Novel 13-Vertex Metallocarborane Complexes Formed by Polyhedral Expansion of 1,2-Dicarba-*closo*-dodecaborane(12) ($1,2\text{-}B_{10}C_2H_{12}$)

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Abstract: 1,2-Dicarba-*closo*-dodecaborane(12) was found to undergo a two-electron reduction with sodium metal in tetrahydrofuran to form a $B_{10}C_2H_{12}^{2-}$ ion. This ion serves as a ligand in the formation of a variety of transition metal complexes which include $[(\pi\text{-}C_5H_5)M(\pi\text{-}B_{10}C_2H_{12})]$ (M = Fe(III) and Co(III)), $[(\pi\text{-}B_{10}C_2H_{12})_2M']^{n-}$ (M′ = Co(III), Fe(II), and Ni(II)), and $[(\pi\text{-}B_{10}C_2H_{12})M''(CO)_3]^{2-}$ (M″ = Mo and W). The preparation, characterization, and structures of these complexes are discussed. In each case, a closo polyhedral structure is proposed with the metal atom located at one of the 13 vertices.

The preparation of the $B_{10}C_2H_{12}^{2-}$ ion by reduction of the corresponding *closo*-carborane with sodium naphthalide and the subsequent formation of the metallocarborane complex, $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$, have been reported in a recent communication.[2] We now wish to report a series of transition metal complexes based upon the $B_{10}C_2H_{12}^{2-}$ ion.

The method of preparing metallocarborane ligands by reduction of the parent *closo*-carborane has been termed "polyhedral expansion" since the resulting transition metal complexes contain a polyhedral framework with one more vertex than the parent carborane—the new vertex presumably being occupied by the transition metal.[3] π-Cyclopentadienyl cobalt complexes of $B_6C_2H_8^{2-}$, $B_6C_2H_8^{4-}$, $B_8C_2H_{10}^{2-}$, and $B_8C_2H_{10}^{4-}$ have been prepared by this method,[3-5] but those of the $B_{10}C_2H_{12}^{2-}$ ion are structurally unique. Previously, the largest known polyhedral carborane derivatives have been the 12-atom icosahedral species exemplified by the $B_{10}C_2H_{12}$ carboranes and the transition metal complexes of the $B_9C_2H_{11}^{2-}$ dicarbollide ion.[6-8] The complexes of transition metals with the $B_{10}C_2H_{12}^{2-}$ ion exhibit metallocarborane polyhedra containing, for the first time, 13 vertices.

Nomenclature. The nomenclature associated with the transition metal complexes of the isomeric $B_{10}C_2H_{12}^{2-}$ ions conforms to the recently adopted rules.[9] In naming these complexes, we have chosen to follow the convention that a *nido*-carborane ligand is bonded to the metal. Accordingly, the systematic name for $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$, Figure 1, is π-cyclopentadienyl-π-dodecahydro-7,9-dicarba-*nido*-dodecaboratocobalt. In each of the complexes reported here, the metal atom presumably occupies vertex number 13 of the resulting 13-atom closo polyhedron.

Preparation and Characterization of the π-Cyclopentadienyl-π-$B_{10}C_2H_{12}$ Complexes of Iron and Cobalt. The reaction of the $B_{10}C_2H_{12}^{2-}$ ion with an excess of sodium cyclopentadienide and an excess of either anhydrous $FeCl_2$ or $CoCl_2$ resulted in the formation of π-cyclopentadienyl-π-dodecahydrodicarba-*nido*-dodecaboratocobalt(III) or -iron(III). The isolated cobalt complex contains a formal cobalt(III) due to an oxidation of cobalt(II) to cobalt(III) with the concomitant formation of a black, insoluble, ferromagnetic powder presumed to be cobalt metal, whereas the iron complex must be air-oxidized to the formal iron(III) species.

$$\begin{array}{c} C_5H_5^- + B_{10}C_2H_{12}^{2-} + MCl_2 \longrightarrow (\pi\text{-}C_5H_5)M^{II}(\pi\text{-}B_{10}C_2H_{12}) \\ (\pi\text{-}C_5H_5)M^{III}(\pi\text{-}B_{10}C_2H_{12}) \xleftarrow{-e} \end{array}$$

The violet $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}B_{10}C_2H_{12})$ (I) is paramagnetic, having an effective magnetic moment of 2.12 BM, and is easily reduced (Table I) with aqueous sodium borohydride to an orange anionic iron(II) species.

Table I. Reduction Potentials[a] for the $\pi\text{-}C_5H_5\text{-}\pi\text{-}B_{10}C_2H_{12}$ and $(\pi\text{-}B_{10}C_2H_{12})_2$ Metal Complexes

Compound	$E_{1/2}$ *vs.* sce	
	$M^{IV} + 2e^- \rightarrow M^{II}$	$M^{III} + e^- \rightarrow M^{II}$
I		+0.16
II		−0.72
III		−1.15
IV		−1.16
V		−0.33
VI		−0.02
VII	−0.03	

[a] Cyclic voltammetry in acetonitrile with 0.1 *F* tetraethylammonium perchlorate as supporting electrolyte, platinum button electrode.

The 60-MHz ^1H nmr spectrum (Table II) of the diamagnetic $[(\pi\text{-}C_5H_5)Fe^{II}(\pi\text{-}B_{10}C_2H_{12})]^-$ ion consisted of a sharp singlet of area 5 and a single broad resonance of area 2 which were assigned to the five equivalent cyclopentadienyl protons and to two equivalent polyhedral C–H units, respectively. The 80.5-MHz ^{11}B nmr spectrum (Figure 2 and Table III) exhibited seven doublets of area ratio 1:1:1:1:2:2:2 which indicated

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[1] National Science Foundation Trainee, 1968–1971; National Defense Education Act Title IV Predoctoral Fellow, 1971–1972.

[2] G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 2541 (1971).

[3] W. J. Evans and M. F. Hawthorne, *ibid.*, **93**, 3063 (1971).

[4] G. B. Dunks and M. F. Hawthorne, *ibid.*, **92**, 7213 (1970).

[5] W. J. Evans and M. F. Hawthorne, in preparation.

[6] M. F. Hawthorne, D. C. Young, T. A. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

[7] H. W. Ruhle and M. F. Hawthorne, *Inorg. Chem.*, **7**, 2279 (1968).

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[9] "Nomenclature of Boron Compounds," *Inorg. Chem.*, **7**, 1945 (1968).

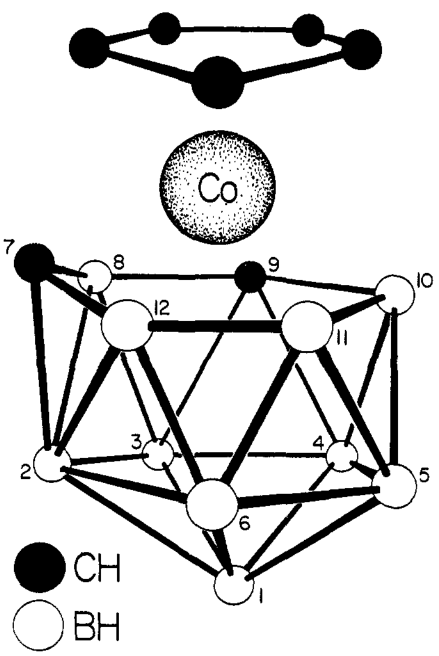

Figure 1. The structure of π-cyclopentadienyl-π-dodecahydro-7,9-dicarba-*nido*-dodecaboratocobalt, $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}7,9\text{-}B_{10}C_2H_{12})$.

Table II. ^1H Nmr Data for the π-$B_{10}C_2H_{12}$ Metal Complexes

Compound[a]	Resonance, τ[e] (rel area)	Assignment
I[b]	Sharp singlet, 5.80 (5)	Cyclopentadienyl protons
	Broad singlet, 7.00 (2)	Carborane C–H
II	Sharp singlet, 4.48 (5)	Cyclopentadienyl protons
	Broad singlet, 5.57 (2)	Carborane C–H
III	Sharp singlet, 4.48 (5)	Cyclopentadienyl protons
	Broad singlet, 5.10 (1)	Carborane C–H
	Broad singlet, 7.08 (1)	Carborane C–H
IV	Sharp singlet, 4.54 (5)	Cyclopentadienyl protons
	Broad singlet, 5.32 (1)	Carborane C–H
	Broad singlet, 6.60 (1)	Carborane C–H
V[c]	Broad singlet, 5.42	Carborane C–H
VI[c]	Broad singlet, 6.84	Carborane C–H
VII[d]	Broad singlet, 6.09	Carborane C–H
VIII[c]	Broad singlet, 6.70	Carborane C–H
IX[c]	Broad singlet, 7.67	Carborane C–H

[a] In acetone-d_6. [b] Reduced to the Fe^{II} complex. [c] Sodium salt. [d] Oxidized to the Ni^{IV} complex. [e] Relative to tetramethylsilane.

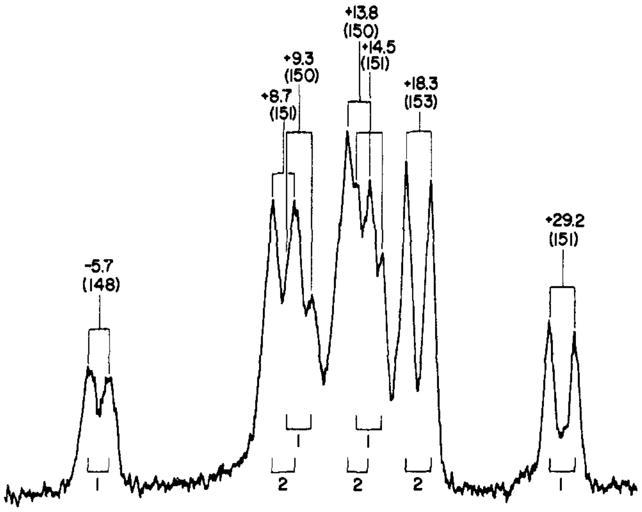

Figure 2. The 80.5-MHz ^{11}B nmr spectrum of $[(\pi\text{-}C_5H_5)Fe^{II}(\pi\text{-}B_{10}C_2H_{12})]^-$ taken in acetone. Chemical shifts (parts per million relative to $BF_3\cdot O(C_2H_5)_2$) and coupling constants (hertz) are indicated. Relative areas appear beneath the peaks.

that the carborane framework consisted of four unique boron atoms and three nonequivalent pairs of boron atoms.

The elemental analysis of I is given in Table IV. The electronic and infrared spectra are given in Tables V and VI, respectively.

The reaction of NaC_5H_5 and $Na_2B_{10}C_2H_{12}$ with $CoCl_2$ resulted in a product having the formulation $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$ (II). The red II was found to undergo a thermal rearrangement to an orange isomer, III, in hexane at reflux and the orange isomer further rearranged to a red-orange isomer, IV, in benzene at reflux. In the solid state, both II and III were successively converted to IV upon heating and then melted at 250–251°. Isomers II, III, and IV exhibited virtually identical mass spectra with cutoffs at *m/e* 270 corresponding to the $^{11}B_{10}{}^{12}C_7{}^1H_{17}{}^{59}Co^+$ ion. The elemental analyses, electronic spectra, and infrared spectra for the three products are shown in Tables IV, V, and VI, respectively.

The 60-MHz ^1H nmr spectrum, Table II, of the red isomer, II, exhibited a sharp singlet of area 5 assigned to the cyclopentadienyl protons and a broad singlet of area 2 assigned to two equivalent carborane C–H units. The spectra of both III and IV showed, in addition to the sharp singlet of area 5, two broad singlets of area 1, assigned to the two types of nonequivalent carborane C–H units.

The 80.5-MHz ^{11}B nmr spectrum, Table III, of II consisted of doublets of area ratio 1:1:1:1:2:2:2 again suggesting a carborane framework with three unique pairs and four unique boron atoms. The ^{11}B nmr spectrum of the orange isomer, III, contained eight doublets of area ratio 1:1:1:1:1:1:2:2. Since we can envisage no structure with nonequivalent carborane C–H units and two pairs of equivalent boron atoms, we feel that the two doublets of area 2 arise from the coincidental overlap of four area 1 resonances. The spectrum of the red-orange isomer, IV, contained ten doublets of equal area.

The above data suggest that the red, orange, and red-orange products are indeed structural isomers of one another with II being more symmetrical than either III or IV. The three isomers probably retain the gross configuration of 13-atom polyhedra and differ from each other only in the positions of the carbon atoms within the polyhedral framework. The nmr data are insufficient to assign definitely the positions of the carbon atoms in II, III, and IV. X-Ray diffraction studies for III and IV are in progress.

The X-ray crystal structure[10] of II indicates that the complex exists as a pair of enantiomers with the carbon atoms located at positions 7 and 9 or 7 and 11. The rapid equilibration of these two enantiomers at room temperature is consistent with the observed nmr spectra since the molecule would then exhibit a plane of symmetry on a time averaged basis. The low-temperature 80.5-MHz ^{11}B nmr spectra, Figure 3, of II shows

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(10) We are grateful to Professor Melvyn Churchill for informing us of these results prior to publication.

Table III. The 80.5-MHz ^{11}B Nmr Spectra of the π-$B_{10}C_2H_{12}$ Metal Complexes[a]

Compound	Rel intens	Chemical shifts, δ^e (J_{B-H} in Hz)
I[b]	1:2:1:2:1:2:1	−5.7 (148), +8.7 (151), +9.3 (150), +13.8 (150), +14.5 (151), +18.3 (153), +29.2 (151)
II	1:2:1:2:1:2:1	−12.9 (135), −1.0 (135), −0.4 (134), +4.2 (145), +6.2 (170), +11.1 (145), +16.4 (153)
III	1:1:1:1:1:2:2:1	−21.2 (140), −8.0 (138), −6.3 (149), −4.7 (140), +2.5 (170), +6.1 (170), +8.3 (161), +12.8 (153)
IV	1:1:1:1:1:1:1:1:1:1	−7.9 (145), −5.4 (169), −3.5 (145), −2.4 (161), +3.6 (145), +7.9 (145), +9.3 (169), +12.5 (145), +14.9 (145), +16.9 (145)
V	1:3:2:1:2:1	−17.9 (151), −4.5 (127),[c] +1.9 (151), +4.0 (172), +10.0 (158), +14.3 (162)
VI	1:2:1:3:2:1	−8.3 (127), +4.9 (130), +9.1 (141), +11.3 (134),[c] +17.2 (140), +25.7 (148)
VII[d]	1:1:1:1:4:2	+2.7 (147), +6.7 (174), +9.0 (141), +11.3 (154), +13.3 (161),[c] +16.5 (181)
VIII	1:2:1:3:2:1	−1.4 (130), +1.2 (148), +3.7 (138), +8.3 (134),[c] +14.7 (127), +22.6 (145)
IX	2:1:1:3:2:1	−2.4 (140), −1.0 (136), +4.6 (137), +6.9 (130),[c] +14.7 (134), +20.5 (141)

[a] Determined in acetone. [b] Reduced to Fe^{II}. [c] Overlapping doublets. [d] Oxidized to Ni^{IV}, acetonitrile solution. [e] Relative to $BF_3 \cdot O(C_2H_5)_2$.

Table IV. Elemental Analyses

Compound		% C	% H	% B	% N	% Metal
I	Calcd	31.67	6.41	40.83		21.07
	Found	31.75	6.24	39.95		21.29
II	Calcd	31.33	6.34	40.35		21.98
	Found	31.61	6.88	40.12		21.76
III	Calcd	31.33	6.34	40.35		21.98
	Found	31.52	6.55	39.77		21.86
VI	Calcd	31.33	6.34	40.35		21.98
	Found	31.36	6.50	40.20		21.85
V	Calcd	30.19	9.22	45.28	2.94	12.37
	Found	29.96	9.43	45.54	2.88	12.13
VI	Calcd	39.73	10.59	35.76	4.63	9.27
	Found	39.93	10.74	35.98	4.48	9.11
VII	Calcd	39.51	10.62	35.59	4.61	9.67
	Found	39.43	10.67	35.71	4.73	9.78
IX	Calcd	43.75	7.64	18.75	4.86	16.67
	Found	43.54	7.94	18.59	4.65	16.96

Table V. Electronic Spectra of the π-(C_5H_5)-π-$B_{10}C_2H_{12}$ and $(\pi\text{-}B_{10}C_2H_{12})_2$ Metal Complexes

	λ_{max}, mμ (ϵ)[a]
I	488 (233) sh, 419 (336) sh, 259 (7410), 234 (7100)
II	450 (465), 296 (8850), 256 (17,900), 230 (13,000) sh
III	446 (490), 285 (8400), 254 (26,800), 225 (9100) sh
IV	475 (516), 279 (10,500), 252 (20,000), 225 (11,000) sh
V	588 (254), 300 (16,600), 262 (21,200) sh, 235 (26,800)
VI	498 (771), 362 (4740), 287 (24,200), 235 (32,600)
VII	492 (976) sh, 390 (9600), 264 (13,300), 231 (14,500) sh

[a] In spectroquality acetonitrile.

Table VI. Infrared Spectra (cm^{-1}, Nujol Mull)

I	3050 (m), 2517 (s), 1237 (w), 1190 (w), 1150 (w), 1109 (m), 1086 (w), 1034 (w), 1007 (m), 985 (w), 934 (w), 847 (s), 773 (w)
II	3045 (m), 2501 (s), 1419 (m), 1409 (m), 1376 (m), 1191 (w), 1122 (w), 1090 (m), 1062 (m), 1022 (m), 1005 (s), 983 (m), 897 (m), 878 (w), 856 (s), 842 (s), 778 (m), 768 (m), 739 (m), 727 (m)
III	3072 (m), 2521 (s), 1195 (w), 1158 (w), 1125 (w), 1081 (w), 1024 (m), 995 (m), 984 (m), 851 (m), 843 (m), 778 (w)
IV	3060 (m), 2515 (s), 1421 (m), 1288 (w), 1133 (w), 1049 (m), 993 (m), 981 (m), 948 (w), 900 (w), 851 (m), 828 (m), 778 (w), 741 (w)
V	2569 (s), 1200 (w), 1176 (m), 1154 (w), 1127 (w), 1090 (m), 1071 (w), 1048 (m), 1029 (m), 1006 (s), 975 (m), 950 (w), 896 (w), 878 (w), 856 (w), 832 (w), 785 (m), 734 (w)
VI	2569 (s), 1284 (w), 1200 (w), 1261 (m), 1245 (w), 1221 (w), 1093 (w), 1074 (w), 1055 (w), 1045 (w), 1024 (w), 991 (m), 971 (w), 856 (w), 884 (w), 777 (m), 732 (w), 717 (w)
VII	2501 (s), 1308 (w), 1184 (m), 1155 (w), 1091 (w), 1082 (w), 1031 (m), 1005 (m), 978 (m), 908 (w), 889 (w), 823 (w), 796 (w), 727 (m)
VIII	2488 (s), 1990 (w), 1890 (s), 1735 (s), 1304 (w), 1187 (w), 1165 (m), 1087 (w), 1027 (w), 1002 (m), 788 (w), 725 (w)
IX	2049 (s), 1895 (s), 1780 (s), 1296 (w), 1254 (w), 1176 (m), 1154 (m), 1069 (w), 1017 (w), 1008 (w), 1000 (m), 990 (m), 813 (w), 787 (w), 757 (w), 727 (w), 718 (w)

that an apparent symmetry plane prevails down to −30°. At −90°, the molecule has become asymmetric, presumably having been "frozen" into a mixture of the 7,9 and 7,11 isomers.

At temperatures above −30°, the interconversion between the 7,9 and 7,11 isomers is apparently quite rapid. The mechanism that we propose for this interconversion is shown in Figure 4 and involves a twofold, diamond-square-diamond rearrangement[11] which may be either stepwise or concerted. In either case, a time-averged structure would contain a plane of symmetry.

Preparation and Characterization of the $(\pi\text{-}B_{10}C_2H_{12})_2$ Metal Complexes. The preparation of the π-cyclopentadienyl-π-$B_{10}C_2H_{12}$ metal complexes for both cobalt(III) and iron(III), described above, suggested that $(\pi\text{-}B_{10}C_2H_{12})_2$ derivatives might also be prepared. In the latter case, the metal atom would simultaneously occupy the 13th vertex in two 13-atom carborane polyhedra. Such complexes were prepared with formal cobalt(III), iron(II), and nickel(II) according to the general equation

$$2B_{10}C_2H_{12}^{2-} + M^n \longrightarrow [(\pi\text{-}B_{10}C_2H_{12})_2M]^{n-4}$$

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(11) W. N. Lipscomb, *Science*, **153**, 373 (1966).

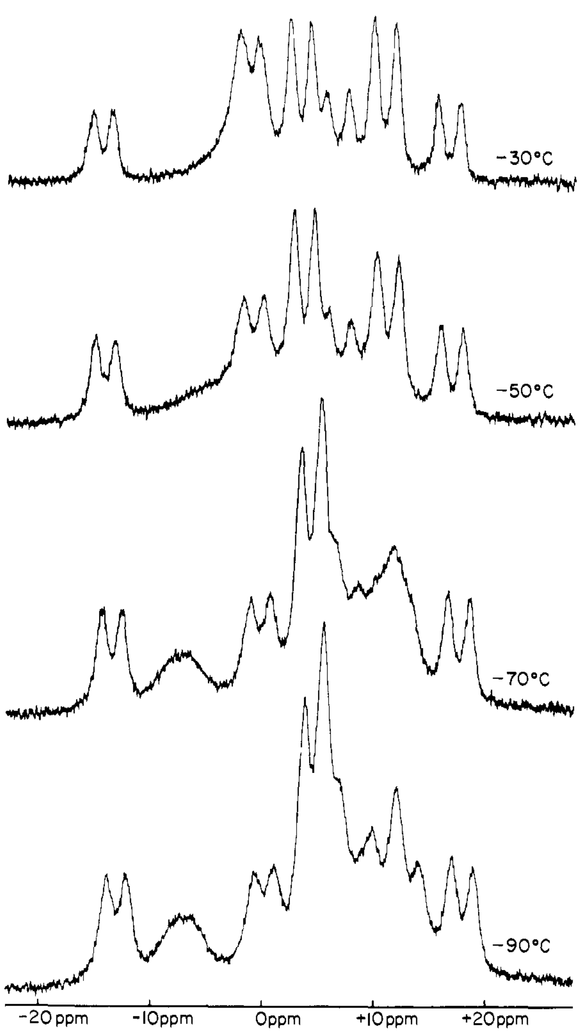

Figure 3. The temperature-dependent 80.5-MHz ^{11}B nmr spectrum of red (π-C_5H_5)Co^{III}(π-$B_{10}C_2H_{12}$) (II) taken in dimethyl ether. The presence of at least seven magnetically nonequivalent boron atoms at −90° indicates total asymmetry in the molecule.

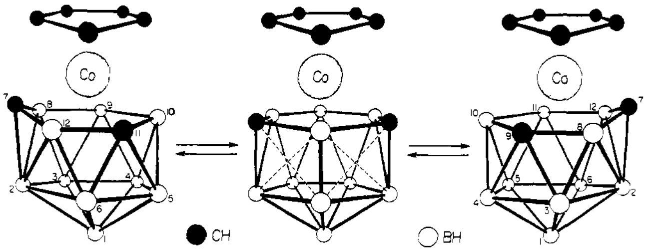

Figure 4. Proposed mechanism of the rapid interconversion between the (π-C_5H_5)Co^{III}(π-7,9-$B_{10}C_2H_{12}$) and (π-C_5H_5)Co^{III}-(π-7,11-$B_{10}C_2H_{12}$) enantiomers showing an intermediate or transition-state structure containing a plane of symmetry.

where M = Fe, Co, or Ni. In each case, the anhydrous metal salt (either the chloride or the acetylacetonate) was added directly to a stoichiometric amount of $Na_2B_{10}C_2H_{12}$ in tetrahydrofuran under nitrogen. The anionic metal complexes were isolated and recrystallized as the tetraethylammonium salts. The elemental analyses for these three products are presented in Table IV.

The bis complexes were slowly solvolyzed in acidic or basic media and very slowly by ethanol. The nickel derivative could be heated to 150° and the iron derivative to 240° before decomposition occurred. The cobalt complex decomposed at 230°, but was found to undergo another change at lower temperatures. A dichloromethane solution of the green $[(C_2H_5)_4N][(\pi\text{-}B_{10}C_2H_{12})_2Co^{III}]$ (V) slowly changed at the reflux temperature to a reddish color, presumably due to a thermal rearrangement and the production of a second isomer. Cyclic voltammetry of the recrystallized red product showed two reversible waves; −0.33 (*vs.* sce) and −0.72 V. The pure green isomer exhibited only one wave at −0.33 V. Thus far, attempts to prepare the pure red isomer have failed giving only inseparable mixtures of the red and green products. It is assumed that the two isomers differ only in the positions of the two carbon atoms within each of the polyhedral frameworks as was the case for the three (π-C_5H_5)Co^{III}(π-$B_{10}C_2H_{12}$) complexes described above.

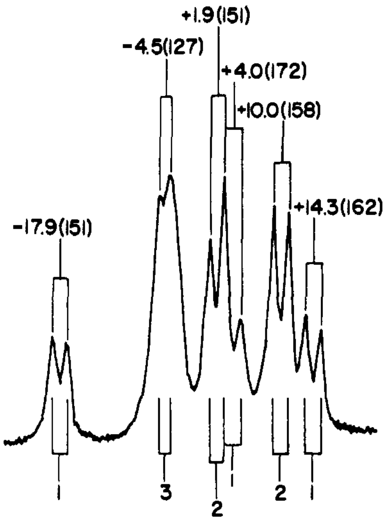

Figure 5. The 80.5-MHz ^{11}B nmr spectrum of $[(C_2H_5)_4N][(\pi\text{-}B_{10}C_2H_{12})_2Co^{III}]$ in acetone.

Cyclic voltammetry and controlled potential coulometry of $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})_2Fe^{II}]$ (VI) also showed a reversible, one-electron wave whereas $[(C_2H_5)_4N]_2$-$[(\pi\text{-}B_{10}C_2H_{12})_2Ni^{II}]$ (VII) underwent a two-electron oxidation to a formal nickel(IV) complex. Cyclic voltammetry data are given in Table I. The electronic and infrared spectra of the (π-$B_{10}C_2H_{12}$)$_2$ metal complexes, V, VI, and VII are presented in Tables V and VI.

The nmr spectra of the three bis complexes were very similar. The 60-MHz ^1H nmr spectra, Table II, of the sodium salts of the complexes (obtained by the metathetical reaction of the tetraethylammonium salts and sodium tetraphenylborate in acetone) all showed a single, broad resonance assigned to four equivalent polyhdedral C–H units. The 80.5-MHz ^{11}B nmr spectra (Table III) of V, Figure 5, and VI exhibited doublets of area ratio 1 : 1 : 1 : 1 : 2 : 2 : 2 with an area 2 resonance and an area 1 resonance overlapping to give an area 3 resonance. The spectra indicated a polyhedral framework consisting of three unique pairs and four unique boron atoms.

A normal ^{11}B nmr spectrum for VII was not obtained. Rounded peaks appeared instead of the usual, sharp, well-defined doublets probably due to the presence of paramagnetic species. Although a solid-state magnetic susceptibility study showed the complex

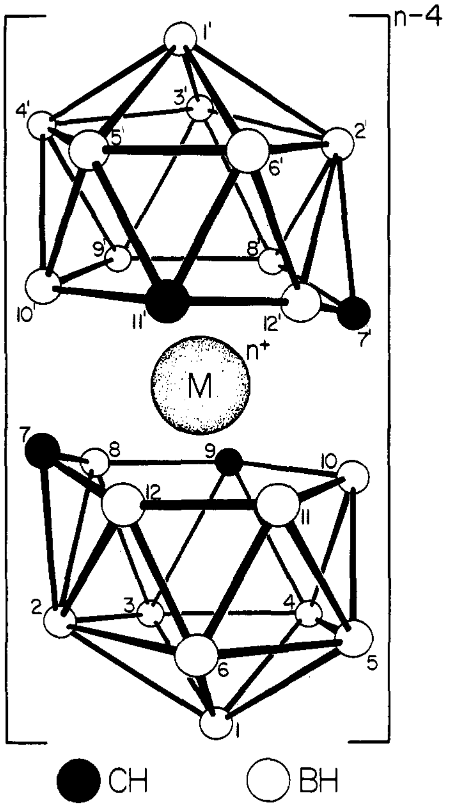

Figure 6. Proposed structure of the $(\pi\text{-}B_{10}C_2H_{12})_2$ metal complexes. M is Co(III), Fe(II), or Ni(II).

to be diamagnetic, it is possible that in solution an equilibrium exists between two spin states with one of them being paramagnetic. Anomalous magnetic behavior has also been reported for $[(\pi\text{-}7,9\text{-}B_9C_2H_{11})_2\text{-}Ni^{II}]^{2-}$ while the isomeric $[(\pi\text{-}7,8,\text{-}B_9C_2H_{11})_2Ni^{II}]^{2-}$ complex has a normal high-spin magnetic moment of 2.90 BM.[12] An acceptable ^{11}B nmr spectrum of VII was obtained, however, by oxidizing the sample to the formal nickel(IV) species with an excess of iodine. The spectrum showed doublets of area ratio 1:1:1:1:2:2:2 where a doublet of area 4 appeared due to the coincidental overlap of two area 2 resonances.

The fluxional behavior of the $B_{10}C_2H_{12}^{2-}$ ligand described above for II appears to prevail in V, VI, and VII with the ligand rapidly interconverting between the 7,9 and 7,11 isomers and the metal atom occupying position 13 within each of the carborane polyhedra (Figure 6).

Preparation and Characterization of the π-$B_{10}C_2H_{12}$-Molybdenum and -Tungsten Tricarbonyl Dianions. The chemistry of the $B_{10}C_2H_{12}^{2-}$ ion has shown certain similarities to that of the $B_9C_2H_{11}^{2-}$ dicarbollide ion,[6] and we were curious as to whether the $B_{10}C_2H_{12}^{2-}$ ion would displace carbon monoxide from certain metal carbonyls. No thermal or photochemical substitution of the $B_{10}C_2H_{12}^{2-}$ ligand for carbon monoxide was observed upon reaction with $Cr(CO)_6$, $Mn(CO)_5Br$, or $Fe(CO)_5$.

Simple displacement of carbon monoxide from either $Mo(CO)_6$ or $W(CO)_6$ was possible when $Na_2B_{10}C_2H_{12}$ and the metal hexacarbonyl were exposed to ultraviolet radiation in a tetrahydrofuran solution.

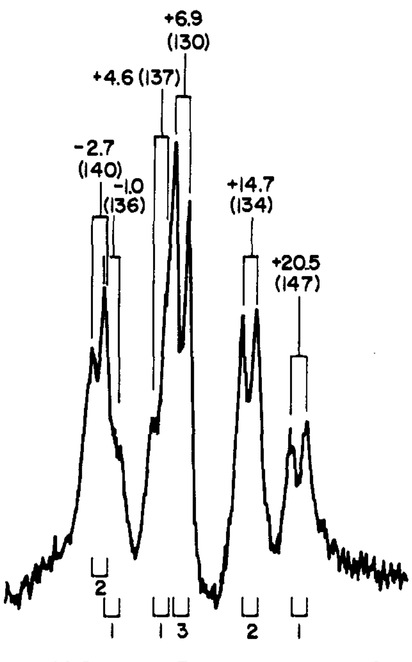

Figure 7. The 80.5-MHz ^{11}B nmr spectrum of $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})Mo(CO)_3]$ taken in acetone.

$$B_{10}C_2H_{12}^{2-} + M(CO)_6 \xrightarrow{h\nu} [(\pi\text{-}B_{10}C_2H_{12})M(CO)_3]^{2-} + 3CO$$
$$M = Mo \text{ or } W$$

Both complexes, isolated and recrystallized as their tetraethylammonium salts, were extremely air-sensitive and were handled under pure nitrogen. The salt $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})W(CO)_3]$ (VIII) was so air-sensitive that a satisfactory elemental analysis was not obtained.

The infrared spectra of VIII and $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})Mo(CO)_3]$ (IX) are given in Table VI.

Both VIII and IX were diamagnetic and their nmr spectra were similar to those of the other metal complexes of the $B_{10}C_2H_{12}^{2-}$ ion. Each 60-MHz ^1H nmr spectrum, Table II, contained a single broad resonance attributed to two equivalent polyhedral C–H units. The 80.5-MHz ^{11}B nmr spectra of IX, Figure 7, and VIII (Table III) exhibited signals of area ratio 1:1:1:2:2:3. The coincidental overlap of two resonances accounted for the doublet of area 3. The proposed structure of VIII and IX is shown in Figure 8. Once again, the complexes are presumably interconverting between the 7,9 and 7,11 isomers.

Conclusion. The results reported herein indicate that metallocarboranes may assume polyhedral structures larger than 12-atom icosahedra *via* a "polyhedral expansion" reaction common to *closo*-carboranes. Fluxional behavior is indicated for some of these 13-atom metallocarboranes. Additional investigations into the reactions and derivative chemistry of these complexes are under way.

Experimental Section

Physical Measurements. Ultraviolet–visible spectra were measured with a Beckman DB spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Proton nmr spectra were obtained by means of a Varian A-60D and the 80.5-MHz ^{11}B nmr spectra with an instrument designed and constructed by Professor F. A. L. Anet of this department. The electrochemical apparatus for cyclic voltammetry and controlled potential coulometry was based on the

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(12) D. V. Howe, Ph.D. Dissertation, University of California, Riverside, Calif., 1970.

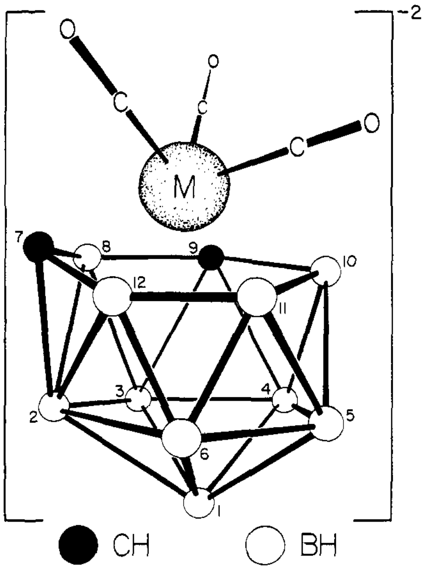

Figure 8. The proposed structure of the π-7,9-$B_{10}C_2H_{12}$-molybdenum and -tungsten tricarbonyl dianions.

design of Lawless and Hawley.[13] Mass spectra were obtained using an Associated Electrical Industries MS-9 spectrometer and magnetic susceptibilities measured utilizing a Cahn Model RG electrobalance in conjunction with a Varian Model V-4004 electromagnet, Model V-2300 A power supply, and Model V-2301A current regulator.

Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Galbraith Laboratories, Knoxville, Tenn.

Materials. Cobalt and nickel acetylacetonates were obtained from Research Organic/Inorganic Chemical Corp. Molybdenum and tungsten carbonyls were purchased from Climax Molybdenum Co. Anhydrous sublimed ferric chloride, hydrogen reduced iron powder, naphthalene, tetraethylammonium bromide, and tetramethylammonium chloride were obtained from Matheson Coleman and Bell. Sodium hydride, as a 60% dispersion in mineral oil, was purchased from Metal Hydrides, Inc. Baker "Analyzed Reagent" silica gel, 60–200 mesh, was employed in column chromatography. All of the above were used without further purification.

1,2-Dicarba-*closo*-dodecarborane(12) was sublimed under high vacuum prior to use. Anhydrous $CoCl_2$ was prepared by heating (at 100° under high vacuum for 3 days) $CoCl_2 \cdot 6H_2O$ obtained from Mallinckrodt Chemical Co. Dicyclopentadiene from Aldrich Chemical Co. was converted to C_5H_6 immediately prior to use.

Tetrahydrofuran (THF) was freshly distilled from $LiAlH_4$ and collected under nitrogen. Hexane, benzene, dichloromethane, acetone, ethanol, and acetonitrile were reagent grade. Ultraviolet-visible spectra and cyclic voltammetry measurements were made in Matheson Coleman and Bell Spectroquality acetonitrile.

$Na_2B_{10}C_2H_{12}$. In a 1-l., 3-necked flask fitted with a mechanical stirrer and a nitrogen inlet were placed 1.15 g (50 mg-atoms) of sodium metal cut into small pieces, 3.6 g (25 mmol) of freshly sublimed 1,2-$B_{10}C_2H_{12}$, 150 ml of THF, and approximately 0.2 g of naphthalene. The flask was stoppered and the contents were stirred at room temperature until the sodium had been consumed (about 3 hr). The $Na_2B_{10}C_2H_{12}$ was then used *in situ* for the preparation of transition metal complexes.

NaC_5H_5. In a 500-ml, three-necked flask fitted with a mechanical stirrer, nitrogen inlet, and an outlet at the bottom containing a coarse glass frit and closed with a Teflon stopcock was placed 3.0 g (75 mmol of a 60% oil dispersion) of NaH. The NaH was washed with two 30-ml portions of THF which were then decanted to remove the oil. THF (200 ml) was added to the flask. A mixture of 5 g (75 mmol) of freshly distilled C_5H_6 and 10 ml of THF was added to the flask dropwise over a 0.5-hr period from an addition funnel. The contents of the flask were stirred at room temperature for an additional 3 hr. The pink solution of NaC_5H_5 could then be filtered through the bottom outlet of the flask into another reaction flask with a minimum exposure to air.

$(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}B_{10}C_2H_{12})$ (I). A solution of 20 mmol of $Na_2B_{10}C_2H_{12}$ and 40 mmol of NaC_5H_5, both prepared as above, was placed in a 1-l. flask fitted with a mechanical stirrer and a nitrogen inlet. The preparation of all metal complexes was done in a nitrogen atmosphere. The flask was cooled to 0° and a gray-white slurry of $FeCl_2$ in THF, prepared by the reaction of 5.2 g (32 mmol) of $FeCl_3$ and 4.0 g (72 mg-atoms) of iron powder in 100 ml of THF at reflux for 3 hr, was added slowly. The reaction mixture was stirred for 15 hr while slowly warming to room temperature. A stream of oxygen was passed through the solution for 0.5 hr after which the solution was filtered through Celite. Silica gel (30 g) was added to the fitrate and the solvent removed by rotary evaporation. The solid was placed atop a (4 × 30 cm) silica gel chromatography column prepared with hexane. The column was eluted with hexane which was slowly enriched with dichloromethane. Four major bands were separated which contained, in order of elution, a mixture of ferrocene and naphthalene, green $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}7,9\text{-}B_9C_2H_{11})$, violet $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}B_{10}C_2H_{12})$ (0.8342 g, 3.1 mmol, 15%), and a purple band which moved extremely slowly on the column. This final band was not isolated but was presumed to be the $(\pi\text{-}B_{10}C_2H_{12})_2$ complex of iron(II).

One side product of this reaction was the previously unreported $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}7,9\text{-}B_9C_2H_{11})$ which could also be prepared by the direct combination of $C_5H_5^-$, $FeCl_2$, and 7,9-$B_9C_2H_{11}^{2-}$. We wish to include the characterization data here. *Anal.* Calcd for $C_7H_{16}B_9Fe$: C, 33.20; H, 6.32; B, 38.48; Fe, 22.07. Found: C, 33.32; H, 6.23; B, 38.07; Fe, 22.17. The 60-MHz ^1H nmr spectrum in acetone-d_6 (obtained after the reduction of the complex to a formal iron(II) species with aqueous sodium borohydride and isolated as the tetramethylammonium salt) consisted of three singlets of area ratio 5:12:2 at τ 5.71 (cyclopentadienyl protons), τ 6.52 (methyl protons), and τ 8.20 (carborane C–H), respectively. The 80.5-MHz ^{11}B nmr spectrum (also of the reduced species) exhibited doublets of area ratio 3:1:2:1:2 at +10.5 (126), +15.4 (156), +17.3 (139), +19.8 (148), and +24.2 (148) [chemical shift, parts per million relative to $BF_3 \cdot O(C_2H_5)_2$ (B–H coupling constants, Hz)]. The infrared spectrum (Nujol mull) included absorptions at 2535 (s), 1147 (w), 1109 (m), 1038 (w), 1004 (w), 984 (w), 947 (w), 920 (w), 841 (s), 733 (w), and 702 (w) cm^{-1}.

Reduction of $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}B_{10}C_2H_{12})$. To 0.265 g (1 mmol) of violet I dissolved in a solution of 10% acetonitrile in water was added an aqueous solution of excess $NaBH_4$, and the mixture was heated on a steam bath for 1 hr. After the solution had become orange, it was cooled to room temperature and added to an aqueous solution of excess tetramethylammonium chloride. The resulting orange precipitate was filtered, washed with water, and recrystallized by the slow rotary evaporation of solvent from a dichloromethane–hexane mixture.

$(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$ (II). To a solution of 25 mmol of $Na_2B_{10}C_2H_{12}$, prepared as above, was added a solution of 75 mmol of NaC_5H_5. The flask was cooled in an ice bath, and a slurry of 12 g (92 mmol) of finely ground anhydrous $CoCl_2$ in 50 ml of THF was added from an addition funnel. The contents of the flask were stirred for 15 hr while slowly warming to room temperature. The addition funnel and nitrogen inlet were removed and, in order to convert any cobalticene formed to a cobalticinium salt, a stream of oxygen was passed through the solution with occasional stirring for 0.5 hr. The reaction mixture was then filtered through Celite to remove cobalt metal. Approximately 30 g of silica gel was added to the filtrate, and the solvent was removed at room temperature using a rotary evaporator and a water aspirator. The solid was then chromatographed on silica gel in the manner described for $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}B_{10}C_2H_{12})$. Seven major bands were separated consisting of, in order of elution: naphthalene, 1,2-$B_{10}C_2H_{12}$ (2.55 g, 17.7 mmol), orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$, III (0.1054 g, 0.4 mmol), yellow $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}7,8\text{-}B_9C_2H_{11})$, red $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$, II (2.16 g, 8 mmol), the yellow cobalticinium salt of $B_9C_2H_{12}^-$, a red-brown band which consisted of a mixture of isomers of $[(\pi\text{-}C_5H_5)_2Co]^+[Co(\pi\text{-}B_{10}C_2H_{12})_2]^-$ (1.73 g, 4.0 mmol). II and III were recrystallized from hexane–dichloromethane mixtures by the slow removal of the solvent on a rotary evaporator.

Rearrangement of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$. To a 25-ml round-bottom flask were added 0.268 g (1 mmol) of red II and 20 ml of hexane. A reflux condenser topped with a nitrogen inlet was connected, and the solution was heated at reflux for 15 hr. After cooling to room temperature, 10 g of silica gel was added and the solvent removed using a rotary evaporator and a water aspirator. The solid was placed on a 2.5 × 30-cm silica gel column and eluted with

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[13] J. D. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969).

hexane gradually enriched with dichloromethane. The bands that were separated, in order of elution, were red-orange $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_{10}C_2H_{12})$, IV (trace), orange III (0.1575 g, 0.6 mmol, 60%), and red II (0.1011 g, 0.37 mmol, 37%).

In a 200-ml round-bottom flask were placed 1.0444 g (3.8 mmol) of red II and 100 ml of benzene. A reflux condenser topped with a nitrogen inlet was connected and the flask was heated at reflux for 24 hr. The mixture was chromatographed as above yielding only one band. The solvent was evaporated and 0.7344 g (2.7 mmol, 71%) of red-orange IV was isolated.

$(C_2H_5)_4N[(\pi\text{-}B_{10}C_2H_{12})_2Co^{III}]$ (V). To a solution of 12.5 mmol of $Na_2B_{10}C_2H_{12}$, prepared as above, in 100 ml of THF was added 2.1 g (6.2 mmol) of cobalt(III) acetylacetonate directly as a solid. After stirring at room temperature for 12 hr, the mixture was filtered through Celite. The solvent was removed from the filtrate by rotary evaporation using a water aspirator. The resulting dark green oil was redissolved in a minimum amount of ethanol and added to an ethanol solution of excess tetraethylammonium bromide. The precipitate was filtered, washed with water, and redissolved in dichloromethane. The addition of hexane, followed by cooling to 0°, resulted in the formation of 1.3 g (2.7 mmol, 44%) of large, dark green crystals.

$[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})_2Fe^{II}]$ (VI). $FeCl_3$ (2.0 g, 12.5 mmol) and 1.0 g (18 mg-atoms) of iron powder were stirred in 50 ml of THF at reflux for 3 hr under nitrogen giving a cloudy, gray slurry of $FeCl_2$. The $FeCl_2$ slurry was added to a solution of 25 mmol of $Na_2B_{10}C_2H_{12}$ in 100 ml of THF. After stirring at room temperature for 12 hr, the mixture was filtered through Celite and then rotary evaporated with a water aspirator to a dark purple oil. The oil was redissolved in ethanol and added to an ethanol solution of excess tetraethylammonium bromide. The resulting precipitate was filtered, washed with ethanol, and redissolved in acetone. The addition of ethanol followed by slow rotary evaporation of the solvent produced 2.5 g (4.2 mmol, 34%) of purple crystals of $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})_2Fe^{II}]$.

$[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})_2Ni^{II}]$ (VII). To a 25 mmol solution of $Na_2B_{10}C_2H_{12}$ in 100 ml of THF was added 3.2 g (12.5 mmol) of nickel(II) acetylacetonate. The mixture was stirred at room temperature for 12 hr and then filtered through Celite. The complex was isolated as the tetraethylammonium salt in the manner already described for the corresponding complexes of cobalt and iron. The precipitate was redissolved in 20% acetonitrile in dichloromethane. The addition of hexane followed by slow cooling to 0° resulted in the formation of 2.4 g (4.0 mmol, 32%) of orange-brown crystals of $[(C_2H_5)_4N]_2[\pi\text{-}B_{10}C_2H_{12})_2Ni^{II}]$.

Oxidation of $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})_2Ni^{II}]$. To a 0.3 g (0.5 mmol) sample of VII dissolved in 2 ml of acetonitrile was added a large excess of iodine crystals, and the mixture was allowed to stir at room temperature for 10 hr. The 80.5-MHz ^{11}B nmr spectrum of the product was obtained directly from the reaction mixture without isolation of the nickel(IV) species.

$[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})W(CO)_3]$ (VIII). To a solution of 12.5 mmol of $Na_2B_{10}C_2H_{12}$ in 100 ml of THF was added 4.4 g (12.5 mmol) of $W(CO)_6$. The mixture was stirred under rigorous exclusion of air for 48 hr while being irradiated with a Pen-ray ultraviolet lamp. The flask was then transferred to a nitrogen-filled drybox where the solvent was removed *via* rotary evaporation using a mechanical vacuum pump. The solid was redissolved in ethanol and added to an ethanol solution of tetraethylammonium bromide. The resulting orange precipitate was filtered, washed with ethanol, and recrystallized by the slow rotary evaporation of an acetone–ethanol solution. Pale orange, microcrystalline $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})W(CO)_3]$ (1.1 g, 1.9 mmol, 15%) was isolated.

$[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12}]Mo(CO)_3]$ (IX). In the manner described immediately above, a solution of 12.5 mmol of $Na_2B_{10}C_2H_{12}$ and 3.3 g (12.5 mmol) of $Mo(CO)_6$ in 100 ml of THF was irradiated for 24 hr. After precipitation with tetraethylammonium bromide and recrystallization from acetone–ethanol, 3.0 g (5.1 mmol, 41%) of bright, yellow needles of $[(C_2H_5)_4N]_2[(\pi\text{-}B_{10}C_2H_{12})Mo(CO)_3]$ was obtained.

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