Article

Metal-Rich Metallaboranes: Synthesis, Structures and Bonding of Bi- and Trimetallic Open-Faced Cobaltaboranes

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Abstract: Synthesis, isolation, and structural characterization of unique metal rich cobaltaborane clusters are reported. They were obtained from reactions of monoborane as well as modified borohydride reagents with cobalt sources. For example, the reaction of $[Cp*CoCl]_2$ with $[LiBH_4 \cdot THF]$ and subsequent photolysis with excess $[BH_3 \cdot THF]$ (THF = tetrahydrofuran) at room temperature afforded the 11-vertex tricobaltaborane *nido*-$[(Cp*Co)_3B_8H_{10}]$ (**1**, $Cp* = \eta^5\text{-}C_5Me_5$). The reaction of $Li[BH_2S_3]$ with the dicobaltaoctaborane(12) $[(Cp*Co)_2B_6H_{10}]$ yielded the 10-vertex *nido*-2,4-$[(Cp*Co)_2B_8H_{12}]$ cluster (**2**), extending the library of dicobaltadecaborane(14) analogues. Although cluster **1** adopts a *classical* 11-vertex-*nido*-geometry with one cobalt center and four boron atoms forming the open pentagonal face, it disobeys the Polyhedral Skeletal Electron Pair Theory (PSEPT). Compound **2** adopts a perfectly symmetrical 10-vertex-*nido* framework with a plane of symmetry bisecting the basal boron plane resulting in two {CoB$_3$} units bridged at the base by two boron atoms and possesses the expected electron count. Both compounds were characterized in solution by multinuclear NMR and IR spectroscopies and by mass spectrometry. Single-crystal X-ray diffraction analyses confirmed the structures of the compounds. Additionally, density functional theory (DFT) calculations were performed in order to study and interpret the nature of bonding and electronic structures of these complexes.

Keywords: cobaltaborane; decaborane; eleven-vertex cluster; *nido* cluster; metallaborane; mixed-metal cluster; ten-vertex cluster

1. Introduction

Polyhedral cage expansion for the synthesis of large clusters has been the objective of boron-rich metallaborane and metallacarborane chemistry over the last six decades [1–6]. Molecular boron-rich clusters have found their place in many fields ranging from ceramics and polymers to boron neutron capture therapy and nanomaterials [7–10]. Those applications along with more fundamental studies of their specific and somewhat unique bonding and electronic structures have been the driving force towards the development of this chemistry [7,11,12]. In particular, following the pioneering work of Hawthorne et al. [13], several groups such as those of Evans [14], Welch [15], Xie [16,17], and ours [18–20] have contributed in enriching the library of the large 12–16 vertex single cage polymetalla(hetero)borane clusters over the years. The already extensive array of metal-laborane clusters continues to grow in direct proportion with the advent of novel synthetic methods [9,11,17,21–33]. However, it is difficult to come up with an integrated scheme aimed at the synthesis of polyhedra bearing definite geometry and composition. This is largely due to the undefined and uncontrolled nature of cluster growth from metal synthons or small preformed clusters. Even the most sought-after strategies like

condensation involving monoborane reagents, insertion or fragmentation involving borane or metal carbonyl fragments and cluster fusion [34] rarely exhibit metallaboranes with a high metal−to−boron ratio [35–39].

Among the several strategies aimed towards cluster expansion that have been conceived over the years, the reaction of cyclopentadienyl halides or hydrides with monoborane reagents such as BH₃·THF (THF = tetrahydrofuran), [BHCl₂·SMe₂], or [LiBH₄·THF], is a strategy that has been thoroughly optimized [40,41] and has proven to be very useful for yielding a variety of higher vertex metallaborane clusters adopting unique polyhedral cage geometries and structural features [41–45]. Although, in most cases, the metallaboranes are generated in small yields with a low metal−to−boron ratio, it was the strategy that involved pyrolyzing [Cp*RhCl₂]₂ in large excess of [BH₃·THF], that allowed us to isolate 15- and 16-vertex rhodaborane clusters [18]. Although fused clusters [46] or single cage clusters bearing 5–11 vertices are reported with the cobalt system [20,46–52], isolation of analogous single cage supraicosahedral cobaltaboranes has not been successful up until now despite the fact that both rhodium and cobalt are group-9 metals. Indeed, our recent reports include the formation of a range of high-nuclearity cobaltaborane clusters, such as the hypoelectronic 9-vertex *closo*-[(Cp*Co)₂B₇H₆OMe], hypoelectronic octadecahedral 11-vertex *closo*-[(Cp*Co)₃B₈H₇R] (R = H or Me), and icosahedral 12-vertex *closo*-[(Cp*Co)₃B₈H₈S] species obtained from the reaction of [Cp*CoCl]₂ with [LiBH₄·THF] and subsequent thermolysis with 2-mercaptobenzothiazole in toluene [50]. Our renewed quest for higher nuclearity cobaltaboranes made us look for modified synthetic strategies and although the objective of isolating a single cage supraicosahedral cobaltaborane was not achieved, the treatment of [Cp*CoCl]₂ with [LiBH₄·THF] followed by photolysis with excess BH₃·THF afforded the 11-vertex-(hyper)*nido*-[(Cp*Co)₃B₈H₁₀] cluster (**1**). Group-9 metallaboranes have continually monopolized the field not only for novelty in geometries but also for the possibility to draw on the open cage molecules like [(Cp*M)₂B₆H₁₀] [M = Co and Rh] and [(Cp*Rh)₂B₈H₁₂] for further reactivities [53]. We have ourselves contributed significantly to this area by enriching the library of mono- and dicobaltadecaborane(14) analogues in the past [50–52]. Most recently, we have explored and reported the chemistry of dicobaltaoctaborane(12) with chalcogenated borohydride, Li[BH₂E₃] [E = S, Se, or Te] which resulted in the characterization of novel chalcogenated analogues of dicobaltadecaborane(14) [54]. Careful analysis of the reaction between [(Cp*Co)₂B₆H₁₀] and Li[BH₂S₃] led to the isolation of 2,4-[(Cp*Co)₂B₈H₁₂] (**2**), a new dicobaltadecaborane(14) analogue. The main results are presented in this article.

2. Results and Discussion

2.1. Reaction of (Cp*CoCl)₂ with [LiBH₄·THF] and [BH₃·THF]

The reaction of [Cp*CoCl]₂ with an eight-fold excess of [LiBH₄·THF] followed by photolysis with excess of BH₃·THF at room temperature for 16 h led to the formation of a green crystalline solid in 10% yield which was characterized as a novel open-faced 11-vertex cobaltaborane, (hyper)*nido*-[(Cp*Co)₃B₈H₁₀] (**1**). The reaction also yielded cobaltaboranes reported in the recent past like [(Cp*Co)₂B₆H₁₀] and [(Cp*Co)B₉H₁₄] [52] (Scheme 1) and a few other compounds which could not be isolated due to lesser yields and transient natures. Preparative thin-layer chromatography (TLC) allowed separation of **1** from the reaction mixture and hence enabled the characterisation of the pure compound. Multinuclear NMR (see Figures S1−S4 for spectra) and IR spectroscopies and solid-state structure determination by X-ray diffraction analysis helped establish the composition and structure of **1**. A detailed account of the spectroscopic and structural characterizations of **1** follows.

[(Cp*Co)₃B₈H₁₀], **1**. The room temperature ¹¹B{¹H} NMR of **1** shows the presence of four resonances between 71.4 and 19.7 ppm. The ¹H{¹¹B} NMR spectrum of **1** suggests the existence of two different Cp* environments appearing at 1.9 and 1.7 ppm with a relative ratio of 1:2. This is also corroborated by the ¹³C{¹H} NMR spectrum. In addition to the

chemical shifts corresponding to B-H_t protons, the ^{1}H{^{11}B} NMR spectrum also shows a sharp upfield resonance in the hydride region at δ = −20.43 ppm which may typically be arising due to two equivalent Co-H-B protons. The infrared (IR) spectrum shows broad bands around 2438 cm^{-1} owing to stretching frequencies of the terminal B-H_t bonds. Although the spectroscopic data indicated the formation of a large cluster, they were not sufficient to help conceptualize the actual identity of **1**. A clear identification was obtained only after the crystal structure determination of **1** which was carried out with crystals obtained by slow evaporation of a concentrated hexane/CH$_2$Cl$_2$ (90:10) solution of **1** kept at −10 °C.
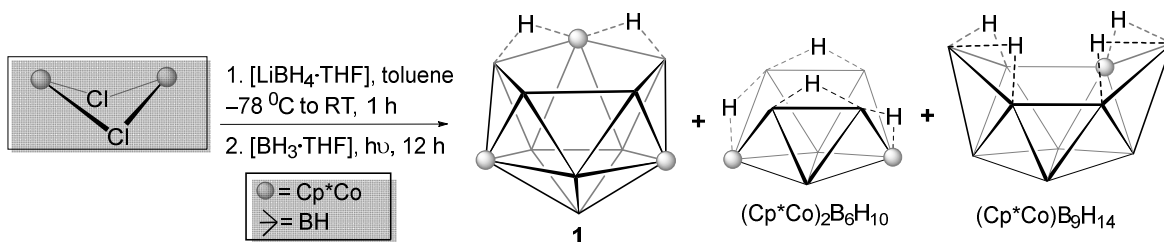
Scheme 1. Synthesis of the open-faced tricobaltaborane cluster **1**.

The molecular structure of **1** (Figure 1) adopts a classical 11-vertex *nido* core that can be formally generated by the removal of an apical vertex of the ubiquitous 12-vertex icosahedron (Figure 2). The molecule has two minor disordered components with atoms B8 and B8′, each with 50% occupancy. Despite the lack of precision in some of the bond distances and angles of the cluster owing to the restraints set to resolve this disorder, the crystallographic data reasonably allow a clear determination of the structure. Only one of the residues (with B8′) is discussed and shown in Figure 1. The five atoms of the open face (Co1, B4, B5, B7, and B8′) of the cluster are four-connected vertices while the remaining six ones are all five-connected vertices (Figure 1). This is in agreement with the NMR results discussed above which indicate that the higher chemical shifts in the ^{11}B NMR spectrum corresponds to the high connected B atoms with the chemical shifts for B1 and B2 accidentally eclipsing at 71.4 ppm thus displaying four resonances in the ratio 2:2:2:2. A crystallographic mirror plane passing through the atoms Co1, B1, and B2 bisects the molecule into two symmetrical entities, thereby rendering the chemical environments of Cp* ligands attached to Co2 and Co3 as equivalent.

The polyhedral cage geometry of cluster **1** looks reminiscent of that of classical 11-vertex *nido* geometry of related clusters such as [C$_2$B$_9$H$_{11}$]$^{2-}$, [(Cp*Rh)$_3$B$_8$H$_9$(OH)$_3$] [55], [*nido*-7,8,9-PC$_2$B$_8$H$_{11}$] [56], [8,8-η^2-{η^2-(BH$_3$)·dppm}-*nido*-8,7-RhSB$_9$H$_{10}$] [57], [9,9-η^2-{η^2-(BH$_3$)·dppm}-*nido*-9,7,8-RhC$_2$B$_8$H$_{11}$] [57], and [(μ-PPh$_2$)(PPh$_3$)$_2$Pt$_2$B$_9$H$_6$(O^{i}Pr)$_3$] [58] for instance which all possess 13 skeletal electron pairs (SEP), i.e., (*n* + 2) SEPs if *n* is the number of occupied vertices according to the Polyhedral Skeletal Electron Pair Theory (PSEPT) [59]. Interestingly, however, with only 12 skeletal electron pairs (SEPs), cluster **1** is two electrons short of the formal (*n* + 2) SEP count expected for *nido* clusters as required by the PSEPT [59]. As stated earlier, in addition to the BH_t and Cp* protons, the ^{1}H{^{11}B} NMR spectrum shows the presence of only a single resonance for two bridging Co-H-B protons. The presence of two B-H-B protons which would have afforded a *nido* species with the "expected" electron count could not be traced from ^{1}H NMR.
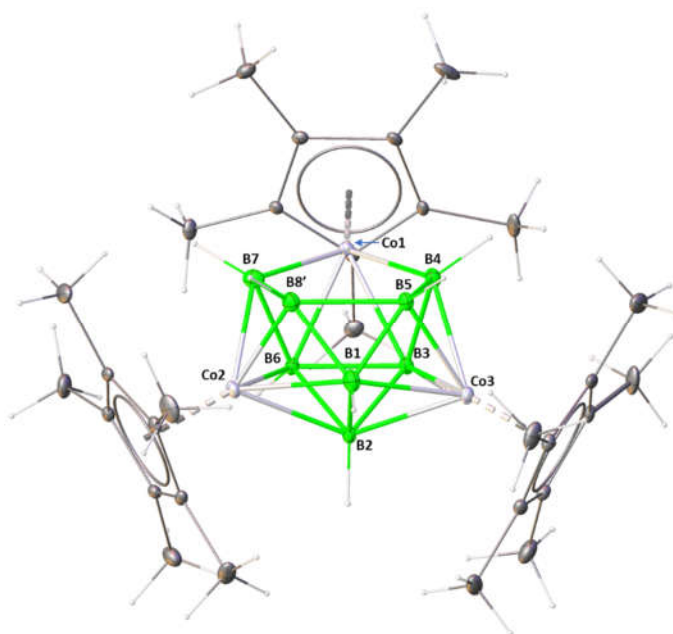
Figure 1. Molecular structure and atom labels of one of the residues of **1**. Selected bond lengths (Å) and bond angles (°) of **1**: B1–B2 1.82(2), B1–Co3 2.051(14), B1–Co2 2.063(16), B2–Co3 2.084(13), B6–B7 1.78(2), B4–Co1 2.067(14), B7–Co1 2.030(14), B7–B8'–B5 113.0(17), and B7–Co1–B4 87.4(6). Co–*H*–B bridging hydrogens could not be located.
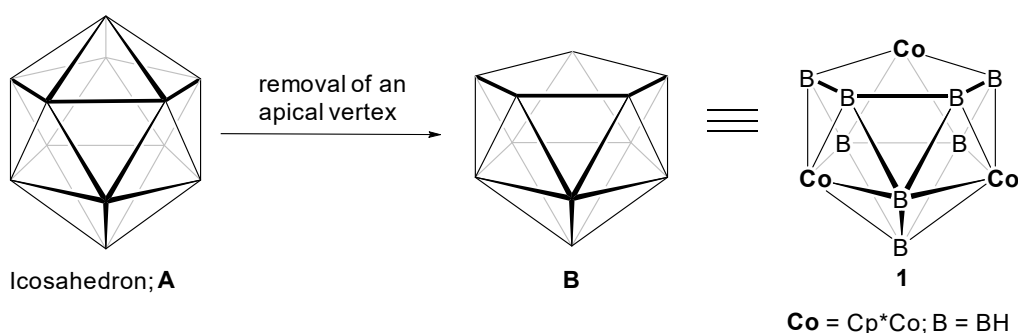

Figure 2. Schematic representation of stepwise generation of the cluster framework of **1** (**B**) from an icosahedron (**A**).

To the best of our knowledge cluster **1** is the first example of electron-poor 11-vertex−12-SEP (hyper)*nido* species of this kind in the metallaborane cluster domain. Nevertheless, isoelectronic and isostructural examples are known in metallacarborane chemistry. Indeed, cluster **1** can be compared both electronically and structurally to some 11-vertex−12-SEP *nido* clusters such as [9,9-L_2-*nido*-9,7,8-$MC_2B_8H_{11}$] (**I**: L= PPh_3, M = Ir; **II**: L = PEt_3, M = Rh) [60] and [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**III**) [61,62] (Chart 1). 11-vertex−12-SEP metalla(hetero)borane compounds exist such as [1-PPh_3-{1,3-(μ-dppm)}-*isonido*-1,2-$RhSB_9H_8$] [**IV**; dppm = $CH_2(PPh_2)_2$] [63,64], or [1,1,1-(H)$(PMe_3)_2$-*isonido*-1,2-$IrSB_9H_9$] (**V**) [65] (Figure 3), but they are not isostructural with **1**. While the latter is generated from the icosahedron by removing one vertex (Figure 2), the geometry reported for the 11-vertex *isonido* clusters [63–65] is derived from an 11-vertex octadecahedron by the removal of one connectivity of the apical vertex thereby generating a distorted quadrilateral open face (**D**; top of Figure 3).
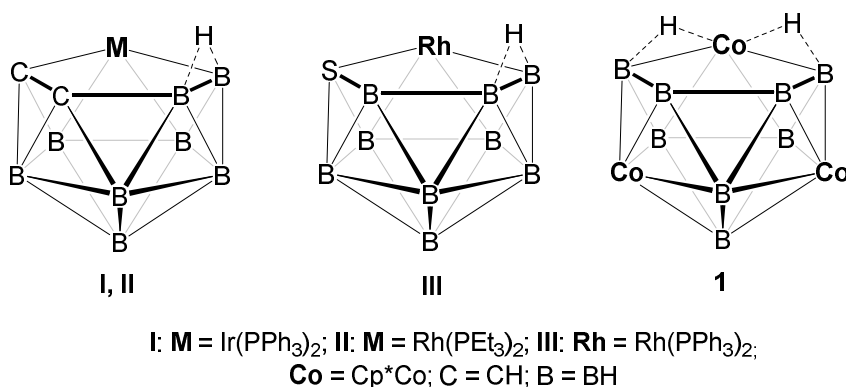
I: **M** = Ir(PPh₃)₂; II: **M** = Rh(PEt₃)₂; III: **Rh** = Rh(PPh₃)₂;
Co = Cp*Co; C = CH; B = BH

Chart 1. Examples of 11-vertex−12-SEP (skeletal electron pairs) *nido*-metalla(hetero)borane clusters.
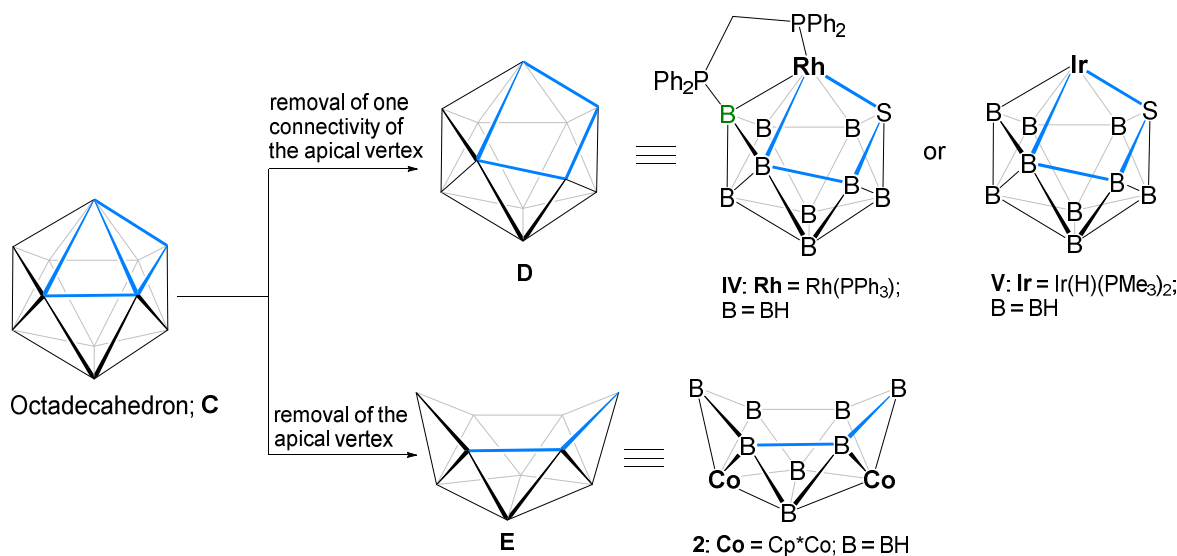

Figure 3. Schematic representation of stepwise generation of the 11-vertex *isonido* (**D**) and 10-vertex *nido* (**E**) cluster frameworks from an octadecahedron (**C**) and their examples.

Density functional theory (DFT) calculations were carried out at the B3LYP/LANL2DZ level of theory (see computational details in Section 3) on model compound **1′** (Cp analogue of **1**) to analyse the electronic structure and nature of bonding in the electron deficient molecule **1**. Optimized bond distances in **1′** are in accordance with those experimentally measured for the solid-state structure of **1** (Table S1). The molecular orbital (MO) analysis of **1′** (Table S2) shows a large energy gap of 2.79 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in agreement with the electron count of 12 SEPs and the fact that only two bridging hydrogen atoms are present in the structure. The HOMO of **1′** is mainly localized on the metal centres and the five-connected inner-core boron atoms, whereas the LUMO is predominantly localized on the metal centres with considerable participation of the boron atoms of the open face of the cluster (Figure 4). We may wonder if cluster **1** could be reduced and reach the expected count of 13 SEPs to obey the PSEPT. It turns out that the LUMO + 1 is energetically close to the LUMO, separated only by 0.4 eV. This indicates that reduction of **1** is unlikely.
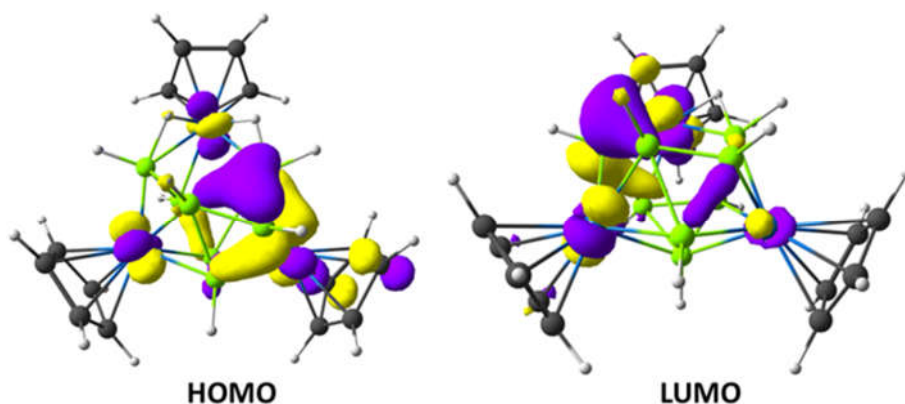
Figure 4. Frontier molecular orbitals of **1'**. Contour value: ±0.05 [e/bohr³]^½.

2.2. Reactivity of [(Cp*Co)$_2$B$_6$H$_{12}$] with Li[BH$_2$S$_3$]

Reactions of the open-cage dicobaltaoctaborane(12) analogue [(Cp*Co)$_2$B$_6$H$_{12}$] with chalcogenated borohydride Li[BH$_2$E$_3$] (E = S, Se, or Te) which were recently carried out in our group, resulted in the formation of novel chalcogenated analogues of dicobaltadecaborane(14), namely [(Cp*Co)$_2$B$_6$E$_2$H$_6$] (E = S, Se, or Te) [54]. The room temperature reaction between [(Cp*Co)$_2$B$_6$H$_{12}$] and Li[BH$_2$S$_3$] yielded another compound which could not be isolated earlier due to less yield. Performing the reaction at a larger scale followed by careful analysis of the reaction mixture led to the isolation of 2,4-[(Cp*Co)$_2$B$_8$H$_{12}$] (**2**), i.e., a novel dicobaltadecaborane(14) analogue (Scheme 2). This compound was characterized by ^{1}H, ^{11}B{^{1}H} and ^{13}C{^{1}H} NMR (Figures S5−S8) and IR spectroscopies, mass spectrometry (Figure S9), and single-crystal X-ray diffraction analysis.
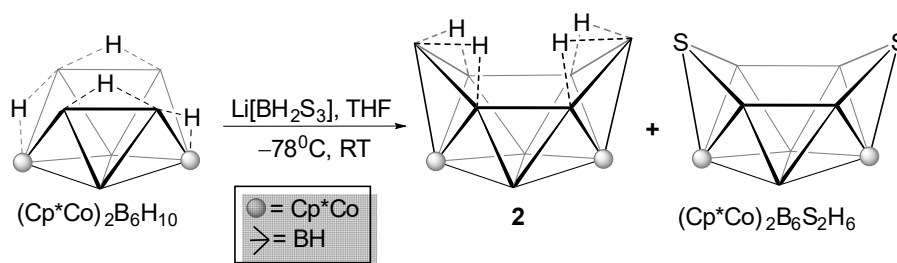
Scheme 2. Synthesis of a symmetric dicobaltaborane analogue of decaborane(14).

Dicobaltadecaborane(14) analogue, **2**. Cluster **2** was isolated as a yellow solid in 15% yield. The mass spectrometric data for **2** showed molecular ion peaks at m/z 487.2692 which corresponds to the molecular formula [C$_{20}$H$_{42}$B$_8$Co$_2$]$^+$. The ^{11}B{^{1}H} NMR showed chemical shifts at δ = 26.6, 11.4, and 5.6 ppm, whereas ^{1}H NMR showed a single chemical shift for 30 Cp* protons at δ = 1.69 ppm, and additionally, chemical shifts at δ = 4.38, 2.94, and 2.31 ppm which correspond to B-H_t protons. A distinct up-field resonance was observed at δ = −4.25 ppm which may be assigned to four equivalent B-H-B bridging protons. The chemical shifts displayed in the ^{13}C{^{1}H} NMR spectrum also corroborated with a single Cp* environment in the molecule. The infrared (IR) spectrum showed broad bands centered around 2493 cm^{-1} owing to stretching frequencies of the terminal B-H bonds.

Slow evaporation of a concentrated hexane/CH$_2$Cl$_2$ (80:20) solution of **2** kept at −10 °C yielded crystals suitable for X-ray diffraction analysis. The solid-state X-ray structure of **2** (Figure 5), determined by single-crystal X-ray diffraction measurements clearly shows that it is a 10-vertex open *nido*-dicobaltaborane which is in absolute agreement with the

spectroscopic as well as mass spectrometric data. It is apparent from its solid state X-ray structure that compound **2** adopts the same structural arrangement as the symmetric dimetalla *nido*-2,4-[(Cp*M)$_2$B$_8$H$_{12}$] (M = Rh and Ir) [27,55] previously reported, analogues of decaborane(14). In the structure, a crystallographic mirror plane including the B6-B8 vector bisects the molecule into two equivalent {CoB$_3$} units. As a result, the two Co atoms that reside on either side of the crystallographic mirror plane are chemically equivalent and hence correspond to the presence of single Cp* environment in the ^{1}H and ^{13}C{^{1}H} NMR spectra. The bridging hydrogen atoms lie on the open face of the six-membered ring and their presence is confirmed both by ^{1}H NMR and X-ray diffraction studies. We noted that the average B-B bond length in **2** is somewhat shorter as compared to the Rh and Ir analogues [27,55] and follows the trend (Co < Rh < Ir) down the triad. A {Cp*Co} unit being isolobal with a BH unit, the cluster is isostructural and isoelectronic with nido-decaborane(14) which can be generated from the removal of the six-connected apical vertex of an octadecahedron (see bottom of Figure 3). Indeed, **2** can be regarded as a 10-vertex nido metallaborane cluster with 12 SEPs, as expected according to the PSEPT. **2** is then a new member of the series of ten-vertex−12-SEP polyhedral borane, carborane, or metallaborane clusters having the same SEP count and geometry. We have tried to compare its structural data and chemical shift values with a set of comparable cobaltaboranes with the formal electron count of 12 SEPs (Table 1). The unique feature of this reaction here (Scheme 2) is the insertion of two BH units in octaborane(12) that leads to cluster growth from 8 to 10 vertices.
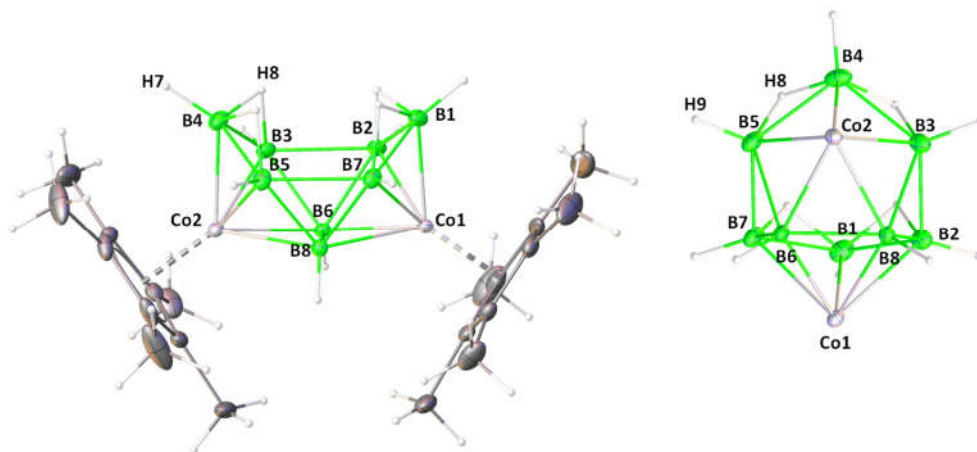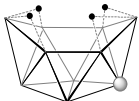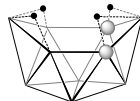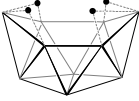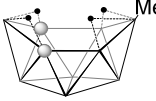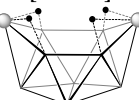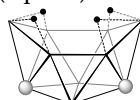

Figure 5. Molecular structure and atom labels for **2**: frontal view (left) and bottom angular view (right, Cp* ligands attached to Co are omitted for clarity). Selected bond lengths (Å) and bond angles (°): B1–Co1 1.972(5), B2–B3 1.971(7), B2–Co1 2.043(5), B3–B4 1.807(8), B3–Co2 2.043(4), B5–Co2 2.041(5), B7–Co1 2.046(4), B3–B2–Co1 115.5(2), B4–B3–B2 116.3(4), B3–B4–B5 103.9(3), and B2–Co1–B7 89.1(2).

Table 1. Selected structural and spectroscopic parameters of 10-vertex−12-SEP *nido*-cobaltaborane clusters. [a]

Geometry	d(B-B)$_{av}$ [Å]	^{11}B NMR (δ,ppm)	Ref.	Geometry	d(B-B)$_{av}$ [Å]	^{11}B NMR (δ,ppm)	Ref.
6-[(Cp*Co)B$_9$H$_{13}$]	1.78	20.5, 15.4, 5.2, −1.2, −12.4, −29.8	[47]	3,5-[(Cp*Co)$_2$B$_8$H$_{12}$]	1.80	42.4, 30.1, 25.3, 20.1, 9.1, 6.3, −1.2, −12.9	[52]
5-[(Cp*Co)B$_9$H$_{13}$]	1.78	29.4, 27.1, 12.5, 4.1, 3.5, 1.7, −1.1, −14.5, −36.9	[52]	6-Cl-5,7-[(Cp*Co)$_2$B$_8$H$_{12}$]	-	49.9, 23.1, 19.4, 7.1, −7.1, −40.7	[47]

Cluster				Cluster		
2-[(CpCo)B₉H₁₃]	-	17.0, 14.6, 9.0, 1.7, −38.2	[49]	5,7-[(Cp*Co)₂B₈H₁₂]	1.80	57.3, 24.4, 6.0, −7.4, 40.3	[47]
[B₁₀H₁₄]	1.78	11.7, 9.7, 0.28, −36.5	[66]	[(Cp*Co)₂B₈H₁₁] Me	1.76	54.0, 29.7, 22.2, 8.7, 3.3, −40.1	[51]
6,9-[(Cp*Co)₂B₈H₁₂]	2.02	20.8, 2.3	[47]	2,4-[(Cp*Co)₂B₈H₁₂]	1.81	26.6, 11.4, 5.6	This wok

a ◯ = Cp*Co; ⟩ = BH; • = H.

In order to acquire an insight into the structure and bonding of **2**, we further did DFT calculations at the B3LYP/LANL2DZ level of theory (see computational details in Section 3 on model **2′** (Cp analogue of **2**) as well as on its group-9 metallaborane model analogues **3′** (Cp analogue of 2,4-[(Cp*Rh)₂B₈H₁₂] and **4′** (Cp analogue of 2,4-[(Cp*Ir)₂B₈H₁₂]) for comparison. The optimized geometrical parameters obtained for **2′** compare fairly well with the corresponding crystallographically characterized data of **2** (Table S1). Additionally, the gauge-including atomic orbitals-density functional theory (GIAO-DFT calculated ¹¹B chemical shift values agree well with those observed experimentally (Table 2) and are of sufficient accuracy to confirm assignments that are consistent with the empirical ones based simply on boron connectivity and environment (see above).

A molecular orbital analysis suggests a significant HOMO-LUMO energy gap (> 4 eV) for the three compounds in the order **2′** < **3′** < **4′** (Figure 6). Inspection of the nodal properties of the frontier MOs reveals that HOMOs weigh heavily on the respective metal centres, while the LUMOs are delocalized both on the metal centres and the five-connected inner-core boron atoms. Metal−metal Wiberg bond indices computed for **2′**, **3′**, and **4′** are very weak and close to each other (ca. 0.06), reflecting the nonappearance of bonding interaction between the metal centres in such species.

Table 2. Experimentally observed and calculated ¹H and ¹¹B chemical shifts for **2–4** species and **2′–4′** models, respectively.

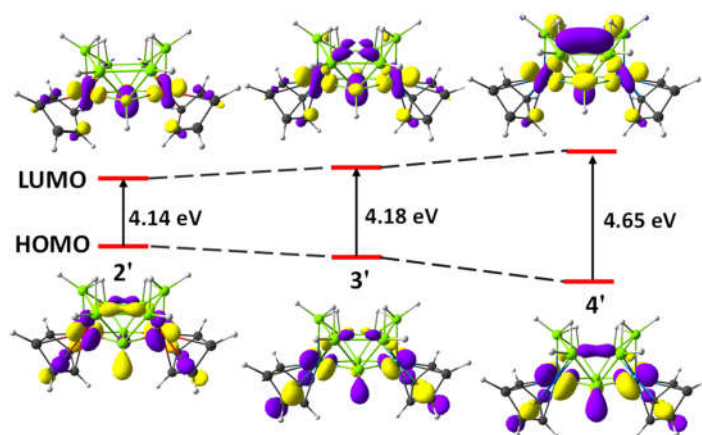| Cluster	¹H NMR δ (ppm)		¹¹B NMR δ (ppm)		Ref.
	Expt.	Calc.	Expt.	Calc.	
2/2′	−4.25	−6.22	26.6, 11.4, 5.6	20.0, 11.0, 3.0	This work
3/3′	−3.52	−5.43	21.1, 9.4, 1.9	16.2, 6.5, 0.8	56 (expt.)
4/4″	−3.73	−5.45	1.8, −0.2, −12.9	7.3, −1.7, −11.0	27 (expt.)

Figure 6. Frontier molecular orbital diagram of **2′**, **3′**, and **4′** (see text). Contour value: ±0.05 [e/bohr^3]$^{1/2}$.

3. Materials and Methods

3.1. General Methods and Instrumentation

All of the experiments were conducted under an argon atmosphere using standard Schlenk and glove-box techniques. Solvents were distilled prior to use under argon. Cp*H, CoCl$_2$, *n*-BuLi in hexane, LiBH$_4$ (2.0 M in THF), BH$_3$·THF, and S powder were used as received (Sigma Aldrich, Bangalore, India). (Cp*CoCl)$_2$ [67,68], [(Cp*Co)$_2$B$_6$H$_{10}$] [52], and Li[BH$_2$S$_3$] [69,70] were synthesized as per literature. Thin-layer chromatography, using silica gel TLC plates by Merck supported with 250-μm diameter aluminum, was done to separate the reaction mixtures. A 500 MHz Bruker FT-NMR spectrometer (Bruker, Billerica, MA, USA), JASCO FT/IR-4100 (JASCO, India) and Agilent Technologies: 6545-Q-TOF LC/MS (Agilent, Santa Clara, CA, USA) spectrometer were used respectively to record NMR, Infrared (IR) spectra, and ESI (Electrospray Ionization) mass. In ^{1}H NMR spectra, the chemical shifts for residual protons in the deuterated solvents were used as reference (CDCl$_3$, δ = 7.26 ppm, C$_6$D$_6$, δ = 7.16) while a sealed tube containing [Bu$_4$N(B$_3$H$_8$)] [71] in benzene-*d$_6$* (δ_B, ppm, −30.07) was used as an external reference for ^{11}B{^{1}H} NMR spectra. The light source for the photoreaction described in this report was Oriel Instrument with a 500 W Hg/Xe arc lamp equipped with liquid and colored glass filters, irradiating at 280–780 nm.

Synthesis of **1**: [Cp*CoCl]$_2$ (0.1 g, 0.22 mmol) was suspended in toluene (15 mL) in a flame-dried Schlenk tube and was cooled to −78°C, [LiBH$_4$·THF] (0.6 mL, 1.20 mmol) was added to it and the reaction mixture was allowed to warm slowly to room temperature and was left to stir for another hour. [BH$_3$·THF] (3 mL) was added to the reaction mixture and the resultant mixture was slowly warmed to room temperature was allowed to stir for 30 min, and finally kept for photolysis at room temperature for 12 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum and the residue was dissolved in hexane and passed through Celite. The solvent was evaporated under vacuum and the residue was purified using preparative silica-gel TLC plates by eluting with hexane/CH$_2$Cl$_2$ (80:20) mixture that yielded green solid 1 (0.010 g, 10%) and known red solids [(Cp*Co)$_2$B$_6$H$_{10}$] (0.025 g, 24%), [(Cp*Co)$_3$B$_4$H$_4$] (0.018 g, 19%), and a few compounds which could not be isolated. The known cobaltaboranes were characterized with reference to their spectroscopic data reported earlier.

1: ^{11}B NMR (160 MHz, C$_6$D$_6$, 22 °C): δ = 71.5, 31.4, 24.5, 19.7 ppm; ^{1}H{^{11}B} NMR (500 MHz, C$_6$D$_6$, 22 °C): δ = 8.08 (br, 4H, B*H$_t$*), 5.16 (s, 2H, B*H$_t$*), 4.08 (s, 2H, B*H$_t$*), 1.94 (s, 15H, Cp*), 1.70 (s, 30H, Cp*) −20.43 (br, 2H, Co-*H*-B) ppm; ^{13}C NMR (100 MHz, C$_6$D$_6$, 22 °C) = 96.0, 93.4 (*C*$_5$Me$_5$), 10.4, 9.6 ppm (C$_5$*Me*$_5$); IR (dichloromethane): $\bar{\nu}$ = 2438 (B*H$_t$*) cm^{-1}.

Synthesis of **2**: In a flame-dried Schlenk tube, [(Cp*Co)$_2$B$_6$H$_{10}$] (0.05 g, 0.107 mmol) was suspended in 5 mL of dry THF at room temperature. A freshly prepared solution of Li[BH$_2$S$_3$] in THF (10 mL, 0.428 mmol) was added dropwise to the red solution of [(Cp*Co)$_2$B$_6$H$_{10}$]. The reaction mixture was allowed to stir at room temperature for 24 h. The solvent was dried under vacuum and the residue was extracted into *n*-hexane/CH$_2$Cl$_2$ (85:15 *v/v*) mixture and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic work-up by using TLC plates. Elution with an *n*-hexane/CH$_2$Cl$_2$ (85:15 *v/v*) mixture yielded the air-stable yellow solid (Compound **2**) (0.020 g, 38%) and the known compound [(Cp*Co)$_2$B$_6$H$_6$S$_2$] (0.016 g, 28 %) [57].

2: MS (ESI+): *m/z* calculated for C$_{20}$H$_{42}$B$_8$Co$_2{}^+$ 487.2747, found 487.2692; ^{11}B NMR (160 MHz, CDCl$_3$, 22 °C): δ = 26.6, 11.4, 5.6 ppm; ^{1}H NMR (500 MHz, CDCl$_3$, 22 °C): δ = 4.38 (s, 2H, B*H$_t$*), 2.94 (s, 2H, B*H$_t$*), 2.31 (s, 4H, B*H$_t$*), 1.69 (s, 30H, Cp*), −4.25 (br, 4H, B-*H*-B) ppm; ^{13}C NMR (100 MHz, CDCl$_3$, 22 °C) = 97.0 (*C$_5$Me$_5$*), 9.8 ppm (C$_5$*Me$_5$*); IR (dichloromethane): $\bar{v}$ = 2493 (B*H$_t$*) cm^{-1}.

3.2. Single Crystal X-ray Diffraction Analysis

Crystallographic and structural refinement data for **1** and **2** are given in Table 3. Bruker AXS Kappa APEXII CCD diffractometer, (Bruker, Billerica, MA, USA) with graphite monochromatic Mo K$_\alpha$ (λ = 0.71073 Å) radiation at 296 K was used to collect and integrate crystal diffraction data. Heavy atom methods like SHELXT-2014 and SHELXS-97 [72–74] were used to solve the structures while SHELXL-2018 and SHELXL-2014 [73] were used for structure-refinements, respectively. Olex2 [75] was used for drawing molecular structures.

Table 3. Crystallographic and structural refinement data for **1** and **2**.

Compound	1	2
CCCDC No.	2043679	2060786
Empirical formula	C$_{30}$H$_{53}$B$_8$Co$_3$	C$_{20}$H$_{42}$B$_8$Co$_2$
Formula weight	676.99	486.87
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.785 (4)	8.3902 (2)
b (Å)	11.638 (6)	40.6669 (12)
c (Å)	16.993 (9)	8.5097 (2)
α (°)	96.244 (18)	90
β (°)	96.56 (2)	119.0361 (11)
γ (°)	101.532 (18)	90
Volume (Å^3)	1675.6 (15)	2538.60 (12)
Z	2	4
ρ_{calc}(g/cm^{-3})	1.342	1.274
μ (mm^{-1})	1.487	1.312
F (000)	708	1024
2θ range for data collection (°)	3.6–44.9	2–50
Independent reflections	3990	4472
Final R indices [I >= 2σ (I)]	R_1 = 0.0889, wR_2 = 0.2412	R_1 = 0.0439, wR_2 = 0.0958
Parameters	452	329

3.3. Computational Details

Gaussian 09 program package [76] was used for geometry optimizations of all model clusters. Computations were done with the Cp ligands in place of Cp* to reduce the computational effort (for optimized model clusters see Figures S10–S13). Gas-phase optimizations without any solvent effect or symmetry constraints, were done with the

hybrid Becke–Lee–Yang–Parr (B3LYP) functional [77] in combination with the LANL2DZ (Los Alamos National Laboratory 2 Double-Zeta) basis set [78] for all the atoms from the EMSL (Environmental Molecular Sciences Laboratory) Basis Set Exchange Library [79]. Frequency calculations were carried out for all structures to check the nature of the stationary states and the absence of any imaginary frequency to confirm that the optimized geometries were genuine minima on the potential energy hypersurface. NMR chemical shifts were computed by employing the gauge-including atomic orbitals (GIAOs) method [80–82] using the optimized geometries at the B3LYP/LANL2DZ level. Chemical shifts corresponding to ^{11}B NMR were computed in relation to B_2H_6 (B3LYP shielding constant for ^{11}B NMR: 83.6 ppm) and were then converted to the standard [$BF_3 \cdot OEt_2$] scale by adding 16.6 ppm (the experimental δ (^{11}B) value of B_2H_6) to the computed values. ^{1}H NMR chemical shift calculations were done with TMS ($SiMe_4$) as the internal standard. Chemcraft [83] was used for generating orbital graphics and optimized structure plots. Natural Bond Orbital (NBO) analyses [84] allowed for arrival of the Wiberg Bond Indices (WBI) [85].

4. Conclusions

Results described in this article have demonstrated the scope of new methodologies for the synthesis of high-nuclearity cobaltaborane clusters. Firstly, one of the new routes described here has led to the isolation of a novel and unprecedented 11-vertex–12-SEP disobedient cobaltaborane cluster with a (*hyper*)*nido* M_3B_8 core. The second route has allowed for synthesis and characterization of a classic example of sequentially generated higher nuclearity cluster with a 10-vertex–12-SEP *nido* core via cluster growth on a preformed template. Indeed, cobaltaboranes and cobaltaheteroboranes constitute a showcase for dynamic and unique structural features and as a result, we are always on the lookout for possibilities of generating novel sophisticated cobaltaborane frameworks. Amongst the several synthetic strategies that are recognized in this domain, the applicability of the ones reported here may be vital and might lead to the generation of sophisticated high-nuclearity metallaborane frameworks of other group-9 metals. The unusual formation of **1** and the open-faced geometries of both **1** and **2** should imply enhanced reactivity to such species. Further efforts are currently devoted to that purpose.

computational facilities and Dr. Babu Varghese and Mr. Venkatachalam Ramkumar for Single Crystal X-ray Diffraction data analyses.

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