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**Synthesis and structural characterization of a diruthenium pentalene complex,  
[Cp\*Ru{(Cp\*Ru)<sub>2</sub>B<sub>6</sub>H<sub>14</sub>}(Cp\*Ru)]**

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**Abstract.** Treatment of *nido*-[1,2-(Cp\*Ru)<sub>2</sub>(μ-H)<sub>2</sub>B<sub>3</sub>H<sub>7</sub>], **1** with five equivalents of Te powder led to the isolation of diruthenium pentalene analogue [(Cp\*Ru){(Cp\*Ru)<sub>2</sub>B<sub>6</sub>H<sub>14</sub>}(RuCp\*)], **2** and a metal indenyl complex [(Cp\*Ru)<sub>2</sub>B<sub>2</sub>H<sub>6</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)], **3**. The [(Cp\*Ru)<sub>2</sub>B<sub>6</sub>H<sub>14</sub>] fragment in **2** may be considered as a true metal-boron analogue of η<sup>5</sup>-η<sup>5</sup>-pentalene ligand (C<sub>8</sub>H<sub>6</sub>) and [(Cp\*Ru)B<sub>2</sub>H<sub>6</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)] fragment in **3** is an analogue of η<sup>5</sup>-indenyl ligand. The solid state X-ray structures were unambiguously determined by crystallographic analysis of compounds **2** and **3**. Further, the density functional theory (DFT) calculations were performed to investigate the bonding and the electronic properties of **2a** (Cp analogue of **2**). The frontier molecular orbital analysis of both **2a** and **2b** (Cp analogue of [(Cp\*Ru)B<sub>8</sub>H<sub>14</sub>(RuCp\*)]) reveals a lower HOMO–LUMO gap indicating less thermodynamic stability.

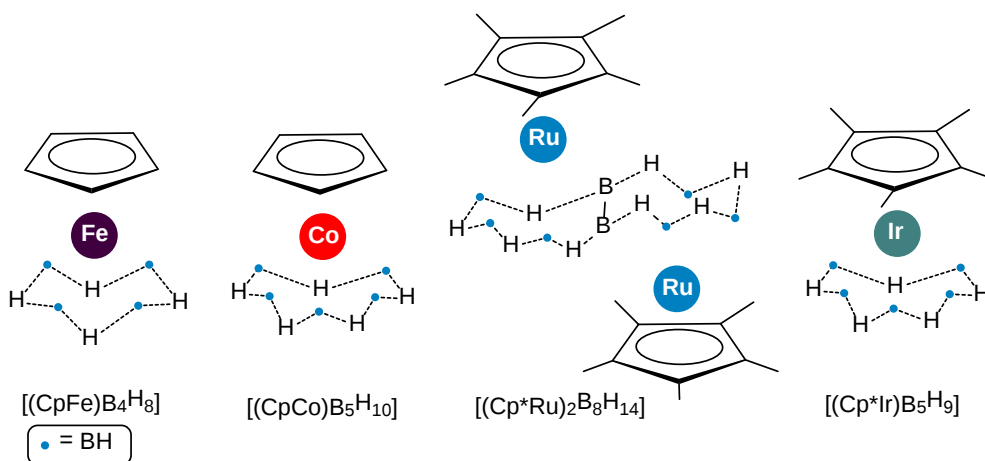
**Keywords.** Ruthenium; boron; pentalene; indenyl; metallaborane

## 1. Introduction

Over the past several decades, the significant research efforts in the field of transition metal boron chemistry have established several sandwich type metallaborane compounds.<sup>1–4</sup> In majority of these boron containing polyhapto π-ligand based sandwich complexes, metal atoms are sandwiched mainly by two types of polyhapto π-ligands (Chart 1).<sup>1–4</sup> The first such type of sandwich molecule [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)FeB<sub>5</sub>H<sub>10</sub>] was reported by Grimes and coworkers in 1977.<sup>1</sup> Later in 1984, Grimes reported [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)CoB<sub>4</sub>H<sub>8</sub>]<sup>2</sup> that showed the connection of isolobal analogy between (η<sup>4</sup>-C<sub>4</sub>H<sub>4</sub>) and (η<sup>4</sup>-B<sub>4</sub>H<sub>8</sub>) fragment. Fehlner and coworkers in 2005 reported a novel

dinuclear ruthenium-pentalene analogue ( $[(\text{Cp}^*\text{Ru})\text{B}_8\text{H}_{14}(\text{RuCp}^*)]$ ).<sup>3</sup> Successively, they reported  $[(\eta^5\text{-C}_5\text{Me}_5\text{Ir})\text{B}_5\text{H}_9]$  which was an analogue of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}]$ , in which  $[\text{B}_5\text{H}_9]^{2-}$  moiety is isoelectronic with the  $[\eta^5\text{-C}_5\text{H}_5]^-$  ligand.<sup>4</sup>

As a part of our research efforts in the field of transition-metal-boron chemistry, we have isolated and characterized a wide range of metallaborane compounds of group 4-9<sup>5-10</sup> starting from novel boron-rich metallaboranes such as 15- and a 16-vertex rhodaborane clusters<sup>10b-c</sup> to complexes with a one boron for example,  $\sigma$ -borane,<sup>9a-d</sup> boryl,<sup>9e</sup> trimetallic bridging borylene<sup>9f-g,10d</sup> complexes. Recently, we have synthesized various metallaheteroboranes through the activation of heterocumulenes<sup>9h</sup>, diaryl-dichalcogenide ligands<sup>6a-c</sup> or chalcogen powders.<sup>7a-c</sup> As a result, we have thermolysed the *nido*-[1,2-( $\text{Cp}^*\text{Ru}$ )<sub>2</sub>( $\mu\text{-H}$ )<sub>2</sub>B<sub>3</sub>H<sub>7</sub>] with Te powder that resulted in the formation of a diruthenium pentalene analogue **2** and a metal indenyl complex **3**. In this report, we describe the detailed structural characterization and bonding of these sandwich molecules.



**Chart 1.** Selected examples of sandwich complexes containing polyhapto borane ligands analogous to organic  $\pi$ -ligands.

## 2. Experimental

### 2.1 General considerations

All the manipulations were conducted under an Ar/N<sub>2</sub> atmosphere using standard Schlenk techniques or glove box. Solvent were distilled prior to use under Argon. LiBH<sub>4</sub>.THF 2.0 M, Cp<sup>\*</sup>H, Tellurium powder (Aldrich) were used as received.  $[\text{Cp}^*\text{RuCl}_2]_2$ <sup>11</sup> and *nido*-[1,2-( $\text{Cp}^*\text{Ru}$ )<sub>2</sub>( $\mu\text{-H}$ )<sub>2</sub>B<sub>3</sub>H<sub>7</sub>]<sup>12</sup> was prepared according to the literature methods. The external reference  $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ <sup>13</sup> for the <sup>11</sup>B NMR, was synthesized with the literature method. Preparative thin-layer chromatography was performed with Merck 105554 TLC Silica gel 60 F<sub>254</sub>, layer thickness 250  $\mu\text{m}$  on aluminum sheets (20 x 20 cm). The NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer. The residual solvent protons were used as reference ( $\delta$ , ppm,

CDCl<sub>3</sub>, 7.26; C<sub>6</sub>D<sub>6</sub>, 7.16), while a sealed tube containing [Bu<sub>4</sub>N(B<sub>3</sub>H<sub>8</sub>)] in [D<sub>6</sub>]-benzene ( $\delta_B$ , ppm, -30.07) was used as an external reference for the <sup>11</sup>B NMR. The Infrared spectra were recorded on a Jasco FT/IR-1400 spectrometer. Mass spectra were recorded on Bruker MicroTOF-II mass spectrometer in ESI ionization mode. The CV measurements were carried out on a CH potentiostat, model 668.

## 2.2 Synthesis of compound 2

Compound **1** (0.1 g, 0.19 mmol) was taken in a flame-dried Schlenk tube and dissolved in toluene (15 mL). The resulting solution was heated with five equivalents of Te powder (0.123 g, 0.95 mmol) at 80 °C for 18 hours. The reaction mixture was filtered through Celite using hexane. The filtrate was concentrated and the residue was chromatographed on silica gel TLC plates. Elution with a hexane/CH<sub>2</sub>Cl<sub>2</sub> (90:10 v/v) mixture yielded orange **2** (0.09 g, 4.5%) and yellow **3**<sup>14</sup>.

**2**: MS (ESI<sup>+</sup>): *m/z* calculated for [C<sub>40</sub>H<sub>74</sub>B<sub>6</sub>Ru<sub>4</sub> + H<sup>+</sup>], 1029.2, found, 1029.3; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, *d*<sub>6</sub>-benzene, 22 °C):  $\delta$  = 21.5 (s, 1B), 14.2 (s, 1B), 11.5 (s, 1B), 9.5 (s, 1B), -1.9 (s, 1B), -30.6 (s, 1B); <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-benzene, 22 °C):  $\delta$  = 5.45 (br, BH<sub>t</sub>), 4.82 (br, BH<sub>t</sub>), 3.39 (br, BH<sub>t</sub>), 2.96 (br, BH<sub>t</sub>), 1.98 (s, 15H, Cp\*), 1.91 (s, 15H, Cp\*), 1.89 (s, 15H, Cp\*), 1.82 (s, 15H, Cp\*), -0.78 (br, 1H, B-H-B), -1.50 (br, 1H, B-H-B), -2.56 (br, 1H, B-H-B), -4.48 (br, 1H, B-H-B), -11.08 (br, 1H, Ru-H-B), -12.17 (br, 1H, Ru-H-B), -12.47 (br, 1H, Ru-H-B), -14.04 (br, 1H, Ru-H-B), -11.85 (s, 1H, Ru-H-Ru), -14.66 (s, 1H, Ru-H-Ru); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, *d*<sub>6</sub>-benzene, 22 °C):  $\delta$  = 95.2, 94.8, 87.5, 86.6 (s, C<sub>5</sub>Me<sub>5</sub>), 12.3, 12.2, 11.7, 10.5 (s, C<sub>5</sub>Me<sub>5</sub>); IR (DCM, cm<sup>-1</sup>): 2962 (C-H), 2354, 2406 and 2480 (B-H<sub>t</sub>). Raman (DCM, cm<sup>-1</sup>): 289 (Ru-Ru).

## 2.3 X-ray structure determination

The crystal data for **2** and **3** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation at 150 K. The structures were solved by heavy atom methods using SHELXS-97<sup>15a</sup> or SIR92<sup>15b</sup> and refined using SHELXL-97.<sup>15c</sup>

**Table1.** Crystal data and structural refinement for compounds **2** and **3**

| Compound                                                     | <b>2</b>                                                                        | <b>3</b>                                                                        |
|--------------------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| CCDC no.                                                     | 1828946                                                                         | 1828947                                                                         |
| Empirical formula                                            | C <sub>40</sub> H <sub>64</sub> B <sub>6</sub> Ru <sub>4</sub>                  | C <sub>27</sub> H <sub>42</sub> B <sub>2</sub> Ru <sub>2</sub>                  |
| Formula weight                                               | 1014.05                                                                         | 590.36                                                                          |
| Temperature/K                                                | 150(2)                                                                          | 150(2)                                                                          |
| Crystal system                                               | triclinic                                                                       | orthorhombic                                                                    |
| Space group                                                  | <i>P</i> -1                                                                     | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                           |
| <i>a</i> /Å                                                  | 11.1227(9)                                                                      | 11.4420(6)                                                                      |
| <i>b</i> /Å                                                  | 14.2888(11)                                                                     | 14.4265(9)                                                                      |
| <i>c</i> /Å                                                  | 15.6289(13)                                                                     | 16.3603(9)                                                                      |
| $\alpha$ /°                                                  | 70.293(3)                                                                       | 90                                                                              |
| $\beta$ /°                                                   | 86.130(3)                                                                       | 90                                                                              |
| $\gamma$ /°                                                  | 70.142(3)                                                                       | 90                                                                              |
| Volume/Å <sup>3</sup>                                        | 2196.3(3)                                                                       | 2700.6(3)                                                                       |
| <i>Z</i>                                                     | 2                                                                               | 4                                                                               |
| $\rho_{\text{calc}}$ /g/cm <sup>3</sup>                      | 1.533                                                                           | 1.452                                                                           |
| $\mu$ /mm <sup>-1</sup>                                      | 1.375                                                                           | 1.13                                                                            |
| <i>F</i> (000)                                               | 1020                                                                            | 1208                                                                            |
| 2 $\theta$ range for data collection/°                       | 5.834 to 49.998                                                                 | 6.122 to 54.948                                                                 |
| Reflections collected                                        | 28291                                                                           | 15672                                                                           |
| zIndependent reflections                                     | 7709 [ <i>R</i> <sub>int</sub> = 0.0606,<br><i>R</i> <sub>sigma</sub> = 0.0614] | 6158 [ <i>R</i> <sub>int</sub> = 0.0551, <i>R</i> <sub>sigma</sub> =<br>0.0629] |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                     | 1.163                                                                           | 1.104                                                                           |
| Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.0595, <i>wR</i> <sub>2</sub> =<br>0.1356              | <i>R</i> <sub>1</sub> = 0.0453, <i>wR</i> <sub>2</sub> = 0.0900                 |
| Final <i>R</i> indexes [all data]                            | <i>R</i> <sub>1</sub> = 0.0780, <i>wR</i> <sub>2</sub> =<br>0.1495              | <i>R</i> <sub>1</sub> = 0.0551, <i>wR</i> <sub>2</sub> = 0.0939                 |

#### 2.4 Computational details

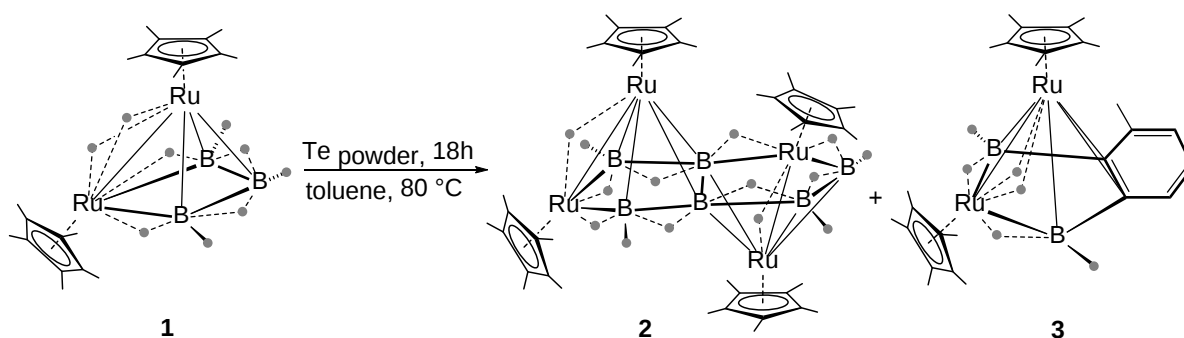
Quantum chemical calculations were performed on compounds **2a**, **2b** and **3a** (Cp analogues of **3 nido**-[(Cp\**Ru*)<sub>2</sub>B<sub>2</sub>H<sub>8</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)] using density functional theory (DFT) as implemented in the Gaussian09 package.<sup>16</sup> The calculations were carried out with the Cp analogue compounds instead of Cp\* in order to save computing time. Without any symmetry constraints, all the geometry optimizations were carried out in gaseous state, (no solvent effect) using PBE0 functional<sup>17</sup> in combination with triple- $\zeta$  quality basis set Def2-TZVP. The calculated <sup>11</sup>B chemical shielding values, determined at the PBE0/Def2-TZVP level of calculations, were referenced to B<sub>2</sub>H<sub>6</sub> (PBE0/Def2-TZVP, B shielding constant 85.9 ppm), and these chemical shift values ( $\delta$ ) were then converted to the standard BF<sub>3</sub>·OEt<sub>2</sub> scale using the experimental value of +16.6 ppm for

B<sub>2</sub>H<sub>6</sub>. The <sup>1</sup>H chemical shifts were referenced to TMS (SiMe<sub>4</sub>). The computation of the NMR shielding tensors employed gauge-including atomic orbitals (GIAOs),<sup>18</sup> using the implementation of Schreckenbach, Wolff, Ziegler, and co-workers.<sup>19</sup> The ChemCraft package<sup>20</sup> was used for the visualizations. The two-dimension electron density and Laplacian electronic distribution plots were generated using Multiwfn package.<sup>21</sup>

### 3. Results and Discussion

#### 3.1 Synthesis of [(Cp\*Ru){(Cp\*Ru)<sub>2</sub>B<sub>6</sub>H<sub>14</sub>}(RuCp\*)], **2**

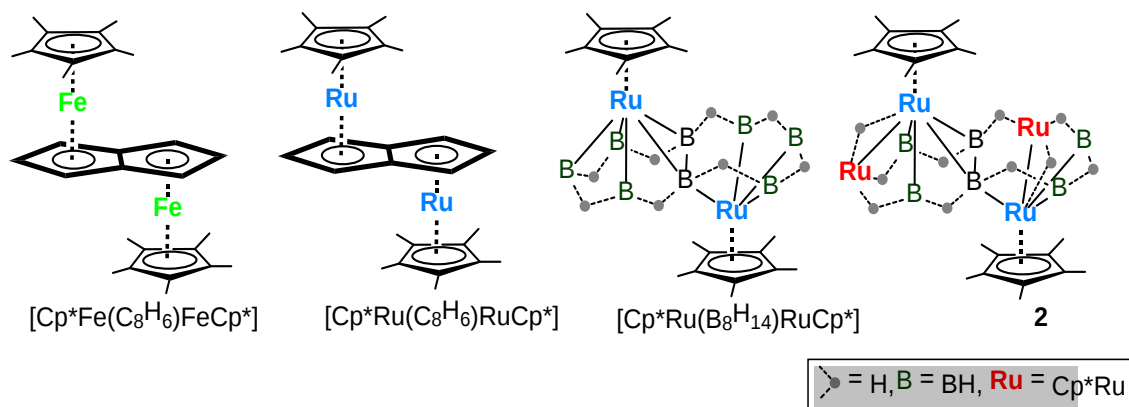
As shown in Scheme 1, the thermolysis of *nido*-**1** with five equivalents of Te powder yielded a moderately air stable solid **2**. Compound **2** isolated as orange solid in its purest form by thin-layer chromatography (TLC) and characterized by <sup>11</sup>B{<sup>1</sup>H}, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR, IR spectroscopy and a single-crystal X-ray diffraction study. In parallel to the formation of compound **2**, reaction also yielded compound **3** in very less yield.<sup>14</sup> Compound **3** was characterised with limited spectroscopic data and a single-crystal X-ray diffraction analysis.



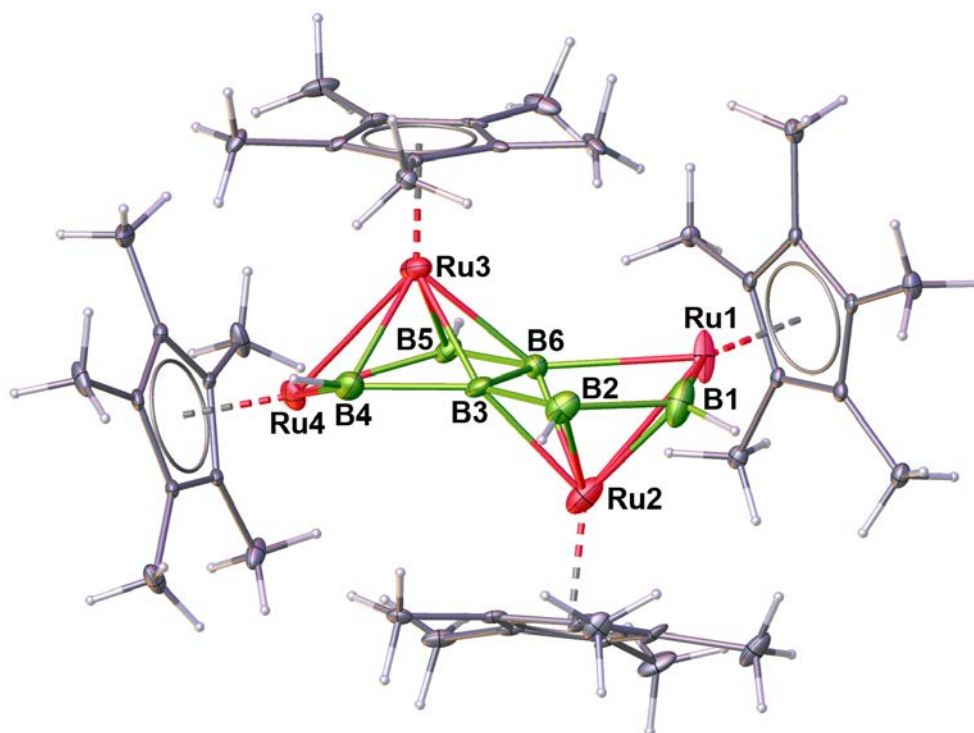
**Scheme 1.** Synthesis of compounds **2** and **3**.

The solid-state X-ray structure of **2**, shown in Figure 1, can be viewed as a fused structure in which two diruthenaborane cages fused in a transoid fashion with two common boron atoms, to generate a planar Ru<sub>2</sub>B<sub>6</sub> fragment. The framework is analogous to that of isoelectronic dinuclear pentalene complexes [Cp\*M(C<sub>8</sub>H<sub>6</sub>)MCp\*], (M = Fe or Ru)<sup>22</sup> and [(Cp\*Ru)(B<sub>8</sub>H<sub>14</sub>)(RuCp\*)]<sup>3</sup> (Chart 2). In compound **2** the ruthenium atoms are bonded symmetrically to the Cp\* ligands. The average Ru-B distance is found to be larger (*d*<sub>Ru-B</sub> 2.228 Å) as compared to [(Cp\*Ru)B<sub>8</sub>H<sub>14</sub>(RuCp\*)] (*d*<sub>Ru-B</sub> 2.15 Å). The average distance between two Ru is 2.837 Å. As shown in Figure 1, two Ru atoms (Ru2 and Ru3) are bridged by Cp\* and [(Cp\*Ru)<sub>2</sub>B<sub>6</sub>H<sub>14</sub>] fragment, in which the ends of B<sub>4</sub>H<sub>x</sub> (x = 6 or 8) are bonded by two Ru atoms (Ru1 and Ru4) forming cyclic metal-boron rings. These cyclic RuB<sub>4</sub>H<sub>x</sub> (x = 6 or 8) units are fused by a B-B bond (B3-B6) resulting a fused dimetallacycle. The B6-Ru1-B1-B2-B3 ring is puckered with the Ru1 lying 0.128 Å out of the least square plane defined by boron atoms B1-B2-B3-B6 (mean

deviation from the plane = 0.045 Å). Similarly, in the Ru4 B6-B5-Ru4-B4-B3 ring the Ru4 lies 0.528 Å out of the least square plane defined by boron atoms B6-B5-B3-B4 (mean deviation from the plane = 0.003 Å).



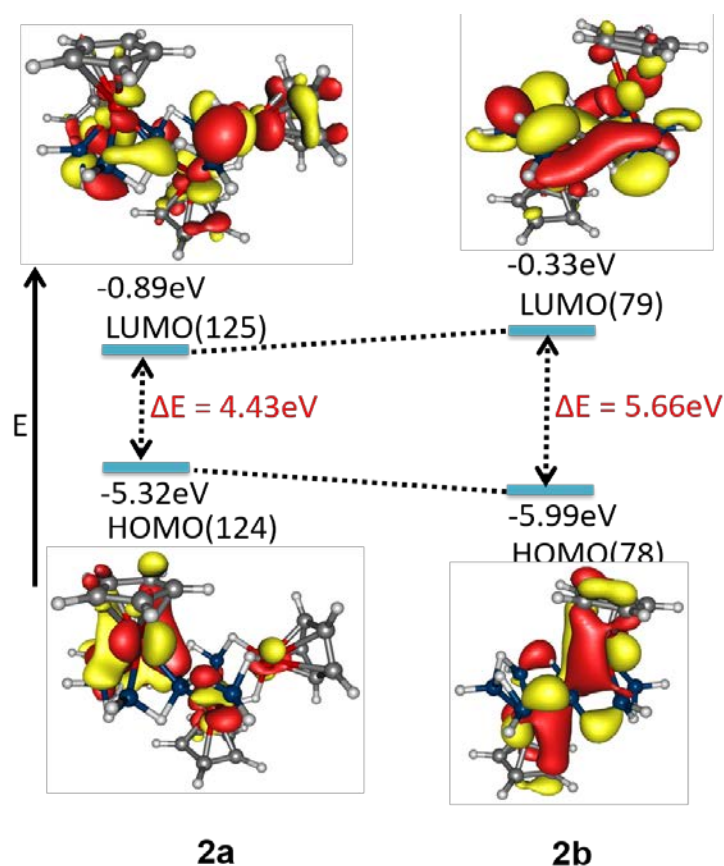
**Chart 2.** Dimetala pentalene complex [Cp\*M(pentalene)MCp\*] (M = Fe and Ru), pentalene analogue [Cp\*Ru(B<sub>8</sub>H<sub>14</sub>)RuCp\*] and a metallaborane analogue of diruthenium pentalene, 2.



**Figure 1.** Molecular structure of compound 2. Selected interatomic distances (Å) and angles (°): Ru1-Ru2 2.854(7), Ru3-Ru4 2.821(5), Ru1-B6 2.402(10), Ru1-B1 2.99(13), B1-B2 1.811(14), B3-B6 1.789(12), B1-Ru1-B6 81.0(4), B2-B3-B4 135.7(7), Ru1-B6-B5 133.9(5).

Consistence with the X-ray structure determination, the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum reveals six different resonances ( $\delta$  = 21.58, 14.23, 11.59, 9.53, -1.95 and -30.66 ppm) reflecting the lack of

symmetry in the molecule. In addition to Cp\* protons, the  $^1\text{H}$  NMR spectrum of **2** shows up-field resonances at  $\delta = -0.78, -1.50, -2.56$  and  $-4.48$  for B-H-B,  $-11.08, -12.17, -12.47$  and  $-14.04$  for B-H-Ru and  $-11.85$  and  $-14.66$  ppm for the presence of Ru-H-Ru protons. Assignment of the Ru-Ru stretching vibration in compound **2** is evidenced by a single resonance-enhanced band at  $289\text{ cm}^{-1}$ , which falls within the reported range.<sup>23</sup>

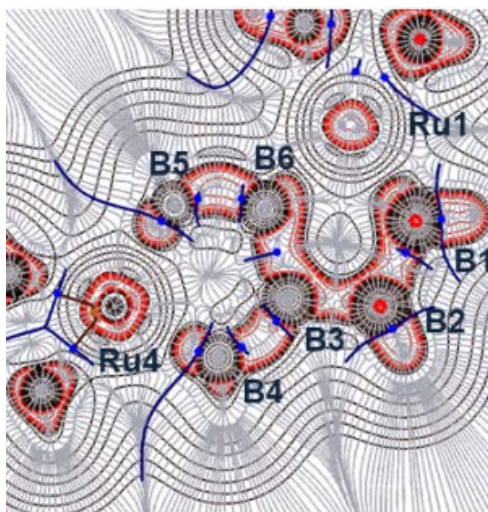


**Figure 2.** Frontier molecular orbitals of **2a** and **2b** (isocontour value  $\pm 0.03 [e/\text{Bohr}^3]^{1/2}$ ).

To gain some insight into the electronic structure and bonding nature of **2a** (Cp analogue of **2**), we carried out the density functional theory (DFT) calculations<sup>16</sup> and compared with **2b**. The optimized structure of **2a** (Figure S13 and Table S1) is in good match with its X-ray structure. Further, the DFT calculations helped us to confirm the position of the bridging hydrogen atoms that could not be located by X-ray diffraction studies. The DFT computed energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for **2a** of 4.43 eV at PBE0 level is consistent with its high thermodynamic stability. However, the HOMO–LUMO gap for **2a** is much lesser than its parent metallaborane **2b** (5.66 eV). This led us to compare their MO diagrams (Figure 2). Analyses of the frontier orbitals for **2a** reveals a significant increase in HOMO energy (ca. 0.67 eV) and decrease in LUMO energy (ca.

0.56 eV) with respect to **2b**. Consequently, it leads to the decrease in HOMO–LUMO gap of **2a** compared to **2b** (Figure 2). Previous theoretical calculations on compound **2b** showed that the LUMO of  $B_8H_{14}^{2-}$ , which is essentially vacant orbitals centered at  $B_8H_{14}^{2-}$  ligand, is destabilized and higher in energy due to the electropositive nature of B.<sup>24</sup> In contrast, the presence of two 2 electron donor  $\{Cp^*RuH\}$  fragments in the central  $[(Cp^*Ru)_2B_6H_{14}]^{2-}$  ligand of **2a** destabilizes the HOMO and stabilizes the LUMO, resulting in a smaller HOMO/LUMO gap of **2a** (compared to **2b**). This may be attributed to the presence of electron rich  $\{Cp^*RuH\}$  fragments compared to the BH units.

To understand the bonding of the nearly planar  $[Cp^*Ru_2B_6H_{14}]^{2-}$  unit and the nature of Ru-B and B-B bonding in **2a**, the topological analyses<sup>25</sup> were carried out. As shown in Figure 3, the results show an area of charge concentration along each Ru-B and B-B bonds in  $[Ru_2B_6]$  plane indicating the  $\sigma/\pi$  delocalized bonds between Ru and B atoms. In addition, the boron-metal interaction has more covalent character as compared to B-B bonds in **2a**. This is also indicated by higher values of the electron density ( $\rho$ ) and a negative value of the energy density  $[H(r)]$  at bcps (Table S3).



**Figure 3.** Contour line diagram of the Laplacian of the electron density,  $\nabla^2\rho(r)$  of **2a** in the plane of  $[Ru_2B_6]$  generated using the Multiwfn program package at the PBE0/Def2-TZVP level of theory. Solid red lines show areas of charge concentration ( $-\nabla^2\rho(r) > 0$ ), while dashed black lines indicate areas of charge depletion ( $-\nabla^2\rho(r) < 0$ ). Solid brown and blue lines indicate bond paths and zero-flux-surfaces, respectively, and blue dots indicate bond critical points (BCPs).

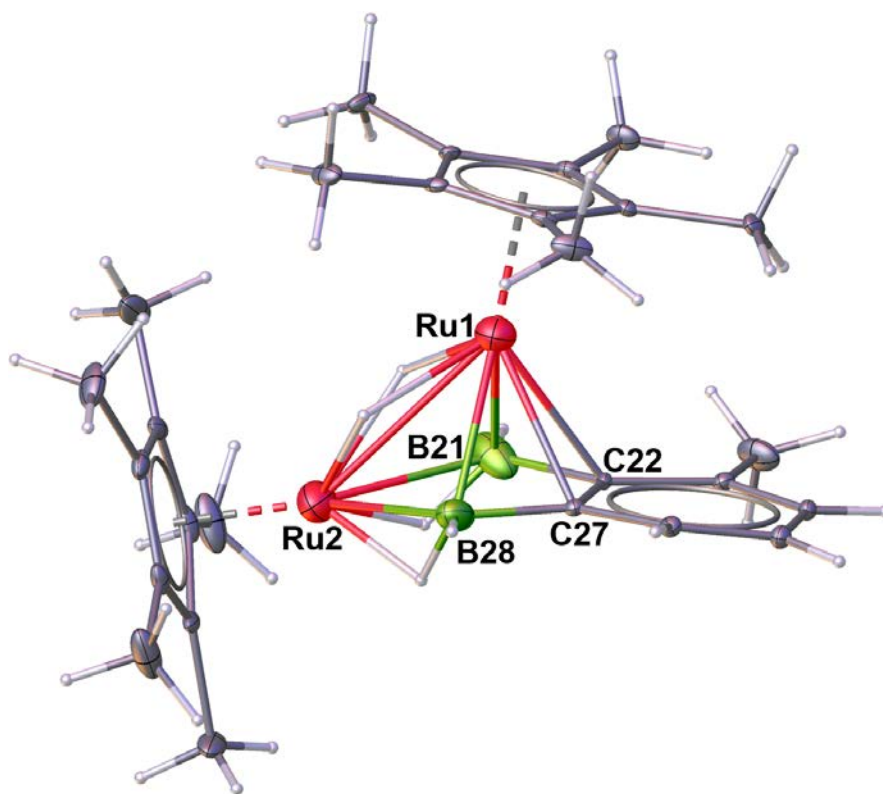
Compound **2** is a redox active molecule and which has been concluded from its cyclic voltammetric studies. The cyclic voltammogram of  $[Cp^*Ru(C_8H_6)RuCp^*]$  exhibits one reversible oxidation wave and an irreversible wave at 0.29 V higher potential.<sup>22b</sup> The irreversible behaviour

is attributed to the oxidation reaction of the Cp\* ligand, analogous to the behaviour of [Cp\*<sub>2</sub>Ru] on oxidation. Compound **2** in a similar way exhibits three successive one-electron oxidations with the first two are separated by approximately 0.4 V while the 2<sup>nd</sup> and 3<sup>rd</sup> potentials are separated by 0.23 V. The first redox event 2<sup>0</sup>/2<sup>+</sup> is quasi-reversible, but the second and third oxidations 2<sup>+</sup>/2<sup>2+</sup> and 2<sup>2+</sup>/2<sup>3+</sup> are irreversible as shown by the lack of a return wave. The cyclic voltammogram of **2** is similar to that of [(Cp\*Ru)B<sub>8</sub>H<sub>14</sub>(RuCp\*)]<sup>3</sup> that shows two successive one-electron oxidations separated by approximately 0.8 V (Figure S5 in SI).

### 3.2 Solid state X-ray structure of **3**

Although compounds **2** and **3** were isolated from same reaction, all of our attempts to reproduce **3** were failed. However, with the limited spectroscopic data and an X-ray crystallographic analysis, we have characterized compound **3**. The <sup>11</sup>B{<sup>1</sup>H} chemical shifts appeared at  $\delta$  = -16.8 and -19.2 ppm with equal intensity arise from the two different boron environments. The <sup>1</sup>H NMR spectrum of **3** displayed two signals ( $\delta$  = 1.87 and 1.51 ppm) corresponding to Cp\* protons in 1:1 ratio. Further, it predicts the presence of three up-fielded resonances at  $\delta$  = -10.84, -11.16 and -12.23 ppm. These observed up-fielded chemical shifts may be due to the presence of Ru-H-B and Ru-H-Ru hydrogens.

The solid-state X-ray structure of compound **3** may be considered as an eight-sep *nido*-[(Cp\*Ru)<sub>2</sub>B<sub>2</sub>H<sub>8</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)] cluster (Figure 4). Compound **3** [(Cp\*Ru)<sub>2</sub>B<sub>2</sub>H<sub>8</sub>C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)] can be viewed as an edge fused ruthenaborane cluster in which a toluene ring being fused to a pentagonal pyramidal ring Ru<sub>2</sub>B<sub>2</sub>C<sub>2</sub>. The structure of **3** is analogous to the isoelectronic ruthenium indenyl complex with a central indenyl ligand [( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)Ru( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)] (R = Me).<sup>26</sup> The C-C bond length in **3** that is fused with the pentagonal pyramid ring is about 1.43 Å, which can be considered to have a partial double bond character. The respective C-C bond in **3** is slightly longer than the C=C bond length of toluene (1.40 Å), but shorter as compared to similar reported indenyl compounds,<sup>27</sup> which indeed longer than normal C=C length (1.33 Å). The Ru-Ru bond distance (2.9578 Å) is considerably longer than the reported diruthena-boranes<sup>12,28</sup> The RuB<sub>2</sub>C<sub>6</sub> fragment in **3** is a true analogue of the  $\eta^5$ -indenyl ligand and this further illustrates the similarity of the properties of boron and its immediate neighbour carbon and their tendency to form similar structures by using the concept of isolobal analogy.<sup>29</sup>



**Figure 4.** Molecular structure of compound **3**. Selected bond distances (Å) and angle (°): Ru1-Ru2 2.9578(8), Ru1-B21 2.349(12), Ru2-B21 2.391(11), Ru2-B28 2.386(10) C22-C27 1.43(3) Ru1-C22-B21 71.00(8), B21-Ru2-B28 76.4(4), B21-C22-C27 117.7(15), and C23-C22-C27 120.6 (17).

#### 4. Conclusions

In this article, we have synthesised and structurally characterized the metallaborane analogue of diruthena pentalene and an indenyl complex. Diruthena pentalene complex **2** is a notable entry in to the class of pentalene complexes containing main group and transition metals. On the other hand, compound **3** that contains a {RuB<sub>2</sub>C<sub>6</sub>} fragment is a true analogue of  $\eta^5$ -indenyl ligand. Theoretical calculations adequately explained the electronic structure of **2**. Further we have demonstrated that the HOMO-LUMO gap decreases when two of the BH fragments in the parent molecule were replaced by two 2 electron {Cp\**RuH*} fragments.

#### Supplementary Information (SI)

Supplementary data contains the X-ray crystallographic files in CIF format for **2** and **3**, CCDC 1828946 (**2**) and 1828947 (**3**) for this work. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). All additional information pertaining to characterization of the complexes **2-3** using ESI-MS technique, IR spectra and multinuclear NMR spectra (Figure S1 - Figure S8), computational details are given in the Supplementary Information available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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## **Table of Contents**

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Manuscript title: Synthesis and structural characterization of a diruthenium pentalene complex,  $[\text{Cp}^*\text{Ru}\{(\text{Cp}^*\text{Ru})_2\text{B}_6\text{H}_{14}\}(\text{Cp}^*\text{Ru})]$

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Synopsis of the paper:

Treatment of *nido*-[1,2-( $\text{Cp}^*\text{Ru}$ )<sub>2</sub>( $\mu\text{-H}$ )<sub>2</sub>B<sub>3</sub>H<sub>7</sub>] with Te powder led to the isolation of diruthenium pentalene analogue  $[(\text{Cp}^*\text{Ru})\{(\text{Cp}^*\text{Ru})_2\text{B}_6\text{H}_{14}\}(\text{RuCp}^*)]$  and a metal indenyl complex  $[(\text{Cp}^*\text{Ru})_2\text{B}_2\text{H}_6\text{C}_6\text{H}_3(\text{CH}_3)]$ .

