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Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

$B_{10}H_{12}CNH_3$, $B_9H_9CH^-$, $B_{11}H_{11}CH^-$, and Metallomonocarboranes[1]

By W. H. Knoth

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Acidification of $B_{10}H_{13}CN^{2-}$ and $B_{10}H_{12}CN \cdot S(CH_3)_2^-$ forms the monocarboranes $B_{10}H_{12}CNH_3$ and $B_{10}H_{11}(OH)CNH_3$, respectively. Further reactions of these have led to the *closo*-carborane anions $B_9H_9CH^-$ and $B_{11}H_{11}CH^-$, to a series of metallomonocarboranes based on the $B_{10}H_{10}CH^{3-}$ and $B_{10}H_{10}CNH_3^{2-}$ anions, and to the *nido*-carborane $B_9H_{11}CN(CH_3)_3$.

The reactions of decaborane with aqueous sodium cyanide to form $B_{10}H_{13}CN^{2-}$ and with sodium cyanide in dimethyl sulfide to form $B_{10}H_{12}CN \cdot S(CH_3)_2^-$, both in quite good yield, were described earlier.[2] It has now been found that acidification of these anions *via* ion exchange converts them to the *C*-aminocarboranes $B_{10}H_{12}CNH_3$ and $B_{10}H_{11}(OH)CNH_3$, respectively, making these the most readily accessible carboranes known. In its simplest form, the preparation of $B_{10}H_{12}CNH_3$ consists merely of dissolving decaborane in aqueous sodium cyanide, passing the resulting clear solution through an acidic ion-exchange column, and evaporating the effluent to dryness. The $B_{10}H_{12}(CN)OH^{2-}$ anion appears to be an intermediate in the preparation of $B_{10}H_{11}(OH)CNH_3$; it can be prepared by refluxing an aqueous solution of $NaB_{10}H_{12}CN \cdot S(CH_3)_2$ and is converted to $B_{10}H_{11}(OH)CNH_3$ upon acidification.

The aminocarborane $B_{10}H_{12}CNH_3$ is the parent member of a series which was reported earlier by Hyatt, Owen, and Todd.[3] They treated decaborane with alkyl isocyanides and obtained mono-*N*-alkylated derivatives, $B_{10}H_{12}CNH_2R$.[4] The two routes are compared in the equations

$$B_{10}H_{14} + 2NaCN \xrightarrow[-HCN]{H_2O} Na_2B_{10}H_{13}CN \xrightarrow{H^+} B_{10}H_{12}CNH_3 \quad (1)$$

$$B_{10}H_{14} + RNC \longrightarrow B_{10}H_{12}CNH_2R \quad (2)$$

On the basis of ^{11}B nmr analysis and the isoelectronic relationship of the $B_{10}H_{12}CNH_2R$ system with $B_9C_2H_{13}$,[5] Todd has proposed[3] the structure shown in Figure 1A, with which we concur. The infrared spectrum of $B_{10}H_{12}CNH_3$ is shown in Figure 2.

The simplest apparent route for the formation of $B_{10}H_{12}CNH_3$ involves interaction of the nitrile carbon atom attached to B-6 in $B_{10}H_{13}CN^{2-}$ with boron atoms 7, 8, and 9 of the decaborane basket to give the relationships shown in Figure 1. Applying this scheme to the formation of $B_{10}H_{11}(OH)CNH_3$ leads to the structure shown in Figure 1B in which the hydroxyl group is on B-8, adjacent to the carbon atom in the open pentagonal face. Such a structure would be comprised of a *dl* pair; no attempt at resolution has been made. A degradation reaction which supports this structure is discussed below. The ^{11}B nmr spectrum of $B_{10}H_{11}(OH)CNH_3$ at 32.1 MHz is not conclusive. It does exhibit a low-field singlet which must represent the hydroxyl-bonded boron atom. Low-field shifts resulting from hydroxyl substitution in boranes have been observed previously.[6]

An *N*-substituted aminocarborane, $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$ (Figure 1C), which is also a member of this series, can be prepared by the reaction of $NaB_{10}H_{12}CN \cdot S(CH_3)_2$ with benzoyl chloride

$$NaB_{10}H_{12}CN \cdot S(CH_3)_2 + C_6H_5COCl \longrightarrow NaCl + C_6H_5CONHCB_{10}H_{11}S(CH_3)_2 \quad (3)$$

The assigned formulation is supported by the presence of amide absorption in the infrared spectrum and the absence of nitrile absorption. Boron-11 nmr is inconclusive. Thermolysis of $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$ at 160–165° results in the loss of dimethyl sulfide and the formation of $C_6H_5CONHCB_{10}H_{11}$.

Methylation of $B_{10}H_{12}CNH_3$ and of $B_{10}H_{11}(OH)CNH_3$ with dimethyl sulfate proceeds smoothly to form $B_{10}H_{12}CN(CH_3)_3$ and $B_{10}H_{11}(OH)CN(CH_3)_3$. Reaction of the latter with sodium hydroxide in aqueous tetrahydrofuran gives $B_9H_{11}CN(CH_3)_3$. Infrared analysis demonstrates the absence of a hydroxy group, suggesting that B-8 in Figure 1B has been removed. This reforms a decaborane-like basket structure with the carbon atom at the 6 position (Figure 3) and, in fact, $B_9H_{11}CN(CH_3)_3$ is isoelectronic with $B_{10}H_{14}$, being equivalent to $B_{10}H_{12}^{2-}$. The ^{11}B nmr spectrum of $B_9H_{11}CN(CH_3)_3$ (Figure 4) exhibits boron atom sets of 2:2:2:1:1:1, consistent with the assigned structure and thereby lending support to the structure proposed for the precursor $B_{10}H_{11}(OH)CNH_3$. The unmethylated analog $B_9H_{11}CNH_3$ is obtained, together with $B_{10}H_{12}CNH_3$, when $B_{10}H_{13}CN^{2-}$ is acidified with concentrated hydrochloric acid instead of *via* ion exchange.

Treatment of $B_{10}H_{12}CN(CH_3)_3$ with sodium hydride at ambient temperature liberates 1 equiv of hydrogen, forming the $B_{10}H_{11}CN(CH_3)_3^-$ anion. This reacts with oxalyl chloride to give, after work-up with water, $B_{10}H_{11}(COOH)CN(CH_3)_3$. Thermolysis of this acid in refluxing xylene results in intramolecular dehydration

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(1) For preliminary reports of this work, see W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 1274, 3342 (1967).

(2) W. H. Knoth and E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **20**, 66 (1961).

(3) D. E. Hyatt, D. A. Owen, and L. J. Todd, *Inorg. Chem.*, **5**, 1749 (1966).

(4) This reaction was also discovered by W. R. Hertler, U. S. Patent 3,429,923 (Feb 25, 1969).

(5) R. A. Wiesboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **86**, 1642 (1964).

(6) W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *ibid.*, **86**, 3973 (1964).

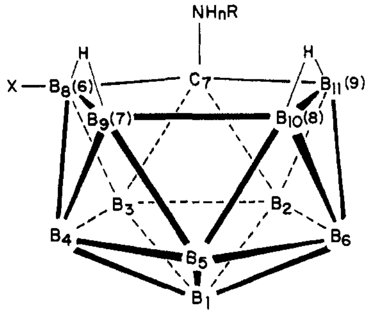

Figure 1.—Skeletal structures, where numbers in parentheses refer to original atom positions in decaborane: (A) $B_{10}H_{12}$-CNH_2R (R = H, alkyl, *n* = 2, X = H); (B) $B_{10}H_{11}(OH)CNH_3$ (R = H, *n* = 2, X = OH); (C) $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$ (R = C_6H_5CO, *n* = 1, X = $S(CH_3)_2$).

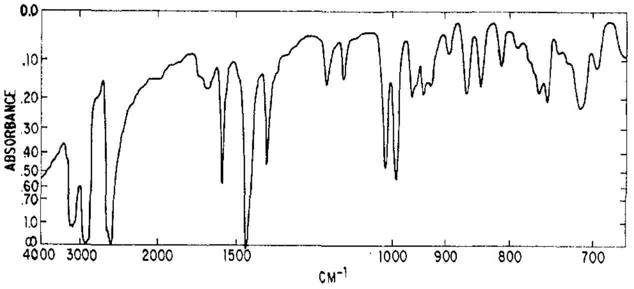

Figure 2.—Infrared spectrum (Nujol mull) of $B_{10}H_{12}CNH_3$.

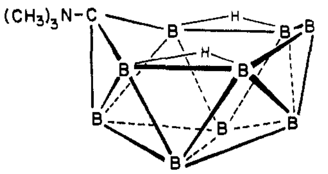

Figure 3.—$B_9H_{11}CN(CH_3)_3$ (terminal hydrogen atoms omitted).

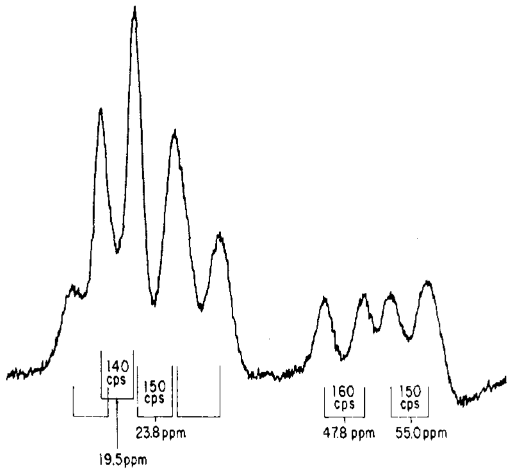

Figure 4.—The 32.1-MHz ^{11}B nmr spectrum of $B_9H_{11}CN(CH_3)_3$ in acetonitrile, referred to $(CH_3O)_3B$.

and the formation of $B_{10}H_{10}(CO)CN(CH_3)_3$. This evolves carbon monoxide upon further heating (170–

$$B_{10}H_{12}CN(CH_3)_3 \xrightarrow{NaH} H_2\uparrow + NaB_{10}H_{11}CN(CH_3)_3 \xrightarrow[2.\ H_2O]{1.\ (COCl)_2} B_{10}H_{11}(COOH)CN(CH_3)_3 \xrightarrow{\sim140°} B_{10}H_{10}(CO)CN(CH_3)_3 \xrightarrow{\sim170°} B_{10}H_{10}CN(CH_3)_3 \quad (4)$$

180°), giving $B_{10}H_{10}CN(CH_3)_3$. Another route to the latter compound has been reported by Todd,[7] who obtained it from the reaction of $B_{10}H_{12}CN(CH_3)_3$ with sodium hydride and iodine. The ^{11}B nmr spectrum for $B_{10}H_{10}CN(CH_3)_3$ prepared by the oxalyl chloride route is identical with that reported by Todd. The position of the carboxyl group in $B_{10}H_{11}(COOH)CN(CH_3)_3$ has not been established.

Deamination reactions of $B_{10}H_{12}CN(CH_3)_3$ and $B_9H_{11}CN(CH_3)_3$ follow quite different courses. Deamination of $B_{10}H_{12}CN(CH_3)_3$ by reaction with sodium gives the expected $B_{10}H_{12}CH^-$ as a major product and $B_{10}H_{10}CH^-$ as a minor product.[8] Both the $B_{10}H_{10}CH^-$ anion and $B_{10}H_{10}CN(CH_3)_3$ are isoelectronic and presumably isostructural with $B_9C_2H_{11}$.[9] The deamination of $B_9H_{11}CN(CH_3)_3$ with sodium does not give the expected $B_9H_{11}CH^-$. Instead, hydrogen is lost spontaneously and the *closo* anion 1-$B_9H_9CH^-$ is formed. This anion is a carba derivative of $B_{10}H_{10}^{2-}$ and has the carbon atom at an apical position (Figure 5). This structure is based on the ^{11}B nmr spectrum (Figure 6A) which exhibits a low-field doublet (one boron atom) assigned to the boron atom at the other apical position and two nonequivalent sets of four boron atoms each, representing the two equatorial belts. The infrared spectrum of CsB_9H_9CH is shown in Figure 7.

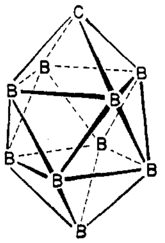

Figure 5.—Skeletal structure of 1-$B_9H_9CH^-$.

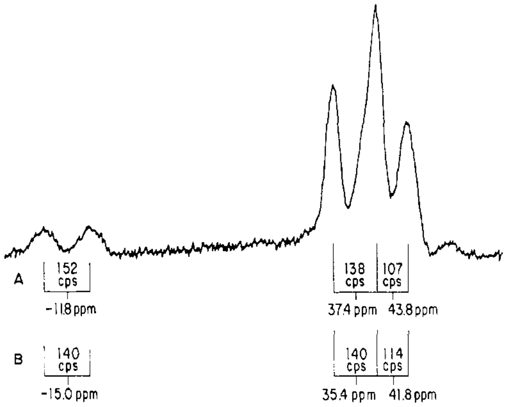

Figure 6.—The 19.2-MHz ^{11}B nmr spectra in acetonitrile, referred to $(CH_3O)_3B$: (A) Cs-1-B_9H_9CH; (B) Cs-1-$B_9H_9CSi(CH_3)_3$.

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(7) D. E. Hyatt, F. R. Scholer, L. J. Todd, and J. L. Warner, *Inorg. Chem.*, **6**, 2229 (1967).

(8) Todd has used sodium hydride for this deamination and has converted $B_{10}H_{12}CH^-$ to $B_{10}H_{10}CH^-$ by reaction with sodium hydride and iodine.[7]

(9) (a) T. E. Berry, F. N. Tebbe, and M. F. Hawthorne, *Tetrahedron Lett.*, 715 (1965); (b) C. Tsai and W. E. Streib, *J. Amer. Chem. Soc.*, **88**, 4513 (1966).

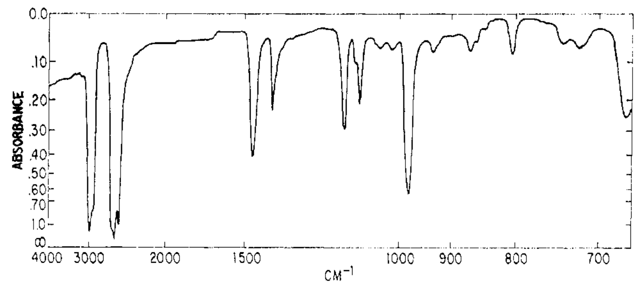

Figure 7.—Infrared spectrum (Nujol mull) of Cs-1-B_9H_9CH.

Another route to the $B_9H_9CH^-$ carborane is thermolysis of $CsB_{10}H_{12}CH$ at 320–330° (eq 5); this route gives $B_{11}H_{11}CH^-$ as a coproduct.

$$2CsB_{10}H_{12}CH \longrightarrow CsB_9H_9CH + CsB_{11}H_{11}CH + 2H_2 \quad (5)$$

This disproportionation is reminiscent of the thermolytic behavior of $Cs_2B_{11}H_{13}$[10] (eq 6) which is isoelectronic with $CsB_{10}H_{12}CH$.

$$2Cs_2B_{11}H_{13} \xrightarrow{250°} 2H_2 + 2Cs_2B_{11}H_{11} \xrightarrow{600°} CsB_{10}H_{10} + Cs_2H_{12}H_{12} \quad (6)$$

Just as $B_9H_9CH^-$ is a monocarborane analog of $B_{10}H_{10}^{2-}$ and of $B_8C_2H_{10}$, so is $B_{11}H_{11}CH^-$ a monocarborane analog of $B_{12}H_{12}^{2-}$ and of $B_{10}C_2H_{12}$. The ^{11}B nmr spectrum of $B_{11}H_{11}CH^-$ (Figure 8) displays boron atom sets of 1:5:5, consistent with an icosahedral structure comprised of one carbon and eleven boron atoms (Figure 9). The infrared spectrum of $CsB_{11}H_{11}CH$ is shown in Figure 10. The chemical properties of $B_9H_9CH^-$ and of $B_{11}H_{11}CH^-$ have not been extensively investigated but seem to reflect both polyhedral borane and carborane character. For example, bromination of $B_{11}H_{11}CH^-$ proceeds readily in aqueous solution but to a lesser extent than for $B_{12}H_{12}^{2-}$ under the same conditions. At 5° $B_{12}H_{12}^{2-}$ is easily converted to $B_{12}H_6Br_6^{2-}$,[11] whereas at the same temperature $B_{11}H_{11}CH^-$ and excess bromine give a mixture of $B_{11}H_{10}BrCH^-$ and $B_{11}H_9Br_2CH$. In common with $B_{10}C_2H_{12}$, both $B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ readily form *C*-lithio derivatives when treated with alkyllithium reagents. $B_9H_9CLi^-$ has been carbonated to form $B_9H_9CCOOH^-$ and treated with trimethylchlorosilane to form $B_9H_9CSi(CH_3)_3^-$. The near identity of the ^{11}B nmr spectrum of $B_9H_9CSi(CH_3)_3^-$ with that of $B_9H_9CH^-$ (Figure 6) confirms that the substitution has occurred at the carbon atom.

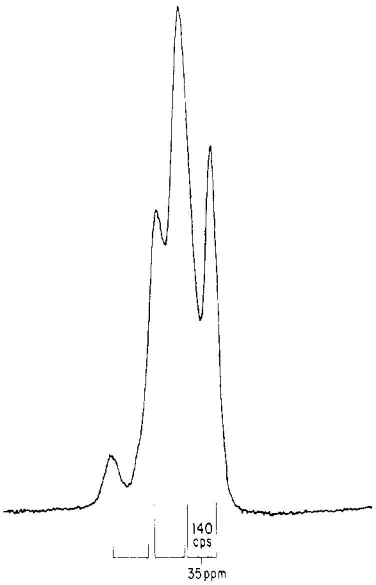

Figure 8.—The 32.1-MHz ^{11}B nmr spectrum of $CsB_{11}H_{11}CH$ in acetonitrile, referred to $(CH_3O)_3B$.

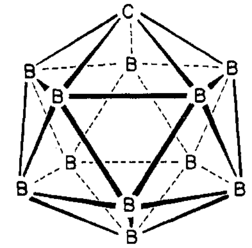

Figure 9.—Skeletal structure of $B_{11}H_{11}CH^-$.

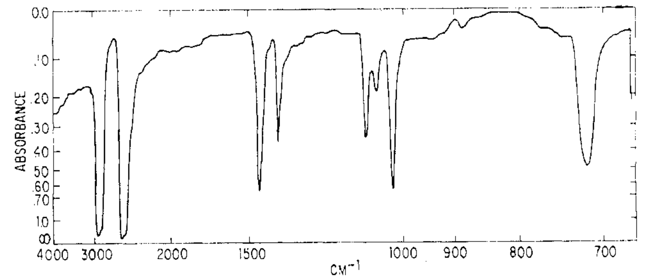

Figure 10.—Infrared spectrum (Nujol mull) of $CsB_{11}H_{11}CH$.

Hawthorne and coworkers have prepared a series of metallocarboranes, exemplified by $(B_9C_2H_{11})_2Fe^-$ and $(B_9C_2H_{11})_2Co^{2-}$, in which $B_9C_2H_{11}^{2-}$ is complexed to a transition metal atom.[12] These complexes are formally similar to metallocenes because in both cases the metal is bonded to a pentagonal face which can contribute six electrons in three bonding molecular orbitals. Because $B_9C_2H_{11}^{2-}$, $B_{10}H_{10}CH^{3-}$, and $B_{10}H_{10}CNH_3^{2-}$ are isoelectronic, it might be expected that the latter two anions would form similar transition metal complexes. Treatment of $B_{10}H_{12}CH^-$ and $B_{10}H_{12}CNH_3$ with base and various transition metal halides has given such complexes as shown in Table I.[13] The structure proposed for these complexes by analogy with the $B_9C_2H_{11}^{2-}$ complexes is shown in Figure 11.

The $B_{10}C$ ligands stabilize high formal metal oxidation states more readily than does $B_9C_2H_{11}^{2-}$. This can be seen in the preferred nickel oxidation state (IV) in the nickel complexes and, even more strikingly, in the oxidation of the yellow-orange diamagnetic ($B_{10}H_{10}$-

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[10] F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).

[11] W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *ibid.*, **3**, 159 (1964).

[12] Metallocarboranes have recently been reviewed: L. J. Todd, *Advan. Organometal. Chem.*, **8**, 87 (1970).

[13] Metallocarborane complexes derived from $B_{10}H_{10}CH^{2-}$ and $B_{10}H_{10}CNH_2R^{2-}$ were communicated by Todd and coworkers simultaneously with our preliminary communication:[1] D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *J. Amer. Chem. Soc.*, **89**, 3342 (1967).

TABLE I

Carborane	Metal halide	Base[a]	Product	Formal metal oxidn state in isolated product
$B_{10}H_{12}CH^-$	$CrCl_3$	A	$(B_{10}H_{10}CH)_2Cr^{3-}$	III
$B_{10}H_{12}CH^-$	$MnCl_2$	A	$(B_{10}H_{10}CH)_2Mn^{2-}$	IV
$B_{10}H_{12}CH^-$	$CoCl_2$	A, B	$(B_{10}H_{10}CH)_2Co^{3-}$	III
$B_{10}H_{12}CH^-$	$NiCl_2$	A, B	$(B_{10}H_{10}CH)_2Ni^{2-}$	IV
$B_{10}H_{12}CH^-$	$FeCl_2$	A	$(B_{10}H_{10}CH)_2Fe^{3-}$	III
$B_{10}H_{12}CNH_3$	$MnCl_2$	A	$(B_{10}H_{10}CNH_2)_2Mn^{2-}$	IV
$B_{10}H_{12}CNH_3$	$CoCl_2$	B	$(B_{10}H_{10}CNH_3)_2Co^-$	III
$B_{10}H_{12}CNH_3$	$NiCl_2$	B	$(B_{10}H_{10}CNH_3)_2Ni$	IV
$B_{10}H_{12}CNH_3$	$FeCl_2$	A	$(B_{10}H_{10}CNH_3)_2Fe^-$	III

[a] Base: A, *n*-butyllithium in tetrahydrofuran; B, aqueous sodium hydroxide.

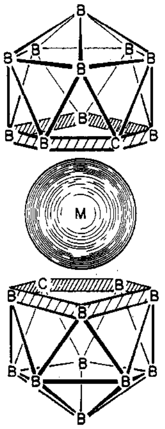

Figure 11.—Skeletal structure proposed for metallocarboranes derived from $B_{10}H_{10}CH^{3-}$ and $B_{10}H_{10}CNH_3^{2-}$.

$CH)_2Co^{3-}$ ion to an almost black, paramagnetic $(B_{10}H_{10}CH)_2Co^{2-}$ ion which contains cobalt in a formal oxidation state of IV.

Reaction of $B_{10}H_{12}CNH_2CH_2C_6H_5$ with $NiCl_2$ in aqueous sodium hydroxide has given $(B_{10}H_{10}CNH_2CH_2C_6H_5)_2Ni$. Another N-alkylated complex, $[B_{10}H_{10}CNH(CH_3)_2]_2Ni$, has been prepared by the methylation of $(B_{10}H_{10}CNH_3)_2Ni$ with dimethyl sulfate. The stability of these complexes was further demonstrated by the reaction of $(B_{10}H_{10}CNH_3)_2Ni$ with nitrous acid to form $(B_{10}H_{10}COH)_2Ni^{2-}$ and of $(B_{10}H_{10}CH)_2Co^{3-}$ with chlorine in acetonitrile at 0° to give a mixture of chlorinated products of average composition $(B_{10}H_{2.5}Cl_{7.5}CH)_2Co^{3-}$. The manganese complexes are significantly less stable than the others; they decompose spontaneously in moist acetonitrile over a period of several days.

Experimental Section

$B_{10}H_{12}CNH_3$.—A mixture of decaborane (24 g, 0.2 mol), sodium cyanide (30 g, 0.61 mol), and water (300 ml) was stirred until a clear solution formed. This was passed through a column containing excess Amberlite IR 120 (H) resin. The effluent was evaporated to dryness on a steam bath leaving a residue comprised of $B_{10}H_{12}CNH_3$ and a little boric acid. The residue was extracted with ether. Evaporation of the extracts left $B_{10}H_{12}CNH_3$ which, to remove the final traces of ether, was again dissolved in water and evaporated to dryness. The yield of $B_{10}H_{12}CNH_3$, a crystalline white solid, was 21.5 g, 75%. The compound does not melt to 400°. *Anal.* Calcd for $B_{10}H_{12}CNH_3$: B, 72.5; C, 8.0; H, 10.1; N, 9.4. Found: B, 73.0; C, 8.0; H, 10.1; N, 9.5. Uv λ_{max} 287 (ϵ 1.4). No protons bonded to carbon could be detected by nmr. The infrared spectrum is shown in Figure 2.

In a similar preparation, run on half the scale, the ion-exchange effluent was basified with 100 ml of 20% aqueous sodium hydroxide. The addition of tetramethylammonium chloride (20 g) precipitated 11.6 g (64%) of $(CH_3)_4NB_{10}H_{12}CNH_2$. Two grams of this was recrystallized from 300 ml of water which contained 5 g of tetramethylammonium hydroxide pentahydrate and then dried under vacuum at 80° (dec pt 295–300°). *Anal.* Calcd for $(CH_3)_4NB_{10}H_{12}CNH_2$: B, 48.6; C, 27.0; H, 11.7; N, 12.6. Found: B, 48.6; C, 25.6; H, 11.6; N, 12.4.

The addition of dioxane (5 ml) to a solution of $B_{10}H_{12}CNH_3$ (3.9 g, 26 mmol) in water (20 ml) precipitated a dioxanate of $B_{10}H_{12}CNH_3$. Recrystallization of this from water gave 3.2 g (52%) of $B_{10}H_{12}CNH_3 \cdot C_4H_8O_2$, a crystalline white solid which does not melt below 400°. *Anal.* Calcd for $B_{10}H_{12}CNH_3 \cdot C_4H_8O_2$: B, 45.5; C, 25.4; H, 9.7; N, 5.9; H by evolution, 1890 cm³/g. Found: B, 46.2; C, 25.3; H, 9.7; N, 5.8; H by evolution, 1889 cm³/g.

Reaction of $B_{10}H_{13}CN^{2-}$ with Hydrochloric Acid.—$Cs_2B_{10}H_{13}CN$ (30.7 g, 74.5 mmol) was added in one portion to 12 *M* hydrochloric acid (100 ml). Vigorous bubbling ensued. When the solid had essentially all dissolved, the still-bubbling mixture was filtered. The addition of dioxane (50 ml) to the filtrate precipitated a solid which was washed seven times with small amounts of cold water to leave a mixture of $B_{10}H_{12}CNH_3 \cdot C_4H_8O_2$ and $B_9H_{11}CNH_3 \cdot C_4H_8O_2$. *Anal.* Calcd for $B_{10}H_{12}CNH_3 \cdot C_4H_8O_2$: B, 45.5; C, 25.4; H, 9.7; N, 5.9. Calcd for $B_9H_{11}CNH_3 \cdot C_4H_8O_2$: B, 43.2; C, 26.6; H, 9.8; N, 6.2. Found: B, 44.2; C, 25.9; H, 9.9; N, 6.0. Uv $\lambda_{max}^{CH_3CN}$ 286 (*k* 7.69), 245 (*k* 9.09). Confirmation that the product was a mixture of $B_{10}H_{12}CNH_3$ and $B_9H_{11}CNH_3$ dioxanates was obtained by methylation as described below for the conversion of $B_{10}H_{12}CNH_3$ to $B_{10}H_{12}CN(CH_3)_3$. Infrared, ultraviolet and proton nmr comparisons with the pure species showed that the methylated product was a mixture of $B_9H_{11}CN(CH_3)_3$ and $B_{10}H_{12}CN(CH_3)_3$ in a ratio of about 7:3.

$B_{10}H_{12}CN(CH_3)_3$.—The effluent from the passage of an aqueous solution of $Cs_2B_{10}H_{13}CN$ (20 g, 48.4 mmol) through an ion-exchange column packed with an excess of a strongly acidic ion-exchange resin (Amberlite IR 120 (H)) was basified with sodium hydroxide and stirred with two successive 10-ml portions of dimethyl sulfate. The solution was kept basic with sodium hydroxide as needed. $B_{10}H_{12}CN(CH_3)_3$ (8.3 g, 90%) precipitated and was recrystallized from aqueous acetonitrile to obtain 7.5 g (81%) of $B_{10}H_{12}CN(CH_3)_3$, mp 345–350°, as a colorless crystalline solid. *Anal.* Calcd for $B_{10}H_{12}CN(CH_3)_3$: B, 56.5; C, 25.1; H, 11.0; N, 7.3. Found: B, 56.1; C, 25.8; H, 11.0; N, 7.5. Uv $\lambda_{max}^{CH_3CN}$ 284 (ϵ 1.4). Thin layer chromatography on silica gel using 4:1 dichloroethylene–acetonitrile as eluent detected only one component, R_f 0.77. Proton nmr in CD_3CN revealed a sharp singlet at τ 6.84.

The presence of one acidic hydrogen in $B_{10}H_{12}CN(CH_3)_3$ was demonstrated. A solution of $B_{10}H_{12}CN(CH_3)_3$ (0.9582 g) in 25 ml of tetrahydrofuran was stirred with 1 g of 50% sodium-in-oil dispersion. The mixture was filtered; the filter cake was rinsed three times with tetrahydrofuran. The combined filtrate and washings were diluted with 100 ml of water, precipitating recovered $B_{10}H_{12}CN(CH_3)_3$. Titration of this mixture required 48.8 ml of 0.1 *N* HCl, indicating a neutralization equivalent of 195 for $B_{10}H_{12}CN(CH_3)_3$ (calcd for $B_{10}H_{12}CN(CH_3)_3$ as a monobasic acid, 191).

The ^{11}B nmr spectrum was identical with that reported for $B_{10}H_{12}CN(CH_3)_3$ prepared *via* methylation of $B_{10}H_{12}CNH_2CH_3$ which was prepared from decaborane and methyl isocyanide.[3]

$B_{10}H_{10}CH^-$ and $B_{10}H_{12}CH^-$.—$B_{10}H_{12}CN(CH_3)_3$ (5.8 g, 30.4 mmol) was added to a mixture of sodium dispersion (3.5 g, 50% in oil, 75 mg-atoms) in a nitrogen atmosphere, resulting in immediate hydrogen evolution. The mixture was refluxed for 7 hr and then filtered. The grayish white filter cake was added slowly to water (150 ml). Essentially no sodium was left. The resulting solution was filtered; addition of excess trimethylammonium chloride precipitated $(CH_3)_3NHB_{10}H_{12}CH$ which was recrystallized from water (2.0 g, 34% yield). *Anal.* Calcd for $(CH_3)_3NHB_{10}H_{12}CH$: B, 56.0; C, 24.9; H, 11.9; N, 7.2; neutralization equiv, 193; apparent mol wt, 96; H by evolution, 2320 cm^3/g. Found: B, 56.1; C, 25.4; H, 12.3; N, 7.2; neutralization equiv, 200; apparent mol wt (boiling point in CH_3CN), 94; H by evolution, 2358 cm^3/g.

The ^{11}B nmr spectrum has been reported.[7] The initial filtrate was evaporated and the residue was extracted with water. Addition of trimethylammonium chloride to the filtered extracts precipitated $(CH_3)_3NHB_{10}H_{10}CH$ in 60% yield. Dissolution in ethanol and addition of tetramethylammonium hydroxide gave the corresponding tetramethylammonium salt, which was recrystallized from aqueous ethanol. *Anal.* Calcd for $(CH_3)_4NB_{10}H_{10}CH$: B, 52.7; C, 29.2; H, 11.3; N, 6.8; apparent mol wt, 103; H by evolution, 2080 cm^3/g. Found: B, 52.8; C, 28.5; H, 11.1; N, 6.8; apparent mol wt (boiling point in CH_3CN), 102; H by evolution, 2090 cm^3/g. Uv $\lambda_{max}^{CH_3CN}$ 287 (ϵ 125), 235 (ϵ 3300). The ^{11}B nmr spectrum was identical with that reported in the literature.[7]

The following is an alternate procedure which is preferred if only $B_{10}H_{12}CH^-$ and no $B_{10}H_{10}CH^-$ is desired. A mixture of $B_{10}H_{12}CN(CH_3)_3$ (20 g, 105 mmol), 400 ml of tetrahydrofuran, and 18 g (0.39 g-atom) of 50% sodium dispersion in oil was refluxed for 18 hr in a nitrogen atmosphere. The mixture was cooled to room temperature and ethanol (100 ml) was added. After reaction ceased, the mixture was concentrated until a gummy residue was left. This was extracted with 200 ml of water. The extracts were filtered and the filtrate was acidified with hydrochloric acid. The addition of excess trimethylammonium chloride precipitated crude $(CH_3)_3NHB_{10}H_{12}CH$. This was purified by brief digestion in 300 ml of boiling water and then dried, *in vacuo*, at 80°. The yield from several preparations ranged from 11.4 to 14.6 g (56–72%). The product was identical by infrared analysis with that prepared above.

$B_{10}H_{11}(COOH)CN(CH_3)_3$.—A slurry of $B_{10}H_{12}CN(CH_3)_3$ (15 g, 78 mmol) in tetrahydrofuran (100 ml) was added to sodium hydride dispersion (50% NaH in oil, 15 g, 310 mmol) in tetrahydrofuran (75 ml) in a nitrogen atmosphere. After hydrogen evolution ceased (about 15 min), the mixture was filtered into a flask containing oxalyl chloride (20 ml) and tetrahydrofuran (75 ml). Gas evolution (presumably carbon monoxide, 1.2 l., 63%) commenced. After it stopped, the solution was concentrated on a steam bath to 190 ml. Dilution with water (500 ml) gave an oil which solidified on stirring. This solid was removed and extracted with four 50-ml portions of 5% aqueous sodium hydroxide. The filtered extracts were acidified with hydrochloric acid which precipitated $B_{10}H_{11}(COOH)CN(CH_3)_3$ (3.8 g, 20%). The analytical sample was recrystallized from aqueous glyme (dec pt (loss of water) 145°). *Anal.* Calcd for $B_{10}H_{11}(COOH)CN(CH_3)_3$: B, 46.0; C, 25.6; H, 8.9; N, 6.0. Found: B, 45.6; C, 27.3; H, 9.5; N, 5.9. The infrared spectrum (Nujol mull) included a strong absorption at 1660 cm^{-1} consistent with the presence of the carboxyl group. This compound becomes insoluble on storage at room temperature; the decomposition products have not been identified.

$B_{10}H_{10}(CO)CN(CH_3)_3$.—A slurry of $B_{10}H_{11}(COOH)\cdot CN(CH_3)_3$ (3.8 g, 16 mmol) in xylene (100 ml) was boiled for 5 min. Most of the solid dissolved. The mixture was filtered and the filtrate was concentrated until a slurry of crystals was obtained. Filtration gave $B_{10}H_{10}(CO)CN(CH_3)_3$ (2.1 g, 60%, dec pt (loss of CO) 170–180°). *Anal.* Calcd for $B_{10}H_{10}(CO)CN(CH_3)_3$: C, 27.6; H, 8.8. Found: C, 27.6; H, 9.1. Uv $\lambda_{max}^{CH_3CN}$ 295 (ϵ 2900), 247 (ϵ 11,300). The infrared spectrum exhibited an intense $C\equiv O$ stretching frequency at 2310 cm^{-1}.

$B_{10}H_{10}CN(CH_3)_3$.—A 2.1-g (10-mmol) sample of $B_{10}H_{10}(CO)CN(CH_3)_3$ was heated *in vacuo* at 170–180° for 20 hr. The product (1.6 g, 85%) had no $C\equiv O$ absorption in the infrared spectrum. The ^{11}B nmr spectrum was identical with that reported[7] for $B_{10}H_{10}CN(CH_3)_3$.

$B_{10}H_{11}(OH)CNH_3\cdot C_4H_8O_2$.—An aqueous solution of $NaB_{10}H_{12}CN\cdot S(CH_3)_2$ (30 g, 130 mmol) was passed through an ion-exchange column which contained excess Amberlite IR 120 (H) resin. Evaporation of the effluent left a residue which was extracted with four 50-ml portions of water. The addition of dioxane (5 ml) to each portion of the extracts caused the separation of $B_{10}H_{11}(OH)CNH_3\cdot C_4H_8O_2$ from the first three portions (20 g, 61%). *Anal.* Calcd for $B_{10}H_{11}(OH)CNH_3\cdot C_4H_8O_2$: B, 42.7; C, 23.7; H, 9.1. Found: B, 41.8; C, 24.7; H, 9.4. Uv $\lambda_{max}^{CH_3CN}$ 286 (ϵ 124).

$B_{10}H_{11}(OH)CN(CH_3)_3$.—A warm aqueous solution of $CsB_{10}H_{12}CN\cdot S(CH_3)_2$ (63 g, 18 mmol) was passed through an ion-exchange column packed with excess Amberlite IR 120 (H) resin. Evaporation of the effluent on a steam bath left a residue which was extracted with 60 ml of water. The extract was stirred with 10% aqueous sodium hydroxide (30 ml) and dimethyl sulfate (3.0 ml) precipitating $B_{10}H_{11}(OH)CN(CH_3)_3$ (1.9 g, 50%). The analytical sample (mp <400°) was recrystallized from aqueous acetonitrile. *Anal.* Calcd for $B_{10}H_{11}(OH)CN(CH_3)_3$: B, 52.2; C, 23.2; H, 10.2; N, 6.8; H by evolution, 2060 cm^3/g. Found: B, 52.2; C, 23.5; H, 10.4; N, 6.5; H by evolution, 2025 cm^3/g. The infrared spectrum confirmed the presence of a hydroxyl group.

$B_{10}H_{12}(CN)OH^{2-}$.—A solution of $NaB_{10}H_{12}CN\cdot S(CH_3)_2$ (10 g, 43 mmol) in 75 ml of water was refluxed for 2.5 hr and then cooled. Twenty milliliters of 50% aqueous cesium hydroxide solution was added to precipitate a solid which was recrystallized from water. The first crystals deposited were yellow, followed by a deposition of colorless crystals of different shape. The mixture was again recrystallized and the fractions were separated. The yellow crystals (0.7 g) were found to be $Cs_2B_{10}H_{13}CN$ by X-ray analysis (yellow color due to an impurity); the colorless crystals (1.1 g) were $Cs_2B_{10}H_{12}(CN)OH$. *Anal.* Calcd for $Cs_2B_{10}H_{12}(CN)OH$: Cs, 62.0; B, 24.9; C, 2.8; H, 3.0; N, 3.3. Found: Cs, 60.3; B, 24.8; C, 3.2; H, 3.2; N, 3.2. Uv $\lambda_{max}^{H_2O}$ 255 (ϵ 7800).

The infrared analysis showed the presence of CN, BH, and OH groups. Passage of $Cs_2B_{10}H_{12}(CN)OH$ through an acidic ion-exchange column followed by treatment of the effluent with sodium hydroxide and dimethyl sulfate gave $B_{10}H_{11}(OH)CN(CH_3)_3$.

$B_9H_{11}CN(CH_3)_3$.—A mixture of tetrahydrofuran (10 ml), 5% aqueous sodium hydroxide (12 ml), and $B_{10}H_{11}(OH)CN(CH_3)_3$ (1.2 g, 5.8 mmol) was stirred for 16 hr. Dilution with water (100 ml) precipitated a mixture of $B_9H_{11}CN(CH_3)_3$ and $B_{10}H_{11}(OH)CN(CH_3)_3$ which was treated with additional aqueous sodium hydroxide–tetrahydrofuran for another 16 hr. Dilution of this solution with water precipitated $B_9H_{11}CN(CH_3)_3$ (0.6 g, 58%). The analytical sample (mp 256–258°) was recrystallized from aqueous acetonitrile. *Anal.* Calcd for $B_9H_{11}CN(CH_3)_3$: B, 54.2; C, 26.8; H, 11.3. Found: B, 53.6; C, 27.1; H, 11.3. Uv $\lambda_{max}^{CH_3CN}$ 287 (ϵ 234), 243 (ϵ 3160). Thin layer chromatography on silica gel with 18:1 dichloroethane–acetonitrile as eluent revealed only one component (R_f 0.79). Proton nmr showed a single sharp spike which was at τ 6.78 in acetonitrile-d_3. The infrared spectrum lacked the hydroxyl absorption exhibited in the spectrum of the starting borane.

$B_9H_9CH^-$.—a. A mixture of $B_9H_{11}CN(CH_3)_3$ (5.6 g, 31.4 mmol), tetrahydrofuran (160 ml), and sodium dispersion (50% in oil, 6 g, 125 mg-atoms) was refluxed in a nitrogen atmosphere for 6 hr. This mixture was filtered. The filter cake was dissolved in ethanol (100 ml) and refiltered. The new filtrate was concentrated to leave a residue which was extracted with water (100 ml). Filtration of the extracts gave 1.3 g of recovered $B_9H_{11}CN(CH_3)_3$. The filtrate was allowed to stand for 3 days; 0.2 g of a crystalline solid ("A"), mp 141°, was formed. This material is described further below. Solid "A" was removed by filtration; the addition of tetramethylammonium chloride to the filtrate precipitated $(CH_3)_4NB_9H_9CH$ (0.7 g, 15%). *Anal.* Calcd for $(CH_3)_4NB_9H_9CH$: B, 50.4; C, 31.1; H, 11.4; N, 7.2; apparent mol wt, 96; H by evolution, 1970 cm^3/g. Found: B, 50.7; C, 31.7;, H, 11.5; N, 7.2; apparent mol wt (freezing point in $(CH_3)_2SO$), 103; H by evolution, 2003 cm^3/g.

Boron nmr analysis suggested the presence of a trace amount of $(CH_3)_4NB_9H_{11}CH$. A $B_9H_9CH^-$ salt which was free of $B_9H_{11}CH^-$ by nmr analysis (Figure 6) was obtained in a similar preparation

(40% yield) by precipitation with cesium hydroxide in place of tetramethylammonium chloride. The infrared spectrum is shown in Figure 7. *Anal.* Calcd for CsB_9H_9CH: B, 38.6. Found: B, 38.6.

Solid "A," isolated above, has not been identified. The infrared spectrum has a widely split terminal B–H absorption (2520 and 2430 cm^{-1}) and absorptions at 1850 and 1560 cm^{-1} which are assigned to bridging hydrogen but which are unusually strong for such absorptions. The proton nmr spectrum has a sharp spike at τ 7.3 for $(CH_3)_3N$. Analysis suggests a boron:carbon ratio of 5:1. *Anal.* Calcd for $B_5H_{11}CN(CH_3)_3$: B, 39.6; C, 35.3; H, 14.8; N, 10.3. Found: B, 41.4, 41.2; C, 35.6; H, 14.7; N, 10.3. The ^{11}B nmr spectrum at 19.2 MHz is complex.

b. The preceding preparation of $B_9H_9CH^-$ was based on pure $B_9H_{11}CN(CH_3)_3$ prepared in several steps from $B_{10}H_{12}CNS(CH_3)_2^-$. The $B_9H_9CH^-$ anion can also be prepared from the $B_9H_{11}CN(CH_3)_3$–$B_{10}H_{12}CN(CH_3)_3$ mixture obtainable from $B_{10}H_{13}CN^{2-}$ and concentrated hydrochloric acid followed by methylation as described above.

A mixture of $B_9H_{11}CN(CH_3)_3$ and $B_{10}H_{12}CN(CH_3)_3$ (15.5 g) was mixed with 400 ml of tetrahydrofuran and 14 g of 50% sodium dispersion in oil and refluxed overnight in a nitrogen atmosphere. The solution was cooled and 100 ml of ethanol was added. Filtration was followed by evaporation of the filtrate and extraction of the residue with 100 ml of water. The extract was filtered through Celite and mixed with a large excess of 50% aqueous cesium hydroxide with accompanying chilling in a water–ice bath. A solid precipitated and was recrystallized from water to obtain 3.5 g of CsB_9H_9CH, identified by infrared and ^{11}B nmr analysis. An important aspect of the preparation is isolation of the product as a cesium salt in preference to a tetramethylammonium or trimethylammonium salt. If the latter salts are isolated directly, the product is contaminated with $B_{10}H_{12}CH^-$ salts.

$B_{11}H_{11}CH^-$.—A solution of $CsB_{10}H_{12}CH$ (8 g, 30 mmol) in triethylamine–borane (50 ml) was heated to 170–180° for 5 hr in a nitrogen atmosphere. The triethylamine–borane was removed *in vacuo*, leaving a thick slurry. This was washed with benzene (30 ml), leaving $CsB_{11}H_{11}CH$ (3 g, 36%). The analytical sample was recrystallized from water. *Anal.* Calcd for $CsB_{11}H_{11}CH$: B, 43.0; C, 4.4; H, 4.4; H by evolution 1710, cm^3/g. Found: B, 42.6; C, 4.6; H, 4.5; H by evolution, 1723 cm^3/g.

Extraction of the benzene washings with several portions of petroleum ether (bp 38–51°) left an insoluble oil. Dilution of this oil with excess trimethylamine left a white gum which was digested in hot benzene to obtain 3 g of additional $CsB_{11}H_{11}CH$ for a total yield of 72%. The ^{11}B nmr spectrum is shown in Figure 8 and the infrared spectrum in Figure 10.

$B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ from $B_{10}H_{12}CH^-$.—$CsB_{10}H_{12}CH$ (3.8 g, 14.3 mmol) was heated *in vacuo* at 320–330° for 6.75 hr. The product was fractionally recrystallized to obtain two readily separated products. The less soluble was CsB_9H_9CH; the more soluble was $CsB_{11}H_{11}CH$. In a separate experiment $CsB_{10}H_{12}CH$ (0.502 g, 1.89 mmol) was heated at 325° for 4 hr. Hydrogen (1.98 mmol, 104%) was evolved.

$B_9H_9CCOOH^-$.—Seven milliliters of a solution of *n*-butyllithium in hexane (1.6 *M*) was added to a solution of CsB_9H_9CH (2.5 g, 10 mmol) in 75 ml of tetrahydrofuran in a nitrogen atmosphere. The resulting cloudy solution was refluxed for 10 min and then cooled. Ten grams of solid carbon dioxide was volatilized through a −78° trap into the reaction solution. Solids formed during this period. The mixture was filtered; the filter cake was dissolved in 20 ml of water. Excess tetrapropylammonium hydroxide was added and the mixture was filtered through Celite. Acidification of the filtrate with hydrochloric acid precipitated $(C_3H_7)_4NB_9H_9CCOOH$. Part was recrystallized from water for analysis; normal recrystallization was difficult and recrystallization of the remainder was accomplished by Soxhlet extraction with water for several days. The total yield was 1.0 g (29%). *Anal.* Calcd for $(C_3H_7)_4NB_9H_9CCOOH$: B, 27.8; C, 48.1; H, 10.9. Found: B, 27.5; C, 48.4; H, 11.1. Uv $\lambda_{max}^{CH_3CN}$ λ 225 (sh) (ϵ 1950). The infrared spectrum confirmed the presence of a carboxyl group.

$B_9H_9CSi(CH_3)_3^-$.—Ten milliliters of a 1.6 *M* solution of *n*-butyllithium in hexane was added to a solution of CsB_9H_9CH (1.5 g, 6 mmol) in 50 ml of glyme. The temperature rose to 55°. When it dropped to 50°, trimethylchlorosilane (2 ml, 15.8 mmol) was added. The mixture was evaporated to dryness; the residue was dissolved in a small amount of water and tetramethylammonium chloride was added to precipitate a white solid. Proton nmr suggested this was a mixture of $(CH_3)_4NB_9H_9CH$ and $(CH_3)_4NB_9H_9CSi(CH_3)_3$ in a ratio of 2.3:1, and the infrared spectrum was consistent with this. This mixture was fractionally recrystallized from aqueous alcohol; the silylated species was the more soluble and was not obtained analytically pure. The final fraction was analyzed. *Anal.* Calcd for $(CH_3)_4NB_9H_9CSi(CH_3)_3$: B, 36.6; C, 36.2; H, 11.3. Found: B, 35.0; C, 32.7, 34.2; H, 10.9, 11.2. The proton nmr spectrum of this material in CD_3CN had a peak for $(CH_3)_4N$ at τ 7.15 and one for $(CH_3)_3Si$ at τ 9.87 relative to external TMS. The peak ratios indicated about 96% purity. The ^{11}B nmr spectrum was very similar to that of $B_9H_9CH^-$, consistent with substitution on carbon (Figure 6).

$B_{11}H_{11}CSi(CH_3)_3^-$.—Three milliliters of an *n*-butyllithium solution (1.6 *M* in hexane) was added to $CsB_{11}H_{11}CH$ (0.38 g, 1.4 mmol) in dimethoxyethane (25 ml) in a nitrogen atmosphere. After the mixture was stirred for 2 min, trimethylchlorosilane (7.5 ml) was added and stirring was continued for 10 min. The mixture was filtered. The filtrate was evaporated and the residue was dissolved in water. Treatment with tetramethylammonium chloride precipitated a solid which was fractionally recrystallized from aqueous ethanol. The initial fractions were $(CH_3)_4NB_{11}H_{11}CH$; subsequent fractions were mixtures of $(CH_3)_4NB_{11}H_{11}CH$ and $(CH_3)_4NB_{11}H_{11}CSi(CH_3)_3$ as demonstrated by infared and proton nmr analyses. The final fraction had the highest percentage of silylated product. The nmr spectrum in CD_3CN exhibited a singlet at τ 6.45 ($(CH_3)_4N$, relative intensity 12) and one at τ 9.55 ($(CH_3)_3Si$, relative intensity 7). Greater purity was not obtained.

$C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$ and $C_6H_5CONHCB_{10}H_{11}$.—Solid $NaB_{10}H_{12}CN \cdot S(CH_3)_2$ (15 g, 65 mmol) was added in small portions with stirring to benzoyl chloride (100 ml) with cooling as needed to keep the temperature below 50°. After completion of the addition, stirring was continued 10 min and the mixture was filtered. The filter cake was extracted with six 100-ml portions of hot ethyl acetate. The filtrate was diluted with excess petroleum ether, causing the separation of an oil. The oil was dissolved in ethyl acetate. Slow concentration of the ethyl acetate solution caused the separation of 9.1 g (52%) of $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$. Further purification was achieved by dissolving this product (1.6 g) in hot acetonitrile (50 ml) followed by the addition of water until the solution became cloudy. Crystalline $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$ (1.2 g; mp softened at 150°, followed by resolidification and final melting at 191–192°) separated on cooling. *Anal.* Calcd for $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$: B, 34.5; C, 38.4; H, 7.4; N, 4.5; S, 10.2. Found: B, 34.7; C, 38.3; H, 7.1; N, 4.8; S, 10.2. Uv $\lambda_{max}^{CH_3CN}$ 225 (ϵ 14,000). The infrared spectrum includes absorptions for N–H, B–H, and C=O. No nitrile absorption is apparent.

Thermolysis of this compound (3.25 g) at 160–165° *in vacuo* for 3 days resulted in complete loss of methyl sulfide. *Anal.* Calcd for $C_6H_5NHCB_{10}H_{11}$: B, 43.0; C, 38.2; H, 6.8; N, 5.6. Found: B, 43.4; C, 38.2; H, 7.2; N, 5.4. Uv $\lambda_{max}^{CH_3CN}$ 283 (ϵ 14,200), 245 (ϵ 9250); dec pt 200–202°.

The isomeric formulation $C_6H_5CONH_2CB_{10}H_{10}$ is discounted for the product because the ^{11}B nmr spectrum of such a species should resemble that of $(CH_3)_3NCB_{10}H_{10}$.[7] There is no such resemblance; the ^{11}B spectrum of $C_6H_5CONH_2CB_{10}H_{11}$ is a complex multiplet. Possibly $C_6H_5CONHCB_{10}H_{11}$ has a structure in which the nitrogen is bridging to the boron atom which was bonded to methyl sulfide in the precursor $C_6H_5CONHCB_{10}H_{11}S(CH_3)_2$ (see Figure 1C).

$(B_{10}H_{10}CH)_2Cr^{3-}$.—Fifty milliliters of a solution of *n*-butyllithium (1.6 *M* in hexane) was added to a solution of $(CH_3)_3NHB_{10}H_{12}CH$ (3.0 g, 15.5 mmol) in 100 ml of tetrahydrofuran in a nitrogen atmosphere. The solution was cooled to 10° with an ice–water bath and 3 g (19 mmol) of chromium(III) chloride was added with stirring, resulting in a temperature rise to 28°. The cooling bath was removed and the mixture was allowed to stand overnight. The mixture was filtered to obtain a dark blue filter cake which was extracted with 50 ml of water. The extracts were filtered through Celite to get a dark blue filtrate which was treated with 15 ml of 50% aqueous cesium hydroxide. Filtration gave a dark blue solid which has not been identified and a red filtrate. Concentration of the red filtrate precipitated 1.2 g (11%) of $Cs_3(B_{10}H_{10}CH)_2Cr\cdot H_2O$ as a red solid which was recrystallized from water and dried at 80° under vacuum. *Anal.* Calcd for $Cs_3(B_{10}H_{10}CH)_2Cr\cdot H_2O$: B, 29.6; C, 3.3; H, 3.3. Found: B, 30.2; C, 3.5; H, 3.1. Uv $\lambda_{max}^{H_2O}$ 490 (ϵ 242), 375 (ϵ 1700), 390 (ϵ 23,600), 240 (ϵ 20,800). The infrared spectrum (Nujol mull) included major bands at 2500 (B–H), 1085, 1065, and 1015 cm^{-1} plus bands indicating water of hydration.

$(B_{10}H_{10}CH)_2Mn^{2-}$.—One hundred and fifty milliliters of *n*-butyllithium solution (1.6 *M* in hexane, 0.24 mol) was added to a solution of $(CH_3)_3NHB_{10}H_{12}CH$ (9 g, 46 mmol) in tetrahydrofuran (250 ml) at ambient temperature in a nitrogen atmosphere. The mixture was cooled in an ice–water bath and manganous chloride (9 g, 71 mmol) was added. The cooling bath was removed and the mixture was stirred for 1.5 hr. The supernatant liquid was decanted; the dark residue was dissolved in water (150 ml) and acidified with hydrochloric acid. Trimethylammonium chloride (15 g) was added. The resulting dark precipitate was removed and extracted with boiling water (100 ml). The insoluble portion was recrystallized twice from aqueous alcohol to obtain 2.3 g of $[(CH_3)_3NH]_2(B_{10}H_{10}CH)_2Mn$ as shiny black crystals. *Anal.* Calcd for $[(CH_3)_3NH]_2(B_{10}H_{10}CH)_2Mn$: C, 21.9; H, 9.7; B, 49.5; Mn, 12.6; N, 6.4. Found: C, 22.6; H, 9.5; B, 49.5; Mn, 11.7; N, 6.2. Uv $\lambda_{max}^{CH_3CN}$ 553 (ϵ ~970), 383 (ϵ ~9600), 340 (ϵ ~10,500), 270 (ϵ ~21,400). The extinction coefficients are approximate because fading occurred slowly in solution. The infrared spectrum (Nujol mull) included major bands at 3130 (N–H), 2500 (B–H), 1075, 1050, 995, and 975 (cation absorption) cm^{-1}. Allowing a sample of $[(CH_3)_3NH]_2(B_{10}H_{10}CH)_2Mn$ to stand in moist acetonitrile for several days resulted in complete fading of the initial dark color and deposition of MnO_2.

$(B_{10}H_{10}CNH_2)_2Mn^{2-}$.—One hundred and sixty milliliters of butyllithium solution (1.6 *M* in hexane, 0.26 mol) was added to a solution of $B_{10}H_{12}CNH_3$ (10 g, 67 mmol) in glyme (400 ml) at ambient temperature in a nitrogen atmosphere. The resulting mixture was cooled in an ice bath. Manganous chloride (6 g, 48 mmol) was added and the mixture was refluxed for 2 hr. The glyme was decanted to leave a dark residue which was extracted with water (80 ml). Tetramethylammonium chloride (15 g) was added to the extract, precipitating a gummy solid. Extraction with boiling water gave crystalline solid "A" plus a residue which was extracted with aqueous alcohol to obtain crystalline solid B. Solids A (0.6 g) and B (1.9 g) were identical by infrared analysis. *Anal.* Calcd for $[(CH_3)_4N]_2(B_{10}H_{10}CNH_2)_2Mn$: C, 23.6; H, 9.1; B, 42.6; Mn, 10.8. Found: C, 24.4; H, 9.7; B, 43.2; Mn, 11.5. Uv $\lambda_{max}^{CH_3CN}$ 545 (ϵ ~1250), 400 (ϵ ~9400), 348 (ϵ ~8400), 277 (ϵ ~22,000). The extinction coefficients are approximate because slow fading occurred in solution. Allowing a sample of $[(CH_3)_4N]_2(B_{10}H_{10}CNH_2)_2Mn$ to stand in moist acetonitrile for several days resulted in complete fading of the initial dark color and deposition of MnO_2.

$(B_{10}H_{10}CH)_2Fe^{3-}$.—A solution of $(CH_3)_3NHB_{10}H_{12}CH$ (3.0 g, 15.5 mmol) in 100 ml of THF was treated with 50 ml of a 1.6 *M* hexane solution of *n*-butyllithium in a nitrogen atmosphere. The temperature rose to about 55° and a grease separated. The mixture was cooled to 5° in an ice bath and 3 g (27.6 mmol) of anhydrous ferrous chloride was added in one portion with stirring. The cooling bath was removed after 1 hr and the mixture was stirred overnight. The tetrahydrofuran was decanted and the residue was washed once with a small amount of tetrahydrofuran. The residue was then extracted with 100 ml of water. The extracts were filtered and $FeCl_3$ (0.2 g) was added to the filtrate. Air was bubbled through for 1 hr and the mixture was filtered through Celite. The filtrate was treated with 25 ml of 50% aqueous cesium hydroxide solution and chilled to precipitate a dark crystalline solid. This was recrystallized from water to obtain 3.6 g, 32%, of $Cs_3(B_{10}H_{10}CH)_2Fe\cdot H_2O$ as large shiny black crystals. *Anal.* Calcd for $Cs_3(B_{10}H_{10}CH)_2Fe\cdot H_2O$: B, 29.4; C, 3.3; H, 3.3; Fe, 7.6. Found: B, 29.2; C, 3.4; H, 3.4; Fe, 8.0. Uv $\lambda_{max}^{H_2O}$ 575 (ϵ 266), 372 (ϵ 1100), 274 (ϵ 21,200). Polarographic reduction in water occurred irreversibly at −1.3 V (*vs.* sce) and oxidation at greater than −0.2 V. The infrared spectrum (Nujol mull) confirmed the presence of water of hydration and included major bands at 2500 (B–H), 1090, 1050, and 1020 cm^{-1}.

$(B_{10}H_{10}CNH_3)_2Fe^{-}$.—Fifty milliliters of *n*-butyllithium solution (1.6 *M* in hexane) was added to a solution of $B_{10}H_{12}CNH_3$ (3.0 g, 20 mmol) in 100 ml of tetrahydrofuran in a nitrogen atmosphere. The resulting mixture was cooled to 7° in a water–ice bath and $FeCl_2$ (3.0 g, 24 mmol) was added with stirring. The ice bath was removed and stirring was continued for 1 hr. The supernatant liquid was decanted and the dark residue was washed once with a small amount of tetrahydrofuran. The residue was then dissolved in 40 ml of water and the solution was filtered through Celite. The filtrate was acidified with hydrochloric acid and the addition of excess tetramethylammonium chloride then precipitated 2.8 g (66%) of dark green $(CH_3)_4N(B_{10}H_{10}CNH_3)_2Fe$ which was recrystallized from water. *Anal.* Calcd for $(CH_3)_4N(B_{10}H_{10}CNH_3)_2Fe$: B, 51.0; C, 17.0; H, 9.0; N, 9.9; Fe, 13.1. Found: B, 50.0; C, 17.1; H, 9.5; N, 9.8; Fe, 13.3. Uv $\lambda_{max}^{H_2O}$ 585 (ϵ 270), 400 (sh) (ϵ 960), 292 (ϵ 19,300), 273 (ϵ 20,600).

$(B_{10}H_{10}CH)_2Co^{3-}$.—Three grams (15.5 mmol) of $(CH_3)_3NHB_{10}H_{12}CH$ was dissolved in 75 ml of 50% aqueous sodium hydroxide. This solution was added to a solution of $CoCl_2\cdot 6H_2O$ (12 g, 50 mmol) in 25 ml of water and the resulting mixture was heated 10 min on a steam bath with occasional agitation. Then it was diluted with 100 ml of water and filtered through Celite to obtain a dark yellow filtrate. The addition of 30 ml of 50% aqueous cesium hydroxide solution to this filtrate precipitated a dingy yellow solid which was recrystallized from water. The yield of $Cs_3(B_{10}H_{10}CH)_2Co\cdot H_2O$ was 3.8 g (66%). The analytical sample was recrystallized a second time. *Anal.* Calcd for $Cs_3(B_{10}H_{10}CH)_2Co\cdot H_2O$: B, 29.3; C, 3.2; H, 3.2; Co, 8.0. Found: B, 29.6; C, 3.1; H, 3.3; Co, 8.0. Uv $\lambda_{max}^{H_2O}$ 420 (ϵ 360), 275 (ϵ 41,300). The ^{11}B nmr spectrum consisted of a poorly resolved multiplet. This salt did not reduce silver nitrate even in boiling water; instead an insoluble yellow solid, presumably the corresponding silver salt, precipitated. The infrared spectrum (Nujol mull) confirmed the presence of water of hydration and included major bands at 2480 (B–H), 1090, 1050, and 1015 cm^{-1}.

The $(B_{10}H_{10}CH)_2Co^{3-}$ anion can also be prepared from *n*-butyllithium, $(CH_3)_3NHB_{10}H_{12}CH$, and cobalt chloride in tetrahydrofuran as described for the preparation of $(B_{10}H_{10}CH)_2Fe^{3-}$, but the aqueous preparation is simpler.

$(B_{10}H_{10}CH)_2Co^{2-}$.—A solution of $(NH_4)_4Ce(SO_3)_4\cdot 2H_2O$ (8 g, 7 mmol) in water (50 ml) and concentrated sulfuric acid (2 ml) was added to $Cs_3(B_{10}H_{10}CH)_2Co\cdot H_2O$ (3.9 g, 5.3 mmol) in water (100 ml). An immediate blue-green color resulted. The solution was filtered. Tetramethylammonium hydroxide was added but not in sufficient amount to basify the solution. A blue precipitate of $[(CH_3)_4N]_2(B_{10}H_{10}CH)_2Co$ formed. This was removed by filtration; the filtrate (yellow) was treated with more $(NH_4)_2Ce(SO_4)_4$ to precipitate additional $[(CH_3)_4N]_2(B_{10}H_{10}CH)_2Co$. The crude product was dissolved in acetonitrile. The solution was filtered and concentrated slowly at room temperature. Black crystals of $[(CH_3)_4N]_2(B_{10}H_{10}CH)_2Co$ separated and were dried at room temperature *in vacuo*. *Anal.* Calcd for $[(CH_3)_4N]_2(B_{10}H_{10}CH)_2Co$: C, 25.5; H, 9.8; B, 46.0; N, 6.0; Co, 12.6. Found: C, 25.9; H, 9.9; B, 45.4; N, 6.2; Co, 12.2. Uv $\lambda_{max}^{CH_3CN}$ 627 (ϵ 141), 410 (ϵ 590), 285 (ϵ 31,000). The infrared spectrum (Nujol mull) included major bands at 2520, 1085, 1040, 995, and 945 (cation absorption) cm^{-1}. The ^1H nmr spectrum in CD_3CN had a greatly broadened peak for $(CH_3)_4N$, shifted to higher field than normal, consistent with the presence of a paramagnetic species.

$(B_{10}Cl_{7.5}H_{2.5}CH)_2Co^{3-}$.—A solution of $Cs_3(B_{10}H_{10}CH)_2Co \cdot H_2O$ (6.8 g, 9.2 mmol) in acetonitrile (100 ml) was cooled to 5° in an ice–water bath. Chlorine was bubbled through the solution with continued cooling. The temperature rose to 20°; chlorination was continued until the temperature fell to 10°. The solution was then evaporated to dryness. The residual solid was recrystallized twice from water and dried at 80° *in vacuo* to obtain 2.4 g of $Cs_3(B_{10}Cl_{7.5}H_{2.5}CH)_2Co \cdot H_2O$ as a moderately water-soluble orange solid. *Anal.* Calcd for $Cs_3(B_{10}Cl_{7.5}H_{2.5}CH)_2Co \cdot H_2O$: B, 17.2; Cl, 42.4; Co, 4.7. Found: B, 18.0; Cl, 43.3; Co, 5.5. Uv $\lambda_{max}^{H_2O}$ 330 (ϵ 42,000).

$(B_{10}H_{10}CNH_3)_2Co^-$.—A solution of $B_{10}H_{12}CNH_3$ (3.0 g, 20 mmol) in 25 ml of 50% aqueous sodium hydroxide was added to a solution of $CoCl_2 \cdot 6H_2O$ (11 g, 47 mmol) in 15 ml of water. The mixture was allowed to stand for 2 min with occasional swirling and stirring. It was then diluted with 30 ml of water and filtered through Celite and washed down with water. The volume of combined filtrate plus washings was 90 ml. This solution was cooled in an ice bath and acidified with 20 ml of 12 *M* hydrochloric acid. Ten grams of tetramethylammonium chloride was added, precipitating a yellow solid. This was recrystallized from 5% aqueous tetramethylammonium hydroxide to obtain $[(CH_3)_4N]_2B_{10}H_{10}CNH_2CoB_{10}H_{10}CNH_8$. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}H_{10}CNH_2CoB_{10}N_{10}CNH_3$: C, 23.9; H, 9.9; N, 11.2; Co, 11.8. Found: C, 23.9; H, 10.2; N, 11.0; Co, 11.9. Uv $\lambda_{max}^{CH_3CN}$ 422 (ϵ 460), 281 (ϵ 42,000).

Passage of this salt through a strongly acidic ion-exchange column followed by neutralization of the effluent to pH 5.5 with tetramethylammonium hydroxide precipitated $(CH_3)_4N(B_{10}H_{10}CNH_3)_2Co$. *Anal.* Calcd for $(CH_3)_4N(B_{10}H_{10}CNH_3)_2Co$: C, 16.9; H, 8.9; N, 9.8. Found: C, 16.6; H, 9.0; N, 9.7. Uv $\lambda_{max}^{H_2O}$ 426 (ϵ 358), 284 (ϵ 34,400).

$(B_{10}H_{10}CH)_2Ni^{2-}$.—A solution of nickel(II) chloride hexahydrate (12 g, 50 mmol) in 25 ml of water was added to a solution prepared from $(CH_3)_3NHB_{10}H_{12}CH$ (3.0 g, 15.5 mmol) and 75 ml of 50% sodium hydroxide. The resulting mixture was heated for 10 min on a steam bath with occasional agitation. It was then diluted with 100 ml of water and filtered through Celite to obtain a dark yellow filtrate. The addition of 30 ml of 50% aqueous cesium hydroxide to this filtrate precipitated a dark solid. Recrystallization from water gave 1.5 g of a dark solid. Passage of air for 1 hr through the filtrate from the isolation of the crude product precipitated additional material which was combined with the recrystallized product. Recrystallization of the combined solids from water gave 1.1 g (42%) of $Cs_2(B_{10}H_{10}CH)_2Ni$ as grayish black needles. *Anal.* Calcd for $Cs_2(B_{10}H_{10}CH)_2Ni$: B, 35.8; C, 4.1; H, 3.7; Ni, 10.3. Found: B, 35.6; C, 3.5; H, 3.3; Ni, 10.3. Uv $\lambda_{max}^{H_2O}$ 290 (ϵ 38,400). The infrared spectrum (Nujol mull) included major bands at 2500 (B–H), 1090, 1045, and 1010 cm^{-1}.

Pure $Cs_2(B_{10}H_{10}CH)_2Ni$ is yellow-orange. However, unless special precautions are taken, there ususally is enough Ni(III) salt present to give a dark color to the final product, as in the above preparation, even though the product is analytically pure. Complete oxidation to a bright yellow-orange salt can be achieved in any of several ways: several recrystallizations from water using decolorizing carbon, the slow addition of dilute hydrogen peroxide to a solution of the product until the color lightens, or passing air through an aqueous solution of the product with a trace of ferric chloride present.

The $(B_{10}H_{10}CH)_2Ni^{2-}$ anion can also be prepared from $(CH_3)_3NHB_{10}H_{12}CH$, *n*-butyllithium, and nickel chloride in tetrahydrofuran, as described above for the preparation of $(B_{10}H_{10}CH)_2Fe^{3-}$, but the aqueous preparation is simpler.

$(B_{10}H_{10}CNH_3)_2Ni$.—A solution of $B_{10}H_{12}CNH_3$ (10 g, 6.7 mmol) in 20% aqueous sodium hydroxide (100 ml) was added to a solution of $NiCl_2 \cdot 6H_2O$ (38 g, 0.16 mol) in water (50 ml). This mixture was heated on a steam bath for 30 min and then filtered through Celite. The filtrate was mixed with 50% aqueous cesium hydroxide solution to precipitate $Cs_2(B_{10}H_{10}CNH_2)_2Ni$. This was recrystallized from water and then passed, in aqueous solution, through a strongly acidic ion-exchange column. The effluent was evaporated to obtain 4.8 g (40%) of $(B_{10}H_{10}CNH_3)_2Ni$ as a crystalline orange solid. The analytical sample was recrystallized from water and dried at 80° *in vacuo*. *Anal.* Calcd for $(B_{10}H_{10}CNH_3)_2Ni$: C, 6.8; H, 7.4; B, 61.4; Ni, 16.6. Found: C, 7.0; H, 7.6; B, 60.8; Ni, 16.2. Uv $\lambda_{max}^{CH_3CN}$ 410 (ϵ 2170), 318 (ϵ 25,700), 282 (ϵ 24,400).

$[B_{10}H_{10}CNH(CH_3)_2]_2Ni$.—Dimethyl sulfate (12 g, 95 mmol) was added to a solution of $(B_{10}H_{10}CNH_3)_2Ni$ (5 g, 14 mmol) in 10% aqueous sodium hydroxide (100 ml). The mixture was stirred for 3 hr to obtain a dark red solution. Acidification with hydrochloric acid precipitated $[B_{10}H_{10}CNH(CH_3)_2]_2Ni$. This was redissolved in 100 ml of water plus 12 ml of 10% aqueous sodium hydroxide to obtain a dark red solution. This was filtered; 35% of the filtrate was treated with 50% cesium hydroxide solution to precipitate $CsB_{10}H_{10}CN(CH_3)_2NiB_{10}H_{10}CNH(CH_3)_2$ (0.5 g, 19%). This recrystallized from water as a yellow crystalline solid. *Anal.* Calcd for $CsB_{10}H_{10}CN(CH_3)_2NiB_{10}H_{10}CNH(CH_3)_2$: C, 13.4; H, 6.0; N, 6.9. Found: C, 13.3; H, 6.1; N, 5.2.

The remainder of the basic solution was acidified with dilute hydrochloric acid to obtain 2.5 g (67%) of $[B_{10}H_{10}CNH(CH_3)_2]_2Ni$, an orange solid which was washed with water and dried at 80° *in vacuo*. *Anal.* Calcd for $[B_{10}H_{10}CNH(CH_3)_2]_2Ni$: C, 17.6; H, 8.4; B, 53.0; N, 6.8; Ni, 14.3. Found: C, 17.7; H, 8.4; B, 53.0; N, 7.2; Ni, 14.3. Uv $\lambda_{max}^{CH_3CN}$ 437 (ϵ 2100), 330 (ϵ 16,500), 288 (ϵ 28,000).

$(B_{10}H_{10}CNH_2CH_2C_6H_5)_2Ni$.—A solution of $NiCl_2 \cdot 6H_2O$ (3.7 g, 15.5 mmol) in water (5 ml) was added to $B_{10}H_{12}CNH_2(CH_2C_6H_5$ (1 g, 4.2 mmol) in 20% aqueous sodium hydroxide (25 ml). The mixture was heated on a steam bath for 4 min and then filtered through Celite. The acidification of the filtrate precipitated 0.8 g of an orange solid which was recrystallized twice from aqueous alcohol. *Anal.* Calcd for $(B_{10}H_{10}CNH_2CH_2C_6H_5)_2Ni$: C, 36.0; H, 7.2; N, 5.2. Found: C, 35.5; H, 7.8; N, 5.0. Uv $\lambda_{max}^{CH_3CN}$ 427 (ϵ 1990), 318 (ϵ 21,000), 287 (ϵ 22,700).

$(B_{10}H_{10}COH)_2Ni^{2-}$.—Hydrochloric acid (12 *M*, 5 ml, 60 mmol) was added dropwise with stirring to a solution of $(B_{10}H_{10}CNH_3)_2Ni$ (1 g, 2.8 mmol) and sodium nitrite (5 g, 72 mmol) in water (75 ml). During the addition the temperature rose to 30°. Stirring was continued for 30 min. Tetramethylammonium chloride (2 g, 19 mmol) was added and the resulting yellow-orange precipitate was recrystallized from water to obtain 0.9 g (64%) of $[(CH_3)_4N]_2(B_{10}H_{10}COH)_2Ni$. Infrared analysis confirmed the presence of the hydroxyl group. *Anal.* Calcd for $[(CH_3)_4N]_2(B_{10}H_{10}COH)_2Ni$: C, 24.0; H, 9.2; N, 5.6; Ni, 11.8. Found: C, 24.0; H, 9.4; N, 5.7; Ni, 11.7. Uv $\lambda_{max}^{CH_3CN}$ 302 (ϵ 41,700).