J. Am. Chem. Soc. **1996,** *118,* 8164−8165

Clusters as Ligands. Coordination of an Electronically Unsaturated Chromaborane to an Iron Tricarbonyl Fragment

Hisako Hashimoto, Maoyu Shang, and Thomas P. Fehlner*

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

Received May 15, 1996

We have shown that the 42 cluster valence electron (cve) dimetallaborane cluster, $Cp^*_2Cr_2B_4H_8$, (**1**), $Cp^* = \eta^5\text{-}C_5Me_5$, is electronically unsaturated based on its observed core geometry (Chart 1a).[1] However, the unsaturation introduced by the Cp*Cr fragments is delocalized over the cluster framework rather than localized in a Cr−Cr multiple bond. As expected, this molecule reacts with species possessing Lewis basicity, e.g., with CO to produce $Cp^*_2Cr_2(CO)_2B_4H_6$[2] and with CS_2 to produce $Cp^*_2Cr_2B_4H_6S_2CH_2$.[3] We have now explored the reaction of **1** with a low-valent, later transition metal center and show that **1** behaves as a complex 4-electron ligand in coordinating a $Fe(CO)_3$ fragment to yield an unusual mixed metal metallaborane.[4−8]

Treatment of **1** with $Fe_2(CO)_9$ at 50 °C results in the formation of a dark brown compound $Cp^*_2Cr_2B_4H_8Fe(CO)_3$ (**2**) in quantitative yield by NMR.[9] The mass spectrometric data suggest that **2** is a simple $Fe(CO)_3$ adduct of **1**. At low temperature the ^{11}B NMR spectrum of **2** shows four inequivalent boron sites and the ^1H NMR spectrum shows two types of terminal protons (broad overlapping signals), a single Cp* methyl resonance, and two types of M−H−B bridging protons. Terminal BH and CO stretching frequencies are observed in the IR spectrum and the presence of the latter is confirmed by the ^{13}C NMR spectrum. These data suggest that the $Fe(CO)_3$ fragment is asymmetrically bound to **1**.

The solid-state structure of **2** is shown in Figure 1 and is consistent with the solution data.[10] The $Fe(CO)_3$ fragment is attached to **1** by two Cr−Fe bonds and two μ_3-Cr−Fe−B bridging hydrogens. The metal−metal distances are consistent with single bonds; however, the Cr−Cr distance is significantly shorter than that in **1** (2.870(2) Å) whereas the Cr−B(1−4) and B(1)−B(4) distances are longer. Note that **2** retains the other two μ_2-Cr−H−B bridging hydrogens of **1**.

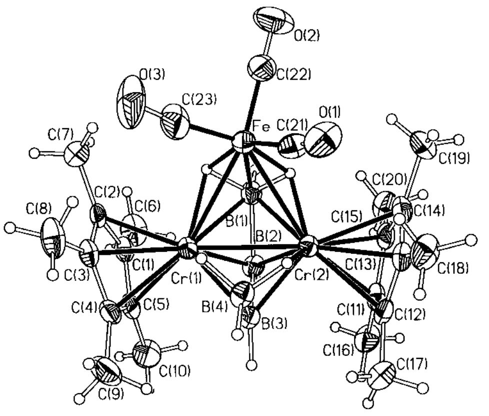
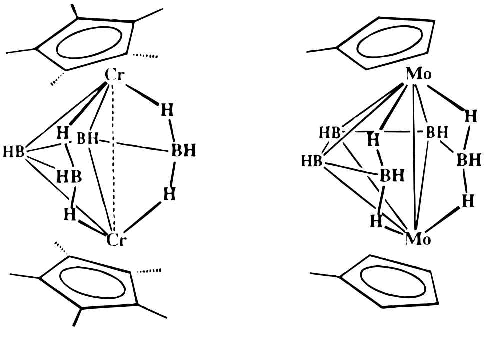


Figure 1. Molecular Structure of $Cp^*_2Cr_2B_4H_8Fe(CO)_3$, **2**. Selected bond distances (Å) and angles (deg): Fe−Cr(1) = 2.746(1), Fe−Cr(2) = 2.740(1), Fe−B(1) = 2.181(8), Cr(1)−Cr(2) = 2.710(1), Cr(1)−B(1) = 2.250(8), Cr(1)−B(2) = 2.090(7), Cr(1)−B(3) = 2.093(7), Cr(1)−B(4) = 2.178(8), Fe−H(2) = 1.58(7), Fe−H(3) = 1.65(7), Cr(1)−H(2) = 1.89(6), Cr(1)−H(7) = 1.69(6), B(1)−H(2) = 1.34(7), B(1)−H(3) = 1.24(7), B(3)−B(2)−B(1) = 127.3(6), B(2)−B(3)−B(4) = 119.4(6).

Chart 1



(**a**) (**b**)

Compound **2** exhibits dynamic behavior in the NMR. As the temperature is raised the signals at δ −8.0 and −16.2 in the ^1H spectrum disappear into the baseline at 22 °C before coalescing at 50 °C into a single peak at δ −11.9. Near 22 °C, the broad signals at δ 129.5 and 105.8 in the ^{11}B NMR coalesce into one at δ 117.5 while those at δ 46.0 and 4.1 ppm coalesce into one at δ 27.3. The free energy of activation derived from either the ^1H or ^{11}B NMR studies is 51 kJ mol^{-1} and suggests a single fluxional process. This process must be one in which the $Fe(CO)_3$ fragment retains its connection with the two Cr atoms and swings between the two BH_3 moieties of **1** thereby pairwise averaging the four boron signals and averaging the two M−H−B proton signals.

As $Fe(CO)_3$ is isolobal to BH, **2** is formally related to the 46 cve $Cp'_2Mo_2B_5H_9$, $Cp' = \eta^5\text{-}C_5H_4Me$,[11] which is viewed as saturated with a $Mo_2B_3H_3$ trigonal-bipyramidal core face-capped by two BH_3 fragments (Chart 1b). Thus, **2**, as an analog to $Cp_2Mo_2B_5H_9$, has 56 cve and obeys the electron counting rules.[12−15] Although this is a perfectly valid viewpoint, **2** and

---

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

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

[3] Hashimoto, H.; Shang, M.; Fehlner, T. P. *Organometallics* **1996**, *15*, 1963.

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

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

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

[7] Housecroft, C. E. In *Inorganometallic Chemistry*; Fehlner, T. P., Ed.; Plenum Press: New York, 1992; p 73.

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

[9] The reaction of **1** (100 mg, 0.235 mmol) with $Fe_2(CO)_9$ (172 mg, 0.558 mmol) in toluene (2 mL) for 3 days at 50 °C gave a dark brown complex **2** (101 mg, 0.178 mmol) in 76% isolated yield. Spectroscopic data for **2**: MS (EI), $P^+ = 566$, 4 boron atoms, calcd for weighted average of $^{12}C_{23}{}^1H_{38}{}^{11}B_4{}^{56}Fe^{52}Cr_2{}^{16}O_3$, $^{12}C_{23}{}^1H_{38}{}^{10}B^{11}B_3{}^{56}Fe^{52}Cr^{53}Cr^{16}O_3$, $^{12}C_{22}{}^{13}C^1H_{38}{}^{10}B^{11}B_3{}^{56}Fe^{52}Cr_2{}^{16}O_3$ 566.1376, obsd 566.1371. ^{11}B NMR (toluene + C_6D_6, −20 °C): δ 129.5 (br, fwhm = 380 Hz, {^1H}, s, fwhm = 320 Hz), 105.8 (br, fwhm = 360 Hz, {^1H}, s, fwhm = 310 Hz), 46.0 (br, fwhm = 290 Hz, {^1H}, s, fwhm = 290 Hz), 4.1 (br, fwhm = 390 Hz, {^1H}, s, fwhm = 320 Hz). ^1H NMR ($C_6D_5CD_3$, −40 °C): δ 7 (br, 2H, BH_t), ≈2 (br, 2H, BH_t), 1.79 (s, 30H, Cp*), −8.0 (br s, fwhm = 70 Hz, 2H, μBH), −16.2 (br s, fwhm = 39 Hz, 2H, μBH). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C): δ 220.4 (br s, CO), 109.9 (C_5Me_5), 12.4 ($C_5\mathit{Me}_5$). IR (KBr, cm^{-1}): 2988 (vw), 2979 (vw), 2963 (vw), 2914 (m), 2873 (vw sh, CH), 2494 (m), 2484 (m sh), 2466 (w), 2446 (w, BH), 1978 (vs), 1916 (vs), 1905 (vs, CO), 1378 (m), 1026 (m) 588 (s), others.

[10] Crystallographic data for **2**, monoclinic, $P2_1/n$, $a = 8.4967(6)$ Å, $b = 20.730(2)$ Å, $c = 15.2484(10)$ Å, $\beta = 90.277(6)°$, $V = 2685.8(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.399$ g cm^{-3}. Of 3651 reflections collected (CAD4 diffractometer, Mo Kα, 293 K), 3502 were independent and 2636 were observed ($>2\sigma(F_o{}^2)$). All non-hydrogen atoms were anisotropically refined. The borane hydrogen atoms were refined isotropically, while the methyl ones were included in the final refinement as idealized riding atoms (C−H = 0.96 Å). $R_1 = 0.0508$, $R_2 = 0.1073$ for 2636 observed unique reflections ($I > 2\sigma(I)$) and $R_1 = 0.0755$, $R_2 = 0.1254$ for all 3502 unique reflections including those with negative intensities.

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

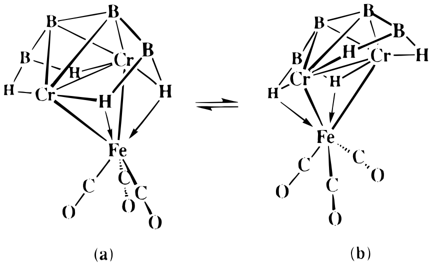
S0002-7863(96)01638-1 CCC: $12.00

$Cp'_2Mo_2B_5H_9$ differ significantly. That is, the $Cp^*{}_2Cr_2B_4H_8$ fragment in **2** retains the qualitative shape of **1** including the positions of the bridging hydrogen atoms and the fluxional behavior of **2** also distinguishes it from the Mo compound. Thus, an alternate view of **2** as a $Cp^*{}_2Cr_2B_4H_8$ ligand coordinated to a $Fe(CO)_3$ fragment is considered.

The spectroscopic signature of the carbonyl ligands on iron supports an analysis of **2** as a complex coordination compound. The IR stretching frequencies are $\approx$100 cm^{-1} below those of any neutral ferraborane[16-18] or a metallacarborane containing both CpCo and $Fe(CO)_3$ fragments.[19] The frequency range is similar to that found for $Fe(CO)_3\{P(OPh)_3\}_2$ or ferraborane monoanions. The IR data suggest a buildup of charge on Fe which is corroborated by the low-field chemical shift of the ^{13}C NMR resonance for the CO ligands.

Fenske–Hall molecular orbital (MO) calculations provide additional justification for this view.[20,21] The distortion in the geometry of **1** on coordination, principally the longer B(1)–B(4) distance and the shorter Cr–Cr distance, results in stabilization of the LUMO and destabilization of the HOMO so that they become nearly degenerate. These two orbitals have the appropriate symmetry to participate in bonding interactions with the half-occupied π symmetry orbitals of the $Fe(CO)_3$ fragment. The empty σ orbital of the $Fe(CO)_3$ fragment interacts with a lower-lying, filled B–H–Cr orbital generating a bonding, donor–acceptor interaction in which the BH_2 group of **1** acts in the manner of a bidentate borohydride ligand (Chart 2a)[22] or an electron-rich neutral borane.[23-25] The Fe center satisfies the 18-electron rule and coordinated **1** satisfies the cluster electron counting rules (44 cve). The fluxional behavior of **2** involves alternating chelating interactions between the Fe atom and the two BH_3 groups of **1** which are equivalent in the free ligand (Chart 2b). This behavior is reminiscent of that observed for the chelating $[\eta^2\text{-nido-}C_2B_9H_{12}]^-$ ligand.[26]

Chart 2



The view of **2** as a $Fe(CO)_3$ fragment coordinated by a chelating chromaborane cluster reveals the presence of both Lewis acidic sites and hydridic sites on **1** and connects this reaction to that of **1** with CS_2. In the latter case, the hydride is transferred completely to carbon and a coordinated H_2CS_2 ligand is observed. A complete analysis of this system, including the isoelectronic cobalt analog of **2**, will be forthcoming.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, positional and equivalent isotropic thermal parameters, bond distances and angles, and general displacement parameter expressions (16 pages). See any current masthead page for ordering and Internet access instructions.

JA9616387

---

(12) Wade, K. *New Scientist* **1974**, *62*, 615.

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

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

(15) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: New York, 1990.

(16) Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organometallics* **1983**, *2*, 825.

(17) Jacobsen, G. B.; Andersen, E. L.; Housecroft, C. E.; Hong, F.-E.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. *Inorg. Chem.* **1987**, *26*, 4040.

(18) Vites, J. C.; Housecroft, C. E.; Eigenbrot, C.; Buhl, M. L.; Long, G. J.; Fehlner, T. P. *J. Am. Chem. Soc.* **1986**, *108*, 3304.

(19) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1976**, *15*, 1343.

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

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

(22) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

(23) Katoh, K.; Shimoi, M.; Ogino, H. *Inorg. Chem.* **1992**, *31*, 670.

(24) Shimoi, M.; Katoh, K.; Ogino, H. *J. Chem. Soc., Chem. Commun.* **1990**, 811.

(25) Snow, S. A.; Shimoi, M.; Ostler, C. D.; Thompson, B. K.; Kodama, G.; Parry, R. W. *Inorg. Chem.* **1984**, *23*, 511.

(26) Belmont, J. A.; Soto, J.; King, R. E., III; Donaldson, A. J.; Hewes, J. D.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1989**, *111*, 7475.