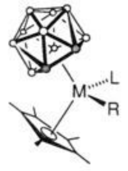
Early Metal Dicarbollide Chemistry. Characterization of an Unusual Bridging $C_2B_9H_{11}^{2-}$ Bonding Mode in $(C_5Me_5)_2(C_2B_9H_{11})_2Hf_2Me_2$

Donna J. Crowther, Dale C. Swenson, and
Richard F. Jordan*

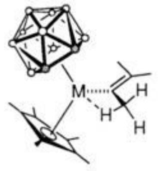
Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

Received June 8, 1995

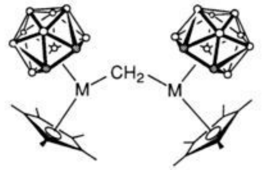
The alkane elimination reaction of Cp^*MMe_3 ($Cp^* = C_5Me_5$; M = Zr, Hf) with $C_2B_9H_{13}$ yields new metallocarborane complexes of stoichiometry $[Cp^*(C_2B_9H_{11})MMe]_n$ (**1a**, M = Zr; **1b**, M = Hf).[1] These species polymerize ethylene and oligomerize propylene, form Lewis base adducts, insert 2-butyne, and undergo thermal elimination of methane yielding **2**−**4**, respectively. NMR data for **2**−**4** and X-ray crystallographic results for **3a** and **4a** establish that these compounds adopt bent metallocene structures with η^5-$C_2B_9H_{11}$ ("dicarbollide", "dc") ligands, similar to the structures of d^0 $Cp_2M(R)(L)_x^{n+}$ species.[2] However, development of the analogy between $(Cp)(C_2B_9H_{11})M(R)$ and $Cp_2M(R)^+$ species has been hindered because the structures of the parent compounds **1a**,**b** are unknown. Here we report that **1b** adopts an unsymmetrical dinuclear structure with an unusual bridging dicarbollide ligand.



2a,b



3a,b



4a,b

The ^1H NMR spectrum of **1b** (toluene-d_8) contains two Cp* resonances, two Hf−Me resonances, and four dicarbollide C−H resonances.[3] Two of the latter resonances (δ 3.74, 3.22) appear in the range observed for η^5-$C_2B_9H_{11}$ complexes **2**−**4** (δ 2.22−3.37) while the other two appear at higher field (δ 1.85, 1.53), in the range observed for $C_2B_9H_{12}^-$ salts (δ 1.7−1.9).[4] These data indicate that in noncoordinating solvents **1b** adopts an unsymmetrical structure of nuclearity 2 or higher and suggest that only one dicarbollide ligand is bound in an η^5 manner. Consistent with these conclusions, the ^{13}C NMR spectrum of **1b** contains two C_5Me_5, two $C_5\mathit{Me}_5$, and two Hf−Me resonances, as well as two (broad) dicarbollide C−H resonances. The solid state CP-MAS ^{13}C NMR spectrum of **1b** is similar to the solution spectrum and establishes that the solid state and solution structures are very similar. The ^{11}B NMR spectrum of **1b** is complex and uninformative, and reproducible solution molecular weight data could not be obtained due to solubility limitations. The ^1H NMR spectrum of **1b** is essentially unchanged between 212 and 350 K, at which temperature methane elimination and formation of **4b** are rapid. Thus **1b** is not fluxional in this temperature range. As these data do not allow a structural assignment for **1b**, an X-ray crystallographic study was undertaken.[5]

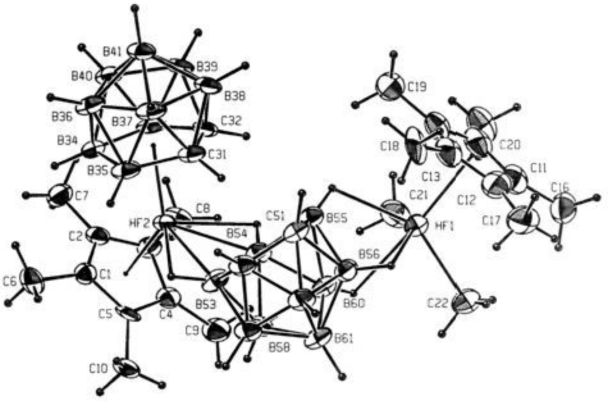


Figure 1. ORTEP view of **1b** showing 35% probability ellipsoids. Centroids are abbreviated as follows: C(100), C(1)−C(5) ring; C(200), C(11)−C(15) ring; B(300), C(31)−B(35) ring; B(400), B(55)−B(56)−B(60) face; B(500), B(53)−B(54) midpoint. Bond lengths (Å) and angles (deg): Hf(1)−C(200) 2.24; Hf(1)−C(21) 2.239(6); Hf(1)−C(22) 2.228(6); Hf(1)−B(55) 2.658(4); Hf(1)−B(56) 2.653(4); Hf(1)−B(60) 2.654(4); Hf(1)−H(55) 2.26; Hf(1)−H(56) 2.28; Hf(1)−H(60) 2.32; Hf(2)−C(100) 2.22; Hf(2)−B(300) 2.04; Hf(2)−B(53) 2.502(5); Hf(2)−B(54) 2.459(4); Hf(2)−H(53) 2.30; Hf(2)−H(54) 2.27; C(200)−Hf(1)−B(400) 131.5; C(200)−Hf(1)−C(21) 108.6; C(200)−Hf(1)−C(22) 106.8; B(400)−Hf(1)−C(21) 101.9; B(400)−Hf(1)−C(22) 101.9; C(21)−Hf(1)−C(22) 102.9(4); C(100)−Hf(2)−B(300) 135.4; C(100)−Hf(2)−B(500) 113.5; B(300)−Hf(2)−B(500) 111.0.

As illustrated in Figure 1, **1b** adopts a dinuclear structure composed of $Cp^*(\eta^5$-$C_2B_9H_{11})Hf^+$ and $Cp^*HfMe_2^+$ fragments bridged by a $C_2B_9H_{11}^{2-}$ group. The $Cp^*(\eta^5$-$C_2B_9H_{11})Hf^+$ unit (Hf(2)) has a bent metallocene structure with a symmetrically coordinated η^5-$C_2B_9H_{11}^{2-}$ ligand. The Hf(2)−B(η^5-dc) and Hf(2)−C(η^5-dc) distances (2.48−2.53 Å) and centroid−Hf(2)−centroid angle (135.4°) are comparable to those in **3a** and **4a**. The μ-$C_2B_9H_{11}^{2-}$ group binds to Hf(2) via two B−H−Hf bridges involving B−H units on the open C_2B_3 face (B(53),

---

[1] (a) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455. (b) Crowther, D. J.; Jordan, R. F. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 121. (c) Analogous Ti chemistry: Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993.

[2] Reviews: (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (b) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. (c) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283. (d) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (e) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57.

[3] Compound **1b**. A solution of $C_2B_9H_{13}$ (1.30 g, 9.68 mmol) in toluene (30 mL) was added by cannula over 15 min to precooled (−78 °C) solution of Cp^*HfMe_3 (3.20 g, 8.93 mmol) in toluene (40 mL) under a N_2 atmosphere. The N_2 was removed under vacuum and the reaction vessel warmed to 23 °C. The evolution of CH_4 began near 0 °C, and the initially colorless reaction mixture turned bright yellow. The reaction mixture was maintained at ambient temperature and degassed occasionally over 48 h. Half of the toluene was removed under vacuum, and hexane (50 mL) was added by vacuum transfer at −78 °C, resulting in precipitation of a yellow solid. The bright yellow product was collected by filtration, washed with hexane (3 × 20 mL), and dried under high vacuum for 15 h (3.55 g, 86.6%). The crude product was recrystallized from toluene/hexane (1/1) at −35 °C (2.60 g, 63.4% final yield). ^1H NMR (toluene-d_8, 300 MHz): δ 3.74 (s, 1H, dc CH), 3.22 (s, 1H, dc CH), 2.10 (s, 15H, C_5Me_5), 1.85 (s, 1H, dc CH), 1.70 (s, 15H, C_5Me_5), 1.53 (s, 1H, dc CH), 0.03 (s, 3H, Hf−Me), −0.22 (s, 3H, Hf−Me). $^{13}C\{^1H\}$ NMR (toluene-d_8, 75.5 MHz): δ 129.1 (C_5Me_5), 121.5 (C_5Me_5), 59.0 (br, $C_2B_9H_{11}$), 58.3 (br, $C_2B_9H_{11}$), 49.1 (Hf−Me), 47.8 (Hf−Me), 13.4 ($C_5\mathit{Me}_5$), 11.6 ($C_5\mathit{Me}_5$). CP-MAS ^{13}C NMR: δ 130.0 (br), 122.5, 54.0, 45.5, 16.6 (br), 12.5. Anal. Calcd for $C_{26}H_{58}B_{18}Hf_2$: C, 33.86; H, 6.34. Found: C, 33.97; H, 6.33.

[4] (a) Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009. (b) Buchanan, J.; Hamilton, E. J. M.; Reed, D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 677.

[5] Crystals of **1b**·toluene were obtained by slow cooling of a concentrated toluene solution. Crystal data: orange plate, monoclinic, $a = 17.330(4)$ Å, $b = 10.763(4)$ Å, $c = 24.524(7)$ Å, $\beta = 98.22(2)°$, $V = 4527(2)$ Å^3, space group $P2_1/n$, Z = 4, fw = 1014.4, calcd density 1.49 Mg/m^3. Data in the range 4−50° were collected at 291 K using Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined by full matrix least squares techniques. The C(11)−C(20) Cp* group and the toluene are disordered and were treated as described in the supporting information. All H atoms were located except for those on the disordered Cp* group and the toluene. The positions of the H atoms H(31)−H(35), H(51)−H(56), and H(60) were refined with the B−H distances restrained to 1.10 Å. Additionally, the Hf(1)−H(55) distance was restrained to 2.30 Å. The remaining H atoms were placed in calculated positions, and all H atoms were assigned calculated thermal parameters. See the supporting information for details. An empirical absorption correction was applied. Final $R = 0.035$ for 2692 reflections with $F > 4\sigma(F)$. Final $wR_2 = 0.108$ on F^2 for 3268 reflections and 420 parameters.

0002-7863/95/1517-10403$09.00/0

B(54)). The donor B−H units are centered in the metallocene wedge and lie in the "equatorial" plane between the two η^5-ligands; i.e., B(53) and B(54) are nearly equidistant from the centroid−Hf(2)−centroid plane,[6] and the dihedral angle between the B(53)−Hf(2)−B(54) and centroid−Hf(2)−centroid planes is 89.3°. The Hf(2)−B(μ-dc) distances (2.46 and 2.50 Å) are almost identical to the Hf(2)−B(η^5-dc) distances, despite the fact that Hf(2) lies outside of the open C(51)−B(55) face and overlap of the μ-dc^{2-} donor orbitals and Cp*(η^5-$C_2B_9H_{11}$)Hf$^+$ acceptor orbitals is consequently not optimal.[7,8] The Hf(2)−H(53) and Hf(2)−H(54) distances (2.30, 2.27 Å) are indicative of significant Hf−H interactions. Overall, the geometry around Hf(2) is similar to that in **3a**, **4a**, and other d^0 bent metallocenes containing Cp* and dicarbollide ligands.[9] The Cp*HfMe$_2^+$ unit (Hf(1)) binds the μ-dc^{2-} group via three B−H−Hf bridges involving the remaining B−H unit on the C_2B_3 face (B(55)) and two adjacent B−H units on the lower ring (B(56), B(60)). The B−H−Hf interactions involving Hf(1) are characterized by longer Hf−B distances (2.65−2.66 Å) but similar Hf−H distances (2.26−2.32 Å) compared to the Hf(2)−H−B interactions. This difference reflects the greater charge and HOMO coefficients on the B atoms on the open face versus the other cage positions of $C_2B_9H_{11}^{2-}$.[8] The geometry and B−H−Hf interactions at Hf(1) are very similar to the Zr geometry and B−H−Zr interactions in [Cp*ZrMe$_2$][$CB_{11}H_{12}$], a tight ion pair which is held together by three B−H−Zr bridges.[10]

On the basis of these structural results, **1b** may reasonably be represented as the ion pair [Cp*HfMe$_2$][Cp*(η^5-$C_2B_9H_{11}$)-Hf(η^2-$C_2B_9H_{11}$)]. This structure differs considerably from the unsymmetrical dinuclear Cp*$_2$M(μ-X)MCp*$_2$X (X = Cl, Me) structures typically observed for sterically comparable d^0 Cp*$_2$-MX species.[11] The preference for a dicarbollide-bridged structure rather than a Me-bridged structure for **1b** reflects the basicity of the B−H bonds and the distribution of charge over both the open face and the exterior of the $C_2B_9H_{11}^{2-}$ cage.[8]

The unusual bonding interactions in **1b** have precedent in other heterocarborane structures. The dihapto −(μ-H)$_2$− coordination of the μ-$C_2B_9H_{11}^{2-}$ group to Hf(2) is reminiscent of the structure of Et$_2$Al($C_2B_9H_{12}$), in which a Et$_2$Al$^+$ unit coordinates $C_2B_9H_{12}^{2-}$ via two B−H−Al bridges involving B−H units on the C_2B_3 face.[12] Several exo-polyhedral [L$_n$M]-[$R_2C_2B_9H_{10}$] species have been reported in which metal cations bind $R_2C_2B_9H_{10}^-$ anions via B−H−M bridges similar to those at Hf(1) in **1b**. Notable examples include [Rh(PPh$_3$)$_2$][7-Me-8-Ph-7,8-$C_2B_9H_{10}$] and [Ir(PPh$_3$)$_2$H$_2$][$C_2B_9H_{12}$], in which the Rh^{I} and Ir^{III} centers coordinate the carboranyl anions via B−H−M bridges involving one B−H unit on the C_2B_3 face and one on the lower B_5 ring.[13] The structure of **1b** is perhaps most comparable to that of [Et$_2$Al][(η^5-$C_2B_9H_{11}$)$_2$Al], in which a dicarbollide ligand binds to one Al in an η^5 mode and to the other via two B−H Al bridges.[14] This species is an unsymmetrical dimer of EtAl($C_2B_9H_{11}$).

The unusual structure of **1b** raises interesting questions about the formation and reactivity of **1a**,**b**, the mechanism by which these species catalyze olefin polymerization, and the relationships between (Cp)($C_2B_9H_{11}$)M(R) and Cp$_2$M(R)$^+$ species in general.[1,9] Studies of these issues are ongoing.

Acknowledgment. This work was supported by NSF Grant CHE-9413022. The CP-MAS spectrum of **1b** was obtained by Dr. Richard Eckman at Exxon Chemical.

Supporting Information Available: Details of the X-ray crystallographic analysis of **1b** (37 pages); observed and calculated structure factors for **1b** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA951860W

---

(6) B(53) and B(54) lie 0.80 and 0.90 Å from the C(100)−Hf(2)−B(100) plane.

(7) The dihedral angle between the B(53)−Hf(2)−B(54) and C(51)−B(55) planes is 121.1°. Analysis of H−H distances indicates that displacement of the Cp*(η^5-$C_2B_9H_{11}$)Hf(2) unit to increase or decrease this angle would result in increased steric crowding between the Cp* or η^5-$C_2B_9H_{11}$ groups and the μ-$C_2B_9H_{11}$ group.

(8) The Cp*(η^5-$C_2B_9H_{11}$)Hf$^+$ acceptor orbitals lie in the plane between the η^5 ligands. See ref 1b. The dc^{2-} donor orbitals project out from the C_2B_3 plane and tilt somewhat toward the center of the C_2B_3 ring. See: (a) Hamilton, E. J. M.; Welch, A. J. *Polyhedron* **1990**, *9*, 2407. (b) Goursot, A.; Pénigault, E.; Chermette, H.; Fripiat, J. G. *Can. J. Chem.* **1986**, *64*, 1752. (c) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363. (d) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602.

(9) For bent metallocenes incorporating η^5-$C_2B_9H_{11}^{2-}$ or η^5-$R_2C_2B_4H_4^{2-}$ ligands, see ref 1 and the following: (a) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (b) Marsh, R. E.; Schaefer, W. P.; Bazan, G. C.; Bercaw, J. E. *Acta Crystallogr.* **1992**, *C48*, 1416. (c) Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992**, *11*, 3098. (d) Uhrhammer, R.; Su, Y.; Swenson, D. C.; Jordan, R. F. *Inorg. Chem.* **1994**, *33*, 4398. (e) Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769. (f) Manning, M. J.; Knobler, C. B.; Khattar, R.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2009. (g) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Organometallics* **1991**, *10*, 3964. (h) Siriwardane, U.; Zhang, H.; Hosmane, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 9637. (i) Zhang, H.; Jia, L.; Hosmane, N. S. *Acta Crystallogr.* **1993**, *C49*, 453. (j) Houseknecht, K. L.; Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 1163.

(10) Crowther, D. J.; Borkowsky, S. L.; Swenson, D.; Meyer, T. Y.; Jordan, R. F. *Organometallics* **1993**, *12*, 2897.

(11) (a) Watson, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554.

(12) (a) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687. (b) Churchill, M. R.; Reis, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1314.

(13) (a) Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979. (b) Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2990. (c) Doi, J. A.; Teller, R. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 80.

(14) (a) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046. (b) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367. (c) Churchill, M. R.; Reis, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1317.