

Synthesis and Structural Characterization of Novel Organohydroborate Hafnocene Complex ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{($\mu\text{-H}$)₂BC₈H₁₄}Cl

Jang-Hoon Chung^{†,*} and Sang Mock Lee[‡]

[†]Department of Chemistry and Department of Nano Science and Engineering, Myongji University, Yongin, Gyeonggi 449-728, Korea. *E-mail: chungjh@mju.ac.kr

[‡]Materials Center, Samsung Advanced Institute of Technology, Yongin, Gyeonggi 446-712, Korea
Received February 14, 2006

Key Words : Organohydroborate, Hafnocene, Metallocene

The compound B(C₆F₅)₃ and its variations have been widely employed as alkyl carbanion abstracting reagents to produce metallocene cations for olefin polymerization.¹⁻³ Weakly coordinating anions containing boron can greatly improve the activity of metallocene catalysts used in industrial olefin polymerization⁴ and thus group IV and V metallocene complexes of the organohydroborate anions have been intensively investigated.⁵ Recently, many organohydroborate metallocene complexes have been reported by Shore and co-workers.⁶⁻⁸ A common structural feature of those complexes is the three-center two electron M-H-B bond, like that observed in transition metal tetrahydroborate complexes but the reactivity and fluxional behavior of organohydroborate complexes are unlike those of the tetrahydroborate analogues.⁶ Although many of those metallocenes have been synthesized, few complexes could be used in the olefin polymerization and then this laboratory has been involved in the chemistry of the cyclic organohydroborate anions, and their group IV metallocene derivatives for the catalyst.⁹

Described here is recent work that led to the preparation of a novel cyclic organohydroborate hafnocene complex ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{($\mu\text{-H}$)₂BC₈H₁₄}Cl. The hafnocene complex contains the three-center two electron bond Hf-H-B¹⁰ in which the hydride abstraction for olefin polymerization may occur.

Experimental Section

General Procedures. All operations were carried out on a standard high vacuum line or in a drybox under a nitrogen atmosphere. Diethyl ether, THF, hexane, and toluene were dried over sodium-benzophenone, distilled, and stored in a sealed flask. ($\eta^5\text{-C}_5\text{H}_5$)₂HfCl₂ and ($\mu\text{-H}$)₂(BC₈H₁₄)₂ (9-BBN dimer) were purchased from Aldrich and used as received. Potassium hydride (35% dispersion in mineral oil) was purchased from Aldrich and was washed with hexane prior to use. K[H₂BC₈H₁₄] was prepared by literature procedure.¹¹ NMR spectra were recorded on a Bruker AM-250 NMR spectrometer. ¹H NMR spectra were obtained at 250.11 MHz, and referenced to residual solvent protons. ¹¹B NMR spectra were obtained at 80.3 MHz, and externally referenced to BF₃OEt₂ in C₆D₆ (δ = 0.00 ppm). Infrared spectra were recorded on a Mattson Polaris Fourier Transform

Spectrometer with 2 cm⁻¹ resolution.

X-Ray Structural Determination. Single crystal X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffraction system, which employs graphite monochromated Mo K α radiation (λ = 0.71073 Å). A single crystal of ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{($\mu\text{-H}$)₂BC₈H₁₄}Cl was mounted on the tip of a glass fiber coated with Fomblin oil (pentafluoropolyether), and crystallographic data were collected at -123 °C. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).¹² The empirical absorption correction was applied with the SORTAV program¹³ provided by MaXus software.¹⁴ The structure was solved by direct methods and refined using SHELXL-97 (difference electron density calculations and full matrix least-squares refinements) structure solution package.¹⁵ Data merging was performed using the the data preparation program supplied by SHELXTL-97. The hydrogen atoms of Cp rings and bridge hydrogen atoms were located and refined isotropically. All other hydrogen atoms were calculated and fixed during the refinement.

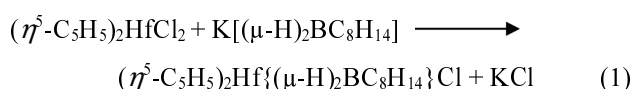
Preparation of ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{($\mu\text{-H}$)₂BC₈H₁₄}Cl. In the drybox a solution of K[H₂BC₈H₁₄] (2.0 mmol in 15 mL of diethyl ether) was added dropwise to 759 mg (2.0 mmol) of ($\eta^5\text{-C}_5\text{H}_5$)₂HfCl₂ dissolved in 20 mL of diethyl ether. The solution was stirred overnight at room temperature. The KCl was removed by filtration and a white solid was obtained upon removal of the solvent under dynamic vacuum. The solid was redissolved in toluene for crystallization. 642 mg (69% yield) of ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{($\mu\text{-H}$)₂BC₈H₁₄}Cl was obtained. ¹H NMR (C₆D₆, 30 °C) 5.86 (s), 2.16-1.41 (br m), 0.52 (br s) ppm; ¹¹B NMR (C₆D₆, 30 °C) 33.29 (br s) ppm; IR (KBr) 2916 (s), 2888 (s), 2834 (s), 1657 (w), 1444 (s), 1384 (m), 1325 (m), 1283 (s), 1260 (vs), 1199 (s), 1163 (m), 1197 (s), 1020 (vs), 953 (m), 886 (m), 870 (m), 799 (vs), 744 (s) cm⁻¹.

Reaction of ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{($\mu\text{-H}$)₂BC₈H₁₄}Cl with K[($\mu\text{-H}$)₂BC₈H₁₄]. ($\eta^5\text{-C}_5\text{H}_5$)₂Hf{($\mu\text{-H}$)₂BC₈H₁₄}Cl (1.0 mmol, 465 mg), K[H₂BC₈H₁₄] (1.0 mmol), and a stir bar were added to a 50 mL flask in the drybox. After degassing, 25 mL of diethyl ether was transferred into the flask at -78

°C. The flask was warmed to room temperature and the content was stirred overnight. The KCl was removed by filtration and a white solid was obtained upon removal of the solvent under dynamic vacuum. 336 mg (61% yield) of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2\text{Cl}$ was obtained. ^1H NMR (C_6D_6 , 30 °C) 5.56 (s), 2.11-1.43 (br m), -2.56 (br s), -3.37 (br s) ppm; ^{11}B NMR (C_6D_6 , 30 °C) 27.26 (br s) ppm; IR (KBr) 2981 (m), 2914 (vs), 2870 (vs), 2841 (vs), 2025 (m), 1660 (m), 1470 (m), 1435 (s), 1410 (s), 1315 (s), 1205 (m), 1043 (m), 818 (vs) cm^{-1} .

Results and Discussion

The cyclic organohydroborate hafnocene complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2\text{Cl}$ was obtained in the reaction of a 1 : 1 molar ratio of $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}_2$ with $\text{K}[(\mu\text{-H})_2\text{BC}_8\text{H}_{14}]$ at room temperature in diethyl ether (eq. 1). The hafnocene complex has a double hydrogen-bridged bidentate cyclic organohydroborate ligand. The reaction of the hafnocene complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2\text{Cl}$ with $\text{K}[(\mu\text{-H})_2\text{BC}_8\text{H}_{14}]$ at room temperature in diethyl ether produced the cyclic organohydroborate hafnocene complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2$ which was earlier reported.^{9(b)}



The molecular structure of the hafnocene complex was determined from a single crystal X-ray diffraction analysis. Crystallographic data and the selected bond distances and bond angles are provided in Table 1 and 2, respectively. The molecular structure is depicted in Figure 1. The structure of the complex consists of $(\eta^5\text{-C}_5\text{H}_5)_2\text{HfCl}$ fragment bound to a bidentate cyclic organohydroborate ligand $(\mu\text{-H})_2\text{BC}_8\text{H}_{14}$ group through two bridging hydrogens. The coordination geometry around the metal in the complex can be described as a distorted tetrahedron consisting of a coordination sphere of B, Cl, and the centroids of the two Cp rings at the corners of the tetrahedron. In this complex, the hafnium is associated with 18 valence electrons. There are two independent molecules in the asymmetric unit cell of the complex. As

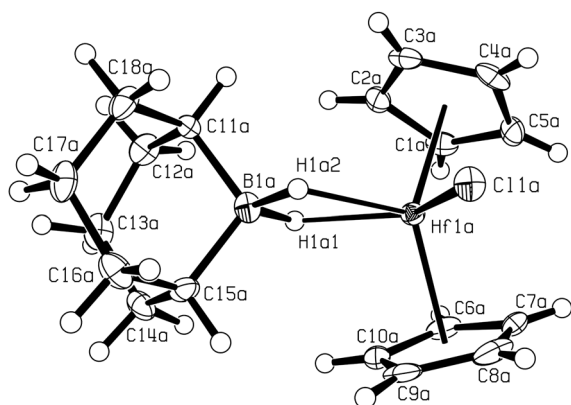


Figure 1. Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2\text{Cl}$ with 50% probability thermal ellipsoids. Hydrogens attached to carbon atoms are omitted for clarity.

Table 1. Crystallographic data for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2\text{Cl}$

Empirical formula	$\text{C}_{18}\text{H}_{26}\text{BClHf}$
Formula weight	467.14
Temperature	150(2) K
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	18.720(2)
b, Å	13.753(1)
c, Å	13.273(1)
β , deg	92.377(4)
V, Å ³	3414.3(5)
Z	8
Density (calcd, g/cm^3)	1.818
μ , mm^{-1}	6.258
2 θ range (deg)	2.18 to 27.50
No. of reflns collected	68564
No. of ind reflns	7832
Data/restraints/params	7832/0/451
$R_1[I > 2\sigma(I)]^a$	0.0279
$wR_2(\text{all data})^b$	0.0407
Goodness of fit on F^2	0.973

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}.$$

Table 2. Selected Bond Distances and Angles for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2\text{Cl}^a$

Bond Distances (Å)	A	B
Hf-C _{pcentroid} (C1-C5)	2.180(2)	2.182(2)
Hf-C _{pcentroid} (C6-C10)	2.181(2)	2.184(2)
Hf-Cl	2.4881(8)	2.4776(9)
Hf-B	2.574(4)	2.567(4)
Hf-H1	2.00(3)	2.09(3)
Hf-H2	2.10(3)	2.02(3)
B-H1	1.23(3)	1.17(3)
B-H2	1.18(3)	1.25(3)
B-C11	1.601(5)	1.612(6)
B-C15	1.607(5)	1.590(5)
Bond Angles (deg)		
C _{pcentroid} -Hf-C _{pcentroid}	130.01(7)	130.23(7)
C _{pcentroid} (C1-C5)-Hf-B	106.4(1)	106.3(1)
C _{pcentroid} (C6-C10)-Hf-B	107.3(1)	107.3(1)
C _{pcentroid} (C1-C5)-Hf-Cl	104.82(5)	103.23(7)
C _{pcentroid} (C6-C10)-Hf-Cl	103.85(5)	104.43(5)
B-Hf-Cl	100.76(9)	101.13(1)
B-Hf-H1	27.9(8)	26.7(8)
B-Hf-H2	26.9(7)	28.6(8)
C1-Hf-H1	128.7(8)	129.7(8)
C1-Hf-H2	74.1(8)	74.6(8)
H1-Hf-H2	54.7(10)	55.2(11)
Hf-B-H1	49.3(13)	53.2(14)
Hf-B-H2	53.8(13)	50.6(13)
H1-B-H2	102.8(1)	103.7(1)

^aThere are two unique molecules (A & B) in the asymmetric unit cell of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Hf}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}_2\text{Cl}$.

shown in Table 2, the selected bond distances and bond angles of the molecule A are in accord with those of the molecule B. For the molecule A, the $\text{Cp}_{\text{centroid}}\text{-Hf-Cp}_{\text{centroid}}$, $\text{Cp}_{\text{centroid}(\text{C1-C5})}\text{-Hf-B}$, $\text{Cp}_{\text{centroid}(\text{C1-C5})}\text{-Hf-Cl}$, and B-Hf-Cl angles are 130.01(7), 106.4(1), 104.82(5), and 100.76(9), respectively. These angles are generally in agreement with those observed for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}\text{Cl}$.^{6(b)} The Hf-B distance of 2.574(4) and the Hf- $\text{Cp}_{\text{centroid}(\text{C1-C5})}$ distance of 2.180(2) are consistent with other systems with bidentate Hf-H-B bridges.⁹ The bridge hydrogens of Hf-H-B bonds were located and the position and isotropic thermal parameters were refined. Hf-H1, Hf-H2, B-H1, and B-H2 distances are 2.00(3), 2.10(3), 1.23(3), and 1.18(3) Å, respectively. Hf-B-H1, Hf-B-H2, H1-Hf-H2, H1-B-H2, Cl-Hf-H1, and Cl-Hf-H2 angles are 49.3(13), 53.8(13), 54.7(10), 102.8(1), 128.7(8), and 74.1(8), respectively. These distances and angles are comparable to those of previously reported hafnocene and zirconocene systems with bidentate Hf-H-B bridges.^{6,9}

The ^1H and ^{11}B NMR spectra of the hafnocene complex are in accord with the solid-state structure determined by the single crystal X-ray analysis. This organohydroborate hafnocene complex has a four-membered $\text{Hf}(\mu\text{-H})_2\text{B}$ ring consisting of the electron-deficient three-center two electron bond Hf-H-B.¹⁶ The NMR spectra indicate the formation of the Hf-H-B bridge. The ^{11}B resonance is a broad singlet at 33.29 ppm which narrows upon proton decoupling. This is indicative of the presence of Hf-H-B bridge. This resonance is further downfield from the signal at -15.9 ppm produced by the parent salt, $\text{K}[(\mu\text{-H})_2\text{BC}_8\text{H}_{14}]$ but is a typical chemical shift of the boron atom of the electron deficient bridge in the organohydroborate transition metal complex.¹⁷ The ^1H NMR spectrum shows a broad signal at 0.52 ppm that falls within the range observed for the bridging hydrogen of other organohydroborate early transition metallocene complex with d^0 configuration.¹⁸ The proton resonance appears as a broad signal since the hydrogen is bonded to the quadrupolar boron nucleus and thus the signal is assigned to the Hf-H-B bridging hydrogen.^{19,20}

Supplementary material. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 268201). Copy 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>).

References

- Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.
- Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 5541.
- (a) Abbenhuis, H. C. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1058. (b) Mcknibht, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (c) Kaminsky, W. J. *Chem. Soc., Dalton Trans.* **1998**, 1413.
- (a) LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560. (b) Choukroun, R.; Douzic, B.; Donnadieu, B. *Organometallics* **1997**, *16*, 5517.
- Liu, F.-C.; Du, B.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1999**, *38*, 3228.
- (a) Chen, X.; Lim, S.; Plecnik, C. E.; Liu, S.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2004**, *43*, 692. (b) White, J. P., III; Deng, H.; Shore, S. G. *Inorg. Chem.* **1991**, *30*, 2337.
- (a) Liu, S.; Liu, F.-C.; Renkes, G.; Shore, S. G. *Organometallics* **2001**, *20*, 5717. (b) Liu, F.-C.; Liu, J.; Meyers, E. A.; Shore, S. G. *J. Am. Chem. Soc.* **2000**, *122*, 6106.
- Jordan, G. T.; Liu, F.-C.; Shore, S. G. *Inorg. Chem.* **1997**, *36*, 5597.
- (a) Chung, J.-H.; Shore, S. G. *Bull. Korean Chem. Soc.* **2005**, *26*, 707. (b) Chung, J.-H.; Shore, S. G. *Bull. Korean Chem. Soc.* **2005**, *26*, 1447.
- Baker, R. T.; Ovenall, D. W.; Calabrese, J. C.; Westcott, S. A.; Taylor, N. J.; William, I. D.; Marder, T. B. *J. Am. Chem. Soc.* **1990**, *112*, 9399.
- Köster, R.; Seidel, G. *Inorg. Synth.* **1983**, *22*, 198.
- Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode in Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Methods in Enzymology 276; Academic Press: New York, 1997; pp 307-326.
- (a) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.
- Mackay, S.; Gilmore, C. J.; Edwards, C.; Tremayne, M.; Stuart, N.; Shankland, K. *MaXus: A Computer Program for the Solution and Refinement of Crystal Structures from Diffraction Data*; University of Glasgow, Scotland; Nonius BV: Delft, The Netherlands and Mac-Science Co. Ltd.: Yokohama, Japan, 1998.
- Sheldrick, G. M. *SHELXL-97: A Structure Solution and Refinement Program*; University of Göttingen: Germany, 1998.
- Ho, N. N.; Bau, R.; Plecnik, C. E.; Shore, S. G.; Wang, X.; Schultz, A. J. *J. Organomet. Chem.* **2002**, *654*, 216.
- (a) Chini, R.; Longoni, G.; Albano, V. G. *Adv. Organomet. Chem.* **1976**, *14*, 285. (b) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37.
- Chen, X.; Liu, S.; Plecnik, C.; Liu, F.-C.; Fraenkel, G.; Shore, S. G. *Organometallics* **2003**, *22*, 275.
- James, B. D.; Nanda, R. K.; Wallbridge, M. G. H. *Inorg. Chem.* **1964**, *3*, 1798.
- (a) Frost, P. W.; Howard, J. A. K.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1362. (b) Baker, M. V.; Field, L. D. *J. Chem. Soc., Chem. Commun.* **1984**, 996. (c) Esteruelas, M. A.; Jean, Y.; Lledos, A.; Oro, L. A.; Ruiz, N.; Volatron, F. *Inorg. Chem.* **1994**, *33*, 3609.