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## ARTICLE

# Synthesis and chemistry of the open-cage cobaltaheteroborane cluster $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\}_2\text{B}_2\text{H}_2\text{Se}_2]$ : A combined experimental and theoretical study<sup>S</sup>

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<sup>S</sup>Dedicated to the memory of Professor Ken Wade in recognition of his important and inspiring contribution to cluster chemistry.

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Reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{CoCl}]_2$  with a two-fold excess of  $[\text{LiBH}_4\cdot\text{thf}]$  followed by heating with an excess of Se powder produces the dicobaltaselenaborane species  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\}_2\text{B}_2\text{H}_2\text{Se}_2]$ , **1**, in good yield. The geometry of **1** resembles a *nido* pentagonal  $[\text{Co}_2\text{B}_2\text{Se}_2]$  bipyramid with a missing equatorial vertex. It can alternatively be seen as an open cage triple-decker cluster. Isolation of **1** permits its reaction with  $[\text{Fe}_2(\text{CO})_9]$  to give heterometallic diselenametallaborane  $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\}\text{Fe}(\text{CO})_3\text{B}_2\text{H}_2\text{Se}_2]$ , **2**. The geometry of **2** is similar to that of **1** with one of the  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}]$  groups replaced by the isolobal, two-electron fragment  $[\text{Fe}(\text{CO})_3]$ . Both new compounds have been characterized by mass spectrometry, <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR spectroscopy. The structural architectures have been unequivocally established by crystallographic analysis. In addition, density functional theory calculations were performed to investigate the bonding and electronic properties. The large HOMO-LUMO gaps computed for both clusters are consistent with their thermodynamic stability. Natural bond order calculations predict the absence of metal-metal bonding interaction.

## Introduction

The chemistry of molecular (hetero)boranes has developed over the last decades to the point where it now occupies an important place between organic and inorganic chemistries, with overlaps into materials science, biology and medicine.<sup>1</sup> This development has been greatly aided by significant contributions from computational chemistry, X-ray crystallography and NMR spectroscopy.<sup>2</sup> Many (hetero)borane compounds are now structurally characterized and find unique applications in many diverse fields from new materials<sup>3</sup> to homogeneous catalysis<sup>4</sup> to medicine (boron-neutron capture therapy (BNCT) for tumours) or drugs.<sup>5</sup>

In contrast to (hetero)boranes, metallaheteroborane chemistry is far less developed.<sup>2</sup> There is a need for the design of new synthetic routes for the preparation of novel metallaheteroboranes under mild conditions. The main synthetic procedure consists of the insertion of heteroatoms in the pre-formed polyboranes which upon subsequent boron replacement by respective isolobal transition-metal fragments, results in the formation of metallaheteroboranes.<sup>6,7</sup> Alternatively, insertion of heteroatoms into already formed metallaboranes can also generate metallaheteroboranes.<sup>8</sup> Apart from carboranes and metallacarboranes,<sup>1</sup> thia boranes and thiametallaboranes are the most wide-ranging main group polyhedral heteroboranes which have been reported. On the other hand, examples of metallaheteroborane clusters containing heavier group 16 elements are limited.<sup>9,10</sup>

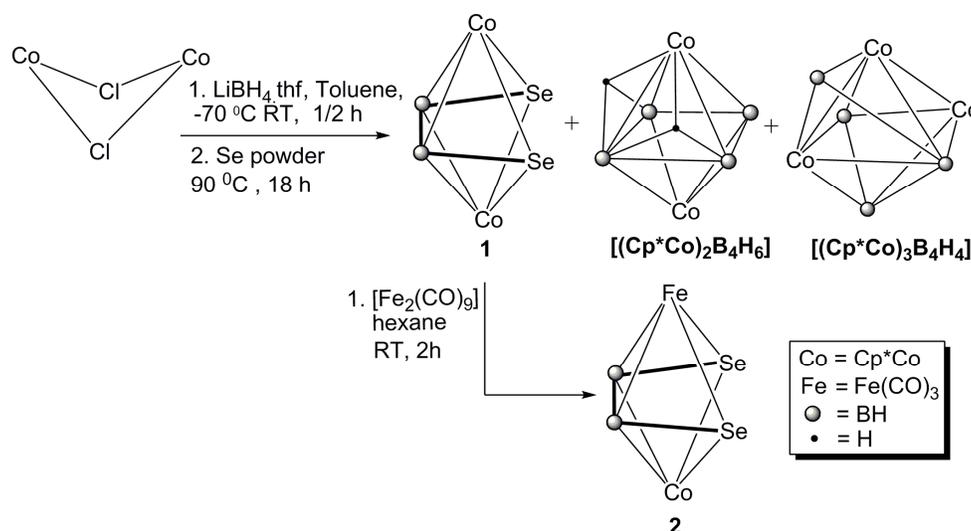
Using key results from our earlier works on dimetallachalcoboranes with group 6 transition metals and inspired by the isolation of  $[(\text{CpCo})_2\text{B}_2\text{H}_2\text{S}_2]$  by Sneddon<sup>11</sup> and recently  $[(\text{Cp}^*\text{Co})_2\text{B}_2\text{H}_2\text{S}_2]$  by one of us,<sup>12</sup> we have continued to explore the cobalt system with various chalcogen sources. We describe in this paper the synthesis and characterization of a novel dicobaltaheteroborane and its reactivity with some transition-metal carbonyls.

## Results and discussion

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

Reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{CoCl}]_2$  with two-fold excess of  $[\text{LiBH}_4\cdot\text{thf}]$  followed by heating with Se powder results in the formation of crystalline dicobaltaselenaborane **1** in good yield. The reaction also yields the known compounds  $[(\text{Cp}^*\text{Co})_2\text{B}_4\text{H}_6]$ <sup>13</sup> and  $[(\text{Cp}^*\text{Co})_3\text{B}_4\text{H}_4]$ ,<sup>13</sup> in low yields (Scheme 1). Although produced as a mixture, these compounds can easily be separated by TLC and spectroscopically and structurally characterized.

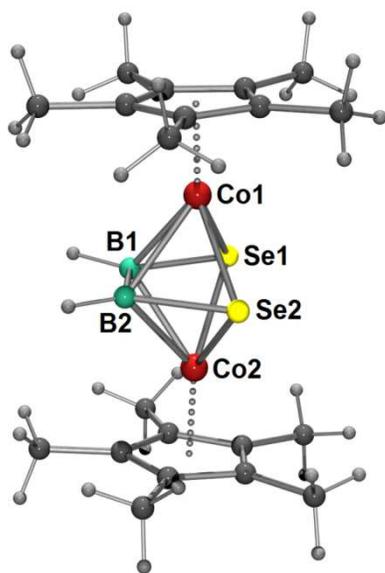
Compound **1** is reasonably air stable and can be handled especially in its pure crystalline state. The <sup>11</sup>B NMR spectrum at room temperature shows one boron peak at  $\delta = 33.5$  ppm, which is consistent with a tri- or tetra-coordinated boron environment. The <sup>1</sup>H NMR spectrum reveals two broad peaks that correspond



**Scheme 1.** Synthesis and reactivity of dicobaltaselenaborane cluster **1**.

to B-H terminal protons at  $\delta = 3.76$  and 3.67 ppm. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra imply two Cp\* ligands. These spectroscopic data rationalize the presence of  $C_2$  symmetry for this molecule. To confirm this spectroscopic assignment, an X-ray analysis was undertaken and the framework geometry of compound **1** became clear thereafter.

Compound **1** crystallizes in the monoclinic  $P2_1/c$  space group with the asymmetric unit consisting of two Co atoms separated by 3.144 Å and each ligated to a Cp\* ligand, two B-H units along with two  $\mu_3$ -Se atoms. The non-bonded distance of 3.336 Å between the Se1 and Se2 atoms is longer than that in the cluster  $[(\eta^5\text{-C}_5\text{Me}_5\text{Mo})_2\text{B}_4\text{H}_4\text{Se}_2]^{14}$  that exhibits a flattened *nido* heptagonal bipyramid. The average B-Se distance of 2.02 Å is comparable to those encountered for other selenaborane clusters.<sup>10</sup> The average Co-Se distance of 2.38 Å and average Co-B distance of 2.16 Å in compound **1** are similar to those observed for  $[(\text{Co})_6(\mu_3\text{-Se})_8(\text{PEt}_3)\cdot\text{thf}]^{15}$  and in earlier reported cobaltaboranes,<sup>16</sup> respectively.



**Fig. 1** Molecular structure of  $[\{(\eta^5\text{-C}_5\text{Me}_5\text{Co})_2\text{B}_2\text{H}_2\text{Se}_2\}]$ , **1**. Selected bond lengths (Å) and angles ( $^\circ$ ): Co(1) - B(1) 2.128(5), Co(1) - B(2) 2.201(5), Co(1) - Se(1) 2.3804(6), Co(2) - B(1) 2.117(5), Co(2) - Se(1) 2.3792(6), Se(1) - B(1) 1.985(6), Se(2) - B(2) 2.070(6), B(1) - B(2) 1.726(7), B(1) - H(1) 1.190(19), B(1) - Co(1) - B(2) 46.96(18), B(1) - Co(1) - Se(1) 51.87(15), B(2) - Co(1) - Se(1) 88.02(13), Se(1) - Co(1) - Se(2) 88.90(2).

The X-ray structure of **1** shows the geometry of the cluster to be a *nido* six-vertex-pentagonal bipyramid, from which one atom is missing in the equatorial plane (Fig. 1). The cluster has  $C_{2v}$  symmetry with two Co atoms in the apical positions, two boron atoms and two Se atoms in equatorial positions of the parent pentagonal bipyramid. The boron and selenium atoms, present in the equatorial positions, lie in the same plane (maximum deviation of  $0.02^\circ$ , Table 1). The Cp\* rings bonded to each Co atom and the open  $[\text{B}_2\text{Se}_2]$  ring are almost parallel to each other (dihedral angles,  $\text{B}_2\text{Se}_2/\text{Cp}^* 0.28/2.45^\circ$  avg.  $2.28^\circ$ ) and the Co atoms are located nearly over the centroid of the Cp\* rings leading to almost parallel mutual orientation of all three rings. Hence, the title compound can be described as a triple-decker complex in which two metal atoms are sandwiched between two Cp\* and the open  $[\text{Se}_2\text{B}_2\text{H}_2]$  ring.<sup>11</sup>

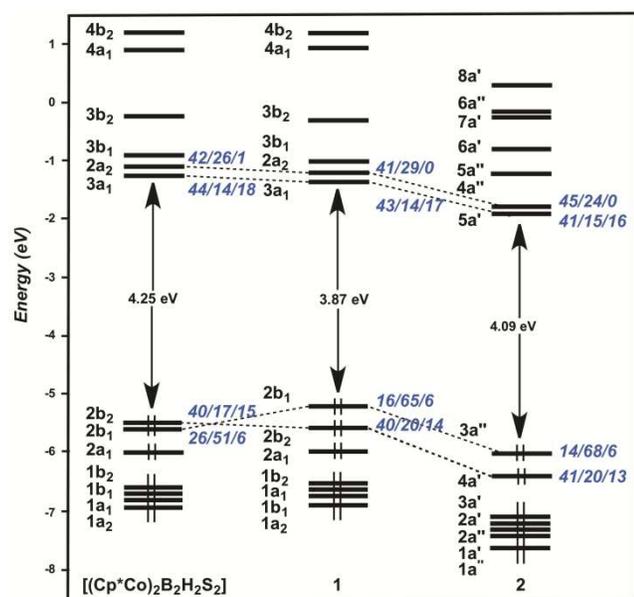
The Cp\* ligands linked to the cobalt atoms connect one molecule to another to form infinite 1D chains *via* C-H $\cdots\pi$  interactions ( $d_{\text{avg}}\text{H}\cdots\text{C}(\text{Cp}^*) = 2.85$  Å) parallel to the  $c$  axis (Fig. 2). In addition, 2D layers are generated *via* nonconventional hydrogen-hydrogen C-H $\cdots$ H-B interactions ( $d(\text{H}(\text{C})\cdots\text{H}(1)) = 2.14$  Å;  $\angle\text{C}9-\text{H}9\text{C}\cdots\text{H}1 = 143.3^\circ$ ,  $\angle\text{B}1-\text{H}1\cdots\text{H}9\text{C} = 104.7^\circ$ ; (Fig. S1) and subsequently, a 3D architecture is generated with some additional weak van der Waals interactions along the  $a$  axis (Fig. S2). Such weak nonconventional hydrogen-hydrogen bonds often play key roles in molecular self-assembly in a crystal lattice.<sup>17</sup>

Such an open *nido* cage is consistent with the  $n+2$  skeletal electron pair (sep) count, i.e., 8 seps,  $[2(\text{Cp}^*\text{Co}) \times 2 + 2(\mu_3\text{-Se}) \times 4 + 2(\text{BH}) \times 2]/2$ , expected according to the Wade-Mingos electron counting rules.<sup>18</sup> To gain some insight into the electronic structure and bonding nature of **1**, density functional theory (DFT) calculations<sup>19</sup> were carried out. The important structural parameters and calculated  $^{11}\text{B}$  NMR chemical-shift

**Table 1** Experimental and calculated structural parameters of **1**, **2** and  $[(\text{Cp}^*\text{Co})_2\text{B}_2\text{H}_2\text{S}_2]$ 

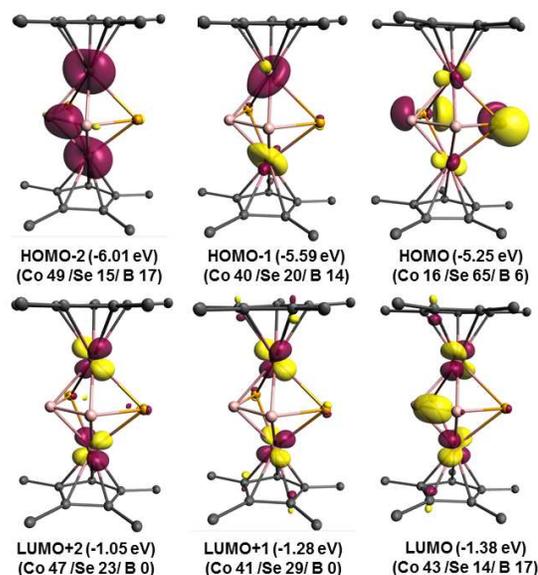
Complexes	$d[\text{M}-\text{M}]^a$ Å		$d[\text{E}-\text{E}]^b$ Å		Dihedral angles(°)				$^{11}\text{B}$ NMR	
	Exptl.	Calcd.	Exptl.	Calcd.	M-B-B/B-B-M <sup>c</sup> ...Se-B-B-Se <sup>d</sup>				Exptl.	Calcd.
$[(\text{Cp}^*\text{Co})_2\text{B}_2\text{H}_2\text{S}_2]$	3.072	3.073	3.136	3.125	105.1	106.1	0.02	0.00	22.7	16.53
<b>1</b>	3.144	3.156	3.336	3.315	105.2	109.3	0.27	0.00	33.5	31.8
<b>2</b>	3.238	3.219	3.335	3.355	108.4	108.9	2.002	0.01	31.2	26.4

<sup>a</sup>  $d[\text{M}-\text{M}]$  = distance between metal atoms, <sup>b</sup>  $d[\text{E}-\text{E}]$  = Distance between chalcogen atoms, <sup>c</sup> M-B-B/B-B-M = dihedral angle between the adjacent M-B-B and B-B-M planes (butterfly core), <sup>d</sup> Se-B-B-Se = deviation of the equatorial plane from the mean plane.

**Fig. 2** Illustration of 1D chain parallel to the  $c$  axis via C-H... $\pi$  interactions in **1**.**Fig. 3** MO diagrams for compounds  $[(\text{Cp}^*\text{Co})_2\text{B}_2\text{H}_2\text{S}_2]$  (left), **1** (middle), and **2** (right).  $\text{M}_2/\text{E}_2/\text{B}_2$  ( $\text{E} = \text{S}, \text{Se}$ ) percentage contributions of the first frontier molecular orbitals are given in italics.

values for **1** are listed in Table 1. They are in good agreement with the values experimentally measured. Density functional theory (DFT) calculations show a large energy gap of 3.87 eV computed at the PBE0 level between the highest occupied molecular orbital (HOMO) and the lowest unoccupied

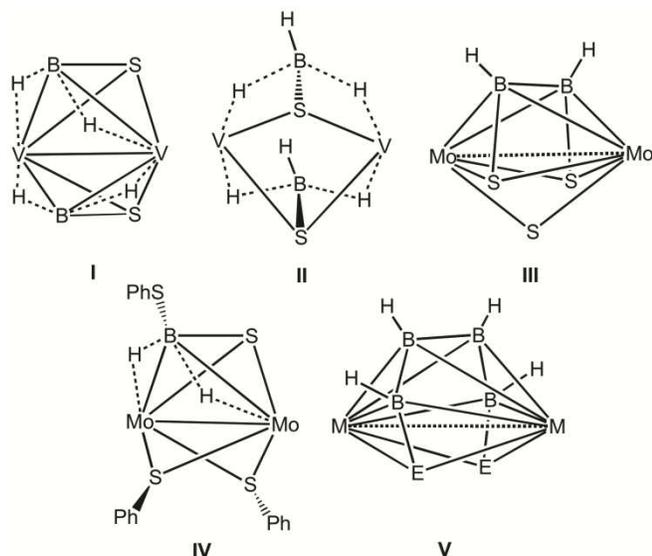
molecular orbital (LUMO) for **1**, consistent with high thermodynamical stability. The larger HOMO-LUMO gap computed for its sulfur analog cluster  $[(\text{Cp}^*\text{Co})_2\text{B}_2\text{H}_2\text{S}_2]$  led us to compare their MO diagrams (Fig. 3). Analysis of the frontier orbitals for both compounds indicates an increase in energy of the HOMO in **1** and a slight decrease in energy of the LUMO, leading to shrinking of the HOMO-LUMO gap of 0.38 eV as compared to  $[(\text{Cp}^*\text{Co})_2\text{B}_2\text{H}_2\text{S}_2]$  (Fig. 3). A look at the

**Fig. 4** DFT calculated frontier molecular orbitals of **1** (hydrogen atoms are removed for clarity).  $\text{M}_2/\text{Se}_2/\text{B}_2$  percentage contributions are given (isocontour value  $\pm 0.06$  [ $\text{e}/\text{bohr}^3$ ]<sup>1/2</sup>).

molecular orbital composition of the HOMOs of **1** (Fig. 4) shows that the HOMO of  $b_1$  symmetry is heavily localized on the selenium atoms and to a lesser extent on the metal atoms with a small participation of the boron atoms. The HOMO-1 ( $2b_2$ ), on the other hand is mainly Co in character with some contribution of selenium and boron atoms. Interestingly, this contrasts with the sulfur analog  $[(Cp^*Co)_2B_2H_2S_2]$  where the HOMO  $2b_2$  is localized on the metal atoms and the HOMO-1  $2b_1$  is strongly weighted on the sulfur atoms. This inversion can be attributed to the weaker electronegativity of Se compared to that of S.

### Reactivity of *nido*- $[(Cp^*Co)_2B_2H_2Se_2]$ , **1** with $[Fe_2(CO)_9]$

The chemistry of heterometallic systems has been intensively studied, in part due to the promise of catalytic reactivity or enhanced stoichiometric reactivity from the cooperative activation and synergistic interaction of metal centers with differing electronic properties. Although there are a large number of reports on bimetallic thiaaborane clusters<sup>20</sup> (Chart 1), there are very few examples of bimetallic selenaborane clusters. Therefore, a quest to find clusters that contain different transition metals led us to try to isolate heterobimetallic (Co-Fe) metallaheteroborane clusters. As a result, we performed the reaction of **1** with  $[Fe_2(CO)_9]$  in hexane at room temperature, from which  $[(Cp^*Co)Fe(CO)_3B_2H_2Se_2]$ , **2**, (Scheme 1) was obtained.

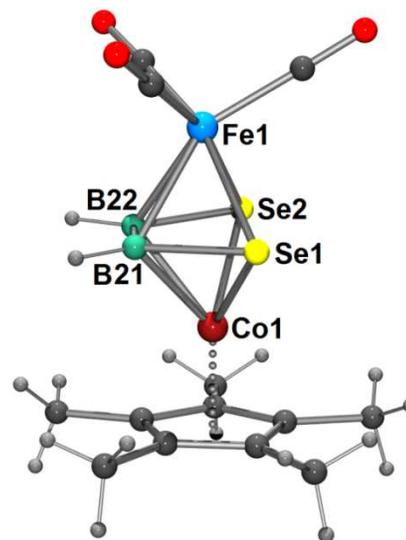


**Chart 1** Selected bimetallic metallachalcogenoboranes complexes: (I:  $[(CpV)_2(\mu_3-S)_2B_2H_4]$ , II:  $[(CpV)_2(\mu_3-S)_2B_2H_6]$ , III:  $[(Cp^*Mo)_2(\mu_3-S)_3(\mu_2-S)B_2H_2]$ , IV:  $[(Cp^*Mo)_2(\mu-SPh)_2(\mu_3-S)BH_2(SPh)]$ , V:  $[(Cp^*M)_2B_4H_4E_2]$ , (E = S, Se, Te and M = Mo, W in V)).

### $[Cp^*CoFe(CO)_3B_2H_2Se_2]$ , **2**

Compound **2** was isolated in modest yield and characterized spectroscopically and by single crystal X-ray diffraction. The IR spectrum shows three frequencies, 2063, 2021, and 1998  $cm^{-1}$  in the carbonyl region. Both experimental and DFT calculated NMR chemical shifts (Table S1) for  $^1H$  and  $^{11}B$  NMR spectra confirm the presence of a plane of symmetry in cluster **2**. The up-field region NMR chemical shift for  $Cp^*$  peaks in  $^1H$  NMR spectrum contains half the number of protons for **2** in comparison to **1** via integration. This confirms the substitution of one of  $Cp^*Co$  unit in **2** by an  $Fe(CO)_3$  fragment.

This was further elucidated from an X-ray structure determination. Compound **2** crystallizes in the monoclinic  $P2_1/n$  space group with the asymmetric unit consisting of one Co(I) atom bonded to a  $Cp^*$  ligand, one  $Fe(CO)_3$  unit, two B-H units along with two  $\mu_3$ -Se atoms. Overall, the core geometry of **2** can be well visualized as a pentagonal bipyramid with one equatorial vertex missing (between Se1 and Se2), analogous to **1**. The Co–B and Co–Se bond lengths are 2.11–2.21 and 2.36–2.37 Å, respectively, and Fe–B and Fe–Se bond lengths are 2.21 and 2.45 Å, respectively, similar overall to those reported for related Co and Fe metallaborane complexes.<sup>16</sup>



**Fig. 5** Molecular structure of  $[(\eta^5-C_5Me_5)CoFe(CO)_3B_2H_2Se_2]$ , **2**. Selected bond lengths (Å) and angles ( $^\circ$ ) Co(1) – B(22) 2.111(6), Co(1) – B(21) 2.135(6), Co(1) – Se(1) 2.3690(8), Fe(1) – B(21) 2.214(6), Se(2) – B(22) 1.979(6), B(21) – B(22) 1.700(8), Co(1) – B(21) – Fe(1) 96.2(2), B(21) – B(22) – Co(1) 67.1(3), B(21) – B(22) – Co(1) 67.1(3), Se(2) – B(22) – Fe(1) 71.39(19).

After the successful isolation of **2** from **1**, our objective was to isolate the diferraselenaborane species. As a result, we performed the reaction using an excess of  $[Fe_2(CO)_9]$  under various reaction conditions. Although computational results obtained on the hypothetical molecule  $[Fe_2(CO)_9]_2B_2H_2Se_2$  show its thermodynamic stability with a HOMO-LUMO energy gap of 4.47 eV at the PBE0 level of theory, all of our attempts to isolate this molecule failed. In **2**, the  $Cp^*$  ligand bonded to the cobalt atom of one molecule, is oriented to establish intermolecular weak C–H $\cdots$ Se hydrogen bonding interactions<sup>21</sup> with a selenium atom of an adjacent molecule ( $dH(9C)\cdots Se(1) = 2.90$  Å,  $\angle C(9)–H(9C)\cdots Se(1) = 152.3^\circ$ ) leading to an infinite 1D chain parallel to the *ac* plane (Fig. S3). The adjacent chains are closely packed via weak intermolecular C–H $\cdots$ B interactions<sup>22</sup> ( $dH(6C)\cdots B(22) = 3.19$  Å,  $\angle C9–H9C\cdots Se1 = 153.6^\circ$ ), forming layers parallel to the *ab* plane (Fig. S4). Furthermore, the 2D networks are linked together by unconventional weak intermolecular C–H $\cdots$ H–C hydrogen-hydrogen bonds ( $dH7C\cdots H8C = 2.37$  Å,  $\angle C7–H7C\cdots H8C = 160.2^\circ$ ;  $\angle C8–H8C\cdots H7C = 161.4^\circ$ ) and other weak van der Waals interactions to generate an extended 3D architecture along the *a* axis (Fig. S5).

As expected cluster **2** possesses 8 seps, similar to **1**. This is because of the similar electronic bonding properties of  $[Fe(CO)_3]$  fragment in **2**, which is isolobal to  $[Cp^*Co]$  fragment

in **1**. Therefore, in order to analyze the effect of the metal fragment in these species, the DFT computed molecular orbital diagram of compound **2** was analyzed and compared to that of **1**. The HOMO-LUMO energy gap computed at the PBE0 level for **2**, ca. 4.09 eV, is consistent with its high thermodynamic stability. In comparison to **1**, **2** is even more stable owing to the larger HOMO-LUMO gap (Fig. 3). Moving from **1** to **2**, i.e., replacement of one Cp\*Co unit by the isolobal fragment [Fe(CO)<sub>3</sub>], shows some energy stabilization of the LUMOs and HOMOs, particularly the latter leading to an energy gap between the frontier orbitals higher by ca. 0.22 eV in **2**. Overall, the metal/nonmetal character is similar in **1** and **2**. However, we note that in **2**, both LUMOs and HOMOs are more distributed over the cobalt atom.

Finally, natural bond order (NBO) calculations were carried out to analyze possible through-space metal-metal interactions in these compounds. The very weak computed Wiberg bond indices (WBI) on the natural atomic orbital (NAO) basis of 0.031 for Co-Co interaction in **1** and 0.034 for Co-Fe interaction in **2** clearly indicate the absence of bonding interaction between the metal atoms.

## Conclusions

Results described herein demonstrate the synthesis of the “open cage” triple-decker molecule [(Cp\*Co)<sub>2</sub>B<sub>2</sub>H<sub>2</sub>Se<sub>2</sub>] and its [Cp\*CoFe(CO)<sub>3</sub>B<sub>2</sub>H<sub>2</sub>Se<sub>2</sub>] derivative. Both are *nido* pentagonal bipyramids expected according to the Wade-Mingos electron counting rules. The thermodynamic stability of these species is confirmed by DFT calculations, which show large HOMO-LUMO gaps. This work opens a new area for the synthesis of other metallaheteroboranes.

## Experimental Section

### General Procedures and Instrumentation

All the operations were conducted using standard Schlenk techniques under an Ar/N<sub>2</sub> atmosphere. Solvents were pre-distilled under Argon. All other reagents Cp\*H, CoCl<sub>2</sub>, n-BuLi in hexane, [LiBH<sub>4</sub>·thf], Se powder and [Fe<sub>2</sub>(CO)<sub>9</sub>] (Aldrich) were used as received. [Cp\*CoCl]<sub>2</sub><sup>23</sup> and the external reference, [Bu<sub>4</sub>N(B<sub>3</sub>H<sub>8</sub>)],<sup>24</sup> for <sup>11</sup>B NMR were synthesized by literature methods. Thin layer chromatography was carried out on 250 mm aluminum-supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded with a 400 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, CDCl<sub>3</sub>, 7.26), while a sealed tube containing [Bu<sub>4</sub>N(B<sub>3</sub>H<sub>8</sub>)] in C<sub>6</sub>D<sub>6</sub> (<sup>11</sup>B, ppm, -30.07) was used as an external reference for the <sup>11</sup>B NMR. Mass spectra were recorded on Bruker Micro TOF – II mass spectrometer. Infrared spectra were obtained on a Nicolet iS10 IR spectrometer.

**Synthesis of [(Cp\*Co)<sub>2</sub>B<sub>2</sub>H<sub>2</sub>Se<sub>2</sub>], **1**.** Into a pre-dried Schlenk tube a brown solution of [Cp\*CoCl]<sub>2</sub> (0.2 g, 0.44 mmol) in dry toluene (12 cm<sup>3</sup>) [LiBH<sub>4</sub>] (0.6 ml, 1.09 mmol) was added *via* syringe at -70 °C and allowed to stay for half an hour after addition of [LiBH<sub>4</sub>] and slowly warmed to room temperature. Then Se powder (0.06 g, 0.8 mmol) was added to the deep brown solution and the mixture was heated at 90 °C for 18 hours. Solvent was evacuated and the residue was extracted into hexane - CH<sub>2</sub>Cl<sub>2</sub> (70:30) and passed through Celite. After removal of solvent the resulting solid was separated by TLC on silica gel TLC plates. Elution with hexane-CH<sub>2</sub>Cl<sub>2</sub> (85:15 v/v) yielded violet [(Cp\*Co)<sub>2</sub>B<sub>2</sub>H<sub>2</sub>Se<sub>2</sub>], **1** (0.08 g, 30%), known

brown [(Cp\*Co)<sub>2</sub>B<sub>4</sub>H<sub>6</sub>], (0.02 g, 10%) and yellow [(Cp\*Co)<sub>3</sub>B<sub>4</sub>H<sub>4</sub>], (0.04 g, 20%).

**1:** MS (MALDI): m/z 571 [M]<sup>+</sup>; isotope envelope C<sub>20</sub>H<sub>32</sub>B<sub>2</sub>Co<sub>2</sub>Se<sub>2</sub>: requires 571. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 22 °C): δ = 33.5 (br, 2B), <sup>1</sup>H NMR (22 °C, 400 MHz, CDCl<sub>3</sub>): δ = 3.76 (br, 1H, 1BH<sub>i</sub>), 3.67 (br, 1H, 1BH<sub>i</sub>), 1.65 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), <sup>13</sup>C NMR (22 °C, 100 MHz, CDCl<sub>3</sub>): δ = 105.2 (s, C<sub>5</sub>Me<sub>5</sub>), 10.7, (s, C<sub>5</sub>Me<sub>5</sub>). IR (cm<sup>-1</sup>): 2413w (B-H<sub>i</sub>).

**Synthesis of [Cp\*CoFe(CO)<sub>3</sub>B<sub>2</sub>H<sub>2</sub>Se<sub>2</sub>], **2**.** In a flame-dried Schlenk tube, compound **1** (0.01 g, 0.015 mmol) was dissolved in hexane (10 ml) and [Fe<sub>2</sub>(CO)<sub>9</sub>] (0.01 g, 0.028 mmol) was added to the solution. The reaction mixture was allowed to stir at room temperature for two hours. Solvent was removed and the solid was extracted into hexane - CH<sub>2</sub>Cl<sub>2</sub> (50:50) and passed through Celite. After removal of solvent, the residue was purified on silica gel TLC plates. Elution with a hexane-CH<sub>2</sub>Cl<sub>2</sub> (90 : 10 v/v) mixture yielded air-stable brown [(Cp\*Co)Fe(CO)<sub>3</sub>B<sub>2</sub>H<sub>2</sub>Se<sub>2</sub>], **2** (0.004 g, 42%).

**2:** MS (MALDI): m/z 517 [M]<sup>+</sup>; isotope envelope C<sub>13</sub>H<sub>17</sub>B<sub>2</sub>CoFeO<sub>3</sub>Se<sub>2</sub>: requires 517. <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>, 22 °C): δ = 31.2 (br, 2B), <sup>1</sup>H NMR (22 °C, 400 MHz, CDCl<sub>3</sub>): δ = 3.92 (br, 1H, 1BH<sub>i</sub>), 3.85 (br, 1H, 1BH<sub>i</sub>), 1.77 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), <sup>13</sup>C NMR (22 °C, 100 MHz, CDCl<sub>3</sub>): δ = 107.6 (s, C<sub>5</sub>Me<sub>5</sub>), 10.9, (s, C<sub>5</sub>Me<sub>5</sub>). IR (cm<sup>-1</sup>): 2434w (B-H<sub>i</sub>), 2063, 2021, and 1998 (terminal C-O stretching).

### X-ray crystal structure determinations of **1** and **2**

For each compound, a crystal of appropriate size and shape was selected, coated in Paratone-N oil, and mounted on a Kapton loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow at low-temperature. Crystal data for **1** and **2**, were collected at 150(2) K on a Bruker APEXII AXS diffractometer, equipped with a CCD detector, using Mo K<sub>α</sub> radiation (λ = 0.71073 Å). The structures were solved by direct methods using the SIR97<sup>25</sup> program and then refined with full-matrix least-squares methods based on F<sup>2</sup> (SHELXL-97),<sup>26</sup> with the aid of the WINGX program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters, except boron-linked hydrogen atoms that were introduced into the structural model through Fourier difference map analysis. Hydrogen atoms were finally included in their calculated positions.

*Crystal data for 1.* CCDC 1058306, C<sub>20</sub>H<sub>32</sub>B<sub>2</sub>Co<sub>2</sub>Se<sub>2</sub>, M<sub>r</sub> = 569.86, monoclinic, space group P2<sub>1</sub>/c, a = 10.3512(8) Å, b = 16.2372(10) Å, c = 14.1030(9) Å, V = 2226.5(3) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.7 g cm<sup>-3</sup>, μ = 4.761 mm<sup>-1</sup>, F(000) = 1136, R<sub>1</sub> = 0.0485, wR<sub>2</sub> = 0.1333, 7447 independent reflections [2θ ≤ 63.18°] and 245 parameters.

*Crystal data for 2.* CCDC 1058307, C<sub>13</sub>H<sub>17</sub>B<sub>2</sub>CoFeO<sub>3</sub>Se<sub>2</sub>, M<sub>r</sub> = 515.59, monoclinic, space group P2<sub>1</sub>/n, a = 8.2464(4) Å, b = 23.0294(11) Å, c = 9.6550(5) Å, β = 108.887(2)°, V = 1734.86(15) Å<sup>3</sup>, Z = 4, ρ<sub>calcd</sub> = 1.974 g cm<sup>-3</sup>, μ = 5.993 mm<sup>-1</sup>, F(000) = 1000, R<sub>1</sub> = 0.0435, wR<sub>2</sub> = 0.0912, 12271 independent reflections [2θ ≤ 54.96°] and 210 parameters.

### Computational details

Quantum chemical calculations were performed on compounds **1**, **2** and model compounds [(Cp\*Co)<sub>2</sub>B<sub>2</sub>H<sub>2</sub>S<sub>2</sub>] and [{Fe(CO)<sub>3</sub>}<sub>2</sub>B<sub>2</sub>H<sub>2</sub>Se<sub>2</sub>] using density functional theory (DFT) as implemented in Gaussian09 program package.<sup>19</sup> All compounds were fully optimized in gaseous state (no solvent effect) with and without symmetry constraints using the PBE0 functional<sup>27</sup> and with a triple- $\zeta$  quality basis set Def2TZVP for all atoms. The NMR chemical shifts ( $\delta$ ) were computed by using the gauge-including atomic orbitals (GIAOs) approximation.<sup>28</sup> The projected <sup>11</sup>B chemical shielding values, determined at PBE0/Def2TZVP level of calculations, were referenced to B<sub>2</sub>H<sub>6</sub> (PBE0/Def2TZVP, B shielding constant 89.5 ppm), and these chemical shift values ( $\delta$ ) were then converted to the standard BF<sub>3</sub>.OEt<sub>2</sub> scale using the experimental value of +16.6 ppm for B<sub>2</sub>H<sub>6</sub>. <sup>1</sup>H chemical shifts were referenced to TMS. The AOMix prograde<sup>29</sup> was used for the MO composition analysis. Wiberg bond indices (WBI)<sup>30</sup> were obtained from a natural bond orbital (NBO)<sup>31</sup> analysis.

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### Notes and references

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Electronic Supplementary Information (ESI) available: For crystal packing diagrams for **1** and **2**; CCDC reference numbers 1058306-1058307 or other electronic format see DOI: 10.1039/b000000x/

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### Table of Content Entry Only

## Synthesis and chemistry of the open-cage cobaltaheteroborane cluster $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\}_2\text{B}_2\text{H}_2\text{Se}_2]$ : A combined experimental and theoretical study

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An open cage triple-decker molecule with three planar rings almost parallel to each other (see picture).

