Cyclic Hydroborate Complexes of Metallocenes. 1. Organodiborate Ring Transformations Promoted by Zirconocene and Hafnocene Dichlorides. Syntheses and Structures of Zirconocene and Hafnocene Boracyclopentane Derivatives

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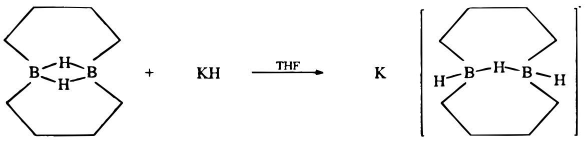
The anion $[H_2B_2(\mu\text{-H})(\mu\text{-C}_4H_8)_2]^-$, **II**, reacts with zirconocene dichloride and with hafnocene dichloride to form $(\eta^5\text{-C}_5H_5)_2ZrCl\{(\mu\text{-H})_2BC_4H_8\}$, **III**, and $(\eta^5\text{-C}_5H_5)_2HfCl\{(\mu\text{-H})_2BC_4H_8\}$, **IV**, complexes, which contain a boracyclopentane ring that is bound to the metal through hydrogen bridges. In these reactions, 0.5 mol of the transannular hydrogen-bridged 10-membered ring compound $B_2(\mu\text{-H})_2(\mu\text{-C}_4H_8)_2$ is also formed. A possible reaction pathway for the formation of these complexes is proposed on the basis of time-lapse ^{11}B NMR spectroscopy. The methyl-substituted complex $(\eta^5\text{-C}_5H_5)_2Zr(CH_3)\{(\mu\text{-H})_2BC_4H_8\}$, **V**, is prepared from the reaction of **III** with CH_3Li. The molecular structure of **III** was reported earlier. The structures of **IV** and **V** are reported here. Crystal data for **IV**: space group $P2_1/n$ (No. 14), $a = 8.565(1)$ Å, $b = 14.786(3)$ Å, $c = 11.120(3)$ Å, $\beta = 96.17(2)°$, $Z = 4$. Crystal data for **V**: space group *Pbca* (No. 61), $a = 8.436(1)$ Å, $b = 16.343(2)$ Å, $c = 20.827(2)$ Å, $Z = 8$.

Introduction

The reaction of $B_2(\mu\text{-H})_2(\mu\text{-C}_4H_8)_2$, **I**, with KH (reaction 1)[1] produces the organodiborate anion $[H_2B_2(\mu\text{-H})(\mu\text{-C}_4H_8)_2]^-$, **II**, which contains a transannular B−H−B bridge. Complex **II** normally functions as a hydride transfer agent.[2] Like alkoxyborohydrides and trialkylborohydrides, it reduces metal carbonyls to metal carbonyl hydrido carbonylate ions,[3] alkyl halides to alkanes,[4] and ketones and aldehydes to alcohols.[4] The very stable and relatively inert organodiborane, **I**,[5] is regenerated in these hydride transfer reactions.

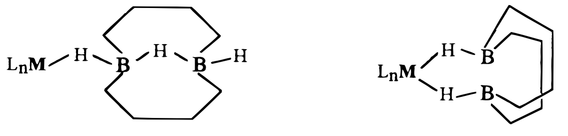


(1)

I **II**

It occurred to us that **II** might also act as a ligand for the formation of hydrogen-bridged complexes with d- and f-block metals. In principle, the two terminal hydrogens could enable compound **II** to coordinate to the metal center through a single hydrogen-bridge bond (structure **1** in Chart 1) or chelate to the metal through two hydrogen-bridge bonds (structure **2** in Chart 1). The potential for **II** to serve as a chelating ligand in metal complexes was particularly appealing to us since the products would be metallo analogues of the the *arachno* borane B_3H_9, which to date has not been isolated.

Chart 1

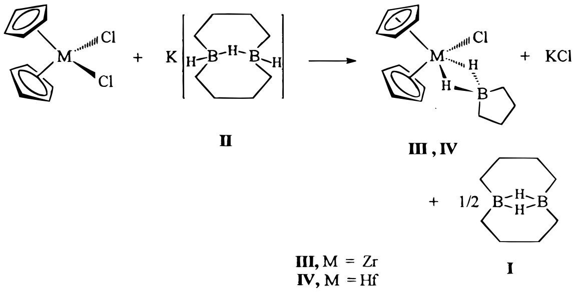


1 **2**

In our attempts to isolate such complexes, a unique type of ring transformation occurred in reaction of **II** with zirconocene and with hafnocene dichlorides. Earlier, in a preliminary report,[6] we described the zirconocene complex $(\eta^5\text{-C}_5H_5)_2ZrCl\{(\mu\text{-H})_2BC_4H_8\}$, **III**, which was isolated from this reaction. Presented here are details of syntheses and structural characterizations of **III** and $(\eta^5\text{-C}_5H_5)_2HfCl\{(\mu\text{-H})_2BC_4H_8\}$, **IV**, formed from the reaction of **II** with zirconocene dichloride and with hafnocene dichloride. Additionally, the reactions of **III** with CH_3Li and C_6H_5Li are described and the structure of $(\eta^5\text{-C}_5H_5)_2Zr(CH_3)\{(\mu\text{-H})_2BC_4H_8\}$, **V**, is also reported.

Results and Discussion

$(\eta^5\text{-C}_5H_5)_2ZrCl\{(\mu\text{-H})_2BC_4H_8\}$, III, and $(\eta^5\text{-C}_5H_5)_2HfCl\{(\mu\text{-H})_2BC_4H_8\}$, IV. In reactions of **II** with the electron-deficient 16-electron metal centers of zirconocene dichloride and hafnocene dichloride, the complexes $(\eta^5\text{-C}_5H_5)_2ZrCl\{(\mu\text{-H})_2BC_4H_8\}$, **III**, and $(\eta^5\text{-C}_5H_5)_2HfCl\{(\mu\text{-H})_2BC_4H_8\}$, **IV,** are formed (reaction 2). The transannular hydrogen-bridged organodiborane, **I**, is also generated.



(2)

II **III, IV** **I**

III, M = Zr
IV, M = Hf

Compounds **III** and **IV** are white solids, stable at room temperature under vacuum. In solution, both compounds are highly soluble in THF and benzene, moderately soluble in

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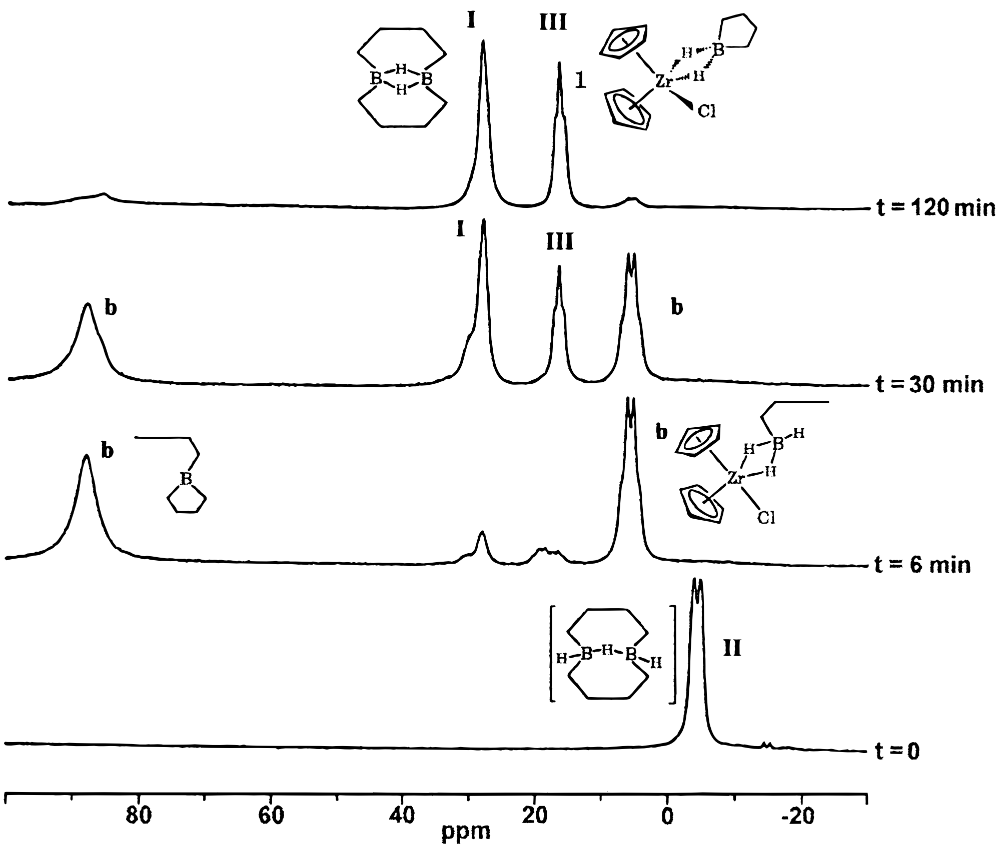

Figure 1. Time-lapse ^{11}B NMR spectra of the reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ with $\text{K}[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]$.

diethyl ether, and insoluble in hexanes. Over time (*ca.* 30 min), THF solutions of **III** and **IV** decompose slightly at room temperature to form a small amount of **I**, metallocene dichloride, and $(\eta^5\text{-C}_5\text{H}_5)_2\text{MH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ (M = Zr, Hf).[7]

NMR spectra are consistent with the boracyclopentane ring, BC_4H_8, binding to the zirconocene and hafnocene atoms through $\text{M}(\mu\text{-H})_2\text{B}$ interactions. Boron-11 NMR spectra of **III** and **IV** consist of a triplet, that arises from coupling with bridge protons, at +16.7 ppm ($J(^{11}\text{B},^1\text{H}) = 56$ Hz) and +12.4 ppm ($J(^{11}\text{B},^1\text{H}) = 55$ Hz), respectively. These resonances are downfield relative to those of their bis(tetrahydroborate) analogs.[8a,b] The ^{1}H NMR spectrum of **III** in the bridge region consists of two broad signals at 0.19 and −2.17 ppm for the two inequivalent bridging hydrogens. Only one bridging hydrogen is clearly visible in the ^{1}H NMR spectrum; it is observed at −0.95 ppm for **IV**. The second resonance, at approximately 1 ppm, is partially obscured by the α-CH_2 signals of the borocyclopentane ring.

While the bridging hydrogens are not equivalent in the static structures of **III** and **IV**, coalescence of the bridge signals occurs at about 50 °C for both compounds where the average signal appears at −0.97 ppm for **III** and 0.15 ppm for **IV**. Neither the ^{1}H nor the ^{11}B NMR spectra provide clues for the exchange pathway. However, it is reasonable to assume that during the process one of the Zr−H−B bonds is broken to permit rotation of the remaining Zr−H−B bond into the site fromerly occupied by the broken Zr−H−B bond followed by reassembly of the broken bond.

The reaction pathway for the formation of **III** has been studied by means of time-elapse boron-11 NMR spectra (Figure 1), which provide insight into the intermediates produced in the formation of **III**. Six minutes after the reaction was initiated, all of the $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$, **II**, was consumed, and two new signals appeared at +88.1 (s) and +5.8 ppm (q, $J(^{11}\text{B},^1\text{H}) = 71$ Hz) in a 1:1 ratio. Over the next 2 h, these signals disappeared while those for $\text{B}_2(\mu\text{-H})_2(\mu\text{-C}_4\text{H}_8)_2$, **I** (+28.2 ppm),[9] and **III** appeared in a 1:1 ratio that remained constant as they increased in intensity with time. Scheme 1 depicts a proposed reaction pathway based upon these spectra. A reasonable initial step would involve coordination of $[\text{H}_2\text{B}_2(\mu\text{-H})(\mu\text{-C}_4\text{H}_8)_2]^-$ to the 16-electron Zr through a hydrogen-bridge bond to form **a**, an 18-electron complex. Departure of Cl^- from **a** and rapid molecular rearrangement could result in the formation of the intermediate **b**. ^{11}B NMR spectra support the presence of **b**. The broad downfield resonance is indicative of a trialkylborane.[1b,10] The coupling constant for the upfield quartet is intermediate for terminal and bridge B−H coupling, which is consistent with the bridge hydrogens rapidly exchanging with the terminal hydrogen. (Rapid exchange of bridging and terminal hydrogens of metallo tetrahydroborates at room temperature is well-known.[8a,11]) Formation of **III** could result in

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[7] Shore, S. G.; Liu, J.; Jordan, G. T., IV; Liu, F.-C.; Meyers, E. A.; Gaus, P. L. Cyclic Organohydroborate Anions as Hydride Transfer Agents in Reactions with Organic and Organometallic Compounds. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: London, 1997; pp 84−91.

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Scheme 1

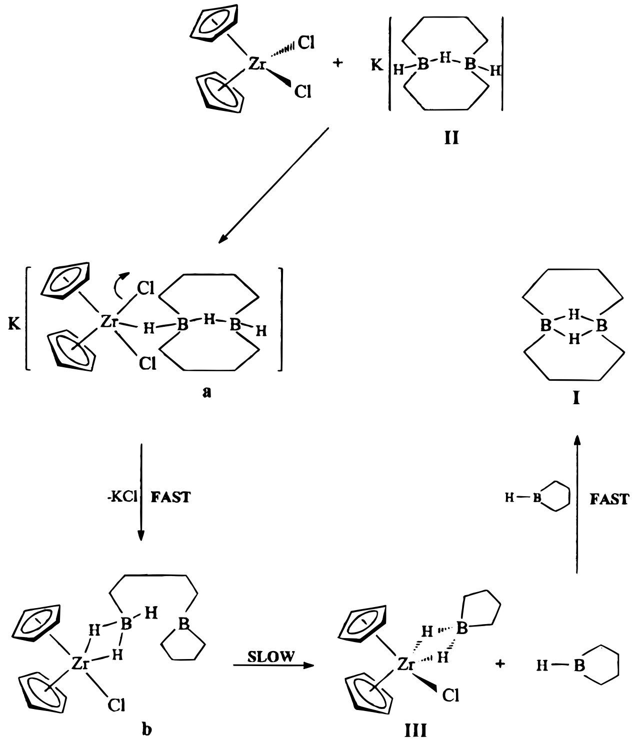


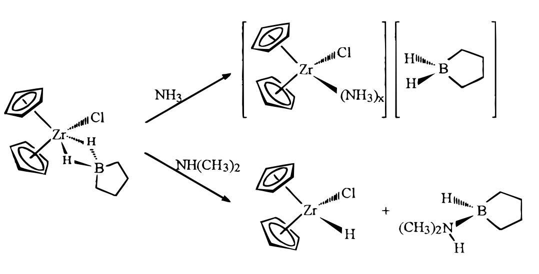
Table 1. ^{11}B NMR Data for the Cleavage of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with Excess Amines

L	δ, ppm	J_{B-H}, Hz[a]
$NH(CH_3)_2$	−2.4	89, d
$NH_2(CH_3)$	−6.3	90, d
NH_3	−20.8	76, t

[a] d = doublet, t = triplet.

elimination of the cyclic borane $HB(C_4H_8)$, which rapidly dimerizes to the transannular hydrogen-bridged organoborane **I**.

Qualitative studies of reactions of **III** with Lewis bases, NH_3, $NH_2(CH_3)$, and $NH(CH_3)_2$, were carried out using the liquid Lewis base as the solvent (Table 1). In ammonia, the bridge system undergoes heterolytic cleavage at −40 °C to yield $[H_2BC_4H_8]^-$ and the solvent-separated cation $[(\eta^5\text{-}C_5H_5)_2ZrCl(NH_3)_x]^+$ (reaction 3a). Evidence for the ionic product is given by a clean ^{11}B NMR spectrum which is a sharp triplet at −20.8 ppm ($J(^{11}B,^1H)$ = 76 Hz) at −40 °C that is assigned to $[H_2BC_4H_8]^-$. This reaction parallels the unsymmetrical cleavage of B_2H_6 by NH_3 to give $[BH_2(NH_3)_2][BH_4]$.[12] The hydrogen-bridge system of **III** is cleaved homolytically by methylamines (reaction 3b). The ^{11}B NMR spectrum for the reaction with $NH(CH_3)_2$ consists of a doublet at −2.4 ppm ($J(^{11}B,^1H)$ = 89 Hz) at −40 °C that is assigned to $NH(CH_3)_2HBC_4H_8$.



(3a)

(3b)

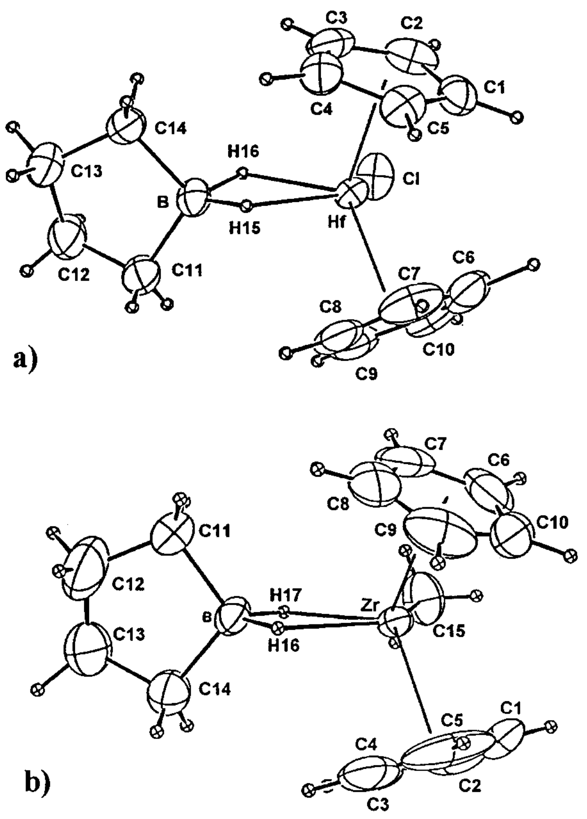
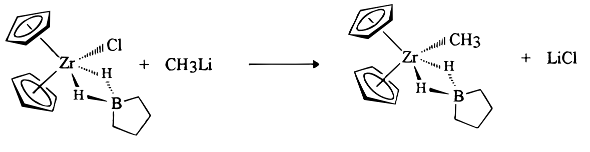


Figure 2. Molecular structures of (a) $(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$ and (b) $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$ (50% probability thermal ellipsoids).

$(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$. The reaction of **III** with CH_3Li in THF (reaction 4) produces **V**. While suitable crystals were obtained for a single-crystal X-ray analysis of **V**, a side product of $(\eta^5\text{-}C_5H_5)_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$[7] was also formed which could not be fully separated from **V** to give pure **V** other than a relatively small number of crystals. Compound **V** is very soluble in THF and benzene and slightly soluble in hexanes.



(4)

The ^{11}B NMR spectrum of **V** is a broad triplet at 20.1 ppm ($J(^{11}B,^1H)$ = 61 Hz). This resonance is 3.4 ppm further downfield from that of the parent complex **III**. Two broad signals of the inequivalent bridging hydrogens are found at −1.51 and −3.52 ppm in the ^1H NMR spectrum. The resonance of the methyl group appears at −0.12 ppm, which is consistent with $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ (−0.39 ppm)[13] and $(\eta^5\text{-}C_5H_5)_2ZrCl(CH_3)$ (0.42 ppm).[15]

From the reaction of **III** with C_6H_5Li at −45 °C was obtained an oily residue that appeared to contain the phenyl-substituted metallocene $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)\{(\mu\text{-}H)_2BC_4H_8\}$ on the basis of its NMR spectra. The ^{11}B NMR spectrum in pentane shows a triplet at 24 .1 ppm ($J(^{11}B,^1H)$ = 55 Hz). The bridge hydrogens are observed as two broad signals at −0.71 and −3.34 ppm in the ^1H NMR spectrum.

X-ray Structures of $(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$, IV, and $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$, V. The molecular

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Table 2. Crystallographic Data for $(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$, $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$, and $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$

empirical formula	$C_{14}H_{20}BClHf$	$C_{14}H_{20}BClZr$	$C_{15}H_{23}BZr$
fw	413.06	325.80	305.38
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	*Pbca* (No. 61)
a, Å	8.565(1)	8.594(1)	8.436(1)
b, Å	14.786(3)	14.807(3)	16.343(2)
c, Å	11.120(2)	11.170(3)	20.827(2)
β, deg	96.17(1)	96.42(2)	90
V, Å^3	1400.1(4)	1412.6(5)	2871.4(7)
Z	4	4	8
ρ(calcd), g cm^{-3}	1.959	1.532	1.413
T, °C	−60	−60	−60
λ, Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	75.5	9.3	7.3
transm coeff, %	30.85−99.96	94.03−99.90	92.26−99.96
$R_F{}^a$	0.017	0.018	0.025
$R_{wF}{}^b$	0.022	0.027	0.030
k_c	0.02	0.02	0.02

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. [c] $w = [\sigma(|F_o|)^2 + (k|F_o|)^2]^{-1}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$, $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$, and $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$

Bond Lengths

$(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$		$(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$		$(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$	
Hf−Cl	2.474(1)	Zr-Cl	2.494(7)	Zr−C15	2.286(7)
av Hf−C(1−5)[a]	2.471[9]	av Zr−C(1−5)[a]	2.491[7]	av Zr−C(1−5)[a]	2.486[9]
av Hf−C(6−10)[a]	2.487[3]	av Zr−C(6−10)[a]	2.501[4]	av Zr−C(6−10)[a]	2.498[10]
Hf−B	2.527(5)	Zr−B	2.572(3)	Zr−B	2.560(6)
Hf−H15	1.85(7)	Zr−H15	2.00(3)	Zr−H16	1.96(4)
Hf−H16	2.00(6)	Zr−H16	1.97(3)	Zr−H17	2.03(5)
C11−B	1.601(7)	C11−B	1.611(4)	C11−B	1.611(8)
C11−C12	1.516(8)	C11−C12	1.517(4)	C11−C12	1.487(9)
C12−C13	1.514(8)	C12−C13	1.508(5)	C12−C13	1.40(1)
C13−C14	1.526(7)	C13−C14	1.521(5)	C13−C14	1.51(1)
C14−B	1.626(7)	C14−B	1.606(4)	C14−B	1.605(9)
B−H15	1.19(6)	B−H15	1.24(2)	B−H16	1.20(4)
B−H16	1.18(6)	B−H16	1.22(3)	B−H17	1.11(5)

Angles

$(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$		$(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$		$(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$	
Cl−Hf−B	100.4(1)	Cl−Zr−B	100.47(7)	C15−Zr−B	98.9(3)
Cl−Hf−H15	126(2)	Cl−Zr−H15	128.2(7)	C15−Zr−H16	126(1)
Cl−Hf−H16	75(2)	Cl−Zr−H16	73.7(8)	C15−Zr−H17	74(1)
H15−Hf−H16	52(2)	H15−Zr−H16	55(1)	H16−Zr−H17	51(2)
C12−C11−B	103.2(4)	C12−C11−B	105.0(3)	C12−C11−B	104.1(5)
C11−C12−C13	105.8(4)	C11−C12−C13	106.8(3)	C11−C12−C13	110.5(6)
C12−C13−C14	106.4(4)	C12−C13−C14	106.2(3)	C12−C13−C14	108.9(6)
C13−C14−B	105.0(4)	C13−C14−B	102.2(3)	C13−C14−B	104.1(6)
C11−B−C14	104.3(4)	C11−B−C14	105.0(3)	C11−B−C14	103.9(5)
H15−B−H16	92(4)	H15−B−H16	97(2)	H16−B−H17	97(3)
Hf−H15−B	111(4)	Zr−H15−B	102(2)	Zr−H16−B	106(2)
Hf−H16−B	103(4)	Zr−H16−B	105(2)	Zr−H17−B	106(3)

[a] The standard deviation (σ_l) for the average bond length of Hf−C is calculated according to the equations[19]

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

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

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.

structures of **IV** and **V** were determined by single-crystal X-ray diffraction analyses, and they are shown in Figure 2. Crystallographic data and selected bond distances and bond angles are given in Tables 2 and 3. For purposes of comparison, data for **III**, the structure of which was reported earlier,[6] are also given in these tables.

The molecular structure of **IV** is nearly identical to that of complex **III**, which was reported earlier [6] and is not unexpected.[15] The structures of **III** and **IV** each consist of a Cp_2-MCl fragment bound to a BC_4H_8 ring through two hydrogen bridges, which were located, and their positions were refined. The Zr−B and Hf−B distances of 2.572(3) and 2.537(5) Å, respectively, are all consistent with other systems with bidentate Zr−H−B bridges.[16] For the hydrogen-bridge system of **III** and **IV** the metal−H distances range from 1.85(7) to 2.00(6) Å, while the B−H distances range from 1.18(6) to 1.24(2) Å. These distances are close to those reported for $(\eta^5\text{-}C_5H_5)_2Zr(H)$-$(BH_3CH_3)$.[16a]

The geometry around the metal in compounds **III** and **IV** is best described as a distorted tetrahedron consisting of a coordination sphere of B, Cl, and the centroids of the two Cp rings. The centroid−M−centroid angle is 129.3° and the Cl−M−B angle is approximately 100° in both compounds. The Cp rings are in an eclipsed conformation. The Zr−C distance for the Cp rings range from 2.469(3) to 2.508(3) Å, with an average distance of 2.50 Å in complex **III**. In complex **IV**, the Hf−C distances range from 2.444(5) to 2.497(5) Å, with an average distance of 2.48 Å. In both structures, the Cl is displaced from the least-squares plane through M, B, H15, H16 by 0.409(1) Å in **III** and 0.532(1) Å in **IV**.

The configuration around the metal center in **V** is like that in structures **III** and **IV**. The Zr−B distance of 2.560(6) Å is 0.01 Å shorter than that in **III**. The Zr−H distances are 1.96(4) and 2.03(5) Å, while the B−H distances are 1.11(5) and 1.20(4) Å. The Cp rings are eclipsed but are not as symmetrically aligned as in **III**. The centroid−Zr−centroid angle is opened up, slightly, to nearly 133°. The Zr−C distances for the Cp rings range from 2.520(6) to 2.462(7) Å, with an average distance of 2.49 Å. The Zr−C15 distance is 2.286(7) Å which is comparable to Zr−C distance of $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$ (2.25 Å).[17] This methyl carbon resides 0.075(5) Å out of the least-squares plane defined by Zr, B, H16, and H17.

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. $K[B_2(C_4H_8)_2H_3]$ was prepared by a literature procedure.[1] Cp_2ZrCl_2, Cp_2HfCl_2, and CH_3Li (1.4 M solution in diethyl ether) were purchased from Aldrich and used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. proton (δ(TMS) = 0.00 ppm) and ^{11}B NMR ($\delta(BF_3\cdot Et_2O$ in $C_6D_6)$ = 0.00 ppm) spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 and 80.253 MHz at 303 K, respectively. 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. 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 based on measured ψ scans was applied.

The structures were solved by employing a combination of MULTAN 11/82 and difference Fourier techniques with analytical scattering factors used throughout the structure refinement and both real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms. All the crystallographic computations were carried out on a DEC Vax station 3100 computer, using the MoLEN[18] suite of programs. After all non-hydrogen atoms were located and refined, bridging hydrogen atoms between zirconium and the boron center were located from difference Fourier maps. The bridge hydrogen displacement parameters were refined for compound **III** but fixed for compound **IV**. Remaining hydrogen atoms on Cp rings, the methyl group, and the C_4H_8 fragment were placed at calculated positions by assuming ideal geometries with d(C−H) = 0.95 Å and B(H) = 1.3B(C) Å^2. Then with the positional and thermal parameters of all hydrogen atoms fixed, the non-hydrogen atoms were refined anisotropically. New hydrogen positions were calculated again, and this procedure was repeated until the parameters of non-hydrogen atoms were refined to convergence (final shift/error ≤ 0.03).

Preparation of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$. A solution of $K[B_2(C_4H_8)_2H_3]$ (4.49 mmol in 20 mL of THF) was added dropwise to 1.23 g (4.21 mmol) of Cp_2ZrCl_2 dissolved in 20 mL of THF. The solution was stirred overnight at room temperature and then filtered. THF and $B_2(\mu\text{-}H)_2(C_4H_8)_2$ were removed under dynamic vacuum. The resulting pale yellow solid was dissolved in a minimal amount of THF, and the solution was layered with hexanes at room temperature. Colorless crystals were formed, which were washed with hexanes and dried under vacuum to give 0.977 g (3.00 mmol) of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$, **III**, 71.3% yield. Crystals suitable for X-ray structure determination were grown from THF solution at −78 °C. ^{11}B NMR (THF-d_8): δ 16.7 (t, J_{B-H} = 56 Hz). ^1H NMR (THF-d_8): δ 6.34 (s, Cp), 1.44 (br s, 4H, β-H), 0.92 (br s, 4H, α-H), 0.19 (br s, μ-H), −2.17 (br s, μ-H). IR (KBr): 3122 (s), 3107 (s), 3090 (m), 2933 (s), 2919 (s), 2851 (s), 2811 (m), 2759 (m), 2558 (br, w), 2320 (vw), 2278 (w), 2065 (s), 2004 (vs), 1925 (s), 1905 (s), 1852 (s), 1368 (vs), 1182 (m), 1123 (m), 1065 (w), 1014 (s), 957 (m), 928 (w), 808 (vs), 607 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{20}BClZr$: C, 51.61; H, 6.19; B, 3.32; Cl, 10.88; Zr, 28.00. Found: C, 51.43; H, 6.15; B, 3.21; Cl, 10.99; Zr, 27.34.

Preparation of $(\eta^5\text{-}C_5H_5)_2HfCl\{(\mu\text{-}H)_2BC_4H_8\}$. A solution of $K[B_2(C_4H_8)_2H_3]$ (1.07 mmol in 20 mL of THF) was added dropwise to 0.379 g (1 mmol) of Cp_2HfCl_2 in 20 mL of THF. The solution turned cloudy immediately, and the reaction mixture was stirred overnight and then filtered. THF and $B_2(\mu\text{-}H)_2(C_4H_8)_2$ were removed under dynamic vacuum. The resulting white solid was dissolved in a minimal amount of THF, and the solution was layered with hexanes at 0 °C to produce colorless crystals. The crystals were washed with hexanes and dried under vacuum to give 0.175 g (0.424 mmol) of $(\eta^5\text{-}C_5H_5)_2Hf(Cl)\{(\mu\text{-}H)_2BC_4H_8\}$, **IV**, 42.4% yield. Crystals suitable for X-ray structure determination were grown from THF solution at −78 °C. ^{11}B NMR (THF-d_8): δ 12.4 (t, J_{B-H} = 55 Hz). ^1H NMR (THF-d_8): δ 6.26 (s, Cp), 1.45 (br s, 4H, β-H), 0.85 (br s, 4H, α-H), −0.95 (br s, μ-H). IR (KBr): 3123 (s), 3109 (s), 3092 (m), 2934 (s), 2920 (s), 2850 (s), 2812 (m), 2582 (br, w), 2331 (w), 2278 (w), 2067 (s), 2010 (vs), 1943 (s), 1920 (s), 1878 (s), 1821 (m), 1407 (vs), 1183 (m), 1124 (m), 1056 (w), 1013 (s), 958 (m), 930 (w), 811 (vs), 610 (w) cm^{-1}. Anal. Calcd for $C_{14}H_{20}BClHf$: C, 40.71; H, 4.88; B, 2.62; Cl, 8.58. Found: C, 40.18; H, 4.91; B, 1.30; Cl, 8.48.

Preparation of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$. In a two-neck round-bottom flask attached to a vacuum extractor, 0.70 mmol of $LiCH_3$ (0.5 mL of 1.4 M solution) was dissolved in 8 mL of THF. A tip-tube containing 0.229 g (0.703 mmol) of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ was connected to the second neck of the reaction flask. Under stirring at −45 °C, methyllithium was slowly added to the $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ solution. The reaction mixture was warmed to 0 °C over a 3 h period and then stirred for an additional 10 min at room temperature. The solvent was quickly removed under vacuum, behind a white solid, which was extracted with 10 mL of ether. Slow evaporation of the solvent produced a white crystalline solid of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)\{(\mu\text{-}H)_2BC_4H_8\}$, **V**. ^{11}B NMR (THF-d_8): δ 20.1 (t, J_{B-H} = 61 Hz). ^1H NMR (THF-d_8): δ 6.05 (s, Cp), 1.36 (br s, 4H, β-H), 0.80 (br s, 4H, α-H), −0.12 (s, CH_3), −1.51 (br s, μ-H), −3.52 (br s, μ-H). IR (KBr): 3118 (w), 3102 (w), 2923 (s), 2911 (s), 2844 (s), 2811 (m), 2578 (br, w), 2319 (vw), 2278 (vw), 2067 (m), 1995 (s), 1967 (s), 1906 (m), 1856 (m), 1818 (m), 1405 (vs), 1177 (m), 1116 (m), 1055 (vw), 1015 (s), 958 (m), 954 (m), 915 (vw), 800 (vs) cm^{-1}.

Reaction of III with C_6H_5Li. To a 15 mL Et_2O/THF (2:1) solution of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ (0.430 g, 1.32 mmol) was added 10 mL of 0.14 M LiC_6H_5 over a 5 min period at −45 °C. The reaction was stirred for 2.5 h at −45 °C and 1 h at 0 °C under a continuous flow of N_2. After stirring, the solvent was removed under vacuum,

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leaving an oily residue. Repeated extraction of the oil with ether or pentane failed to produce a crystalline solid. ^{11}B NMR (pentane): δ 24.1 (t, $J_{B-H} = 55$ Hz). ^{11}B NMR (THF-d_8): δ 22.0 (br). ^{1}H NMR (THF-d_8): δ 7.55−6.72 (mult), 6.06 (s, Cp), 144 (br s, 4H, β-H), 0.93 (br s, 4H, α-H), −0.71 (br s, μ-H), −3.34 (br s, μ-H).

Reactions of III with Amines. In each reaction, *ca*. 0.1 mmol of $(\eta^5\text{-}C_5H_5)_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ was added to a 5 mm NMR tube connected to a 9 mm Solv-Seal joint. The corresponding amine (0.9 mL) was condensed into the tube at −196 °C. Each NMR tube was flame-sealed and kept at −196 °C until the tube was ready to be placed into the precooled NMR probe (−40 °C). ^{11}B NMR ($NH(CH_3)_2$): δ −2.4 (d, $J_{B-H} = 89$ Hz). ^{11}B NMR (NH_2CH_3): δ −6.3 (d, $J_{B-H} = 90$ Hz). ^{11}B NMR (NH_3): δ −20.8 (d, $J_{B-H} = 76$ Hz).

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Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **IV** and **V** (13 pages). For supporting information for **III**, see ref 6. Ordering information is given on any current masthead page.

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