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Cyclopentadienylcobalt Azaboranes Violating the Wade-Mingos Rules: A Degree 3 Vertex for the Nitrogen Atom

Amr A. A. Attia,[1] Alexandru Lupan,*[1] and R. Bruce King*[2]

[1] *Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania*
[2]*Department of Chemistry and Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia, 30602, USA*

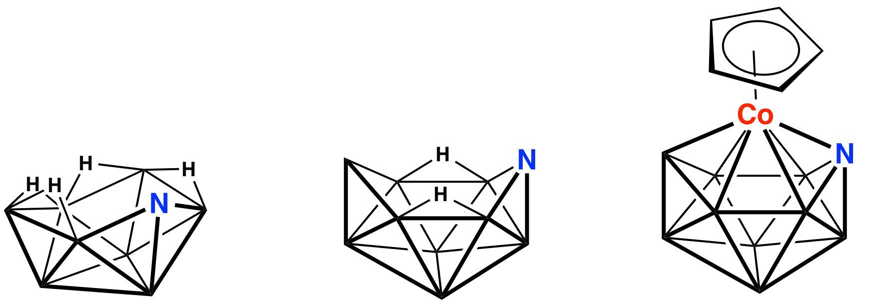
Abstract

The experimentally realized chemistry of polyhedral azaboranes includes the very stable cobalt derivative $CpCoNHB_9H_9$, which has been synthesized and structurally characterized by X-ray crystallography. The structures and energetics of the complete series of cobaltaazaboranes $CpCoNHB_{n-2}H_{n-2}$ have now been studied by density functional theory. Low-energy structures are found for the 8- and 9-vertex systems based on non-spherical deltahedra providing a degree 3 vertex for the nitrogen atom and thus violating expectations from the Wade-Mingos rules. Thus the lowest energy $CpCoNHB_6H_6$ structure is an antipodally bicapped octahedron with the nitrogen atom at a degree 3 vertex rather than the most spherical bisdisphenoid. For the 9-vertex $CpCoNHB_7H_7$ system the lowest energy structures are based on the most spherical tricapped trigonal prism. However, isomeric $CpCoNHB_7H_7$ structures at ~13 kcal/mol in energy above these structures are found with a central capped bisdisphenoid having the nitrogen atom at the degree 3 capping vertex. In contrast to the 8- and 9-vertex systems, the low-energy $CpCoNHB_{n-2}H_{n-2}$ structures for the 10 to 12 vertex systems are based on the most spherical deltahedra. For the 10- and 11-vertex systems all of the low-energy structures have the nitrogen atom at a degree 4 vertex. The predicted Co–N and Co–B distances in the lowest energy $CpCoNHB_9H_9$ structure are very close to the experimental values.

* e-mail: alupan@chem.ubbcluj.ro (A. Lupan) and rbking@chem.uga.edu (R. B. King)

1. Introduction

The chemistry of polyhedral azaboranes originated with the synthesis by Muetterties and co-workers[1] of the *arachno* azadecaborane derivative $B_9H_{13}NH$ (Figure 1) from decaborane in low yield as its monoanion $B_9H_{12}NH^-$. Subsequently Heřmánek, Schaeffer, and their coworkers used the nitrosation of decaborane followed by acidification to obtain the *arachno* azanonaborane $B_8H_{12}NH$.[2] Todd and co-workers[3] showed that careful control of the nitrosation of decaborane gave the *nido* azadecaborane derivative $B_9H_{11}NH$, having a structure closely related to that of decaborane (Figure 1). The 11-vertex *closo* cobaltaazaborane derivative $CpCoNHB_9H_9$ (Cp = η^5-C_5H_5) was synthesized from $B_9H_{11}NH$ by reaction with NaCp/$CoCl_2$.



***arachno*-$B_8H_{12}NH$** ***nido*-$B_9H_{11}NH$** ***closo*-$CpCoNHB_9H_9$**

Figure 1. Some experimentally known azaborane derivatives. In Figures 1 and 2 unlabeled vertex atoms are boron atoms and terminal hydrogen atoms are omitted for clarity.

The NH vertices found in the azaboranes are donors of four skeletal electrons in accord with the Wade-Mingos rules.[4,5,6] The initial azaborane syntheses often lead to electron-rich *nido* and *arachno* structures as exemplified by the metal-free structures in Figure 1. Nevertheless, the 10-vertex and 12-vertex *closo* structures B_9H_9NH and $B_{11}H_{11}NH$ have been synthesized and structurally characterized by X-ray crystallography (Figure 2).[7] The 10-vertex azaborane B_9H_9NH has the nitrogen atom at a degree 4 rather than a degree 5 vertex of the bicapped square antiprismatic B_9N cage. The NH vertices in the azaboranes can be deprotonated with bases and the resulting anions alkylated to give NR vertices without disturbing the azaborane cage structure. In addition, azaborane cages can be expanded by thermal reactions with borane adducts $BH_3{\cdot}L$ (L = Me_2S, THF, etc.).[8,9] This method was used to synthesize the *closo* icosahedral azadodecaborane, $B_{11}H_{11}NH$.

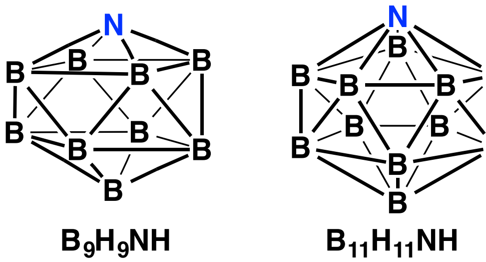
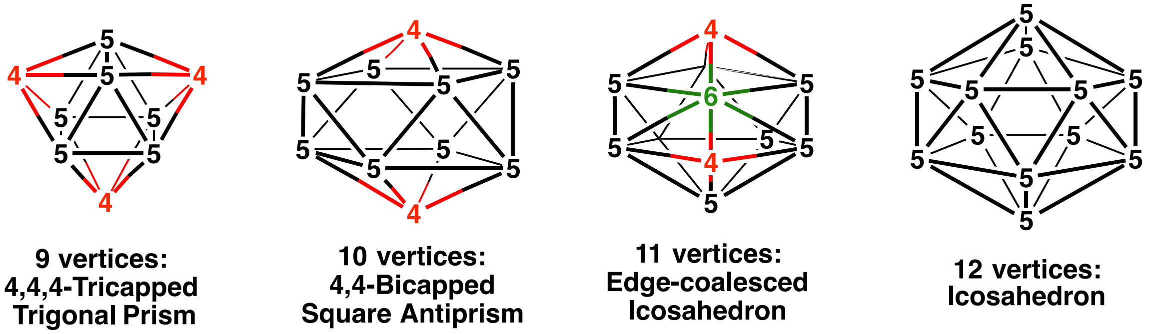


Figure 2. The two known *closo* azaboranes. Hydrogen atoms are omitted for clarity.

The synthesis of the 11-vertex $CpCoNHB_9H_9$ raises the question whether other cobaltaazaboranes $CpCoNHB_{n-2}H_{n-2}$ with different numbers of vertices can be synthesized. As noted above, metal-free polyhedral azaboranes are available for the syntheses of such species. According to the Wade-Mingos rules[4,5,6] such *n*-vertex cobaltaazaboranes $CpCoNHB_{n-2}H_{n-2}$ have the $2n + 2$ skeletal electrons required for the most spherical deltahedra (Figures 3 and 4). We now report density functional theory studies on such cobaltaazaboranes having from eight to twelve vertices. This work has led to the discovery of low-energy structures violating the Wade-Mingos rules by having central $CoNB_{n-2}$ polyhedra that are not the most spherical deltahedra. This can be related to the preference of the nitrogen atom for vertices of lower degrees. The most extreme example occurs in the 8-vertex system where the lowest energy $CpCoNHB_6H_6$ structure is not the most spherical 8-vertex deltahedron, namely the bisdisphenoid, but instead the D_{3d} antipodally bicapped octahedron with two degree 3 vertices and six degree 5 vertices (Figure 4). The nitrogen atom in this $CpCoNHB_6H_6$ structure is located at one of the degree 3 vertices.



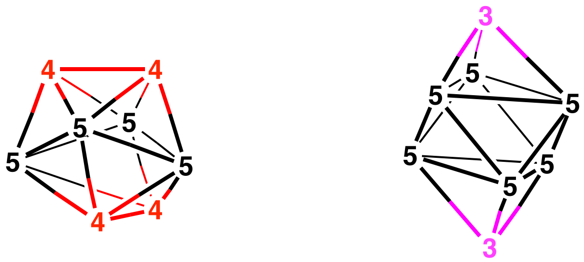
9 vertices: **4,4,4-Tricapped Trigonal Prism**

10 vertices: **4,4-Bicapped Square Antiprism**

11 vertices: **Edge-coalesced Icosahedron**

12 vertices: **Icosahedron**

Figure 3. The most spherical *closo* deltahedra having from 9 to 12 vertices found in *n*-vertex metallaboranes having $2n + 2$ Wadean skeletal electrons. In Figures 3 and 4, vertices of degrees 3, 4, 5, and 6 are purple, red, black, and green, respectively.



Bisdisphenoid
("D_{2d} Dodecahedron")

D_{3d} Antipodally
Bicapped Octahedron

Figure 4. Comparison of the bisdisphenoid and the antipodally bicapped octahedron, both of which are 8-vertex deltahedra.

2. Theoretical Methods

Full geometry optimizations were carried out on the $\mathrm{CpCoN}B_{n-2}\mathrm{H}_{n-1}$ systems (n = 8 to 12) at the B3LYP/6-31G(d) level of theory.[10,11,12,13] The lowest energy structures were then reoptimized at a higher level, i.e., M06L/6-311G(d,p), and these are the structures presented in the manuscript.[14] The initial structures were chosen by systematic substitution of one BH vertex by a CpCo vertex in various polyhedral frameworks, followed by all possible substitutions of a boron atom in the resulting cobaltaborane by a nitrogen atom. The large number of different starting structures for the optimizations included 101 structures of the 8-vertex clusters $\mathrm{CpCoNB_6H_7}$, 68 structures of the 9-vertex clusters $\mathrm{CpCoNB_7H_8}$, 97 structures of the 10-vertex clusters $\mathrm{CpCoNB_8H_9}$, 140 structures of the 11-vertex clusters $\mathrm{CpCoNB_9H_{10}}$, and 35 structures of the 12-vertex clusters $\mathrm{CpCoNB_{10}H_{11}}$ (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 optimizations were continued by following the normal modes corresponding to imaginary frequencies to insure that genuine minima were obtained.

All calculations were performed using the Gaussian 09 package[15] 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.

The $\mathrm{CpCoNHB}_{n-2}\mathrm{H}_{n-2}$ (n = 8 to 12) structures are numbered as **B(n–2)NCo-x** where **n** is the total number of polyhedral vertices, and **x** is the relative order of the structure on the energy scale (M06L/6-311G(d,p) including zero-point corrections). The lowest energy optimized structures discussed in this paper are depicted in Figures 5 to 9. Only the lowest energy and thus potentially chemically significant structures are considered in detail in this paper. All of the low-energy structures reported in this paper are closed-shell structures with substantial HOMO-LUMO gaps ranging from 1.5 to 3.3 eV (Tables S1B to S5B of the Supporting Information). More comprehensive lists of structures, including higher energy structures, are given in the Supporting Information.

3. Results

Four $CpCoNHB_6H_6$ structures of the 8-vertex $CpCoNHB_6H_6$ system were found within 15 kcal/mol of the global minimum (Figure 5 and Table 1). The central $CoNB_6$ polyhedron in the lowest energy such structure **B6NCo-1** is not the most spherical 8-vertex deltahedron expected by the Wade-Mingos rules[4,5,6] but instead an antipodally bicapped octahedron with two degree 3 vertices capping opposite faces (Figure 4). This allows the nitrogen atom in **B6NCo-1** to occupy one of the degree 3 vertices so that the local tetrahedral environment of the nitrogen atom is similar to that of an ammonium ion. The formal positive charge on such a nitrogen atom can be balanced by a formal negative charge on the antipodally situated tetrahedral borate ion with a local environment similar to BH_4^-.

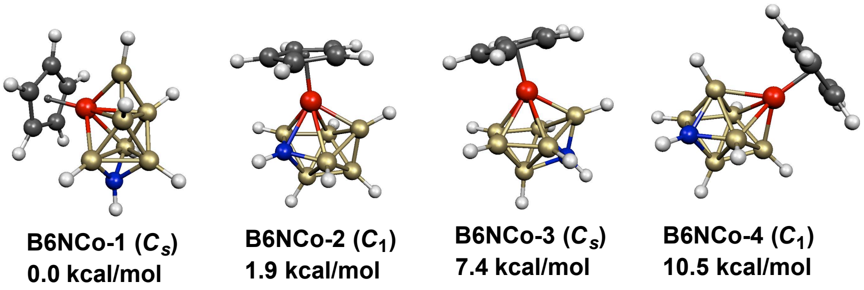


Figure 5. The four optimized $CpCoNHB_6H_6$ structures within 15 kcal/mol of the global minimum.

The remaining low-energy $CpCoNHB_6H_6$ structures have a central $CoNB_6$ bisdisphenoid as expected by the Wade-Mingos rules (Figures 4 and 5; Table 1).[4,5,6] The two lowest energy such structures, namely **B6NCo-2** and **B6NCo-3** lying 3.8 and 7.4 kcal/mol, respectively, in energy above **B6NCo-1**, have the cobalt and nitrogen atoms at degree 5 and 4 vertices, respectively. This is in accord with the expected preferences of cobalt for high degree vertices and nitrogen for low degree vertices. Structure **B6NCo-2** has a Co–N polyhedral edge of length 1.957 Å whereas in **B6NCo-3** the cobalt and nitrogen atoms do not occupy adjacent vertices. The higher energy $CpCoNHB_6H_6$

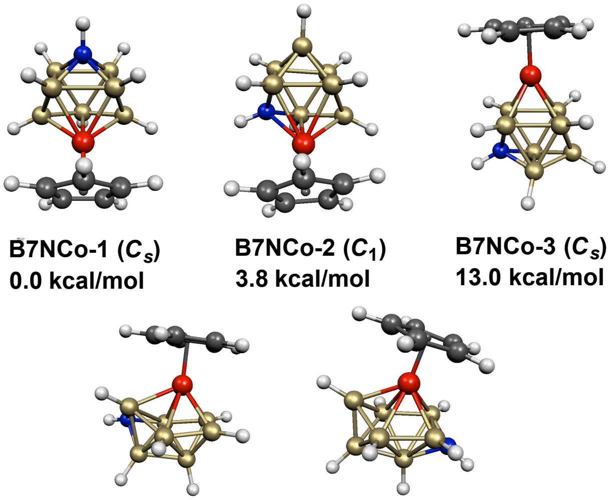
structure **B6NCo-4**, lying 10.5 kcal/mol in energy above **B6NCo-1**, has the cobalt and nitrogen atoms at non-adjacent degree 4 vertices.

Table 1. Details of the four 8-vertex $CpCoNHB_6H_6$ structures within 15 kcal/mol of the global minimum. Adjacent Co–N distances corresponding to polyhedral edges are indicated in *italic*s.

Structure (symmetry)	ΔE kcal/mol	Vertex Degrees Co	N	Co–N distance	HOMO-LUMO Gap, eV	Polyhedron
B6NCo-1 (C_s)	0.0	5	3	2.678 Å	2.90	Bicap octahed
B6NCo-2 (C_1)	1.9	5	4	*1.957 Å*	2.31	Bisdisphenoid
B6NCo-3 (C_s)	7.4	5	4	2.724 Å	2.27	Bisdisphenoid
B6NCo-4 (C_1)	10.5	4	4	3.028 Å	2.27	Bisdisphenoid

The three lowest energy structures of the 9-vertex $CpCoNHB_7H_7$ system are all based on the most spherical deltahedron, namely the tricapped trigonal prism (Figure 6 and Table 2). The lowest energy such structure, namely **B7NCo-1**, is the unique tricapped trigonal prism structure with the cobalt atom at a degree 5 vertex and the nitrogen atom at a non-adjacent degree 4 vertex. The next $CpCoNHB_7H_7$ structure in energy, namely **B7NCo-2** at 3.8 kcal/mol above **B7NCo-1**, also has the cobalt and nitrogen atoms at degree 5 and degree 4 vertices, respectively. However, in **B7NCo-2** the cobalt and nitrogen atoms are adjacent forming a deltahedral edge of length 1.915 Å. The third $CpCoNHB_7H_7$ structure **B7NCo-3**, lying 13.0 kcal/mol in energy above **B7NCo-1**, is the unique tricapped trigonal prismatic structure with both the cobalt and nitrogen atoms at degree 4 vertices. These degree 4 vertices in the tricapped trigonal prism are necessarily non-adjacent. The low HOMO-LUMO gap of 1.53 eV for **B7NCo-3** relative to the HOMO-LUMO gaps greater than 2 eV for the isomeric $CpCoNHB_7H_7$ structures (Table 2) may relate to the presence of the cobalt atom at a degree 4 rather than a degree 5 vertex in the $CoNB_7$ tricapped trigonal prism.

The next two 9-vertex $CpCoNHB_7H_7$ structures in terms of energy, namely **B7NCo-4** and **B7NCo-5** at 13.2 and 15.3 kcal/mol, respectively, above **B7NCo-1**, violate the Wade-Mingos rules[4,5,6] by having central $CoNB_7$ capped bisdisphenoids rather than the most spherical tricapped trigonal prism. Such capped bisdisphenoids have a single degree 3 vertex for the nitrogen atom as well as two degree 4 vertices, five degree 5 vertices, and one degree 6 vertex. Interestingly, the cobalt atom in both **B7NCo-4** and **B7NCo-5** occupies a degree 5 vertex not adjacent to the nitrogen atom at the degree 3 vertex rather than the degree 6 vertex, which necessarily is adjacent to the degree 3 vertex. In **B7NCo-4** the cobalt atom is located at a degree 5 vertex adjacent to the unique degree 6 vertex. However, in **B7NCo-5** the cobalt atom is located at a degree 5 vertex not adjacent to the degree 6 vertex.



B7NCo-1 (C_s)
0.0 kcal/mol

B7NCo-2 (C_1)
3.8 kcal/mol

B7NCo-3 (C_s)
13.0 kcal/mol

B7NCo-4 (C_1)
13.2 kcal/mol

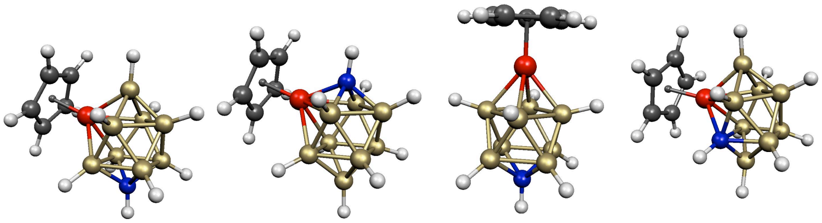
B7NCo-5 (C_s)
15.3 kcal/mol

Figure 6. The five optimized $CpCoNHB_7H_7$ structures within 17 kcal/mol of the global minimum.

Table 2. Details of the five $CpCoNHB_7H_7$ structures within 17 kcal/mol of the global minimum. Adjacent Co–N distances corresponding to polyhedral edges are indicated in *italic*s.

Structure (symmetry)	Δ*E* kcal/mol	Vertex Degrees Co	N	Co–N distance	HOMO-LUMO Gap, eV	Polyhedron
B7NCo-1 (C_s)	0.0	5	4	2.905 Å	2.35	Tricap trig prism
B7NCo-2 (C_1)	3.8	5	4	*1.915 Å*	2.08	Tricap trig prism
B7NCo-3 (C_s)	13.0	4	4	2.984 Å	1.53	Tricap trig prism
B7NCo-4 (C_1)	13.2	5	3	2.682 Å	2.15	Cap bisdisphenoid
B7NCo-5 (C_s)	15.3	5	3	2.659 Å	3.23	Cap bisdisphenoid

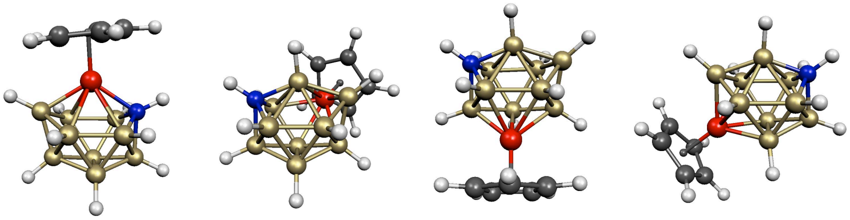
Unlike the $CpCoNHB_nH_n$ structures with 8 and 9 vertices, the low-energy $CpCoNHB_nH_n$ structures with 10, 11, and 12 vertices are all based on the most spherical deltahedra (Figure 3). For the 10-vertex $CpCoNHB_8H_8$ system the lowest energy structure **B8NCo-1** is the unique bicapped square antiprismatic structure with the cobalt and nitrogen atoms at non-adjacent degree 5 and 4 vertices, respectively (Figure 7). The unique $CpCoNHB_8H_8$ structure **B8NCo-2** with the cobalt and nitrogen atoms at adjacent degree 5 and 4 vertices, respectively, lies 7.5 kcal/mol in energy above **B8NCo-1**. The unique structure **B8NCo-3** with both the cobalt and nitrogen atoms at degree 4 vertices is a much higher energy structure, lying 19.0 kcal//mol. above **B8NCo-1**. The next $CpCoNHB_8H_8$ structure in energy, namely **B8NCo-4** at 28.5 kcal/mol above **B8NCo-1**, has the cobalt and nitrogen atoms at adjacent degree 5 vertices. The potential energy surface of the 10-vertex system $CpCoNHB_8H_8$ is obviously much simpler than that of the 8- and 9-vertex $CpCoNHB_{n-2}H_{n-2}$ (n = 8, 9) systems since only two $CpCoNHB_8H_8$ structures lie within the 17 kcal/mol energy cutoff point used for the 8- and 9-vertex structures (Tables 1 and 2).



B8NCo-1 (C_s) **0.0 kcal/mol** **B8NCo-2 (C_s)** **7.5 kcal/mol** **B8NCo-3 (C_{4v})** **19.0 kcal/mol** **B8NCo-4 (C_1)** **28.5 kcal/mol**

Figure 7. The four optimized $CpCoNHB_8H_8$ structures within 36 kcal/mol of the global minimum.

The lowest energy 11-vertex $CpCoNHB_9H_9$ structure **B9NCo-1** is the unique structure with the cobalt and nitrogen atoms located at the degree 6 vertex and one of the degree 4 vertices of the most spherical 11-vertex deltahedron (Figure 8). The cobalt and nitrogen atoms in **B9NCo-1** are necessarily in adjacent positions forming a deltahedral edge of length 1.946 Å. The next three $CpCoNHB_9H_9$ structures in terms of energy, namely **B9NCo-2**, **B9NCo-3**, and **B9NCo-4** lying 5.8, 11.7, and 15.2 kcal/mol above **B9NCo-1**, are the three possible structures with the nitrogen atom at a degree 4 vertex and the cobalt atom at a non-adjacent degree 5 vertex.

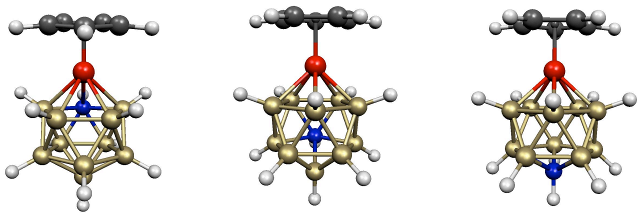


B9NCo-1 (C_s) **0.0 kcal/mol** **B9NCo-2 (C_1)** **5.8 kcal/mol** **B9NCo-3 (C_1)** **11.7 kcal/mol** **B9NCo-4 (C_s)** **15.2 kcal/mol**

Figure 8. The four optimized $CpCoNHB_9H_9$ structures within 17 kcal/mol of the global minimum.

The cobaltaazaborane $CpCoNHB_9H_9$ has been synthesized and shown by X-ray crystallography to have the lowest energy structure **B9NCo-1** in accord with our theoretical predictions.[3] The predicted Co–N distance in **B9NCo-1** of 1.946 Å is essentially identical with the experimental Co–N distance of 1.942(7) Å. In addition the predicted five Co–B deltahedral edges in sequence around the base of the $CoNB_5$ hexagonal subpyramid in **B9NCo-1** of 2.030, 2.305, 2.197, 2.197, and 2.305 Å are very close to the experimental values of 2.040, 2.309, 2.263, 2.252, and 2.314 Å.

Three structures are possible for the 12-vertex $CpCoNHB_{10}H_{10}$ system in which the central $CoNB_{10}$ unit is a “regular” icosahedron with all degree 5 vertices. These are the only low-energy $CpCoNHB_{10}H_{10}$ structures, lying within 3.5 kcal/mol of each other (Figure 9). The lowest energy such $CpCoNHB_{10}H_{10}$ structure **B10NCo-1** has the cobalt and nitrogen atoms in adjacent positions forming a 2.027 Å icosahedral edge and is thus the *ortho* isomer. The highest energy icosahedral $CpCoNHB_{10}H_{10}$ structure **B10NCo-3** is the *para* isomer with the cobalt and nitrogen atoms in antipodal positions. The lowest energy non-icosahedral $CpCoNHB_{10}H_{10}$ lies a gigantic 43.3 kcal/mol above **B10NCo-1** and thus is probably not chemically relevant. This C_s structure has the cobalt atom at a unique degree 6 vertex, the nitrogen atom at a unique degree 3 vertex, three degree 4 vertices, seven degree 5 vertices, and two equivalent quadrilateral faces.



B10NCo-1 (C_s)
0.0 kcal/mol

B10NCo-1 (C_s)
0.7 kcal/mol

B10NCo-3 (C_{5v})
3.5 kcal/mol

Figure 9. The three possible optimized $CpCoNHB_{10}H_{10}$ structures with a central $CoNB_{10}$ icosahedron having all degree 5 vertices.

4. Discussion

In metallaboranes containing heteroatoms the transition metals typically prefer higher degree vertices whereas carbon and nitrogen prefer lower degree vertices. This difference in the preferred vertex degrees of various vertex atoms can lead to deviations from sphericity. As a result, low-energy polyhedra different from the most spherical deltahedra (Figure 3) found in the deltahedral borane dianions $B_nH_n^{2-}$ (n = 6 to 12) having $2n + 2$ Wadean skeletal electrons[4,5,6] might be found in isoelectronic polyhedral metallaboranes in which some of the boron vertices are replaced by heteroatom vertices. For the cobaltadicarbaboranes $CpCoC_2B_{n-3}H_{n-1}$, also with $2n + 2$ Wadean skeletal electrons, the lowest energy structures are the same deltahedra found in the $B_nH_n^{2-}$ anions.[16] However, for the isoelectronic ferratricarbaboranes $CpFeC_3B_{n-4}H_{n-1}$, 8-vertex $CpFeC_3B_4H_7$ structures based on the less spherical hexagonal bipyramid are found to be of comparable energy to the most spherical bisdisphenoidal isomers.[17] This can be related to the possibility of the three carbon atoms occupying three non-adjacent degree 4 vertices in the hexagonal bipyramid but not in the bisdisphenoid. In addition, low energy 10-vertex $CpFeC_3B_6H_9$ structures based on the *isocloso* 10-vertex deltahedron with three non-adjacent degree 4 vertices for the carbon atoms are comparable in energy with isomeric structures based on the most spherical bicapped square antiprism.

The preference of the nitrogen atom in the polyhedral cobaltaazaboranes $CpCoNHB_{n-2}H_{n-2}$ for lower degree vertices can lead to deviations from the most spherical deltahedra in the lowest energy structures. Such deviations from the most spherical deltahedra can even provide degree 3 vertices for the nitrogen atoms, which then have a local environment similar to the ammonium ion. Thus in the 8-vertex system the lowest energy $CpCoNHB_6H_6$ structure **B6NCo-1** has a central $CoNB_6$ antipodally bicapped octahedron rather than a bisdisphenoid. This provides two degree 3 vertices, one of which is occupied by the nitrogen atom. However, only slightly higher energy isomeric $CpCoNHB_6H_6$ structures are based on the most spherical bisdisphenoid. For the 9-vertex $CpCoNHB_7H_7$ system the three lowest energy structures are the three possible structures based on the most spherical tricapped trigonal prism with the nitrogen atom at a degree 4 vertex. However, the central $CoNB_7$ polyhedron in the next two $CpCoNHB_7H_7$ structures in terms of relative energy is a most spherical 8-vertex bisdisphenoid with one of the triangular face capped by the ninth vertex. This capping vertex provides a degree 3 vertex for the nitrogen atom. The lowest energy $CpCoNHB_6H_6$ structure **B6NCo-1** (Figure 5) and the $CpCoNHB_7H_7$ structures **B7NCo-4** and **B7NCo-5** (Figure 6) represent unprecedented examples of metallaborane structures having a degree 3 vertex in a deltahedron with at least 8 vertices.

All of the central polyhedra in the 10- to 12-vertex $CpCoNHB_{n-2}H_{n-2}$ systems ($n = 10, 11, 12$) are the most spherical deltahedra (Figure 2). These deltahedra for the 10- and 11-vertex systems have two degree 4 vertices. One of these degree 4 vertices is occupied by the nitrogen atom in all of the low-energy structures. The unique 10-vertex $CpCoNHB_8H_8$ structure with the cobalt atom at a degree 5 vertex and the nitrogen atom at a non-adjacent degree 4 vertex is the lowest energy structure by a significant margin of 7.5 kcal/mol (Figure 7). Similarly the unique 11-vertex $CpCoNHB_9H_9$ structure with the cobalt atom at the unique degree 6 vertex and the nitrogen atom at a degree 4 vertex is the lowest energy structure by 5.8 kcal/mol.

Three structures of the 12-vertex system $CpCoNHB_{10}H_{10}$ are possible with a central $CoNB_{10}$ "regular" icosahedron with all degree 5 vertices. All three such structures have similar energies within 3.5 kcal/mol and lie more than 43 kcal/mol in energy below the lowest energy structure not based on a "regular" icosahedron.

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Supporting Information. Table S1A: Initial $CpCoNHB_6H_6$ structures; Table S1B: Distance table for the lowest-lying $CpCoNHB_6H_6$ structures; Table S1C: Energy ranking for all the $CpCoNHB_6H_6$ structures; Table S2A: Initial $CpCoNHB_7H_7$ structures; Table S2B: Distance table for the lowest-lying $CpCoNHB_7H_7$ structures; Table S2C: Energy ranking for all the $CpCoNHB_7H_7$ structures; Table S3A: Initial $CpCoNHB_8H_8$ structures; Table S3B: Distance table for the lowest-lying $CpCoNHB_8H_8$ structures; Table S3C: Energy ranking for all the $CpCoNHB_8H_8$ structures; Table S4A: Initial $CpCoNHB_9H_9$ structures; Table S4B: Distance table for the lowest-lying $CpCoNHB_9H_9$ structures; Table S4C: Energy ranking for all the $CpCoNHB_9H_9$ structures; Table S5A: Initial $CpCoNHB_{10}H_{10}$ structures; Table S5B: Distance table for the lowest-lying $CpCoNHB_{10}H_{10}$ structures; Table S5C. Energy ranking for all the $CpCoNHB_{10}H_{10}$ structures; Complete Gaussian09 Reference (reference 15).

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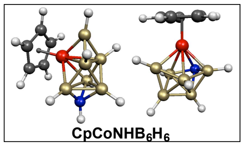
Graphical Abstract

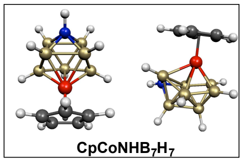
Cyclopentadienylcobalt Azaboranes Violating the Wade-Mingos Rules: A Degree 3 Vertex for the Nitrogen Atom

Amr A. A. Attia, Alexandru Lupan,*
and R. Bruce King*

The structures and energetics of the cobaltaazaboranes $CpCoNHB_{n-2}H_{n-2}$ (n = 8 to 12) have been investigated by density functional theory. In addition to structures based on the most spherical deltahedra, low-energy 8- and 9-vertex structures are found based on the antipodally bicapped octahedron and capped bisdisphenoid, respectively, with the nitrogen atom at a degree 3 vertex.



$CpCoNHB_6H_6$



$CpCoNHB_7H_7$