496 *Inorg. Chem.* **1998,** *37,* 496−502

Cyclic Hydroborate Complexes of Metallocenes II: Reactivity of $(\mu\text{-H})_2(BC_5H_{10})_2$ and Its Cyclic Derivative, $[H_2BC_5H_{10}]^-$; Synthesis of $(\eta^5\text{-}C_5H_5)_2MCl(\mu\text{-H})_2BC_5H_{10}$ (M = Zr, Hf)

Jianping Liu, Edward A. Meyers, and Sheldon G. Shore*

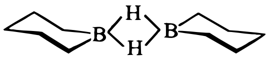
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received October 10, 1997

Reactions of the organodiborane $(\mu\text{-H})_2(BC_5H_{10})_2$, **1**, with the Lewis bases, $N(CH_3)_3$, $P(CH_3)_3$, NH_3, and H^-, produced the cyclic adducts $LHBC_5H_{10}$ ($L = N(CH_3)_3$, $P(CH_3)_3$, NH_3, H^-) through symmetrical cleavage of the hydrogen bridge system. The salt $[(NH_3)_2BC_5H_{10}][H_2BC_5H_{10}]$ was produced through unsymmetrical cleavage of the hydrogen bridge system. An improved, synthesis of the anion $[H_2BC_5H_{10}]^-$, **3**, is described. It can function as a hydride transfer reducing agent in its reactions with BH_3THF and 4-*tert*-butylcyclohexanone. In its reactions with $(\eta^5\text{-}C_5H_5)_2MCl_2$ it serves as a chelating agent to produce $(\eta^5\text{-}C_5H_5)_2MCl(\mu\text{-H})_2BC_5\underline{H}_{10}$ (M = Zr, **4**; Hf, **5**). The molecular structures of **1** and **4** are reported here. Crystal data for **1**: space group $P\bar{1}$, $a = 6.415(3)$ Å, $b = 9.260(4)$ Å, $c = 10.291(5)$ Å, $\alpha = 114.53(4)°$, $\beta = 104.25(4)°$, $\gamma = 90.01(4)°$, $Z = 2$. Crystal data for **4**: space group $P2_1/c$, $a = 12.584(2)$ Å, $b = 9.511(1)$ Å, $c = 12.813(2)$ Å, $\beta = 100.26(1)°$, $Z = 4$.

Introduction

Hydroboration of 1,4-pentadiene to produce the organodiborane $(\mu\text{-H})_2(BC_5H_{10})_2$,[1] **1**, was first reported by Köster. Later this reaction was studied in detail and an improved synthesis of **1** was developed.[2] However, the reported chemistry of **1** is limited to its reactions with olefins[3a] and bulky amines.[3b] Unlike the transannular hydrogen-bridged diborane $(\mu\text{-H})_2B_2(\mu\text{-}C_4H_8)_2$,[4] **2**, **1** is believed to possess a more conventional diborane structure based upon chemical studies.[1]



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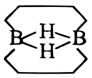

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In view of the ease with which **1** can be prepared and in view of its potential as a ready source for cyclic boracyclohexane derivatives, it has been of interest to us to expand the known chemistry of this compound. We report here a single-crystal X-ray diffraction analysis of the structure of **1**; its reactions with nucleophiles; its conversion to the cyclic organohydroborate anion, $[H_2BC_5H_{10}]^-$, **3**. This anion was prepared in essentially quantitative yield. It was shown to function as a facile hydride transfer agent in its reduction of BH_3THF and 4-*tert*-butylcyclohexanone. It can also serve as a chelating ligand in its reactions with $(\eta^5\text{-}C_5H_5)_2MCl_2$ (M = Zr, **4**; Hf, **5**) to form cyclic organohydroborate complexes. Some derivative chemistry of **4** has been outlined because organohydroborate metal complexes have received significantly less attention[5] than the many tetrahydroborate metal complexes that have been prepared and studied.[6,7]

Results and Discussion

Molecular Structure of $(\mu\text{-H})_2(BC_5H_{10})_2$. The organodiborane $(\mu\text{-H})_2(BC_5H_{10})_2$, **1**, was prepared through the reaction of 1,4-pentadiene with BH_3THF according to a method reported earlier.[2a] The boron-11 NMR spectrum of **1** consists of a triplet at +25.6 ppm ($J_{BH} = 42$ Hz) in ether in accord with that

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Table 1. Crystallographic Data for $(\mu\text{-H})_2(BC_5H_{10})_2$ and $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-H})_2BC_5H_{10}$

empirical formula	$C_{10}H_{22}B_2$	$C_{15}H_{22}BClZr$
formula wt, amu	163.91	339.83
space group	$P\bar{1}$	$P2_1/c$
a, Å	6.415(3)	12.584(2)
b, Å	9.260(4)	9.511(1)
c, Å	10.291(5)	12.813(2)
α, deg	114.53(4)	90
β, deg	104.25(4)	100.26(1)
γ, deg	90.01(4)	90
vol, Å^3	535.4	1508.8
Z	2	4
ρ(calcd), g cm^{-3}	1.017	1.496
crystal size, mm	0.6 × 0.5 × 0.4	0.5 × 0.5 × 0.4
T, °C	−60	25
λ, Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	0.5	8.8
transm coeff, %	−	97.88−99.93
$R_F{}^a$	0.075	0.019
$R_{wF}{}^b$	0.100	0.030
k^c	0.04	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 2. Selected Positional Parameters and Their Esd's for $(\mu\text{-H})_2(BC_5H_{10})_2$

atom	x	y	z	B (Å^2)^{a,b}
C11	0.2328(5)	0.2172(4)	0.1131(3)	2.65(7)
C12	0.3401(5)	0.2913(4)	0.2806(4)	3.23(8)
C13	0.1785(5)	0.3648(4)	0.3687(4)	3.38(8)
C14	−0.0101(5)	0.2426(4)	0.3359(3)	3.20(8)
C15	−0.1379(5)	0.1680(4)	0.1723(3)	2.59(7)
C21	0.7628(5)	0.6176(4)	0.2055(3)	2.88(7)
C22	0.8218(5)	0.7984(4)	0.2856(3)	3.16(8)
C23	0.6469(5)	0.8837(4)	0.3548(3)	3.36(8)
C24	0.4267(5)	0.8488(4)	0.2396(3)	3.06(8)
C25	0.3458(5)	0.6710(4)	0.1592(3)	2.82(7)
B1	0.0218(5)	0.1009(4)	0.0725(3)	2.14(7)
B2	0.5269(5)	0.5735(4)	0.0954(4)	2.38(8)
H1	0.071(5)	−0.031(4)	0.066(3)	4.4(9)
H2	0.478(4)	0.425(3)	0.030(3)	2.2(6)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. ^{b} Hydrogen atoms were located and refined isotropically.

reported in the literature.[2b] Colorless crystals of $(\mu\text{-H})_2(BC_5H_{10})_2$ were obtained at room temperature by slow sublimation of crude $(\mu\text{-H})_2(BC_5H_{10})_2$ under vacuum. When the crystals were cooled they became cloudy between −20 °C and −40 °C, but as the temperature was lowered further they became clear again. Single-crystal X-ray diffraction analyses indicated that a phase change had occurred. Two X-ray data sets were collected: one at 5 °C and one at −60 °C. The phase change involves a change in space group and lattice parameters, but the cell volumes are approximately equal. Since the molecular structures of the $(\mu\text{-H})_2(BC_5H_{10})_2$ molecules in the two crystalline forms are virtually identical, only the one at −60 °C is discussed here. However, the Supporting Information that is associated with this work provides information obtained from both the data set at −60 and 5 °C. Crystallographic data are listed in Table 1. Atom positional parameters and selected bond distances and angles are given in Tables 2 and 3. The ORTEP of $(\mu\text{-H})_2(BC_5H_{10})_2$ from the X-ray data obtained at −60 °C is shown in Figure 1.

In the triclinic space group, $P\bar{1}$ (−60 °C), there are two independent half-molecules in the asymmetric unit which generate two independent molecules through the center of inversion. Compound **1** exists as two boracyclohexane rings that are joined together by two hydrogen bridges. The molecule has crystallographically imposed C_{2h} symmetry. The B−H bond distances range from 1.24(4) to 1.29(3) Å and the B−B distances are 1.810(8) and 1.809(8) Å. The H−B−H and B−H−B angles range from 88(3) to 92(2)°. These parameters are consistent with those observed in the B_2H_6 molecule.[8] The C−B bond distances are in the range of 1.575(5) − 1.585(5) Å which is typical for carbon−boron single bonds.[9]

Table 3. Selected Bond Distances (Å) and Angles (°) for $(\mu\text{-H})_2(BC_5H_{10})_2{}^a$

Bond Distances			
C11−C12	1.533(5)	C23−C24	1.537(6)
C11−B1	1.585(5)	C24−C25	1.523(6)
C12−C13	1.520(6)	C25−B2	1.575(5)
C13−C14	1.530(6)	B1−H1	1.24(4)
C14−C15	1.529(6)	B1−H1#1	1.27(4)
C15−B1	1.575(5)	B2−H2	1.25(3)
C21−C22	1.526(6)	B2−H2#	1.29(3)
C21−B2	1.585(5)	B1···B1#1	1.810(8)
C22−C23	1.522(6)	B2···B2#2	1.809(8)

Bond Angles			
C12−C11−B1	110.6(3)	C22−C21−B2	110.6(3)
C11−C12−C13	111.6(3)	C21−C22−C23	112.3(3)
C12−C13−C14	112.3(3)	C22−C23−C24	112.4(3)
C13−C14−C15	112.2(4)	C23−C24−C25	112.2(4)
C14−C15−B1	109.6(3)	C24−C25−B2	110.0(3)
C11−B1−C15	115.9(3)	C21−B2−C25	116.2(3)
C11−B1−H1	110(2)	C21−B2−H2	111(2)
C11−B1−H1#1	114(2)	C21−B2−H2#2	113(1)
C15−B1−H1	111(2)	C25−B2−H2	115(1)
C15−B1−H1#1	114(2)	C25−B2−H2#2	110(1)
H1−B1−H1#1	88(3)	H2−B2−H2#2	89(2)
B1−H1−B1#1	92(3)	B2−H2−B2#2	91(2)

^{a} Symmetry transformation used to generate equivalent atoms: #1, $-x, -y, -z$; #2, $1 - x, 1 - y, -z$.

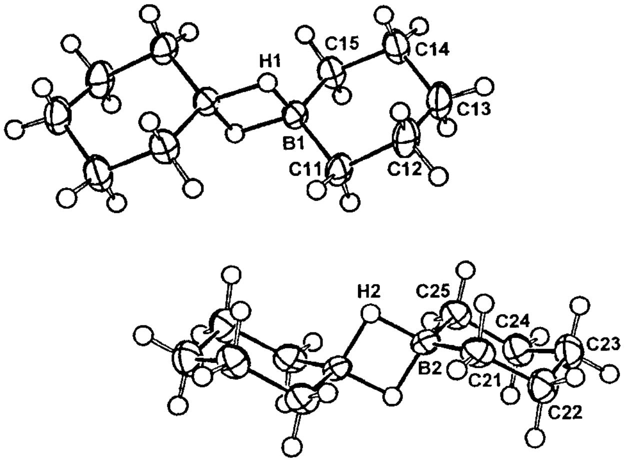

Figure 1. ORTEP plot of the molecular structure of $(\mu\text{-H})_2(BC_5H_{10})_2$ with 25% probability thermal ellipsoids.

Reaction of $(\mu\text{-H})_2(BC_5H_{10})_2$, 1, with $N(CH_3)_3$, $P(CH_3)_3$, and NH_3. Qualitative studies of reactions of **1** with Lewis bases were undertaken. Reactions of **1** with $N(CH_3)_3$ and $P(CH_3)_3$ produce symmetrical cleavage products (reactions 1 and 2) similar to those reactions of B_2H_6, first observed by Burg and Schlesinger,[10a] and the reactions of the organodiboranes $B_2H_{2+x}Me_{4-x}$[10b] and **2**.[4] Boron-11 NMR spectra consist of a doublet at 1.01 ppm (J_{BH} = 94 Hz) at 0 °C for the product of

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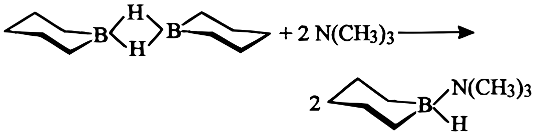
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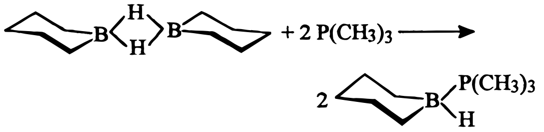
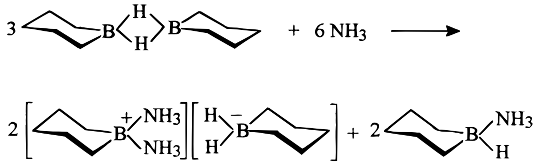

(2)

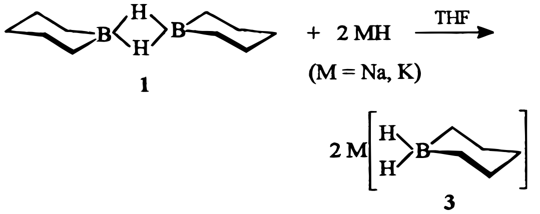
reaction 1 and a doublet of doublets at −20.9 ppm (J_{BH} = 89 Hz, J_{BP} = 52 Hz) for the product of reaction 2. Coupling between boron and phosphorus (J_{BP} = 52 Hz) was observed in the proton decoupled ^{11}B and ^{31}P NMR spectra. Symmetrical cleavage products from both reactions 1 and 2 are white solids upon removal of solvents. They are stable in solution and in the solid state at room temperature under vacuum.

Reaction of **1** with NH_3 produces both unsymmetrical and symmetrical cleavage products in a 1:1 molar ratio (reaction 3) based upon the ^{11}B NMR spectrum of the reaction mixture which consists of a singlet at −5.95 ppm assigned to $[(NH_3)_2BC_5H_{10}]^-$, a triplet at −19.50 ppm (J_{BH} = 73 Hz) assigned to $[H_2BC_5H_{10}]^-$, and a doublet at −11.20 ppm (J_{BH} = 85 Hz) assigned to $(NH_3)HBC_5H_{10}$. These ^{11}B NMR data are in excellent agreement with those assignments made for the ammonia adducts of organoboranes ($[(NH_3)_2BMe_2]^-$: −5.7 (s) ppm; $(NH_3)HBMe_2$: −12.5 (d, J_{BH} = 85 Hz)).[10b] Upon removal of liquid NH_3, the unsymmetrical cleavage product, $[(NH_3)_2BC_5H_{10}]^-[H_2BC_5H_{10}]^-$, decomposes to form the starting material **1**. In contrast, the symmetrical cleavage product, $(NH_3)HBC_5H_{10}$, is stable.


(3)

The reaction of **1** with NH_3 (reaction 3) is believed to be the first example of apparent symmetrical cleavage of the hydrogen bridge system of a diborane molecule by liquid NH_3. Previous work showed no NMR evidence for symmetrical cleavage, only unsymmetrical cleavage by liquid ammonia was observed. The tendency for symmetrical cleavage increases $CH_3NH_2 < (CH_3)_2NH < N(CH_3)_3$ when the Lewis base serves as the solvent for the reaction.[11] For the organodiboranes, $B_2H_{2+x}Me_{4-x}$[10b] and **2**,[4] similar results were also observed in that liquid ammonia produced only unsymmetrical cleavage products. But as in the case of B_2H_6 the trend for symmetrical cleavage products increased $CH_3NH_2 < (CH_3)_2NH < N(CH_3)_3$.[4,10b] This earlier work suggests that with increasing steric bulk of the amine ligand symmetrical cleavage of the hydrogen bridge system of the diborane is favored.

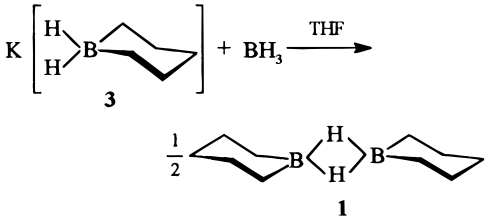
Synthesis and Reactivities of M[H$_2$BC$_5$H$_{10}$] (M = Na, K). Hydride ion from alkali metal hydrides MH (M = Na, K) reacts with **1** to produce the cyclic organohydroborate anion $[H_2BC_5H_{10}]^-$, **3**, (reaction 4). The cyclic hydroborate salts of **3** appear to be stable in THF and in the solid state under nitrogen. The sodium salt of **3** produces a sharp triplet at −22.13 ppm (J_{BH} = 72 Hz) in the ^{11}B NMR spectrum, consistent with the spectra of its lithium salt (−18.9 ppm, t, J_{BH} = 68 Hz)[12] and other dialkylborohydrides, $[H_2B(CH_3)_2]^-$ (−23.9 ppm, J_{BH} = 78 Hz)[10b] and $[H_29\text{-}(BBN)]^-$.[13] In the ^{1}H NMR spectrum of **3**, a quartet of quintets centered at 0.64 ppm is assigned to the two B−H hydrogens which couple not only to ^{11}B (J_{BH} = 72 Hz) but also to the four α hydrogens of the boracyclohexane ring (J_{HH} = 3 Hz). Upon boron decoupling, the signal collapses to a single quintet confirming the assignment. Signals in the ^{1}H NMR spectrum at 0.28, 1.31, and 1.45 ppm are assigned to the α-, γ-, and β-hydrogen atoms of the methylene groups of the ring, based on earlier work.[4]



(4)

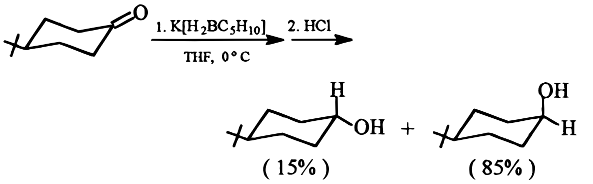
The anion **3** was reported earlier as the lithium salt by Brown and co-workers.[12] However, no reaction chemistry was reported and the procedure for the preparation of this anion is much more involved than that described here. In our reactions with metal hydride, the anion **3** was produced in almost 100% yield and purity.

$K[H_2BC_5H_{10}]$ is an effective hydride donor reagent. When one equivalent $K[H_2BC_5H_{10}]$ is added to BH_3THF, hydride ion is immediately transferred to BH_3 to form a precipitate of KBH_4 and **1** (reaction 5).



(5)

When $K[H_2BC_5H_{10}]$ reacts with 4-*tert*-butylcyclohexanone (reaction 6), 85% of the trans isomer and 15% of the *cis*-4-*tert*-butylcyclohexanol are produced. The ratio of isomers is comparable to that produced by other hydride reducing agents.[14]



(6)

Anion **3** functions as a chelating agent in its reactions with zirconocene dichloride and hafnocene dichloride to produce $(\eta^5\text{-}C_5H_5)_2MCl(\mu\text{-}H)_2BC_5H_{10}$ (M = Zr, **4**, and Hf, **5**) (reaction 7). The formation of **4** and **5** involves a simple metathesis reaction with the formation of KCl and a neutral transition metal−boron species. Interestingly, when the anion, $[(\mu\text{-}H)_2B_2H(\mu\text{-}C_4H_8)]^-$, reacts with zirconocene dichloride and hafnocene dichloride, a

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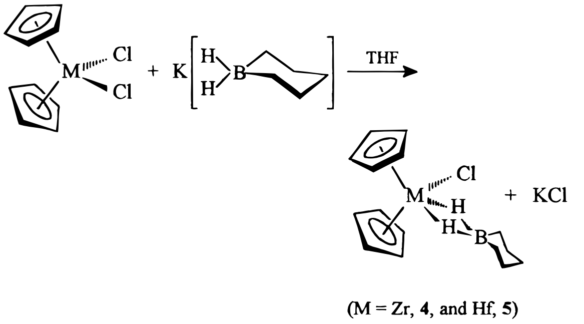

(7)

ring transformation of the anion occurs and the boracyclopentane derivative (η^5-C_5H_5)$_2$MCl(μ-H)$_2$$BC_4H_8$ (M = Zr, Hf) is formed.[15]

NMR spectra of **4** and **5** are similar. The ^{11}B NMR spectrum of **4** consists of a broad triplet at +13.6 ppm, similar to the spectrum of (η^5-C_5H_5)$_2$MCl(μ-H)$_2$$BC_4H_8$ (M = Zr, Hf).[15] The coupling pattern is consistent with a boron atom bonded to two hydrogen atoms, and the coupling constant of J_{B-H} = 53 Hz, is within the range expected for a bridging hydrogen interaction. This suggests and as indicated in the X-ray structure discussed below that two three-center hydrogen bridges exist between the boron atom and the metal center. In **5**, the triplet appears at +9.3 ppm. Although the ^{11}B NMR spectrum indicates that equivalent bridge hydrogens exist with respect to the boron atom, clearly the ^1H NMR spectrum displays inequivalence of the two bridging hydrogen atoms in the complex at room temperature. The ^1H NMR spectrum of **4** in d_8-THF contains two broadened signals +0.24 and −2.07 ppm, which are in the range common for bridging hydrogen interactions.[15] Equivalence of these two hydrogens is temperature dependent, as coalescence into a single resonance at −0.86 ppm occurs above 55 °C, which is similar to that observed in the boracyclopentane derivative (η^5-C_5H_5)$_2$MCl(μ-H)$_2$$BC_4H_8$ (M = Zr, Hf).[15] Clues for the exchange pathway could not be deduced from ^1H and ^{11}B NMR spectra. However, a reasonable assumption is 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 formerly occupied by the broken Zr−H−B bond followed by reassembly of the broken bond.[15]

Qualitative studies of reactions of **4** with Lewis bases, $N(CH_3)_3$ and NH_3, were carried out using the liquid Lewis base as the solvent. Boron-11 NMR spectra indicate that the hydrogen bridge system is cleaved symmetrically by $N(CH_3)_3$ in that a doublet signal occurs at 0.33 ppm (J_{BH} = 88 Hz) that is consistent with the formation of $(CH_3)_3NHBC_5H_{10}$ in the reaction. Liquid ammonia cleaves the double hydrogen bridge system both symmetrically and unsymmetrically as observed in the reaction of **1** with liquid NH_3. Evidence for symmetrical cleavage is provided by a doublet in the ^{11}B NMR spectrum at −11.64 ppm (J_{BH} = 78 Hz) that is consistent with the formation of $(NH_3)HBC_5H_{10}$. In the unsymmetrical cleavage reaction of **4** with liquid NH_3 there are two possible ways in which the bridge can be cleaved unsymmetrically and both of these routes appear to occur in the reaction with NH_3 (Scheme 1). In one case (pathway 1 in Scheme 1) the cleavage produces a boronium ion $[(NH_3)_2BC_5H_{10}]^+$ (−6.27 ppm (s)) and presumably a zirconocene anion. In the other pathway (pathway 2 in Scheme 1) unsymmetrical cleavage leads to the formation of a zirconocene cation and the cyclic hydroborate anion $[H_2BC_5H_{10}]^-$ (−19.37 ppm (t, J_{BH} = 72 Hz)), produced in the reaction of **1** with liquid NH_3 (reaction 3).

Molecular Structure of (η^5-C_5H_5)$_2$ZrCl(μ-H)$_2$$BC_5H_{10}$, 4. Colorless crystals of **4** were formed from a THF solution layered with hexane at −25 °C. Crystallographic data are given in Table 1. Selected positional parameters and bond distances and angles are given in Tables 4 and 5. The ORTEP of (η^5-C_5H_5)$_2$ZrCl(μ-H)$_2$$BC_5H_{10}$ is shown in Figure 2.

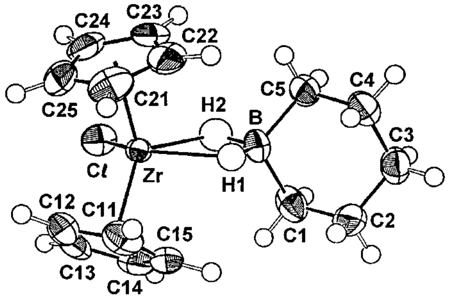

Figure 2. ORTEP plot of molecular structure of (η^5-C_5H_5)$_2$ZrCl(μ-H)$_2$$BC_5H_{10}$ with 50% probability thermal ellipsoids.

The solid-state structure of (η^5-C_5H_5)$_2$ZrCl(μ-H)$_2$$BC_5H_{10}$ closely approximates that of (η^5-C_5H_5)$_2$ZrCl(μ-H)$_2$$BC_4H_8$,[15] but it contains a boracyclohexane ring in place of a boracyclopentane ring. The geometry around the Zr center consists of a distorted tetrahedron that is defined by B, Cl, and two centroids of the two $C_5H_5^-$ rings. The angle of the centroid−Zr−centroid is 129.97(6)° and the angle of Cl−Zr−B is 101.12(6)°; and the distances of Zr−H1, Zr−H2, and Zr−B are 2.06(2), 2.10(2), and 2.593(2) Å, respectively, in close agreement with those parameters in (η^5-C_5H_5)$_2$ZrCl(μ-H)$_2$$BC_4H_8$.[15]

Experimental Section

Materials. All manipulations were carried out on a standard high vacuum line or in a drybox under an atmosphere of dry, pure N_2. Tetrahydrofuran was dried over Na/benzophenone for 4 days followed by distillation into a storage bulb which also contained Na/benzophenone. Hexane was stirred over concentrated sulfuric acid for 2 days and then decanted and washed with water. Finally it was dried by stirring it with CaH_2 for 6 days followed by distillation into a storage bulb containing Na. Previously dried solvents were freshly distilled into the reaction flasks prior to use. 1,4-pentadiene, BH_3THF (1.0 M in THF), 4-*tert*-butylcyclohexanone, and $P(CH_3)_3$ (Aldrich) were used as received. $N(CH_3)_3$ and NH_3 were purchased from Matheson. $N(CH_3)_3$ was dried over CaH_2 under vacuum at 0 °C for 1 day. NH_3 was dried over Na. Zirconocene dichloride and hafnocene dichloride (Strem) was used as received. (μ-H)$_2$$(BC_5H_{10})_2$ was prepared according to the reported method.[2a]

All IR spectra were recorded with 2 cm^{-1} resolution using a Mattson-Polaris FT-IR spectrometer. Boron-11 NMR {$\delta(Et_2OBF_3)$ = 0.00 ppm}, proton NMR {$\delta[Si(CH_4)_4]$ = 0.00 ppm}, and phosphorus-31 NMR {$\delta(H_3PO_4)$ = 0.00 ppm} were obtained on either a Bruker AM-250 or a MSL-300 instrument. Elemental analyses were performed in Galbraith Laboratories, Inc., Knoxville, Tennessee.

Reaction of (μ-H)$_2$$(BC_5H_{10})_2$ with Liquid $N(CH_3)_3$. A 0.024 g quantity of (μ-H)$_2$$(BC_5H_{10})_2$ (0.14 mmol) was placed in a 5 mL flask which was equipped with an NMR tube and a magnetic stir bar. The flask was sealed with a vacuum line adaptor in the drybox. On the vacuum line, the flask was evacuated and $N(CH_3)_3$ (ca. 3 mL) was condensed into the flask at −78 °C. The mixture was stirred for 2 min at −35 °C and then was transferred to the NMR tube at −20 °C. The NMR tube was flame-sealed, and ^{11}B NMR spectra were recorded. ^{11}B NMR ($N(CH_3)_3$): 1.01 (d, J_{BH} = 94 Hz) ppm at 0 °C; 0.73 (d, J_{BH} = 92 Hz) ppm at −25 °C; and 0.61 (d, J_{BH} = 94 Hz) ppm at −40 °C.

After $N(CH_3)_3$ was pumped away from the reaction mixture, a white solid was obtained. The ^{11}B NMR spectrum was recorded in THF at room temperature. ^{11}B NMR (THF): 0.29 (d, J_{BH} = 93 Hz) ppm.

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Scheme 1

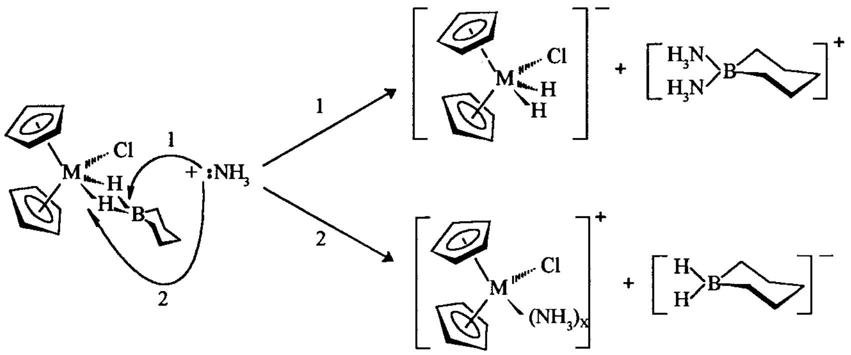

Table 4. Selected Positional Parameters and Their Esd's for $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-}H)_2BC_5H_{10}$

atom	*x*	*y*	*z*	*B* (Å^2)^{a,b}
Zr	0.31882(1)	0.03645(2)	0.21108(1)	2.347(4)
Cl	0.48139(4)	0.08391(7)	0.13207(4)	4.17(1)
B	0.2038(2)	0.2583(3)	0.1527(2)	3.37(4)
C1	0.2241(2)	0.4007(2)	0.2183(2)	4.66(5)
C2	0.1218(2)	0.4482(2)	0.2558(2)	4.61(6)
C3	0.0268(2)	0.4605(2)	0.1654(2)	4.31(5)
C4	0.0036(2)	0.3240(3)	0.1061(2)	4.20(5)
C5	0.1002(2)	0.2709(3)	0.0614(2)	4.25(5)
C11	0.3000(2)	−0.0075(3)	0.3988(2)	4.46(5)
C12	0.3960(2)	−0.0735(3)	0.3843(2)	4.68(5)
C13	0.4681(2)	0.0312(3)	0.3685(2)	4.43(5)
C14	0.4182(2)	0.1601(3)	0.3721(2)	4.23(5)
C15	0.3155(2)	0.1360(3)	0.3932(2)	4.07(5)
C21	0.2027(2)	−0.1757(2)	0.1905(2)	4.95(5)
C22	0.1524(2)	−0.0830(3)	0.1158(2)	4.79(5)
C23	0.2190(2)	−0.0639(3)	0.0400(2)	4.73(5)
C24	0.3102(2)	−0.1479(2)	0.0687(2)	4.51(5)
C25	0.3011(2)	−0.2155(2)	0.1630(2)	4.68(5)
H1	0.189(1)	0.168(2)	0.214(1)	2.4(4)
H2	0.278(2)	0.224(2)	0.127(2)	4.4(5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] Hydrogen atoms H1 and H2 were located and refined isotropically.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-}H)_2BC_5H_{10}$^{a}

	Bond Distances		
Zr−C*l*	2.4802(5)	B−H2	1.09(2)
Zr−B	2.593(2)	B−C1	1.590(4)
av Zr−C(11−15)^a	2.503[6]	B−C5	1.593(3)
av Zr−C(21−25)^a	2.497[9]	C1−C2	1.521(4)
Zr−H1	2.06(2)	C2−C3	1.514(4)
Zr−H2	2.10(2)	C3−C4	1.507(3)
B−H1	1.19(2)	C4−C5	1.519(3)
	Bond Angles		
C*l*−Zr−B	101.12(6)	H1−B−H2	103(1)
C*l*−Zr−H1	127.4(5)	Zr−H1−B	102(1)
C*l*−Zr−H2	77.3(6)	Zr−H2−B	104(1)
H1−Zr−H2	50.9(7)	B−C1−C2	110.8(2)
C1−B−C5	110.9(2)	B−C5−C4	110.7(2)
C1−B−H1	107.1(9)	C1−C2−C3	112.3(2)
C1−B−H2	111(1)	C2−C3−C4	112.0(2)
C5−B−H1	109.5(9)	C3−C4−C5	112.4(2)
C5−B−H2	115(1)		

[a] The standard deviation (σ_l) for the average bond length of Zr−C is calculated according to the following equations (see ref 17):

$$\langle l\rangle = \sum_m l_m/m$$

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

where $\langle l\rangle$ is the mean length, l_m is the length of the mth bond, and m is the number of bonds.

Reaction of $(\mu\text{-}H)_2(BC_5H_{10})_2$ with $P(CH_3)_3$. A 0.012 g quantity of $(\mu\text{-}H)_2(BC_5H_{10})_2$ (0.07 mmol) was placed in a 5 mL flask which was equipped with an NMR tube and a magnetic stir bar. The flask was sealed with a vacuum line adaptor in the drybox. On the vacuum line, the flask was evacuated and $P(CH_3)_3$ (ca. 2 mL) was condensed into the flask at −78 °C. The mixture was stirred at room temperature for 2 min. Then $P(CH_3)_3$ was removed under reduced pressure and a white solid was obtained. Finally, THF was condensed into the flask and the solution was transferred to the NMR tube. ^{11}B and ^{31}P NMR spectra were recorded at room temperature. ^{11}B NMR (THF): −20.9 (dd, J_{BH} = 89 Hz, J_{BP} = 52 Hz) ppm. ^{31}P NMR (THF): −7.67 (br, J_{PH} unresolved, J_{BP} = 54 Hz) ppm.

Reaction of $(\mu\text{-}H)_2(BC_5H_{10})_2$ with Liquid NH_3. A 0.024 g quantity of $(\mu\text{-}H)_2(BC_5H_{10})_2$ (0.14 mmol) was placed in a 5 mL flask which was equipped with an NMR tube and a magnetic stir bar. The flask was sealed with a vacuum line adaptor in the drybox. On the vacuum line, the flask was evacuated and NH_3 (ca. 3 mL) was condensed into the flask at −78 °C. The mixture was stirred for 5 min at −35 °C, and then the liquid was transferred to the NMR tube at −40 °C. The NMR tube was flame sealed and ^{11}B NMR spectra were taken at −40 °C. ^{11}B NMR ($N(CH_3)_3$): −5.95 (s), −11.20 (d, J_{BH} = 85 Hz), −19.50 (t, J_{BH} = 73 Hz) ppm.

After NH_3 was pumped away from the reaction mixture, a white solid was obtained. ^{11}B NMR spectra were taken in THF at room temperature. ^{11}B NMR (d_8-THF): 54.92 (s) ppm (from partial decomposition of $(\mu\text{-}H)_2(BC_5H_{10})_2$ in THF), 24.96 (t, br, unresolved) ppm (from $(\mu\text{-}H)_2(BC_5H_{10})_2$), 12.62 (d, J_{BH} = 123 Hz) ppm (from partial decomposition of $(\mu\text{-}H)_2(BC_5H_{10})_2$ in THF), −10.42 (d, J_{BH} = 92 Hz) ppm (from symmetrical cleavage product $(NH_3)HBC_5H_{10}$).

Preparation of $M[H_2BC_5H_{10}]$ (M = Na, K). A 0.205 g quantity of $(\mu\text{-}H)_2(BC_5H_{10})_2$ (1.25 mmol) was dissolved in THF (10 mL) and KH (0.12 g, 2.99 mmol) was added into the flask at room temperature under N_2. The mixture was stirred for 0.5 h at room temperature and filtered. A white solid was obtained when solvent was pumped away. Hydrolysis analysis showed that 98% theoretical amount of H_2 was released from the reaction of $K[H_2BC_5H_{10}]$ with hydrochloric acid. NMR (d_8-THF): ^{11}B, −19.95 (t, J_{BH} = 73 Hz) ppm; ^1H, 1.48 (4 H, m), 1.32 (2 H, m), 0.77 (2 H, q, J_{BH} = 73 Hz), 0.28 (4 H, m) ppm. IR (cm^{-1}, in THF): 2974 (m), 2858 (m), 2780 (m), 2179 (sh, s), 2106 (vs), 2044 (sh, s), 1934 (w), 1692 (s), 1567 (m), 1418 (sh, m), 1385 (m), 1337 (w), 1141 (vw), 1069 (m), 910 (m), 800 (vw), 745 (w), 682 (vw). IR (cm^{-1}, in KBr): 2902 (s), 2868 (s), 2831 (s), 2784 (s), 2288 (sh, w), 2226 (sh, m), 2160 (sh, s), 2136 (vs), 2080 (s), 1985 (m), 1438 (s), 1414 (m), 1323 (vw), 1276 (sh, w), 1241 (s), 1223 (sh, m), 1210 (sh, w), 1181 (sh, m), 1170 (s), 1116 (s), 1081 (m), 1055 (s), 1015 (vw), 979 (vw), 960 (m), 935 (m), 868 (m), 756 (m), 717 (w), 693 (w), 506 (m).

In the reaction of NaH with $(\mu\text{-}H)_2(BC_5H_{10})_2$, 0.043 g (0.26 mmol) of $(\mu\text{-}H)_2(BC_5H_{10})_2$ was dissolved in THF (5 mL) and NaH (0.016 g, 0.67 mmol) was added. After 2 h of stirring, solvent was removed from the solution and a white solid was isolated. NMR (d_8-THF): ^{11}B,

−22.13 (t, J_{BH} = 71 Hz); ^{1}H, 1.45 (4 H, m), 1.31 (2 H, m), 0.64 (2 H, quartet of quintet, J_{BH} = 72.3 Hz, J_{HH} = 3.23 Hz), 0.28 (4 H, m) ppm.

Hydride Transfer Reaction of $[H_2BC_5H_{10}]^-$. (1) Reaction of $K[H_2BC_5H_{10}]$ with BH_3THF. A 10 mL quantity of a 0.1 M solution of $K[H_2BC_5H_{10}]$ was added to a 50 mL flask containing a magnetic stir bar and BH_3THF (1.0 M, 1 mL) while stirring constantly at room temperature. White solid was precipitated from the solution immediately. The mixture was stirred for 30 min and filtered. The white solid left on the frit was characterized as KBH_4 by IR, powder XRD, and ^{11}B NMR. THF was removed from the filtrate to leave a colorless crystalline solid in the flask which was identified as $(\mu\text{-H})_2(BC_5H_{10})_2$ from its ^{11}B NMR spectrum (25.01 (t, br) ppm) in THF.

(2) Reduction of 4-*tert*-Butylcyclohexanone by $K[H_2BC_5H_{10}]$. A flask equipped with a sidearm tube and a magnetic stir bar was charged with 4-*tert*-butylcyclohexanone (0.0312 g, 0.202 mmol) and THF (10 mL). $K[H_2BC_5H_{10}]$, 20 mL (0.202 mmol) THF solution was placed in the sidearm tube. The flask was sealed with a vacuum line adaptor. After this apparatus was brought out of the drybox, the flask and sidearm were cooled to 0 °C for 30 min. $K[H_2BC_5H_{10}]$ in THF was then slowly added to the flask with constant stirring. The mixed solution was stirred for 2 h at 0 °C. HCl, 3 M, was then added into the solution. The mixture was stirred for 1 h. The reaction solution was extracted with ether three times, and the combined ether extracts was treated with 3 M NaOH and then with water. Finally the ether solution was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure at room temperature to yield the crude product. Then the crude product was pumped on for 2 h at room temperature to give the final product, 0.02891 g, 92% isolated yield product. It was identified by comparison of its NMR spectra with the reported spectra.[14] For the *trans*-4-*tert*-butylcyclohexanol, ^{1}H NMR ($CDCl_3$): 0.84 (s, 9 H), 0.9−2.1 (m, 10 H), 3.51 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): 25.6, 27.6, 36.0, 47.1, 71.2 ppm. For the *cis*-4-*tert*-butylcyclohexanol, ^{1}H NMR ($CDCl_3$): 0.86 (s, 9 H), 0.9−2.1 (m, 10 H), 4.03 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): 20.9, 32.3, 33.4, 48.0, 65.8 ppm.

Preparation of $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-H})_2BC_5H_{10}$. A 0.146 g quantity of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ (0.50 mmol) was dissolved in THF (10 mL) in a 50 mL flask, and $K[H_2BC_5H_{10}]$ (0.50 mmol, 15 mL) THF solution was added to the flask with constant stirring at room temperature under N_2. The mixture was stirred overnight at ambient temperature and then filtered. The white precipitate was characterized as KCl by powder XRD. Upon removal of most of the THF from the filtrate and addition of Et_2O, a white solid was obtained. Et_2O was removed, and white solid was dried under vacuum for 2 h (0.142 g, 84%). NMR (d_8-THF): ^{11}B, 13.66 (t, br, J_{BH} = 53 Hz) ppm; ^{1}H, 6.34 (10 H on Cp^- rings, s), 1.49 (4 H, m), 1.39 (2 H, m), 0.89 (4 H, m), 0.24 (1 H, s, br), −2.07 (1 H, s, br) ppm. IR (cm^{-1}, in THF): 3106 (s), 2975 (m), 2862 (m), 2016 (vs), 1818(m), 1754 (m), 1656 (w), 1555 (w), 1384 (vs), 1327 (m), 1219 (vw), 1069 (w), 1013 (w), 910 (vw), 806 (m), 741 (m), 610 (vw). IR (cm^{-1}, in KBr): 3116 (m), 3089 (m), 2912 (s), 2900 (s), 2878 (s), 2834 (m), 2807 (w), 2012 (vs), 1997 (s), 1970 (m, sh), 1943 (sh, m), 1813 (w), 1715 (w), 1442 (m), 1419 (w), 1374 (vs), 1337 (s), 1292 (w), 1276 (w), 1254 (m), 1214 (m), 1190 (vw), 1126 (vw), 1090 (w), 1021 (sh, m), 1014 (s), 956 (m), 812 (vw), 849 (sh, m), 829 (sh, m), 809 (s), 740 (m), 610 (w), 575 (w). Broad bands with maximum at 2102 cm^{-1} (in KBr) and 2012 cm^{-1} (in THF) for B−H stretching, 1374 cm^{-1} (in KBr) and 1337 cm^{-1} (in THF) for M−H stretching, and other bands for organic ring. Anal. Calcd for $C_{15}H_{22}BClZr$: C, 53.02; H, 6.52; B, 3.18; Cl, 10.43. Found: C, 51.22; H, 6.04; B, 2.63; Cl, 10.15.

Preparation of $(\eta^5\text{-}C_5H_5)_2HfCl(\mu\text{-H})_2BC_5H_{10}$. A 0.191 g quantity of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ (0.502 mmol) was dissolved in THF (10 mL) in a 50 mL flask, and $K[H_2BC_5H_{10}]$ (0.536 mmol, 15 mL) THF solution was added to the flask with constant stirring at room temperature under N_2. The mixture was stirred overnight at ambient temperature and then filtered. The white precipitate was characterized as KCl by powder XRD. Upon removal of THF from the filtrate and addition of Et_2O, a white solid was obtained. Et_2O was removed, and white solid was dried under vacuum for 2 h (0.152 g, 71%). NMR (d_8-THF): ^{11}B, 9.32 (t, J_{BH} = 57 Hz) ppm; ^{1}H 6.25 (10 H on Cp^- rings, s), 1.49 (4 H, m), 1.43 (2 H, m), 0.86 (4 H, m) ppm. Anal. Calcd for $C_{15}H_{22}BClHf$: C, 42.18; H, 5.19; B, 2.53; Cl, 8.30. Found: C, 40.03; H, 4.71; B, 2.46; Cl, 8.22.

Reaction of $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-H})_2BC_5H_{10}$ with $N(CH_3)_3$ and NH_3. Both reactions were carried out in a similar manner. In the drybox, $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-H})_2BC_5H_{10}$ was placed in an NMR tube which was attached to a 9 mm solv-seal joint. The NMR tube was sealed with a vacuum line adaptor. On the vacuum line, $N(CH_3)_3$ or NH_3, 1 mL, was condensed into the NMR tube at −78 °C, and then the NMR tube was flame-sealed. ^{11}B NMR spectra were recorded at −40 °C.

For the reaction with $N(CH_3)_3$, ^{11}B NMR (in $N(CH_3)_3$) yielded a feature at 0.33 (d, J_{BH} = 88 Hz) ppm. For the reaction with NH_3, ^{11}B NMR (in NH_3) yielded features at −6.27 (s), −11.64 (d, J_{BH} = 78 Hz), and −19.37 (t, J_{BH} = 72 Hz) ppm.

X-ray Crystal Structure Determinations. A crystal of suitable size was mounted in a glass capillary under N_2. Crystallographic data were collected 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 was applied based on measured ψ scans for $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-H})_2BC_5H_{10}$. Crystallographic data are listed in Table 1.

Structures were solved by the direct method MULTAN 11/82 and difference Fourier synthesis. Analytical atomic scattering factors were used throughout the structure refinement with both the 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 MolEN.[16] Full-matrix least-squares refinements were employed.

$(\mu\text{-H})_2(BC_5H_{10})_2$ undergoes a reversible phase transformation between −20 and −40 °C. Two data sets of reflections, one at 5 °C and the other at −60 °C, were collected from the same single crystal. Because the molecular structures of the $(\mu\text{-H})_2(BC_5H_{10})_2$ molecules in the two space groups are identical, only the one structure at −60 °C is discussed here. The reflection data set at −60 °C was collected in the 2θ range from 4 to 50° ($0 \le h \le 7$, $-11 \le k \le 11$, $-12 \le l \le 12$). There are 198 variable parameters refined based upon 1885 independent reflections with 1072 reflections [$I > 3\sigma(I)$]. After all of the non-hydrogen atoms were located and refined, all hydrogen atoms were located from the difference Fourier maps. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically to convergence (final shift/error ≤ 0.03). The highest residual peak on the final difference Fourier map was 0.380 e/Å^3 at a distance of 0.803 Å from C25 for crystal structure at −60 °C.

For $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-H})_2BC_5H_{10}$, the reflection data set was collected in the range of 2θ from 4° to 50° ($0 \le h \le 15$, $0 \le k \le 11$, $-15 \le l \le 15$). There are 172 variable parameters refined based upon 2654 independent reflections with 2282 reflections [$I > 3\sigma(I)$]. After all of the non-hydrogen atoms were located and refined, two bridging hydrogen atoms between Zr and B centers were located from the difference Fourier maps. Remaining hydrogen atoms on both C_5H_5 rings and the C_5H_{10} fragment were placed at calculated positions assuming ideal geometries with C−H distances of 0.95 Å. The thermal parameters of the hydrogen atoms were set to B(H) = 1.3B(C) Å^2. Positional and thermal parameters of these calculated hydrogen atoms were fixed during the refinement. The two bridge hydrogen atoms were located and refined isotropically. All non-hydrogen atoms were refined anisotropically. New hydrogen positions were calculated and this procedure was repeated until the parameters of non-hydrogen atoms were refined to convergence (final shift/error ≤ 0.03). The highest residual peak on the final difference Fourier map was 0.308 e/Å^3 at a distance of 0.830 Å from the chlorine atom.

Acknowledgment. This work was supported by the National Science Foundation through CHE94-09123 and CHE97-00394.

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(16) *MolEN Crystal Structure Analysis Program*; Enraf-Nonius: Delft, The Netherlands, 1990.

(17) Stout, G. H.; Jensen, L. H. In *X-ray Structure Determination*, 2nd ed.; Wiley: New York, 1989; pp 406−408.

Supporting Information Available: Tables of crystallographic data, positional parameters, completed bond distances and angles, anisotropic thermal parameters for $(\eta^5\text{-}C_5H_5)_2ZrCl(\mu\text{-}H)_2BC_5H_{10}$, $(\mu\text{-}H)_2(BC_5H_{10})_2$ (5 °C), and $(\mu\text{-}H)_2(BC_5H_{10})_2$ (−60 °C) and figures of ORTEP for $(\mu\text{-}H)_2(BC_5H_{10})_2$ (5 °C), and the unit cell packing diagrams for both $(\mu\text{-}H)_2(BC_5H_{10})_2$ structures at 5 and −60 °C (16 pages). Ordering information is given on any current masthead page.

IC971275R