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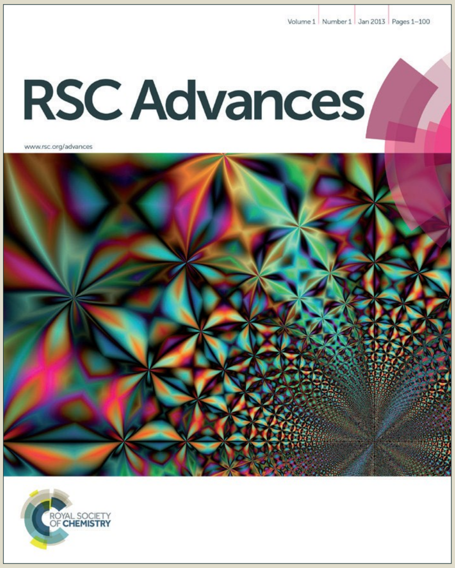

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Cyclopentadienylironphosphacarboranes: Fragility of Polyhedral Edges in the 11-Vertex System

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Abstract

The lowest energy $CpFeCHP(CH_3)B_{n-3}H_{n-3}$ (n = 8 to 12) structures, including the experimentally known $CpFeCHP(CH_3)B_8H_8$, have been investigated by density functional theory. The central $FeCPB_{n-3}$ polyhedra in all of the lowest energy such structures are the most spherical *closo* deltahedra. The heteroatoms are so located to 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 $CpFeCHP(CH_3)B_8H_8$ 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.

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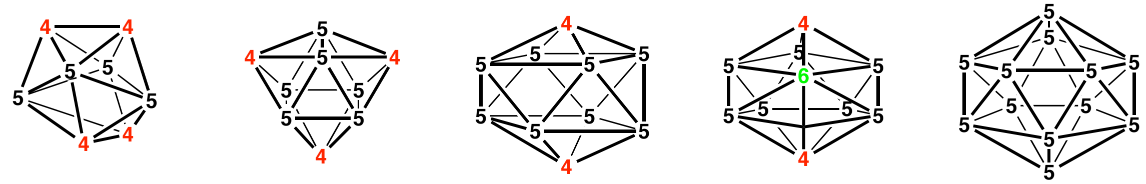
1. Introduction

The chemistry of metallaboranes was initiated by Hawthorne and co-workers in the 1960s [1], first with 12-vertex icosahedral systems and later with 10- and 11-vertex polyhedral systems using decaborane, $B_{10}H_{14}$ as the boron hydride raw material. Shortly thereafter Grimes and co-workers [2] first synthesized smaller polyhedral metallaboranes with as few as six vertices using pentaborane, B_5H_9 as the boron hydride raw material. Most of the early work used polyhedral ligands derived from dicarbaboranes in a search for neutral species isoelectronic with the most spherical *closo* deltahedral borane anions $B_nH_n^{2-}$ ($n = 6$ to 12) [3, 4]. Such species have $2n + 2$ skeletal electrons according to the Wade-Mingos rules [5, 6, 7, 8].



8 vertices:
Bisdisphenoid
(“D_{2d} Dodecahedron”)

9 vertices:
4,4,4-Tricapped
Trigonal Prism

10 vertices:
4,4-Bicapped
Square Antiprism

11 vertices:
“Edge-coalesced
Icosahedron”

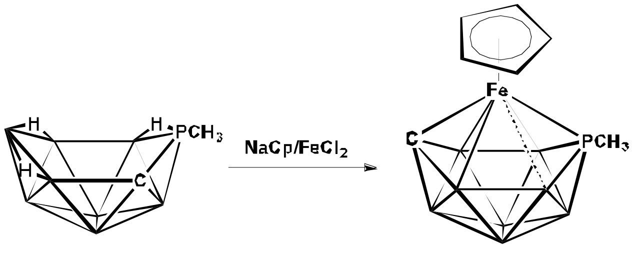
12 vertices:
Icosahedron

Figure 1. The most spherical *closo* deltahedra having from 8 to 12 vertices. Degree 4, 5, and 6 vertices are colored in red, black, and green, respectively.

The early work on metallaboranes used a CpCo (Cp = η^5-C_5H_5) vertex to replace a BH vertex in a polyhedral dicarbaborane structure. A CpCo vertex is isolobal with a BH vertex and, like a BH vertex, is a donor of two skeletal electrons. The early work on metallaboranes often involved stable neutral $CpCoC_2B_nH_{n+2}$ species. In subsequent work main group heteroatoms were introduced into the cages of such metallaborane structures. In this connection phosphorus can be considered as a “carbon copy” [9] since a bare phosphorus atom donates three skeletal electrons like a CH vertex. Thus replacement of two CH groups by bare phosphorus atoms in the dicarbaboranes $C_2B_{n-2}H_n$ gives the diphosphaboranes $P_2B_{n-2}H_{n-2}$. The icosahedral diphosphaborane $P_2B_{10}H_{10}$ was first synthesized in relatively low yield by Todd and co-workers in 1989 [10]. Much more recently the yield in the synthesis of $P_2B_{10}H_{10}$ has been greatly improved [11] so that it is now available in quantities as a reagent for the synthesis of metalladiphosphaboranes. In this connection an isomer of the cobalt complex $CpCoP_2B_9H_9$ has been synthesized from $P_2B_{10}H_{10}$ and structurally characterized by X-ray crystallography. Ferradiphosphacarboranes isomers of the stoichiometries $CpFeCP_2B_8H_9$ [12] and $CpFeC_2PB_8H_{10}$ [13, 14] isoelectronic with $CpCoP_2B_9H_9$ have also been synthesized.

A complication in the development of the chemistry of metalladiphosphaboranes isoelectronic with metalladicarbaboranes is the basicity of the lone pairs on the phosphorus vertices. This is demonstrated by synthesis of the cobalt hydride $HCo(\eta^1\text{-}P_2B_{10}H_{10})_2(PEt_3)_2$ derived from $HCo(CO)_4$ by replacement of two CO groups with Et_3P ligands and the remaining two CO groups by $\eta^1\text{-}B_{10}H_{10}P_2$ ligands bonding to the cobalt through a lone pair from one of the phosphorus vertices [15]. The basicity of a vertex phosphorus atom in a polyhedral borane can be quenched by alkylation analogous to the conversion of a phosphine R_3P: to a phosphonium ion $[R_3PR']^+$. An RP vertex is a four-electron donor in a polyhedral borane structure. Thus species $CpFeCHP(R)B_{n-3}H_{n-3}$ have the $2n + 2$ skeletal electrons for a most spherical deltahedral structure (Figure 1) and are isoelectronic with $B_nH_n^{2-}$, $C_2B_{n-2}H_n$, $CpCoC_2B_{n-3}H_{n-1}$, and $CpCoP_2B_{n-3}H_{n-3}$.

Sneddon and co-workers [16] have used the anion $[CH_3PCHB_8H_{11}]^-$ having a decaborane-like structure to synthesize the iron complex $CpFeCHP(CH_3)B_8H_8$ (Figure 2). In the $[CH_3PCB_8H_{12}]^-$ anion the carbon atom is located at a degree 4 vertex adjacent to the phosphorus atom located at a degree 3 vertex. However, in the reaction of the anion with a CpFe source the carbon atom migrates so that both the carbon and phosphorus atoms are located at the two degree 4 vertices of the resulting most spherical 11-vertex deltahedron, namely the so-called “edge-coalesced icosahedron” (Figures 1 and 2). The iron atom in this structure is located at the unique degree 6 vertex of this deltahedron. However, one of the bonds from the iron atom to an adjacent boron atom is abnormally long (dashed line in Figure 2) suggesting that a degree 6 iron atom cannot form strong bonds to all six adjacent atoms. This phenomenon suggested a more detailed study of this and related systems using density functional theory. In order to provide a broad perspective of the nature of these ferraphosphacarbaboranes, we included in this study the complete series of $CpFeCHP(CH_3)B_{n-3}H_{n-3}$ systems having 8 to 12 vertices.



$CH_3PCHB_8H_{11}$ $CpFeP(CH_3)CHB_8H_8$

Figure 2. The phosphacarbaborane and its conversion to $CpFeP(CH_3)CHB_8H_8$. Unmarked atoms are boron atoms and external hydrogen atoms are omitted for clarity. The dashed line corresponds to an elongated Fe···B edge.

2. Theoretical Methods

In order to reduce computational costs the full geometry optimizations were initially carried out on the $CpFeCHPHB_{n-3}H_{n-3}$ systems (n = 8 to 12) at the B3LYP/6-31G(d) [17, 18, 19, 20] level of theory. The lowest energy structures were then reoptimized at a higher level, i. e., M06L/6-311G(d,p) [21] and these are the results presented in the paper. The initial structures were chosen by systematic substitution of one BH vertex in $B_nH_n^{2-}$ by a CpFe unit, then another BH vertex by a PH vertex, followed by all possible substitutions of the remaining BH vertices by a CH vertex. However, in order to keep the number of possible structures manageable, structures with degree 3 CpFe vertices capping a triangular face were excluded from consideration because of the general preference of transition metal units for higher degree vertices. The large number of different starting structures for the optimizations included 593 structures of the 8-vertex clusters $CpFeCHPHB_5H_5$, 439 structures of the 9-vertex clusters $CpFeCHPHB_6H_6$, 648 structures of the 10-vertex clusters $CpFeCHPHB_7H_7$, 938 structures of the 11-vertex clusters $CpFeCHPHB_8H_8$, and 304 structures of the 12-vertex clusters $CpFeCHPHB_9H_9$ (see the Supporting Information). It is thus assured that the number of polyhedral frameworks is representative enough and covers all geometries of interest. 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. The PH vertices in the lowest energy $CpFeCHPHB_{n-3}H_{n-3}$ structures were then replaced by PCH_3 vertices and the structures reoptimized to give the $CpFeCHP(CH_3)B_{n-3}H_{n-3}$ structures reported in this paper and related to the experimental $CpFeCHP(CH_3)B_8H_8$ structure [14].

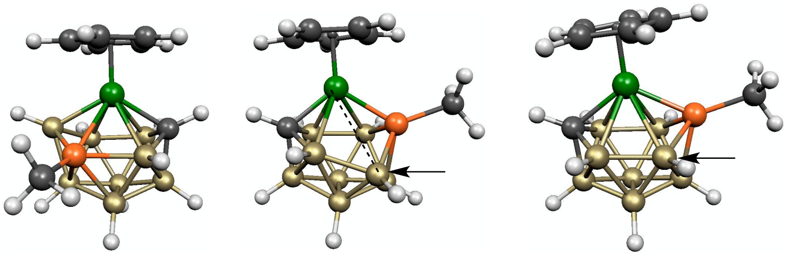
All calculations were performed using the Gaussian 09 package [22] with the default settings for the SCF cycles and geometry optimization, namely the fine grid (75,302) for numerically evaluating the integrals, 10^{-8} hartree for the self-consistent field convergence, maximum force of 0.000450 hartree/bohr, RMS force of 0.000300 hartree/bohr, maximum displacement of 0.001800 bohr, and RMS displacement of 0.001200 bohr. ^{11}B NMR chemical shifts were calculated at the gauge invariant atomic orbital (GIAO) – B3LYP/6-311+G(d,2p) level and referenced to $BF_3{:}OEt_2$.

The $CpFeCHP(CH_3)B_{n-3}H_{n-3}$ (n = 8 to 12) structures are numbered as **B(*n*-3)CPFe-*x*** where ***n*** is the total number of polyhedral vertices, and ***x*** is the relative order of the structure on the energy scale (M06L/6-311G(d,p) including zero-point corrections). The lowest energy optimized structures discussed in this paper are depicted in Figures 3, 5, 6, 7, and 8. Only the lowest energy and thus potentially chemically significant structures are considered in detail in this paper. All of the structures reported in this paper are closed-shell structures with substantial HOMO-LUMO gaps ranging from 1.7 to 3.5 eV (Table S6 of the Supporting Information). More comprehensive lists of structures, including higher energy structures, are given in the Supporting Information.

3. Results and Discussion

3.1 The 11-vertex System CpFeCHP(CH$_3$)B$_8$H$_8$

The one experimentally known CpFeCHP(CH$_3$)B$_{n-3}$H$_{n-3}$ system is the 11-vertex system CpFeCHP(CH$_3$)B$_8$H$_8$ (Figure 2) [16]. The experimental structure is derived from the most spherical *closo* 11-vertex deltahedron (Figure 1) with the iron atom located at the unique degree 6 vertex and the phosphorus and carbon atoms located at the two degree 4 vertices. However, one of the Fe-B edges is lengthened to 2.636 Å relative to the ~2.4 Å lengths of the other three Fe-B edges. Our theoretical study predicts three CpFeCHP(CH$_3$)B$_8$H$_8$ structures within 15 kcal/mol of the global minimum **B8CPFe-1** (Figure 3 and Table 1). This global minimum does not correspond to the experimental CpFeCHP(CH$_3$)B$_8$H$_8$ structure since its phosphorus atom is located at a degree 5 rather than a degree 4 vertex.



B8CPFe-1
0.0 kcal/mol

B8CPFe-2
3.1 kcal/mol

B8CPFe-3
3.5 kcal/mol

Figure 3. The three lowest energy CpFeCHP(CH$_3$)B$_8$H$_8$ structures. A dashed line indicates the long Fe$\cdots$B distance in **B8CPFe-2** and an arrow indicates the mobile boron atom interconverting **B8CPFe2** and **B8CPFe-3**.

Table 1. The three CpFeCHP(CH$_3$)B$_8$H$_8$ structures within 11 kcal/mol of the lowest energy structure.

Structure	ΔE	Vertex Degrees			Heteroatom	
(symmetry)	kcal/mol	Fe	C	P	Edges, Å	Polyhedron
B8CPFe-1 (C_s)	0.0	6	4	5	Fe–P(2.327), Fe–C(1.980)	11-v deltahedron
B8CPFe-2 (C_1)	3.1	5	4	4	Fe–P(2.146), Fe–C(1.912)	Fe$\cdots$B(3.095)$\Rightarrow$f$_4$
B8CPFe-3 (C_s)	3.5	6	4	4	Fe–P(2.158), Fe–C(1.960)	Fe–B(2.410)

The next two closely energetically spaced CpFeCHP(CH$_3$)B$_8$H$_8$ structures **B8CPFe-2** and **B8CPFe-3**, lying ~3 kcal/mol in energy above **B8CPFe-1**, are closely related to the experimental structure [16] since in both of these structures both the phosphorus and carbon atoms are located at the degree 4 vertices. The Fe-B edges in the C_s structure **B8CPFe-3** are not exceptional with two short ~2.27 Å Fe-B edges and two longer ~2.41 Å Fe-B edges. However, in **B8CPFe-2** one of the Fe···B edges has lengthened to ~3.09 Å (dashed line in Figure 3) whereas the other Fe-B edges remain in the range 2.14 to 2.36 Å. The lengthening of one of the Fe···B edges in **B8CPFe-2** has the effect of converting two adjacent triangular faces into a quadrilateral face and reducing the degree of the iron vertex from 6 to 5. This effectively converts the 11-vertex *closo* polyhedron into an 11-vertex *isonido* polyhedron with the same number of skeletal electrons [23, 24, 25]. The experimental CpFeCHP(CH$_3$)B$_8$H$_8$ structure lies between **B8CPFe-2** and **B8CPFe-3** with its elongated Fe···B edge of 2.636 Å. The experimental Fe–P and Fe–C distances of 2.134 and 1.955 Å, respectively, for CpFeCHP(CH$_3$)B$_8$H$_8$ [16] are close to the predicted values for **B9CPFe-3** of 2.158 and 1.960 Å as well as those for **B9CPFe-2** of 2.146 and 1.912 Å.

In order to provide additional insight regarding the experimental CpFeCHP(CH$_3$)B$_8$H$_8$ structure relative to the predicted structures **B8CPFe-2** and **B8CPFe-3**, **g**eometry optimizations starting from the X-ray coordinates of the experimental structure [16] were performed. This led to a structure identical to **FeB8CP-3** in both geometry and energy**.** In addition, scanning the fragile Fe-B bond in **FeB8CP-2** to reach the same Fe-B bond length as in **FeB8CP-3** provided an energy barrier of 0.77 kcal/mol (Figure 4). This low energy barrier suggests fluxional behavior between **FeB8CP-2** and **FeB8CP-3.** In addition, the experimental ^{11}B NMR spectrum of CpFeCHP(CH$_3$)B$_8$H$_8$ is closer to the calculated ^{11}B NMR spectrum of **FeB8CP-3** than to that of **FeB8CP-2** (Table 2). This is consistent with the elongated Fe···B edge of length 2.636 Å being closer to the 2.410 Å value for **FeB8CP-3** than to the 3.095 Å value for **FeB8CP-2**.

Table 2. Summary of ^{11}B NMR shifts. The numbering of the boron atoms (in parentheses) is relative to the X-ray crystal structure [16].

	^{11}B NMR chemical shifts in ppm
B8CPFe measured	4.7(9), –1.9(8), –18.1(6,7), –22.4(4,5), –24.7(10,11) [a]
B8CPFe-2 calculated	4.2(9), –4.5(7), –7.4(4), –9.9(8), –12.5(5), –18(11), –22.2(10), –33.7(6)
B8CPFe-3 calculated	3.4(9), –3.9(8), –15.9(6,7), –24.3(4,5), –28.7(10,11)

[a] values taken from reference 16.

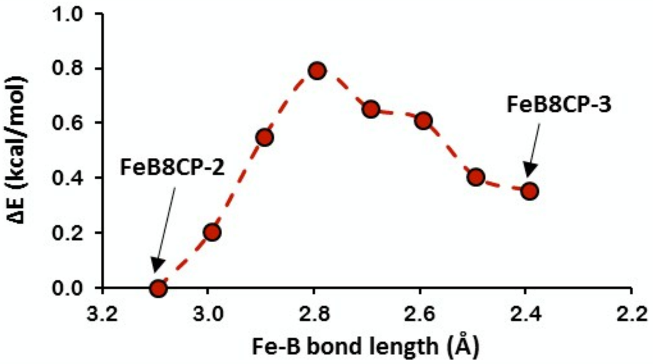


Figure 4. Relative energy as a function of the fragile Fe-B bond length in the **B8CPFe-2/B8CPFe-3** system of CpFeCHP(CH$_3$)B$_8$H$_8$ structures.

3.2 The 12-vertex System CpFeCHP(CH$_3$)B$_9$H$_9$

The eight CpFeCHP(CH$_3$)B$_9$H$_9$ structures within ~26 kcal/mol of the lowest energy structure all have a central FeCPB$_9$ regular icosahedron and thus all degree 5 vertices (Figure 4 and Table 2). The four lowest energy of these structures, lying within 10 kcal/mol of the lowest energy structure **B9CPFe-1**, are the four possible structures with adjacent iron and phosphorus vertices (i. e., an Fe–P edge) and non-adjacent phosphorus and carbon vertices (no P–C edges). These four structures differ in the locations of the carbon vertices relative to the iron and phosphorus vertices. The four higher energy CpFeCHP(CH$_3$)B$_9$H$_9$ structures, at energies between 19.5 and 26.1 kcal/mol above **B9CPFe-1**, have either non-adjacent iron and phosphorus atoms or adjacent phosphorus and carbon atoms.

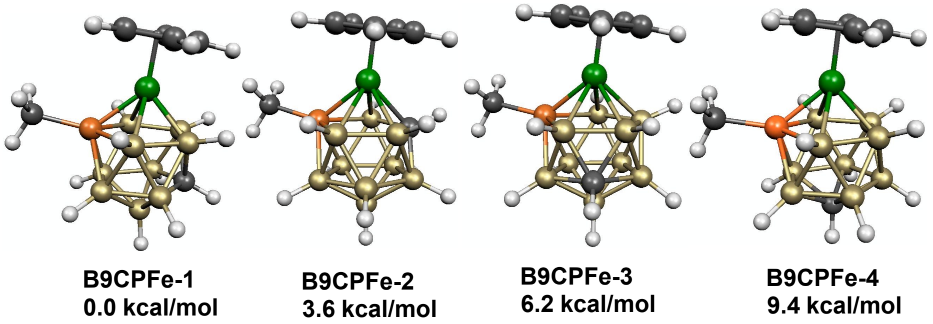


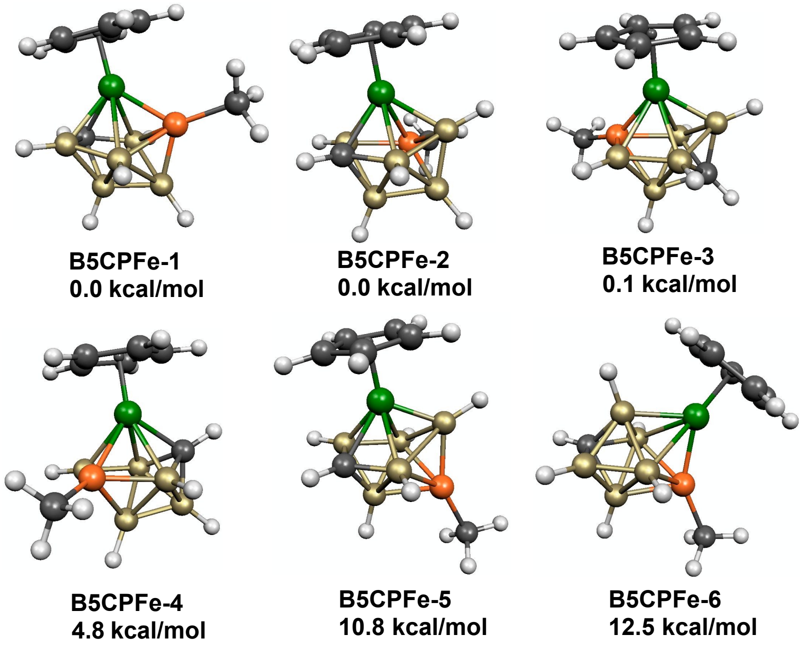
Figure 5. The four lowest energy CpFeCHP(CH$_3$)B$_9$H$_9$ structures.

Table 3. The four lowest energy CpFeCHP(CH$_3$)B$_9$H$_9$ structures within 19 kcal/mol of the lowest energy structure.

Structure (symmetry)	ΔE kcal/mol	Heteroatom Edges, Å	HOMO-LUMO Gap, eV
B9CPFe-1 (C_s)	0.0	Fe–P(2.101), Fe···C(3.151), P···C(3.357)	3.2
B9CPFe-2 (C_1)	3.6	Fe–P(2.117), Fe–C(2.040), P···C(2.909)	3.0
B9CPFe-3 (C_1)	6.2	Fe–P(2.092), Fe···C(3.158), P···C(2.960)	3.0
B9CPFe-4 (C_s)	9.4	Fe–P(2.082), Fe···C(3.693), P···C(2.905)	3.0

3.3 CpFeCHP(CH_3)$B_{n-3}H_{n-3}$ (n = 8, 9, 10) systems.

All six of the lowest energy 8-vertex CpFeCHP(CH_3)B_5H_5 structures (Figure 6 and Table 4) have a central FeCPB$_5$ bisdisphenoid, which is the most spherical 8-vertex *closo* deltahedron (Figure 1). The four lowest energy CpFeCHP(CH_3)B_5H_5 structures, lying within 4.8 kcal/mol of **B5CPFe-1**, have the iron atoms at degree 5 vertices and Fe-P edges but differ in the location of the carbon vertex relative to the iron and phosphorus vertices. There is then a jump in relative energy to **B5CPFe-5**, lying 10.8 kcal/mol above **B5CPFe-1**, which has the iron atom at a degree 5 vertex but not adjacent to the phosphorus atom (i. e., no Fe–P edge). The next CpFeCHP(CH_3)B_5H_5 structure **B5CPFe-6**, lying 12.5 kcal/mol in energy above **B5CPFe-1**, has the iron atom at a degree 4 vertex. However, this iron atom is directly bonded to the phosphorus atom through an Fe–P edge.



B5CPFe-1
0.0 kcal/mol

B5CPFe-2
0.0 kcal/mol

B5CPFe-3
0.1 kcal/mol

B5CPFe-4
4.8 kcal/mol

B5CPFe-5
10.8 kcal/mol

B5CPFe-6
12.5 kcal/mol

Figure 6. The six lowest energy CpFeCHP(CH_3)B_5H_5 structures.

The five lowest energy structures for the nine-vertex CpFeCHP(CH_3)B_6H_6 system, lying within 8.5 kcal/mol of the lowest energy structure **B6CPFe-1**, are all based on the tricapped trigonal prism (Figure 7 and Table 5), which is the most spherical 9-vertex *closo* deltahedron (Figure 1). All five structures have the iron atom at a degree 5 vertex and an Fe–P edge. The four lowest energy structures have the carbon atom at a degree 4 vertex whereas the fifth CpFeCHP(CH_3)B_6H_6 structure **B6CPFe-5** has the carbon atom at a degree 5 vertex.

Table 4. The six CpFeCHP(CH_3)B_5H_5 structures within 15 kcal/mol of the lowest energy structure.

Structure	ΔE	Vertex Degrees			Heteroatom	HOMO-LUMO
(symmetry)	kcal/mol	Fe	C	P	Edges, Å	Gap, eV
B5CPFe-1 (C_1)	0.0	5	4	4	Fe–P(2.095),Fe–C(2.014)	2.4
B5CPFe-2 (C_1)	0.0	5	4	5	Fe–P(2.222), Fe–C(1.999)	2.5
B5CPFe-3 (C_1)	0.1	5	4	4	Fe–P (2.165)	2.7
B5CPFe-4 (C_1)	4.8	5	4	4	Fe–P(2.174),Fe–C(1.940)	2.4
B5CPFe-5 (C_1)	10.8	5	4	4	Fe–C(2.001)	2.9
B5CPFe-6 (C_1)	12.5	4	4	4	Fe–P(2.038)	1.7

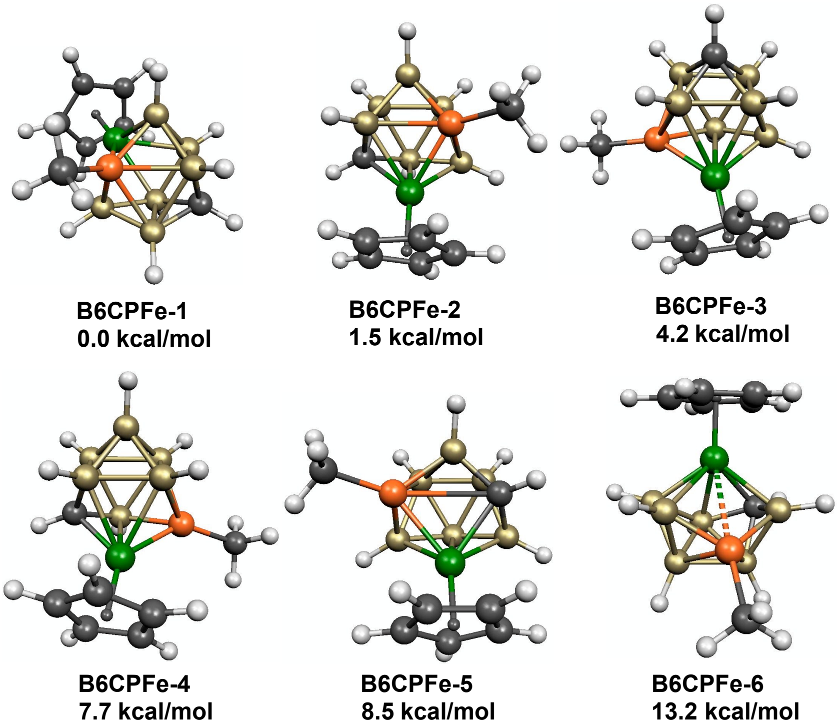


Figure 7. The six lowest energy CpFeCHP(CH_3)B_6H_6 structures.

The sixth CpFeCHP(CH_3)B_6H_6 structure **B6CPFe-6**, lying 13.2 kcal/mol in energy above **B6CPFe-1**, is the only low-energy CpFeCHP(CH_3)$B_{n-3}H_{n-3}$ structure found in this work that is not based on one of the most spherical *closo* deltahedra in Figure 1. Instead the structure of **B6CPFe-6** is based a central 9-vertex *isocloso* deltahedron with the iron atom at the unique degree 6 vertex and the phosphorus atom at an adjacent degree 5 vertex (Figure 7 and Table 5). However, the Fe···P edge is lengthened from the typical 2.0 to 2.3 Å distance to 2.770 Å in **B6CPFe-6** (see dashed line in Figure 7). Considering this lengthened Fe···P edge as no longer an edge leads to an *isonido* 9-vertex structure [23, 24, 25] having a quadrilateral face with a degree 5 iron vertex and a degree 4 phosphorus vertex. Such an *isonido* $CpFeCHP(CH_3)B_6H_6$ structure **B6CPFe-6** is as consistent with its 20 skeletal electrons ($= 2n + 2$ for $n = 9$) as the *closo* tricapped trigonal prismatic structures for the five lowest energy $CpFeCHP(CH_3)B_6H_6$ structures. This lengthening of one of the Fe–P edges to the degree 6 iron vertex in the 9-vertex *isocloso* structure **B6CPFe-6** is analogous to the lengthening of one of the Fe–B edges to the likewise degree 6 iron vertex in the 11-vertex *closo* structure **B8CPFe-2** discussed above. Note that the 11-vertex *closo* deltahedron can also function as an 11-vertex *isocloso* deltahedron since it has a degree 6 vertex.

Table 5. The six $CpFeCHP(CH_3)B_6H_6$ structures within 15 kcal/mol of the lowest energy structure.

Structure (symmetry)	ΔE kcal/mol	Vertex Degrees Fe	C	P	Heteroatom Edges, Å	HOMO-LUMO Gap, eV
B6CPFe-1 (C_s)	0.0	5	4	5	Fe–P(2.233)	2.0
B6CPFe-2 (C_1)	1.5	5	4	5	Fe–P(2.176), Fe–C(1.947)	2.2
B6CPFe-3 (C_1)	4.2	5	4	4	Fe–P(2.098)	2.0
B6CPFe-4 (C_1)	7.7	5	4	4	Fe–P(2.097), Fe–C(1.940)	1.9
B6CPFe-5 (C_1)	8.5	5	5	5	Fe–P(2.251), Fe–C(2.143)	2.4
B6CPFe-6 (C_1)*	13.2	6	4	5	Fe–P(2.770), Fe–C(1.937)	2.0

* This structure has a central $FeCPB_6$ *isocloso* deltahedron.

The three lowest energy structures in the 10-vertex system $CpFeCHP(CH_3)B_7H_7$, which lie within 2.4 kcal/mol of the lowest energy structure **B7CPFe-1**, have the iron atom located at a degree 5 vertex, the phosphorus atom adjacent to the iron atom forming an Fe–P edge, and the carbon located at a degree 4 vertex (Figure 8 and Table 6). The central $FeCPB_7$ polyhedron in these three structures is the bicapped square antiprism, which is the most spherical *closo* 10-vertex deltahedron (Figure 1). After these three $CpFeCHP(CH_3)B_7H_7$ structures there is a large jump in energy to **B7CPFe-4**, which lies 14.7 kcal/mol above **B7CPFe-1**. Structure **B7CPFe-4** has the carbon atom as well as the iron and phosphorus atoms located at degree 5 vertices. Thus both of the degree 4 vertices in the central bicapped square antiprism of **B7CPFe-4** are occupied by boron atoms.

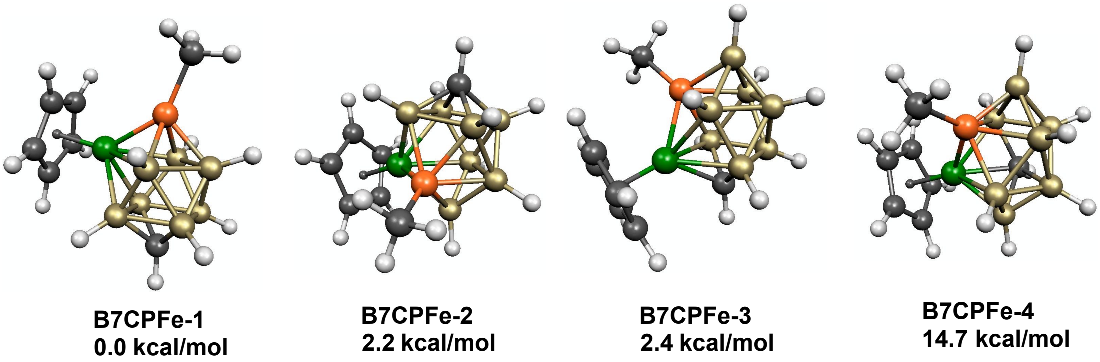


Figure 8. The four lowest energy CpFeCHP(CH_3)B_7H_7 structures.

Table 6. The four CpFeCHP(CH_3)B_7H_7 structures within 18 kcal/mol of the lowest energy structure.

Structure (symmetry)	ΔE kcal/mol	Vertex Degrees Fe	C	P	Heteroatom Edges, Å	HOMO-LUMO Gap, eV
B7CPFe-1 (C_s)	0.0	5	4	5	Fe–P(2.073)	2.6
B7CPFe-2 (C_1)	2.2	5	4	5	Fe–P(2.169)	2.6
B7CPFe-3 (C_1)	2.4	5	4	5	Fe–P(2.162), Fe–C(1.949)	2.6
B7CPFe-4 (C_1)	14.7	5	5	5	Fe–P(2.120), Fe–C(2.080)	2.8

4. Conclusions

The central $FeCPB_{n-3}$ polyhedra in all of the lowest energy CpFeCHP(CH_3)$B_{n-3}H_{n-3}$ structures (n = 8 to 12) are the most spherical *closo* deltahedra (Figure 1) as suggested by the Wade-Mingos rules for these $2n + 2$ skeletal electron systems [5, 6, 7, 8]. The heteroatoms in the $FeCPB_{n-3}$ polyhedra are so located to have adjacent iron and phosphorus atoms and non-adjacent phosphorus and carbon atoms in the lowest energy structures. In addition, the carbon atoms prefer energetically to be located at degree 4 rather than degree 5 or 6 vertices in accord with previous theoretical studies on metalladicarbaboranes [26] and metallatricarbaboranes [27]. The iron atoms prefer energetically to be located at the highest degree vertex, normally a degree 5 vertex except for the 11-vertex *closo* deltahedron, which has a degree 6 vertex for the iron atom.

The iron atom at the degree 6 vertex in the lowest energy 11-vertex CpFeCHP(CH_3)B_8H_8 structures is adjacent to the phosphorus and carbon atoms as well as four boron atoms. However, one of the Fe–B bonds in the 11-vertex CpFeCHP(CH_3)B_8H_8 structure appears to be fragile, readily elongating to ~3.1 Å in one of the low-energy structures. This effectively converts the 11-vertex *closo* deltahedron having 18 triangular faces into a polyhedron having a single quadrilateral face as well as 16 triangular faces. This elongation of an Fe–B bond is also observed in the experimental $CpFeCHP(CH_3)B_8H_8$ structure [16], which has one elongated Fe–B deltahedral edge of ~2.6 Å in addition to three normal Fe–B edges of 2.3 to 2.4 Å.

Acknowledgment. Funding from the Romanian Ministry of Education and Research, (Grant PN-II-RU-TE-2014-4-1197) and the U. S. National Science Foundation (Grant CHE-1057466) is gratefully acknowledged.

Supporting Information. Table S1A: Initial $CpFeCHPHB_5H_5$ structures; Table S1B: Distance table for the lowest-lying $CpFeCHPCH_3B_5H_5$ structures; Table S1C: Energy ranking for all of the $CpFeCHPHB_5H_5$ structures; Table S2A: Initial $CpFeCHPHB_6H_6$ structures; Table S2B: Distance table for the lowest-lying $CpFeCHPCH_3B_6H_6$ structures; Table S2C: Energy ranking for all of the $CpFeCHPHB_6H_6$ structures; Table S3A: Initial $CpFeCHPHB_7H_7$ structures; Table S3B: Distances table for the lowest-lying $CpFeCHPCH_3B_7H_7$ structures; Table S3C: Energy ranking for all of the $CpFeCHPHB_7H_7$ structures; Table S4A: Initial $CpFeCHPHB_8H_8$ structures; Table S4B: Distance table for the lowest-lying $CpFeCHPCH_3B_8H_8$ structures; Table S4C: Energy ranking for all of the $CpFeCHPHB_8H_8$ structures; Table S5A: Initial $CpFeCHPHB_9H_9$ structures; Table S5B: Distance table for the lowest-lying $CpFeCHPCH_3B_9H_9$ structures; Table S5C: Energy ranking for all of the $CpFeCHPHB_9H_9$ structures; Complete Gaussian09 reference (reference 22).

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Graphical Abstract

Cyclopentadienyliron-phosphacarboranes: Fragility of Polyhedral Edges in the 11-Vertex System

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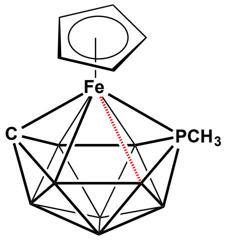
The central FeCPB$_{n-3}$ polyhedra in all of the lowest energy CpFeCHP(CH$_3$)B$_{n-3}$H$_{n-3}$ (n = 8 to 12) structures are the most spherical *closo* deltahedra with adjacent iron and phosphorus atoms and non-adjacent phosphorus and carbon atoms. One of the Fe–B bonds from the degree 6 iron vertex in the 11-vertex CpFeCHP(CH$_3$)B$_8$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.



CpFeP(CH$_3$)CHB$_8$H$_8$