ORGANOMETALLICS

Volume 16, Number 7, April 1, 1997

Communications

Synthesis, Structure, and Reactivity of a Novel Hafnium Carboranyl Hydride Complex

Masayasu Yoshida, Donna J. Crowther, and Richard F. Jordan*

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

Received January 28, 1997[⊗]

*Summary: The reaction of $Cp^*_2(C_2B_9H_{11})_2Hf_2Me_2$ (**1b**; $Cp^* = C_5Me_5$) with H_2 yields the novel hafnium carboranyl hydride complex $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5{:}\eta^1\text{-}C_2B_9H_{10})Hf(Cp^*)(H)$ (**4**), in which the two metal centers are linked by a C-metalated $\mu\text{-}\eta^5{:}\eta^1\text{-}C_2B_9H_{10}$ ligand and Hf−H−Hf and B−H−Hf bridges. Complex **4** catalyzes the hydrogenation of internal alkynes to cis-alkenes. It is proposed that the active species in this reaction is the mononuclear hydride $Cp^*(C_2B_9H_{11})Hf(H)$ (**5**), which is formed by hydrogenolysis of **4** and undergoes rapid alkyne or alkene insertion and Hf-C hydrogenolysis steps.*

Group 4 metal dicarbollide complexes of the general type $Cp(\eta^5\text{-}C_2B_9H_{11})M\text{-}R$ are neutral, isoelectric analogues of the $Cp_2M(R)^+$ cations which play a key role in metallocene-based olefin polymerization catalysis.[1−3] The methyl complexes $Cp^*_2(C_2B_9H_{11})_2M_2Me_2$ (**1a**, M = Zr; **1b**, M = Hf; $Cp^* = C_5Me_5$) undergo 2-butyne insertion and thermolysis reactions leading to the bent-metallocene species $Cp^*(C_2B_9H_{11})MC(Me){=}CMe_2$ (**2a,b**) and $\{Cp^*(C_2B_9H_{11})M\}_2(\mu\text{-}CH_2)$ (**3a,b**) and also polymerize ethylene and oligomerize propylene. Recently we reported that the parent compound **1b** adopts an unsymmetrical dinuclear structure composed of $[Cp^*(C_2B_9H_{11})Hf]^+$ and $[Cp^*HfMe_2]^+$ fragments linked by an unusual bridging $C_2B_9H_{11}{}^{2-}$ group (Scheme 1). To probe the role of dinuclear species in the chemistry of $Cp(C_2B_9H_{11})M(R)$ compounds, we are investigating the reactivity of **1b** with other substrates. Here we describe the structure and reactivity of a unique hafnium carboranyl hydride complex formed by hydrogenolysis of **1b**.

The reaction of **1b** with H_2 (4 atm) in benzene (23 °C, 45 min) yields a mixture of the dinuclear hydride complex $(Cp^*)(\eta^5\text{-}C_2B_9H_{11})Hf(\mu\text{-}\eta^5{:}\eta^1\text{-}C_2B_9H_{10})Hf(Cp^*)(H)$ (**4**) and **3b** (Scheme 1). Analytically pure **4** precipitates from the reaction mixture as a bright yellow powder and was isolated by simple filtration. The solubility of **4** in benzene is very poor, while that of **3b** is relatively high, which facilitates the isolation of **4**. The **4**/**3b** product ratio is 83/17, as determined by ^1H NMR just before the onset of the precipitation of **4**.

The molecular structure of **4** was determined by X-ray crystallography (Figure 1).[4] Complex **4** has a dinuclear structure in which a $Cp^*(\eta^5\text{-}C_2B_9H_{10})Hf{-}H$ metallocene unit (Hf(1)) is bonded via a dicarbollide carbon to a second $Cp^*(\eta^5\text{-}C_2B_9H_{11})Hf$ fragment (Hf(2)), resulting in a $\eta^5{:}\eta^1\text{-}C_2B_9H_{10}$-bridged structure. The centroid−Hf−centroid angles at Hf(1) (137.6°) and Hf(2) (132.8°) and the Hf−Cp* centroid distances (2.20, 2.22 Å) are normal.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(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) Jordan, R. F. New Organometallic Models for Ziegler-Natta Catalysts. In *Proceedings of the World Metallocene Conference*; Catalyst Consultants Inc.: Spring House, PA, 1993; pp 89−96.

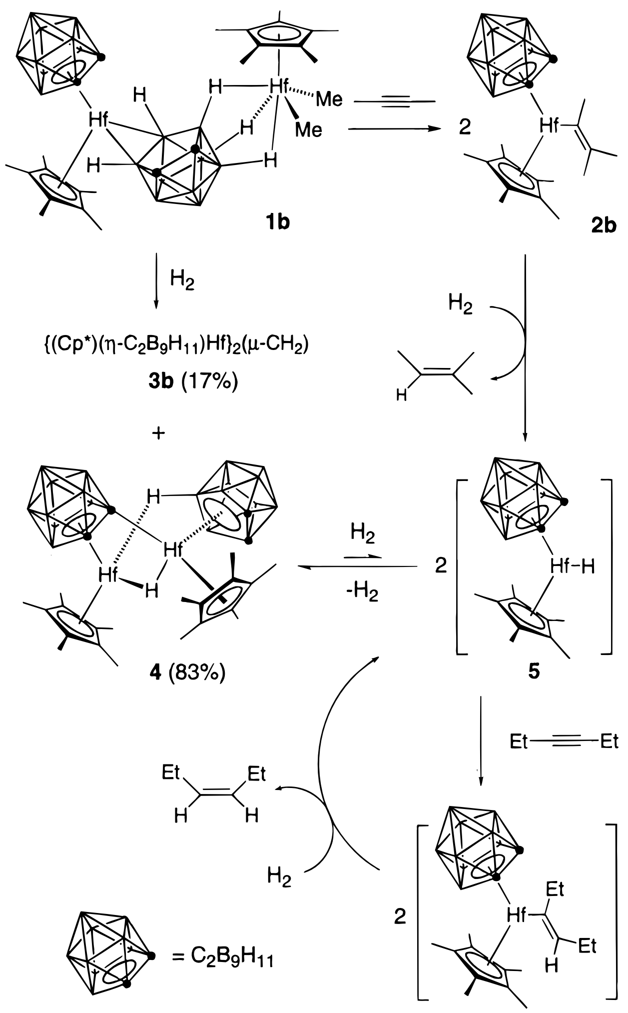
(2) Analogous Ti chemistry: Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993.

(3) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403.

(4) Crystals of $\mathbf{4}\cdot 2CH_2Cl_2$ were obtained by slow cooling of a concentrated CH_2Cl_2 solution. Crystal data: yellow prism, triclinic, $a = 10.5809(2)$ Å, $b = 13.6836(2)$ Å, $c = 15.1096(2)$ Å, $\alpha = 101.818(1)°$, $\beta = 91.517(1)°$, $\gamma = 99.036(1)°$, $V = 2110.80(6)$ Å^3, space group $P\bar{1}$, $Z = 2$, fw = 1062.07, calcd density 1.671 Mg/m^3, goodness of fit on F^2 1.033. Final $R = 0.0493$; final wR2 = 0.1029 for 5305 reflections with $I > 2\sigma(I)$.

S0276-7333(97)00058-7 CCC: $14.00

Scheme 1



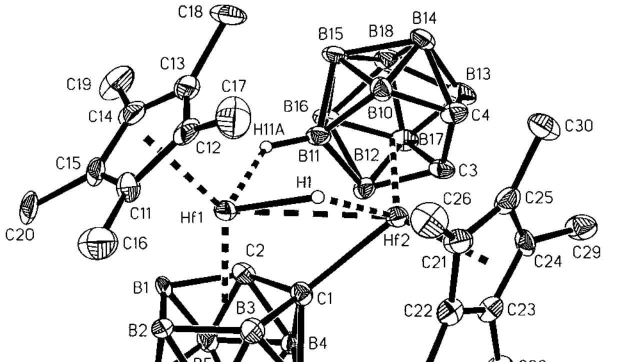


Figure 1. Molecular structure of (Cp*)(η^5-$C_2B_9H_{11}$)Hf(μ-η^5:η^1-$C_2B_9H_{10}$)Hf(Cp*)(H) (**4**).

The C(3)−B(12) dicarbollide ligand binds to Hf(2) in a symmetrical η^5 manner; the Hf(2)−B(10,11,12) and Hf(2)−C(3,4) distances (2.48−2.54 Å) and the Hf(2)−{C(3)−B(12) centroid} distance (2.07 Å) are similar to those observed for **1b**, **2a**, and **3a**.[1,3] In contrast, the C(1)-B(3) dicarbollide ligand binds to Hf(1) in an unsymmetrical fashion. The Hf(1)−C(1,2) and the Hf(1)−B(3) distances (2.36−2.46 Å) are significantly shorter than the (normal) Hf(1)−B(1,2) distances (2.51−2.55 Å), and the Hf−centroid distance (1.96 Å) is also short. These effects result from the presence of the electropositive Hf(2) at C(1), which renders C(1) and the adjacent C(2) and B(3) atoms electron-rich. The twist angle between the two centroid−Hf−centroid planes is 74°, which minimizes steric interactions between the two metallocene units and also allows for three-center, two-electron Hf(1)−H(1)- - -Hf(2) and B(11)−H(11A)- - -Hf(1) bridges.[5] Both Hf centers are four-coordinate due to the μ-H interactions.

NMR data establish that the dinuclear structure of **4** is maintained in solution and provide insight into the dynamic properties of this species. The ^1H NMR spectrum of **4** contains two Cp* resonances (δ 2.36, 2.16), three η^5-dicarbollide C−H resonances (δ 3.16, 3.04, 2.53), and a single Hf−H resonance at δ 8.81 (1H). The presence of a hydride ligand is confirmed by the ^2H NMR spectrum of the corresponding deuterio complex (**4-*d***, *vide infra*), which contains a Hf−D resonance at δ 8.78 (1D). The ^{13}C NMR spectrum of **4** contains two sets of Cp* resonances, three η^5-dicarbollide C−H resonances (δ 74.4, 52.8, 51.6), and a dicarbollide C−Hf resonance (δ 119.6) which does not split in the ^1H-coupled spectrum. This pattern of dicarbollide ^{13}C resonances is characteristic of the μ-η^5:η^1-$C_2B_9H_{10}$ unit observed in the solid state. The ^{11}B NMR spectrum of **4** is complex, as expected due to the low symmetry.[6] However, two low-field resonances at δ 16.2 and 6.2, which are assigned to B(11) and B(10), B(12) (see Figure 1 for numbering scheme), exhibit low J_{BH} values (95 and 78 Hz, respectively) indicative of bridging B−H−Hf interactions. The remaining resonances exhibit normal J_{BH} values (140−170 Hz) characteristic of terminal B−H units.[7] These observations are consistent with rapid rotation about the Hf(2)−(C(3)−B(12) centroid) axis and concomitant exchange of B(10)−H, B(11)−H, and B(12)−H between terminal and Hf(1)−H−B positions in solution.

The IR spectrum of **4** (KBr) contains ν(Hf−H) and δ-(Hf−H) bands at 1428 and 680 cm^{-1}, which shift to 1010 and 471 cm^{-1} in the spectrum of **4-*d***. The low ν(Hf−H) value is consistent with a bridging Hf−H species.[8−10]

Complex **4** catalyzes the hydrogenation of internal alkynes to alkenes.[11] For example, **4** catalyzes the hydrogenation (1 atm of H_2) of 3-hexyne to *cis*-3-hexene (0.41 turnovers/min, 23 °C, CH_2Cl_2) and subsequent slower hydrogenation of *cis*-3-hexene to *n*-hexane (ca. 0.2 turnovers/min). Several observations provide insight into the mechanism of this reaction (Scheme 1).

---

(5) Distances (Å): Hf(1)−H(1), 1.86; Hf(2)−H(1), 1.97; Hf(1)−H(11A), 2.03; Angles (deg): Hf(1)−H(1)−Hf(2), 117.9; Hf(1)−H(11A)−B(11), 134.1.

(6) All B−H resonances split in the ^1H-coupled ^{11}B spectrum.

(7) (a) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687. (b) Fontaine, X. L. R.; Greenwood, M. N.; Kennedy, J. D.; Nestor, K.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1990**, 681.

(8) ν(Hf−H) for terminal Hf−H: (a) $Cp^*_2HfH_2$, 1590 cm^{-1}; Cp^*_2Hf(H)Ph, 1630 cm^{-1}; Cp^*_2Hf(H)Et, 1630 cm^{-1}: Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97. (b) Cp^*_2Hf(H)(PHPh), 1643 cm^{-1}; Cp^*_2Hf(H)(PPh_2), 1630 cm^{-1}: Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 1760. (c) $Cp^*_2Hf(H)(CH_2)_6Hf(H)Cp^*_2$, 1612 cm^{-1}; Cp^*_2-Hf(H)(crotyl), 1578 cm^{-1}: Bercaw, J. E.; Moss, J. R. *Organometallics* **1992**, *11*, 639.

(9) ν(Hf−H) for bridging Hf−H: (a) [Cp*Hf(H)Me{P^tBu_2}]$_2$, 1510 cm^{-1}: Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670. (b) [Cp*Hf(H)$_2$Cl]$_4$, 1575 cm^{-1}: Booij, M.; Blenkers, J.; Sinnema, J. C. M.; Meetsma, A.; Bolhuis, F. v.; Teuben, J. H. *Organometallics* **1988**, *7*, 1029.

(10) The IR spectrum of **4** contains a ν(B−$H_{terminal}$) absorbance at 2560 cm^{-1} which shifts to 1920 cm^{-1} in the spectrum of **4-*d***. Distinct ν(B−$H_{bridging}$) absorbances could not be identified.

(i) **4** is the only organometallic species detectable by NMR during the reaction. (ii) **4** does not react detectably with alkynes in the absence of H_2 or with H_2 in the absence of alkynes. (iii) Exposure of **4** to D_2 (4 atm) results in rapid (<5 min, 23 °C, CD_2Cl_2) and complete exchange of deuterium into the Hf−H and carborane C−H sites (as well as extensive exchange into the B−H sites) to yield **4-*d***. These observations indicate that **4** undergoes rapid reversible Hf−C hydrogenolysis, presumably to yield $[Cp^*(C_2B_9H_{11})HfH]_n$ (n = 1 or 2), but the equilibrium between these species strongly favors **4** at low H_2 pressure.[12] (iv) An induction period (ca. 1 h) is observed before significant alkyne hydrogenation occurs. (v) Hydrogenolysis of **2b** yields **4** and 2-methyl-2-butene (4 atm, 23 °C, <10 min), which indicates that the presumed initial product $Cp^*(C_2B_9H_{11})HfH$ (**5**) rapidly condenses with H_2 loss to yield **4**. (vi) Complex **2b** catalyzes the hydrogenation (1 atm) of 3-hexyne to *cis*-3-hexene (5.9 turnovers/min) without an induction period.

Observations i−vi are consistent with the mechanism in Scheme 1. The reaction of **4** or **2b** with H_2 yields the unobserved mononuclear hydride **5**, which undergoes conventional alkyne insertion and Hf−C hydrogenolysis steps. The lower activity observed when **4** rather than **2b** is used as the catalyst precursor and the induction period in the former case are believed to be due to slow conversion of **4** to **5**. Note that the rapid H/D exchange of **4** does not require rapid formation of **5** but rather may involve reversible formation of a $[Cp^*(\eta^5\text{-}C_2B_9H_{11})HfH]_2$ species which must dissociate to form **5**. Kinetic studies may help to clarify this point.

The mechanism of the reaction of **1b** with H_2 to yield **4** is obscure. The intermediate hydride species $Cp^*{}_2(C_2B_9H_{11})_2Hf_2(H)Me$ (**6**), which has an unsymmetrical dinuclear structure analogous to that of **1b**, is observed in ^1H NMR monitoring experiments.[13] It is possible that **6** reacts further with H_2 to yield **5**, which condenses to **4**. The regioselectivity of dicarbollide metalation in the formation of **4** (from **5** or other precursors) reflects the fact that the dicarbollide C−H bonds are more acidic than the B−H bonds and thus are more reactive in σ-bond metathesis with Hf−R bonds.[14]

This work shows that dinuclear compounds play a key role in the chemistry of d^0 $Cp(\eta^5\text{-}C_2B_9H_{11})MR$ systems but suggests that mononuclear complexes may be critical for catalysis. Further reactivity studies of **4** will be reported in due course.

Acknowledgment. This work was supported by NSF Grant No. CHE-9413022 and Mitsui Petrochemical Industries, Ltd. We are grateful to Dr. Victor G. Young, Jr., and the University of Minnesota X-ray Crystallographic Laboratory for the X-ray analysis.

Supporting Information Available: Text and tables giving synthetic procedures and characterization data for new compounds and details of the X-ray structure determination of **4** (34 pages). Ordering information is given on any current masthead page.

OM970058V

---

(11) Homogeneous alkyne hydrogenation catalysts: (a) Frolov, V. M. *Platinum Met. Rev.* **1996**, *40*, 8. (b) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. H. *J. Am. Chem. Soc.* **1994**, *116*, 9103. (c) Cabeza, J. A.; Fernandez-Colinas, J. M.; Garcia-Granda, S.; Llamazares, A.; Lopez-Ortiz, F.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 426. (d) Evans, W. J. *J. Organomet. Chem.* **1983**, *250*, 217. (e) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672. (f) Evans, W. J.; Engerer, S. C.; Piliero, P. A.; Wayda, A. L. *J. Chem. Soc., Chem. Commun.* **1979**, 1007.

(12) The ^2H NMR spectrum of **4-*d*** contains one Hf−D resonance (δ 8.78, 1H), three dicarbollide C−D resonances (δ 3.13, 3.04, 2.57), and dicarbollide B−D resonances (δ 4 to −1, broad).

(13) ^1H NMR (C_6D_6) of **6**: δ 7.96 (s, 1H, Hf−H), 2.45 (s, 1H, dicarbollide CH), 1.93 (s, 15H, Cp*), 1.73 (s, 15H, Cp*), 1.47 (s, 1H, dicarbollide CH), 0.48 (s, 3H, Me); the remaining dicarbollide CH resonances are obscured by resonances of **1b** or **4**.

(14) Similarly, the reaction of *o*-carborane with *n*-BuLi results in C-lithiation: (a) Zakharkin, L. I.; Grebenikov, A. V.; Kazantsev, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 2077. (b) Gomez, F. A.; Hawthorne, M. F. *J. Org. Chem.* **1992**, *57*, 1384.