Origins of Unsaturation in Group 6 Metallaboranes. Synthesis, Crystal Structure, and Molecular Orbital Calculations for $(Cp^*MoCl)_2B_3H_7$ (Cp* = Pentamethylcyclopentadienyl)

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Unsaturation in transition metal cluster compounds is rare and often difficult to establish.[1−4] Within the realms of metallaborane chemistry unsaturated species—that is, those which are formally electron deficient with respect to the number of skeletal pairs required to sustain the observed molecular geometry—are unknown. We have recently reported the synthesis and structural characterization of the cluster $(Cp^*Cr)_2B_4H_8$ (**3**)[5,6] (Cp* = pentamethylcyclopentadienyl) which, having five skeletal electron pairs and a bicapped tetrahedral geometry, is formally two electrons deficient in terms of Wade's rules.[7] The reactivity of this species (*e.g.*, with CO and Na metal) further demonstrate its unsaturation.[6] However, attempts to explain how **3** sustains its observed molecular geometry despite having a deficiency of cluster electrons and too few atoms to adopt a capped structure based on a polyhedron with fewer vertices have been frustrated by the lack of saturated metallaborane analogues containing later transition metal fragments. We have now been successful in isolating and structurally characterizing the cluster $(Cp^*MoCl)_2B_3H_7$ (**1**), an intermediate in the cluster condensation route from Cp^*MoCl_4 to $(Cp^*Mo)_2B_5H_9$ (**4**) using excess BH_3·THF.[8] Comparison of the geometry and electronic structure of this new complex with those of $(Cp^*Co)_2B_3H_7$ (**2**), which has a further two pairs of electrons and is saturated,[9,10] allows definitive conclusions to be reached concerning the role of the Cp*M fragment (M = Cr or Mo) in stabilizing unsaturated metallaborane clusters.

Reaction of Cp^*MoCl_4 with 5 equiv of BH_3·THF in toluene produces the green, very air- and moisture-sensitive cluster **1** which has been characterized by ^{11}B and ^1H NMR, IR, and single-crystal X-ray diffraction.[11] The molecular structure (Figure 1) is best viewed as a trigonal bipyramid; the required number of skeletal electron pairs is six, and since the electron count for $(Cp^*MoCl)_2B_3H_7$ (**1**) is only *five* pairs, this implies that the molecule is unsaturated. Superficially there are similarities between this molecule and the dicobalt species **2**.[9,10] Each contains a pair of metal centers bridged by similar B_3H_7 units. Closer inspection reveals significant differences between the two species consistent with the differing electron counts. $(Cp^*Co)_2B_3H_7$ is a seven skeletal pair molecule and adopts a 2,4-*nido* structure based on the octahedron.[9,10] The Co−Co distance (3.36 Å) is consistent with the absence of any bonding interaction implied for two metal atoms occupying nonadjacent basal vertices.[9,10] For **1**, the Mo−Mo distance is somewhat shorter (3.096 Å), and although by itself this distance is ambiguous as to the extent of bonding between the two molybdenum centers, it certainly does not rule out a Mo−Mo single bond. In addition, it is interesting to note that the B_3 ligand is significantly more "opened out" in **1** than in **2**. Hence, the B−B bond lengths are longer [1.839 *vs* 1.705 Å (mean)] and the B−B−B angle somewhat wider (117.9° *vs* 100.6°) than in the cobalt compound.[9,10] This is consistent with the three borons occupying the two apical and one basal positions of a trigonal bipyramid, rather than of an octahedron.[12]

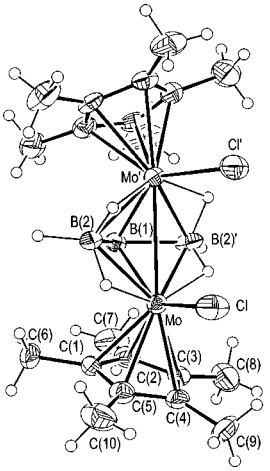

Figure 1. Molecular structure of $(Cp^*MoCl)_2B_3H_7$, **1**. Selected bond distances (Å) and angles (°): Mo−Mo′ 3.0958(12), Mo−Cp*(centroid) 2.002(3), Mo−Cl 2.423(2), Mo−B(1) 2.144(8), Mo−B(2) 2.286(8), Mo−H(3) 1.74(6), B(1)−B(2) 1.838(11), B(1)−H(1) 1.06(14), B(2)−H(2) 1.27(5), B(2)−H(3) 1.26(6), B(2)−H(4) 1.06(7), B(2)−B(1)−B(2)′ 117.8(9), Cp*(centroid)−Mo(1)−Mo(2)−Cp*(centroid) 17.23(10).

Comparison of the geometric parameters for **1** with those found in the saturated cluster $(C_5H_4MeMo)_2B_5H_9$[13] reveals that the Mo−Mo distance is significantly longer (*ca.* 10%) than that found in the B_5 species (which is described as having an Mo−Mo single bond). Clearly this distance (3.096 Å) is long enough to preclude multiple bonding between the molybdenum centers,[14−16] this being one possible response to the electronic

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(11) Reaction of Cp^*MoCl_4 with 5 equiv of BH_3·THF in a dilute toluene solution (*ca.* 50 mM in BH_3·THF) at 55 °C over a period of 72 h produces the cluster **1** in *ca.* 5% yield. The principal reaction product is the metallaborane **4**, and a series of ^{11}B NMR monitored reactions have confirmed that the reactive species **1** is actually an intermediate in the formation of the Mo_2B_5 species. Compound **1** has been characterized by ^{11}B and ^1H NMR, IR, and single-crystal X-ray diffraction. Spectroscopic data for **1**: ^{11}B NMR (toluene, 21 °C), [$J(^{11}B-^1H)$ in parentheses] δ 105.5 [d, 1B (155 Hz)], δ 34.2 [br, 2B]; ^1H NMR ([$^2H_6$]benzene, 21 °C), δ −4.8 [pcq, 4H (MoHB) (70 Hz)], δ 1.66 [s, 30H (Cp*)], δ 3.4 [br, 2H (BH_t)], δ 8.5 [br, 1H (BH_t)]; IR (KBr, cm^{-1}) 2982 w, 2962 w, 2916 s, 2855 w sh, ν(C−H); 2498 s, 2455 s, ν(B−H_t); 1475 m, 1448 w sh, 1415 w, 1377 s, 1071 w, $\delta(CH_3)$; 752 s, 675 w sh, 664 m, $\rho(CH_3)$ [δ = deformation mode, ρ = rocking mode]. Crystallographic data for **1**: tetragonal, $P4_32_12$, a = 8.5231(13) Å, b = 8.5231(13) Å, c = 32.956(7) Å, V = 2394.0(7) Å^3, Z = 4, D_{calcd} = 1.589 g cm^{-3}. Of the 2422 reflections collected (CAD4 diffractometer, Mo Kα, 293 K), 2099 were independent and 1826 were observed [$I > 2\sigma(I)$]. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were located in subsequent Fourier synthesis. Both methyl and borane hydrogens were included in the final refinement, the former as idealized riding atoms (C−H = 0.96 Å), the latter isotropically. R_1 = 0.0420, wR_2 = 0.0944 for observed unique reflections [$I > 2\sigma(I)$], and R_1 = 0.0542, wR_2 = 0.1053 for all 2099 unique reflections including those with negative intensities.
(12) The two chloride ligands in **1** adopt terminal positions, rather than the μ_2-bridging coordination mode seen in $(Cp^*MoCl)_2B_4H_{10}$. The Mo−Mo distance is longer (3.096 *vs* 2.710 Å) and the angle between the two Cp* rings is somewhat larger (49.68° *vs* 9.85°).
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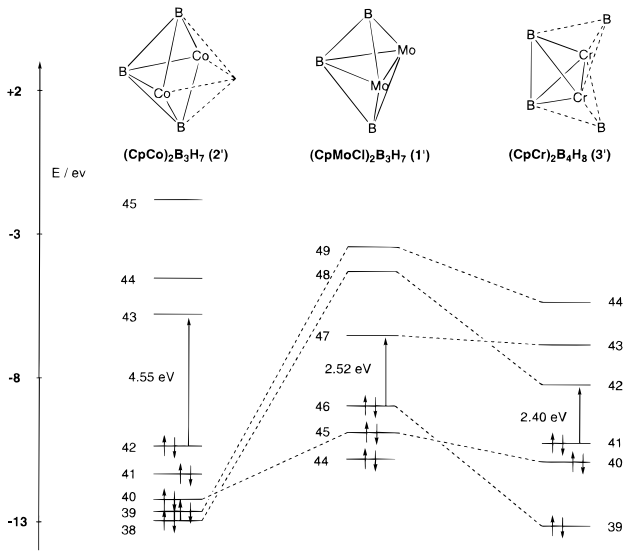

Figure 2. Comparison of relevant features of the molecular orbital schemes for $(CpMoCl)_2B_3H_7$, $(CpCo)_2B_3H_7$, and $(CpCr)_2B_4H_8$.

unsaturation of the cluster. The observed Mo−Mo distance is, however, shorter than that observed in both $[CpMo(CO)_3]_2$ (3.22 Å)[17] and $Mo_2(CO)_{10}^{2-}$ (3.123 Å)[18] , which are described as having single bonds, and considerably shorter than the 3.575 Å found in the cation $[\{(MeO)_3P\}_2(OC)_2Mo(\mu\text{-}Cl)_3Mo(CO)_2\text{-}\{P(OMe)_3\}_2]^{n+}$, which has no Mo−Mo bond.[19] In addition to a longer Mo−Mo distance, the Mo−B linkages are somewhat shorter than the corresponding distances in $(C_5H_4MeMo)_2B_5H_9$.[13] It is interesting to note that the principal geometric differences between the saturated Mo_2B_5 and unsaturated Mo_2B_3 species (namely the longer M−M distance and shorter M−B distances) are mirrored by similar changes between saturated and unsaturated derivatives of the Cr_2B_4 system [*e.g.* between the unsaturated parent chromaborane **3** and the saturated derivative $(Cp^*Cr)_2B_4H_8Fe(CO)_3$[5,6,20]]. It would therefore appear that the geometric response to unsaturation is similar in **1** and **3**, and Fenske−Hall calculations carried out on the two systems might be expected to display some common features.

A comparison of the molecular orbital (MO) pictures for $(CpMoCl)_2B_3H_7$ (**1′**) and $(CpCo)_2B_3H_7$ (**2′**) (Figure 2) reveals a somewhat larger HOMO/LUMO gap for the cobalt compound (4.55 *vs* 2.52 eV).[21−23] Furthermore, in the molybdenum species, MOs 45 and 49 constitute a Mo−Mo σ bonding/antibonding pair of orbitals; MO 45 is filled whereas MO 49 is empty, and the energy gap between the two is nearly 7 eV. By contrast, the corresponding molecular orbitals in **2′** lie much deeper in energy (MOs 39 and 40) and *both* are filled. This allows the accommodation of one of the two extra pairs of electrons present in the cobalt system, and consequently, the Co−Co interaction is effectively nonbonding, a difference further reflected by the M_2 Mulliken overlap populations [+0.13 for **1′**, −0.03 for **2′**]. These findings are consistent not only with the description of **1′** and **2′** in terms of a trigonal bipyramid and an octahedron, respectively, but also with the fact that the "t_{2g}" orbitals of the later transition metal are both filled and more core-like in nature and therefore less likely to interact usefully with ligand-based orbitals. This is further exemplified by MO 38 for the cobalt compound (**2′**) which lies at −12.94 eV; the corresponding MO for **1′** (48) lies at −4.27 eV. Both MOs are essentially M−B antibonding, and the much better metal−borane energy match in the molybdenum case shifts this orbital to much higher energy. Consequently, this MO is occupied in **2′** but unoccupied in **1′**. In essence, the combination of a metal−metal bond in **1′** and the better metal−borane energy match shifts two MOs to a much higher energy in $(Cp^*MoCl)_2B_3H_7$ with the consequence that these orbitals are unfilled and **1′** has two fewer bonding MOs and two fewer skeletal pairs than **2′** (five *vs* seven).

The ability of the metal t_{2g} orbitals to interact with those of the ligand in such a way that the unfilled cluster bonding orbital is shifted to high energy also accounts for the unsaturation in $(CpCr)_2B_4H_8$ (**3′**); the HOMO/LUMO gaps for both compounds [2.52 eV for **1′**, 2.40 eV for **3′**] are well within the range expected for stable metallaboranes (see Figure 2). For **3′** it was found that, relative to the bonding in the saturated chromaboranes $(CpCr)_2B_4H_8Fe(CO)_3$ and $(CpCr)_2B_4H_6(CO)_2$, there was a lengthening of Cr−Cr bond and shortening of the Cr−B bonds.[5,6,24] Since the LUMO for **3′** is Cr−Cr bonding but Cr−B antibonding, this causes a shift to higher energy and this orbital is unoccupied—with the consequence that **3′** has one fewer occupied MO than its saturated counterparts.[24] It is interesting, therefore, that **1** shows similar lengthening of Mo−Mo and shortening of Mo−B bonds with respect to saturated molybdaboranes; given that the LUMO for **1′** is of similar character to that of **3′**, these geometric changes cause a similar elevation in the LUMO energy, and the cluster skeleton contains one fewer pair of bonding electrons than expected.

The metal−metal bonding in **1′** and **3′** is similar in nature. In each case the SHOMO is a filled $\sigma(d_{z^2})$ bonding orbital with the corresponding (empty) antibonding orbital lying much higher in energy. The Mulliken overlap populations for each M_2 unit are also consistent with the presence of an M−M bond for both molecules (+0.13 for **1′**, +0.06 for **3′**); the higher value for **1′** is in line with the stronger metal−metal bonding expected for the heavier transition metal [and indeed is only slightly less than the value calculated for the $(CpMo)_2B_5H_9$ molecule (0.14)].

In conclusion, $(Cp^*MoCl)_2B_3H_7$ represents a rare example of an unsaturated metallaborane cluster, and the first for which direct comparison is possible with a saturated later transition metal species containing the same borane fragment. Comparison with $(Cp^*Co)_2B_3H_7$ shows that the existence of a metal−metal bond together with the elevation of M−B antibonding orbitals resulting from a better metal−borane energy match is vital in stabilizing a structure with two fewer electron pairs than the cobalt counterpart. Similar behavior observed for $(Cp^*Cr)_2B_4H_8$ identify this as a more general phenomenon in which a good energy match between Cp*M (M = Cr, Mo) and borane fragment orbitals can cause elevation of the LUMO and support one fewer skeletal bonding pair than predicted.

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Supporting Information Available: Tables of crystal data, positional and equivalent isotropic thermal parameters, bond distances and angles, and general displacement parameter expressions (13 pages). See any current masthead page for ordering and Internet access instructions.

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