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Synthesis, Structural Characterization, and Reactions of Cyclic Organohydroborate Half-Zirconocene Compounds

Errun Ding, Fu-Chen Liu, Shengming Liu, Edward A. Meyers, and Sheldon G. Shore*

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

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Cyclic organohydroborate complexes of zirconium monocyclopentadienyl $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$, **1**, and $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$, **2**, were prepared from the reaction of $CpZrCl_3$ with 3 mol of $K[H_2BC_5H_{10}]$ and $K[H_2BC_8H_{10}]$, respectively, in diethyl ether. Compounds **1** and **2** react with the hydride ion abstracting agent $B(C_6F_5)_3$ to form the same salt $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2[HB(C_6F_5)_3]_2$, **5**. The complexes $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, **3**, and $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ [where $Cp^* = C_5(CH_3)_5$], **4**, were prepared from the reaction of $CpZrCl_3$ and Cp^*ZrCl_3 with $K[H_2BC_8H_{10}]$ in 1:2 molar ratios, respectively. An α-hydrogen of a BC_8H_{14} unit forms an *agostic* interaction with Zr in compound **3** but not in **4**. All of the compounds were characterized by single-crystal X-ray diffraction analysis.

Introduction

While the chemical literature is rich with descriptions of structures and properties of metallohydroborate systems in general,[1] hydroborate derivatives of metallocenes, especially organohydroborate derivatives have received significantly less attention.[2] Relatively recently, however, several cyclic organohydroborate derivatives of Group 4 and Group 5 metallocenes have been prepared in this laboratory[3] and some of these complexes have been the subject of hydride abstraction reactions to give cationic and neutral products as a function of the coordinating ability of the solvent.

To our knowledge there are only two reports of monocyclopentadienyl hydroborates,[4,5] $CpZr\{(\mu\text{-}H)_2BH_2\}_3$ and $[CpTi(Cl)BH_4]_2$. In view of the paucity of such complexes, we have initiated an investigation of the preparation and study of monocyclopentadienyl zirconium cyclicorganohydroborate derivatives. They are of interest to us with respect to potential hydride abstraction reactions which might produce new types of cationic species. Furthermore, as has been pointed out earlier,[6] cationic species derived from Group 4 half-sandwich complexes can be electronically unsaturated and sterically less hindered than their metallocene analogues. These features suggest that the cationic species produced might exhibit higher activities for reactions with sterically crowded

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* Author to whom correspondence should be addressed. E-mail: shore.1@osu.edu.

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Table 1. Products of Reactions of $CpZrCl_3$ or Cp^*ZrCl_3 and $K[H_2BC_5H_{10}]$ and $K[H_2BC_8H_{14}]$

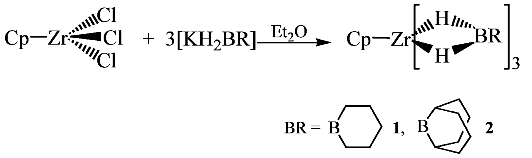
ratio of reactants	products
$CpZrCl_3$:3$K[H_2BC_5H_{10}]$	$CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$
$CpZrCl_3$:2$K[H_2BC_5H_{10}]$	$CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$
$CpZrCl_3$:1$K[H_2BC_5H_{10}]$	$CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$
$CpZrCl_3$:3$K[H_2BC_8H_{14}]$	$CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$
$CpZrCl_3$:2$K[H_2BC_8H_{14}]$	$CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$
$CpZrCl_3$:1$K[H_2BC_8H_{14}]$	$CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$
Cp^*ZrCl_3:2$K[H_2BC_8H_{14}]$	$Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$
Cp^*ZrCl_3:1$K[H_2BC_8H_{14}]$	$Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$

substances.[7,8] Here we describe the synthesis and characterization of cyclic organohydroborate derivatives of half-zirconocene compounds.

Results and Discussion

Formation and Properties of $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$, 1, $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$, 2, $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, 3, $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, 4, and $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2[HB(C_6F_5)_3]_2$, 5. Complexes $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$, **1**, and $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$, **2**, were obtained in 33% and 38% yields from the reaction of $CpZrCl_3$ with 3 mol of $K[H_2BC_5H_{10}]$ and $K[H_2BC_8H_{14}]$, respectively, in diethyl ether (reaction 1 and Table 1).

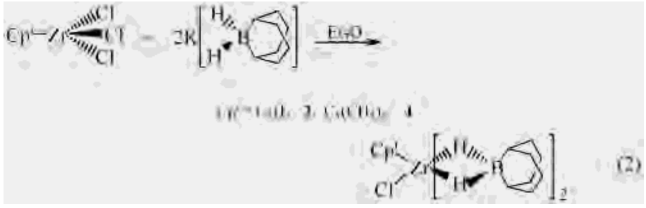
These compounds are white solids that are stable at room temperature in the absence of air. They are soluble in THF and diethyl ether but slowly decompose to $(C_5H_{10}B)(\mu\text{-}H)_2(BC_5H_{10})$, $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$, and unidentified products in solution.



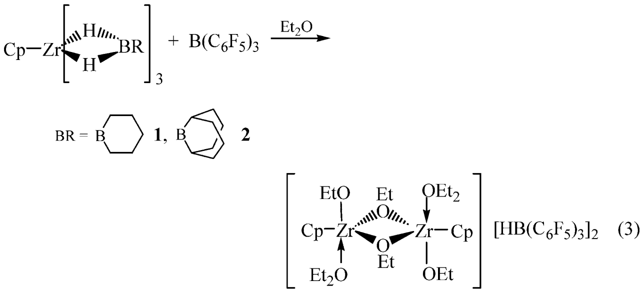
(1)

Complexes $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, **3**, and $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, **4**, were prepared by employing 1:2 molar ratios of reactants (reaction 2 and Table 1).

Solid compound **4** is stable under N_2 at room temperature for at least 2 months without apparent decomposition. Compound **3** on the other hand, under the same conditions decomposes within 1 month.



Reactions of $CpZrCl_3$ with $K[H_2BC_5H_{10}]$ in 1:1 and 1:2 molar ratios were performed in anticipation of producing the stoichiometric derivatives, but only complex **1** was produced in each case, as indicated in Table 1. Boron-11 spectra of the two reaction systems show the signal for **1** (14.49 ppm) that is observed in the optimized preparation of this complex employing a 1:3 ratio of reactants. They also contain a signal at 25.56 ppm due to the organodiborane, $(C_5H_{10}B)(\mu\text{-}H)_2(BC_5H_{10})$. Reactions with $CpZrCl_3$ and Cp^*ZrCl_3 with $K[H_2BC_8H_{14}]$, in 1:1 ratios produced the 1:2 complexes**,** **3**, and **4**, respectively, and $(C_8H_{14}B)(\mu\text{-}H)_2(BC_8H_{14})$.



5

Reaction of $B(C_6F_5)_3$, with **1** and with **2** in diethyl ether produced $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2[HB(C_6F_5)_3]_2$, **5,** which contains a doubly charged cation (reaction 3).

This reaction parallels the reaction of $Cp_2ZrH(\mu\text{-}H)_2(BC_4H_8)$ with $B(C_6F_5)_3$ in diethyl ether to produce $[Cp_2Zr(OEt)(OEt_2)][HB(C_6F_5)_3]$[3h] in which the cation, $[Cp_2Zr(OEt)(OEt_2]^+$, has structural features in common with the dication, $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2^{2+}$, of Compound **5**. From the study of the formation of $[Cp_2Zr(OEt)(OEt_2)]^+$, a plausible reaction pathway for the formation of $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2^{2+}$ is outlined in Scheme 1. In this scheme the initial step is hydride ion abstraction from a bridge site which is followed by elimination of 0.5 mol of the organodiborane, a very stable species. The resulting cation, with the charge localized on the zirconium atom is susceptible to symmetrical hydrogen bridge cleavage by the nucleophilic solvent ether, resulting in the elimination of another half mole of organodiborane and yielding a terminal hydrogen on zirconium. This hydrogen transfers to an ethyl group of a coordinated ether to yield ethane gas and a coordinated ethoxyl group on the zirconium. This sequence is repeated. The cyclic organoborane ligand is eliminated; a second ethoxyl group is generated on the zirconium cation which forms the dimeric dication $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2^{2+}$ of compound **5** through ethoxyl bridges. In this sequence key steps involve the transfer of hydrogen from a metal to the carbon of a coordinated ether to generate an alkoxyl group. Such hydrogen transfer is well documented.[9,3h]

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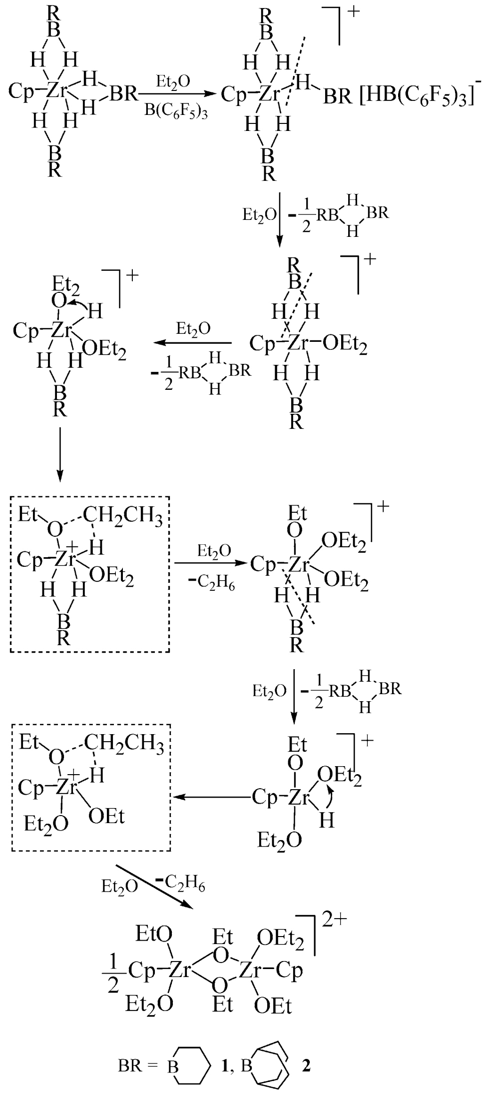
Scheme 1



Compound **5** is a white solid that is stable in the absence of air. In diethyl ether it shows no apparent sign of decomposition. The ^{11}B NMR spectrum of **5** in THF-d_8 consists of a doublet at $\delta = -27.08$ ppm ($J_{\mathrm{B-H}} = 93.2$ Hz). In the ^{1}H NMR spectrum of **5**, the signal of the Cp hydrogens appears at $\delta = 6.50$ ppm. Two signals at 4.17 (4H, q, $J = 7$ Hz) and 1.22 ppm (6H, t, $J = 7$ Hz) are assigned to an ethoxyl group, and two signals at 3.39 (4H, q, $J = 7$ Hz) and 1.12 ppm (6H, t, $J = 7$ Hz) are consistent with free diethyl ether which is displaced from the cation of **5** by THF-d_8 in the NMR tube.

We also attempted to abstract hydride from **2** with $B(C_6F_5)_3$ in toluene. But the product is too unstable to isolate. The ^{11}B NMR spectrum in toluene consists of a doublet at -24.46 ppm, which indicates the formation of an anion with a BH bond. But this signal disappeared very soon at room temperature. There is no apparent reaction of **3** or **4** with $B(C_6F_5)_3$ in diethyl ether or toluene, but reactions do take place in THF. A colorless oil was obtained after 2 days, which was dissolved in pyridine to produce a green oil. The ^{11}B NMR spectrum of the $[HB(C_6F_5)_3]^-$ anion appeared at -25.70 ppm. We could not isolate a pure product.

Molecular Structures of Compounds 1−5. The solid-state structures of **1**−**5** were determined by single-crystal X-ray diffraction analyses. Structures are shown in Figures 1−3. Crystallographic data and selected bond distances and angles are given in Tables 2−7.

Crystals of **1**, suitable for X-ray diffraction, were obtained by crystallization from benzene-d_6 and crystals of **2** were grown in a diethyl ether solution. Their molecular structures closely resemble each other (see Figure 1). They have *pseudo* mirror symmetry. In these complexes the zirconium is associated with 18 valence electrons, each cyclic organohydroborate ligand contributes a pair of electrons through each hydrogen bridge. Structural parameters fall within normal ranges. For compound **1**, the angles cent−Zr−H32 = 158°, cent−Zr−B1 = 108.7°, cent−Zr−B2 = 108.2°, cent−Zr−B3 = 130.7°, are similar to the corresponding angles in compound **2**, cent−Zr−H132 = 158°, cent−Zr−B11 = 109.3°, cent−Zr−B12 = 108.6°, cent−Zr−B13 = 130.7°. The average Zr bridge hydrogen bond lengths in **1** (1.97 Å) and **2** (1.956 Å).

Suitable single crystals of $CpZr(Cl)\{(\mu\text{-}H)_2B(C_8H_{14})\}_2$, **3**, and $Cp^*Zr(Cl)\{(\mu\text{-}H)_2B(C_8H_{14})\}_2$, **4**, were grown from diethyl ether solutions at ambient temperature. The molecular structures of **3** and **4** are shown in Figure 2. The average Zr bridge hydrogen bond lengths in **3** (1.99 Å) and **4** (1.98 Å) are also close to those in **1** and **2**. In these complexes, zirconium is formally associated with 16 valence electrons, but interestingly, in compound **3**, the "electron deficiency" of zirconium appears to be partially compensated for by an *agostic* interaction with an α-H of a BC_8H_{14} unit. The Zr−(α-H111) distance is 2.31(3) Å which is significantly less than the sum of the zirconium covalent radius and the hydrogen van der Waals radius, 2.70 Å, (Zr = 1.50 Å,[11] H = 1.20 Å[12]). Note that the participating BC_8H_{14} unit is positioned to facilitate *agostic* interaction, but this is not the case for the nonparticipating BC_8H_{14} unit. The Zr−(α-H12A) distance, 3.559 Å is the closest distance of an α-H on the nonparticipating BC_8H_{14} unit. There is no apparent corresponding *agostic* interaction in complex **4**, $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$. The shortest Zr−(α-H9) distance is 3.265 Å. The closest α-carbons of both BC_8H_{14} units to zirconium are essentially equidistant from the metal, 3.241 and 3.300 Å. These distances are significantly longer than the shortest α-carbon to zirconium distance in **3**, 2.698(3) Å, in the BC_8H_{14} unit that participates in the *agostic* interaction. The absence of an *agostic* interaction between an α-C−H hydrogen and zirconium in complex **4** may be attributed to the enhanced electron donating ability of the Cp*Zr unit due to the electron releasing ability of its methyl groups.

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Table 2. Crystallographic Data for $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$ **1**, $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ **2**, $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ **3**, $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ **4**, and $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2[HB(C_6F_5)_3]_2$ **5**

empirical formula	$C_{20}H_{41}B_3Zr$	$C_{29}H_{53}B_3Zr$	$C_{21}H_{37}B_2ClZr$	$C_{26}H_{47}B_2ClZr$	$C_{62}H_{52}B_2F_{30}O_6Zr_2$
fw (amu)	405.18	525.36	437.80	578.01	1667.10
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1$	$P\bar{1}$
a, Å	9.9708 (10)	15.9725 (10)	33.4957 (10)	8.9621(10)	12.2391 (10)
b, Å	11.0604 (10)	10.5422(10)	6.9309 (10)	16.6582(10)	12.7093 (10)
c, Å	11.8022 (10)	17.6995(10)	21.0313 (10)	10.2454(10)	12.8877 (10)
α, deg	70.076(10)	90	90	90	61.459 (10)
β, deg	79.616 (10)	108.509 (10)	121.615 (10)	93.522(10)	76.237 (10)
γ, deg	63.938(10)	90	90	90	69.907 (10)
V, Å^3	1098.12 (18)	2826.2 (4)	4157.9 (6)	1526.7(2)	1647.3 (2)
Z	2	4	8	2	1
r (calcd), g cm^{-3}	1.225	1.235	1.399	1.257	1.681
T, °C	25	−123	−123	−123	−60
m, mm^{-1}	0.500	0.404	0.659	0.468	0.452
$R_1{}^a$ [$I > 2.0$ s (I)]	0.0217	0.0289	0.0415	0.0334	0.0453
w$R_2{}^b$ (all data)	0.0585	0.0676	0.0789	0.0880	0.1306

[a] $R_1 = F_o - F_c/F_o$. [b] $wR_2 = \{w(F_o^2 - F_c^2)^2/3w(F_o^2)^2\}^{1/2}$.

Table 3. Bond Lengths and Angles for $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$ **1**

Bond Lengths (Å)			
av Zr−C(1−5)	2.4632	Zr−H(1B)	2.015(19)
Zr−B(1)	2.542(2)	B(1)−C(15)	1.595(3)
Zr−B(2)	2.544(2)	B(1)−C(11)	1.599(3)
Zr−B(3)	2.567(2)	B(1)−H(1A)	1.22(2)
Zr−H(1A)	1.95(2)	B(1)−H(1B)	1.229(19)
Bond Angles (deg)			
B(1)−Zr−H(1A)	27.7(6)	H(3A)−Zr−H(3B)	54.8(8)
B(1)−Zr−H(1B)	28.4(5)	Zr−B(1)−H(1A)	48.2(10)
H(1A)−Zr−H(1B)	55.7(8)	Zr−B(1)−H(1B)	51.2(9)
H(1B)−Zr−H(2A)	148.4(8)	H(1A)−B(1)−H(1B)	98.5(13)
H(1A)−Zr−H(2B)	69.0(9)	H(2A)−B(2)−H(2B)	97.8(14)
H(2A)−Zr−H(2B)	57.1(9)	H(3A)−B(3)−H(3B)	95.8(13)

Table 4. Bond Lengths and Angles for $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ **2**

Bond Lengths (Å)			
av Zr−C(1−5)	2.478	Zr(1)−H(112)	1.988(18)
Zr(1)−B(12)	2.541(2)	B(11)−C(11)	1.589(3)
Zr(1)−B(11)	2.544(2)	B(11)−C(15)	1.590(3)
Zr(1)−B(13)	2.556(2)	B(11)−H(111)	1.210(19)
Zr(1)−H(111)	1.924(18)	B(11)−H(112)	1.186(19)
Bond Angles (deg)			
B(11)−Zr(1)−H(111)	27.1(6)	H(121)−Zr(1)−H(122)	56.4(8)
B(11)−Zr(1)−H(112)	26.9(5)	H(131)−Zr(1)−H(132)	55.7(7)
H(111)−Zr(1)−H(112)	53.7(8)	Zr(1)−B(11)−H(111)	46.5(8)
H(111)−Zr(1)−H(121)	126.4(8)	Zr(1)−B(11)−H(112)	49.4(9)
H(112)−Zr(1)−H(121)	149.1(7)	H(111)−B(11)−H(112)	95.1(12)
B(12)−Zr(1)−H(122)	27.9(6)	H(121)−B(12)−H(122)	92.6(12)
H(111)−Zr(1)−H(122)	73.2(8)	H(131)−B(13)−H(132)	96.7(11)
H(112)−Zr(1)−H(122)	123.9(8)		

Table 5. Bond Lengths and Angles for $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ **3**

Bond Lengths (Å)			
Zr(1)−B(11)	2.344(4)	Zr(1)−H(11B)	2.00(3)
Zr(1)−Cl(1)	2.4190(9)	Zr(1)−H(111)	2.31(3)
avZr(1)−C(1−5)	2.472	B(11)−C(115)	1.578(5)
Zr(1)−B(12)	2.567(4)	B(11)−C(111)	1.606(5)
Zr(1)−C(111)	2.698(3)	B(11)−H(11A)	1.20(3)
Zr(1)−H(11A)	1.98(3)	B(11)−H(11B)	1.18(3)
Bond Angles (deg)			
B(11)−Zr(1)−Cl(1)	102.78(10)	H(11A)−Zr(1)−H(11B)	53.3(12)
B(11)−Zr(1)−B(12)	113.63(12)	H(12A)−Zr(1)−H(12B)	53.9(11)
Cl(1)−Zr(1)−B(12)	104.19(9)	Cl(1)−Zr(1)−H(111)	75.3(7)
B(11)−Zr(1)−H(11A)	30.7(9)	Zr(1)−B(11)−H(11A)	57.7(14)
Cl(1)−Zr(1)−H(11A)	133.5(9)	Zr(1)−B(11)−H(11B)	58.4(15)
B(11)−Zr(1)−H(11B)	30.1(8)	H(11A)−B(11)−H(11B)	97(2)
Cl(1)−Zr(1)−H(11B)	84.7(9)		

Table 6. Bond Lengths and Angles of $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ **4**

Bond Lengths (Å)			
Zr(1)−Cl(1)	2.4178(7)	Zr(1)−H(2A)	2.11(5)
avZr(1)−C(1A)	2.488	Zr(1)−H(2B)	1.93(3)
Zr(1)−B(2)	2.488(8)	B(1)−C(1)	1.541(13)
Zr(1)−B(1)	2.491(12)	B(1)−C(5)	1.640(14)
Zr(1)−H(1A)	1.78(5)	B(1)−H(1A)	1.37(5)
Zr(1)−H(1B)	2.12(7)	B(1)−H(1B)	0.57(7)
Bond Angles (deg)			
Cl(1)−Zr(1)−B(2)	99.4(2)	H(1A)−Zr(1)−H(2B)	125.3(17)
Cl(1)−Zr(1)−B(1)	100.5(3)	H(2A)−Zr(1)−H(2B)	58.4(16)
Cl(1)−Zr(1)−H(1A)	79.6(16)	Zr(1)−B(1)−H(1A)	44(2)
B(1)−Zr(1)−H(1A)	32.1(15)	Zr(1)−B(1)−H(1B)	44(7)
Cl(1)−Zr(1)−H(1B)	107(2)	H(1A)−B(1)−H(1B)	88(8)
B(1)−Zr(1)−H(1B)	10.7(19)	H(2A)−B(2)−H(2B)	100(3)
H(1A)−Zr(1)−H(2A)	159.6(12)		

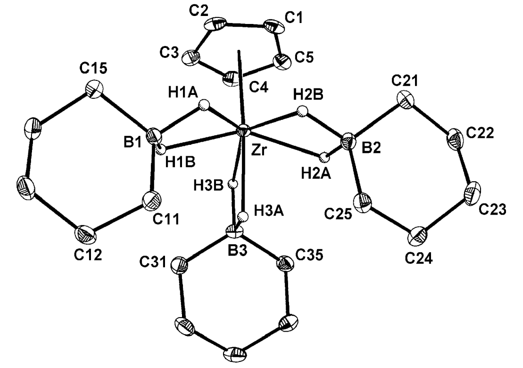
The Zr−Cl distance in complex **3** and in complex **4**, 2.419(9) Å and 2.417(8) Å agree well with the terminal Zr−Cl distance in $CpZrCl_3$, 2.419(3),[10] which in the solid state is a polymer CpZr units bound to single terminal Cl and two double Cl bridges. Formally the zirconium in this solid is associated with 16 valence electrons such as the zirconium in **3** and **4**. These bond distances are significantly shorter than the Zr−Cl distance, 2.4802(5) Å, in $Cp_2Zr(Cl)\{(\mu\text{-}H)_2BC_5H_{10}\}$[3f] which contains an 18 valence electron zirconium atom and is consistent with the sum of the Zr−Cl covalent radii, 2.49 Å (Zr = 1.50 Å,[11] Cl = 0.99 Å[12]). The "short" Zr−Cl distances in **3** and **4** and $CpZrCl_3$ might be indicative of a pπ-dπ back-bonding contribution or alternatively partial ionic character ($Zr^{\delta+}$- $Cl^{\delta-}$) similar to that proposed[11,13] for "short" Zr−O bonds. The average Zr bridge hydrogen bond lengths in **3** (1.99 Å) and **4** (1.98 Å) are also close to those in **1** and **2** and in cyclic organoborate zirconocene compounds reported earlier.[3]

Crystals of **5,** suitable for X-ray diffraction, were obtained by crystallization from the mixed solvent diethyl ether/hexane. The molecular structure of **5**, shown in Figure 3, has a crystallographically imposed center of symmetry. Two $[CpZr(OEt)(OEt_2)]$ fragments are linked by two OC_2H_5 bridging groups through oxygen atoms. The zirconium atoms are associated with 14 valence electrons. The Zr−O distance for the $Zr-OEt_2$ linkage, Zr1−O3 = 2.255(2) Å, and the Zr−O distance for the terminal Zr−OEt linkage, Zr1−O2 = 1.896(2) Å, are in agreement with the distances observed

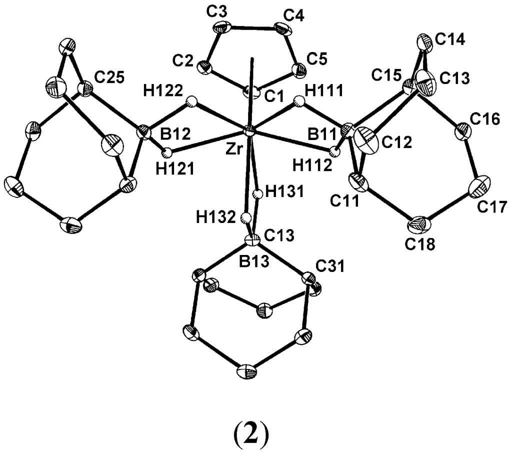
Table 7. Bond Lengths and Angles for $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2[HB(C_6F_5)_3]_2$ **5**

Bond Lengths (Å)			
Zr(1)−O(2)	1.896(2)	O(2)−C(13)	1.423(5)
Zr(1)−O(1)	2.147(2)	C(11)−C(12)	1.490(7)
Zr(1)−O(3)	2.255(2)	C(13)−C(14)	1.469(7)
avZr(1)−C(1−5)	2.505	C(15)−C(16)	1.504(7)
Zr(1)−Zr(1)#1[a]	3.5080(7)	C(17)−C(18)	1.492(7)
O(1)−C(11)	1.464(5)		
Bond Angles (deg)			
O(2)−Zr(1)−O(1)#1[a]	130.66(11)	O(1)−Zr(1)−O(3)	138.86(10)
O(2)−Zr(1)−O(1)	87.73(10)	C(11)−O(1)−Zr(1)#1[a]	118.8(2)
O(1)#1[a]−Zr(1)−O(1)	70.37(10)	C(11)−O(1)−Zr(1)	125.4(2)
O(2)−Zr(1)−O(3)	87.89(11)	Zr(1)#1[a]−O(1)−Zr(1)	109.63(10)
O(1)#1[a]−Zr(1)−O(3)	82.01(10)	C(13)−O(2)−Zr(1)	161.2(3)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, -y + 2, -z + 1$.

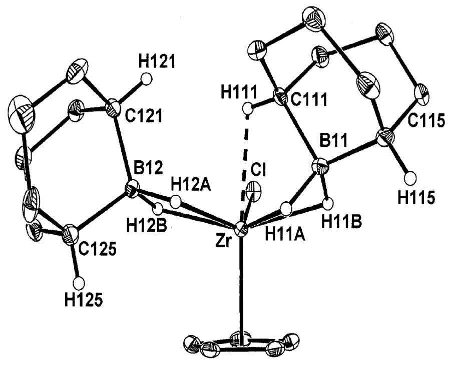


(1)

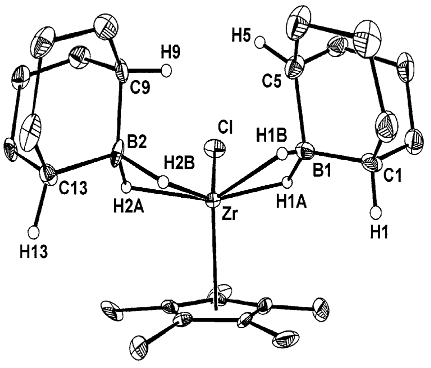


(2)

Figure 1. Molecular structures of $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$ **1** and $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ **2** with 25% thermal ellipsoids.



(3)



(4)

Figure 2. Molecular structures of $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ **3** and $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ **4** with 25% thermal ellipsoids.

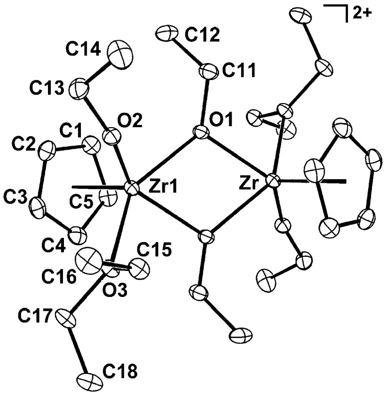


Figure 3. Molecular structures of $[CpZr(OEt)(OEt_2)(\mu\text{-}OEt)]_2^{2+}$ **5** with 15% thermal ellipsoids.

for the equivalent linkages in the cation $[Cp_2Zr(OEt)(OEt_2)]^+$, 2.209(8) Å and 1.884(8) Å, respectively.[3h,13] The zirconium−oxygen distance in the $Zr-OEt_2$ linkage agrees well with the sum of the covalent radii, 2.23 Å (Zr = 1.50 Å,[11] O = 0.73 Å[12]). While the "short" distance of the ethoxyl-zirconium bond can be attributed to a contribution from pπ-dπ bonding, a persuasive, alternative argument can be made for a partial ionic contribution to the bonding ($Zr^{\delta+}$- $Ol^{\delta-}$).[11] The zirconium−oxygen distance of the bridging ethoxyl group Zr1−O1 = 2.145(2) Å is intermediate between the Zr−O distance of the $Zr-OEt_2$ linkage and the Zr−O distance of Zr−OEt linkage. The sum of the angles around the bridging oxygen is 354° (Zr1−O1−Zr = 109.63(10)°, Zr−O1−C11 = 118.8(2)°, Zr1−O1−C11 = 125.4(2)°). This oxygen is 0.26 Å out of the Zr1 − Zr − C11 plane (Figure 4) which suggests some sp^2 character. A convincing example of sp^2 hybridized oxygen is provided by Erker and co-workers[14] in which the sum of the angles around planar three-coordinated oxygen to zirconium atoms is 359°, with an average angle of 119.9°. In this example, the average Zr−O distance is 2.060 Å.

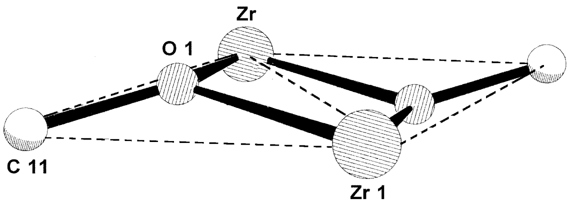


Figure 4. Elevation of O1 with respect to to the Zr1−Zr−C11 plane.

Experimental Section

General Procedures. All manipulations were carried out on a standard high-vacuum line or in a drybox under a nitrogen atmosphere. Diethyl ether, hexane, tatrahydrofuran (THF), and toluene were distilled under nitrogen from sodium benzophenone. All solvents for vacuum-line manipulations were stored in a vacuum over Na/K alloy. Deuterated solvents were obtained from Cambridge Isotope Laboratories (all 99 atom % D) and were vacuum-transferred from Na/K alloy. $CpZrCl_3$, Cp^*ZrCl_3, $B_2(\mu\text{-H})_2(C_8H_{14})$ (9-BBN dimer), and $B(C_6F_5)_3$ were purchased from Aldrich and used as received. Potassium hydride (35 wt % dispersion in mineral oil) was purchased from Aldrich and was washed with hexane prior to use. $B_2(\mu\text{-H})_2(C_5H_{10})$,[15] $K[H_2BC_5H_{10}]$,[16] and $K[H_2BC_8H_{14}]$[17] were prepared by literature procedures. NMR spectra were recorded on a Bruker AM-250 NMR spectrometer operating at 250.11 at 303 K, and boron-11 spectra were externally referenced to BF_3OEt_2(δ = 0.00 ppm). 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 one of two instruments, an Enraf-Nonius CAD4 diffractometer or an Enraf-Nonius Kappa CCD diffractometer. Both instruments employ graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å).

The Enraf-Nonius CAD4 diffractometer was used to obtain structural data from compounds **1** and **5** at 25 and −60 °C. Suitable single crystals were mounted and sealed inside glass capillaries of 0.3 or 0.5 mm diameter under N_2. 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 the 2θ range of 24−30°. Diffraction data were corrected for Lorentz and polarization effects and empirical absorption (empirically from ψ-scan data).

The Enraf-Nonius Kappa CCD diffractometer was employed to collect data from compounds **2**, **3**, and **4**. A single crystal was mounted on the tip of a glass fiber coated with Fomblin oil (a perfluoropolyether), and crystallographic data were collected at −123 °C. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined by employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects by use of the Denzo-SMN package (Nonius BV, 1999).[18] Absorption correction was applied with the SORTAV program[19] provided by MaXus software.[20] All of the structures were solved by direct methods and refined with the SHELXTL-97 (difference electron density calculation, full matrix least-squares refinements) structure solution package.[21] All non-hydrogen atoms were located and refined anisotropically. All bridging hydrogen atoms and the *agostic* hydrogen atom in **3** were located and refined isotropically. One molecule of solvent crystallizes with one molecule of **4**. All other hydrogen atoms were calculated under the assumption of standard -CH geometries.

Preparation of $CpZr\{(\mu\text{-H})_2BC_5H_{10}\}_3$, 1. $CpZrCl_3$ (525.4 mg, 2.0 mmol), $K[H_2BC_5H_{10}]$ (484.3 mg, 6.0 mmol), and a stir bar were added to a 100 mL flask. After degassing, 15 mL of diethyl ether was transferred into the flask at −78 °C. The flask was warmed to room temperature and the contents were stirred for 3 h, after which the KCl was removed by filtration and a white solid was obtained upon removal of the solvent under vacuum. This white solid was redissolved in ether and kept at −40 °C for crystallization. A 268 mg (33.1% yield) of off-white crystalline $CpZr\{(\mu\text{-H})_2BC_5H_{10}\}_3$ was obtained. ^{11}B NMR (ether) δ = 14.49 (t) ppm; ^{11}B NMR (benzene-d_6) δ = 14.40 (t) ppm; ^1H NMR (THF-d_8) δ = 5.729 (s, Cp), 1.47 (br s, β-H), 1.64 (br s, γ-H), 1.11 (br s, α-H), 0.10 (br s, μ-H) ppm; IR (KBr) 3113 (vw), 3106 (vw), 2909 (vs), 2903 (vs), 2852 (m), 2840 (s), 2806 (w), 2654 (vw), 2642 (vw), 2038 (vw), 1969 (w), 1944 (m), 1951 (m), 1873 (s), 1840 (m), 1766 (w), 1566 (vw), 1454 (s), 1443 (s), 1421 (vs), 1395 (vs), 1334 (s), 1292 (w), 1279 (w), 1265 (vw), 1220 (m), 1212 (w), 1197 (m), 1106 (vw), 1097 (w), 1068 (vw), 1034 (vw), 1017 (m), 1006 (w), 955 (m), 916 (vw), 848 (w), 832 (w), 823 (s), 788 (vw), 748 (vw), 723 (vw) cm^{-1}. Anal. Calcd for $C_{20}H_{41}B_3Zr$: C, 59.28; H, 10.20. Found: C, 59.11; H, 10.17.

Preparation of $CpZr\{(\mu\text{-H})_2BC_8H_{14}\}_3$, 2. $CpZrCl_3$ (262.7 mg, 1.0 mmol), $K[H_2BC_8H_{14}]$ (486.3 mg, 3.0 mmol), and a stir bar were

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(21) SHELXTL (version 5.10), Bruker Analytical X-ray systems, 1997.

added to a 100 mL flask. After degassing, 15 mL of diethyl ether was transferred into the flask at −78 °C. The flask was warmed to room temperature and the contents were stirred for 12 h, after which the KCl was removed by filtration and a white solid was obtained upon removal of the solvent under vacuum. This white solid was redissolved in ether and kept at −40 °C for crystallization. White crystalline $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ was obtained in 38% yield. ^{11}B NMR (ether) $\delta = 21.96$ ppm; ^{11}B NMR (benzene-d_6) $\delta = 20.26$ ppm; ^1H NMR (benzene-d_6) $\delta = 5.82$ (s, Cp), 2.10−1.82 (m, β-H), 1.63 (br s, α- and γ-H), 0.27 (br, μ-H) ppm; IR (KBr) 3107 (m), 2979 (s), 2915 (vs), 2904 (vs), 2882 (vs), 2866 (vs), 2834 (vs), 2563 (m), 2001 (s), 1935 (w), 1853 (s), 1761 (m), 1646 (w), 1563 (s), 1464 (vs), 1406 (vs), 1323 (vs), 1216 (vs), 1163 (s), 1069 (s), 1047 (s), 1016 (s), 935 (s), 819 (vs), 703 (m) cm^{-1}. Anal. Calcd for $C_{29}H_{53}B_3Zr$: C, 66.30; H, 10.17. Found: C, 66.55; H, 10.13.

Preparation of $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, 3. A solution of $K[H_2BC_8H_{14}]$ (324.2 mg, 2.0 mmol) in 50 mL of diethyl ether was added dropwise to a solution of $CpZrCl_3$ (262.7 mg,1 mmol) in 100 mL of diethyl ether. After the solution was stirred at room temperature for 12 h, the white solid (KCl) was removed by filtration and a white product was obtained after removal of the solvent under vacuum. This white solid was redissolved in ether and kept at −40 °C for crystallization. White crystalline $CpZr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ was obtained in 46% yield. ^{11}B NMR (ether) $\delta = 19.29$ ppm; ^{11}B NMR (benzene-d_6) $\delta = 19.07$ ppm; ^1H NMR (benzene-d_6) $\delta = 5.89$ (s, Cp), 1.95−1.89 (m, β-H), 1.72 (br s, β- and γ-H), 1.62−1.59 (m, α-H), −0.13 (br s, μ-H) ppm; IR (KBr) 3101 (m), 2954 (s), 2881 (vs), 2872 (vs), 2831 (vs), 2657 (w), 1988 (m), 1967 (m), 1930 (s), 1862 (w), 1795 (w), 1664 (w), 1685 (m), 1440 (m), 1450 (s), 1345 (vs), 1320 (vs), 1299 (s), 1212 (s), 1115 (m), 1048 (m), 1021 (m), 929 (m), 822 (s) cm^{-1}. Anal. Calcd for $C_{21}H_{37}B_2ClZr$: C, 57.61; H, 8.52. Found: C, 57.30; H, 8.32.

Preparation of $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$, 4. A solution of $K[H_2BC_8H_{14}]$ (324.2 mg, 2.0 mmol) in 50 mL of diethyl ether was added dropwise to a solution of Cp^*ZrCl_3 (332.8 mg, 1.0 mmol) in 100 mL of diethyl ether. After the solution was stirred at room temperature for 12 h, the white solid (KCl) was removed by filtration and a white product was obtained after removal of the solvent under vacuum. This white solid was redissolved in ether and kept at −40 °C for crystallization. White crystalline $Cp^*Zr(Cl)\{(\mu\text{-}H)_2BC_8H_{14}\}_2$ was obtained in 46% yield. ^{11}B NMR (ether) $\delta = 19.29$ ppm; ^{11}B NMR (benzene-d_6) $\delta = 17.50$ ppm; ^1H NMR (benzene-d_6) $\delta = 1.92$ (br s, -CH_3, α- and β-H in BBN), 1.62 (br s, γ-H), 0.46 (br s, μ-H) ppm; IR (KBr) 2979 (m), 2948 (s), 2923 (vs), 2887 (vs), 2834 (vs), 2663 (m), 1993 (m), 1935 (m), 1786 (m), 1485 (m), 1447 (s), 1401 (s), 1385 (vs), 1316 (s), 1212 (m), 1115 (m), 1069 (m), 1030 (m), 926 (m), 817 (m), 700 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{47}B_2ClZr$: C, 61.84; H, 9.33. Found: C, 62.19; H, 9.68.

Preparation of $[CpZr(OEt)(OEt2)(\mu\text{-}OEt)]_2[HB(C_6F_5)_3]_2$, 5. $CpZr\{(\mu\text{-}H)_2BC_5H_{10}\}_3$ (126.1 mg, 0.31 mmol) or $CpZr\{(\mu\text{-}H)_2BC_8H_{14}\}_3$ (162.9 mg, 0.31 mmol) and $B(C_6F_5)_3$ (162 mg, 0.32 mmol) were dissolved in 5 mL of diethyl ether. During this process, C_2H_6 gas evolved. About 10 mL of hexane was put on the top of the ether solution. About 1 week later, 231.2 mg (0.277 mmol, 89.2% yield) of white crystalline solid was isolated. ^{11}B NMR (THF-d_8) $\delta = -27.08$ (d, $J_{B-H} = 93.2$ Hz) ppm; ^1H NMR (THF-d_8) $\delta = 6.50$ (s, Cp), 4.17 (q, $J = 7$ Hz), 3.39 (q, $J = 7$ Hz), 1.22 (t, $J = 7$ Hz) ppm; $^1H\{^{11}B\}$ NMR (THF-d_8) $\delta = 3.79$ (br s, BH) ppm; IR (KBr) 3123 (br, vw), 2982 (m), 2940 (w), 2884 (w), 2373 (w), 1643 (s), 1640 (vw), 1548 (w), 1511 (vs), 1466 (vs), 1384 (s), 1274 (s), 1185 (vw), 1108 (vs), 1078 (s), 1020 (s), 968 (vs), 930 (m), 894 (m), 880 (w), 863 (w), 846 (w), 840 (m), 852 (s), 765 (m), 757 (m), 730 (vw), 664 (w), 637(vw), 604 (vw), 569 (m), 541 (m), 524 (w), 467 (vw), 447 (vw), 421 (vw) cm^{-1}. Anal. Calcd for $C_{62}H_{52}B_2F_{30}O_6Zr_2$: C, 44.67; H, 3.14. Found: C, 43.99; H, 3.34.

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Supporting Information Available: Tables of crystallographic data, position parameters, bond lengths, and bond and anisotropic thermal parameters for all complexes (**1**−**5**). Crystallographic data in CIF format for all complexes (**1**−**5**). This material is available free of charge via the Internet at http://pubs.acs.org.

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