Inorg. Chem. **2003**, *42*, 1758–1763

Inorganic Chemistry

Article

Syntheses and Structures of Metallocene Methyltrihydroborate Derivativies: $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, and $Cp_2Ti\{(\mu\text{-}H)_2BHCH_3\}$

Fu-Chen Liu,* Ko-Yu Chen, and Jung-Hua Chen

Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan, ROC

Gene-Hsian Lee and Shie-Ming Peng

Department of Chemistry, National Taiwan University, Taipai 106, Taiwan, ROC

Received October 3, 2002

Downloaded by NATIONAL TAIWAN UNIV on August 18, 2009
Published on February 13, 2003 on http://pubs.acs.org | doi: 10.1021/ic020597e

In reactions of zirconocene dichloride, Cp_2ZrCl_2, with 1 equiv and an excess amount of $LiBH_3CH_3$, the methyltrihydroborate complexes, $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, **1**, and $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, **2**, were isolated. The reaction of titanocene dichloride, Cp_2TiCl_2, with an excess amount of $LiBH_3CH_3$ produced the monosubstituted methyltrihydroborate complex, $Cp_2Ti\{(\mu\text{-}H)_2BHCH_3\}$, **3**. The titanium was reduced from Ti(IV) to Ti(III), producing a 17-electron, paramagnetic titanocene complex. Under a dynamic vacuum at room temperature, compound **2** decomposed and produced the zirconium hydride compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$. Single crystal X-ray structures of **1**, **2**, and **3** were determined. Crystal data for **1**: space group $P2_1/c$, $a = 13.7921(3)$ Å, $b = 13.4227(3)$ Å, $c = 13.0868(3)$ Å, $\beta = 91.6448(12)°$, $Z = 8$. Crystal data for **2**: space group $Pna2_1$, $a = 15.2949(4)$ Å, $b = 9.3417(2)$ Å, $c = 9.3211(2)$ Å, $Z = 4$. Crystal data for **3**: space group $Fmm2$, $a = 9.1795(3)$ Å, $b = 13.0993(5)$ Å, $c = 8.8520(3)$ Å, $Z = 4$.

Introduction

Although many tetrahydroborate metal complexes have been studied extensively since the 1950s,[1] little is known concerning metal organohydroborate chemistry. In our previous work, we prepared and studied many cyclic organodihydroborate metallocene complexes.[2] The cyclic organodihydroborate and the tetrahydroborate complexes differ in their properties. For example, both of the tetrahydroborate complex, $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$,[3] and the organodihydroborate complex, $Cp_2ZrH\{(\mu\text{-}H)_2BC_5H_{10}\}$,[4] display the intramolecular hydrogen exchange at elevated temperature. However, their exchange behavior is different, and the hydrogen exchange of the tetrahydroborate complex, $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$, occurs at higher temperature. In addition, the organodihydroborate complex, $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$, reacts with Lewis acid $B(C_6F_5)_3$ in the diethyl ether to produce $[Cp_2Zr(OC_2H_5)(OC_4H_{10})][HB(C_6F_5)_3]$,[5] while the reaction of $Cp_2Zr\{(\mu\text{-}H)_2BH_2\}_2$ with $B(C_6F_5)_3$ produces $[Cp_2Zr(OC_4H_{10})\{(\mu\text{-}H)_2BH_2\}][HB(C_6F_5)_3]$.[6] These results suggest that the cyclic

---

* Corresponding author. E-mail: fcliu@mail.ndhu.edu.tw. Fax: 886-3-8661487.

(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. (c) Barton, L.; Srivastava, D. K. Metallaboranes. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press Inc.: New York, 1995; pp 275−372. (d) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193.

(2) (a) Shore, S. G.; Liu, F.-C. Cationic Metallocenes Derived from Cyclic Organohydroborate Metallocene Complexes. In *Contemporary Boron Chemistry*; Davidson, M. G., Hughes, A. K., Marder, T. B., Wade, K., Eds.; The Royal Society of Chemistry: London, 2000; pp 28−35. (b) Shore, S. G.; Liu, J.; Jordan, G. T., IV; Liu, F.-C.; Meyers, E. A.; Gaus, P. L. Cyclic Organohydroborate Anions as Hydride Transfer Agents in Reactions with Organic and Organometallic Compounds. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: London, 1997; pp 84−91. (c) Shore, S. G.; Jordan, G. J., IV; Liu, J.; Liu, F.-C.; Meyers, E. A.; Gaus, P. L. Cyclic Organohydroborate Anions: Hydride Transfer Reactions in the Reduction of Metal Carbonyls and Organic Functional Groups; Reactions with Zirconocene and Hafnocene Dichlorides. In *The Borane, Carborane and Carbocation Continuum*; Casanova, J., Ed.; John Wiley & Sons: New York, 1998; pp 351−366.

(3) Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 3397.

(4) (a) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293. (b) Chow, A.; Liu, F.-C.; Fraenkel, G.; Shore, S. G. *Magn. Reson. Chem.* **1998**, *36*, S145.

(5) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 6106.

10.1021/ic020597e CCC: $25.00

© 2003 American Chemical Society
Published on Web 02/13/2003

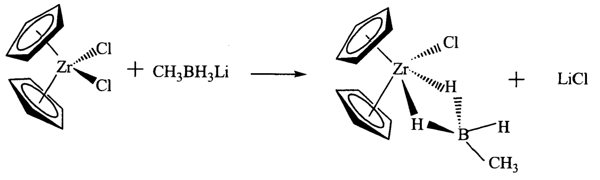
Downloaded by NATIONAL TAIWAN UNIV on August 18, 2009
Published on February 13, 2003 on http://pubs.acs.org | doi: 10.1021/ic020597e

organodihydroborate metallocene complexes have weaker Zr−H−B interaction than those of the tetrahydroborate metallocene complexes.

In our recent work, we have been interested in investigation of the methyltrihydroborate complexes. In our initial thought, the chemical behavior of the methyltrihydroborate ligand will lie between those of the organodihydroborate and the tetrahydroborate ligands, and the different behavior between the organodihydroborate and the tetrahydroborate complexes could be rationalized through the study of the organotrihydroborate complexes. The methyltrihydroborate complexes were first reported by Schlesinger,[7] and more recently by Edelstein et al.[8] In this contribution, we want to report the preparations, structures, and properties of the methyltrihydroborate derivatives of the zirconocene and titanocene.

Results and Discussion

Formation and Properties of $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, 1, $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, 2, and $Cp_2Ti\{(\mu\text{-}H)_2BHCH_3\}$, 3. In reactions of Cp_2ZrCl_2 with 1 equiv and an excess amount of $LiBH_3CH_3$ in ether solution, the methyltrihydroborate complexes $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, **1**, and $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, **2**, were obtained, as shown in eqs 1 and 2. The reaction of Cp_2ZrCl_2 with excess $LiBH_3CH_3$ was studied previously by Edelstein et al.[8a] They were unsuccessful in their attempt to synthesize the methyltrihydroborate disubstituted product $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, but they obtained the zirconium hydride compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ after sublimation. We were able to isolate compound **2** by a procedure in which the ether solvent was not removed completely after the reaction. It was removed slowly until the solution was saturated. Upon cooling this saturated solution at −35 °C, compound **2** was isolated as a crystallized product.



(1)

The chemical shifts of the NMR spectra of **1** and **2** are consistent with the hydrogen-bridged interaction between the zirconium center atom and the boron atom. The ^{11}B NMR spectra of **1** and **2** consist of a quartet at 3.84 ppm ($J(^{11}B, {}^1H) = 76$ Hz) and −6.82 ppm ($J(^{11}B, {}^1H) = 75$ Hz), respectively. These chemical shifts are downfield relative to that of the free methyltrihydroborate anion which appears at −30.9 ppm.[9] The correlation between the chemical shifts and the number of substituted hydroborates was not found. The chemical shift of the disubstituted compound $Cp_2Zr\{(\mu\text{-}H)_2B(C_6F_5)_2\}_2$ (−12.9 ppm)[10] appears at higher field than that of the monosubstituted compound $Cp_2ZrCl\{(\mu\text{-}H)_2B(C_6F_5)_2\}$ (−10.3 ppm);[11] however, the chemical shift of the monosubstituted complex $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$[12] (13.7 ppm) appears at higher field than that of the disubstituted complex $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$[4a] (24.6 ppm). An interesting result was also observed for compounds **1** and **2**. The ^{11}B−H coupling constants of the two compounds (76 (**1**) and 75 (**2**) Hz) are about the same as that observed for the free anion, $LiBH_3CH_3$.[9,13] Normally, the B−H coupling constant of the free hydroborate is larger than that is found in the complex.[4a,12]

In the ^1H NMR spectra, the signals of the BH_3 hydrogens of compound **1** appear at 0.24 ppm as a broad signal, and they appear as a broad quartet at 0.64 ppm in compound **2** due to the fast exchange of the bridge and terminal hydrogens on the NMR time scale. The magnetic equivalence of bridge and terminal hydrogen atoms of the hydroborate complexes at ambient temperature is well-known.[1a] The resonances of the methyl group in compounds **1** and **2** appear at 0.16 and 0.53 ppm, respectively. These signals are broad due to interaction with the nuclear quadrupoles of the boron-11 atoms to which they are attached.

To further study the properties of compound **2**, it was dissolved in the ether solution, and the volatile species were removed under a dynamic vacuum at ambient temperature for 2 h. Figure 1a shows the boron spectrum of this solution before the volatile species were removed. In addition to the chemical shift of compound **2**, a small signal assigned to $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$[8a,14] which appeared at 18.2 ppm was observed. The formation of $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ is due to the decomposition of compound **2** at room temperature. After the removal of the solvent and volatile decomposition product from this solution, the remaining material was redissolved in ether. As shown in the boron-11 NMR spectrum in Figure 1b, compound **2** was absent, and the major product was $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$. In a separated reaction of Cp_2ZrCl_2 with an excess amount of $LiBH_3CH_3$ at about 30 °C, in addition to the major product of compound **2**, a significant amount of $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ was also observed. Single crystal X-ray cell parameters and boron-11, proton, and IR spectra are in accord with those reported for $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$. Thus, compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ is formed according to eq 3, where the neutral,

---

(6) (a) Unpublished result. (b) Compound $[Cp_2Zr(THF)((\mu\text{-}H)_2BH_2)][BPh_4]$ was reported: Choukroan, R.; Douziech, B.; Donnadieu, B. *Organometallics* **1997**, *16*, 5517.

(7) Schlesinger, H. I.; Brown, H. C.; Horvitz, L.; Bond, A. C.; Tuck, L. D.; Walker, A. C. *J. Am. Chem. Soc.* **1953**, *97*, 27.

(8) (a) Kot, W. K.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1987**, *26*, 1339. (b) Shinomoto, R.; Gamp, E.; Edelstein, N. M.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1983**, *22*, 2351. (c) Shinomoto, R.; Zalkin, A.; Edelstein, N. M. *Inorg. Chem. Acta* **1987**, *139*, 97. (d) Brennan, J.; Shinomoto, R.; Zalkin, A.; Edelstein, N. M. *Inorg. Chem.* **1984**, *23*, 4143. (e) Shinomoto, R.; Zalkin, A.; Edelstein, N. M.; Zhang, D. *Inorg. Chem.* **1987**, *26*, 2868. (f) Shinomoto, R.; Brennan, J.; Edelstein, N. M.; Zalkin, A. *Inorg. Chem.* **1985**, *24*, 2896.

(9) Singaram, B.; Cole, T. E.; Brown, H. C. *Organometallics* **1984**, *3*, 774.

(10) Spence, R. E. v. H.; Parks, D. J.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1230.

(11) Spence, R. E. v. H.; Piers, W. E.; Sun, Y.; Parvez, M.; MacGillivray, L. R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 2459.

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

(13) Biffar, W.; Nöth, H.; Sedlak, D. *Organometallics* **1983**, *2*, 579.

(14) The boron chemical shift of $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ we measured is 18.2 ppm in the diethyl ether. It is 2 ppm upfield of that reported in ref 8a.

Downloaded by NATIONAL TAIWAN UNIV on August 18, 2009
Published on February 13, 2003 on http://pubs.acs.org | doi: 10.1021/ic020597e

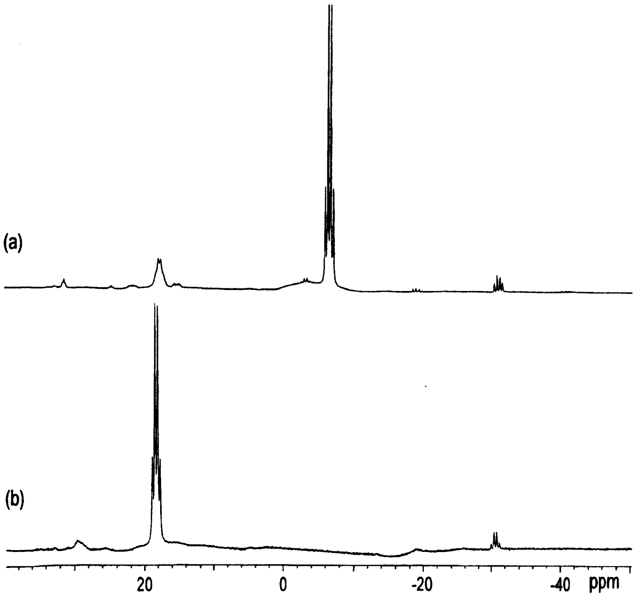
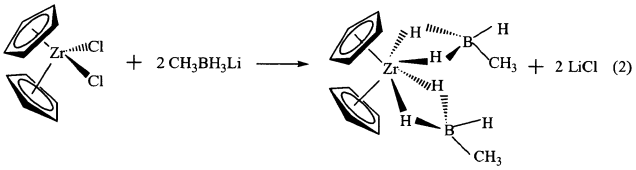
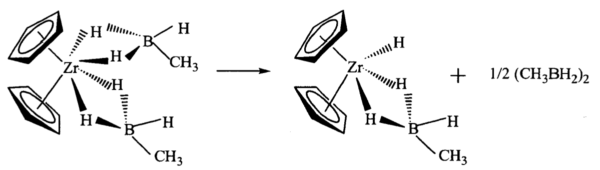


Figure 1. (a) ^{11}B NMR spectrum of $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$ in ether solution. (b) The solvent and the volatile species in part a was removed under vacuum at room temperature and redissolved in ether solution for ^{11}B NMR spectrum.

volatile diborane, $(CH_3BH_2)_2$, is removed under a dynamic vacuum. An alternative decomposition mechanism may produce the ionic pair $[Cp_2Zr(H_3BCH_3)]^+ + [CH_3BH_3]^-$, and if it occurred, adding an excess amount of $[CH_3BH_3]^-$ will prevent the decomposition of $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$. We did not find any boron signal which can be assigned to the species $[Cp_2Zr(H_3BCH_3)]^+$. In addition, the previous study by Edelstein et al.[8] also implied that the formation of the ionic pair did not occur. In their reaction, an excess amount of $LiBH_3CH_3$ was used, and the zirconium hydride compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ was obtained after sublimation. They mentioned that the product before the sublimation has similar NMR and IR spectra as that of the compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$. It is clear that the compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$ was formed during the removal of the solvent and the unreacted $LiBH_3CH_3$ did not prevent the formation of the zirconium hydride $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$.



(2)

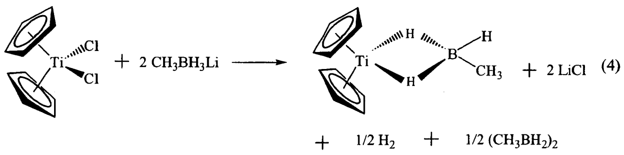


(3)

The weak Zr−H−B bonding in compound **2** is unprecedented. While compounds $Cp_2Zr\{(\mu\text{-}H)_2B(C_6F_5)_2\}_2$[10] and $Cp_2Zr\{(\mu\text{-}H)_2BC_5H_{10}\}_2$[4a] are stable under a dynamic vacuum, compound $Cp_2Zr\{(\mu\text{-}H)_2BH_2\}_2$[15] can be sublimed under reduced pressure at 120 °C without apparent decomposition. It reacts with trimethylamine to produce the zirconium hydride complex $Cp_2ZrH\{(\mu\text{-}H)_2BH_2\}$. To our knowledge, compound **2** possesses the weakest Zr−H−B bonding among the hydroborate complexes ever reported. Since the methyl group of the methyltrihydroborate ligand is not likely to cause the steric hindrance and weaken the Zr−H−B bond, the electronic effect may play a major role in this weak Zr−H−B interaction. In compound **2**, zirconium is formally associated with 20 valence electrons, the same as compound $Cp_2Zr\{(\mu\text{-}H)_2BH_2\}_2$; however, the electron donor ability of the methyl group on the methyltrihydroborate ligand releases more electron density to the zirconium atom. Since excess electron density accumulates on the central atom, a weak Zr−H−B interaction is expected, and one possible mechanism for release of the charge density on the zirconium atom is the rupture of the Zr−H−B bond to produce the more stable, 18-electron, compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$.

Compound **1** is a white solid that is stable at room temperature under nitrogen atmosphere or vacuum. It can be sublimed under reduced pressure at 60 °C. On the other hand, compound **2** is only stable under nitrogen atmosphere at low temperature, and it decomposes under reduced pressure or at elevated temperature. Compound **2** is very soluble in ether solution and slightly soluble in toluene or benzene solution. The solubility of compound **2** in ether solution is far better than that of the compound **1**; thus, crystallization is a good method for the purification of compound **1** if contamination of compound **2** is found.

Compound $Cp_2Ti\{(\mu\text{-}H)_2BHCH_3\}$, **3**, was prepared from the reaction of Cp_2TiCl_2 with an excess amount of $LiBH_3CH_3$ in ether solution, as shown in eq 4. During the reaction, the solution becomes purple in color and hydrogen gas evolved.



(4)

In this reaction, Ti(IV) is reduced to Ti(III), producing a 17-electron species. Thus, the ^{11}B and ^{1}H NMR spectra of compound **3** are NMR silent due to the paramagnetic property of the Ti(III). Compound **3** is very soluble in ether solution, thereby producing low yields by crystallization. It is stable under a nitrogen atmosphere, but very air sensitive. It decomposes and turns yellow upon exposure to air.

Molecular structures of 1, 2, and 3. The molecular structures of **1**, **2**, and **3** were determined by single-crystal X-ray diffraction analysis, and they are shown in Figures 2−4. Crystallographic data and selected bond distances and bond angles are given in Tables 1−4.

The molecular structures of **1** and **2** are shown in Figures 2 and 3. The coordination geometry of the zirconium atom in the molecular structures of **1** and **2** is best described as a distorted tetrahedron. At the corners of the tetrahedron are

---

(15) (a) James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1967**, *6*, 1979. (b) Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1964**, *3*, 1798.

Downloaded by NATIONAL TAIWAN UNIV on August 18, 2009
Published on February 13, 2003 on http://pubs.acs.org | doi: 10.1021/ic020597e

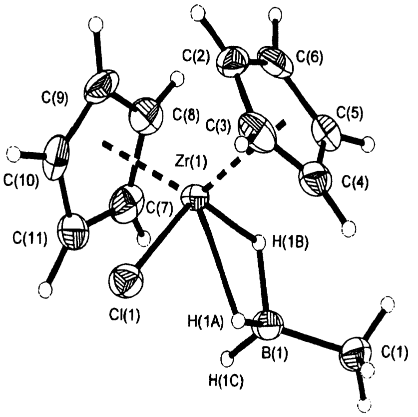


Figure 2. Molecular structure of $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, **1**, showing 50% probability thermal ellipsoids.

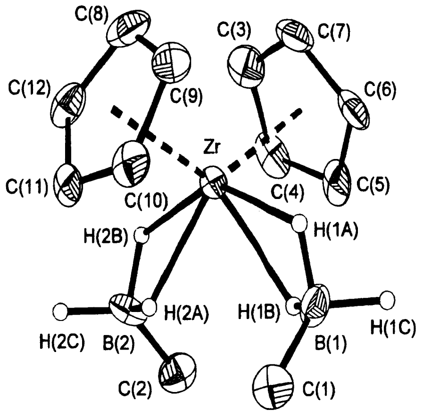


Figure 3. Molecular structure of $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, **2**, showing 50% probability thermal ellipsoids.

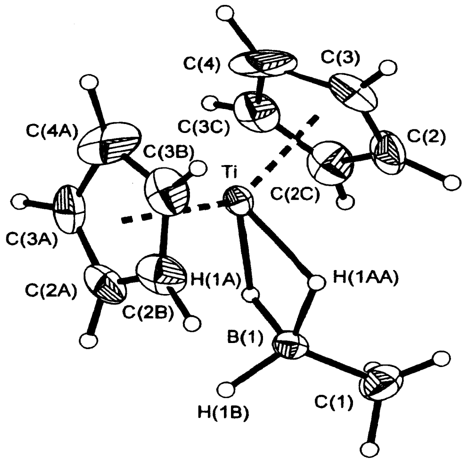


Figure 4. Molecular structure of $Cp_2Ti\{(\mu\text{-}H)_2BHCH_3\}$, **3**, showing 30% probability thermal ellipsoids.

the centers of the two Cp rings, a boron atom which is connected to the zirconium through two bridge hydrogens, and a Cl (**1**), or a second boron atom (**2**) which is also connected to the zirconium through two bridge hydrogens. Two independent molecules of **1** were found in the unit cell. These two molecules have similar bond distances and angles. The bridge hydrogens in compounds **1** and **2** were located and refined isotropically.

Table 1. Crystallographic Data for $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, **1**, $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, **2**, and $Cp_2Ti\{(\mu\text{-}H)_2BHCH_3\}$, **3**

empirical formula	$C_{11}H_{16}BClZr$	$C_{12}H_{22}B_2Zr$	$C_{11}H_{16}BTi$
fw	285.72	279.14	206.95
T (K)	150(1)	150(1)	150(1)
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$Pna2_1$	$Fmm2$
a (Å)	13.7921(3)	15.2949(4)	9.1795(3)
b (Å)	13.4227(3)	9.3417(2)	13.0993(5)
c (Å)	13.0868(3)	9.3211(2)	8.8520(3)
β (deg)	91.6448(12)		
V (Å^3)	2421.72(9)	1331.80(5)	1064.41(6)
Z	8	4	4
ρ_{calcd} (g/cm^3)	1.567	1.392	1.291
cryst size (mm^3)	0.30 × 0.08 × 0.01	0.12 × 0.20 × 0.20	0.12 × 0.07 × 0.05
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ limits (deg)	2.12−27.50	2.55−27.50	3.11−27.50
index ranges	$-17 \leq h \leq 17$ $-17 \leq k \leq 17$ $-16 \leq l \leq 16$	$-19 \leq h \leq 17$ $-12 \leq k \leq 11$ $-12 \leq l \leq 12$	$-11 \leq h \leq 11$ $-16 \leq k \leq 16$ $-11 \leq l \leq 10$
reflns collected	18244	7406	2814
unique reflns	5539	2699	662
unique reflns [$I > 2.0\sigma(I)$]	1152	576	436
completeness to θ (%)	99.8	99.6	99.7
μ (mm^{-1})	1.087	0.791	0.753
max/min transm	0.894, 0.819	0.911, 0.855	0.967, 0.921
data/restraints/ params	5539/40/278	2699/8/155	662/4/47
R1[a] [$I > 2.0\sigma(I)$]	0.0502	0.0537	0.0516
wR2[b] (all data)	0.1318	0.1194	0.1367
R_{int}	0.0756	0.0473	0.0377
GOF on F^2	1.024	1.167	1.082

[a] $R1 = \sum||F_o|| - |F_c||/\sum||F_o|$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Table 2. Selected Interatomic Distances (Å) and Bond Angles [deg] for $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, **1**[a]

Zr(1)−H(1B)	1.96(4)	H(1B)−Zr(1)−H(1A)	53(1)
Zr(1)−H(1A)	2.00(3)	H(1B)−Zr(1)−Cl(1)	126.5(9)
Zr(1)−Cl(1)	2.494(1)	H(1A)−Zr(1)−Cl(1)	74.2(8)
Zr(1)−B(1)	2.578(3)	H(1C)−B(1)−H(1A)	115(3)
B(1)−H(1C)	1.19(3)	H(1C)−B(1)−H(1B)	115(3)
B(1)−H(1A)	1.18(3)	H(1A)−B(1)−H(1B)	95(3)
B(1)−H(1B)	1.24(3)	C(1)−B(1)−Zr(1)	132.4(4)
B(1)−C(1)	1.572(7)		

[a] Average values of the two independent molecules in the unit cell.

Table 3. Selected Interatomic Distances (Å) and Bond Angles [deg] for $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, **2**

Zr−H(1B)	2.100(10)	B(2)−H(2C)	1.099(10)
Zr−H(1A)	2.12(9)	B(2)−H(2A)	1.101(10)
Zr−H(2B)	2.17(9)	B(2)−H(2B)	1.106(10)
Zr−H(2A)	1.99(8)		
Zr−B(1)	2.612(9)	H(1B)−Zr−H(1A)	47.1(11)
Zr−B(2)	2.599(8)	H(2B)−Zr−H(2A)	47.7(10)
B(1)−C(1)	1.601(12)	H(1B)−B(1)−H(1A)	100(5)
B(2)−C(2)	1.616(11)	H(2B)−B(2)−H(2A)	100(5)
B(1)−H(1C)	1.100(10)	B(2)−Zr−B(1)	99.7(3)
B(1)−H(1A)	1.102(10)	C(1)−B(1)−Zr	117.8(6)
B(1)−H(1B)	1.101(10)	C(2)−B(2)−Zr	117.8(6)

Table 4. Selected Interatomic Distances (Å) and Bond Angles [deg] for $Cp_2Ti\{(\mu\text{-}H)_2BHCH_3\}$, **3**

Ti−B(1)	2.402(12)	H(1A)−Ti−H(1AA)	56(6)
Ti−H(1A)	1.75(8)	H(1A)−B(1)−H(1AA)	88(8)
B(1)−H(1A)	1.20(8)	C(1)−B(1)−Ti	138(4)
B(1)−H(1B)	1.150(10)	H(1A)−B(1)−H(1B)	92(4)
B(1)−C(1)	1.611(19)		

The average Zr−Cl distance in compound **1** is 2.494(2) Å. It is comparable to the Zr−Cl distances observed in the cyclic organohydroborate complexes $Cp_2ZrCl\{(\mu\text{-}H)_2BC_5H_{10}\}$ (2.4802(5) Å)[12] and $Cp_2ZrCl\{(\mu\text{-}H)_2BC_4H_8\}$ (2.494(7) Å).[16] The average Zr−B distance of compound **1** is 2.578(6) Å. This distance is in the range of the Zr−B distances (2.572-

Downloaded by NATIONAL TAIWAN UNIV on August 18, 2009
Published on February 13, 2003 on http://pubs.acs.org | doi: 10.1021/ic020597e

(3)−2.593(2) Å) found in the cyclic organodihydroborate complexes[12,16] and compound $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$.[8a]

The bridge Zr−H distances of compound **1** are in the range 1.94(5)−2.00(5) Å, and the bridge B−H distances are in the range 1.17(5)−1.28(5) Å. These distances are consistent with those reported for the other alkylhydroborate complexes.[4a,5,12,16,17]

The Zr−B distances in compound **2** indicate a weak interaction between the zirconium and the methyltrihydroborate anion. The two Zr−B distances in compound **2** are 2.599(8) and 2.612(9) Å, respectively. These distances are longer than those of other alkylhydroborate complexes which appear in the range 2.548(4)−2.596(3) Å.[4a,5,12,16,17] As we mentioned earlier, the electronic effect may account for this weak Zr−H−B bonding which results in the longer Zr−B distances.

The bridge Zr−H distances of compound **2** are in the range 1.99(8)−2.17(9) Å, and the bridge B−H distances are in the range 1.101(10)−1.106(10) Å. The Zr−H distances are comparable to those of other alkylhydroborate complexes which appear in the range 1.97(3)−2.15(9) Å; however, the bridge B−H distances are in the short limit of those of other alkylhydroborate complexes[4a,5,12,16,17] which are in the range 1.10(9)−1.32(5) Å.

The two bridge H−Zr−H angles of compound **2** are 47.1(11)° and 47.7(10)°. These two angles are smaller than those of other alkylhydroborate complexes which appear in the range 51.6(11)−55(2)°.[4a,5,12,16,17] It appears that these small angles produce long Zr−B distances and the resulting weak Zr−H−B interaction.

The coordination geometry of the titanium atom in compound **3** is best described as distorted trigonal. The centers of the two Cp rings and the boron atom which is connected to the titanium through two bridge hydrogens define the distorted trigonal coordination geometry of the metal center. The boron atom deviates 0.6 Å from the plane defined by the two centers of the two Cp rings and the titanium atom. The methyltrihydroborate ligand displays a 50% disorder where two positions of the boron and the carbon atoms are found. There are two crystallographically imposed mirror planes. One passes through the Ti and the two bridge hydrogens, and the other passes through Ti, C(4), B(1), B(1A), C(1), and C(1A), to generate the rest of the molecule. The terminal and the two bridge hydrogens on the boron atom were located and refined isotropically. The Ti−B distance of 2.402(12) Å is consistent with those of other titanocene complexes reported in the literature.[18] From the trend of the Ti−B distances of $Cp_2Ti\{(\mu\text{-}H)_2BH_2\}$[18a] (2.37(1) Å), compound **3** (2.402(12) Å), $Cp_2Ti\{(\mu\text{-}H)_2BC_4H_8\}$[18b] (2.409(4) Å), and $Cp_2Ti\{(\mu\text{-}H)_2BC_5H_{10}\}$[18b] (2.446(3) Å), it may be suggested that the steric effect of the substituted group on the boron atom plays a role in the Ti−B distance, where the bigger the group is, the longer the Ti−B distance is. The bridge Ti−H distance of 1.75(8) Å is the same as that found in $Cp_2Ti\{(\mu\text{-}H)_2BH_2\}$;[18a] however, it is shorter than that of other titanocene organohydroborate complexes which appear in the range 1.83(3)−1.90(1) Å. The bridge B−H distance of 1.20(8) Å falls in the range 1.18(3)−1.35(3) Å, which is that of other titanocene organohydroborate complexes.

Experimental Section

General Procedures. All manipulations were carried out on a standard high vacuum line or in a drybox under the atmosphere of nitrogen. Diethyl ether was dried over Na/benzophenone and was freshly distilled prior to use. $LiBH_3CH_3$ was prepared according to the literature method.[9] Elemental analyses were recorded on a Hitachi 270-30 spectrometer. Proton spectra (δ(TMS) 0.00 ppm) were recorded on a Varian Mercury 200 spectrometer operating at 199.975 MHz. ^{11}B spectra (externally referenced to $BF_3\cdot OEt_2$ (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.

X-ray Crystal Structure Determination. Suitable single crystals were mounted and sealed inside glass fibers under nitrogen. Crystallographic data collections were carried out on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(1) K. Cell parameters were retrieved and refined using *DENZO-SMN*[19] software on all reflections. Data reduction was performed with the *DENZO-SMN*[19] software. An empirical absorption was based on the symmetry-equivalent reflections and was applied to the data using the *SORTAV*[20] program. Structure analysis was made by using *SHELXTL* program on a personal computer. The structure was solved using the *SHELXS-97*[21] program and refined using *SHELXL-97*[22] program by full-matrix least-squares on F^2 values. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the borons were found from the d-Fourier map and 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 Table 1.

Preparation of $Cp_2ZrCl\{(\mu\text{-}H)_2BHCH_3\}$, 1. In the drybox, 37.6 mg (1.05 mmol) of $LiBH_3CH_3$ and 294 mg (1.01 mmol) of Cp_2ZrCl_2 were charged to a flask. The flask was evacuated, and about 15 mL of 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 the product (223.0 mg, 78% yield) were obtained after crystallization in Et_2O at −35 °C. ^{11}B NMR (d_8-THF): δ 3.84 ppm (q, $J_{B-H} = 76$ Hz). ^1H NMR (d_8-THF): δ 6.33 (Cp), 0.16 (CH_3), and 0.24 ppm (br, BH_3). IR(KBr): 3101(w),

---

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

(17) (a) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 3293. (b) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1999**, *38*, 2169. (c). Liu, F.-C.; Du, B.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1999**, *38*, 3228.

(18) (a) Melmed, K. M.; Coucouvanis, D.; Lippard, S. J. *Inorg. Chem.* **1973**, *12*, 232. (b) Liu, F.-C.; Plečnik, C. E.; Liu, S.; Liu, J.; Meyers, E. A.; Shore, S. G. *J. Organomet. Chem.* **2001**, *627*, 109.

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

(20) (a) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426.

(21) *SHELXS-97*: Sheldrick, G. M. *Acta Crystallogr., Sect. A*, **1990**, *46*, 467.

(22) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

2927(w), 2899(vw), 2873(vw), 2865(vw), 2836(vw), 2729(vw), 2378(m), 2346(w), 2223(vw), 2113(w), 2020(m), 1924(m), 1855(vw), 1438(m), 1377(s), 1337(s), 1303(m), 1264(m), 1119(s), 1071(w), 1016(s), 991(w), 923(vw), 903(vw), 811(vs), 772(w), 737(m), 694(vw), 669(vw), 609(vw) cm^{-1}. Anal. Calcd for $C_{11}H_{16}BClZr$: C, 46.24; H, 5.64. Found: C, 46.41; H, 5.41.

Preparation of $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$, 2. Cp_2ZrCl_2 (293.0 mg, 1.0 mmol) and $LiBH_3CH_3$ (107.0 mg, 3.0 mmol) were put in a flask under nitrogen. 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 overnight. The LiCl formed was separated from the solution through filtration, and the solvent was reduced to about 5 mL. This ether solution was kept at −35 °C for crystallization. A 230 mg (82.4%) portion of $Cp_2Zr\{(\mu\text{-}H)_2BHCH_3\}_2$ was isolated. ^{11}B NMR (C_6H_6): δ −6.82 ppm (q, J_{B-H} = 75 Hz). ^{11}B NMR (OEt_2): δ −6.30 ppm (q, J_{B-H} = 75 Hz). ^{1}H NMR (C_6D_6): δ 5.65 (s, Cp), 0.64 ppm (q, br, BH_3), and 0.53 (s, br, CH_3). IR(KBr): 3109(w), 2963(vw), 2921(w), 2896(w), 2828(vw), 2357(w), 2200(vw), 2109(w), 2081(w), 2019(w), 1994(w), 1968(w), 1945(w), 1937(w), 1924(w), 1920(w), 1912(w), 1449(w), 1438(w), 1432(w), 1420(w), 1376(m), 1364(m), 1341(m), 1301(m), 1262(m), 1234(m), 1212(m), 1103(s), 1062(m), 1023(m), 1010(m), 934(vw), 846(m), 820(vs), 732(w), 694(w), 670(vw), 663(vw), 603(vw) cm^{-1}. Anal. Calcd for $C_{12}H_{22}B_2Zr$: C, 51.63; H, 7.94. Found: C, 49.81; H, 7.62.

Preparation of $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$. A 105 mg portion of compound **2** was dissolved in 10 mL of Et_2O. Then, the solvent and volatile species were removed under a dynamic pump for 2 h. The white solid left was characterized through IR, NMR, and the X-ray diffraction analyses. All of these analyses are consistent with the result of $Cp_2ZrH\{(\mu\text{-}H)_2BHCH_3\}$.[8a]

Preparation of $Cp_2Ti(\mu\text{-}H)_2BHCH_3\}$, 3. A 50 mL flask was charged with 172 mg (4.8 mmol) of $LiBH_3CH_3$ and 500 mg (2.0 mmol) of Cp_2TiCl_2. The flask was evacuated, and about 20 mL of Et_2O was condensed at −78 °C. The system was warmed to room temperature and stirred for 6 h. During the reaction, H_2 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 217 mg (52.4% yield) portion of purple crystals was obtained. ^{11}B NMR (d_8-THF): silence. ^{1}H NMR (d_8-THF): silence. IR(KBr): 3117(vw), 3088(vw), 2919(w), 2833(vw), 2392(m), 2249(vw), 2077(vw), 1990(vw), 1890(m), 1833(m), 1422(w), 1384(s), 1292(w), 1263(w), 1133(m), 1014(m), 904(vw), 804(vs), 709(vw) cm^{-1}. Anal. Calcd for $C_{11}H_{16}BTi$: C, 63.85; H, 7.79. Found: C, 61.30; H, 7.41.

Acknowledgment. This work was supported by the National Science Council of the ROC through Grant NSC 91-2113-M-259-010.

Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and interatomic distances and angles for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC020597E

Downloaded by NATIONAL TAIWAN UNIV on August 18, 2009
Published on February 13, 2003 on http://pubs.acs.org | doi: 10.1021/ic020597e