

Conference paper

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Heterometallic boride clusters: synthesis and characterization of butterfly and square pyramidal boride clusters*

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Abstract: A number of heterometallic boride clusters have been synthesized and structurally characterized using various spectroscopic and crystallographic analyses. Thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with $[\text{Cp}^*\text{WH}_3(\text{B}_4\text{H}_8)]$ (**1**) yielded $[(\text{Cp}^*\text{W}(\text{CO})_2)_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$ (**2**), $[(\text{Cp}^*\text{W}(\text{CO})_2)_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_2\{\text{Ru}(\text{CO})_2\}(\mu\text{-H})]$ (**3**), $[(\text{Cp}^*\text{W}(\text{CO})_2)_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_4]$ (**4**) and a ditungstaborane cluster $[(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{Ru}(\text{CO})_3]$ (**5**) ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$). Compound **2** contains 62 cluster valence-electrons, in which the boron atom occupies the semi-interstitial position of a M_4 -butterfly core, composed of two tungsten and two ruthenium atoms. Compounds **3** and **4** can be described as hetero-metallic boride clusters that contain 74-cluster valence electrons (cve), in which the boron atom is at the basal position of the M_5 -square pyramidal geometry. Cluster **5** is analogous to known $[(\text{Cp}^*\text{W})_2\text{B}_5\text{H}_9]$ where one of the BH vertices has been replaced by isolobal $\{\text{Ru}(\text{CO})_3\}$ fragment. Computational studies with density functional theory (DFT) methods at the B3LYP level have been used to analyze the bonding of the synthesized molecules. The optimized geometries and computed ^{11}B NMR chemical shifts satisfactorily corroborate with the experimental data. All the compounds have been characterized by mass spectrometry, IR, ^1H , ^{11}B and ^{13}C NMR spectroscopy, and the structural architectures were unequivocally established by crystallographic analyses of clusters **2–5**.

Keywords: boride; cluster compounds; IMEBORON-16; ruthenium; semi-interstitial; tungsten.

Introduction

Discrete and extended transition metal clusters that contain interstitial atoms form an interesting class of compounds due to their combined fundamental aspects as well as applied research [1–5]. As a result, compounds containing main group elements such as carbon, nitrogen and phosphorous at the interstitial environment have been well documented in the literature [6–18]. In this perspective, the field of boride clusters essentially is very rich. As doping of the bulk metal clusters with boron diversifies the physical and electronic properties, this can be utilized as common strategy for studying both the electronics as well as surface chemistries of the metal borides [19–29]. Several reviews and articles have demonstrated that the area of metal-rich

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metallaboranes as well as boron-rich metallaboranes are expanding briskly [30–54]. The incorporation of an orbital rich atom like boron into the created cavity not only posed substantial challenges to the synthetic chemists, but also created opportunities to further develop this area [55–57]. Although the first example of a boride cluster $[\text{Co}_6(\text{CO})_{18}\text{B}]$ was reported by Schmid and coworkers in 1975 [58], the first X-ray diffraction study of $[\text{HRu}_6(\text{CO})_{17}\text{B}]$ was reported almost 14 years later by Shore [59].

Over the past decade, our effort in synthesizing metallaboranes using boranes, metal halides and metal carbonyls allowed us to isolate a variety of boride clusters with varying metal to boron ratio [60–68]. Recently, we have reported a novel μ_9 -boride cluster, generated from the reaction of an open cage rhodaborane $[(\text{Cp}^*\text{Rh})_2\text{B}_6\text{H}_{10}]$ and $[\text{Co}_2(\text{CO})_8]$ [68]. In this article, we present the synthesis and structural characterization of various mixed-metal boride clusters and a hetero bimetallic tungstaborane cluster from the thermolytic reaction of *nido*- $[\text{Cp}^*\text{WH}_3(\text{B}_4\text{H}_8)]$ [69] and $[\text{Ru}_3(\text{CO})_{12}]$. In addition, the computational studies on the ground of density functional theory (DFT) have been undertaken to analyze the bonding and stability of the synthesized clusters.

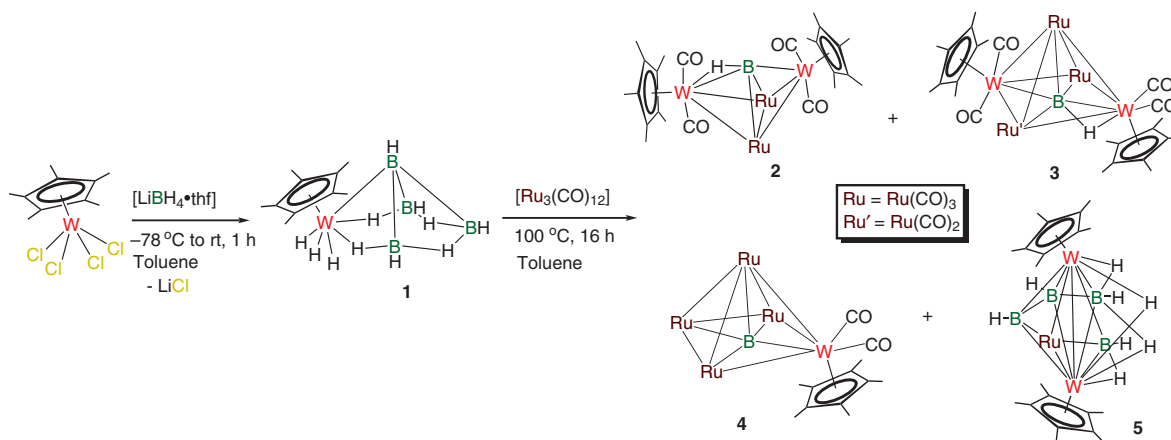
Results and discussion

As shown in Scheme 1, thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with **1**, obtained from the metathesis reaction of $[\text{Cp}^*\text{WCl}_4]$ with $\text{LiBH}_4 \cdot \text{thf}$, led to the formation of a series of mixed metal clusters **2–5**. Clusters **2–4** represent interstitial boride compounds in which the boron atoms are in μ_4 and μ_5 -connected; whereas compound **5** showed trigonal bipyramidal core. Detailed characterization of **2–5** using various multinuclear NMR, IR, mass spectrometry and single crystal X-ray diffraction studies are described below.

$[\{\text{Cp}^*\text{W}(\text{CO})_2\}_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$ (**2**)

Compound **2** was isolated as moderately air stable orange crystals which were characterized by ^1H , ^{11}B , ^{13}C NMR, IR and by single-crystal X-ray crystallography. The ^{11}B NMR displayed a single resonance in the down field region at $\delta = 128.8$ ppm. The ^1H NMR spectrum showed a single resonance corresponding to Cp^* protons and one up field chemical shift at $\delta = -18.95$ ppm. The presence of the CO ligands was confirmed by ^{13}C NMR and IR spectroscopy. The mass spectrum of **2** suggests the molecular formulation of $\text{C}_{30}\text{H}_{31}\text{BO}_{10}\text{Ru}_2\text{W}_2$.

In order to confirm the spectroscopic assignments and to determine the solid state structure of **2**, the X-ray structure analysis was undertaken. The crystal structure of **2**, shown in Fig. 1, corresponds to a butterfly



Scheme 1: Synthesis of mixed metal clusters **2–5**.

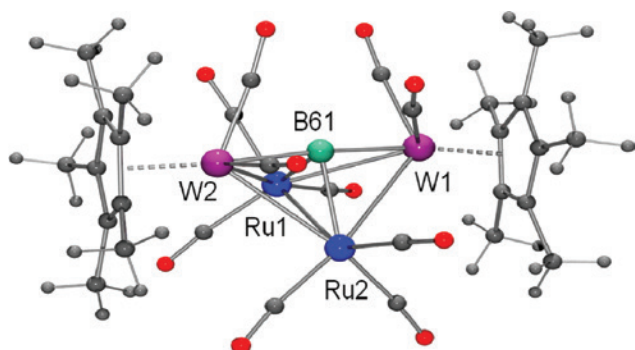


Fig. 1: Molecular structure and labeling diagram for **2** (the bridging hydrogen atom could not be located). Selected bond lengths (Å) and angles (°) are as follows **2**: W1-B61 2.123(5), W1-Ru2 2.982(4), W1-Ru1 3.025(4), W2-Ru1 2.967(5), W2-B61 2.118(5), Ru1-B61 2.202(5), Ru2-B61 2.195(5). B61-W1-Ru2 47.33(14), Ru2-W1-Ru1 56.264(12), W2-B61-W1 174.8(3), Ru2-B61-Ru1 80.24(17).

core and consists of two tungsten and two ruthenium atoms, where each tungsten atoms occupy the wing tip position and the boron atom occupies the semi-interstitial position. The observed W-B and Ru-B bond distances are consistent with the known tungstaboranes [69–71], ruthenaboranes [72, 73], and M_4 -boride clusters, for example $[\text{Cp}^*\text{Mo}(\text{CO})_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_3(\mu\text{-H})_2]$ [64], $[\{\text{Cp}^*\text{Mo}(\text{CO})_2\}_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$ [65], $[\{\text{Cp}^*\text{Ru}(\text{CO})_2\}_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}\{\text{Ru}(\text{CO})_2\}(\mu\text{-H})]$ [61] and $[\text{H}\{\text{Cp}^*\text{W}(\text{CO})_2\}\{\text{Ru}(\text{CO})_3\}_3(\mu_4\text{-B})(\mu\text{-H})]$ [74]. Therefore, the boron atom is in bonding contact with all the four metal atoms. Each tungsten atom accompanied with two terminal CO ligands and a Cp^* ligand, whereas the hinge ruthenium atoms possess three carbonyl ligands each. The molecule possesses a C_2 axis that passes through the boron atom and bisects the Ru-Ru bond. Furthermore, ignoring the Cp^* ligands, compound **2** shows approximately C_{2v} symmetry with a σ -plane along with the C_2 axis. The observed ^{11}B NMR chemical shift of **2** is in agreement with other structurally characterized boride clusters (Table 1). The boron atom in **2** positioned in such a way that it connects both the wing-tip ruthenium atoms in a linear fashion with the W1-B61-W2 angle of 174.78° . Compound **2** contains 62-cluster valence electrons (cve) and consequently isostructural and isoelectronic to $[\{\text{Cp}^*\text{Mo}(\text{CO})_2\}_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$.

$[\{\text{Cp}^*\text{W}(\text{CO})_2\}_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_2\{\text{Ru}(\text{CO})_2\}(\mu\text{-H})]$, (**3**) and $[\{\text{Cp}^*\text{W}(\text{CO})_2\}_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_4]$, (**4**)

Compounds **3** and **4** have been isolated as brown and purple solids in 10.3% and 16.2% yield, respectively. The constitution of **3** and **4** were ascertained by X-ray diffraction studies on suitable single crystals obtained at -4°C in hexane- CH_2Cl_2 solution. The molecular structure of **3** and **4**, shown in Fig. 2a and b, are seen to be consistent with the solution spectroscopic data. The solid state structure displays the existence of a “boride” boron atom partially encapsulated in the square pyramidal base. The overall structures of **3** and **4** are virtually similar. The square base of compound **3** is composed of two Ru and two tungsten atoms, whereas it is three ruthenium atoms and a tungsten atom for **4**. The boron atom lies ca. 0.31 Å below the square face, made of M1-Ru1-M2-Ru4 (M1 = W and M2 = W or Ru) that is analogous to boride clusters $[\text{Cp}^*\text{RuCO}\{\text{Ru}(\text{CO})_3\}_4\text{B}]$ [61], $[\text{Cp}^*\text{Mo}(\text{CO})_2\{\text{Ru}(\text{CO})_3\}_4\text{B}]$ [66] and $[\text{Ru}_5(\text{CO})_{15}\text{B}\{\text{AuPPh}_3\}]$ [83]. Thus, clusters **3** and **4** can be viewed as *nido*-square pyramidal with boron in the semi-interstitial position, similar to that of $[\{\text{Cp}^*\text{W}(\text{O})\}\{\text{Cp}^*\text{W}(\text{CO})_2\}\{\text{Ru}(\text{CO})_3\}_3(\mu_5\text{-C})]$ [84].

Alternatively, the geometry of clusters **3** and **4** can also be considered as 74-electron complex, in which the B atom contributes three valence electrons to the square pyramidal framework. The average Ru-Ru distances is usual as compared to other $M_5\text{B}$ boride clusters, such as $[\text{Cp}^*\text{RuCO}\{\text{Ru}(\text{CO})_3\}_4\text{B}]$ (2.770 Å – 2.907 Å) and $[\text{Ru}_5(\text{CO})_{15}\text{B}\{\text{AuPPh}_3\}]$, (2.804 – 3.054 Å).

The ^{11}B NMR showed a single boron peak at $\delta = 189.8$ for **3**, whereas compound **4** shows a resonance at $\delta = 182.0\text{ ppm}$, that is comparable with other related structurally characterized μ_5 -boride clusters (Table 1).

Table 1: Compounds 2–4 and some selected structurally characterized boride clusters and their ^{11}B chemical shifts.

Complex	Geometry	$\delta (^{11}\text{B})$ ppm	Ref.
$[\text{HFe}_4(\text{CO})_{12}\text{BH}_2]$	Butterfly	116	[75]
$[\text{HFeRu}_3(\text{CO})_{12}\text{BH}_2]$	Butterfly	114	[76]
$[\text{HRu}_4(\text{CO})_{12}\text{BH}_2]$	Butterfly	109.9	[77]
$[\text{HOs}_4(\text{CO})_{12}\text{BH}_2]$	Butterfly	119.7	[78]
$[\text{HOs}_5(\text{CO})_{16}\text{B}]$	bb	184.4	[78]
$[\text{HRu}_6(\text{CO})_{17}\text{B}]$	oh	193.8	[59]
$[\text{Ru}_6(\text{CO})_{17}\text{B}][\text{PPN}]$	oh	196	[59]
$[\text{Ru}_6(\text{CO})_{17}\text{B}][\text{HNMe}_3]$	oh	202.2	[79]
$[\text{H}_2\text{Ru}_6(\text{CO})_{18}\text{B}][\text{PPN}]$	tp	205.9	[80]
$[\text{CoMn}_2(\text{CO})_{13}\text{B}]$	tpl	195.8	[50]
$[\text{Fe}_4\text{Au}_3(\text{CO})_{12}(\text{PPh}_3)_3\text{B}]$	bb	183	[82]
$[\text{Cp}^*\text{CoHRu}_3(\text{CO})_9\text{B}(\mu\text{-H})_2]$	Butterfly	89.5	[62]
$[\text{HCpW}(\text{CO})_2\{\text{Ru}(\text{CO})_3\}_3\text{B}(\mu\text{-H})]$	Butterfly	131.9	[74]
$[(\text{Cp}^*\text{Ru})_2\{\text{Ru}_2(\text{CO})_8\}\text{BH}]$	Butterfly	207.7	[61]
$[\text{H}_2\text{Cp}^*\text{RhRu}_3(\text{CO})_8(\text{PPh}_3)\text{BH}]$	Butterfly	149	[81]
$[\text{HCp}^*\text{IrRu}_3(\text{CO})_{10}\text{BH}_2]$	Butterfly	92.7	[81]
$[(\text{Cp}^*\text{Rh})_2\{\text{Co}_6(\text{CO})_{12}\}(\mu\text{-H})(\text{BH})\text{B}]$	ttp	101.2	[68]
$[\text{H}_2\text{Cp}^*\text{RhRu}_3(\text{CO})_8(\text{PPh}_3)\text{BH}]$	Butterfly	149	[81]
$[(\text{Cp}^*\text{Rh})(\mu_6\text{-B})\{\text{Ru}(\text{CO})_3\}_4\{\text{RuH}(\text{CO})_2\}]$	oh	177.6	[65]
$[(\text{Cp}^*\text{Mo}(\text{CO})_2)(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_3(\mu\text{-H})_2]$	Butterfly	123.1	[64]
$[(\text{Cp}^*\text{Mo}(\text{CO})_2)(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$	Butterfly	128.4	[65]
$[(\text{Cp}^*\text{Ru}(\text{CO})_2)(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}\{\text{Ru}(\text{CO})_2\}(\mu\text{-H})]$	Butterfly	207.7	[61]
$[\text{Cp}^*\text{RuCo}\{\text{Ru}(\text{CO})_3\}_4\text{B}]$	sq	174.6	[61]
$[\text{Ru}_5(\text{CO})_{15}\text{B}(\text{AuPPh}_3)]$	sq	172.5	[34]
$[(\text{Cp}^*\text{W}(\text{CO})_2)_2(\mu_4\text{-B})\{\text{Ru}(\text{CO})_3\}_2(\mu\text{-H})]$ (2)	Butterfly	128.8	this work
$[(\text{Cp}^*\text{W}(\text{CO})_2)_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_2\{\text{Ru}(\text{CO})_2\}(\mu\text{-H})]$ (3)	sq	189.8	this work
$[(\text{Cp}^*\text{W}(\text{CO})_2)_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_4]$ (4)	sq	182.0	this work

bb, bridged butterfly; oh, octahedral; tp, trigonal prism; tpl, trigonal planar; ttp, tricapped trigonal prism; sq, square pyramidal.

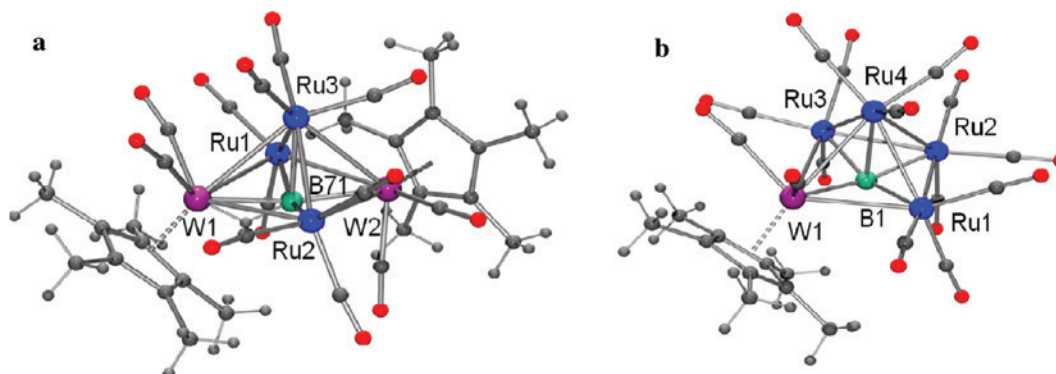


Fig. 2: Molecular structure and labeling diagrams for (a) **3** and (b) **4**. Selected bond lengths (Å) and angles (°) of **3**: W1–Ru1 2.993(5), W1–Ru2 3.00(5), W1–Ru3 3.089(5), W1–B71 2.163(6), W2–B71 2.203(6), W2–Ru1 2.968(5), W2–Ru2 3.030(5), W2–Ru3 2.994(5), Ru1–B71 2.258(5), Ru2–B71 2.162(5). Ru1–W1–Ru2 54.711(12), W1–B71–W2 168.5(3), Ru2–B71–Ru1 77.12(17), W1–B71–Ru1 85.19(19), W2–B71–Ru1 83.41(19). **4**: B1–Ru1 2.093(4), B1–Ru3 2.094(4), B1–W1 2.156(4), Ru1–Ru4 2.7930(4), Ru1–B1–Ru3 159.13(19), Ru1–B1–Ru2 85.56(14), Ru3–B1–Ru2 86.29(14), Ru1–B1–W1 90.86(15), Ru3–B1–W1 92.62(15), Ru1–B1–Ru4 79.68(12), W1–B1–Ru4 83.97(13).

The computed ^{11}B NMR chemical shifts of **3** and **4** employing gauge-including atomic orbitals (GIAO) method and B3LYP functional corroborates well with the experimental values [85] (Table S1). The ^1H NMR spectrum of **4** displayed a single resonance corresponding to the Cp^* protons, however ^1H NMR suggests presence of

two types of Cp* ligand for **3** along with a broad upfield resonance at $\delta = -4.96$ ppm due to W-H-B. The ^{13}C NMR also confirms the presence of the Cp* ligands. The IR spectrum of **4** shows the presence of two types of terminal CO ligands, whereas compound **3** shows three signals corresponding to terminal CO ligands.

Clusters **3** and **4** contain 7 skeletal electron pair (sep) [86–89] thus, they are isoelectronic and isolobal to each other if we assume $[\text{Ru}(\text{CO})_3]$ and $[\text{Cp}^*\text{W}(\text{CO})_2\text{H}]$ are isolobal (both are 14 electron fragments) [90]. To study this substitution effect, we have performed the DFT calculations on the model complexes $[\{\text{CpW}(\text{CO})_2\}_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_2\{\text{Ru}(\text{CO})_2(\mu\text{-H})\}]$ and $[\{\text{CpW}(\text{CO})_2\}_2(\mu_5\text{-B})\{\text{Ru}(\text{CO})_3\}_4]$, the Cp analogs of **3** and **4**, respectively. The DFT calculated geometries are in close agreement with the observed structures. An increased of HOMO-LUMO gap has been observed while shifting from **3** to **4** (2.61 eV for **3** vs. 2.92 eV for **4**, Fig. S19). Further, the electronic structures of clusters **2–4** are almost similar where the HOMO and LUMO are largely centered on the metal centers and the boron based orbitals are more ‘core’ like which also support the encapsulated pictures of the boron atoms.

$[(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{Ru}(\text{CO})_3]$ (**5**)

Although, compound **5** was produced as a mixture along with the compounds **2–4**, it was separated by preparative thin-layer chromatography (TLC), allowing characterization of the pure materials. It was isolated as greenish brown solid (11.4 % yield). The ^{11}B NMR of compound **5** displayed three resonances at $\delta = 77.7$, 40.2 and 34.0 ppm, that rationalize the presence of three different boron environments. In addition to the resonances for BH_i protons, the ^1H NMR spectrum showed signal at $\delta = 2.26$ ppm corresponding to the Cp* ligand and two upfield signals at $\delta = -7.10$ and -12.85 ppm that may be due to the W-H-B protons. The ^{13}C NMR spectra contain signals attributable to terminal CO ligand and Cp* ligand. The mass spectrum of **5** showed molecular ion peak at m/z 877.

The framework geometry of **5** was unambiguously established by its solid state structure determination. As shown in Fig. 3, the structure of **5** can be viewed as a bicapped trigonal bipyramid, in which the $\{\text{W}_2\text{B}_2\text{Ru}\}$ trigonal bipyramid core is capped by B1 and B4 at the triangular $\{\text{W}_2\text{B}\}$ and $\{\text{W}_2\text{Ru}\}$ faces. The solid state X-ray structure of **5** is analogous to that of well known ditungstaborane $[(\text{Cp}^*\text{W})_2\text{B}_5\text{H}_9]$ [69], **I** (Table S2). One of the major differences between **I** and **5** is the presence of a isolobal ‘ C_{3v} ’ $[\text{Ru}(\text{CO})_3]$ fragment instead of a BH fragment. This led us to perform a detailed electronic structure and bonding analysis of **5** in the context of known **I**. The molecular orbital (MO) analysis of **I** and **5** shows that the HOMOs are largely localized on the tungsten atoms which are essentially W-W δ^* bonding. Interestingly, this is stabilized in **5** with two strong W-Ru interactions (Fig. 4). However, in both the compounds the LUMOs are corresponding to the W-W bonding with

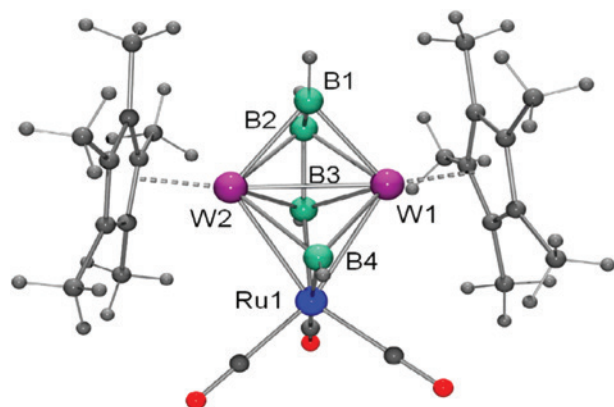


Fig. 3: Molecular structure and labeling diagram for **5**. Selected bond lengths (Å) and angles (°) of **5**: B1-B2 1.76(3), B1-W1 2.27(2), B1-W2 2.27(2), B2-B3 1.74(3), B3-Ru1 2.14(2), B4-Ru1 2.17(2), B4-W2 2.43(2), Ru1-W1 2.783(16), Ru1-W2 2.81(15), W1-W2 2.819(9); B2-B1-W1 63.7(9), W1-B1-W2 76.9(7), B3-B2-B1 123.8(16), W1-B4-W2 71.7(6), B3-Ru1-B4 93.9(9).

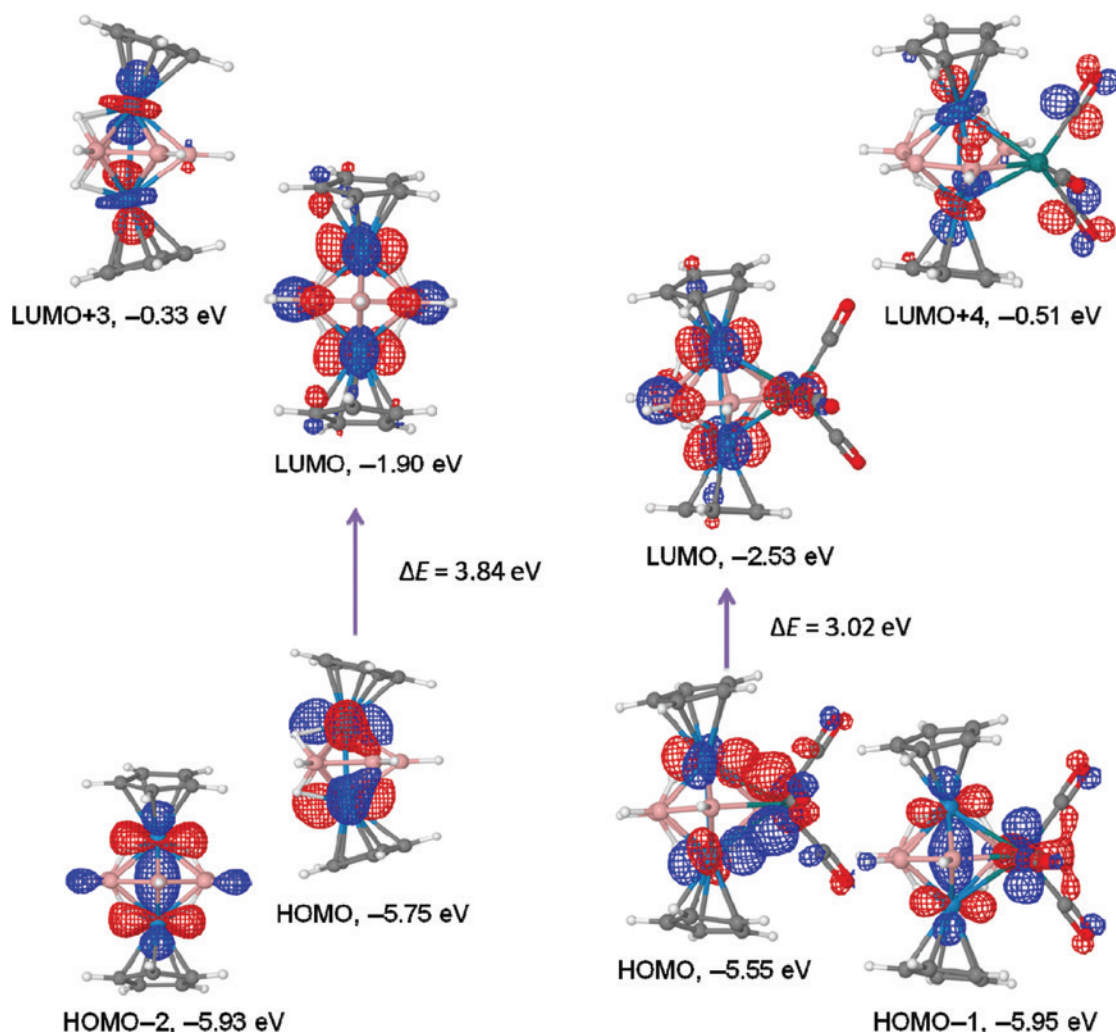


Fig. 4: Frontier molecular orbital diagram of **1** (left) and **5** (right).

δ -symmetry, which are destabilized by the antibonding interactions with the σ - orbitals of the boron moieties. A comparison of the MO diagrams of **5** and **1** (Fig. 4) show a larger HOMO/LUMO gap for **1** (3.84 eV for **1** vs. 3.02 eV for **5**). As shown in Fig. 4, the HOMO-1 and LUMO + 4 of **5** represents the W-W σ bonding and antibonding interactions, respectively, having an energy gap of 6.46 eV. On the other hand, corresponding MOs of **1** can be found in HOMO-2 and LUMO + 3, respectively, in which the energy gap between them is 6.26 eV.

Conclusions

The structure, bonding and chemistry of the transition metals boride clusters continuing to flourish the chemists due to their unique physical, chemical and electrical properties. Herein, we have described the synthesis and structurally characterized different types of hetero-metallic boride clusters. These clusters obey Wade-Mingos rule of the polyhedral skeleton electron counts and are unique considering the environment of the boron centers and the cluster geometries. Compound **2** represent semi-interstitial butterfly boride clusters, whereas **3** and **4** are square pyramidal heterometallic boride clusters. In addition, we have isolated an interesting ditungstaborane **5** that showed an $[\text{Ru}(\text{CO})_3]$ fragment insertion into the $[(\text{Cp}^*\text{W})_2\text{B}_5\text{H}_9]$ cage. The experimental results are well accompanied and rationalized and the bonding analyses of the synthesized clusters are explained with the help of DFT studies.

Experimental section

General procedures and instrumentation

All the experiments were conducted under an argon atmosphere using standard Schlenk techniques. Solvents were distilled prior to use under argon environment. $\text{LiBH}_4 \cdot \text{thf}$, W(CO)_6 , PCl_5 , Cp^*H and nBuLi were purchased from Aldrich chemicals and used as received. MeI was purchased from Aldrich and freshly distilled prior to use. $[\text{Cp}^*\text{WCl}_4]$ [91, 92] and the external reference $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ [93] for ^{11}B NMR were synthesized according to literature method. TLC was performed on a 250 mm dia aluminum-supported silica gel plates (MERCK TLC Plates). The NMR spectra were recorded on 500 MHz Bruker FT-NMR spectrometer. The residual solvent protons were used as reference (δ , ppm, CDCl_3 , 7.26), whereas a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in C_6D_6 (δ_{B} , ppm, -30.07) was used as an external reference for ^{11}B NMR. Infrared spectra were obtained on a Jasco FT/IR-1400 spectrometer. Electrospray mass (ESI-MS) spectra were recorded on a Qtof Micro YA263 HRMS Instruments.

Synthesis of 2–5

In a flame-dried Schlenk tube $[\text{Cp}^*\text{WH}_3(\text{B}_4\text{H}_8)]$ (**1**), (0.180 g, 0.48 mmol) in 10 mL of toluene was heated with $[\text{Ru}_3(\text{CO})_{12}]$ (0.06 g, 0.093 mmol) at 100°C for 28 h. From the brown color solution the volatile components were removed under vacuum and the remaining residue was extracted into hexane and passed through celite. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/ CH_2Cl_2 (70:30 v/v) mixture yielded orange **2** (0.068 g, 0.059 mmol 12.46%), brown **3** (0.064 g, 0.049 mmol 10.30%), purple **4** (0.088 g, 0.078 mmol 16.19%) and greenish brown **5** (0.048 g, 0.055 mmol 11.38%).

2: HRMS (ESI⁺): m/z calculated for $[\text{C}_{30}\text{H}_{31}\text{O}_{10}\text{BW}_2\text{Ru}_2\text{Na}]$: 1156.9013; found: 1156.9020; $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , 22°C): $\delta = 128.8$ (br, 1B); ^1H NMR (500 MHz, CDCl_3 , 22°C): $\delta = 2.18$ (s, 30H, Cp^*), -18.95 (br, 1H, Ru-H – Ru); ^{13}C NMR (125 MHz, CDCl_3 , 22°C): $\delta = 200.7$ ($\underline{\text{CO}}$), 198.2 ($\underline{\text{CO}}$), 100.5 (s, $\underline{\text{C}_5\text{Me}_5}$), 10.6 (s, $\underline{\text{C}_5\text{Me}_5}$). IR (CH_2Cl_2 , cm^{-1}): $\bar{\nu} = 2017, 1971, 1950, 1852$ (CO).

3: HRMS (ESI⁺): m/z calculated for $[\text{C}_{32}\text{H}_{31}\text{O}_{12}\text{W}_2\text{Ru}_3\text{BNa}]$: 1314.7955; found: 1314.7948; $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, CDCl_3 , 22°C): $\delta = 189.8$ (br, 1B); ^1H NMR (500 MHz, CDCl_3 , 22°C): $\delta = 2.11$ (s, 15H, Cp^*), 2.07 (s, 15H, Cp^*), -4.96 (br, 1H, W-H-B); ^{13}C NMR (125 MHz, CDCl_3 , 22°C): $\delta = 206.1, 205.1, 200.0, 198.4$ ($\underline{\text{CO}}$), 101.2, 99.4 (s, $\underline{\text{C}_5\text{Me}_5}$), 12.1, 11.1 (s, $\underline{\text{C}_5\text{Me}_5}$); IR (CH_2Cl_2 , cm^{-1}): $\bar{\nu} = 2042, 2003, 1958, 1933, 1901$ (CO).

4: HRMS (ESI⁺): m/z calculated for $[\text{C}_{24}\text{H}_{16}\text{B}_1\text{O}_{14}\text{W}_1\text{Ru}_4]$: 1130.6294; found: 1130.6319; $^{11}\text{B}\{^1\text{H}\}$ NMR (22°C , 160 MHz, CDCl_3): $\delta = 182.0$ (s, 1B); ^1H NMR (22°C , 500 MHz, CDCl_3): $\delta = 2.03$ (s, 15H, Cp^*); ^{13}C NMR (22°C , 125 MHz, CDCl_3): $\delta = 206.6, 202.7, 197.9, 190.9, 189.2$ ($\underline{\text{CO}}$), 114.5 (s, $\underline{\text{C}_5\text{Me}_5}$), 13.8 (s, $\underline{\text{C}_5\text{Me}_5}$); IR (CH_2Cl_2 , cm^{-1}): $\bar{\nu} = 2030, 2000, 1959$ (CO).

5: HRMS (ESI⁺): m/z calculated for $[\text{C}_{23}\text{H}_{39}\text{B}_4\text{O}_3\text{W}_2\text{Ru}]$: 877.1333; found: 877.1326; $^{11}\text{B}\{^1\text{H}\}$ NMR (22°C , 160 MHz, CDCl_3): $\delta = 77.7$ (s, 2B), 40.2 (s, 1B), 34.0 (s, 1B); ^1H NMR (22°C , 500 MHz, CDCl_3): $\delta = 6.60$ (b, B-H₁), 5.96 (b, B-H₁), 5.63 (b, B-H₁), 2.26 (s, 30H, Cp^*), -7.10 (b, B-H-W), -12.85 (b, B-H-W); ^{13}C NMR (22°C , 125 MHz, CDCl_3): $\delta = 197.3$ ($\underline{\text{CO}}$), 105.8 (s, $\underline{\text{C}_5\text{Me}_5}$), 11.3 (s, $\underline{\text{C}_5\text{Me}_5}$); IR (CH_2Cl_2 , cm^{-1}): $\bar{\nu} = 2005, 1941$ (CO).

X-ray structure determination

Suitable X-ray quality crystals of **2–5** were grown by slow diffusion of a hexane- CH_2Cl_2 solution. The crystal data for **2** and **3** were collected and integrated using D8 VENTURE Bruker AXS and for **4** and **5** were using Bruker Kappa apexII CCD single crystal diffractometer, equipped with graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71078 \text{ \AA}$) radiation.

Table 2: Crystallographic data and structure refinement information for clusters 2–5.

	2	3	4	5
Empirical formula	C ₃₀ H ₃₀ BO ₁₀ Ru ₂ W ₂	C ₃₂ H ₃₁ BO ₁₂ Ru ₃ W ₂	C ₂₄ H ₁₅ BO ₁₄ Ru ₄ W	C ₂₃ H ₃₄ B ₄ O ₃ RuW ₂
Formula weight	1131.19	1289.29	1126.30	870.51
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pcc/n</i>	<i>P21/c</i>	<i>P21/n</i>	<i>P21/n</i>
<i>a</i> (Å)	17.2521(14)	21.4876(17)	11.0472(3)	12.0780(8)
<i>b</i> (Å)	30.468(3)	9.0740(7)	15.5394(4)	16.4329(12)
<i>c</i> (Å)	12.4547(12)	18.4479(12)	18.4264(4)	15.2013(11)
α (°)	90	90	90	90
β (°)	90	103.850(3)	95.9405(9)	110.498(3)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	6546.6(10)	3492.4(4)	3146.22(14)	2826.1(3)
<i>Z</i>	8	4	4	4
<i>D</i> _{calc} (g/cm ³)	2.295	2.452	2.378	2.046
<i>F</i> (000)	4248	2416	2104	1632
μ (mm ⁻¹)	7.965	7.892	5.582	8.669
θ Range (°)	2.94–27.48	2.45–27.49	2.27–26.73	2.24–21.25
No. of reflns collected	60732	41166	24585	10597
No. of unique reflns [<i>I</i> > 2 σ (<i>I</i>)]	7504	7990	5549	2825
Goodness-of-fit on <i>F</i> ²	1.114	1.042	1.058	1.043
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0292, w <i>R</i> 2 = 0.0663	<i>R</i> 1 = 0.0295, w <i>R</i> 2 = 0.0713	<i>R</i> 1 = 0.0189, w <i>R</i> 2 = 0.0373	<i>R</i> 1 = 0.0530, w <i>R</i> 2 = 0.1155
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0328, w <i>R</i> 2 = 0.0678	<i>R</i> 1 = 0.0388, w <i>R</i> 2 = 0.0758	<i>R</i> 1 = 0.0242, w <i>R</i> 2 = 0.0393	<i>R</i> 1 = 0.0989, w <i>R</i> 2 = 0.1410

Data collection for **2** and **3** were carried out at 150 K and for compound **4** and **5** at 296 K, respectively, using ω - ϕ scan modes. Multi-scan absorption correction has been employed for the data using SADABS [94] program. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 [95] and refined using SHELXL-2014 [96]. Crystallographic data and structure refinement information has been shown in Table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1574739 (**2**), 1574738 (**3**), 1574737 (**4**) and 1574736 (**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details

All the calculations (DFT) were carried out with the program package Gaussian 09 (Rev. C. 01) [97] and were performed on a parallel cluster system. The ground-state geometries were optimized without symmetry constraints using the B3LYP functional [98–100] in combination with mixed basis set: SDD with effective core potential for Ru and W and 6-31g* for C, B, H, O [101–103]. To reduce the computational cost all the calculations were carried out with the Cp analog model compounds, instead of Cp*. The model geometries were fully optimized in gaseous state (without solvent effect) without any symmetry constraints. The optimized geometries were confirmed to be local minima by performing frequency calculations and obtaining only positive (real) frequencies. The NMR chemical shifts were calculated on the optimized geometries at the aforementioned level. Computation of the NMR shielding tensors employed GIAOs [104–108]. The ¹¹B NMR chemical shifts were calculated relative to B₂H₆ (B3LYP B shielding constant 93.5 ppm) and converted to the usual [BF₃ · OEt₂] scale using the experimental d(¹¹B) value of B₂H₆, 16.6 ppm [109].

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