z = 8$. Crystal data for **3**: space group $P2_1/n$, $a = 9.674(2)$ Å, $b = 14.047(2)$ Å, $c = 14.512(3)$ Å, $\beta = 102.53(2)°$, $Z = 4$.

Introduction

Recently, we investigated the chemistry of $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$, which was prepared from the reaction of $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$ with KH (reaction 1).[1] This anion is a very good hydride transfer agent. It reduces metal carbonyls to metal carbonyl hydrido carbonylate ions, alkyl halides to alkanes, and ketones and aldehydes to alcohols.[2] The driving force for these reduction reactions is the formation of $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$, a stable and relatively inert organodiborane. In addition to the hydride transfer ability, we also found a unique ring disproportionation reaction of $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ in the reactions with zirconocene and hafnocene dichlorides to produce the double hydrogen bridged cyclopentaborate derivatives $Cp_2MCl\{(\mu\text{-}H)_2BC_4H_8\}$ (M = Zr, Hf) (reaction 2).[3] While many metal tetrahydroborate complexes have been prepared and studied,[4] little is known concerning metal organohydroborate chemistry,[5] and only two metallocene complexes with cyclic hydroborate and alkyl ligands have been reported.[3a,6] In the present report procedures for the preparation and the characterization of new cyclic organohydroborate derivatives of zirconocene dichloride are described.



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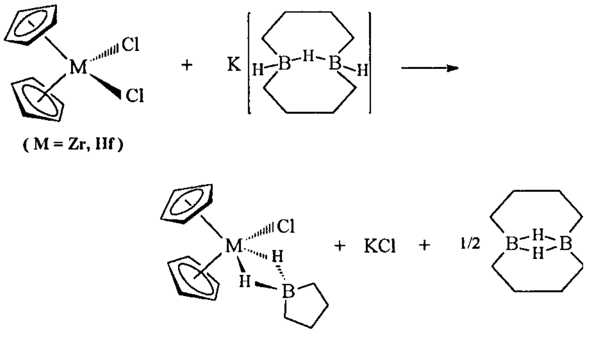

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Results and Discussion

$Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, 1. Three methods were developed for the synthesis of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**. It was prepared from the reaction of Cp_2ZrCl_2 with $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ in a 1:2 molar ratio (reaction 3); the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ (reaction 4); and the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with LiH in THF (reaction 5), which is similar to the preparation of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$.[6] However, reaction 5 is significantly slower than reactions 3 and 4 due to the limited solubility of lithium hydride. In reaction 3 disproportionation of the organodiborate anion $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ as well as hydride displacement of chloride occurs to form 1.5 mol of the organodiborane, $B_2(\mu\text{-}H)_2(\mu\text{-}C_4H_8)_2$, as well as 1 mol of **1**. Compound **1** is the

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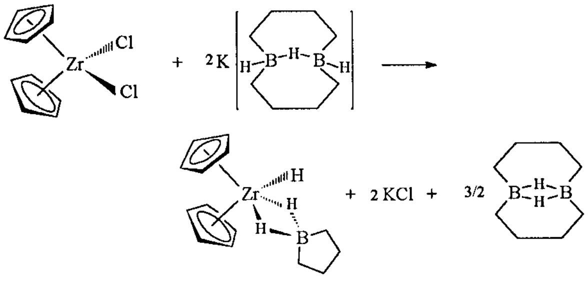
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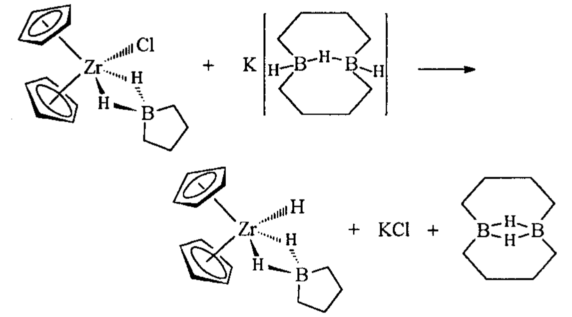
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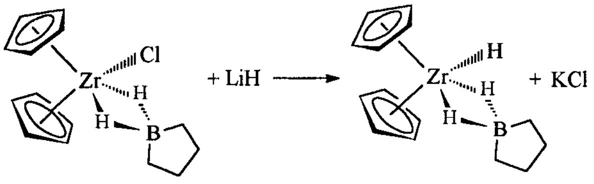
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analogue of the previously reported $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$,[6] which differs from **1** in that it contains the BC_5H_{10} ring.

The ^{11}B NMR spectrum of **1** in Et_2O consists of a triplet at $\delta = 30.9$ ppm ($J_{B-H} = 61.4$ Hz), which is about 14 ppm further downfield from the signal produced by the parent compound, $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$.[3] The ^1H NMR spectrum of **1** gives rise to two broad, apparent doublets at $\delta = -3.10$ and -4.25 ppm, ascribed to the two bridge hydrogens. The doublet appearance of these signals is due to the partial thermal decoupling of the boron nucleus;[5l,7] they collapse to singlets upon boron decoupling. The terminal hydride signal appears at $\delta = 3.95$ ppm as a broad signal that sharpens upon boron decoupling. This relatively high field chemical shift is comparable to the chemical shifts of Zr−H hydride in $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ (4.16 ppm),[5a] $(C_5Me_5)_2Zr\{(\mu\text{-}H)_2BH_2)(\mu\text{-}H)_2\}_2$ (3.91 ppm),[8] and $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ (4.06 ppm).[6] A weak interaction also exists between the terminal hydride and the two bridge hydrogens. The signal from the terminal hydrogen becomes a triplet at −20 °C upon boron decoupling, with a coupling constant of about 1 Hz. Preliminary variable temperature ^1H NMR spectra indicate that this molecule is fluxional in a manner similar to that reported for $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$[6] in that bridge hydrogens, Zr−H terminal hydrogen, and Cp hydrogens are involved, as a function of temperature, in hydrogen exchange processes. The ^1H NMR spectrum of **1** in the boracyclopentane region consists of two broad signals at $\delta = 1.70$ (4H, β-H) and 0.99 ppm (4H, α-H). Splitting of the signals occurs at low temperature. At −60 °C in d_8-toluene, the β hydrogen resonance is split into two overlapped signals at $\delta = 2.11$ and 2.08 ppm, while the resonance of the four α hydrogens is split into two overlapped signals at $\delta = 1.32$ and 1.21 ppm.

The IR spectrum of **1** is consistent with the bidentate hydrogen-bridge structure.[4a] The broad band at 1597 cm^{-1} is assigned to the Zr−H stretching mode, which agrees with bands observed in the IR spectra of $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ (1595 cm^{-1}),[5a] $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$ (1620 cm^{-1}),[9] and $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ (1618 cm^{-1}).[6]

In the solid state at room temperature under nitrogen, compound **1** is stable for several months. In benzene or Et_2O no detectable decomposition is observed for several weeks. It is more stable than $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$.[3] Compound **1** is more soluble in Et_2O than $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$, but it is less soluble than $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$.[3a]

For the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ two possible products were considered. One product would be that actually isolated (reaction 4), $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**, formed through hydride transfer from the organodiborate to zirconium to displace the chloride. The other possible product considered, $Cp_2Z\{(\mu\text{-}H)_2BC_4H_8\}_2$, but not observed, would have been formed through disproportionation of the organodiborate anion, $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$, as observed in the preparation of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$[3] (reaction 2). Possible kinetic and thermal factors that resulted in the preferential formation and isolation of **1** rather than $Cp_2Z\{(\mu\text{-}H)_2BC_4H_8\}_2$ were considered. Scheme 1 is similar to an earlier proposed scheme[3] for the preparation of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ from the reaction of Cp_2ZrCl_2 with $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ that is based upon time dependent NMR spectra that provide evidence for intermediate species. In the present case proximity of the borocyclopentane ring of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ might sterically prevent or significantly hinder the $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ anion from approaching the Zr center. Instead, transferring the hydride to zirconium with the breaking of the B−H bond would be more easily achieved.

In order to avoid the problems associated with the disproportionation of $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$, the anion $Li[H_2BC_4H_8]$[10] was chosen as an alternative reagent for the reaction with $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ in an attempt to prepare $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}_2$. This reaction did not yield Cp_2Zr-

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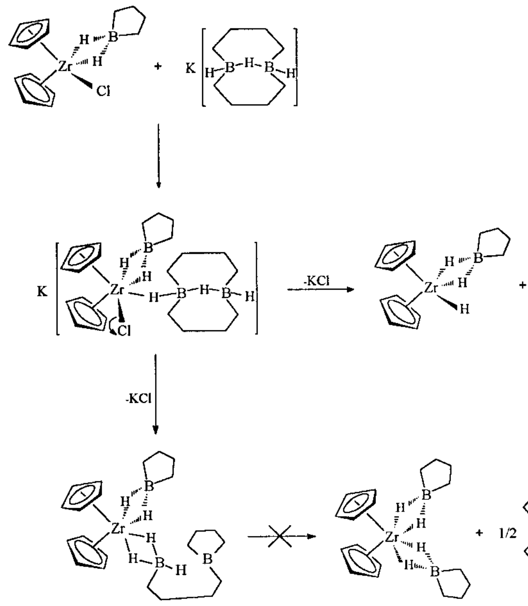
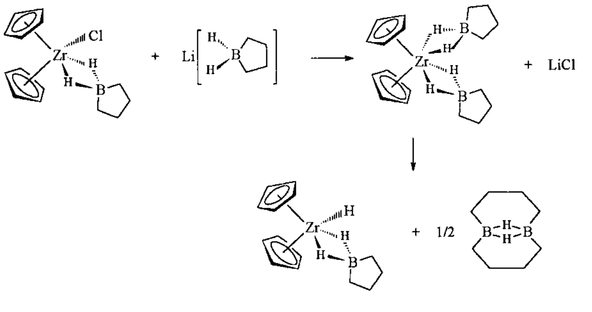
(10) $Li[H_2BC_4H_8]$ was prepared from the reaction of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ with LiH.

Scheme 1. Proposed Mechanism for the Reaction of $Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$ with $K[H_2B_2(\mu-H)(\mu-C_4H_8)_2]$



$\{(\mu-H)_2BC_4H_8\}_2$, but produced **1** instead as the final isolated product.

Upon reaction of $Li[H_2BC_4H_8]$ with $Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$ in THF, time-elapsed $^{11}B\{^1H\}$ NMR spectra[11] showed a new, broad signal at about 28 ppm, which then splits into two overlapping signals at $\delta = 30.2$ and 28.2 ppm, with the intensity of the former larger than the latter. From previous studies, the signal at 28.2 ppm is assigned to $\{B_2(C_4H_8)H_2\}$,[12] and the signal at 30.2 ppm corresponds to $Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$, **1**. If $[H_2BC_4H_8]^-$ functioned solely as a hydride transfer agent, then $Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$ and $\{B_2(C_4H_8)H_2\}$ would be produced in equal amounts in the ^{11}B NMR spectrum initially. However, the broad signal that initially appears at 28 ppm might indicate the formation of $Cp_2Zr\{(\mu-H)_2BC_4H_8\}_2$. Table 1 presents the selected chemical shifts of bis(cyclopentadienyl) zirconium boracyclopentane and boracyclohexane derivatives. The replacement of a boracyclohexane ring by a boracyclopentane ring appears to shift the boron signal of the complex downfield. It is reasonable to assume that the new peak at 28 ppm is due to the formation of $Cp_2Zr\{(\mu-H)_2BC_4H_8\}_2$. However, since the NMR signal diminishes with time, it appears that this compound is unstable and disproportionates into $Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$ and $\{B_2(C_4H_8)H_2\}$ as described in reaction 6.



(6)

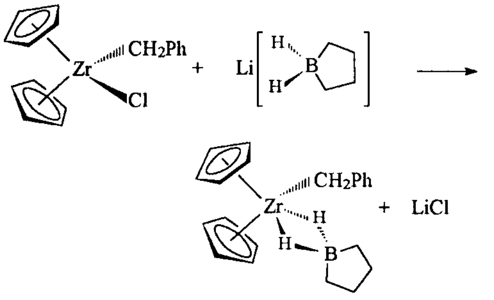
While Scheme 1 suggests that the pathway for the formation of **1** is more favorable than that for the formation of $Cp_2Zr\{(\mu-H)_2BC_4H_8\}_2$, based upon steric considerations, consideration of reaction 6 suggests that this compound is also thermally less stable than **1**.

Table 1. Selected ^{11}B Chemical Shifts (ppm) of Cyclic Hydroborate Complexes

compd	δ	compd	δ
$Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$[a]	16.7	$Cp_2ZrCl\{(\mu-H)_2BC_5H_{10}\}$[b]	13.7
$Cp_2Zr(CH_3)\{(\mu-H)_2BC_4H_8\}$[c]	20.1	$Cp_2Zr(CH_3)\{(\mu-H)_2BC_5H_{10}\}$[d]	18.2
$Cp_2Zr(Ph)\{(\mu-H)_2BC_4H_8\}$[c]	22.0	$Cp_2Zr(Ph)\{(\mu-H)_2BC_5H_{10}\}$[e]	19.4
$Cp_2Zr(CH_2Ph)\{(\mu-H)_2BC_4H_8\}$	22.1	$Cp_2Zr(CH_2Ph)\{(\mu-H)_2BC_5H_{10}\}$	19.4
$Cp_2ZrH\{(\mu-H)_2BC_4H_8\}$	30.9	$Cp_2ZrH\{(\mu-H)_2BC_5H_{10}\}$[d]	28.2
		$Cp_2Zr\{(\mu-H)_2BC_5H_{10}\}_2$[d]	24.6

[a] Reference 3. [b] Reference 21. [c] Reference 3a. [d] Reference 6. [e] Reference 14.

$Cp_2Zr(CH_2Ph)\{(\mu-H)_2BC_4H_8\}$, 2. Attempts to prepare $Cp_2Zr(CH_2Ph)\{(\mu-H)_2BC_4H_8\}$, **2**, from the reaction of $Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$ with $PhCH_2MgCl$ were complicated by a competing reaction. While the major product isolated is a single hydrogen bridge compound $Cp_2Zr\{(\mu-H)(BC_4H_8)CH_2Ph\}\{(\mu-H)_2BC_4H_8\}$,[13] compound **2** appears as a minor product that exists in solution. The reaction of $Cp_2ZrCl(CH_2Ph)$ with $K[H_2B_2(\mu-H)(\mu-C_4H_8)_2]$ produces small amounts of **2** based on ^{11}B NMR. The major product is a species in which the organohydroborate ligand coordinates to the Zr atom via a tridentate hydrogen-bridged bond ($\delta = 10.3$ ppm, q, $J_{B-H} = 73$ Hz; $\delta = 91.8$ ppm, s). The coupling constant is similar to that of the intermediate observed ($\delta = 5.8$ ppm, q, $J_{B-H} = 71$ Hz; $\delta = 88.1$ ppm, s) for the formation of $Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$.[3] It seems reasonable that the reaction of $Cp_2ZrCl(CH_2Ph)$ with $K[H_2B_2(\mu-H)(\mu-C_4H_8)_2]$ produces the intermediate $Cp_2Zr(CH_2Ph)\{(\mu-H)_3BC_4H_8B(C_4H_8)\}$. However, conversion of this intermediate to the final product, compound **2**, was hampered by the steric effect of the accessory ligands around the Zr atom. It discourages the rearrangement of the organohydroborate ligand and produces low yields of **2**. Consequently, compound **2** was prepared from the reaction of $Cp_2ZrCl(CH_2Ph)$ with $Li[H_2BC_4H_8]$[10] as shown in reaction 7.



(7)

The ^{11}B NMR spectrum of **2** in d_6-benzene consists of a triplet at $\delta = 22.1$ ppm, which is consistent with that of $Cp_2Zr(CH_3)\{(\mu-H)_2BC_4H_8\}$ (20.1 ppm)[3a] and $Cp_2Zr(Ph)\{(\mu-H)_2BC_4H_8\}$ (22.0 ppm).[3a] The ^1H NMR spectrum of **2** in d_6-benzene consists of one broad signal at $\delta = 2.13$ ppm, which is assigned to the methylene group. The two signals of the bridging hydrogens appear at $\delta = -1.09$ and -3.70 ppm.

It is of interest to compare the steric effect of the ligands $H_2B(C_4H_8)$ and CH_2Ph in the compounds $Cp_2ZrCl(X)$ (X = $H_2B(C_4H_8)$ and CH_2Ph). In reaction 7, the reaction of $Cp_2ZrCl(CH_2Ph)$ with $Li[H_2BC_4H_8]$ produces the double hydrogen bridged compound **2**. However, the hydrido compound, compound **1**, was formed when $Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$ reacted with

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(11) Time-elapsed $^{11}B\{^1H\}$ NMR spectra of the reaction of $Cp_2ZrCl\{(\mu-H)_2BC_4H_8\}$ with $Li[H_2BC_4H_8]$ in THF is provided in the Supporting Information.

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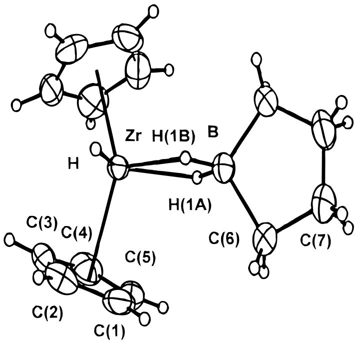
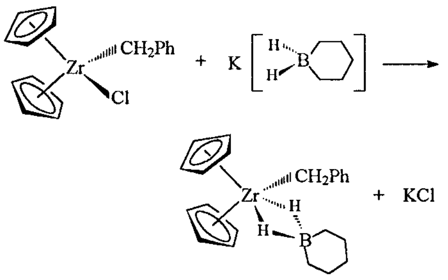


Figure 1. Molecular structure of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**, showing 50% probability ellipsoids.

$Li[H_2BC_4H_8]$ (reaction 6), probably due to the benzyl ligand having a steric requirement smaller than that of the cyclic organoborate ligand, $H_2B(C_4H_8)$.

$Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$, 3. Compound **3** is prepared from the reaction of $Cp_2ZrCl(CH_2Ph)$ with $K[H_2BC_5H_{10}]$ in THF (reaction 8). The ^{11}B NMR spectrum of **3** in Et_2O consists of a broad triplet at $\delta = 19.1$ ppm, which is comparable to that in $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$ (18.23 ppm)[6] and $Cp_2Zr(Ph)\text{-}\{(\mu\text{-}H)_2BC_5H_{10}\}$ (19.4 ppm).[14] The ^1H NMR spectrum of **3** in d_6- benzene displays two broad signals assigned to the two bridge hydrogens at $\delta = -0.91$ and -3.57 ppm. The signal of the methylene group appears as a sharp singlet at $\delta = 2.08$ ppm.



(8)

Compounds **2** and **3** are stable under a nitrogen atmosphere for several months without decomposition. They are more soluble than compound **1** in diethyl ether and benzene solution.

There are only a limited number of tetrahydroborate metal complexes that also contain an alkyl ligand,[15] and only two examples of an organohydroborate metal complex with an alkyl ligand have been reported previously.[3a,6] Direct alkylation of $Cp_2Zr(Cl)(H_2BR')$ ($R' = C_4H_8$, C_5H_{10}) via alkyllithium reagents is affected by competing reactions; the alkyl anion can in principle bond to the boron atom or the zirconium atom, to give a mixture of products. However, this problem can be overcome by choosing another synthetic route. By changing the starting material from $Cp_2ZrCl\{(\mu\text{-}H)_2BX\}$ ($X = C_4H_8$ and C_5H_{10}) and R^- (R = alkyl group) to $Cp_2Zr(Cl)R$ and $[H_2BX]^-$, only one active site, the Zr center, is available on the metal complexes, $Cp_2Zr(Cl)R$, for reaction with the organohydroborate anion, and the alkyl-substituted organohydroborate zirconocene complexes are produced in good yield.

Molecular Structures. The molecular structures of **1**−**3** were determined by single-crystal X-ray diffraction analyses, and they are shown in Figures 1−3. Crystallographic data and selected positional parameters, bond distances, and bond angles are given in Tables 2−8.

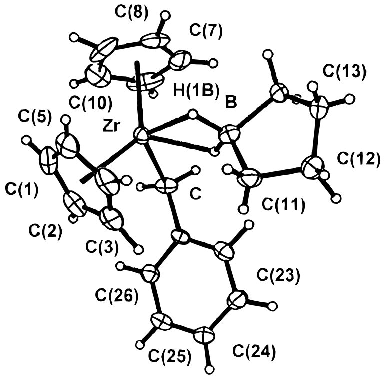


Figure 2. Molecular structure of $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$, **2**, showing 30% probability ellipsoids.

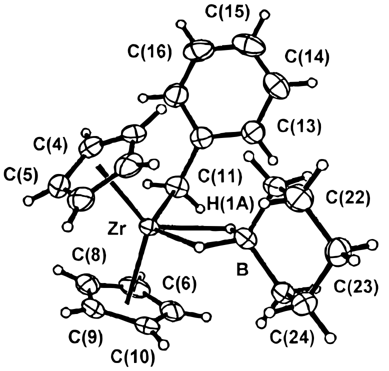


Figure 3. Molecular structure of $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$, **3**, showing 50% probability ellipsoids.

Table 2. Crystallographic Data for $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$, and $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$

empirical formula	$C_{14}H_{21}BZr$	$C_{21}H_{27}BZr$	$C_{22}H_{29}BZr$
fw, amu	291.34	381.46	395.48
space group	*Pnam*	*Pbca*	$P2_1/n$
a, Å	9.836(2)	8.3882(10)	9.674(2)
b, Å	10.186(2)	16.6669(10)	14.047(2)
c, Å	13.393(3)	27.0063(10)	14.512(3)
β, deg			102.53(2)
vol, Å^3	1341.8(5)	3775.6(5)	1925.2(6)
Z	4	8	4
ρ(calcd), g cm^{-3}	1.442	1.342	1.364
cryst size, mm	0.65 × 0.28 × 0.45	0.30 × 0.38 × 0.33	0.27 × 0.20 × 0.35
T, °C	−60	−60	−60
radiation (λ,Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	0.790	0.579	0.571
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
2θ limits, deg	4−50	4−45	4−50
±h	0, 11	0, 9	0, 11
±k	0, 12	0, 17	0, 16
±1	−15, 15	0, 29	−17, 17
no. of rflns measd	2407	2453	3668
no. of unique rflns	1227	2453	3384
no. of unique rflns [$I \geq 2.0\sigma(I)$]	1161	1338	2812
no. of variables	86	216	225
R1[a] [$I \geq 2.0\sigma(I)$]	0.0298	0.0462	0.0228
wR2[b] (all data)	0.0783	0.1364	0.0576
R_{int}	0.0152		0.0150
GOF	1.180	1.214	1.042

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

The coordination geometry about the zirconium atom in the three structures is best described as a distorted tetrahedron. Occupying the corners of the tetrahedron are the centers of the two Cp rings, a cyclic hydroborate ring (BC_4H_8 in **1** and **2**;

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(14) Liu, F.-C. Ph.D. Dissertation, The Ohio State University, 1998.

(15) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2361.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**

atom	*x*	*y*	*z*	$U(eq)^{a,b}$
Zr	7026(1)	4209(1)	2500	27(1)
C(1)	7290(4)	4061(4)	656(2)	61(1)
C(2)	6347(4)	3101(3)	915(2)	57(1)
C(3)	5201(3)	3737(4)	1285(2)	55(1)
C(4)	5432(3)	5091(4)	1240(2)	58(1)
C(5)	6725(4)	5274(4)	839(2)	60(1)
B	9364(4)	5285(4)	2500	35(1)
C(6)	10270(3)	5711(3)	3457(2)	43(1)
C(7)	11589(5)	6133(7)	3004(3)	106(2)
H	7580(50)	2650(50)	2500	51(12)
H(1A)	8270(50)	5820(40)	2500	48(14)
H(1B)	9020(50)	4150(40)	2500	41(12)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Hydrogen atoms from H to H(1B) were located and refined isotropically.

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, **1**[a]

	Bond Lengths		
av Zr−C(1−5)[b]	2.483[5]	B−H(11)	1.21(5)
Zr−centroid	2.184	B−H(12)	1.20(4)
Zr(1)−B	2.548(4)	B−C(6)	1.620(4)
Zr(1)−H	1.68(5)	C(6)−C(7)	1.495(5)
Zr(1)−H(11)	2.05(5)	C(7)−C(7)#1	1.351(8)
Zr(1)−H(12)	1.96(5)		
	Angles		
centroid−Zr−centroid	136.2	H(11)−Zr(1)−H(12)	55(2)
centroid−Zr−B	109.1	C(6)−B−C(6)#1	104.6(3)
centroid−Zr−H	98.1	C(6)−B−Zr(1)	127.7(2)
centroid−Zr−H(11)	101.9	C(6)−B−H(11)	111.7(11)
centroid−Zr−H(12)	111.9	C(6)−B−H(12)	114.3(11)
B−Zr(1)−H	97(2)	H(11)−B−H(12)	101(3)
H−Zr(1)−H(11)	124(2)	C(7)−C(6)−B	103.5(3)
H−Zr(1)−H(12)	69(2)	C(7)#1−C(7)−C(6)	113.9(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, y, -z + {}^1/_2$. [b] The standard deviation (σ_l) for the average bond length of Zr−C is calculated according to the equations[23] $\langle l\rangle = \sum_m l_m/m$ and $\sigma_l = [\sum_m (l_m - \langle l\rangle)^2/m(m-1)]^{1/2}$, where $\langle l\rangle$ is the mean length, l_m is the length of the *m*th bond, and *m* is the number of bonds.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$, **2**

atom	*x*	*y*	*z*	$U(eq)^{a,b}$
Zr	2440(1)	6208(1)	1278(1)	34(1)
C(1)	2218(15)	5525(7)	2101(4)	69(3)
C(2)	1335(14)	6227(8)	2136(3)	67(3)
C(3)	−14(13)	6150(7)	1817(4)	67(3)
C(4)	102(14)	5410(7)	1594(4)	61(3)
C(5)	1452(15)	5021(6)	1754(4)	65(3)
C(6)	5242(13)	6669(7)	1133(7)	83(5)
C(7)	4713(14)	6376(9)	678(5)	74(4)
C(8)	4524(14)	5586(9)	733(5)	71(4)
C(9)	4837(15)	5352(7)	1201(7)	85(4)
C(10)	5325(13)	6016(11)	1457(4)	80(4)
B	755(13)	6246(7)	484(4)	39(3)
C(11)	−1153(11)	6208(6)	472(3)	53(3)
C(12)	−1570(12)	6420(7)	−60(4)	63(3)
C(13)	−233(12)	6133(6)	−372(3)	54(3)
C(14)	1308(10)	6302(6)	−87(3)	44(2)
C	2445(13)	7599(5)	1455(3)	48(2)
C(21)	875(10)	7988(5)	1567(3)	35(2)
C(22)	−277(12)	8143(5)	1220(3)	45(2)
C(23)	−1720(11)	8477(5)	1331(4)	50(3)
C(24)	−2051(10)	8715(6)	1817(3)	53(3)
C(25)	−922(12)	8585(6)	2168(3)	50(3)
C(26)	524(11)	8232(6)	2054(3)	43(2)
H(1A)	1390(90)	6830(40)	720(30)	40(20)
H(1B)	1110(110)	5720(50)	670(30)	60(30)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Hydrogen atoms from H(1A) to H(1B) were located and refined isotropically.

Table 6. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$, **2**

	Bond Lengths		
av Zr−C(1−5)[a]	2.51[2]	B−H(1A)	1.27(7)
av Zr−C(6−10)[a]	2.50[1]	B−H(1B)	1.10(9)
Zr−centroid$_{C1-C5}$	2.215	B−C(11)	1.60(2)
Zr−centroid$_{C6-C10}$	2.208	B−C(14)	1.61(2)
Zr−C	2.367(8)	C(11)−C(12)	1.52(2)
Zr−B	2.568(11)	C(12)−C(13)	1.48(2)
Zr−H(1A)	2.04(7)	C(13)−C(14)	1.53(2)
Zr−H(1B)	2.15(9)		
	Angles		
centroid−Zr−centroid	131.5	H(1A)−Zr−H(1B)	53(3)
centroid$_{C1-C5}$−Zr−B	109.1	H(1A)−B−H(1B)	107(6)
centroid$_{C6-C10}$−Zr−B	106.1	C(11)−B−H(1A)	117(3)
centroid$_{C1-C5}$−Zr−H(1A)	119.6	C(14)−B−H(1A)	108(3)
centroid$_{C6-C10}$−Zr−H(1A)	107.3	C(11)−B−H(1B)	105(5)
centroid$_{C1-C5}$−Zr−H(1B)	99.1	C(14)−B−H(1B)	115(5)
centroid$_{C6-C10}$−Zr−H(1B)	99.0	C(11)−B−C(14)	105.6(8)
centroid$_{C1-C5}$−Zr−C	104.2	C(12)−C(11)−B	103.9(8)
centroid$_{C6-C10}$−Zr−C	102.8	C(13)−C(12)−C(11)	106.8(8)
C−Zr−B	98.4(4)	C(12)−C(13)−C(14)	107.0(7)
C−Zr−H(1A)	70(2)	C(13)−C(14)−B	103.2(7)
C−Zr−H(1B)	122(2)	C(21)−C−Zr	117.6(6)

[a] The standard deviation (σ_l) for the average bond length of Zr−C is calculated according to the equations[23] $\langle l\rangle = \sum_m l_m/m$ and $\sigma_l = [\sum_m (l_m - \langle l\rangle)^2/m(m-1)]^{1/2}$ where $\langle l\rangle$ is the mean length, l_m is the length of the *m*th bond, and *m* is the number of bonds.

BC_5H_{10} in **3**), which is connected to the zirconium atom through two bridge hydrogens, and a hydride ligand in **1** and a benzyl group in **2** and **3**. In compound **1**, a crystallographically imposed mirror plane passes through the terminal hydride, Zr, H(1A), H(1B), and B and generates the second half of the molecule. The C(7)−C(7)#1 distance 1.351(8) Å is calculated to be shorter than a normal C−C distance. This discrepancy might be due to the plane of the BC_4H_8 ring being canted with respect to a plane that passes through B and is perpendicular to the mirror plane. It might also be due to rotation of these atoms around the axis passing through B and bisecting the bond. In either case, the projection of the C(7)−C(7)#1 distance upon this plane normal to the mirror plane would be shorter than the actual C(7)−C(7)#1 disatnce.

The Zr−B distances of **1**, **2**, and **3** are 2.548(4), 2.568(11), and 2.587(2) Å, respectively. These distances fall within the range observed for zirconium borahydride complexes that have a double hydrogen bridge between the zirconium and the boron atoms.[4a] The $Cp_{centroid}$−Zr−$Cp_{centroid}$ angle and the $Cp_{centroid}$−Zr distances are 136.2° and 2.184 Å in **1**; 131.5° and 2.215 and 2.208 Å in **2**; 130.3° and 2.215 and 2.204 Å in **3**. These angles and distances reflect the steric effect of the benzyl ligand in compounds **2** and **3**, compared to the hydride ligand in **1**. The Zr−H bridge bond distances are in the range 1.96−2.15 Å, and the B−H bridge bond distances are in the range 1.05−1.27 Å. These distances fall within the ranges observed for zirconium borohydride complexes with double hydrogen bridge bonds.[4a] The Zr−H terminal bond of 1.68(5) Å in **1** appears to be significantly shorter than that found in (η^5-C_5Me_5)Zr(η-C_8H_8)H (1.81 Å),[16] $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ (1.786(4) Å),[6] $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ (1.79(4) Å),[5a] and $\{ZrH(-H)(\eta\text{-}C_5H_4Me)_2\}_2$ (1.78(2) Å).[17] However, it is comparable to the Zr−H bond

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(16) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 821.

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$, **3**

atom	*x*	*y*	*z*	*U*(eq)[a,b]
Zr	6960(1)	3200(1)	8327(1)	24(1)
C(1)	5952(3)	1663(2)	8761(2)	43(1)
C(2)	5270(2)	1829(2)	7819(2)	40(1)
C(3)	6275(2)	1780(2)	7268(2)	37(1)
C(4)	7592(2)	1563(2)	7858(2)	38(1)
C(5)	7385(3)	1480(2)	8783(2)	43(1)
C(6)	7709(3)	4721(2)	9226(2)	41(1)
C(7)	8944(2)	4180(2)	9291(2)	47(1)
C(8)	8813(3)	3353(2)	9797(2)	46(1)
C(9)	7505(3)	3390(2)	10070(1)	41(1)
C(10)	6829(2)	4232(2)	9717(1)	38(1)
C(11)	8485(2)	3559(2)	7313(2)	35(1)
C(12)	8067(2)	3276(2)	6304(2)	33(1)
C(13)	7043(2)	3787(2)	5668(2)	37(1)
C(14)	6632(3)	3519(2)	4733(2)	49(1)
C(15)	7216(3)	2730(2)	4397(2)	54(1)
C(16)	8230(3)	2219(2)	5005(2)	53(1)
C(17)	8659(3)	2489(2)	5945(2)	44(1)
B	4811(2)	4217(2)	7512(2)	29(1)
C(21)	3804(2)	3818(2)	6562(1)	35(1)
C(22)	2250(2)	3797(2)	6638(2)	42(1)
C(23)	1762(2)	4754(2)	6933(2)	39(1)
C(24)	2649(2)	5080(2)	7882(2)	40(1)
C(25)	4211(2)	5191(2)	7853(1)	34(1)
H(1A)	6000(20)	4231(14)	7455(14)	26(5)
H(1B)	4940(20)	3644(15)	8144(15)	32(5)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor [b] Hydrogen atoms H(1A) and H(1B) were located and refined isotropically.

Table 8. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$, **3**

Bond Lengths			
av Zr−C(1−5)[a]	2.515[4]	B-H(1B)	1.21(2)
av Zr−C(6−10)[a]	2.51[1]	B-C(25)	1.606(3)
Zr−centroid$_{C1-C5}$	2.215	B-C(21)	1.606(3)
Zr−centroid$_{C6-C10}$	2.204	C(21)-C(22)	1.531(3)
Zr−C(11)	2.354(2)	C(22)-C(23)	1.518(3)
Zr−B	2.587(2)	C(23)-C(24)	1.527(3)
Zr−H(1A)	2.01(2)	C(24)-C(25)	1.529(3)
Zr−H(1B)	2.01(2)	C(11)-C(12)	1.487(3)
B−H(1A)	1.17(2)		
Angles			
centroid-Zr−centroid	130.3	H(1A)-B-H(1B)	97(2)
centroid$_{C1-C5}$−Zr−B	110.6	C(12)-C(11)-Zr	119.1(2)
centroid$_{C6-C10}$-Zr−B	106.1	C(25)-B-C(21)	111.6(2)
centroid$_{C1-C5}$−Zr−H(1A)	123.7	C(25)-B-H(1A)	115.7(10)
centroid$_{C6-C10}$−Zr−H(1A)	103.7	C(21)-B-H(1A)	111.6(10)
centroid$_{C1-C5}$−Zr−H(1B)	97.1	C(25)-B-H(1B)	108.6(10)
centroid$_{C6-C10}$−Zr−H(1B)	101.1	C(21)-B-H(1B)	111.3(10)
centroid$_{C1-C5}$−Zr−C(11)	104.5	C(22)-C(21)-B	111.6(2)
centroid$_{C6-C10}$−Zr−C(11)	102.0	C(23)-C(22)-C(21)	111.9(2)
C(11)-Zr-B	98.39(8)	C(22)-C(23)-C(24)	111.9(2)
C(11)-Zr-H(1A)	73.7(6)	C(23)-C(24)-C(25)	111.8(2)
C(11)-Zr-H(1B)	125.0(6)	C(24)-C(25)-B	110.4(2)
H(1A)-Zr-H(1B)	52.5(8)		

[a] The standard deviation (σ_l) for the average bond length of Zr−C is calculated according to the equations[23] $\langle l \rangle = \sum_m l_m/m$ and $\sigma_l = [\sum_m (l_m - \langle l \rangle)^2/m(m-1)]^{1/2}$, where $\langle l \rangle$ is the mean length, l_m is the length of the *m*th bond, and *m* is the number of bonds.

lengths reported for $(\eta^5\text{-}C_8H_{11})Zr(H)(dmpe)$ (1.67 Å).[18] However, ESDs were not reported. The Zr−C bond distances of **2** and **3** are 2.367(8) and 2.354(2) Å, respectively. These distances are comparable to the previously reported Zr−C distance of 2.310(7) Å in $Cp_2Zr(CH_2Ph)_2$.[13]

Experimental Section

General Procedures. All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of nitrogen. Diethyl ether and THF were dried over Na/benzophenone and freshly distilled prior to use. Hexane was dried over CaH_2 and freshly distilled prior to use. Cp_2ZrCl_2, KH, LiH, $BH_3{\cdot}THF$ (1 M in THF), and benzylmagnesium chloride (1.0 M in Et_2O) were purchased from Aldrich and used as received. $\{B_2(C_4H_8)_2H_2\}$,[12] $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$,[1] $Cp_2ZrCl(CH_2Ph)$,[19] $\{(\mu\text{-}H)BC_5H_{10}\}_2$,[20] $K[H_2BC_5H_{10}]$,[21] and $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$[3a] were prepared by literature procedures. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. ^1H (δ(TMS) = 0.00 ppm) and ^{11}B NMR spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 and 80.253 MHz at 303 K. Boron-11 spectra were externally referenced to $BF_3{\cdot}OEt_2$ ($\delta = 0.00$ ppm). Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer with 2 cm^{-1} resolution.

X-ray Crystal Structure Determination. Crystallographic data were collected at −60 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Crytallographic computations were carried out using the SHELXTL software package.[22] Structure solution involved the DIRECT method. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 24−30°. All reflection data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied based on measured ψ scans. All of the non-hydrogen atoms in complexes **1**−**3** were located and refined anisotropically. All of the bridge hydrogen atoms in the complexes **1**−**3** and the Zr−H in **1** were located and refined isotropically. The C−H hydrogens were placed in calculated positions, riding on the atoms to which they are bonded.

Preparation of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, 1. Method 1. In the drybox a 3.94 mmol quantity of $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ in 15 mL of THF solution was added dropwise to 576.6 mg (1.97 mmol) of Cp_2ZrCl_2 in 5 mL of THF. After the solution was stirred at room temperature overnight, THF and diborane were removed and the resulting white solids were extracted with diethyl ether. After removal of the diethyl ether, 504 mg (1.73 mmol, 87.8% yield) of white solid product was isolated.

Method 2. $K[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]$ (1.05 mmol) in 15 mL of THF solution was added dropwise to 342.7 mg (1.05 mmol) of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ in 6 mL of THF in the drybox. Within minutes the solution became cloudy due to the formation of KCl. After the solution was stirred at room temperature for 3 h, the THF and the diborane were removed under vacuum overnight and the resulting residue was extracted with Et_2O. Removal of the solvent from the filtrate gave 280 mg (96.1% yield) of white solid product.

Method 3. A 263 mg (0.81 mmol) amount of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$, 7.5 mg (0.94 mmol) of lithium hydride, and 15 mL of THF were put in a flask in a drybox. The solution was stirred at room temperature until all of the starting material was consumed. The reaction was monitored by ^{11}B NMR spectroscopy. After the reaction, THF was removed under vacuum and ether was introduced to extract the product. A white solid product was obtained following solvent removal after filtration (184 mg, 78% yield). Single crystals suitable for X-ray diffraction were obtained from an Et_2O solution at −40 °C by slow evaporation. ^{11}B NMR (Et_2O): $\delta = 30.9$ ppm (t, $J_{B-H} = 61.4$ Hz). ^1H NMR (d_6-benzene): $\delta = 5.60$ (s, Cp), 3.95 (br, Zr−H), 1.80 (br, 4H, β-H), 1.11 (br, 4H, α-H), −3.26 (br, μ-H), and −4.25 ppm (br, μ-H). ^1H NMR (d_8-toluene): $\delta = 5.61$ (s, Cp), 3.88 (br, Zr−H), 1.70 (br,

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4H, β-H), 0.99 (br, 4H, α-H), −3.25 (br, μ-H), and −4.34 ppm (br, μ-H). IR (KBr): 3113 (vw), 3099 (vw), 3075 (m), 2917 (s), 2908 (s, sh), 2844 (s), 2806 (w), 2644 (vw, br), 2280 (vw), 2064 (w), 2007 (vw), 1908 (s, br), 1848 (w, sh), 1820 (m, br), 1597 (m, br), 1577 (m, sh), 1462 (m), 1426 (vs, br), 1329 (w), 1308 (w), 1176 (w), 1121 (w), 1063 (vw), 1033 (w), 1012 (s), 965 (vw), 916 (vw), 818 (vs), 801 (s), 751 (w), 661 (w), 560 (vw), 539 (vw) cm^{-1}. Anal. Calcd for $C_{14}H_{21}BZr$: C, 57.71; H, 7.27. Found: C, 57.07; H, 7.14.

Preparation of $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_4H_8\}$, 2. A 1 mmol quantity of $Li[H_2BC_4H_8]$ in 10 mL of THF was added dropwise to 348 mg (1 mmol) of $Cp_2ZrCl(CH_2Ph)$ dissolved in 10 mL of THF. After the solution was stirred at room temperature for 3 h, the THF was removed under vacuum and the resulting white solid was extracted with Et_2O and hexanes. A yellow-brown solid was obtained after removal of the solvent from the filtrate. Pale yellow crystals of the product (160.2 mg, 42% yield) were obtained after recrystallization in Et_2O at −40 °C. ^{11}B NMR (d_6-benzene): $\delta = 22.1$ ppm (t). ^{1}H NMR (d_6-benzene): $\delta = 7.35-6.95$ (m, Ph), 5.49 (s, Cp), 2.13 (s, CH_2), 1.93 (br, 4H, β-H), 1.17 (br, 2H,α-H), 1.07 (br, 2H, α-H), −1.09 (br, μ-H), and −3.70 ppm (br, μ-H). IR (KBr): 3107 (w), 3089 (vw), 3073 (vw), 3050 (vw), 3019 (vw), 2989 (vw), 2921 (m, sh), 2903 (s), 2851 (m), 2841 (m), 2806 (w), 2277 (vw, br), 2115 (vw, br), 2069 (w), 2002 (m), 1974 (m), 1908 (w), 1857 (w), 1814 (vw, br), 1665 (w, br), 1593 (s), 1547 (vw), 1486 (s), 1461 (m), 1427 (s), 1412 (s), 1304 (vw), 1293 (vw), 1252 (vw), 1234 (vw), 1207 (m), 1181 (w), 1138 (vw), 1119 (vw), 1084 (vw), 1065 (vw), 1030 (m), 1016 (s), 1011 (m), 992 (m), 954 (vw), 913 (vw), 897 (vw), 839 (m), 815 (vs), 803 (s), 754 (s), 703 (s), 602 (vw), 550 (vw), 531 (vw), 471 (vw, br), 412 (vw) cm^{-1}. Anal. Calcd for $C_{21}H_{27}BZr$: C, 66.12; H, 7.13. Found: C, 65.42; H, 6.64.

Preparation of $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$, 3. In a drybox, 1.0 mmol of $K[H_2BC_5H_{10}]$ in 10 mL of THF was added dropwise to 348 mg (1.0 mmol) of $Cp_2ZrCl(CH_2Ph)$ in 10 mL of THF. The orange solution became cloudy and the color changed to yellow-green. After the solution was stirred at room temperature for 3 h, the THF was removed under vacuum and the resulting solid was extracted with Et_2O. A yellow-green, oily residue was obtained after removal of the Et_2O from the yellow-green filtrate. Pale yellow crystals (245.7 mg, 62.1% yield) were obtained after dissolving this oily residue in Et_2O and cooling to −40 °C. ^{11}B NMR (Et_2O): $\delta = 19.1$ ppm (t). ^{1}H NMR (d_6-benzene): $\delta = 7.32-6.89$ (m, Ph), 5.42 (s, Cp), 2.08 (s, CH_2), 1.83 (br, 6H, β,γ-H), 1.04 (br, 4H, α-H), −0.91 (br, μ-H), and −3.57 ppm (br, μ-H). IR (KBr): 3104 (vw), 3090 (vw), 3064 (vw), 3046 (vw), 3017 (w), 3012 (w), 2939 (m), 2912 (s), 2904 (s), 2891 (s), 2880 (s), 2867 (m, sh), 2833 (s), 2809 (m), 2273 (vw), 2051 (vw), 1997 (m, br), 1981 (m, sh), 1947 (w), 1913 (vw, sh), 1874 (vw), 1823 (m), 1763 (vw), 1593 (s), 1484 (s), 1457 (w), 1445 (m), 1417 (m), 1391 (vs, br), 1336 (m), 1306 (vw), 1290 (vw), 1274 (w), 1265 (vw), 1217 (m), 1205 (m), 1178 (vw), 1125 (vw), 1100 (vw), 1090 (w), 1074 (vw), 1048 (w), 1030 (m, sh), 1022 (s), 1014 (s), 992 (m), 957 (m), 932 (vw), 918 (vw), 890 (vw), 843 (m), 828 (s), 820 (s), 810 (vs), 806 (vs), 784 (w), 750 (s), 699 (s), 661 (vw), 614 (vw), 578 (vw), 550 (vw), 533 (w), 403 (vw) cm^{-1}. Anal. Calcd for $C_{22}H_{29}BZr$: C, 66.81; H, 7.39. Found: C, 66.41; H, 7.28.

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Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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