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From *closo* to *isocloso* Structures and Beyond in Cobaltaboranes with 9 to 12 Vertices

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Density functional theory (DFT) studies predict the dianions $CpCoB_{n-1}H_{n-1}^{2-}$ (n = 9, 10, 11, 12; Cp = η^5-C_5H_5) to have structures based on the most spherical deltahedra found in the isoelectronic boranes $B_nH_n^{2-}$. In the $CpCoB_8H_8^{2-}$ dianion the non-equivalent structures with the cobalt atom at a degree 4 vertex and at a degree 5 vertex are essentially degenerate in terms of energy (within ∼1 kcal/mol). For the $CpCoB_{n-1}H_{n-1}^{2-}$ dianions (n = 10, 11, 12) the cobalt atom prefers energetically the vertices of the lowest possible degree (four for n = 10 and 11, five for n = 12). Structures for the neutral species $CpCoB_{n-1}H_{n-1}$ (n = 10, 11, 12) based on *isocloso* deltahedra with the cobalt atom at a degree 6 vertex are preferred energetically by 9, 19, and 53 kcal/mol, respectively, over alternative structures. However, for $CpCoB_8H_8$ the *closo* tricapped trigonal prismatic structure with the cobalt atom at a degree 5 vertex is energetically preferred by ∼9 kcal/mol over the *isocloso* deltahedral structure with the cobalt atom at a degree 6 vertex. The lowest energy structures predicted for the dications $CpCoB_8H_8^{2+}$ and $CpCoB_9H_9^{2+}$ are highly oblate (flattened) deltahedra with the cobalt atom at a degree 7 vertex. A complicated potential energy surface was found for $CpCoB_{10}H_{10}^{2+}$ including non-deltahedral structures with a single quadrilateral or pentagonal face. The predicted lowest energy structures for both $CpCoB_{11}H_{11}$ and $CpCoB_{11}H_{11}^{2+}$ are based on the same 12-vertex deltahedron with three degree 6, six degree 5, and three degree 4 vertices, and thus topologically different from the regular icosahedron normally found in boron chemistry.

1. Introduction

The borane dianions $B_nH_n^{2-}$ ($6 \le n \le 12$) are of considerable interest because of their unusual stabilities compared with the reactive and frequently unstable neutral boron hydrides, such as those originally obtained by Stock.[1] These $B_nH_n^{2-}$ dianions have structures based on the so-called "most spherical" deltahedra with the maximum possible number of vertices of degrees 4 and 5.[2] In this context a deltahedron is a polyhedron in which all faces are triangles, and the degree of a polyhedral vertex is the number of edges meeting at that vertex. The deltahedra found in the deltahedral borane dianions having from 9 to 12 vertices are depicted in Figure 1.

These deltahedral boranes with n vertices have particularly high stabilities when the number of skeletal electrons is $2n + 2$, in accord with the Wade−Mingos rules.[3−6] To count the skeletal electrons to apply the Wade−Mingos rules, the BH vertices are considered as formal donors of two skeletal electrons since one of the three boron valence electrons is used to form the B−H bond thereby leaving only two electrons for skeletal bonding. The stability of the deltahedral boranes with n vertices and $2n + 2$ skeletal electrons can be viewed as an extension of the concept of aromaticity from two dimensions in benzene and related planar compounds to the third dimension.[7−9]

A major breakthrough in borane chemistry was the discovery by Hawthorne and co-workers[10] that one or two boron vertices in borane derivatives can be replaced by transition metal units. Compounds with CpCo (Cp = η^5-C_5H_5) vertices in place of BH vertices in borane structures are of particular interest since CpCo vertices, as formal donors of two skeletal electrons, are isoelectronic and isolobal with BH vertices. Thus derivatives of the type $CpCoB_{n-1}H_{n-1}^{2-}$ are isoelectronic with the very stable borane anions $B_nH_n^{2-}$. However, in the original work of Hawthorne and co-workers on metallaboranes[10] two of the boron vertices were replaced by carbon vertices leading to

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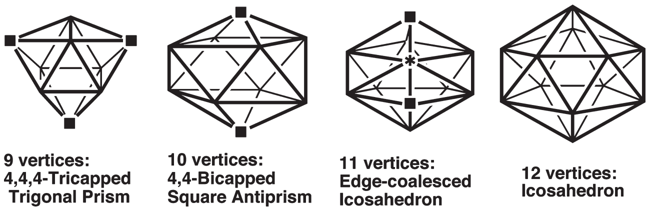

Figure 1. Most spherical (*closo*) $B_nH_n^{2-}$ deltahedra ($9 \le n \le 12$). In Figures 1 and 2 the degree 4 and 6 vertices are designated by ■ and *, respectively, and the degree 5 vertices are unlabeled.

neutral cobaltadicarbaboranes $CpCoC_2B_{n-3}H_{n-1}$ isoelectronic with the cobaltaborane dianions $CpCoB_{n-1}H_{n-1}^{2-}$. This provided the practical benefits of working with neutral molecules rather than dianions but introduced the complication of isomers arising from different locations of the two carbon atoms in the CoC_2B_n deltahedron.

The subsequent development of metallaborane chemistry involving polyhedra other than the icosahedron, particularly by Kennedy and co-workers,[11−14] led to a variety of deltahedral metallaborane structures based on deltahedra topologically distinct from the *closo* deltahedra. This led to the identification of a new class of less spherical deltahedra for metallaboranes and metallacarboranes called either *isocloso*[15] or *hypercloso*[16−18] deltahedra; the former terminology will be used in this paper. These *isocloso* metallaborane deltahedra are derived from the *closo* metal-free borane deltahedra by one or more diamond-square-diamond processes,[19,20] typically generating a degree 6 vertex for the metal atom. Of particular interest are the 9- and 10-vertex structures based on a deltahedron with the transition metal at a degree 6 vertex whereas (Figure 2) the corresponding metal-free deltahedron has only degree 4 and 5 vertices (Figure 1). What is even more interesting is the fact that such "anomalous" metallaborane deltahedra are also "disobedient" in not having the $2n + 2$ skeletal electrons expected from the Wade−Mingos rules[3−6] but only $2n$ skeletal electrons.[11]

Experimental work suggests the existence of two types of metallaboranes, namely, n-vertex *closo* metallaboranes having the $2n + 2$ skeletal electrons suggested by the Wade−Mingos rules[3−6] for the most spherical deltahedra (Figure 1) and n vertex *isocloso* metallaboranes having only $2n$ skeletal electrons and deltahedral structures with a single degree 6 vertex for the metal atom. For the nine- and ten-vertex systems the *closo* and *isocloso* deltahedra are topologically different (Figures 1 and 2). However, for the 11-vertex system even the *closo* deltahedron has a unique degree 6 vertex (Figure 1), since an 11-vertex deltahedron with only degree 4 and 5 vertices is topologically impossible.[21] In this case the 11-vertex *closo* and *isocloso* polyhedra are identical. For the 12-vertex system the icosahedron, which has exclusively degree 5 vertices, is the *closo* deltahedron. However, an *isocloso* 12-vertex deltahedron with two degree 6 and two degree 4 vertices is found in the molybdenum anion[22] $[\{(\eta^3\text{-}C_3H_5)(OC)_2Mo\}(PhC)_2B_9H_9]^-$.

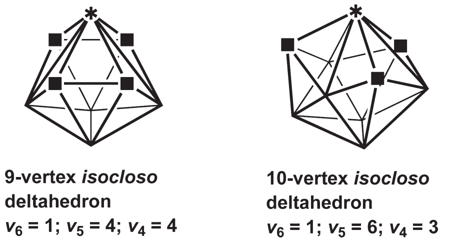

Figure 2. Nine- and ten-vertex *isocloso* metallaborane deltahedra. These are different from the corresponding nine- and ten-vertex *closo* deltahedra and have the transition metal atom at the unique degree 6 vertex.

The research described in this paper uses density functional theory (DFT) to investigate the preferred structures for the cobaltaborane dianions $CpCoB_{n-1}H_{n-1}^{2-}$ with the *closo* electron count of $2n + 2$ skeletal electrons and those of the neutral cobaltaboranes $CpCoB_{n-1}H_{n-1}$ with the *isocloso* electron count of $2n$ skeletal electrons. In addition, the electron poorer dications $CpCoB_{n-1}H_{n-1}^{2+}$ with only $2n - 2$ skeletal electrons are also investigated.

2. Theoretical Methods

Full geometry optimizations were carried out on the $CpCoB_{n-1}H_{n-1}$ systems at the B3LYP/6-31G(d)[23−26] level of theory. In addition, optimizations at the B3LYP/6-31+G(d) level were carried out for all of the $CpCoB_{n-1}H_{n-1}^{2-}$ dianions, since diffuse functions are important for the negatively charged species. The starting points for the optimizations were 3 structures of the 9-vertex clusters $CpCoB_8H_8^z$, 6 structures of the 10-vertex clusters $CpCoB_9H_9^z$, 11 structures of the 11-vertex clusters $CpCoB_{10}H_{10}^z$, and 2 structures of the 12-vertex clusters $CpCoB_{11}H_{11}^z$ with $z = -2, 0, +2$ as listed in Table S1 of the Supporting Information. These starting structures were generated by replacing one of the vertices in the original B_nH_n cluster with an isolobal CpCo unit. 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.[27]

The structures, total and relative energies, and relevant interatomic distances for all calculated systems are given in Tables S2−S6 of the Supporting Information. Structures are numbered as $(\mathbf{B}_{n-1}\mathbf{Co})$*e*-x where n is the number of vertices, e is the number of apparent skeletal electrons, and x is the relative order of the structure on the energy scale. The skeletal electron number e assumes that the CpCo and BH vertices are donors of two skeletal electrons. Only the lowest energy and

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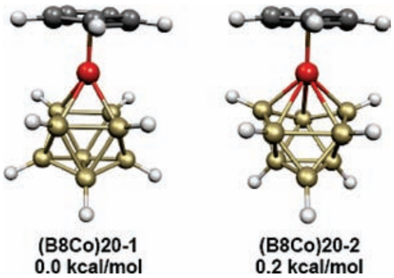

Figure 3. Optimized structures of $CpCoB_8H_8^{2-}$.

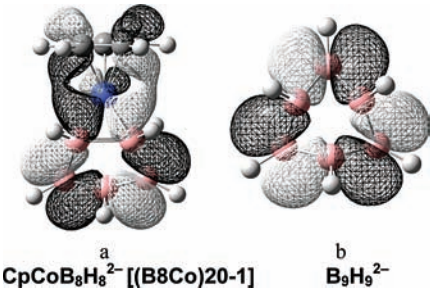

Figure 4. Comparison of the HOMOs of $CpCoB_8H_8^{2-}$ (**B8Co20−1**) with $B_9H_9^{2-}$.

thus potentially chemically significant structures are considered in detail in this paper. However, more comprehensive lists of structures, including higher energy structures, are given in the Supporting Information.

All calculations were performed using the Gaussian 98 package[28] 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.

3. Results

3.1. Nine-Vertex $CpCoB_8H_8$ Structures. Both low energy structures of $CpCoB_8H_8^{2-}$ (Figure 3) are based on the expected tricapped trigonal prism, the *closo* deltahedron for a nine-vertex system (Figure 1), in accord with the Wade−Mingos rules[3−6] for this 20 (= $2n + 2$ for $n = 9$) skeletal electron system. Structure **(B8Co)20−1** with the cobalt atom at a degree 4 vertex is predicted to lie 1.0 kcal/mol above structure **(B8Co)20−2** with the cobalt atom at a degree 5 vertex at the B3LYP/6-31G(d) level, but 0.2 kcal/mol lower in energy at the B3LYP/6-31+G(d) level. On this basis one might consider **(B8Co)20−1** and **(B8Co)20−2** quasidegenerate, with a slight preference however for the latter. This is supported by the molecular orbital (MO) analysis which show that the nondegenerate highest occupied molecular orbital (HOMO) of **(B8Co)20−1** (Figure 4a) is very similar to that of the parent $B_9H_9^{2-}$ cluster (Figure 4b).[29] Thus any deformation of **(B8Co)20−2** toward increasing the degree of the vertex holding the Co atom (moving down to right the CpCo unit), increases the out-of-phase overlap of the CpCo fragment with that of the B_8H_8 fragment so the energy of the resulting polyhedron **(B8Co)20−2** becomes higher than that of **(B8Co)20−1**.

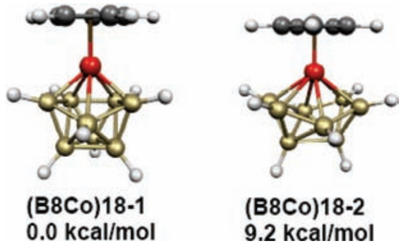

Figure 5. Optimized structures of $CpCoB_8H_8$.

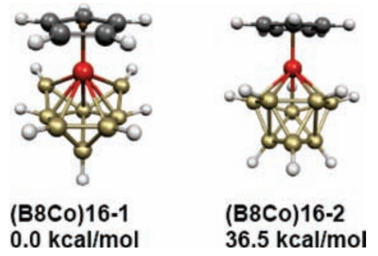

Figure 6. Optimized structures of $CpCoB_8H_8^{2+}$.

The neutral molecule $CpCoB_8H_8$ has only 18 (= $2n$ for $n = 9$) skeletal electrons and thus might be expected to exhibit an *isocloso* structure (Figure 2) with the cobalt atom at the unique degree 6 vertex. The *isocloso* structure **(B8Co)18−2** (Figure 5) is found, but at 9.2 kcal/mol above the global minimum **(B8Co)18−1**. The structure of this global minimum **(B8Co)18−1** is very similar to the low energy structure **(B8Co)20−2** of the $CpCoB_8H_8^{2-}$ dianion (Figure 3), namely, a tricapped trigonal prism with the cobalt atom at a degree 5 vertex. The *closo* $CpCoB_8H_8$ structure with the cobalt atom at a degree 4 vertex was found to be a transition state at 29.4 kcal/mol above the global minimum **(B8Co)18−1** with a large imaginary vibrational frequency at 257*i*. Following the corresponding normal mode leads to the global minimum **(B8Co)18−1** with the cobalt atom at a degree 5 vertex of the tricapped trigonal prism.

The global minimum of the electron poor dication $CpCoB_8H_8^{2+}$, namely, **(B8Co)16−1** (Figure 6), has a very different type of structure, which can be described as a seven-vertex pentagonal bipyramid with the eighth and ninth BH vertices capping a pair of triangular faces sharing an axial vertex, where the cobalt atom is located. The degree of the cobalt vertex thus increases from 5 to 7 with these two capping atoms. The central pentagonal bipyramid in **(B8Co)16−1** is the *closo* deltahedron for a seven-vertex system and thus is the polyhedron expected by the Wade−Mingos rules[3−6] for 16 (= $2n + 2$ for $n = 7$) skeletal electrons. The two capping BH vertices in the **(B8Co)16−1** structure contribute two skeletal electrons each but no new bonding orbitals in accord with the observed skeletal electron count.

A tricapped trigonal prismatic structure with the cobalt atom at a degree 5 vertex, namely, **(B8Co)16−2** (Figure 6), is also found for $CpCoB_8H_8^{2+}$ but at a relatively high energy of 36.5 kcal/mol above the global minimum **(B8Co)16−1**. This structure is similar to the

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[28] *Gaussian 98*, Revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002. The complete reference is given in the Supporting Information.

[29] McKee, M. L.; Wang, Z. X.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **2000**, *122*, 4781.

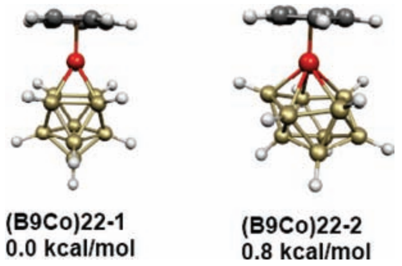

Figure 7. Optimized structures of $CpCoB_9H_9^{2-}$.

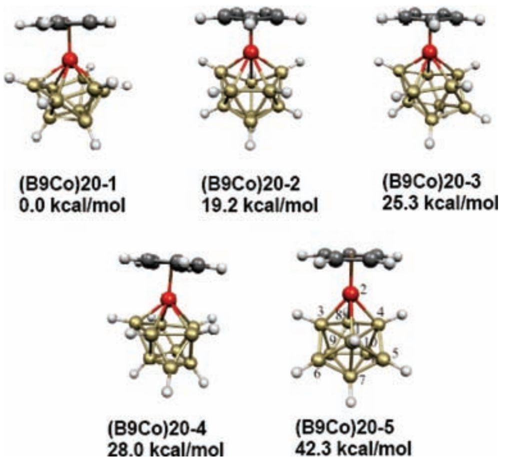

Figure 8. Optimized structures of $CpCoB_9H_9$.

global minima of $CpCoB_8H_8^{2-}$ and $CpCoB_8H_8$, namely, **(B8Co)20−1** (Figure 3) and **(B8Co)18−1** (Figure 5), respectively.

3.2. Ten-Vertex $CpCoB_9H_9$ Structures. Both low energy structures of $CpCoB_9H_9^{2-}$ (Figure 7) are based on the expected bicapped square antiprism, the *closo* deltahedron for a ten-vertex system (Figure 1), in accord with the Wade−Mingos rules[3−6] for this 22 skeletal electron system ($22 = 2n + 2$ for $n = 10$). The lowest energy structure **(B9Co)22−1** has the cobalt atom at a degree 4 vertex rather than a degree 5 vertex. Nevertheless, the structure **(B9Co)22−2** with the cobalt atom at a degree 5 vertex lies only 0.8 kcal/mol (1.7 kcal/mol at the B3LYP/6-31+G(d) level) above the **(B9Co)22−1** global minimum, thereby showing an increased preference of the cobalt atom for the degree four vertex than in the nine vertex system $CpCoB_8H_8^{2-}$.

The lowest energy structure for the neutral $CpCoB_9H_9$ molecule is the *isocloso* structure **(B9Co)20−1** with the cobalt atom at the unique degree 6 vertex (Figure 8) in accord with the 20 skeletal electrons ($20 = 2n$ for $n = 10$). The two higher energy *isocloso* structures **(B9Co)20−2** and **(B9Co)20−4** at 19.2 and 28.0 kcal/mol, respectively, above the global minimum **(B9Co)20−1**, have the cobalt atom at a degree 5 rather than the unique degree 6 vertex. These structures differ in that the degree 5 vertex bearing the cobalt atom is adjacent to the unique degree 6 vertex in **(B9Co)20−2** but two edges away from the degree 6 vertex in **(B9Co)20−4**. The *isocloso* $CpCoB_9H_9$ structure **(B9Co)20−5** (Figure 8) with the cobalt atom at a degree 4 vertex lies at a still higher energy of 42.3 kcal/mol.

Another relatively high energy structure for $CpCoB_9H_9$ is also found based on the *closo* 10-vertex deltahedron, namely, the bicapped square antiprism. Thus structure **(B9Co)20−3** with the cobalt atom at a degree 5 vertex of the bicapped square antiprism (Figure 8) lies 25.3 kcal/mol above **(B9Co)20−1**. The corresponding bicapped square antiprism structure for $CpCoB_9H_9$ with the cobalt atom at a degree 4 vertex similar to structure **(B9Co)22−1** for $CpCoB_9H_9^{2-}$ (Figure 7) is not a genuine minimum but instead a transition state at 48.5 kcal/mol above **(B9Co)20−1** with a large imaginary vibrational frequency at 367*i*. Following the corresponding normal mode leads to the *isocloso* structure **(B9Co)20−2** by a diamond-square-diamond process, which increases the degree of the cobalt vertex from 4 to 5 as well as the degree of one of the boron vertices from 5 to 6.

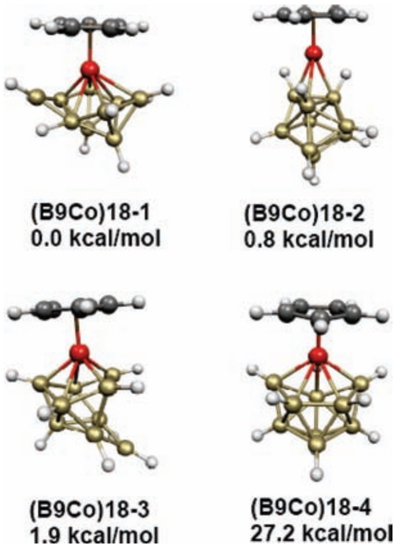

Figure 9. Optimized structures of $CpCoB_9H_9^{2+}$.

Four optimized structures were found for the electron-poor dication $CpCoB_9H_9^{2+}$ (Figure 9). The lowest energy structure **(B9Co)18−1** is a relatively oblate (flattened) structure derived from an *isocloso* nine-vertex CoB_8 deltahedron (Figure 2) with the ninth boron atom capping a CoB_2 triangular face. The cobalt atom in **(B9Co)18−1** is thus located at a degree 7 vertex similar to the cobalt atom in the $CpCoB_8H_8^{2+}$ global minimum **(B8Co)16−1** (Figure 6). The *isocloso* nine-vertex deltahedral core of **(B9Co)18−1** is consistent with the 18 skeletal electrons in $CpCoB_9H_9^{2+}$. Again, as in **(B8Co)16−1**, the degree 3 capping BH vertex in **(B9Co)18−1** contributes the usual two skeletal electrons but no new bonding skeletal orbitals.

Two relatively low lying $CpCoB_9H_9^{2+}$ structures based on distorted bicapped square antiprisms (Figure 9) lie within only ~2 kcal/mol of **(B9Co)18−1** suggesting a highly fluxional system. In structure **(B9Co)18−2** at only 0.8 kcal/mol above **(B9Co)18−1** the cobalt atom occupies a degree 4 vertex whereas in structure **(B9Co)18−3** at 1.9 kcal/mol above **(B9Co)18−1** the cobalt atom occupies a degree 5 vertex.

The final $CpCoB_9H_9^{2+}$ structure **(B9Co)18−4** (Figure 9) at 27.2 kcal/mol above **(B9Co)18−1** is based on an *isocloso* deltahedron. However, the cobalt atom in **(B9Co)18−4** is not located at the unique degree 6 vertex but instead at a degree 5 vertex adjacent to a degree 6 vertex. The $CpCoB_9H_9^{2+}$ structure **(B9Co)18−4** is closely

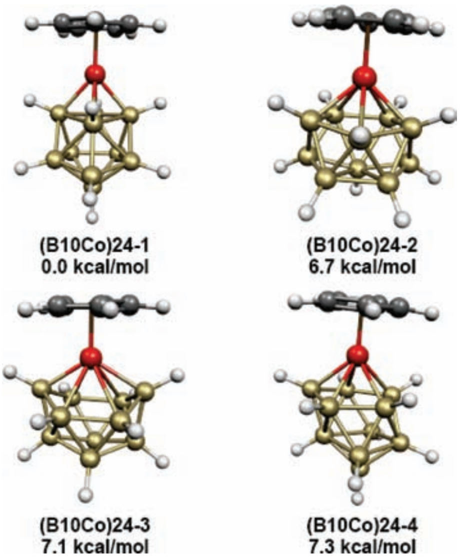

Figure 10. Optimized structures of $CpCoB_{10}H_{10}^{2-}$.

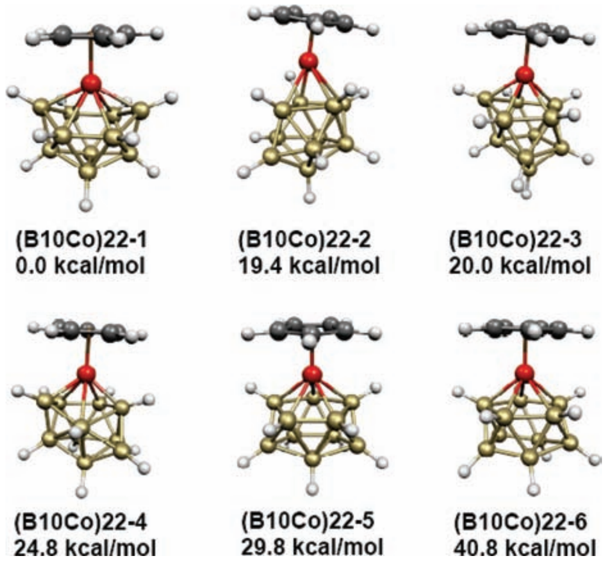

Figure 11. Optimized structures of $CpCoB_{10}H_{10}$.

related to the $CpCoB_9H_9$ structure (**B9Co**)**20−2**. The *isocloso* $CpCoB_9H_9^{2+}$ structure with the cobalt atom at the unique degree 6 vertex similar to the $CpCoB_9H_9$ structure (**B9Co**)**20−1** in Figure 8 is a transition state at only 6.3 kcal/mol above (**B9Co**)**18−1** but with an imaginary vibrational frequency of 140*i*. Following the corresponding normal mode leads to the $CpCoB_9H_9^{2+}$ global minimum (**B9Co**)**18−1** (Figure 9).

3.3. Eleven-Vertex $CpCoB_{10}H_{10}$ Structures. An 11-vertex deltahedron with only degree 4 and degree 5 vertices can be shown to be topologically impossible.[21] Therefore, even the most spherical *closo* 11-vertex deltahedron (Figure 1) must contain a degree 6 vertex so that for the 11-vertex systems the *closo* and *isocloso* polyhedra are topologically equivalent. This most spherical *closo* 11-vertex deltahedron has vertices of five different types, namely, a unique degree 6 vertex, two equivalent degree 4 vertices, and three types of degree 5 vertices (four vertices adjacent to the vertices of degree 4 and 6; two vertices adjacent to vertices of degree 4 and 5, and two vertices adjacent only to vertices of degree 5). This leads to a larger number of structures of similar energies relative to structures based on the more symmetrical most spherical 9- and 10-vertex deltahedra, namely, the tricapped trigonal prism and the bicapped square antiprism, respectively (Figure 1).

Four structures were found for $CpCoB_{10}H_{10}^{2-}$ based on cobalt substitution at the five types of vertices in the most spherical 11-vertex deltahedron (Figure 10) since optimization of the structure having the cobalt atom at the degree 5 vertex adjacent to the degree 6 vertex ends up with the same structure as that obtained by starting from the one with the cobalt atom in the degree four vertex. The global minimum (**B10Co**)**24−1** has the cobalt atom at one of the degree 4 vertices. The next two structures, namely, (**B10Co**)**24−2** and (**B10Co**)**24−3** at 6.7 and 7.1 kcal/mol, respectively, above (**B10Co**)**24−1** have the cobalt atom at one of the degree 5 and degree 6 vertices, respectively. In the lower energy of these structures, namely, (**B10Co**)**24−2**, the cobalt atom is at a degree 5 vertex two edges away from the unique degree 6 vertex. However, in the higher energy of these structures, namely, (**B10Co**)**24−3**, the cobalt atom is at the unique degree 6 vertex. Structure (**B10Co**)**24−3** turns out to be a transition state with an imaginary vibrational frequency of 36 cm^{-1}. Following the corresponding normal mode leads to (**B10Co**)**24−1**. Thus it can be estimated that the barrier for the degenerate transformation of (**B10Co**)**24−1** into (**B10Co**)**24−1** (exchanging the positions of the cobalt atom at the degree four vertices) is about 7.1 kcal/mol at the B3LYP/6 + 31G(d) level of theory. The fourth structure with the cobalt atom in the degree five vertex lies relatively close to the others (7.3 kcal/mol).

The four lowest energy structures for the neutral $CpCoB_{10}H_{10}$ (Figure 11), like those of $CpCoB_{10}H_{10}^{2-}$, are based on the same 11-vertex deltahedron with the cobalt atom at one of the five non-equivalent vertices. However, in this case the lowest energy structure, namely, (**B10Co**)**22−1**, has the cobalt atom at the unique degree 6 vertex. Furthermore, this structure lies $\sim$19 kcal/mol in energy below any of the other $CpCoB_{10}H_{10}$ structures indicating that it is a particularly favorable structure. A related MB_{10} polyhedron is found in the experimentally known[30,31] isoelectronic (η^6-Me_6C_6)$RuB_{10}H_{10}$, which has been structurally characterized by X-ray crystallography. The next $CpCoB_{10}H_{10}$ structure, namely, (**B10Co**)**22−2** at 19.4 kcal/mol above (**B10Co**)**22−1**, has the cobalt atom at a degree 4 vertex. The $CpCoB_{10}H_{10}$ structures (**B10Co**)**22−3** and (**B10Co**)**22−4**, at 20.0 and 24.8 kcal/mol, respectively, above (**B10Co**)**22−1**, have the cobalt atom at the degree 5 vertices. In (**B10Co**)**22−3** the degree 5 vertex with the cobalt atom is two edges away from the unique degree 6 vertex whereas in (**B10Co**)**22−4** the cobalt atom is at a degree 5 vertex adjacent to the degree 6 vertex.

The two highest energy $CpCoB_{10}H_{10}$ structures, namely, (**B10Co**)**22−5** and (**B10Co**)**22−6** at 29.8 and 40.8 kcal/mol, respectively, above (**B10Co**)**22−1** (Figure 11), have a CoB_{10}

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[31] Bown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D; Thornton-Pett, M. *Dalton Trans.* **1988**, 925.

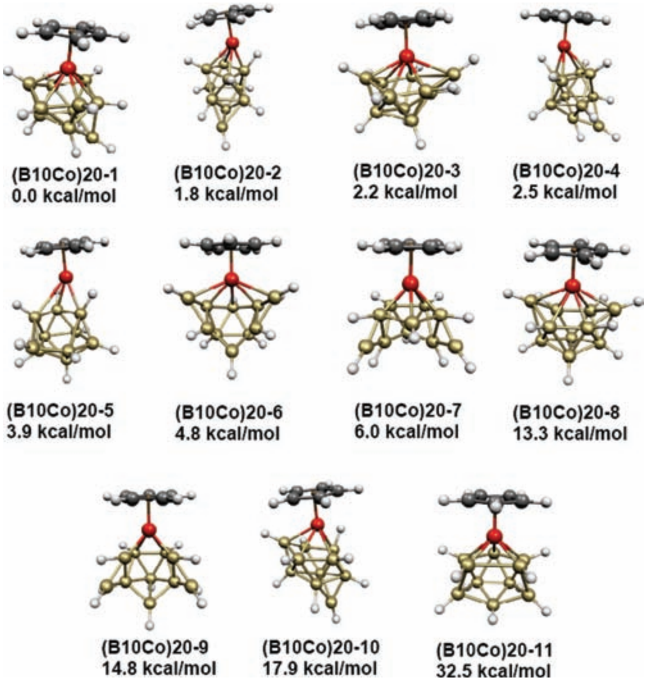
(B10Co)20-1 0.0 kcal/mol
(B10Co)20-2 1.8 kcal/mol
(B10Co)20-3 2.2 kcal/mol
(B10Co)20-4 2.5 kcal/mol
(B10Co)20-5 3.9 kcal/mol
(B10Co)20-6 4.8 kcal/mol
(B10Co)20-7 6.0 kcal/mol
(B10Co)20-8 13.3 kcal/mol
(B10Co)20-9 14.8 kcal/mol
(B10Co)20-10 17.9 kcal/mol
(B10Co)20-11 32.5 kcal/mol

Figure 12. Optimized structures of $CpCoB_{10}H_{10}^{2+}$.

polyhedron with one quadrilateral face so that there are no degree 6 vertices. In both structures the cobalt atom is located at a degree 5 vertex. These structures may be derived from a CoB_{11} icosahedron by removing the boron vertex antipodal to the cobalt atom. The resulting pentagonal face is then distorted by making a new diagonal edge thereby converting the pentagonal face into a triangular face and a quadrilateral face.

A total of 11 structures were found for the $CpCoB_{10}H_{10}^{2+}$ dication (Figure 12) indicating a complicated potential energy surface. This arises, at least partially, from the relatively low symmetry of the 11-vertex system, which leads to a large number of structural possibilities.

Three of the $CpCoB_{10}H_{10}^{2+}$ structures (Figure 12) are based on the 11-vertex deltahedron (Figure 1) including the global minimum **(B10Co)20−1** as well as the higher energy structures **(B10Co)20−8** and **(B10Co)20−10** at 13.3 and 17.9 kcal/mol, respectively, above **(B10Co)20−1**. In structure **(B10Co)20−8** the cobalt atom is located at the unique degree 6 vertex whereas in structures **(B10Co)20−1** and **(B10Co)20−10** the cobalt atom is located at a degree 5 vertex.

The electron poverty of $CpCoB_{10}H_{10}^{2+}$ also leads to structures based on a ten-vertex CoB_9 deltahedron with the remaining BH vertex functioning as a degree 3 vertex capping one of the triangular faces. Structure **(B10Co)20−3** at only 2.2 kcal/mol above **(B10Co)20−1** is based on a ten-vertex *isocloso* deltahedron (Figure 2) with the cobalt atom at the unique degree 6 vertex. However, the capped triangular face is a CoB_2 face so that the cobalt vertex degree increases to seven analogous to the lowest energy structures for $CpCoB_nH_n^{2+}$, namely, **(B8Co)16−1** (Figure 6) and **(B9Co)18−1** (Figure 9), respectively. The underlying *isocloso* 10-vertex deltahedron in **(B10Co)20−3** is expected to require the 20 skeletal electrons (= $2(n-1)$ for $n = 11$) available in $CpCoB_{10}H_{10}^{2+}$.

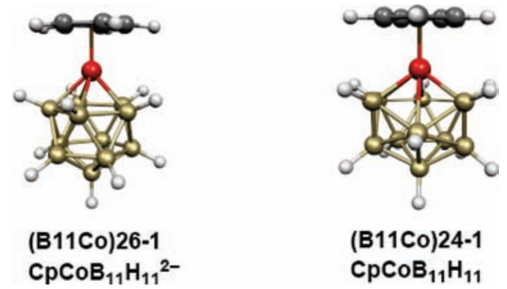
(B11Co)26-1 $CpCoB_{11}H_{11}^{2-}$
(B11Co)24-1 $CpCoB_{11}H_{11}$

Figure 13. Optimized structures of $CpCoB_{11}H_{11}^{2-}$ and $CpCoB_{11}H_{11}$.

The second $CpCoB_{10}H_{10}^{2+}$ structure based on a capped 10-vertex deltahedron is **(B10Co)20−4** (Figure 12), which is also a relatively low energy structure at only 2.5 kcal/mol above **(B10Co)20−1**. However, in this case the underlying 10-vertex deltahedron is the "most spherical" bicapped square antiprism (Figure 1) rather than the underlying *isocloso* deltahedron in **(B10Co)20−3**. The cobalt atom is located at a degree 4 vertex and the capped face is a pure B_3 face so that the degree of the cobalt vertex remains 4 after the capping.

The $CpCoB_{10}H_{10}^{2+}$ energy surface is complicated by five non-deltahedral structures with a quadrilateral face and thus with only 26 edges rather than the 27 edges required for an 11-vertex deltahedron with only triangular faces. Such structures arise from distortion lengthening one of the boron−boron distances so that it is too long to correspond to a polyhedral edge. The $CpCoB_{10}H_{10}^{2+}$ structures **(B10Co)20−2**, **(B10Co)20−5**, **(B10Co)20−7**, **(B10Co)20−9**, and **(B10Co)20−11** (Figure 12), at 1.8, 3.9, 6.0, 14.8, and 32.5 kcal/mol, respectively, above **(B10Co)20−1** all fall into this category. In **(B10Co)20−5**, **(B10Co)20−7**, and **(B10Co)20−11** the cobalt atom is located at a degree 5 vertex whereas in **(B10Co)20−2** and **(B10Co)20−9** the cobalt atom is located at a degree 4 vertex. The eleventh $CpCoB_{10}H_{10}^{2+}$ structure, namely, **(B10Co)20−6**, at 4.8 kcal/mol above **(B10Co)20−1**, is even a more open structure, indicated by its B−B and Co−B distances, to be based on an 11-vertex polyhedron with only 25 edges and one pentagonal face in addition to 15 triangular faces.

3.4. Twelve-Vertex $CpCoB_{11}H_{11}$ Structures. The potential energy surfaces for the 12-vertex $CpCoB_{11}H_{11}^{z}$ ($z = -2, 0, +2$) clusters are considerably less complicated than those for the 9- to 11-vertex systems. For $CpCoB_{11}H_{11}^{2-}$ the icosahedral structure **(B11Co)26−1** (Figure 13) is the lowest energy structure. The next higher lying $CpCoB_{11}H_{11}^{2-}$ structure found in this work is a non-icosahedral structure at more than 75 kcal/mol above **(B11Co)26−1** and therefore chemically irrelevant. The great relative stability of the icosahedral $CpCoB_{11}H_{11}^{2-}$ structure **(B11Co)26−1** is in accord with the Wade−Mingos rules[3−6] predicting an icosahedral structure for a 12-vertex 26-skeletal electron (= $2n + 2$ for $n = 12$) system.

The lowest energy structure **(B11Co)24−1** for neutral $CpCoB_{11}H_{11}$ is based on a non-icosahedral polyhedron (Figure 13) with three degree 6 vertices, six degree 5 vertices, and three degree 4 vertices. The cobalt atom, as expected, occupies one of the degree 6 vertices so that the 12-vertex deltahedron in **(B11Co)24−1** can be considered

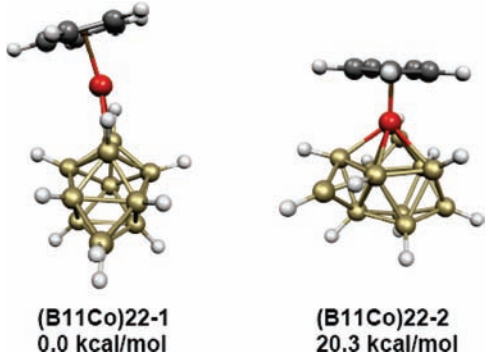

Figure 14. Optimized structures of $CpCoB_{11}H_{11}^{2+}$.

as an *isocloso* 12-vertex deltahedron. However, the deltahedron in **(B11Co)24−1** is different from that found experimentally[22] in $[\{(\eta^3\text{-}C_3H_5)(OC)_2Mo\}(PhC)_2B_9H_9]^-$, which has only two degree 6 vertices, two degree 4 vertices, and eight degree 5 vertices.

The icosahedral structure for neutral $CpCoB_{11}H_{11}$, similar to the structure **(B11Co)26−1** (Figure 2) for the dianion $CpCoB_{11}H_{11}^{2-}$, is a transition state at 52.4 kcal/mol above **(B11Co)24−1** with a large imaginary vibrational frequency at $537i$ cm^{-1}. Following the corresponding normal mode leads to structure **(B11Co)24−1**.

Two structures were found for the dication $CpCoB_{11}H_{11}^{2+}$ (Figure 14). The lowest energy $CpCoB_{11}H_{11}^{2+}$ structure **(B11Co)22−1** can be derived from the most spherical 10-vertex B_{10} deltahedron, namely, a bicapped square antiprism (Figure 1), by capping two of the triangular faces with necessarily degree 3 vertices. One of these caps is the cobalt vertex and the other cap is the eleventh boron vertex. The central 10-vertex deltahedron in **(B11Co)22−1** follows the Wade−Mingos rules[3−6] in this 22 skeletal electron system ($= 2n + 2$ for $n = 10$). The higher energy $CpCoB_{11}H_{11}^{2+}$ structure, namely, **(B11Co)22−2** at 20.3 kcal/mol above **(B11Co)22−1** (Figure 14), is based on a CoB_{11} deltahedron with three degree 6 vertices, six degree 5 vertices, and three degree 4 vertices similar to the deltahedron in the $CpCoB_{11}H_{11}$ structure **(B11Co)24−1** (Figure 12). Again the cobalt atom in **(B11Co)22−2** is located at one of the degree 6 vertices.

4. Discussion

4.1. Dianions $CpCoB_{n-1}H_{n-1}^{2-}$.

The $CpCoB_{n-1}H_{n-1}^{2-}$ dianions have $2n + 2$ skeletal electron and thus by the Wade−Mingos rules[3−6] are expected to have structures based on the most spherical deltahedra (Figure 1). In the cases $n = 9, 10, 11, 12$ such structures were found to be the lowest energy structures. For the 12-vertex system $CpCoB_{11}H_{11}^{2-}$ the icosahedral structure was found to lie more than 75 kcal/mol below any other structures.

The most spherical deltahedra with nine and ten vertices, namely, tricapped trigonal prism and bicapped square antiprism, respectively (Figure 1), have two nonequivalent sites, namely, degree 4 and degree 5 vertices. The energy differences between the $CpCoB_{n-1}H_{n-1}^{2-}$ ($n = 9, 10$) structures with the cobalt atoms at degree 4 or degree 5 vertices are predicted by our DFT calculations to be less than 2 kcal/mol (Figures 3 and 7). For the nine-vertex $CpCoB_8H_8^{2-}$ the structure with the cobalt atom at the degree 4 vertex is only slightly preferred. However, for the ten-vertex $CpCoB_9H_9^{2-}$, the structure with the cobalt atom at the degree 4 vertex is preferred by 0.8 kcal/mol (Figure 7).

The 11-vertex system is more complicated since the most spherical 11-vertex deltahedron (sometimes called the "edge-coalesced icosahedron") has five types of vertices, namely, a unique degree 6 vertex, one type of degree 4 vertices, and three types of degree 5 vertices. The three types of degree 5 vertices are distinguished by their locations relative to the degree 6 and degree 4 vertices. From the five possible *closo*-$CpCoB_{10}H_{10}^{2-}$ structures four were found by optimizations (Figure 10), two of them collapsing in the global minimum. Here the energy span was somewhat greater than in the 9- and 10-vertex systems with structure **(B10Co)24−3** having the cobalt atom at the degree 6 vertex being predicted to lie 7.1 kcal/mol above **(B10Co)24−1** having the cobalt atom at a degree 4 vertex. Among the structures having the cobalt atom at a degree five vertex, the preferred one is with this atom having only degree five vertices as neighbors.

4.2. Neutral Molecules $CpCoB_{n-1}H_{n-1}$.

The neutral molecules $CpCoB_{n-1}H_{n-1}$ are $2n$ skeletal electron systems and thus might be expected to prefer structures based on *isocloso* deltahedra with the cobalt atom at a degree 6 vertex. For the 9- and 10- vertex systems the *isocloso* deltahedra (Figure 2) have a unique degree 6 vertex and thus are topologically different from the corresponding *closo* deltahedra (Figure 1), which do not have any degree 6 vertices. For the 10-vertex system the *isocloso* structure **(B9Co)20−1** with the cobalt atom at the unique degree 6 vertex (Figure 8) is indeed highly preferred energetically, lying ~19 kcal/mol below the next lower energy structure. Note that in the *isocloso* 10-vertex deltahedron (Figure 2) the three degree 4 vertices are isolated from each other without any edges directly connecting two degree 4 vertices. Instead the three degree 4 vertices of the *isocloso* 10-vertex deltahedron alternate with three of the degree 5 vertices to form a skew hexagon surrounding the degree 6 vertex bearing the cobalt atom in **(B9Co)20−1**.

The *isocloso* 9-vertex deltahedron (Figure 2) is quite different from the *isocloso* 10-vertex deltahedron in that the four degree 4 vertices are in two edge-connected pairs as part of the skew hexagon of four degree 4 vertices and two degree 5 vertices surrounding the degree 6 vertex bearing the cobalt atom. The direct edge-connection of pairs of degree 4 vertices in the *isocloso* 9-vertex deltahedron is apparently less favorable than the isolation of degree 4 vertices in the *isocloso* 10-vertex deltahedron as indicated by the fact that the *isocloso* 9-vertex structure **(B8Co)18−2** for $CpCoB_8H_8$ lies ~9 kcal/mol above the global minimum **(B8Co)18−1**, which is a *closo* structure with the cobalt atom at a degree 5 vertex (Figure 3). Thus the lowest energy structures for $CpCoB_8H_8$ and $CpCoB_8H_8^{2-}$ are based on the same underlying polyhedron, despite the obvious difference of two in their skeletal electron counts.

The topological requirement of a degree 6 vertex for an 11-vertex deltahedron[21] makes the *closo* and *isocloso* 11-vertex deltahedra identical, namely, the "edge-coalesced icosahedron" (Figure 1). This 11-vertex deltahedron can thus function as either a *closo* or *isocloso* deltahedron depending upon the skeletal electron count. For $CpCoB_{10}H_{10}$ with 22 skeletal electrons ($22 = 2n$ for $n = 11$) the structure **(B10Co)22−1** with the cobalt atom at the unique degree 6 vertex is preferred over any other structure by ~19 kcal/mol (Figure 11). This differs from $CpCoB_{10}H_{10}^{2-}$ with 24 skeletal electrons ($24 = 2n + 2$ for $n = 11$), for which the lowest energy structure **(B10Co)24−1** has the cobalt atom at a degree 4 vertex and the energy separations are much smaller (Figure 10).

The icosahedron is so favorable in boron chemistry[32,33] that a diamond-square-diamond rearrangement[19,20] of an icosahedron to give an alternative *isocloso* 12-vertex deltahedron with at least one degree 6 vertex might be expected to be very difficult. Most experimentally known 12-vertex deltahedral clusters retain the fundamental icosahedral topology with only degree 5 vertices, even when the number of skeletal electrons is reduced from 26 ($= 2n + 2$ for $n = 12$) to 24 ($=2n$ for $n = 12$). Thus oxidation of the 26 skeletal electron icosahedral peralkoxyborane dianions $B_{12}(OR)_{12}^{2-}$ to the 24 skeletal electron neutral $B_{12}(OR)_{12}$ retains the icosahedral topology of the central B_{12} unit, albeit with some Jahn−Teller distortion.[34] The one exception so far relating to a 12-vertex non-icosahedral deltahedral metallaborane is the molybdenum anion[22] $[\{(\eta^3\text{-}C_3H_5)(OC)_2Mo\}(PhC)_2B_9H_9]^-$, containing a central MoC_2B_9 deltahedron with two degree 6, two degree 4, and eight degree 5 vertices. Our theoretical studies predict a different type of non-icosahedral but deltahedral structure **(B11Co)24−1** for $CpCoB_{11}H_{11}$ having three degree 6, three degree 4, and six degree 5 vertices (Figure 13). Furthermore, our calculations suggest that neutral icosahedral $CpCoB_{11}H_{11}$ is only a high energy transition state, which spontaneously converts to the non-icosahedral structure **(B11Co)24−1**. More generally, these results on $CpCoB_{11}H_{11}$ suggest that a search for additional non-icosahedral metallaboranes with 24 skeletal electrons is likely to be highly promising and that more than one type of non-icosahedral deltahedron might be found in such metallaboranes.

4.3. Dications $CpCoB_{n-1}H_{n-1}^{2+}$. Oxidation of the dianions $CpCoB_{n-1}H_{n-1}^{2-}$ to the neutral molecules $CpCoB_{n-1}H_{n-1}$, that is, going from a $2n + 2$ skeletal electron system to a $2n$ skeletal electron system, is observed to lead to a preference for structures with the metal atom at a degree 6 vertex. Further oxidation of $CpCoB_{n-1}H_{n-1}$ to the corresponding dications $CpCoB_{n-1}H_{n-1}^{2+}$, that is, going from a $2n$ skeletal electron system to a $2n - 2$ skeletal electron system, is predicted from our theoretical studies to lead to new types of much less spherical deltahedra where the cobalt atom is at a degree 7 vertex. Such structures are based on smaller deltahedra not involving all of the vertex atoms. The remaining vertex atoms not used for the central deltahedron cap faces of the central deltahedron. Since all of the faces of the central deltahedron are triangles, these capping vertices necessarily have a degree of only 3 and are thus readily recognized as such when dissecting the chemically unfamiliar polyhedra predicted for many of the $CpCoB_{n-1}H_{n-1}^{2+}$ structures. Furthermore, the capped face(s) of the central deltahedron in the lowest energy $CpCoB_{n-1}H_{n-1}^{2+}$ structures typically contain the cobalt atom so that the capping process increases the degree of the cobalt vertex in the final $CpCoB_{n-1}H_{n-1}^{2+}$ deltahedron. Thus degree 7 cobalt vertices are found in the lowest energy structures for $CpCoB_8H_8^{2+}$ and $CpCoB_9H_9^{2+}$ leading to rather oblate (flattened) deltahedral structures. The number of vertices in the central deltahedron of these capped $CpCoB_{n-1}H_{n-1}^{2+}$ often relates to the Wade−Mingos rules.[3−6]

Consider the lowest energy structure **(B8Co)16−1** of the $CpCoB_8H_8^{2+}$ dication (Figure 6), which has 16 skeletal electrons by the usual formal electron counting procedure. The central deltahedron in **(B8Co)16−1** is a seven-vertex pentagonal bipyramid with the cobalt atom in one of the axial positions at a degree 5 vertex. The pentagonal bipyramid is the most spherical deltahedron for seven vertices and, as such, would be expected by the Wade−Mingos rules to have $(2)(7) + 2 = 16$ skeletal electrons, which is exactly the number for $CpCoB_8H_8^{2+}$. The two remaining BH vertices cap faces containing the cobalt atom thereby increasing the degree of the cobalt vertex from 5 to 7.

The lowest energy structure **(B9Co)18−1** of the $CpCoB_9H_9^{2+}$ dication also has a degree 7 cobalt vertex (Figure 9). In this case the central deltahedron is a 9-vertex *isocloso* deltahedron (Figure 2) with the cobalt atom at the unique degree 6 vertex. Such an *isocloso* 9-vertex deltahedron would be expected to have the $(2)(9) = 18$ skeletal electrons, which is exactly the number for $CpCoB_9H_9^{2+}$. The remaining BH vertex in **(B9Co)18−1** caps one of the CoB_2 faces of the 9-vertex *isocloso* deltahedron thereby increasing the degree of the cobalt vertex from 6 to 7.

The 11-vertex $CpCoB_{10}H_{10}^{2+}$ dication has 20 skeletal electrons (Figure 12) and is considerably more complicated than the other systems discussed in this paper with 7 structures within ~6 kcal/mol and a total of 11 structures within ~35 kcal/mol of the global minimum. Three of the $CpCoB_{10}H_{10}^{2+}$ structures, namely, **(B10Co)20−1**, **(B10Co)20−8**, and **(B10Co)20−10**, are based on the most spherical 11-vertex deltahedron, namely, the "edge-coalesced icosahedron" (Figure 1). Two of the $CpCoB_{10}H_{10}^{2+}$ structures have central ten-vertex CoB_9 deltahedra with one of the triangular faces capped by the remaining BH vertex. In one of these structures, namely, **(B10Co)20−4**, the central 10-vertex deltahedron is the most spherical deltahedron, namely, the bicapped square antiprism (Figure 1). However, in the other of these capped 10-vertex structures, namely, **(B10Co)20−3**, the central 10-vertex deltahedron is the *isocloso* deltahedron with the cobalt atom originally at the unique degree 6 vertex, which becomes a degree 7 vertex after the capping process. This $CpCoB_{10}H_{10}^{2+}$ structure), at only 2.2 kcal/mol above the global minimum **(B10Co)20−1**, resembles roughly the lowest energy structures for $CpCoB_8H_8^{2+}$, namely, **(B8Co)16−1**, and for $CpCoB_9H_9^{2+}$, namely, **(B9Co)18−1**, in that all three structures are oblate (flattened) and have the cobalt atom at a degree 7 vertex. The $CpCoB_{10}H_{10}^{2+}$ energy surface is complicated by five

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non-deltahedral structures containing a single quadrilateral face, namely, **(B10Co)20−2**, **(B10Co)20−5**, **(B10Co)20−7**, **(B10Co)20−9**, and **(B10Co)20−11** (Figure 11), or, in one case, namely, **(B10Co)20−6**, a single pentagonal face (Figure 11).

The lowest energy structure for $CpCoB_{11}H_{11}^{2+}$, namely, **(B11Co)22−1** (Figure 14) is based on a bicapped 10-vertex deltahedron in accord with the Wade−Mingos rules. The 10-vertex deltahedron, namely, the bicapped square antiprism (Figure 1), requires exactly the 22 skeletal electrons in $CpCoB_{11}H_{11}^{2+}$. A major difference between **(B11Co)22−1** and the lowest energy $CpCoB_nH_n^{2+}$ (n = 8, 9) structures is the presence of the cobalt atom as a capping vertex of degree 3 rather than a degree 7 vertex.

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Supporting Information Available: Table S1: the starting $CpCoB_nH_n$ structures; Table S2: $CpCoB_8H_8^z$ (z = −2, 0, +2) structures and distances; Table S3: $CpCoB_9H_9^z$ (z = −2, 0, +2) structures and distances; Table S4: $CpCoB_{10}H_{10}^z$ (z = −2, 0, +2) structures and distances; Table S5: $CpCoB_{11}H_{11}^z$ (z = −2, 0, +2) structures and distances; Table S6: B3LYP/6-31+G(d) computed $CpCoB_{n-1}H_{n-1}^{2-}$ (n = 9, 10, 11, 12) structures and distances; complete Gaussian 98 reference (reference 28). This material is available free of charge via the Internet at http://pubs.acs.org.