Polyhedral Dinickelaboranes as Analogues of the Dicarbaboranes

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Abstract

The lowest energy structures of the dinickelaboranes $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ ($n = 8$ to 12) are found by density functional theory to be the most spherical *closo* deltahedra similar to those of the isoelectronic dicarbaboranes $\text{C}_2\text{B}_{n-2}\text{H}_n$. The nickel atoms in such dinickelaboranes do not prefer higher degree vertices in contrast to metallaboranes containing earlier transition metals. Similarly, $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ structures having adjacent nickel atoms are of higher energy than isomeric structures having non-adjacent nickel atoms. Thus the brown icosahedral *ortho* $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer with adjacent nickel atoms obtained by Hawthorne and co-workers from $\text{B}_{10}\text{H}_{10}^{2-}$ and Cp_2Ni , $[\text{Cp}_3\text{Ni}_2][\text{BF}_4]$, or $\text{Cp}_2\text{Ni}_2(\text{CO})_2$ and structurally characterized by X-ray crystallography is not the lowest energy isomer but instead a kinetically favored product. However, the structure with non-adjacent nickel atoms suggested by ^{11}B NMR for the $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ isomer isolated in small quantities by Grimes and co-workers from a $\text{B}_5\text{H}_8^-/\text{C}_5\text{H}_5^-/\text{NiBr}_2$ reaction mixture is found to be the lowest energy isomer by ~ 6 kcal/mol. This latter reaction also gives small quantities of a yellow $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer suggested by its ^{11}B NMR spectrum to be the lowest energy *meta* isomer with non-adjacent non-antipodal nickel atoms.

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1. Introduction

The borane dianions $B_nH_n^{2-}$ ($n = 6$ to 12) and their derivatives have structures based on the most spherical so-called *closo* deltahedra, which have the maximum number of degree 4 and 5 vertices [1, 2]. Such borane derivatives are among the most stable and thus least reactive compounds containing B–H bonds. Their special stability has been ascribed to three-dimensional aromaticity embodied in the Wade-Mingos rules [3, 4, 5, 6] conferring special stability on n -vertex systems having $2n + 2$ skeletal electrons such as $B_nH_n^{2-}$ with each BH vertex contributing two skeletal electrons. This interpretation of the deltahedral boranes and isoelectronic carboranes as three-dimensional aromatic systems is supported by analyses using graph theory [7, 8] and tensor surface harmonics [9]. The dicarbaboranes $C_2B_{n-2}H_n$, frequently known simply as “carboranes,” are isoelectronic with borane dianions $B_nH_n^{2-}$ and thus provide neutral species with similar aromatic stability [10]. In the dicarbaboranes each CH vertex contributes three skeletal electrons.

Hawthorne and co-workers [11] first showed that the boron vertices in the dicarbaboranes could be replaced by transition metal vertices to give very stable metallaboranes. The early metallaborane studies replaced BH vertices with CpCo vertices (Cp = η^5 -C₅H₅), where each CpCo vertex is a donor of two skeletal electrons like the BH vertex that it replaces. Thus the cobaltadicarbaboranes $CpCoC_2B_{n-3}H_{n-1}$ and the dicobaltadicarbaboranes $Cp_2Co_2C_2B_{n-4}H_{n-2}$ are stable species and their chemistry has been studied extensively.

An alternative but less developed approach to stable metallaboranes replaces CH vertices in carboranes with CpNi vertices, which are donors of three skeletal electrons like the CH vertices that they replace. Thus dinickelaboranes of the type $Cp_2Ni_2B_{n-2}H_{n-2}$ are isoelectronic with the dicarbaboranes $C_2B_{n-2}H_n$ and provide examples of stable neutral n -vertex metallaboranes having the favorable $2n + 2$ skeletal electrons without the need for carbon vertices in the underlying deltahedron. Two examples of such dinickelaboranes have been synthesized in low to modest yields from reactions of CpNi derivatives with various boranes (Figure 1). Thus the brown 12-vertex species $Cp_2Ni_2B_{10}H_{10}$ is obtained from the reaction of Cp_2Ni , $[Cp_3Ni_2][BF_4]$, or $Cp_2Ni_2(CO)_2$ with $B_nH_n^{2-}$ ($n = 9, 10, 11$) [12] and has been shown by X-ray crystallography to have a central Ni_2B_{10} icosahedron with the nickel atoms in adjacent (*ortho*) positions [13]. Similarly, the 10-vertex species $Cp_2Ni_2B_8H_8$ as well as a second (yellow) 12-vertex $Cp_2Ni_2B_{10}H_{10}$ isomer are among the products isolated from the reaction of a mixture of NaB_5H_8 and NaCp with $NiBr_2$ [14]. The structure of the $Cp_2Ni_2B_8H_8$ species has apparently not been determined by X-ray crystallography. However, its ^{11}B NMR

spectrum suggests a bicapped square antiprism structure with one nickel atom at a degree 4 vertex and the other nickel atom at a non-adjacent degree 5 vertex (Figure 1).

Figure 1. The structures suggested for the known dinickelaboranes $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$. External hydrogen atoms and Cp rings are omitted for clarity. The edges leading to the two degree 4 vertices in $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ are indicated in red.

We now report a density functional theory (DFT) study on the complete series of dinickelaboranes $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ having from 8 to 12 vertices. We show that the structure suggested by ^{11}B NMR for the experimentally known 10-vertex derivative $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ [14] is the lowest energy structure by a margin of ~ 6 kcal/mol thus supporting the structural assignment by NMR. However, the experimental structure for the 12-vertex brown $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer determined by X-ray crystallography [13] is shown to lie ~ 11 kcal/mol in energy above the lowest energy isomer. This provides another example of a synthetic procedure providing a higher energy kinetically stable metallaborane isomer different from the lowest energy thermodynamically preferred isomer. This was previously observed in our original theoretical work on $\text{CpCoC}_2\text{B}_{n-3}\text{H}_{n-1}$ derivatives [15].

2. Theoretical Methods

Full geometry optimizations were carried out on the $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ systems ($n = 8$ to 12) using initially the B3LYP/6-31G(d) [16, 17, 18, 19] level of theory. The lowest-energy structures were then reoptimized at a higher level, i. e., M06L/6-311G(d,p), [20] and these are the structures presented in the manuscript. The initial structures were chosen by systematic substitution of two boron vertices in $\text{B}_n\text{H}_n^{2-}$ with nickel atoms in various n -vertex polyhedra. Thus 50 structures of the 8-vertex clusters $\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$, 52 structures of the 9-vertex clusters $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$, 95 structures of the 10-vertex clusters $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$, 70 structures of the 11-vertex clusters $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$, and 26 structures of the 12-vertex $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ clusters were chosen as starting points for the optimizations (see the Supporting Information). The natures of the stationary points after optimization were checked by calculations of the harmonic vibrational frequencies. If significant imaginary

frequencies were found, the optimization was continued by following the normal modes corresponding to the imaginary frequencies to insure that genuine minima were obtained.

All calculations were performed using the Gaussian 09 package [21] 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 Wiberg bond indices (WBIs) for the Ni-Ni interactions in the optimized $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ ($n = 8$ to 12) structures were obtained from the NBO analysis automatically provided in the Gaussian output [22]. The ^{11}B NMR chemical shift values (in ppm) have been computed by the B3LYP/6-311+G(2d,p) GIAO method and are referenced to $\text{BF}_3\cdot\text{OEt}_2$ (the standard used in the literature).

All of the structures reported in this paper have appreciable HOMO-LUMO gaps of at least 0.8 eV. The lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ ($n = 8$ to 12) structures for a given value of n have even higher HOMO-LUMO gaps of at least 1.8 eV (see Table S6 in the Supporting Information).

The $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ ($n = 8$ to 12) structures are numbered as **B($n-2$)Ni2- 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 2, 3, 5, 6, and 7. Only the lowest energy and thus potentially chemically significant structures are considered in detail in this paper. More comprehensive lists of structures, including higher energy structures, are given in the Supporting Information.

3. Results

3.1 Eight-vertex Structures

Each of the four lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$ structures has a central Ni_2B_6 bisdisphenoid, which is the most spherical *closo* 8-vertex deltahedron having four degree 4 and four degree 5 vertices (Figure 2 and Table 1). The lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$ structure **B6Ni2-1** has the nickel atoms at non-adjacent degree 4 vertices. The corresponding $\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$ structure **B6Ni2-4** with the nickel atoms at adjacent degree 4 vertices is a relatively high-energy structure, lying 20.3 kcal/mol in energy above **B6Ni2-1**. Intermediate in energy at ~ 7 kcal/mol in energy above **B6Ni2-1** are **B6Ni2-2** and **B6Ni2-3** with one nickel atom at a degree 4 vertex and the other nickel atom at a degree 5 vertex. In this case **B6Ni2-2** with the nickel atoms at adjacent vertices is of similar energy to **B6Ni2-3** with the nickel atoms at non-adjacent vertices. The Ni-Ni edge

connecting two degree 4 vertices in **B6Ni2-4** of length 2.311 Å with a corresponding WBI of 0.31 is significantly shorter than the Ni–Ni edge connecting a degree 4 vertex with a degree 5 vertex in **B6Ni2-2** of length 2.391 Å with a correspondingly lower WBI of 0.21.

Figure 2. The four $\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$ structures within 21 kcal/mol of the global minimum.

Table 1. The four lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$ structures. All of the structures have central Ni_2B_6 bisdisphenoids.

Structure (symmetry)	ΔE (kcal/mol)	Nickel vertices		
		Degrees	Ni-Ni distance, Å	WBI
B6Ni2-1 (C_2)	0.0	4,4	3.605	0.10
B6Ni2-2 (C_1)	7.1	4,5	2.391	0.21
B6Ni2-3 (C_s)	7.9	4,5	3.354	0.11
B6Ni2-4 (C_2)	20.3	4,4	2.311	0.31

3.2 Nine-vertex Structures

Each of the five lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ structures has a central Ni_2B_7 tricapped trigonal prism, which is the most spherical *closo* 9-vertex deltahedron (Figure 3 and Table 2). The lowest energy such structure, namely **B7Ni2-1**, has one nickel atom at a degree 4 vertex and the other nickel atom at a non-adjacent degree 5 vertex. The higher energy $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ structures **B7Ni2-3** and **B7Ni2-5**, lying 8.0 and 10.7 kcal/mol, respectively, in energy above **B7Ni2-1**, also have one nickel atom at a degree 4 vertex and the other nickel atom at a degree 5 vertex. However, for **B7Ni2-3** and **B7Ni2-5** the two nickel vertices are adjacent with Ni-Ni distances of ~ 2.39 Å corresponding to WBIs of ~ 0.21 . These Ni-Ni distances and WBIs are essentially identical to those for the nickel atoms in the 8-vertex $\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$ structure **B6Ni2-2** discussed above (Table 1). The

tricapped trigonal prismatic $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ structure **B6Ni2-4**, lying 9.0 kcal/mol in energy above **B7Ni2-1**, has a relatively long 2.794 Å Ni–Ni edge with a low WBI of 0.08. This suggests incipient formation of a capped tetragonal antiprism with the relatively long Ni–Ni edge corresponding to a diagonal of the unique tetragonal face.

Only one tricapped trigonal prismatic $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ structure is possible having both nickel atoms at degree 4 vertices, namely the C_{2v} structure **B7Ni2-2**, lying 3.1 kcal/mol in energy above **B7Ni2-1** (Figure 3 and Table 2). In addition, the higher energy structure **B7Ni2-6**, lying 12.2 kcal/mol in energy above **B7Ni2-1**, has both nickel atoms at degree 4 vertices. However, the central Ni_2B_7 deltahedron in **B7Ni2-6** is not the *closo* 9-vertex tricapped trigonal prism but instead the *isocloso* 9-vertex deltahedron having a unique degree 6 vertex surrounded by four degree 4 vertices (Figure 4). Structure **B7Ni2-6** is the only low-energy $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ ($n = 8$ to 12) found in this work with a central $\text{Ni}_2\text{B}_{n-2}$ polyhedron that is not the most spherical *closo* deltahedron. The *isocloso* **B7Ni2-6** structure is unusual among *isocloso* metallaboranes since the metal atom does not occupy the unique degree 6 vertex. This is one indication that the late transition metal nickel, unlike earlier transition metals, does not have an inherent preference for the highest degree vertices in metallaborane structures.

Figure 3. The six $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ structures within 17 kcal/mol of the global minimum including the unusual structure **B7Ni2-6** having an *isocloso* 9-vertex Ni_2B_7 deltahedron rather than the *closo* tricapped trigonal prism.

Figure 4. Comparison of the 9-vertex *closo* deltahedron (the tricapped trigonal prism) with the 9-vertex *isocloso* deltahedron. Vertices of degrees 4, 5, and 6 are in red, black, and green, respectively.

Table 2. The six lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ structures. The first five structures have central Ni_2B_7 tricapped trigonal prisms. Structure **B7Ni2-6** has a central nine-vertex *isocloso* deltahedron.

Structure (symmetry)	ΔE (kcal/mol)	Nickel vertices		
		Degrees	Ni-Ni distance, Å	WBI
B7Ni2-1 (C_s)	0.0	4,5	3.583	0.09
B7Ni2-2 (C_{2v})	3.1	4,4	3.556	0.10
B7Ni2-3 (C_{2v})	8.0	4,5	2.387	0.22
B7Ni2-4 (C_s)	9.0	5,5	2.794	0.06
B7Ni2-5 (C_1)	10.7	4,5	2.392	0.21
B7Ni2-6 (C_s) ^a	12.2	4,4	3.453	0.08

^a The **B7Ni2-6** structure is based on the 9-vertex *isocloso* deltahedron (Figure 4) rather than the 9-vertex *closo* deltahedron (the tricapped trigonal prism).

3.3 Ten-vertex Structures

Each of the five lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structures has a central Ni_2B_8 bicapped square antiprism, which is the most spherical *closo* 10-vertex deltahedron (Figure 5 and Table 3). The lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structure **B8Ni2-1** is the unique such structure with the nickel atoms at non-adjacent degree 4 and degree 5 vertices and corresponds to the structure suggested on the basis of its ^{11}B NMR spectrum for the $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ isomer that has been synthesized. The fact that **B8Ni2-1** is the lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structure by ~ 6 kcal/mol supports this structural assignment by NMR.

The next $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structure **B8Ni2-2**, lying 5.9 kcal/mol in energy above **B8Ni2-1**, is the unique bicapped square antiprismatic structure with each nickel atom at a degree 4 vertex. This necessarily places the nickel atoms in antipodal positions with a very long $\text{Ni}\cdots\text{Ni}$ distance of 4.565 Å corresponding to a WBI of 0.09 (Figure 5 and Table 3). The next $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structure **B8Ni2-3**, lying 11.2 kcal/mol in energy above

B8Ni2-1, has the nickel atoms at quasi-antipodal degree 5 vertices but at a lesser Ni··Ni distance of 3.577 Å with a WBI of 0.07. Of interest is the observation that the Ni··Ni WBI in **B8Ni2-2** is slightly larger than that in **B8Ni2-3** despite the longer Ni··Ni distance in **B8Ni2-2**.

Figure 5. The five $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structures within 18 kcal/mol of the global minimum.

Table 3. The five lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structures. All of the structures have central Ni_2B_8 bicapped square antiprisms.

Structure (symmetry)	ΔE (kcal/mol)	Nickel vertices		
		Degrees	Ni-Ni distance, Å	WBI
B8Ni2-1 (C_s)	0.0	4,5	3.597	0.09
B8Ni2-2 (C_s)	5.9	4,4	4.565	0.09
B8Ni2-3 (C_2)	11.2	5,5	3.577	0.07
B8Ni2-4 (C_s)	12.4	5,5	2.413	0.19
B8Ni2-5 (C_s)	13.5	4,5	2.382	0.22

The lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structures with adjacent nickel vertices are **B8Ni2-4** and **B8Ni2-5**, lying 12.4 and 13.5 kcal/mol in energy, respectively, above **B8Ni2-1** (Figure 5 and Table 3). In **B8Ni2-4** both nickel atoms are located at degree 5 vertices with an Ni-Ni distance of 2.413 Å corresponding to a WBI of 0.19. In **B8Ni2-5** one nickel atom is located at a degree 4 vertex and the other nickel atom at a degree 5 vertex leading to a somewhat shorter Ni-Ni distance of 2.382 Å corresponding to a slightly higher WBI of 0.22.

3.4 Eleven-vertex Structures

The central Ni_2B_9 polyhedron in each of the five lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structures (Figure 6 and Table 4) is the 11-vertex most spherical *closo* deltahedron, which necessarily has a single degree 6 vertex flanked by two non-adjacent degree 4 vertices [23]. None of the five lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structures has a nickel atom located at the degree 6 vertex. The lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structure with a nickel atom located at the degree 6 vertex is the seventh lowest energy structure lying 13.3 kcal/mol in energy above the lowest energy structure **B9Ni2-1** (see Supporting Information).

The three lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structures all have non-adjacent nickel vertices. Structure **B9Ni2-2**, lying 4.3 kcal/mol in energy above **B9Ni2-1**, is the unique structure with both degree 4 vertices of the underlying 11-vertex *closo* deltahedron occupied by nickel atoms (Figure 6 and Table 4). Structures **B9Ni2-1** as well as **B9Ni2-3** and **B9Ni2-5**, lying 5.5 and 10.3 kcal/mol, respectively, in energy above **B9Ni2-1**, have the nickel atoms at non-adjacent degree 4 and 5 vertices. In **B9Ni2-5** the nickel atoms are located in quasi-antipodal positions with a very long $\text{Ni}\cdots\text{Ni}$ distance of 4.456 Å with a correspondingly very low WBI of 0.05. Structure **B9Ni2-4**, lying 7.8 kcal/mol in energy above **B9Ni2-1**, has the nickel atoms at adjacent degree 4 and 5 vertices. The Ni - Ni distance in **B9Ni2-4** of 2.430 Å is ~ 0.05 Å longer than the Ni - Ni edges between degree 4 and 5 vertices in the 8- and 9-vertex structures corresponding to a somewhat lower WBI of 0.18.

Figure 6. The five $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structures within 13 kcal/mol of the global minimum.

Table 4. The five lowest-energy $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structures. All of the structures have a central Ni_2B_9 *closo* 11-vertex deltahedron and are depicted with the unique degree 6 vertex on the top.

Structure (symmetry)	ΔE (kcal/mol)	Nickel vertices		
		Degrees	Ni-Ni distance, Å	WBI
B9Ni2-1 (C_s)	0.0	4,5	3.619	0.09
B9Ni2-2 (C_{2v})	4.3	4,4	4.146	0.09
B9Ni2-3 (C_i)	5.5	4,5	3.616	0.08
B9Ni2-4 (C_s)	7.8	4,5	2.430	0.18
B9Ni2-5 (C_s)	10.3	4,5	4.456	0.05

3.5 Twelve-vertex Structures

There are three $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomers corresponding to the well-known *ortho*, *meta*, and *para* dicarbaboranes $\text{C}_2\text{B}_{10}\text{H}_{12}$ (Figure 7 and Table 5) [10]. The lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ is the *meta* isomer **B10Ni2-1**. However, the well-characterized $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer is the brown *ortho* isomer **B10Ni2-3**, lying 11.9 kcal/mol in energy above **B10Ni2-1**, and obtained from reactions of $\text{B}_{10}\text{H}_{10}^{2-}$ with Cp_2Ni , $\text{Cp}_2\text{Ni}_2(\text{CO})_2$, or, most efficiently, $[\text{Cp}_3\text{Ni}_2][\text{BF}_4]$. The predicted length of 2.434 Å for the Ni–Ni icosahedral edge in **B10Ni2-3** is close to the experimental value of 2.4233(6) Å determined by X-ray crystallography [13]. The predicted Ni–B edge lengths ranging from ~2.08 to 2.12 Å for **B10Ni2-3** are essentially the same as the experimental Ni–B edge lengths. The formation of the *ortho* $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer **B10Ni2-3** rather than the lowest energy *meta* isomer **B10Ni2-1** in reactions of CpNi systems with polyhedral borane derivatives is an example of the formation of a kinetically favored isomer arising from the synthetic method rather than the thermodynamically favored isomer. However, a yellow $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer, isolated in small quantities from the reaction of B_5H_8^- with NaC_5H_5 and NiBr_2 , appears to be the lowest energy *meta* isomer **B10Ni2-1** based on its ^{11}B NMR spectrum.

Figure 7. The three $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ structures.

Table 5. The three $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ structures.

Structure (symmetry)	ΔE (kcal/mol)	Nickel vertices	
		Ni-Ni distance, Å	WBI
B10Ni2-1 (C_{2v})	0.0	3.612	0.07
B10Ni2-2 (S_{10})	5.0	4.249	0.03
B10Ni2-3 (C_2)	11.9	2.434	0.17

The remaining $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer is the *para* isomer **B10Ni2-2**, lying 5.0 kcal/mol in energy above **B10Ni2-1** (Figure 7 and Table 5). Structure **B10Ni2-2** has unusually high S_{10} point group symmetry with a very low WBI of 0.03 for the antipodal interaction of the nickel atoms at an Ni...Ni distance of 2.434 Å.

3.6 Boron-11 NMR Spectra

Table 6 lists the predicted ^{11}B NMR spectra for the lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ structures as well as the experimental ^{11}B NMR spectra for $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ and $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$. The low-field ^{11}B resonances ranging from 113 to 88 ppm correspond to degree 4 boron vertices whereas the higher field ^{11}B resonances from 55 to -10 ppm correspond to degree 5 boron vertices. The calculated ^{11}B NMR shift values for the lowest energy $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structure **B8Ni2-1** and both $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ structures **B10Ni2-1** and **B10Ni2-3** correspond closely to the experimental values.

Table 6. ^{11}B NMR shift values (in ppm) computed by B3LYP/6-311+G(2d,p) GIAO and referenced to $\text{BF}_3\cdot\text{OEt}_2$. Experimental values, when available, are also provided.

Structure	^{11}B NMR
$\text{Cp}_2\text{Ni}_2\text{B}_6\text{H}_6$ (B6Ni2-1)	113.0, 37.0, 18.1
$\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ (B7Ni2-1)	88.7, 34.8, 26.0, -9.7
$\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ (B8Ni2-1)	94.2, 48.8, 20.3, 6.0, 3.8
$\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ (expt.) ¹⁴	93.6, 47.5, 20.4, 12.2, 6.7
$\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ (B9Ni2-1)	88.0, 46.7, 23.8, 21.8, 8.2, -8.6, -9.8
$\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ (B10Ni2-1)	40.4, 39.4, 21.8, -7.8
Yellow $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ (expt.) ¹⁴	38.9, 20.3, -3.9
$\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ (B10Ni2-2)	21.0, 20.8
$\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ (B10Ni2-3)	64.2, 25.0, 23.8/23.5, 6.0
Brown $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ (expt.) ¹²	54.3, 26.1, 21.3, 6.7

4. Discussion

In most polyhedral metallaboranes the transition metal atoms, such as those in CpM moieties, occupy vertices of relatively high degrees. If carbon vertices are present as CH or CR units in metallacarborane structures, they occupy vertices of relatively low degrees. However, a CpNi vertex in a nickelaborane polyhedron lies in an ambiguous position. As a transition metal moiety a CpNi moiety might be expected to occupy a vertex of relatively high degree comparable to earlier transition metal vertices. However, since a CpNi vertex is isoelectronic with a CH vertex, it might also be expected to occupy relatively low degree vertices. The tendency of CpNi moieties to occupy lower degree metallaborane vertices than similar CpM derivatives of earlier transition metals is suggested by comparison of the experimental bisdisphenoidal structures $\text{Cp}_4\text{M}_4\text{B}_4\text{H}_4$ ($\text{M} = \text{Co}$ [24], Ni [14]). Thus in $\text{Cp}_4\text{Co}_4\text{B}_4\text{H}_4$ the four cobalt atoms occupy the four degree 5 vertices of the bisdisphenoid whereas in $\text{Cp}_4\text{Ni}_4\text{B}_4\text{H}_4$ the four nickel atoms occupy the four degree 4 vertices. Similarly, in the current work we find $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ structures with both nickel atoms at degree 5 vertices to be relatively high energy structures compared with isomeric structures having both nickel atoms at degree 4 vertices or with one nickel atom at a degree 4 vertex and the other nickel atom at a degree 5 vertex. Thus for the $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ systems with $n = 8, 9, 10$, and 11 , the lowest energy structures with both nickel atoms at degree 5 vertices lie ~ 22 , ~ 9 , ~ 11 , and ~ 14 kcal/mol above the corresponding lowest energy isomers. Similarly, for the $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ system (Figure 6) the lowest energy structure with a nickel atom rather than a boron atom located at the unique degree 6 vertex of the 11-vertex *closo* deltahedron lies ~ 13 kcal/mol above the lowest energy isomer. Also in the unusual *isocloso* 9-vertex $\text{Cp}_2\text{Ni}_2\text{B}_7\text{H}_7$ structure **B7Ni2-6** (Figure 3) the unique degree 6 vertex is occupied by a boron atom with nickel atoms at two of the degree 4 vertices.

The tendency of both nickel atoms to avoid degree 5 vertices in $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ structures is not sufficient to lead to low-energy non-icosahedral structures for the 12-vertex $\text{Cp}_2\text{B}_{10}\text{H}_{10}$ system. Of the three possible icosahedral $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ structures, two have been realized experimentally. The reaction of $\text{B}_{10}\text{H}_{10}^{2-}$ with Cp_2Ni , Cp_3Ni_2^+ , or $\text{Cp}_2\text{Ni}_2(\text{CO})_2$ leads to the brown highest energy *ortho* isomer **B10Ni2-3** [12], which has been structurally characterized by X-ray crystallography [13]. This resembles the synthesis of the higher energy derivatives of *ortho* dicarbaborane, $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ rather than the lower energy *meta* and *para* isomers from the reactions of alkynes with decaborane, $\text{B}_{10}\text{H}_{14}$ [10]. Fixing the carbon atoms in adjacent positions from the $\text{C}\equiv\text{C}$ triple bond of the alkyne is apparently responsible for formation of the kinetic *ortho* $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ isomer with retention of the adjacent carbon atoms. The formation of the

kinetically favored higher energy *ortho* $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer **B10Ni2-3** with adjacent nickel atoms rather than the thermodynamically favored isomer **B10Ni2-1** with non-adjacent nickel atoms upon reactions of CpNi derivatives with $\text{B}_{10}\text{H}_{10}^{2-}$ may relate to binuclear Cp_2Ni_2 intermediates, either with an acetylene-like $\text{CpNi}\equiv\text{NiCp}$ structure or a lower energy perpendicular $\text{Ni}_2(\mu\text{-Cp})_2$ structure [25]. With either type of intermediate a strong Ni–Ni bond could fix the nickel atoms in adjacent positions to give the **B10Ni2-3** isomer of $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ as a product rather than one of the two lower energy isomers. However, the lowest energy *meta* $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer **B10Ni2-1** appears to be formed in trace quantities (~10 mg from a typical reaction) from the $\text{B}_5\text{H}_8^-/\text{C}_5\text{H}_5^-/\text{NiBr}_2$ system as a yellow solid.¹⁴ However, this $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer has been characterized only by ^{11}B NMR and mass spectrometry. However, the experimental ^{11}B NMR spectrum for *meta* $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ is close to the calculated ^{11}B NMR spectrum of **B10Ni2-1** (Table 6) thereby supporting the structural assignment.

The Ni–Ni interactions, particularly for those in the structures with adjacent nickel atoms, have been characterized by their Wiberg bond indices (WBI) as obtained by the NBO analysis [22] automatically provided by the Gaussian output. In general, the higher the degree of the nickel vertices forming the Ni–Ni edge, the longer the Ni–Ni distance and the lower the WBI values. Furthermore, larger deltahedra lead to longer Ni–Ni edges and lower WBIs for pairs of nickel vertices of equivalent degrees. Thus for the $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ structures with 8 to 10 vertices and Ni–Ni edges of length ~2.39 Å connecting a degree 4 vertex with a degree 5 vertex, the Ni–Ni edges have WBIs of ~0.21. For the 11-vertex $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structure **B9Ni2-4** the Ni–Ni edge, also between a degree 4 and degree 5 vertex, lengthens to ~2.43 Å with reduction of the corresponding WBI to 0.18. This is similar to the Ni–Ni edges connecting degree 5 vertices in the $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ structure **B8Ni2-4**, the $\text{Cp}_2\text{Ni}_2\text{B}_9\text{H}_9$ structure **B9Ni2-4**, and the $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ structure **B10Ni2-3** having edge lengths ranging from 2.41 to 2.43 Å and WBIs ranging from 0.17 to 0.19. The highest WBI and shortest Ni–Ni distance found for an edge in any of the $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ structures occurs in the only structure with the Ni–Ni edge connecting two degree 4 vertices, namely the bisdisphenoidal 8-vertex structure **B6Ni2-4** with an Ni–Ni edge length of only ~2.31 Å with a correspondingly higher WBI of 0.31. For non-adjacent indirect $\text{Ni}\cdots\text{Ni}$ interactions, particularly those involving nickel atoms in non-adjacent non-antipodal positions, the WBI values range from 0.07 to 0.11. However, for some long $\text{Ni}\cdots\text{Ni}$ antipodal or pseudoantipodal interactions such as those in **B9Ni2-5** and **B10Ni2-2** with $\text{Ni}\cdots\text{Ni}$ distances of ~4.46 and ~4.25 Å, respectively, the corresponding WBIs are much lower at 0.05 and 0.03, respectively.

5. Summary

The lowest energy structures of the dinickelaboranes $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ ($n = 8$ to 12) are the most spherical *closo* deltahedra similar to those of the isoelectronic dicarbaboranes $\text{C}_2\text{B}_{n-2}\text{H}_n$. Structures having both nickel atoms located at degree 5 vertices are of higher energy than isomeric structures having at least one nickel atom located at a degree 4 vertex. Thus nickel atoms in dinickelaboranes do not prefer higher degree vertices in contrast to metallaboranes containing earlier transition metals. Similarly $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ structures having adjacent nickel atoms are of higher energy than isomeric structures having non-adjacent nickel atoms. Thus the brown *ortho* $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer with adjacent nickel atoms obtained by Hawthorne and co-workers from $\text{B}_{10}\text{H}_{10}^{2-}$ and Cp_2Ni , $[\text{Cp}_3\text{Ni}_2][\text{BF}_4]$, or $\text{Cp}_2\text{Ni}_2(\text{CO})_2$ and structurally characterized by X-ray crystallography is not the lowest energy isomer but instead a kinetically favored product. However, the structure with non-adjacent nickel atoms suggested by ^{11}B NMR for the $\text{Cp}_2\text{Ni}_2\text{B}_8\text{H}_8$ isomer isolated in small quantities by Grimes and co-workers from a $\text{B}_5\text{H}_8^-/\text{C}_5\text{H}_5^-/\text{NiBr}_2$ reaction mixture is found to be the lowest energy isomer by ~ 6 kcal/mol. This reaction also gives small quantities of a yellow $\text{Cp}_2\text{Ni}_2\text{B}_{10}\text{H}_{10}$ isomer suggested by its ^{11}B NMR spectrum to be the lowest energy *meta* isomer with non-adjacent non-antipodal nickel atoms.

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Graphical Abstract

Polyhedral Dinickelaboranes as Analogues of the Dicarbaboranes

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Density functional theory of dinickelaboranes $\text{Cp}_2\text{Ni}_2\text{B}_{n-2}\text{H}_{n-2}$ ($n = 8$ to 12), including the experimentally known 10- and 12-vertex systems, indicates an energetic preference for the most spherical *closo* deltahedra having non-adjacent nickel atoms with one such nickel atom at a degree 4 vertex.