

Syntheses, structures, and properties of phenyltrihydroborate complexes of zirconocene and titanocene

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Abstract

The phenyltrihydroborate complexes, $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BPh}\}$, **1**, and $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BPh}\}_2 \cdot (1/2 \text{ toluene})$, **2**, were prepared from the reactions of Cp_2ZrCl_2 with one and two moles of LiBH_3Ph . The Zr–H–B bonds in **2** are stable under vacuum at 100 °C for hours without significant decomposition. An inductive effect has been proposed for this strong interaction. This hydrogen bridge bond can be broken upon reacting with the Lewis base $\text{N}(\text{C}_2\text{H}_5)_3$ to produce $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{BH}_2\text{Ph}$ and the zirconium hydride compound $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BPh}\}$, **3**. Compound **3** also can be prepared from the reaction of Cp_2ZrHCl with LiBH_3Ph . The reaction of **1** with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ is solvent dependent, the metathesis product $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{B}(\text{C}_6\text{F}_5)_2\}$, **4**, was formed in the toluene solution, whereas the ionic complex $[\text{Cp}_2\text{ZrCl}(\text{OEt}_2)][\text{HB}(\text{C}_6\text{F}_5)_3]$, **5**, was isolated from the ether solution. The reaction of titanocene dichloride, Cp_2TiCl_2 , with LiBH_3Ph produced a 17-electron, paramagnetic complex, $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BPh}\}$, **6**. Single crystal X-ray structures of **1**, **2**, **3**, **4**, **5**, and **6** were also determined. A coplanar structure of the four bridge hydrogens in **2** was observed. © 2004 Elsevier B.V. All rights reserved.

Keywords: Phenyltrihydroborate; Organohydroborate; Hydroborate; Crystal structure; Zirconocene; Titanocene

1. Introduction

Many tetrahydroborate metal complexes have been studied extensively during the past 50 years [1], however, only a few examples of the organohydroborate metal complexes have been reported. While most of the known complexes are organodihydroborate compounds, the organotrihydroborate complexes are rare. To our knowledge, there are only several organotrihydroborate anions, including $[\text{BH}_3\text{CH}_3]^-$ [2], $[\text{BH}_3\text{CO}_2\text{R}]^-$ (R = H, CH_3 , C_2H_5) [3], $[\text{BH}_3\text{CN}]^-$ [4], and $[\text{BH}_3\text{C}(\text{SiMe}_3)_3]^-$ [5], that have been used to prepare the corresponding complexes. However, only few complexes were prepared from the $[\text{BH}_3\text{CO}_2\text{R}]^-$ (R = H, CH_3 , C_2H_5) or the

$[\text{BH}_3\text{C}(\text{SiMe}_3)_3]^-$ anions [3,5]. While many methyltrihydroborate, $[\text{BH}_3\text{CH}_3]^-$, and cyanotrihydroborate, $[\text{BH}_3\text{CN}]^-$, complexes have been reported, most of the cyanotrihydroborate anion bonds to the metal through a nitrogen atom and, except for five compounds [2a–c] the methyltrihydroborate complexes involve actinide and lanthanide metals. The chemical properties of these organotrihydroborate complexes are not well studied.

In our recent study, we found that the Zr–H–B bond of the methyltrihydroborate disubstituted complex $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$ [2a] is significantly weaker than that of the tetrahydroborate complex $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BH}_2\}_2$ [6] or the organodihydroborate complex $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$ [7]. While complex $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$ is stable under vacuum at room temperature and complex $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BH}_2\}_2$ can be sublimed under reduced pressure at 120 °C, complex

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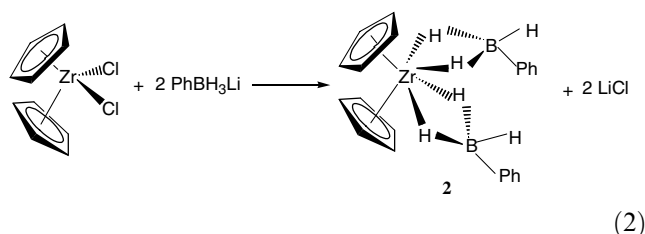
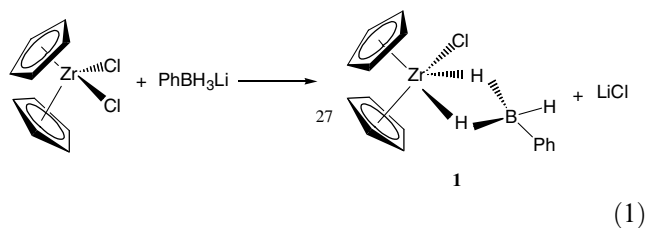
E-mail address: fcliu@mail.ndhu.tw (F.-C. Liu).

$\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$ decomposes to $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BHCH}_3\}$ and $(\text{CH}_3\text{BH}_2)_2$ under vacuum at room temperature [2a]. This weak Zr–H–B bond is unexpected and we proposed that this weak Zr–H–B interaction is caused by the electron releasing property of the methyl group on the boron atom. This effect causes the accumulation of the excess electron density on the central zirconium atom and destabilizes the Zr–H–B interaction. In the present study we are interested to examine this proposition and have selected phenyltrihydroborate complexes for study. We present the syntheses, structures, and the properties of the phenyltrihydroborate derivatives of the zirconocene and titanocene complexes, and we also report the reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BPh}\}$ with the Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$, in non-coordinating and coordinating solvent.

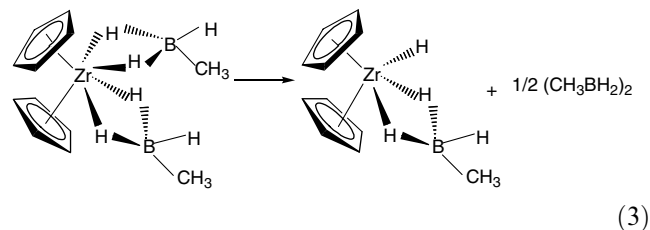
2. Results and discussion

2.1. Formation and properties of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BPh}\}$ (1), $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BPh}\}_2 \cdot (1/2 \text{ toluene})$ (2), $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BPh}\}$ (3), $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{B}(\text{C}_6\text{F}_5)_2\}$ (4), $[\text{Cp}_2\text{ZrCl}(\text{OEt}_2)][\text{HB}(\text{C}_6\text{F}_5)_3]$ (5), and $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BPh}\}$ (6)

The phenyltrihydroborate compounds $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BPh}\}$, **1**, and $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BPh}\}_2 \cdot (1/2 \text{ toluene})$, **2**, were prepared from the reactions of Cp_2ZrCl_2 with one and two moles of LiBH_3Ph , as shown in Eqs. (1) and (2). Compound **2** was crystallized from toluene solution and contained one-half solvent molecule.

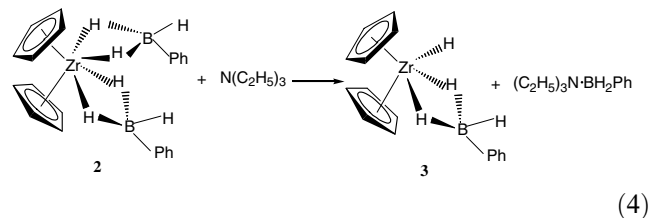


Previously we reported the preparation of the zirconium hydride compound $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BHCH}_3\}$ through the decomposition of the methyltrihydroborate disubstituted compound $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$ under reduced pressure at room temperature [2a] (Eq. (3)). An attempt to prepare the zirconium hydride compound $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BPh}\}$, **3**, using the same method failed.

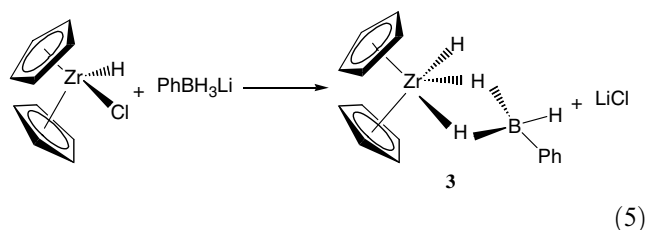


Compound **2** was subjected to sublimation under reduced pressure; however, compound **3** did not form, even when the temperature was raised to 100 °C for 4 h. After heating, most of the crystals turned light pink and the metal luster disappeared. However, the NMR spectra indicated that the compound $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BPh}\}_2$ was still intact, and only the absence of the toluene signals was observed. These NMR spectra suggest that the Zr–H–B bond strength of compound **2** is comparable to that of the tetrahydroborate complex, $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BH}_2\}_2$ [6], which is stable above 100 °C under reduced pressure. From a steric point of view, the phenyl group on the boron atom has a larger steric requirement than that of the methyl group on compound $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$, and this factor might destabilize compound **2**, however, this result was not observed [8]. On the other hand, the inductive effect of the substituent on the boron atom may play a key role for its stability. Formally, the zirconium is associated with 20 valence electrons in compound **2**, the same as the methyltrihydroborate disubstituted compound $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$. Unlike the electron donor methyl substituted group on compound $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$, which directs electron density to the zirconium and weakens the Zr–H–B bond, the electron withdrawing phenyl substituted group on compound **2** relieves the accumulation of excess electron density on the zirconium and stabilizes the Zr–H–B interaction.

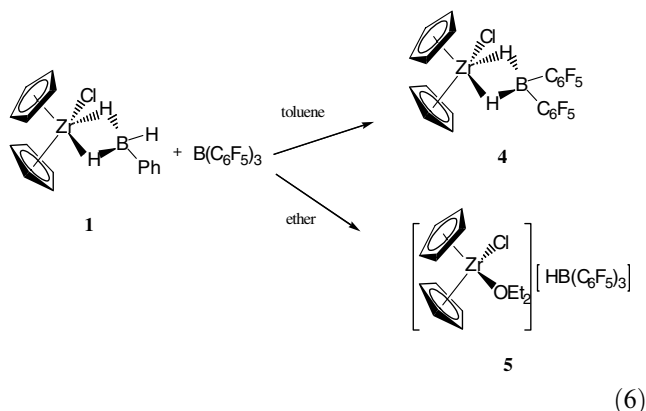
Compound **3** can be prepared from the reaction of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BPh}\}_2$ with $\text{N}(\text{C}_2\text{H}_5)_3$ in toluene solution, as shown in Eq. (4).



These two products, **3** and $(\text{C}_2\text{H}_5)_3\text{N}\cdot\text{BH}_2\text{Ph}$, were isolated from repeated crystallizations and manual separations. The second method to prepare compound **3** is from the reaction of Cp_2ZrHCl with LiBH_3Ph in toluene solution, as shown in Eq. (5). After reacting for one day, only 50% yield of compound **3** was observed from the boron spectra and compound **3** did not increase significantly for further reaction.



The reaction of **1** with $B(C_6F_5)_3$ produces the covalent metathesis product $Cp_2ZrCl\{(\mu-H)_2B(C_6F_5)_2\}$, **4**, in toluene solution, and produces the ionic complex $[Cp_2ZrCl(OEt_2)][HB(C_6F_5)_3]$, **5**, in diethyl ether, as shown in Eq. (6).



These reactions are not balanced since the by-products could not be identified through an NMR study. We could not prepare pure compound **4** on a large scale, since a small amount of by-product could not be removed successfully, however, we isolated a few crystals which were sufficient for the NMR study and the solid state X-ray structure determination. Compound **4** has also been prepared from the reaction of Cp_2ZrHCl with $HB(C_6F_5)_2$ in a NMR tube, and identified through a multinuclear NMR spectroscopy [9]. Compound **5** is soluble in THF and acetonitrile, however, it gradually decomposed in these solvents during the NMR measurements; one of the decomposition products is Cp_2ZrCl_2 .

The boron chemical shifts of compounds **1**, **2**, and **3** appear as a quartet at δ 2.37 ($J_{B-H} = 76$ Hz), -6.0 ($J_{B-H} = 70$ Hz), and 16.62 ppm ($J_{B-H} = 73$ Hz), respectively. The apparent equivalence of bridge and terminal hydrogens of the hydroborate compounds at ambient temperature is well known [1a], which causes the quartet nature of the boron signals. These resonances are downfield with respect to that of lithium phenyltrihydroborate (-26.5 ppm, $J_{B-H} = 75$ Hz). These results are consistent with those obtained from methyltrihydroborate analogs, where the boron chemical shifts of the methyltrihydroborate complexes $Cp_2ZrCl\{(\mu-H)_2BHCH_3\}$ [2a], $Cp_2Zr\{(\mu-H)_2BHCH_3\}_2$ [2a], and $Cp_2ZrH\{(\mu-H)_2BHCH_3\}$ [2b] appear at 3.84, -6.82 , and 18.2 ppm, respectively. The B–H

coupling constants of these organotrihydroborate complexes are comparable with that of the free ligands. This behavior is different from that of the tetrahydroborate or cyclic organodihydroborate complexes, which display smaller coupling constants than that of the free ligands [1a,7,10].

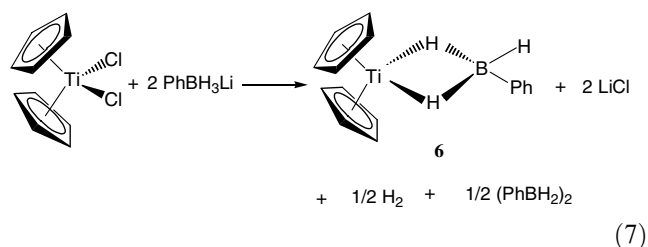
In the 1H NMR spectra, the signals of the BH_3 hydrogens of complexes **1**, **2**, and **3** appeared at 1.00, 1.39, and -0.42 ppm, as a broad quartet, respectively. The terminal and bridge hydrogens in these complexes are indistinguishable in the proton spectra [1a]. The chemical shift of the terminal Zr–H hydride of compound **3** appears at 4.48 ppm, as a broad signal that falls within the range observed for other zirconium hydride complexes [2b, 6b,7,12,13].

The boron signal of compound **4** appears at -10.6 ppm (t, $J_{B-H} = 67$ Hz). This chemical shift and coupling constant are consistent with that of the bis(pentafluorophenyl)borate zirconocene complexes [9,14]. The bridge Zr–H–B hydrogens appear at 0.38 ppm as a broad signal.

The NMR data of compound **5** was collected in deuterated THF where the coordinating ether was replaced by the deuterated THF. The terminal B–H hydrogen appeared at 3.80 ppm as a broad quartet. The anionic borate signal appeared at -25.9 ppm as a doublet ($J_{B-H} = 93$ Hz) in the boron spectrum. These chemical shifts and coupling constant are consistent with other ionic complexes with the same anion [15].

The IR spectrum of compound **3** displays a broad signal at 1597 cm^{-1} assigned to the Zr–H stretching mode, which agrees with bands observed in the IR spectra of other zirconium hydride complexes [2b,6b,7,12].

Compound $Cp_2Ti\{(\mu-H)_2BPh\}$, **6**, was prepared from the reaction of Cp_2TiCl_2 with two moles of $LiBH_3Ph$, as shown in Eq. (7).



During the reaction, hydrogen gas was evolved and the solution turned purple in color. The titanium was reduced from Ti(IV) to Ti(III), producing a 17-electron species. No obvious signal was observed in the ± 100 ppm range in the boron spectra. In the 1H NMR spectrum, three signals were observed in the range 6.55–7.68 ppm. These signals appeared in the range of the aromatic protons and were assigned to the resonances of the phenyl protons, using a proton detected 1H – ^{13}C correlation experiment (heteronuclear multiple quantum

coherence, HMQC). A broad signal that appeared at 7.68 ppm was assigned to the resonance of the β proton of the phenyl group, which is five bonds away from the paramagnetic center. This result is consistent with our previous study of the cyclic organohydroborate complexes of titanocene where the proton signals are NMR silent until they are five bonds away from the paramagnetic center [16].

2.2. Molecular structures

The molecular structures of **1**, **2**, **3**, **4**, **5**, and **6** were determined by single-crystal X-ray diffraction analysis, and they are shown in Figs. 1–6. Crystallographic data and selected bond distances and bond angles are given in Tables 1–4. A complete listing of distances and angles, as well as the atomic coordinates, can be found in the Supporting Information.

The coordination geometry around the zirconium atom in **1**, **2**, **3**, and **4** is best described as a distorted tetrahedron. At the corners of the tetrahedron are the centers of the two Cp rings, a boron atom which is connected to the zirconium through two bridge hydrogens, and a Cl (**1** and **4**), or a second boron atom (**2**) which is also connected to the zirconium through two bridge hydrogens, or a hydrogen atom (**3**). Two independent molecules of **4** were found in the unit cell. These two molecules have slightly different bond distances and angles, and only one molecule is shown in Fig. 4.

In compound **2**, one-half solvent molecule, toluene, was found in the crystal lattice and one Cp ring displayed 50% occupancy. There is a crystallographically imposed mirror plane which passes through the Zr, C(7), C(15), C(16), and C(19), to generate the rest of the molecule. The carbon atoms C(15), C(16), and C(19) are from the solvent, they are not shown in Fig. 2. The four bridge hydrogens are coplanar. The coplanarity of the four bridge hydrogens in $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BH}_2\}_2$ has been

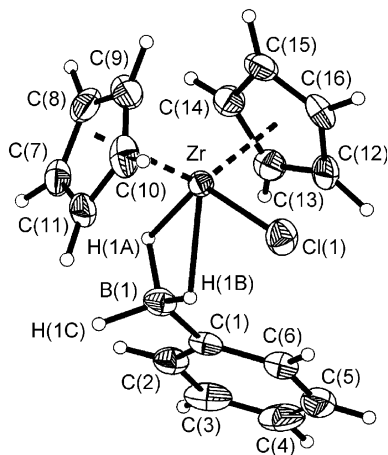


Fig. 1. Molecular structure of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BHPh}\}$ (**1**), showing 50% probability thermal ellipsoids.

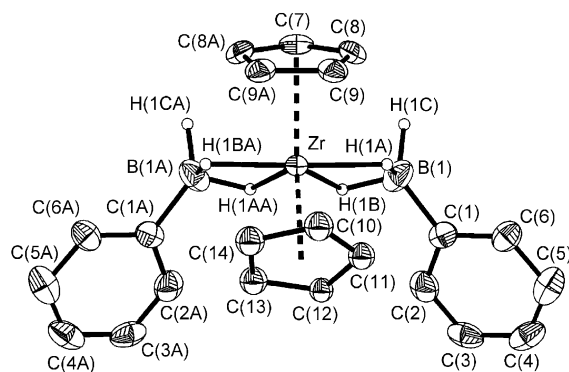


Fig. 2. Molecular structure of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHPh}\}_2 \cdot (1/2 \text{ toluene})$ (**2**), showing 50% probability thermal ellipsoids. Toluene molecule is omitted.

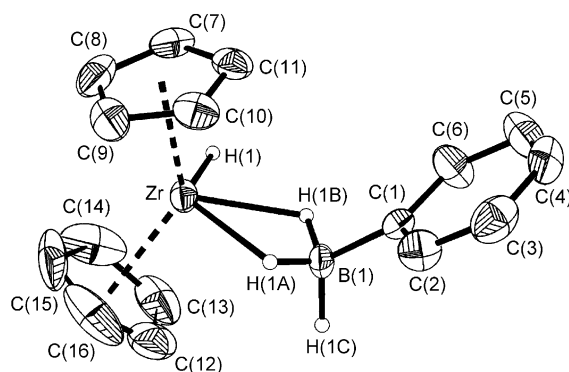


Fig. 3. Molecular structure of $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BHPh}\}$ (**3**), showing 50% probability thermal ellipsoids.

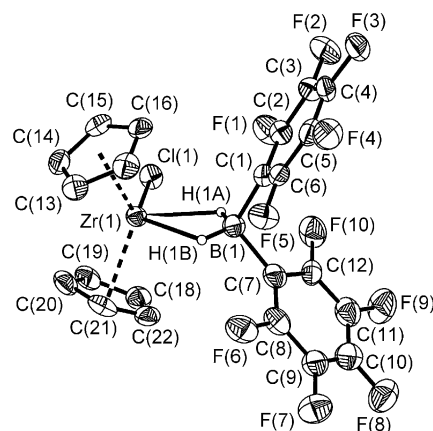


Fig. 4. Molecular structure of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{B}(\text{C}_6\text{F}_5)_2\}$ (**4**), showing 50% probability thermal ellipsoids.

suggested by Hoffmann and Lauher through molecular orbital calculations [17]. Although the solid state structure of $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BH}_2\}_2$ has been reported, hydrogen atoms around the boron atom were not found due to the low quality of the crystal [18]. Some metallocene hydroborate disubstituted complexes have been reported, which include $(\text{C}_5\text{H}_4\text{Me})_2\text{Hf}\{(\mu\text{-H})_2\text{BH}_2\}_2$ [19],

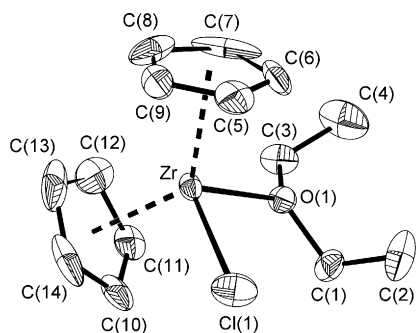


Fig. 5. Molecular structure of the cation $[\text{Cp}_2\text{ZrCl}(\text{OC}_4\text{H}_{10})]^+$ (**5**), showing 30% probability thermal ellipsoids.

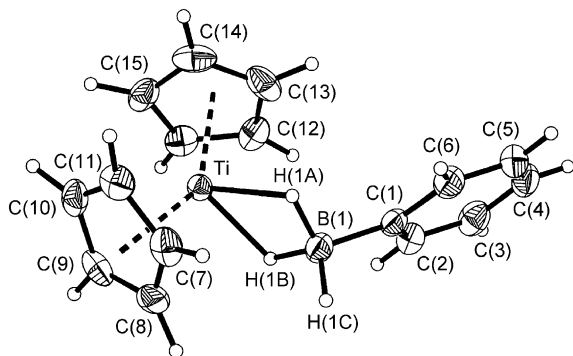


Fig. 6. Molecular structure of $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BHPPh}\}$ (**6**), showing 50% probability thermal ellipsoids.

$\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$ [**7**], $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$ [**2a**], and $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{B}(\text{C}_6\text{H}_5)_2\}_2$ [**9**], the bridge hydrogen atoms in these compounds are not coplanar. In compound **2**, the zirconium atom is 0.1831 Å above, and each boron atom is 0.1719 Å below the plane defined by the four bridge hydrogens. The B–Zr–B angle of **2** is 107.9(3)° which is larger than that in compounds $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BH}_2\}_2$ (103.3(7)°) [**18**], $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}_2$ (89.3°) [**7**] and $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$ (99.7(3)°) [**2a,20**].

The Zr–B distances are 2.592(4) in **1**, 2.628(6) in **2**, and 2.538(11) Å in **3**. These distances reflect the steric bulk of the fourth ligand which is Cl (**1**), BH_3Ph (**2**), and H (**3**), respectively. However, an interesting result is observed when these distances are compared with those in the methyltrihydroborate analogs: $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BHCH}_3\}$ (2.578(6) Å) [**2a**], $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{BHCH}_3\}_2$ (2.599(8) and 2.612(9) Å) [**2a**], and $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BHCH}_3\}$ (2.558(4) Å) [**2b**]. Although the phenyl substituted compounds **1** and **2** have longer Zr–B distances compared with the methyltrihydroborate analogs, compound **3** has a shorter Zr–B distance than that in compound $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BHCH}_3\}$. Obviously, the steric bulk of the phenyl substituted group alone does not account for the discrepancy in these distances. Compared with other ligands, the hydride ligand is

relatively small and the steric effect is minimal. This may suggest the electronic effect dominates the metal–ligand interaction. Support for this argument is given by the two cyclic organodihydroborate compounds, $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ (2.587(7) Å) [**7**] and $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ (2.548(4) Å) [**12**], both have an electron releasing alkyl group, which have Zr–B distances comparable to that in $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BHCH}_3\}$, but are longer than that observed in the electron withdrawing substituted compound **3**.

The Zr–B distance is 2.604(8) Å in **4**. It is slightly longer than that in **1**, however, it is significantly shorter than the Zr–B distances found in the bulky bis(pentafluorophenyl)borate compound $\text{Cp}_2\text{Zr}\{(\mu\text{-H})_2\text{B}(\text{C}_6\text{F}_5)_2\}_2$ (2.696(10) and 2.679(10) Å), due to the steric reason [**14**].

The bridge Zr–H_b and bridge B–H_b distances of compounds **1–4** are listed in Table 3. Comparing with the bridge Zr–H distances (1.96(5)–2.17(9) Å) and the bridge B–H distances (1.10(9)–1.32(5) Å) of the zirconocene hydroborate complexes [**2a,7,9,12,21**], compound **3** has a shorter bridge B–H distance and compound **4** has a longer Zr–H distance. These may account for the short Zr–B distance in **3** and long Zr–B distance in **4**.

The terminal B–H_t bond distances of **1** (1.22(5) Å), **2** (1.21(6) Å), and **3** (1.14(6) Å) are comparable with one of the bridge B–H bond distances and are longer than the other one found in each compound. These results are different compared with those were observed in the tetrahydroborate complexes where the bridge B–H bond distances are 0.06–0.10 Å longer than the terminal B–H bond distances [**1a,21**].

The Zr–Cl distance is 2.4844(13) Å in **1** and 2.460(2) Å in **4**. It is comparable to the Zr–Cl distances observed in other hydroborate complexes [**2a,10,22**].

The terminal Zr–H distance in **3** is 1.70(7) Å. This distance is significantly shorter than that in $(\eta^5\text{-C}_5\text{Me}_5)\text{ZrH}(\eta\text{-C}_8\text{H}_8)$ (1.81 Å) [**23**], $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_5\text{H}_{10}\}$ (1.786(4) Å) [**7**], $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BHCH}_3\}$ (1.78(2) Å) [**2b**], and $\{\text{ZrH}(\mu\text{-H})(\eta\text{-C}_5\text{H}_4\text{Me})_2\}_2$ (1.78(2) Å) [**24**], but is comparable to those distances observed in $\text{Cp}_2\text{ZrH}\{(\mu\text{-H})_2\text{BC}_4\text{H}_8\}$ (1.68(5) Å) [**12**] and $(\eta^5\text{-C}_8\text{H}_{11})\text{ZrH}(\text{dmpe})$ (1.67 Å) [**25**].

The coordination geometry around the zirconium atom in **5** is best described as a distorted tetrahedron, where the centers of the two Cp rings, a chlorine atom, and an oxygen atom occupy the corners of the tetrahedron. The Zr–Cl distance is 2.4148(17) Å and the Zr–O distance is 2.211(3) Å. The Zr–Cl distance is slightly shorter than that in compounds **1**, **4**, and other organohydroborate compound [**2a,10,22**]. The Zr–O distance was consistent with that observed in $[\text{Cp}_2\text{Zr}(\text{OEt})_2](\text{OEt})[\text{HB}(\text{C}_6\text{F}_5)]$ (2.209(8) Å) [**15**] and is slightly longer than the sum of the covalent radii, 2.16 Å [**26**]. These bond distances suggest a weak interaction between the zirconium atom and the ether molecule, which has been

Table 1
Crystallographic data for Cp₂ZrCl{(μ-H)₂BHPh} (1), Cp₂Zr{(μ-H)₂BHPh}₂ · (1/2 toluene) (2), and Cp₂ZrH{(μ-H)₂BHPh} (3)

Empirical formula	C ₁₆ H ₁₈ BClZr	C _{25.5} H ₃₀ B ₂ Zr	C ₁₆ H ₁₉ BZr
<i>F</i> _w	347.78	449.33	313.34
<i>T</i> (K)	150(1)	150(1)	150(1)
Cryst system	Monoclinic	Tetragonal	Monoclinic
Space group	<i>Cc</i>	<i>P4</i> ₂ <i>m</i>	<i>Pn</i>
<i>a</i> (Å)	17.5766(3)	16.9483(2)	6.1535(1)
<i>b</i> (Å)	8.8102(2)	16.9483(2)	8.2688(2)
<i>c</i> (Å)	11.0359(2)	7.9935(1)	14.5763(3)
<i>α</i> (°)			
<i>β</i> (°)	114.0895(9)		99.9431(13)
<i>γ</i> (°)			
<i>V</i> (Å ³)	1560.11(5)	2296.09(5)	730.53(3)
<i>Z</i>	4	4	2
<i>ρ</i> _{calc.} (g/cm ³)	1.481	1.300	1.424
Cryst size (mm ³)	0.40 × 0.32 × 0.25	0.25 × 0.25 × 0.23	0.30 × 0.20 × 0.16
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ Limits (°)	2.54–27.49	1.70–27.50	2.46–27.50
Index ranges	–22 ≤ <i>h</i> ≤ 22 –10 ≤ <i>k</i> ≤ 11 –14 ≤ <i>l</i> ≤ 14	–22 ≤ <i>h</i> ≤ 21 –22 ≤ <i>k</i> ≤ 22 –10 ≤ <i>l</i> ≤ 10	–7 ≤ <i>h</i> ≤ 7 –10 ≤ <i>k</i> ≤ 10 –18 ≤ <i>l</i> ≤ 17
Reflns collected	9597	16177	9723
Unique reflns	3331	2759	3112
Unique reflns [<i>I</i> > 2.0σ(<i>I</i>)]	704	932	320
Completeness to θ (%)	99.8	100.0	99.9
<i>μ</i> (mm ^{–1})	0.859	0.487	0.732
Max/min transm	0.843, 0.738	0.888, 0.821	0.881, 0.799
Data/restraints/parameters	3331/2/185	2759/0/136	3112/2/177
<i>R</i> ₁ ^a [<i>I</i> > 2.0σ(<i>I</i>)]	0.0329	0.0462	0.0387
<i>wR</i> ₂ ^b (all data)	0.0919	0.1153	0.1003
<i>R</i> _{int}	0.0446	0.0731	0.0460
GOF on <i>F</i> ²	1.192	1.118	1.145

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right\}^{1/2}$$

confirmed through a NMR study where the coordinated ether molecule was replaced by the THF molecule.

The coordination geometry of the titanium atom in compound **6** is best described as a trigonal. The centers of the two Cp rings and the boron atom which is connected to the titanium atom through two bridge hydrogens define the trigonal coordination geometry of the metal center. The bond distances of Ti–B, bridge Ti–H_b, and bridge B–H_b are all consistent with those in other titanocene organohydroborate complexes [2a,15,16,27]. The terminal B–H distance of 1.14(2) Å is shorter than the bridge B–H distances.

3. Experimental

3.1. General procedures

All manipulations were carried out using a standard high vacuum line or in a drybox under an atmosphere of nitrogen. Diethyl ether and toluene were dried over Na/benzophenone and were freshly distilled prior to use. Cp₂ZrCl₂, Cp₂TiCl₂, and LiAlH₄ were purchased from Aldrich and used as received. PhB(OH)₂ and

B(C₆F₅)₃ were purchased from Strem and used as received. LiBH₃Ph was prepared according to the literature method [11a]. Elemental analyses were recorded on a Hitachi 270–30 spectrometer. ¹H NMR spectra (δ (TMS) 0.00 ppm) were recorded on a Varian Mercury 200 spectrometer operating at 199.975 MHz or recorded on a Varian Unity Inova 600 spectrometer operating at 599.948 MHz. ¹¹B spectra (externally referenced to BF₃ · OEt₂ (δ 0.00 ppm)) were recorded on a Varian Unity Inova 600 operating at 192.481 MHz. Infrared spectra were recorded on a Jasco FT/IR-460 Plus spectrometer with 2 cm^{–1} resolution.

3.2. X-ray crystal structure determination

Suitable single crystals of **1**, **2**, **3**, **4**, **5**, and **6** were mounted and sealed inside glass capillaries under nitrogen. Crystallographic data collections were carried out on a Nonius KappaCCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150(1) K. Cell parameters were retrieved and refined using DENZO-SMN [28] software on all reflections. Data reduction was performed with the DENZO-SMN [28] software. An empirical absorption was based on the symmetry-equivalent reflections and

Table 2
 Crystallographic data for Cp₂ZrCl{(μ-H)₂B(C₆F₅)₂} (4), [Cp₂ZrCl(OC₄H₁₀)] [HB(C₆F₅)] (5), and Cp₂Ti{(μ-H)₂BHPh} (6)

Empirical formula	C ₂₂ H ₁₂ B ₂ ClF ₁₀ Zr	C ₃₂ H ₂₁ BClF ₁₅ OZr	C ₁₆ H ₁₈ BTi
<i>F</i> _w	603.8	843.97	269.01
<i>T</i> (K)	150(1)	150(1)	150(1)
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
<i>a</i> (Å)	7.3519(1)	12.5124(6)	11.47130(10)
<i>b</i> (Å)	16.2967(3)	20.5626(10)	14.3734(2)
<i>c</i> (Å)	18.1612(3)	12.9849(6)	16.7301(2)
α (°)	89.9137(7)		
β (°)	89.1789(7)	106.118(1)	
γ (°)	83.7631(6)		
<i>V</i> (Å ³)	2162.82(6)	3209.5(3)	2758.49(6)
<i>Z</i>	4	4	8
ρ_{calc} (g/cm ³)	1.854	1.747	1.296
Cryst size (mm ³)	0.25 × 0.25 × 0.10	0.23 × 0.20 × 0.15	0.25 × 0.20 × 0.10
Radiation (λ , Å)	Mo K α (0.71073)	Mo K α (0.71073)	Mo K α (0.71073)
2 θ Limits (°)	1.12–27.50	1.91–27.50	2.43–27.50
Index ranges	−9 ≤ <i>h</i> ≤ 9 −21 ≤ <i>k</i> ≤ 21 −23 ≤ <i>l</i> ≤ 23	−15 ≤ <i>h</i> ≤ 16 −26 ≤ <i>k</i> ≤ 26 −16 ≤ <i>l</i> ≤ 15	−14 ≤ <i>h</i> ≤ 14 −18 ≤ <i>k</i> ≤ 18 −21 ≤ <i>l</i> ≤ 21
Refins collected	29319	29319	20458
Unique refins	9824	7372	3166
Unique refins [<i>I</i> > 2.0 σ (<i>I</i>)]	1184	1672	1128
Completeness to θ (%)	98.6	99.9	99.9
μ (mm ^{−1})	0.727	0.541	0.598
Max/min transm	0.943, 0.821	0.9233, 0.8857	0.945, 0.859
Data/restraints/parameters	9824/1/648	7372/0/464	3166/0/176
<i>R</i> ₁ ^a [<i>I</i> > 2.0 σ (<i>I</i>)]	0.0785	0.0707	0.0364
<i>wR</i> ₂ ^b (all data)	0.2344	0.1787	0.0985
<i>R</i> _{int}	0.0655	0.0525	0.0507
GOF on <i>F</i> ²	1.098	1.062	1.051

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$$

$$^b wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2) \}^{1/2}$$

Table 3

Selected bond distances (Å) and bond angles (°) for Cp₂ZrCl{(μ-H)₂BHPh} (1), Cp₂Zr{(μ-H)₂BHPh}₂ · (1/2 toluene) (2), Cp₂ZrH{(μ-H)₂BHPh} (3), Cp₂ZrCl{(μ-H)₂B(C₆F₅)₂} (4), and Cp₂Ti{(μ-H)₂BHPh} (6)

	1	2	3	4	6
<i>Bond distances</i>					
M–B	2.592(4)	2.628(6)	2.538(11)	2.604(8) 2.619(8)	2.417(2)
M–H _{bridge}	2.06(4) 2.10(5)	1.90(5) 2.09(6)	2.09(7) 2.07(7)	2.302(10) 2.18(8) 2.17(7) 2.30(8)	1.875(18) 1.904(18)
B–H _{bridge}	1.15(4) 1.23(4)	1.16(5) 1.22(6)	1.04(8) 1.11(7)	1.15(9) 1.03(8) 1.109(8) 1.36(8)	1.221(18) 1.218(18)
B–H _{terminal}	1.22(5)	1.21(6)	1.14(6)		1.14(2)
Zr–Cl	2.4844(13)			2.460(2) 2.456(2)	
Zr–H _{terminal}			1.70(7)		
<i>Bond angles</i>					
B–Zr–B		107.9(3)			
B–Zr–Cl	100.10(11)			99.2(2) 110.5(2)	
B–Zr–H _{terminal}			97(2)		

Table 4
Selected bond distances (Å) and bond angles (°) for
[Cp₂ZrCl(OC₄H₁₀)] [HB(C₆F₅)₃] (**5**)

Bond distances	
Zr–O(1)	2.211(3)
Zr–Cl(1)	2.4148(17)
O(1)–C(1)	1.461(6)
O(1)–C(3)	1.498(7)
C(1)–C(2)	1.489(9)
C(3)–C(4)	1.452(11)
Bond angles	
O(1)–Zr–Cl(1)	96.53(11)
C(1)–O(1)–C(3)	114.7(4)
C(1)–O(1)–Zr	120.4(3)
C(3)–O(1)–Zr	120.9(3)

was applied to the data using the SORTAV [29] program. The structure was solved using the SHELXS-97 [30] program and refined using SHELXL-97 [31] program by full-matrix least-squares on F^2 values. All non-hydrogen atoms, except for C10–C19 in compound **2**, were refined with anisotropic thermal parameters. Hydrogen atoms attached to the zirconium and the boron atoms, and the carbon atoms C10–C19 in compound **2** were located from the difference Fourier map and were refined isotropically. Hydrogen atoms attached to the carbons were fixed at calculated positions and refined using a riding mode. Detailed crystal data are listed in Tables 1 and 2.

3.3. Preparation of complexes

3.3.1. Cp₂ZrCl{(μ-H)₂BHPh} (**1**)

Cp₂ZrCl₂ (438 mg, 1.50 mmol) and LiBH₃Ph (152 mg, 1.55 mmol) were charged to a flask in the drybox. The flask was evacuated and 20 ml of the diethyl ether was condensed to the flask at –78 °C. The system was warmed to room temperature and stirred overnight. The LiCl formed was separated from the solution through filtration. A white solid was obtained after removal of the solvent from the filtrate. Colorless crystals of **1** (438 mg, 84% yield) were obtained after crystallization in Et₂O at –35 °C. ¹¹B NMR (d₈-THF): δ 2.37 ppm (q, J_{B-H} = 76 Hz). ¹H NMR (d₈-THF): δ 7.27–6.29 (m, 5H, Ph), 6.32 (s, 10H, Cp), and 1.00 ppm (br, 3H, BH₃). IR(KBr): 3110(m), 3087(vw), 3065(vw), 3050(vw), 3011(vw), 2953(vw), 2924(vw), 2855(vw), 2692(vw), 2400(w), 2366(w), 2348(vw), 2271(vw), 2185(vw), 2087(m), 1992(w), 1936(vw), 1439(m), 1436(m), 1345(s), 1305(m), 1279(m), 1263(m), 1185(w), 1156(vw), 1126(vw), 1092(m), 1070(w), 1014(m), 926(vw), 826(vs), 770(vw), 720(s), 700(m), 671(vw), 651(vw), 610(vw), 581(vw), 548(vw), and 471(vw) cm⁻¹. Anal. Calc. for C₁₆H₁₈BClZr: C, 55.25; H, 5.22. Found: C, 55.52; H, 5.14%.

3.3.2. Cp₂Zr{(μ-H)₂BHPh}₂ · (1/2 toluene) (**2**)

In the drybox, 407 mg (4.2 mmol) of LiBH₃Ph and 584.7 mg (2.0 mmol) of Cp₂ZrCl₂ were charged into a flask. The flask was evacuated, and 20 ml of toluene was condensed to the flask at –78 °C. The system was warmed to room temperature over a 1 h period and stirred for additional 10 h. The LiCl was separated from the solution through filtration and the solvent was reduced to about 10 ml. The toluene solution was kept at –35 °C for crystallization. A 776 mg (86.3% yield) of colorless product was isolated. ¹¹B NMR (C₆H₆): δ –6.0 ppm (q, J_{B-H} = 70 Hz). ¹H NMR (C₆D₆): δ 7.65–7.27 (m, 10H, Ph), 7.17–6.95 (m, Ph, toluene), 5.51 (s, 10H, Cp), 2.07 (s, CH₃, toluene), and 1.39 ppm (br, 6H, BH₃). IR(KBr): 3140(vw), 3103(w), 3084(vw), 3060(w), 2997(w), 2375(m), 2345(w), 2256(vw), 2172(w), 2094(m), 1484(vw), 1460(vw), 1438(w), 1342(m), 1253(s), 1175(w), 1124(vw), 1085(m), 1023(m), 929(vw), 848(w), 824(vs), 766(vw), 728(s), 701(m), 671(w), 537(vw), and 464(vw) cm⁻¹. Anal. Calc. for C_{25.5}H₃₀B₂Zr: C, 68.16; H, 6.73. Found: C, 67.82; H, 6.65%.

3.3.3. Cp₂ZrH{(μ-H)₂BHPh} (**3**)

Method 1. In the drybox, 899 mg (2.0 mmol) of Cp₂Zr{(μ-H)₂BHPh}₂ · (1/2 toluene) was charged into a flask. The flask was evacuated, and 20 ml of toluene was condensed to the flask at –78 °C. A 0.28 ml (2.0 mmol) of N(C₂H₅)₃ was measured and transferred to the flask at –78 °C. The flask was warmed to room temperature and continued to stir for 4 h. The cloudy solution turned clear after stirring at room temperature for few minutes. After the reaction the toluene was removed and the resulting white solid was dissolved in the diethyl ether and kept at –35 °C for crystallization. Both compounds, Cp₂ZrH{(μ-H)₂BHPh} and (C₂H₅)₃N · BH₂Ph, were crystallized and they were isolated through manual separation and repeated recrystallization. A 455 mg (72.6% yield) of Cp₂ZrH{(μ-H)₂BHPh} and a 289 mg (75.6% yield) of (C₂H₅)₃N · BH₂Ph were obtained.

Method 2. A 234.9 mg (2.4 mmol) of LiBH₃Ph and 515 mg (2.0 mmol) of Cp₂ZrHCl were charged to a flask covered with aluminum foil. The flask was evacuated and about 20 ml of toluene was condensed into the flask at –78 °C. The system was warmed to room temperature and stirred overnight. The LiCl was removed through filtration and an oily species was obtained after removal of the solvent under vacuum. The oily species was allowed to stand at room temperature for days and a 60 mg (9.6% yield) of colorless crystals was obtained. Analysis data for Cp₂ZrH{(μ-H)₂BHPh}: ¹¹B NMR (toluene): δ 17.40 ppm (q, J_{B-H} = 75 Hz). ¹H NMR (C₆D₆): δ 7.48–7.10 (m, 5H, Ph), 5.53 (s, 10H, Cp), 4.48 (s, 1H, ZrH), and –0.42 ppm (br, 3H, BH₃). IR(KBr): 3102(w), 3063(w), 3003(w), 2964(w), 2774(vw), 2394(m), 2346(w), 2265(vw), 2173(vw), 2033(w), 2008(w), 1962(m), 1924(m), 1920(m),

1912(m), 1597(br, m), 1432(m), 1420(m), 1396(s), 1389(s), 1261(m), 1181(m), 1088(s), 1066(m), 1028(m), 1014(s), 915(vw), 812(vs), 716(s), 698(m), 653(w), 583(w), and 458(vw) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{19}\text{BZr}$: C, 61.33; H, 6.11. Found: C, 61.42; H, 6.06%. Analysis data for $(\text{C}_2\text{H}_5)_3\text{N} \cdot \text{BH}_2\text{Ph}$: ^{11}B NMR (toluene): δ -6.78 ppm (t, $J_{\text{B-H}} = 97$ Hz). ^1H NMR (C_6D_6): δ 7.81–7.29 (m, 5H, Ph), 2.86 (br, q, 2H, BH_2), 2.22 (q, 6H, CH_2 , $J_{\text{H-H}} = 7.3$ Hz), and 0.74 ppm (t, 9H, CH_3 , $J_{\text{H-H}} = 7.3$ Hz). IR(KBr): 3080(vw), 3064(w), 3045(w), 2999(s), 2976(m), 2943(w), 2912(w), 2877(w), 2816(vw), 2418(w), 2349(br, vs), 2295(m), 2276(w), 2256(w), 2210(vw), 2191(vw), 2092(vw), 1560(vw), 1475(m), 1460(m), 1452(m), 1444(w), 1429(w), 1414(vw), 1381(s), 1356(w), 1340(vw), 1261(vw), 1198(s), 1173(m), 1151(s), 1126(w), 1107(s), 1088(m), 1068(w), 1055(w), 1034(m), 1011(m), 993(w), 904(vw), 889(vw), 854(vw), 823(vw), 800(vw), 776(m), 760(m), 737(s), 708(s), 638(m), and 449(vw) cm^{-1} . Anal. Calc. for $\text{C}_{12}\text{H}_{22}\text{BN}$: C, 75.41; H, 11.60; N, 7.33. Found: C, 75.05; H, 11.50; N, 7.30%.

3.3.4. Reaction of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BHPPh}\}$ with $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene

In the drybox, 347.8 mg (1.00 mmol) of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BHPPh}\}$ and 342.0 mg (0.67 mmol) of $\text{B}(\text{C}_6\text{F}_5)_3$ were charged into a 50 ml flask. The flask was evacuated and 20 ml of the toluene was condensed to the flask at -78 °C. The flask was warmed to room temperature and continued to stir overnight. The solution was separated from the solids through filtration and the solids were washed with two portions of 20 ml of toluene. The solution were combined and white solids were obtained after removal of the volatile species. Several crystals of $\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{B}(\text{C}_6\text{F}_5)_2\}$ were obtained from a hexane/toluene mixed solvent system. ^{11}B NMR (toluene): δ -10.6 ppm (t, $J_{\text{B-H}} = 67$ Hz). ^1H NMR (C_6D_6): δ 5.63 (s, 10H, Cp) and 0.38 ppm (br, q, 2H, BH_2).

3.3.5. $[\text{Cp}_2\text{ZrCl}(\text{OC}_4\text{H}_{10})][\text{HB}(\text{C}_6\text{F}_5)_3]$ (5)

$\text{Cp}_2\text{ZrCl}\{(\mu\text{-H})_2\text{BHPPh}\}$, (347.8 mg, 1.0 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (512.0 mg, 1.0 mmol) were charged into a flask in the drybox. The flask was evacuated and 15 ml of diethyl ether was condensed to the flask at -78 °C. The system was warmed to room temperature gradually and stop stirring after a clear solution was formed. Pale yellow-green crystals were grown gradually. After standing at room temperature for 10 h, the crystals of $[\text{Cp}_2\text{ZrCl}(\text{OC}_4\text{H}_{10})][\text{HB}(\text{C}_6\text{F}_5)_3]$ were separated from the solution through filtration. These crystals were washed with two portions of 10 ml ether and were dried under vacuum. A 674.0 mg (79.9% yield) of pale yellow-green crystals was obtained. ^{11}B NMR (THF): δ -25.9 ppm (q, $J_{\text{B-H}} = 93$ Hz). ^1H NMR (d_8 -THF): δ 6.85 (s, 10H, Cp), 3.80 (br, q, 1H, BH), 3.38 (q, 2H, CH_2), 1.11 ppm (t, 3H, CH_3). IR(KBr): 3123(m), 3095(w),

3001(w), 2987(w), 2947(vw), 2908(vw), 2873(vw), 2366(br, m), 2339(w), 2027(vw), 1863(vw), 1776(vw), 1639(s), 1601(w), 1550(w), 1512(s), 1460(br, vs), 1390(m), 1375(m), 1321(w), 1273(s), 1184(w), 1115(s), 1101(s), 1072(s), 1014(m), 970(vs), 906(m), 879(w), 825(s), 754(s), 723(m), 685(vw), 654(m), 602(w), 563(w), 521(w), 469(vw), and 409(vw) cm^{-1} . Anal. Calc. for $\text{C}_{32}\text{H}_{21}\text{BClF}_{15}\text{OZr}$: C, 45.54; H, 2.51. Found: C, 45.60; H, 2.49%.

3.3.6. $\text{Cp}_2\text{Ti}\{(\mu\text{-H})_2\text{BHPPh}\}$ (6)

In the drybox, 470 mg (4.8 mmol) of LiBH_3Ph and 500 mg (2.0 mmol) of Cp_2TiCl_2 were charged to a flask. The flask was evacuated and about 20 ml of diethyl ether was condensed to the flask at -78 °C. The system was warmed to room temperature and stirred for 6 h. During the reaction, H_2 gas evolved and the solution became purple in color. The LiCl was removed by filtration and the volatile materials were removed under vacuum. The purple solid left in the flask was dissolved in Et_2O and kept at -35 °C for crystallization. A 518 mg (96.3% yield) of purple crystals were obtained. ^{11}B NMR (d_8 -THF): not observed. ^1H NMR (d_8 -THF): δ 7.68(br, s), 6.89(s), and 6.55(s) ppm. IR(KBr): 3117(vw), 3091(vw), 3066(w), 3045(vw), 2999(w), 2969(vw), 2928(vw), 2029(vw), 2003(w), 1911(m), 1896(m), 1820(w), 1804(w), 1431(m), 1389(vs), 1365(m), 1343(w), 1309(w), 1263(w), 1176(w), 1156(w), 1120(w), 1064(w), 1015(s), 997(w), 916(vw), 906(vw), 819(m), 804(vs), 779(w), 739(m), 710(s), 666(vw), 604(w), 558(w), 487(vw), and 436(vw) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{18}\text{BTi}$: C, 71.44; H, 7.74. Found: C, 71.66; H, 7.63%.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 238550 (compound 1), 238551 (compound 2), 238552 (compound 3), 238553 (compound 4), 238554 (compound 5), 238555 (compound 6). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.09.026.

References

- [1] (a) T.J. Marks, J.R. Kolb, *Chem. Rev.* 77 (1977) 263;
(b) K.B. Gilbert, S.K. Boocock, S.G. Shore, Compounds with bonds between a transition metal and boron, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press Inc., New York, 1982, pp. 879–945;
(c) L. Barton, D.K. Srivastava, *Metallaboranes*, in: G. Wilkinson, E.W. Abel, F.G.A. Stone (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press Inc., New York, 1995, pp. 275–372;
(d) M. Ephritikhine, *Chem. Rev.* 97 (1997) 2193.
- [2] (a) F.-C. Liu, K.-Y. Chen, J.-H. Chen, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* 42 (2003) 1758;
(b) W.K. Kot, N.M. Edelstein, A. Zalkin, *Inorg. Chem.* 26 (1987) 1339;
(c) R. Shinomoto, E. Gamp, N.M. Edelstein, D.H. Templeton, A. Zalkin, *Inorg. Chem.* 22 (1983) 2351;
(d) R. Shinomoto, A. Zalkin, N.M. Edelstein, *Inorg. Chem. Acta* 139 (1987) 97;
(e) J. Brennan, R. Shinomoto, A. Zalkin, N.M. Edelstein, *Inorg. Chem.* 23 (1984) 4143;
(f) R. Shinomoto, A. Zalkin, N.M. Edelstein, D. Zhang, *Inorg. Chem.* 26 (1987) 2868;
(g) R. Shinomoto, J. Brennan, N.M. Edelstein, A. Zalkin, *Inorg. Chem.* 24 (1985) 2896.
- [3] (a) J.C. Bommer, K.W. Morse, *Inorg. Chem.* 22 (1983) 592;
(b) J.C. Bommer, K.W. Morse, *Inorg. Chem.* 18 (1979) 531;
(c) J.C. Bommer, K.W. Morse, *Inorg. Chem.* 19 (1980) 587.
- [4] (a) D.G. Holah, A.N. Hughes, N.I. Khan, *Can. J. Chem.* 62 (1984) 1016;
(b) B.G. Segal, S.J. Lippard, *Inorg. Chem.* 16 (1977) 1623;
(c) K.M. Melmed, T.-I. Li, J.J. Mayerle, S.J. Lippard, *J. Am. Chem. Soc.* 96 (1974) 69;
(d) R. Hedelt, C. Schulzke, D. Rehder, *Inorg. Chem. Commun.* 3 (2000) 300.
- [5] P. Paetzold, L. Geret, R. Boese, *J. Organomet. Chem.* 381 (1990) 1.
- [6] (a) R.K. Nanda, M.G.H. Wallbridge, *Inorg. Chem.* 3 (1964) 1798;
(b) B.D. James, R.K. Nanda, M.G.H. Wallbridge, *Inorg. Chem.* 6 (1967) 1979.
- [7] F.-C. Liu, J. Liu, E.A. Meyers, S.G. Shore, *Inorg. Chem.* 37 (1998) 3293.
- [8] The closest non-bonded contact distance of the phenyl group with other atoms is 3.405 Å in C(1A)—(13).
- [9] R.E. von H. Spence, W.E. Piers, Y. Sun, M. Parvez, L.R. MacGillivray, M.J. Zaworotko, *Organometallics* 17 (1998) 2459.
- [10] J. Liu, E.A. Meyers, S.G. Shore, *Inorg. Chem.* 37 (1998) 496.
- [11] (a) B. Singaram, T.E. Cole, H.C. Brown, *Organometallics* 3 (1984) 774;
(b) W. Biffar, H. Nöth, D. Sedlak, *Organometallics* 2 (1983) 579.
- [12] F.-C. Liu, B. Du, J. Liu, E.A. Meyers, S.G. Shore, *Inorg. Chem.* 38 (1999) 3228.
- [13] P.T. Wolczanski, J.E. Bercaw, *Organometallics* 1 (1982) 793.
- [14] R.E. von H. Spence, D.J. Parks, W.E. Piers, M.-A. MacDonald, M.J. Zaworotko, S.J. Rettig, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1230.
- [15] F.-C. Liu, J. Liu, E.A. Meyers, S.G. Shore, *J. Am. Chem. Soc.* 122 (2000) 6106.
- [16] F.-C. Liu, C.E. Plečnik, S. Liu, J. Liu, E.A. Meyers, S.G. Shore, *J. Organomet. Chem.* 627 (2001) 109.
- [17] J.W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* 98 (1976) 1729.
- [18] B. Sztáray, E. Rosta, Z. Böcskey, L. Szepes, *J. Organomet. Chem.* 582 (1999) 267.
- [19] P.L. Johnson, S.A. Cohen, T.J. Marks, J.M. Williams, *J. Am. Chem. Soc.* 100 (1978) 2709.
- [20] The B–Zr–B angles of other metallocene hydroborate disubstituted compounds were not reported.
- [21] R.W. Broach, I.-S. Chuang, T.J. Marks, J.M. Williams, *Inorg. Chem.* 22 (1983) 1081.
- [22] (a) G.T. Jordan IV, S.G. Shore, *Inorg. Chem.* 35 (1996) 1087;
(b) G.T. Jordan IV, F.-C. Liu, S. Shore, *J. Inorg. Chem.* 36 (1997) 5597.
- [23] W.J. Highcock, R.M. Mills, J.L. Spencer, P. Woodward, *J. Chem. Soc., Dalton Trans.* (1986) 821.
- [24] S.B. Stones, J.L. Peterson, *Inorg. Chem.* 20 (1981) 2889.
- [25] M.B. Fischer, E.J. James, T.J. McNeese, S.C. Nyburg, B. Posin, W. Wong-Ng, S.S. Wreford, *J. Am. Chem. Soc.* 102 (1980) 4941.
- [26] (a) W.A. Howard, G. Parkin, *J. Am. Chem. Soc.* 116 (1994) 606;
(b) W.A. Howard, M. Waters, G. Parkin, *J. Am. Chem. Soc.* 115 (1993) 4917.
- [27] (a) K.M. Melmed, D. Coucouvanis, S.J. Lippard, *Inorg. Chem.* 12 (1973) 232;
(b) G.I. Mamaeva, I. Hargittai, V.P. Spiridonov, *Inorg. Chim. Acta* 25 (1977) L123.
- [28] DENZO-SMN Z. Otwinowsky, W. Minor, Processing of X-ray diffraction data collected in oscillation mode, in: C.W. Carter Jr., R.M. Sweet (Eds.), *Methods in Enzymology*, vol. 276: *Macromolecular Crystallography, Part A*, Academic Press, New York, 1997, pp. 307–326.
- [29] (a) R.H. Blessing, *Acta Crystallogr. Sect. A* 51 (1995) 33;
(b) R.H. Blessing, *J. Appl. Crystallogr.* 30 (1997) 421–426.
- [30] SHELXS-97 G.M. Sheldrick, *Acta Crystallogr., Sect. A* 46 (1990) 467.
- [31] G.M. Sheldrick, SHELXL-97, University of Göttingen: Göttingen, Germany, 1997.