Reactions of an Electronically Unsaturated Chromaborane. Coordination of CS_2 to $(\eta^5\text{-}C_5Me_5)_2Cr_2B_4H_8$ and Its Hydroboration to a Methanedithiolato Ligand

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

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

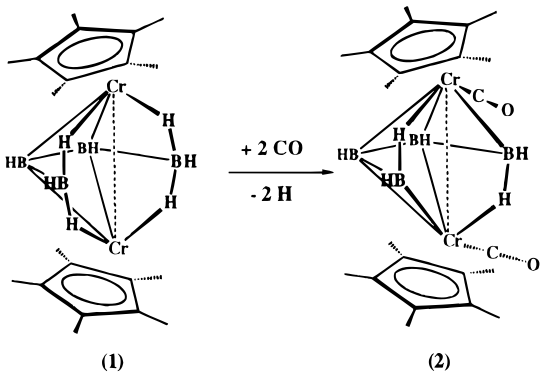
Received March 7, 1996[⊗]

*Summary: The reaction of the electronically unsaturated $Cp^*{}_2Cr_2B_4H_8$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$) cluster with CS_2 yields the saturated $Cp^*{}_2Cr_2(CH_2S_2B_4H_6)$ (**3**) cluster in better than 90% isolated yield. Both solution spectroscopic and solid-state crystallographic data show that **3**, with C_2 point symmetry, contains an intracluster bridging methanedithiolato H_2CS_2 ligand in which the S atoms of the ligand have replaced two transoid BHCr bridging hydrogens in **1**, which in turn have added to the carbon atom. The three compounds **1**, $Cp^*{}_2Cr_2(CO)_2B_4H_6$ (**2**), and **3** exhibit similar cluster geometries but possess 42, 44, and 46 cluster valence electrons, respectively.*

The three principal steps in metal-assisted transformations of molecules are (1) facile addition of a ligand to a metal site, (2) chemical modification of the bound ligand within the coordination sphere of the metal, and (3) elimination of the modified ligand from the metal site.[1] Many systems, stoichiometric as well as catalytic, have been delineated in which mononuclear metal complexes act as the site of ligand transformation.[2] Transition-metal clusters have significant potential for different and even more demanding transformations, e.g., complex hydrogenations.[3−6] As ligand dissociation from saturated clusters is often competitive with cluster degradation, the importance of electronically unsaturated clusters in facilitating the first step in the process is well recognized.[7,8] However, only a few unsaturated clusters are known,[9] with the net result that our understanding of ligand transformations on clusters is much less developed than that of mononuclear complexes.

Recently, we have described a chromaborane cluster, $Cp^*{}_2Cr_2B_4H_8$ (**1**; $Cp^* = \eta^5\text{-}C_5Me_5$), that is unsaturated in the sense of possessing 2 fewer cluster valence electrons than the 44 required by the bicapped-tetrahedral cluster geometry it exhibits.[10,11] In contrast to other unsaturated dimetal systems, in which the unsaturation is expressed in short metal−metal multiple bonds,[1] the unsaturation in **1** appears to be spread over the entire cluster skeleton. The description of **1** as an unsaturated cluster is supported by the compound's tendency to add CO ligands under mild conditions. Thus, as shown in Scheme 1, **1** adds two CO molecules and loses 2H to form $Cp^*{}_2Cr_2(CO)_2B_4H_6$ (**2**), a 44-electron saturated cluster with the same bicapped-tetrahedral geometry as **1**. As **1** possesses potentially reactive B−H hydrogens, a suitable substrate might well experience both coordination and reduction, i.e., metal-assisted hydroboration.[12−15] In support of this hypothesis we now describe the reaction of CS_2 with **1** and its consequent conversion to a methanedithiolato ligand.

Scheme 1



Compound **1** reacts[16] cleanly with CS_2 to form a single product, $Cp^*{}_2Cr_2(CH_2S_2B_4H_6)$ (**3**), in quantitative yield by ^{11}B NMR. The mass spectrum of **3** is consistent with a formula containing four B and two Cr atoms, and the parent ion mass corresponds to a simple CS_2 adduct of **1**. The NMR data suggest that **3** has two-fold symmetry; i.e., in the ^1H NMR a single Cp* resonance and

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) Elschenbroich, C.; Salzer, A. *Organometallics*; VCH: New York, 1989.

(2) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(3) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(4) Kaesz, H. D.; Knobler, C. B.; Andrews, M. A.; Buskirk, G. V.; Szostak, R.; Strouse, C. E.; Lin, Y. C.; Mayr, A. *Pure Appl. Chem.* **1982**, *54*, 131.

(5) Studies in Surface Science and Catalysis; Gates, B., Guczi, L., Knözinger, H., Eds.; Elsevier: New York, 1986; Vol. 29.

(6) *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990.

(7) Laplaza, C. E.; Cummins, C. C. *Science* **1995**, *268*, 861.

(8) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; p 329.

(9) Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; p 201.

(10) Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1994**, *116*, 8408.

(11) Ho, J.; Deck, K. J.; Nishihara, Y.; Shang, M.; Fehlner, T. P. *J. Am. Chem. Soc.* **1995**, *117*, 10292.

(12) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671.

(13) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679.

(14) Westcott, S. A.; Marder, T. A.; Baker, R. T. *Organometallics* **1993**, *12*, 975.

(15) Hartwig, J. F.; Huber, S. *J. Am. Chem. Soc.* **1993**, *115*, 4908.

0276-7333/96/2315-1963$12.00/0

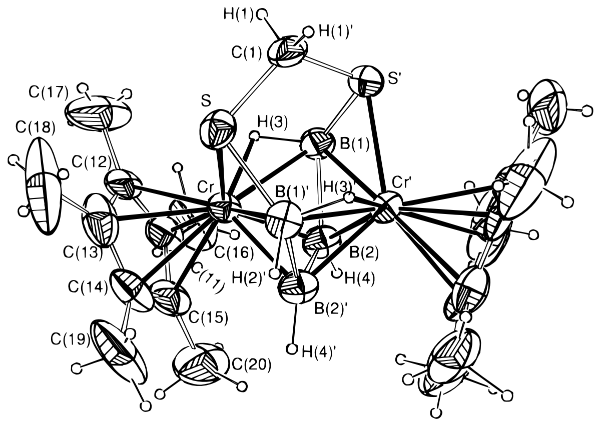
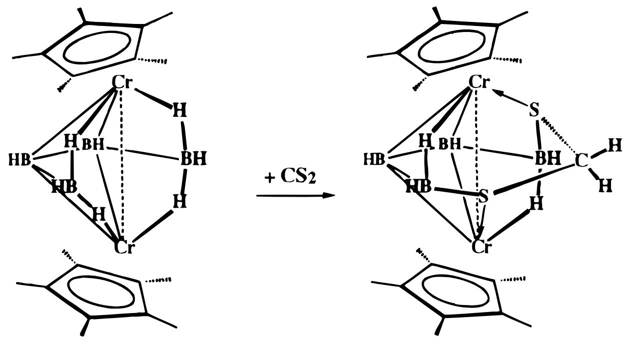


Figure 1. Molecular structure of $Cp^*_2Cr_2(CH_2S_2B_4H_6)$ (**3**). Selected bond distances (Å) and angles (deg): Cr−Cr′ = 2.912(1), Cr−S = 2.283(2), Cr−B(1) = 2.242(7), Cr−B(1)′ = 2.283(6), Cr−B(2) = 2.073(7), Cr−B(2)′ = 2.026(6), Cr−H(3) = 1.62(6), B(1)−H(3) = 1.18(6), S−C(1) = 1.809(5), C(1)−H(1) = 0.96(6); S−C(1)−S′ = 114.2(4), S−C(1)−H(1) = 110(4), S−C(1)−H(1)′ = 109(4), H(1)−C(1)−H(1)′ = 105(5).

three distinct, equal-intensity BH resonances (two terminal and one Cr−B bridging) are observed along with a sharp singlet of comparable intensity assigned to methylene protons (confirmed by a $^{13}C-^1H$ HETCOR measurement). The ^{11}B NMR spectrum shows two resonances similar to those of **1**; however, one of them is shifted to high field, which would be consistent with an interaction with a donor atom. In the IR, absorptions for CS stretching vibrations[17] are observed as well as bands for both BH and CH vibrations.

A solid-state, single-crystal X-ray diffraction structure determination[18] revealed a geometry for **3** (Figure 1) fully consistent with the spectroscopic solution-state data. The cluster **3** is located on a crystallographic C_2 axis which passes through the methylene carbon C(1) and the center of the B(2)−B(2′) bond. A methanedithiolato H_2CS_2 moiety, which originates from the added CS_2 molecule, is attached to the B_4H_6 fragment, forming a seven-membered $CH_2S_2B_4H_6$ ring sandwiched between the two Cp*Cr fragments such that each sulfur atom bridges one of the Cr atoms. Thus, **3** can be formally generated from **1** by the replacement of two trans BHCr bridging hydrogens by the two sulfur atoms of CS_2, with the hydrogen atoms being transferred to the carbon atom of CS_2 to form a H_2CS_2 moiety with nearly tetrahedral geometry around the carbon atom (Scheme 2).

Scheme 2



(1) (3)

The cluster structure of **3** is qualitatively the same as those of **1** and **2**. There are some quantitative differences: the Cr−Cr distance is longer in **3** (2.917(1) vs 2.870 (2), 2.792(1) Å, respectively); the E−Cr−Cr−E dihedral angle is larger for **3** (E = S) than for **2** (E = C) (57.10(5) vs 49.0(2)°, respectively), and the angle between the Cp* ligands in **3** is larger than that in **1** and **2** (43.2(7) vs 28.1(8), 30.4(20)°, respectively). If the H_2CS_2 fragment contributes the expected 6 electrons to the cluster bonding network, then **3** would be a 46-electron cluster. Thus, we have the curious situation of three clusters, **1**−**3**, exhibiting the same cage geometry but three different cluster electron counts. The origin of this behavior requires the detail of a molecular orbital treatment which will be described elsewhere.

Both borane and metal clusters containing a bridging methanedithiolato ligand have been reported previously.[19−24] The C−S bond distance in **3** (1.809(5) Å) is slightly shorter than those observed for the methanedithiolato-bridged transition-metal clusters, but it is comparable to the C−S single-bond distance observed in the thiaborane clusters. Although the H_2CS_2 ligands in these compounds are the same, their origins differ. With one exception, the earlier examples are formed from metal-bound sulfur atoms plus a source of CH_2 fragments or from the fragmentation of a cyclic organosulfur ring. The exception[22] is the reaction of CS_2 with the unsaturated $H_2Os_3(CO)_{10}$ cluster, which leads to its reduction to an S-bound H_2CS_2 moiety. The difference in this reaction is that two clusters are required for the reduction, thereby producing a bridged cluster dimer, $(\mu\text{-}S_2CH_2)\{HOs_3(CO)_9\}_2$, as a principal product. Apparently the chromaborane cluster **1** is capable of delivering at least two reducing equivalents to the bound substrate, permitting complete ligand reduction by a single

---

(16) The reaction of **1** (135 mg, 0.317 mmol) with CS_2 (60 μL, 1.0 mmol) in 4 mL of toluene for 40 h at 40 °C gave the dark green complex **3** (146 mg, 0.291 mmol) in 92% yield. Spectroscopic data for **3**: MS (CI), $P^+ = 502$; MS (EI), $P^+ = 502$, 4 boron atoms, calcd for weighted average of $^{12}C_{21}{}^1H_{38}{}^{11}B_4{}^{52}Cr_2{}^{32}S_2$, $^{12}C_{21}{}^1H_{38}{}^{10}B_2{}^{11}B_2{}^{52}Cr_2{}^{34}S_2$, $^{12}C_{21}{}^1H_{38}{}^{10}B{}^{11}B_3{}^{52}Cr{}^{53}Cr_2{}^{32}S_2$, and $^{12}C_{20}{}^{13}C{}^1H_{38}{}^{10}B{}^{11}B_3{}^{52}Cr_2{}^{32}S_2$ 502.1619, obsd 502.1610. ^{11}B NMR (toluene, 24 °C): δ 121.2 m, FWHM = 157 Hz, $\{^1H\}$, s, FWHM = 99 Hz; −9.7 m, FWHM = 300 Hz, $\{^1H\}$, s, FWHM = 150 Hz. ^1H NMR (C_6D_6, 24 °C): δ 7.8 br q, FWHM = 505 Hz, 2H, BH; 2.17 s, 2H, CH_2; 1.72 s, 30H, Cp*; −13.0 br d, FWHM = 185 Hz, 2H, CrHB. ^1H NMR ($C_6D_5CD_3$, −80 °C): δ 7.8 br s, FWHM = 111 Hz, 2H, BH; 2.14 s, 2H, CH_2; 1.77 s, 30H, Cp*; 1.0 br s, FWHM = 97 Hz, 2H, BH; −12.9 br s, FWHM = 42 Hz, 2H, CrHB. $^{13}C\{^1H\}$ NMR ($C_6D_5CD_3$, 24 °C): δ 102.1 C_5Me_5, 42.8 CH_2 (correlated with the CH_2 signal at 2.14 ppm in the ^1H NMR by a $^{13}C-^1H$ HETCOR measurement), 11.7 C_5Me_5. IR (KBr, cm^{-1}): 2971 w, 2953 w, 2904 m, 2855 w, CH; 2489 m, 2421 m, BH; 1377 m, 1027 m, CS.

(17) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

(18) Crystallographic data for **3**: $C_{21}H_{38}Cr_2B_4S_2$, monoclinic, $C2/c$, $a = 20.436(2)$ Å, $b = 14.500(2)$ Å, $c = 8.5648(8)$ Å, $\beta = 94.923(7)°$, $V = 2528.7(4)$ Å^3, $Z = 4$, D(calcd) = 1.318 g cm^{-3}. Of 3706 reflections collected (CAD4 diffractometer, Mo Kα, 293 K), 1763 were independent and 1369 were observed ($>3\sigma(F_o^2)$). All non-hydrogen atoms were anisotropically refined and all hydrogen atoms found and either refined or involved only in the structure factor calculation. $R_1 = 0.046\ 85$, $R_2 = 0.068\ 10$.

(19) Kang, S. O.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 3281.

(20) McKenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1983**, *105*, 5329.

(21) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

(22) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.

(23) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(24) Seyferth, D.; Womack, G. B.; Gallagher, M. K.; Cowie, M.; Hames, B. W.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1987**, *6*, 283.

cluster. Note that the reaction of CS_2 with $CpMoH_2$ gives a 10% yield of a product which has been spectroscopically characterized as $Cp_2Mo(\mu\text{-}S_2CH_2)$;[25] however, the path by which it is formed is unclear.

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, general displacement parameter expressions, and least-squares planes and a figure giving the ^1H NMR spectrum of **3** (11 pages). Ordering information is given on any current masthead page.

OM960180E

---

(25) Okuda, J. *Z. Naturforsch., B* **1990**, *45*, 753.