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Article

Synthesis, Structures and Chemistry of the Metallaboranes of Group 4–9 with M₂B₅ Core Having a Cross Cluster M–M Bond

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Abstract: In an attempt to expand the library of M₂B₅ bicapped trigonal-bipyramidal clusters with different transition metals, we explored the chemistry of [Cp*WCl₄] with metal carbonyls that enabled us to isolate a series of mixed-metal tungstaboranes with an M₂B₅{B₄M′} {M = W; M′ = Cr(CO)₄, Mo(CO)₄, W(CO)₄} core. The reaction of in situ generated intermediate, obtained from the low temperature reaction of [Cp*WCl₄] with an excess of [LiBH₄·thf], followed by thermolysis with [M(CO)₅·thf] (M = Cr, Mo and W) led to the isolation of the tungstaboranes [(Cp*W)₂B₄H₈M(CO)₄], 1–3 (1: M = Cr; 2: M = Mo; 3: M = W). In an attempt to replace one of the BH—vertices in M₂B₅ with other group metal carbonyls, we performed the reaction with [Fe₂(CO)₉] that led to the isolation of [(Cp*W)₂B₄H₈Fe(CO)₃], 4, where Fe(CO)₃ replaces a {BH} core unit instead of the {BH} capped vertex. Further, the reaction of [Cp*MoCl₄] and [Cr(CO)₅·thf] yielded the mixed-metal molybdaborane cluster [(Cp*Mo)₂B₄H₈Cr(CO)₄], 5, thereby completing the series with the missing chromium analogue. With 56 cluster valence electrons (cve), all the compounds obey the cluster electron counting rules. Compounds 1–5 are analogues to the parent [(Cp*W₂B₅H₉)] (M = Mo and W) that seem to have generated by the replacement of one {BH} vertex from [(Cp*W₂B₅H₉)] or [(Cp*Mo₂B₅H₉)] (in case of 5). All of the compounds have been characterized by various spectroscopic analyses and single crystal X-ray diffraction studies.

Keywords: chromaborane; metallaborane; mixed-metal cluster; molybdaborane; tungstaborane

1. Introduction

Metallaboranes are a class of compounds intermediate between borane cages on one side and transition metal clusters on the other [1–22]. Thus, they provide a platform for the evaluation of electronic compatibility or incompatibility of metal and borane fragments. One of the most studied and explored cluster systems in metallaborane chemistry is the M₂B₅ system reported by us [23–33] and others [34–41]. Earlier, Fehlner and co-workers showed an attractive route for the synthesis of electronically unsaturated metallaboranes, i.e., those, which are formally electron deficient with respect to the number of skeletal electron pairs (sep), required to maintain the observed molecular geometry [34–36,42,43]. This synthetic utility is derived from the tendency of the unsaturated cluster to react with fragments, which can readily donate further electrons to the cluster framework. For example, [(Cp*Cr)₂B₄H₈] was synthesized by treating [(Cp*Cr)₂B₄H₈] with {BH} sources [35,36]. Following a
similar procedure molybdenum and tungsten analogues were isolated by the same group followed by the chlorinated rhenium analogue \([\text{Cp}^*\text{ReH}]\text{B}_3\text{Cl}_3\) \([37–40]\). Later in 2008 our group was successful in synthesizing a tantalum analogue \([(\text{Cp}^*\text{TaH})\text{B}_5\text{Cl}_5]\) \([37–40]\). Following this, a vanadaborane \([(\text{Cp}^*\text{V})_2\text{B}_3\text{H}_{11}]\) was isolated under similar reaction conditions \([30]\).

As part of our continuous interest on metallaborane chemistry of group 4–9 transition metals \([23–33,44–50]\), we have synthesized a variety of metallaboranes by cluster expansion reactions using transition metal carbonyls or small organic molecules \([46,47,51]\). Recently, we have reported an account of the chemistry of Mo system with group 6 metal carbonyls that generated several \([(\text{Cp}^*\text{Mo})_2\text{B}_2\text{H}_2\text{M}]\text{CO}_4\) derivatives in which one of the \([\text{BH}]\) vertices have been replaced by either \text{Cp}^*\text{M} or metal carbonyl fragments \([49]\). Apart from their significant geometries, these molecules were found to show interesting bonding interactions, as well as electronic structures. Looking at the geometry of the molybdenum systems, tungsten and chromium systems became of interest. Thus, we were interested to see whether the chemistry associated with a \((\text{Cp}^*\text{W})\) fragment would mimic \((\text{Cp}^*\text{Mo})\) or display other interesting variations. Thus, we performed the reaction of an in situ generated intermediate, obtained from the low temperature reaction of \([\text{Cp}^*\text{WCl}_4]\) with an excess of \([\text{LiBH}_4\text{thf}]\), followed by thermolysis with \([\text{M(CO)}_5\text{thf}]\) (M = Cr, Mo and W) that indeed led to the formation of \([(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{Cr(CO)}_4]_1\), \([(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{Mo(CO)}_4]_2\) and, \([(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{W(CO)}_4]_3\). Besides group 6 metal carbonyls, we were also interested to replace the \(\text{B–H}\) fragments of \(\text{B}_5\) core using other metal carbonyl fragments. Thus, we performed the same chemistry using \([\text{Fe}_2\text{(CO)}_9]\) that led to the isolation of an interesting mixed-metal tungstaborane, \([(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{Fe(CO)}_3]_4\). In this report we describe the chemistry of both tungsten and molybdenum derivatives. In addition, we also provide a complete overview of the \(\text{M}_2\text{B}_3\) system of group 4–9 metals.

2. Results and Discussion

2.1. Synthesis and Characterization of Tungstaboranes \([(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{M(CO)}_4]_1–3 (1: M = \text{Cr}; 2: M = \text{Mo}; 3: M = \text{W})\)

As shown in Scheme 1, the reaction of in situ generated intermediate, obtained from the low temperature reaction of \([\text{Cp}^*\text{WCl}_4]\) with an excess of \([\text{LiBH}_4\text{thf}]\), followed by thermolysis with \([\text{M(CO)}_5\text{thf}]\) (M = Cr, Mo and W) yielded the air and moisture sensitive brown solids 1, 2 and 3 along with the reported compounds \([(\text{Cp}^*\text{W(CO)}_2)_2\text{B}_2\text{H}_2\text{M}]\text{CO}_4\), (M = Mo; W) \([50]\) and \([(\text{Cp}^*\text{W})_2\text{B}_3\text{H}_5]\) \([40]\) in moderate yields. The $^{11}\text{B}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectrum of compound 1 showed four signals at $\delta = 70.2, 62.2, 36.5$ and $25.0$ ppm in $1:1:1:1$ ratio indicating the presence of four boron atoms. A similar pattern of $^{11}\text{B}\{^1\text{H}\}$ NMR was also observed for the molybdaborane \([(\text{Cp}^*\text{Mo})_2(\mu-H)_2(\mu_3-H)_2\text{B}_3\text{H}_5\text{M}]\text{CO}_4\) \([49]\). The $^1\text{H}$ NMR spectrum showed four signals in the upfield region, which signifies the presence of four different types of $\text{W–H–B}$ protons. Further, the $^1\text{H}$ NMR rationalizes the presence of \text{Cp}^* ligand. The $^{11}\text{B}\{^1\text{H}\}$ and $^1\text{H}$ NMR of 2 and 3 nearly resemble that of 1, with the four non-equivalent of boron atoms, one chemically equivalent \text{Cp}^* ligand and four different types of $\text{W–H–B}$ protons. The infrared (IR) spectra of 1, 2 and 3 showed the stretching frequencies corresponding to the CO ligands and BH$_3$. Further, the ESI-MS (HR MS) showed a close association among compounds 2 and 3.
In order to confirm the spectroscopic assignments and to determine the solid-state structures of 1–3, X-ray structure analyses were undertaken. The solid-state structures of 1–3, shown in Figure 1, are consistent with the observed spectroscopic data. The asymmetric unit of 1 contains two independent molecules (one is shown in Figure 1), having similar geometric parameters. Although, the bridging hydride ligands and the $B-H$ terminal hydrogen atoms could not be located in the solid state X-ray structure, their positions were fixed based on $^1H$ NMR spectroscopy, as shown in Scheme 1. The core geometry of 1–3 is very similar to our recently reported molybdaboranes $\{[\text{Cp}^*\text{Mo}](\mu-H)_2(\mu_3-H)_2B_3H_4W(CO)_4]\}$ and $\{[\text{Cp}^*\text{Mo}(\mu-H)_2B_3H_4W(CO)_4]\}$ [49]. If the classical skeletal electron counting formalism [52–54] is applied, the 6-sep clusters 1–3 can be viewed as electron-deficient $nido$ species derived from an 8-vertex $oblato$-closo hexagonal bipyramidal cluster, with a cross cluster M–M bond [34–36]. Alternatively, these 6-sep species can be seen as adopting a trigonal bipyramidal geometry in which the central $[W_2B_3]$ unit is capped by $[\text{BH}_3]$ and a group 6 metal carbonyl fragment $(\text{CrCO})_3$ for 1, $[\text{MoCO}]_4$ for 2 and $[W(CO)]_4$ for 3 at the two $[W_2B]$ triangular faces. The W–W bond distances in 1–3 and $[\text{Cp}^*\text{W}]_2B_3H_5(\mu-H)_4$ are comparable (ca. 2.84 Å for 1–3; 2.82 Å for $[\text{Cp}^*\text{W}]_2B_3H_5(\mu-H)_4$) (Table 1). Compounds 1–3 are thus analogous to $[\text{Cp}^*\text{W}]_2B_3H_5(\mu-H)_4$ possessing 56 cve (6 sep) and obey the usual electron counting rules [52–54].

Scheme 1. Synthesis of the tungstaboranes 1–3.

Figure 1. Molecular structures and labeling diagrams of 1, 2 and 3. Bridging hydride ligands and hydrogen atoms attached to the boron atoms could not be located. Selected bond lengths (Å) and bond angles (°) 1: W3–W4 2.824(3), Cr2–W3 2.869(9), Cr2–W4 2.895(10), B5–Cr2 2.32(9), B6–B7 1.67(11), B7–B8 1.79(7), B6–W3 2.15(9), B5–W4 2.27(7), B5–W3 2.43(8), W3–Cr2–W4 58.7(2), B7–B6–B5 129(6), W4–B5–W3 74(2), Cr2–B5–W3 74(2), B6–B5–Cr2 125(4). 2: W1–B2 2.20(7), W1–B4 2.32(5), W1–W2 2.84(2), W1–Mo1 2.98(9), W2–B1 2.19(7), W2–Mo1 3.04(2), B1–B2 1.74(10), B2–B3 1.69(7), W4–Mo2 3.015(2), Mo2–B11 2.439(8), B2–W1–B3 45.0(3), B2–W1–W2 50.28(19), B2–W1–Mo1 95.23(18), W2–W1–Mo1 62.87(13). 3: W12–W13 2.83(10), W12–W11 2.96(10), W12–B11 2.35(3), W12–B12 2.20(2), W12–B13 2.19(2), W13–B12 2.28(2), W13–B11 2.20(2), B11–B12 1.75(3), B12–B13 1.66(3), B13–B14 1.73(3); W12–W11–W13 56.54(2), B11–W12–B12 45.0(9), B11–B12–B13 123.9(18), W12–B11–W13 76.9(9).
Table 1. Selected structural parameters and chemical shifts (\(^1\text{H}\) and \(^{11}\text{B}\) NMR) of metallaboranes 1–5 and other related clusters.

| Metallaborane | \(\text{Avg.}d\) [\(\text{M–M}\)] (Å) | \(\text{Avg.}d\) [\(\text{M–B}\)] (Å) | \(\text{Avg.}d\) [\(\text{B–B}\)] (Å) | \(^{11}\text{B}\) NMR (ppm) | Ref. |
|---------------|---------------------------------|--------------------------------|---------------------------------|------------------------------|-----|
| [{\([\text{Cp}^*\text{Cr}])_2\text{B}_2\text{H}_3\text{Fe}(\text{CO})_3\}] | 2.71                           | 2.15                           | 1.72                           | -                            | [34]|
| [{\([\text{Cp}^*\text{Cr}])_2\text{B}_2\text{H}_6(\text{CO})_3\}] | 2.69                           | 2.13                           | 1.69                           | -                            | [35]|
| [{\([\text{Cp}^*\text{Mo}])_2\text{B}_2\text{H}_3\text{Fe}(\text{CO})_3\}] | 2.82                           | 2.26                           | 1.71                           | 49.2, 46.9, 26.8             | [40]|
| [{\([\text{Cp}^*\text{Mo}])_2\text{B}_2\text{H}_3\text{H}_3\text{W}(\text{CO})_4\}] | 2.82                           | 2.24                           | 1.72                           | 27.9, 41.9, 81.2             | [49]|
| [{\([\text{Cp}^*\text{W}]_2\text{B}_2\text{H}_3\text{H}_3\text{W}(\text{CO})_4\}] | 2.91                           | 2.24                           | 1.73                           | 103.0, 77.9, 77.0            | [49]|
| [{\([\text{Cp}^*\text{W}]_2\text{B}_2\text{H}_3\text{H}_4\text{Cr}(\text{CO})_3\}] | 2.84                           | 2.38                           | 1.73                           | 70.6, 62.2, 36.5, 25.0       | This work |
| [{\([\text{Cp}^*\text{W}]_2\text{B}_2\text{H}_3\text{H}_4\text{Fe}(\text{CO})_3\}] | 2.83                           | 2.27                           | 1.71                           | 70.1, 60.1, 39.1, 25.6       | This work |
| [{\([\text{Cp}^*\text{W}]_2\text{B}_2\text{H}_3\text{H}_4\text{W}(\text{CO})_4\}] | 2.89                           | 2.24                           | 1.71                           | 70.2, 60.1, 35.5, 26.1       | This work |
| [{\([\text{Cp}^*\text{W}]_2\text{B}_2\text{H}_3\text{H}_4\text{Fe}_2(\text{CO})_3\}] | 2.82                           | 2.28                           | 1.74                           | 79.0, 76.2, 41.0, 35.9       | This work |
| [{\([\text{Cp}^*\text{Mo}])_2\text{B}_2\text{H}_3\text{H}_4\text{Fe}_2(\text{CO})_3\}] | 2.82                           | 2.23                           | 1.72                           | 83.5, 81.3, 41.3, 27.1       | This work |

2.2. Synthesis and Characterization of Mixed Metal Tungstaborane [{\([\text{Cp}^*\text{W}]_2\text{B}_2\text{H}_3\text{Fe}(\text{CO})_3\}]_4, 4

After successfully isolating clusters 1–3 with group 6 metal carbonyls, we were interested to explore similar chemistry with other metal carbonyls. In this context, we performed the reaction with group 8 metal carbonyls. As shown in Scheme 2, the reaction of in situ generated intermediate, obtained from the low temperature reaction of [{\([\text{Cp}^*\text{WCl}])_2\text{B}_2\text{H}_3\text{Fe}(\text{CO})_3\}] with an excess of [{\([\text{LiBH}_4]+\text{thf}\})], followed by thermolysis with [{\text{Fe}_2(\text{CO})_4}] yielded the air and moisture sensitive brown solid, 4 in moderate yield. The \(^{11}\text{B}\)\(^1\text{H}\) NMR of compound 4 displayed four resonances at \(\delta = 79.0, 76.2, 41.0,\) and 35.8 ppm, that rationalize the presence of four different boron environments. In addition to the resonances for \(\text{BH}_3\) protons, the \(^1\text{H}\) NMR spectrum showed a signal at \(\delta = 2.24\) ppm corresponding to the \(\text{Cp}^*\) ligands and two upfield signals at \(\delta = -6.97\) and \(-12.92\) ppm, that are probably due to \(\text{W}–\text{H}–\text{B}\) protons. The presence of CO ligands is confirmed by the IR spectrum. The mass spectrum of 4 showed a molecular ion peak at \(m/z\) 853.1456.

The framework geometry of 4 was established by its solid-state structure determination. As shown in Figure 2, it depicts a bicapped trigonal bipyramidal geometry, in which the \([\text{W}_2\text{B}_2\text{Fe}]\) trigonal bipyramidal core is capped by the boron atoms B42 and B41 at the triangular \([\text{W}_2\text{B}]\) and \([\text{W}_2\text{Fe}]\) faces similar to compounds 1–3. One of the major differences is the position of the \(\text{Fe}(\text{CO})_3\) unit in the molecule. While in 1–3 the metal carbonyl fragment caps one of the \([\text{W}_2\text{B}]\) triangular faces, in compound 4 it is part of the triangular faces with tungsten \([\text{W}_2\text{Fe}]\). The geometry of compound 4 resembles that of the tungsten-ruthenium complex [{\([\text{Cp}^*\text{W}]_2\text{B}_2\text{H}_3\text{Ru}(\text{CO})_3\}] [33] where \(\text{Ru}(\text{CO})_3\) occupies the same position as that of \(\text{Fe}(\text{CO})_3\). The \(\text{W}–\text{W}\) bond distance in 4 is comparable to that of 1–3. This type of \(\text{M}_2\text{B}_5\) molecule is rare. With 56 cve (6 sep), compound 4 also obeys the electron counting rules and is an analog of [{\([\text{Cp}^*\text{W}]_2\text{B}_5\text{H}_5(\mu-\text{H})_4\}].
2.3. Synthesis and Characterization of the Molybdaborane [(Cp*Mo)₂B₄H₈Cr(CO)₄], 5

Recently, we were successful in isolating various mixed-metal molybdaboranes [49,50] by treating the intermediate, obtained from the reaction of Cp*MoCl₄ and LiBH₄, with [W(CO)₅·thf]. Following the same procedure we performed the reaction with [Cr(CO)₅·thf] and as expected, the reaction enabled us to isolate compound 5 (Scheme 3). Details of its spectroscopic and structural characterization are discussed below.

Compound 5 was obtained as a green solid in moderate yield along with the known compound [(Cp*Mo)₂B₃H₄] [37,38]. The ¹¹B [¹H] NMR spectrum of 5 resembles that of 1–4 with four distinct boron environments at δ = 83.5, 81.3, 41.3, and 27.1 ppm. The ¹H NMR spectrum shows four signals in the upfield region, which signifies the presence of four different types of hydride ligands (δ = −6.48, −10.56, −11.89, −15.42 ppm). Further, the ¹H NMR rationalizes the presence of one equivalent Cp* ligand. Presence of the CO ligands was confirmed by IR measurements. The ESI-MS (HR SM) showed a molecular ion peak at m/z [(M + Na)⁺] = 705.0523, which corresponds to the molecular formula C₂₄H₃₈B₄O₄Mo₂CrNa.

To confirm the spectroscopic assignments, an X-ray crystallographic analysis was undertaken. The core geometry of 5 is similar to the recently reported molybdaboranes [(Cp*Mo)₂(μ-H)₂(μ3-H)₂B₄H₄W(CO)₄] and [(Cp*Mo)₂(μ-H)₂B₄H₄W(CO)₅] [49]. The asymmetric unit
of 5 contains two independent molecules, which differ slightly in terms of geometric parameters (one is shown in Figure 3). Although, the bridging hydride ligands could not be located in the solid-state X-ray structure, their positions were fixed based on $^1$H NMR, as shown in Scheme 3. With 6 sep, it adopts the expected trigonal bipyramidal geometry in which the central [Mo$_2$B$_3$] unit is capped by [BH$_3$] and the chromium carbonyl fragment [Cr(CO)$_4$] at the two [Mo$_2$B] triangular faces. The Mo–Mo bond distance is in accordance with the reported mixed molybdaboranes (Table 1). Compound 5 is thus an additional entry to the class of mixed-metal molybdaborane clusters.

In metallaborane chemistry, the mutually synergistic interactions of metal and organic ligands can generate molecules with interesting and diverse geometries. As evident in Table 2, it was shown earlier that group 4 metals from the reaction of [Cp$_2$MCl$_2$] (M = Zr, Hf) with LiBH$_4$ and [BH$_3$·thf] generated fused clusters [(Cp$_2$M)$_2$B$_3$H$_11$] (M = Zr/Hf) [55,56] where two arachno-ZrB$_3$ moieties are fused with the B$_3$ unit. As expected according to Mingos’s formalism it possesses an electron count of 54 cve. Under similar reaction conditions group 5 metals vanadium and tantalum give [(CpV)$_2$B$_3$H$_11$] [30] and [(Cp*$^\text{Ta}$)$_2$B$_3$H$_11$] [23] respectively, with a geometry that resembles a nido hexagonal bipyramid with a single missing equatorial vertex. A similar structural interpretation has been suggested for the [(Cp*$^\text{M}$)$_2$B$_5$H$_9$] systems (M = Cr [34–36], Mo [37,38], and W [40]), as well as for [(Cp*$^\text{Re}$)$_2$B$_5$Cl$_3$] [39]; in each case, the trigonal bipyramidal M$_2$B$_3$ unit is capped by two BH$_3$ fragments over the M$_2$B faces. A comparison of the structural parameters and chemical shifts of these analogues is shown in Table 2. Another interesting molecule from group 5 is [(Cp*$^\text{Ta}$)$_2$B$_5$H$_11$Cl$_2$] [23] having a contrasting geometry. It has a nido structure based on a closo dodecahedron by removing one five-connected vertex. Apart from these M$_2$B$_5$ molecules, group 8 and 9 metals generate monometallic clusters viz. [($\eta^5$-C$_5$H$_5$)FeB$_2$H$_9$] [57], [Cp*$^\text{Ru}$B$_2$H$_9$] [58], [($\eta^5$-C$_5$H$_5$)CoB$_2$H$_9$] [59] and [($\eta^5$-C$_5$Me$_5$)IrB$_2$H$_9$] [60] showing interesting sandwich structures mimicking their organometallic counterpart ferrocene. These molecules provided an additional bridge between metallaborane and organometallic chemistry.

Figure 3. Molecular structure and labeling diagram of 5. Bridging hydride ligands could not be located. Selected bond lengths (Å) and bond angles (°): 5: Mo1–Mo2 2.821(9), Mo1–Cr1 2.923(13), B31–B32 1.733(14), B32–B33 1.706(14), B33–B34 1.723(13), B31–Mo1 2.245(10); Mo1–Cr1–Mo2 57.9(3), Mo1–B311–Mo2 76.4(3), B31–B32–B33 118.4.
Table 2. Selected structural data and $^{11}$B chemical shifts of different M$_2$B$_5$ clusters from Group 4–9 metals.

| Metallaborane                          | Geometry | Sep | Avg.$d$ [M–M] (Å) | Avg.$d$ [M–B] (Å) | Avg.$d$ [B–B] (Å) | $^{11}$B NMR (ppm) | Ref.   |
|----------------------------------------|----------|-----|-------------------|-------------------|-------------------|-------------------|--------|
| [(Cp$_2$M)$_2$B$_3$H$_{11}$] M = Zr, Hf |          | 10  | b                 | 2.50 (Zr)         | 1.78 (Zr)         | 8.1, 2.5, −4.1 (Zr) | [55,56]|
| [M$_2$B$_3$H$_{11}$] M = CpV, Cp$^+$Ta |          | 6   |                   | 2.76 (V)          | 2.23 (V)          | −1.8, 3.4, 21.9 (V) | [23,30]|
| [Cp$^+$TaB$_3$H$_{11}$Cl$_2$]          |          | 8   |                   | 3.22              | 2.38              | 77.7, 18.8, 15, −10 | [23]   |
| [(Cp$^+$M)$_2$B$_3$H$_6$] M = Cr, Mo, W |          | 6   |                   | 2.62 (Cr)         | 2.15 (Cr)         | 25.0, 86.2, 91.5 (Cr) | [36–38,40]|
| [(Cp$^+$Mo)$_2$B$_3$EH$_3$X]           |          | 6   |                   | 2.78 (S)          | 2.21 (S)          | 101.1, 76.7, 40.3, 10.1 (S) | [31]   |
| E = S, Se; X = H                       |          |     |                   | 2.77 (Se)         | 2.24 (Se)         | 100.7, 76.7, 41.8, 16.8 (Se) |       |
| E = Te; X = Cl                        |          |     |                   | 2.84 (Te)         | 2.17 (Te)         | 95.5, 73.2, 40.7, 26.7 (Te) |       |
Table 2. Cont.

| Metallaborane                                                                 | Geometry | Sep * | Avg. \(d\) [M–M] (Å) | Avg. \(d\) [M–B] (Å) | Avg. \(d\) [B–B] (Å) | \(^{11}B\) NMR (ppm) | Ref. |
|-----------------------------------------------------------------------------|----------|-------|-----------------------|-----------------------|-----------------------|---------------------|------|
| \([\text{Cp}^\ast\text{Re}]_2\text{B}_2\text{H}_2\text{M}\) \(\text{M} = \text{Fe(CO)}_3\) | 6       | 2.76  | 2.20                  | 1.74                  | 28.1, 48.3, 88.3      | [39] |
| \([\text{Cp}^\ast\text{W}]_2\text{B}_2\text{H}_2\text{M}\) \(\text{M} = \text{Cr(CO)}_4\) | 6       | 2.82  | 2.38                  | 1.74                  | 70.2, 25.6 (Mo)       | This work          |
| \([\text{Cp}^\ast\text{W}]^2\text{B}_2\text{H}_2\text{M}\) \(\text{M} = \text{Mo(CO)}_4\) | 6       | 2.84  | 2.23                  | 1.71                  | 70.1, 25.6 (Mo)       | This work          |
| \([\text{Cp}^\ast\text{W}]_2\text{B}_2\text{H}_2\text{M}\) \(\text{M} = \text{W(CO)}_4\) | 6       | 2.83  | 2.27                  | 1.71                  | 70.2, 25.6 (Mo)       | This work          |
| \([\text{Cp}^\ast\text{Cr}]_2\text{B}_2\text{H}_2\text{M}\) \(\text{M} = \text{Cr(CO)}_4\) | 6       | 2.70  | 2.15                  | 1.71                  | 27.3, 117.5 (Fe)      | [35] |

* Skeletal electron pair count. * No M–M bond.
3. Materials and Methods

3.1. General Procedures and Instrumentation

All the manipulations were conducted under an argon atmosphere using standard Schlenk techniques. Solvents were distilled prior to use under an argon atmosphere. [Cp*MoCl₄], [Cp*WCl₄], [M(CO)₅·thf] (M = Cr, Mo, and W) were prepared according to literature methods [61–63], while other chemicals, such as [LiBH₄]·2.0 M in thf, Cp*H, n-BuLi, [Cr(CO)₆], [Mo(CO)₆], W(CO)₆, and Fe₂(CO)₉ were obtained commercially (Sigma-Aldrich, St. Louis, MO, USA) and used as received. Mel was purchased from Aldrich and freshly distilled prior to use. The external reference for the ¹¹B NMR, [Bu₄N(B₃H₆)] was synthesized with the literature method [64]. Preparative thin layer chromatography (TLC) was carried on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates, Merck, Darmstadt, Germany). NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometer (Bruker, Billerica, MA, USA). The residual solvent protons were used as a reference (δ, ppm, CDCl₃; 7.26), while a sealed tube containing [Bu₄N(B₃H₆)] in [D₈] [64] benzene (δB, ppm, −30.07) was used as an external reference for the ¹¹B NMR. Infrared spectra were recorded on a Nicolet iS10 spectrometer (JASCO, Easton, MD, USA). The photo-reactions described in this report were conducted in a Luzchem LZC-4 V photo reactor (Luzchem, Ottawa, Canada), with irradiation at 254–350 nm. MALDI-TOF mass spectra were recorded on a Bruker Ultraflextreme (Bruker, Billerica, MA, USA) by using 2,5-dihydroxybenzoic acid as a matrix and a ground steel target plate.

Synthesis of 1–3: In a flame-dried Schlenk tube [Cp*WCl₄] (0.1 g, 0.22 mmol) in 15 mL of toluene was treated with a 5-fold excess of [LiBH₄·thf] (0.55 mL, 1.1 mmol) at −78 °C and allowed to stir at room temperature for one hour. After removal of toluene, the residue was extracted into hexane and filtered through Celite. The brownish-green hexane extract was dried in vacuo, and taken up in 15 mL of THF and heated at 65 °C with [M(CO)₅·thf] (M = Cr, Mo, and W) for 22 h. The solvent was evaporated in vacuo and residue was extracted into hexane and passed through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (75:15 v/v) mixture yielded brown 1 (0.011 g, 6%) (in case of [Cr(CO)₅·THF]) along with known [(Cp*W)Cl₂·thf] (0.048 g, 31%), greenish brown 2 (0.014 g, 7%) (in case of [Mo(CO)₅·THF]) along with earlier reported [(Cp*W)Cl₂·B₂H₆Mo(CO)₄] (0.028 g, 13%), [(Cp*W)Cl₂·B₂H₆] (0.050 g, 32%) and green 3 (0.013 g, 6%) (in case of [W(CO)₅·thf]) along with earlier reported [(Cp*W)Cl₂·B₂H₂W(CO)₄] (0.046 g, 20%) and [(Cp*W)Cl₂·B₂H₂] (0.044 g, 29%).

1: ¹¹B[¹H] NMR (22 °C, 128 MHz, CDCl₃): δ = 70.6 (br, 1B), 62.2 (br, 1B), 36.5 (br, 1B), 25.0 (br, 1B); ¹H NMR (22 °C, 400 MHz, CDCl₃): δ = 4.12 (br, 2H, BH₄), 3.66 (br, 2H, BH₄), 2.22 (s, 15H, Cp*), 2.21 (s, 15H, Cp*), −6.88 (br, 1H, W–H–B), −10.71 (br, 1H, W–H–B), −11.69 (br, 1H, µ₃-H), −14.27 (br, 1H, µ₂-H); IR (hexane) ν/cm⁻¹: 2525 w(BH₄, 1922, 1855 w(CO).
2: HR-MS (high resolution mass spectrometry) (ESI⁺): m/z calculated for [C₂₄H₃₈O₄B₄W₂MoK⁺]: 939.0853; found 939.0834; ¹¹B[¹H] NMR (22 °C, 128 MHz, CDCl₃): δ = 70.1 (br, 1B), 60.1 (br, 1B), 39.1 (br, 1B), 25.6 (br, 1B); ¹H NMR (22 °C, 400 MHz, CDCl₃): δ = 6.38, (br, 4H, BH₄), 2.20 (s, 30H, Cp*), −6.21 (br, 1H, W–H–B), −8.53 (br, 1H, W–H–B), −11.06 (br, 1H, µ₃-H), −13.0 (br, 1H, µ₂-H); IR (hexane) ν/cm⁻¹: 2482 w(BH₄), 2011, 1945, 1878 w(CO).
3: HR-MS (ESI⁺): m/z calculated for [C₂₄H₃₈O₄B₄W₃H⁺]: 987.1749; found 987.1727; ¹¹B[¹H] NMR (22 °C, 128 MHz, CDCl₃): δ = 70.3 (br, 1B), 60.1 (br, 1B), 35.5 (br, 1B), 26.1(br, 1B); ¹H NMR (22 °C, 400 MHz, CDCl₃): δ = 6.05 (br, 2H, BH₄), 5.78 (br, 2H, BH₄), 2.18 (s, 30H, Cp*), −6.74 (br, 1H, W–H–B), −7.05 (br, 1H, W–H–B), −10.90 (br, 1H, µ₃-H), −13.13 (br, 1H, µ₂-H); IR (hexane) ν/cm⁻¹: 2467 w(BH₄), 2028, 1984, 1926, 1878, 1835 w(CO).

Synthesis of 4: In a flame-dried Schlenk tube [Cp*WCl₄] (0.1 g, 0.22 mmol) in 15 mL of toluene was treated with a 5-fold excess of [LiBH₄·thf] (0.55 mL, 1.1 mmol) at −78 °C and allowed to stir at room temperature for one hour. After removal of toluene, the residue was extracted into hexane and filtered through Celite. The brownish-green hexane extract was dried in vacuo, and taken up in 15 mL of THF and heated at 65 °C with [M(CO)₅·thf] (M = Cr, Mo, and W) for 22 h. The solvent was evaporated in vacuo and residue was extracted into hexane and passed through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (75:15 v/v) mixture yielded brown 1 (0.011 g, 6%) (in case of [Cr(CO)₅·THF]) along with known [(Cp*W)Cl₂·thf] (0.048 g, 31%), greenish brown 2 (0.014 g, 7%) (in case of [Mo(CO)₅·THF]) along with earlier reported [(Cp*W)Cl₂·B₂H₆Mo(CO)₄] (0.028 g, 13%), [(Cp*W)Cl₂·B₂H₆] (0.050 g, 32%) and green 3 (0.013 g, 6%) (in case of [W(CO)₅·thf]) along with earlier reported [(Cp*W)Cl₂·B₂H₂W(CO)₄] (0.046 g, 20%) and [(Cp*W)Cl₂·B₂H₂] (0.044 g, 29%).
through a frit using Celite. The brownish-green hexane extract was dried in vacuo, and taken in 15 mL of THF and heated at 65 °C with Fe$_2$(CO)$_9$ for 22 h. The solvent was evaporated in vacuo and residue was extracted into hexane and passed through celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH$_2$Cl$_2$ (75:15 v/v) mixture yielded green 4 (0.020 g, 11%) along with known [(Cp*W)$_2$B$_5$H$_9$] (0.040 g, 26%).

4: HR-MS (ESI$^+$): m/z calculated for [C$_{23}$H$_{38}$O$_3$B$_4$W$_2$Fe+Na$^+$]: 853.1459; found 853.1456; $^{11}$B NMR (22 °C, 128 MHz, CDCl$_3$): $\delta$ = 79.0 (br, 1B), 76.2 (br, 1B), 41.0 (br, 1B), 35.8 (br, 1B); $^1$H NMR (22 °C, 400 MHz, CDCl$_3$): $\delta$ = 6.37, (br, 2H, BH$_t$), 6.05, (br, 2H, BH$_t$), 2.24 (s, 30H, Cp*), $-$6.79 (br, 2H, W–H–B), $-$12.92 (br, 2H, W–H–B); IR (hexane) $\nu$/cm$^{-1}$: 2482 w(BH$_t$), 1984, 1918 w(CO).

Synthesis of 5: In a flame-dried Schlenk tube [Cp*MoCl$_4$]$_2$ (0.1 g, 0.27 mmol) in 10 mL of toluene was treated with a 5-fold excess of [LiBH$_4$·thf] (0.7 mL, 1.4 mmol) at $-78$ °C and allowed to stir at room temperature for one hour. After removal of toluene, the residue was extracted into hexane and filtered through a frit using Celite. The brownish-green hexane extract was dried in vacuo, and taken in 10 mL of THF and heated at 65 °C with [Cr(CO)$_5$·thf] for 18 hours. The solvent was evaporated in vacuo and residue was extracted into hexane and passed through celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH$_2$Cl$_2$ (80:10 v/v) mixture yielded dark brown 5 (0.026 g, 14%) along with known [(Cp*Mo)$_2$B$_5$H$_9$] (0.042 g, 29%).

5: HR-MS (ESI$^+$): m/z calculated for [C$_{24}$H$_{38}$O$_7$B$_4$Mo$_2$Cr+Na$^+$]: 705.0553; found 705.0523; $^{11}$B NMR (22 °C, 128 MHz, CDCl$_3$): $\delta$ = 83.5 (br, 1B), 81.3 (br, 1B), 41.3 (br, 1B), 27.1 (br, 1B); $^1$H NMR (22 °C, 400 MHz, CDCl$_3$): $\delta$ = 6.29, (br, 2H, BH$_t$), 5.89, (br, 2H, BH$_t$), 2.06 (s, 30H, 2Cp*), $-$6.48 (br, 1H, Mo–H–B), $-$10.56 (br, 1H, Mo–H–B), $-$11.89 (br, 1H, $\mu_3$-H), $-$15.42 (br, 1H, $\mu_3$-H); IR (hexane) $\nu$/cm$^{-1}$: 2474 (BH$_t$), 1996, 1941, 1886, 1851 (CO).

3.2. X-ray Structure Analysis

Single crystals of 1–5 suitable for X-ray diffraction were grown from hexane/CH$_2$Cl$_2$ solution at $-10$ °C. Crystal data for 2, 3, 4 and 5 were collected and integrated using D8 VENTURE Bruker AXS single crystal diffractometer and for 1 Bruker Kappa apexII CCD single crystal diffractometer, equipped with graphite monochromated Mo Kα ($\lambda$ = 0.71073 Å) radiation (details Table 3). Data collection for 1 was carried out at 296 K and for 2, 3, 4 and 5 at 150 K, using $\omega$–$\varphi$ scan modes. Multi-scan absorption correction has been employed for the data using SADABS [65–67] program. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 [65–67] and refined using SHELXL-2014 [65–67]. The structures were drawn using Olex2 [68]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1893708 (1), CCDC-1893709 (2), CCDC-1893711 (3), CCDC-1893712 (4) and CCDC-1893713 (5) (see Supplementary Materials). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table 3. Crystallographic data and structure refinement information for 1–5.

|        | 1            | 2            | 3            | 4            | 5            |
|--------|--------------|--------------|--------------|--------------|--------------|
| **Empirical formula** | C\textsubscript{24}H\textsubscript{37}B\textsubscript{4}O\textsubscript{4}CrW\textsubscript{2} | C\textsubscript{24}H\textsubscript{30}B\textsubscript{4}O\textsubscript{4}MoW\textsubscript{2} | C\textsubscript{24}H\textsubscript{30}B\textsubscript{4}O\textsubscript{4}W\textsubscript{3} | C\textsubscript{23}H\textsubscript{38}B\textsubscript{4}O\textsubscript{4}FeW\textsubscript{2} | C\textsubscript{24}H\textsubscript{38}B\textsubscript{4}O\textsubscript{4}CrMo\textsubscript{2} |
| **Formula weight** | 852.47 | 889.36 | 977.27 | 829.32 | 677.66 |
| **Crystal system** | Orthorhombic | Triclinic | Triclinic | Monoclinic | Monoclinic |
| **Space group** | P\textsubscript{ca}2\textsubscript{1} | P\textsubscript{\textit{1}} | P\textsubscript{\textit{1}} | P\textsubscript{2\textsubscript{1}/n} | P\textsubscript{2\textsubscript{1}/c} |
| **a (Å)** | 23.323(5) | 16.3096(16) | 19.9272(18) | 16.685(13) | 19.454(2) |
| **b (Å)** | 14.555(3) | 18.8186(18) | 19.390(2) | 16.2795(16) | 21.905(2) |
| **c (Å)** | 17.009(7) | 19.9272(18) | 19.390(2) | 15.073(17) | 94.494(4) |
| **α (°)** | 90.000(10) | 85.532(3) | 85.443(4) | 90 | 90 |
| **β (°)** | 90.000(10) | 71.947(3) | 79.671(3) | 110.538(4) | 90 |
| **γ (°)** | 90 | 89.111(3) | 70.858(3) | 90 | 90 |
| **V(Å\textsuperscript{3})** | 5774(3) | 5797.1(10) | 5780.6(10) | 2686.6(5) | 5626.2(9) |
| **Z** | 8 | 8 | 8 | 4 | 8 |
| **D_{\text{calc}} (g/cm\textsuperscript{3})** | 1.961 | 2.038 | 2.246 | 2.050 | 1.600 |
| **F(000)** | 3240 | 3328 | 3584 | 1576 | 2736 |
| **μ (mm\textsuperscript{-1})** | 8.346 | 8.370 | 11.937 | 9.097 | 1.285 |
| **θ Range (°)** | 3.2–22.1 | 2.27–27.51 | 2.26–27.50 | 2.50–27.52 | 2.57–27.46 |
| **no. of reflns collected** | 8977 | 26525 | 26460 | 6147 | 12768 |
| **no. of unique reflns [I > 2σ(I)]** | 3645 | 22650 | 22550 | 5606 | 10014 |
| **goodness-of-fit on F\textsuperscript{2}** | 0.997 | 1.065 | 1.104 | 1.063 | 1.081 |
| **final R indices [I > 2σ(I)]** | R\textsubscript{1} = 0.0879, wR\textsubscript{2} = 0.1580 | R\textsubscript{1} = 0.0349, wR\textsubscript{2} = 0.0819 | R\textsubscript{1} = 0.0965, wR\textsubscript{2} = 0.1988 | R\textsubscript{1} = 0.0379, wR\textsubscript{2} = 0.1175 | R\textsubscript{1} = 0.0810, wR\textsubscript{2} = 0.1827 |
| **R indices (all data)** | R\textsubscript{1} = 0.2386, wR\textsubscript{2} = 0.2215 | R\textsubscript{1} = 0.0458, wR\textsubscript{2} = 0.0880 | R\textsubscript{1} = 0.1133, wR\textsubscript{2} = 0.2103 | R\textsubscript{1} = 0.0421, wR\textsubscript{2} = 0.1236 | R\textsubscript{1} = 0.1054, wR\textsubscript{2} = 0.2014 |
4. Conclusions

In summary, we have described the synthesis of various homo and heterometallic tungstaborane clusters [(Cp*W)3B3H3M], 1–4: M = Cr(CO)3; 2: M = Mo(CO)3; 3: M = W(CO)3; 4: M = Fe(CO)3] with different metal carbonyl fragments. Reaction of [Cp*MoCl4] and [Cr(CO)5·thf] yielded the mixed-metal molydababorane cluster [(Cp*Mo)2B3H3Cr(CO)3]. Compounds 1–5 are analogous to their parent tungstaborane/molydababorane [(Cp*M)2B3H3|M = W, Mo] that seem to have been generated by the replacement of one [BH] vertex from [(Cp*W)2B2H4] or [(Cp*Mo)2B2H4] (in case of 5). One of the major differences in these molecules is the position of the Fe(CO)3 unit in compound 4. While in 1–3 the metal carbonyl fragment caps one of the [W2B] triangular faces, in compound 4, Fe(CO)3 is part of the triangular [W2Fe] faces. This type of M2B5 molecule is rare. These results further demonstrate the use of metal carbonyls to generate molecular clusters that show exciting geometry and bonding interactions.

Supplementary Materials: The following are available online at http://www.mdpi.com/2304-6740/7/3/27/s1. It contains 1H, 11B·1H, 13C·1H NMR and mass spectra; X-ray analysis details and CIF and the checkCIF.

Author Contributions: R.B. (Ranjit Bag) and S.S. conceived and designed the experiment; R.B. (Ranjit Bag) and S.S. performed the synthesis and the spectroscopic analysis; results were discussed with R.B. (Rosmita Borthakur) and S.G. project administration. T.R., V.D. and J.-F.H. performed the X-ray analysis. Borthakur), B.M. and S.G.; R.B. (Rosmita Borthakur) prepared the manuscript with feedback from S.G. and J.-F.H.; T.R., V.D. and J.-F.H. performed the X-ray analysis.

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