

A Novel Heterometallic μ_9 -Boride Cluster: Synthesis and Structural Characterization of $[(\eta^5\text{-C}_5\text{Me}_5\text{Rh})_2\{\text{Co}_6(\text{CO})_{12}\}(\mu\text{-H})(\text{BH})\text{B}]$

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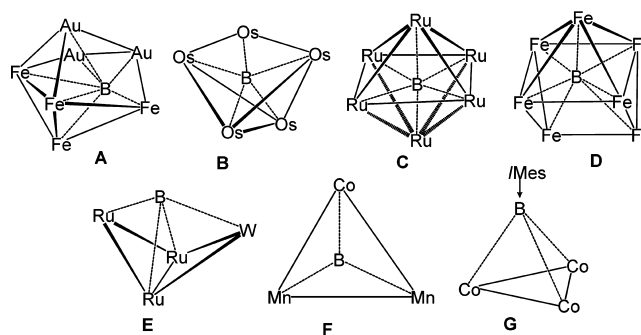
S Supporting Information

ABSTRACT: The preparation, characterization, and electronic structure of the first heterometallic μ_9 -boride cluster $[(\text{Cp}^*\text{Rh})_2\{\text{Co}_6(\text{CO})_{12}\}(\mu\text{-H})(\text{BH})\text{B}]$ has been reported. The interstitial boron atom in the title cluster is within the bonding contact of eight metal and one boron atom in a unique tricapped trigonal prism geometry.

Transition metals clusters that contain interstitial atoms, particularly the main group elements, constitute a considerable subgroup of chemistry.¹ The most discussed are those of comprising carbon and nitrogen in the interstitial position.^{2–4} In these metal clusters, the atom in the cavity can be accommodated either in an octahedron or in a trigonal prism displaying a wide range of geometries with a varying number of transition metals. In addition, clusters having hydrogen and other lighter elements as interstitial atoms have also been described.⁵ Moving to the lower row of the periodic table, atoms of the p-block elements necessitate larger cavities in which the elements are to be housed. However, the driving force for the incorporation of electron-rich phosphorus or an orbital-rich atom like boron into the created cavity is different from each other. Thus, while the latter has posed substantial challenges for synthetic chemists, it has also created opportunities to further develop chemistry of an important metal cluster theme.

Over time, the progress of metallaborane chemistry has considerably expanded in the shadow of organometallic chemistry.^{6,7} Further, several reviews and articles have illustrated that the growth of metal-rich metallaboranes, distinct from the larger boron cage clusters (boron-rich), is relatively significant.^{8,9} The typical feature that deals the boride clusters¹⁰ is the greater number of boron-to-metal bonding contacts at the expense of boron–hydrogen bonds (Chart 1). Since an early report of a potential boride cluster,¹¹ few groups have addressed the synthesis of them in a systematic way. Using the isolobal analogy between H and $[\text{AuPR}_3]$, Housecroft was successful making boride clusters with gold atoms forming part of the metal shell (Chart 1, A).¹² Shore has used $[\text{H}_3\text{Os}_3(\text{CO})_9\text{BCO}]$ as a thermal precursor for a five osmium atom boride (Chart 1, B).¹³ Contemporary to this work, Fehlner focused on iron analogs and successfully made $[\text{AsPh}_4]_2[\text{HFe}_7(\text{CO})_{20}\text{B}]$ (Chart 1, D).¹⁴ A very recent development of the Braunschweig group is the isolation of an electron-precise lowest coordinated boride and a unique tetrahedral boride (Chart 1, F and G)¹⁵ clusters having novel structural types.

Chart 1. Different Types of Transition Metal Boride Clusters (G: IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)



Having synthesized a wide range of metallaboranes containing group 4 to 9 transition metals,^{16–19} a variety of reactivity patterns were investigated, and the reactions with metal carbonyls have been found to be the most successful for making metal borides.^{10,18} As a result, after developing a fruitful synthetic route to $[(\text{Cp}^*\text{Rh})_2\text{B}_6\text{H}_{10}]$, **1**,¹⁹ we were interested making boride clusters from various metal carbonyls. Reaction of **1** with $[\text{Fe}_2(\text{CO})_9]$ yielded condensed structure;¹⁹ however, a room temperature reaction with $[\text{Co}_2(\text{CO})_8]$ led to the isolation of the first M_8 -boride, $[(\text{Cp}^*\text{Rh})_2\{\text{Co}_6(\text{CO})_{12}\}(\mu\text{-H})(\text{BH})\text{B}]$, **2**, along with $[(\text{Cp}^*\text{Rh})_2\{\text{Co}_2(\text{CO})_7\}]$, **3** (Supporting Information, SI). The ¹¹B NMR spectroscopy used to monitor the reaction shows that two resonances appeared at δ 101 and 90 ppm.²⁰ The ¹¹B chemical shift values indicate the formation of a greater number of M–B bonds at the expense of B–H bonds. After chromatographic separation, compounds **2** and **3** have been isolated as brown and orange solids in moderate yields. The ¹H NMR spectrum of **2** shows the presence of two different Cp* ligands and a high field resonance for the bridging proton.

The evidence for the structural composition came from a single-crystal X-ray crystallographic analysis.^{20,21} The molecular structure of **2**, shown in Figure 1(a), is a distorted tricapped trigonal prism where two Rh and four Co atoms are arranged in an approximately trigonal prismatic fashion with the encapsulation of a single boron atom (B1). The other two Co atoms (Co2 and Co2') and the boron atom B2 are in the capping positions of three square faces. Although the ¹H NMR shows two types of Cp* protons due to the presence of bridging hydrogen, the core geometry (without all ancillary ligands) has C_{2v} symmetry. If we

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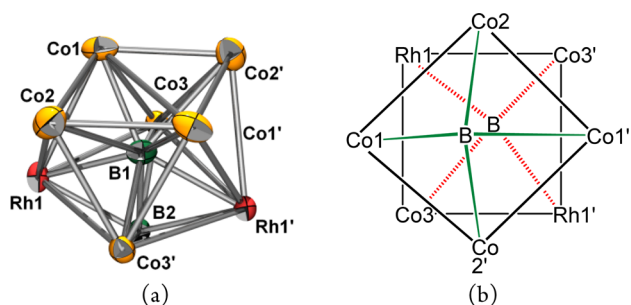


Figure 1. (a) Molecular structure and labeling diagram for **2** (Cp*, carbonyl ligands, and terminal B–H proton are omitted for clarity). Selected bond lengths (Å): Rh1–B1 2.138(10), Co1–B1 2.010(16), B1–B2 1.810(3), B1–Rh1' 2.138(9), and Rh1–B2 2.128(8). (b) Representation of C_2 axes.

consider the square made of Co1–Co2–Co1'–Co2', the C_2 axes are passing through the diagonals, middle of the edges, and two boron atoms (Figure 1(b)). The Co–B and Rh–B distances in the trigonal prism core are within the expected range.¹⁹ The average distance between the capping Co and the interstitial boron of 2.384 Å is longer compared to the average $Co_{\text{cage}}\text{–B}$ bond (2.031 Å). Table 1 lists a wide variety of structurally characterized metal boride clusters having varied bonding modes.

It is noteworthy to mention that **2** corresponds to the building block (Figure 2) from which solid-state metal borides are considered to be constructed.²² Depending on whether the face-capping atoms are metal or boron, one can generate solid-state borides with isolated B atoms, B_2 units, B_n chains, etc.²² by fusing such building blocks in an extended array. Three square faces of the core geometry of **2** are capped by two Co and one B. Thus, **2** can be considered as a solid-state boride with B_2 units.

¹¹B chemical shift values are sensitive to the environment, with interstitial atoms being characterized by unusually low-field chemical shifts and a sharp signal. Thus, the chemical shift of B1 (δ 101 ppm) certainly demands some comments. B1 is directly bonded to eight metal atoms; however, the chemical shift appeared unusual in the upfield region. The change in connectivity associated with B1 is that it is also linked to another boron atom rather than fully connected to the metal atoms. The resonance at δ 90 ppm can be attributed to the five-connected boron (B2), as it shows a doublet in the proton-coupled ¹¹B spectrum.

To gain insight into the electronic structure of **2**, we carried out the density functional theory (DFT) of **2'** (Cp analog of **2**; Figure S2, SI). Metal–boron bonding was further probed by using NBO (natural bond orbital)^{25a} analysis and the Wiberg

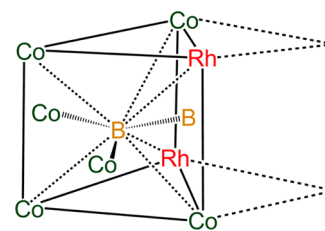


Figure 2.

Bond index (WBI).^{25b} Optimization of the geometry at the BP86/def2-SV(P) level reveals geometries in agreement with the experimental structure (Table S1, SI). Computed ¹¹B chemical shifts are in accord with the experimental values (Table S2, SI). DFT molecular orbitals show that both σ - and π -type orbitals are involved in the M–B1 bonding interactions. A σ -type overlap of a sp_z hybrid of boron with d_z^2 -type orbitals of the metal atoms has been observed in HOMO-39. The π -type interactions of p_x and p_y orbitals of boron with d orbitals of rhodium atoms are evident in HOMO (Figure S3, SI).

The structure of **2'** is complicated; hence, no reasonable NBO-type Lewis structures could be found. Therefore, WBI has been used to understand the bonding interaction. A high WBI value indicates a strong coupling of B1, both with B2 (WBI: 0.43) and Rh (WBI: 0.37). Similarly, a strong coupling of B1 has also been observed with the cage Co atoms (WBI: 0.41).

To understand the bonding, geometry, and electronic structure, synthesis of the homometallic analog of **2** became of interest. Thus, we have synthesized the Co-precursor, that is, [(Cp*Co)₂B₆H₁₀], **4**. The identity of **4** has been confirmed by spectroscopic study along with a single-crystal X-ray analysis.²¹ The solid-state structure of **4**, shown in Figure 3, is similar to [B₈H₁₂],^{26a} [C₂B₆H₁₀],^{26b} [(Cp*Ru)₂B₆H₁₂],^{26c} and [(Cp*Rh)₂B₆H₁₀].¹⁹

Isolation of **4** allowed us to carry out the reaction with [Co₂(CO)₈] to generate [(Cp*Co)₂{Co₆(CO)₁₂}(μ-H)(BH)–B]. Unfortunately, no sign of [(Cp*Co)₂{Co₆(CO)₁₂}(μ-H)(BH)B] was observed, even under forcing conditions which finally led to the decomposition of starting material. The theoretical study shows that a large HOMO–LUMO gap (Figure S5, SI) exists in **2'** compared to **2''** (homometallic analog of **2**; Figure S4, SI); thus, the results are consistent with the experimental findings.

In conclusion, the results described here are the isolation of the first μ_9 -boride cluster where the interstitial boron atom is in contact with eight metal atoms. The reactivity of [(Cp*M)₂B₆H₁₀] (M = Co and Rh) with [Co₂(CO)₈] exemplify

Table 1. Selected Structural Parameters and Chemical Shifts (¹¹B) of Different Boride Clusters

compound	core geometry	connectivity ^a	δ (¹¹ B) ppm	refs
[CoMn ₂ (CO) ₁₃ B]	[CoMn ₂] trigonal	3	195.8	15a
[Co(CO) ₉ BIMes]	[Co ₃ IMes] tetrahedra	3	89	15b
[HRu ₄ (CO) ₁₂ BH ₂]	[Ru ₄] butterfly	4	109.9	23
[HOs ₅ (CO) ₁₆ B]	[Os ₅] bb ^c	5	184.4	13
[HRu ₆ (CO) ₁₇ B]	[Ru ₆] octahedra	6	193.8	23c
[H ₂ Ru ₆ (CO) ₁₈ B][PPN]	[Ru ₆] trigonal prism	6	205.9	24
[Fe ₄ Au ₃ (CO) ₁₂ (PPh ₃) ₃ B]	[Au ₃ Fe ₄] bb ^c	7	183	14
[(Cp*MoSe) ₂ Fe ₆ (CO) ₁₃ –B ₂ (BH) ₂]	fused cluster ^b	8	106.2	18
2	[Rh ₂ Co ₆ B] ttp ^d	9	101.2	this work

^aConnectivity to the full interstitial boron atom. ^bFused cubane [Mo₂Se₂Fe₂B₂] and a tricapped trigonal prism [Fe₆B₃]. ^cBridged butterfly.

^dTricapped trigonal prism core.

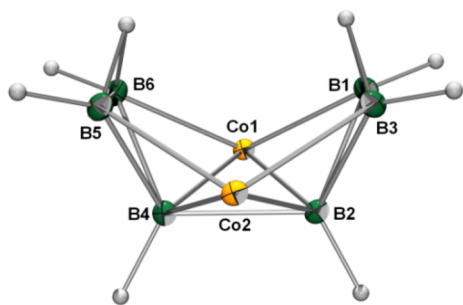
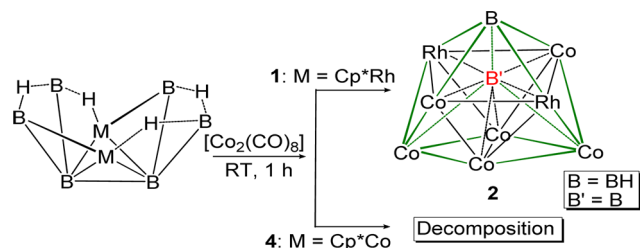


Figure 3. Molecular structure and labeling diagram for **4**. Selected bond lengths (Å): Co1–B1 2.026(4) and B1–B2 1.744(5).

Scheme 1. Synthesis of μ_9 -Boride Cluster **2**^a



^a(Cp* and carbonyl ligands are not shown for clarity).

the significance of the transition metals in determining their properties. In addition to the structural characterization, the DFT calculations were also used to verify the bonding situation of the boride clusters.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data, experimental and computational details, and X-ray crystallographic files for **2**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(20) The ¹¹B NMR of the crystals (obtained after two weeks at −3 °C) shows another set of resonances along with **2**. The resonances at δ 101.2 and 89.8 ppm are assigned for **2**, and the resonances at δ 78.6 and 65.4 ppm are assigned for [(η^5 -C₅Me₅Rh)₂{Co₄(CO)₁₀}(μ-H)(BH)B] (**2a**) (SI). Therefore, it is assumed that compound **2a** (Figure S1, SI) might have formed during slow crystallization at −3 °C.

(21) See Supporting Information for X-ray details.

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