Inorg. Chem. **1999,** *38,* 2169−2173

Cyclic Hydroborate Complexes of Metallocenes. IV. Weak Unsupported Single Hydrogen Bridges in $Cp_2Zr\{(\mu\text{-}H)B(X)CH_2Ph\}\{(\mu\text{-}H)_2BX\}$ ($X = C_5H_{10}$, C_4H_8)

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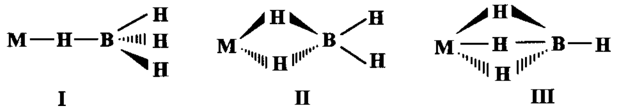
Received November 24, 1998

The compounds $Cp_2Zr\{(\mu\text{-}H)(BC_5H_{10})CH_2Ph\}\{(\mu\text{-}H)_2BC_5H_{10}\}$, **1**, and $Cp_2Zr\{(\mu\text{-}H)(BC_4H_8)CH_2Ph\}\{(\mu\text{-}H)_2BC_4H_8\}$, **2**, were prepared in yields of 59% and 51%, respectively, from the reactions of $Cp_2ZrCl\{(\mu\text{-}H)_2BX\}$ ($X = C_5H_{10}$, C_4H_8) with $PhCH_2MgCl$. Single-crystal X-ray diffraction analyses indicate the presence of an unsupported Zr−H−B bond in these complexes. In solution at low temperature ^1H NMR spectra are consistent with the presence of the unsupported Zr−H−B bridge in complexes **1** and **2**. However, NMR spectra at room temperature indicate that the hydrogen bridge is dissociated into $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ and $B(C_5H_{10})CH_2Ph$ in the case of complex **1**, and $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ and $B(C_4H_8)CH_2Ph$ in the case of complex **2**. It is possible to pump away the $B(C_4H_8)CH_2Ph$ from solid **2** at room temperature, leaving behind $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$. These results suggest that the Zr−H bond acts as an electron pair donor to trivalent boron in the formation of **1** and **2**. Crystal data for $Cp_2Zr\{(\mu\text{-}H)(BC_5H_{10})CH_2Ph\}\{(\mu\text{-}H)_2BC_5H_{10}\}$: monoclinic, $P2_1/m$ (No. 11), $a = 9.392(5)$ Å, $b = 13.250(4)$ Å, $c = 9.841(6)$ Å, $\beta = 95.70(4)°$, $Z = 2$. Crystal data for $Cp_2Zr\{(\mu\text{-}H)(BC_4H_8)CH_2Ph\}\{(\mu\text{-}H)_2BC_4H_8\}$: orthorhombic, *Pbca* (No. 61), $a = 18.1630(10)$ Å, $b = 19.0497(10)$ Å, $c = 13.0393(10)$ Å, $Z = 8$.

Introduction

The M−H−B three-center, two-electron bond is present in covalent hydroborate metal complexes in which the hydroborate serves as a monodentate, bidentate, or tridentate ligand (Chart 1). Tridentate and bidentate linkages between metal and boron atoms are more common than monodentate linkages.[1] IR spectroscopy has been applied as the principal technique for the identification of monodentate interaction of a hydroborate anion with a metal for most of the complexes that have been reported to contain an unsupported M−H−B bond.[1a,2] However, there are some monodentate complexes that have been structurally characterized by single-crystal X-ray or neutron diffraction analyses. These are $[Cu\{(\mu\text{-}H)BH_3\}(PMePh_2)_3]$,[3] $[Cu\{(\mu\text{-}H)BH_3\}\{(PPh_2CH_2)_3CMe\}]$,[4] $[FeH\{(\mu\text{-}H)BH_3\}(dmpe)_2]$ (dmpe = bis(dimethylphosphino)ethane),[5] $[Hf_2\{N(SiMe_2CH_2PMe_2)_2\}_2H_3(BH_4)_3]$,[6] $[V\{(\mu\text{-}H)BH_3\}_2\{dmpe\}_2]$,[7] $\{Cr(Py)_4\{(\mu\text{-}H)BH_3\}_2\}$ (Py = pyridine),[8] $\{Cr_3(TMEDA)_2(Py)_4((\mu\text{-}H)_2BH_2)_4\}\{(\mu\text{-}H)BH_3\}_2\}$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine),[8] and $\{RuH\{(\mu\text{-}H)BH_3\}(Me_8[16]aneS_4)$.[9] Monodentate, unsupported M−H−B bridges have also been observed in the following compounds: $\{M(CO)_5((\mu\text{-}H)B_2H_3\cdot 2PMe_3)\}$ (M = Cr, W),[10] and $\{Cp_2Ta(PMe_3)\{(\mu\text{-}H)BH_2(Si(t\text{-}Bu)_2H)\}$.[11]

Chart 1



Described here is recent work that led to the preparation and isolation of the following complexes with unsupported single hydrogen bridges: $Cp_2Zr\{(\mu\text{-}H)B(X)CH_2Ph\}\{(\mu\text{-}H)_2BX\}$ ($X = C_5H_{10}$ (**1**), C_4H_8 (**2**)). To our knowledge these are the first demonstrated examples of the formation of a single M−H−B bond in which the M−H bond acts as an electron pair donor to a trivalent boron to form the hydrogen-bridged bond.[12] In previous examples[3−11] the B−H bond serves as the electron pair donor to the unsaturated metal center.

Results and Discussion

Formation of $Cp_2Zr\{(\mu\text{-}H)B(X)CH_2Ph\}\{(\mu\text{-}H)_2BX\}$ ($X = C_5H_{10}$,[1] C_4H_8[2]). In an attempt to prepare the benzyl-substituted cyclic hydroborate complex $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$ from the reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$[13] with $PhCH_2$-

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(1) (a) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263. (b) Gilbert, K. B.; Boocock, S. K.; Shore, S. G. Compounds with Bonds between a Transition Metal and Boron. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press Inc.: New York, 1982; pp 879−945.

(2) Marks, T. J.; Kennelly, W. J.; Kolb, J. R.; Shimp, L. A. *Inorg. Chem.* **1972**, *11*, 2540.

(3) (a) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Shore, S. G.; Schmitkons, T.; Fratini, A. V.; Morse, K. W.; Wei, C.-Y.; Bau, R. *J. Am. Chem. Soc.* **1981**, *103*, 5165. (b) Bommer, J. C.; Morse, K. W. *Inorg. Chem.* **1980**, *19*, 587. (c) Kutal, C.; Grutsch, P.; Atwood, J. L.; Rogers, R. D. *Inorg. Chem.* **1978**, *17*, 3558.

(4) (a) Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096. (b) Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2768.

(5) (a) Bau, R.; Yuan, H. S. H.; Baker, M. V.; Field, L. D. *Inorg. Chim. Acta* **1986**, *114*, L27. (b) Baker, M. V.; Field, L. D. *J. Chem. Soc., Chem. Commun.* **1984**, 996.

(6) Fryzuk, M. D.; Rettig, S. J.; Westerhaus, A.; Williams, H. D. *Inorg. Chem.* **1985**, *24*, 4316.

(7) Jensen, J. A.; Girolami, G. S. *Inorg. Chem.* **1989**, *28*, 2107.

(8) Dionne, M.; Hao, S.; Gambarotta, S. *Can. J. Chem.* **1995**, *73*, 1126.

(9) Yoshida, T.; Adachi, T.; Ueda, T.; Akao, H.; Tanaka, T.; Goto, F. *Inorg. Chim. Acta* **1995**, *231*, 95.

(10) Katoh, K.; Shimoi, M.; Ogino, H. *Inorg. Chem.* **1992**, *31*, 670.

(11) Jiang, Q.; Carroll, P. J.; Berry, D. H. *Organometallics* **1993**, *12*, 177.

(12) Ir−H···B interaction in *fac*-$[IrH(PMe_3)_3(\eta^2\text{-}CH_2BHC_8H_{14})]$ has been suggested. Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; Williams, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399.

(13) Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 496.

10.1021/ic981347u CCC: $18.00

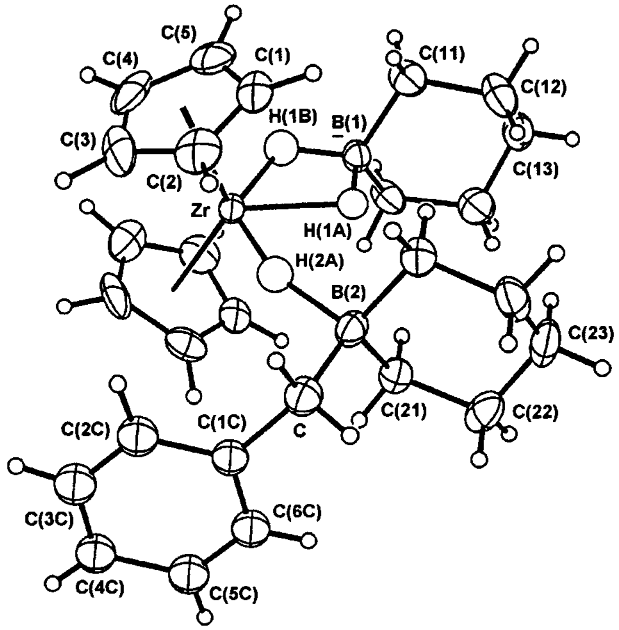

Figure 1. Molecular structure of $Cp_2Zr\{(\mu\text{-}H)BC_5H_{10}(CH_2Ph)\}\{(\mu\text{-}H)_2BC_5H_{10}\}$ showing 50% probability ellipsoids.

MgCl, a complicated sequence of reactions occurred that resulted in the isolation of $Cp_2Zr\{(\mu\text{-}H)B(C_5H_{10})CH_2Ph\}\{(\mu\text{-}H)_2BC_5H_{10}\}$, **1**, a compound that contains an unsupported single hydrogen bridge in the solid state. The reaction produces a mixture of several organoborate species. Boron-11 NMR spectra at room temperature indicate that the initial major products are $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$[14] and an organoborate anion ($\delta = -15.2$ ppm) that is believed to be $[B(C_5H_{10})(CH_2Ph)_2]MgCl$,[15] an intermediate that decreases in concentration with time. Minor initial components $Cp_2Zr(CH_2Ph)\{(\mu\text{-}H)_2BC_5H_{10}\}$[16] and $B(C_5H_{10})CH_2Ph$ increase in concentration as the concentration of the intermediate species decreases. Similar competing reactions resulting in complicated products are also observed in the direct alkylation of the cyclic hydroborate complexes $Cp_2ZrCl\{(\mu\text{-}H)_2X\}$ ($X = BC_4H_8$, BC_5H_{10}).[13,17] Crystallization from the reaction mixture yielded two types of crystals that were manually separated: $Cp_2Zr\{(\mu\text{-}H)B(C_5H_{10})CH_2Ph\}\{(\mu\text{-}H)_2BC_5H_{10}\}$, **1** (59% yield), colorless crystals identified from a single-crystal X-ray diffraction analysis, and the previously reported compound $Cp_2Zr(CH_2Ph)_2$[18] (10% yield), orange crystals that were identified by ^1H NMR spectroscopy and confirmed by single-crystal X-ray diffraction analysis.[19]

The reaction of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ with $PhCH_2MgCl$ forms the complex $Cp_2Zr\{(\mu\text{-}H)B(C_4H_8)CH_2Ph\}\{(\mu\text{-}H)_2BC_4H_8\}$, **2** (51% yield, colorless crystals), in a sequence of steps, followed by NMR spectroscopy, with intermediate species similar to those in the formation of **1**.

Molecular Structures of 1 and 2. The molecular structures of **1** and **2** are shown in Figures 1 and 2. Crystallographic data and selected positional parameters, bond distances, and bond angles are given in Tables 1−5. The X-ray analyses show that the structures of complexes **1** and **2** are closely related. In the solid state, each complex contains an unsupported single hydrogen Zr−H−B bridge that connects the $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}$ and $BC_5H_{10}(CH_2Ph)$ units in **1** and the $Cp_2Zr\{(\mu\text{-}H)_2BC_4H_8\}$ and $BC_4H_8(CH_2Ph)$ units in **2**. The Zr−H bond of the parent zirconocene hydride organohydroborate acts as an electron pair donor to the boron of the alkyl borane.

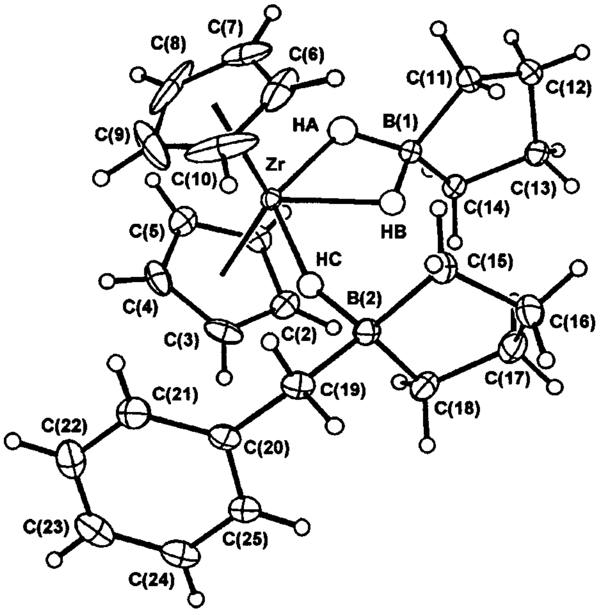

Figure 2. Molecular structure of $Cp_2Zr\{(\mu\text{-}H)BC_4H_8(CH_2Ph)\}\{(\mu\text{-}H)_2BC_4H_8\}$ showing 25% probability ellipsoids.

Table 1. Crystallographic Data for $Cp_2Zr\{(\mu\text{-}H)BC_5H_{10}(CH_2Ph)\}\{(\mu\text{-}H)_2BC_5H_{10}\}$, **1**, and $Cp_2Zr\{(\mu\text{-}H)BC_4H_8(CH_2Ph)\}\{(\mu\text{-}H)_2BC_4H_8\}$, **2**

empirical formula	$C_{27}H_{40}B_2Zr$	$C_{25}H_{36}B_2Zr$
fm, amu	477.44	449.38
space group	$P2_1/m$	$Pbca$
a, Å	9.392(5)	18.1630(10)
b, Å	13.250(4)	19.0497(10)
c, Å	9.841(6)	13.0393(10)
β, deg	95.70(4)	
vol, Å^3	1218.7(11)	4511.6(5)
Z	2^c	8
ρ(calcd), g cm^{-3}	1.301	1.323
cryst size, mm	0.35 × 0.45 × 0.34	0.25 × 0.20 × 0.28
T, °C	−60	−60
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	0.463	0.495
scan mode	$\omega - 2\theta$	$\omega - 2\theta$
2θ limits, deg	4−45	4−50
$\pm h$	−10, 10	−21, 21
$\pm k$	0, 14	0, 22
$\pm l$	−10, 10	0, 15
no. of rflns measd	3430	7926
no. of unique rflns	1675	3965
no. of unique rflns $[I > 2.0\sigma(I)]$	1336	2558
no. of variables	151	265
R1^a $[I > 2.0\sigma(I)]$	0.0378	0.0341
wR2^b (all data)	0.0894	0.0894
R_{int}	0.0466	0.0298
GOF	1.041	1.015

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [c] The asymmetric unit for **1** is one half of a molecule. Therefore, there are 4 asymmetric units in the unit cell.

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(14) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293.

(15) This chemical shift is consistent with chemical shifts reported for tetraalkyl borate anions. Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; p 384.

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

(17) (a) Jordan, G. T., IV; Liu, F.-C.; Shore, S. G. *Inorg. Chem.* **1997**, *36*, 5597. (b) Jordan, G. T., IV; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 1087.

(18) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972**, *11*, 654.

(19) The molecular structure, crystallographic data, positional parameters, bond distances, and bond angles of $Cp_2Zr(CH_2Ph)_2$ are provided in the Supporting Information.

Table 2. Atomic coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Cp_2Zr\{(\mu\text{-H})BC_5H_{10}(CH_2Ph)\}\{(\mu\text{-H})_2BC_5H_{10}\}$, **1**

atom	*x*	*y*	*z*	*U*(eq)^{a,b}
Zr	9797(1)	2500	7909(1)	23(1)
C(1)	9862(5)	4369(3)	7705(4)	40(1)
C(2)	11025(5)	4114(3)	8607(5)	43(1)
C(3)	10508(6)	3705(3)	9775(4)	52(1)
C(4)	9016(6)	3725(3)	9567(5)	52(1)
C(5)	8614(5)	4137(3)	8282(5)	44(1)
B(1)	8124(7)	2500	5665(6)	27(1)
C(11)	7556(4)	3501(3)	4894(4)	39(1)
C(12)	7733(5)	3440(3)	3364(4)	46(1)
C(13)	7056(6)	2500	2729(6)	38(2)
B(2)	12548(7)	2500	6179(6)	31(2)
C(21)	12194(4)	1491(3)	5284(4)	33(1)
C(22)	12943(4)	1541(3)	3973(4)	41(1)
C(23)	12550(6)	2500	3174(6)	46(2)
C	14105(6)	2500	7058(6)	33(1)
C(1C)	14453(7)	1651(6)	8106(7)	30(2)
C(2C)	14344(8)	1816(6)	9495(8)	37(2)
C(3C)	14546(9)	1053(7)	10435(9)	42(2)
C(4C)	14939(17)	110(11)	10102(16)	39(2)
C(5C)	15036(9)	−92(7)	8647(9)	40(2)
C(6C)	14832(9)	695(6)	7725(8)	35(2)
H(1A)	9415(51)	2500	5863(48)	26(13)
H(1B)	8069(54)	2500	6965(54)	35(15)
H(2A)	11385(51)	2500	7302(51)	33(15)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Hydrogen atoms from H(1A) to H(2A) were located and refined isotropically.

Table 3. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp_2Zr\{(\mu\text{-H})BC_5H_{10}(CH_2Ph)\}\{(\mu\text{-H})_2BC_5H_{10}\}$, **1**^{a}

	Bond Lengths		
av Zr−C(1−5)^b	2.480[5]	B(2)−H(2A)	1.63(5)
Zr−centroid$_{(C1-C5)}$	2.179	B(1)−C(11)	1.593(5)
Zr−B(1)	2.580(6)	C(11)−C(12)	1.534(6)
Zr−B(2)	3.232(6)	C(12)−C(13)	1.506(5)
Zr−H(1A)	2.01(5)	B(2)−C	1.624(8)
Zr−H(1B)	1.79(5)	B(2)−C(21)	1.618(5)
Zr−H(2A)	1.66(5)	C(21)−C(22)	1.532(5)
B(1)−H(1A)	1.21(5)	C(22)−C(23)	1.521(5)
B(1)−H(1B)	1.29(5)	C−C(1C)	1.539(8)
	Bond Angles		
centroid−Zr−centroid	133.3	C(11)#1−B(1)−C(11)	112.7(4)
centroid$_{(C1-C5)}$−Zr−B(1)	108.5	C(12)−C(11)−B(1)	111.1(4)
centroid$_{(C1-C5)}$−Zr−H(1A)	113.0	C(13)−C(12)−C(11)	111.6(4)
centroid$_{(C1-C5)}$−Zr−H(1B)	100.0	C(12)−C(13)−C(12)#1	111.6(5)
centroid$_{(C1-C5)}$−Zr−H(2A)	100.1	C−B(2)−C(21)	114.6(3)
B(1)−Zr−H(1A)	27.1(14)	C−B(2)−C(21)#1	114.6(3)
B(1)−Zr−H(2A)	101(2)	C(21)−B(2)−C(21)#1	111.5(5)
H(1A)−Zr−H(1B)	54(2)	C(22)−C(21)−B(2)	109.6(4)
H(1A)−Zr−H(2A)	74(2)	C(23)−C(22)−C(21)	111.3(4)
H(1B)−Zr−H(2A)	128(2)	C(22)#1−C(23)−C(22)	113.4(5)
H(1A)−B(1)−H(1B)	89(3)	C(1C)−C−B(2)	118.5(4)
C(11)#1−B(1)−H(1A)	111.1(11)	Zr−H(2A)−B(2)	158.5(33)
C(11)−B(1)−H(1A)	111.1(10)	H(2A)−B(2)−C	105.5(18)
C(11)#1−B(1)−H(1B)	115.4(9)	H(2A)−B(2)−C(21)	104.7(9)
C(11)−B(1)−H(1B)	115.4(9)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, -y + {}^1/_2, z$. [b] The standard deviation (σ_l) for the average bond length of Zr−C is calculated according to the equations[25] $\langle l \rangle = \sum_m l_m/m$ and $\sigma_l = [\sum_m(l_m - \langle l \rangle)^2/m(m-1)]^{1/2}$, where $\langle l \rangle$ is the mean length, l_m is the length of the *m*th bond, and *m* is the number of bonds.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Cp_2Zr\{(\mu\text{-H})BC_4H_8(CH_2Ph)\}\{(\mu\text{-H})_2BC_4H_8\}$, **2**

atom	*x*	*y*	*z*	*U*(eq)^{a,b}
Zr	1256(1)	6302(1)	2617(1)	23(1)
C(1)	2025(2)	6409(2)	732(2)	42(1)
C(3)	812(2)	6656(2)	892(3)	48(1)
C(4)	1167(2)	7241(2)	1314(3)	49(1)
C(5)	1911(2)	7079(2)	1417(3)	42(1)
C(6)	1088(4)	6277(2)	4487(3)	77(2)
C(7)	1741(3)	6563(3)	4342(3)	73(2)
C(8)	1643(5)	7170(4)	3880(4)	114(3)
C(9)	913(7)	7276(4)	3755(5)	157(5)
C(10)	579(2)	6707(5)	4135(5)	115(3)
B(1)	1916(2)	5126(2)	2762(3)	31(1)
C(11)	2089(2)	4678(2)	3781(3)	39(1)
C(12)	2602(2)	4088(2)	3429(3)	44(1)
C(13)	2391(2)	3945(2)	2324(3)	41(1)
C(14)	2259(2)	4669(2)	1838(2)	36(1)
B(2)	−323(2)	5489(2)	2487(3)	31(1)
C(15)	−264(2)	4956(2)	3465(3)	40(1)
C(16)	−380(2)	4229(2)	3001(3)	49(1)
C(17)	−12(2)	4262(2)	1953(3)	51(1)
C(18)	−234(1)	4973(2)	1503(3)	42(1)
C(20)	−1098(2)	6564(2)	1699(3)	35(1)
C(21)	−1061(2)	7771(2)	1144(4)	56(1)
C(23)	−1213(2)	7579(2)	152(3)	56(1)
C(24)	−1299(2)	6882(2)	−72(3)	54(1)
C(25)	−1244(2)	6380(2)	687(3)	45(1)
HA	2145(18)	5708(17)	2809(24)	44(9)
HB	1258(16)	5284(16)	2651(22)	32(8)
HC	259(17)	5941(16)	2451(21)	31(9)

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

In general, bond distances involving Zr, H, and B are comparable for equivalent components of complexes **1** and **2**. However, because complex **1** is disordered in the solid state, uncertainties in its bond distances are larger than in **2** and significant differences occur in the "observed" Zr−H and H−B distances of **1** and **2** and their H−B distances in the unsupported Zr−H−B bond. We believe that the Zr−H and H−B distances in this bond in complex **2** are more accurate than those in **1**. In complex **2** the Zr−H distance of the Zr−H−B bond is 1.95(3) Å, longer than that for the terminal Zr−H bond 1.68(5) Å in $Cp_2ZrH\{(\mu\text{-H})_2BC_4H_8\}$. Upon forming a Zr−H−B bridge, lengthening of the Zr−H distance is to be expected. Recent *ab initio* DFT calculations for the hypothetical compound $Cp_2NbH_2(\mu\text{-H})BH_3$ showed a "strong interaction" between BH_3 and the central hydride of Cp_2NbH_3,[20] that lengthens the Nb−H distance by 0.08 Å with respect to uncomplexed Cp_2NbH_3. In the case of **1** the Zr−H distance is apparently shortened to 1.66(5) Å from 1.79(5) Å in $Cp_2ZrH\{(\mu\text{-H})_2BC_5H_{10}\}$, an observation we consider to be unrealistic due to the disordered nature of the structure. The B−H distance in the unsupported B−H−B bond of **2** is 1.36(3) Å, a reasonable value for a B−H distance in a three-center bond.[1] In the case of **1** the corresponding B−H component appears to be unreasonably long, 1.63(5) Å.

NMR Studies of 1 and 2. NMR spectra[21] of **1** and **2** indicate the formation of the unsupported Zr−H−B bridge at low temperature. In d_8-toluene, the single-bridge Zr−H−B hydrogen exibits a high-field shift at −60 °C. It appears at −2.32 ppm in **1** and −0.16 ppm in **2**, which are 6.36 and 4.07 ppm upfield from the chemical shift of the Zr−H hydrogen in the uncomplexed zirconocene hydrides, $Cp_2ZrH\{(\mu\text{-H})_2BC_5H_{10}\}$ and $Cp_2ZrH\{(\mu\text{-H})_2BC_4H_8\}$, at the same temperature. However, NMR spectra[21] in solution at room temperature (^{11}B and ^1H) indicate that **1** and **2** are dissociated in diethyl ether and in benzene.

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[20] Camanyer, S.; Maseras, F.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertràn, J. *Angew Chem., Int. Ed. Engl.* **1997**, *36*, 265.

[21] Proton spectra of $Cp_2ZrH\{(\mu\text{-H})_2BC_5H_{10}\}$, $Cp_2ZrH\{(\mu\text{-H})_2BC_4H_8\}$, $Cp_2Zr\{(\mu\text{-H})BC_5H_{10}(CH_2Ph)\}\{(\mu\text{-H})_2BC_5H_{10}\}$, and $Cp_2Zr\{(\mu\text{-H})BC_4H_8(CH_2Ph)\}\{(\mu\text{-H})_2BC_4H_8\}$ are provided in the Supporting Information.

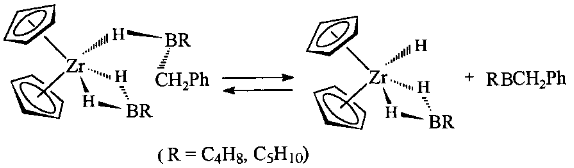
Table 5. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp_2Zr\{(\mu\text{-}H)BC_4H_8(CH_2Ph)\}\{(\mu\text{-}H)_2BC_4H_8\}$, **2**

Bond Lengths			
av Zr−C(1−5)[a]	2.479[6]	B(1)−C(11)	1.610(5)
av Zr−C(6−10)[a]	2.455[5]	B(1)−C(14)	1.613(5)
Zr−centroid$_{(C1-C5)}$	2.175	C(11)−C(12)	1.530(5)
Zr−centroid$_{(C6-C10)}$	2.179	C(12)−C(13)	1.516(5)
Zr−B(1)	2.548(4)	C(13)−C(14)	1.536(5)
Zr−B(2)	3.263(4)	B(2)−C(19)	1.621(5)
Zr−HA	1.99(3)	B(2)−C(18)	1.625(5)
Zr−HB	1.94(3)	B(2)−C(15)	1.633(5)
Zr−HC	1.95(3)	C(15)−C(16)	1.524(5)
B(1)−HA	1.18(3)	C(16)−C(17)	1.523(5)
B(1)−HB	1.24(3)	C(17)−C(18)	1.530(5)
B(2)−HC	1.36(3)		

Bond Angles			
centroid−Zr−centroid	133.2	C(11)−B(1)−HB	114.3(14)
centroid$_{(C1-C5)}$−Zr−B(1)	107.5	C(14)−B(1)−HB	114.5(14)
centroid$_{(C6-C10)}$−Zr−B(1)	109.8	C(19)−B(2)−HC	102.8(13)
centroid$_{(C1-C5)}$−Zr−HA	100.6	C(18)−B(2)−HC	106.2(12)
centroid$_{(C6-C10)}$−Zr−HA	100.1	C(15)−B(2)−HC	111.6(12)
centroid$_{(C1-C5)}$−Zr−HB	111.9	C(11)−B(1)−C(14)	104.8(3)
centroid$_{(C6-C10)}$−Zr−HB	114.4	C(12)−C(11)−B(1)	105.1(3)
centroid$_{(C1-C5)}$−Zr−HC	100.0	C(13)−C(12)−C(11)	105.2(3)
centroid$_{(C6-C10)}$−Zr−HC	101.8	C(12)−C(13)−C(14)	105.7(3)
B(1)−Zr−HA	26.8(9)	C(13)−C(14)−B(1)	103.7(3)
B(1)−Zr−HB	28.1(8)	C(19)−B(2)−C(18)	118.0(3)
B(1)−Zr−HC	97.8(9)	C(19)−B(2)−C(15)	114.6(3)
HA−Zr−HB	55.0(12)	C(18)−B(2)−C(15)	103.5(3)
HA−Zr−HC	124.6(14)	C(16)−C(15)−B(2)	104.2(3)
HB−Zr−HC	69.6(12)	C(17)−C(16)−C(15)	105.0(3)
HA−B(1)−HB	97(2)	C(16)−C(17)−C(18)	105.3(3)
C(11)−B(1)−HA	113(2)	C(17)−C(18)−B(2)	105.0(3)
C(14)−B(1)−HA	114(2)	C(20)−C(19)−B(2)	119.0(3)
Zr−HC−B(2)	159.9(20		

[a] The standard deviation (σ_l) for the average bond length of Zr−C is calculated according to the equations[25] $\langle l\rangle = \sum_m l_m/m$ and $\sigma_l = [\sum_m(l_m - \langle l\rangle)^2/m(m-1)]^{1/2}$, where $\langle l\rangle$ is the mean length, l_m is the length of the mth bond, and m is the number of bonds.

The ^{11}B NMR spectrum of **1** in ether solution consists of two signals. One signal (δ 28.22 ppm, $J_{B-H} = 54.9$ Hz) very closely corresponds to that produced by free $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$. The second signal ($\delta$ 83.58 (s)) is consistent with signals produced by alkyl boranes.[22] The two signals occur in a 1:1 ratio. Upon proton decoupling, the signal assigned to $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ collapses to a singlet while the singlet assigned to the alkyl borane at 83.58 ppm does not sharpen. The boron-11 NMR spectrum is consistent with complete dissociation of **1** in solution as shown in eq 1. By the same token the ^1H NMR spectrum of **1** in d_6-benzene consists of signals that closely match the spectrum of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ and a set of signals that can be assigned to $BC_5H_{10}(CH_2Ph)$. The ^1H NMR spectrum of the Zr−H hydrogen has a chemical shift of 4.00 ppm, which is only slightly higher (but within experimental error) than that observed (3.94 ppm) for solutions containing only $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ as the solute. Furthermore, the chemical shifts of the $Zr(\mu\text{-}H)_2B$ hydrogens (−3.26 and −4.16 ppm) are in excellent agreement with those observed for the free $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$ molecule (−3.26 and −4.16 ppm).



(1)

Boron-11 NMR resonances of **2** appear at $\delta = 90.50$ (s) and 30.70 ppm (t, $J_{B-H} = 61.0$ Hz) and are assigned to the two components $BC_4H_8(CH_2Ph)$ and $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$.[15] Upon proton decoupling, the signal at 30.70 ppm collapses to a singlet and the signal at 90.50 ppm is unchanged. The proton NMR resonances of component $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$ of **2** is almost identical to that of the free molecule of $Cp_2ZrH\{(\mu\text{-}H)_2BC_4H_8\}$, except for a 0.04 ppm upfield shift.

If any association occurs in solution at room temperature, it is undoubtedly very weak. When solvent Et_2O was pumped from solution of **2** to a dynamic vacuum of 10^{-5} Torr at room temperature for 24 h, 70% of the alkyl borane, $BC_4H_8(CH_2Ph)$, was removed. A similar result has been observed for $Cp_3Zr(\mu\text{-}H)Al(C_2H_5)_3$,[23] which crystallizes as an unsupported single hydrogen bridged compound, but is also apparently dissociated in solution.

Experimental Section

General Procedures. All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of nitrogen. Diethyl ether was dried over Na/benzophenone and freshly distilled prior to use. Hexane was dried over CaH_2 and freshly distilled prior to use. Cp_2ZrCl_2, KH, $BH_3{\cdot}THF$ (1 M solution in THF), and benzylmagnesium chloride (1.0 M in Et_2O) were purchased from Aldrich and used as received. $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$[13] and $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$[17] were prepared by literature procedures. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Room temperature ^1H (δ(TMS) = 0.00 ppm) and ^{11}B NMR spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 and 80.253 MHz at 303 K. $^1H\{^{11}B\}$ (δ(TMS) = 0.00 ppm) NMR spectra at 213 K were recorded on a Bruker AM-500 NMR spectrometer operating at 500.13 MHz. Boron-11 spectra were externally referenced to $BF_3{\cdot}OEt_2$ (δ = 0.00 ppm). Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer with 2 cm^{-1} resolution.

X-ray Crystal Structure Determination. Crystallographic data were collected at −60 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Crystallographic computations were carried out using the SHELXTL software package.[24] Structure solution involved a DIRECT method. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 24−30°. All reflection data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied based on measured ψ scans. All of the non-hydrogen atoms in the complexes $Cp_2Zr\{(\mu\text{-}H)BC_5H_{10}(CH_2Ph)\}\{(\mu\text{-}H)_2BC_5H_{10}\}$, **1**, and $Cp_2Zr\{(\mu\text{-}H)BC_4H_8(CH_2Ph)\}\{(\mu\text{-}H)_2BC_4H_8\}$, **2**, were located and refined anisotropically. All of the bridge hydrogen atoms were located and refined isotropically. The C−H hydrogens were placed in calculated positions, riding on the atoms to which they are bonded.

The structure of complex **1** was refined in space groups $P2_1$ and $P2_1/m$. Solution in $P2_1$ was unsatisfactory due to negative thermal parameters of several atoms and wide variation in C−C distances. X-ray analysis in $P2_1/m$ was successful. Complex **1** resides on a crystallographically imposed mirror plane. The asymmetric unit is one half of a molecule, and the mirror operation generates the other half of the molecule. The benzyl group is disordered; it appears on both sides of the mirror plane. The mirror plane passes through Zr, H(1A), H(1B), H(2A), B1, B2, C(13), C(23), and C. However, because the structure is disordered, it is possible that these atoms are also disordered and are positioned with partial occupancies just off either side of the mirror plane, with the averaged positions on the mirror plane. Such a situation

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(22) (a) Saturnino, D. J.; Yamauchi, M,; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063. (b) Good, C. D.; Ritter, D. M. *J. Am. Chem. Soc.* **1962**, *84*, 1162. (c) Nöth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: Berlin, 1978; pp 115−124.

(23) Kopf, J.; Vollmer, H.-J.; Kaminsky, W. *Cryst. Struct. Commun.* **1980**, *9*, 985.

(24) SHELXTL (version 5), solution and refinement of molecular structures. Siemens Energy & Automation, Inc., 1994.

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

could contribute to the "short" Zr−H and "long" B−H distances observed in the unsupported Zr−H−B bond.

Preparation of $Cp_2Zr\{(\mu\text{-}H)BC_5H_{10}(CH_2Ph)\}\{(\mu\text{-}H)_2BC_5H_{10}\}$, 1. $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$ (330 mg, 0.97 mmol) was placed in 15 mL of Et_2O in a two-necked flask and cooled to −40 °C. Benzylmagnesium chloride (1 mmol, 1 mL, 1.0 M in Et_2O) was injected into the system by syringe under nitrogen. The system was warmed to room temperature over a 3 h period and stirred for an additional 3 h. Initially the mixture was yellow-green in color, but it turned yellow upon warming. After stirring at room temperature, the color further changed to orange. The Et_2O was removed under vacuum, and the resulting solid was extracted with hexane. Removal of the hexane from the filtrate resulted in a pale yellow solid, which was dissolved in Et_2O and crystallized at −40 °C. Orange crystals of $Cp_2Zr(CH_2Ph)_2$ (21 mg, 10% yield) and colorless crystals of **1** (137 mg, 59.1% yield) were obtained.

Data for 1. ^{11}B NMR (Et_2O): δ 83.58 (s) and 28.22 ppm (t, J_{B-H} =54.9 Hz). ^1H NMR (d_6-benzene): δ 7.17−6.91 (m, Ph), 5.58 (s, Cp), 4.00 (br, 1H), 2.45 (s, CH_2), 1.74 (br, 7H), 1.50 (br, m, 5H), 1.11 (br, m, 8H), −3.26 (br, μ-H), and −4.16 ppm (br, μ-H). ^1H NMR (d_8-toluene): δ 7.16−6.87 (m, Ph), 5.58 (s, Cp), 3.89 (br, 1H), 2.43 (s, CH_2), 1.69 (br, 6H), 1.52 (br, m, 4H), 1.41 (br, m, 2H), 1.09 (br, m, 4H), 1.00 (br, 4H), −3.00 (br, μ-H), and −4.10 ppm (br, μ-H). IR (KBr): 3117 (w), 3111 (w), 3095 (vw, sh), 3073 (vw), 3050 (vw), 3020 (vw, sh), 3011 (w), 2988 (vw), 2925 (s, sh), 2901 (vs), 2889 (s), 2841 (s), 2827 (s), 2814 (m, sh), 2646 (vw), 1936 (s), 1898 (s), 1882 (s, sh), 1834 (m), 1788 (m, br), 1744 (m, br), 1594 (m), 1490 (m), 1458 (m, sh), 1426 (s), 1409 (vs), 1370 (w, sh), 1341 (m), 1292 (w), 1280 (w), 1275 (w), 1263 (vw, sh), 1226 (w, sh), 1212 (s), 1201 (m, sh), 1180 (w), 1175 (vw), 1153 (vw), 1129 (vw), 1111 (vw), 1092 (m), 1074 (m), 1067 (m), 1015 (s), 958 (s), 927 (vw), 903 (w), 887 (w), 881 (w), 822 (s), 814 (s), 800 (s), 764 (s), 744 (vw, sh), 705 (s), 662 (w), 582 (w), 551 (m), 491 (m), 458 (vw) cm^{-1}. Anal. Calcd for $C_{27}H_{40}B_2Zr$: C, 67.92; H, 8.44. Found: C, 66.88; H, 8.23.

Preparation of $Cp_2Zr\{(\mu\text{-}H)BC_4H_8(CH_2Ph)\}\{(\mu\text{-}H)_2BC_4H_8\}$, 2. The preparation method of **2** is similar to that described above except 0.95 mmol of $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ and 0.98 mL of benzylmagnesium chloride were used. After reaction, 108.7 mg (50.9% yield) of colorless **2** and 32 mg (15.9% yield) of orange $Cp_2Zr(CH_2Ph)_2$ were isolated from Et_2O at −40 °C. Crystals of **2** suitable for X-ray diffraction were also obtained from this solution.

Data for 2. ^{11}B NMR (Et_2O): δ 90.50 (s) and 30.70 ppm (t, J_{B-H} = 61.0 Hz). ^1H NMR (d_6-benzene): δ 7.20−6.96 (m, Ph), 5.60 (s, Cp), 3.91 (br, 1H), 2.63 (s, CH_2), 1.80 (br, 4H), 1.57 (br, m, 4H), 1.01 (br, m, 8H), −3.10 (br, μ-H), and −4.25 ppm (br, μ-H). ^1H NMR (d_8-toluene): δ 7.17−6.93 (m, Ph), 5.59 (s, Cp), 3.83 (br, 1H), 2.63 (s, CH_2), 1.74 (br, m, 4H), 1.59 (br, m, 4H), 1.05 (br, m, 8H), −3.30 (br, μ-H), and −4.40 ppm (br, μ-H). IR (KBr): 3123 (vw), 3105 (w), 3095 (vw), 3077 (vw), 3058 (vw), 3019 (vw, br), 2918 (s, br), 2861 (m, sh), 2849 (s), 2806 (vw, sh), 2649 (vw, br), 2059 (vw), 2008 (vw), 1912 (m, br), 1892 (w, sh), 1825 (w), 1597 (w), 1491 (w), 1462 (m, sh), 1444 (s), 1430 (s), 1399 (s), 1368 (s), 1343 (s), 1289 (m, sh), 1238 (m, sh), 1217 (w, sh), 1180 (w), 1123 (vw, br), 1066 (m), 1014 (m), 957 (vw), 931 (vw), 906 (w), 885 (vw), 870 (vw), 801 (vs), 754 (m), 729 (m, br), 701 (s), 658 (vw), 607 (vw), 538 (vw), 528 (vw), 473 (vw) cm^{-1}. Anal. Calcd for $C_{25}H_{36}B_2Zr$: C, 66.82; H, 8.08. Found: C, 65.23; H, 7.90.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE 97-00394. NMR spectra were obtained at the Ohio State University Campus Chemical Instrument Center.

Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **1**, **2**, and $Cp_2Zr(CH_2Ph)_2$ and proton spectra of $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$, $Cp_2ZrH\{(\mu\text{-}H)_2\ BC_5H_{10}\}$, **1**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981347U