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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Abstract. Treatment of *nido*-[1,2-(Cp*Ru)₂(μ-H)₂B₃H₇], **1** with five equivalents of Te powder led to the isolation of diruthenium pentalene analogue [(Cp*Ru){(Cp*Ru)₂B₆H₁₄}(RuCp*)], **2** and a metal indenyl complex [(Cp*Ru)₂B₂H₆C₆H₃(CH₃)], **3**. The [(Cp*Ru)₂B₆H₁₄] fragment in **2** may be considered as a true metal–boron analogue of η⁵-η⁵-pentalene ligand (C₈H₆) and [(Cp*Ru)B₂H₆C₆H₃(CH₃)] fragment in **3** is an analogue of η⁵-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)B₈H₁₄(RuCp*)]) reveals a lower HOMO–LUMO gap indicating less thermodynamic stability.

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

1. Introduction

Over the past several decades, significant research efforts in the field of transition metal boron chemistry have established several sandwich type metallaborane compounds.^{1–4} In the majority of these boron containing polyhaptic π-ligand based sandwich complexes, metal atoms are sandwiched mainly by two types of polyhaptic π-ligands (Chart 1).^{1–4} The first such type of sandwich molecule [(η⁵-C₅H₅)FeB₅H₁₀] was reported by Grimes and coworkers in 1977.¹ Later in 1984, Grimes reported [(η⁵-C₅H₅)CoB₄H₈]² that showed the connection of isolobal analogy between (η⁴-C₄H₄) and (η⁴-B₄H₈) fragments. Fehlner and coworkers in 2005 reported a novel dinuclear ruthenium–pentalene analogue [(Cp*Ru)B₈H₁₄(RuCp*)].³ Successively, they reported [(η⁵-C₅Me₅Ir)B₅H₉] which was an analogue of [(η⁵-C₅H₅)₂Fe], in which [B₅H₉]^{2–} moiety is iso-electronic with the [η⁵-C₅H₅][–] ligand.⁴

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^{5–10} starting from novel boron-rich metallaboranes such as 15- and a 16-vertex rhodaborane clusters^{10b–c} to complexes with a one boron, for example, σ-borane,^{9a–d} boryl,^{9e} trimetallic bridging borylene^{9f–g, 10d} complexes. Recently, we have synthesized various metallaheteroboranes through the activation of heterocumulenes^{9h}, diaryl-dichalcogenide ligands^{6a–c} or chalcogen powders.^{7a–c} As a result, we have thermolysed the *nido*-[1,2-(Cp*Ru)₂(μ-H)₂B₃H₇] 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.

2. Experimental

2.1 General considerations

All the manipulations were conducted under an Ar/N₂ atmosphere using standard Schlenk techniques or glove box.

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Chart 1. Selected examples of sandwich complexes containing polyhapto borane ligands analogous to organic π -ligands.

Solvents were distilled prior to use under Argon. LiBH_4 , THF 2.0 M, Cp^*H , Tellurium powder (Aldrich) were used as received. $[\text{Cp}^*\text{RuCl}_2]_2$ ¹¹ and *nido*-[1,2-(Cp^*Ru)₂(μ -H)₂ B_3H_7]¹² was prepared according to the literature methods. The external reference $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ ¹³ for the ¹¹B NMR, was synthesized with the literature method. Preparative thin-layer chromatography was performed with Merck 105554 TLC Silica gel 60 F₂₅₄, layer thickness 250 μm on aluminum sheets (20 $\times$ 20 cm^2). The NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer. The residual solvent protons were used as a reference (δ , ppm, CDCl_3 , 7.26; C_6D_6 , 7.16), while a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in $[\text{D}_6]$ -benzene (δ_{B} , ppm, −30.07) was used as an external reference for the ¹¹B 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 h. 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_2Cl_2 (90:10 v/v) mixture yielded orange **2** (0.09 g, 4.5%) and yellow **3**¹⁴.

2: MS (ESI⁺): m/z calculated for $[\text{C}_{40}\text{H}_{74}\text{B}_6\text{Ru}_4 + \text{H}^+]$, 1029.2, found, 1029.3; ¹¹B{¹H} NMR (160 MHz, d_6 -benzene, 22 °C): δ = 21.5 (s, 1B), 14.2 (s, 1B), 11.5 (s, 1B), 9.5 (s, 1B), −1.9 (s, 1B), −30.6 (s, 1B); ¹H NMR (500 MHz, d_6 -benzene, 22 °C): δ = 5.45 (br, BH_t), 4.82 (br, BH_t), 3.39 (br, BH_t), 2.96 (br, BH_t), 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); ¹³C{¹H} NMR (125 MHz, d_6 -benzene, 22 °C): δ = 95.2, 94.8, 87.5, 86.6 (s, C_5Me_5), 12.3, 12.2, 11.7, 10.5 (s, C_5Me_5); IR (DCM, cm^{-1}): 2962 (C-H), 2354, 2406 and 2480 (B-H_t). Raman (DCM, cm^{-1}): 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 α (λ = 0.71073 Å) radiation at 150 K. The structures were solved by heavy atom methods using SHELXS-97^{15a} or SIR92^{15b} and refined using SHELXL-97 (Table 1).^{15c}

2.4 Computational details

Quantum chemical calculations were performed on compounds **2a**, **2b** and **3a** (Cp analogues of **3** *nido*-[1,2-(Cp^*Ru)₂ $\text{B}_2\text{H}_8\text{C}_6\text{H}_3(\text{CH}_3)]$) using density functional theory (DFT) as implemented in the Gaussian 09 package.¹⁶ 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 a gaseous state, (no solvent effect) using PBE0 functional¹⁷ in combination with triple- ζ quality basis set Def2-TZVP. The calculated ¹¹B chemical shielding values, determined at the PBE0/Def2-TZVP level of calculations, were referenced to B_2H_6 (PBE0/Def2-TZVP, B shielding constant 85.9 ppm), and these chemical shift values (δ) were then converted to the standard $\text{BF}_3\cdot\text{OEt}_2$ scale using the experimental value of +16.6 ppm for B_2H_6 . The ¹H chemical shifts were referenced to TMS (SiMe_4). The computation of the NMR shielding tensors employed gauge-including atomic orbitals (GIAOs),¹⁸ using the implementation of Schreckenbach, Wolff, Ziegler, and co-workers.¹⁹ The ChemCraft package²⁰ was used for the visualizations. The two-dimensional electron density and

Table 1. Crystal data and structural refinement for compounds **2** and **3**.

Compound	2	3
CCDC no.	1828946	1828947
Empirical formula	C ₄₀ H ₆₄ B ₆ Ru ₄	C ₂₇ H ₄₂ B ₂ Ru ₂
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 ₁ 2 ₁ 2 ₁
<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)
α /°	70.293(3)	90
β /°	86.130(3)	90
γ /°	70.142(3)	90
Volume/Å ³	2196.3(3)	2700.6(3)
<i>Z</i>	2	4
ρ_{calc} /g/cm ³	1.533	1.452
μ /mm ⁻¹	1.375	1.13
<i>F</i> (000)	1020	1208
2 θ range for data collection/°	5.834 to 49.998	6.122 to 54.948
Reflections collected	28291	15672
<i>z</i> Independent reflections	7709 [<i>R</i> _{int} = 0.0606, <i>R</i> _{sigma} = 0.0614]	6158 [<i>R</i> _{int} = 0.0551, <i>R</i> _{sigma} = 0.0629]
Goodness-of-fit on <i>F</i> ²	1.163	1.104
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0595, <i>wR</i> ₂ = 0.1356	<i>R</i> ₁ = 0.0453, <i>wR</i> ₂ = 0.0900
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0780, <i>wR</i> ₂ = 0.1495	<i>R</i> ₁ = 0.0551, <i>wR</i> ₂ = 0.0939

Laplacian electronic distribution plots were generated using Multiwfn package.²¹

3. Results and Discussion

3.1 Synthesis of [(Cp**Ru*){(Cp**Ru*)₂B₆H₁₄}(*Ru*Cp*)], **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 ¹¹B{¹H}, ¹H and ¹³C{¹H} NMR, IR spectroscopy and a single-crystal X-ray diffraction study. In parallel to the formation of compound **2**, the reaction also yielded compound **3** in very less yield.¹⁴ Compound **3** was characterised with limited spectroscopic data and a single-crystal X-ray diffraction analysis.

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 Ru₂B₆ fragment. The framework is analogous to that of isoelectronic dinuclear pentalene complexes [Cp*M(C₈H₆)MCp*], (M = Fe or Ru)²² and [(Cp**Ru*)(B₈H₁₄)(*Ru*Cp*)]³ (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*_{Ru-B} 2.228 Å) as compared to [(Cp**Ru*)B₈H₁₄(*Ru*Cp*)] (*d*_{Ru-B} 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*)₂B₆H₁₄] fragment, in which the ends of B₄H_x (*x* = 6 or 8) are bonded by two Ru atoms (Ru1 and Ru4) forming cyclic metal-boron rings. These cyclic RuB₄H_x (*x* = 6 or 8) units are fused by a B–B bond (B3–B6) resulting in 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).

Consistent with the X-ray structure determination, the ¹¹B{¹H} NMR spectrum reveals six different resonances (δ = 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 ¹H NMR spectrum of **2** shows up-field resonances at δ = –0.78, –1.50, –2.56 and –4.48 for B–H–B, δ = –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

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

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).

in compound **2** is evidenced by a single resonance-enhanced band at 289 cm^{-1} , which falls within the reported range.²³

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) calculations¹⁶ and compared with **2b**. The optimized structure of **2a** (Figure S13 and Table S1 in Supplementary Information) 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 less 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 $\text{B}_8\text{H}_{14}^{2-}$, which is essentially vacant orbitals centered at $\text{B}_8\text{H}_{14}^{2-}$ ligand, is destabilized and higher in energy due to the

Chart 2. Dimetala pentalene complex $[\text{Cp}^*\text{M}(\text{pentalene})\text{MCp}^*]$ ($\text{M} = \text{Fe}$ and Ru), pentalene analogue $[\text{Cp}^*\text{Ru}(\text{B}_8\text{H}_{14})\text{RuCp}^*]$ and a metallaborane analogue of diruthenium pentalene, **2**.

Figure 2. Frontier molecular orbitals of **2a** and **2b** (isocontour value ± 0.03 [e/Bohr³]^{1/2}).

electropositive nature of B.²⁴ In contrast, the presence of two 2 electron donor {Cp^{*}RuH} fragments in the central [(Cp^{*}Ru)₂B₆H₁₄]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^{*}Ru₂B₆H₁₄]²⁻ unit and the nature of Ru–B and B–B bonding in **2a**, the topological analyses²⁵ 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 [Ru₂B₆] plane indicating the σ / π 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 (ρ) and a negative value of the energy density [$H(r)$] at bcps (Table S3 in Supplementary Information).

Compound **2** is a redox active molecule which has been concluded from its cyclic voltammetric studies. The cyclic voltammogram of [Cp^{*}Ru(C₈H₆)RuCp^{*}] exhibits one reversible oxidation wave and an irreversible wave at 0.29 V higher potential.^{22b} The irreversible behaviour is attributed to the oxidation reaction of the Cp^{*} ligand, analogous to the behaviour of [Cp^{*}₂Ru] on oxidation. Compound **2** in a similar way

Figure 3. Contour line diagram of the Laplacian of the electron density, $\nabla^2\rho(r)$ of **2a** in the plane of [Ru₂B₆] 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).

exhibits three successive one-electron oxidations with the first two are separated by approximately 0.4 V while the 2nd and 3rd potentials are separated by 0.23 V. The first redox event **2**⁰/**2**⁺ is quasi-reversible, but the second and third oxidations **2**⁺/**2**²⁺ and **2**²⁺/**2**³⁺ are irreversible as shown by the lack of a return wave. The cyclic voltammogram of **2** is similar to that of [(Cp^{*}Ru)B₈H₁₄(RuCp^{*})]³ that shows two successive one-electron oxidations separated by approximately 0.8V (Figure S5 in Supplementary Information).

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

Although compounds **2** and **3** were isolated from the same reaction, all of our attempts to reproduce **3** were unsuccessful. However, with the limited spectroscopic data and an X-ray crystallographic analysis, we have characterized compound **3**. The ¹¹B{¹H} chemical shifts appeared at $\delta = -16.8$ and -19.2 ppm correspond to the two different boron environments. The ¹H 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.

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).

The solid-state X-ray structure of compound **3** may be considered as an eight-step *nido*-[(Cp**Ru*)₂B₂H₈C₆H₃(CH₃)] cluster (Figure 4). Compound **3** [(Cp**Ru*)₂B₂H₈C₆H₃(CH₃)] can be viewed as an edge-fused ruthenaborane cluster in which a toluene ring being fused to a pentagonal pyramidal ring Ru₂B₂C₂. The structure of **3** is analogous to the isoelectronic ruthenium indenyl complex with a central indenyl ligand [(η⁵-C₅R₅)Ru(η⁵-C₉H₇)] (R = Me).²⁶ 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,²⁷ which indeed longer than the normal C=C length (1.33 Å). The Ru–Ru bond distance (2.9578 Å) is considerably longer than the reported diruthena-boranes.^{12,28} The RuB₂C₆ fragment in **3** is a true analogue of the η⁵-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.²⁹

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 {RuB₂C₆} fragment is a true analogue of η⁵-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**Ru*H} 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. All additional information pertaining to characterization of the complexes **2–3** using ESI-MS technique, IR spectra and multinuclear NMR spectra (Figures S1–S8), and computational details are given in the Supplementary Information available at www.ias.ac.in/chemsci.

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