

*Dedicated to Professor Luminița Silaghi-Dumitrescu
on the occasion of her 65th anniversary*

THE EFFECT OF ELECTRON-RICH HETEROATOMS IN METALLABORANE CLUSTERS

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ABSTRACT. The experimentally synthesized and structurally characterized metallaborane clusters containing highly electronegative heteroatoms namely (S, P, and Se) were studied by density functional theory in order to provide an insight into the influence of these heteroatoms on the polyhedral framework of metallaboranes.

Keywords: *Metallaboranes, Density functional theory, heteroatoms, electronegativity.*

INTRODUCTION

The most stable boranes are the deltahedral borane dianions $B_nH_n^{2-}$ which adopt the geometries of the most spherical deltahedra having in general vertices of degrees 4 and 5. Such boranes have $2n + 2$ skeletal electrons, as required by the Wade-Mingos rules [1,2,3,4]. BH vertices can be replaced by isoelectronic CH vertices leading to stable neutral $C_2B_{n-2}H_n$. In 1960s Hawthorne successfully substituted BH vertices in dicarbaboranes with transition metal units such as CpCo (Cp = η^5 -C₅H₅) leading to neutral cobaltadicarbaboranes [5].

Phosphorous and carbon have similar electronegativities owing to their diagonal relationship in the periodic table. However, replacement of a CH vertex by a phosphorus atom in carborane cages leads to the possibility

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of new chemistry arising from the basic properties of the phosphorus external lone pair. The first icosahedral diphosphaborane $P_2B_{10}H_{10}$ was initially synthesized in low yield in 1989 [6]. Subsequent improvements in the synthesis of $P_2B_{10}H_{10}$ made it more readily available to synthesize the cobaltadiphosphaborane $CpCoP_2B_9H_9$ [7]. Other work led to the synthesis of various ferradiphosphacarboranes such as $CpFeCP_2B_8H_9$ [8].

One important aspect in the chemistry of the metalladiphosphaboranes is the basicity of the phosphorus lone pairs. A phosphorus vertex is a four skeletal electron donor so that a $CpFeCPB_{n-3}H_{n-2}$ structure has $2n+2$ skeletal electrons and thus exhibits most spherical *closo* deltahedral geometries. The 11-vertex iron complex $CpFeCHP(CH_3)B_8H_8$ has been synthesized [9] in which the iron atom is located in the unique degree 6 vertex while the carbon and phosphorus atoms are located in the only two available degree 4 vertices. Interestingly one of the Fe-B bonds is abnormally long suggesting that a degree 6 vertex is not favored. Related to the ferracarbaphosphaboranes are the isoelectronic ferrathiacarboranes $CpFeCHSB_{n-3}H_{n-3}$. Two examples of such species have been synthesized by Kudinov and coworkers [10], namely the icosahedral 12-vertex $CpFeC(NHMe_3)SB_9H_9$ and the 11-vertex $CpFeC[B(OH)_2]SB_8H_8$.

The 10- and 12-vertex cobaltthiaboranes were first synthesized by Sneddon and co-workers in low yield [11]. A more efficient synthesis of $CpCoSB_{10}H_{10}$ was recently carried out by Welch and co-workers [12]. X-ray crystallography showed an icosahedral structure with adjacent cobalt and sulfur atoms. [12]. The synthesis of $B_9H_9E_2$ ($E = S$ or Se) species having two sulfur or selenium vertex atoms has been reported [13]. Such species appear to have nido structures derived by removal of a vertex from a regular icosahedron to leave a pentagonal face. A similar introduction of a $CpCo$ unit into the diselenaborane $B_9H_9Se_2$ gives a low yield of a novel 12-vertex nido species $CpCoSe_2B_9H_9$ having a bent pentagonal face.[13]

This study aimed at investigating the effect of the electron-rich heteroatoms, namely S, P and Se, on the polyhedral framework of metallaborane clusters by using density functional theory. We review our results in this area.

RESULTS AND DISCUSSION

A. Phosphorus as a "carbon copy" and its heavier congeners

The low energy 8-vertex $CpCoP_2B_5H_5$ structures are based on the most spherical deltahedron namely the D_{2d} bisdisphenoid. The lowest such structure has the cobalt atom located in a degree 5 vertex and the phosphorus

atoms located in non-adjacent degree 4 vertices (figure 1). All of the 9-vertex $\text{CpCoP}_2\text{B}_6\text{H}_6$ structures have central CoP_2B_6 tricapped trigonal prisms. The lowest energy $\text{CpCoP}_2\text{B}_6\text{H}_6$ structure has the phosphorus atoms located in non-adjacent positions with one at a degree 4 vertex and the other located at a degree 5 vertex. The latter is adjacent to the cobalt atom located in the only adjacent degree 5 vertex that is not adjacent to the degree 4 phosphorus atom. [14]

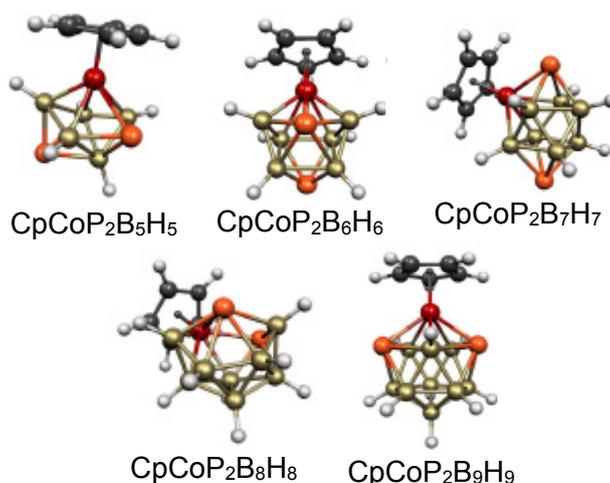


Figure 1. The lowest energy $\text{CpCoP}_2\text{B}_{n-2}\text{H}_{n-2}$ structures.

The geometries of the 10-vertex cobaltadiphosboranes $\text{CpCoP}_2\text{B}_7\text{H}_7$ are based on the D_{4d} bicapped square antiprism. The lowest energy such structure is the unique structure having both phosphorus atoms located at degree 4 vertices. The 11-vertex $\text{CpCoP}_2\text{B}_8\text{H}_8$ system is based on the 11-vertex most spherical deltahedron. This C_{2v} deltahedron has a single degree 6 vertex, and consequently two degree 4 vertices. The lower symmetry leads inherently to a more complicated potential energy surface. The lowest energy such structure has a $\text{P}\cdots\text{P}$ edge that is too long for a direct bond thereby leading to a polyhedron with a quadrilateral face including a $\text{P}\cdots\text{P}$ diagonal. The lowest energy 12-vertex $\text{CpCoP}_2\text{B}_9\text{H}_9$ structures are all regular icosahedra. The most stable such structure has two Co-P edges and non-adjacent P atoms. [14]

The lowest energy 8-vertex $\text{CpFeCHP}(\text{CH}_3)\text{B}_5\text{H}_5$ structures are all bisdisphenoids having the iron atoms located mainly in degree 5 vertices with phosphorus and carbon atoms in non-adjacent positions (Figure 2).

The 9-vertex systems are based on the most spherical *closo* tricapped trigonal prism having the iron atom located at a degree 5 vertex. In all such structures the phosphorus atom is adjacent to the iron atom while the carbon atom prefers a degree 4 vertex. The situation is similar for the 10-vertex $\text{CpFeCHP}(\text{CH}_3)\text{B}_7\text{H}_7$ system exhibiting also the geometry of the corresponding most spherical deltahedron, namely the bicapped tetragonal antiprism. Such structures have the carbon and phosphorus atoms located in the only two degree 4 vertices. [15]

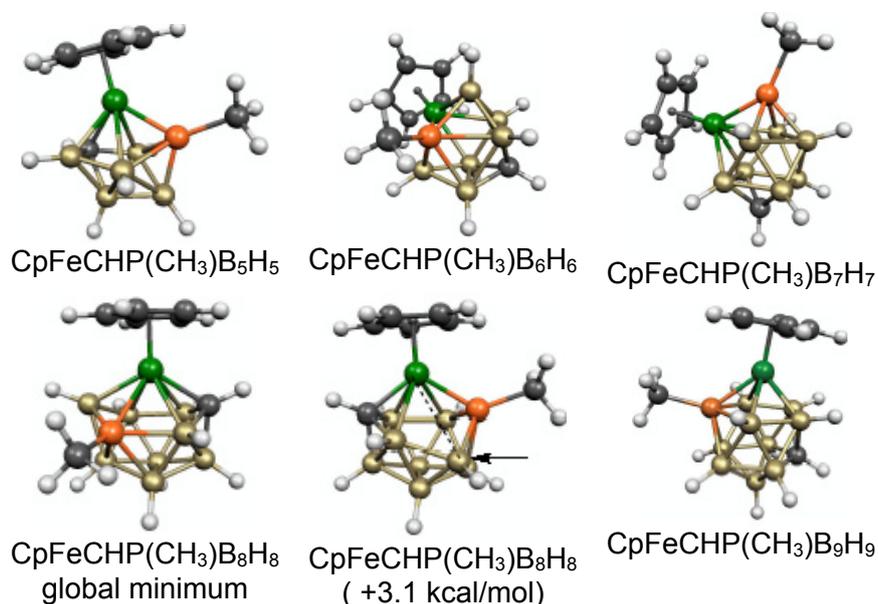


Figure 2. The lowest energy $\text{CpFeCHP}(\text{CH}_3)\text{B}_{n-3}\text{H}_{n-3}$ structures.

The experimental $\text{CpFeCHP}(\text{CH}_3)\text{B}_8\text{H}_8$ structure is not the global minimum but a slightly higher energy structure (+3.1 kcal/mol) having the phosphorus atom located in a degree 4 vertex. Lengthening one of the Fe-B bonds converts the two adjacent deltahedral faces into a single quadrilateral face thus reducing the degree of the iron vertex from 6 to 5. [15]

The 12-vertex structures based on the FeCPB_9 framework clearly favor the regular icosahedron over any other arrangement of the 12 vertex atoms. The most stable such structure has an Fe-P edge with the carbon vertex placed antipodally to the phosphorus vertex. [15]

B. The electron rich sulfur and selenium vertices: a route to more open structures

A sulfur vertex contributes four skeletal electrons so that a $\text{CpCoSB}_{n-2}\text{H}_{n-2}$ system has $2n + 2$ skeletal electrons and thus prefers a close deltahedral bisdisphenoid geometry according to the Wade-Mingos rules. The lowest energy $\text{CpCoSB}_6\text{H}_6$ structure is a bisdisphenoid having the cobalt atom at a degree 5 vertex and the sulfur atom at a non-adjacent degree 4 vertex (Figure 3). The lowest energy 9-vertex cobaltathiaborane structures are tricapped trigonal prisms having the cobalt atom located in a degree 5 vertex and the sulfur atom in the non-adjacent degree 4 vertex. The same location pattern was found for the lowest energy $\text{CpCoSB}_8\text{H}_8$ structure based on the most spherical 10-vertex deltahedron, namely the bicapped tetragonal antiprism. This trend continues for the 11-vertex $\text{CpCoSB}_9\text{H}_9$ family in which the low-energy structures are all isomers of the corresponding *closo* deltahedron. The most stable such structure is the unique isomer having the cobalt atom located in the unique degree 6 vertex and the sulfur atom located in an adjacent degree 4 vertex. [16]

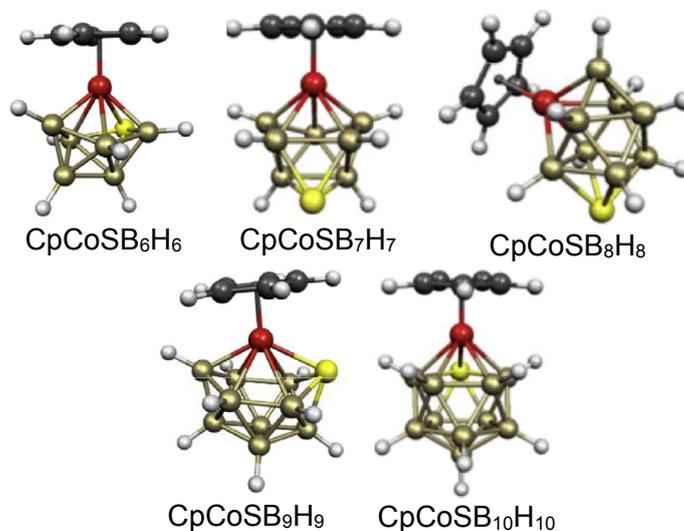


Figure 3. The lowest-energy $\text{CpCoSB}_{n-2}\text{H}_{n-2}$ structures.

For the 12-vertex $\text{CpCoSB}_{10}\text{H}_{10}$ structures, isomers based on the icosahedron have much lower energies than those based on any other possible 12-vertex polyhedra such as the cuboctahedron or anticuboctahedron. The lowest-energy cobaltathiaborane icosahedron has a direct Co-S edge.

The highest energy such structure has the cobalt and sulfur atoms located on at antipodal vertices. [16]

Various ferrathiocarboranes such as $\text{CpFeC}(\text{NHCMe}_3)\text{SB}_9\text{H}_9$ and $\text{CpFeC}[\text{B}(\text{OH})_2]\text{SB}_8\text{H}_8$, have been synthesized and structurally characterized by X-ray crystallography [17]. The ferrathiocarboranes are isoelectronic with the dicobaltadecaboranes and the cobaltathiaboranes. The question arises regarding the geometrical preferences of the ferrathiocarboranes $\text{CpFeCHSB}_n\text{H}_n$ as compared with the previously discussed iron phosphacarboranes $\text{CpFeCHP}(\text{CH}_3)\text{B}_{n-3}\text{H}_{n-3}$ and whether two heteroatoms known to exhibit a preference for a lower vertex degree, namely sulfur and carbon in this case, would induce deviations from the deltahedral sphericity.

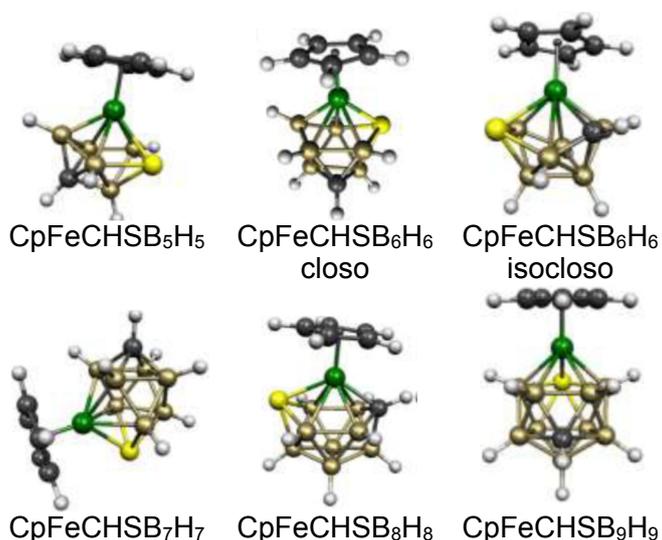


Figure 4. The lowest-lying $\text{CpFeCHSB}_{n-3}\text{H}_{n-3}$ structures.

The lowest energy 8-vertex $\text{CpFeCHSB}_5\text{H}_5$ structures are based on the most spherical deltahedron, namely the bisdisphenoid with the iron atom in a degree 5 vertex directly connected to a degree 4 vertex sulfur atom. The carbon atom is located in the only other degree 4 vertex which is non-adjacent to either iron or sulfur atoms (figure 4). [18] The lowest energy 9-vertex iron thiocarborane $\text{CpFeCHSB}_6\text{H}_6$ structure is a *closo* tricapped trigonal prismatic which is very close in energy to an *isocloso* isomer. The low-energy *closo* structure is the unique structure having the iron atom located in a degree 5 vertex and sulfur and carbon atoms located in degree 4 vertices but not with adjacent iron and carbon atoms and with a direct Fe-S bond. The 10-vertex $\text{CpFeCHSB}_7\text{H}_7$ global minimum structure is the most spherical deltahedron having the heteroatoms at degree 4 vertices with the

added preference for iron-sulfur adjacency. The most stable $\text{CpFeCHSB}_8\text{H}_8$ structure is the unique *closo/isocloso* isomer with both heteroatoms located at degree 4 vertices and the iron atom located in the unique degree 6 vertex. [18] This is the experimentally reported polyhedral arrangement for the boronic acid $\text{CpFeC}[\text{B}(\text{OH})_2]\text{SB}_8\text{H}_8$ [17]. The lowest energy 12-vertex structure $\text{CpFeCHSB}_9\text{H}_9$ is reported to be the only isomer having adjacent iron and sulfur atoms as well as non-adjacent and non-antipodal iron and carbon atoms. [18]

While a CH vertex is a donor of 3 skeletal electrons, a group 16 element vertex (S or Se) has an external lone pair thus leaving 4 skeletal electrons for skeletal bonding. Thus a thia- or selenaborane has the $2n + 2$ skeletal electrons necessary for a spherical cage. This can also be predicted for neutral boranes having extra hydrogen atoms. In practice such "extra" hydrogen atoms cannot remain on a closed polyhedron. However removal of a vertex leaves an open face which is suitable for edge-capping extra hydrogens. Such species are called *nido*-boranes. The ability of each sulfur and selenium atom to provide four skeletal electrons provides the possibility of *nido* metallaborane structures without bridging hydrogen atoms. Such species having 11 vertices obtained by removal of a vertex from an icosahedron (and consequently having a pentagonal opened face) have been reported [19].

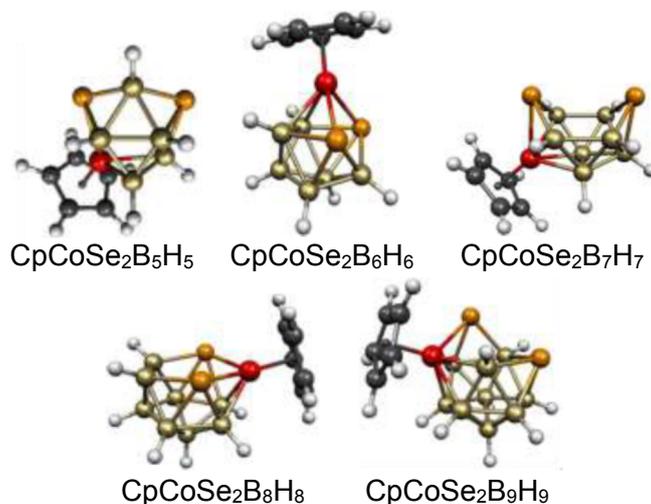


Figure 5. The lowest-lying $\text{CpCoSe}_2\text{B}_{n-3}\text{H}_{n-3}$ structures.

The most stable 8-vertex cobaltaselenaborane $\text{CpCoSe}_2\text{B}_5\text{H}_5$ structure originates from the 9-vertex most spherical deltahedron by the removal of a degree 5 vertex leading to a pentagonal open face providing two degree 3 vertices for the selenium atoms (Figure 5). [20]

The lowest energy 9-vertex $\text{CpCoSe}_2\text{B}_6\text{H}_6$ structures are generated by the removal of a degree 4 vertex from the *closo* 10-vertex most spherical deltahedron, namely the bicapped tetragonal antiprism. This leaves a large tetragonal open face. The 10-vertex $\text{CpCoSe}_2\text{B}_7\text{H}_7$ system is a simple one, derived from the 11-vertex most spherical *closo* deltahedron by removal of the single degree 6 vertex. This decreases the degrees of the two former two degree 4 vertices to just 3 where the two selenium atoms are located. This structure resembles the well-known structure of nido decaborane, $\text{B}_{10}\text{H}_{14}$. The lowest energy $\text{CpCoSe}_2\text{B}_9\text{H}_9$ structure originates from a regular icosahedron by distorting a vertex so that two edges are broken leaving a degree 4 vertex as well as two degree 3 vertices for the selenium atoms. [20]

CONCLUSIONS

Density functional theory results show that the lowest energy $\text{CpCoP}_2\text{B}_{n-3}\text{H}_{n-3}$ ($n = 8$ to 12) structures have the cobalt atom at a degree 5 or 6 vertex and the phosphorus atoms at degree 4 vertices with strong preference of the phosphorus atoms to occupy non-adjacent vertices. The lowest energy structures of the isoelectronic $\text{CpFeCHP}(\text{CH}_3)\text{B}_{n-3}\text{H}_{n-3}$ ($n = 8$ to 12) have adjacent iron and phosphorus atoms and non-adjacent phosphorus and carbon atoms. One of the Fe–B bonds from the degree 6 iron vertex in the 11-vertex $\text{CpFeCHP}(\text{CH}_3)\text{B}_8\text{H}_8$ structure appears to be fragile, readily elongating to ~ 3.1 Å in one of the low-energy structures, consistent with experimental observation on this system. The lowest energy structures for the $\text{CpCoSB}_n\text{H}_n$ ($n = 6$ – 10) systems were found to be the *closo* deltahedra in accord with expectations for these $2n + 2$ Wadean skeletal electron systems. The sulfur atoms in these structures were shown to prefer locations at the lowest degree vertices. Results on the ferrathiacarboranes $\text{CpFeCHSB}_{n-3}\text{H}_{n-3}$ ($n = 8$ – 12) indicate energetic preferences for deltahedral structures having the iron atoms located at degree 5 or 6 vertices, the carbon and sulfur atoms located at degree 4 vertices, and Fe–S edges. The lowest energy $\text{CpCoSe}_2\text{B}_{n-3}\text{H}_{n-3}$ ($n = 8$ – 12) structures have central $\text{CoSe}_2\text{B}_{n-3}$ nido polyhedra derived from *closo* or *isocloso* deltahedron by removal of a vertex. This leads to an “open” non-triangular face having four to six edges. The two selenium vertices in such structures are located on this open face reflecting the general preference of selenium for low-degree vertices.

THEORETICAL METHODS

Full geometry optimizations have been carried out at the M06L/6-311G(d,p) level of theory. The natures of the stationary points after optimization were checked by calculations of the harmonic vibrational frequencies. If significant imaginary frequencies were found, the optimization was continued by following the normal modes corresponding to imaginary frequencies to insure that genuine minima were obtained.

All calculations were performed using the Gaussian 09 package [21] with the default settings for the SCF cycles and geometry optimization, namely the fine grid (75,302) for numerically evaluating the integrals, 10^{-8} hartree for the self-consistent field convergence, maximum force of 0.000450 hartree/bohr, RMS force of 0.000300 hartree/bohr, maximum displacement of 0.001800 bohr, and RMS displacement of 0.001200 bohr.

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