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ARTICLE

Chemistry of Group 9 Dimetallaborane Analogues of Octaborane(12)

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We report the synthesis, isolation and structural characterization of several moderately air stable *nido*-metallaboranes that represent boron rich open cage systems. The reaction of $[\text{Cp}^*\text{CoCl}]_2$, ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), with $[\text{BH}_3 \cdot \text{thf}]$ in toluene at ice cold temperature, followed by thermolysis in boiling toluene produced $[(\text{Cp}^*\text{Co})\text{B}_9\text{H}_{13}]$, **1** $[(\text{Cp}^*\text{Co})_2\text{B}_8\text{H}_{12}]$, **2** and $[(\text{Cp}^*\text{Co})_2\text{B}_6\text{H}_{10}]$ **3**. Building upon our earlier reactivity studies on rhodaboranes, we continue to explore the reactivity of dicobalt analogues of octaborane(12) cluster **3** with $[\text{Fe}_2(\text{CO})_9]$ and $[\text{Ru}_3(\text{CO})_{12}]$ at ambient conditions that yielded novel fused clusters $[\text{Fe}_2(\text{CO})_6(\text{Cp}^*\text{Co})_2\text{B}_6\text{H}_{10}]$, **4** and $[\text{Ru}_4(\text{CO})_{11}(\text{Cp}^*\text{Co})_2\text{B}_3\text{H}_3]$, **5** respectively. In an attempt to synthesizing heterometallic metallaborane compound we performed the reaction of $[(\text{Cp}^*\text{Rh})_2\text{B}_6\text{H}_{10}]$, **6** with $[\text{Cp}^*\text{IrH}_4]$ that yielded a Ir-Ir double bonded compound $[(\text{Cp}^*\text{Ir})_2\text{H}_3][\text{B}(\text{OH})_4]$, **7**. All the new compounds have been characterized by IR, ^1H , ^{11}B , ^{13}C NMR spectroscopy, and the molecular structures were unambiguously established by X-ray diffraction analysis.

Introduction

Metallaboranes are the real hybrid systems that empirically intersect the polyhedral boranes with transition metal clusters, which, in some ways, resembles to organometallic chemistry and possess an extensive chemistry.¹ These clusters have been showing their enormous importance in recent years due to exceptional structural frame works, variable degrees of reactivity, and lately their catalytic activities.²⁻⁶ Due to the optimistic implementations of isolobal analogy combined with the cluster electron-counting rules, the metallaborane clusters have been perceived considerable credence till date.^{7,8} The main-group atoms or fragments which can be substituted by the isolobal transition-metal fragments generate species which are often more stable and more readily deliberated by X-ray analysis.⁹ For example, $\{\text{BH}\}$ unit is isolobal with a two-electron $[\text{M}(\text{CO})_3]$ or $[\text{Cp}^*\text{M}]$ fragment ($\text{M}(\text{CO})_3$, $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; Cp^*M , $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$, $\text{Cp}^* = \eta^5\text{-C}_5\text{H}_5, \eta^5\text{-C}_5\text{Me}_5$). In this regard, transition metal carbonyls such as $[\text{Fe}_2(\text{CO})_9]$ and $[\text{Co}_2(\text{CO})_8]$ have been used successively due to their potential as versatile reagents for metal cluster building reactions.¹⁰

As a result, after successive isolation of compound $[(\text{Cp}^*\text{Co})_2\text{B}_6\text{H}_{10}]$, **3** the chemistry was elaborated by means of a cluster expansion reaction with $[\text{Fe}_2(\text{CO})_9]$ in hexane, which led us to isolate a fused cluster, $[\text{Fe}_2(\text{CO})_6(\text{Cp}^*\text{Co})_2\text{B}_6\text{H}_{10}]$, **4**. Extension of this approach toward $[\text{Ru}_3(\text{CO})_{12}]$ resulted the formation of the unusual heterometallic boride cluster $[\text{Ru}_4(\text{CO})_{11}(\text{Cp}^*\text{Co})_2\text{B}_3\text{H}_3]$, **5**. Current investigations in our lab focus on synthesis of novel heterometallic clusters in a way to synthesize the polyhedral metallaboranes having mixed transition metals units within the constraints.¹¹ In this regard, we explored the reaction of $[\text{Cp}^*\text{IrH}_4]$ with $[(\text{Cp}^*\text{M})_2\text{B}_6\text{H}_{10}]$ where $\text{M} = \text{Co}$ and Rh . The reaction of $[\text{Cp}^*\text{IrH}_4]$ with compound **3** led to decomposition of starting material, however

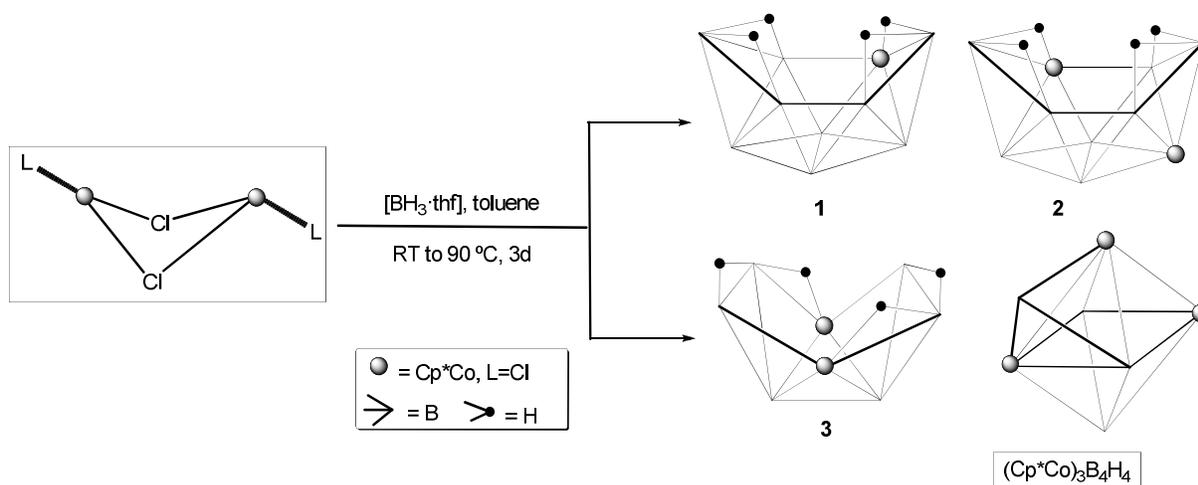
$[\text{Cp}^*\text{IrH}_4]$ with $[(\text{Cp}^*\text{Rh})_2\text{B}_6\text{H}_{10}]$ resulted a dimerized compound, in which the reduction happened at iridium center to avail an unusual double bonded Ir atoms.

Results and discussion

Synthesis and characterization of decaborane(14) analogues **1** and **2**:

As shown in Scheme 1, the reaction of $[\text{Cp}^*\text{CoCl}]_2$ with excess of $[\text{BH}_3 \cdot \text{thf}]$ in toluene at 0 °C, followed by thermolysis for longer period resulted new clusters $[\text{nido-5-(Cp}^*\text{Co)B}_9\text{H}_{13}]$, **1** and $[\text{nido-3,5-(Cp}^*\text{Co})_2\text{B}_8\text{H}_{12}]$, **2** in moderate yields. The reaction also yielded metallaborane clusters $[(\text{Cp}^*\text{Co})_3\text{B}_4\text{H}_4]$,²¹ and $[(\text{Cp}^*\text{Co})_2\text{B}_6\text{H}_{10}]$,¹² **3** in good yields. Although they are produced in a mixture, these compounds can be separated by TLC which allowed spectroscopic and structural characterization of pure materials. Compounds **1** and **2** are reasonably air stable and can be handled in air for extended periods without apparent change, especially in the pure crystalline state. Spectroscopic and structural characterizations of **1** and **2** from the NMR, IR, mass spectrometry and X-ray diffraction studies are discussed below.

[nido-5-(Cp*Co)B₉H₁₃], 1: Compound **1** has been isolated as a red solid in 20% yield. The ^{11}B NMR spectrum at room temperature shows nine resonances at $\delta = 29.4, 27.1, 12.5, 4.1, 3.5, 1.7, -1.1, -14.5$ and -36.9 ppm indicates the absence of a plane of symmetry in the molecule. The down field resonance at 29.4 ppm in ^{11}B NMR spectra is corresponding to the unique four connected boron atom B1 which is attached to one cobalt and three boron atoms. Besides the BH terminal protons, one equivalent of Cp^* protons were also observed in the ^1H NMR spectrum. In addition, one distinct up field sharp resonances centered at $\delta = -20.78$ ppm which is assigned to one equivalent of Co-H-B. The IR spectrum features bands at 2461 and 2490 cm^{-1} owing to the terminal B-H stretches.



Scheme 1. Synthesis of mono, di-cobaltaborane clusters.

The solid state X-ray structure, determined by single crystal X-ray diffraction studies, (Fig. 1), clearly shows that **1** is isoelectronic and isostructural with decaborane-14 and is in agreement with the above spectroscopic data. All the boron atoms are connected to the terminal hydrogen atoms and the Cp* ligand is attached to the Co vertex. The interesting structural feature presented in **1** is the presence of C–H···B interactions, which seem to play a well defined role in the crystal lattice.¹³ Indeed, in the crystals of **1** each molecule interacts with two nearest neighbours via C–H···B contacts (3.003 Å), forming an infinite one-dimensional chain (Fig. 2). Alignment of those chains lead to the generation of flat layers, which interacted through C–H···π interaction into a lamellar three dimensional structure (Fig. S1, supporting information).

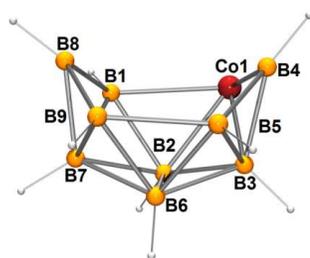


Fig. 1. Molecular structure of **1**. Cp* ligand is removed for clarity. Selected interatomic distances (Å) and angle (°): Co(1)-B(1) 2.202(12), Co(1)-B(4) 2.028(8), Co(1)-B(2) 2.091(13), B(1)-B(8) 1.725(18), B(1)-B(7) 1.767(18), B(1)-B(2) 1.778(10) B(5)-B(6) 1.790(15), B(1)-Co(1)-B(4) 100.4(4), B(3)-B(2)-Co(1) 64.4(5), B(2)-B(6)-Co(1) 113.8(8), B(3)-Co(1)-B(1) 88.9(4), B(2)-B(3)-B(4) 114.4(7).

[nido-3,5-(Cp*Co)₂B₈H₁₂], 2: Compound **2** have been isolated as brown solids in 18% yields. The ¹¹B NMR spectrum rationalizes the presence of eight ¹¹B resonances at room temperature distributed between the regions δ = 42 to -12 ppm with equal intensity ratio. Comparing the ¹¹B {¹H} chemical shift values with decaborane-14, B6 boron atom of **2** (Fig. 3) corresponds to the most up fielded one. In addition to the Cp* ligand and terminal B–H protons, the ¹H NMR of **2** shows four distinct up fielded broad resonances corresponding to B–H–B and an Co–H–B centred at δ = -3.2, -4.1, -4.8 and -19.1 ppm. The IR spectrum of *nido-2* feature bands in the region of 2428 and 2451 cm⁻¹ due to the terminal B–H stretches.

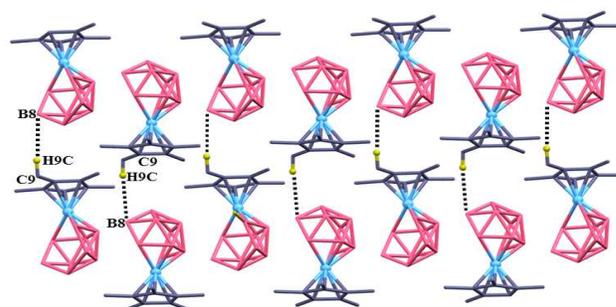


Fig. 2. 2D layer packing of **1** showing C–H···B interaction view along *a* axis (hydrogen atoms except those, which have been taken part in the hydrogen bonding, are removed for clarity) Color code: C: violet; Co: cyan; B: pink; H: yellow.

The solid state structure of **2**, shown in Fig. 2, confirms the structural inferences made on the basis of spectroscopic results. The molecular structure of **2** shows that there are degrees 3, 4, and 5 vertices, in which one cobalt atom occupies the degree four vertex and another cobalt atom occupies degree five vertex. Based on the electron counting rules, the framework geometry of **1** and **2** should be *nido* cluster derived from eleven-vertex *closo*-octadecahedron with a missing vertex of connectivity six. By analogy with the Ir,¹⁴ Co,¹⁵ Ru¹⁶ and Rh¹⁷ analogues compounds **1** and **2** can be considered

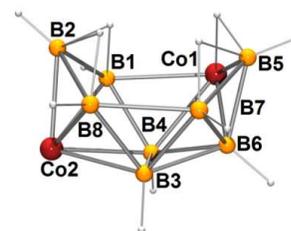
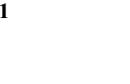
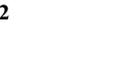


Fig. 3. Molecular structure of **2**. Cp* ligands are removed for clarity. Selected interatomic distances (Å) and angle (°): Co(1)-B(1) 2.182(7), Co(2)-B(2) 1.953(7), B(1)-B(2) 1.853(9) B(3)-B(4) 1.777(7), B(7)-B(8) 1.954(10); B(5)-Co(1)-B(1) 100.6(2), B(1)-B(4)-Co(2) 65.0(3), B(1)-B(4)-B(6) 116.0(4), B(7)-B(3)-B(8) 67.5(4), Co(1)-B(5)-B(7) 67.5(4).

Table 1. Selected structural parameter of ten vertex *nido* clusters^a having variety of metal boron ratio

Geometry ^b	Formula	Avg. <i>d</i> [B–B][Å] ^c	refs.	Geometry ^b	Formula	Avg. <i>d</i> [B–B][Å] ^c	refs.
	5-[(Cp*Co)B ₉ H ₁₃]	1.78	This work		3,5-[(Cp*Rh) ₂ B ₈ H ₁₂]	1.81	17b
	3,5-[(Cp*Co) ₂ B ₈ H ₁₂]	1.80	This work		3,5,7-[(Cp*Rh) ₃ -B ₇ H ₁₁]	1.83	17b
	[B ₁₀ H ₁₄]	1.78	16b		2,4-[(Cp*Ir) ₂ -B ₈ H ₁₂]	2.13	14
	1-[(Cp [#] Ru)B ₉ H ₁₃] ^d	2.16	16		6,9-[(Cp*Co) ₂ B ₈ H ₁₂]	2.02	15a
	2-[(Cp*Rh)B ₉ H ₁₃]	1.94	17a		6-Cl-5,7-[(Cp*Co) ₂ B ₈ H ₁₁]	-	15a
	2,4-[(Cp*Rh) ₂ B ₈ H ₁₂]	1.97	17a		9-Me-5,7-[(Cp*Co) ₂ B ₈ H ₁₁]	1.76	17b

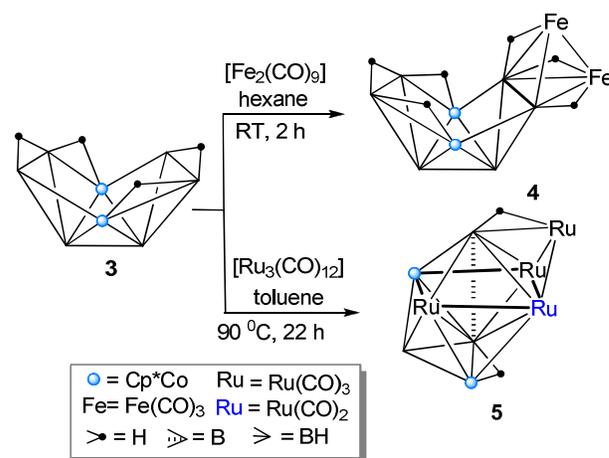
^a all clusters possess 11 sep; ^d < = BH; ^c open face; ^d Cp[#] = η⁶-C₆Me₆;

as total sep of 12. Both *nido*-1 and *nido*-2 are the case of a polyhedral cluster, similar to ten vertex boranes, carboranes or metallaboranes having same skeletal electron pairs (sep) and geometry. Therefore, we have tried to contrast their structural data and chemical shifts values with a set of similar cluster types of formal electron counts of 12 (Table 1).¹⁴⁻¹⁷ The bridging hydrogens of **1** have not been located by X-ray diffraction studies; however, their connectivity have assertively been determined by ¹H NMR and are expected to be situated on the open face of the six-membered ring.

Metal fragment addition to *nido*-[(Cp*Co)₂B₆H₁₀], **3:** The cluster build up reactions are now well-known;¹⁰ however, high yield and precise stoichiometry examples are limited. After finding an improved synthetic route to [(Cp*Co)₂B₆H₁₀], **3** and the resourcefulness of metal carbonyl compounds as important building block for cluster growth reaction, tempted us to verify the reactivity of **3** with metal carbonyl compounds. Therefore, the room temperature reaction of **3** with [Fe₂(CO)₉] in hexane yielded condensed cluster [Fe₂(CO)₆(Cp*Co)₂B₆H₁₀], **4** whereas the reaction of [Ru₃(CO)₁₂] with **3** at elevated temperature yielded a boride cluster [Ru₄(CO)₁₁(Cp*Co)₂B₃H₃], **5**. Details of the structural characterizations of **4** and **5** are discussed below.

[Fe₂(CO)₆(Cp*Co)₂B₆H₁₀], **4:** Compound **4** has been isolated in modest yield and characterized spectroscopically as well as by a single crystal X-ray diffraction study. The IR spectrum in the carbonyl region shows four terminal carbonyl

frequencies. The frequencies 2063, 2021, 1998 and 1992 cm⁻¹ have been assigned to a [Fe₂(CO)₆] fragment as they are not unlike those reported for [Fe₂(CO)₆Se₂]¹⁸ and [B₂H₆Fe₂(CO)₆]¹⁹. Unlike **3**, cluster **4** does not possess plane of

**Scheme 2.** Metal fragment addition to *nido*-[(Cp*Co)₂B₆H₁₀].

symmetry which has been confirmed by ¹H and ¹¹B NMR spectra. Comparing the upfield ¹H NMR values of **3** and **4** it is reasonable to say that the resonances at δ = -9.2, -11.7 and -

11.9 ppm are assigned to three B-H-Fe protons while the resonances at $\delta = -20.4$ and -20.7 ppm are assigned to two Co-H-B protons. Compound **4** can take part in C-H \cdots O bonding interactions (Fig. S2). The molecules are self-assembled through hydrogen bonded network in such a way to arrange themselves in a 2D layer parallel to *c*-axis. The 2D layers are further self-assembled by the weak C-H \cdots O intermolecular hydrogen bonds (C13-H13a \cdots O4 = 3.555 Å, C14-H14c \cdots O4 = 3.573 Å) formed between the CO group of one molecule and the hydrogen atom of Cp* unit of another molecule (Fig. S2). The 2D sheets are further arranged into 3D framework through C-H \cdots O, C=O \cdots π interactions and van der Waal interactions (Fig. S3).

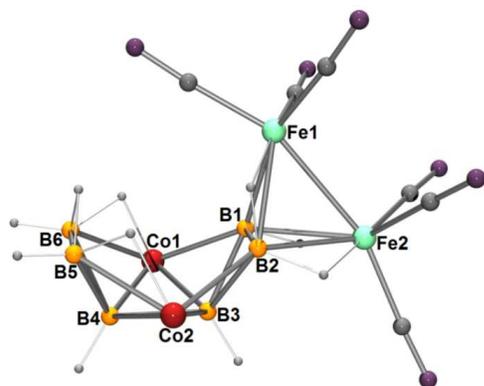


Fig. 4. Molecular structure and labeling diagram for **4**. Cp* ligands are excluded for clarity. Selected bond lengths (Å) and angles (°) for **4**: Co(1)-B(1) 2.074(2), B(1)-B(2) 1.687(3), Fe(1)-B(1) 2.121(2), Fe(1)-Fe(2) 2.5779(5); B(1)-Co(1)-B(6) 102.09(11), B(1)-B(2)-Fe(2) 68.03(12), B(1)-Fe(1)-B(2) 46.23(9), Co(1)-B(1)-B(2) 118.58(16).

As far as total electron count is concerned, this condensed cluster can be described by fusion of smaller clusters fragments in accordance with Mingos fusion formalism.⁷ This formalism states, the total electron count of such condensed cluster is equal to the sum of the electron counts for the parent polyhedra minus the electron count of the shared unit(s) (atom, pair of atoms etc.). As a result of which cluster **4** (cluster valence electrons, cve = 84) can be viewed as formed from the condensation of [*nido*-(η^5 -C₅Me₅Co)₂B₆H₁₀] (cve = 56) and [Fe₂(CO)₉] (cve = 34) with elimination of three CO molecules (cve = 6). The mno rule²⁰ is also consistent with cluster **4**. Considering {Cp*Rh} as two electron fragment, the total skeletal electron count (sep) for **4** is 12. The mno rule also gives *m* = 2, *n* = 10 and *o* = 0 for *m*+*n*+*o* = 12 (where *m* is the number of polyhedra, *n* the number of vertices in the fused cluster, and *o* the number of single vertex shared atoms).

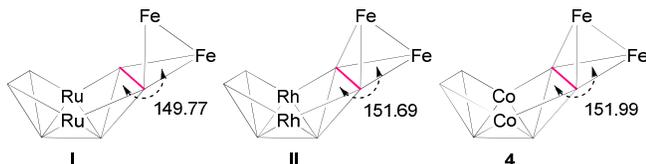


Chart 1. Comparison of [$\{\text{Fe}_2(\text{CO})_6\}(\text{Cp}^*\text{Ru})_2(\text{CO})(\text{B}_6\text{H}_{10})$], [$\{\text{Fe}_2(\text{CO})_6\}(\text{Cp}^*\text{Rh})_2(\text{B}_6\text{H}_{10})$] and **4**.

The existence of compound **4** led us to draw a structural comparison with [$\{\text{Fe}_2(\text{CO})_6\}(\text{Cp}^*\text{Ru})_2(\text{CO})(\text{B}_6\text{H}_{10})$]^{10c} and [$\{\text{Fe}_2(\text{CO})_6\}(\text{Cp}^*\text{Rh})_2(\text{B}_6\text{H}_{10})$]^{12a} clusters having same geometry.

The important geometrical differences among these three compounds are illustrated in Chart 1 and Table S1. As the shapes of these clusters are same, the differences given in Table S1 are exclusively in terms of the structural constraints. On the other hand, the differences in fused B-B distances (1.68–1.71 Å) and dihedral angles (152.0–149.7°) may be due to the presence of more electron dense metal in the cluster core.

[Ru₄(CO)₁₁(Cp*Co)₂B₃H₃], **5**: The development of isolobal analogy discloses the similarities between electronic structures of compounds of different atomic compositions. Since [Fe(CO)₃] fragment is isoelectronic to [Ru(CO)₃], we performed the reaction of **3** with [Ru₃(CO)₁₂] that yielded boride cluster **5**. The isolation of transition metal interstitial borides has gained an exclusively advanced area of cluster chemistry.²¹ The existence of three ¹¹B resonances at $\delta = 122.1$, 99.3, and 85.1 ppm (1:1:1) are noticed in ¹¹B spectrum. Among them the resonance at $\delta = 122.1$ ppm has been assigned to μ_7 -boride boron (B3; Fig. 5). In addition, the ¹H NMR spectrum reveals one terminal B-H protons at $\delta = 6.41$ ppm along with two up field resonances. The presence of two Cp* ligands are confirmed by ¹H and ¹³C NMR spectroscopy. The IR spectrum of **5** features bands at 2490 cm⁻¹ attributed to the terminal B-H stretches. The strong absorptions at 2054, 2032, 2003 and 1993 cm⁻¹ correspond to the terminal carbonyl groups.

The molecular structure of **5** shown in Fig. 5 reveals that the cage geometry is tricapped octahedron geometry with one semi-interstitial boron atom of coordination number 7. The octahedral core consists of the four metal atoms (Co1, Ru2, Ru3 and Ru4) in the equatorial plane and two boron atoms (B2 and B3) in the apical positions. Further, the three triangular faces, Co1-B3-Ru4, B3-Ru3-Ru4 and B2-Ru2-Ru3 are capped by B1, Co2 and Ru4 respectively. Compound **5** is best described as a tricapped octahedron. On the basis of the capping principle, the skeletal electron count is determined by the central polyhedron, that is, the Ru₃Co₁B₂ octahedron, and is seven sep. But for **5**, eight sep are available and the observed structures do not obey the counting rules.⁷ Although there are several instances of tricapped octahedron among the families of higher nuclearity metal carbonyl cluster complexes, they are very rare in metatallaborane cluster families. In fact, this is a rare structural characterization of heterometallic boride cluster having cobalt and ruthenium metals as prime cluster constituents.

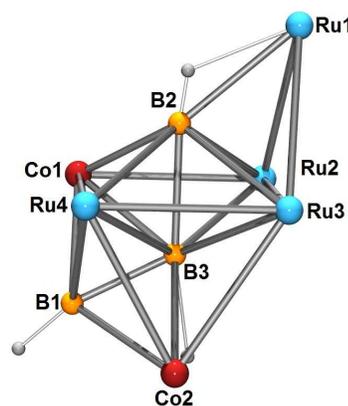
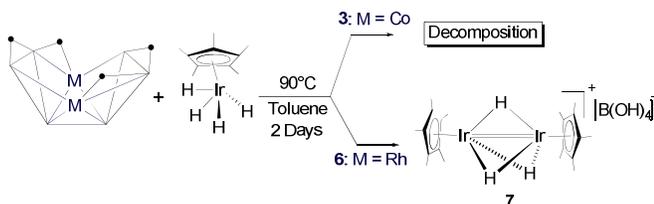


Fig. 5. Molecular structure and labeling diagram for **5**. Cp* and carbonyl ligands are excluded for clarity. Selected bond lengths (Å) and angles (°) for **5**: Co(1)-B(1) 2.060(9), B(1)-B(3) 1.631(12), B(2)-B(3) 1.914(11), B(3)-Ru(3) 2.215(8); Ru(4)-Co(1)-Ru(2) 97.17(4), Co(1)-B(3)-Co(2) 134.6(4), B(1)-B(3)-B(2) 115.8(6), Ru(2)-B(3)-Ru(3) 80.4(3), Ru(3)-B(3)-Ru(4) 76.5(2).

Reactivity of $[(Cp^*M)_2B_6H_{10}]$, (3**: $M = Co$; **6**: $M = Rh$) toward $[Cp^*IrH_4]$:** The chemistry of heterometallic systems has been intensively studied, in part due to the promise of enhanced stoichiometric or catalytic reactivity from the cooperative activation and synergistic interaction of metal centers with differing electronic properties. Thus, in an extension to prepare heterobimetallic (Rh-Ir) metallaborane complex, we performed the reaction of $[(Cp^*M)_2B_6H_{10}]$, (**3**: $M = Co$; **6**: $M = Rh$) with $[Cp^*IrH_4]$ in toluene at 90 °C. For compound **3**, the reaction led to decomposition, however the reaction of **6** and $[Cp^*IrH_4]$ afforded an extremely polar yellow solid $[(Cp^*Ir)_2H_3][B(OH)_4]$, **7** (Scheme 3). Compound **7** has been isolated in modest yield, and characterized spectroscopically as well as by single-crystal X-ray diffraction analysis. The ^{11}B NMR spectroscopy reveals a very sharp peak at $\delta = -0.94$ ppm, whereas, the 1H NMR spectroscopy reveals resonances for Cp^* proton at $\delta = 2.09$ ppm and hydride regions at $\delta = -15.6$ ppm in 10:1 ratio. The mass spectrum of **7** showed a good isotopic distribution which is in agreement with the molecular weight of the cationic species. IR absorption bands at 1518 and 1496 cm^{-1} , are also evidence of the bridging Ir-hydride stretch as the terminal hydride ligands generally give rise to the IR bands in the range from 2200 to 1600 cm^{-1} and bridging hydride ligands from 1600 to 800 cm^{-1} .²²



Scheme 3: Reactivity of $[(Cp^*M)_2B_6H_{10}]$ with iridium hydride

The spectroscopic findings became clear after the X-Ray diffraction analysis was undertaken. The molecule in its asymmetric unit contains two units, $[Cp^*Ir]_2$ and $[B(OH)_4]$. As shown in Fig. 6, the Cp^* moieties are in a mutually staggered conformation and C_5 axis is passing through the iridium atoms. The bridging hydride atoms and the hydrogens of $[B(OH)_4]$ unit could not be located in the X-ray study whereas their presence are inferred by 1H NMR data. The Ir-Ir bond length (2.459(2) Å) in **7** is significantly shorter than those previously reported for the formal Ir-Ir double bonds found in the carbonyl-bridged analogues $[Cp^*_2Ir_2(\mu-CO)_2]$ (2.554(1) Å),²⁴ $[Ir_2(\mu-PPh_2)_2(CO)_2(PPh_3)_2]$ (2.551(1) Å)²⁵ and $[Cp^*_2Ir_2(\mu-H)_2(\mu_2-\eta^1, \eta^1-N_2C_3H_3)]$ (2.663(1) Å).²⁶

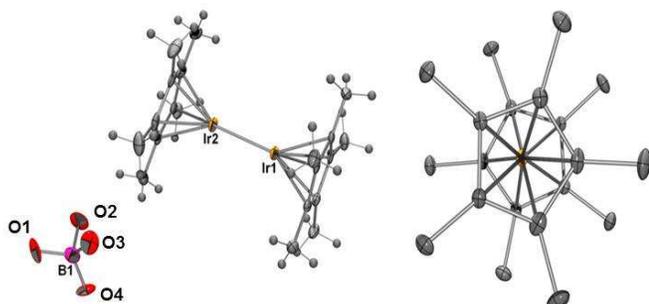


Fig. 6. Molecular structure and labeling diagram for **7**. Thermal ellipsoids are shown at the 20% probability. Front view (left) and side view $[B(OH)_4]^-$ removed for clarity(right). Relevant bond lengths (Å) and angles (deg): Ir1-Ir2 2.459(3), B1-O1 1.280(2), B1-O2 1.380(2); O3-B1-O2 112.8(18), O3-B1-O1 115.0(17).

Conclusions

Mono- and di-cobaltaborane analogues of decaborane(14) have been synthesized and structurally characterized. It is exciting to see at what degree it might be likely to replace the BH units by $\{Cp^*Co\}$ fragment or metal carbonyl fragments ($\{Fe(CO)_3\}$ or $\{Co_2(CO)_5\}$) in B_{10} cage and what would be the structural discrepancy from the parent molecules. The reactivity of *nido*- $[(Cp^*Co)_2B_6H_{10}]$ with $[Fe_2(CO)_9]$ led us to isolate novel fused clusters, whereas, the reaction with $[Ru_3(CO)_{12}]$ generates a semi-interstitial tricapped octahedral boride which is very uncommon in metallaboranes families. Therefore, not only borane addition increased cluster nuclearity but also cluster condensation can be considered as an additional viable pathway for increasing nuclearity in the cluster framework.

Experimental Section

General Procedures and Instrumentation

All the operations were carried out under an Ar/ N_2 atmosphere using standard Schlenk and glovebox techniques. Solvent were dried and deoxygenated under Argon and freshly distilled prior to use. Cp^*H , $CoCl_2$, $n-BuLi$ in cyclohexane, were used as received. $[Cp^*CoCl]_2$,²⁶ 6^{12a} , $[Cp^*IrH_4]$ ²⁷ and the external reference $[Bu_4N(B_3H_8)]$,²⁸ for the ^{11}B NMR were synthesized by the literature method. Thin layer chromatography was carried on 250 mm dia aluminium supported silica gel TLC plates (MERCK TLC Plates) to separate products. NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ , ppm, $CDCl_3$, 7.26), while a sealed tube containing $[Bu_4N(B_3H_8)]$ in C_6D_6 (^{11}B , ppm, -30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were recorded on a Nicolet iS10 spectrometer. The mass spectra were recorded on Bruker MicroTOF-II mass spectrometer. The microanalyses for C and H were performed on Perkin Elmer Instruments series II model 2400.

Synthesis of 1 and 2. Into a brown colour solution of $[Cp^*CoCl]_2$, (0.2 g, 0.44 mmol) in dry toluene (12 cm^3) $[BH_3 \cdot thf]$ (2 ml, 1.51 mmol) was added by syringe at 0 °C. The resulting deep brown solution was thermolized at 90 °C for 3 days. The solvent was removed in vacuo and the remaining residue was extracted in hexane and passed through Celite. After removal of hexane the resulting solid was subjected to thin layered chromatographic work up using silica gel TLC plates. Elution with hexane: CH_2Cl_2 (85:15 v/v) yielded red $[(Cp^*Co)B_9H_{13}]$, **1** (0.03 g, 20 %), green $[(Cp^*Co)_2B_8H_{12}]$ **2** (0.04 g, 18%), red $[(Cp^*Co)_2B_6H_{10}]$, **3** (0.03 g, 15%) and yellow $[(Cp^*Co)_3B_4H_6]$, (0.03 g, 12%).

1: ^{11}B NMR (128 MHz, $CDCl_3$, 22 °C): $\delta = 29.4$ (br, 1B), 27.1 (br, 1B), 12.5 (br, 1B), 4.1 (d, 1B), 3.5 (br, 1B), 1.7 (d, 1B), -1.1 (br, 1B), -14.5 (br, 1B), -36.9 (br, 1B). 1H NMR (400 MHz, $CDCl_3$, 22 °C): $\delta = 6.81$ (br, 2BH_i), 5.72 (br, 2BH_i), 4.01 (br, 2BH_i), 3.82 (br, 1BH_i), 3.21 (br, 2BH_i), 1.74 (s, 15H, Cp*), -2.82 (br, 2B-H-B), -3.51 (br, 1B-H-B), -18.43 (s, Co-H-B). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): $\delta = 92.9$ (s, $\eta^5-C_5Me_5$), 90.2 (s, $\eta^5-C_5Me_5$), 14.2 (s, $\eta^5-C_5Me_5$), 10.3 (s, $\eta^5-C_5Me_5$). IR (hexane) ν/cm^{-1} : 2461w, 2490w (BH_i). Elemental analysis (%) calcd for $C_{10}H_{28}B_9Co$: C, 39.22; H, 9.21. Found: C, 39.75; H, 9.01.

2: MS (ESI⁺): m/z 527 (M+K)⁺, calculated mass for $^{12}C_{20}^{1}H_{42}^{11}B_8^{59}Co_2^{39}K$ 527.2332, obsd, 527.2322. ^{11}B NMR (128 MHz, $CDCl_3$, 22 °C): $\delta = 42.4$ (br, 1B), 30.1 (br, 1B), 25.3 (d, $J_{B-H} = 136$ Hz, 1B), 20.1 (br, 1B), 9.1 (br, 1B), 6.3 (br, 1B), -1.2 (br, 1B) -12.9 (d, $J_{B-H} = 139$ Hz, 1B). 1H NMR (400 MHz,

CDCl_3 , 22 °C): δ = 6.96 (br, 2BH₁), 5.68 (br, 2BH₁), 3.74 (br, 2BH₁), 1.68 (s, 15H, 1Cp*), 1.64 (s, 15H, 1Cp*), 9.1 (br, 1B), 1.24 (br, 1BH₁), -3.19 (s, B-H-B), -4.07 (s, B-H-B), -4.87 (s, B-H-B), -19.13 (Co-H-B). ¹³C NMR (100 MHz, CDCl_3 , 22 °C): δ = 94.1 (s, $\eta^5\text{-C}_5\text{Me}_5$), 90.2 (s, $\eta^5\text{-C}_5\text{Me}_5$), 9.9 (s, $\eta^5\text{-C}_5\text{Me}_5$), 9.1 (s, $\eta^5\text{-C}_5\text{Me}_5$). IR (hexane) ν/cm^{-1} : 2428w, 2451w (BH₁).

Synthesis of 4. To a flame-dried Schlenk tube compound **3** (0.005 g, 0.0115 mmol) was dissolved in hexane (10 ml) and $[\text{Fe}_2(\text{CO})_9]$ (0.002g, 0.0054 mmol) was added to the solution. The reaction mixture was allowed to stir at room temperature for two hours. The solvent was dried and the solid was extracted into hexane by passing through Celite. The filtrate was concentrated and kept at -40 °C to remove $[\text{Fe}_3(\text{CO})_{12}]$. After removal of solvent, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with a hexane/ CH_2Cl_2 (95:5 v/v) mixture yielded air stable brown $[\text{Fe}_2(\text{CO})_6(\text{Cp}^*\text{Co})_2\text{B}_6\text{H}_{10}]$, **4** (0.016 g, 60%).

4: MS (ESI⁺): m/z 661 (M-3CO)⁺, calculated mass for ¹²C₂₃¹H₄₁¹¹B₆⁵⁹Co₂⁵⁶Fe₂¹⁶O₃ 661.0977, obsd, 661.0984. ¹¹B NMR (22 °C, 128 MHz, CDCl_3) δ = 45.5 (d, J_{B-H} = 143, 1B), 32.0 (d, J_{B-H} = 151, 1B), 26.9 (d, J_{B-H} = 122, 1B), 25.3 (d, J_{B-H} = 134, 1B), 9.1 (br, 1B), -5.5 (d, J_{B-H} = 128, 1B). ¹H NMR (22 °C, 400 MHz, CDCl_3) δ = 4.98 (partially collapsed quartet (pcq), (br 1BH₁), 4.25 (br, 1BH₁), 4.10 (pcq, 1BH₁), 3.34 (br, 1BH₁), 1.74 (s, 15H; 1Cp*), 1.70 (s, 15H, 1Cp*), -3.49 (br, 2B-H-B), -9.20 (d, 1B-H-Fe), -11.71 (br, 1B-H-Fe), -11.93 (br, 1B-H-Fe), -20.45 (br, 1Co-H-B), -20.67 (br, 1Co-H-B). ¹³C NMR (22 °C, 100 MHz, CDCl_3): δ = 100.5 (s, C₅Me₅), 98.7 (s, C₅Me₅), 11.2 (s, C₅Me₅), 8.3 (s, C₅Me₅). IR (hexane) ν/cm^{-1} : 2468, 2512 (BH₁), 2063, 2021, 1998 and 1992 (CO).

Synthesis of 5. To a flame-dried Schlenk tube, compound **3** (0.005 g, 0.0115 mmol) was dissolved in toluene (12 ml) and $[\text{Ru}_3(\text{CO})_{12}]$ (0.002g, 0.0054 mmol) was added to the solution. Then the reaction mixture was allowed for thermolysis at room 90 °C for 22 hours. The solvent was evacuated and the solid was extracted into hexane by passing 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 (90:10 v/v) mixture yielded air stable yellowish brown product $[\text{Ru}_4(\text{CO})_{11}(\text{Cp}^*\text{Co})_2\text{B}_3\text{H}_3]$, **5** (0.0018g, 12%).

5: ¹¹B NMR (22 °C, 128 MHz, CDCl_3) δ = 122.1 (s, 1B), 99.3 (br, 1B), 85.1 (br, 1B). ¹H NMR (22 °C, 400 MHz, CDCl_3) δ = 6.41 (pcq, 1BH₁), 1.74 (s, 15H; 1Cp*), 1.70 (s, 15H; 1Cp*), -5.56 (br, 1B-H-Ru), -14.93 (br, 1B-H-Co). ¹³C NMR (22 °C, 100 MHz, CDCl_3): δ = 100.5 (s, $\eta^5\text{-C}_5\text{Me}_5$), 98.7 (s, $\eta^5\text{-C}_5\text{Me}_5$), 11.2 (s, $\eta^5\text{-C}_5\text{Me}_5$), 8.3 (s, $\eta^5\text{-C}_5\text{Me}_5$). IR (hexane) ν/cm^{-1} : 2490 (BH₁), 2054, 2032, 2003, 1993 (CO). Elemental analysis (%) calcd for C₃₁H₃₃B₃Co₂O₁₁Ru₄: C, 32.76; H, 2.93. Found: C, 32.79; H, 2.31.

Synthesis of 7. To a flame-dried Schlenk tube, compound **6** (0.04 g, 0.35 mmol) was dissolved in toluene (10 ml) and $[\text{Cp}^*\text{IrH}_4]$ (0.015g, 3.49 mmol) was added to this solution. The reaction mixture was allowed for thermolysis at 90 °C for 2 days. The solvent was dried and the solid was extracted into n-hexane and CH_2Cl_2 mixture (30:70) by passing 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 (5:95 v/v) mixture yielded air stable red product $[(\text{Cp}^*\text{Ir})_2\text{H}_3][\text{B}(\text{OH})_4]$, **7** (0.021g, 13%).

7: MS (MALDI): m/z 537 [M]⁺; isotope envelope C₁₀H₃₃Ir₂: requires 537. ¹¹B NMR (22 °C, 128 MHz, CDCl_3) δ = -0.94 (s, 1B). ¹H NMR (22 °C, 400 MHz, CDCl_3) δ = -15.6 (3 Ir-H-Ir), 4.16 (4H, OH), 2.09 (s, 15H, Cp*). ¹³C NMR (22 °C,

100 MHz, CDCl_3) δ = 103.2 (s, $\eta^5\text{-C}_5\text{Me}_5$), 11.4 (s, $\eta^5\text{-C}_5\text{Me}_5$). IR (hexane) ν/cm^{-1} : 1518, 1496 w Ir-H-Ir stretch.

X-ray Structure Determination.

Crystal data for **1** and **2** were collected and integrated using Super Nova, Dual, Cu at zero, Eos equipped with graphite-monochromated Cu K α radiation (λ = 1.5418 Å) radiation at 296 K. Crystal data for **4** was collected and integrated using OXFORD DIFFRACTION SUPER NOVA CCD system with graphite monochromated Mo-K α (λ = 0.71073 Å) radiation at 296 K. The crystal data for compounds **5** and **7** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-K α (λ = 0.71073 Å) radiation at 296 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97.²⁵

Crystal data for **1**: CCDC 1026973, C₁₀H₂₄B₉Co, M_r = 300.51, Monoclinic, space group *P*2₁, a = 9.6223(8) Å, b = 9.0222(8) Å, c = 10.1966(13) Å, β = 100.638(6)°, V = 870.00(15) Å³, Z = 2, ρ_{calcd} = 1.147 g·cm⁻³, μ = 7.515 mm⁻¹, F(000) = 312, R₁ = 0.0592, wR₂ = 0.0860, 3019 independent reflections [$\theta \leq 67.453^\circ$] and 223 parameters.

Crystal data for **2**: CCDC 1026974, C₂₀H₄₂B₈Co₂, M_r = 486.87, Triclinic, space group *P*-1, a = 8.3422(4) Å, b = 11.7052(6) Å, c = 13.3262(10) Å, α = 85.485(5)°, β = 86.826(5)°, γ = 76.377(4)°, V = 1259.82(13) Å³, Z = 2, ρ_{calcd} = 1.283 g·cm⁻³, μ = 1.322 mm⁻¹, F(000) = 512, R₁ = 0.0643, wR₂ = 0.1342, 5457 independent reflections [$\theta \leq 27.500^\circ$] and 313 parameters.

Crystal data for **4**: CCDC 1026975, C₂₆H₄₀B₆Co₂Fe₂O₆, M_r = 743.00, Monoclinic, space group *P*2₁/*n*, a = 8.7762(2) Å, b = 18.3446(5) Å, c = 20.7153(6) Å, β = 93.051(2)°, V = 3330.35(15) Å³, Z = 4, ρ_{calcd} = 1.482 g·cm⁻³, μ = 1.869 mm⁻¹, F(000) = 1520, R₁ = 0.0343, wR₂ = 0.0884, 7645 independent reflections [$\theta \leq 27.500^\circ$] and 419 parameters.

Crystal data for **5**: CCDC 1026976, Crystal data for **5**: C₃₁H₃₃B₃Co₂O₁₁Ru₄, M_r = 1136.14, Monoclinic space group *P*2₁, a = 9.5232(2) Å, b = 19.2392(5) Å, c = 11.2114(3) Å, β = 112.8620(10)°, V = 1892.77(8) Å³, Z = 2, ρ_{calcd} = 1.993 g·cm⁻³, μ = 2.466 mm⁻¹, F(000) = 1104, R₁ = 0.0259, wR₂ = 0.0557, 5738 independent reflections [$\theta \leq 24.998^\circ$] and 476 parameters.

Crystal data for **7**: CCDC 1026977, Crystal data for **7**: C₂₀H₃₄Br₂O₄, M_r = 733.68, Monoclinic space group *P*2₁/*c*, a = 10.4560(3) Å, b = 21.0575(6) Å, c = 11.1328(2) Å, β = 109.3220(10)°, V = 2313.12(10) Å³, Z = 4, ρ_{calcd} = 2.107 g·cm⁻³, μ = 11.515 mm⁻¹, F(000) = 1380, R₁ = 0.0364, wR₂ = 0.0945, 5541 independent reflections [$\theta \leq 28.4^\circ$] and 291 parameters.

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Notes and references

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Electronic Supplementary Information (ESI) available: For crystal packing diagram for **1** and **4**; CCDC reference numbers 1026973-1026977 or other electronic format see DOI: 10.1039/b000000x/

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Table of Content Entry Only**Chemistry of Group 9 Dimetallaborane Analogues of Octaborane(12)**

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Reaction of octaborane(12) analogue with metal carbonyl compounds yielded condensed metallaborane (A) and boride cluster (B) (see picture).

