J. Am. Chem. Soc. **1998,** *120,* 8283−8284

Synthesis and Structure of the Metallaborane $Cp^*_3(\mu\text{-H})W_3B_8H_8$ from the Thermolysis of $Cp^*H_3WB_4H_8$ ($Cp^* = \eta^5\text{-}C_5Me_5$). A Close-Packed 11-Atom Boron-Rich Cluster

Andrew S. Weller, Maoyu Shang, and Thomas P. Fehlner*

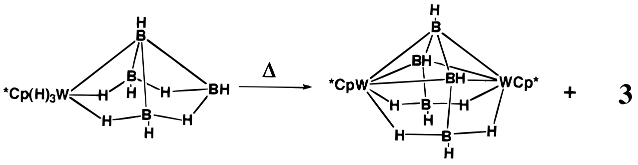
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556

Received April 2, 1998

Elemental metals exhibit close-packed solid-state structures, whereas elemental boron, a near metal,[1] features interconnected icosahedral cages. Metal borides possess structures that range from metal lattices containing interstitial boron atoms at one compositional extreme to boron cage networks containing metal atoms in voids at the other.[2] Similarly, metallaboranes exhibit molecular cluster structures with interstitial boron atoms for metal-rich compounds[3] and boron cages with one or more vertexes subrogated by metal fragments for boron-rich compounds.[4−6] For some time we have had an interest in metallaboranes in which the numbers of metal and boron atoms are more nearly equal in the expectation that the competing structural tendencies of the two elements might lead to unusual behavior.[7] Although examples of such compounds are limited, for metals in groups 8 and 9, normal borane cage-like behavior is observed,[8] albeit with some interesting exceptions.[9−13]

Recently, we have developed the syntheses of group 6 metallaboranes based on the reactions of $[Cp^*MCl_n]_2$ (M = Cr,[14] Mo,[15] and $Cp^* = \eta^5\text{-}C_5Me_5$) with monoboranes and have isolated a number of novel compounds. In two instances, the lower number of valence electrons and the higher metal orbital energies of the group 6 Cp*M fragments relative to group 9 metals, for example, lead to the observation of electronic unsaturation in the cluster bonding network.[16,17] Since these clusters are small, sufficient capping to compensate for the missing electrons is not possible. In larger clusters, additional capping would be expected. If highly capped structures were formed, close-packed structures would be expected.[18] The metal cluster, $[H_4Os_{10}(CO)_{24}]^{2-}$, for example, has a tetra capped octahedral structure and constitutes a 10-atom cluster with close-packed metals.[19]

Chart 1



1

2

An extension of our synthetic approach to tungsten resulted in the isolation of a number of new compounds. In addition, these procedures allow $Cp^*H_3WB_4H_8$, **1**, a compound previously isolated in 1% yield as the spectroscopically characterized C_5H_4-^{i}Pr derivative,[20] to be generated in good yield. Crystallographic characterization of **1** has confirmed the postulated structure shown in Chart 1. Since **1** is well set up for the loss of H_2, we have explored its condensation by simple thermolysis. Larger boron-rich tungstaboranes result in which the spatial arrangement of the boron and metal atoms in one compound approximates a close-packed structure rather than a single borane cage. In effect, the low Cp*W fragment electron count induces the borane fragments to compensate by adopting a highly capped structure. Note that tungstaboranes are rare; only four structurally characterized tungstaboranes have been reported previously, and all contain a single metal atom.[21−24]

As summarized in Chart 1, the pyrolysis of **1**[25] yields $Cp^*_2W_2B_5H_9$, **2**, the analogue of $Cp^*_2M_2B_5H_9$ (M = Cr, Mo) (Chart 1),[26] and a second compound that has been identified as $Cp^*_3(\mu\text{-H})W_3B_8H_8$, **3**, on the basis of its spectroscopic properties[27] and a solid-state structure determination.[28] The geometric structure of **3** is shown in Figure 1 and Chart 2c where it is seen to consist of a $Cp^*_3W_3(\mu\text{-H})$ triangle joined in a complex way to 8 BH fragments. All of the B−B, B−W, and W−W distances can be considered bonding, although two of the last are somewhat

---

* E-mail: Fehlner.1@nd.edu.

[1] Fehlner, T. P. *Adv. Inorg. Chem.* **1990**, *35*, 199.

[2] Lundström, T. In *Boron and Refractory Borides*; Matkovich, V. I., Ed.; Springer-Verlag: Berlin, 1977.

[3] Housecroft, C. E. *Coord. Chem. Rev.* **1995**, *143*, 297.

[4] Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519.

[5] Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *34*, 211.

[6] Grimes, R. N. In *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982; p 269.

[7] Housecroft, C. E.; Fehlner, T. P. *Adv. Organomet. Chem.* **1982**, *21*, 57.

[8] Fehlner, T. P. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; p 287.

[9] Bowser, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 4623.

[10] Bowser, J. R.; Bonny, A.; Pipal, J. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1979**, *101*, 6229.

[11] Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 904.

[12] Kennedy, J. D. *Inorg. Chem.* **1986**, *25*, 111.

[13] Baker, R. T. *Inorg. Chem.* **1986**, *25*, 109.

[14] Ho, J.; Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1995**, *117*, 10292.

[15] Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1998**, *120*, 2586.

[16] Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1994**, *116*, 8408.

[17] Aldridge, S.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1997**, *119*, 11120.

[18] Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: New York, 1990.

[19] Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M. D.; Braga, D.; McPartlin, M. *Chem. Commun.* **1983**, 241.

[20] Bullick, H. J.; Grenbenik, P. D.; Green, M. L. H.; Hughes, A. K.; Leach, J. B.; McGowan, P. C. *J. Chem. Soc., Dalton Trans.* **1995**, 67.

[21] Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Macpherson, I.; Thornton-Pett, M. *Chem. Commun.* **1987**, 1987.

[22] Drew, M. G. B.; Baker, P. K.; Beckett, M. A.; Severs, L. M. *Polyhedron* **1992**, *11*, 3095.

[23] Grenbenik, P. D.; Leach, J. B.; Green, M. L. H.; Walker, N. M. *J. Organomet. Chem.* **1988**, *345*, C31.

[24] Beckett, M. A.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1986**, 795.

[25] In a typical experiment, a solution of $Cp^*H_3WB_4H_8$ (120 mg, 0.32 mmol, in 5 mL of toluene) was heated to 110 °C for 20 min in a Young's tube. Purification by preparative thin-layer chromatography afforded yellow **2**, $Cp^*_2W_2B_5H_9$ (40 mg, 36% based on W) and apricot **3**, $Cp^*_3(\mu\text{-H})W_3B_8H_8$ (30 mg, 19%) as the major products as microcrystalline solids.

[26] Aldridge, S.; Hashimoto, H.; Kawamura, K.; Shang, M.; Fehlner, T. P. *Inorg. Chem.* **1998**, *37*, 928.

[27] Spectroscopic data for **3**: MS (FAB+), $P^+ = 1055$, 3 W, 8 B atoms, calcd for weighted average of isotopomers lying within the instrument resolution, 1055.3596, obsd 1055.3560. ^{11}B NMR (d_8-toluene, 21 °C, δ ppm, J(BH) Hz, 96.236 MHz), 94.3 (1 B, d, 128), 82.5 (4 B, br, overlapping resonances), 24.1 (2 B, d, 128), −22.7 (1 B, br). ^{1}H NMR (d_8-toluene, 80 °C, δ ppm, J(BH) Hz, 300 MHz), 10.21 (1 BH_t, q, 129), 9.43 (2 BH_t, q, 125), 7.19 (2 BH_t, q, 130), 3.80 (2 BH_t, q, 129), 2.0 (s, 30 H, 2 Cp*), 1.87 (s, 15 H, 1 Cp*), −2.64 (1 BH_t, partially collapsed q, ∼170), −15.34 [1 H, W−H−W, ^1J(WH) 67]. IR (KBr, $\nu(BH_t)$, cm^{-1}): 2527 m, 2480 m, 2432 m.

[28] Crystallographic data for **3**: orthorhombic, $Cmc2_1$ (No. 36), $a = 17.8507(13)$, $b = 14.1146(12)$, $c = 13.7229(12)$ Å, $V = 3457.6(5)$ Å^3, $Z = 4$, fw = 1052.76, $D_c = 2.022$ g/cm^3. Data (Mo Kα) were collected on an Enraf-Nonius CAD4 diffractometer at 293 K. Structure solution and refinement were performed on a PC by using the SHELXTL package.[3] The hydride was refined isotropically with the isotropic thermal parameter fixed to 1.2 times the equivalent isotropic thermal parameter of its bonded W atom. The refinement converged to a final value of $R_1 = 0.0349$ and $wR_2 = 0.0929$ for observed unique reflections ($I > 2\sigma(I)$) and $R_1 = 0.0363$ and $wR_2 = 0.1000$ for all unique reflections including those with negative intensities.

S0002-7863(98)01101-9 CCC: $15.00

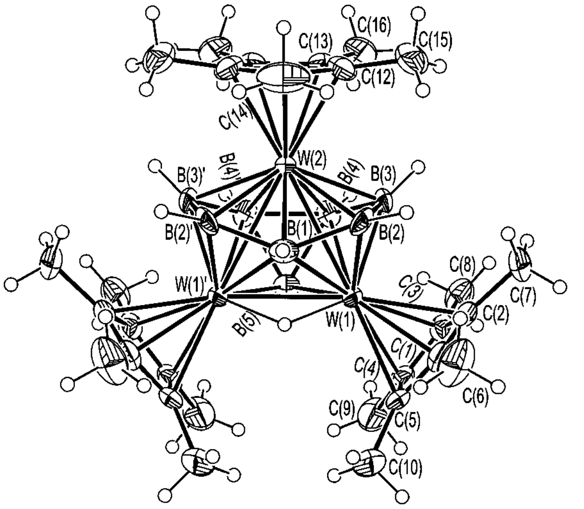
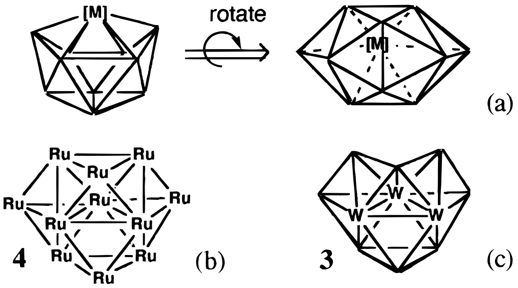


Figure 1. The molecular structure of $Cp^*_3(\mu\text{-H})W_3B_8H_8$, **3**. Selected bond distances (Å): W(1)−B(3) 2.077(13), W(1)−B(2) 2.16(2), W(1)−B(5) 2.226(13), W(1)−B(4) 2.331(12), W(1)−B(1) 2.52(2), W(1)−W(1′) 2.8008(7), W(1)−W(2) 3.0597(6), W(1)−H(1) 1.58(7), W(2)−B(2) 2.231(10), W(2)−B(3) 2.254(12), W(2)−B(1) 2.26(2), W(2)−B(4) 2.339(13), B(1)−B(2) 1.71(2), B(2)−B(3) 1.83(2), B(4)−B(5) 1.78(2), B(4)−B(4′) 1.79(2).

Chart 2



long (see below). The W−W bridging hydrogen is found in the structure determination, and its position is confirmed by the ^{183}W satellites in the ^{1}H NMR spectrum (a doublet, $^1J_{WH} = 67$ Hz, of intensity 31% due to the ^{183}W−H−W isotopomer (calcd abundance 33%) plus the outer lines of a triplet of intensity 3% due to the ^{183}W−H−^{183}W isotopomer (calcd abundance 2.7%)).

The prescribed geometry for an 11-vertex, closed main-group cage is shown in Chart 2a, and examples of monometal metallaboranes with the expected 12 skeletal electron pairs (sep) as well as 11 sep are known.[29,30] If the W(1,1′)−W(2) distances are considered to be nonbonding, **3** is a single cage; however, a comparison of parts 2a and c of Chart 2 reveals a distinctively different geometry for **3**. In addition, **3** can only have 7, 10, or 13 sep, depending on whether the Cp*W is considered as a −1-, 1-, or 3-electron donor to the cage.[31−33] These observations forced a different analysis of the structure.

The 11-atom transition metal cluster $[Ru_{11}H(CO)_{27}]^{3-}$, **4**, exhibits a hexagonal close-packed metal core (Chart 2b).[34] It possesses 146 cluster valence electrons (cve) consistent with its 11-atom close-packed structure,[35] and therefore, a M_3E_8 cluster of identical geometry should exhibit 66 cve.[18,36] In fact, **3** does possess 66 cve, and its geometry is very similar to that of **4**. For both **3** and **4**, the bottom two layers (Chart 2b and c) can be seen to be derived from the A, B layers of a close-packed structure. (In **3**, B(3, 3′) are 0.511(4) Å below the plane of the W_3 triangle.) The top layer of **4** is positioned to give A, B, A stacking as are the B(2, 2′) atoms of **3**. However, B(1) is in a position corresponding to A, B, C stacking. For spheres of equal radii, an arrangement of this type is not possible, but due to the disparity in W and B radii, it is preferred in **3** since it permits B−B bonding in the third layer. Despite the difference, the number of bonded edges in **3** and **4** remain equal.

The feature that distinguishes a close-packed structure of **3** from a single cage is the presence or absence, respectively, of bonding between W(2) and W(1, 1′). Unfortunately, the W(2)−W(1) distance of 3.0597(6) Å is ambiguous: it could be bonding or nonbonding. Fenske−Hall calculations[37,38] on **3** reveal a substantial HOMO−LUMO gap consistent with the cve count. More importantly, MOs associated with the W_3H triangle and reminiscent of the Walsh orbitals of cyclopropane can be identified. Thus, the HOMO at −12.19 eV consists of the symmetric bonding combination of W d_{z^2} orbitals pointed toward the center of the W_3 triangle and an unoccupied antibonding partner is found at −2.02 eV. Furthermore, the W(2)−W(1) Mulliken overlap population is 0.08 which compares favorably with 0.13 for $Cp^*_2W_2B_5H_9$ with $d_{W-W} = 2.8170(8)$ Å. The calculations support the description of **3** as a close-packed metallaborane.

Finally, we note that **3** is isoelectronic with a hypothetical $Cp^*_3(H)W_3C_8$ molecule which can be considered a ligated metal analogue of a metallocarbohedrene or “met-car”.[39] The latter compounds, which consist of early transition metals and carbon atoms, have also been described as close-packed main-group transition metal clusters, and their proposed structures have been of considerable theoretical interest.[40] We suggest that the factors driving close-packing in **3** are the same as those responsible for the close-packed met-car structures. Full details of this new chemistry and that of the other new tungstaboranes will be forthcoming.

Acknowledgment. The assistance of Mr. Donald Schifferl with the NMR experiments as well as the generous support of the National Science Foundation are gratefully acknowledged.

Supporting Information Available: Information on data collection and reduction and structure solution and refinement, tables of crystallographic parameters, atomic coordinates and equivalent isotropic temperature factors, bond distances and bond angles, and anisotropic temperature factors for **3** (17 pages, print/PDF). An X-ray crystallographic file, in CIF format, for **3** is available on the Web only. See any current masthead page for ordering information and Web access instructions.

JA981101O

---

(29) Adams, K. J.; McGrath, T. D.; Thomas, R. L.; Weller, A. S.; Welch, A. J. *J. Organomet. Chem.* **1997**, *527*, 283.

(30) Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1986**, 517.

(31) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(32) Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 29.

(33) Albright, T. A.; Burdett, J. K.; Whangbo, H.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(34) Bailey, P. J.; Beswick, M. A.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Ramirez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1992**, 3159.

(35) Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1980**, *197*, 233.

(36) Mingos, D. M. P. In *Inorganometallic Chemistry*; Fehlner, T. P., Ed.; Plenum: New York, 1992; p 179.

(37) Fenske, R. F. *Pure Appl. Chem.* **1988**, *27*, 61.

(38) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

(39) Cartier, S. F.; May, B. D.; Castleman, A. W., Jr. *J. Phys. Chem.* **1996**, *100*, 8175.

(40) Bénard, M.; Rohmer, M.-M.; Poblet, J.-M.; Bo, C. *J. Phys. Chem.* **1995**, *99*, 16913.