

## Synthesis and Structural Characterization of Novel Anionic Thulium(III) Cyclic Organohydroborate Complex with Agostic Interactions

### $\{K(\eta^6-C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$

Sungin Ha, Minah Song, Daeyoung Park, Ansoo Kang,<sup>†</sup> Sangbong Moon,<sup>‡</sup> and Jang-Hoon Chung<sup>\*</sup>

*Department of Chemistry, Myongji University, Kyunggido 449-728, Korea. \*E-mail: chungjh@mju.ac.kr*

<sup>†</sup>*Department of Chemical Engineering, Myongji University, Yongin, Kyunggido 449-728, Korea*

<sup>‡</sup>*Elchem Tech Co., Ltd., New T Castle 1001, Gasandong, Geumchungu, Seoul 153-759, Korea*

*Received July 23, 2011, Accepted August 16, 2011*

**Key Words** : Cyclic organohydroborate, Three-centered two-electron bond, Agostic interaction, Thulium complex

A number of transition metal hydroborate complexes have received considerable attention for a while.<sup>1</sup> Recently, the complexes containing cyclic organohydroborates as ligands have been prepared and studied.<sup>2</sup> Those complexes have the M-H-B (M: transition metal) three-centered two-electron bonds in which B-H or M-H bond may serve as the electron pair donor to an unsaturated metal center or a trivalent boron to form the hydrogen-bridged bond.<sup>3</sup> Additionally, the cyclic organohydroborate ligands such as  $[H_2BC_8H_{14}]^-$  form agostic interactions between the  $\alpha$ -C-H hydrogens as well as the B-H hydrogens and the metals in the complexes.<sup>4</sup> Agostic interactions have attracted considerable interest since they lead to C-H activation,<sup>5</sup> which can be important for catalytic chemistry.<sup>6</sup> We have been involved in the chemistry of the lanthanide cyclic organohydroborate complexes because strong  $\alpha$ -H agostic interactions in the efficient organolanthanide catalysts may play a significant role in the stabilization of the reactive species in polymerization.<sup>7</sup>

Described here is detail of the synthesis and crystal structure of a novel anionic thulium cyclic organohydroborate complex,  $\{K(\eta^6-C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$ , which is prepared quantitatively in the reaction of  $TmCl_3$  with  $K[H_2BC_8H_{14}]$  (1:4 molar ratio). This anionic thulium complex has electron deficient, three-centered two-electron bonds Tm-H-B. An interesting feature in the molecular structure is the existence of agostic interactions between Tm(III) and the  $\alpha$ -C-H bonds of the cyclic organohydroborate  $H_2BC_8H_{14}$  group.<sup>8,9</sup>

### 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.  $TmCl_3$  and  $(\mu-H)_2(BC_8H_{14})_2$  (9-borabicyclo-[3,3,1]nonane, 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.  $K[H_2BC_8H_{14}]$  was prepared by

literature procedure.<sup>10</sup> Infrared spectra were recorded on a Mattson Polaris Fourier Transform Spectrometer with  $2\text{ cm}^{-1}$  resolution.

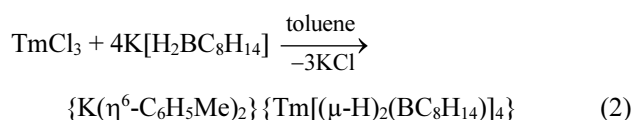
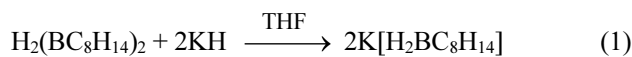
**X-ray Structural Determination.** Single crystal x-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffraction system, which employs graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). A single crystal of  $\{K(\eta^6-C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$  was mounted on the tip of a glass fiber coated with Fomblin oil (Aldrich). Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. Data integration was carried out for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).<sup>11</sup> The absorption corrections were applied using the SORTAV program<sup>12</sup> provided by MaXus software.<sup>13</sup> 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.<sup>14</sup>

**Preparation of  $\{K(\eta^6-C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$ .** 275.3 mg (1.0 mmol) of  $TmCl_3$  and 640.4 mg (4.0 mmol) of  $K[H_2BC_8H_{14}]$  were put into a flask in the dry box. After degassing, 30 mL of toluene was transferred into the flask at  $-78\text{ }^\circ\text{C}$ . The solution was warmed to room temperature and stirred for 48 hours. During this process the solution turned cloudy due to the formation of KCl which was removed by filtration. Volatile components were removed by means of dynamic high vacuum leaving a white solid. The solid was redissolved in ether and the solution was filtered to remove impurities. A white solid  $\{K(\eta^6-C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$  was obtained in 71% yield upon removal of the solvent under vacuum. Crystal, suitable for x-ray diffraction, was obtained by crystallization from toluene. IR (KBr,  $\nu_{BNN}$ ) 2978 (m), 2938 (s), 2795 (m), 2198 (m), 2067 (sh), 2013 (s), 2001 (s), 1925 (sh), 1727 (m), 1653 (s), 1496 (m), 1438 (w), 1420 (w), 1212 (m), 1109 (m), 1062 (m), 1019 (w)  $\text{cm}^{-1}$ .

### Results and Discussion

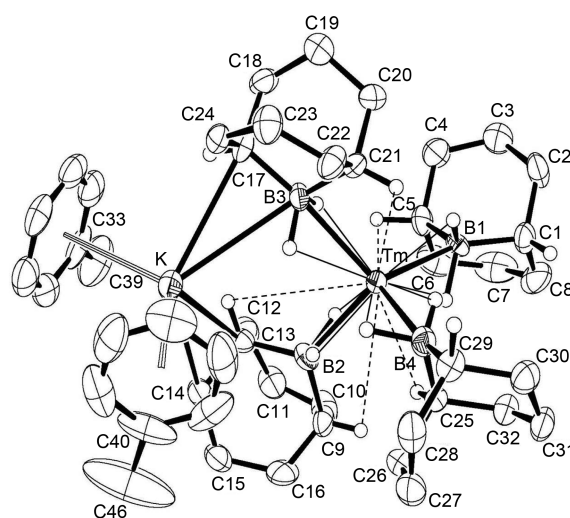
The cyclic organohydroborate thulium complex  $\{K(\eta^6-$

$C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$  was obtained in the reaction of a 1:4 molar ratio of  $TmCl_3$  with  $K[H_2BC_8H_{14}]$  in toluene at room temperature (eq. 1 & 2). The complex is stable in toluene solution. The solid is stable under a nitrogen atmosphere at room temperature for a week while decomposition occurs when it is exposed to air.



The molecular structure of the thulium 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 complex is an ionic compound that consists of the cation  $\{K(\eta^6-C_6H_5Me)_2\}^+$  and the anion  $\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}^-$ . The coordination geometry about Tm(III) center can be described as a distorted tetrahedron formed by four cyclic organohydroborate ligands,  $(\mu-H)_2BC_8H_{14}$  (9-BBN). Each 9-BBN ligand is attached to Tm (III) through two Tm-H-B bridges which are three-centered two-electron bonds. The molecular structure clearly shows that strong agostic interactions occur between Tm and  $\alpha$ -C-H bonds. The  $(\mu-H)_2BC_8H_{14}$  unit involving B2 atom coordinates symmetrically to Tm. However, in the three other cases, each  $(\mu-H)_2BC_8H_{14}$  unit is asymmetrically bound to Tm(III) by bringing one of the two  $\alpha$ -C-H hydrogens sufficiently close to Tm(III) for an agostic interaction. Thus, the 9-BBN can be considered to function as a pseudotridentate ligand because of the agostic interaction of one of two  $\alpha$ -C-H hydrogens in addition to two Tm-H-B three-centered two-electron bonds. The hydrogen atoms bonded to the bridgehead  $\alpha$ -carbon atoms (C(1), C(5), C(9), C(13), C(17), C(21), C(25), and C(29)) were refined isotropically to investigate the agostic interactions with Tm. The  $Tm \cdots \alpha-H(21)$  and  $Tm \cdots \alpha-H(25)$  distances, 2.56(5) and 2.47(5) Å, are significantly shorter than the other  $Tm \cdots \alpha-H(17)$  and  $Tm \cdots \alpha-H(29)$  distances, 4.56(6) and 4.51(4) Å due to strong agostic interactions. The  $Tm \cdots \alpha-H(5)$  distance, 3.16(6) is also shorter than another  $Tm \cdots \alpha-H(1)$  distance, 4.19(4), although the agostic interaction between Tm and  $\alpha-H(5)$  is weaker than those between Tm and  $\alpha-H(21)$ , and  $\alpha-H(25)$ . The  $\alpha-C(5)-B1-Tm$ ,  $\alpha-C(21)-B3-Tm$ , and  $\alpha-C(25)-B4-Tm$  angles, 103.8(4), 82.2(2), and 85.5(4)°, is much smaller than the corresponding  $\alpha-C(1)-B1-Tm$ ,  $\alpha-C(17)-B3-Tm$ , and  $\alpha-C(29)-B4-Tm$  angles, 148.5(5), 170.9(4), and 165.4(5)° due to the agostic interactions.

The bridge hydrogens of Tm-H-B were located and the position and isotropic thermal parameters were refined. The average Tm-H (bridge hydrogen), and  $Tm \cdots B$  distances are 2.17, and 2.561 Å, respectively. The average B-Tm-B angle is 109.4°. These distances and angles fall within the ranges previously observed for other systems with bidentate Ln-H-B bridges (Ln: lanthanide metal).<sup>2,6</sup> The interactions of K



**Figure 1.** Molecular structure of  $\{K(\eta^6-C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$  with 50% probability thermal ellipsoids. Bridging Tm-H-B and  $\alpha$ -C-H hydrogens are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms are omitted for clarity (Tm  $\cdots$  H: agostic interaction).

with C(13), C(14), C(17), and B3 of  $(\mu-H)_2BC_8H_{14}$  ligand force the two  $(\mu-H)_2BC_8H_{14}$  units toward each other and then the B3-Tm-B2 angle, 97.33(16)°, is considerably distorted from the regular tetrahedral angle of 109.5°. The bands between 2067 and 1929  $cm^{-1}$ , and at around 2795  $cm^{-1}$  in IR spectrum are assigned to Tm-H-B, and -C-H stretches, respectively. These observations of IR spectrum are consistent with other systems with Ln-H-B (Ln: lanthanide metal) and  $\alpha$ -C-H.<sup>15</sup> The molecular structure shows that the potassium cation is bound to two toluene ligands and com-

**Table 1.** Crystallographic Data for  $\{K(\eta^6-C_6H_5Me)_2\}\{Tm[(\mu-H)_2(BC_8H_{14})]_4\}$

Empirical formula	$C_{46}H_{80}B_4KTm$
fw	884.37
space group	$Pca2_1$
a, Å	19.5681(3)
b, Å	12.3045(1)
c, Å	18.9084(2)
V, Å <sup>3</sup>	4552.68(9)
Z	4
$\rho$ (calcd), g/cm <sup>3</sup>	1.290
T, °C	-123
$\lambda$ , Å	Mo K $\alpha$ (0.71073)
$\theta$ range (deg)	2.08-27.51
$hkl$ ranges	-25 24, -15 15, -21 24
Reflections collected	53957
Independent reflections	10158
$\mu$ , mm <sup>-1</sup>	2.070
GOF	1.096
$R_1$ [ $I^2 > 2\sigma(I)$ ] <sup>a</sup>	0.0370
$wR_2$ (all data) <sup>b</sup>	0.0807

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

**Table 2.** Selected bond distances (Å) and angles (°) for {K( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>Me)<sub>2</sub>} {Tm[( $\mu$ -H)<sub>2</sub>(BC<sub>8</sub>H<sub>14</sub>)<sub>4</sub>]}

---

*bond distances*

Tm...B(1) 2.587(7)	Tm...B(2) 2.665(5)
Tm...B(3) 2.493(5)	Tm...B(4) 2.497(9)
Tm...C(5) 3.348(6)	Tm...C(21) 2.792(4)
Tm...C(25) 2.866(5)	Tm...C(29) 4.041(6)
Tm...H(1) 4.19(4)	Tm...H(5) 3.16(6)
Tm...H(9) 3.73(4)	Tm...H(13) 3.78(4)
Tm...H(17) 4.56(6)	Tm...H(21) 2.56(5)
Tm...H(25) 2.47(5)	Tm...H(29) 4.51(4)
C(5)-H(5) 1.08(6)	C(21)-H(21) 1.01(4)
C(25)-H(25) 1.17(5)	C(9)-H(9) 0.91(4)
Tm-H(1B1) 2.20(5)	Tm-H(2B1) 2.14(6)
Tm-H(1B2) 2.23(4)	Tm-H(2B2) 2.09(5)
Tm-H(1B3) 2.17(4)	Tm-H(2B3) 2.20(5)
Tm-H(1B4) 2.11(7)	Tm-H(2B4) 2.23(5)
C(13)-K 3.315(5)	C(14)-K 3.240(5)
C(17)-K 3.238(6)	B(3)-K 3.360(5)
K-H(13) 2.69(5)	K-H(17) 2.90(5)
K-H(2B3) 2.72(5)	

*bond angles*

B3-Tm-B4 114.7(2)	B3-Tm-B1 115.2(2)
B4-Tm-B1 109.6(3)	B3-Tm-B2 97.33(16)
B4-Tm-B2 111.7(3)	B1-Tm-B2 107.6(2)
C5-B1-Tm 103.8(4)	C1-B1-Tm 148.7(5)
C9-B2-Tm 126.9(3)	C13-B2-Tm 126.3(3)
C17-B3-Tm 170.9(4)	C21-B3-Tm 82.2(2)
C29-B4-Tm 165.4(5)	C25-B4-Tm 85.5(4)
B(3)-C(21)-Tm 62.2(2)	B(4)-C(25)-Tm 60.3(3)
Tm-C(21)-H(21) 66(3)	Tm-C(25)-H(25) 59(2)
K-C(13)-H(13) 42(3)	K-C(14)-H(14A) 42.8
K-C(14)-H(14B) 88.8	K-C(17)-H(17) 61(3)

---

pletes its coordinating sphere by making K-C(13), K-C(14), K-C(17), and K-B3 interactions from ( $\mu$ -H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub> ligands. A bridging hydrogen H(2B3) of Tm-H-B bonds also interacts with K<sup>+</sup> as a  $\mu_3$ -H ligand to give a Tm-( $\mu_3$ -H)-K interaction. Two  $\eta^6$ -toluene solvent molecules occupy the coordination sphere of potassium which shows the preference of the potassium cation to interact with two arene rings in a multi-hapto fashion.<sup>16</sup>

**Supplementary Material.** Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 826609). 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).

**Acknowledgments.** This work was supported by the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Program, funded by the Ministry of Science

and Technology of Korea. We thank Dr. Judith Gallucci in the Department of Chemistry of The Ohio State University for providing the crystal structure results.

## References

- (a) Makhaev, V. D. *Russ. Chem. Rev.* **2000**, *69*, 727. (b) Fischer, P. J.; Young, J. V. G.; Ellis, J. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 189. (c) Xu, Z.; Lin, Z. *Coord. Chem. Rev.* **1996**, *156*, 139. (d) Sun, Y.; Piers, W. E.; Rettig, S. J. *Organometallics* **1996**, *15*, 4110. (e) Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661. (f) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.
- (a) Chen, X.; Lim, S.; Plecnik, C. E.; Liu, S.; Du, B.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2004**, *43*, 692. (b) Chen, X.; Liu, S.; Plecnik, C. E.; Liu, F.-C.; Fraenkel, G.; Shore, S. G. *Organometallics* **2003**, *22*, 275. (c) Lacroix, F.; Plecnik, C. E.; Liu, S.; Liu, F.-C.; Meyers, E. A.; Shore, S. G. *J. Organomet. Chem.* **2003**, *22*, 275. (d) Ding, E. R.; Liu, F.-C.; Liu, S.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2002**, *41*, 5329.
- 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.
- (a) Hamilton, E. J. M.; Park, J. S.; Chen, X.; Liu, S.; Sturgeon, M. R.; Meyers, E. A.; Shore, S. G. *Organometallics* **2009**, *28*, 3973. (b) Aznavour, K.; Yousufuddin, M.; Bau, R.; McIntyre, G.; Mason, S. A.; Chen, X.; Lim, S.; Plecnik, C. E.; Liu, S.; Du, B.; Meyers, E. A.; Shore, S. G. *J. Mol. Struct.* **2008**, *890*, 277. (c) Chen, X.; Liu, S.; Du, B.; Meyers, E. A.; Shore, S. G. *Eur. J. Inorg. Chem.* **2007**, 5563. (d) Ding, E.; Du, B.; Shore, S. G. *J. Organomet. Chem.* **2007**, *692*, 2148.
- (a) Sun, Y.; Metz, M.; Stern, C. L.; Marks, T. J. *Organometallics* **2000**, *19*, 1625. (b) Chen, Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287.
- (a) Beswick, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2410. (b) Moscardi, G.; Piemontesi, F.; Resconi, L. *Organometallics* **1999**, 5264.
- Lee, S. M.; Ha, S.; Song, M.; Kang, A.; Moon, S.; Chung, J.-H. *Bull. Korean Chem. Soc.* **2009**, *30*, 3117.
- (a) Klimpel, M. G.; Grlitzer, H. W.; Tafipolsky, M.; Spiegler, M.; Scherer, W.; Anwender, R. *J. Organomet. Chem.* **2002**, *647*, 236. (b) Giesbrecht, G. R.; Gordon, J. C.; Brady, J. T.; Clark, D. L.; Keogh, D. W.; Michalezyk, R.; Scott, B. L.; Watkin, J. G. *Eur. J. Inorg. Chem.* **2002**, 723. (c) Hieringer, W.; Eppinger, J.; Anwender, R.; Herrmann, W. A. *J. Am. Chem. Soc.* **2000**, *122*, 11983. (d) Click, D. R.; Scott, B. L.; Watkin, J. G. *Chem. Commun.* **1999**, 633.
- Zhu, X.; Wong, W.-K.; Lo, W.-K.; Wong, W.-Y. *Chem. Commun.* **2005**, 1022.
- Köster, R.; Seidel, G. *Inorg. Synth.* **1983**, *22*, 198.
- Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276(A), p 307.
- (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.
- Chen, X.; Lim, S.; Plecnik, C. E.; Liu, S.; Du, B.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2005**, *44*, 6052.
- (a) Fukin, G. K.; Lindeman, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 8329. (b) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303. (c) Clark, D. L.; Hollis, R. V.; Scott, B. L.; Watkin, J. G. *Inorg. Chem.* **1996**, *35*, 667.