

Directed Synthesis of Chromium and Molybdenum Metallaborane Clusters. Preparation and Characterization of $(\text{Cp}^*\text{Cr})_2\text{B}_5\text{H}_9$, $(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9$, and $(\text{Cp}^*\text{MoCl})_2\text{B}_4\text{H}_{10}$

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Cluster formation by metal-mediated condensation of single boron fragments has been shown to be one of several effective synthetic routes to new metallaboranes,^{1–4} although in many cases there is little control over the nuclearity of the product.^{5–11} We have been particularly interested in the reaction of dimeric species such as $[\text{Cp}^*\text{MCl}]_2$ ($\text{M} = \text{Co}$ or Cr) with BH_4^- or $\text{BH}_3\cdot\text{L}$ as a method of controlling the number of metal atoms in the product.^{12,13} In the chromium case, reaction with $\text{BH}_3\cdot\text{thf}$ yields the electronically “unsaturated” cluster $(\text{Cp}^*\text{Cr})_2\text{B}_4\text{H}_8$, **1**, which is noteworthy not only from a structural standpoint,¹³ but also for the opportunity it represents in bringing about complexation and chemical modification of small molecules.^{14,15} In addition, it provides a rare opportunity for the controlled synthesis of larger clusters *via* addition of further mononuclear boron fragments. Here we report the synthesis of $(\text{Cp}^*\text{Cr})_2\text{B}_5\text{H}_9$, **2**, by addition of a BH fragment to **1**. Given the two-step synthesis of **2** from $[\text{Cp}^*\text{CrCl}]_2$ and monoboron fragments, synthesis of the analogous molybdenum cluster, $(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9$, **3**, by the use of a dimeric metal precursor and $\text{BH}_3\cdot\text{thf}$ establishes this as a more general method of controlled cluster synthesis. Furthermore, when the metal dimer used is the Mo(III) species $[\text{Cp}^*\text{MoCl}_2]_2$, the highly unusual cluster $(\text{Cp}^*\text{MoCl})_2\text{B}_4\text{H}_{10}$, **4**, is isolated and structurally characterized.

Reaction of **1** with a 3-fold excess of $\text{BHCl}_2\cdot\text{SMe}_2$ in toluene at 55 °C over a period of 72 h produces the cluster **2** in ca. 45% yield. Removal of volatiles *in vacuo*, extraction with hexane and filtration through pre-dried Celite yields a dark green-brown solution from which brown plate-like crystals can be grown by concentration and cooling. **2** is moderately air sensitive in the solid phase, much more so in solution, and is characterized by measurement of its ¹³C, ¹¹B, and ¹H NMR spectra (including selective decoupling), solid-phase IR spectrum, and mass spectrum.¹⁶

The mass spectrum of **2** is consistent with a formula containing two Cr and five B atoms and the parent ion mass corresponds to addition of a BH unit to **1**. The ¹¹B NMR data indicate the presence of a pair of equivalent borons and a unique boron, each linked directly to a metal center and a single terminal hydrogen and another pair of equivalent borons each linked to two bridging hydrogens and one terminal hydrogen. Furthermore, the ¹H and ¹³C spectra imply two equivalent Cp* ligands, four equivalent CrHB protons and three distinct BH_i groups (2:2:1). These NMR data are consistent with a molecular geometry **I** (Figure 1), a finding reinforced by the similar spectra reported for the structurally characterized $(\text{C}_5\text{H}_4\text{MeMo})_2\text{B}_5\text{H}_9$ and recently confirmed by an X-ray crystallographic study. Both compounds are best viewed as 46-electron clusters based around a $\text{M}_2\text{B}_3\text{H}_3$ trigonal bipyramidal core ($\text{M} = \text{Cr}$ or Mo) capped by two BH₃ fragments.¹⁷ Alternatively, from a synthetic standpoint, **2** can be thought of as formally derived from **1** by insertion of a BH fragment into the B(2)–B(3) bond.

Given the sequential synthesis of **2** by addition of monoboron fragments to a dimeric metal precursor, it was thought that reduction of $[\text{Cp}^*\text{MoCl}_2]_2$ followed by reaction with $\text{BH}_3\cdot\text{thf}$ might provide a viable synthetic route to **3**, in that the related compound $(\text{C}_5\text{H}_4\text{MeMo})_2\text{B}_5\text{H}_9$ has been previously isolated in 0.75–1.5% yield from the reaction of $(\text{C}_5\text{H}_4\text{Me})\text{MoCl}_4$ and LiBH_4 .¹⁷ Accordingly, the reduction of $[\text{Cp}^*\text{MoCl}_2]_2$ with 1 equiv of LiEt_3BH , followed by reaction with $\text{BH}_3\cdot\text{thf}$, gave an orange-brown crystalline solid shown on the basis of ¹¹B and ¹H NMR measurements to be $(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9$, **3** [by comparison with the spectra reported for $(\text{C}_5\text{H}_4\text{MeMo})_2\text{B}_5\text{H}_9$].¹⁸ **3** is produced cleanly (there being no other metallaborane products detected by ¹¹B NMR) in yields of 50–60%. This approach therefore represents a high yield targeted synthesis of M_2B_5 clusters of chromium and molybdenum. Difference in reactivity between the chromium and molybdenum systems is reflected in the isolation of the unsaturated M_2B_4 intermediate (**1**) in the chromium case, with addition of the fifth boron requiring more forcing conditions, in contrast to the clean one-step synthesis of the Mo_2B_5 cluster.

Extension of this approach to include reactions of the Mo(III) dimer $[\text{Cp}^*\text{MoCl}_2]_2$ with monoboranes leads to the formation of a mixture of **3** and the novel Mo(III) cluster $(\text{Cp}^*\text{MoCl})_2\text{B}_4\text{H}_{10}$, **4**, in yields of up to 45% (see Figure 1). **4** has been characterized by ¹¹B and ¹H NMR, IR, mass spectrometry and single-crystal X-ray diffraction.¹⁹ The molecular structure (Figure 2) shows two Cp*Mo units linked by a pair of bridging chlorides and in a side-on fashion by a B₄H₁₀ unit. Bridging of the dimetal unit by B(1) and B(2) is similar to the coordination of the B₂H₆²⁻ ligand to a dimetal species in $[(\text{C}_5\text{Me}_4\text{Et})\text{Nb}(\text{B}_2\text{H}_6)]_2^{20}$ and $[(\text{DTolF})_2\text{TaB}_2\text{H}_6]_2$ [DTolF =

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(16) Spectroscopic data for **2**: MS (EI), P⁺ = 438, 2 Cr, 5 B atoms, calcd for weighted average of ¹²C₂₀¹H₃₉¹¹B₅⁵²Cr₂, ¹²C₂₀¹H₃₉¹¹B₄¹⁰B⁵²C₅₃, Cr₂, ¹²C₂₀¹H₃₉¹¹B₃⁵³Cr₂, ¹²C₁₉¹³C¹H₃₉¹¹B₄¹⁰B⁵²Cr₂, 438.2351, obsd 438.2353. ¹¹B NMR (toluene, 21 °C), $[J(^{11}\text{B}-^1\text{H})$ in parentheses] δ 91.5 [d, 2B (104 Hz)], δ 86.2 [d, 1B (124 Hz)], δ 25.0 [overlapping d of t, 2B (120, 65 Hz)]. ¹H NMR ($[\text{C}_5\text{H}_5]$ toluene, 21 °C), δ -6.2 [pcq, 4H (CrHB) (70 Hz)], δ 1.81 [s, 30H (Cp*)], δ 3.2 [br, 1H (BH₁)], δ 4.6 [pcq, 2H (BH₂) (115 Hz)], δ ≈ 6.7 [br, 2H (BH₃)]. ¹³C{¹H} NMR (CD₂Cl₂, 21 °C) δ 108.1 [10C (Cp*, CCH₃)], δ 12.9 [10C (Cp*, CCH₃)]. IR (KBr, cm⁻¹) 2963 m, 2908 s, 2870 w sh, $\nu(\text{C}-\text{H})$; 2476 s, 2452 s, $\nu(\text{B}-\text{H})$; 1376 s, 1075 m, $\delta(\text{CH}_3)$; 753 s, 683 w, $\rho(\text{CH}_3)$. [δ = deformation mode, ρ = rocking mode].

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(18) Reduction of $[\text{Cp}^*\text{MoCl}_2]_2$ (140 mg, 0.23 mmol) by 2 equiv of LiEt_3BH in toluene at room temperature followed by removal of volatiles *in vacuo* and reaction with a 3-fold excess of $\text{BH}_3\cdot\text{thf}$ (also in toluene) produced an orange solution from which tiny orange crystals of $(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9$ could be isolated. Identification was made by comparison of the measured NMR spectra with those reported for $(\text{C}_5\text{H}_4\text{MeMo})_2\text{B}_5\text{H}_9$ (listed in parentheses). ¹¹B NMR (hexane, 21 °C) δ 62.9 [op-sided doublet – accidental overlap of two signals, 3B] (δ 61.6, 2B and 59.7, 1B) δ 25.8 [m, 2B] (27.8, 2B). ¹H NMR (toluene, 21 °C) δ -6.99 [pcq, 4H] (-7.01, 4H), δ 1.92 [s, 30H] (-), δ 3.85 [br, 1H] (3.94, 1H), 5.37 [br, 2H] (5.53, 2H), 6.22 [b, 2H], (6.34, 2H).

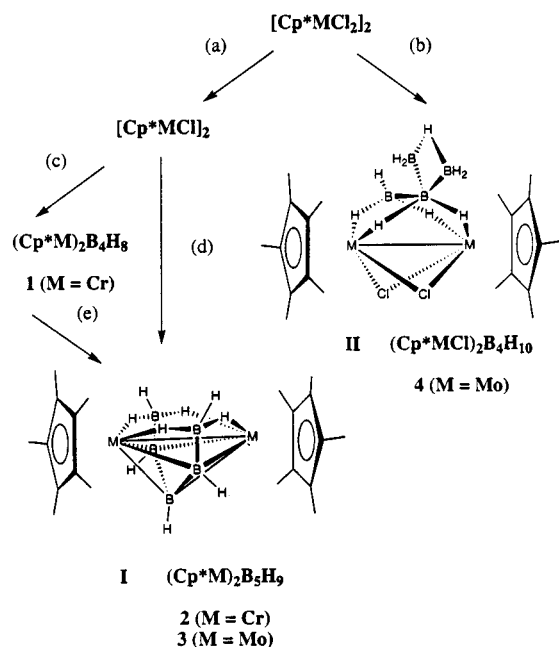


Figure 1. Reactions of dichromium and dimolybdenum precursors with mono-boron reagents. Conditions: (a) M = Cr, +LiEt₃BH, 21 °C; M = Mo, +LiEt₃BH, 21 °C or BH₃·thf, slow; (b) M = Mo, +BH₃·thf, -BH₂Cl, 21 °C; (c) M = Cr, +BH₃·thf, 21 °C; (d) M = Mo, +BH₃·thf, -BH₂Cl, 45 °C; (e) M = Cr, +BHCl₂·SMe₂, 55 °C.

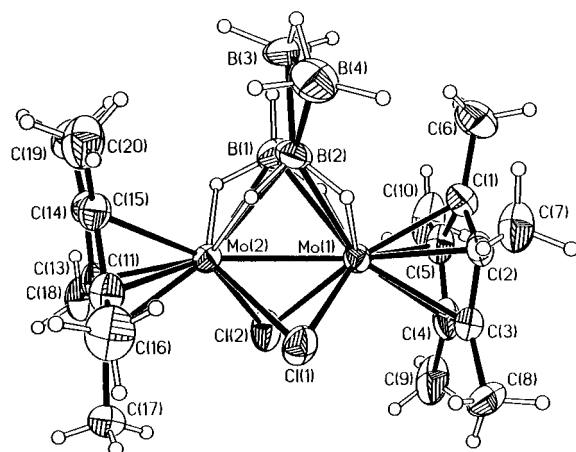


Figure 2. Molecular structure of $(\text{Cp}^*\text{MoCl})_2\text{B}_4\text{H}_{10}$, **4**. Selected bond distances (Å) and angles (°): Mo(1)–Mo(2) 2.7113(13), Mo(1)–Cp*(centroid) 1.934(3), Mo(2)–Cp*(centroid) 1.939(3), Mo(1)–Cl(1) 2.468(3), Mo(2)–Cl(1) 2.463(3), Mo(1)–B(1) 2.42(2), Mo(1)–B(2) 2.42(2), B(1)–B(2) 1.70(2), B(2)–B(3) 1.77(2), B(2)–B(4) 1.87(2), B(3)–B(4) 1.79(3), Mo(1)–H(2) 1.82(2), B(1)–H(2) 1.08(2), Mo(1)–Cl(1)–Mo(2) 66.71(8), Mo(1)–Cl(2)–Mo(2) 66.21(8), B(3)–B(2)–B(4) 58.6(10), Cp*(centroid)–Mo(1)–Mo(2)–Cp*(centroid) 7.99(10).

(*p*-tolyl)NCHN(*p*-tolyl),²¹ the B–B and B–H_b distances for **4** being within the range of values expected for this mode of coordination. The Mo–Mo bond length and Mo(μ -Cl)Mo angles are also consistent with a single bond linking the two Mo(III) centers, as would be expected based on the electron count.^{22,23}

The structure of **4** can be considered as a dimolybdenum unit bridged by two chlorides and by a B₂H₆²⁻ ligand in which the single terminal hydrogen attached to B(2) has been replaced by a B₂H₅ unit. The H₂B···BH₂ unit is planar and approximately perpendicular to the plane defined by the BBHB unit. Furthermore, the B(2)–B(3) and B(2)–B(4) distances are similar to the analogous values in both [CpCo(Me₃Si)₂C₂B₄H₃][B₂H₅]²⁴ and B₃H₇NH₃²⁵ in which the B₂H₅ unit is viewed as being linked to a third boron atom *via* a three-center boron–boron–boron bond. It seems likely that a similar bonding situation occurs in **4**.

If we consider, then, that a terminal hydrogen from a B₂H₆²⁻ unit has been replaced by B₂H₅, **4** represents the first example of a metal complex containing a B₄H₁₀²⁻ ligand. Assembly of this ligand from monoboron precursors demonstrates the ability of transition metal centers to mediate not only B–B but also BBB three-center bond formation. In addition, termination of the BH₃ condensation process at a point where the molybdenum dimer still bears two bridging chlorides offers **4** as a model compound for possible intermediates in the formation of larger M₂B_x clusters. As it stands, **4** represents a novel example of an early transition metal metallaborane with low boron content, a little investigated type of metallaborane.

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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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(19) Reaction of [Cp*MoCl₂]₂ with a 5-fold excess of BH₃·thf in toluene at 45 °C for 120 h yields a mixture of **3** and **4**, as determined by ¹¹B NMR spectroscopy. **3** is easily removed by washing with hexane and crystals of **4** can then be grown by layering a toluene solution with hexane. Spectroscopic data for **4**: MS (EI), P⁺ = 587, 2 Mo, 2 Cl, 4 B atoms, calcd for weighted average of 81 isotopomers falling within the resolution limits of the spectrometer at the measured ion peak, 587.1078, obsd 587.1107. ¹¹B NMR (toluene, 21 °C), δ -56.7 [br, 1B], fwhm = 760 Hz, {¹H} fwhm = 630 Hz; δ -27.2 [d, 1B (110 Hz)], fwhm = 910 Hz, {¹H} fwhm = 550 Hz; δ -11.9 [br, 1B], fwhm = 1320 Hz, {¹H} fwhm = 720 Hz; δ -8.0 [b, 1B], fwhm = 1440 Hz, {¹H} fwhm = 1020 Hz. ¹H NMR ([²H₈]toluene, 21 °C), δ -12.4 [pcq, 4H (MoHB)], δ 0.44 [br, 1H (BHB)], δ 1.76 [s, 30H (Cp*)], δ \approx 2.5 [br, 4H (BH₃)], δ \approx 3.6 [br, 1H (BH₃)]. IR (KBr, cm⁻¹) 2979 m, 2960 m, 2912 s, 2857 w sh, ν (C–H); 2493 s, 2462 s, 2426 vs, ν (B–H_a); 1994 m br, ν (B–H_b); 1376 s, 1028 m, δ (CH₃); others. Crystallographic data for **4**: monoclinic, P2₁/c, *a* = 11.5162(11) Å, *b* = 15.261(2) Å, *c* = 14.815(2) Å, β = 103.183(10)°, *V* = 2535.1(5) Å³, *Z* = 4, *D*_{calcd} = 1.537 g cm⁻³. Of the 3717 reflections collected (CAD4 diffractometer, Mo K α , 293 K), 3523 were independent and 2910 were observed [*I* > 2 σ (*I*)]. All non-hydrogen atoms were anisotropically refined. Both methyl and borane hydrogens were included in the final refinement, the former as idealized riding atoms (C–H = 0.96 Å), the latter with bond length restraints. *R*₁ = 0.0708, *wR*₂ = 0.2148 for observed unique reflections [*I* > 2 σ (*I*)] and *R*₁ = 0.083, *wR*₂ = 0.2290 for all 3523 unique reflections including those with negative intensities.

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