

Conference paper

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Chemistry of early and late transition metallaboranes: synthesis and structural characterization of periodinated dimolybdaborane $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_3\text{I}_5]$

Abstract: Thermolysis of an in situ generated intermediate $[(\text{Cp}^*\text{Ta})_2(\text{BH}_3)_2\text{Cl}_2]$, **1** generated from the reaction of $[\text{Cp}^*\text{TaCl}_4]$, ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and $[\text{LiBH}_4\cdot\text{thf}]$, in presence of $[\text{Ru}_3(\text{CO})_{12}]$ yielded *pileo*- $[\text{Cp}^*\text{TaCl}(\mu\text{-Cl})\text{-B}_2\text{H}_4\text{Ru}_3(\text{CO})_8]$, **2** having two electrons fewer than seven pairs required for the observed square pyramidal geometry. Cluster **2** is the first example of an unsaturated cluster comprising early and late transition metals in a square pyramid core. This reaction also yielded $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)(\text{B}_2\text{H}_4\text{Cl}_2)]$, **3** as a by-product. In addition, the reaction of $[\text{Cp}^*\text{MoCl}_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with $[\text{LiBH}_4\cdot\text{thf}]$ in presence of excess $[\text{MeI}]$ at mild condition led to the isolation of periodinated dimolybdatetaborane $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_3\text{I}_5]$, **4** that hints a possible existence of $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_8]$. After the isolation of periodinated **4**, we extended this chemistry towards the late transition metallaborane $[(\text{Cp}^*\text{Rh})_3\text{B}_4\text{H}_4]$, **5** using $[\text{PtBr}_2]$ as brominating source. Although all the attempts to isolate perbrominated rhodaborane failed, we have isolated partially brominated rhodaborane clusters $[(\text{Cp}^*\text{Rh})_3(\text{BH})(\text{BBr})_3]$, **6** and $[(\text{Cp}^*\text{Rh})_3(\text{BH})_3(\text{BBr})]$, **7**. All the compounds were characterized by IR and ^1H , ^{11}B and ^{13}C NMR spectroscopy in solution, and the solid-state structures of **2**, **4** and **6** were established by crystallographic analysis.

Keywords: boron; IMEBORON-XV; molybdenum; perhalogenation; rhodium; tantalum.

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Introduction

The origin of polyhedral metallaborane cage chemistry lies at the confluence of main group and organometallic chemistry [1, 2]. However, due to the large diversity in the structural patterns that are continually revealed, the key focus of work in this area has been directed at the “first order” chemistry that is, preparation and structural characterization of metallaboranes [1–6]. By contrast, the “second order” chemistry, i.e., the reaction chemistry of the metallaboranes is sparsely examined, even though the redox flexibility of the clusters allied with many metal centers. In attempts to address this area, so far others and we have studied variety of reaction chemistry utilizing high yield metallaboranes compounds [7–11].

The substitution of B–H hydrogen of boranes and carboranes is a well-known reaction [12, 13]. Such studies which led to the per-halogenated [14, 15], hydroxylated [16, 17] or alkylated [18–20] products (Chart 1),

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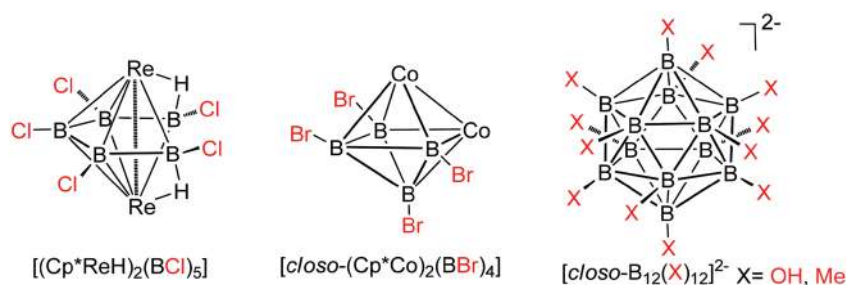


Chart 1 Per-substituted metallaboranes and boranes.

continue to be a significant interest for their potential applications as hydrophobic space-filling pharmacophores [21], weakly coordinating anions [22–24], components of radioimaging [25] and as targets for boron neutron capture therapy [26]. Between the hydroxylated and halogenated derivatives, the former one may possess more interesting chemistry due to their greater reactivity relative to the inert halogenated species. Although the per-substitution of carboranes and boranes are well documented, examples in metallacarboranes [12, 13] or metallaboranes [11] are handful that prompted the chemists to synthesize these clusters.

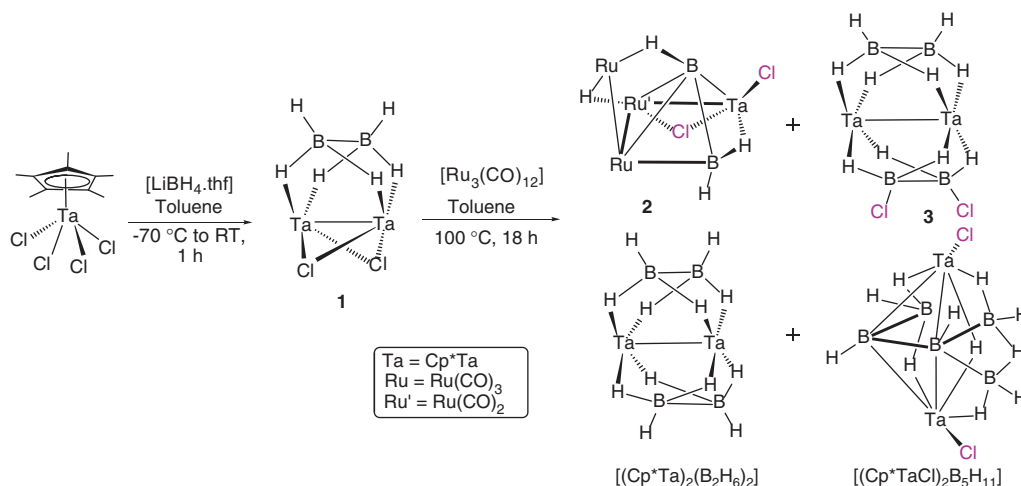
Following to the earlier report on the isolation of perchlorinated rhenaborane $[(\text{Cp}^*\text{Re})_2\text{B}_5\text{Cl}_5\text{H}_2]$ from the reaction of $[(\text{Cp}^*\text{ReH}_2)_2\text{B}_4\text{H}_4]$ with $[\text{BHCl}_2\cdot\text{SMe}_2]$, we practiced this chemistry on tungsten system, that offered partial chlorination of the framework geometry [27]. Recently, we have reported a perbrominated cluster $[(\text{Cp}^*\text{Co})_2\text{B}_4\text{H}_2\text{Br}_4]$ [28] obtained from the reaction of $[(\text{Cp}^*\text{Co})_2\text{B}_4\text{H}_6]$ and $[\text{PtBr}_2]$. In the present study, we report the reactivity of $[(\text{Cp}^*\text{Ta})_2(\text{BH}_3)_2\text{Cl}_2]$, **1** with $[\text{Ru}_3(\text{CO})_{12}]$ that yielded a *pileo*- $[\text{Cp}^*\text{TaCl}(\mu\text{-Cl})\text{B}_2\text{H}_4\text{Ru}_3(\text{CO})_8]$, **2** and a chlorinated tantalaborane $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)(\text{B}_2\text{H}_4\text{Cl}_2)]$, **3**. Further, we attempted to generate perhalogenated dimetallaborane compounds using various halogenating sources. In one case (Mo-system), we are succeeded in isolating perhalogenated metallaborane; in another (Rh-system), only partial halogenation in the framework geometry took place.

Results and discussion

Synthesis of tantalaboranes **2** and **3**

While studying the reactivity of several metallaborane clusters of group 5–9 [29–37] with various organic and inorganic compounds, use of $[\text{Fe}_2(\text{CO})_9]$ and $[\text{Ru}_3(\text{CO})_{12}]$ turned out to be the most profitable procedures [34–40]. As a result, we performed the reaction of $[(\text{Cp}^*\text{Ta})_2(\text{BH}_3)_2\text{Cl}_2]$, **1** with $[\text{Ru}_3(\text{CO})_{12}]$ that led to the isolation of $[\text{Cp}^*\text{TaCl}(\mu\text{-Cl})\text{B}_2\text{H}_4\text{Ru}_3(\text{CO})_8]$, **2** and $[(\text{Cp}^*\text{Ta})_2(\text{B}_2\text{H}_6)(\text{B}_2\text{H}_4\text{Cl}_2)]$, **3** in moderate yields (Scheme 1). Compound **2** is reasonably stable in air, thus, can be separated by thin-layer chromatography, allowing the characterization of pure materials. The ^{11}B NMR spectrum of **2** displays two distinct resonances at $\delta = 112.9$ and 57.9 ppm. The ^1H NMR shows a single resonance for Cp* protons at $\delta = 1.90$ ppm along with three upfield chemical shifts at $\delta = -7.63$, -7.79 , -16.61 ppm. The broad resonances at $\delta = -7.63$ and -7.79 ppm have been assigned for Ru-H-B and Ta-H-B, respectively. The sharp peak at $\delta = -16.61$ ppm stands for Ru-H-Ru. The IR spectrum shows intense bands at 2056, 2029 and 1953 cm^{-1} , characteristic of terminal carbonyl groups and a band at 2417 cm^{-1} for the terminal B–H stretch.

The molecular structure of **2**, shown in Fig. 1, is fully consistent with solution spectroscopic data. The structure can be defined as capped square pyramid where the square is composed Ta1-Ru1-Ru2-B2 and B1 is at the pyramidal position. Further Ru3 is capped on the B1-Ru1-Ru2 face. Another interesting feature of **2** is the bridged chlorine atom between one Ta and one Ru atom. The square pyramidal geometry of compound, **2** can be compared with tantalaborane $[\text{Cp}^*\text{TaCl}_2\text{B}_4\text{H}_8]$ [32]. The two clusters display similar B–B distances and the metal–apical boron distances whereas, the metal–basal boron distance (2.269 Å) is significantly shorter in **2**



Scheme 1 Synthesis of tantalaboranes **2** and **3**.

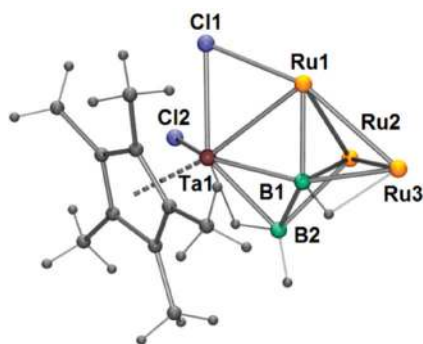


Fig. 1 Molecular structure of $[\text{Cp}^*\text{TaCl}(\mu\text{-Cl})\text{B}_2\text{H}_4\text{Ru}_3(\text{CO})_6]$, **2** (carbonyl ligands on Ru atoms were omitted for clarity). Selected bond lengths (Å) and angles (°): Ta1-B1 2.270(7), Ta1-B2 2.268(7), Ta1-Cl1 2.4752(17), Ta1-Cl2 2.4047(17), B1-B2 1.714(10), Ru1-B1 2.112(7), Ru2-B1 2.234(6), Ru2-B2 2.327(7), Ru3-B1 2.190(7), Ru1-Ru2 2.9091(7), Ru1-Ta1 2.8151(6); Ta1-B1-B2 67.8(3), Ta1-B1-Ru1 79.9(2), Ru2-B1-Ta1 95.5(2), Ru3-B1-Ta1 159.4(4), Ru1-B1-Ru2 84.0(2).

as compared to $[\text{Cp}^*\text{TaCl}_2\text{B}_4\text{H}_8]$ (2.413 Å). Similarly, the average Ru-B and Ru-Ru distance of 2.178 Å and 2.835 Å are well matched to those of analogues *pileo*- $[2,3\text{-}(\text{Cp}^*\text{Ru})_2(\mu\text{-H})\text{B}_4\text{H}_7]$ [8]. Compound **2**, to the best of our knowledge is the first structurally known metallaborane having both early and late transition metal atoms in the capped square pyramidal arrangement [Chart 2 (I-V)] [41–45]. The bond length of bridged chloride ligand between Ta-Ru can be compared with reported Cl-bridged and unbridged metal clusters, $[\text{Ru}_3(\text{CO})_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$, $[(\text{Cp}^*\text{Rh})\text{Ru}_4\text{H}_2(\mu\text{-Cl})(\text{CO})_{12}\text{B}]$ [45] and $[\text{Ru}_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_3(\text{CO})_7]$ [46]. Interestingly, all the Ru atoms in **2** have 18 electrons around the metal center, however, the Ta-centre possesses 16 electrons (considering two electrons from the bridged chlorine atom).

Considering cluster **2** as fused cluster, the Mingos's fusion formalism gave $66e$ [$\text{Ru}_2\text{Ta}_1\text{B}_2$ square pyramid (54) + Ru_3B tetrahedron (50) – Ru_2B triangle (38) = 66e]. On the other hand, the total electron count of cluster can generally be determined by adding the valence electrons contributed by the metal atoms and the electrons donated to the metals by the ligands [47, 48]. Thus, the total number of cluster valence electrons (cve) available for **2** is 64 [Cp^*TaCl (11e) + $\mu\text{-Cl}$ (3e) + 2B (6e) + 4H (4e) + 3 Ru (24e) + 8CO (16e) = 64e], two electrons short to the capped square pyramidal geometry. It might be due to the fact that Cp^*TaCl is not a “conical” fragment rather a ML_4 fragment with one frontier orbital less. So the cluster **2** is electronically unsaturated cluster and having both early and late transition metal atoms in the cluster core.

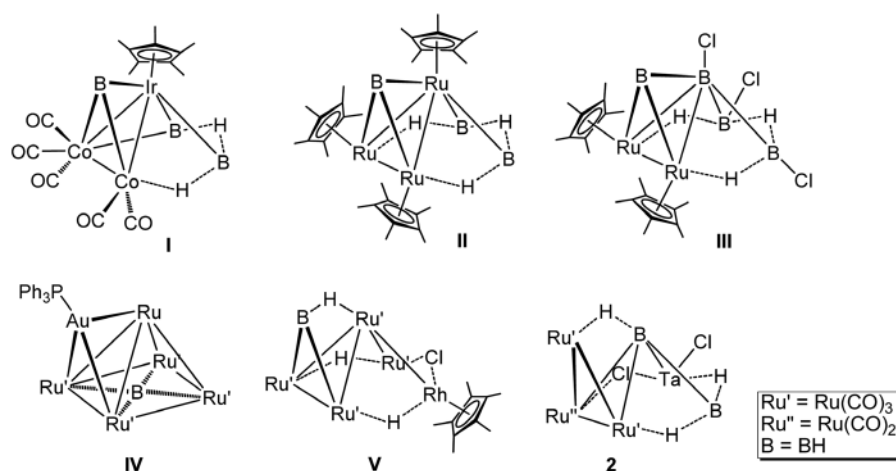


Chart 2 pileo-square pyramidal metallaborane clusters.

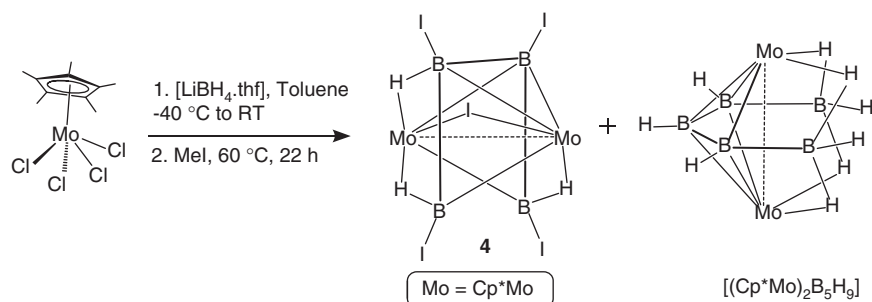
Cluster **3** was obtained as orange red solid in 20 % yield and characterized by spectroscopic and mass spectrometric data. In the mass spectrum, the highest envelope was observed at m/z 757, consistent with $[(Cp^*Ta)_2(B_2H_6)(B_2H_4Cl_2)]$. The ^{11}B NMR displays two resonances at $\delta = 12.5$ and -5.7 ppm in 1:1 ratio indicating a higher symmetric arrangements. The 1H NMR spectrum shows resonances for the Cp^* protons at $\delta = 2.42$ ppm and broad peaks at $\delta = -9.02$ and -10.41 ppm for Ta-H-B hydrogens along with B-H terminal signal at 3.98 ppm. Further in an attempt to find the position of hydrogen atoms in **3**, 2D $^{11}B\{^1H\}/^1H\{^{11}B\}$ HSQC experiment was undertaken. The study shows that the boron at $\delta = -5.7$ ppm coupled with both the protons at $\delta = -10.41$ and 3.98 ppm; whereas the boron at $\delta = 12.5$ ppm coupled with proton at -9.02 ppm. This suggests that the boron resonating at 12.5 ppm devoid of any terminal hydrogen. Further, to observe the fluxionality of **3**, the variable-temperature $^1H\{^{11}B\}$ and $^{11}B\{^1H\}$ NMR was recorded. The result signifies the absence of any possibility of fluxionality in **3**. The IR spectrum shows a band at 2403 cm^{-1} due to the terminal B-H stretch.

Synthesis of periodinated $[(Cp^*Mo)_2B_4I_5H_3]$, **4**

The high yield synthesis of dimolybdaboranes allowed us to synthesize their stable derivatives [49–53]. Earlier, we have described the synthesis of B-H substituted dimolybdaboranes [50] from the reaction of $[Cp^*MoCl_4]$ and $[LiBH_4\cdot thf]$, followed by the addition of $[BHCl_2\cdot SMe_2]$. Further, extension of this chemistry towards dichalcogenide ligands [49], RE-ER [R = Ph, CH_2Ph , 2,6-(t Bu) $_2$ C $_6$ H $_2$ OH, (CH $_3$) $_3$ C]; E = S, Se] yielded variety of hybrid clusters. Recently we have reported the B-iodination of $[(Cp^*Mo)_2B_4H_4S_2]$ and $[(Cp^*Mo)_2B_5H_9]$ using NaI, which led to the isolation of iodinated dimolybdathiorborane derivatives [51]. However, all our attempts to synthesis periodinated $[(Cp^*Mo)_2(BI)_5H_4]$ or $[(Cp^*Mo)_2B_4I_5S_2]$ failed. Therefore, in a challenge to synthesize periodinated molybdaborane, we have renewed this chemistry in different reaction conditions and iodine sources. As a result, thermolysis of an in situ generated intermediate, produced from $[Cp^*MoCl_4]$ and $[LiBH_4\cdot thf]$, in presence of MeI afforded periodinated dimolybdetetraiodoborane $[(Cp^*Mo)_2B_4H_3I_5]$, **4** (Scheme 2).

The solid state structure of the compound **4**, shown in Figure 2, was ascertained by X-ray structure analysis. The molecule has near perfect C_s symmetry and can be viewed as bicapped tetrahedron geometry. The Mo1-Mo_1-B2-B3 atoms are arranged in tetrahedra whereas the other two B-I moieties [B1(I1) and B4(I4)] are in capping position (Figure 2). The total cluster valence electrons for compound **4** is 44 which is isoelectronic to rhenaborane cluster $[(Cp^*ReH)_2B_4H_8]$ [54] and $[(Cp^*Cr)_2(CO)_2B_4H_6]$ [55]. The Mo-Mo distance of 2.729 Å in **4** is considerably longer than the analogues $[(Cp^*Mo)_2B_2S_2H_2(\mu-\eta^1-S)]$ (2.635 Å) and $[(Cp^*Mo)_2B_2H_5(BSePh)_2(\mu-\eta^1-SePh)]$ (2.694 Å) [49]. Although the average Mo-B distances in **4** and $[(Cp^*Mo)_2B_2H_5(BSePh)_2(\mu-\eta^1-SePh)]$ are similar (2.274 Å, 2.275 Å respectively), the B-B distances of former is 0.5 Å longer than the later.

The ^{11}B NMR spectrum of **4** displays four distinct resonances at $\delta = 53.3, 36.1, 31.3, 13.9$ ppm. The 1H NMR shows two signals for Cp^* protons at $\delta = 1.98$ and 1.90 ppm along with three upfield chemical shifts at



Scheme 2 Synthesis of $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_3\text{I}_5]$ 4.

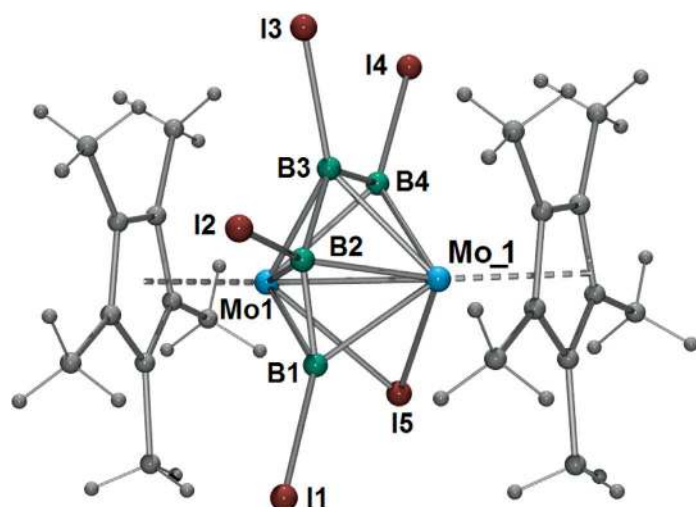


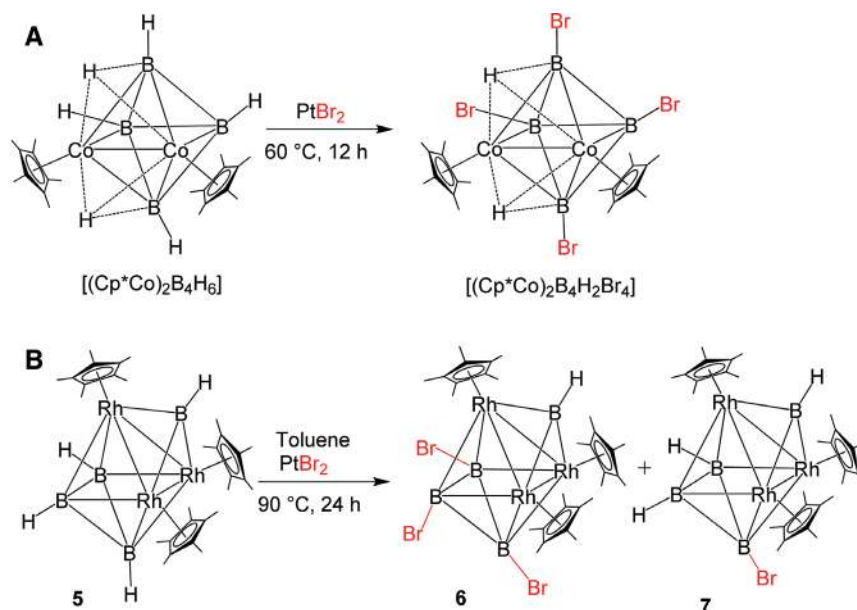
Fig. 2 Molecular structure of $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_3\text{I}_5]$ 4. Selected bond lengths (\AA) and angles ($^\circ$): B1-B2 1.570(3), B2-B3 1.679(16), B3-B4 1.840(3), B1-I1 2.199(12), B3-I3 2.178(12), B1-Mo1 2.297(9), B2-Mo1 2.272(8), I5-Mo1 2.815(9); B2-B1-I1 132.5(12), B2-B1-Mo1 69.0(5), I1-B1-Mo1 140.7(4), B1-B2-B3 128.0(11), Mo1-Mo1-I5 61.00(11).

$\delta = -4.75, -6.01$ and -8.39 ppm. Although, the bridging hydrogens could not be located in the solid state structure, but their presence has been ascertained by ^1H NMR spectroscopy.

Synthesis of brominated rhodaborane clusters

Although the metallaboranes offer reaction potentials similar to those of polyhedral boranes and transition metal clusters [56–60], the additional feature is the competition between the metal and boron sites. For example, borane displacement vs. metal fragment displacement, ligand substitution at boron vs. metal sites, removal of M-H-B vs B-H-B protons [61–63]. Nevertheless, the isolation of chlorinated tantalaborane 3 and the existence of perbrominated cobaltaborane [28], led us to extend this chemistry to Rh-system. As a result, we have performed the reaction of $[(\text{Cp}^*\text{Rh})_3(\text{B}_4\text{H}_4)]$, 5 with PtBr_2 , that yielded partial brominated rhodaboranes $[(\text{Cp}^*\text{Rh})_3(\text{BH})(\text{BBr})_3]$, 6 and $[(\text{Cp}^*\text{Rh})_3(\text{BH})_3(\text{BBr})]$, 7 (Scheme 3). Prolonged reaction time or drastic reaction conditions were unsuccessful for perbromination in 5.

The mass spectrometric data of 6 suggests a molecular formula of $\text{C}_{30}\text{H}_{46}\text{B}_4\text{Br}_3\text{Rh}_3$. The $^{11}\text{B}\{^1\text{H}\}$ NMR reveals the presence of three resonances in 1 : 2 : 1 ratio whereas the coupled ^{11}B NMR shows different pattern. The resonances at $\delta = 89.3$ and 62.6 ppm showed no coupling in ^{11}B NMR suggests the B-Br environment. The ^1H NMR shows one broad peak at 8.62 ppm for BH_4 proton; two peaks for Cp* protons at 2 : 1 ratio. The IR spectrum shows a broad band at 2423 cm^{-1} for the terminal B-H stretches. The molecular structure of compound



Scheme 3 A) Synthesis of *closo*- $[(Cp^*Co)_2B_4H_2Br_4]$; B) Synthesis of **6** and **7**.

6 confirms the structural inferences made on the basis of spectroscopic results. The solid state structure of **6** is shown in Fig. 3, where this compound is seen to be a cluster analogue of **5** and $[(Cp^*Co)_3B_4H_4]$ [64]. The substitution at the terminal B–H changes the internal distances. The average Rh–Rh distance lengthens from 2.667 Å (in **5**) to 2.691 Å (in **6**) whereas; the distance of unique borylene atom (B4) to the triangular metal plane shortens from 1.388 Å (in **5**) to 1.354 Å (in **6**). The average B–Br bond distances of 1.97 Å in **6** are very close $[(Cp^*Co)_2(BBr)_4H_2]$ [28]. The geometry of cluster **7** is established by comparison of its spectroscopic data with those for capped octahedral cluster **5** and other related species [65, 66].

Conclusions

In this contribution we report the synthesis and structural characterization of *pileo*- $[Cp^*TaCl(\mu-Cl)-B_2H_4Ru_3(CO)_8]$, **2** and a partial chlorinated-tantalaborane $[(Cp^*Ta)_2(B_2H_6)(B_2H_4Cl_2)]$, **3** from the thermolysis

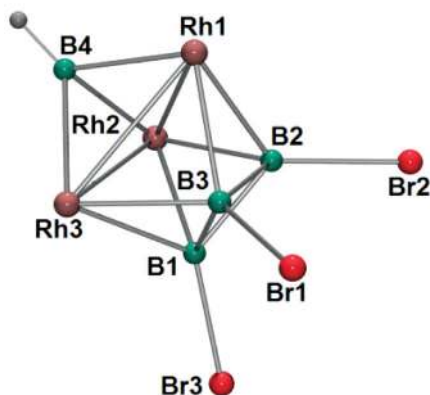


Fig. 3 Molecular structure of $[(Cp^*Rh)_3(BH)(BBr)_3]$, **6** (the Cp^* ligands on the Rh are excluded for clarity). Selected bond lengths (Å) and angles ($^\circ$): Rh1–Rh2 2.6914(11), Rh2–Rh3 2.697(11), Rh1–B2 2.092(14), B2–B3 1.71(2), B1–B2 1.69(2), Rh1–B4 2.049(13), B2–Br2 1.979(13), B1–Br3 1.963(14); Rh1–Rh2–Rh3 60.00(3), Rh1–B2–Rh2 79.9(5), B1–B2–B3 59.2(8).

of **1** and $[\text{Ru}_3(\text{CO})_{12}]$. Compound **2** can be considered as a hypoelectronic cluster as it possesses two electrons less than required for a square pyramidal geometry. In addition, we report, for the first time, the isolation and characterization of a periodinated dimolybdatetetraborane $[(\text{Cp}^*\text{Mo})_2\text{B}_4\text{H}_3\text{I}_5]$, **4** that provides a direct evidence for the existence of its parent molecule.

Experimental section

General procedures and instrumentation

All the syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques. Solvents were dried by common methods and distilled under N_2 before use. Compound **1** [29], $[(\text{Cp}^*\text{Rh})_3(\text{BH})_4]$ [8] and $[\text{Cp}^*\text{MoCl}_4]$ [67] were prepared according to literature methods, while other chemicals $[\text{Cp}^*\text{TaCl}_4]$, $[\text{LiBH}_4\cdot\text{thf}]$, $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{PtBr}_2]$ were obtained commercially and used as received. The external reference for the ^{11}B NMR, $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ was synthesized as per literature methods [68]. Thin layer chromatography was carried on 250 mm dia aluminum supported silica gel TLC plates (Merck TLC Plates). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ , ppm, d_6 -benzene, 7.16) while a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in d_6 -benzene (δ_{B} , ppm, -30.07) was used as an external reference for the ^{11}B NMR. The infrared spectra were recorded on a Nicolet iS10 spectrometer. MALDI-TOF mass-spectra of the compounds were obtained on a Bruker Ultraflex extreme using 2,5-dihydroxybenzoic acid as a matrix and a ground steel target plate. Microanalyses for C and H were performed on Perkin Elmer Instruments series II model 2400.

Synthesis of **2** and **3**

To a flame-dried Schlenk tube $[\text{Cp}^*\text{TaCl}_4]$ (0.12 g, 0.26 mmol) was suspended in toluene (15 mL) and $[\text{LiBH}_4\cdot\text{thf}]$ (0.8 mL, 1.56 mmol) was added at -78°C . The solution turned purple after warming to room temperature over 10 min. It was stirred at room temperature for 1 h, volatiles were removed, and it was extracted with hexane. The filtrate was dried and redissolved in toluene (15 mL). The resulting solution was pyrolyzed in presence of $[\text{Ru}_3(\text{CO})_{12}]$ (0.16 g, 0.26 mmol) at 100°C for 18 h. The solvent was evaporated and the residue was extracted into hexane and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic workup on silica gel TLC plates. Elution with a hexane/ CH_2Cl_2 (80:20 v/v) mixture yielded yellow **2** (0.024 g, 10 %) and orange-red **3** (0.04 g, 20 %) along with other tantalaboranes reported earlier [31]. **2**: MS (MALDI): m/z 941 $[\text{M}+\text{H}]^+$. Isotope envelope $\text{C}_{18}\text{H}_{20}\text{B}_2\text{Cl}_2\text{O}_8\text{Ru}_3\text{Ta}$: requires 941. m/z 717 $[\text{M}+\text{H}-8\text{CO}]^+$. Isotope envelope $\text{C}_{10}\text{H}_{20}\text{B}_2\text{Cl}_2\text{Ru}_3\text{Ta}$: requires 717. ^{11}B NMR (22°C , 128 MHz, d_6 -benzene): $\delta = 112.9$ (br, 1B), 57.9 (br, 1B). ^1H NMR (22°C , 400 MHz, d_6 -benzene): $\delta = 4.56$ (br, 1H, BH_t), 1.90 (s, 15H, Cp*), -7.63 (br, 1H, Ru-H-B), -7.79 (br, 1H, Ta-H-B), -16.61 (s, 1H, Ru-H-Ru). ^{13}C NMR (22°C , 100 MHz, d_6 -benzene): $\delta = 198.3$, 191.3 (CO), 102.3 (C_5Me_5), 10.3 (C_5Me_5). IR (hexane) ν/cm^{-1} : 2417w (BH_t), 2056, 2029, 1953 (CO). Elemental analysis (%) calcd for $\text{C}_{18}\text{H}_{19}\text{B}_2\text{Cl}_2\text{O}_8\text{Ru}_3\text{Ta}$: C, 22.99; H, 2.04. Found: C, 23.68; H, 1.96. **3**: MS (MALDI): m/z 757 $[\text{M}+\text{H}]^+$. Isotope envelope $\text{C}_{20}\text{H}_{41}\text{B}_4\text{Cl}_2\text{Ta}_2$: requires 757. ^{11}B NMR (22°C , 128 MHz, d_6 -benzene): $\delta = 12.5$ (br, 2B), -5.7 (br, 2B). ^1H NMR (22°C , 400 MHz, d_6 -benzene): $\delta = 3.98$ (br, H, 2BH_t), 2.42 (s, 30H, 2Cp*), -9.02 (d, 4H, Ta-H-B), -10.41 (br, 4H, Ta-H-B). ^{13}C NMR (22°C , 100 MHz, d_6 -benzene): $\delta = 103.5$ (C_5Me_5), 9.1 (C_5Me_5). IR (hexane) ν/cm^{-1} : 2403w (BH_t).

Synthesis of **4**

In a flame-dried Schlenk tube $[\text{Cp}^*\text{MoCl}_4]$ (0.1 g, 0.27 mmol) in 10 mL of toluene was treated with 5-fold excess of $[\text{LiBH}_4\cdot\text{thf}]$ (0.7 mL, 1.4 mmol) at -40°C and allowed to stir at room temperature for 1 h. After removal of

toluene, the residue was extracted into hexane and filtered through a frit using Celite. The yellowish-green hexane extract was dried in vacuo, redissolved in 10 mL of toluene and refluxed at 60 °C with excess MeI 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 for chromatographic separation. Elution with hexane:CH₂Cl₂ (80:20 v/v) mixture afforded green **4** (0.015 g, 5 %) along with reported [(Cp*Mo)₂B₅H₉] [52]. **4**: MS (MALDI): m/z 1144 [M]⁺. Isotope envelope C₂₀H₃₃B₄I₅Mo₂: requires 1144. ¹¹B NMR (22 °C, 400 MHz, *d*₆-benzene): δ = 53.3 (br, 1B), 36.1 (br, 1B), 31.3 (br, 1B), 13.9 (br, 1B). ¹H NMR (22 °C, 400 MHz, *d*₆-benzene): δ = 1.98 (s, 15H, 1Cp*), 1.90 (s, 15H, 1Cp*) -4.75 (br, 1H, Mo-H-B), -6.01 (br, 1H, Mo-H-B), -8.39 (br, 1H, Mo-H-B). ¹³C NMR (22 °C, 500 MHz, *d*₆-benzene): δ = 101.3, 99.3 (C₅Me₅), 11.1, 10.7 (C₅Me₅).

Synthesis of **6** and **7**

An orange solution of [(Cp*Rh)₃B₄H₄] **5** (0.21 g, 0.27 mmol) in toluene (15 mL) was stirred in the presence of [PtBr₂] (0.09 g, 0.27 mmol) at 90 °C about 24 h. The solvent was dried and the residue was extracted into hexane and subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/CH₂Cl₂ (75:25 v/v) mixture yielded two orange compounds **6** (0.046 g, 17 %) and **7** (0.07 g, 30 %). **6**: MS (MALDI): m/z 998 [M+H]⁺. Isotope envelope C₃₀H₄₆B₄Br₃Rh₃: requires 998. ¹¹B NMR (22 °C, 128 MHz, *d*₆-benzene): δ = 128.3 (br, 1B), 89.3 (br, 2B), 62.6 (br, 1B). ¹H NMR (22 °C, 400 MHz, *d*₆-benzene): δ = 8.62 (br, 1H, BH₁), 1.92 (s, 30H, 2Cp*), 1.81 (s, 15H, 1Cp*). ¹³C NMR (22 °C, 100 MHz, *d*₆-benzene): δ = 100.5 (C₅Me₅), 11.2 (C₅Me₅). IR (hexane) ν/cm⁻¹: 2423w (BH₁). Elemental analysis (%) calcd for C₃₀H₄₆B₄Br₃Rh₃: C, 36.06; H, 4.64. Found: C, 37.18; H, 4.43. **7**: MS (MALDI): m/z 840 [M+H]⁺. Isotope envelope C₃₀H₄₈B₄BrRh₃: requires 840. ¹¹B NMR (22 °C, 128 MHz, *d*₆-benzene): δ = 128.3 (br, 1B), 75.8 (br, 2B), 69.6 (br, 1B). ¹H NMR (22 °C, 400 MHz, *d*₆-benzene): δ = 8.96 (br, 1H, BH₁), 4.75 (br, 2H, BH₁), 1.96 (s, 30H, 2Cp*), 1.79 (s, 15H, 1Cp*). ¹³C NMR (22 °C, 100 MHz, *d*₆-benzene): δ = 106.1 (C₅Me₅), 12.7 (C₅Me₅). IR (hexane) ν/cm⁻¹: 2469w (BH₁). Elemental analysis (%) calcd for C₃₀H₄₈B₄BrRh₃: C, 42.83; H, 5.75. Found: C, 41.88; H, 6.01.

X-ray structure determination

The crystal data for **2** was collected and integrated using an Oxford Diffraction Super Nova CCD system equipped with graphite-monochromated Cu-Kα radiation (λ = 1.54184) radiation at 150 K. The crystal data for **4**, **6** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 296 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97 [69, 70].

- **Crystal data for 2**: CCDC 997761; C₁₈H₁₈B₂Cl₂O₈Ru₃Ta, M_r = 939.00, monoclinic space group *P*-1, a = 15.6941(4) Å, b = 12.5641(3) Å, c = 13.4897(3) Å, β = 95.183(2)°, V = 2649.05(11) Å³, Z = 4, ρ_{calcd} = 2.354 g·cm⁻³, μ = 23.197 mm⁻¹, F(000) = 1756, R₁ = 0.0372, wR₂ = 0.1000, 5201 independent reflections [2θ ≤ 72.66°] and 324 parameters.
- **Crystal data for 4**: CCDC 997762; C₂₀H₃₀B₄I₅Mo₂, M_r = 1140.06, Orthorhombic space group Cmc21, a = 10.8891(6) Å, b = 17.9178(6) Å, c = 15.5816(6) Å, β = 90°, V = 3040.1(2) Å³, Z = 4, ρ_{calcd} = 2.491 g cm⁻³, μ = 5.911 mm⁻¹, F(000) = 2076, R₁ = 0.0472, wR₂ = 0.1175, 2768 independent reflections [2θ ≤ 50.0°] and 164 parameters.
- **Crystal data for 6**: CCDC 1007647; C₃₀H₄₆B₄Br₃Rh₃, M_r = 761.66, monoclinic space group *P*-1, a = 10.9363(4) Å, b = 16.767(3) Å, c = 17.995(3) Å, β = 95.183(2)°, V = 2649.05(11) Å³, Z = 4, ρ_{calcd} = 2.354 g·cm⁻³, μ = 23.197 mm⁻¹, F(000) = 1756, R₁ = 0.0372, wR₂ = 0.1000, 5201 independent reflections [2θ ≤ 72.66°] and 324 parameters.

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