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# Heterometallic Triply-Bridging *Bis*-Borylene Complexes

Ranjit Bag,<sup>[a]</sup> Sourav Kar,<sup>[a]</sup> Suvam Saha,<sup>[a]</sup> Suman Gomosta,<sup>[a]</sup> Beesam Raghavendra,<sup>[a]</sup> Thierry Roisnel,<sup>[b]</sup> and Sundargopal Ghosh<sup>\*[a]</sup>

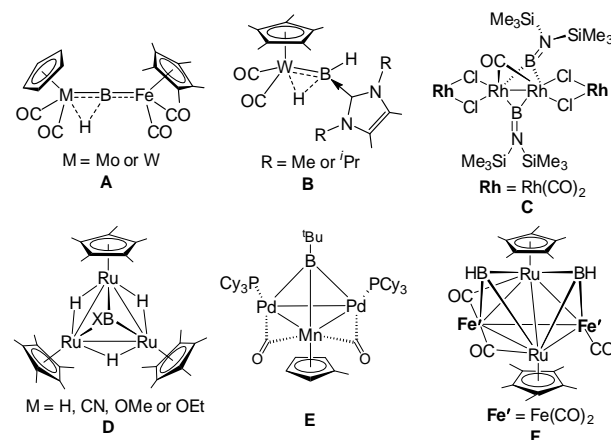
Dedicated to Professor Goutam Kumar Lahiri on the occasion of his 60<sup>th</sup> birthday

**Abstract:** Triply bridging *bis*-(hydrido(borylene)) and *bis*-borylene species of groups 6, 8 and 9 transition metals are reported. Mild thermolysis of  $[\text{Fe}_2(\text{CO})_9]$  with an *in situ* produced intermediate, generated from the low temperature reaction of  $[\text{Cp}^*\text{WCl}_4]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) and  $[\text{LiBH}_4\cdot\text{THF}]$  afforded triply-bridging *bis*-(hydrido(borylene)),  $[(\mu_3\text{-BH})_2\text{H}_2(\text{Cp}^*\text{W}(\text{CO})_2)_2\{\text{Fe}(\text{CO})_2\}]$  (**1**) and *bis*-borylene,  $[(\mu_3\text{-BH})_2(\text{Cp}^*\text{W}(\text{CO})_2)_2\{\text{Fe}(\text{CO})_3\}]$  (**2**). The chemical bonding analyses of **1** show that the B-H interactions in *bis*-(hydrido(borylene)) species is stronger as compared to the M-H ones. Frontier molecular orbital analysis shows a significantly larger energy gap between HOMO-LUMO for **2** as compared to **1**. In an attempt to synthesize the ruthenium analogue of **1**, a similar reaction has been performed with  $[\text{Ru}_3(\text{CO})_{12}]$ . Although we failed to get the *bis*-(hydrido(borylene)) species, the reaction afforded triply-bridging *bis*-borylene species  $[(\mu_3\text{-BH})_2(\text{WCp}^*(\text{CO})_2)_2\{\text{Ru}(\text{CO})_3\}]$  (**2'**), an analogue of **2**. In search for the isolation of bridging *bis*-borylene species of Rh, we have treated  $[\text{Co}_2(\text{CO})_8]$  with *nido*- $[(\text{RhCp}^*)_2(\text{B}_3\text{H}_7)]$ , which afforded triply-bridging *bis*-borylene species  $[(\mu_3\text{-BH})_2(\text{RhCp}^*)_2\text{Co}_2(\text{CO})_5(\mu\text{-CO})]$  (**3**). All the compounds have been characterized by means of single-crystal X-ray diffraction study;  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$  NMR spectroscopy; IR spectroscopy and mass spectrometry.

## Introduction

The rapidly growing field of subvalent species<sup>1</sup> is witnessing a dramatic change with the entry of borylene (:BR) species because of their unique electronic structure and extensive reactivity.<sup>2,3</sup> Although in 1960s Timms reported the synthesis of free borylene (:BF) in the gas phase, because of their highly reactive nature isolation of free borylenes are only achievable under drastic conditions as an intermediate.<sup>2</sup> Later, the borylene fragment has been stabilized and structurally characterized by trapping it in the transition metals coordination sphere.<sup>4</sup> In 1998, Braunschweig *et al.*<sup>5</sup> and Cowley *et al.*<sup>6</sup> reported the first structurally characterized terminal borylene complexes. Since then, the search for different types of borylene complexes using various synthetic methods has been augmented immensely.

Based upon the coordination nature of boron and the number of boron-metal bonds, borylene ligands can be classified as terminal, bridging, semibridging, and triply bridging (Chart 1).<sup>7-12</sup> Borylenes possess classical 2c-2e bonds, unlike metallaboranes, where M-B bonds are composed of nonclassical multicenter-2e bonds. Apart from their fascinating structural features, the chemistry associated with borylene has been enriching the field of organometallic and organic synthesis. For example, acid induced B-N bond break,<sup>3e</sup> the borylene transfer to organic species to synthesize diboraheterocyclic and borirenes complexes,<sup>3e,13</sup> metal-fragment addition,<sup>3e,14</sup> cycloaddition and dimerization,<sup>15</sup> nucleophilic substitution and addition,<sup>3e,13,16</sup> and auxiliary ligand exchange.<sup>17</sup> In addition, very recently Braunschweig *et al.* have shown nitrogen fixation using a dicoordinate borylene species.<sup>18</sup>



**Chart 1.** Different types of transition metal borylene complexes: hydridoborylene (**A**), hydrido(hydroborylene) (**B**), *bis*-borylene (**C**), homometallic triply bridged borylene (**D**), heterometallic triply bridged borylene (**E**) and heterometallic triply bridged *bis*-borylene (**F**).

Furthermore, after the isolation of triply bridging borylene species  $[(\mu_3\text{-BX})(\text{RuCp}^*)_3(\mu\text{-H})_3]$  ( $\text{X} = \text{H or CN}$ ) (**D**) followed by their fascinating chemistry, the synthesis of them using various transition metals became of interest.<sup>10</sup> In that connection, a series of homo and hetero-metallic triply bridging borylene complexes has been reported by us.<sup>12,19</sup> In addition, we have synthesized and structurally characterized triply bridging bis-borylene  $[(\text{RuCp}^*)(\mu\text{-CO})(\mu_3\text{-BH})_2\text{Fe}_2(\text{CO})_5]$  (**F**).<sup>12</sup> Although examples of structurally characterized triply-bridging borylene species are known, the synthesis strategies for the isolation of triply-bridging bis-borylene complexes met with little success.<sup>12,19a,d</sup> Thus, we explored the chemistry of group 6 transition metals with boranes and metal carbonyls. Herein, we report the synthesis, structure and bonding of various type of triply bridging borylenes. The density functional theory (DFT)

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calculations and electron counting rules provided further insight into the electronic structures and the bonding of these molecules.

existence was ascertained by the characteristic proton chemical shift.

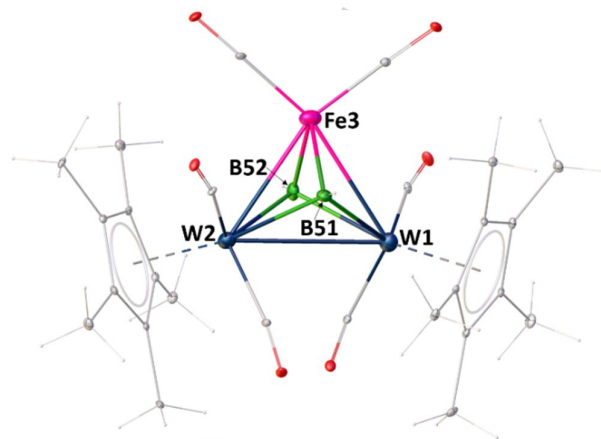
## Results and Discussion

### Reactivity of $[\text{Cp}^*\text{WCl}_4]$ with boranes and metal carbonyls.

In the course of our continuing efforts to synthesize borylene species, we have been exploring numerous approaches using different metal carbonyl precursors. Using these methodologies recently, we have reported a series of borylene complexes. In order to explore this chemistry with group 6, we have performed thermolysis reaction of  $[\text{Fe}_2(\text{CO})_9]$  with an *in situ* produced intermediate, generated from the reaction of  $[\text{Cp}^*\text{WCl}_4]$  and  $[\text{LiBH}_4\cdot\text{THF}]$ , which afforded triply-bridging *bis*-{hydrido(borylene)} metal complex (**1**) and *bis*-borylene complex (**2**) (Scheme 1). In a pursuit to synthesize the ruthenium-borylene species, a similar reaction has been carried out with  $[\text{Ru}_3(\text{CO})_{12}]$ , which afforded triply-bridging *bis*-borylene complex (**2'**). All these species were isolated using thin layer chromatography (TLC) and characterized by means of various NMR spectroscopic; IR spectroscopic and mass spectrometric data. The characterizations of these compounds are described below.

**Bis-{hydrido(borylene)}, 1.** Compound **1** was isolated as orange solid in low yield. A downfield resonance at  $\delta = 80.0$  ppm is observed in  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum. The molecular ion peak of **1** at  $m/z$  888.0894 corresponds to  $[\text{C}_{26}\text{H}_{34}\text{O}_6\text{B}_2\text{W}_2\text{Fe}]^+$ . The peak at  $\delta = 1.97$  ppm in  $^1\text{H}$  NMR spectrum corresponds to  $\text{Cp}^*$  ligands. Further, the  $^1\text{H}$  NMR spectrum exhibits resonances at -9.20 (W-H-B) and 9.31 (B-H) ppm. The IR spectroscopic data has also confirmed the existence of B-H and CO ligands. However, the mass and spectroscopic data were not sufficient to establish the exact core structure of this molecule.

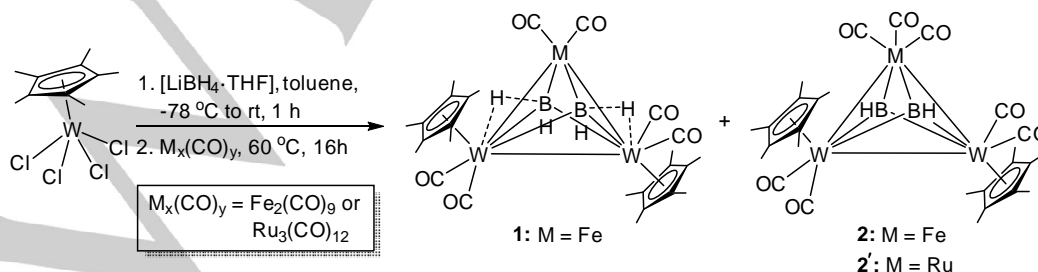
An explicit explanation evaded us till an X-ray structure showed the molecular formula of **1** as  $[(\mu_3\text{-BH})_2\text{H}_2(\text{Cp}^*\text{W}(\text{CO})_2)_2(\text{Fe}(\text{CO})_2)]$ . As represented in Figure 1, solid state structure of **1** signifies a trigonal bipyramid  $\text{W}_2\text{FeB}_2$  core, in which the axial positions are occupied with two B atoms and the equatorial positions are occupied with one Fe and two W atoms. The W-W bond length of 3.0491(4) Å is marginally longer in **1** with respect to W-W bond distances of reported tuginstaboranes.<sup>20</sup> The Fe-B bond distances of **1** are slightly shorter as compared to Fe-B bond distances of reported metallaboranes.<sup>21</sup> Although the bridging W-H-B hydrogens were not positioned from single crystal X-ray diffraction, their



**Figure 1.** Molecular structure and labeling diagram of **1**. Selected bond lengths (Å) and angles (°): W2-W1 3.0491(4), Fe3-W1 2.7773(11), W2-Fe3 2.7893(11), W1-B51 2.287(9), W1-B52 2.310(8), Fe3-B52 2.042(9), Fe3-B51 2.045(8); W1-Fe3-W2 66.43(2), W2-B52-W1 83.1(3), Fe3-B51-W1 79.5(3).

Based on the available literature (Chart 1), compound **1** can be considered as *bis*-{hydrido(borylene)} species. In 2013, Braunschweig and co-workers reported a new class of borylene called hydridoborylene (**A**).<sup>7</sup> Recently, Tobita and co-workers reported the synthesis of W-hydrido(hydroborylene) species (**B**).<sup>8</sup> Compound **1** may be considered as the newest and unique entry to this series. The presence of a broad down-field  $^{11}\text{B}$  chemical shift for **1** is comparable to aminoborylene species  $[\text{W}(\text{CO})_5\text{BN}(\text{SiMe}_3)_2]$  (86.6 ppm);<sup>6</sup> hydridoborylene complexes  $[(\text{OC})_2\text{MCP}(\text{HBN}(\text{SiMe}_3)_2)]$  (M = Cr (70.7 ppm); Mo (74.4 ppm) and W (81.6 ppm));<sup>7</sup> and hydrido(hydroborylene) complexes  $[\text{WCp}^*(\text{CO})_2(\text{H})(\text{BH}\cdot\text{NHC})]$  (NHC =  $^{\text{Me}}\text{IPr}$  (74.4 ppm);  $^{\text{Me}}\text{IMe}$  (74.0 ppm)).<sup>8</sup> The  $^1\text{H}$  NMR spectrum of **1** exhibits a broad peak at  $\delta = -9.20$  ppm, which may be due to the existence of hydrido ligand. The presence of the bridging W-H-B interaction has been indicated by broadening of this peak.

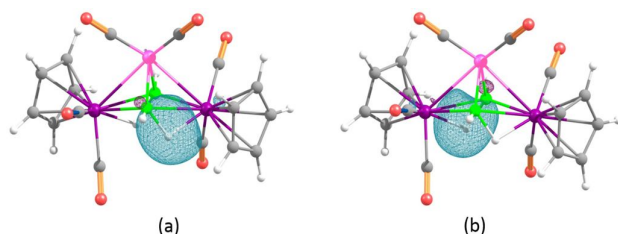
Computational studies have been carried out at the b3lyp/def2-tzvp level of theory to analyze the bonding scenario of **1**.<sup>22</sup> The HOMO-LUMO energy gap of 2.894 eV indirectly supports the thermodynamic stability of **1**. The NBO calculations of **1** illustrate that the B-H bonding interaction is significantly stronger as compared to the W-H interaction in W-H-B. In addition, the wiberg bond indices (WBI) shows that WBI values for B-H interaction (0.46-0.53) is higher compared to that of W-H



**Scheme 1.** Synthesis of triply-bridging *bis*-{hydrido(borylene)} metal complex (**1**) and *bis*-borylene complexes (**2** and **2'**).

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interaction (0.35–0.41). The calculated  $^1\text{H}$  NMR further supported the W-H-B interaction.<sup>23</sup> Further, to check bonding nature of Fe-B bonds of **1**, we have looked at the Laplacian electron density plot along the B53–Fe3–B51 plane which displayed bond critical points (bcp) between all these Fe-B bonds (Figure S23(a)). A charge concentrated area along the Fe-B bonds has been found with high covalent character, which was also revealed by a negative energy density value [ $H(r) = -0.055$ ] and average electron density ( $\rho(r) = 0.123$ ) at BCPs of Fe-B bonds. All these bcp and atoms (one Fe and two B) are connected by bond paths (Figure S23(a)).

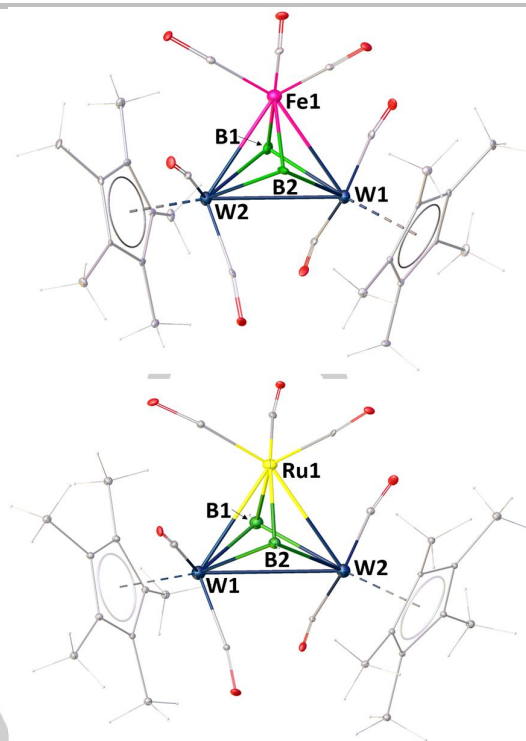


**Figure 2.** (a) and (b) showed natural bonding orbital (NBOs) obtained from NBO analysis showing W-H-B bonding.

**Triply-bridging *bis*-borylene complexes, **2** and **2'**.** As shown in Scheme 1, triply-bridging *bis*-borylene complex **2** was isolated along with *bis*-(hydrido(borylene)), **1**. A molecular ion peak of **2**, observed at  $m/z$  914.0702, that suggests the composition of  $[\text{C}_{27}\text{H}_{32}\text{O}_7\text{B}_2\text{W}_2\text{Fe}]^+$ . Although the  $^1\text{H}$  NMR spectrum exhibits resonances at  $\delta = 2.01$  and 10.20 ppm that correspond to  $\text{Cp}^*$  and terminal B-H protons respectively, there were no up-field resonances. A down-field resonance at  $\delta = 102.8$  ppm is observed in  $^{11}\text{B}$  NMR. All these spectroscopic data along with mass spectrometric data suggest **2** as a *bis*-borylene species, which was further confirmed by X-ray diffraction analysis.

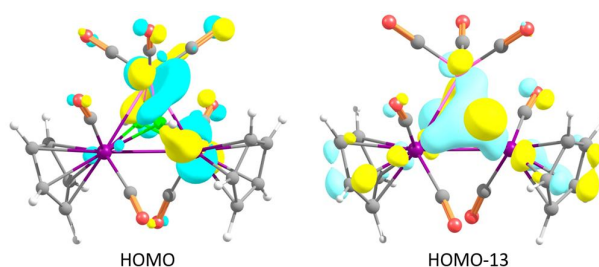
The X-ray structure of **2**, represented in Figure 3(top), corroborated well with all the spectroscopic data. The structure of **2** can also be viewed as a trigonal bipyramid geometry where the trimetallic triangular equatorial positions are occupied by two tungsten atoms and one iron atom and two B-H units are linked with three metal atoms in  $\mu_3$ -fashion. The W-W bond length of **2** (3.0516(7) Å) is comparable with that of **1**. The W-Fe bond distances of 2.785(2) Å and 2.814(2) Å of **2** are consistent with the W-Fe bond lengths of **1**.

In an effort to isolate the Ru analogue of **1**, we performed the same reaction in presence of  $[\text{Ru}_3(\text{CO})_{12}]$ . The reaction yielded brown solid **2'**. The chemical shift pattern of **2'** is almost similar to that of **2** in  $^1\text{H}$  NMR. The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum displays a down-field peak at  $\delta = 102.4$  ppm. A peak at  $m/z$  961.0460 is observed in the mass spectrum of **2'** that corresponds to  $[\text{C}_{27}\text{H}_{32}\text{O}_7\text{B}_2\text{W}_2\text{Ru}+\text{H}]^+$ . The X-ray structures of **2'**, presented in Figure 3(bottom), confirmed the structural interpretations which have been done based on the spectroscopic results. The core geometry of **2'** is alike to that of **2**, the presence of Ru instead of Fe is the only difference. The Ru-B bond distances of **2'** are comparable with the reported Ru-B bond distances.<sup>24</sup> The Ru-W bond lengths of 2.923(3) Å and 2.897(3) Å of **2'** are consistent with the W-Ru bond distances (2.986(3) Å and 2.981(3) Å) of  $[\text{HRu}_3\text{WCp}(\text{CO})_{10}(\text{PPh}_3)\text{BH}]$ .<sup>25</sup>



**Figure 3.** Molecular structures and labeling diagrams of **2** (top) and **2'** (bottom). Selected bond lengths (Å) and angles ( $^\circ$ ): **2**: W1-W2 3.0516(7), Fe1-W1 2.814(2), Fe1-W2 2.785(2), B1-Fe1 2.03(2), B1-W2 2.307(19); B1-Fe1-B2 89.8(7). **2'**: W1-W2 3.0585(15), W1-B1 2.18(4), W1-B2 2.23(3), W2-Ru1 2.923(3), Ru1-B2 2.18(3), W2-B1 2.37(4), B2-W2 2.37(3); B1-W1-Ru1 85.9(14).

**Electronic structure comparison of **1**, **2** and **2'**.** The molecular structures of **1**, **2** and **2'** are very similar. The only difference between these three 6 skeletal electron pairs (SEP)<sup>26,27</sup> cores is the absence of two W-H-B protons in **2** and **2'** that is balanced by an extra CO ligand. Seeing **1** and **2** as 52 cve (cluster valence electron) with trigonal bipyramid geometry ( $\text{M}_3\text{B}_2$  core), one can construct **1** by removing one CO and adding two hydrogens into **2**. The MOs comparison of **1** and **2** displays a larger gap between HOMO and LUMO for **2** (Table S1), which suggests a higher thermodynamic stability for **2** compared to **1**. Whereas, in case of triply bridging borylene species, moving from Fe (**2**) to Ru (**2'**), the HOMO-LUMO energy gap increases (Table S1). Furthermore, the HOMO, HOMO-1, HOMO-5 and HOMO-13 of **2** show considerable overlap between B atom, two W and one Fe atom that indicate that {BH} unit is bridged



**Figure 4.** Selected frontier MOs of **2** showing  $\mu_3$ -B bonding mode with two W and one Fe atoms.

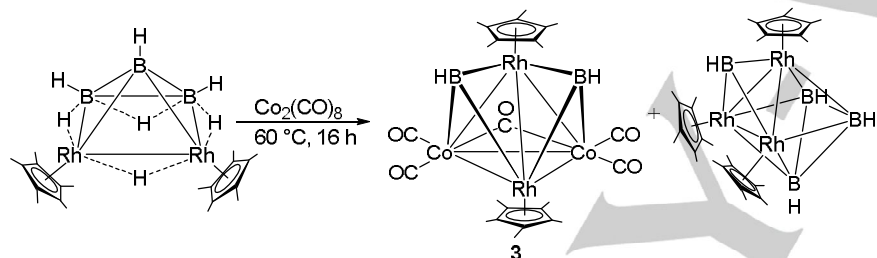


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between two W and one Fe atom in  $\mu_3$ -fashion (Figures 4 and S21). Furthermore, the interactions have also been confirmed from average WBI values for W-B (0.58) and Fe-B (0.54).

### Reactivity of *nido*-(Cp\* $\text{Rh}_2(\text{B}_3\text{H}_7)$ ) with $[\text{Co}_2(\text{CO})_8]$ .

In order to extend this chemistry with other transition metals, the thermolysis reaction of *nido*-(Cp\* $\text{Rh}_2(\text{B}_3\text{H}_7)$ )<sup>28</sup> with  $[\text{Co}_2(\text{CO})_8]$  has been performed (Scheme 2). The reaction afforded yellow solid **3** and known *pileo*-(Cp\* $\text{Rh}_3\text{B}_4\text{H}_4$ )<sup>29</sup>. The molecular ion peak was observed at  $m/z$  757.9167 in the mass spectrum. The  $^1\text{H}$  NMR spectrum of **3** indicates single Cp\* environment appearing at  $\delta$  = 1.81 ppm. In addition, a broad peak at  $\delta$  = 8.73 ppm is detected in  $^1\text{H}$  NMR spectrum, that corresponds to terminal B-H.  $^{13}\text{C}$  NMR spectroscopy confirmed the presence of CO and Cp\* ligands.  $^{11}\text{B}$  NMR spectrum of **3** displays a downfield peak at  $\delta$  = 125.5 ppm. Although a higher molecular-ion peak and NMR spectra of **3** specify the formation of borylene species, to predict the structure of **3** these spectroscopic data were not sufficient. To get the structure single crystal X-ray analysis of **3** has been carried out.



**Scheme 2.** Synthesis of triply bridging *bis*-borylene complex, **3**.

The X-ray analysis of **3** displays the molecular formula as  $[(\mu_3\text{-BH})_2(\text{Cp}^*\text{Rh})_2\text{Co}_2(\text{CO})_5(\mu\text{-CO})]$ . The molecular structure of **3** comprises of a  $\text{Rh}_2\text{Co}_2$  tetrahedron, in which Rh1-Co1-Rh2 and Rh1-Co2-Rh2 faces are symmetrically bridged in  $\mu_3$ -fashion by borylene ligand (BH) (Figure 5). The core structure of **3** alike of our previously reported triply bridging *bis*-borylene,  $[(\text{Cp}^*\text{Ru})(\mu_3\text{-BH})(\mu\text{-CO})_2\text{Fe}_2(\text{CO})_5]$ .<sup>12</sup> On the other hand, compound **3** can be

viewed as bicapped tetrahedral, having 6 SEP. The Rh-Rh bond length of 2.6285(16) Å in **3** is significantly shorter as compared to Rh-Rh bond distances of *nido*-(Cp\* $\text{Rh}_2(\text{B}_3\text{H}_7)$ )<sup>27</sup> (2.8491(4) Å) and *pileo*-(Cp\* $\text{Rh}_3\text{B}_4\text{H}_4$ )<sup>29</sup> (ca. 2.667 Å); however, comparable with  $[(\text{Cp}^*\text{Rh})_2(\mu\text{-CO})(\mu_3\text{-BH})(\text{Mo}(\text{CO})_5)]^{19d}$  (2.6339 (3) Å). The average Rh-B and B-Co bond lengths of 2.055 Å and 1.985 Å respectively lie in the range of those reported transition-metal borylene complexes.<sup>19a,d</sup>

Although we do not have any direct evidence in support of the formation of these triply-bridging borylene, or bicapped tetrahedron species, **1-3**, the existence of heterometallic octahedral species  $[\text{Co}(\text{CO})_3(\text{Cp}^*\text{Rh})_2\text{B}_3\text{H}_3\text{Cl}]$ , produced from the reaction of *nido*-(Cp\* $\text{Rh}_2(\text{B}_3\text{H}_6\text{Cl})$ ) and  $[\text{Co}_2(\text{CO})_8]$ ,<sup>30</sup> provides some hints for their formation. Thus, we strongly believe that the formation of **3** might have occurred through a similar intermediate  $[\text{Co}(\text{CO})_3(\text{Cp}^*\text{Rh})_2\text{B}_3\text{H}_4]$ , which on reaction with one cobalt carbonyl fragment yielded **3** with the replacement of one of the BH vertices of the intermediate.

## Conclusions

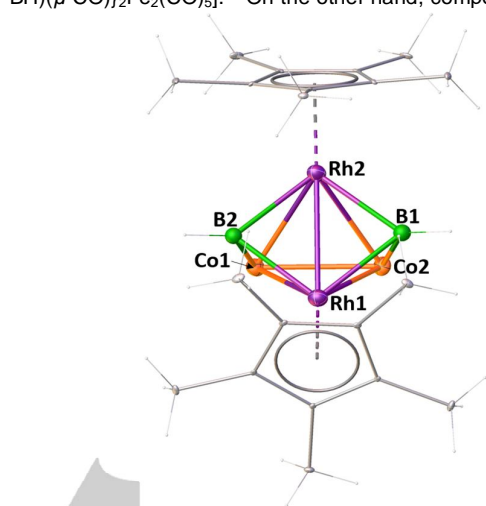
In summary, we have isolated and structurally characterized some unique heterometallic *bis*-(hydrido(borylene)) species **1** and triply-bridging *bis*-borylene complexes **2** and **2'**. The density functional theory calculations and electron counting rules provided salient insight into the electronic structures and bonding of

these novel molecules. Furthermore, theoretical studies show that addition of one CO and removal of two bridging H atoms from *bis*-(hydrido(borylene)) (**1**), generated triply-bridging *bis*-borylene complex (**2**), which has significantly higher HOMO-LUMO energy gap. In addition, we have synthesized 6 SEP triply-bridging *bis*-borylene species **3** which contain a tetrahedral core, capped by two borylene ligands.

## Experimental Section

**General Procedures and Instrumentation.** Employing glove box or standard Schlenk line techniques, all processes were carried out under dry argon. Solvents were distilled using sodium/benzophenone. Using three freeze-pump-thaw cycles  $\text{CDCl}_3$  was degassed.  $[\text{Cp}^*\text{WCl}_4]$ <sup>31</sup> and  $[\text{Cp}^*\text{RhCl}_2]$ <sup>32</sup> were prepared following literature procedures, while  $[\text{LiBH}_4\cdot\text{THF}]$ ,  $[\text{Ru}_3(\text{CO})_{12}]$ ,  $[\text{Co}_2(\text{CO})_8]$  and  $[\text{Fe}_2(\text{CO})_9]$  were obtained commercially.  $^{11}\text{B}\{^1\text{H}\}$  NMR external reference,  $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$  was prepared following literature technique.<sup>33</sup> Chromatography was performed using 250  $\mu\text{m}$  aluminium supported silica gel Merck TLC sheets. Utilizing Bruker FT-NMR (500 MHz) spectrometers NMR spectra were recorded. The residual solvent protons have been employed as reference ( $\delta$ , ppm,  $\text{CDCl}_3$ , 7.26;  $d_6$ -benzene, 7.16), while for the  $^{11}\text{B}\{^1\text{H}\}$  NMR a sealed tube holding  $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$  in  $d_6$ -benzene ( $\delta$ , ppm, -30.07) had been employed as an external reference. Utilizing a FT/IR-1400 (JASCO) spectrometer IR spectra were recorded. Using an Agilent 6545 Q-TOF LC/MS instrument ESI-MS spectra were recorded.

**Synthesis of **1** and **2**:** In a moisture free Schlenk tube  $[\text{Cp}^*\text{WCl}_4]$ , (0.1 g, 0.21 mmol) was taken in 10 mL of toluene, followed by addition of 5-fold excess of  $[\text{LiBH}_4\cdot\text{THF}]$  (0.7 mL) at -78 °C. It was brought to room



**Figure 5.** Molecular structures and labeling diagrams of **3**. For clarity the CO ligands are omitted. Selected bond lengths (Å) and angles (°): Rh2-Rh1 2.6285(16), B2-Rh1 2.04(2), B1-Rh1 2.07(2), Rh1-Co1 2.608(2), Co1-Co2 2.372(3), Co1-B2 1.98(2), Co2-B1 1.99(2); Co2-B1-Rh2 78.6(8).

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temperature by stirring for 1 h. After removing toluene, extraction was carried out using hexane. Under vacuo the brown hexane filtrate was dried. 10 mL of THF was added to it in presence of  $[\text{Fe}_2(\text{CO})_9]$  and heated at 60 °C for 16 h. After that solvent was removed and extraction was done using hexane. Using TLC plates the residue was chromatographed. Elution with a  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (20:80 v/v) afforded orange **1** (0.010 g, 11 %) and yellow **2** (0.020 g, 21 %) along with known  $[(\text{Cp}^*\text{W})_2\text{B}_4\text{H}_8\text{Fe}(\text{CO})_3]^{34}$  (0.010 g, 12 %) and  $[(\text{Cp}^*\text{W})_2\text{B}_5\text{H}_9]^{35}$  (0.020 g, 27 %).

**1:** MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{M}]^+$  888.0933, found 888.0894;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 80.0 ppm (s, 2B);  $^1\text{H}$  NMR (500 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 9.31 (br, 2H, B-H), 1.97 (s, 30H,  $\text{C}_5\text{Me}_5$ ), -9.20 ppm (br, 2H, W-H-B);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 99.4 ( $\text{C}_5\text{Me}_5$ ), 10.4 ppm ( $\text{C}_5\text{Me}_5$ ); IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 2498 (w, B-H), 2032, 1992, 1941, 1871 (CO).

**2:** MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{M}]^+$  914.0730, found 914.0702;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 102.8 ppm (s, 2B);  $^1\text{H}$  NMR (500 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 10.20 (br, 2H, B-H), 2.01 ppm (s, 30H,  $\text{C}_5\text{Me}_5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 99.9 ( $\text{C}_5\text{Me}_5$ ), 10.2 ppm ( $\text{C}_5\text{Me}_5$ ); IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 2003, 1942 (CO).

**Synthesis of 2':** In a solution of  $[\text{Cp}^*\text{WCl}_4]$  (0.1 g, 0.21 mmol) of toluene (10 mL) 5-fold excess of  $[\text{LiBH}_4\cdot\text{THF}]$  (0.7 mL) was added at -78 °C and allowed to come to room temperature by stirring for 1 h. After that toluene was removed, extraction was carried out into hexane using Celite. The brown filtrate was dried. It was taken in THF (10 mL) along with  $[\text{Ru}_3(\text{CO})_{12}]$ , followed by heating at 60 °C for 16 h. After that solvent was removed and extraction was done using hexane. Using TLC plates the residue was chromatographed. Elution with a  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (20:80 v/v) afforded yellow **2'** (0.013 g, 13 %) along with known  $[(\text{WCp}^*(\text{CO})_2)_2\{\text{Ru}(\text{CO})_3(\mu_4\text{-B})_2(\mu\text{-H})\}]^{36}$  (0.020 g, 17 %) and  $[(\text{WCp}^*(\text{CO})_2)\{\text{Ru}(\text{CO})_3\}_4(\mu_5\text{-B})]^{37}$  (0.031 g, 13 %).

**2':** MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{M}+\text{H}]^+$  961.0511, found 961.0460;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 102.4 ppm (s, 2B);  $^1\text{H}$  NMR (500 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 10.60 (br, 2H, B-H), 2.03 ppm (s, 30H,  $\text{C}_5\text{Me}_5$ ),  $^{13}\text{C}$  NMR (125 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 99.7 (s,  $\text{C}_5\text{Me}_5$ ), 10.3 ppm (s,  $\text{C}_5\text{Me}_5$ ); IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ): 2518(w, B-H), 2024, 1945, 1922 (CO).

**Synthesis of 3:** To the solution of *nido*- $[(\text{Cp}^*\text{Rh})_2(\text{B}_3\text{H}_7)]$  (0.15 g, 0.29 mmol) in 15 mL of hexane 2 equiv. of  $[\text{Co}_2(\text{CO})_8]$  (0.198g, 0.58 mmol) was added at room temperature. It was left to stir for additional 16 h at 60 °C. After removal of solvent, extraction was carried out using hexane through celite. After that it was concentrated and placed at -40 °C for removing  $[\text{Co}_4(\text{CO})_{12}]$ . Using TLC plates the residue was chromatographed. Elution with a  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (20:80 v/v) afforded yellow **3** (0.044 g, 20 %) and known *pileo*- $[(\text{Cp}^*\text{Rh})_3\text{B}_4\text{H}_4]^{29}$  (0.017 g, 12 %).

**3:** MS (ESI<sup>+</sup>):  $m/z$  calculated for  $[\text{M}]^+$  757.9221, found 757.9167;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 125.5 ppm (s, 2B);  $^1\text{H}$  NMR (500 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 8.73 (br, 2H, B-H), 1.81 ppm (s, 30H,  $\text{C}_5\text{Me}_5$ ),  $^{13}\text{C}$  NMR (125 MHz, 22 °C,  $\text{CDCl}_3$ ):  $\delta$  = 211.0 (s, CO), 100.9 (s,  $\text{C}_5\text{Me}_5$ ), 10.3 ppm (s,  $\text{C}_5\text{Me}_5$ ).

**X-ray structure determination.** Using slow diffusion method crystals of **1**, **2**, **2'** and **3** were grown from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  solution. The crystal data for **1** was collected and integrated utilizing Bruker D8 Venture AXS diffractometer, for **2** using Bruker APEX-II CCD diffractometer, for **2'** using Oxford Diffraction Super Nova single crystal diffractometer, for **3** utilizing Bruker axs kappa apex3 CMOS Diffractometer, facilitated with graphite monochromated  $\text{MoK}\alpha$  ( $\lambda$  = 0.71078 Å) radiation at 150 K (for **1**) and 296 K (for **2**, **2'** and **3**), respectively. Employing SADABS<sup>37</sup> program multi-scan absorption correction has been done. Using SHELXS-97 or SIR92<sup>38</sup> all the structures has been solved by heavy atom methods. Whereas, the refinement is done using SHELXL-2014<sup>39</sup>. CCDC-1908922

(**1**), 1953765 (**2**), 1908926 (**2'**) and 1964900 (**3**) contain crystallographic data, which are accessible at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Crystal data of 1:**  $\text{C}_{26}\text{H}_{34}\text{B}_2\text{O}_6\text{FeW}_2$ ,  $M_r$  = 887.72, Monoclinic,  $P2_1/n$ ,  $a$  = 8.5096(8) Å,  $b$  = 22.094(2) Å,  $c$  = 15.1025(15) Å,  $\alpha$  = 90°,  $\beta$  = 90.451(4),  $\gamma$  = 90°,  $V$  = 2839.4(5) Å<sup>3</sup>,  $Z$  = 4,  $\rho_{\text{calcd}}$  = 2.077 g/cm<sup>3</sup>,  $F(000)$  = 1688,  $\mu$  = 8.624 mm<sup>-1</sup>,  $R_1$  = 0.0436,  $wR_2$  = 0.1085, 6498 independent reflections [ $2\theta \leq 55.03^\circ$ ] and 326 parameters.

**Crystal data of 2:**  $\text{C}_{27}\text{H}_{30}\text{B}_2\text{FeO}_7\text{W}_2$ ,  $M_r$  = 911.68, Orthorhombic,  $Fdd2$ ,  $a$  = 15.9987(4) Å,  $b$  = 79.603(2) Å,  $c$  = 9.1771(2) Å,  $\alpha$  = 90°,  $\beta$  = 90°,  $\gamma$  = 90°,  $V$  = 11687.5(5) Å<sup>3</sup>,  $Z$  = 16,  $\rho_{\text{calcd}}$  = 2.072 g/cm<sup>3</sup>,  $F(000)$  = 6912,  $\mu$  = 8.386 mm<sup>-1</sup>,  $R_1$  = 0.0367,  $wR_2$  = 0.0634, 4946 independent reflections [ $2\theta \leq 49.992^\circ$ ] and 362 parameters.

**Crystal data of 2':**  $\text{C}_{27}\text{H}_{32}\text{B}_2\text{O}_7\text{RuW}_2$ ,  $M_r$  = 958.91, Orthorhombic,  $Fdd2$ ,  $a$  = 16.2626(6),  $b$  = 79.337(2) Å,  $c$  = 9.2643(4) Å,  $\alpha$  = 90°,  $\beta$  = 90°,  $\gamma$  = 90°,  $V$  = 11953.0(8) Å<sup>3</sup>,  $Z$  = 16,  $\rho_{\text{calcd}}$  = 2.131 g/cm<sup>3</sup>,  $F(000)$  = 7232,  $\mu$  = 8.220 mm<sup>-1</sup>,  $R_1$  = 0.0688,  $wR_2$  = 0.1800, 4579 independent reflections [ $2\theta \leq 49.996^\circ$ ] and 362 parameters.

**Crystal data of 3:**  $\text{C}_{25}\text{H}_{32}\text{B}_2\text{Co}_2\text{O}_5\text{Rh}_2$ ,  $M_r$  = 757.80, Monoclinic,  $Cc$ ,  $a$  = 8.8032(5),  $b$  = 37.947(2) Å,  $c$  = 25.8258(14) Å,  $\alpha$  = 90°,  $\beta$  = 98.6300(10)°,  $\gamma$  = 90°,  $V$  = 8529.4(8) Å<sup>3</sup>,  $Z$  = 12,  $\rho_{\text{calcd}}$  = 1.770 g/cm<sup>3</sup>,  $F(000)$  = 4512,  $\mu$  = 2.319 mm<sup>-1</sup>,  $R_1$  = 0.0602,  $wR_2$  = 0.0864, 14340 independent reflections [ $2\theta \leq 49.508^\circ$ ] and 962 parameters.

**Computational details.** Gaussian 09<sup>40</sup> program was used for the optimization of all the molecules by means of b3lyp<sup>41</sup> functional along with def2-tzvp basis set from EMSL<sup>42</sup> Library. Calculations were done on Cp analogue compounds to avoid extra computing time. Initiating from the X-ray coordinates, optimizations were done in gaseous state. Employing same level of theory frequency calculations were completed. The GIAO<sup>43</sup> method was employed for the calculations of  $^{11}\text{B}$  and  $^1\text{H}$  chemical shifts. The b3lyp/def2-tzvp optimized structures has been used for calculating the NMR chemical shifts by means of the hybrid B3LYP and def2-tzvp. With respect to  $\text{B}_2\text{H}_6$ , the  $^{11}\text{B}\{^1\text{H}\}$  NMR chemical shifts has been computed (shielding constant 84.3 ppm) and changed to  $[\text{BF}_3\cdot\text{OEt}_2]$  scale utilizing the experimental  $\delta(^{11}\text{B})$  value of  $\text{B}_2\text{H}_6$  (16.6 ppm). Whereas, for computing  $^1\text{H}$  NMR chemical shift, TMS( $\text{SiMe}_4$ ) has been taken as the internal standard (shielding constant 31.92 ppm). Employing NBO partitioning scheme, natural bonding analyses have been accomplished.<sup>44</sup> Utilizing Multiwfn V.3.4 package<sup>45</sup> the QTAIM analysis<sup>46</sup> was executed. Using the visualization programs, such as Gaussview<sup>47</sup> and Chemcraft<sup>48</sup> optimized structures and orbital graphics have been produced.

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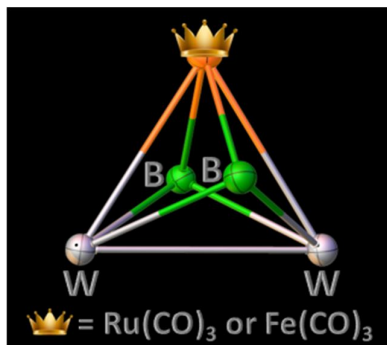
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*Bis*-(hydrido(borylene)),  $[(\mu_3\text{-BH})_2(\mu\text{-H})_2\{\text{Cp}^*\text{W}(\text{CO})_2\}_2\{\text{Fe}(\text{CO})_2\}]$  and triply bridging *bis*-borylene species,  $[(\mu_3\text{-BH})_2\{\text{Cp}^*\text{W}(\text{CO})_2\}_2\{\text{M}(\text{CO})_3\}]$  (M= Fe or Ru) have been isolated and structurally characterized utilizing the coordination sphere of transition metals. In addition, we have synthesized another triply bridging *bis*-borylene species  $[(\mu_3\text{-BH})_2\text{-(Cp}^*\text{Rh})_2\text{Co}_2(\text{CO})_5(\mu\text{-CO})]$ .



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Heterometallic Triply-Bridging *Bis*-Borylene Complexes