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PAPER

Synthesis, Characterization and Crystal Structure Analysis of Cobaltaborane and Cobaltaheteroborane Clusters

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Cluster expansion reactions of cobaltaboranes have been carried out using mono metal-carbonyls, metal halides and dichalcogenide ligands. Thermolysis of an in-situ generated intermediate, obtained from the reaction of $[Cp^*CoCl]_2$ ($Cp^* = C_5Me_5$) and $[LiBH_4 \cdot thf]$, with three equivalents of $[Mo(CO)_3(CH_3CN)_3]$
10 followed by reaction with methyl iodide yielded *isocloso*-$[(Cp^*Co)_3B_6H_7Co(CO)_2]$, (**1**) and *closo*-$[(Cp^*Co)_2B_2H_5Mo_2 (CO)_6I]$, (**2**). Cluster **1** is ascribed to *isocloso* structure based on a 10-vertex bicapped square antiprism geometry. In a similar manner, reaction of $[Cp^*CoCl]_2$ with $[LiBH_4 \cdot thf]$ and dichalcogenide ligand RS-SR (R = 1-OH-2,6-(^tBu)$_2$-C$_6$H$_2$) yielded *nido* cluster $[(Cp^*Co)_2B_2H_2S_2)]$, (**3**). In parallel to the formation of compounds **1-3**, these reactions also yielded known cobaltaboranes
15 $[(Cp^*Co)_2B_4H_6]$, (**4**) and $[(Cp^*Co)_3B_4H_4]$ in good yields. After the isolation of compound **4** in good yield, we verified its reactivity with $PtBr_2$ which yielded *closo*-$[(Cp^*Co)_2B_4H_2Br_4]$, (**5**). To the best of our knowledge this is the second perhalogenated metallaborane cluster to be recognized. All the new compounds have been characterized by elemental analysis, IR, ^1H, ^{11}B, and ^{13}C NMR spectroscopy and the geometric structures were unequivocally established by X-ray diffraction analysis of compounds **1**, **2**,
20 **3** and **5**. Geometries obtained from the electronic structure calculations employing density functional theory (DFT) are in close agreement with the solid state X-ray structures. In addition, we have analyzed the variation of stability of the model compounds **1'** (**1'**: Cp analogue of **1**, Cp = C$_5$H$_5$), $[(CpCo)_4B_6H_6]$, (**1a**) and $[(CpRh)_4B_6H_6]$, (**1b**).

Introduction

25 An area of continuing importance in polyhedral metallaborane chemistry is the progress of new and efficient methods, leading to expanded cluster cage.[1-3] Although for the past few decades Fehlner and others[4-9] have worked on boron-transition metal clusters, development in this area has been slow; only the most
30 stable/least reactive compounds are characterized restricting the scope of the chemistry particularly when the first row transition metals are of interest. Nevertheless, due to availability of few recent convenient routes to metallaboranes, the progress of synthetic chemistry has permitted a spotlight on the reactivity.[10,11]
35 As a result, recent years witnessed significant development of many interesting polyhedral cage structures, which includes the expansions of single clusters beyond the icosahedrons to contribute species with 13-16 vertices.[12-14] In addition, the study of metallaboranes has flourished and recently has been finding
40 applications in other areas of chemistry.[15] The polyhedral borane chemistry are alike to the organic compounds in aspect of biomedicine[16] however, due to the presence of unusual chemical, biochemical and physical properties they offer a unique and enhanced performance. The *exo*-cluster substitution chemistry of
45 metallaboranes differs considerably from those of pure boranes and carboranes.[17] The absence of useful synthetic routes and any

systematic derivative chemistry of metallaborane has inhibited the development of these compounds. However, a recent study by Hawthorne's group on *exo*-cluster substitution,[18] led us to explore
50 the development of synthetic routes of B-functionalized metallaborane species. Introduction of substituents on the boron in metallaboranes is important if one wishes to make complexes that are resistant to deboronation by electrophiles.[19] Further, the halogenations of metallaborane clusters has specific interest,
55 since they are important in preparing functionalized clusters for assembly into larger arrays, extended polymetallic clusters and B–B linked systems.[19d]

Recently in our laboratory we have reported a series of low to high boron content metallaborane compounds of group 4-9 that
60 turned our attention towards synthesizing hybrid-metallaborane clusters. As a result, we explored their chemistry with mono metal-carbonyls, dichalcogenides and metal halides that yielded various novel hybrid-clusters, **1-5**. In addition, the experimental findings captivated us to carry out theoretical study using DFT,
65 that analyses the electronic structure and bonding of these molecules. In the following, we report the synthesis, structural characterization and electronic structure of several novel hypoelectronic hybrid clusters.
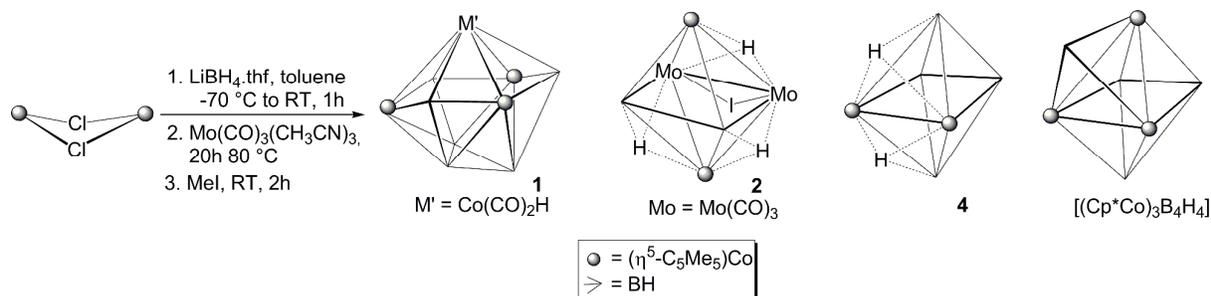
Scheme 1 Synthesis of metal-rich metallaborane clusters **1**, **2** and **4**.

Results and Discussion

As shown in Scheme 1, the reaction of [Cp*CoCl]$_2$ with excess of [LiBH$_4$·thf] in toluene at -70 ºC, followed by thermolysis in presence of [Mo(CO)$_3$(CH$_3$CN)$_3$] for 20 h resulted a dark green solution, which on further reaction with MeI yielded *isocloso*-[(Cp*Co)$_3$B$_6$H$_7$Co(CO)$_2$] (**1**), *closo*-[(Cp*Co)$_2$B$_2$H$_5$Mo$_2$(CO)$_6$I] (**2**), [(Cp*Co)$_2$B$_4$H$_6$] (**4**), and [(Cp*Co)$_3$B$_4$H$_4$] in moderate yields. Although they are produced in a mixture, these compounds can be separated by TLC which allowed spectroscopic and structural characterization of pure materials. Note that all the compounds except **2**, have also been isolated in the absence of MeI particularly in the pure crystalline state. The spectroscopic and structural characterizations of **1**, **2**, **3** and **5** from the NMR, IR, mass spectrometry and X-ray diffraction studies are discussed below.

Isocloso-[(Cp*Co)$_3$B$_6$H$_7$Co(CO)$_2$] (**1**)

Compound **1** has been isolated as an orange solid in 12% yield. From the mass spectral analysis combined with ^{1}H, ^{13}C and ^{11}B NMR spectra, **1** is formulated as [(Cp*Co)$_3$B$_6$H$_7$Co(CO)$_2$]. Consistent with the solid state structure (determined by X-ray diffraction), the ^{11}B NMR spectrum of **1** at room temperature shows two resonances at δ = 125.4 and 33.6 ppm in equal intensity. This evidently indicates that the molecule is highly symmetrical. The downfield resonance at δ = 125.4 ppm has been assigned to four coordinated boron atoms B(1,4,6), whereas the upfiled resonance is corresponding to the five connected vertices B(2,3,5). Beside the BH terminal protons, one equivalent of Co-H proton was observed in the ^{1}H NMR spectrum. To probe any fluxionality that may be present for the molecule **1** in solution, variable temperature ^{1}H and ^{11}B NMR was recorded. At -85 ˚C the Cp* resonances remained the same as those observed at room temperature. Similarly, there was no change of chemical shift for Co-H proton at δ = -19.46 ppm. These results clearly support no fluxionality in molecule **1**.

The framework geometry of **1** was unambiguously established by its solid state X-ray structure determination (Fig. 1) of a suitable single crystal grown by slow evaporation of hexane solution at −10 °C. Fig. 1 represents a novel 10-vertex closed geometry in which the Co$_3$B$_6$ cage by its 6-membered (Co$_2$B$_4$) open face coordinated to the unique Co atom of vertex connectivity six. Three among the four cobalt atoms have connected with Cp* ligands and the unique six connected cobalt atom is attached to [H(CO)$_2$] fragment. The most common

structure for ten-vertex *closo* cage systems is bicapped square antiprism (D$_{4d}$), and **1** is attributed to a 10-vertex *isocloso* geometry similar to that of [(Cp*Rh)$_4$B$_6$H$_6$].[14] Both the structures are based on a 10-vertex *closo*-bicapped square antiprism geometry by one diamond square diamond (DSD) rearrangement to yield *isocloso*-**1** (Chart 1). In the present case, all four cobalt vertices bonded to Cp* seem impossible due to steric hindrance. The six-membered face of compound **1** is distorted from a regular chair conformation as the absolute values of torsion angles about the bonds of the 6-membered cycle of [(Cp*Co)$_3$B$_6$H$_7$Co(CO)$_2$] vary from 41.03 to 45.88°; whereas, in the case of Rh-analogue it is 51.8−52.8°. The change in the structural parameters between **1** and [(Cp*Rh)$_4$B$_6$H$_6$][14] might be due to the presence of an heavier group metal center in the six-membered ring of compound [(Cp*Rh)$_4$B$_6$H$_6$]. Each Cp* moiety in the X-ray structure of **1** has C-H•••Π interaction with the neighboring molecules in the ab-plane[20] (Fig. 2).
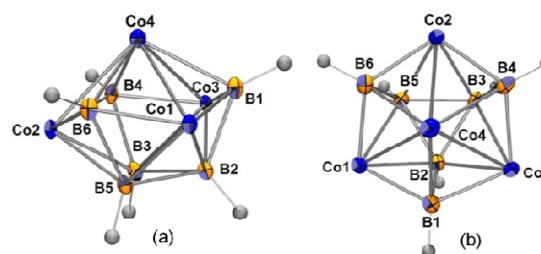
Fig. 1 Molecular structure and labeling diagram of [(Cp*Co)$_3$B$_6$H$_7$Co(CO)$_2$] **1**. (a) side view and (b) top view (Cp*, carbonyls and terminal hydrogens are not shown for clarity). Selected bond lengths (Å) and angles (°): B(3)-Co(2) 2.077(7), B(3)-Co(3) 2.146(7), B(5)-B(6) 1.827(10), B(5)-Co(2) 2.108(7), B(5)-Co(1) 2.095(7), B(6)-Co(1) 1.982(8); B(3)-Co(3)-Co(4) 76.4(3), B(2)-Co(3)-Co(4) 76.87(19), B(4)-Co(3)-B(2) 92.7(3), B(1)-Co(3)-B(2) 50.8(3), B(4)-Co(2)-Co(4) 56.3(2), B(6)-Co(2)-Co(4) 54.1(2), B(3)-Co(2)-Co(4) 78.6(2), B(5)-Co(2)-Co(4) 78.1(2).
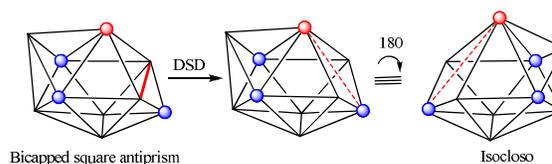
Chart 1 Heavy red lines indicate the B-B interaction broken in the diamond-square-diamond (dsd) rearrangement, whereas the light red lines indicate those formed.

According to the electron counting rules,[19d,21] the framework geometry of **1** should be considered as a ten-vertex *isocloso* geometry based on bicapped square anti prism structure. Cluster **1** is 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 10 (Table 1). The terminal hydrogen on cobalt at **1** have not been located by X-ray diffraction studies; however, its connectivity have been assertively determined by ^{1}H NMR and are expected to be situated on the unique cobalt atom at degree six vertices. The framework geometry of **1** is similar to that of $[(Cp^*Rh)_4B_6H_6]$ with the replacement of $\{Cp^*Rh\}$ group(s) by the isoelectronic $\{Co(CO)_2H\}$ and $\{Cp^*Co\}$ fragment(s). The average B−B (1.74 Å) and M−B bond lengths (2.14 Å) follow the cobaltaboranes trend. But the disparity in bond lengths between boron atoms (ranging from 1.69 to 1.86 Å) may be due to the *isocloso* nature of the framework. Three of the B atoms in **1** occupies the five connecting vertex, whereas rest of the B atoms are having the vertex connectivity of four. The six-membered ring (B1-Co1-B6-Co2-B4-Co3) that bounds to the unique cobalt centre has a chair conformation as observed in glucose or cyclohexane.

Table 1 Selected structural parameters and ^{11}B chemical shift values for **1** and various ten vertex *isocloso* clusters.

Compounds	Avg.*d* [M-B][Å]	Avg.*d* [B-B][Å]	^{11}B NMR [ppm]	Ref.
1	2.08	1.79	62.5, 34.5	_^{a}
$[(Cp^*Rh)_3B_7H_7]$	2.14	2.00	35.4, 18.8, 11.2, -2.5, -18.9	14a
$[(Cp^*Rh)_4B_6H_6]$	2.22	2.01	38.7, 21.4	14b
X-RuC$_2$B$_7$H$_7$^{b}	2.24	2.131	108.0, 19.2, 14.6, -2.06, -11.0	24
$[(CpFe)_2C_2B_6H_8]$	2.15	2.16	8.5, -1.8, -18.1, -28.1, -36.8, -142.9	25a
$[OsH(PPh_3)_2(Ph)(OMe)CB_8H_7]$	2.38	1.72	80.8, 77.7, 19.1, 15.9, -4.2,-19.6, -21.4	25b
$[(pcym)RuB_9H_9]^c$	2.25	1.71	91.3, 28.0, -15.6	25c

^{a} this work; ^{b} X = Me$_2$(CH$_2$CHCH$_2$C$_6$H$_4$Ph$_2$P)$_3$; ^{c} pcym = l-Me-4-^{iso}Pr-C$_6$H$_4$

The intriguing electron deficiency nature of **1** led us to carry out the DFT calculations. The DFT calculated values are in good agreement with the experimental observations and reproduces the experimental geometry and the ^{11}B chemical shifts using gauge-including atomic orbital density functional theory [GIAO-DFT] method (Table S2, supporting information†). The DFT frontier molecular orbitals demonstrate substantial bonding interaction between the cobalt and boron atoms in HOMO-1 and HOMO-3. The WBI (Wiberg Bond Index)^{22} value of 0.46 supports the existence of Co-B bonding interactions. Further, as shown in Fig. 3, a considerable amount of overlap between two cobalt atoms has been observed in HOMO-2, which may be due to electron poor nature of **1**. In order to establish the identity of **1a** (Cp anologue of **1'**) and relate its stability with analogous **1'** and **1b**, the DFT calculation was caried out. Although a large HOMO-

LUMO gap (>3 eV) shows the thermodynamic stability, energetically **1a** may not be achievable due to the steric repulsion between the Cp ligands (Table S3, supporting information). Considering the bonding topology in **1**, Co1-B1-Co3 and B6-Co2-B4 shows 2-electron 3-center bonds (3c-2e) in hexagonal face. In addition, we have shown by natural bond orbital (NBO) analysis^{23a,b} that all the triangular faces below the hexagonal belt show exclusively 3c-2e bonds.^{23c,d}

Closo-$[(Cp^*Co)_2B_2H_5Mo_2(CO)_6I]$ (2)

Compound **2** has been isolated as brown solid. The IR spectrum features bands at 2475 and 2022 cm^{-1} owing to the terminal B−H stretches and carbonyl ligands respectively. The ^{11}B NMR spectrum at room temperature shows a single resonance at δ = 75.7 ppm indicating high symmetry. Beside the BH terminal protons, two equivalents of Cp* protons and μ$_3$-H were also observed in the ^{1}H NMR spectrum. The framework geometry of **2** became clear when a solid state structure was determined (Fig. 4). Both the Mo atoms are having terminal carbonyl ligands and each cobalt is attached with Cp* group. Considering $\{Cp^*Co\}$ and the bridged iodine as two and three electron fragments respectively,^{26a} $[(Cp^*Co)_2B_2H_5Mo_2(CO)_6I]$ possesses seven skeleton electron pair (sep), consistent with the skeleton electron count of *closo* six vertex polyhedra. The average B−B (1.79 Å) and Co−B bond lengths (2.05 Å) are comparable to those observed with other cobaltaborane clusters.^{26b,27} The B-Mo bond length in **2** was found to be 2.153(6) Å, which is significantly longer compare to those observed in $[(Cp*Mo)_2B_3H_3SCo_2(CO)_6]$ (2.290(4) Å) and $[(Cp*Mo)_2B_3H_3TeCo_2(CO)_5]$ (2.243(7) Å).^{28} Metallaborane frameworks containing bridging hydrogen(s) typically reveal *nido* or *arachno* shapes because of the spatial and electronic demands of the bridge atoms.^{29} As a result, the *closo*-clusters with bridging hydrogen atoms are rare in metallaborane or in organometallic chemistry.^{26b} To the best of our knowledge compound **2** is the third example in this category.
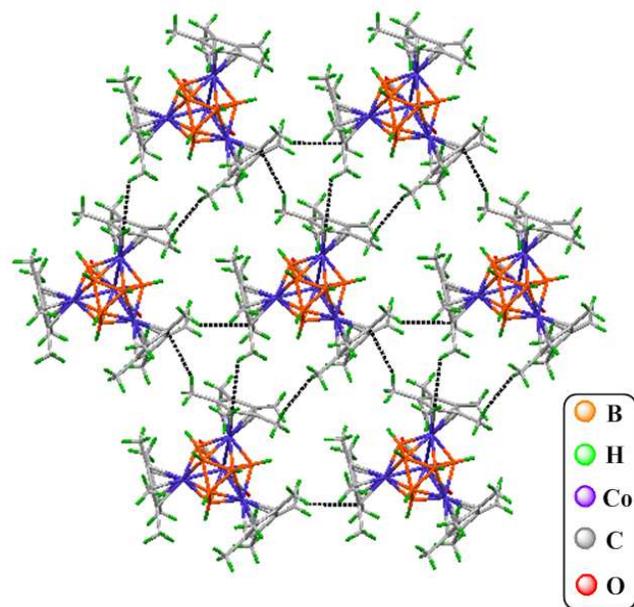
Fig. 2 Layer of molecule **1** linked through C-H•••π interactions.
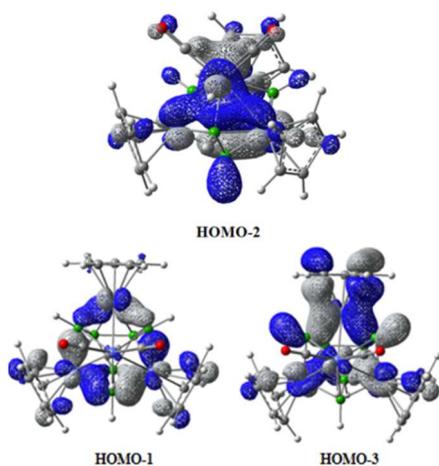
Fig. 3 Frontier molecular orbital diagram of **1'** (**1'**: Cp analogue of **1**, Cp = C₅H₅).

The single crystal X-ray diffraction study of **2** shows that the crystal lattice is essentially stabilized by two short intermolecular contacts. Of these, the C-H•••O hydrogen bond (C22-H22C•••O1_$1, with H22C•••O1_$1 = 2.570 Å and angle C22-H22C•••O1_$1 = 148.07° (symm $1: -1/2+x, 1/2-y, 1/2+z)) generates 1D hydrogen bonded chain parallel to [101] direction. These chains are further interlinked by H15A•••I1_$2 (symm$2: 1.5-x, -1/2+y, 1.5-z) short contacts to form a 2D network. As the adjacent 1D sheets are related through two fold screw translations, they run in opposite directions. These parallel sheets are further stabilized through several week C-H•••O interactions (Fig. 5).
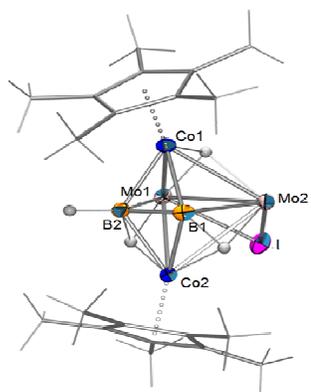
Fig. 4 Molecular structure and labelling diagram of *closo*-**2**. Selected bond lengths (Å) and angles (°): B(1)-B(2) 1.761(6), B(1)-Co(1) 2.030(4), B(1)-Mo(2) 2.463(4), B(2)-Co(2) 2.053(4), Co(1)-Mo(1) 2.8123(6), Co(1)-Mo(2) 2.8301(6), Co(2)-Mo(2) 3.0077(6), Co(2)-Mo(1) 3.0408(5), Mo(1)-I(1) 2.8039(4); B(2)-B(1)-Co(1) 64.31(19), Co(1)-B(1)-Co(2) 117.7(2), B(2)-B(1)-Mo(2) 104.1(2), Co(1)-B(1)-Mo(2) 77.43(13).

Cobaltathiaborane [(Cp*Co)₂B₂H₂S₂] (3)

As shown in Scheme 2, the reaction of [Cp*CoCl]₂ with excess of [LiBH₄·thf] in toluene at -78 ºC, followed by treatment with dichalcogenides, RS-SR (R = 1-OH-2,6-(ᵗBu)₂-C₆H₂) for 16 h yielded **3** along with **4** and [(Cp*Co)₃B₄H₄]. Thus, the disulfide ligand acts as a source of sulfur that eventually yielded **3**. A key development in borane chemistry is the finding that one or two boron vertices in borane/carborane can be replaced by transition metal fragments.[30] Compounds with one or more Cp*Co vertices in place of BH vertices in borane structures are of specific interest, since Cp*Co is a formal donor of two skeletal electrons and isoelectronic and isolobal to BH. Further, since a cage sulfur atom is a four electron donor, isoelectronic to BH²⁻, the incorporation of a sulphur atom into a borohydrides or metallaborane framework demands the replacement of BH₃ fragments. Thus, the formation of cobaltathiaborane **3** might have occurred by the replacement of two BH₃ fragment in [(Cp*Co)₂B₄H₈]. The first sulfur incorporated polyhedral boron cluster was reported by Mutterties in 1967.[31] Since then, several thiaboranes and metallathiaboranes have been discovered. Note that the Cp analogue of dicobaltathiaborane **3**, [(CpCo)₂B₂H₂S₂] was first prepared by Sneddon from the reaction of cobalt vapour with B₅H₉, C₅H₆ and H₂S.[33]
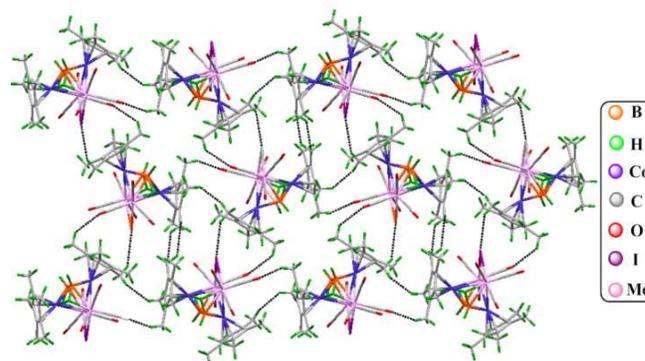
Fig. 5 Crystal packing diagram of *closo*-**2**.

Compound **3** has been isolated as a purple solid. The IR spectrum features bands at 2467 cm⁻¹ owing to the terminal B−H stretching. The ¹¹B NMR spectrum at room temperature shows single sharp signal at δ = 22.7 ppm indicating the presence of a plane of symmetry with respect to the plane bisecting the B-B bond. Both the boron atoms are connected to the terminal hydrogen atoms and the sulfur ligands are triply bridged to Co₂B fragment. The molecular structure of **3**, shown in Fig. 6, is seen to be consistent with the solution spectroscopic data. The Co-S bond length (2.255(8) Å) in **3** is somewhat longer than that observed in its Cp analogues (2.239(2) Å) and other cobaltathiaboranes. For example, [(CpCo)₂B₉H₈S] (2.232 Å) and [CpCoB₆H₈S₂] (2.235 Å).[26,32,33] All the Co-B, B-S and B-B bond lengths are in the range associated with bonding interactions, observed in other cobaltathiaboranes, [(CpCo)₂B₉H₈S], and [(CpCo)₂B₅H₇S].
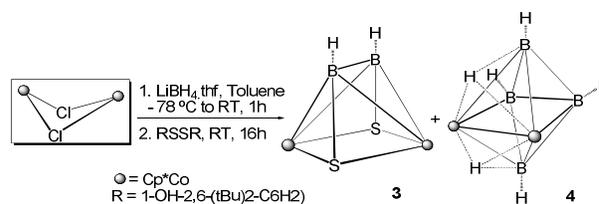
Scheme 2 Synthesis of cobaltathiaborane cluster **3**

Compound **3** has the same core geometry to its Cp analogue and another complex [S₂Os₄(CO)₁₂].[33] Changing the ancillary ligand from Cp to Cp*, compound **3** crystallizes in *C2/c* space

group rather than $P2_1/c$. The dihedral angle between the Cp* and {B$_2$S$_2$} planes in **3** is 2.26°, whereas in the case of [(CpCo)$_2$B$_2$H$_2$S$_2$] the planes are parallel. The Co(1)-S(1)-Co(2) and Co(1)-S(2)-Co(2) angles are 86.22° and 85.80° respectively, 5 which are deviated from [(CpCo)$_2$B$_2$H$_2$S$_2$] and [S$_2$Os$_4$(CO)$_{12}$].
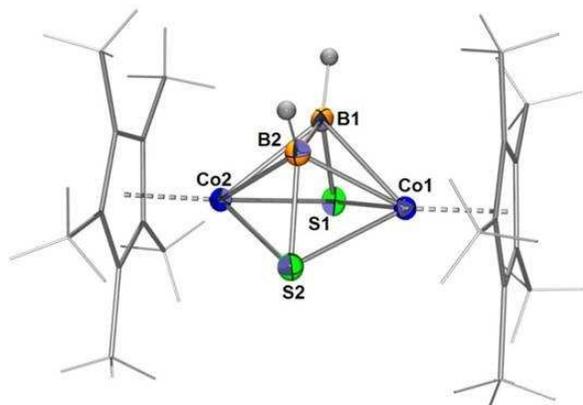
Fig. 6 Molecular structure and labelling diagram of **3**. Selected bond lengths (Å) and angles (°): B(1)-B(2) 1.733(5), B(1)-S(1) 1.823(3), B(1)-Co(1) 2.111(3), S(1)-Co(1) 2.2465(8); B(1)-S(1)-Co(1) 61.46(10), Co(1)-10 S(1)-Co(2) 86.22(3), B(1)-Co(1)-B(2) 48.43(13), B(1)-Co(1)-S(1) 49.34(9), S(1)-Co(1)-S(2) 88.25(3), B(2)-Co(2)-S(2) 48.94(9), B(1)-Co(2)-S(2) 84.93(9), S(1)-Co(2)-S(2) 88.24(3).
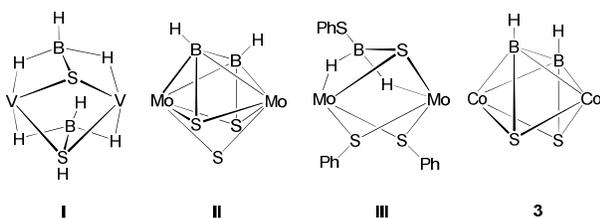
15 **Chart 2** Triply bridged sulfur ligands observed in dinuclear metallaborane complexes, (**I**: [(CpV)$_2$(μ$_3$-S)$_2$(BH$_3$)$_2$], **II**: [(Cp*Mo)$_2$(μ$_3$-S)$_3$(BH)$_2$], **III**: [(Cp*Mo)$_2$(μ-SPh)$_2$(μ$_3$-S)(H$_2$BSPh)]).

Table 2 Selected structural parameters and ^{11}B NMR of **3** and other related compounds

Compounds	sep^a	Avg. d [M-M][Å]	Avg. d [M-B][Å]	^{11}B NMR [ppm]	Ref.
3	8	3.07	2.12	22.8	-^{b}
[(CpCo)$_2$B$_2$H$_2$S$_2$]	8	3.06	2.16	17.6	33
[(Cp*Mo)$_2$B$_2$S$_2$H$_2$ (μ-η1-S)]	6	2.63	2.48	18.8	34
[(Cp*Mo)$_2$B$_2$H$_5$ (BSePh)$_2$(μ-η1-SePh)]	6	2.70	2.27	78.8, 54.0, 19.2	34
[(CpV)$_2$S$_2$B$_2$H$_6$]	6	2.77	2.38	-24.6	16
[(Cp*Cr)$_2$B$_4$H$_8$]	5	2.87	2.06	34.3, 126.5	35
[(Cp*ReH$_2$)$_2$B$_4$H$_4$]	6	2.81	2.17	1.30, 68.7	36
[(Cp*Ta)$_2$B$_4$H$_{10}$]	5	2.89	2.38	0.3, 16.6	37
[(Cp*Mo)$_2$B$_4$H$_7$ (μ-PPh$_2$)]	6	2.73	2.20	4.16, 34.3, 47.2	38

20 ^{a}sep = skeletal electron pair, ^{b}this work.

As evident from the X-ray analysis of **3**, it is clear that the molecules and their two-fold equivalents are linked through two C-H•••π interaction between the five membered ring (C1-C2-C3-C4-C5) and H10A. The distance between H10A and Cp* plane is 25 2.66897 Å, indicating the formation of a week dimer. The connection does not extend further to form a C-H•••Π bonded chain but forms a weak dimer. In addition, these chains are linked through a week S•••H interaction between S2 and H7C_$2 (symm $2: 1-x, 1-y, 1-z).
30

Perbromination of [(Cp*Co)$_2$B$_4$H$_6$] using PtBr$_2$

Although few reports are available on the chlorination of boranes and polyboranes (Eqn 1)^{39a}, it is not clear which factors actually dominates the substitution chemistry. Therefore, it is desirable to 35 have systematic and efficient methods for achieving B-perhalogenation of metallaborane compounds. All our attempts to prepare perhalogenated metallaborane or metallaheteroborane using different halogen sources such as BHCl$_2$.SMe$_2$, NaI etc. were failed.^{40} The first example of a dinuclear metallaborane 40 fully chlorinated at boron is reported earlier in 2004 (Eqn 2).^{41} In the Following, we present the result of the reaction of [(Cp*Co)$_2$B$_4$H$_6$], **4** with PtBr$_2$ to afford B-Br inserted **5** in less yield (Eqn 3).

$$Na_2[B_{12}H_{12}] \xrightarrow[\text{2. 100 °C, 24h}]{\text{1. Cl}_2\text{, 5h, rt}} [B_{12}Cl_{12}]^{2-} \qquad \text{Eqn 1}$$

$$[(Cp^*ReH_2)_2B_4H_4] \xrightarrow[\text{75 °C, 20h}]{BHCl_2.SMe_2} [(Cp^*Re)_2B_5Cl_5H_2] \qquad \text{Eqn 2}$$

$$\underset{(4)}{[(Cp^*Co)_2B_4H_6]} \xrightarrow[\text{60 °C, 12h}]{PtBr_2} \underset{(5)}{[(Cp^*Co)_2B_4Br_4H_2]} \qquad \text{Eqn 3}$$
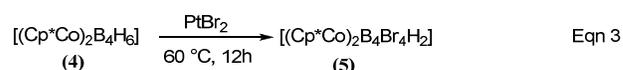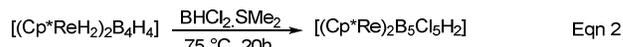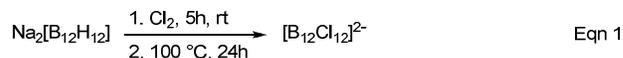
45 Compound **5** has been isolated as an orange solid in 7% yield. The ^{11}B{^{1}H} NMR spectrum of **5** shows no coupling with hydrogen confirms the substitution of all of the terminal protons in [(Cp*Co)$_2$B$_4$H$_6$] by bromine atoms and rationalizes the presence of two types of boron environments at δ = 43.0 and 11.8 50 ppm. The observed ^{11}B NMR chemical shifts for **5** are shielded by 17.5 and 2.8 ppm when compared with parent compound [(Cp*Co)$_2$B$_4$H$_6$]. The ^{1}H NMR spectrum reveals the presence of two unique Cp* and μ$_3$-H protons at δ = 1.89 and -11.31 ppm respectively.

55 The molecular structure of **5**, shown in Fig. 7(a), is seen to be fully consistent with the solution spectroscopic data. Compound **5** can be derived from [(Cp*Co)$_2$B$_4$H$_6$] by the replacement of four B-H terminal hydrogens by its isoelectronic bromine atoms. Thus, the qualitative cluster shapes of [(Cp*Co)$_2$B$_4$H$_6$] and **5** are 60 same, and the differences are sought in the magnitude of the structural parameters. The Co–Co bond length of 2.4995(7) Å is shorter as compared to those of parent cobaltaborane.^{25} The B–Br distance of 1.934 Å is consistent with the existence of a single B-Br bond, being somewhat shorter than the corresponding 65 'unexceptional' distance observed in [8,9,10,11,12,13-Br$_6$-1,2-(-(CH$_2$)$_3$-1,2-C$_2$B$_{11}$H$_5$] (1.94(1) Å).^{42} As half of the molecule forms the asymmetric unit, each molecule has two bromine acceptor and two carbon donors building C-H•••Br interaction to form 2D sheet (Fig. 7(b)).
70

(a)

(b)
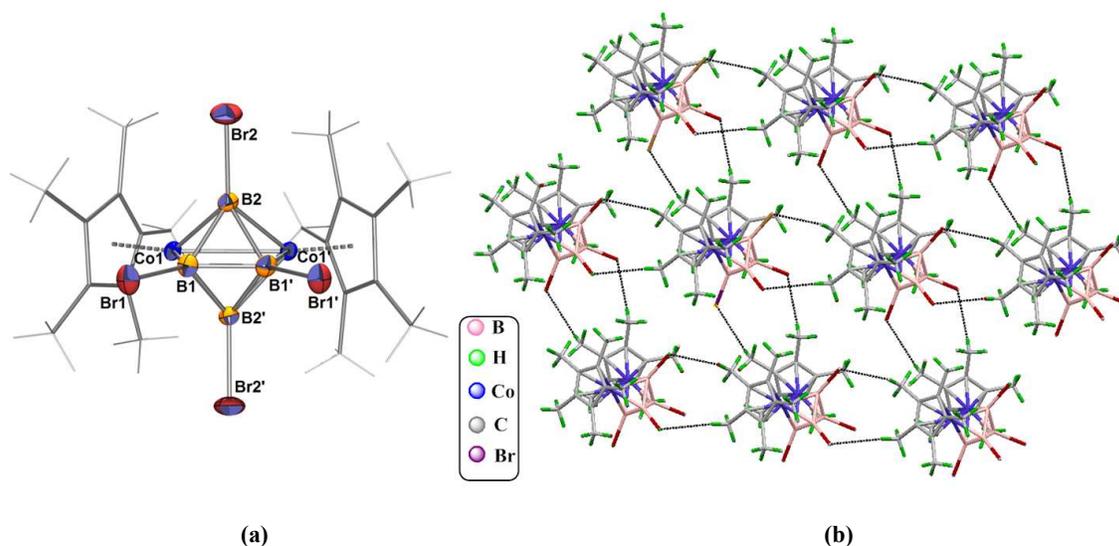
Fig. 7 (a) Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Co(1)-B(2) 2.122(7), Br(1)-B(1) 1.960(7), B(1)-B(2) 1.707(10), B(1')-B(2') 1.713(9); B(1)-Co(1)-B(2) 48.6(3), B(2')-Co(1')-B(2') 71.7(3), B(2)-B(1)-Co(1) 68.9(4), Br(1)-B(1)-Co(1) 132.2(4), B(1)-B(2)-Br(2) 129.1(5), B(1')-B(2')-Br(2') 129.7(5), B(1)-B(2)-Co(1) 97.4(4); (b) Two-dimensional sheet of **5** through the C-H•••Br interaction parallel to the ac-plane.

HOMO-2
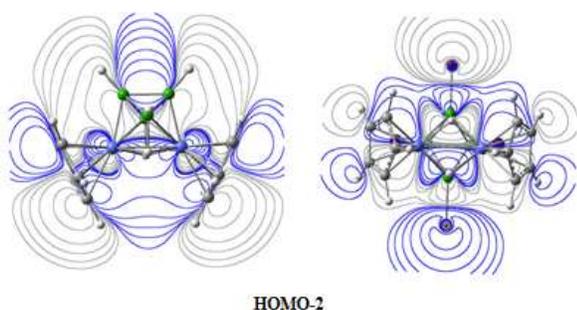
Fig. 8 Frontier molecular orbital diagram of **4'** and **5'**.

To understand the electronic structure, DFT calculations were carried out on model compounds **4'** and **5'** (Cp analogues of compound **4** and **5** respectively). The DFT frontier molecular orbital study shows a significant destabilization of the highest occupied molecular orbitals (HOMOs) of **5** suggesting higher reactivity compared to its parent molecule **4** (Table S3). Further, the MOs show strong bonding interaction between two boron atoms (B2 and B1') and the cobalt atoms (HOMO-2, Fig. 8). In addition, we have also observed in compound **5** three centered two electron B-B-B bonds in the triangular faces using NBO analysis.

Conclusion

A novel 10-vertex metal-rich hypoelectronic cobaltaborane [Co_4B_6], and 6-vertex *closo*-[$Co_2Mo_2B_2$] have been synthesized and structurally characterized. The experimental results were accompanied and rationalized by means of the DFT studies, which reveal geometries in agreement with the structure determinations. The DFT study further illustrates the extra stability of the ten vertex *isocloso* cluster over its rhodium analogue. Metallaborane frameworks containing bridging hydrogen(s) typically represent *nido* or *arachno* shapes because of the spatial and electronic demands of the bridge atoms.[43] Nevertheless, compound **5** represents one of the rare examples showing *closo* structure containing two μ_3-H protons, which is rare in metallaborane chemistry or in organometallic chemistry.

Experimental Section

General Procedures and Instrumentation. All the operations were conducted under an Ar/N_2 atmosphere using standard Schlenk techniques. Solvents were distilled prior to use under Argon. All the other reagents Cp*H, $CoCl_2$, (1-OH-2,6-(^{t}Bu)$_2$-C_6H_2)$_2S_2$, *n*-BuLi in hexane, [LiBH$_4$·thf] (Aldrich) were used as received. [Cp*CoCl]$_2$[44] and the external reference, [Bu$_4$N(B$_3$H$_8$)],[45] for the ^{11}B NMR were synthesized as per the literature method. Thin layer chromatography was carried on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates). The NMR spectra were recorded on 400 and 500 MHz Bruker FT-NMR spectrometer. The residual solvent protons were used as reference (δ, ppm, CDCl$_3$, 7.26), while a sealed tube containing [Bu$_4$N(B$_3$H$_8$)] in C$_6$D$_6$ (δ B, ppm, -30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were obtained on a Nicolet iS10 IR spectrometer. Microanalyses for C, H, and N were performed on Perkin Elmer Instruments series II model 2400. Mass spectra were recorded on Bruker Micro TOF – II mass spectrometer.

Synthesis of 1-3: In a Flame-dried Schlenk tube, [Cp*CoCl]$_2$, (0.5 g, 1.09 mmol) was suspended in toluene (20 cm^3) and cooled to -70 °C. [LiBH$_4$.thf] (2.17 mL, 4.36 mmol) was added via syringe and the reaction mixture was warmed slowly over 20 minutes to room temperature and left stirring for an additional hour. The reaction mixture was thermolysed in presence of [Mo(CO)$_3$(CH$_3$CN)$_3$], (0.9 g, 3.27 mmol) at 80 °C for 20 h. The solution was allowed to come to room temperature. MeI (0.14 g, 1 mmol) was added and stirred at room temperature for 2h. The solvent was removed in vacuo and the residue was extracted into hexane. After removal of solvent from filtrate, the residue was subjected to chromatographic work up using silica gel TLC plates. Elution with

hexane:CH_2Cl_2 (80:20 *v/v*) yielded orange $[(Cp^*Co)_3B_6H_7Co(CO)_2]$ (**1**) (0.1 g, 12%), brown $[(Cp^*Co)_2B_2H_5IMo_2(CO)_6]$ (**2**) (0.06 g, 6%), brown $[(Cp^*Co)_2B_4H_6]$ (**4**) (0.05 g, 9%), and yellow $[(Cp^*Co)_3B_4H_4]$ (0.07 g, 10%). Under the same reaction conditions, using (1-OH-2,6-($^tBu)_2$-$C_6H_2)_2$ S_2 (2.54 g, 5.36 mmol) in place of $[Mo(CO)_3(CH_3CN)_3]$ yielded purple $[(Cp^*Co)_2B_2S_2H_2]$, (**3**) (0.1 g, 19%).

Note that compounds **4** and $[(Cp^*Co)_3B_4H_4]$ have been synthesized and characterized in comparison with the spectroscopic data reported earlier by Grimes *et al.* by the reaction of Cp^*Li, $CoCl_2$ with $[B_5H_8]^-$.[27]

1: MS(MALDI): m/z 769 $[M]^+$, isotope envelope. $C_{32}H_{52}B_6Co_4O_2$ requires 769; ^{11}B NMR (128 MHz, $CDCl_3$, 22 °C): δ = 125.4 (s, J_{B-H} = 138 Hz, 3B), 33.6 (s, J_{B-H} = 133 Hz, 3B), ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 5.23 (br, $3BH_t$), 3.58 (br, $3BH_t$), 2.10 (s, 45H, $3Cp^*$), -19.46 (s, Co*H*), ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 92.9 (s, η^5-C_5Me_5), 14.1 (s, η^5-C_5Me_5); IR (hexane, cm^{-1}): 2461w, 2490w (BH_t), 1995s (*CO*). Anal. Calcd (%) for $C_{32}H_{51}B_6Co_4O_2$: C 50.022, H 6.69. Found: C 49.43, H 7.39.

2: MS(MALDI): m/z 900 $[M]^+$, isotope envelope. $C_{26}H_{34}B_2Co_2IMo_2O_6$ requires 900; ^{11}B NMR (128 MHz, $CDCl_3$, 22 °C): δ = 75.7 (br, 2B), ^{1}H NMR (400 MHz, $CDCl3$, 22 °C): δ = 1.57 (s, 15H, Cp^*), 1.51 (s, 15H, Cp^*), -15.20 (2 μ_3H), -19.78 (1μ_3H); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 94.4 (s, η^5-C_5Me_5), 93.9 (s, η^5-C_5Me_5), 8.9 (s, η^5-C_5Me_5), 8.7 (s, η^5-C_5Me_5); IR (hexane, cm^{-1}): 2475w (BH_t), 2022s (*CO*).

3: MS(MALDI): m/z 476.1 $[M]^+$, isotope envelope. $C_{20}H_{32}B_2Co_2S_2$ requires 476.1; ^{11}B NMR (128 MHz, $CDCl_3$, 22 °C): δ = 22.7 (2B), ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 3.78 (br, $2BH_t$), 2.17 (s, 30H, $2Cp^*$); ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): δ = 88.1 (s, η^5-C_5Me_5), 13.0 (s, η^5-C_5Me_5); IR (hexane, cm^{-1}): 2467w (BH_t). Anal. Calcd (%) for $C_{20}H_{32}B_2Co_2S_2$: C 50.45, H 5.41. Found: C 48.99, H 6.02.

Synthesis of $[(Cp^*Co)_2B_4H_2Br_4]$, 5: In a typical reaction, $[(Cp^*Co)_2B_4H_6]$ (0.08 g, 0.18 mmol) in hexane (10 mL) was stirred with 3 equivalents of $PtBr_2$ (0.2 g, 0.55 mmol) for 12 h at 60 °C. The solvent was removed in vacuo, the residue was extracted in hexane, and passed through Celite. The mother liquor was concentrated and the residue was chromatographed on silica gel TLC plates. Elution with a hexane/CH_2Cl_2 (3:1) mixture yielded orange **5**, (0.01 g, 7%).

5: MS(MALDI): m/z 683 $[M^+-2Br]$, isotope envelope. $C_{20}H_{32}B_4Br_2Co_2$ requires 683; ^{11}B NMR (128 MHz, $CDCl_3$, 22 °C): δ = 43.0 (br, 2B), 11.8 (br, 2B); ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C): δ = 1.89 (s, 30H, $2Cp^*$), -11.31 (Co-H-B); ^{13}C NMR (100 MHz, $CDCl3$, 22 °C): δ = 92.7 (s, η^5-C_5Me_5), 11.2 (s, η^5-C_5Me_5). IR (hexane, cm^{-1}): 2856s, 2925s, 2960s (CH_3).

Molecular Orbital Calculations. The full geometry optimizations were carried out on model compounds **1'-5'** (Cp analogues of **1-5**) using DFT as implemented in Gaussian09 program package.[46] The geometry optimization were carried out in gas phase (no solvent effect) using B3LYP functional.[47,48] In order to assess the nature of the stationary point on the potential energy surface, we performed additional harmonic frequency calculations at the same level of theory on the optimized geometry and obtained zero point energy corrections to the energy values reported herein. The geometry optimizations have been carried out with B3LYP functional with mixed basis sets 6-31g* for all the main group elements e.g. carbon, oxygen, boron, sulphur, 3-21g for iodine and SDD (Stuttgart/Dresden double-ζ) for Co, Rh, Mo atoms.[47-50] The crystallographic coordinates has been used as a starting geometry for complete geometry optimizations. We also computed the NMR shielding tensors at the B3LYP/GIAO[51] level of theory. The ^{11}B NMR chemical shifts were calculated relative to B_2H_6 (B3LYP B shielding constant 93.5 ppm) and converted to the usual $BF_3.OEt_2$ scale using the experimental δ([11]B) value of B_2H_6, 16.6 ppm.[52] Further, NBO analysis was carried out using the NBO routine within the Gaussian 09.

X-ray Structure Determination. Suitable X-ray quality crystals of **1**, **2**, **3** and **5** were grown by slow diffusion of a hexane:CH_2Cl_2 (9.5:0.5 *v/v*) solution and single crystal X-ray diffraction studies were undertaken. Crystal data for **3** were collected and integrated using Bruker AXS (Kappa Apex II) diffractometer equipped with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation at 150 K. The crystal data for **1**, **2** and **5** were collected and integrated using OXFORD DIFFRACTION XALIBUR-S CCD system equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) radiation at 150K (Table 3). The structure was solved by heavy atom methods using SHELXS-97[53] and refined using SHELXL-97[54] (Sheldrick, G.M., University of Göttingen). CCDC 945313 (**1**), 971697 (**2**), 971698 (**3**), 971699 (**5**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Notes and references

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† Electronic Supplementary Information (ESI) available: [cif files]. See DOI: 10.1039/b000000x/

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Table 3. Crystallographic data for compounds **1**, **2**, **3** and **5**

Chemical formula	$C_{32}H_{51}B_6Co_4O_2$ (**1**)	$C_{26}H_{34}B_2Co_2IMo_2O_6$ (**2**)	$C_{20}H_{32}B_2Co_2S_2$ (**3**)	$C_{20}H_{32}B_4Br_4Co_2$ (**5**)
Formula weight	768.31	900.79	476.1	753.2
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	*Cc*	*P21/n*	*C2/c*	*Fdd*2
a (Å)	19.9069(9)	9.3527(2)	28.0135(16)	9.6049(2)
b (Å)	11.4558(4)	17.1264(3)	8.5928(3)	35.0685(9)
c (Å)	16.9951(9)	20.0330(3)	19.9723(12)	16.3289(3)
α (°)	90.00	90.00	90.00	90.0
β (°)	115.311(6)	92.060(2)	114.615(4)	90.0
γ (°)	90.00	90.00	90.00	90.0
V(Å^3)	3503.7(3)	3206.77(10)	4370.7(4)	5500.1(2)
Z	4	4	8	4
D_{calc} (Mg/m^3)	1.457	1.866	1.468	1.814
F (000)	1588	1756	2000	2912
μ (mm^{-1})	1.889	1.495	1.764	16.288
θ Range (°)	2.98-25.99	2.47-23.98	0.998 -25.00	5.04-72.09
Goodness of fit	1.168	1.030	1.075	1.076
Reflections collected	14040	28639	17170	10217
Independent reflections	6298	5634	3849	2522
Parameters	413	382	245	141
R1, wR2 [$I>2\sigma(I)$]	0.0480, 0.1467	0.0500, 0.0858	0.0393, 0.0972	0.0481, 0.1381
R1, wR2 (all data)	0.0500, 0.1487	0.0941, 0.0966	0.0513, 0.1060	0.0499, 0.1415

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● = B   ● = Mo   ● = Cp*Co   ● = I   ● = Br   ● = O   ○ = H
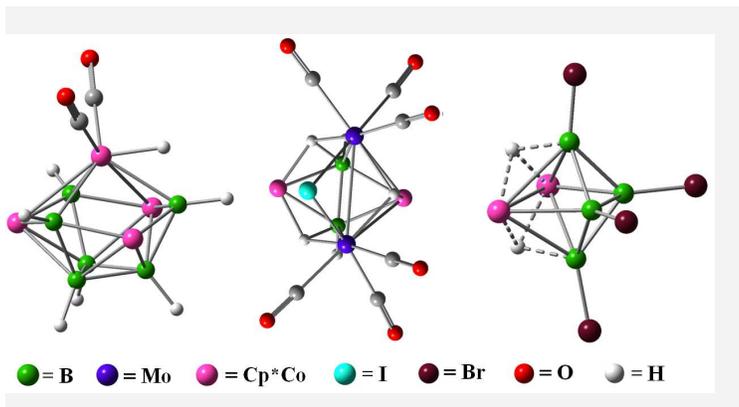
Novel class of cobaltaborane and cobaltaheteroborane clusters, *isocloso*-[(Cp*Co)$_3$B$_6$H$_7$Co(CO)$_2$], *closo*-[(Cp*Co)$_2$B$_2$H$_5$Mo$_2$(CO)$_6$I], *nido*-[(Cp*Co)$_2$B$_2$H$_2$S$_2$)], and *closo*-[(Cp*Co)$_2$B$_4$H$_2$Br$_4$] have been synthesized and structurally characterized (see picture).

5

Dudekula Sharmila, Rongala Ramalakshmi, Kiran Kumarvarma Chakrahari, and Sundargopal Ghosh*.......Page No. – Page No.

Synthesis, Characterization and Crystal Structure Analysis of Cobaltaborane and Cobaltaheteroborane Clusters.

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