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Hypoelectronic Isomeric Diiridaboranes [(Cp*Ir)₂B₆H₆]: The “Rule-Breakers” (Cp* = η⁵-C₅Me₅)

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In an effort to synthesize supraicosahedral iridaboranes, pyrolysis of [Cp*IrCl₂]₂ with excess [BH₃·thf] afforded isomeric iridaborane clusters [(Cp*Ir)₂B₆H₆], **1** and **2**. The geometry of **1** is dodecahedron similar to that of [B₈H₈]²⁻, whereas **2** exhibits cluster shape that can be derived from a nine vertex tricapped trigonal prism by removing one of the capped vertices. The existence of large HOMO-LUMO gap further rationalizes the *isocloso* structures for these isomers.

Boron like carbon, shares extensive catenation properties; however, due to the intrinsic electron-deficient nature it favours three-dimensional hyper-coordinated compounds with non-classical bonding.¹⁻⁴ The continuation of well-known relationship between geometry and the number of skeletal electron pairs (*sep*) for borane cages provides link between borane, heteroborane, carbocation, transition metal cluster and Zintl phase cluster chemistries.⁵⁻⁹ As a result, it has been observed that the metallaborane clusters containing late transition metals mimic classic organometallic compounds. For example, [(Cp*Ru)C₈H₆(RuCp*)]^{0,+} vs [(Cp*Ru)B₈H₁₄(RuCp*)]^{0,+}, [(CO)₄Fe(η²-C₂H₄)] vs [(CO)₄Fe]B₂H₅, [(η⁵-C₅H₅)Co(η⁴-C₄H₄)] vs [(η⁵-C₅H₅)Co]B₄H₈ and [(η⁵-C₅H₅)Fe(η⁵-C₅H₅)] vs [(η⁵-C₅H₅)Fe]B₅H₁₀.¹⁰

The rapid progress in this field¹⁻¹⁴ has been quite beyond potential and often proved a challenge to many well-established cluster electron-counting rules.¹⁵ For instance, Kennedy and co-workers have observed that metallaboranes with *closo* geometries deviate from most spherical deltahedra and do not possess the expected (n+1) *sep*, rather n *sep*.^{4c,8,16} Such “disobedient” metallaborane skeletons are often found as *isocloso* or *hypercloso* deltahedra. Further, a series of hypoelectronic *closo*-rhenaboranes [(Cp*Re)₂B_nH_n], n = 7–10, have been isolated and structurally characterized that

possess(n-2) *sep*.¹⁷ Also, there are precedents in the literature that metallaboranes of earlier transition metals exhibit structures with high metal-coordination number and cross-cluster bond.^{4a,17}

Our continuous drive in this field for a decade enabled us to isolate for the first time a 15- and a 16-vertex rhodaborane clusters [(Cp*Rh)₂B₁₃H₁₃] and [(Cp*Rh)₃B₁₂H₁₂Rh(Cp*RhB₄H₉)] respectively with 2n skeletal electron pairs.^{14,18} These results of ours^{14,18} and others,^{19,20} prompted us to explore the iridium system, as most of the reported iridaboranes are often hydrogen rich and open clusters albeit being in the same group as rhodium.²⁰ Although the main objective of isolating supraicosahedral iridaboranes was not achieved, the reaction of [Cp*IrCl₂]₂ with [BH₃·thf] enabled us to isolate 8-vertex iridaboranes [(Cp*Ir)₂B₆H₆] (**1** and **2**)²¹ as moderately stable yellow and red crystalline solids (Chart 1, Scheme S1, ESI[†]).

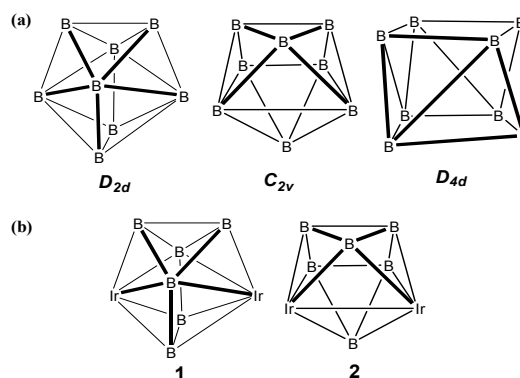


Chart 1 (a) Isomeric clusters of [B₈H₈]²⁻ (b) core structures of **1** and **2**

The composition and structures of **1** and **2** were established from mass spectrometry, multinuclear NMR spectroscopy, IR and X-ray diffraction studies (ESI[†]). The polyhedral structure of **1**, shown in Fig. 1, is a dodecahedron similar to that of borane ion²² [B₈H₈]²⁻ with two electron less than that of [B₈H₈]²⁻. On the otherhand, **2** exhibits cluster shape that can be derived from a nine vertex tricapped

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[†]Electronic Supplementary Information (ESI) available: X-ray analysis of **1**, **2** and **3**, CCDC references number 1429317,1429319, 1429318. Synthesis details, full computational details. See DOI: 10.1039/x0xx00000x

trigonal prism by removing one of the capped vertices. To follow cluster electron-counting rules,¹⁵ the 8-vertex dodecahedron **1** and the bicapped trigonal prism **2** require 9 and 10 skeletal electron pairs (sep) respectively while only 8 sep are available for them. Thus, they are *hypo*-electronic *i.e.*, fewer valence electrons than required by its geometric structure and violates Wade-Mingos rule.^{15a-c}

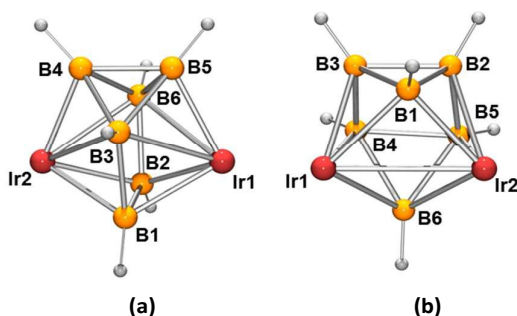


Fig. 1 Molecular structure and labeling diagram for **1** and **2** (Cp* ligands omitted for clarity) Selected bond lengths (Å) and angles [°] (a) **1**: B1-Ir1 2.042(16), B1-Ir2 2.032(16), B1-B2 1.86(3); B3-B1-Ir2 74.5(8), B3-B1-Ir1 72.6(8), Ir2-B1-Ir1 110.6(8). (b) **2**: B1-Ir1 2.13(2), B2-Ir1 2.08(2), B2-B1-Ir1 62.8(11), B2-B1-Ir2 104.5(13), Ir1-B1-Ir2 80.7(8).

The geometry of **1** can be compared to that of [(Cp*Co)₄B₄H₄]²³ which is a eight vertex polyhedral having highly symmetric (*D*_{2d}) dodecahedron geometry with 16 framework electrons two fewer than a “normal” *closo* eight-vertex polyhedron. The average Ir-B bond length of 2.16 Å is in accord with other iridaboranes.²⁰ However, the average B-B distances of 1.74 (3) Å in **1** is long in comparison with the corresponding distances with other eight-vertex polyhedral geometries (Table 1). It is to be noted that the 16-electron polyhedral *viz.* [B₈Cl₈]²⁴ and [(Cp*Co)₄B₄H₄]²³ has longer B-B distances *i.e.*, 1.78 (4) and 1.86 (1) Å respectively compared to that of the 18-electron systems with avg. B-B distances of 1.56(2) and 1.50(1) Å respectively. The average Ir-B bond length of 2.13 (4) Å in **2** is comparable with that observed for **1** while the average B-B distance is slightly longer than that of **1**. In both **1** and **2** the high coordination number vertices are occupied by the metal atoms. Unlike **1**, **2** has a Ir-Ir bond with a bond distance of 2.7620(11) Å comparable to those previously reported iridaboranes.²⁰

The spectroscopic data reveal that both compounds **1** and **2** contain two Ir and six B atoms. The exact mass measurement of **1** and **2** gave molecular ion corresponding to C₂₀H₃₆B₆Ir₂. The ¹¹B NMR spectrum of **1** at room temperature shows three resonances at δ = 92.1, 64.6 and -23.1 ppm in 1:1:1 ratio, while **2** shows only two peaks at δ = 73.1 and 51.8 ppm in 2:1 ratio indicating the presence of higher symmetry. Apart from the Cp* protons, the ¹H NMR spectrum of **1** also shows a multiplet in the region 10.77–12.31 ppm and a quartet at -3.47 ppm, which may be due to BHT. To understand this correlation ¹H-¹¹B HSQC experiment was performed, which confirmed that the peaks at 12.31 and 10.77 ppm corresponds to BHT for

downfield boron atoms, while the peak at -3.47 ppm corresponds to BHT for upfield boron (δ = -23.0 ppm) atoms. Further, to confirm these assignments we have computed the ¹H and ¹¹B chemical shift values of **1** on the ground of DFT calculations and are found to be consistent with the experimentally observed values (Table S1, ESI[†]). The natural charges and natural valence population values also corroborated well both with ¹H and ¹¹B chemical shift values. The ¹H NMR spectrum of **2** shows BHT for all the boron atoms as a multiplet in the region 8.24–9.09 ppm. Interestingly, the computed ¹¹B chemical shifts for the four four-connect boron atoms for **2** strongly diverge from those of the experimental value of 51.8 ppm (computationally observed: B(2) and B(4) = 8.0 ppm and for B(3) and B(5) = 104 ppm). The resonance at 51.8 ppm for these four boron atoms is not an accidental overlap of two chemical shifts; it is due to a low-barrier fluxional process of the framework boron atoms. Indeed, several calculations on diamond-square-diamond (DSD) rearrangement exchanging boron atoms reveal a barrier of only 6.5 kcal/mol at the BP86/def2-TZVP level of theory.²⁵ The ¹³C NMR spectra imply one equiv of Cp* ligand for both **1** and **2** consistent with its symmetrical structure. The variation in the ¹H and ¹¹B NMR spectra both in **1** and **2** are attributed to two different isomers.

Table 1. Selected structural parameters and avg. (B-B) bond distances of different eight vertex polyhedral boranes.

Compound	Core geometry	Sep	Avg.d[B-B](C)	Refs.
[B ₈ H ₈] ²⁻	[B ₈] ^a	18	1.56 (2)	22
[(CH ₃) ₂ C ₂ B ₆ H ₆]	[C ₂ B ₆] ^a	18	1.50 (1)	24b
[B ₈ Cl ₈]	[B ₈] ^a	16	1.78 (4)	24a
[(Cp*Co) ₄ B ₄ H ₄]	[Co ₄ B ₄] ^a	16	1.86 (1)	23a
[Cp*Ni) ₄ B ₄ H ₄]	[Ni ₄ B ₄] ^a	20	1.93(7)	23b
1	[Ir ₂ B ₆] ^a	16	1.74(3)	this work
2	[Ir ₂ B ₆] ^{btp}	16	1.78 (3)	this work

^a = dodecahedron; ^{btp} = bicapped trigonal prism

An interesting occurrence observed in polyhedral borane chemistry is the isomerization of [B_nH_n]²⁻ ions.^{22,23} Structural non-rigidity has been observed for the polyhedral boranes [B₈H₈]²⁻ and [B₁₁H₁₁]²⁻ and the solid-state X-ray analysis shows [B₈H₈]²⁻ has a *D*_{2d} dodecahedron geometry.^{22b,26} In parallel to this, it has two more stable forms *i.e.* the *D*_{4d} square anti prism and *C*_{2v} bicapped trigonal prism that exist in solution only (Chart 1).^{22b,26} [B₈H₈]²⁻ ion under goes facile polyhedral rearrangement which has been predicted to proceed through a *C*_{2v} structure, formed by breaking one of the B-B bonds. From the extended Huckel MO calculations on polyhedral B_nH_n²⁻ ions for n = 6–9, it was observed that B₈H₈²⁻ is stereochemically non-rigid and has numerous easily accessible geometries, *i.e.*, *D*_{2d}, *D*_{4d} and *C*_{2v}. On the other hand, B₆H₆²⁻, B₇H₇²⁻ and B₉H₉²⁻ have thermodynamically preferred structures as *O*_h, *D*_{5h} and *D*_{3h} respectively.^{22b} Fascinatingly, apart from the isolation of **1** we,

have successfully isolated and structurally characterized the other isomer *i.e.* bicapped trigonal prism (C_{2v}), **2**. This finding led us to perform a computational study to gain some insight on the stability of these clusters and their isomerization.

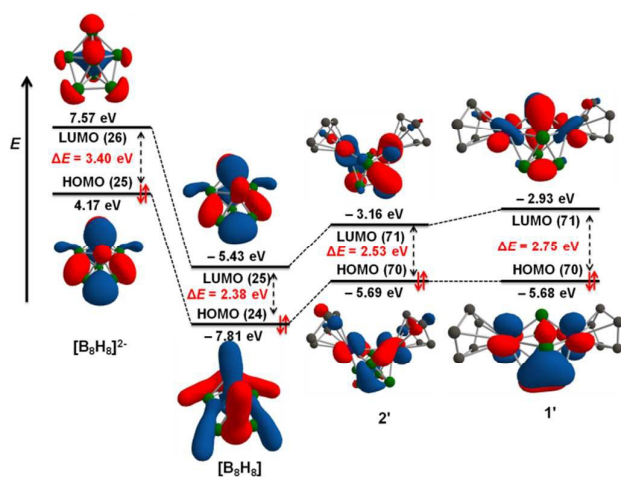


Fig. 2 Frontier molecular orbitals and their respective energies of $[B_8H_8]^{2-}$, $[B_8H_8]$, **2'** and **1'** (isovalue = 0.05). (**1'** and **2'** are Cp analogues of **1** and **2**, ESI^+).

The DFT studies show that there is an enhancement of thermodynamic stability for **1'** and **2'** over *isocloso*- $[B_8H_8]$, despite having two electrons less than that of *closo*- $[B_8H_8]^{2-}$. This may be due to the replacement of two five connected BH vertices of $[B_8H_8]$ with two diffused Cp*Ir fragments.^{13c,d} As shown in Fig. 2, a similar kind of bonding arrangements have been observed for $[B_8H_8]$, **1'** and **2'** that are different from that of $[B_8H_8]^{2-}$. The HOMO of **1'** shows strong bonding interactions along B4-B5, B1-B3 and B2-B6 bonds (HOMO, Figs. 2 and S11; ESI^+), whereas B1 and B2 overlaps in antibonding fashion. These findings have been reflected in their respective bond distances (B4-B5 = 1.629 Å, B1-B3 = 1.754 Å, B2-B6 = 1.799 Å, B1-B2 = 1.877 Å).

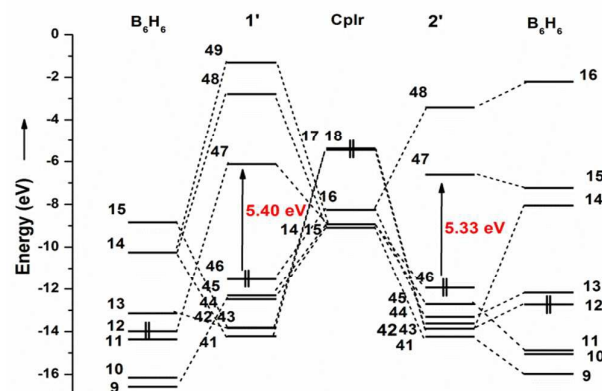


Fig. 3 Interaction diagram of [CpIr] and $[B_6H_6]$ fragments in **1'** and **2'**

In **2**, possible DSD rearrangement has been observed in

LUMO of B2-B3 and B4-B5 (ESI^+). Although the results show similar apparent stabilities for **1'** and **2'**, the key difference between them exists due to the orientation of the borane fragments (Fig. 3). From the interaction diagram, shown in Fig. 3, it is evident that the metal fragment donates two electrons to cluster bonding. Further the calculation demonstrates that although, the eight vertex *closo*- $[B_8H_8]^{2-}$ with 9 sep is more stable than *isocloso*- $[B_8H_8]$, the iridaboranes **1'** and **2'** are stable in *isocloso* geometry with 8 sep only (Table S2, ESI^+).

The creation of new examples for the development of polyhedral borane chemistry, and more broadly on the general field of polyhedral clusters has been of continuous pursuit. Thus after the isolation of isomers **1** and **2**, the third one *i.e.* the square antiprism (D_{4d}), became of interest. As a result, we carried out the same reaction under different reaction conditions with varying amounts of borane as well as temperature. Although the objective of isolating the target was not attained, a nine vertex $[(Cp^*Ir)_2B_7H_7]$ **3**, was produced as a red solid. The solid state X-ray structure of **3**, shown in Fig. 4, shows that it does not display the structural motif expected for a *closo* system of this size, *i.e.*, a tricapped trigonal prism rather it possesses monocapped square anti prism geometry. One of the intriguing features of all the species **1**, **2** and **3** is that all are hypoelectronic in nature with 18 skeletal electrons. Thus, cluster **3** might be considered as an *isonido* structure (Fig. 4) with a four membered open face.^{16d} The average B-B (1.79 Å) and Ir-B bond lengths (2.15 Å) are equivalent to other iridaborane clusters.²⁰

The ^{11}B NMR spectrum of **3** shows three boron environments at $\delta = 102.6, 63.2$ and -4.9 ppm in the ratio of 1:4:2. There are five four connected, (B(1) and B(4-7)) and two five-connected B(2,3) boron atoms in **3**. Thus B(1) and B(4-7) expected to resonate at low field, while B(2,3) at high field. The 1H NMR spectrum of **3** reveals a multiplet due to seven BHt along with one Cp* group.

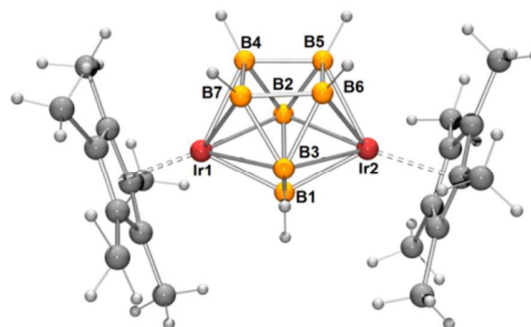


Fig. 4 Molecular structure and labeling diagram for **3**. Selected bond lengths (Å) and angles [$^\circ$]: B1-Ir1 2.051(10), B1-Ir2 2.033(9), B2-Ir1 2.264(9), B2-Ir2 2.239(10), B1-B2 1.849(14); B2-B1-Ir2 70.3(4), B2-B1-Ir1 70.8(4), Ir2-B1-Ir1 119.4(4).

Conclusions

In summary, this work describes for the first time isolation and structural characterization of isomeric iridaborane clusters

[[Cp*Ir]₂B₆H₆]] that resemble the isomeric structures of the parent borane [B₆H₈]²⁻. Further, it would be exciting to see at what degree the BH units in borane cages get replaced by isolobal {Cp*Ir} fragment and what would be the structural variation from the parent boron hydrides.

Acknowledgements

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Notes and references

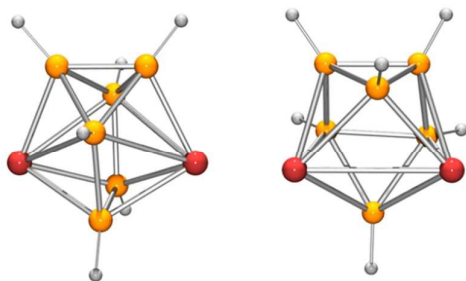
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- Although we do not have any clear evidence regarding the origin, it seems they have generated by sequential cluster growth reaction of [Cp*IrB₃H₃]. Note that, all of our attempts to convert cluster **2** to **1** and vice-versa by pyrolysis were unsuccessful. Therefore, we may conclude that both these clusters must have formed simultaneously.
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**Hypoelectronic Isomeric Diiridaboranes $[(Cp^*Ir)_2B_6H_6]$:
The "Rule-Breakers" ($Cp^* = \eta^5-C_5Me_5$)**

Rosmita Borthakur, Bijan Mondal, Purbasha Nandi and Sundargopal Ghosh*

Isolation of two 8 vertex topological diiridaborane isomers; dodecahedron and bicapped trigonal prism.



Keywords: hypoelectronic, diiridaborane, cluster, dodecahedron, bicapped trigonal prism