

# Synthesis of *closo*- and *nido*-Metalloboranes from Metallocenes

R. N. Leyden, B. P. Sullivan, R. T. Baker, and M. F. Hawthorne\*

Contribution No. 3916 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received November 2, 1977

**Abstract:** Ten- and 12-vertex *closo*- and *nido*-metalloboranes are formed by *nido*-cage closure or polyhedral expansion of *closo*-borane anions employing metallocenes as the metal vertex source. The reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}]$  with *nido*- $(\text{B}_{11}\text{H}_{13})^{2-}$ ,  $(\text{B}_{10}\text{H}_{13})^-$ , or  $(\text{B}_9\text{H}_{12})^-$  in the presence of a catalytic amount of Na/Hg amalgam in glyme yields *closo*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]^-$ , *nido*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]^-$ , and the isomeric *closo*-1- and  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$  anions, respectively. The reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}]$  with  $\text{B}_{10}\text{H}_{14}$  in glyme yields *nido*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{13}]$ , which can be reversibly deprotonated to give the *nido*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]^-$  anion. The reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]$  with *nido*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]^-$  affords the mixed bimetalloborane *closo*- $[(\eta^5\text{-C}_5\text{H}_5)_2\text{CoNi})\text{B}_{10}\text{H}_{10}]^-$ . The reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}]$  or  $[(\eta^5\text{-C}_5\text{H}_5\text{NiCO})_2]$  with *closo*- $(\text{B}_{11}\text{H}_{11})^{2-}$ ,  $(\text{B}_{10}\text{H}_{10})^{2-}$ , or  $(\text{B}_9\text{H}_9)^{2-}$  in glyme produces *closo*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]^-$ ,  $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})_2\text{B}_{10}\text{H}_{10}]$ , and isomeric 1- and  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$ , respectively. The polyhedral expansion of borane anions involves the first example of the oxidative addition of a B-B bond array of a borane to a metal complex. The reaction of  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$  with  $\text{Cl}_2$  in  $\text{CH}_3\text{CN}$  yields the perchloro analogue  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]^-$  which thermally isomerizes to  $[1-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]^-$ . The thermal and photolytic isomerization of *closo*-1- and  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$  and their perchloro analogues is also discussed.

## Introduction

Although considerable interest has been shown with regard to the synthesis and reactivity of *nido*-heteroboranes incorporating transition metals,<sup>1</sup> the synthesis of *closo*-metalloboranes has yet to be fully explored. It is well known that *closo*-carboranes,  $\text{C}_m\text{B}_n\text{H}_{m+n}$ , can be thought of as a formal replacement of  $m\{\text{BH}\}^{2+}$  vertices from the parent *closo*-borane dianions by  $m\{\text{CH}\}^{3+}$  units.<sup>2</sup> Similar vertex replacement by  $\{\eta^5\text{-C}_5\text{H}_5\text{Ni}^{\text{IV}}\}^{3+}$  (isoelectronic to  $\{\text{C-H}\}^{3+}$ )<sup>3</sup> or  $\{\eta^5\text{-C}_5\text{H}_5\text{Co}^{\text{III}}\}^{2+}$  (isoelectronic to  $\{\text{BH}\}^{2+}$ )<sup>3</sup> moieties should yield isolable *closo*-metalloborane species with stabilities reflecting those of the *closo*-carboranes<sup>2</sup> or borane dianions.<sup>4</sup>

Grimes et al.<sup>11,12</sup> have reported the preparation and characterization of two *closo*-cobaltborane species,  $[(\eta^5\text{-C}_5\text{H}_5\text{Co})_2\text{B}_4\text{H}_6]$  and  $[(\eta^5\text{-C}_5\text{H}_5\text{Co})_3\text{B}_3\text{H}_5]$ , both of which contain so-called "extra" hydrogens. We report here the first preparation and characterization of *closo*-metalloboranes containing no "extra" hydrogens.

In two preliminary communications<sup>5,6</sup> we have reported the synthesis of the icosahedral *closo*-nickelboranes  $[1,2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})_2\text{B}_{10}\text{H}_{10}]$ ,  $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]^-$  and the isomeric ten-vertex square antiprismatic species,  $[1\text{- and } [2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$ . In this paper we present the details of these results and of additional metalloboranes both *closo*- and *nido*-, synthesized by employing metallocenes as metal vertex sources.

## Results and Discussion

Two general methods have been developed for the synthesis of *nido*- and *closo*-metalloboranes. The first method is termed *nido*-cage closure. The *nido*-borane species "closes" around the metal atom of the metallocene reagent with expulsion of a cyclopentadienyl moiety. This process may occur with or without loss of molecular hydrogen or possibly by hydride transfer to the cyclopentadienyl ligand and has many precedents in metallocarborane syntheses.<sup>1</sup> The second route to *closo*-metalloboranes may be classified as polyhedral expansion of *closo*-borane anions. In this case a metallocene (i.e.,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}]$ ) reacts with a *closo*-borane anion of  $n$  vertices to give a higher homologue of  $n + 1$  or  $n + 2$  vertices. This process differs from the reductive polyhedral expansion of carboranes or metallocarboranes<sup>8,9</sup> and is the first example of the oxidative addition of a B-B bond array in a *closo*-borane to form a *closo*-metalloborane.

***closo*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]^-$  (I) from *nido*- $(\text{B}_{11}\text{H}_{13})^{2-}$  by *Nido-Cage Closure.*** Solutions of  $(\text{B}_{11}\text{H}_{13})^{2-}$  and nickelocene in acetonitrile remain unchanged indefinitely at room temperature. Addition of a catalytic amount (less than 20% of 1 equiv) of sodium amalgam quickly gives a dark brown solution with evolution of hydrogen. Removal of the acetonitrile and treatment of an aqueous solution of the product mixture with  $(\text{CH}_3)_4\text{NCl}$  yields 63% of the bright yellow I after recrystallization.

The 60-MHz  $^1\text{H}$  NMR spectrum of I consists of two sharp singlets of relative area 5:12 (Table I) which are assigned to the cyclopentadienyl and the tetramethylammonium resonances, respectively. The 80.5-MHz  $^{11}\text{B}$  NMR spectrum consists of three sharp doublets of relative area 1:5:5 (Table II). This is distinctive for a  $\text{C}_{5v}$  icosahedral structure with one heteroatom vertex. The complex I is assigned the structure depicted in Figure 1, which is consistent with these data. It is thus considered to be a formal analogue of  $(\text{CB}_{11}\text{H}_{12})^-$ .<sup>10</sup>

Upon collection of the gas evolved during the reaction it was found that slightly more than 1 mol of  $\text{H}_2$  was produced for each mol of I isolated.

This reaction is also found to proceed at elevated temperatures in a nonreactive solvent in the absence of sodium amalgam. A solution of  $(\{\text{C}_4\text{H}_9\}_4\text{N})_2(\text{B}_{11}\text{H}_{13})$  and nickelocene in 1,2-dimethoxyethane reacts at reflux temperature in several hours. A 52% yield of I as the  $(\{\text{C}_4\text{H}_9\}_4\text{N})^+$  salt is isolated and again the hydrogen gas is found to be slightly in excess of 1 mol for each mol of I isolated.

***nido*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{13}]$  (II) and *nido*- $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]^-$  (III) from  $\text{B}_{10}\text{H}_{14}$  or  $(\text{B}_{10}\text{H}_{13})^-$ .** When nickelocene is added to a solution of decaborane in 1,2-dimethoxyethane or benzene an immediate exothermic reaction ensues. If the reaction is quenched in less than 1 h a 60% yield of a neutral red-brown complex, II, can be isolated. Treatment of II with aqueous base followed by  $(\text{CH}_3)_4\text{NCl}$  results in precipitation of the anionic red complex, III. Significant amounts of  $[(\text{B}_{10}\text{H}_{12})_2\text{Ni}]^{2-}$  are isolated from the initial reaction mixture and at long reaction times this becomes the dominant product. This latter product has also been shown to arise from the interaction of simple  $\text{Ni}^{\text{II}}$  salts with either  $(\text{B}_{10}\text{H}_{13})^-$ <sup>13</sup> or  $(\text{B}_{10}\text{H}_{14})^{2-}$ .<sup>14</sup>

The 100-MHz  $^1\text{H}$  NMR spectrum of II consists of a sharp singlet assigned to the cyclopentadienyl resonance and a broad resonance centered at  $\tau$  10.5 assigned to B-H-B bridging

**Table I.**  $^1\text{H}$  NMR Chemical Shifts ( $\tau$ )<sup>a</sup>

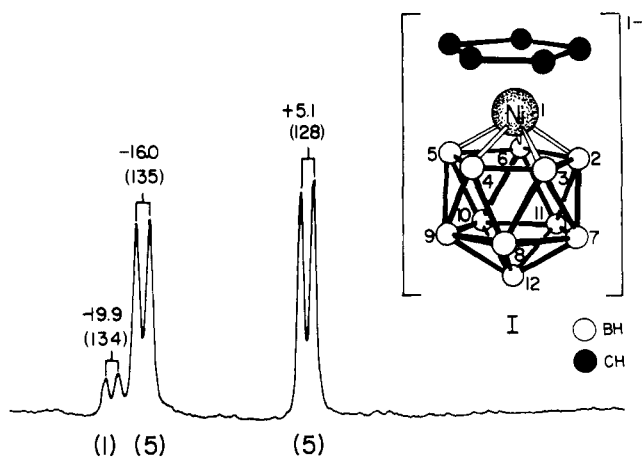
No.	Compd	Solvent	( $\text{C}_5\text{H}_5$ ) <sup>-</sup> (area)	Cation (area)
I	$\{(\text{CH}_3)_4\text{N}\}[(\text{C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]$	$\text{CD}_3\text{CN}$	4.62 (5)	6.95 (12)
II	$\{(\text{C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{13}\}$	Acetone- <i>d</i> <sub>6</sub>	4.92 (5)	<sup>b</sup>
III	$\{(\text{CH}_3)_4\text{N}\}[(\text{C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]$	$\text{CD}_3\text{CN}$	4.83 (5)	6.95 (12)
IV	$\{(\text{C}_6\text{H}_5)_4\text{As}\}[(\text{C}_5\text{H}_5)_2\text{NiCoB}_{10}\text{H}_{10}]$	$\text{CD}_3\text{CN}$	4.58 (5) 5.03 (5)	2.30 (20)
V	$\{(\text{C}_5\text{H}_5\text{Ni})_2\text{B}_{10}\text{H}_{10}\}$	Acetone- <i>d</i> <sub>6</sub>	4.54	
VI	$\{(\text{CH}_3)_4\text{N}\}[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$	$\text{CD}_3\text{CN}$	4.89 (5)	6.95 (12)
VII	$\{(\text{CH}_3)_4\text{N}\}[1-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$	$\text{CD}_3\text{CN}$	4.30 (5)	6.95 (12)
VIII	$\{(\text{CH}_3)_4\text{N}\}[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]$	$\text{CD}_3\text{CN}$	4.36 (5)	6.95 (12)
IX	$\{(\text{CH}_3)_4\text{N}\}[1-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]$	$\text{CD}_3\text{CN}$	4.40 (5)	6.95 (12)

<sup>a</sup> Taken at 100 MHz with  $\text{Me}_4\text{Si}$  internal standard. <sup>b</sup> Also  $\tau$  7.55 (~10) assigned to cage B-H,  $\tau$  8.31 (~2.5) assigned to bridge hydrogens with coincidental overlap.

**Table II.** 80.5-MHz  $^{11}\text{B}$  NMR Spectral Data for the Metalloboranes

No.	Compd	Chemical shift <sup>a</sup> (rel intensity)	Solvent
I	$\{(\text{CH}_3)_4\text{N}\}[(\text{C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]$	+19.9 (1), +16.0 (5), -5.1 (5)	$\text{CH}_3\text{CN}$
II	$\{(\text{C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{13}\}$	+10.5 (3), +4.81 (1), +5.8 (1), -6.7 (3), -26.9 (2)	$\text{CH}_3\text{CN}$
III	$\{(\text{CH}_3)_4\text{N}\}[(\text{C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]$	+11.8 (3), +6.4 (2), -6.0 (3), -25.8 (2)	$\text{CH}_3\text{CN}$
IV	$\{(\text{C}_6\text{H}_5)_4\text{As}\}[(\text{C}_5\text{H}_5)_2\text{CoNiB}_{10}\text{H}_{10}]$	+45.7 (2), +19.8 (1), +10.7 (3), +7.9 (2), -5.2 (2)	$\text{CH}_3\text{CN}$
V	$\{(\text{C}_5\text{H}_5\text{Ni})_2\text{B}_{10}\text{H}_{10}\}$	+54.3 (2), +26.1 (2), +21.3 (4), +6.7 (2)	Glyme
VI	$\{(\text{CH}_3)_4\text{N}\}[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$	+59.0 (1), +12.6 (1), +6.9 (3), -14.7 (2), -21.8 (2)	$\text{CH}_3\text{CN}$
VII	$\{(\text{CH}_3)_4\text{N}\}[1-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$	+78.6 (1), +29.0 (4), -1.3 (4)	$\text{CH}_3\text{CN}$
VIII	$\{(\text{CH}_3)_4\text{N}\}[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]$	+60.5 (1), +18.2 (1), +12.4 (3), -0.6 (2), -11.1 (2)	$\text{CH}_3\text{CN}$
IX	$\{(\text{CH}_3)_4\text{N}\}[1-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]$	+53.4 (1), +38.5 (4), +18.4 (4)	$\text{CH}_3\text{CN}$

<sup>a</sup> With  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as external standard.

**Figure 1.** The structure and  $^{11}\text{B}$  NMR spectrum of  $\{(\text{C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}\}^-$ .

protons. The 60-MHz  $^1\text{H}$  NMR spectrum of III exhibits two sharp singlets assigned to the cyclopentadienyl and tetramethylammonium resonances, respectively. The 80-MHz  $^{11}\text{B}$  NMR spectra of both II and III have a qualitatively similar appearance. The spectrum of II consists of four doublets of relative area 3:2:3:2 with the two high-field doublets partially collapsed due to multiple proton coupling. The spectrum of III also has four doublets of relative area 3:2:3:2. The chemical shifts of both compounds listed in Table II are very close to those of  $[\text{Ni}(\text{B}_{10}\text{H}_{12})_2]^{2-}$ ,<sup>13</sup> which exhibits resonances of relative area 4:1:1:2:2. All three can be interpreted as arising from a 2:2:2:2:1:1 pattern with coincidental overlap as required for an 11-atom icosahedral fragment of pseudo- $\text{C}_{5v}$  symmetry (Figure 2). The charged species, III, is formulated as *nido*- $\{(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}\}^-$ . The species II is then the corresponding protonated product, *nido*- $\{(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{13}\}$ . This formulation is supported by the fact that II can be deprotonated to III by aqueous base and III can be converted to II by treatment with concentrated aqueous HCl in ether.

**Table III.** Cyclic Voltammetric Data<sup>a</sup>

No.	Compd	$E_{1/2}$	
		Oxidn	Redn
I	$\{(\text{CH}_3)_4\text{N}\}[(\text{C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]$	+1.70 <sup>e</sup>	-1.50 <sup>c</sup>
II	$\{(\text{C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{13}\}$	+0.79 <sup>e</sup>	
III	$\{(\text{CH}_3)_4\text{N}\}[(\text{C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}]$	+0.61 <sup>d</sup>	
IV	$\{(\text{C}_6\text{H}_5)_4\text{As}\}[(\text{C}_5\text{H}_5)_2\text{NiCoNi-}\text{B}_{10}\text{H}_{10}]$	+0.45 <sup>c</sup>	-1.55 <sup>b,d</sup>
V	$\{(\text{C}_5\text{H}_5\text{Ni})_2\text{B}_{10}\text{H}_{10}\}$	+1.30 <sup>d</sup> +1.73 <sup>e</sup>	-0.27 <sup>c</sup> -1.35 <sup>c</sup>
VI	$\{(\text{CH}_3)_4\text{N}\}[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$	+0.87 <sup>e</sup>	-1.42
VII	$\{(\text{CH}_3)_4\text{N}\}[1-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$	+0.77 <sup>e</sup>	-1.52
VIII	$\{(\text{CH}_3)_4\text{N}\}[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]$		-0.40 <sup>c</sup>
IX	$\{(\text{CH}_3)_4\text{N}\}[1-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]$		-0.35 <sup>c</sup>

<sup>a</sup> Determined in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte, platinum button electrode. Potentials vs. SCE. <sup>b</sup> Hanging mercury drop electrode. <sup>c</sup> Reversible. <sup>d</sup> Quasi-reversible. <sup>e</sup> Irreversible.

The species III is made in slightly lower yield by treatment of nickelocene with *nido*- $(\text{B}_{10}\text{H}_{13})^-$ . Again prolonged reaction times lead to  $[(\text{B}_{10}\text{H}_{12})_2\text{Ni}]^{2-}$ . This is analogous to the synthesis reported by Muetterties<sup>13</sup> (vide supra). Reductive or basic conditions promote the rapid conversion of III to the bis complex.

The cesium salt of III appears to be completely stable to 180 °C under high vacuum. Pyrolysis of III for 1 h at 230 °C results in loss of a small amount of hydrogen but the residue is a mixture of insoluble materials and unreacted III. Aqueous solutions of III do not immediately react with  $\text{H}_2\text{O}_2$  despite the quasi-reversible oxidation wave at +0.16 V (vs. SCE) seen in the cyclic voltammogram (Table III).

***closo*- $\{(\eta^5\text{-C}_5\text{H}_5)_2\text{CoNi}\}\text{B}_{10}\text{H}_{10}\}^-$  (IV) from *nido*- $\{(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{10}\text{H}_{12}\}$  (III).** Treatment of a solution of cobaltocene and III in 1,2-dimethoxyethane with sodium amalgam results in a mixture from which the green anionic complex, IV, can be isolated as the tetraphenylarsonium salt in 2% yield. An

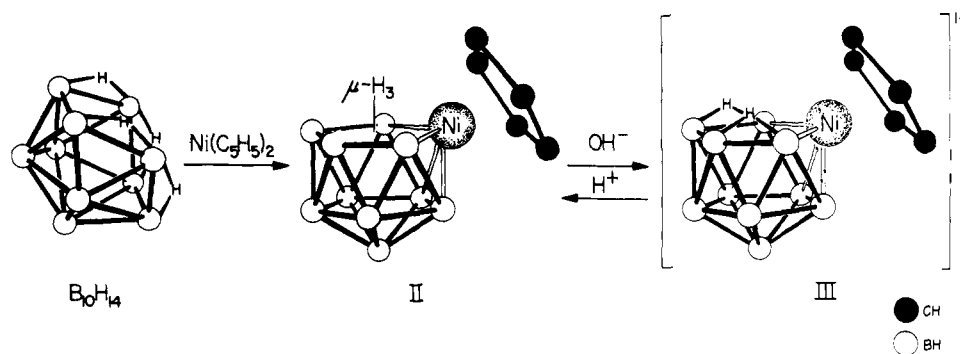


Figure 2. Proposed structure of  $[(C_5H_5Ni)B_{10}H_{13}]$  and  $[(C_5H_5Ni)B_{10}H_{12}]^-$  and their acid-base chemistry.

Table IV. Elemental Analyses for the Metalloboranes

Compd		% C	% H	% As	% B <sup>a</sup>	% Cl	% Co	% N	% Ni <sup>a</sup>
I	Calcd	32.96	8.61		36.26			4.27	17.90
	Found	33.15	8.58		35.90			4.27	17.52
II	Calcd	24.51	7.41		44.12				23.96
	Found	24.40	7.22		43.93				23.11
III	Calcd	33.98	9.19		33.98			4.40	18.45
	Found	34.16	9.25		33.96			4.39	18.48
IV	Calcd	54.50	5.38	10.00	14.40		7.86		7.83
	Found	54.46	5.22	10.15	14.20		7.57		7.89
V	Calcd	32.83	5.52		29.55				32.10
	Found	32.62	5.44		29.88				31.48
VI	Calcd	35.52	8.61						
	Found	35.38	8.51						
VII	Calcd	35.52	8.61		31.97			4.60	19.29
	Found	35.72	8.96		29.12			4.70	18.09
IX	Calcd	17.60	2.79		15.84	51.93			
	Found	17.60	2.75		15.40	51.50			

<sup>a</sup> Elemental analyses of the nickelaboranes were consistently found to have low percentages for boron and nickel presumably owing to the formation of nickel borides during combustion.

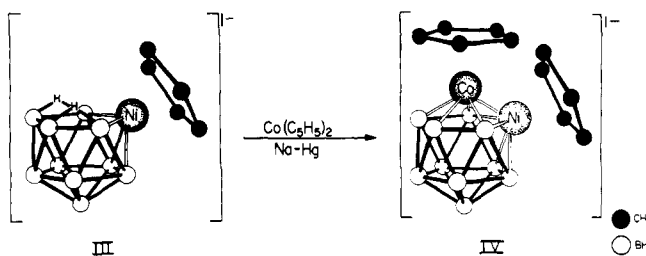


Figure 3. Synthesis and structure of  $[(C_5H_5)_2CoNiB_{10}H_{10}]^-$ .

alternate method involving addition of III to a mixture of  $CoCl_2$ ,  $NaC_5H_5$ , and excess  $NaH$  produces IV in 10% yield.

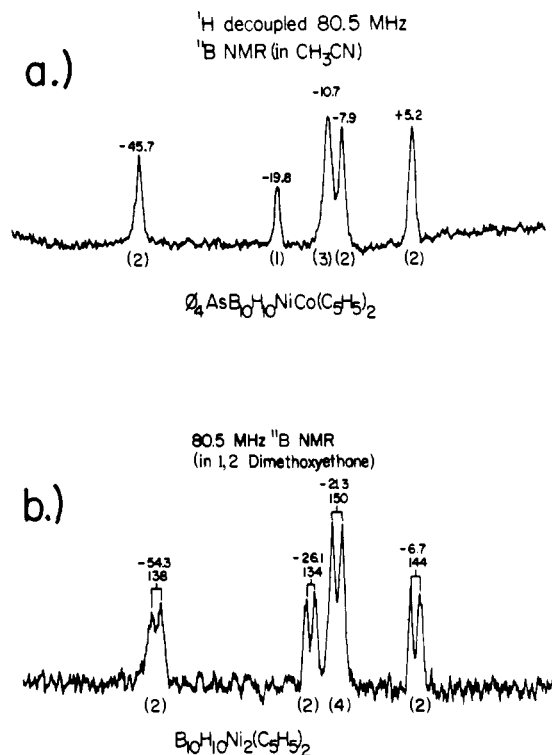
The  $^1H$  NMR spectrum of IV exhibits a broad singlet due to the tetraphenylarsonium cation and two cyclopentadienyl resonances of relative intensities 20:5:5. The  $^{11}B$  NMR spectrum consists of five doublets of relative intensities 2:1:3:2:2. The elemental analysis is consistent with the formulation  $(\{C_6H_5\}_4As)(\{\eta^5-C_5H_5\}_2CoNi)B_{10}H_{10}$  (Table IV). Based upon these data the gross structure of IV is assigned as icosahedral with a formal cyclopentadienyl  $Ni^{IV}$  moiety adjacent to a formal cyclopentadienyl  $Co^{III}$  (see Figure 3). Thus the borane fragment of IV is formally the *arachno*-( $B_{10}H_{10}$ )<sup>6-</sup> ligand and the entire complex is isoelectronic with the previously reported  $[1,2-(\eta^5-C_5H_5Ni)_2B_{10}H_{10}]$  (vide infra). The similarities of these bimetallic species are apparent upon examination of their  $^{11}B$  NMR spectra (Figure 4). The  $^{11}B$  chemical shift positions and overall appearances are similar, the main difference being symmetry lowering in the Co-Ni species.

The sodium salt of IV is quite stable in neutral or slightly basic aqueous solutions. Acidic pH conditions cause decomposition with the deposition of a white solid. Strongly reducing solutions also appear to promote decomposition. This observation may explain the low yield of this compound.

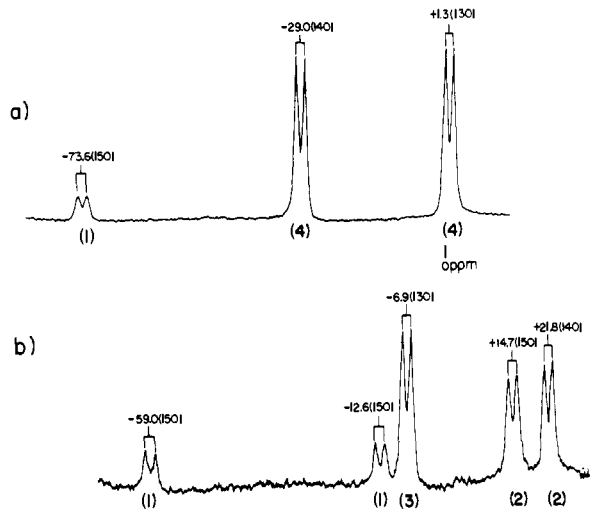
***closo*-[2-( $\eta^5-C_5H_5Ni$ ) $B_9H_9$ ]<sup>-</sup> (VI) and [1-( $\eta^5-C_5H_5Ni$ ) $B_9H_9$ ]<sup>-</sup> (VII) from (*nido*- $B_9H_{12}$ )<sup>-</sup>.** Treatment of a solution of  $(\{CH_3\}_4N)(B_9H_{12})$  and nickelocene in acetonitrile with 1 equiv of sodium amalgam produces a rapid color change from dark green to dark red with noticeable evolution of gas. The red and yellow anionic complexes, VI and VII, can be isolated as  $(\{CH_3\}_4N)^+$  salts by column chromatography on alumina in 18 and 7% yields, respectively. The yield of VII is increased at the expense of VI if care is not taken to minimize the exposure of solutions to heat, light, and acidic conditions. The 80-MHz  $^{11}B$  NMR spectrum of VI exhibits five doublets of relative area 1:1:3:2:2 and the spectrum of VII consists of three doublets of relative area 1:4:4. The  $^1H$  NMR spectrum of both compounds consists of two singlets of relative area 5:12 due to the cyclopentadienyl and the tetramethylammonium resonances, respectively.

The 1:1:3:2:2 pattern of doublets which is observed for compound VI in its  $^{11}B$  spectrum is consistent with a bicapped Archimedean square antiprism with the  $\{C_5H_5Ni\}$  moiety in the equatorial position if there is coincidental overlap of a doublet of area one with a doublet of area two. The 1:4:4 pattern of doublets observed for compound VII is unique for the highly symmetrical bicapped square antiprism with the nickel atom in the apical position (Figures 5 and 6).

The  $^{11}B$  chemical shift of the apical boron atom in VII appears at very low field ( $\sim 74$  ppm). This is another example of



**Figure 4.** <sup>11</sup>B NMR spectra of the icosahedral bimetallocoarboranes: (a)  $(\text{C}_6\text{H}_5)_4\text{As}[(\text{C}_5\text{H}_5)_2\text{CoNiB}_{10}\text{H}_{10}]$ ; (b)  $(\text{C}_5\text{H}_5\text{Ni})_2\text{B}_{10}\text{H}_{10}$ .



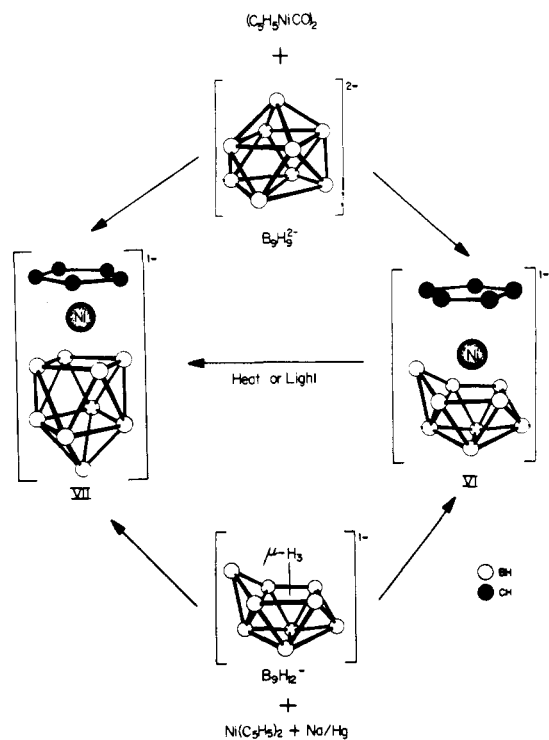
**Figure 5.** <sup>11</sup>B NMR spectra of  $[(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^{2-}$ : (a) the 1 isomer; (b) the 2 isomer.

the “antipodal effect”, i.e., low-field shifts (relative to other shifts occurring in that cluster) which occur at the boron atom placed symmetrically across from a heteroatom.<sup>15,16,17</sup>

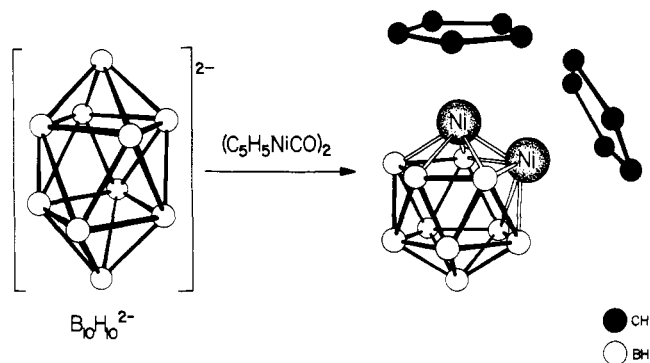
#### Formation of Metalloboranes through Nido-Cage Closure.

The reaction of nickelocene with  $(\text{B}_{11}\text{H}_{13})^{2-}$  or  $(\text{B}_9\text{H}_{12})^-$  appears to depend more upon the electronic properties of the metallocene<sup>18</sup> rather than the nature of the borane. Under the conditions used in the nickelocene reactions both cobaltocene and ferrocene fail to produce the corresponding *closo*-metalloboranes. This result may be due to the decreased lability of the cyclopentadienyl ligand (going from Ni → Co → Fe)<sup>19,20</sup> or the decreased stability of the expected *closo*-metalloboranes (i.e.,  $[(\eta^5\text{-C}_5\text{H}_5\text{Co})\text{B}_{11}\text{H}_{11}]^{2-}$  or  $[(\eta^5\text{-C}_5\text{H}_5\text{Fe})\text{B}_{11}\text{H}_{11}]^{3-}$ ).<sup>21</sup>

**Polyhedral Expansion of Borane Anions.**  $[(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_{11}\text{H}_{11}]^-$  from  $(\text{B}_{11}\text{H}_{11})^{2-}$ . Heating a solution of the *closo*-



**Figure 6.** Synthesis and structure of  $[(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^{2-}$  isomers.



**Figure 7.** Formation of  $[(\text{C}_5\text{H}_5\text{Ni})_2\text{B}_{10}\text{H}_{10}]$  via polyhedral expansion of  $(\text{B}_{10}\text{H}_{10})^{2-}$ .

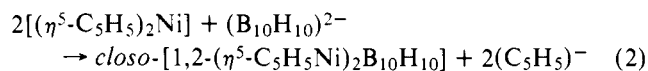
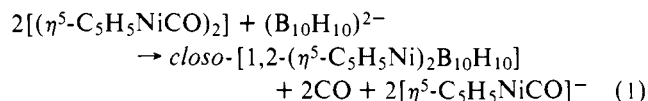
borane anion,  $(\text{B}_{11}\text{H}_{11})^{2-}$ , as the tetrabutylammonium salt, and  $[(\eta^5\text{-C}_5\text{H}_5\text{NiCO})_2]$  in tetrahydrofuran for several hours gives a mixture from which I (as the tetrabutylammonium salt) can be isolated in 23% yield by chromatography. I is also formed in good yield by heating  $[(\text{C}_4\text{H}_9)_4\text{N}]_2(\text{B}_{11}\text{H}_{11})$  with nickelocene in 1,2-dimethoxyethane. The very reactive nickel reagent<sup>22</sup>  $[(\text{C}_5\text{H}_5)_3\text{Ni}_2](\text{BF}_4)$  reacts immediately with  $(\text{B}_{11}\text{H}_{11})^{2-}$  in tetrahydrofuran. The resulting mixture of products in this case is quite complex and I is produced in only low yields (ca. 5%), thus making the former two methods preparatively more suitable.

***closo*-[1,2-( $\eta^5\text{-C}_5\text{H}_5\text{Ni}$ )<sub>2</sub>B<sub>10</sub>H<sub>10</sub>]** (V) from *closo*- $(\text{B}_{10}\text{H}_{10})^{2-}$ . The reaction between *closo*- $(\text{B}_{10}\text{H}_{10})^{2-}$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}]$  or  $[(\eta^5\text{-C}_5\text{H}_5\text{NiCO})_2]$  in 1,2-dimethoxyethane at 25 °C rapidly produces a dark brown solution and a golden brown precipitate, V. Optimum reaction conditions are achieved with the tetraethyl- or tetrabutylammonium salts for solubility reasons.

The <sup>11</sup>B NMR spectrum obtained with this species reveals a 1:1:2:1 pattern. This is the expected symmetry splitting of either an octadecahedron with a cyclopentadienyl nickel moiety occupying the seven-coordinate vertex or a bimetallic nickel analogue of *o*- or *m*-carborane (Figure 7). Mass spectral

data show a parent peak with a cutoff at  $m/e$  363<sup>23</sup> and elemental analysis reveals a Ni:B ratio of 1:5. The structural assignment was thus definitive for a bimetallic analogue of *o*- or *m*-carborane, [1,2-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni)<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (or meta-1,7). The <sup>1</sup>H NMR spectrum shows only one cyclopentadienyl resonance which is also consistent with the structural assignment. Support for the ortho structural assignment<sup>24</sup> for V comes from the similarity between the <sup>11</sup>B spectra of IV and V.

The direct formation of product without an oxidation step and the use of a 2:1 nickel reagent to (B<sub>10</sub>H<sub>10</sub>)<sup>2-</sup> ratio (with yields based on nickel of greater than 50%) substantiate the reaction stoichiometry shown in eq 1 and 2.



Despite variations in the experimental procedure, no evidence could be found for the monometallic intermediate. This is not too surprising considering that the cyclopentadienyl-nickel(IV) moiety prefers low-coordinate vertex positions<sup>26</sup> and that the cage opening reaction is probably initiated by the { $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni} vertex environment. Thus the monometallic octadecahedron might be expected to be an unstable species or reactive intermediate relative to the bimetallic icosahedral product.

**Polyhedral Expansion of (B<sub>9</sub>H<sub>9</sub>)<sup>2-</sup>. Isomers of *closo*-[( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>]<sup>-</sup> from *closo*-(B<sub>9</sub>H<sub>9</sub>)<sup>2-</sup>.** The reaction of [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>NiCO)<sub>2</sub>] with Cs<sub>2</sub>B<sub>9</sub>H<sub>9</sub> in acetonitrile solution at room temperature gives both [1- and [2-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>]<sup>-</sup>, VII and VI (vide infra), and did not proceed to form the bimetallic octadecahedron. This is generally consistent with the high stability of the ten particle square antiprism and the aversion of cyclopentadienylnickel(IV) moiety for very high coordinate positions on the polyhedral surface.<sup>26</sup>

**Formation of *closo*-Metalloboranes via Polyhedral Expansion of *closo*-Borane Anions.** The first polyhedral expansion reactions of carboranes required an initial two-electron reduction of the polyhedron. Numerous examples of the reductive polyhedral expansion of carboranes and heteroatom carboranes<sup>27</sup> have now established the generality of this method. Recently, Stone and co-workers have demonstrated that low-valent platinum reagents are capable of direct insertion into *closo*-carborane cages, thereby by-passing an explicit reduction step.<sup>28,29</sup> Grimes et al. have successfully effected at higher temperatures direct insertion of [Fe(CO)<sub>5</sub>] and [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub>].<sup>30</sup> Both of these processes bear a formal similarity to the oxidative-addition reaction. Attempts to extend this oxidative-addition reaction to the borane anions using [*cis*-(PPh<sub>3</sub>)<sub>2</sub>PtCl<sub>2</sub>] in alcoholic chloroform resulted in the production of an ethoxy-substituted *nido*-platinaborane (Pt<sup>II</sup>) instead of the desired *closo* product (Pt<sup>IV</sup>).<sup>31</sup>

The reaction of nickelocene with the *closo*-borane anions appears, then, to be the first example of the oxidative addition of a boron-boron bond array in a *closo*-boron hydride. The nucleophilic nickelocene molecule (a formally 20-electron complex possessing two unpaired electrons) can be conceptually thought of as donating two electrons to effect the cage opening, followed by cyclopentadienyl ligand loss and oxidative addition of the borane moiety to yield the *closo*-nickelaborane (Ni<sup>IV</sup>).

**Chemistry of the Polyhedral Metalloboranes.** Compounds I-IX are all air and water stable. With the exception of VI and VIII, which isomerize to VII and IX, respectively, they also exhibit high thermal stability. The neutral bimetallic V can be heated to 350 °C and subsequently sublimed at 265 °C in vacuo over a period of hours with only partial decomposition.

These compounds parallel the chemistry and possess the stability of their parent *closo*-boranes. The *nido*-metalloborane; [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni)B<sub>10</sub>H<sub>12</sub>]<sup>-</sup>, appears to be even more hydrolytically stable than its borane analogue (B<sub>11</sub>H<sub>13</sub>)<sup>2-</sup>.

Compound I comes closest to having the stability of its parent, (B<sub>12</sub>H<sub>12</sub>)<sup>2-</sup>, or its monocarbon analogue (CB<sub>11</sub>H<sub>12</sub>)<sup>-</sup>. As an example, the nickel complex can conveniently be separated from less stable impurities by treatment with an aqueous solution of H<sub>2</sub>O<sub>2</sub> which oxidizes the impurities to borate and nickel oxide. Attempts to perform a polyhedral contraction reaction by heating I in ethylene glycol/H<sub>2</sub>O/EtOH-KOH for several days resulted in the recovery of unreacted I. The hydronium salt of I was prepared by passing a solution of the tetramethylammonium salt through a hydrogen-form cation exchange column. This salt is a strong acid and remains unchanged on removal of solvent at room temperature. Heating the residue under vacuum, however, results in decomposition at less than 100 °C.

Treatment of I with DCl in acetonitrile/D<sub>2</sub>O at room temperature over several days results in partial deuteration of the polyhedral boron atoms as evidenced by the infrared spectrum. The <sup>11</sup>B NMR spectrum exhibited a partial collapse of the low-field area one doublet and the highest field area five doublet while the remaining doublet was unchanged.

Exhaustive chlorination of I produces a mixture of species which are only partially chlorinated. Reaction of I with ICl at 0 °C in acetonitrile produced the monoiodinated derivative. The <sup>11</sup>B NMR spectrum indicated that the product was a mixture of isomers and the <sup>1</sup>H NMR spectrum consisted of three closely spaced cyclopentadienyl resonances in the ratio 5:3:1. This suggests a statistical distribution of isomers.

Compound VI can be successfully perchlorinated by treatment with Cl<sub>2</sub> in acetonitrile to yield the bright green [2-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>Cl<sub>9</sub>]<sup>-</sup> (VIII). Compound VIII exhibits five singlets in the <sup>11</sup>B NMR spectrum of relative areas 1:1:3:2:2. While the chemical shifts are slightly different, the splitting pattern is very similar to that of VI. Attempts to chlorinate VII with Cl<sub>2</sub> resulted in a bright red, polar compound which could not be purified in the usual manner by chromatography. However, the deep yellow [1-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>Cl<sub>9</sub>]<sup>-</sup> (IX) is obtained by heating VIII for several minutes at 130 °C.

The mixed metal bimetallic, IV, is the least stable of the *closo*-metalloboranes. As an example, deuteration studies under acidic conditions were impossible to conduct owing to the instability of IV under acidic conditions.

**Isomerization of Ten-Vertex Nickeloboranes.** In a sealed tube, an acetonitrile solution of VI completely isomerizes to VII after several hours at 130 °C. However, in 0.1 M trifluoroacetic acid in 90% CH<sub>3</sub>CN/10% H<sub>2</sub>O in a sealed evacuated tube, the isomerization is essentially complete in much less than 1 h at 80 °C. The isomerization reaction therefore appears to be acid catalyzed. The isomerization of the perchloro species VIII to IX appears to proceed much more rapidly, showing only IX in the <sup>11</sup>B NMR spectrum after several minutes at 130 °C. The isomerization of VIII is relatively insensitive to acid.

The isomerization of the {C<sub>5</sub>H<sub>5</sub>Ni} moiety from the equatorial position in VI to the apical position in VII can also be achieved photochemically. This is the first reported polyhedral photochemistry of a pure metalloborane species.<sup>32</sup> Irradiation from a low-pressure Hg lamp through Pyrex cleanly converted VI to VII in acetonitrile solution while prolonged irradiation of VII caused no change.

Photolysis of IX reversed the thermal isomerization to produce a mixture of VIII and IX on irradiation with a tungsten iodide lamp. The isomerization was so sensitive to light that purification of VIII was complicated by exposure to normal room light. Irradiation of the green complex VIII also produced a mixture of VIII and IX.

Table V. Infrared Spectra for the Metalloboranes<sup>a</sup>

No.	Compd	Absorptions, cm <sup>-1</sup> (intensity) <sup>b</sup>
I	{(CH <sub>3</sub> ) <sub>4</sub> N}[C <sub>5</sub> H <sub>5</sub> Ni-B <sub>11</sub> H <sub>11</sub> ]	2490 (s), 1020 (s), 950 (s), 910 (M (= -29 (m), 728 (m))
II	[η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> NiB <sub>10</sub> H <sub>13</sub> ]	2515 (s), 1415 (m), 1175 (m), 1000 (m) 990 (s), 880 (m), 840 (w), 745 (m)
III	{(CH <sub>3</sub> ) <sub>4</sub> N}[C <sub>5</sub> H <sub>5</sub> Ni-B <sub>10</sub> H <sub>12</sub> ]	2490 (s), 1180 (m), 1040 (m), 995 (s), 950 (s), 885 (m), 843 (w), 827 (m), 742 (m), 725 (m)
IV	{(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As}[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co-NiB <sub>10</sub> H <sub>10</sub> ]	2490 (s), 1600 (m), 1080 (s), 1000 (m), 820 (m), 740 (s), 690 (m)
V	[1,2-(C <sub>5</sub> H <sub>5</sub> Ni) <sub>2</sub> B <sub>10</sub> H <sub>10</sub> ]	2500 (s), 1408 (m), 1015 (s), 905 (m), 890 (m), 850 (s), 840 (s), 745 (m)
VI	{(CH <sub>3</sub> ) <sub>4</sub> N}[2-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> H <sub>9</sub> ]	2490 (s), 1360 (w), 1290 (w), 1230 (w), 1050 (m), 1020 (m), 970 (m), 950 (s), 905 (s), 820 (s), 790 (m)
VII	{(CH <sub>3</sub> ) <sub>4</sub> N}[1-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> H <sub>9</sub> ]	2500 (s), 1170 (w), 1020 (w), 980 (m), 950 (s), 910 (s), 825 (s), 730 (s)
VIII	{(CH <sub>3</sub> ) <sub>4</sub> N}[2-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> Cl <sub>9</sub> ]	1140 (s), 1050 (s), 950 (s), 883 (m), 841 (m), 833 (m), 786 (s), 700 (s)
IX	{(CH <sub>3</sub> ) <sub>4</sub> N}[1-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> Cl <sub>9</sub> ]	1720 (w), 1240 (w), 1190 (w), 1110 (m), 1090 (m), 1020 (m), 1000 (s), 895 (s), 848 (w), 828 (m), 740 (s)

<sup>a</sup> Taken in Nujol mull. <sup>b</sup> s = strong, m = medium, w = weak.

This observation has no known counterpart in boron chemistry; although thermally reversible photochemical isomerizations have been reported,<sup>32,33</sup> the steady state ratio of isomers always favors one isomer exclusively. In the B<sub>9</sub> nickelaboranes a 1:2 equatorial/apical mixture is observed and is accessible photochemically from either isomer. We intend to study this photochemical rearrangement in some detail.

**Infrared and Electronic Spectral Data.** The infrared spectra (Table V) of all the complexes described above exhibited bands in the region 2500–2600 cm<sup>-1</sup> due to terminal B–H stretching vibrations. The spectra of complexes I–IX also contained a band of medium intensity in the region 810–840 cm<sup>-1</sup> assigned to the (C<sub>5</sub>H<sub>5</sub>)<sup>-</sup> ligand. In addition, the spectra of complexes I, III, and VI–IX contained a band at 950 cm<sup>-1</sup> due to the {(CH<sub>3</sub>)<sub>4</sub>N}<sup>+</sup> cation. We were unable to detect bands in the region 1600–1900 cm<sup>-1</sup> in the spectra of II and III which might be assigned to BHB bridge groups. This is not unusual, however, as bands of this type are usually very weak.<sup>45</sup>

The electronic spectral data (Table VI) were generally of little use in providing structural information and no attempt was made to assign the bands to individual electronic transitions. The electronic spectra did, however, prove to be a convenient means of monitoring the thermal isomerization of VI → VII and VIII → IX.

**Electrochemistry of the Metalloboranes.** The values of the oxidation and reduction potentials for the *closo*-metalloboranes are listed in Table III. The qualitative features of the cyclic voltammograms for each of the *closo* compounds are very similar. The reduction waves are all one-electron reversible reductions and the oxidations are all irreversible for the nickelaboranes. The bimetallic compound, V, exhibits two one-electron reductions which is consistent with the observations for bimetallic metallocarboranes.<sup>34</sup> The cobalt–nickel compound in addition exhibits a quasi-reversible oxidation wave which can be assigned to the formal Co<sup>III</sup>–Co<sup>IV</sup> couple.

Table VI. Electronic Spectra (Acetonitrile Solution)

No.	Compd	λ <sub>max</sub> , nm (log ε)
I	{(CH <sub>3</sub> ) <sub>4</sub> N}[(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>11</sub> H <sub>11</sub> ]	271 (4.72)
III	{(CH <sub>3</sub> ) <sub>4</sub> N}[(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>10</sub> H <sub>12</sub> ]	520 sh (1.62), 365 (3.20), 290 (4.33), 266 sh (4.28)
IV	{(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> As}[(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Co-B <sub>10</sub> H <sub>10</sub> ]	308 (4.42), 270 (4.08), 262 (4.11), 240 (4.36)
VI	{(CH <sub>3</sub> ) <sub>4</sub> N}[2-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> H <sub>9</sub> ]	518 (2.69), 329 (3.72), 263 (4.36)
VII	{(CH <sub>3</sub> ) <sub>4</sub> N}[1-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> H <sub>9</sub> ]	349 sh (3.18), 283 (4.73)
VIII	{(CH <sub>3</sub> ) <sub>4</sub> N}[2-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> Cl <sub>9</sub> ]	664 (2.77), 438 (3.41), 355 (4.15), 312 (4.15), 269 (4.02)
IX	{(CH <sub>3</sub> ) <sub>4</sub> N}[1-(C <sub>5</sub> H <sub>5</sub> Ni)-B <sub>9</sub> Cl <sub>9</sub> ]	415 (3.19), 329 (4.59), 258 (3.98), 213 (3.86)

By analogy with the Ni<sup>IV</sup> carborane compounds<sup>25,35</sup> the first reduction wave seen in the cyclic voltammograms for the *closo*-nickelboranes can be assigned to the Ni<sup>IV</sup>–Ni<sup>III</sup> couple. The reduction potential for [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>11</sub>H<sub>11</sub>]<sup>-</sup> is very close to that of the icosahedral monocarbon carborane nickel complex, [1,2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)CB<sub>10</sub>H<sub>11</sub>] (-1.57 V).<sup>25</sup> The icosahedral binickelborane, V, also has a cyclic voltammogram that bears a resemblance to [1,2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)CB<sub>10</sub>H<sub>11</sub>] and suggests the formal similarity of a cyclopentadienylnickel(IV) moiety to a {CH<sub>3</sub>}<sup>3+</sup> group on the icosahedral surface.<sup>25</sup>

Chlorination of the ten-vertex nickel complex shifted the reduction potential by more than 1 V, thus making the nickel atom much more easily reduced. Adding the electron-withdrawing chlorine substituents onto the cage would be expected to decrease the donor ability of the borane ligand thus decreasing the effective electron density around the nickel atom.

The *nido*-metalloborane, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>10</sub>H<sub>12</sub>]<sup>-</sup>, exhibits only a single quasi-reversible oxidation wave at 0.61 V. This may be due to the formal Ni<sup>II</sup>–Ni<sup>III</sup> couple.

## Experimental Section

**Physical Measurements.** The 60-MHz <sup>1</sup>H NMR spectra were obtained using the T-60 Varian instrument, and the 80.5-MHz <sup>11</sup>B spectra were recorded using the cryogenic spectrometer designed by Professor F. A. L. Anet and Dr. C. H. Bradley. Infrared spectra were determined using a Perkin-Elmer Model 137 spectrometer (Table V). Electronic spectra were obtained on the Cary 15 and Beckman Model DB spectrometers (Table VI). Cyclic voltammetry was performed using an instrument based on the design by Hawley.<sup>36</sup> Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Galbraith Laboratories, and the UCLA microanalysts.

**Materials and Procedures.** Unless otherwise stated, reactions were performed in a nitrogen atmosphere using reagent grade solvents which had been previously saturated with nitrogen. Workup was carried out in the presence of oxygen, however, since many *nido* species formed as intermediates undergo relatively easy oxidative closure to a desired *closo* product.<sup>37</sup> Nickelocene,<sup>38</sup> cobaltocene,<sup>38</sup> and salts of *closo*-(B<sub>11</sub>H<sub>11</sub>)<sup>2-</sup>,<sup>39</sup> -(B<sub>10</sub>H<sub>10</sub>)<sup>2-</sup>,<sup>40</sup> and -(B<sub>9</sub>H<sub>9</sub>)<sup>2-</sup>,<sup>41,42</sup> *nido*-(B<sub>9</sub>H<sub>12</sub>)<sup>-</sup>,<sup>43</sup> and (B<sub>11</sub>H<sub>13</sub>)<sup>2-</sup><sup>39</sup> were prepared by published procedures. Cyclopentadienylnickel carbonyl dimer was used as received from Alfa-Ventron Corp. Decaborane was obtained from commercial sources and sublimed at 80 °C under high vacuum. All solvents were distilled under N<sub>2</sub> from an appropriate drying agent as described by Jolly.<sup>44</sup>

{(CH<sub>3</sub>)<sub>4</sub>N}[η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>11</sub>H<sub>11</sub>] (I) from (B<sub>11</sub>H<sub>13</sub>)<sup>2-</sup>. Sodium amalgam (1 g, 0.48%, 2.1 mequiv) was added to 2.0 g (11 mmol) of Na<sub>2</sub>B<sub>11</sub>H<sub>13</sub> and 2.1 g (11 mmol) of nickelocene in 200 mL of acetonitrile. The mixture was stirred for 12 h, the solvent was removed under reduced pressure, and 150 mL of water was added. The solution was carefully treated with H<sub>2</sub>O<sub>2</sub> until the vigorous reaction had ceased. The solution was filtered through Celite and excess tetramethylammonium chloride was added. The dark yellow precipitate

was isolated by filtration and recrystallized from acetone/water to give 2.4 g (63%) of bright yellow needles of I. Similar yields were obtained without the addition of H<sub>2</sub>O<sub>2</sub> but required more lengthy purification.

**I from (B<sub>11</sub>H<sub>11</sub>)<sup>2-</sup>.** A solution of ((C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N)<sub>2</sub>(B<sub>11</sub>H<sub>11</sub>) (0.3 g, 0.5 mmol) and nickelocene (0.1 g, 0.5 mmol) in 1,2-dimethoxyethane was refluxed for 2 h to give a yellow solution. The product was deposited on alumina by removal of the solvent under reduced pressure and added to the top of a previously prepared 30 × 300 mm alumina chromatography column. Eluting with dichloromethane produced a yellow fraction which was identified as the tetrabutylammonium salt of I by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy. This fraction could be recrystallized with difficulty by addition of a small amount of ((C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N)Cl to a solution in acetone/EtOH/H<sub>2</sub>O and slowly removing the solvent under reduced pressure to yield 0.12 g (50%) of ((C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N)((η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>11</sub>H<sub>11</sub>).

**[(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>10</sub>H<sub>13</sub>] (II) from B<sub>10</sub>H<sub>14</sub>.** Nickelocene (1.9 g, 10 mmol) was added to a solution of decaborane (1.2 g, 10 mmol) in 1,2-dimethoxyethane. An immediate reaction ensued with evolution of gas. (If the solvent is slightly wet, gentle heating may be required to initiate the reaction.) After 30 min the volume was reduced on a rotary evaporator and the solution filtered in the air, yielding a crude, brown product. The red-brown II was obtained by recrystallization from benzene, 1.5 g (60%). Further purification was achieved by chromatography on Florisil with hexane/acetone as eluent. The species III was obtained by treating an acetone solution of II with basic aqueous tetramethylammonium chloride.

**[(CH<sub>3</sub>)<sub>4</sub>N][(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>10</sub>H<sub>12</sub>] (III) from (B<sub>10</sub>H<sub>13</sub>)<sup>-</sup>.** Treatment of 4.0 g (32 mmol) of decaborane with 1.7 g of NaH (50% in oil) in 150 mL of 1,2-dimethoxyethane resulted in the formation of NaB<sub>10</sub>H<sub>13</sub>. Addition of 7.0 g (37 mmol) of nickelocene and 20 g of 0.5% sodium amalgam resulted in gas evolution and change of the solution color from green to dark red. The solution was stirred for 45 min and the solvent was removed under reduced pressure. The residue was carefully treated with ice water and filtered through Celite when the foaming subsided. Addition of tetramethylammonium chloride produced a precipitate which was isolated by filtration. The solid was thoroughly extracted with acetone leaving behind the partially soluble ((CH<sub>3</sub>)<sub>4</sub>N)<sub>2</sub>[Ni(B<sub>10</sub>H<sub>12</sub>)<sub>2</sub>]. Addition of ethanol to the acetone solution followed by slow removal of the solvent on a rotary evaporator produced 4.5 g (44% based on B<sub>10</sub>H<sub>14</sub>) of dark red crystals of III after drying under high vacuum.

**[(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As][(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>CoNi)B<sub>10</sub>H<sub>10</sub>] (IV) from [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>10</sub>H<sub>12</sub>]<sup>-</sup> (III).** A solution of NaC<sub>5</sub>H<sub>5</sub> was prepared by the addition of 6 g of NaH (50% in oil) to 5 mL of freshly distilled cyclopentadiene in 100 mL of 1,2-dimethoxyethane. To this were added 3 g of CoCl<sub>2</sub> and 1 g of III and the solution was stirred for 12 h at room temperature. A stream of air was bubbled through the solution for 10 min and the solution filtered through Celite (caution: unreacted NaH may ignite if the filter cake is allowed to dry). The residue was washed once with acetonitrile and the mixture deposited on alumina by removal of the solvent under reduced pressure. The solids were placed on the top of a previously prepared alumina chromatography column. Eluting with dichloromethane gradually enriched with acetonitrile resulted in a red fraction containing a small amount of II and a bright green fraction. The green fraction was further purified by preparative thick layer chromatography on silica gel, then precipitated from an acetone/water solution with tetraphenylarsonium chloride. Recrystallization from ethanol/acetone and drying under high vacuum resulted in 0.25 g (10%) of bright green needles of IV.

**[1,2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)<sub>2</sub>B<sub>10</sub>H<sub>10</sub>] (V). A. From Cyclopentadienylnickel Carbonyl Dimer.** [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>NiCO)<sub>2</sub>] (304 mg, 1 mmol) and K<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (200 mg, 1 mmol) were stirred together in 50 mL of dry 1,2-dimethoxyethane at ambient temperature for 24 h. The solvent was then removed with a water aspirator. The dark brown, sticky residue was then slurried with 200 mL of 50:50 CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> and 20 g of Florisil. This mixture was slowly spun dry, scraped from the wall of the round-bottom flask, and dried at reduced pressure. The Florisil was then mounted on a 25 × 200 mm column of Florisil and eluted progressively with 50–60 °C, 40–45 °C, and boiling CH<sub>2</sub>Cl<sub>2</sub>/hexane mixtures. A very fast band of unreacted dimer came down first, followed by a golden-brown band of the complex, V. Total yield was 86 mg (23%). Continued elution with CH<sub>2</sub>Cl<sub>2</sub> followed by CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN mixtures yielded a dark brown tar containing no B–H (from infrared).

**B. From Nickelocene.** Nickelocene (380 mg, 2 mmol) and K<sub>2</sub>B<sub>10</sub>H<sub>10</sub>

(200 mg, 1 mmol) were brought to reflux in 50 mL dry 1,2-dimethoxyethane with magnetic stirring. The reaction mixture was maintained under reflux until the discharge of the green solution color (approximately 4 h). The workup was achieved as in method A. Total yield of V was 167 mg (45%).

**C. From [(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Ni]<sup>+</sup>, Triscyclopentadienylnickel tetrafluoroborate (200 mg, 0.25 mmol) and K<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (50 mg, 0.13 mmol) were stirred in 25 mL of dry 1,2-dimethoxyethane for 1 h. The reaction was extremely rapid. Isolation and workup were identical with those of method A. Total yield of V was 35 mg (73%).**

**[(CH<sub>3</sub>)<sub>4</sub>N][2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>] (VI) and [(CH<sub>3</sub>)<sub>4</sub>N][1-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>] (VII). A. From (B<sub>9</sub>H<sub>12</sub>)<sup>-</sup>.** To a solution of 1.8 g (10 mmol) of ((CH<sub>3</sub>)<sub>4</sub>N)(B<sub>9</sub>H<sub>12</sub>) and 1.8 g (10 mmol) of nickelocene in 100 mL of acetonitrile was added 50 g of 0.5% sodium amalgam. The solution was stirred for 1 h and then filtered through Celite. The mixture was deposited on alumina by removal of the solvent and placed at the top of a previously prepared 30 × 500 mm alumina chromatography column. Eluting with dichloromethane gradually enriched in acetonitrile first gave small amounts of several neutral compounds which were either unstable or did not contain boron, then the bright yellow fraction VII closely followed by the red complex VI. A green compound overlapped and followed VI. Eluting with CH<sub>3</sub>CN produced a small amount of an orange complex. Recrystallization of the red and yellow complexes was accomplished by adding a small amount of ((CH<sub>3</sub>)<sub>4</sub>N)Cl to an acetone/H<sub>2</sub>O solution and slowly removing the acetone under reduced pressure at ambient temperature. The crystalline products were isolated by filtration and dried under vacuum to yield 0.55 g (18%) of VI and 0.20 g (7%) of VII. The green fraction was evaporated under pressure and the residue (<0.1 g) was dissolved in CD<sub>3</sub>CN. The <sup>1</sup>H NMR spectrum appeared to be a mixture of VI and VII with a third small cyclopentadienyl resonance. The temperature of the NMR probe (35 °C) was sufficient to cause the sample color to change from green to red-yellow indicative of decomposition. The orange complex was recrystallized from acetone/water in the presence of excess ((CH<sub>3</sub>)<sub>4</sub>N)Cl by removal of the acetone under reduced pressure to yield 0.05 g of orange crystals. The <sup>1</sup>H NMR spectrum of the orange complex did not contain a cyclopentadienyl resonance and the <sup>11</sup>B NMR spectrum was similar to that of VI. The compound was not further characterized.

**B. From (B<sub>9</sub>H<sub>9</sub>)<sup>2-</sup>.** [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>NiCO)<sub>2</sub>] (602 mg, 2 mmol) and Cs<sub>2</sub>B<sub>9</sub>H<sub>9</sub> (1.5 g, 4 mmol) were stirred together in acetonitrile at 25 °C for 24 h. The workup was achieved as in A above to yield 240 mg (20%) of ((CH<sub>3</sub>)<sub>4</sub>N)[2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>] and 220 mg (18%) of ((CH<sub>3</sub>)<sub>4</sub>N)[1-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>].

**[(CH<sub>3</sub>)<sub>4</sub>N][2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>Cl<sub>9</sub>] (VIII).** Chlorine gas was bubbled slowly through 0.20 g of VI in 20 mL of acetonitrile maintained at 5 °C with an ice bath. After 30 min the ice bath was removed and Cl<sub>2</sub> continued to bubble through the solution until samples of the solution no longer exhibited a 2500-cm<sup>-1</sup> absorption (B–H) in their infrared spectrum. The solvent was removed under reduced pressure and the residue dissolved in acetone. Aqueous tetramethylammonium chloride was added until the product just began to precipitate, then the acetone was removed slowly by rotary evaporation. The bright green crystals, 0.32 g (80%), were isolated by filtration and dried under vacuum.

**[(CH<sub>3</sub>)<sub>4</sub>N][1-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>Cl<sub>9</sub>] (IX).** Thermal isomerization of VII proved to be an effective way of obtaining the perchlorinated analogue of VII. The green complex VIII (0.1 g) was dissolved in 2 mL of acetonitrile and sealed into a heavy-walled tube under vacuum. The tube was heated to 130 °C for several minutes until the bright green color had changed to yellow-brown. The tube was cooled and the contents chromatographed on a short alumina column with CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN. A small amount of a bright red complex remained at the top of the column while the yellow product, IX, closely followed by a small amount of starting material, was eluted. The solvent was removed from the yellow fraction and the residue recrystallized from ethanol/water (with excess ((CH<sub>3</sub>)<sub>4</sub>N)Cl) to yield 0.09 g of IX. The yellow isomer photochemically isomerizes rapidly to the green isomer and precautions must be taken to avoid exposure of solutions to direct sunlight.

**Isomerization of [2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>]<sup>-</sup> to [1-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>]<sup>-</sup>.**  
**A. Thermal.** The thermal isomerization reaction was monitored using a thermostated UV-vis spectrometer by following the disappearance of the band at 518 nm which is attributed to the equatorial isomer [2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>]<sup>-</sup>. In a typical experiment a standard solution (8.0 × 10<sup>-4</sup> M) of ((CH<sub>3</sub>)<sub>4</sub>N)[2-(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Ni)B<sub>9</sub>H<sub>9</sub>] in degassed CH<sub>3</sub>CN was prepared taking care to minimize exposure to light. The

solution (2 mL) was placed in a 1-cm quartz cell and the 518-nm band was scanned at 60-min intervals. At 70 °C the concentration of the equatorial isomer using Beer's law was halved in 12 h.

In another experiment a sealed Pyrex NMR tube of 20 mg of  $(\text{[CH}_3\text{]}_4\text{N})[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$  in 2 mL of degassed  $\text{CH}_3\text{CN}$  was heated to 130 °C and the isomerization was followed by periodically recording the  $^1\text{H}$  NMR spectrum. The ratio of equatorial to apical isomer was determined by integrating the  $\text{C}_5\text{H}_5$  proton resonances at  $\tau$  4.89 and 4.30, respectively. The isomerization was >95% complete after 90 min at 130 °C.

**B. Acid Catalyzed.** The sample of  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$  was prepared as above except that trifluoroacetic acid was added before the first spectrum was recorded. With  $[\text{CF}_3\text{COOH}] = 1.9 \times 10^{-3}$  M at 70 °C the concentration of the equatorial isomer was halved in only 8 h. With  $[\text{CF}_3\text{COOH}] = 1.0$  M at 80 °C the isomerization was >90% complete in 40 min.

**C. Photolytic.** The photolytic isomerization of  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$  to  $[1-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]^-$  was performed by exposing the sample to a 50-W low-pressure mercury lamp. In a typical experiment 20 mg of  $(\text{[CH}_3\text{]}_4\text{N})[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{H}_9]$  was dissolved in 2 mL of degassed  $\text{CH}_3\text{CN}$  and sealed in a Pyrex NMR tube. The sample was then placed in an immersion well 2 in. from the lamp and the  $^1\text{H}$  NMR spectrum was periodically recorded. The isomerization was >90% complete in 20 min.

**Isomerization of  $[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]^-$  and  $[1-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]^-$ .** **A. Thermal.** The thermal isomerization was monitored using a thermostated UV-vis spectrometer by following the disappearance of the band at 664 nm. With the concentration of  $(\text{[CH}_3\text{]}_4\text{N})[2-(\text{C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]$  equal to  $8.0 \times 10^{-4}$  M the isomerization was only 10% complete at 70 °C over 24 h.

The isomerization was alternatively monitored with  $^1\text{H}$  NMR by integrating the  $(\text{C}_5\text{H}_5)^-$  resonances of the equatorial ( $\tau$  4.36) and apical ( $\tau$  4.40) isomers. The isomerization was >90% complete at 130 °C in 8 h.

**B. Photolytic.** The photolyses of 1- and  $[2-(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{B}_9\text{Cl}_9]^-$  were carried out using a 500-W tungsten iodide lamp and monitoring the solution by  $^1\text{H}$  NMR. After 20 min the photolysis of either the apical or the equatorial isomer resulted in a 2:1 apical/equatorial equilibrium mixture.

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