Preparation and Structure of $(Cp^*Cr)_2B_4H_8$. An Unsaturated Metallaborane Cluster with an Unexpected Structure

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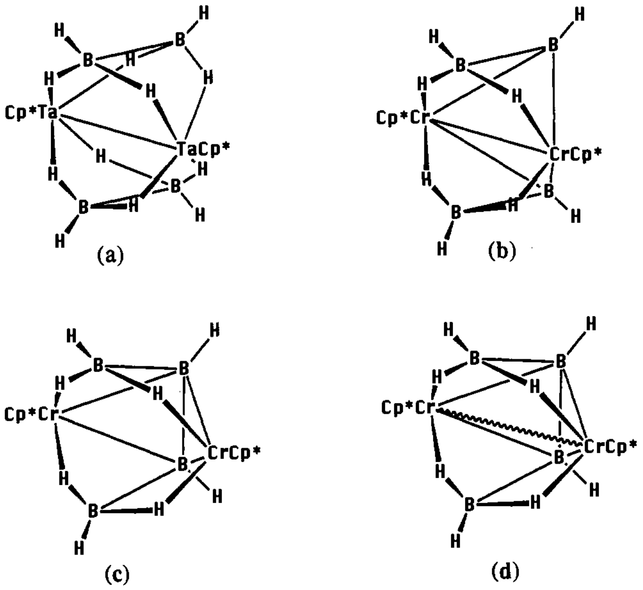
The electron counting rules[1-3] not only correlate cluster structure with formal skeletal electron pairs but also suggest the kinds of fragments that will be ideally suited for cluster bonding.[4] That is, the cluster geometries displayed by *n* cluster fragments usually have $n + 1$, $n + 2$, and $n + 3$ cluster pairs. Hence, a fragment giving rise to many cluster structures, e.g., BH, brings two electrons (and three orbitals) to cluster bonding. The rich chemistry of polyhedral boranes illustrates this point.[5] The fact that transition metal fragments isolobal with BH, e.g., CpCo and $Fe(CO)_3$, readily form clusters with and without boron is also consistent with this idea.[6-9]

Early transition metal fragments behave in an essentially different fashion. The tantalum derivatives $(Cp^*Ta)_2B_2H_6Br_2$, $Cp^* = \eta^5\text{-}(CH_3)_5C_5$, and $(Cp^*Ta)_2(B_2H_6)_2$, Chart 1a,[10] would be unsaturated based on a simple application of the electron counting rules, i.e., the latter has 44 valence shell electrons, which is two fewer than expected for an edge-fused bitetrahedron.[11] The compound can also be viewed as a metal–metal bonded fragment (double bond) with borane ligands chelating the metal–metal axis in a perpendicular fashion.

One wonders how nature would respond to an intermediate situation as represented by the Cp*Cr fragment. This species has three fewer electrons than the Cp*Co fragment and one more than the Cp*Ta fragment, and chelating borane ligands are known for mononuclear complexes of chromium.[12,13] Further, a number of mononuclear chromium–carborane complexes have been reported.[14,15] Nearly all these complexes are paramagnetic, and, in one case,[14] the apparent cluster electron deficiency was suggested to be accommodated in the nonbonding orbitals of the metal fragment.

Recently, we demonstrated that the $[Cp^*CoCl]_2$ dimer is a high-yield source of metallaboranes under mild conditions,[16] and we have now extended this approach to the chromium analogue $[Cp^*CrCl]_2$. The elegant studies of closely related organometallic derivatives by Theopold and co-workers provided an essential stimulus as well as the preparative route to the chromium dimer.[17,18]

Chart 1



(a) (b) (c) (d)

The reaction of paramagnetic $[Cp^*CrCl]_2$ with $BH_3{\cdot}THF$ at −30 °C results in a greenish brown solution and a bright green precipitate. The latter was shown to be $[Cp^*CrCl_2]_2$ by mass spectrometry and ^1H NMR. Extraction with hexane followed by precipitation at −40 °C resulted in a brown, diamagnetic, highly air-sensitive solid, $(Cp^*Cr)_2B_4H_8$, **1**, in 40% ostensible yield based on chromium.[19] Considering that 50% of the $[Cp^*CrCl]_2$ acts as a Cl acceptor, the true yield is 80%. In an alternative approach, the reaction of $[Cp^*CrCl]_2$ with $LiBH_4$ initially produces a dark green-brown, paramagnetic, air-sensitive metallaborane formulated as $[Cp^*CrBH_4]_2$, **2**, in 95% yield.[20] Heating this analogue of $[Cp^*CrCH_3]_2$[18] results in the formation of **1** in good yield.

In the absence of crystallographic data, the molecular formula of **1** and its spectroscopic properties are best fit with the structure shown in Chart 1b. That is, by analogy with the Ta compound (Chart 1a), **1** can be reasonably considered as a 42-electron dimetal compound with B_2 ligands bridging in a perpendicular fashion. The very different boron environments are problematical albeit required by the NMR data. However, if correct, structure **1b** would permit **1** to accommodate its shortage of skeletal electrons by forming a Cr–Cr triple bond. As such, it would be related to the 44-electron (MM double bond) $(CpNbCO)_2(RCCR)_2$[21] as pointed out by Hoffmann.[22]

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(19) Spectroscopic data for **1**. MS (EI): $P^+ = 426$, four boron atoms, calc for weighted average of $^{12}C_{20}{}^1H_{38}{}^{11}B_4{}^{52}Cr_2$, $^{12}C_{20}{}^1H_{38}{}^{10}B^{11}B_3{}^{52}Cr^{53}Cr$ multiplet, 426.2172, obsd, 426.2192. NMR: (^{11}B, hexanes, 22 °C) δ 126.5 d, $J_{BH} = 159$ Hz, {^1H}, s, FWHM = 83 Hz, 2B; 34.3 m, FWHM = 264 Hz, {^1H}, s, FWHM = 97 Hz, 2B; (^1H, C_6D_6, 18 °C) δ 8.5 br, FWHM 460 Hz, 2BH; 3.3 br q, $J_{BH} = 130$ Hz, FWHM = 30 Hz, 2BH; 1.94 s, Cp*; −3.9 partially collapsed q, FWHM = 180 Hz, 4BHCr; (^{13}C, C_6D_6, 18 °C) δ 108.7 s, CCH_3; 12.4 q, CCH_3. IR (KBr, cm^{-1}): 2465 w, 2437 w, 2377 sh, BH.

(20) Spectroscopic data for **2**. MS (EI): $P^+ - H_2 = 402$, two boron atoms, two Cr atoms. NMR: (^{11}B, hexanes, 20 °C) δ −158 br, FWHM = 1100 Hz, 2B; (^1H, C_6D_6, 18 °C) δ 6.7 br, FWHM = 70 Hz, Cp*; −54.3 br s, FWHM = 1400 Hz, 4BHCr; (^{13}C, C_6D_6, 18 °C) δ 121.0, CCH_3; 66.5, CCH_3. IR (hexanes, cm^{-1}): 2460 w, 2101 w,br, BH.

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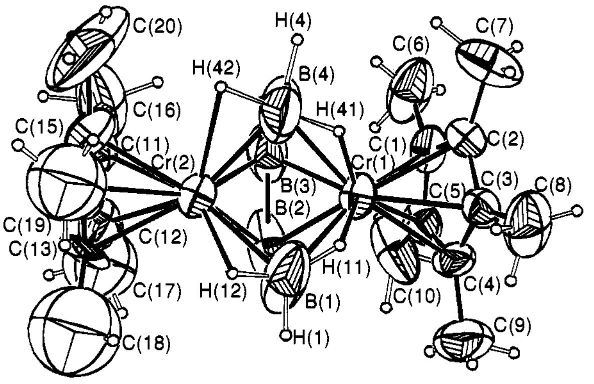

Figure 1. Molecular structure of $(Cp^*Cr)_2B_4H_8$, **1**. Selected bond distances (Å): B(1)–B(2) = 1.75(3), B(2)–B(3) = 1.75(3), B(3)–B(4) = 1.61(3), Cr(1)–B(1) = 2.13(2), Cr(1)–B(2) = 2.01(2), Cr(1)–B(3) = 2.01(2), Cr(1)–B(4) = 2.11(2), Cr(2)–B(1) = 2.15(2), Cr(2)–B(2) = 2.02(1), Cr(2)–B(3) = 2.04(2), Cr(2)–B(4) = 2.12(2). Dihedral angle between the Cp* C_5 planes is 28.1(8)°.

Crystals of **1** were obtained by slow cooling of a hexane solution, and the actual molecular structure in the solid state is shown in Figure 1. This structure,[23] schematically represented in Chart 1c, is fully consistent with the spectroscopic data but signifcantly different from that in Chart 1b. The multiple Cr–Cr bond required by **1b** appears to be missing (d_{CrCr} = 2.870(2) Å compared to an average Cr–Cr distance of 2.715 Å in $[CpCr(\mu_3\text{-}H)]_4$, which is described as lacking metal–metal bonding[17,18]), and instead there is a B–B interaction (d_{BB} = 1.75(3) Å) between two BH fragments of the B_2 ligands of structure **1b**. Rather than an edge-fused bitetrahedral geometry with Cr–Cr bonding, the structure exhibited appears to be a single cage based on a pentagonal bipyramid with apical Cp*Cr fragments and equatorial BH fragments. Geometrically, the structure would be classed as nido, which formally requires 48 valence electrons (eight skeletal pairs). Conventional treatment of the Cp*M fragment[24] would suggest that **1** is six electrons short. In fact, **1** appears to have the structure expected if the metal were cobalt rather than chromium, e.g., compare $(CpCo)_2S_2B_2H_2$ (d_{CoCo} = 3.067 Å).[25,26]

Of course, it is known that a transition metal fragment can "adjust" to its circumstances, e.g., the $CpMn(CO)_2$ fragment is formally a one orbital–zero electron fragment but can act as a three orbital–four electron fragment by utilizing two of its "t_{2g}" filled orbitals.[27] As an extreme example, the $(RO)_3W$ fragment is found to mimic the $(CO)_3Co$ fragment.[28] Fenske–Hall calculations[29] on $(CpCr)_2B_4H_8$ and $(CpCo)_2B_4H_8$ in the cage geometry of **1** show large HOMO–LUMO gaps for both, bonding Cr–Cr and antibonding Co–Co interactions, respectively, and a high-lying filled MO that constitutes a Cr–Cr single bond in the former but an analogous MO which is nonbonding in the latter. (Note that d_{MnMn} = 2.93 Å in $Mn_2(CO)_{10}$,[30] and the observed d_{CrCr} does not precude bonding.) All of these differences between the CpCr and CpCo molecules originate in the higher metal-based orbital energies of the former and the distinctly tilted geometry of the Cp rings in **1**. Thus, in electron counting terms, a better representation of **1** is as a bicapped $Cp^*{}_2Cr_2B_2H_2$ tetrahedron with a long Cr–Cr single bond (structure **1d**). A M_2B_4 bicapped tetrahedron requires 44 cluster valence electrons, and, thus, **1** is still unsaturated.

To test whether the unsaturation of **1** is real, **1** was reacted with CO at room temperature and 1 atm of pressure, thereby producing a brown product that has been spectroscopically characterized as $(Cp^*CrCO)_2B_4H_6$, **3**.[31] Athough the geometric structure of **3** is presently unclear,[32] the facile addition reaction with CO demonstrates that **1** behaves in one essential sense as an unsaturated species.

The synthesis of clusters at temperatures such that reaction barriers are large with respect to kT permits the isolation of kinetic products such as **1** and **2** that do not obey the simple rules. The various factors that are important in stabilizing **1** remain to be explored, and further studies are in progress.

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Supplementary Material Available: Structure solution, tables of crystal data, atomic positional and displacement parameters, and selected distances and bond angles for **1** (11 pages; listing of observed and calculated structure factors (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(23) Crystallographic data for **1**: $C_{20}H_{28}Cr_2B_4$, tetragonal, $P4_2/n$, $a = b$ = 23.720(1) Å, c = 8.4046(7) Å, V = 4728.8(5) Å^3, z = 8, d_{calcd} = 1.509 g/cm^3. Of 3341 reflections collected on a CAD4 diffractometer, 3240 were uniques and 1574 were unique observed $(F_o{}^2) > 3.0\ \sigma(F_o{}^2)$. Hydrogen atoms were located from a difference Fourier map but not refined in the final refinement. R_1 = 0.0672, R_2 = 0.0890.

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(31) Spectroscopic data for **3**. MS (EI): apparent P^+ = 480, four boron atoms, loss of two CO, calcd for weighted average of ${}^{12}C_{22}{}^{1}H_{36}{}^{16}O_2{}^{11}B_4{}^{52}Cr_2$, ${}^{12}C_{22}{}^{1}H_{36}{}^{16}O_2{}^{10}B^{11}B_3{}^{52}Cr^{53}Cr$ multiplet, 480.1914, obsd, 480.1925. NMR: (${}^{11}B$, hexanes, 22 °C) δ 64.8 d, J_{BH} = 140 Hz, {${}^1H$}, s, FWHM = 100 Hz, 2B; 34.9 m, FWHM = 330 Hz, {${}^1H$}, s, FWHM = 190 Hz, 2B; (${}^1H$, $CDCl_3$, 18 °C) δ 1.79 s, Cp*; –6.5 br s, FWHM = 150, int 1, BHCr, –12.7 br s, FWHM = 140 Hz, int 2, BHCr; (${}^{13}C$, $CDCl_3$, 18 °C) δ 104.6 s, CCH_3; 12.1 q, CCH_3. IR (hexane, cm^{-1}): 2478 w, BH; 1914 s, 1871 w, 1857 w, CO.

(32) The data on the 44-electron **3** are consistent with the heavy atom structure of the 44-electron $(CpNbCO)_2(RCCR)_2$, provided that two tautomeric forms are present in solution.