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Limited Occurrence of *Isocloso* Deltahedra with 9 to 12 Vertices in Low-Energy Hypoelectronic Diferradicarbaborane Structures

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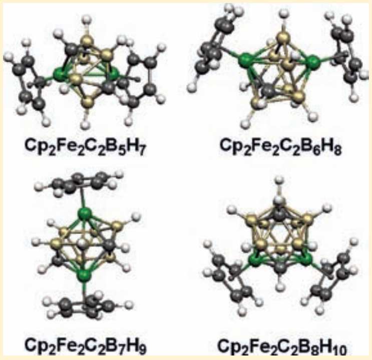
S *Supporting Information*



ABSTRACT: Theoretical studies show that the 10-vertex system $Cp_2Fe_2C_2B_6H_8$ is the only one of the 2*n* skeletal electron $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ systems ($n = 9, 10, 11, 12$) for which a true *isocloso* deltahedron having a single degree 6 vertex is highly favored over alternative structures. This is demonstrated by the occurrence of only the 10-vertex *isocloso* deltahedron as the central $Fe_2C_2B_6$ polyhedron in all nine of the $Cp_2Fe_2C_2B_6H_8$ structures within 8 kcal/mol of the global minimum. Low energy *isocloso* structures are also observed for the 11-vertex $Cp_2Fe_2C_2B_7H_9$. However, interspersed with these *isocloso* structures are $Cp_2Fe_2C_2B_7H_9$ structures based on deltahedra having two or more degree 6 vertices. For the 12-vertex $Cp_2Fe_2C_2B_8H_{10}$, the six lowest energy structures all have central $Fe_2C_2B_8$ deltahedra with two degree 6 vertices, one for each iron atom. The $Cp_2Fe_2C_2B_8H_{10}$ structures having a central $Fe_2C_2B_8$ icosahedron with all degree 5 vertices lie at significantly higher energies, starting at 17.8 kcal/mol above the global minimum. The 9-vertex $Cp_2Fe_2C_2B_5H_7$ system appears to be too small for *isocloso* structures to be favorable, although three such structures are found at energies between 5.5 and 8.0 kcal/mol above the global minimum. Five $Cp_2Fe_2C_2B_5H_7$ structures based on the tricapped trigonal prism lie in an energy below the lowest energy *isocloso* structure. The lowest energy $Cp_2Fe_2C_2B_5H_7$ structure and two higher energy structures within 8.0 kcal/mol of the global minimum have central $Fe_2C_2B_5$ deltahedra with a degree 6 vertex for each iron atom.

1. INTRODUCTION

Hawthorne and co-workers[1] were the first to show that boron vertices in polyhedral boranes and carboranes can be replaced by transition metal vertices to give extensive series of metallaboranes and metallacarboranes. Much of the initial work in this area used CpCo (Cp = cyclopentadienyl) vertices, which are isolobal and isoelectronic with BH vertices and thus donors of two skeletal electrons. Thus, a number of $CpCoC_2B_{n-3}H_{n-1}$ and $Cp_2Co_2C_2B_{n-4}H_{n-2}$ derivatives were synthesized.[2−6] These dicobaltadicarbaboranes all have $2n + 2$ skeletal electrons and exhibit the most spherical deltahedral structures analogous to the $B_nH_n^{2-}$ derivatives in accord with the Wade−Mingos rules.[7−9]

The early studies by Hawthorne and co-workers also included some studies on the synthesis of ferracarboranes containing CpFe vertices.[10] In this connection, a CpFe vertex is a donor of only one skeletal electron assuming the favored 18-electron configuration for the iron atom. Therefore, diferracarboranes of the type $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ have only 2*n* skeletal electrons rather than the $2n + 2$ skeletal electrons required by the Wade−Mingos rules[7−9] for the most spherical deltahedra. For the 10-vertex systems $Cp_2Fe_2C_2B_6H_8$ and $Cp_2Co_2C_2B_6H_8$, this difference in skeletal electron count has a major effect on the shape of the underlying $M_2C_2B_6$ polyhedron (Figure 1). Thus, $Cp_2Co_2C_2B_6H_8$ has a central $Co_2C_2B_6$ bicapped square antiprism analogous to the well-known $B_{10}H_{10}^{2-}$. The different geometry of the central $Fe_2C_2B_6$ unit was originally interpreted as a distorted bicapped square antiprism with an auxiliary Fe−Fe bond between the two iron atoms. This model allows each CpFe vertex to contribute the two skeletal electrons leading to the $2n + 2$ skeletal electrons (= 22 for $n = 10$ in this case) required by the Wade−Mingos rules[7−9] for the bicapped square antiprism geometry for a 10-vertex system. The auxiliary Fe−Fe bond, considered external to the underlying bicapped square antiprism, provides a mechanism for each CpFe vertex to be a donor of two skeletal electrons, while each iron atom attains the favored 18-electron configuration.

This hypoelectronic $Cp_2Fe_2C_2B_6H_8$ structure remained an interesting but isolated anomaly in the literature for a number of years until Kennedy and co-workers discovered several other examples of hypoelectronic metallaborane structures based on deltahedra topologically distinct from the *closo* deltahedra having 2*n* skeletal electrons.[11−14] This led to the proposal of a new class of less spherical deltahedra for metallaboranes and metallacarboranes, which have been called either *isocloso*[15] or *hypercloso*[16−18] deltahedra. The *isocloso* terminology will be used in this Article. These metallaborane deltahedra are derived from the *closo* most spherical metal-free borane deltahedra by a diamond-square-diamond

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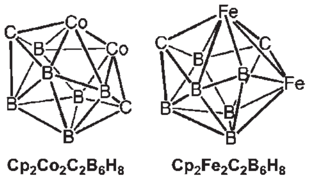
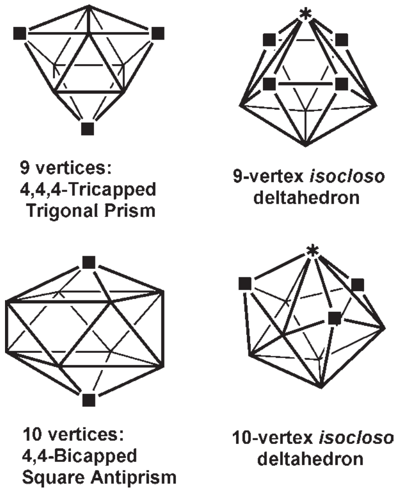


$Cp_2Co_2C_2B_6H_8$ $Cp_2Fe_2C_2B_6H_8$

Figure 1. Comparison of the $Cp_2Co_2C_2B_6H_8$ and $Cp_2Fe_2C_2B_6H_8$ structures synthesized by Hawthorne and co-workers and characterized structurally by X-ray crystallography.



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

9-vertex *isocloso*
deltahedron

10 vertices:
4,4-Bicapped
Square Antiprism

10-vertex *isocloso*
deltahedron

Figure 2. Comparison of the most spherical and the *isocloso* deltahedra having 9 and 10 vertices. The degree 4 and 6 vertices are designated by ■ and *, respectively, and the degree 5 vertices are unlabeled. In the lowest energy *isocloso* metallaborane structures, the degree 6 vertices are occupied by the metal atoms.

process,[19] typically generating a degree 6 vertex for the metal atom. The driving force behind this rearrangement is the preference of transition metals for higher degree vertices relative to carbon or boron atoms. Whereas metal-free boranes and carboranes are known for all of the *closo* most spherical deltahedra from the 6-vertex octahedron to the 12-vertex icosahedron, namely, those with 6 to 12 vertices; metallaborane and dimetallaborane deltahedra distinct from the most spherical deltahedra and with the metal(s) at degree 6 vertices are known only for a more limited range of vertex numbers, namely,, 9 to 12 vertices. The differences between the most spherical and the *isocloso* metallaborane deltahedra having 9 and 10 vertices are illustrated in Figure 2. Since the most spherical 11-vertex deltahedron necessarily has a single degree 6 vertex,[20] there is no change in deltahedral topology in going from the most spherical deltahedron to the *isocloso* 11-vertex deltahedron. In all of the metallaborane structures based on these *isocloso* deltahedra, the unique degree 6 vertices are occupied by transition metal atoms. Furthermore, localized bonding models with combinations of two-center bonds in some of the deltahedral edges and three-center bonds in some of the deltahedral faces can account for the 2*n* skeletal electrons in the *isocloso* deltahedral metallaboranes.[21]

Despite the attractiveness of the chemical bonding models for the hypoelectronic metallaboranes having 2*n* skeletal electrons, the available experimental data, in terms of molecules synthesized and characterized structurally, provide limited support for such models, particularly for systems with other than 10 vertices. Thus, only one example of a 9-vertex *isocloso* metallaborane has been synthesized, namely, the iridaborane $(Me_3P)_2HIrB_8H_7Cl$.[22] Furthermore, the 11-vertex most spherical deltahedron already has a degree 6 vertex, so the most spherical and the *isocloso* 11-vertex deltahedra both have the same topology.

In view of the limited experimental information on hypoelectronic metallaboranes, we have used a different approach to provide insight into the scope of the *isocloso*/*hypercloso* model by effectively synthesizing the lowest energy metallaborane structures in silico using well-established density functional theory methods. Diferraborane structures of the type $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ structures were used for this study for the following reasons:

(1) The 10-vertex system, $Cp_2Fe_2C_2B_6H_8$, was the first experimental example of a hypoelectronic metallaborane found to have a structure different from the corresponding most spherical deltahedron;[10]

(2) The simple substitution of two CpFe vertices for two CpCo vertices in the $Cp_2Co_2C_2B_{n-4}H_{n-2}$ systems, which have been studied extensively experimentally,[1] converts a 2*n* + 2 skeletal electron system predicted by the Wade—Mingos rules[7−9] to exhibit a most spherical deltahedral structure to a 2*n* skeletal electron system of interest in the context of the present work.

2. THEORETICAL METHODS

Full geometry optimizations have been carried out on the $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ systems at the same B3LYP/6-31G(d)[23−26] level of theory used for previous studies on cobaltadicarbaboranes[27] and cobaltaboranes.[28] The initial structures were chosen by the systematic substitution of two boron atoms from $B_nH_n^{2-}$ by two carbon atoms followed by further substitution of all possible different pairs of boron atoms in the resulting dicarbaborane by two CpFe units. This led to a large number of different starting structures. Thus, 249 structures of the 9-vertex clusters $Cp_2Fe_2C_2B_5H_7$, 387 structures of the 10-vertex clusters $Cp_2Fe_2C_2B_6H_8$, 684 structures of the 11-vertex clusters $Cp_2Fe_2C_2B_7H_9$, and 359 structures of the 12-vertex clusters $Cp_2Fe_2C_2B_8H_{10}$ were chosen as starting points for the optimizations (see the Supporting Information). 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 each of the imaginary frequencies to ensure that only genuine minima were obtained.

The structures, total and relative energies, and relevant interatomic distances for all calculated systems are given in the Supporting Information. Structures are numbered as **B(*n*−4)C2Fe2-*x*** where *n* is the number of vertices, and *x* is the relative order of the structure on the energy scale. Only the lowest energy and thus potentially chemically significant structures are considered in detail in this Article. More comprehensive lists of structures, including higher energy structures, are given in the Supporting Information. The energy cutoff points chosen depend upon the distribution of isomer structures and their energies and are indicated in the figure captions. The chosen energy cutoff points led to sets of 7 to 12 structures for a given cluster size discussed in detail in this Article.

All calculations were performed using the Gaussian 09 package[29] 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.

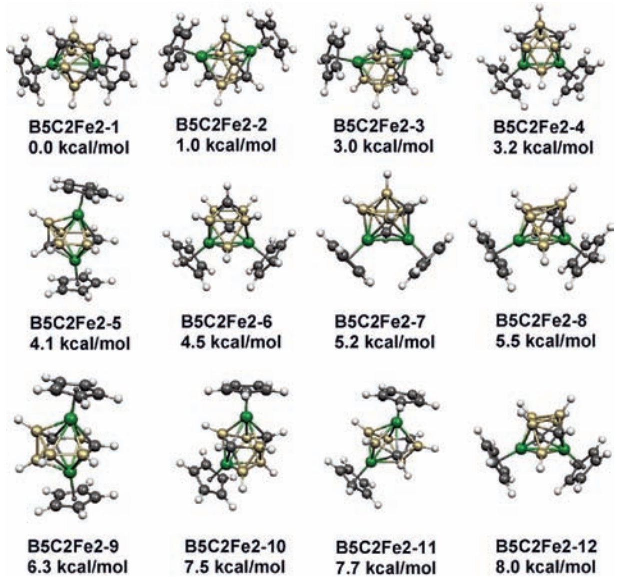


Figure 3. Twelve optimized $Cp_2Fe_2C_2B_5H_7$ structures within 8 kcal/mol of the global minimum.

Table 1. Summary of the 12 $Cp_2Fe_2C_2B_5H_7$ Structures within 8 kcal/mol of the Global Minimum

		vertex degrees		distances[a]		Fe−C	
structure (symmetry)	Δ*E*	Fe	C	Fe−Fe	C−C	edges	comments[b]
B5C2Fe2−1 (C_1)	0.0	6,6	4,4	**2.627**	2.553	1,1	concave
B5C2Fe2−2 (C_2)	1.0	5,5	4,4	3.335	2.570	1,1	TTP
B5C2Fe2−3 (C_1)	3.0	5,5	4,4	3.410	2.605	2,1	TTP
B5C2Fe2−4 (C_s)	3.2	5,5	4,4	**2.417**	2.551	1,1	TTP
B5C2Fe2−5 (C_s)	4.1	6,6	4,4	3.090	3.220	2,1	*oblatocloso*
B5C2Fe2−6 (C_s)	4.5	5,5	4,4	**2.542**	2.590	1,1	TTP
B5C2Fe2−7 (C_1)	5.2	5,5	4,4	**2.456**	2.623	2,1	TTP
B5C2Fe2−8 (C_s)	5.5	6,5	4,4	**2.709**	2.708	2,0	*isocloso*
B5C2Fe2−9 (C_s)	6.3	6,6	4,4	3.126	2.626	2,2	*oblatocloso*
B5C2Fe2−10 (C_1)	7.5	5,5	4,4	3.384	2.606	2,1	TTP
B5C2Fe2−11 (C_1)	7.7	6,5	5,4	3.145	2.451	2,1	*isocloso*
B5C2Fe2−12 (C_1)	8.0	6,5	4,4	**2.626**	3.166	2,1	*isocloso*

[a] The distances in **bold** correspond to direct Fe−Fe bonds (i. e., an edge of the deltahedron). [b] TTP = the D_{3h} 4,4,4-tricapped trigonal prism (i. e., the most spherical 9-vertex deltahedron (Figure 2)).

3. RESULTS

3.1. 9-Vertex $Cp_2Fe_2C_2B_5H_7$ Structures. A total of 26 structures for $Cp_2Fe_2C_2B_5H_7$ were found within 15 kcal/mol of the global minimum indicating a complicated potential energy surface. Among these 26 structures, the 12 structures within 8 kcal/mol of the global minimum are depicted in Figure 3 and listed in Table 1. The nine lowest energy structures (up to 6.3 kcal/mol above the global minimum **B5C2Fe2−1**) have the two carbon atoms at the preferred degree 4 vertices. Structures **B5C2Fe2−2, B5C2Fe2−3, B5C2Fe2−4, B5C2Fe2−6, B5C2Fe2−7**, and **B5C2Fe2−10**, at 1.0, 3.0, 3.2, 4.5, 5.2, and 7.5 kcal/mol above **B5C2Fe2−1**, respectively, all have an underlying $Fe_2C_2B_5$ tricapped trigonal prism and thus are based on the 9-vertex most spherical deltahedron with only degree 4 and 5 vertices. In these structures, the iron atoms are necessarily located at degree 5 rather than degree 6 vertices. These structures differ in the locations of the Fe, C, and B atoms at the nine vertices of the deltahedron. The close energy spacings of these structures suggest a highly fluxional system. The lowest energy $Cp_2Fe_2C_2B_5H_7$ structure having an underlying $Fe_2C_2B_5$ 9-vertex *isocloso* deltahedron with a single degree 6 vertex surrounded by four degree 4 vertices (Figure 2) is **B5C2Fe2−8**, lying 5.5 kcal/mol above **B5C2Fe2−1**. Other *isocloso* $Cp_2Fe_2C_2B_5H_7$ structures within 8 kcal/mol of **B5C2Fe2−1** include **B5C2Fe2−11** and **B5C2Fe2−12** at 7.7 and 8.0 kcal/mol, respectively, above **B5C2Fe2−1**. In these three *isocloso* $Cp_2Fe_2C_2B_5H_7$ structures, one of the iron atoms is located at the unique degree 6 vertex in accord with expectations. These observations indicate that the *isocloso* 9-vertex deltahedron is not particularly favorable for the $Cp_2Fe_2C_2B_5H_7$ system with $2n$ (= 18 for $n = 9$) skeletal electrons, contrary to expectations.

Three of the 12 $Cp_2Fe_2C_2B_5H_7$ structures within 8 kcal/mol of the global minimum **B5C2Fe2−1** are based on 9-vertex deltahedra having two degree 6 vertices and thus resemble topologically the *oblatocloso* $Cp_2Re_2B_7H_7$ deltahedron (Figure 3 and Table 1).[30−33] In all three of these structures, the two iron atoms are located at the two degree 6 vertices. Structures **B5C2Fe2−5** and **B5C2Fe2−9**, lying 4.1 and 6.3 kcal/mol above **B5C2Fe2−1**, resemble *oblatocloso* structures for $Cp_2Re_2B_7H_7$ with the two degree 6 iron vertices in nearly antipodal positions; however, their Fe···Fe distances through the center of the deltahedron are clearly nonbonding distances of ∼3.1 Å. Both structures, **B5C2Fe2−5** and **B5C2Fe2−9**, have the same underlying $Fe_2C_2B_5$ deltahedron with two degree 6 vertices, two degree 5 vertices, and five degree 4 vertices. They differ only in the pair of vertices occupied by the two carbon atoms.

The most unusual $Cp_2Fe_2C_2B_5H_7$ structure is the global minimum structure, **B5C2Fe2−1**, which has two approximately antipodal degree 6 vertices occupied by iron atoms like the structures **B5C2Fe2−5** and **B5C2Fe2−9** (Figure 3 and Table 1). However, structure **B5C2Fe2−1** has a short Fe−Fe distance of 2.627 Å, indicative of an iron−iron bond through the center of the polyhedron. The $Cp_2Fe_2C_2B_5H_7$ polyhedron can be interpreted as a slightly concave deltahedron with the Fe−Fe bond shared by two triangular faces bent toward the center of the polyhedron. The predicted BFeFeB dihedral angle of this concavity is 157.8° as compared with 180° for a coplanar Fe_2B_2 unit.

3.2. 10-Vertex $Cp_2Fe_2C_2B_6H_8$ Structures. A total of nine $Cp_2Fe_2C_2B_6H_8$ structures were found within 8 kcal/mol of the global minimum (Figure 4 and Table 2). All of these structures have an underlying $Fe_2C_2B_6$ *isocloso* 10-vertex deltahedron (Figure 2) with one iron atom at the unique degree 6 vertex and the other iron atom at a degree 5 vertex. The two lowest lying structures, **B6C2Fe2−1** and **B6C2Fe2−2**, have two of the three degree 4 vertices of the 10-vertex *isocloso* deltahedron occupied by carbon atoms. The $Cp_2Fe_2C_2B_6H_8$ isomer isolated in ∼5% yield from the reaction of $C_2B_7H_9^{2-}$ and NaC_5H_5 with $FeCl_2$ by Hawthorne and co-workers[10] is shown by X-ray crystallography to be **B6C2Fe2−2**, which lies only 0.3 kcal/mol above the global minimum **B6C2Fe2−1** and is the lowest energy $Cp_2Fe_2C_2B_6H_8$ structure with a direct Fe−Fe bond. The predicted 2.602 Å length of this Fe−Fe bond is close to the experimental Fe−Fe distance of 2.571 Å. The degree 6 iron atom in **B6C2Fe2−2** is directly bonded to both carbon atoms with predicted distances of 1.962 and 2.010 Å, close to the experimental distances of 1.962 and 1.992 Å. The degree 5 iron atom in **B6C2Fe2−2** is directly bonded to only one of the carbon atoms with a predicted distance of 1.849 Å, close to the experimental distance of 1.873 Å. The

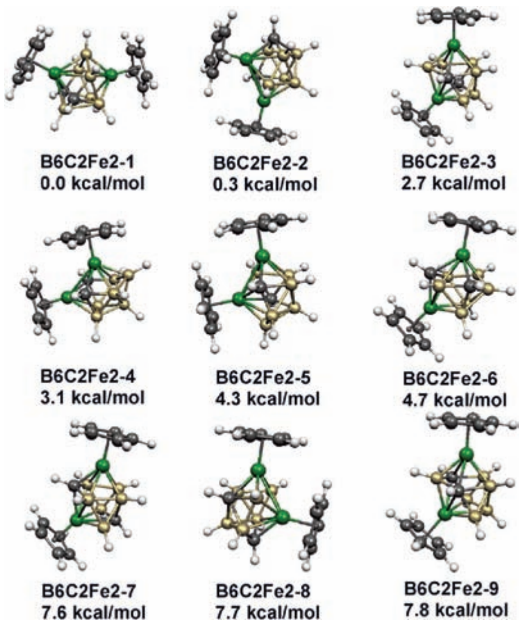


Figure 4. Nine optimized $Cp_2Fe_2C_2B_6H_8$ structures within 8 kcal/mol of the global minimum.

Table 2. Summary of the Nine $Cp_2Fe_2C_2B_6H_8$ Structures within 8 kcal/mol of the Global Minimum

		vertex degrees		distances[a]		Fe−C	
structure (symmetry)	Δ*E*	Fe	C	Fe−Fe	C−C	edges	comments
B6C2Fe2−1 (C_s)	0.0	6,5	4,4	3.311	2.663	2,0	*isocloso*
B6C2Fe2−2 (C_1)	0.3	6,5	4,4	**2.602**	2.705	2,1	*isocloso*
B6C2Fe2−3 (C_1)	2.7	6,5	5,4	3.336	3.042	2,1	*isocloso*
B6C2Fe2−4 (C_s)	3.1	6,5	4,4	**2.551**	2.754	2,2	*isocloso*
B6C2Fe2−5 (C_1)	4.3	6,5	4,4	**2.593**	3.020	2,1	*isocloso*
B6C2Fe2−6 (C_1)	4.7	6,5	4,4	3.371	2.694	2,1	*isocloso*
B6C2Fe2−7 (C_s)	7.6	6,5	5,4	3.387	3.019	2,1	*isocloso*
B6C2Fe2−8 (C_1)	7.7	6,5	5,4	**2.666**	2.601	1,1	*isocloso*
B6C2Fe2−9 (C_s)	7.8	6,5	5,5	3.384	2.583	2,1	*isocloso*

[a] The distances in **bold** correspond to direct Fe−Fe bonds (i. e., an edge of the deltahedron).

green color reported for **B6C2Fe2−2** is consistent with the presence of a direct Fe−Fe bond. Experimental work with the dicobaltadicarbaboranes $Cp_2Co_2C_2B_{n-4}H_{n-2}$ shows that species with direct Co−Co bonds are green, whereas those without direct Co−Co bonds are red.[4]

3.3. 11-Vertex $Cp_2Fe_2C_2B_7H_9$ Structures. The 11-vertex most spherical deltahedron necessarily has a degree 6 vertex so that the most spherical 11-vertex deltahedron is the same as the *isocloso* 11-vertex deltahedron. This deltahedron is found in five of the seven lowest energy $Cp_2Fe_2C_2B_7H_9$ structures, namely, **B7C2Fe2−2, B7C2Fe2−4, B7C2Fe2−5, B7C2Fe2−6,** and **B7C2Fe2−7** lying 2.8, 4.7, 6,5, 6.6, and 6.8 kcal/mol above the global minimum **B7C2Fe2−1**, respectively (Figure 5 and Table 3). These structures differ only in the positions of the iron and carbon atoms on the vertices of the 11-vertex *isocloso* deltahedron. In all of these structures, one of the iron atoms is located at the unique degree 6 vertex and the other iron atom is at one of the degree 5 vertices. In structures **B7C2Fe2−4** and **B7C2Fe2−7**, the two iron atoms are connected by edges of length 2.584 Å and 2.651 Å, respectively, corresponding to an Fe−Fe single bond.

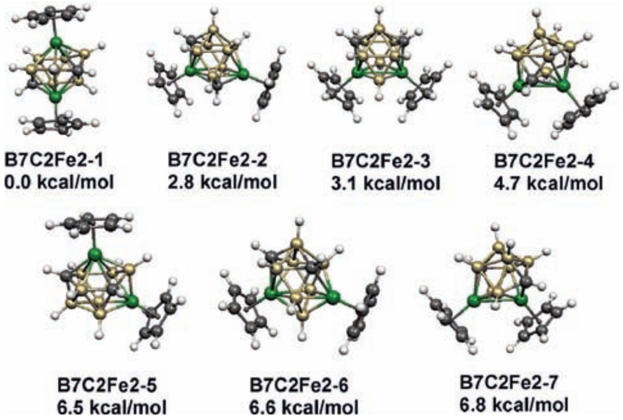


Figure 5. Seven optimized $Cp_2Fe_2C_2B_7H_9$ structures within 8 kcal/mol of the global minimum.

Table 3. Summary of the Seven $Cp_2Fe_2C_2B_7H_9$ Structures within 8 kcal/mol of the Global Minimum

		vertex degrees		distances[a]		Fe−C	
structure (symmetry)	Δ*E*	Fe	C	Fe−Fe	C−C	edges	comments[b],[c]
B7C2Fe2−1 (C_1)	0.0	6,6	5,4	3.286	3.234	2,1	2 ν_6
B7C2Fe2−2 (C_s)	2.8	6,5	4,4	3.421	3.283	2,1	*isocloso*
B7C2Fe2−3 (C_{2v})	3.1	6,6	4,4	**2.713**	2.881	1,1	3 ν_6
B7C2Fe2−4 (C_1)	4.7	6,5	4,4	**2.584**	3.282	2,1	*isocloso*
B7C2Fe2−5 (C_1)	6.5	6,5	5,4	3.396	2.772	2,1	*isocloso*
B7C2Fe2−6 (C_1)	6.6	6,5	4,4	3.378	2.607	1,1	*isocloso*
B7C2Fe2−7 (C_1)	6.8	6,5	5,4	**2.651**	3.330	1,1	*isocloso*

[a] The distances in **bold** correspond to direct Fe−Fe bonds (i. e., an edge of the deltahedron). [b] For these 11-vertex systems, the *isocloso* deltahedron is the same as the most spherical deltahedron, which has a unique degree 6 vertex (ν_6). [c] The numbers of degree 6 vertices are given as $n\ \nu_6$.

Several low-energy $Cp_2Fe_2C_2B_7H_9$ structures are based on less spherical 11-vertex deltahedra having two or even more degree 6 vertices (Figure 5 and Table 3). In such structures, each iron atom is located at a degree 6 vertex. The lowest energy $Cp_2Fe_2C_2B_7H_9$ structure **B7C2Fe2−1** is such a structure having the iron atoms in approximately antipodal positions with a nonbonding Fe···Fe distance of 3.286 Å. Because of this long nonbonding Fe···Fe distance, the **B7C2Fe2−1** structure cannot be considered to be an oblate structure[33] analogous to $Cp_2Re_2B_9H_9$. Furthermore, the central $Fe_2C_2B_7$ polyhedron in **B7C2Fe2−1** with no vertex degree higher than 6 is clearly different from the central Re_2B_9 polyhedron in $Cp_2Re_2B_9H_9$ with a degree 7 rhenium vertex. In the central 9-vertex C_2B_7 unit of **B7C2Fe2−1** an adjacent BBC unit is bonded to both iron atoms, whereas the remaining single carbon atom and five boron atoms are bonded to only a single iron atom.

The remaining $Cp_2Fe_2C_2B_7H_9$ structure, namely, **B7C2Fe2−3** lying 3.1 kcal/mol above the global minimum **B7C2Fe2−1,** is a relatively symmetrical C_{2v} structure with three degree 6 vertices (Figure 5 and Table 3). Two of these degree 6 vertices are

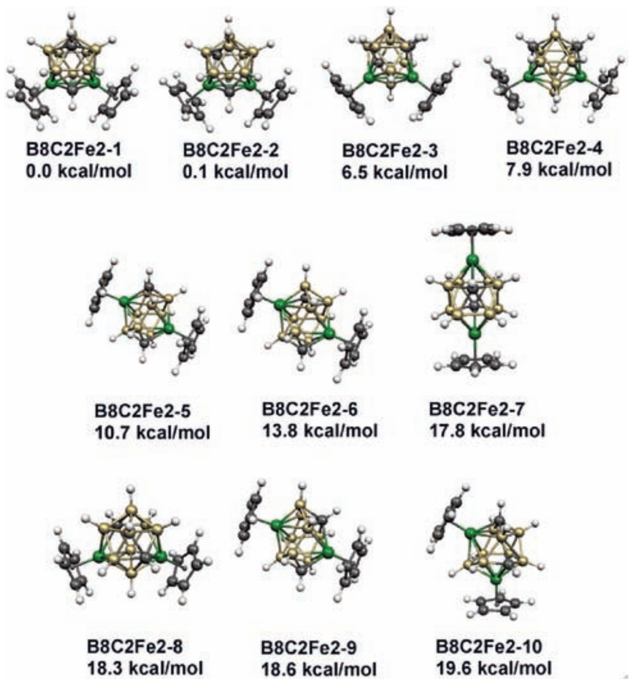


Figure 6. Ten optimized $Cp_2Fe_2C_2B_8H_{10}$ structures within 20 kcal/mol of the global minimum.

Table 4. Summary of the Ten $Cp_2Fe_2C_2B_8H_{10}$ Structures within 20 kcal/mol of the Global Minimum

		vertex degrees		distances[a]		Fe−C	
structure (symmetry)	ΔE	Fe	C	Fe−Fe	C−C	edges	comments[b]
B8C2Fe2−1 (C_s)	0.0	6,6	5,4	**2.642**	2.630	1,1	2 v_6
B8C2Fe2−2 (C_1)	0.1	6,6	5,4	**2.623**	3.225	2,1	2 v_6
B8C2Fe2−3 (C_1)	6.5	6,6	5,5	**2.702**	2.599	1,1	2 v_6
B8C2Fe2−4 (C_{2v})	7.9	6,6	4,4	3.399	2.842	1,1	3 v_6
B8C2Fe2−5 (C_2)	10.7	6,6	4,4	3.537	3.855	1,1	2 v_6
B8C2Fe2−6 (C_1)	13.8	6,6	5,4	3.573	3.575	1,1	2 v_6
B8C2Fe2−7 (C_i)	17.8	5,5	5,5	4.277	3.118	1,1	icosahedron
B8C2Fe2−8 (C_1)	18.3	5,5	5,5	3.579	3.163	1,1	icosahedron
B8C2Fe2−9 (C_1)	18.6	6,6	5,4	3.562	3.342	2,0	2 v_6
B8C2Fe2−10 (C_1)	19.6	6,6	4,4	3.362	2.941	1,1	3 v_6

[a] The distances in **bold** correspond to direct Fe−Fe bonds (i. e., an edge of the deltahedron). [b] The numbers of degree 6 vertices are given as $n\ v_6$.

occupied by iron atoms, which also share a bonding edge of predicted length 2.713 Å. The third degree 6 vertex in **B7C2Fe2−3** is occupied by a boron atom. This boron atom forms an isosceles Fe_2B macrotriangle with the iron atoms having two nonbonding Fe···B edges of length 3.083 Å as well as the bonding Fe−Fe edge of 2.713 Å noted above.

3.4. 12-Vertex $Cp_2Fe_2C_2B_8H_{10}$ Structures. The $Cp_2Fe_2C_2B_8H_{10}$ potential energy surface appears to be simpler than the other $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ ($n = 9, 10, 11$) potential energy surfaces since there are only four structures within 8 kcal/mol of the global minimum **B8C2Fe2−1** (Figure 6 and Table 4). Furthermore, all four structures are nonicosahedral deltahedra having two degree 6 vertices occupied by the iron atoms. In the three lowest energy $Cp_2Fe_2C_2B_8H_{10}$ structures, namely, the global minimum **B8C2Fe2−1** as well as **B8C2Fe2−2** and **B8C2Fe2−3** lying 0.1 and 6.5 kcal/mol, respectively, above this global minimum, the iron atoms share deltahedral edges of lengths 2.642, 2.623, and 2.702 Å, respectively, corresponding to an iron−iron bond. The close energy spacing of only 0.1 kcal/mol between **B8C2Fe2−1** and **B8C2Fe2−2** suggests a highly fluxional system. The $Cp_2Fe_2C_2B_8H_{10}$ structure **B8C2Fe2−4**, lying 7.9 kcal/mol above the global minimum **B8C2Fe2−1**, has a third degree 6 vertex that is occupied by one of the boron atoms. In this structure, the three degree 6 vertices form an Fe_2B isosceles triangle with two 3.198 Å Fe···B edges and one 3.399 Å Fe···Fe edge.

Because of this limited number of low energy $Cp_2Fe_2C_2B_8H_{10}$ structures as well as the lack of icosahedral structures within 8 kcal/mol of the global minimum, the energy range under consideration for $Cp_2Fe_2C_2B_8H_{10}$ was expanded to 20 kcal/mol above **B8C2Fe2−1** in which 10 structures were found (Figure 6 and Table 4). The lowest energy icosahedral structure for $Cp_2Fe_2C_2B_8H_{10}$ is **B8C2Fe2−7** at 17.8 kcal/mol above the global minimum. This lowest energy icosahedral $Cp_2Fe_2C_2B_8H_{10}$ structure **B8C2Fe2−7** has the iron atoms very far apart in antipodal positions with a long nonbonding Fe···Fe distance of 4.277 Å.

No 12-vertex $Cp_2Fe_2C_2B_8H_{10}$ species have been synthesized. However, the known allylmolybdenum carbonyl anion[34] $[(\eta^3\text{-}C_3H_5)Mo(CO)_2C_2Ph_2B_9H_9]^-$ has a central MoC_2B_9 deltahedron very similar to the central $Fe_2C_2B_8$ deltahedron in **B8C2Fe2−5**, lying 10.7 kcal/mol above **B8C2Fe2−1** (Figure 6 and Table 4). In the $[(\eta^3\text{-}C_3H_5)Mo(CO)_2C_2Ph_2B_9H_9]^-$ structure, the two carbon atoms are located at degree 4 vertices, and the molybdenum atom is located at one of the degree 6 vertices. The slightly higher energy $Cp_2Fe_2C_2B_8H_{10}$ structure **B8C2Fe2−6**, lying 13.8 kcal/mol above **B8C2Fe2−1**, has the same central $Fe_2C_2B_8$ deltahedron as **B8C2Fe2−5** but with one of the carbon atoms at a different vertex. Thus, in **B8C2Fe2−5** the two carbon atoms are located in essentially antipodal positions with a relatively long C···C distance of 3.855 Å. However, in **B8C2Fe2−6** the nonbonding C···C distance is significantly shorter at 3.575 Å.

4. DISCUSSION

The conversion of the most spherical *closo* borane deltahedra having, in general, only degree 4 and 5 vertices for structures to less spherical *isocloso*/*hypercloso* metallaborane deltahedra has been assumed to be driven by the preference of transition metals for degree 6 vertices. Furthermore, an analysis of the chemical bonding topology in *isocloso* metallaboranes[21] provides reasonable localized bonding models consisting of two-center two-electron and three-center two-electron bonds for such systems. These observations suggest the existence of *isocloso* metallaboranes having $2n$ rather than $2n + 2$ skeletal electrons for various numbers of vertices from 9 to 12. The structures of such hypoelectronic *isocloso* metallaboranes are assumed to be based on deltahedra having vertices of degree 6 for the metal atoms. Such deltahedra can be derived from the corresponding most spherical deltahedra by diamond-square-diamond transfomations.[19] Such processes generate degree 6 vertices for metal atoms while concurrently converting a corresponding number of the degree 5 vertices to degree 4 vertices. However, the range of such metallaborane structures that have been synthesized and definitively characterized structurally is very limited compared to what might be expected from such a geometrical exercise. For this reason, the theoretical study discussed in this Article was undertaken to assess whether the types of metallaborane structures that can be generated by this geometrical exercise are also favorable energetically. The simple substitution of the two CpCo vertices in the dicobaltadicarbaboranes $Cp_2Co_2C_2B_{n-4}H_{n-2}$ (n = 9, 10, 11, 12) with two CpFe vertices to give the corresponding diferradicarbaboranes $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ is a simple way, at least on paper, to convert *closo* species having $2n + 2$ skeletal electrons to *isocloso* species having only $2n$ skeletal electrons. Furthermore, Hawthorne and co-workers[10] were able to synthesize and characterize structurally by X-ray diffraction both the *closo* $Cp_2Co_2C_2B_6H_8$ with $2n + 2$ skeletal electrons and a bicapped square antiprismatic structure as well as the *isocloso* $Cp_2Fe_2C_2B_6H_8$ structure with the corresponding *isocloso* 10-vertex deltahedral structure with $2n$ skeletal electrons and one of the iron atoms at the unique degree 6 vertex.

The results from this research indicate quite clearly that the 10-vertex *isocloso* deltahedron having a unique degree 6 vertex, six degree 5 vertices, and three degree 4 vertices (Figure 2) is strongly preferred for the 10-vertex system $Cp_2Fe_2C_2B_6H_8$ with $2n$ (= 20 for n = 10) skeletal electrons. Thus, all nine $Cp_2Fe_2C_2B_6H_8$ structures within 8 kcal/mol of the global minimum have such a central $Fe_2C_2B_6$ polyhedron (Figure 4 and Table 2). These nine structures differ only in the locations of the Fe, C, and B atoms on the vertices of this deltahedron.

The 11-vertex most spherical deltahedron already has a degree 6 vertex for a metal atom without rearrangement to a less spherical deltahedron. Therefore, the most spherical 11-vertex deltahedron can also serve as an 11-vertex *isocloso* deltahedron without any polyhedral rearrangement. In fact, five of the seven $Cp_2Fe_2C_2B_7H_9$ structures within 8 kcal/mol of the global minimum, namely, **B7C2Fe2−2**, **B7C2Fe2−4**, **B7C2Fe2−5**, **B7C2Fe2−6**, and **B7C2Fe2−7** at 2.8, 4.7, 6.5, 6.6, and 6.8 kcal/mol, respectively, above **B7C2Fe2−1** (Figure 5 and Table 3), have a central $Fe_2C_2B_7$ *isocloso* 11-vertex deltahedron with one of the iron atoms at the unique degree 6 vertex. These five structures differ only in the locations of the other iron atom and the two carbon atoms relative to this unique degree 6 vertex. The lowest energy $Cp_2Fe_2C_2B_7H_9$ structure **B7C2Fe2−1** is of a different type with a central $Fe_2C_2B_7$ deltahedron having two degree 6 iron vertices in approximately antipodal positions. The seventh of these low energy $Cp_2Fe_2C_2B_7H_9$ structures, namely, **B7C2Fe2−3** at 3.1 kcal/mol above **B7C2Fe2−1**, has a central $Fe_2C_2B_7$ deltahedron with three degree 6 vertices. In **B7C2Fe2−3**, iron atoms are located at two of these degree 6 vertices and a boron atom at the third degree 6 vertex. The three degree 6 vertices in **B7C2Fe2−3** form an isosceles Fe_2B triangle with a bonding Fe−Fe edge of 2.713 Å and two equivalent nonbonding Fe···B edges of 3.083 Å. The general conclusion from these observations on low energy $Cp_2Fe_2C_2B_7H_9$ structures is that the expected *isocloso* structures with one of the iron atoms at the unique degree 6 vertex are still favorable structures. However, alternative structures based on 11-vertex deltahedra with two or three degree 6 vertices and both iron atoms at degree 6 vertices are competitive in energy.

The general stability of icosahedral boranes as well as icosahedral structures for all of the $Cp_2Co_2C_2B_8H_{10}$ isomers that have been synthesized suggest the possibility of low-energy icosahedral structures for $Cp_2Fe_2C_2B_8H_{10}$. However, five of the nine lowest energy $Cp_2Fe_2C_2B_8H_{10}$ structures, namely, the global minimum **B8C2Fe2−1** as well as the structures **B8C2Fe2−2**, **B8C2Fe2−3**, **B8C2Fe2−5**, **B8C2Fe2−6**, and **B8C2Fe2−9** at 0.1, 6.5, 10.7, 13.8, and 18.6 kcal/mol above **B8C2Fe2−1**, are all based on central 12-vertex $Fe_2C_2B_8$ deltahedra with two degree 6 vertices, two degree 4 vertices, and eight degree 5 vertices rather than the twelve degree 5 vertices of the regular icosahedron. In all of these $Cp_2Fe_2C_2B_8H_{10}$ structures, the iron atoms are located at the two degree 6 vertices. The lowest energy $Cp_2Fe_2C_2B_8H_{10}$ structure with a central $Fe_2C_2B_8$ regular icosahedron is the structure **B8C2Fe2−7**, lying 17.8 kcal/mol above the global minimum **B8C2Fe2−1**. Thus, the preference of iron atoms for degree 6 vertices overrides the general tendency of 12-vertex boranes to form icosahedral structures with all degree 5 vertices. The study discussed in this Article provides no theoretical evidence for the still experimentally unknown *isocloso* 12-vertex structures having a single degree 6 vertex, a single degree 4 vertex, and ten degree 5 vertices. Such structures would be analogous to the *isocloso* deltahedra with 9, 10, and 11 vertices (Figure 2).

The 9-vertex *isocloso* deltahedra has its unique degree 6 vertex flanked by the four degree 4 vertices (Figure 2). The concentration of degree 4 vertices makes this *isocloso* deltahedron less favorable than the larger *isocloso* deltahedra having fewer degree 4 vertices. Nevertheless, the 9-vertex *isocloso* deltahedron is found in three of the $Cp_2Fe_2C_2B_5H_7$ structures within 8 kcal/mol of the global minimum, namely, **B5C2Fe2−8**, **B5C2Fe2−11**, and **B5C2Fe2−12** at 5.5, 7.7, and 8.0 kcal/mol above **B5C2Fe2−1**. The 9-vertex most spherical deltahedron, namely, the tricapped trigonal prism (Figure 2), is found in six of the low energy $Cp_2Fe_2C_2B_5H_7$ structures, namely, **B5C2Fe2−2**, **B5C2Fe2−3**, **B5C2Fe2−4**, **B5C2Fe2−6**, **B5C2Fe2−7**, and **B5C2Fe2−10** at 1.0, 3.0, 3.2, 4.5, 5.2, and 7.5 kcal/mol above **B5C2Fe2−1**. These two deltahedra account for nine of the 12 $Cp_2Fe_2C_2B_5H_7$ structures within 8 kcal/mol of **B5C2Fe2−1**.

The three remaining 9-vertex $Cp_2Fe_2C_2B_5H_7$ structures within 8 kcal/mol of the global minimum are all based on deltahedra having two degree 6 vertices where the iron atoms are located. Structures **B5C2Fe2−5** and **B5C2Fe2−9**, lying 4.1 and 6.3 kcal/mol, respectively, above **B5C2Fe2−1**, are based on the same *oblatocloso*[33] $Fe_2C_2B_5$ deltahedron in which the two degree 6 iron vertices are located in approximately antipodal positions. This deltahedron is essentially the same as that for the dirhenaborane[30−33] $Cp_2Re_2B_7H_7$, except that in $Cp_2Fe_2C_2B_5H_7$ structures, the nearly antipodal Fe···Fe distances of ∼3.1 Å are too long for a intrapolyhedral iron−iron bond. These structures differ in the location of the two carbon atoms in the C_2B_7 belt between the two iron vertices.

The most unusual of the $Cp_2Fe_2C_2B_5H_7$ structures is the lowest energy structure **B5C2Fe2−1**, another structure in which both iron atoms are located at degree 6 vertices. The Fe−Fe distance of 2.627 Å suggests a formal iron−iron bond. The two triangular faces sharing this Fe−Fe bond are oriented toward the center of the $Fe_2C_2B_5$ deltahedron creating a slight indentation (concavity). The BFeFeB dihedral angle of this concavity is predicted to be 157.8° as compared with 180° for a planar Fe_2B_2 unit. This unusual concave deltahedron as the lowest energy structure combined with the observation of numerous low-energy tricapped trigonal prism structures suggests that the 9-vertex $Cp_2Fe_2C_2B_5H_7$ system is too small for the true 9-vertex *isocloso* deltahedron (Figure 2) to be an energetically favorable structure.

A limitation in using this study to make more general conclusions on the preferred polyhedra for hypoelectronic metallaboranes with 9 to 12 vertex atoms having $2n$ skeletal electrons lies in the choice of $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ systems for this study. Such systems were chosen because of their relevance to the experimental realization[10] of the lowest energy $Cp_2Fe_2C_2B_6H_8$ structure. However, these $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ systems have the disadvantage of having two metal atoms rather than only a single metal atom. This suggests a possible preference for deltahedra with two degree 6 vertices, one for each iron atom, rather than true *isocloso* deltahedra with only a single degree 6 vertex so that only one of the two iron atoms can be at a degree 6 vertex. A better test for the tendency for systems with 2*n* rather than 2*n* + 2 skeletal electrons to form *isocloso* structures would be a study of the 2*n* skeletal electron $CpMnC_2B_{n-3}H_{n-1}$ systems having only a single metal atom. However, such systems have not yet been realized experimentally and thus are of less interest to most chemists.

5. SUMMARY

The 10-vertex system $Cp_2Fe_2C_2B_6H_8$ is the only $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ system (n = 9, 10, 11, 12) having 2*n* skeletal electrons for which a true *isocloso* deltahedron is highly favored over alternative structures. This is demonstrated by the occurrence of only the 10-vertex *isocloso* deltahedron as the central $Fe_2C_2B_6$ polyhedron in all nine of the $Cp_2Fe_2C_2B_6H_8$ structures within 8 kcal/mol of the global minimum. Low energy *isocloso* structures are also observed for the 11-vertex $Cp_2Fe_2C_2B_7H_9$. However, interspersed with these *isocloso* structures are $Cp_2Fe_2C_2B_7H_9$ structures based on deltahedra with two or more degree 6 vertices. In such structures, each transition metal is located at a degree 6 vertex. For the 12-vertex $Cp_2Fe_2C_2B_8H_{10}$, the four lowest energy structures all have central $Fe_2C_2B_8$ deltahedra with two degree 6 vertices, one for each iron atom. The $Cp_2Fe_2C_2B_8H_{10}$ structures having a central $Fe_2C_2B_8$ icosahedron with all degree 5 vertices lie at significantly higher energies, starting at 17.8 kcal/mol above the global minimum.

The 9-vertex $Cp_2Fe_2C_2B_5H_7$ system appears to be too small for *isocloso* structures to be favorable energetically, although three such structures are found at energies between 5.5 and 8.0 kcal/mol above the global minimum. Five $Cp_2Fe_2C_2B_5H_7$ structures based on the tricapped trigonal prism lie in an energy below the lowest energy *isocloso* structure. The lowest energy $Cp_2Fe_2C_2B_5H_7$ structure and two higher energy structures within 8.0 kcal/mol of the global minimum have central $Fe_2C_2B_5$ deltahedra with a degree 6 vertex for each iron atom.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete Gaussian09 reference (ref 29); Tables 1−12: Initial structures, distance tables, and energy rankings for the $Cp_2Fe_2C_2B_{n-4}H_{n-2}$ structures (n = 9, 10, 11, 12). This material is available free of charge via the Internet at http://pubs.acs.org.

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