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Cyclic Organohydroborate Complexes of Metallocenes. VII. Synthesis, Structure, and Fluxional Behavior of $Cp_2ZrX\{(\mu\text{-}H)_2BC_8H_{14}\}$ (X = H, D, Cl)

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The reaction of $K[H_2BC_8H_{14}]$ with Cp_2ZrCl_2 in a 1:1 molar ratio afforded $Cp_2ZrCl\{(\mu\text{-}H)_2BC_8H_{14}\}$, **1**, which when reacted with KH yielded $Cp_2ZrH\{(\mu\text{-}H)_2BC_8H_{14}\}$, **2**. These complexes were structurally characterized by single-crystal X-ray analysis. Partially deuterated **1** and **2**, complexes $Cp_2ZrCl\{(\mu\text{-}D)(\mu\text{-}H)BC_8H_{14}\}$, **3**, and $Cp_2ZrD\{(\mu\text{-}H)_2BC_8H_{14}\}$, **4**, were prepared. ^2H NMR spectra revealed that in complex **3**, which contains a terminal chloride on zirconium, no exchange of bridge and Cp hydrogens occurred. However, in complex **4**, which includes a terminal hydrogen on zirconium, there was facile mixing of terminal, bridge, and Cp-hydrogens. Furthermore, exchange of terminal zirconium−hydrogen with bridge hydrogen was more rapid than exchange with the Cp-hydrogen. Additionally, this fluxional behavior occurred even at room temperature and in the solid state. Variable-temperature ^1H NMR studies are consistent with these results of dynamic hydrogen exchange in complexes **1** and **2**. The complexes $Cp_2Nb\{(\mu\text{-}H)_2BC_8H_{14}\}$, **7**, and $Cp_2Nb\{(\mu\text{-}D)(\mu\text{-}H)BC_8H_{14}\}$, **8**, have no terminal hydrogen on niobium, and there is no exchange between bridging hydrogens and Cp-hydrogens. The possible participation of the 9-BBN unit ($\{(\mu\text{-}H)_2BC_8H_{14}\}$) hydrogens in dynamic exchange was examined for **2**, the 9-BBN dimer ($(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$), and the 9-BBN anion ($[H_2BC_8H_{14}]^-$) through the partially deuterated complexes $Li[(D)(H)BC_8H_{14}]$, **5**, and $(C_8H_{14}B)(\mu\text{-}D)(\mu\text{-}H)(BC_8H_{14})$, **6**.

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Introduction

Although a number of transition metal tetrahydroborate complexes have been prepared, characterized, and studied, relatively little is known concerning related metal organohydroborate complexes.[1,2] Recently, we have focused on the chemistry of the cyclic organohydroborate anions, $[H_2B_2(\mu\text{-}H)(\mu\text{-}C_4H_8)_2]^-$ (a trans-annular hydrogen-bridged 10-membered ring anion), $[H_2BC_5H_{10}]^-$, and $[H_2BC_8H_{14}]^-$ (the hydroborate anion of the 9-BBN dimer, $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$), and their metallocene derivatives.[3−5] A point of continuing interest is the intramolecular dynamic hydrogen interchange in metallocene derivatives of these hydroborate ligands.

It is well recognized that dynamic intramolecular exchange occurs between terminal metal hydrides and hydrogens that bridge metal and boron atoms in metal tetrahydroborate complexes.[6] However, examples of metallocene complexes in which Cp-hydrogens are also involved in the exchange process are rare.[7,8] Our studies of the organohydroborates $Cp_2ZrH\{(\mu\text{-}H)_2BR_2\}$ (R_2 =

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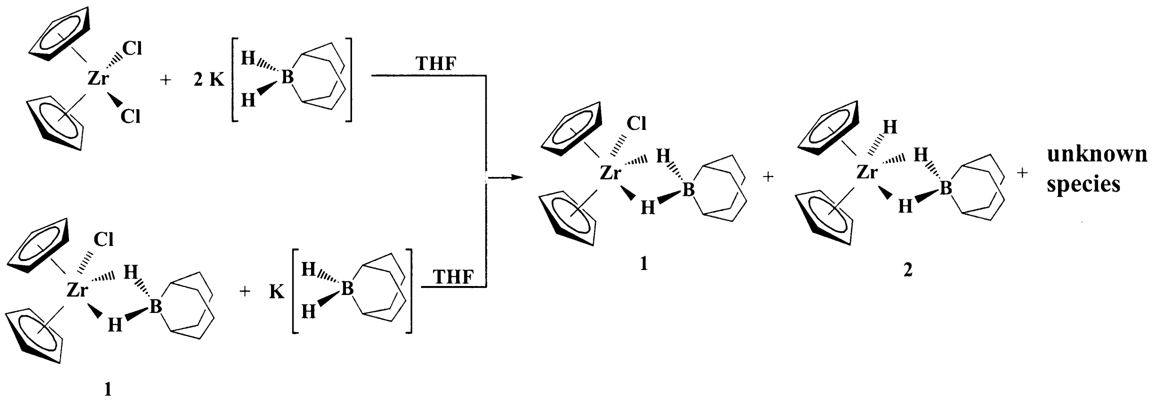
Scheme 1

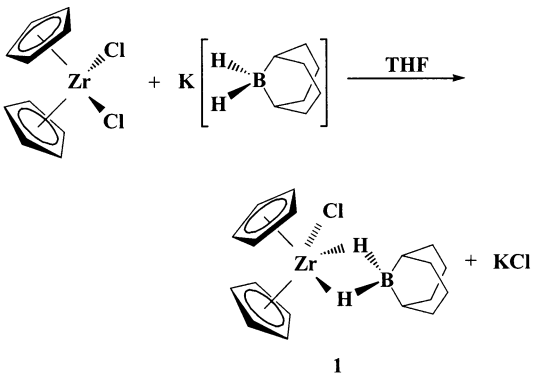


C_4H_8,[9] C_5H_{10}[3c]) indicate that exchange occurs between Zr-H, Zr-H-B, and Cp-H hydrogens, based on temperature-dependent ^{1}H NMR spectra. Additionally, activation parameters for the bridge hydrogen exchange and bridge-terminal hydrogen exchange were determined.[9b] Earlier work[7] reported dynamic intramolecular hydrogen exchange in $Cp_2ZrH\{(\mu\text{-H})_2BH_2\}$. Although our results are generally consistent with this earlier work, there is a significant difference. The earlier study observed that hydrogen interchange involving Cp-H and borohydride hydrogens is more facile than interchange involving Zr-H and borohydride hydrogens.[7] [Due to its fluxional character, on the ^{1}H NMR time scale bridging and terminal hydrogens of the borohydride ligand in $Cp_2ZrH\{(\mu\text{-H})_2BH_2\}$ are equivalent.] On the other hand in the case of the cyclic organohydroborate derivatives, temperature-dependent proton NMR spectra indicate that terminal Zr-H and bridge Zr-H-B hydrogens exchange more rapidly than terminal Zr-H and Cp-hydrogens exchange.[3c,9]

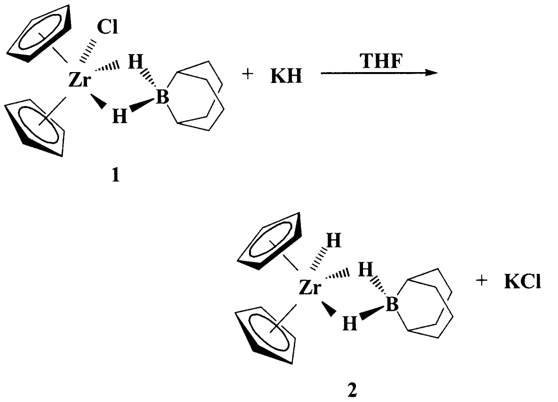
Previously, we proposed that the exchange pathway for bridging hydrogens with Cp-hydrogens requires the presence of a terminal Zr-H hydrogen to facilitate the exchange process.[3c] In the present study we are interested in testing this proposition. We pose the following fundamental question for these metallocene cyclic organohydroborates: Is a terminal hydride on the metal necessary for dynamic intramolecular exchange between bridge and Cp-hydrogen? It is also of interest to determine if the β and γ C-H hydrogens of the 9-BBN unit, $\{(\mu\text{-H})_2BC_8H_{14}\}$, in **2** exchange with the bridge hydrogens since there is precedence for C-H hydrogens exchanging with bridge hydrogens in the 9-BBN dimer, $(C_8H_{14}B)(\mu\text{-H})_2(BC_8H_{14})$.

Results and Discussion

Preparation and NMR Spectra of Complexes 1−6. The reaction between $K[H_2BC_8H_{14}]$ and Cp_2ZrCl_2 in a 1:1 molar ratio produces $Cp_2ZrCl\{(\mu\text{-H})_2BC_8H_{14}\}$, **1**, in an 80% yield (reaction 1). However, the disubstituted complex $Cp_2Zr\{(\mu\text{-H})_2BC_8H_{14}\}_2$ could not be prepared from either the reaction of $K[H_2BC_8H_{14}]$ with Cp_2ZrCl_2 in a 2:1 molar ratio or the reaction of **1** with $K[H_2BC_8H_{14}]$ in a 1:1 molar ratio. Instead mixtures of **1** and $Cp_2ZrH\{(\mu\text{-H})_2BC_8H_{14}\}$), **2**, plus an unidentified boron-containing complex, which possesses an ^{11}B NMR resonance at 6.3 ppm, are produced (Scheme 1). On the other hand, the reaction between $K[H_2BC_5H_{10}]$ and Cp_2ZrCl_2 in a 2:1 molar ratio generates $Cp_2Zr\{(\mu\text{-H})_2BC_5H_{10}\}_2$.[3c] This difference in results is attributed to the larger steric bulk of the $[H_2BC_8H_{14}]^-$ ligand compared to $[H_2BC_5H_{10}]^-$. Treatment of complex **1** with KH in THF at room temperature affords complex **2** in 90% yield (reaction 2).



(1)



(2)

Complexes **1** and **2** are colorless. The solids are stable under a nitrogen atmosphere at room temperature for

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several weeks. However, decomposition occurs when their solutions are exposed to air. Interestingly, when the colorless solution of **2** is stored under nitrogen for an extended period of time at room temperature, the color gradually changes to a faint red, possibly indicating decomposition or the formation of a nitrogen-coordinated compound.[10]

The ^{11}B NMR spectra of **1** and **2** in toluene consist of a broad triplet at δ 17.7 and 32.5 ppm, respectively. These resonances are further downfield from the signal at -15.9 ppm ($^1J_{BH} = 75$ Hz) produced by the parent salt, K[$H_2BC_8H_{14}$], but are similar to the signals of analogous complexes $Cp_2ZrX\{(\mu\text{-}H)_2BR_2\}$ (X = Cl, H; $R_2 = C_4H_8$, C_5H_{10}).[3]

In the ^{1}H NMR spectrum of **1**, the two inequivalent bridging hydrogens give rise to two broad signals at 0.55 and -2.40 ppm. Comparable signals of the two bridging hydrogens appear at -3.17 and -4.12 ppm in the ^{1}H NMR spectrum of **2**. The terminal hydrogen of **2** produces a signal at 3.99 ppm that falls within the range observed for the terminal hydrides of other zirconocene hydroborate compounds, $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ (3.95 ppm),[3b] $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ (4.06 ppm),[3c] $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ (4.16 ppm),[8a] and $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$ (4.53 ppm).[11] Assignment of the α-, β-, and γ-protons of the $\{(\mu\text{-}H)_2BC_8H_{14}\}$ units in **1** and **2** is accomplished by ^{13}C NMR, ^{13}C gated decoupled (GD) NMR, and two-dimensional ^{1}H$-^{13}$C correlation NMR spectra (heteronuclear multiple quantum coherence, HMQC). Since the spectral results are similar for both **1** and **2**, only the data for **2** are discussed below. In the ^{13}C and ^{13}C GD NMR spectra, the triplets at 33.9 and 25.3 ppm are attributed to the β- and γ-carbons, respectively. The α-carbon resonance, δ 29.9 ppm, appears as a broad signal since it is bonded to the quadrupolar ^{11}B nucleus. From the HMQC spectrum, the two sets of proton peaks at 2.11 and 1.73 ppm are assigned to the γ-hydrogens, the resonances at 1.91 and 1.83 ppm are identified as the β-hydrogens, and the chemical shift of the α-hydrogens is 1.39 ppm. The α-hydrogen resonance is upfield relative to the γ-hydrogens in the ^{1}H NMR spectra of complexes **1** and **2**. But for the 9-BBN dimer, $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$, the signal of the α-hydrogens appears at 1.62 ppm between two sets of resonances for the γ-hydrogens (1.95 and 1.51 ppm, based upon their ^{1}H$-^{13}$C HMQC cross-peak). The Cp-hydrogens of complexes **1** and **2** are visible at 5.75 and 5.58 ppm, respectively.

The partially deuterated analogues of **1** and **2**, $Cp_2ZrCl\{(\mu\text{-}D)(\mu\text{-}H)BC_8H_{14}\}$, **3**, and $Cp_2ZrD\{(\mu\text{-}H)_2BC_8H_{14}\}$, **4**, are prepared by the following methods. Compound **3** is formed from the reaction of Li[(D)(H)BC_8H_{14}], **5**, with Cp_2ZrCl_2 (analogous to reaction 1), and complex **4** is prepared by the reaction of LiD with **1** (analogous to reaction 2). Complex **5** is prepared from the reaction of LiD with the 9-BBN dimer. Partially deuterated 9-BBN dimer, $(C_8H_{14}B)(\mu\text{-}D)(\mu\text{-}H)(BC_8H_{14})$, **6**, is obtained by abstracting hydride ion from **5** with $B(C_6F_5)_3$.

Complex **5** was characterized by NMR and IR spectroscopies. Integration of the proton signals of **5** indicates the presence of two THF molecules that are probably coordinated to the Li$^+$ cation. This is consistent with the structure determined by single-crystal X-ray analysis.[13] From the ^{1}H{^{11}B} NMR spectrum of **5**, the signal at 0.77 ppm is assigned to the bridging hydrogens.

According to the ^{13}C and ^{13}C GD NMR spectra of **6**, signals at 33.7 ppm (triplet in the ^{13}C-GD NMR spectrum) and 24.4 ppm (triplet in the ^{13}C-GD NMR spectrum) are designated as the β- and γ-carbons, respectively. The α-carbon, bonded to the boron atom, produces a broad signal at about 20.2 ppm. On the basis of a proton-detected ^{1}H$-^{13}$C correlation (HMQC) spectrum, the different types of hydrogens in **6** are assigned. The β-hydrogens are correlated to two multiplets at 1.85 and 1.67 ppm; the γ-hydrogens correspond to two multiplets at 1.96 and 1.51 ppm; and the α-hydrogens appear as a singlet at 1.63 ppm. The bridging hydrogen of **6** is detected at 1.46 ppm by comparing the ^{1}H and ^{1}H{^{11}B} NMR spectra.

Intramolecular Hydrogen Exchange. The Effect of a Terminal Substituent, X (X = Cl, H), on Zirconium. Our earlier studies showed that intramolecular hydrogen exchange occurs among the Zr-H-B bridging hydrogens, Zr-H terminal hydride, and Cp-hydrogens in $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$[3c] and $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$.[9] Here our principal goal is to determine if dynamic hydrogen exchange takes place between bridging hydrogens and Cp-hydrogens when the terminal H$-$ on Zr is replaced by Cl.

Complexes **1** ($Cp_2ZrCl\{(\mu\text{-}H)_2BC_8H_{14}\}$) and **2** ($Cp_2ZrH\{(\mu\text{-}H)_2BC_8H_{14}\}$) were investigated for dynamic hydrogen exchange. Useful ^{1}H NMR spectra of complex **1** could be obtained only below 330 K due to noticeable decomposition of the complex above that temperature. In the narrow temperature range studied (300$-$330 K), the two bridging hydrogens' signals broaden with increasing temperature but do not fully average; the signal from the Cp-hydrogens does not appear to change. Thus ^{1}H NMR spectra suggest that the only significant dynamic hydrogen interchange occurs between the bridging hydrogens. Above 330 K, signals at 5.86 and 5.58 ppm in the ^{1}H NMR spectra and at 27.3 ppm in the ^{11}B spectrum indicate the formation of complex **2**, zirconocene dichloride,[14] and 9-BBN dimer,[15] respectively, as decomposition products. The ^{2}H NMR spectrum of **3** in toluene reveals only two signals for the bridging deuterium Zr-D-B at room temperature (Figure 1a). After heating **3** at 318 K for 10 h, a new signal is present at 1.4 ppm (Figure 1b), which indicates that **3** has partially decomposed to 9-BBN dimer. No signal corresponding to the presence of Cp-deuterium is observed after heating complex **3**. This confirms that the Cp-hydrogens do not exchange with bridging hydrogens in this complex, and is consistent with what the tem-

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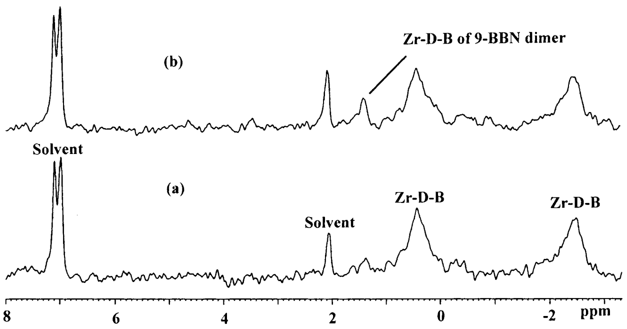

Figure 1. ^{2}H NMR spectra of **3** in toluene (a) before heating and (b) after heating at 318 K for 10 h.

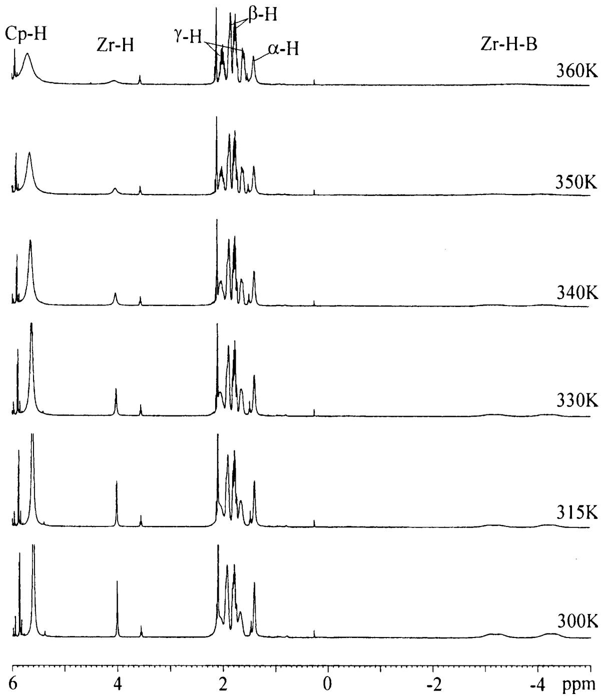

Figure 2. Variable-temperature ^{1}H NMR spectra of **2** in toluene-d_8.

perature-dependent ^{1}H NMR spectra of the undeuterated chloro complex **1** imply.

Proton NMR spectra of complex **2** as a function of temperature are shown in Figure 2. As the temperature rises from ambient, the two bridging hydrogen signals coalesce and then broaden into the baseline. At the same time, the signals assigned to the terminal hydrogen on zirconium and the Cp-hydrogens noticeably broaden. These spectra are in accord with variable-temperature ^{1}H NMR spectra of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$[9] and $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$.[3c] A point of interest here is the fact that the Cp, Zr-H, and Zr-H-B hydrogens are exchanging at temperatures at which **1** does not even display full coalescence of the bridging hydrogen resonances.

The ^{2}H NMR spectrum of **4** in toluene reveals the presence of Zr-D and Zr-D-B (Figure 3a), thus denoting that terminal and bridging hydrogen exchange occurs at room temperature. But there is no evidence for Cp-deuterium in this sample (Figure 3a).

However, upon heating this sample **4** at 318 K for 1 h, the intensities of the terminal and bridging deuterium resonances decrease and a new signal emerges at the chemical shift for Cp-deuterium (Figure 3b). These observations signify that the terminal hydrogen exchanges more rapidly with the bridging hydrogens than with Cp-hydrogens. This result is in accord with preliminary observations of partially deuterated $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$.[9a] Intramolecular hydrogen exchange also occurs in the solid state at room temperature. When an unheated sample of solid **4**, which gives no evidence for Cp-deuterium, is stored in the drybox for several weeks and then dissolved in toluene at room temperature, its ^{2}H NMR spectrum displays the Cp-deuterium resonance in addition to terminal and bridging deuterium resonances.

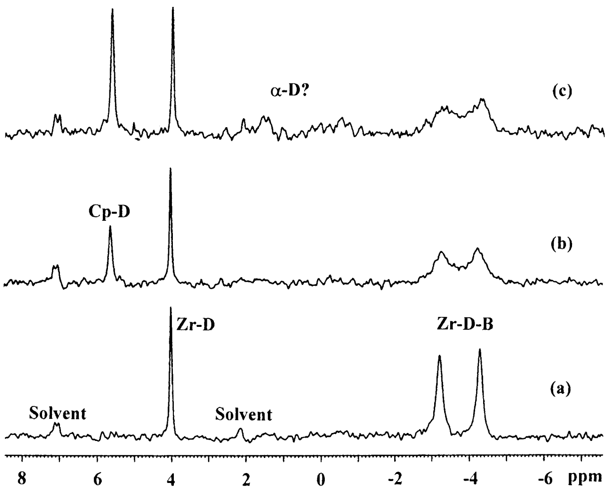

Figure 3. ^{2}H NMR spectra of **4** in toluene (a) before heating, (b) after heating at 318 K for 1 h, and (c) after heating at 358 K for another 1 h.

It is also of interest to determine if bridge hydrogen exchanges with Cp-hydrogen in the absence of a terminal group on the metal. Proton NMR spectra of complex **7**, a niobocene cyclic organohydroborate derivative, were obtained in the temperature range 300−363 K. The spectra show no evidence for exchange of bridge hydrogens with Cp-hydrogens or decomposition. In this molecule there is only one bridging hydrogen signal, due to the mirror symmetry of the molecule. This signal broadens slightly at elevated temperature, but the Cp-hydrogen signal is essentially unchanged.

To confirm the absence of significant interchange between bridging and Cp-hydrogen, partially deuterated $Cp_2Nb\{(\mu\text{-}D)(\mu\text{-}H)BC_8H_{14}\}$, **8**, was prepared by the reaction of Cp_2NbCl_2 with **5** in THF.[3h] Complex **8** in toluene was maintained at 318 K for 10 h. Its ^{2}H NMR spectra before and after heating (Figure 4) give no evidence for Cp-deuterium.

Study of the 9-BBN Unit in 2, 4, and 5 and the 9-BBN Dimer with Respect to Hydrogen Exchange. In the ^{1}H NMR spectrum of **2** (Figure 2) there is a slight broadening of the α-CH hydrogen signal of the $\{(\mu\text{-}H)_2BC_8H_{14}\}$ unit at elevated temperature (360 K). This peak returns to its original shape when the temperature is lowered to ambient (300 K). There are two plausible explanations for these observations. An intriguing possibility is the involvement of the α-hydrogens in the exchange process. But their rate of exchange would be appreciably slower than the other hydrogen exchange processes in the molecule. Another possibility for the temperature dependence of the line

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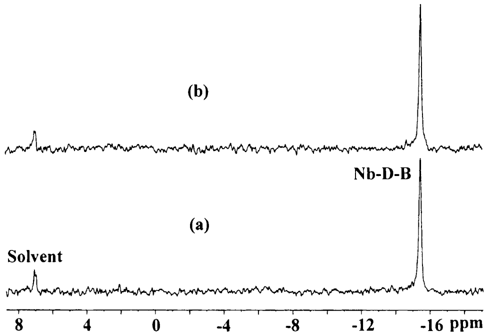

Figure 4. ^2H NMR spectra of **8** in toluene (a) before heating and (b) after heating at 318 K for 10 h.

shape is due to ^{11}B nuclear electric quadrupolar induced relaxation partially averaging long-range $^{11}B-^1H$ coupling. Since the rate of quadrupolar relaxation varies inversely with temperature,[16] its effect on averaging of long-range $^{11}B-^1H$ coupling decreases with increasing temperature and results in a broadened resonance.

After heating $Cp_2ZrD\{(\mu\text{-}H)_2BC_8H_{14}\}$, **4**, to 318 K for 1 h and then at 358 K for another hour, its ^2H NMR spectrum (Figure 3c) reveals a low-intensity signal, just visible at 1.4 ppm. This resonance can be assigned to the bridging deuterium of the 9-BBN dimer, a decomposition product, or the α-carbon-deuterium in **4**. This signal is not present in the ^2H NMR spectrum of **4** before it is heated (Figure 3a). Two unidentified very weak signals at 1.56 and −0.56 ppm are consistent with some decomposition of **4** (Figure 3c). To minimize decomposition, a sample of **4** in toluene was allowed to stand at room temperature for 50 days. The ^2H NMR spectrum displays bridging, terminal, and Cp-deuteriums with a weak signal at 1.4 ppm also present. This signal is too weak to allow a claim for C-H α-hydrogen exchange with bridging deuterium. Furthermore, there is no evidence for exchange of the β- and γ-C-H hydrogens with bridging deuterium.

It is reported that only the β-CH and γ-CH hydrogens in $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$ exchange with the bridging hydrogens, but the α-hydrogens do not. In that account by Köster et al.[15] the evidence for β- and γ-hydrogen rearrangement is provided by ^{13}C NMR spectra. We reexamined the possibility of bridging hydrogens exchanging with β- and γ-hydrogens by ^2H NMR spectroscopy. The bridging deuterium signal of complex $(C_8H_{14}B)(\mu\text{-}D)(\mu\text{-}H)(BC_8H_{14})$, **6**, appears at 1.46 ppm. After **6** is heated in toluene at 358 K for 1 h, the ^2H NMR spectrum displays two new peaks at 1.88 and 1.67 ppm besides the bridging deuterium signal. These are the β- and γ-deuterium resonances, respectively, with no signal representing the α-carbon deuteriums, fully in accord with the report by Köster and co-workers.[15]

Since the neutral 9-BBN diborane undergoes β- and γ-exchange, it was also of interest to examine the deuterated lithium salt of the 9-BBN hydroborate anion, complex $Li[(D)(H)BC_8H_{14}]$, **5**, for such exchange. The ^2H NMR spectrum of **5** at room temperature shows the presence of terminal deuteriums at 0.67 ppm. After heating **5** in toluene at 358 K for 1 h, no new signals appeared in the ^2H NMR spectrum, indicating that no exchange occurred between the boron and carbon hydrogens.

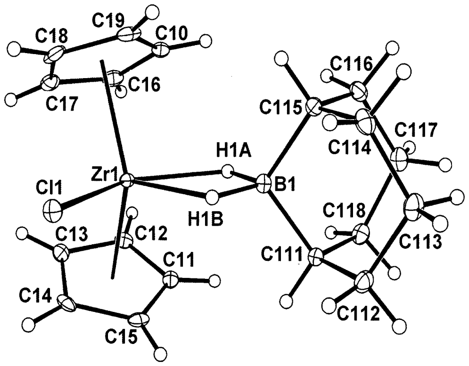

Figure 5. Molecular structure of **1**, showing 15% probability thermal ellipsoids. Hydrogens attached to carbon atoms are shown with arbitrary thermal ellipsoids.

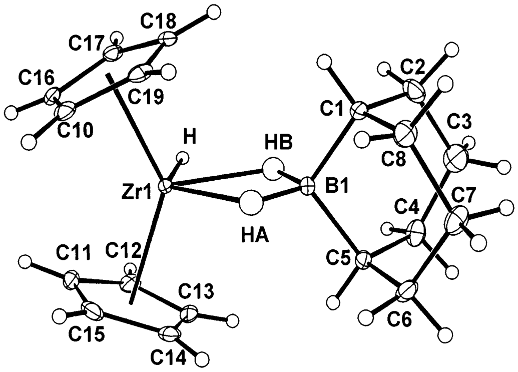

Figure 6. Molecular structure of **2**, showing 15% probability thermal ellipsoids. Hydrogens attached to carbon atoms are shown with arbitrary thermal ellipsoids.

Köster and co-workers account for the exchange of only β- and γ-CH hydrogens in the 9-BBN dimer by assuming a dissociation equilibrium to produce some monomer HBC_8H_{14} at elevated temperature. The monomer is assumed to be the active participant in the exchange process in which the BH hydrogen exchanges with the β- and γ-CH hydrogens through a “topotactical walk mechanism” (Scheme 2). This scheme not only accounts for β-CH and γ-CH hydrogen exchange with BH hydrogen but also provides insight into the lack of exchange in $[(D)(H)BC_8H_{14}]^-$, **5**, which has an electronically saturated boron. Thus there is no need to abstract a C-H hydrogen as illustrated in Scheme 2.

The Köster mechanism requires some symmetric dissociation of the 9-BBN dimer. This mechanism might also account for the absence of β- and γ-hydrogen exchange with boron hydrogen in **2** and **4**. If the Köster mechanism is correct, the lack of β- and γ-CH exchange in these complexes could be attributed to hydrogen bridge systems of complexes **2** and **4** that are more resistant to symmetrical dissociation than the 9-BBN dimer.

Molecular Structures of Complexes 1 and 2. The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis. They are shown in Figures 5 and 6. Crystallographic data and selected bond distances and bond angles are given in Tables 1−3.

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[16] Kaplin, J. I.; Fraenkel, G. *NMR of Chemically Exchanging Systems*; Academic Press: New York, 1980; pp 114−5.

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Scheme 2

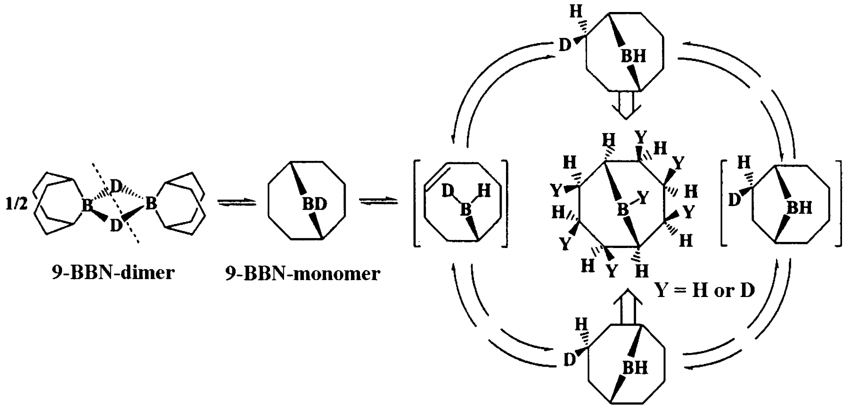

Table 1. Crystallographic Data for 1 and 2[a]

	1	2
formula	$C_{18}H_{26}BClZr$	$C_{18}H_{27}BZr$
mol wt	379.87	345.43
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	18.799(1)	11.961(1)
b (Å)	13.836(1)	10.253(1)
c (Å)	13.328(1)	13.904(1)
β (deg)	92.23(1)	102.79(1)
volume (Å^3)	3464.0(4)	1662.8(2)
Z	8	4
D_c (g/cm^3)	1.457	1.380
F(000)	1568	720
θ range (deg)	2.36−25.02	2.49−25.01
$h\ k\ l$ ranges	−22 22, −16 15, −15 15	−13 14, −12 12, −16 16
cryst size (mm)	0.42 × 0.08 × 0.08	0.46 × 0.31 × 0.12
μ(Mo Kα) (mm^{-1})	0.780	0.650
transmn: max., min.	0.9402, 0.7353	0.9261, 0.7543
no. of reflns collected	19 411	10 236
no. of ind reflns	6109	2931
R_{int}	0.02671	0.0299
completeness to θ	99.8%	100%
no. of data/restraints/params	6109/0/395	2931/0/193
final R indices [$I \geq 2\sigma(I)$][b]	$R_1 = 0.0279$; $wR_2 = 0.0585$	$R_1 = 0.0259$; $wR_2 = 0.0631$
R indices (all)	$R_1 = 0.0419$; $wR_2 = 0.0632$	$R_1 = 0.0309$; $wR_2 = 0.0653$
GOF	1.042	1.112
largest diff peak, e/Å^3	0.460/−0.374	0.373/−0.723

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

The coordination geometry of the zirconium atoms in **1** and **2** can be described as a distorted tetrahedron, consisting of B, Cl, or H, and the centroids of the two Cp rings at the corners of the tetrahedron. The structures of **1** and **2** each consist of a Cp_2ZrX fragment bonded to a BC_8H_{14} group through two bridging hydrogens, which were located and their positions refined. There are two independent molecules in the asymmetric unit cell of **1**. The Zr−B distances of 2.609(3) and 2.593(3) Å in **1** and 2.566(2) Å in **2** are consistent with other systems with bidentate Zr-H-B bridges.[11,17] The shorter Zr−B distance in **2** results from the reduction in steric volume by replacement of the Cl atom on zirconium with a H atom. The steric bulk of the Cl atom also affects the average $Cp_{centroid}$−Zr distances (2.200 and 2.204 Å for **1** and 2.190 Å for **2**) and the $Cp_{centroid}$−Zr−$Cp_{centroid}$ angles (129.6° for **1**; 136.0° for **2**). For the hydrogen-bridge systems of **1** and **2**, the metal−H distances range from 1.96(2) to 2.08(2) Å, while the B−H distances range from 1.19(2) to 1.27(2) Å. The terminal hydrogen in **2** was located and refined isotropically. The Zr−H bond distance of 1.77(2) Å in **2** falls within the limits observed for other zirconocene hydride complexes, $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ (1.7862(4) Å)[3c] and $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ (1.68(5) Å).[3b] The Zr−Cl distances of 2.5080(6) and 2.4971(7) Å in **1** are comparable to the previously reported Zr−Cl distances of 2.4802(5) Å in $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$[3d] and 2.4974(7) Å in $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$.[3f]

Summary and Conclusions

This study provides strong evidence that exchange between bridging and Cp hydrogens in the zirconocene chloro complex $Cp_2ZrCl\{(\mu\text{-}H)_2BC_8H_{14}\}$ and the niobocene complex $Cp_2Nb\{(\mu\text{-}H)_2BC_8H_{14}\}$ does not occur, or is minimal when there is a nonhydridic terminal substituent on zirconium (Cl) or no terminal group on niobium. However, a terminal hydrogen on zirconium participates in intramolecular exchange with bridging and Cp-hydrogens in the hydrido-cyclic organo-

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Table 2. Selected Bond Distances and Angles for 1[a]

Bond Lengths (Å)			
Zr1−Cp$_{\mathrm{Centroid(C11-C15)}}$	2.198	Zr2−Cp$_{\mathrm{Centroid(C21-C25)}}$	2.201
Zr1−Cp$_{\mathrm{Centroid(C16-C10)}}$	2.202	Zr2−Cp$_{\mathrm{Centroid(C26-C20)}}$	2.206
Zr1- -B1	2.609(3)	Zr2- -B2	2.593(3)
Zr1−Cl1	2.5080(6)	Zr2−Cl2	2.4971(7)
Zr1−H1A	1.96(2)	Zr2−H2A	1.96(2)
Zr1−H1B	2.08(2)	Zr2−H2B	2.06(2)
B1−H1A	1.26(2)	B2−H2A	1.27(2)
B1−H1B	1.19(2)	B2−H2B	1.19(2)
B1−C111	1.593(4)	B2−C211	1.593(4)
B1−C115	1.596(4)	B2−C215	1.592(4)

Bond Angles (deg)			
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−Cp$_{\mathrm{Centroid\ (C16-C10)}}$	129.4	Cp$_{\mathrm{Centroid(C21-C25)}}$−Zr2−Cp$_{\mathrm{Centroid\ (C26-C20)}}$	129.7
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−B1	106.5	Cp$_{\mathrm{Centroid(C21-C25)}}$−Zr2−B2	106.4
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−B1	107.2	Cp$_{\mathrm{Centroid(C26-C20)}}$−Zr2−B2	107.3
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−Cl1	105.0	Cp$_{\mathrm{Centroid(C21-C25)}}$−Zr2−Cl2	104.0
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−Cl1	104.2	Cp$_{\mathrm{Centroid(C26-C20)}}$−Zr2−Cl2	104.6
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−H1A	96.5	Cp$_{\mathrm{Centroid(C21-C25)}}$−Zr2−H2A	95.2
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−H1A	96.3	Cp$_{\mathrm{Centroid(C26-C20)}}$−Zr2−H2A	97.3
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−H1B	111.8	Cp$_{\mathrm{Centroid(C21-C25)}}$−Zr2−H2B	114.1
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−H1B	115.3	Cp$_{\mathrm{Centroid(C26-C20)}}$−Zr2−H2B	112.8
B1−Zr1−Cl1	101.14(6)	B2−Zr2−Cl2	101.40(6)
B1−Zr1−H1A	27.6(6)	B2−Zr2−H2A	28.1(7)
B1−Zr1−H1B	26.5(6)	B2−Zr2−H2B	26.5(6)
Cl1−Zr1−H1A	128.8(6)	Cl2−Zr2−H2A	129.5(7)
Cl1−Zr1−H1B	74.7(6)	Cl2−Zr2−H2B	74.9(6)
H1A−Zr1−H1B	54.1(9)	H2A−Zr2−H2B	54.7(9)

[a] There are two unique molecules in the asymmetric unit cell of **1**.

Table 3. Selected Bond Distances and Angles for 2

Bond Lengths (Å)			
Zr1−Cp$_{\mathrm{Centroid(C11-C15)}}$	2.192	Zr1−HB	2.02(2)
Zr1−Cp$_{\mathrm{Centroid(C16-C10)}}$	2.189	B1−HA	1.20(2)
Zr1- -B1	2.566(2)	B1−HB	1.26(2)
Zr1−H	1.77(2)	B1−C1	1.597(3)
Zr1−HA	1.99(2)	B1−C5	1.600(3)

Bond Angles (deg)			
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−B1	109.2		
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−B1	109.6	Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−Cp$_{\mathrm{Centroid(C16-C10)}}$	136.0
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−H	97.9	B1−Zr1−H	95.5(8)
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−H	98.1	B1−Zr1−HA	27.1(7)
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−HA	102.4	B1−Zr1−HB	29.0(5)
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−HA	102.6	H−Zr1−HA	122.6(11)
Cp$_{\mathrm{Centroid(C11-C15)}}$−Zr1−HB	112.1	H−Zr1−HB	66.5(9)
Cp$_{\mathrm{Centroid(C16-C10)}}$−Zr1−HB	111.8	HA−Zr1−HB	56.1(8)

hydroborate zirconocene derivatives. The Zr-H hydrogen undergoes more facile exchange with bridging hydrogen than with the Cp-hydrogen. These results contrast with those observed from $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$, in which the hydrogen of the borohydride ligand interchanges more rapidly with Cp-hydrogen than with Zr-H hydrogen.[7]

The structures of the chloro (Figure 5) and hydrido (Figure 6) complexes of the zirconocene cyclic organohydroborates are similar. The absence of apparent direct exchange between bridging and Cp-hydrogens, in the temperature ranges studied, might be due to the fact that the cyclic organohydroborate ligands are more massive than the $[BH_4]^-$ ligand, which is highly fluxional in $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$.[7] The $[BH_4]^-$ ligand can more easily move into a position conducive for direct hydrogen exchange with Cp-hydrogen than the cyclic organohydroborate ligands.

A possible pathway in which Zr serves as a conduit of hydrogen passage in the exchange reactions of the cyclic organohydroborate derivatives with terminal hydrogen is shown in Scheme 3.

Experimental Section

General Comments. All operations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of nitrogen. Toluene, tetrahydrofuran, and hexane were dried over sodium/benzophenone and freshly distilled prior to use. Cp_2ZrCl_2, Cp_2NbCl_2, $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$, $B(C_6F_5)_3$, KH, and LiD were purchased from Aldrich and used as received. $Cp_2Nb\{(\mu\text{-}H)_2BC_8H_{14}\}$ (**7**)[3h] was prepared by the literature procedure. $Cp_2Nb\{(\mu\text{-}D)(\mu\text{-}H)BC_8H_{14}\}$ (**8**) was prepared by the literature procedure using $Li(THF)_2[(D)(H)\text{-}BC_8H_{14}]$, **5**, instead of $K[H_2BC_8H_{14}]$.[3h] Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. Complexes **3**, **4**, **5**, and **6** are partially deuterated materials that are related to the well-characterized undeuterated complexes $Cp_2ZrCl\{(\mu\text{-}H)_2BC_8H_{14}\}$, $Cp_2ZrH\{(\mu\text{-}H)_2BC_8H_{14}\}$, $Li(THF)_2[H_2\text{-}BC_8H_{14}]$, and $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$. Analyses of these complexes were not attempted in view of the presence of mixed hydrogen isotopes. However, their NMR spectra are clearly consistent with those of the undeuterated species since the chemical shifts of ^1H and ^2H are identical. ^1H (250.1 MHz), ^{13}C (62.9 MHz) (δ (TMS) 0.00 ppm), and ^{11}B (128.4 MHz) (δ ($BF_3{\cdot}OEt_2$) 0.00 ppm) NMR spectra were recorded on a Bruker AM-250 NMR spectrometer. ^2H NMR (61.4 MHz) spectra were recorded on a Bruker DPX-400 NMR spectrometer, and the

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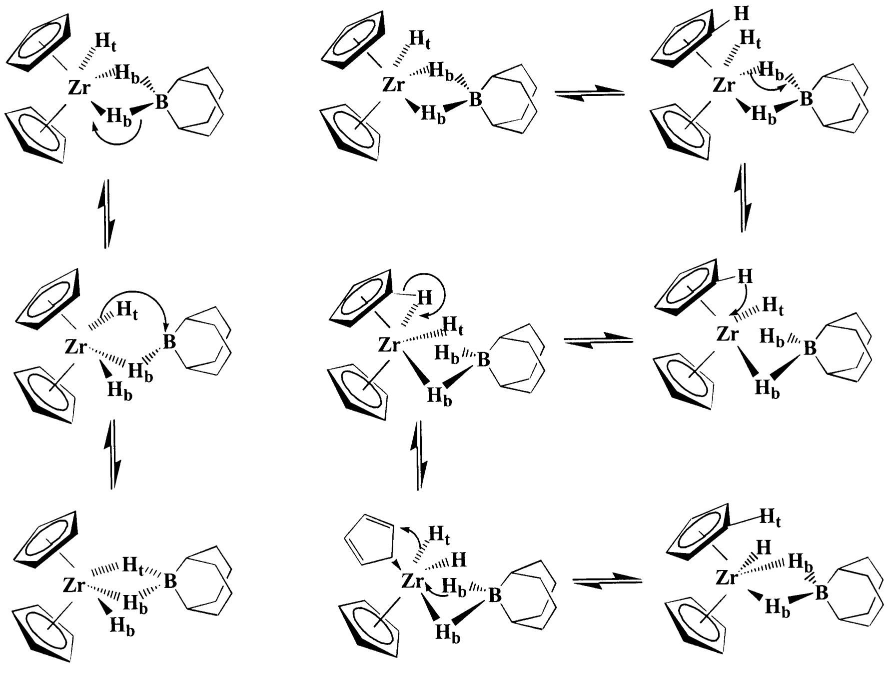
Scheme 3



^1H (500.1 MHz)−^{13}C (125.8 MHz) HMQC spectra were recorded on a Bruker DRX-500 spectrometer. Infrared spectra were recorded on a Mattson Polaris Fourier Transform spectrometer with 2 cm^{-1} resolution.

X-ray Structure Determination. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius KappaCCD diffraction system, which employs graphite-monochromated Mo Kα radiation. A single crystal of **1** and **2** was mounted on the tip of a glass fiber coated with fomblin oil (a perfluoropolyether). Crystallographic data were collected at 150 K for both complexes. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using DENZO.[18] The structures were solved by direct methods and refined using SHELXTL (difference electron density calculations, full least-squares refinements).[19] For both structures, non-hydrogen atoms were located and refined anisotropically. For **1** and **2** the bridge hydrogens and the terminal hydrogen atom of **2** were located and refined isotropically. All other hydrogen atoms were calculated and fixed during the refinement.

Preparation of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_8H_{14}\}$, 1. A solution of $K[H_2BC_8H_{14}]$ (4.0 mmol in 20 mL of THF), which was obtained by filtration of the reaction of 0.488 g (2.0 mmol) of $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$ with 0.176 g (4.4 mmol) of KH in 20 mL of THF, was added dropwise to 1.170 g (4.0 mmol) of Cp_2ZrCl_2 dissolved in 20 mL of THF. The solution was stirred overnight at room temperature and then filtered. The solvent was removed under dynamic vacuum. The resulting white solid was dissolved in a minimum amount of toluene, and colorless needlelike crystals were formed upon slow evaporation of the solvent at room temperature. The crystals were washed with hexane and dried under vacuum, giving 1.210 g (3.18 mmol, 79.5% yield). ^{11}B NMR (toluene-d_8): δ 17.7 (br t). ^1H NMR (toluene-d_8): δ 5.75 (s, 10H, Cp), 2.01 (br s, 6H, 4 β-H and 2 γ-H), 1.91−1.72 (m, 6H, 4 β-H and 2 γ-H), 1.51 (s, 2H, α-H), 0.55 (br d, 1H, μ-H), −2.40 (br d, 1H, μ-H). IR (KBr): 3106(m), 2980(w), 2946(w), 2920(sh), 2873(vs), 2828(s), 1992(s), 1930(w), 1906(w), 1854(w), 1829(m), 1795(w), 1765(w), 1718(w), 1685(w), 1656(m), 1551(w), 1485(w), 1440(m), 1387(vs), 1343(s), 1281(w), 1264(m), 1202(m), 1110(w), 1063(sh), 1041(m), 1013(s), 925(m), 856(m), 809(vs), 738(m), 459(s) cm^{-1}. Anal. Calcd for $C_{18}H_{26}BClZr$: C, 56.91; H, 6.90. Found: C, 56.74; H, 6.94.

Preparation of $Cp_2ZrH\{(\mu\text{-}H)_2BC_8H_{14}\}$, 2. A 0.380 g (1.0 mmol) amount of **1** and 0.044 g (1.1 mmol) of KH were charged into a flask in the drybox. The flask was degassed, and about 20 mL of THF was condensed 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 toluene was introduced to extract the product. The toluene solution was concentrated at room temperature, and colorless crystals formed. The crystals were washed with hexane and dried under vacuum, giving 0.310 g (0.90 mmol, 90.0% yield). ^{11}B NMR (toluene-d_8): δ 32.5 (br t). ^1H NMR (toluene-d_8): δ 5.58 (s, 10H, Cp), 3.99 (s, 1H, H_t), 2.11 (br m, 2H, γ-H), 1.91 (br m, 4H, β-H), 1.83 (br m, 4H, β-H), 1.73 (br m, 2H, γ-H), 1.39 (s, 2H, α-H), −3.17 (br d, 1H, μ-H), −4.12 (br d, 1H, μ-H). ^{13}C NMR (toluene-d_8): δ 104.1 (Cp-C), 33.9 (β-C), 29.9 (br, α-C), 25.3 (γ-C). ^{13}C-GD NMR (toluene-d_8): δ 104.1 (d-quintet, Cp-C, $^1J_{CH} = 174.2$ Hz, $^2J_{CH} = 6.7$ Hz, coupling to bridging and terminal hydrogen), 33.9 (t, β-C, $^1J_{CH} = 123.3$ Hz), 25.3 (t, γ-C, $^1J_{CH} = 111.3$ Hz). IR (KBr): 3108(w), 3074(m), 2975(w), 2920(sh), 2873(vs), 2826(s), 1960(w), 1849(s), 1828(sh), 1794(m), 1733(w), 1699(m), 1651(m), 1557(m), 1539(m), 1425(vs), 1401(sh), 1341(s), 1315(sh, w), 1284(m), 1261(m), 1203(m), 1168(w), 1111(m), 1067(m), 1041(m), 1014(vs), 928(m), 888(m), 865(w), 828(sh), 805(vs), 734(m), 463(m) cm^{-1}. Anal. Calcd for $C_{18}H_{27}BZr$: C, 62.59; H, 7.88. Found: C, 60.94; H, 7.70.

Preparation of $Cp_2ZrCl\{(\mu\text{-}D)(\mu\text{-}H)BC_8H_{14}\}$, 3. The procedure was similar to the preparation of **1** using 0.275 g of $[Li(THF)_2][(D)(H)BC_8H_{14}]$, **5** (1.0 mmol), instead of $K[H_2BC_8H_{14}]$ to react with 0.292 g of Cp_2ZrCl_2 (1.0 mmol). Complex **3** was isolated as colorless crystals (0.287 g, 75.3% yield). ^{11}B NMR (toluene-d_8): δ 18.1 (br t). ^1H NMR (benzene-d_6): δ 5.76 (s, 10H, Cp), 2.01−1.64 (m, 12H, 8β-H and 4γ-H), 1.50 (s, 2H, α-H), 0.66 (br d, μ-H), −2.47 (br d, μ-H). ^2H NMR (toluene): δ 0.43 (s, μ-D), −2.48 (s, μ-D). ^2H NMR (after heating for 10 h at 318 K in toluene and then cooling to room

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(18) Otwinowsky, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology, Vol. 276: Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; pp 307−326.

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temperature, toluene): δ 1.41(s, μ-D of 9-BBN dimer), −0.43 (s, μ-D), −2.43 (s, μ-D). IR (KBr): 3107(m), 2979(w), 2944(w), 2918(sh), 2871(vs), 2827(s), 1986(s), 1933(w), 1848(w), 1828(m), 1793(w), 1768(w), 1752(w), 1734(w), 1714(w), 1698(w), 1682(w), 1649(w), 1633(w), 1557(w), 1538(w), 1519(w), 1504(w), 1483(w), 1468(w), 1438(s), 1386(vs), 1337(s), 1281(m), 1254(m), 1240(w), 1202(m), 1109(w), 1069(m), 1014(s), 925(m), 835(m), 808(vs), 735(m), 458(s) cm^{-1}.

Preparation of $Cp_2ZrD\{(\mu\text{-}H)_2BC_8H_{14}\}$, 4. The procedure was similar to the preparation of **2** using 0.015 g of LiD (1.5 mmol) instead of KH to react with 0.380 g of **1** (1.0 mmol). Complex **4** was isolated as colorless crystals (0.252 g, 72.8% yield). ^{11}B NMR (toluene-d_8): δ 32.2 (br t). ^{1}H NMR (toluene-d_8): δ 5.59 (s, 10H, Cp), 3.99 (s, 1H, H_t), 2.07 (br m, 2H, γ-H), 1.90 (br m, 4H, β-H), 1.84−1.71 (m, 6H, 4β-H and 2γ-H), 1.38 (s, 2H, α-H), −3.25 (br d, μ-H), −4.24 (br d, μ-H). ^{2}H NMR (toluene): δ 3.97 (s, D_t), −3.31 (s, μ-D), −4.26 (s, μ-D). ^{2}H NMR (after heating for 1 h at 85 °C in toluene and then cooling to room temperature, toluene): δ 5.60 (s, Cp-D), 3.97 (s, D_t), 1.40 (s, α-D), −3.27 (s, μ-D), −4.27 (s, μ-D). ^{13}C NMR (toluene-d_8): δ 104.1 (Cp-C), 33.9 (β-C), 29.9 (br s, α-C), 25.3 (γ-C). ^{13}C-GD NMR (toluene-d_8): δ 104.1 (d-quintet, Cp-C, $^1J_{CH}$ = 173.7 Hz, $^2J_{CH}$ = 6.5 Hz, coupling to bridging and terminal hydrogen), 34.0 (t, β-C, $^1J_{CH}$ = 122.2 Hz), 25.3 (t, γ-C, $^1J_{CH}$ = 121.6 Hz). IR (KBr): 3111(w), 3074(m), 2974(m), 2918(sh), 2875(vs), 2825(s), 1960(sh), 1849(s), 1827(s), 1796(m), 1733(w), 1699(m), 1651(m), 1557(m), 1539(m), 1429(vs), 1398(sh), 1321(s), 1261(m), 1203(m), 1168(w), 1111(m), 1067(m), 1038(m), 1013(vs), 927(m), 829(sh), 807(vs), 733(m), 669(m), 501(m), 457(m) cm^{-1}.

Preparation of $[Li(THF)_2][(D)(H)BC_8H_{14}]$, 5. A 50 mL flask was charged with 0.448 g (2.0 mmol) of $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$ and 0.040 g (4.5 mmol) of LiD. The flask was evacuated, and ca. 30 mL of THF was condensed at −78 °C. The system was warmed to room temperature and stirred until all of the starting material was consumed. The reaction was monitored by ^{11}B NMR spectroscopy. After the reaction, the excess LiD was removed by filtration and THF was removed under vacuum. The white solid was washed with hexane and dried under vacuum overnight. Complex **5** was isolated as $[Li(THF)_2][(D)(H)BC_8H_{14}]$ (0.816 g, 2.97 mmol, 74.2% yield). ^{11}B NMR (toluene-d_8): δ −17.5 (asymmetric triplet, ^1J = 68.1 Hz). ^{11}B{H} NMR (toluene-d_8): δ −18.4. ^{1}H NMR (toluene-d_8): δ 3.58 (t, 8H, $O(CH_2CH_2)_2$), 2.42−2.27 (br m, 2H, γ-H), 2.18 (br m, 8H, β-H), 1.98 (s, 2H, γ-H), 1.42 (t, 8H, $O(CH_2CH_2)_2$), 1.12 (s, 2H, α-H). ^{1}H{^{11}B} NMR (toluene-d_8): δ 0.77 (μ-H). ^{2}H NMR (toluene): δ 0.67 (s, μ-D). ^{2}H NMR (after heating for 1 h at 358 K and then cooling to room temperature, toluene): δ 0.70 (s, μ-D). IR (KBr): 2979(m), 2914(vs), 2972(vs), 2834(vs), 1469(s), 1447(s), 1415(vs), 1337(m), 1291(m), 1263(w), 1204(m), 1168(w), 1105(m), 1074(m), 1045(vs), 986(sh), 893(m), 822(m), 800(m), 734(m), 480(m) cm^{-1}.

Preparation of $(C_8H_{14}B)(\mu\text{-}D)(\mu\text{-}H)(BC_8H_{14})$, 6. A 50 mL flask was charged with 0.275 g (1.0 mmol) of **5** and 0.512 g (1.0 mmol) of $B(C_6F_5)_3$. Approximately 20 mL of THF was condensed at −78 °C. The solution was warmed to room temperature and stirred for 1 h. The ^{11}B NMR spectrum of the reaction solution indicated that **5** was consumed. The THF was reduced under vacuum, and dry hexane was added to extract the product. The hexane solution was concentrated, and colorless crystals formed. **6** was recrystallized from toluene, and the crystals were dried under vacuum overnight to give 0.056 g (0.23 mmol, 46.0% yield). ^{11}B NMR (toluene-d_8): δ 27.1 (br m). ^{1}H NMR (toluene-d_8): δ 1.96 (m, 2H, γ-H), 1.85 (br m, 4H, β-H), 1.67 (m, 4H, β-H), 1.63 (s, 2H, α-H), 1.51 (m, 2H, γ-H). ^{1}H{^{11}B} NMR (toluene-d_8): δ 1.46 (m, μ-H). ^{2}H NMR (toluene): δ 1.46 (s, μ-D). ^{13}C NMR (toluene-d_8): δ 33.7 (β-C), 24.4 (γ-C), 20.2 (α-C). ^{13}C-GD NMR (toluene-d_8): δ 33.7 (t, β-C, $^1J_{CH}$ = 124.5 Hz), 24.4 (t, γ-C, $^1J_{CH}$ = 125.8 Hz). IR (KBr): 2982(m), 2952(m), 2926(m), 2884(vs), 2836(s), 1648(m), 1563(m), 1512(m), 1467(s), 1398(m), 1318(m), 1260(s), 1213(s), 1156(s), 1068(vs), 968(m), 916(s), 869(w), 839(w), 804(s), 744(m), 479(m) cm^{-1}. Complex **6** was heated in toluene for 1 h at 358 K and was isolated as colorless crystals, which were characterized by NMR and IR spectroscopies. ^{11}B NMR (toluene-d_8): δ 27.3 (br m). ^{1}H NMR (toluene-d_8): δ 1.96 (m, 2H, γ-H), 1.86 (br m, 4H, β-H), 1.67 (m, 4H, β-H), 1.63 (s, 2H, α-H), 1.51 (m, 2H, γ-H). ^{1}H{^{11}B} NMR (toluene-d_8): δ 1.47 (m, μ-H). ^{2}H NMR (toluene): δ 1.88 (s), 1.67 (s), 1.47 (s, μ-D). ^{13}C NMR (toluene-d_8): δ 33.7 (β-C), 24.4 (γ-C). ^{13}C-GD NMR (toluene-d_8): δ 33.7 (t, β-C, $^1J_{CH}$ = 125.8 Hz), 24.4 (t, γ-C, $^1J_{CH}$ = 124.5 Hz). IR (KBr): 2982(m), 2952(m), 2926(m), 2905(sh), 2885(vs), 2836(s), 1647(w), 1634(w), 1569(vs), 1511(w), 1467(sh), 1445(s), 1398(s), 1358(w), 1318(s), 1301(w), 1260(m), 1213(s), 1160(s), 1104(m), 1066(s), 968(m), 916(s), 865(w), 806(s), 743(m), 477(m) cm^{-1}.

The dimer $C_8H_{14}B(\mu\text{-}H)_2BC_8H_{14}$ was characterized by NMR and IR spectroscopies for comparison with **6**. ^{11}B NMR (toluene-d_8): δ 27.7 (br t). ^{1}H NMR (toluene-d_8): δ 1.95 (m, 2H, γ-H), 1.86 (br m, 4H, β-H), 1.65 (m, 4H, β-H), 1.62 (s, 2H, α-H), 1.51 (m, 2H, γ-H). ^{1}H{^{11}B} NMR (toluene-d_8): δ 1.47 (m, μ-H). ^{13}C NMR (toluene-d_8): δ 33.6 (β-C), 24.4 (γ-C).^{13}C NMR (benzene-d_6): δ 33.6 (β-C), 24.3 (γ-C), 20.2 (br s, α-C). ^{13}C-GD NMR (toluene-d_8): δ 33.7 (t, β-C, $^1J_{CH}$ = 125.8 Hz), 24.4 (t, γ-C, $^1J_{CH}$ = 125.8 Hz). IR (KBr): 2982(m), 2953(m), 2927(m), 2905(sh), 2884(vs), 2836(s), 1569(vs), 1521(w), 1485(w), 1444(s), 1404(w), 1345(w), 1318(m), 1301(w), 1260(m), 1213(m), 1105(s), 1065(s), 1020(s), 916(s), 8690(w), 839(w), 808(s), 744(m), 479(m) cm^{-1}.

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Supporting Information Available: Molecular structure of the second independent molecule for **1**; tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **1** and **2**; relevant additional ^{1}H, ^{2}H, ^{11}B, ^{13}C, ^{1}H−^{13}C, and VT-^{1}H NMR spectra for **1**, **2**, **3**, **4**, **5**, **6**, **7**, and **8**. Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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