



B–H bond iodination of polyhedral dimolybdaborane and dimolybdathiaborane clusters



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ABSTRACT

Reaction of $[\text{Cp}^*\text{MoCl}_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with excess of $[\text{LiBH}_4 \cdot \text{thf}]$ followed by pyrolysis with NaI yielded B–I inserted $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_{9-n}\text{I}_n]$, **1–3** (**1**: $n = 1$; **2**: $n = 2$; **3**: $n = 3$). In parallel to the formation of **1–3**, the reaction also produced known $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$ and $[(\text{Cp}^*\text{Mo})_2(\mu\text{-I})_4]$ in good yields. Under the similar reaction conditions, dimolybdathiaborane $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_4\text{S}_2]$ yielded iodine substituted dimolybdathiaboranes, $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{S}_2\text{H}_{4-n}\text{I}_n]$, **4** and **5** (**4**: $n = 2$; **5**: $n = 3$) in good yields. All the new compounds have been characterized in solution by IR, ^1H and ^{11}B NMR as simple substituted derivatives of $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$ and $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_4\text{S}_2]$. The solid state structures were established unambiguously by crystallographic analysis of compounds **1–5**.

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1. Introduction

Chemistry of polyhedral boranes and carboranes presented decades back through the electrophilic substitution of cage B–H terminal bonds by Hawthorne [1–5], Grimes [6–8] and others [9–15]. Such studies [16–18], in particular to those led to peralkylation, perhydroxylation or perhalogenation, continue to be of significant consideration as the persubstituted borane or carborane clusters bear potential applicability in several areas as targets for anti tumor activity [19], least coordinating anion [20], components of radio imaging reagent [21]. Recently, Hawthorne and co-workers reported the synthesis of a tumor-targeting nano-molecular magnetic resonance imaging contrast agent (MRI CA) derived from a vertex-differentiated icosahedral *closo*- B_{12}^{2-} core [22]. Further, derivative chemistry has been shown to be crucial in some instances [23,24]. For example, iodinated boron clusters are valuable synthons for the preparation of compounds containing the carborane pharmacophore [25]. Unusually, among all the halogenated ortho-carboranes only iodo derivatives are able to participate in palladium-catalyzed cross-coupling reactions, thus providing synthetically valuable coupling products.

The discovery of both cluster electron counting rules and the isolobal principle which bloomed the development of metallaborane chemistry, provide a solid foundation for understanding

the interrelationships between structure and composition of cluster compounds [26–28]. As a result, several metallaboranes of groups 5–9 have been synthesized, in moderate to good yields, which are prone to show different structural varieties [29–37]. Having in hand a wide range of metallaborane and metal-laheteroborane compounds and bearing in mind the utility of halogenated metallaboranes, it is desirable to have systematic and efficient methods for attaining B-perhalogenation of metallaborane compounds that would contribute to their utility. As the *exo*-cluster substitution in metallaborane chemistry differs significantly from those of carboranes, no systematic chemistry has been established for the development of such compounds [38,39]. Earlier we have reported the reaction of $[\text{Cp}^*\text{MCl}_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, $\text{M} = \text{Mo}, \text{W}$) with $[\text{LiBH}_4 \cdot \text{thf}]$ and $\text{BHCl}_2 \cdot \text{SMe}_2$ for the formation of B–Cl substituted products [40,41]. Introduction of substituents on the boron in metallaboranes is important if one wishes to make complexes that are resistant to deboronation (decapitation) by electrophiles [42–45]. Further, halogenation of metallaborane clusters has specific interest, since they are important in preparing functionalized clusters for assembly into larger arrays, extended poly-metallic clusters [43], and B–B linked systems [46,47]. Herein we report the results of the reaction between $[\text{Cp}^*\text{MoCl}_4]$ and $\text{LiBH}_4 \cdot \text{thf}$ followed by mild pyrolysis with NaI to afford iodine substituted molybdaboranes. We have also explored the action of sodium iodide as an agent for B-iodination on the molybdathiaborane $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_4\text{S}_2]$ [48,49], which led to the isolation of iodinated dimolybdathiaborane derivatives.

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2. Result and discussion

2.1. Synthesis and characterization of 1–3

As shown in Scheme 1, reaction of $[\text{Cp}^*\text{MoCl}_4]$ with excess of $[\text{LiBH}_4 \cdot \text{thf}]$ followed by excess of NaI in toluene at 90 °C for 20 h resulted in the formation B–I inserted $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_{9-n}\text{I}_n]$, **1–3** (**1**: $n = 1$; **2**: $n = 2$; **3**: $n = 3$). The reaction was monitored by ^{11}B NMR spectroscopy, which revealed formation of new B–H substituted compounds, as indicated by the sharp resonances in the region between $\delta = 70$ and 20 ppm. In addition to the formation of compounds **1–3**, the reaction also yielded known dimolybdaborane $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$ and one non-boron compound $[(\text{Cp}^*\text{Mo})_2(\mu\text{-I})_4]$. Note that reports on the synthesis of $[(\text{Cp}^*\text{Mo})_2(\mu\text{-I})_4]$ are known in the literature, for example, the reduction of $[\text{Cp}_2^*\text{Mo}_2\text{I}_4]\text{I}_3$ or $[\text{Cp}^*\text{MoI}_3]$ with PMe_3 led to the formation $d^3\text{--}d^3$ binuclear complex $[(\text{Cp}^*\text{Mo})_2(\mu\text{-I})_4]$ in good yields [50,51]. Although the objective of periodination of $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$ cluster was not achieved, a range of B-iodinated metallaboranes and $[(\text{Cp}^*\text{Mo})_2(\mu\text{-I})_4]$ complex have been isolated in moderate to good yields. Descriptions of the characterizations of **1–3** from IR, ^1H , ^{11}B NMR and X-ray diffraction studies follow.

Compounds **1–3** have been isolated as brown solids in 15, 10 and 6% yields respectively. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **1** shows substitution of one of the B–H protons of $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$ by iodine and shows the presence of five types of boron environments at $\delta = 65.0$, 62.3, 51.9, 29.3 and 27.5 ppm. The peak at 51.9 ppm is due to the down field chemical shift of the boron attached to iodine. The ^1H NMR spectra reveals four types of B–H_i protons in the ratio of 1:1:1:1, and the presence of four Mo–H–B protons at $\delta = -6.57$, -7.82 ppm. Similarly, the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **2** rationalized the presence of three types of boron environments in the ratio of 1:2:2 at $\delta = 62.6$, 53.2 and 32.9 ppm respectively. The resonance at $\delta = 53.2$ ppm showed no coupling with hydrogen confirms the B–I environment. Furthermore, the ^1H NMR spectrum of **2** shows the presence of Cp* and Mo–H–B protons. In a similar fashion, compound **3** has been characterized in comparison with the spectroscopic data of **1** and **2**. The NMR data of **3** are consistent with the solid-state X-ray structures, shown in Fig. 2. Although the mono, di and tri-iodo substituted metallaboranes have been isolated, all our attempts to synthesis periodinated clusters were failed. This may be due to the resulting steric hindrance caused by the bulky iodine atoms. Note that prior to this work, on grounds of DFT calculations we demonstrated the role of transition metals and bridging hydrogen in the electrophilic substitution of hydrogen at B–H vertices in $[(\text{Cp}^*\text{M})_2\text{B}_5\text{H}_9]$ ($\text{M} = \text{Mo}$ and W) [40,41].

The molecular structure of **1**, determined by a single-crystal X-ray diffraction study, is shown in Fig. 1. Its geometry is similar to

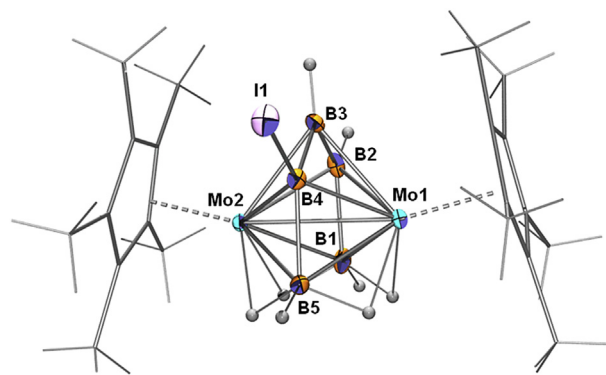


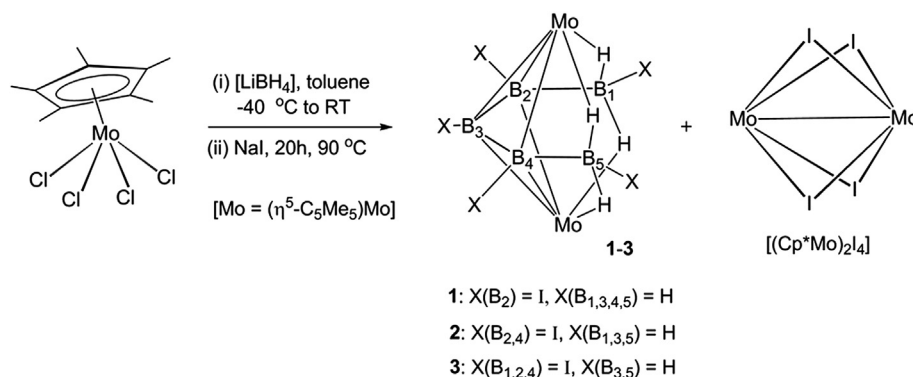
Fig. 1. Molecular structure of $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_8\text{I}]$, **1**. Selected bond lengths (Å) and angles (°): Mo(1)—Mo(2) 2.8134(5), Mo(1)—B(1) 2.313(6), Mo(1)—B(2) 2.198(6), Mo(1)—B(5) 2.323(6), Mo(2)—B(1) 2.329(6), Mo(2)—B(2) 2.209(5), Mo(2)—B(5) 2.325(6), B(1)—B(2) 1.735(8), B(3)—B(4) 1.699(7), B(4)—B(5) 1.747(7), B(4)—I(1) 2.193(5); Mo(1)—B(1)—Mo(2) 74.61(17), Mo(1)—B(2)—Mo(2) 79.35(19), Mo(1)—B(3)—Mo(2) 79.80(18), Mo(1)—B(4)—Mo(2) 78.87(16), Mo(1)—B(5)—Mo(2) 74.49(17).

that of $[(\text{Cp}^*\text{M})_2\text{B}_5\text{H}_9]$ ($\text{M} = \text{Cr}$, Mo , W) [52–54] and is best described as a bicapped *closo* trigonal bipyramid. The Mo–Mo, average B–B and Mo–B bond distances of 2.81, 1.73, and 2.28 Å in **1** are comparable with that of $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$. The molecular structures of **2**, **3** are similar to that of **1**. The difference among these compounds is that the B–H vertices have been replaced by one and two B–I vertices in compounds **2** and **3** respectively. All of the B–B, B–Mo and Mo–Mo distances are lying on the normal single bond range indicating the bonding interactions.

2.2. Synthesis and characterization of 4 and 5

As shown in Scheme 2, reaction of $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_4\text{S}_2]$ with excess of $[\text{LiBH}_4 \cdot \text{thf}]$ and NaI led to the isolation of iodine substituted dimolybdathia boranes $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{S}_2\text{H}_2\text{I}_2]$, **4** and $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{S}_2\text{HI}_3]$, **5**. Description of the characterization of **4** and **5** from X-ray diffraction studies and various spectroscopic data are follows.

Compounds **4** and **5** have been isolated following thin layer chromatography (TLC) in 16, 10% yields respectively. The molecular formula as well as the spectroscopic properties of **4** are best fit with the structure as shown in Fig. 3, and shows the presence of two ^{11}B resonances at $\delta = 83.6$ and -0.2 ppm in 1:1 ratio. The upfield chemical shift at $\delta = -0.2$ ppm has been assigned to the iodinated boron atoms B(1,4), which are attached to sulfur atoms. Beside the Cp* protons, the ^{13}C NMR spectrum also reveals the presence of two equivalents of Cp*. The ^{11}B NMR spectrum for **5** displays three



Scheme 1. Synthesis of B-iodinated dimolybdaboranes, **1–3**.

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