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Chemistry of DimetallaocTABORANE(12) with Chalcogen-based Borate Ligands: Obedient vs Disobedient Clusters

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Supporting Information Placeholder

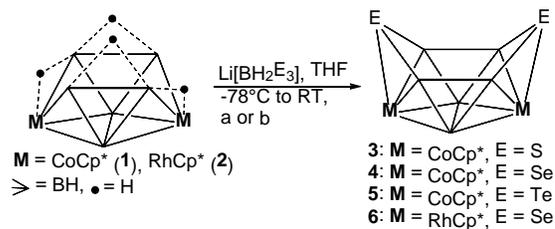
ABSTRACT: Reactions of dimetallaocTABORANES(12) $[(Cp^*M)_2B_6H_{10}]$ (M: Co (**1**) or Rh (**2**); $Cp^* = \eta^5-C_5Me_5$) with different chalcogen sources, such as $Li[BH_2E_3]$ and $Li[BH_3EPh]$ (E = S, Se or Te), led to two unique reaction outcomes. For example, formation of 10-vertex *nido*- $[(Cp^*M)_2B_6E_2H_6]$ (**3**: M = Co, E = S; **4**: M = Co, E = Se; **5**: M = Co, E = Te; **6**: M = Rh, E = Se) from compounds **1-2** is a typical representation of a cluster growth reaction, while the formation of *arachno*- $[(Cp^*Co)_2B_6H_9(EPh)]$ (E: S (**9**); Se (**10**) or Te (**11**)) is a rare method that yielded *arachno* clusters keeping the core geometry identical. Formation of *arachno*-**9-11** is an unique method that converts disobedient cluster **1** to obedient **9-11**. Further, the reactivity of *nido*-**4** with various metal carbonyls presented sequential cluster growth reactions, which afforded 11-vertex *nido*- $[(Cp^*Co)_2B_6Se_2H_6\{Fe(CO)_3\}]$ (**7**) and 13-vertex fused *closo*- $[(Cp^*Co)_2B_6Se_2H_6\{Ru_3(CO)_8\}]$ (**8**). The core geometry of *nido*-**7** is uncommon and very similar to that of $[C_2B_9H_{11}]^{2-}$ with a unique open pentahapto coordinating 5-membered face.

The chemistry associated with polyhedral borane,¹ carborane,^{1b,2} metallaborane,^{1b,3} and metallacarborane⁴ clusters have been strengthening the field of organometallic chemistry for many years. Higher nuclearity boron containing clusters or a combination of boron, carbon or metal, have widespread applications starting from the field of polymers, nanomaterials, ceramics and boron-neutron-capture-therapy.^{1,4,5} Apart from their extensive applications, they have been extremely useful to investigate the unique bonding and very large size electronic structures.^{1c,6} Since 1950 Lipscomb,^{1a} Hawthorne,^{4a} Welch,⁷ Xie,⁸ and us⁹ reported various single-cage clusters enriched with boron, carbon and transition metals however, a unified scheme for the synthesis of polyhedra of specified composition and geometry from molecular synthons is an arduous synthetic task.

Construction of large polyhedra from small clusters is usually undefined and typically uncontrolled.¹⁰ Beginning with the founding work of Hawthorne followed by many main group pioneers, the polyhedron-expansion chemistry has witnessed several synthetic challenges.^{1-4,7-10} For example, a large number of higher nuclearity clusters made of transition metals are synthesized by the fusion of smaller building

blocks such as tetrahedral, trigonal bipyramid and octahedral.¹¹ However, this methodology led to the formation of fused clusters.¹¹ On the other hand, many higher nuclearity single cage metallaborane clusters are synthesized using pentamethylcyclopentadienyl metal chlorides and monoborane reagents, for example, $LiBH_4 \cdot THF$, $BH_3 \cdot THF$, and $BH_3 \cdot SMe_2$, which are also uncontrolled.^{12,13} As a result, search for a unified synthetic strategy become of interest.

In our previous study, we have explored the reactivity of pentamethylcyclopentadienyl based metal halides with various chalcogen-based borate ligands, such as $Li[BH_2E_3]$ or $Li[BH_3EPh]$, which led to the formation of several metallaheteroboranes, albeit in an uncontrolled pathway.^{14,15} Although uncontrolled, the isolation of many interesting molecules from these chalcogen-based ligands tempted us to investigate the same reactions with preformed metallaborane clusters. As a result, we pursued this chemistry with octaborane(12) analogues $[(Cp^*M)_2B_6H_{10}]$ (M: Co (**1**) or Rh (**2**)).^{16,17} Surprisingly, the different chalcogen-based ligands react with octaborane(12) analogues in distinct fashions. Herein, we present some practical synthetic routes for the isolation of two classes of clusters.



Scheme 1. Syntheses of *nido*-**3-6**. (a): RT, 16 h (for **3, 4** and **6**), (b): 80 °C, 16 h (for **5**).

Reaction of $[(Cp^*Co)_2B_6H_{10}]$, **1** with $Li[BH_2E_3]$ (E = S, Se or Te) led to the formation of compounds **3-5** (Scheme 1), which were characterized by ¹H, ¹¹B, and ¹³C NMR and IR spectroscopy as well as mass spectrometry. The ¹H{¹¹B} NMR of **3-5** suggest the existence of single Cp* environments appearing at $\delta = 1.66, 1.66,$ and 1.72 ppm respectively. The ¹¹B{¹H} NMR spectrum of **3** displays two resonances at $\delta = 31.8$ and 22.1 ppm with an intensity ratio of 2:4. The ¹¹B{¹H} NMR spectra of both **4** and **5** also show two chemical shifts similar to that of **3**. The mass spectra of compounds

3-5 show molecular ion peaks at m/z 523.1509 [M]⁺, 618.0316 [M]⁺ and 715.0158 [M]⁺ respectively that indicate the formation of identical core with different chalcogen atoms, i.e., for **3** (S), **4** (Se) and **5** (Te). Although both ¹H{¹¹B} and ¹¹B{¹H} NMR spectra of **3-5** suggest the formation of symmetric clusters, these spectroscopic data were not sufficient enough to identify the core geometries of **3-5**. A clear explanation eluded us until the single crystal X-ray structure analyses of them were carried out.

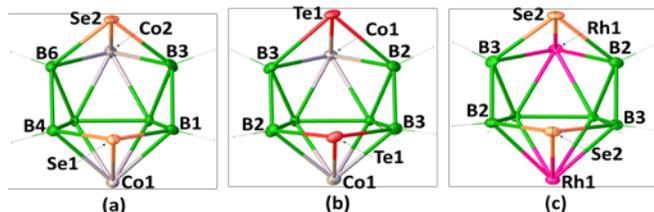


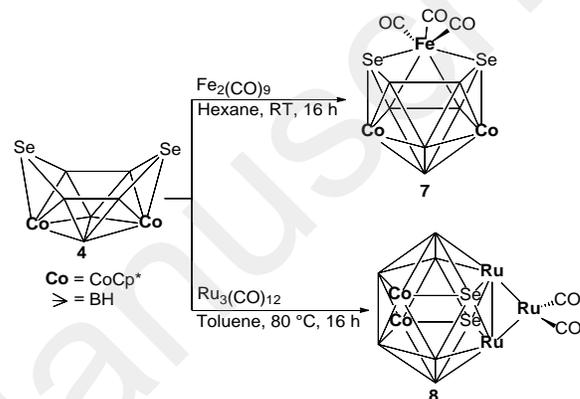
Figure 1. Molecular structures and labelling diagrams of *nido-4* (a), *nido-5* (b) and *nido-6* (c). Cp* attached to metals are omitted for clarity.

The crystal structures of **3-5** correspond to 10-vertex open dicobaltaheteroboranes [(Cp*Co)₂B₆E₂H₆] (E = S (**3**), Se (**4**) and Te (**5**)). All the clusters **3-5** are isostructural and isoelectronic with *nido*-decaborane(14). They can be viewed as 64 cluster valence electron species, which have 12 skeletal electron pairs (SEP). In terms of electron input to cluster, the {Cp*Co} unit is isoelectronic with {BH} unit, whereas chalcogen atom is a source of 4 electrons. The average B-B bond distances of *nido-3-5* are in the normal range, established for the metallaboranes.^{11b,16,17} Consistent with the NMR spectra of *nido-3-5*, the single-crystal X-ray structure analyses also specify the existence of symmetry planes.

One of the unique features of the formation of decaborane analogues *nido-3-5* from octaborane(12) analogue **1** is the direct insertion of two chalcogen atoms that expand the cluster from 8 to 10-vertex. In an order to expand this chemistry to other metals, we have carried out the reaction of [(Cp*Rh)₂B₆H₁₀] with Li[BH₂Se₃] that afforded yellow solid **6**. The ¹H{¹¹B} NMR of **6** shows chemical shift at δ = 1.81 ppm, which indicates the presence of one kind of Cp* environment. ¹¹B{¹H} NMR spectra display two resonances at δ = 21.8 and 21.3 ppm with a relative ratio of 4:2. The mass spectrum shows a molecular ion peak at m/z 704.9850 that corresponds to the molecular formula Rh₂B₆Se₂C₂₀H₃₆. Thus, a similar NMR pattern of **6** and **3-5** along with the mass spectrometric data confirm the composition of **6** as [(Cp*Rh)₂B₆Se₂H₆]. In order to confirm the spectroscopic assignments of **6**, the solid-state X-ray analysis was carried out. As shown in Figure 1(c), the X-ray analysis revealed **6** as the diselenorhodaborane analogue of *nido-3-5*. The average B-B, Rh-Se and Rh-B bond distances of **6** of 1.81 Å, 2.42 Å and 2.20 Å respectively are comparable with reported related rhodaheteroboranes.^{17,18}

While comparing the molecular orbitals of the Cp analogue of *nido-3-5*, it was observed that the HOMO-LUMO energy gap is decreased while changing the chalcogen atoms from S→Te (Table S1). On the other hand, changing the metal from Co to Rh, the HOMO-LUMO energy gap increases (Table S1). The HOMO of *nido-4* is mainly localized on d-orbitals of both metal centres (Figure S56). Whereas, the HOMO-2 is localized on d-orbitals of metals and p-orbitals of both the Se atoms. A similar situation has also been observed for *nido-3* and *nido-5* in HOMO-2 (Figures S55 and S57).

The directed p-orbitals of the Se atoms of *nido-4* in HOMO-2 show its donating ability. As a result, we have explored its reactivity with metal carbonyls aiming further cluster growth reaction. As a result, we have carried out the room temperature reaction of [(Cp*Co)₂B₆Se₂H₆] (**4**) with [Fe₂(CO)₉], which yielded brown solid **7** (Scheme 2). The ¹H{¹¹B} NMR spectrum of **7** shows peak at δ = 1.66 ppm, which corresponds to single Cp* environments. The ¹¹B{¹H} NMR spectrum shows four chemical shifts at δ = 36.9, 27.5, 23.7 and 13.6 ppm. The mass spectrum shows molecular ion peak at 756.9607. As the spectroscopic data was not enough to predict the structure, we have performed single crystal X-ray structural analysis. As shown in Figure S5, the solid-state X-ray analysis of **7** shows as 11-vertex *nido*-[(Cp*Co)₂B₆Se₂H₆{Fe(CO)₃}. The open face of *nido-7* is made of a distorted pentagon Fe₅-Se₂-B₅-B₄-Se₁ and isoelectronic with [C₂B₉H₁₁]²⁻.



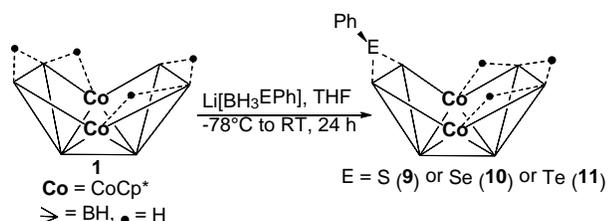
Scheme 2. Syntheses of *nido-7* and *closo-8* (Ru = Ru(CO)₂).

One of the interesting features of the pentagon face of *nido-7* is the presence of more polarized bonds as compared to [C₂B₉H₁₁]²⁻. Furthermore, the HOMO-14 of *nido-7* has p-orbitals on Se atoms which are tilted towards the centre of the pentagon (Figure S59). As a result, one can envisage that *nido-7* can further be capped by 2-electron main group or metal fragments to form 12-vertex *closo*-icosahedral. Hence, we have carried out the reactions of *nido-7* both with [Fe₂(CO)₉] and [Ru₃(CO)₁₂] under thermolytic conditions. Although the objective of isolating a *closo*-cluster was not accomplished from the thermolysis reaction of *nido-7* with [Fe₂(CO)₉], *nido-4* with [Ru₃(CO)₁₂] yielded *closo*-[(Cp*Co)₂B₆Se₂H₆{Ru₃(CO)₈}] (**8**), which is a blend of icosahedron {Co₂Ru₂B₆Se₂} and a triangle {Ru₃}.

The ¹¹B{¹H} NMR spectrum of *closo-8* shows two resonances appearing at δ = 39.4 and 3.9 ppm and the ¹H NMR spectrum shows one chemical shift at δ = 1.73 ppm due to Cp* protons. The mass spectrum shows molecular ion peak at 1144.7386 [M]⁺. The solid-state X-ray structure of *closo-8* (Figure S6) may be considered as a fusion of an icosahedron {Co₂Ru₂B₆Se₂} and a triangle {Ru₃} units, which are fused by Ru-Ru edge. The number of cluster valence electrons required for this fused 13-vertex cluster is 104,¹⁹ which is achieved from the available cluster valence electrons of *closo-8*.

In order to examine the reactivity of Li[BH₃EPh] (E = S, Se or Te) with respect to a similar reaction outcome from **1**, we have carried out the reactions of preformed cobaltaborane **1** with Li[BH₃EPh] (Scheme 3). To our surprise, based on the NMR and other spectroscopic data, the reaction led to a different type of clusters **9-11**. The ¹H NMR spectrum of **9** shows chemical shift at δ = 1.67 ppm indicating one kind of Cp*

environment. In addition to that, it shows two peaks at $\delta = -3.86$ and -21.94 ppm may be due to the presence of B-H-B and Co-H-B protons respectively. The NMR spectroscopic pattern for **10** and **11** are alike to that of **9**. As the spectroscopic data along with the mass spectrometric data were not enough to provide the structure of them, we have performed the single crystal X-ray analysis for **9-10**. The solid-state X-ray structure of **10** (Figure S8) shows that one of the bridging B-H-B hydrogens of **1** is substituted by bridging {SePh} moiety generating **10**. Whereas for **9** and **11**, the bridging B-H-B hydrogen of **1** is substituted by bridging {SPh} and {TePh} units respectively. As bridging {EPh} fragments (E = S, Se or Te) provide 3 cluster bonding electrons to clusters **9-11**, the SEP counts for them amount to 11. Therefore, **9-11** can be considered as *arachno* clusters.



Scheme 3. Syntheses of *arachno-9-11*.

Molecular orbital analysis of compound **1** and *arachno-9-11* using bp86/def2-svp was carried out that established that the HOMO-LUMO energy gap for **1** is moderately higher as compared to *arachno-9-11*. Further, it was observed that the gap between HOMO-LUMO decreased while moving from S→Te (Table S1). The frontier molecular orbitals of *arachno-9-11* show that the HOMOs are mainly localized on d_{z^2} -orbitals of two cobalt centers and the B-B bonds, which are connected to the *exo*-{EPh} fragments. Further, it was observed that part of HOMO-18 of *arachno-9* is comprised of p-orbitals of two B and one S atom, which are delocalized over BBS ring (Figure S61). An analogous bonding situation has also been observed for *arachno-10* and *arachno-11* in HOMO-15 (Figure S62) and HOMO-14 (Figure S63) respectively. The above bonding scenario was further supported by Wiberg Bond Indices (Table S2).

Electron counting rules, along with isolobal analogy, provided a solid foundation to evaluate the structure of a wide range of polyhedral clusters of varying nuclearity.^{6,20-22} However, the well-established cluster electron-counting rules often encountered challenges due to the rapid expansion of the field of polyhedral boron and main-group chemistry.²³ For example, Wade's rule predicts octaborane(12) is of formal *nido*- B_nH_{n+4} constitution. However, the core geometry is of *arachno* type, which can be generated by the removal of two adjacent vertices from 10-vertex *closo*-bicapped square antiprism.²⁴ These clusters are categorized as 'disobedient'.²³ Many such types of metallaborane analogues of octaborane(12) including **1** and **2** are belong to disobedit clusters due to the presence of lesser number of SEP than 11. One of the B-H-B bridging hydrogens in **1** has been replaced by three electron {EPh} fragment that yielded *arachno-9-11*. Thus, one may envisage the conversion of **1** to *arachno-9-11* as disobedit to obedient clusters.

In summary, this paper describes several sequential cluster growth reactions of **1** or **2** by means of $[\text{LiBH}_2\text{E}_3]$ and metal carbonyls. Using a two-step procedure, we were able to synthesize *closo*-icosahedral cluster from **1**. In addition, we have further established a unique method to transform diso-

bedient clusters to obedient one substituting one of the bridging B-H-B hydrogens by three electrons {EPh} fragment. We strongly believe that the novel methods reported in this paper for the synthesis of polyhedral boron clusters from **1** in a sequential and controlled fashion are unique.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, additional experimental data, computational data, and crystallographic data (CIF) for compounds **3-11**. The Supporting Information is available free of charge at <http://pubs.acs.org>.

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Notes

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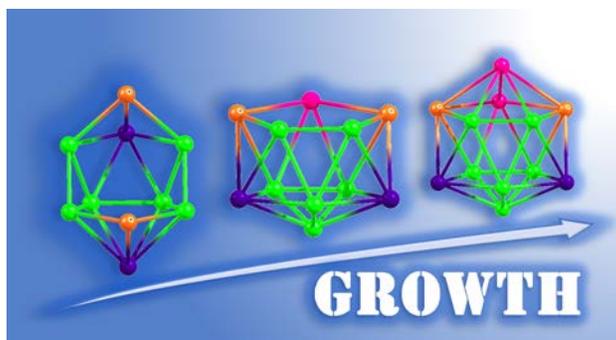
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Sequential cluster growth reactions starting from *nido*- $[(\text{Cp}^*\text{Co})_2\text{B}_6\text{Se}_2\text{H}_6]$ to *closo*- $[(\text{Cp}^*\text{Co})_2\text{B}_6\text{Se}_2\text{H}_6\{\text{Ru}_3(\text{CO})_8\}]$



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