5088 *Inorg. Chem.* **2009**, *48*, 5088–5095
DOI: 10.1021/ic8020904

Inorganic Chemistry
Article

Kinetic versus Thermodynamic Isomers of the Deltahedral Cobaltadicarbaboranes

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Received October 31, 2008

Synthesis of the deltahedral cobaltadicarbaboranes $CpCoC_2B_{n-3}H_{n-1}$ ($n = 9, 10, 11, 12$) typically leads initially to kinetically stable isomers with energies up to ∼20 kcal/mol above the lowest energy isomers. Pyrolyses of these originally produced isomers typically results in isomerization to give more thermodynamically stable isomers. In this connection the relative stabilities of the $CpCoC_2B_{n-3}H_{n-1}$ ($n = 9, 10, 11, 12$) isomers have been investigated using density functional theory. For $CpCoC_2B_{n-3}H_{n-1}$ ($n = 9, 10, 11$) the isomers with both carbon atoms at degree 4 vertices are predicted to have the lowest energies. For $CpCoC_2B_9H_{11}$ the icosahedron is by far the preferred polyhedron. Among the nine possible icosahedral $CpCoC_2B_9H_{11}$ isomers, the unique isomer with the carbon atoms in antipodal (*para*) positions is the global minimum. However, the four $CpCoC_2B_9H_{11}$ isomers with the two carbon atoms in mutual non-antipodal non-adjacent (*meta*) positions lie within ∼5 kcal/mol of the global minimum. These theoretical results are in reasonable agreement with the extensive experimental work on pyrolysis of $CpCoC_2B_{n-3}H_{n-1}$ ($n = 9, 10, 11, 12$) derivatives, mainly in the group of Hawthorne and co-workers during the 1970s.

1. Introduction

A major breakthrough in carborane chemistry, as well as organometallic chemistry, was the discovery by Hawthorne and co-workers[1] that one or two boron vertices in dicarbaborane derivatives can be replaced by transition metal units. This leads to very stable metalladicarbaboranes and dimetalladicarbaboranes. Compounds with CpCo (Cp = η^5-C_5H_5) vertices in place of BH vertices in carborane structures are of particular interest since CpCo vertices, as formal donors of two skeletal electrons, are isolobal with BH vertices. Furthermore, these cobaltadicarbaboranes generally are very stable thermally and oxidatively. Thus the three series of compounds $CpCoC_2B_{n-3}H_{n-1}$, $C_2B_{n-2}H_n$, and $B_nH_n^{2-}$ are all isoelectronic with each other and are $2n + 2$ skeletal electron systems predicted by the Wade−Mingos rules[2−5] to exhibit the most spherical deltahedral structures (e.g., Figure 1 for the systems having 9 to 12 vertices). The number of possible isomers is even larger in these cages with one cobalt atom, two carbon atoms, and a number of boron atoms than in the corresponding metal-free cages.

The source of the two carbon atoms in the syntheses of most metalladicarbaboranes is an alkyne. The transition metal vertex is typically introduced by capping an open face of an intermediate dicarbaborane polyhedron. Since this open face in the polyhedral intermediate normally contains both carbon atoms, the initially produced metalladicarbaborane normally has the two carbon atoms in adjacent (*ortho*) positions, as well as two M−C edges. Pyrolysis of the initially produced metallacarborane gives more thermodynamically stable isomers analogous to the formation of the *meta* and *para* isomers of the icosahedral $C_2B_{10}H_{12}$ carborane by pyrolysis of the initially formed *ortho* $C_2B_{10}H_{12}$ (Figure 2). The more thermodynamically stable cobaltadicarbaborane isomers typically have non-adjacent carbon atoms and/or one or both carbon vertices not directly connected to the cobalt atom through a single edge. The resulting system of metalladicarbaborane isomers can be rather complicated as illustrated by the isolation of seven different isomers[6,7] of the icosahedral cobaltadicarbanonaborane $CpCoC_2B_9H_{11}$. In this paper we will extend the *o*/*m*/*p* terminology to metallacarborane structures by using *ortho* (*o*), *meta* (*m*), and *para* (*p*) to refer to an adjacent pair of vertices (i.e., a pair of vertices connected directly by an edge), a non-adjacent pair of vertices connected by a path of two edges, and an antipodal pair of vertices, respectively, in any

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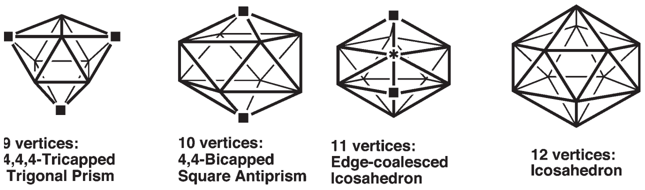

Figure 1. $B_nH_n^{2-}$ deltahedra ($9 \leq n \leq 12$). Degree 4 and 6 vertices are designated by ■ and ∗, respectively. Degree 5 vertices are unlabeled.

type of deltahedral borane structure. The thermodynamic stability of dicarbaboranes is maximized if the carbon atoms occupy the vertices of the lowest degree (typically degree 4 vertices in the structures under consideration here) and are kept as far apart as possible.[8]

Development of the chemistry of metallacarboranes in the 1960s and the 1970s, particularly in the laboratory of Hawthorne and co-workers,[1] was facilitated by the ready availability of decaborane at that time, since decaborane, $B_{10}H_{14}$, from U.S. government stockpiles was the boron raw material for most of the metallacarborane syntheses. However, eventually these stockpiles were depleted and destroyed so that decaborane became much more expensive to use as a starting material for the synthesis of metallaboranes and metallacarboranes. Thus most of the work on the cobaltdicarbaboranes was done before 1980 when decaborane was readily available but determination of molecular structures by single crystal X-ray diffraction was much more difficult than it is now. Therefore, most of the structures of the cobaltadicarbaboranes were established only by indirect methods such as ^{11}B NMR spectra, which provide information only on the following: (1) The symmetry of the cobaltadicarbaborane cage, normally whether it has no symmetry (C_1) or has a 2-fold symmetry element (C_2, C_s, or C_i); (2) The presence of degree 4 boron vertices adjacent to the cobalt vertex as indicated by an unusually low field ^{11}B resonance. The limited number of cobaltadicarbaborane structures that have been determined by X-ray diffraction include that of a mercurated derivative[10] of the 11-vertex system $CpCoC_2B_8H_{10}$ and that of the most readily available isomer of the 12-vertex system[11] $CpCoC_2B_9H_{11}$.

The density functional theory (DFT) study reported in this paper was undertaken in an effort to understand the obviously complicated potential energy surfaces of the $CpCoC_2B_{n-3}H_{n-1}$ systems having 9 to 12 vertices ($n = 9$ to 12). Since very few structures of the relevant cobaltadicarboranes have been definitively established by X-ray diffraction, it was desirable to use DFT to determine the lowest energy structures consistent with the experimental observations.

The only previous DFT studies on cobaltadicarbaboranes were reported by Perekalin and Kudinov.[12] Their work was restricted to the nine isomers of the icosahedral system $CpCoC_2B_9H_{11}$. Our studies reported on this paper are the first DFT studies on the non-icosahedral $CpCoC_2B_{n-3}H_{n-1}$ cobaltadicarbaboranes ($n = 9$, 10, and 11). For comparison, we have also included the 12-vertex icosahedral $CpCoC_2B_9H_{11}$ system in our work. Our results on the 12-vertex $CpCoC_2B_9H_{11}$ isomers are in essential agreement with those of Perekalin and Kudinov.[12]

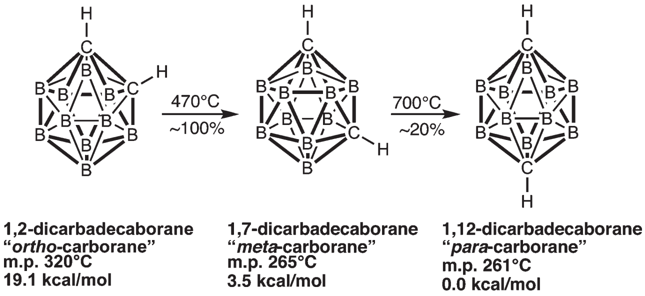

Figure 2. *ortho*, *meta*, and *para* isomers of the icosahedral carborane $C_2B_{10}H_{12}$. Hydrogen atoms on the boron atoms are omitted for clarity. The relative energies of the isomers given in the figure are those obtained from the calculations of Schleyer and Najafian.[9]

2. Theoretical Methods

Full geometry optimizations have been carried on the $CpCoC_2B_{n-3}H_{n-1}$ systems at the B3LYP/6-31G(d)[13−16] level of theory. The initial structures were chosen by systematic substitution of two boron atoms from $B_nH_n^{2-}$ by two carbon atoms followed by substitution of each type of boron atom in the resulting dicarbaborane with a CpCo unit. Thus 22 structures of the 9-vertex clusters $CpCoC_2B_6H_8$, 41 structures of the 10-vertex clusters $CpCoC_2B_7H_9$, 38 structures of the 11-vertex clusters $CpCoC_2B_8H_{10}$, and 16 structures of the 12-vertex clusters $CpCoC_2B_9H_{11}$ were chosen as starting points for the optimizations (see the Supporting Information, Table S1). 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 corresponding normal mode to ensure that genuine minima were obtained. Structures with imaginary frequencies smaller than $25i$ cm^{-1} were considered as minima on the potential energy surface.[17]

The structures, total and relative energies, and relevant interatomic distances for all calculated systems are given in the Supporting Information, Tables S2−S5. Structures are numbered as B(n−3)C2Co-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 paper, although 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 ranged from 25 to 60 kcal/mol above the corresponding global minimum as indicated in the figure captions. The chosen energy cutoff points led to sets of 7 to 10 structures for a given cluster size discussed in detail in this paper.

All calculations were performed using the Gaussian 98 package[18] with the default settings for the self-consistent field (SCF) cycles and geometry optimization, namely, the fine grid (75,302) for numerically evaluating the integrals, 10^{-8} hartree for the SCF 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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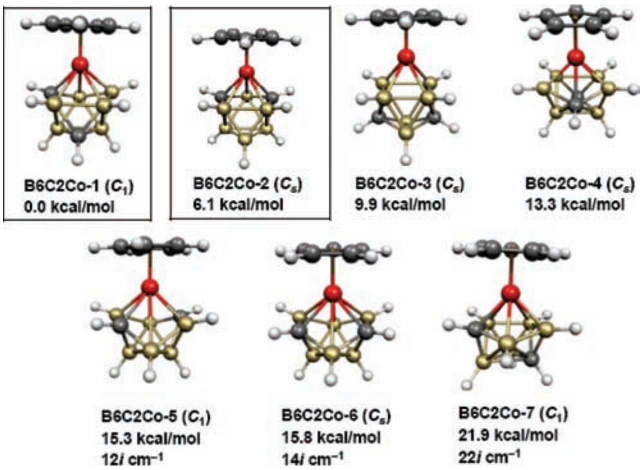

Figure 3. Structures of the 9-vertex $CpCoC_2B_6H_8$ isomers within 25 kcal/mol of the global minimum. Structures known experimentally are enclosed in boxes. Small residual imaginary vibrational frequencies are listed for the higher energy structures. The corresponding normal modes were not followed.

3. Results and Discussion

3.1. Nine-vertex $CpCoC_2B_6H_8$ Isomers. Seven distinct isomers among 22 total isomers were found for $CpCoC_2B_6H_8$ within 25 kcal/mol of the global minimum (Figure 3 and Table 1). In the four lowest energy structures the CoC_2B_6 polyhedron is the tricapped trigonal prism, which is the most spherical 9-vertex deltahedron (Figure 1). In the global minimum B6C2Co-1 the CpCo unit is located at a degree 5 vertex, and the two carbon atoms are located at two of the three degree 4 vertices so that there is only one Co−C edge. The next higher lying $CpCoC_2B_6H_8$ isomer, namely, B6C2Co-2 at 6.1 kcal/mol above B6C2Co-1, is very similar except both carbon atoms are at the two of the degree 4 vertices that are adjacent to the degree 5 CpCo vertex. Isomers B6C2Co-1 and B6C2Co-2 are the only $CpCoC_2B_6H_8$ structures that have been realized experimentally[19] consistent with these two structures being the lowest energy predicted $CpCoC_2B_6H_8$ structures. Furthermore, the B6C2Co-2 isomer of $CpCoC_2B_6H_8$ is converted to the lower energy B6C2Co-1 isomer upon pyrolysis at 150 °C for 5 h,[19] consistent with our DFT predictions. Although no $CpCoC_2B_6H_8$ isomers have been characterized structurally, the metalladicarbanonaboranes $[B_6H_8C_2Mn(CO)_3]^-$ (ref 20) and $H(Ph_3P)_2CoC_2B_6H_8$ (ref 21) have been shown by X-ray diffraction to have the same MC_2B_6 deltahedra as the $CpCoC_2B_6H_8$ global minimum B6C2Co-1 (Figure 3).

The next two isomers for $CpCoC_2B_6H_8$ in terms of energy (Figure 3 and Table 1) are also based on a CoC_2B_8 tricapped trigonal prism. In isomer B6C2Co-3, at 9.9 kcal/mol in energy above B6C2Co-1, the cobalt atom and both carbon atoms are located at the degree 4 vertices so that there are no direct Co−C edges in the deltahedron. The higher energy of structure B6C2Co-3 relative to B6C2Co-1 and B6C2Co-2 relates to the energetic disadvantage of having the cobalt atom located at a degree 4 vertex rather than a degree 5 vertex. However, the MC_2B_6 polyhedron of B6C2Co-3 is found in the platinadicarbanonaborane $(Me_3P)_2PtC_2Me_2B_6H_6$, which has been characterized by X-ray diffraction.[22] This suggests that a $(Me_3P)_2Pt$ unit, unlike a CpCo unit, prefers to be located at a degree 4 rather than a degree 5 vertex. This relates to the fact that $(Me_3P)_2Pt$ and CpCo units are not strictly isolobal. Thus $(Me_3P)_2Pt$, unlike CpCo, is not conical and thus has one less frontier orbital to interact with the carborane cage. This relates to the stability of square planar platinum complexes with metal−ligand bonds in only two dimensions leading to a 16-electron configuration rather than the usual 18-electron configuration.

Table 1. Structures, Energies (E in hartree), and Relative Energies (ΔE in kcal/mol) of the 9-Vertex $CpCoC_2B_6H_8$ Isomers within 25 kcal/mol of the Global Minimum

isomer	E	ΔE	vertex degrees Co	vertex degrees C	comments
B6C2Co-1 (C_1)	−1806.42132	0.0	5	4,4	Co−C
B6C2Co-2 (C_s)	−1806.41159	6.1	5	4,4	2 Co−C
B6C2Co-3 (C_s)	−1806.40559	9.9	4	4,4	No Co−C
B6C2Co-4 (C_s)	−1806.40010	13.3	5	5,4 (*m*)	Co−C
B6C2Co-5 (C_1)	−1806.39686	15.3	6	4,4 (*p*)	*isocloso* deltahedron
B6C2Co-6 (C_s)	−1806.39614	15.8	6	4,4 (*m*)	*isocloso* deltahedron
B6C2Co-7 (C_1)	−1806.38657	21.9	5	5,4 (*m*)	Co−C

Isomer B6C2Co-4, at 13.3 kcal/mol above the global minimum B6C2Co-1, has the cobalt atom located at the preferred degree 5 vertex. However, one of the carbon atoms in B6C2Co-4 is located at a less favorable degree 5 vertex. The latter relates to the higher energy of this structure relative to B6C2Co-1 and B6C2Co-2. The other carbon in B6C2Co-4 is in a *meta* position relative the cobalt atom, that is, two edges away from the cobalt atom.

The highest energy $CpCoC_2B_6H_8$ isomer within 25 kcal/mol of the global minimum B6C2Co-1, namely, B6C2Co-7 at 21.9 kcal/mol above B6C2Co-1, also has a CoC_2B_6 tricapped trigonal prism framework (Figure 3 and Table 1). Isomer B6C2Co-7 resembles isomer B6C2Co-4 in that the cobalt atom and one of the carbon atoms are located at degree 5 vertices and the other carbon atom is located at a degree 4 vertex. Furthermore in both B6C2Co-7 and B6C2Co-4 the two carbon atoms are in *meta* positions relative to each other and there is one Co−C edge. However, in B6C2Co-4 the Co−C edge is a “vertical” edge of the underlying trigonal prism connecting two degree 5 vertices whereas in B6C2Co-7 the Co−C edge is an edge connecting a degree 5 vertex with a degree 4 vertex.

In the remaining two $CpCoC_2B_6H_8$ structures within 25 kcal/mol of the global minimum B6C2Co-1, namely, B6C2Co-5 and B6C2Co-6 (Figure 3 and Table 1), the CoC_2B_8 deltahedron is not the tricapped trigonal prism but instead is an alternative 9-vertex C_{2v} deltahedron with one degree 6 vertex and four degree 4 vertices. This deltahedron can be derived from the tricapped trigonal prism by a sequence of two diamond-square-diamond (dsd) processes (Figure 4).[23,24] All four of the degree 4

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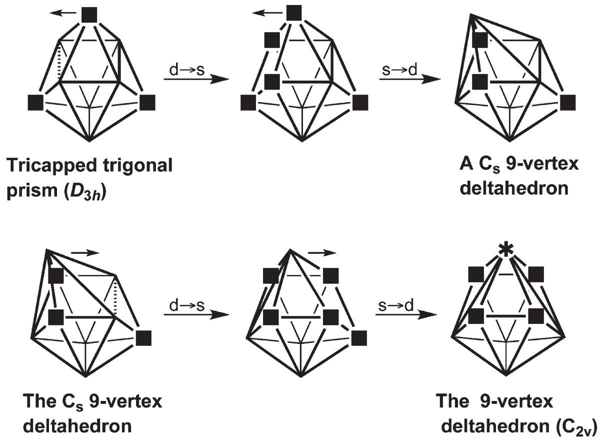

Figure 4. Sequence of diamond-square-diamond (dsd) processes converting the tricapped trigonal prism (the most spherical 9-vertex deltahedron) into the C_{2v} 9-vertex deltahedron found in structures B6C2Co-5 and B6C2Co-6 of $CpCoC_2B_6H_8$. Degree 4 and 6 vertices are designated by ■ and ∗, respectively. Degree 5 vertices are unlabeled.

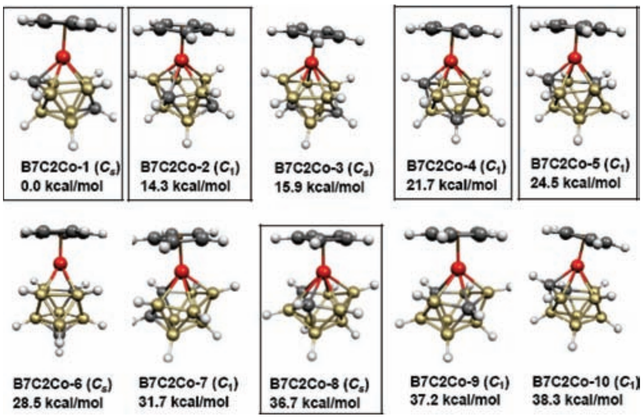

Figure 5. Structures of the 10-vertex $CpCoC_2B_7H_9$ within 40 kcal/mol of the global minimum. Structures known experimentally are in boxes.

vertices in the final 9-vertex deltahedron are connected by an edge to the unique degree 6 vertex. In both B6C2Co-5 and B6C2Co-6 the cobalt atom is at the unique degree 6 vertex, and the carbon atoms are at two of the degree 4 vertices. In B6C2Co-5 at 15.3 kcal/mol above B6C2Co-1 the two carbon atoms are in *para* positions relative to each other. However, in B6C2Co-6 at 15.8 kcal/mol the two carbon atoms are in *meta* positions relative to each other. This difference in the locations of the carbon atoms in these $CpCoC_2B_6H_8$ structures is seen to make relatively little difference, that is, only 0.5 kcal/mol, in the relative energies of B6C2Co-5 and B6C2Co-6.

3.2. Ten-Vertex $CpCoC_2B_7H_9$ Isomers. Ten isomers among 41 total isomers for the 10-vertex system $CpCoC_2B_7H_9$ were found within 40 kcal/mol of the global minimum (Figure 5 and Table 2). Nine of these ten isomers have a CoC_2B_7 bicapped square antiprism, which is the most spherical 10-vertex deltahedron. However, structure B7C2Co-8 for $CpCoC_2B_7H_9$ is based on an isocloso 10-vertex deltahedron with the cobalt atom at the unique degree 6 vertex and carbon atoms at two of the three degree 4 vertices.

Table 2. Structures, Energies (E in hartree), and Relative Energies (ΔE in kcal/mol) of the 10-Vertex $CpCoC_2B_7H_9$ Isomers within 40 kcal/mol of the Global Minimum

			vertex degrees		
isomer	E	ΔE	Co	C	Co−C edges
B7C2Co-1 (C_s)	−1831.92102	0.0	5	4,4	1
B7C2Co-2 (C_1)	−1831.89815	14.3	5	4,5 (*m*)	1 (deg 5)
B7C2Co-3 (C_s)	−1831.89566	15.9	5	4,5 (*m*)	0
B7C2Co-4 (C_1)	−1831.88637	21.7	5	4,5 (*m*)	1 (deg 4)
B7C2Co-5 (C_1)	−1831.88195	24.5	5	4,5 (*m*)	2
B7C2Co-6 (C_s)	−1831.87551	28.5	4	4,5 (*m*)	1
B7C2Co-7 (C_1)	−1831.87043	31.7	5	4,5 (*o*)	1
B7C2Co-8 (C_s)	−1831.86248	36.7	6 (*isocloso*)	4,4	2
B7C2Co-9 (C_1)	−1831.86180	37.2	5	5,5 (*m*)	2
B7C2Co-10 (C_1)	−1831.86000	38.3	5	4,5 (*o*)	2

The lowest energy $CpCoC_2B_7H_9$ isomer, namely, B7C2Co-1, is the unique isomer with a carbon atom at each of the two degree 4 vertices capping the underlying square antiprism and the cobalt atom at a degree 5 vertex. Note that the carbon atoms are separated as much as possible in *para* positions. This isomer is also indicated to be favorable by being more than 14 kcal/mol below the next lowest energy $CpCoC_2B_7H_9$ isomer. The carbon atoms in isomer B7C2Co-1 are necessarily in *para* (antipodal) relative positions at the degree 4 vertices. Although $CpCoC_2B_7H_9$ has not been characterized structurally, several related metalladicarbadecaboranes $[B_7H_7C_2H(OH)M(CO)_3]^z$ (z = 0, M = Ru; z = −1, M = Mn, Re) with a MC_2B_7 deltahedron analogous to B7C2Co-1 have been structurally characterized by X-ray diffraction.[25]

The next four $CpCoC_2B_7H_9$ isomers in terms of energy (Figure 5 and Table 2) all have the cobalt at a degree 5 vertex and the carbon atoms in relative *meta* positions with one of the carbon atoms located at a degree 4 vertex and the other carbon atom at a degree 5 vertex. Isomers B7C2Co-2 and B7C2Co-4, at 14.3 and 15.9 kcal/mol in energy, respectively, above B7C2Co-1, all have one of the two carbon atoms directly bonded to cobalt through a Co−C deltahedral edge. In B7C2Co-2 this Co−C edge is to the carbon at a degree 5 vertex. However, in the higher energy isomer B7C2Co-4 this Co−C edge is to the carbon located at a degree 4 vertex. The isomer B7C2Co-3, at 15.9 kcal/mol above B7C2Co-1, does not have a Co−C edge. The highest energy of these four isomers, namely, B7C2Co-5 at 24.5 kcal/mol above B7C2Co-1, has Co−C edges to both carbon atoms.

The next $CpCoC_2B_7H_9$ isomer B7C2Co-6, at 28.5 kcal/mol above B7C2Co-1, is the only structure within 40 kcal/mol of the global minimum B7C2Co-1 with the cobalt atom located at a degree 4 rather than a degree 5 vertex. This isomer has one Co−C edge, necessarily to the degree 5 vertex carbon atom.

The lowest energy $CpCoC_2B_7H_9$ isomer with adjacent carbon atoms is B7C2Co-7 at 31.7 kcal/mol (Figure 5 and Table 2). In B7C2Co-7 one carbon is located at a degree 4 vertex, the other carbon atom is located at a degree 5 vertex, and there is a single Co−C edge. Isomer B7C2Co-10, at 38.3 kcal/mol above B7C2Co-1, also has adjacent carbon atoms, one located at a degree 4 vertex and the other at a degree 5 vertex. However, there are two Co−C edges in B7C2Co-10 whereas B7C2Co-7 has only one Co−C edge.

The final $CpCoC_2B_7H_9$ isomer with a bicapped square antiprismatic central CoC_2B_7 unit and within 40 kcal/mol of the global minimum B7C2Co-1, namely, B7C2Co-9 at

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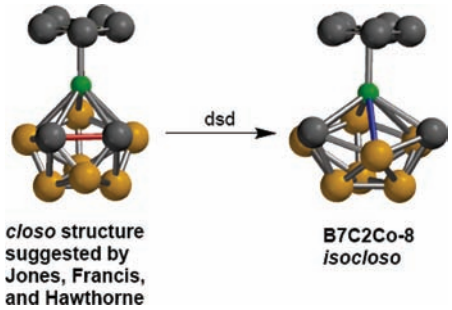

Figure 6. Diamond-square-diamond (dsd) relating the C_s *closo* $CpCoC_2B_0H_9$ structure proposed by Jones, Francis, and Hawthorne[26] to the *isocloso* structure B7C2Co-8, also of C_s symmetry. In these structures hydrogen atoms are omitted for clarity and Co, C, and B atoms are indicated by green, gray, and yellow circles, respectively.

37.2 kcal/mol above B7C2Co-1, has two Co−C edges and the carbon atoms in meta positions.

One $CpCoC_2B_7H_9$ structure within 40 kcal/mol of B7C2Co-1, namely, B7C2Co-8 at 36.7 kcal/mol above B7C2Co-1, was found based on an isocloso 10-vertex deltahedron with one degree 6 vertex, two degree 4 vertices, and seven degree 5 vertices (Figure 5 and Table 2). Formation of an *isocloso* rather than the usual *closo* 10-vertex structure allows the cobalt atom to be located at a favorable degree 6 vertex and the two carbon atoms to be located at favorable degree 4 vertices. Furthermore, an attempt to optimize the closo stucture suggested by Jones, Francis, and Hawthorne (JFH)[26] for their $CpCoC_2B_7H_9$ isomer IA (Figure 4 of their paper[26]) led instead to the isocloso isomer by rupture of the C−C edge (red edge in Figure 6) and formation of a new Co−B edge (blue edge in Figure 6). In this way the degree 5 vertices for the cobalt and carbon atoms are converted to the degree 6 vertex for the cobalt atom and degree 4 vertices for the carbon atoms. Our DFT studies thus suggest that isomer IA suggested in the JFH paper[26] is really the isocloso structure B7C2Co-8. The structural assignment in the JFH paper is based solely on the C_s symmetry indicated by the ^{11}B NMR without any definitive structural determinations by X-ray crystallography. Furthermore, alternative isocloso structures for metallaboranes were not yet recognized in 1972 when the JFH work was done.

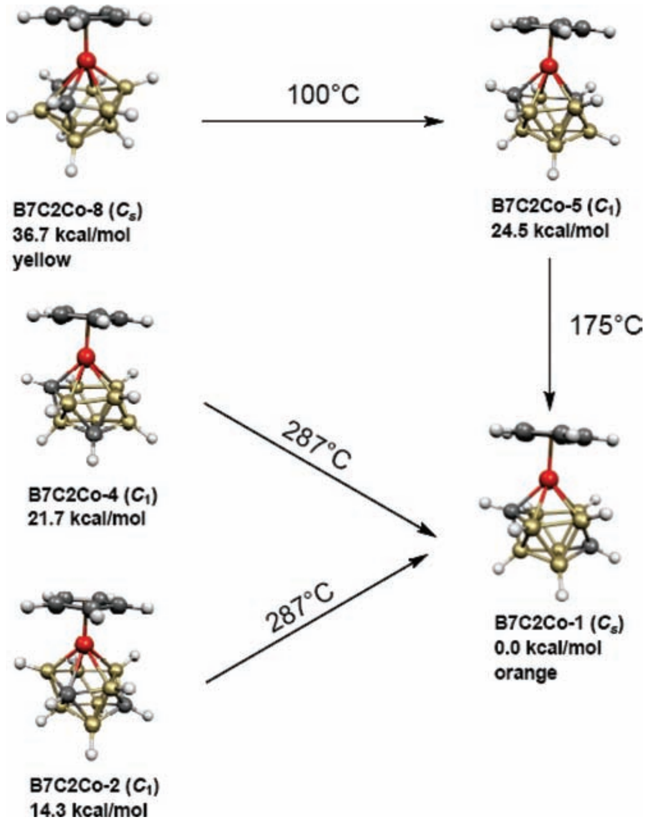

Figure 7. Thermal rearrangements of $CpCoC_2B_7H_9$ isomers.

Five of the ten $CpCoC_2B_7H_9$ isomers depicted in Figure 5 and listed in Table 2 have been realized experimentally. Their relationships through thermal interconversions are depicted in Figure 7.[19] The starting isomers B7C2Co-4, and B7C2Co-2 of $CpCoC_2B_7H_9$ are all obtained by reactions of various isomeric $B_7C_2H_9^{2-}$ anions with $CoCl_2$ in the presence of NaC_5H_5. The *isocloso* $CpCoC_2B_7H_9$ isomer B7C2Co-8 was isolated by chromatography from a complicated mixture obtained by the polyhedral contraction[26] of $CpCoC_2B_9H_{11}$ with KOH/H_2O_2. Since the pentagonal open face in the dicarbaborane anions used in these syntheses contain one or both of the carbon atoms, the initial $CpCoB_7C_2H_9$ products correspondingly have one or two Co−C edges. Isomer B7C2Co-3, although lower in energy than the experimentally known B7C2Co-4, B7C2Co-5, and B7C2Co-8 isomers, is not accessible by this chemistry since it has no Co−C edges. The thermal rearrangements depicted in Figure 7 lead to lower energy $CpCoB_7C_2H_9$ isomers with fewer Co−C edges, carbon atoms at degree 4 rather than degree 5 vertices, and more widely separated carbon atoms.

3.3. Eleven-Vertex $CpCoC_2B_8H_{10}$ Isomers. The most spherical 11-vertex deltahedron has C_{2v} symmetry with a unique degree 6 vertex flanked by two degree 4 vertices. The remaining eight vertices of this deltahedron have degree 5 (Figure 1). All 11 $CpCoC_2B_8H_{10}$ isomers within 25 kcal/mol of the global minimum among 38 total isomers are based on this deltahedron (Figure 8 and Table 3). The lowest energy $CpCoC_2B_8H_{10}$ isomer B8C2Co-1 has the cobalt atom located at the unique degree 6 vertex and the carbon atoms located at the two degree 4 vertices, thereby preserving the full C_{2v} symmetry of the deltahedron despite three different vertex types. This maximum symmetry of the 11-vertex deltahedron in isomer B8C2Co-1 minimizes the number of distinct boron atoms and thus facilitates its identification by high-resolution ^{11}B NMR spectroscopy. The $CpCoC_2B_8H_{10}$ isomer B8C2Co-1 has been synthesized,[27] and the structure of a chloromercuri derivative $CpCoC_2B_8H_9HgCl$ has been determined by X-ray diffraction.[10]

The next three $CpCoC_2B_8H_{10}$ isomers in terms of energy also have the two carbon atoms located at the two degree 4 vertices of the 11-vertex deltahedron similar to B8C2Co-1, but the cobalt atom is located at a degree 5 vertex rather than a degree 6 vertex (Figure 8 and Table 3). Isomer B8C2Co-2 of $CpCoC_2B_8H_{10}$, at 2.3 kcal/mol in

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(26) Jones, C. J.; Francis, J. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1972**, *94*, 8391.

(27) Evans, W. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 3063.

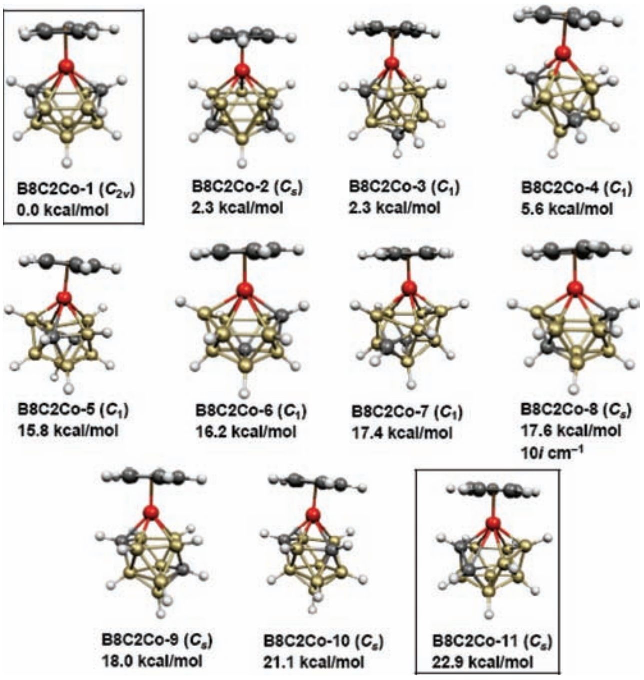

Figure 8. Structures of the eleven 11-vertex $CpCoC_2B_8H_{10}$ within 25 kcal/mol of the global minimum. The two structures known experimentally are enclosed in boxes.

Table 3. Structures, Energies (*E* in hartree), and Relative Energies (ΔE in kcal/mol) of the 11-Vertex $CpCoC_2B_8H_{10}$ Isomers within 20 kcal/mol of the Global Minimum

isomer	*E*	ΔE	vertex degrees Co	 C	comments
B8C2Co-1 (C_{2v})	−1857.36947	0.0	6	4,4 (*m*)	2Co−C
B8C2Co-2 (C_s)	−1857.36579	2.3	5	4,4 (*m*)	No Co−C
B8C2Co-3 (C_1)	−1857.36575	2.3	5	4,4 (*m*)	Co−C
B8C2Co-4 (C_1)	−1857.36046	5.6	5	4,4 (*m*)	Co−C
B8C2Co-5 (C_1)	−1857.34421	15.8	5	4,5 (*p*)	Co−C (deg 5)
B8C2Co-6 (C_1)	−1857.34358	16.2	6	4,5 (*m*)	Co−C (deg 4)
B8C2Co-7 (C_1)	−1857.34166	17.4	5	4,5 (*o*)	No Co−C
B8C2Co-8 (C_s)	−1857.34134	17.6	6	4,5 (*p*)	Co−C (deg 4)
B8C2Co-9 (C_1)	−1857.34071	18.0	5	4,5 (*p*)	Co−C (deg 4)
B8C2Co-10 (C_s)	−1857.33575	21.1	5	4,5 (*m*)	2Co−C
B8C2Co-11 (C_s)	−1857.33302	22.9	6	4,5 (*o*)	2Co−C

energy above B8C2Co-1, has no Co−C edges and both carbon atoms are in *meta* positions relative to the cobalt atom. Isomer B8C2Co-3 of $CpCoC_2B_8H_{10}$, also at 2.3 kcal/mol in energy above B8C2Co-1, has a single Co−C edge and the other carbon atom is in a pseudo-antipodal (*para*) position relative to the cobalt atom. Isomer B8C2Co-4 of $CpCoC_2B_8H_{10}$, at 5.6 kcal/mol above B8C2Co-1, also has a single Co−C edge but the other carbon atom is in a *meta* position relative to the cobalt atom. The fact that the four lowest lying isomers of $CpC_2B_8H_{10}$ in terms of energy all have the two carbon atoms at the two degree 4 vertices of the 11-vertex deltahedron suggests that the presence of the carbon atoms at the degree 4 vertices is the most important factor determining the relative energies of the $CpCoC_2B_8H_{10}$ isomers.

The remaining seven $CpCoC_2B_8H_{10}$ isomers within 25 kcal/mol of the global minimum B8C2Co-1 have one carbon atom located at a degree 5 vertex and the other carbon atom located at a degree 4 vertex (Figure 8 and Table 3). The jump in relative energy from the highest energy isomer with two degree 4 carbon vertices, namely, B8C2Co-4, to the lowest energy of these isomers with a degree 5 carbon vertex, namely, B8C2Co-5, is ~10 kcal/mol, again indicating the energy favorability of carbon atoms at degree 4 vertices. Three of these isomers, namely, B8C2Co-6, B8C2Co-8, and B8C2Co-11 at 16.2 kcal/mol, 17.6 kcal/mol, and 22.9 kcal/mol, respectively, have the cobalt atom located at the degree 6 vertex with the carbon atoms in relative *meta*, *para*, and *ortho* positions, respectively. Isomers B8C2Co-6 and B8C2Co-8 have one Co−C edge to the degree 4 carbon vertex. However, the higher energy isomer B8C2Co-11 has two Co−C edges.

The remaining four $CpCoC_2B_8H_{10}$ isomers, namely, B8C2Co-5, B8C2Co-7, B8C2Co-9, and B8C2Co-10 at 15.8 kcal/mol, 17.4 kcal/mol, 18.0 kcal/mol, and 21.1 kcal/mol in energy, respectively, above the global minimum B8C2Co-1 all have the cobalt atom located at a degree 5 vertex, one carbon atom located at a degree 4 vertex, and the other carbon atom located at a degree 5 vertex (Figure 8 and Table 3). These isomers differ in the relative positions of the carbon atoms. Thus in isomers B8C2Co-5, B8C2Co-7, B8C2Co9, and B8C2Co-10 the carbon atoms are in *para*, *ortho*, *para*, and *meta* positions, respectively. The two $CpCoC_2B_8H_{10}$ isomers with the carbon atoms in *para* positions, namely, B8C2Co-5 and B8C2Co-9, differ by their single Co−C edges being from the cobalt atom to the degree 5 carbon atom and the degree 4 carbon atom, respectively.

The global minimum $CpCoC_2B_8H_{10}$ isomer, namely, B8C2Co-1, is obtained by the reaction of $C_2B_8H_{10}$ with sodium followed by reaction of the resulting $C_2B_8H_{10}{}^{2-}$ dianion with $CoCl_2$ and NaC_5H_5.[27] A different $CpCoC_2B_8H_{10}$ isomer is obtained by oxidative degradation of *ortho*-$CpCoC_2B_9H_{11}$ with hydrogen peroxide in alkaline media. This product is formulated as the B8C2Co-11 isomer based on the proximity of the carbon atoms in the starting material and the non-equivalence of all eight boron atoms in the ^{11}B NMR spectrum indicating the lack of symmetry. This isomer, which has not been structurally characterized by X-ray diffraction, is reported to rearrange to the lowest energy $CpCoC_2B_8H_{10}$ isomer, namely, B8C2Co-1, upon pyrolysis in cyclooctane at 150 °C. Isomer B8C2Co-11 of $CpCoC_2B_8H_{10}$, although of relatively high energy, is the lowest energy isomer with adjacent carbon atoms and the cobalt atom at a degree 6 vertex. However, formulation of this alkaline oxidative degradation product as B8C2Co-11 assumes that the proximity of the two carbon atoms is maintained during the reaction. Note that a much lower energy isomer with no symmetry such as B8C2Co-3 at only 2.3 kcal/mol above B8C2Co-1 would also lead to a similar ^{11}B NMR spectrum. This system clearly merits reinvestigation since this report is more than 35 years old.

Some experimental data are available on the analogous 11-vertex cobaltdicarbaboranes $CpCoC_2Me_2B_8H_8$ in which the hydrogens on the two carbon atoms have been replaced by methyl groups. The analogous oxidative alkaline degradation product of $CpCoC_2Me_2B_9H_9$ is formulated as isomer B9C2Co-11 of $CpCoC_2Me_2B_8H_8$. Pyrolysis of this isomer $CpCoC_2Me_2B_8H_8$ in boiling octane gives not only a blue isomer formulated with the global minimum structure B9C2Co-1 but also a second

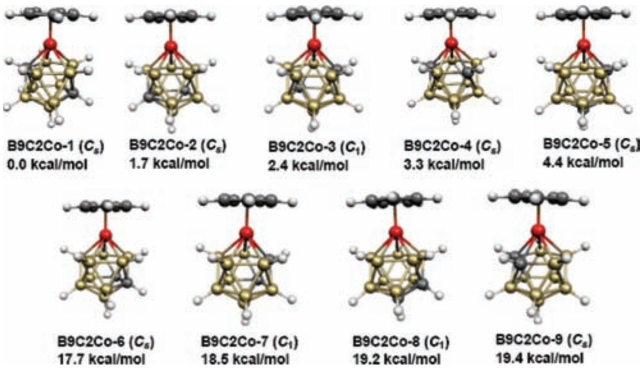

Figure 9. Structures of the nine 12-vertex $CpCoC_2B_9H_{11}$ isomers within 50 kcal/mol of the global minimum.

isomer formulated with the low energy structure B9C2Co-2 at only 2.3 kcal/mol above B9C2Co-1 for the $CpCoC_2B_8H_{10}$ derivatives. This formulation is very plausible in terms of energetics. However, because of the lack of X-ray structures, this system also merits reinvestigation.

3.4. Twelve-Vertex $CpCoC_2B_9H_{11}$ Structures. All nine possible icosahedral $CpCoC_2B_9H_{11}$ structures were found to be true minima (Figure 9 and Table 4). Any non-icosahedral $CpCoC_2B_9H_{11}$ structures, such as structures analogous to the experimentally obtained structure of the anion $[(\eta^3C_3H_5)Mo(CO)_2C_2Ph_2B_9H_9]^-$ based on a 12-vertex deltahedron with two degree 6 vertices, two degree 4 vertices, and eight degree 5 vertices, were found to be more than 50 kcal/mol above the global minimum B9C2Co-1 and thus are not considered in this paper. Our calculations on $CpCoC_2B_9H_{11}$ using the B3LYP/6-31G(d) method are in essential agreement with the DFT calculations of Perekalin and Kudinov (PK)[12] using the PBEPBE method with the DGDZPV basis set with regard to the relative energies of the nine isomers (Table 4). The $CpCoC_2B_9H_{11}$ isomers in Table 4 are designated as *xy-z* where *x* and *y* relate to the relative positions of each carbon atom to the cobalt atom in the icosahedron and *z* relates to the relative positions of the two carbon atoms. In both cases the relative positions are designated as adjacent or *ortho* (*o*), non-adjacent non-antipodal or *meta* (*m*), and antipodal or *para* (*p*) analogous to the designations used for the metal free $C_2B_{10}H_{12}$ isomers in Figure 2.

The relative position of the two carbon atoms in the $CpCoC_2B_9H_{11}$ isomers is the most important factor in determining their relative energies. Thus, the $CpCoC_2B_9H_{11}$ global minimum B9C2Co-1 is the unique icosahedral isomer *om-p* with the carbon atoms in antipodal (*para*) positions. The four icosahedral $CpCoC_2B_9H_{11}$ isomers with the two carbons in relative *meta* positions, namely, B9C2Co-2, B9C2Co-3, B9C2Co-4, and B9C2Co-5, all lie in the narrow energy range of 1.7 kcal/mol for B9C2Co-2 to 4.4 kcal/mol for B9C2Co-5, using the global minimum B9C2Co-1 energy as the reference point. The final four icosahedral $CpCoC_2B_9H_{11}$ isomers, namely, B9C2Co-6, B9C2Co-7, B9C2Co-8, and B9C2Co-9, which have the two carbons in adjacent (*ortho*) positions, that is, forming a C−C edge in the icosahedron, are the highest energy isomers having significantly higher relative energies in the range from 17.7 kcal/mol for B9C2Co-6 to 19.4 kcal/mol for B9C2Co-9, again using the global minimum B9C2Co-1 energy as the reference point.

Table 4. Structures, Energies (E in hartree), and Relative Energies (ΔE in kcal/mol) of the 12-Vertex $CpCoC_2B_8H_{10}$ Isomers within 50 kcal/mol of the Global Minimum

isomer	E	ΔE	$\Delta E_{PK}{}^a$	C and Co arrangement
B9C2Co-1 (C_s)	−1882.87408	0.0	0.0	*om-p*
B9C2Co-2 (C_s)	−1882.87141	1.7	1.1	*mm:m*
B9C2Co-3 (C_1)	−1882.87025	2.4	2.5	*om:m*
B9C2Co-4 (C_s)	−1882.86881	3.3	3.7	*oo-m*
B9C2Co-5 (C_s)	−1882.86710	4.4	3.8	*op-m*
B9C2Co-6 (C_s)	−1882.84586	17.7	15.4	*mm-o*
B9C2Co-7 (C_1)	−1882.84458	18.5	16.6	*om-o*
B9C2Co-8 (C_1)	−1882.84343	19.2	16.2	*mp-o*
B9C2Co-9 (C_s)	−1882.84320	19.4	17.6	*oo-o*

[a] Data of Perekalin and Kudinov.[12]

Extensive experimental work has been done on the pyrolysis of $CpCoC_2B_9H_{11}$ and its derivatives where the hydrogens attached to the carbon atoms are replaced by other groups.[7] The most accessible carborane starting material for the synthesis of $CpCoC_2B_9H_{11}$ is *ortho*-$C_2B_{10}H_{12}$ (Figure 2), which is the product initially formed from acetylene and decaborane derivatives. Removal of a BH vertex from *ortho*-$C_2B_{10}H_{12}$ with a strong base followed by introduction of a CpCo unit into the resulting anion $C_2B_9H_{12}^-$ using $CoCl_2$/NaCp gives the highest energy icosahedral $CpCoC_2B_9H_{11}$ isomer, namely, the *oo-o* isomer B9C2Co-9 (Figure 9 and Table 4) at nearly 20 kcal/mol above the $CpCoC_2B_9H_{11}$ global minimum B9C2Co-1. The formation of the high energy *oo-o* isomer B9C2Co-9 in this reaction relates to the retention of the C−C bond in the original acetylene, as well as location of the two carbon atoms on the open pentagonal face of the intermediate $C_2B_9H_{12}^-$ anion. Pyrolysis of B9C2Co-9 requires temperatures around ~400 °C and leads to rearrangement to give a complicated mixture containing many of the other $CpCoC_2B_9H_{11}$ isomers, characterized by their ^{11}B and ^{1}H NMR spectra, as well as their chromatographic and electrochemical properties. The five lowest energy isomers with separated carbon atoms predominate in the pyrolysis mixture. The limiting products in the pyrolysis of $CpCoC_2B_9H_{11}$ at the highest temperatures of ~700 °C in a dynamic system are the three lowest energy $CpCoC_2B_9H_{11}$ isomers, namely, B9C2Co-1, B9C2Co2, and B9C2Co-3 (Figure 8 and Table 4). The only $CpCoC_2B_9H_{11}$ isomer found in the B9C2Co-9 pyrolysis product retaining the adjacent carbon atoms is B9C2Co-7, and this rearranges further with separation of the carbon atoms upon heating beyond 500 °C.

The two $CpCoC_2B_9H_{11}$ isomers B9C2Co-6 and B9C2Co-8 (Figure 9 and Table 4) are the only $CpCoC_2B_9H_{11}$ isomers that have not been identified in the pyrolysis mixtures. Both "missing" isomers B9C2Co-6 and B9C2Co-8 have adjacent carbon atoms and thus are relatively high energy $CpCoC_2B_9H_{11}$ isomers. However, tying the two carbons in the CoC_2B_9 cage together with a trimethylene bridge forces the two carbons to remain in *ortho* position upon rearrangement so that the pyrolysis products of the trimethylene derivative $CpCoC_2(CH_2)_3B_9H_9$ include the trimethylene analogues of the "missing" $CpCoC_2B_9H_{11}$ isomers B9C2Co-6 and B9C2Co-8.[7]

3.5. HOMO−LUMO Gaps in the Cobaltadicarbaboranes. An indication of the stability of a computed structure besides its energy is a large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In this connection the HOMO−LUMO gaps have been investigated for the structures reported in this paper (see the Supporting Information, Tables S6 to S9). The nine-vertex $CpCoC_2B_6H_8$ structures based on the most spherical deltahedron (Figure 3), namely, the tricapped trigonal prism (Figure 1) have HOMO−LUMO gaps in the range 4.0 to 4.2 eV. However, the two nine-vertex structures based on the isocloso nine-vertex deltahedron with the cobalt atom at a degree 6 vertex, namely, structures B6C2Co-5 and B6C2Co-6 (Figure 3 and Table 1), have smaller HOMO−LUMO gaps in the range 3.7 ± 0.07 eV. Similarly for the 10-vertex $CpCoC_2B_7H_9$ structures based on the most spherical deltahedron, namely, the bicapped square antiprism (Figure 5 and Table 2), the HOMO−LUMO gaps fall in the range 4.0 to 4.7 eV. However, the isocloso $CpCoC_2B_7H_9$ structure B7C2Co-8 (Figure 5 and Table 2) has the much smaller HOMO−LUMO gap of 3.35 eV.

All of the 11-vertex $CpCoC_2B_8H_{10}$ isomers (Figure 8 and Table 3) have the same CpC_2B_8 skeleton, namely, the edge-coalesced icosahedron (Figure 1). The $CpCoC_2B_8H_{10}$ isomers with the cobalt atom at a degree 5 vertex have HOMO−LUMO gaps of 3.91 to 4.68 eV whereas structures with the cobalt atom at a degree 6 vertex have lower HOMO−LUMO gaps of 3.40 to 3.95 eV.

The 12-vertex $CpCoC_2B_9H_{11}$ isomers within 25 kcal/mol of the global minimum are all based on CoC_2B_9 icosahedra with the cobalt atom necessarily at a degree 5 vertex (Figure 9 and Table 4). The HOMO−LUMO gaps for these $CpCoC_2B_9H_{11}$ isomers fall in the range 4.75 to 5.26 eV. The higher HOMO−LUMO gaps of the icosahedral cobaltadicarbaboranes with 12 vertices relative to those of the non-icosahedral cobaltadicarboranes with fewer than 12 vertices may relate both to the high symmetry of the icosahedron and the high stability of icosahedral borane structures relative to borane structures based on other polyhedra.

4. Summary

The most important factor in determining the stabilities of the cobaltadicarbaborane derivatives $CpCoC_2B_{n-3}H_{n-1}$ ($n = 9, 10, 11$) is the degree of the carbon vertices. Thus, for the nine-vertex system $CpCoC_2B_6H_8$ the three lowest energy isomers all have both carbon atoms located at two of the three degree 4 vertices of the nine-vertex deltahedron, namely, the tricapped trigonal prism. For the 10-vertex system $CpCoC_2B_7H_9$, the unique isomer with both carbon atoms located at the two degree 4 vertices of the 10-vertex deltahedron, namely, the bicapped square antiprism, is the global minimum lying more than 14 kcal/mol below the next lowest energy isomer. For the 11-vertex system $CpCoC_2B_8H_{10}$ the four isomers with both carbon atoms located at the two degree 4 vertices of the 11-vertex deltahedron lie more than 10 kcal/mol below the next lowest energy isomer.

The icosahedron is by far the preferred polyhedron for the 12-vertex system $CpCoC_2B_9H_{11}$. Since the icosahedron has no degree 4 vertices, the carbon atoms in $CpCoC_2B_9H_{11}$ must necessarily be located at degree 5 vertices. Among the nine possible icosahedral $CpCoC_2B_9H_{11}$ isomers, the unique isomer with the carbon atoms in antipodal (*para*) positions is the global minimum. However, the four $CpCoC_2B_9H_{11}$ isomers with the two carbon atoms in mutual non-antipodal non-adjacent (*meta*) positions lie within ~5 kcal/mol of the global minimum.

The syntheses of the $CpCoC_2B_{n-3}H_{n-1}$ derivatives ($n = 9, 10, 11, 12$) often use alkynes as the source of the two carbon atoms in the $CpCoC_2B_{n-3}$ deltahedron. The initially produced isomers are therefore relatively high-energy kinetic isomers having adjacent carbon atoms derived from the original alkyne. The thermal rearrangements of these initially produced high-energy isomers provide routes to lower energy isomers. At sufficiently high temperatures these rearrangements lead to the lowest energy thermodynamic isomers, typically either with both carbon atoms located at degree 4 vertices (for $n = 9, 10, 11$) or with the carbon atoms as widely separated as possible (for the icosahedral systems with $n = 12$). The relatively high temperatures required for the isomerizations of the $CpCoC_2B_{n-3}H_{n-1}$ derivatives (even >400 °C in some cases) indicates not only their high thermal stabilities but also the high activation energies for the isomerization processes.

Acknowledgment. We are indebted to the National Science Foundation for support of this work under Grant CHE-0716718. Part of this work was undertaken with the financial support from CEEX-42 SUPRAMOL program, Romania.

Supporting Information Available: Table S1, initial structures (left) and the codes of the optimized structures derived from for $CpCoC_2B_{n-3}H_{n-1}$; Table S2, optimized structures of $CpCoC_2B_6H_8$; Table S3, optimized structures of $CpCoC_2B_7H_9$; Table S4, optimized structures of $CpCoC_2B_8H_{10}$; Table S5, Optimized structures of $CpCoC_2B_9H_{11}$; Table S6, HOMO−LUMO gaps for the $CpCoC_2B_6H_8$ structures; Table S7, HOMO−LUMO gaps for the $CpCoC_2B_7H_9$ structures; Table S8, HOMO−LUMO gaps for the $CpCoC_2B_8H_{10}$ structures; Table S9, HOMO−LUMO gaps for the $CpCoC_2B_9H_{11}$ structures; complete Gaussian 98 reference (reference 18). This material is available free of charge via the Internet at http://pubs.acs.org.