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Cyclic Hydroborate Complexes of Metallocenes III. Syntheses and Structures of Zirconocene Boracyclohexane Derivatives $Cp_2Zr(X)\{(\mu\text{-}H)_2BC_5H_{10}\}$ (X = H, CH_3, $H_2BC_5H_{10}$)[†]

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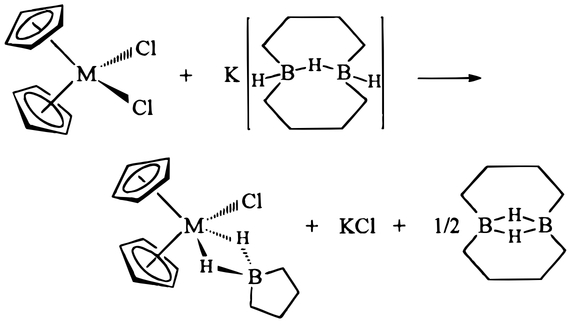
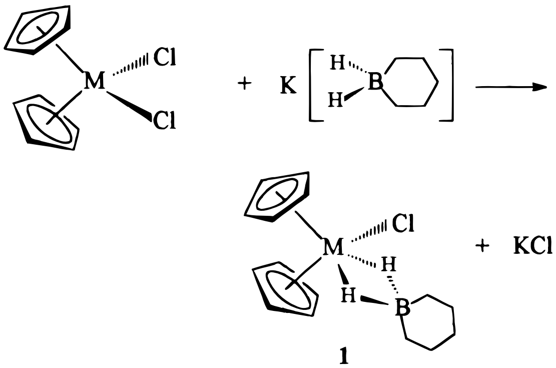
In reactions of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$, **1**, with LiH, Cl^- is replaced to produce $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$, **2**. Reaction of **1** with $K[H_2BC_5H_{10}]$ yields $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$, **4**. The methyl-substituted compound $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$, **3**, is prepared from the reaction of $Cp_2ZrCl(CH_3)$ with $K[H_2BC_5H_{10}]$. The synthetic route for the preparation of **3** prevents side reactions that occur in the direct alkylation of zirconocene organohydroborate complexes. Proton NMR spectra of **2** at elevated temperatures indicate that intramolecular hydrogen exchange occurs among Zr−H−B hydrogens, terminal H on Zr, and Cp hydrogens. The structures of **2**, **3**, and **4** are reported. Crystal data for **2**: space group *Abm*2 (No. 39), $a = 11.423(2)$ Å, $b = 14.138(3)$ Å, $c = 9.025(5)$ Å, $Z = 4$. Crystal data for **3**: space group *Pbca* (No. 61), $a = 8.469(4)$ Å, $b = 16.828(9)$ Å, $c = 21.897(8)$ Å, $Z = 8$. Crystal data for **4**: space group *C*2/*c* (No. 15), $a = 16.222(7)$ Å, $b = 9.434(2)$ Å, $c = 13.131(5)$ Å, $\beta = 102.97(3)°$, $Z = 4$.

Introduction

Many tetrahydroborate metal complexes have been prepared and studied.[1,2] The complexes $Cp_2Zr(BH_4)_2$[3,4] and $Cp_2ZrH(BH_4)$[3,4] are among the earliest reported. With the exception of X-ray structural analyses, these compounds were studied in detail. However, organohydroborate metal complexes have received much less attention.[5] Recently we reported on the disproportionation of the bis(tetramethylene)diborate anion, $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$, in its reactions with zirconocene and hafnocene dichloride[6,7] to produce the double hydrogen-bridged cyclopentaborate derivative $Cp_2MCl\{(\mu\text{-}H)_2BC_4H_8\}$ (M = Zr, Hf; reaction 1). It was also shown that the cyclic hydroborate anion $[H_2BC_5H_{10}]^-$ serves as a chelating ligand in its reaction with zirconocene and hafnocene dichlorides to form complexes[8] (reaction 2) analogous to those formed in reaction 1. Here we report extensions of these studies to the preparation, structures, and properties of $Cp_2ZH\{(\mu\text{-}H)_2BC_5H_{10}\}$, **2**, $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$, **3**, and $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$, **4**.



(1)



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(2)

Results and Discussion

$Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$, 2. (A) Formation of 2. Compound **2** is prepared from the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$, **1**, with LiH in THF (reaction 3a). This reaction was monitored to completion by ^{11}B NMR spectroscopy (2 days at room temperature). During the reaction, the starting material and compound **2** were the only species observed in ^{11}B NMR spectra. However, we believe that formation of compound **2** might occur through two parallel pathways. In one pathway, reaction 3a, nucleophilic displacement of Cl^- by H^- would produce complex **2** directly. In the second pathway or alternative reaction route, reaction 3b, the H^- ion could attack the boron atom to cleave the hydrogen bridge system to generate Cp$_2$-

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[†] Dedicated to Prof. Dr. Heinrich Nöth on the occasion of his 70th birthday.

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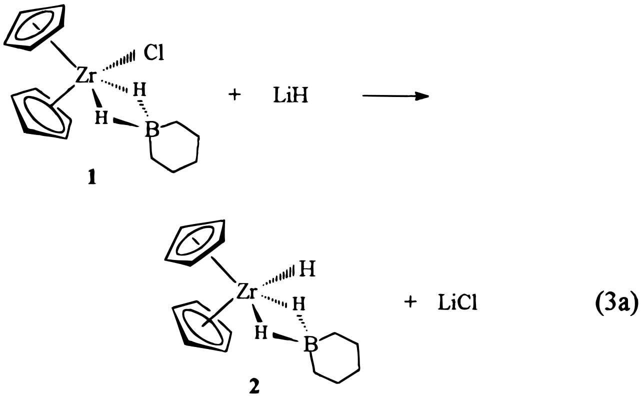
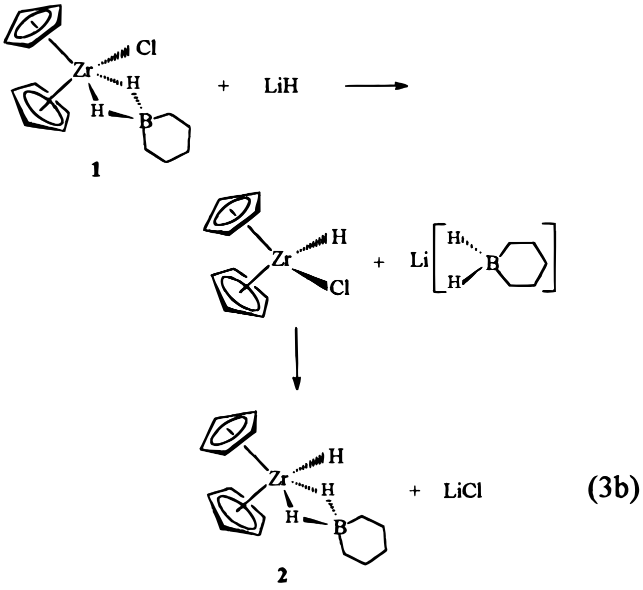


(3a)

ZrClH and $[H_2BC_5H_{10}]^-$, which then react with each other, the $[H_2BC_5H_{10}]^-$ anion displacing Cl^- from Cp_2ZrClH to form compound **2**. Indeed, in a separate reaction of Cp_2ZrClH with $K[H_2BC_5H_{10}]$, pure compound **2** was produced.



(3b)

The IR spectrum of **2** is consistent with the bidentate hydrogen-bridge structure.[1] The broad band that is assigned to the Zr−H stretching mode appears at 1618 cm^{-1}, within the range 1540−1650 cm^{-1} reported for M−H (M = Zr, Hf) stretching,[9] and is in agreement with those values observed for $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$ (1620 cm^{-1}),[10] $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3)$ (1595 cm^{-1}),[5a] and $[(C_5Me_5)Zr\{(\mu\text{-}H)_2BH_2\}H(\mu\text{-}H)_2]_2$ (1628 cm^{-1}).[9]

Compound **2** is stable under a nitrogen atmosphere. After exposure to air for 18 h, the integrated ^{11}B NMR spectrum indicated that 46% of the complex had undergone decomposition. Compound **2** is also stable in benzene solution at room temperature for several weeks. However, a white solid forms immediately when this solution is exposed to the air.

(B) NMR Spectra of 2. The ^{11}B NMR spectrum of **2** in ether solution consists of a triplet at $\delta = 28.18$ ppm (t, $J_{B-H} = 55.6$ Hz) which is about 15 ppm downfield from the parent compound, $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$.[8] In the ^1H NMR spectrum, the two bridge hydrogens give rise to two broad signals at $\delta = -3.26$ and -4.16 ppm that are split into what appear to be doublets. They collapse to two singlets upon decoupling ^{11}B from the proton signals. Interestingly the shapes of the two bridge hydrogen signals, undecoupled from ^{11}B, are similiar to those of the BH_4^- hydrogens signals of $(PPh_3)_2Cu\{(\mu\text{-}H)_2BH_2\}$[11] at ambient temperature and $Zr(BH_4)_4$[12] at −70 °C and are due to partial thermal decoupling of the boron nuclei. The terminal hydride on zirconium produces a broad signal at $\delta = 4.06$ ppm that falls within the range observed for terminal hydride in $Cp_2ZrH(BH_4)$ (4.53 ppm),[3] $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ (4.16 ppm),[5a] and $[(C_5Me_5)Zr\{(\mu\text{-}H)_2BH_2\}H(\mu\text{-}H)_2]_2$ (3.91 ppm).[9] These chemical shifts differ significantly from the higher-field values observed for the chemical shifts of hydride in complexes of the intermediate and late transition metals.[13] The low-field chemical shift is attributed to the fact that since early transition metal atoms have d^0 configuration, there is no shielding effect on the proton attached to the metal atom.[3]

Although there is no direct bond between the terminal hydride on zirconium and the boron atom, there is evidence for interaction since the broad ^1H signal of the terminal hydride sharpens upon ^{11}B decoupling. The ^1H NMR spectrum of the boracyclohexane ring consists of two broad signals at $\delta = 1.68$ ppm (6H, β,γ-H) and 0.99 ppm (4H, α-H). Splitting of the two signals occurs at low temperature. At −60 °C, the signals of the β- and γ-hydrogens are separated ($\delta = 1.91$ and 2.17 ppm). At this temperature the four α-hydrogens are also split into two overlapping signals ($\delta = 1.30$ and 1.24 ppm).

(C) Intramolecular Hydrogen Exchange in 2. Proton NMR spectra of **2** (Figures 1 and 2) at elevated temperatures indicate that intramolecular hydrogen exchange occurs among Zr−H−B hydrogens, terminal H on Zr, and Cp hydrogens. In Figure 1 the two signals of the bridge hydrogens broaden as the temperature is raised, coalesce between 50 and 60 °C, and then broaden into the baseline as the temperature is raised. As this process occurs, the signal assigned to the terminal hydrogen

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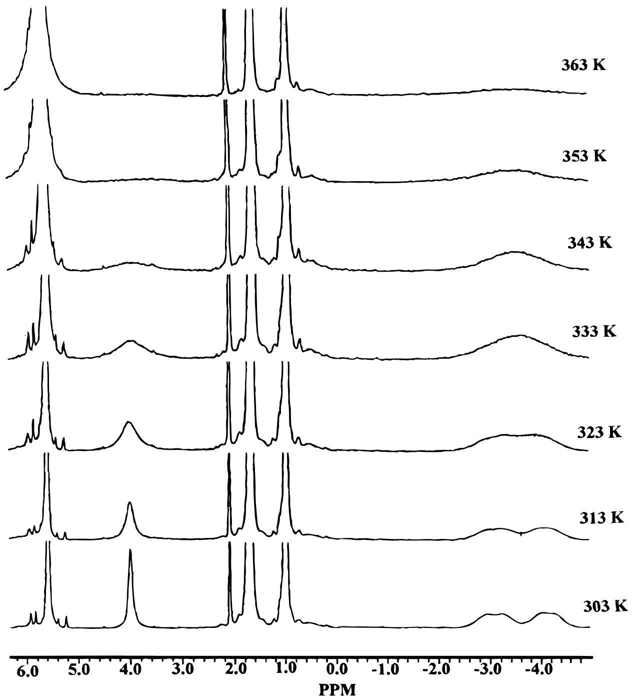


Figure 1. Variable-temperature ^{1}H NMR spectra of CpH{(μ-H)$_2$-BC$_5$H$_{10}$} in toluene-d_8 displaying the bridge and terminal hydride region.

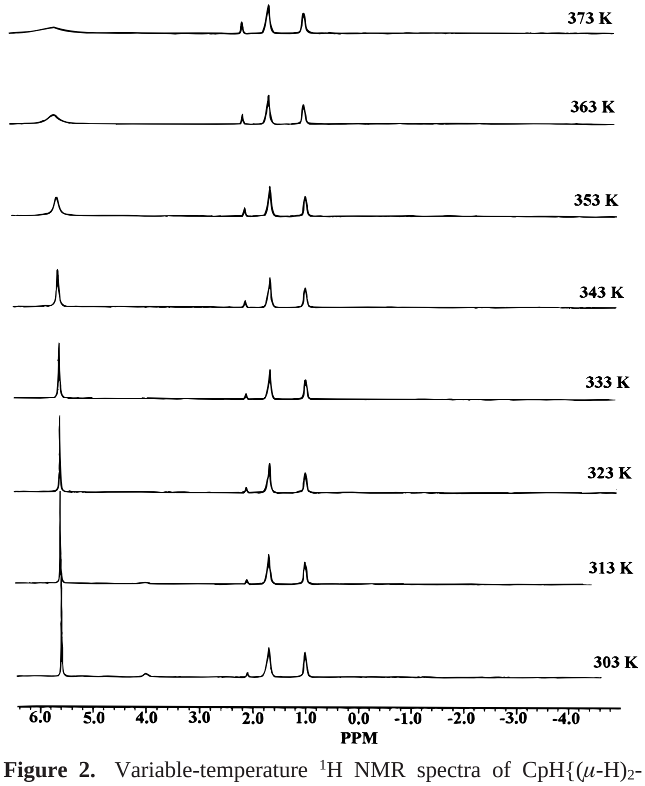
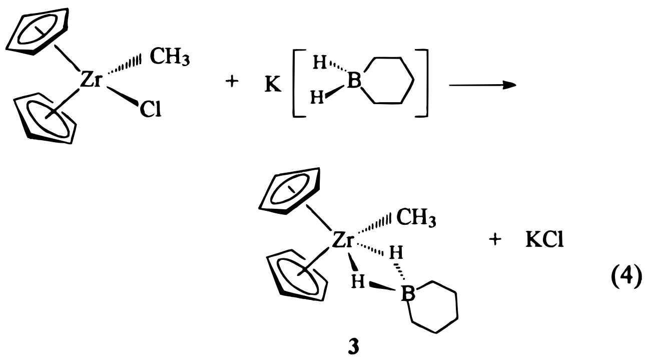


Figure 2. Variable-temperature ^{1}H NMR spectra of CpH{(μ-H)$_2$-BC$_5$H$_{10}$} in toluene-d_8.

on zirconium also broadens into the baseline, and noticeable broadening of the signal assigned to Cp hydrogens occurs. In Figure 2, the broadening of the Cp proton signal is more clearly represented in a spectrum of lower magnification than in Figure 1. Thus in compound **2** the sequence of hydrogen exchange with increasing temperature appears to be the initial interchange of Zr−H−B hydrogen followed by exchange of these hydrogens with the terminal hydrogen on zirconium and with further increase in temperature, significant exchange of these hydrogens with the Cp hydrogens occurs. On the other hand, in the case of Cp$_2$ZrH(μ-H)$_2$BH$_2$ it was shown[14] that the Zr−H−B hydrogens exchange with Cp hydrogens before exchange with the terminal H on Zr occurs as the temperature is increased.

A possible exchange process that involves the Zr−H−B, the Zr−H hydrogen, and the C−H hydrogens on the Cp ring is shown in Scheme 1. To account for the exchange of the terminal hydride, a single hydrogen bridge intermediate with one broken B−H$_b$ bond is proposed. The exchange of the terminal hydride and the bridge hydrogens can be accomplished by rotation about the single hydrogen bridge intermediate, followed by B−H$_t$ bond formation. The exchange of the Cp hydrogens with terminal hydride and bridge hydrogens might involve rearrangement of the bonding of the Cp ring to zirconium, proceeding through $\eta^5 \rightarrow \eta^1 \rightarrow \eta^5$ bonding modes. The Zr−H hydrogen, is then abstracted by the η^1-Cp ligand to restore the η^5 bonding mode of the Cp ring. Line shape analyses of the exchange process for the terminal and bridge hydrogens have been reported.[15]

Cp$_2$Zr(CH$_3$){(μ-H)$_2$BC$_5$H$_{10}$}, 3. Compound **3** is obtained in high yield (84%) from the reaction of Cp$_2$ZrCl(CH$_3$) with K[H$_2$BC$_5$H$_{10}$] in THF solution (reaction 4).



The ^{11}B NMR spectrum of **3** in ether solution consists of a triplet at δ = 18.23 ppm (t, J_{B-H} = 58.6 Hz). The ^{1}H NMR spectrum in benzene-d_6 consists of two broad signals of the two bridging hydrogens at δ = −1.26 and −3.39 ppm, collapse of the two bridge signals occurs at about 60 °C. The chemical shift of the methyl group occurs at δ = 0.09 ppm which is in the range observed for zirconium methyl complexes, Cp$_2$Zr(CH$_3$)$_2$ (−0.39 ppm)[16] and Cp$_2$ZrCl(CH$_3$) (0.42 ppm),[17] and is consistent with Cp$_2$Zr(CH$_3$){(μ-H)$_2$BC$_4$H$_8$} (−0.12 ppm)[7] and Cp$_2$Zr(CH$_3$){(μ-H)$_2$BH$_2$} (0.17 ppm).[18]

Compound **3** is stable under nitrogen atmosphere and in a vacuum. It is very soluble in THF, diethyl ether, toluene, and benzene; however, its solubility in hexane is limited.

An alternative route was also attempted for the preparation of **3**. This involved the reaction of Cp$_2$ZrCl{(μ-H)$_2$BC$_5$H$_{10}$} with methyllithium but it produced a mixture of products besides compound **3**. On the basis of the ^{11}B NMR spectrum of the reaction mixture, the reaction products include CH$_3$BC$_5$H$_{10}$ (84.6 ppm (s)),[19] Cp$_2$ZrH{(μ-H)$_2$BC$_5$H$_{10}$} (28.1 ppm (t)), Cp$_2$Zr(CH$_3$){(μ-H)$_2$BC$_5$H$_{10}$} (18.0 ppm (t)), and one unidentified organoborate (−21.5 ppm). These products probably arise from competing reactions in which the methyllithium can displace

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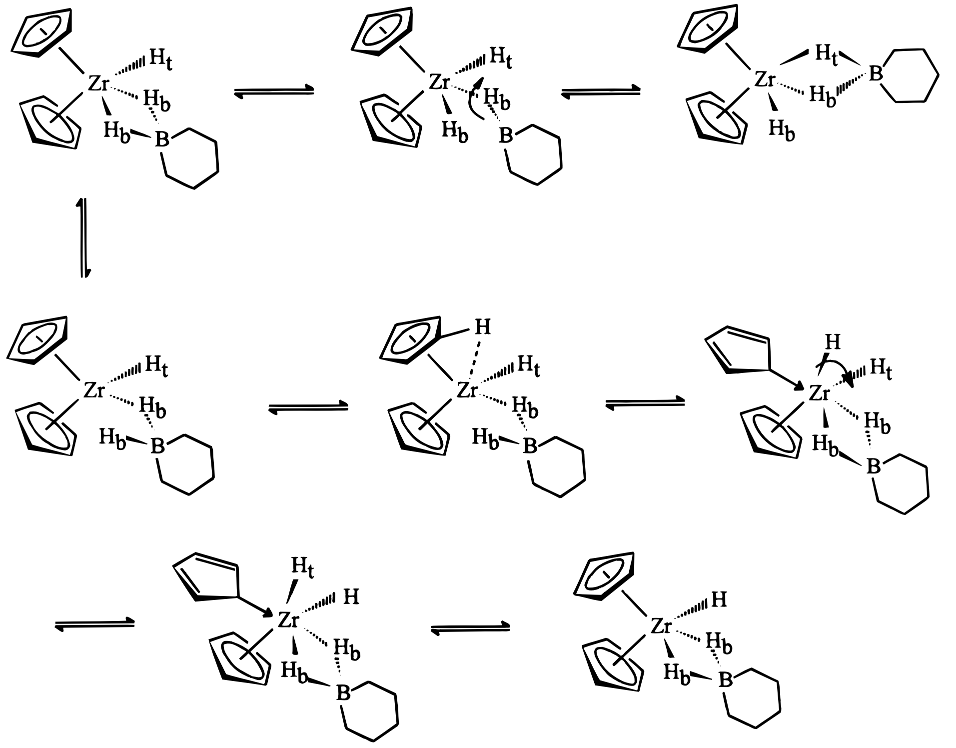
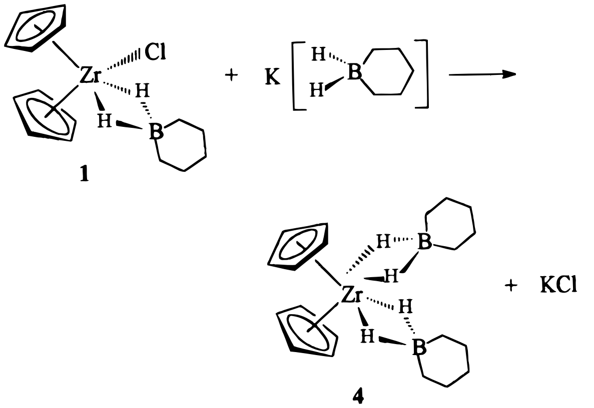
Scheme 1. A Plausible Mechanism of Hydrogen Exchange of $Cp_2Zr(H)\{(\mu\text{-}H)_2BC_5H_{10}\}$



terminal Cl or bridging H from $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$. Similar competing pathways in the reaction of methyllithium with $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ can account for the mixture of products formed.[7]

$Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$, 4. The reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$ with $K[H_2BC_5H_{10}]$ in THF (eq 5) produces compound **4**, the organoboron analogue of $Cp_2Zr\{(\mu\text{-}H)_2BH_2\}_2$,[3] a compound that has been reported to have weak interaction between BH_4^- and the metal center,[1] on the basis of IR spectroscopy. The B−H$_b$ stretching mode is higher in frequency, while the Zr−H$_b$ stretching mode is lower in frequency than other tetrahydroborate metal complexes. A similar argument can be made for compound **4** on the basis of its IR spectrum since the B−H$_b$ stretching mode at 2009 cm^{-1} is at higher frequency than observed for other zirconacene complexes with only a single boracyclohexane ring, while the Zr−H$_b$ stretching mode at 1382 cm^{-1} is at lower frequency.



(5)

The ^{11}B NMR spectrum of **4** consists of a triplet at $\delta = 24.57$ ppm (t, $J_{B-H} = 40.2$ Hz) which is consistent with the double hydrogen-bridged structure. The chemical shift occurs at about the same position as the neutral organodiborane $\{(\mu\text{-}H)\text{-}BC_5H_{10}\}_2$, but the coupling constant is about 15 Hz less than occurs for the other compounds discussed here and in a previous report.[7] In the ^1H NMR spectrum, two bridge hydrogens appear as a broad signal at $\delta = -2.82$ ppm at ambient temperature and the signal from the other bridge hydrogens is believed to be overlapped with the signals of the boracyclohexane rings. An averaged signal appears at −0.93 ppm at 60 °C which suggests that the overlapped signal occurs at about 1 ppm. Compound **4** is stable under an atmosphere of nitrogen; it is less soluble in THF, ether, and benzene than compound **2**.

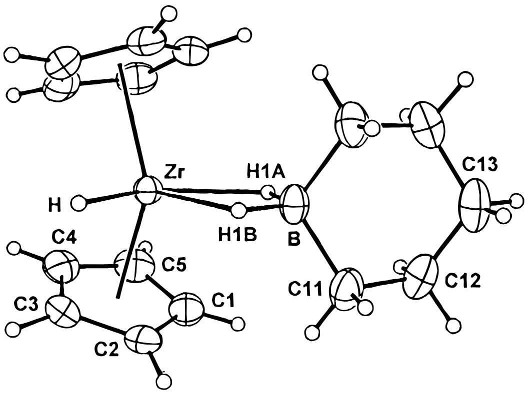


Figure 3. Molecular structure of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ with 50% probability thermal ellipsoids.

Molecular Structures of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$, $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$, and $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$. The molecular structures of **2**, **3**, and **4** were determined by single-crystal X-ray diffraction analyses, and they are shown in Figures 3−5. Crystallographic data and selected bond distances and bond angles are given in Tables 1−4.

The coordination geometry of the zirconium atom in the molecular structures of **2**, **3**, and **4** is best described as a distorted tetrahedron. At the corners of the tetrahedron are the centers of two Cp rings, a boracyclohexane ring which is connected to

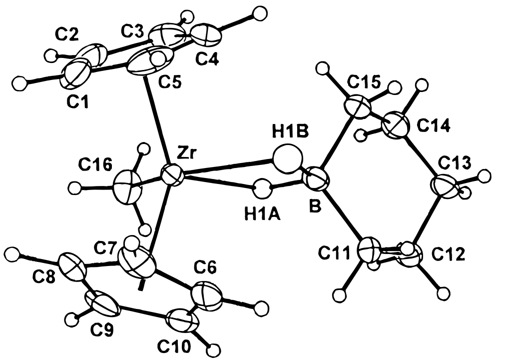


Figure 4. Molecular structure of $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$ with 30% probability thermal ellipsoids.

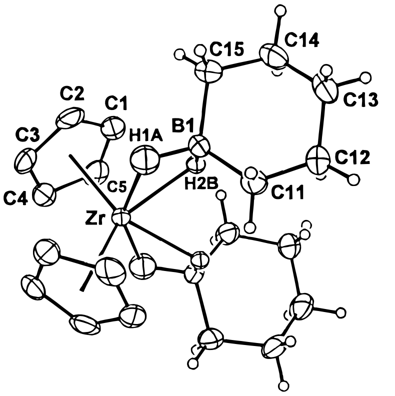


Figure 5. Molecular structure of $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$ with 50% probability thermal ellipsoids.

the zironium atom through two hydrogen bridges, and an H (**2**), CH_3 (**3**), or a second boracyclohexane ring connected to the zirconium atom through two hydrogen bridges (**4**) at the fourth corner of the tetrahedron.

The centroid−Zr−centroid angles decrease in the order 135.0° in **2**, 131.5° in **3**, and 127.0° in **4**, which reflects the increased steric bulk of the fourth ligand in the squence of structures **2**, **3**, and **4**. This effect of the fourth ligand is also observed in the $Cp_{(centroid)}$−Zr and Zr−B distances. The $Cp_{(centroid)}$−Zr distances are 2.184, 2.207, and 2.214 Å and the Zr−B distances are 2.570(5), 2.587(7), and 2.596(3) Å for **2**, **3**, and **4**, respectively. The Zr−B distances fall within the range observed for zirconium borohydride complexes that have a double hydrogen bridge connecting the zirconium and boron atoms.[2a−c,g,20] All of the bridge hydrogens in **2**, **3**, and **4** and the terminal hydrogen in **2** were located. These hydrogens were refined, with the exception of **2** in which positional and thermal parameters were fixed. The Zr−H bridge bond distances are in the range of 1.98−2.28 Å, and the B−H bridge bond distances are in the range of 1.15−1.32 Å. These distances fall within the ranges previously observed for zirconium borohydrides with double hydrogen bridges.[1] Likewise the Zr−H terminal bond distance of 1.79 Å in **2** falls within the range observed for zirconium hydride complexes: $(\eta^5\text{-}C_5Me_5)Zr(\eta\text{-}C_8H_8)H$ (1.81 Å),[21] $\{ZrH(\mu\text{-}H)(\eta\text{-}C_5H_4Me)_2\}_2$ (1.78 Å),[22] $Cp_2ZrH(BH_3CH_3)$ (1.79 Å),[5a] $(\eta^5\text{-}C_8H_{11})ZrH(dmpe)$ (1.67 Å)[23] (dmpe = 1,2-bis(dimethylphosphino)ethane), and $Zr_2H_4(BH_4)_4(dmpe)_2$ (1.74 Å).[2c]

In complex **2** the asymmetric unit is half the molecule. The second half of the moleule is generated by a crystallographically imposed mirror plane on which the terminal hydride H, Zr, H(1A), H(1B), B, and C(13) reside. It is of interest to compare the steric effect in compounds **2** and **3**. The hydride ligand in compound **2** lies on the same crystallographic mirror plane that contains Zr, H(1A), H(1B), B, and C(13). However, when the hydride ligand is replaced by the methyl group in compound **3**, it does not reside on a plane. From a least-squares plane calculated for Zr, B, and C(13), equivalent to that in compound **2**, the carbon of the methyl group resides 0.08(4) Å below this plane, the bridge hydrogen H(1A) resides 0.14(5) Å below this plane, and H(1B) resides 0.25(6) Å above this plane.

In complex **4** the asymmetric unit is half of the molecule. The second half of **4** is generated by a crystallographically imposed 2-fold axis that passes through the Zr atom. A least-squares plane was calculated with Zr, H(1A), H(2B), and B. The dihedral angle between this plane and the equivalent plane generated by the 2-fold axis is 49.3°. A molecular orbital calculation of $Cp_2Zr(BH_4)_2$ by Hoffmann and Lauher[24] favors an idealized coplanar structure for all four bridging hydrogen atoms in which one of the four donor molecular orbitals (b_2) provided by the two BH_4^- groups does not possess the correct symmetry for the bond formation with the Cp_2Zr center. The twisted structure of the four bridging hydrogens in **4** may be due to the repulsion of the two bulky organoborate rings; however, the absence of proper symmetry for bond formation between the metal center and the organoborate ligand should also be considered since the four bridging hydrogens in $(C_5H_4Me)_2Hf(BH_4)_2$,[25] which contains the less bulky borohydride ligands, are also not coplanar.

Experimental Section

General Procedures. All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of nitrogen. THF and diethyl ether 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, 1,4-pentadiene, KH, LiH, $BH_3\cdot THF$ (1 M solution in THF), and CH_3Li (1.4 M solution in diethyl ether) were purchased from Aldrich and used as received. $\{(\mu\text{-}H)BC_5H_{10}\}_2$,[26] $K[H_2BC_5H_{10}]$,[8] $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$,[8] and $Cp_2ZrCl(CH_3)$[27] 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 $BF_3\cdot OEt_2$ (δ = 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 on a COMPAQ PC computer using SHELEXTL software package.[28] Structure solution involved a 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

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Table 1. Crystallographic Data for $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$, $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$, and $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$

empirical formula	$C_{15}H_{23}BZr$	$C_{26}H_{25}BZr$	$C_{20}H_{34}B_2Zr$
fw (amu)	305.36	319.39	387.31
space group	*Abm*2	*Pbac*	*C*2/*c*
a, Å	11.423(2)	8.469(4)	16.222(7)
b, Å	14.138(3)	16.828(9)	9.434(2)
c, Å	9.025(2)	21.897(8)	13.131(5)
β, deg			102.97(3)
vol, Å^3	1457.5(5)	3121(3)	1958.2(3)
Z	4	8	4
ρ(calcd), g cm^{-3}	1.392	1.360	1.314
crystal size, mm	0.40 × 0.45 × 0.55	0.28 × 0.08 × 0.33	0.40 × 0.15 × 0.25
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}	0.731	0.559	0.559
scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
2θ limits, deg	4−50	4−45	4−50
$\pm h$	0, 13	0, 9	−19, 19
$\pm k$	0, 16	−18, 18	0, 11
$\pm l$	0, 10	−23, 23	0, 15
no. of reflcns measd	1399	8175	1723
no. of unique reflcns	717	2029	1522
no. of unique reflcns [$I > 2.0\sigma(I)$]	706	1262	3911
no. of variables	85	171	113
R$_1$[a] [$I > 2.0\sigma(I)$]	0.0238	0.0415	0.0284
wR$_2$[b] [all data]	0.0624	0.0853	0.0755
R$_{int}$	0.000	0.1018	0.0334
GOF	1.130	1.054	1.066

[a] $R_1 = \sum||F_o| - |F_c|/\sum|F_o|$. [b] $wR_2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (°) for $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$[a]

Bond Lengths			
av Zr−C(1−5)[29,30]	2.490[6]	B−H(1A)	1.211(5)
Zr−centroid	2.184	B−H(1B)	1.148(5)
Zr−B	2.570(5)	B−C(11)	1.601(4)
Zr−H	1.7862(4)	C(11)−C(12)	1.533(6)
Zr−H(1A)	1.9777(6)	C(12)−C(13)	1.515(7)
Zr−H(1B)	2.2817(9)	C(13)−C(12)#1	1.515(7)

Bond Angles			
centroid−Zr−centroid	135.0	C(4)−C(5)−C(1)	107.8(3)
centroid−Zr−B	109.7	C(11)#1−B−C(11)	111.4(4)
centroid−Zr−H	96.8	C(11)#1−B−Zr	124.1(2)
centroid−Zr−H(1A)	102.7	C(11)−B−Zr	124.1(2)
centroid−Zr−H(1B)	112.5	C(11)#1−B−H(1A)	109.6(2)
B−Zr−H	99.89(11)	C(11)−B−H(1A)	109.6(2)
B−Zr−H(1A)	27.10(11)	Zr−B−H(1A)	48.1(2)
B−Zr−H(1B)	26.53(11)	C(11)#1−B−H(1B)	107.8(2)
H−Zr−H(1A)	126.99(4)	C(11)−B−H(1B)	107.8(2)
H−Zr−H(1B)	73.36(2)	Zr−B−H(1B)	62.6(2)
H(1A)−Zr−H(1B)	53.63(2)	H(1A)−B−H(1B)	110.6(4)
C(5)−C(1)−C(2)	107.3(4)	C(12)−C(11)−B	109.2(3)
C(3)−C(2)−C(1)	107.9(4)	C(13)−C(12)−C(11)	112.1(3)
C(4)−C(3)−C(2)	108.4(3)	C(12)−C(13)−C(12)#1	113.5(7)
C(3)−C(4)−C(5)	108.6(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1, *x*, $-y + {}^3/_2$, *z*.

data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied based on measured ψ scans.

Preparation of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$, 2. A 330 mg (0.97 mmol) amount of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$ and 8.5 mg (1.07 mmol) of lithium hydride were put in a flask that contained a stir bar. The flask was degassed, and about 20 mL of THF was transferred into the flask. The system was warmed and 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. The ether solution was concentrated to about one-half of the volume, and about 20 mL of hexane was added to the system to induce precipitation. A white product was obtained following solvent removal after filtration (0.20 g, 67.5% yield). Single crystals suitable for X-ray structure determination were obtained from ether solution by slow evaporation of the solvent at −40 °C. ^{11}B NMR (ether): δ 28.18 (t, $J_{B-H} = 55.6$ Hz). ^{1}H NMR (benzene-d_6): δ 5.58 (s, Cp), 4.06 (br, Zr−H), 1.74 (br, 6H, β,γ-H), 1.06 (br, 4H, α-H), −3.26 (br, μ-H), and −4.16 (br, μ-H). ^{1}H NMR (toluene-d_8): δ 5.59 (s, Cp), 3.99 (br, Zr−H), 1.68 (br, 6H, β,γ-H), 0.99 (br, 4H, α-H), −3.08 (br, μ-H), and −4.14 (br, μ-H). IR (KBr): 3130 (w), 3098 (vw), 3079 (m), 2919 (s), 2904 (s),

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(29) The standard deviation for the average bond length of Zr−C is calculated according to the equations[30]

$$\langle l \rangle = \sum\nolimits_m l_m/m$$

$$\sigma_l = \left[\sum\nolimits_m (l_m - \langle l \rangle)^2/(m(m-1))\right]^{1/2}$$

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.

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Table 3. Selected Interatomic Distances (Å) and Bond Angles (°) for $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$

Bond Lengths			
av Zr−C(1−5)[29,30]	2.498[13]	B−H(1A)	1.19(4)
av Zr−C(6−10)[29,30]	2.503[20]	B−H(1B)	1.32(5)
Zr−centroid$_{(C1-C5)}$	2.205	B−C(11)	1.587(10)
Zr−centroid$_{(C6-C10)}$	2.208	B−C(15)	1.617(8)
Zr−C(16)	2.289(5)	C(11)−C(12)	1.527(8)
Zr−B	2.587(7)	C(12)−C(13)	1.513(8)
Zr−H(1A)	2.10(4)	C(13)−C(14)	1.503(10)
Zr−H(1B)	2.05(5)	C(14)−C(15)	1.516(9)
Bond Angles			
centroid−Zr−centroid	131.5	C(11)−B−Zr	126.2(4)
centroid$_{(C1-C5)}$−Zr−B	108.9	C(15)−B−Zr	122.1(5)
centroid$_{(C6-C10)}$−Zr−B	107.7	C(11)−B−H(1A)	111(2)
centroid$_{(C1-C5)}$−Zr−C(16)	101.8	C(15)−B−H(1A)	110(2)
centroid$_{(C6-C10)}$−Zr−C(16)	102.5	Zr−B−H(1A)	53(2)
centroid$_{(C1-C5)}$−Zr−H(1A)	116.9	Zr−B−H(1B)	52(2)
centroid$_{(C6-C10)}$−Zr−H(1A)	110.2	C(11)−B−H(1B)	115(2)
centroid$_{(C1-C5)}$−Zr−H(1B)	93.2	C(15)−B−H(1B)	104(2)
centroid$_{(C6-C10)}$−Zr−H(1B)	103.1	H(1A)−B−H(1B)	104(3)
C(16)−Zr−B	99.2(2)	C(11)−B−C(15)	111.6(5)
C(16)−Zr−H(1A)	72.3(10)	C(12)−C(11)−B	112.5(5)
C(16)−Zr−H(1B)	128.7(13)	C(13)−C(12)−C(11)	111.9(6)
B−Zr−H(1A)	27.0(10)	C(14)−C(13)−C(12)	112.5(5)
B−Zr−H(1B)	30.3(13)	C(13)−C(14)−C(15)	112.3(5)
H(1A)−Zr−H(1B)	57(2)	C(14)−C(15)−B	111.1(6)

Table 4. Selected Interatomic Distances (Å) and Bond Angles (°) for $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$[a]

Bond Lengths			
av Zr−C(1−5)[29,30]	2.514[9]	C(12)−C(13)	1.524(4)
Zr−centroid	2.214	C(12)−C(11)	1.529(4)
Zr(1)−B(1)	2.596(3)	C(11)−B(1)	1.612(4)
Zr(1)−H(1A)	1.99(3)	C(15)−C(14)	1.523(4)
Zr(1)−H(2B)	2.06(2)	C(15)−B(1)	1.605(4)
B(1)−H(1A)	1.23(3)	C(13)−C(14)	1.514(4)
B(1)−H(2B)	1.15(2)		
Bond Angles			
centroid−Zr−centroid	127.0	Zr(1)−B(1)−H(1A)	48(2)
centroid$_{C(1-5)}$−Zr−B1	102.6	Zr(1)−B(1)−H(2B)	50.1(11)
centroid$_{C(1-5)\#1}$−Zr−B1	111.5	C(15)−B(1)−Zr(1)	133.5(2)
centroid$_{C(1-5)}$−Zr−H(1A)	98.4	C(11)−B(1)−Zr(1)	114.1(2)
centroid$_{C(1-5)}$−Zr−H(2B)	95.0	C(11)−B(1)−H(1A)	114(2)
centroid$_{C(1-5)\#1}$−Zr−H(1A)	94.6	C(11)−B(1)−H(2B)	112.1(12)
centroid$_{C(1-5)\#1}$−Zr−H(2B)	131.6	C(15)−B(1)−H(2B)	110.0(11)
B(1)#1−Zr(1)−B1	98.3	C(15)−B(1)−H(1A)	111(2)
B(1)#1−Zr(1)−H(1A)	124.0(9)	C(15)−B(1)−C(11)	112.4(2)
B(1)−Zr(1)−H(1A)	27.2(9)	C(12)−C(11)−B(1)	109.3(2)
B(1)#1−Zr(1)−H(2B)	78.6(7)	C(14)−C(15)−B(1)	110.2(2)
B(1)−Zr(1)−H(2B)	25.4(7)	C(13)−C(12)−C(11)	112.2(2)
H(1A)−Zr(1)−H(2B)	51.6(11)	C(13)−C(14)−C(15)	112.6(2)
H(1A)−B(1)−H(2B)	96(2)	C(14)−C(13)−C(12)	113.1(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, y, $-z + {}^3/_2$.

2893 (s), 2875 (s), 2851 (s), 2814 (m), 2720 (vw), 2644 (vw), 2277 (vw), 2157 (vw), 1970 (vw, sh), 1915 (m), 1864 (s), 1837 (s), 1812 (s), 1775 (m), 1741 (m), 1656 (w), 1636 (w, sh), 1618 (m, br), 1536 (w, sh), 1500 (vw), 1454 (s, sh), 1446 (s, sh), 1422 (vs, br), 1368 (m, sh), 1337 (m), 1305 (m), 1276 (m), 1218 (s), 1199 (w), 1120 (vw), 1100 (vw), 1092 (w), 1068 (m), 1013 (s), 956 (s), 920 (w), 905 (vw, sh), 841 (m, sh), 836 (m, sh), 827 (s,), 810 (vs), 779 (m, sh), 754 (w, sh), 660 (m), 615 (vw), 581 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{23}BZr$: C, 59.00; H, 7.59. Found: C, 58.33; H, 7.49.

Preparation of $Cp_2Zr(CH_3)\{(\mu\text{-}H)_2BC_5H_{10}\}$, 3. A 1 mmol quantity of $K[H_2BC_5H_{10}]$ in about 10 mL of THF was added dropwise to 272.2 mg (1 mmol) of $Cp_2ZrCl(CH_3)$ in about 10 mL of THF in a drybox. During the process the solution turned cloudy due to the formation of KCl. After the reaction mixture had been stirred at room temperature for 3 h, THF was pumped away and the resulting white solid was extracted with ether. White solids were obtained after ether had been removed from the filtrate (270 mg, 84.5% yield). Single crystals suitable for X-ray structure determination were obtained from the ether solution at −40 °C by slow evaporation of the solvent. ^{11}B NMR (ether): δ 18.23 (t, $J_{B-H} = 58.6$ Hz). ^{1}H NMR (benzene-d_6): δ 5.55 (s, Cp), 1.78 (br, 6H, β,γ-H), 1.09 (br, 4H, α-H), 0.09 (s, CH_3), −1.26 (br, μ-H), and −3.39 (br, μ-H). IR (KBr): 3136 (vw), 3119 (vw), 3093 (vw), 2915 (s), 2901 (s), 2867 (m, sh), 2839(s), 2809 (m), 2679 (vw), 2648 (vw), 2278 (vw, br), 2107 (vw), 2070 (vw, br), 1999 (w, sh), 1969 (m), 1949 (m), 1919 (w, sh), 1877 (w), 1827 (w, br), 1745 (vw, br), 1642 (vw, br), 1443 (m), 1427 (m), 1391 (s, br), 1336 (m), 1292 (vw), 1275 (w), 1261 (vw), 1217 (w), 1194 (vw), 1126 (vw, br), 1101 (vw, sh), 1094 (w), 1072 (w), 1036 (w), 1017 (s), 954 (w), 927 (vw, br), 816 (s), 802 (vs), 741 (w, br), 676 (vw, br), 582 (vw, br), 448 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{25}BZr$: C, 60.17; H, 7.89. Found: C, 59.96; H, 7.77.

Preparation of $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$, 4. An 81.8 mg (0.5 mmol) amount of $\{(\mu\text{-}H)BC_5H_{10}\}_2$, 42 mg (1.05 mmol) of potassium hydride, and about 10 mL of THF were put into a flask. After the reaction mixture was stirred at room temperature for 3 h, the unreacted potassium hydride was removed by filtration and a white solid was left when THF was removed from solution under vacuum. A 0.33 g (0.97 mmol) quantity of $Cp_2ZrCl\{(\mu\text{-}H)_2\ BC_5H_{10}\}$ was then added to the above flask.

The flask was degassed and about 20 mL of THF was condensed into the flask at −78 °C. The system was slowly warmed to room temperature over a 5 h period. During this process the solution turned cloudy due to the formation of KCl. After the reaction, the THF was removed and ether was introduced to extract the product. After the ether was removed under vacuum, a 0.30 g (79.8% yield) quantity of white powder was obtained. Single crystals suitable for X-ray structure determination were obtained from the ether solution at −40 °C by slow evaporation of the solvent. ^{11}B NMR (ether): δ 24.57 (t, $J_{B-H} = 40.2$ Hz). ^{11}B NMR (benzene-d_6): δ 24.07 (t). ^{1}H NMR (benzene-d_6): δ 5.59 (s, Cp), 1.76 (br, 6H, β,γ-H), 1.51 (br, 6H, β,γ-H), 1.04 (br, 4H, α-H), 0.95 (br, 4H, α-H), and −2.82 (br, 2μ-H). IR (KBr): 3116 (vw), 3107 (w), 3090 (vw), 2907 (vs), 2899 (vs), 2881 (vs), 2862 (s, sh), 2832 (s), 2808 (s), 2663 (vw), 2653 (vw), 2427 (vw), 2348 (vw), 2274 (vw), 2245 (vw), 2196 (vw), 2166 (vw), 2130 (w), 2104 (w, sh), 2067 (m, sh), 2009 (s, br), 1953 (m, sh), 1929 (m), 1879 (vw), 1850 (vw), 1832 (vw), 1737 (vw, br), 1645 (vw, br), 1564 (vw, br), 1453 (m), 1443 (s), 1416 (m), 1383 (s), 1364 (s, sh), 1344 (s), 1337 (s), 1324 (m, sh), 1281 (s), 1273 (s), 1234 (s), 1210 (m, sh), 1174 (w), 1096 (m), 1070 (w), 1027 (m), 1013 (s), 1010 (s), 975 (vw), 952 (w, sh), 940 (w), 929 (w, sh), 911 (w), 845 (m, sh), 835 (s), 824 (s), 813 (vs), 804 (s), 763 (w), 735 (vw, br), 718 (vw), 601 (vw), 548 (vw), 453 (vw) cm^{-1}. Anal. Calcd for $C_{20}H_{34}B_2Zr$: C, 62.02; H, 8.85. Found: C, 61.94; H, 8.75.

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Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **2**, **3**, and **4** (17 pages). Ordering information is given on any current masthead page.

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