

N_2O . The proposed mechanism is quite complicated and involves copper(II) in combination with NO functioning as the nitrosylating agent of the amine. By comparison with our study, one might expect that the lability of Cu(II) and the fact that no dinitrogen complex of either oxidation state of copper has been reported is suggestive that the *N*-nitroso amine simply breaks away from the copper center and then undergoes further decomposition.

The reaction of $\text{Ru}(\text{NH}_3)_6^{3+}$ with $\text{S}_2\text{O}_3^{2-}$, OH^- , and O_2 to produce $(\text{NH}_3)_5\text{RuNH}_2\text{SO}_3^{2+}$ has been demonstrated⁵² to proceed only in basic solution. Considering the substitution inertness of $\text{Ru}(\text{NH}_3)_6^{3+}$ and the high yields obtained for the sulfamate product, it would appear that attack also proceeds on $\text{Ru}-\text{NH}_2^-$. However, one cannot rule out initial attack by $\text{S}_2\text{O}_3^{2-}$ upon the octahedron, which facilitates removal of the ammine proton.

In conclusion, we have determined the kinetics and mechanism of the reaction between NO and $\text{Ru}(\text{NH}_3)_6^{3+}$ from pH 3 to ~ 11 . Beyond pH 8.3, the reaction is first order in Ru(III), NO, and OH^- , with attack by NO upon the deprotonated ammine complex. A

(52) J. N. Armor and H. Taube, *Inorg. Chem.*, **10**, 1570 (1971).

dramatic variation of $\sim 10^6$ exists in the rate constants for the acid and base components of the rate law. In acid solution, substitution of the coordinated ammine is important; however, in basic solution, the reaction may proceed *via* a concerted or stepwise attack of NO and OH^- upon $\text{Ru}(\text{NH}_3)_6^{3+}$. The dinitrogen complex is not produced when either $\text{Ru}(\text{NH}_3)_6^{3+}$ or $\text{Ru}(\text{NH}_3)_6^{2+}$ is treated with NO_2^- in alkaline solution. In general, this suggests that any metal ammine complex which is used in this synthetically useful preparation for dinitrogen complexes ought to be one which undergoes reaction with NO_{aq} and has easily dissociable ammine protons (along with other criteria for metal-nitrogen complex stabilization).^{53,54}

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(53) Yu. G. Borod'ko and A. E. Shilov, *Russ. Chem. Rev.*, **38**, 355 (1969).

(54) J. E. Fergusson and J. L. Love, *Rev. Pure Appl. Chem.*, **20**, 33 (1970).

Derivative Chemistry of Metallocarboranes. Nido 11-Atom Metallocarboranes and Their Lewis Base Adducts

Christopher J. Jones, James N. Francis, and M. Frederick Hawthorne*

Contribution No. 3135 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received May 10, 1973

Abstract: The reaction between $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ or $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ and pyridine affords the nido adducts $X[9-(\eta\text{-C}_5\text{H}_5)\text{-}11\text{-C}_5\text{H}_5\text{N-}7,8,9\text{-C}_2\text{CoB}_9\text{H}_{10}]$ and $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}11'\text{-C}_5\text{H}_5\text{N-}7',8'\text{-C}_2\text{B}_9\text{H}_{10}]^-$, respectively. Oxidation of these species with FeCl_3 affords the substituted closo compounds $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}7\text{-C}_5\text{H}_5\text{N-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_9]^+$ and $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}7'\text{-C}_5\text{H}_5\text{N-}2',4'\text{-C}_2\text{B}_9\text{H}_9]$. Analogous compounds were prepared from $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ with piperidine in place of pyridine. The unsubstituted nido metallocarboranes $X[9-(\eta\text{-C}_5\text{H}_5)\text{-}7,8,9\text{-C}_2\text{CoB}_9\text{H}_{11}]^-$ and $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}7',8'\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$ were prepared by degradation of the icosahedral compounds $[3-(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$ and $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]^-$. These compounds could be reversibly protonated to give $X[9-(\eta\text{-C}_5\text{H}_5)\text{-}7,8,9\text{-C}_2\text{CoB}_9\text{H}_{12}]$ and $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}7',8'\text{-C}_2\text{CoB}_9\text{H}_{12}]^-$ which eliminate hydrogen on heating to give $[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ and $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',3'\text{-C}_2\text{B}_9\text{H}_{10}]^-$. The chemical changes resulting from the replacement of a polyhedral $\{\text{BH}\}^{2+}$ moiety by $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ or $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^{2+}$ are discussed.

Although a large number of metallocarboranes have been prepared¹⁻¹⁷ since the first report of $[1,2\text{-}$

(1) M. F. Hawthorne and G. B. Dunks, *Science*, **178**, 462 (1972).

(2) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

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

(4) T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 5475 (1969).

(5) G. B. Dunks, Ph.D. Dissertation, University of California, Riverside, Calif., 1970.

(6) W. J. Evans and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 3063 (1971).

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

(8) L. J. Todd, A. R. Burke, A. P. Garber, H. T. Silverstein, and B. N. Storhoff, *Inorg. Chem.*, **9**, 2175 (1970).

(9) J. L. Little, P. S. Welcker, N. J. Loy, and L. J. Todd, *Inorg. Chem.*, **9**, 63 (1970).

(10) L. J. Todd, *et al.*, *J. Organometal. Chem.*, **50**, 93 (1973).

$\text{C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Fe-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]^-$ in 1965,^{18,19} compara-

(11) J. L. Spencer, M. Green, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1178 (1972).

(12) L. G. Sneddon and R. N. Grimes, *J. Amer. Chem. Soc.*, **94**, 7161 (1972).

(13) R. N. Grimes, *J. Amer. Chem. Soc.*, **93**, 261 (1971).

(14) V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, **95**, 2830 (1973).

(15) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Amer. Chem. Soc.*, **94**, 1865 (1972).

(16) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Amer. Chem. Soc.*, **95**, 3046 (1973).

(17) J. W. Howard and R. N. Grimes, *Inorg. Chem.*, **11**, 263 (1972).

(18) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Amer. Chem. Soc.*, **87**, 1818 (1965).

(19) The first commo metallocarborane was originally treated as a π -bonded metal complex of the (3)-1,2-B₂C₂H₁₁²⁻ ligand (ref 18). However, using the newest IUPAC nomenclature rules this compound should be named as a commo polyhedral structure, *i.e.*, $[1,2,3\text{-C}_2\text{FeB}_9\text{H}_{11}(3\text{-commo-}3')1',2',3'\text{-C}_2\text{FeB}_9\text{H}_{11}]^-$. Since a reader not versed in the details of replacement nomenclature might be led to the

tively little is known about the chemistry of metallocarborane polyhedra themselves. A variety of substitution reactions involving terminal B-H groups has been observed^{8,20-23} as well as thermal rearrangements involving carbon atom migration.^{4,7,24,25} However, reactions involving structural changes within the polyhedral framework are limited to replacement of {BH}²⁺ by {(η-C₅H₅)Co}²⁺ or {1,2,3-C₂CoB₉H₁₁}⁺ to give polymetallics,^{26,27} insertion of {(η-C₅H₅)Co}²⁺ or "polyhedral nido" and removal of {BH}²⁺ or "polyhedral nido." Consequently, we have investigated the chemistry of metallocarboranes further and have isolated a variety of compounds containing 11-atom polyhedra comprised of one cobalt, two carbon, and eight boron atoms. The chemical reactions observed parallel those of the structurally similar carboranes although significant differences in reactivity were found.

Adducts Containing Nido Metallocarborane Polyhedra. Both X[1-(η-C₅H₅)-2,4,1-C₂CoB₈H₁₀] and X-[1-(η-C₅H₅)-3,1'-Co-2',4'-C₂B₈H₁₀] reacted with pyridine to give the red adducts I and II in 85 and 70% yield, respectively. The 100-MHz ¹H nmr spectrum of I exhibited resonances owing to the C₅H₅⁻ pyridine, and two nonequivalent carborane CH groups (in addition, a broad resonance was observed at -7.0 ppm which we assign to a bridge proton). The ¹H nmr spectrum of II similarly showed a resonance at +9.2 ppm assigned to a bridge proton, other resonances attributable to pyridine, nonequivalent carborane CH groups, and the ammonium cation (Table I). The mass spectrum exhibited a cutoff at *m/e* 325 consistent with the molecular formula C₁₂H₂₀B₈NCo. However, the ion at the parent peak array was unlike that suggested that hydrogen was being lost from the molecular ion, as has been noted previously for metallocarborane.²⁹ The 80.5-MHz ¹¹B nmr spectrum of I (Figure 1a) consisted of seven resonances of area 1 and a singlet of area 1 at -4.3 ppm. This was consistent with the presence of a methyl substituent on boron and the absence of a nido substituent. The 80.5-MHz ¹¹B nmr spectrum of II (Figure 2a) was complicated by the extensive decoupling of the terminal {BH} groups. The spectrum was simplified by ¹H decoupling of the terminal {BH} groups and could be qualitatively fitted to the overall structure of I and [3-(η-C₅H₅)-1,2,3-C₂CoB₉H₁₁].

If the compound contains two iron atoms, we have simplified the structure contained in this paper in such a way as to observe the same numbering while eliminating the nido description. Thus, the compound in question appears here as [1,2-C₂B₈H₁₁-3,3'-Fe-1',2'-C₂B₉H₁₁]⁻ with the point of polyhedral fusion designated by -3,3'-Fe-.

(20) M. F. Hawthorne, L. F. Warren, K. P. Callahan, and N. F. Travers, *J. Amer. Chem. Soc.*, **93**, 2407 (1971).

(21) J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, **10**, 594 (1971).

(22) J. N. Francis, C. J. Jones, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 4878 (1972).

(23) B. M. Graybill and M. F. Hawthorne, *Inorg. Chem.*, **8**, 1799 (1969).

(24) L. F. Warren and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 1157 (1970).

(25) M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 6679 (1972).

(26) C. J. Jones and M. F. Hawthorne, *Inorg. Chem.*, **12**, 608 (1973).

(27) J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, **10**, 863 (1971).

(28) W. J. Evans and M. F. Hawthorne, *J. Chem. Soc., Chem. Commun.*, 611 (1972).

(29) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 8391 (1972).

Table I. 100-MHz ¹H Nmr Spectral Data (shifts in ppm relative to (CH₃)₄Si)

Compound and solvent	Resonance	Assignment
I, X[9-(η-C ₅ H ₅)-11-C ₅ H ₅ N-7,8,9-C ₂ CoB ₈ H ₁₀] in CD ₃ CN	-5.02	Cyclopentadienide
	-2.59	Carborane CH
	-3.49	
	+11.1	H bridge
II, [(CH ₃) ₄ N]X[1,2-C ₂ B ₉ H ₁₁ -3,9'-Co-11'-C ₅ H ₅ N-7',8'-C ₂ B ₈ H ₁₀] in CD ₃ CN	-7.0 to -9.0	Pyridine
	-3.09	Tetramethylammonium
	-2.64	
	-2.83	Carborane CH
-3.20		
III, X[9-(η-C ₅ H ₅)-11-C ₅ H ₅ N-NH-7,8,9-C ₂ CoB ₈ H ₁₀] in (CD ₃) ₂ CO	-3.65	H bridge
	+9.2	
	-7.0 to -9.0	Pyridine
	-4.83	Cyclopentadienide
IV, X[1-(η-C ₅ H ₅)-7-C ₅ H ₅ N-2,4,1-C ₂ CoB ₈ H ₁₀][PF ₆] in CD ₃ CN	-3.26	Carborane CH
	-3.56	
	+11.0	H bridge
	-0.5 to -2.5	Piperidine CH
V, X[1,2-C ₂ B ₉ H ₁₁ -3,1'-Co-7'-C ₅ H ₅ N-2',4'-C ₂ B ₈ H ₉] in (CD ₃) ₂ CO	-5.67	Cyclopentadienide
	-4.16	
	-6.15	Carborane CH
	-7.0 to -9.0	
VI, X[1-(η-C ₅ H ₅)-7-C ₅ H ₅ N-2,4,1-C ₂ CoB ₈ H ₉] in C ₆ D ₆	-5.55	Pyridine
	-5.76	0.5 CH ₂ Cl ₂ of solvation
	-4.21	
	-2.96	Carborane CH
-2.54		
VII, [(CH ₃) ₄ N]X[1,2-C ₂ B ₉ H ₁₁ -3,9'-Co-7',8'-C ₂ B ₈ H ₁₁] in CD ₃ CN	-7.0 to -9.0	Pyridine
	-5.42	0.5 CH ₂ Cl ₂ of solvation
	-4.52	
	-4.84	Cyclopentadienide
-2.96		
VIII, [(CH ₃) ₄ N]X[1,2-C ₂ B ₉ H ₁₁ -3,9'-Co-7',8'-C ₂ B ₈ H ₁₂] in CD ₃ CN	-0.5 to -2.5	Piperidyl
	-3.42 ^a	Tetramethylammonium
	-2.16 ^b	
	-2.46 ^b	Carborane CH
-2.85 ^b		
IX, [(CH ₃) ₄ N][1,2-C ₂ B ₉ H ₁₁ -3,1'-Co-2',3'-C ₂ B ₈ H ₁₀] in CD ₃ CN	-3.34 ^b	H bridge
	+3.95 ^b	
	-3.06	Tetramethylammonium
	-2.22	
X, [(CH ₃) ₄ N]X[9-(η-C ₅ H ₅)-7,8,9-C ₂ CoB ₈ H ₁₁] in CD ₃ CN	-2.94	Carborane CH
	-3.40	
	-4.02	H bridge
	+1.53 ^b	
XI, X[9-(η-C ₅ H ₅)-7,8,9-C ₂ CoB ₈ H ₁₂] in CDCl ₃	+6.10 ^b	Tetramethylammonium
	-3.06	
	-4.18	Carborane CH
	-6.62	
XII, X[9-(η-C ₅ H ₅)-7,8,9-C ₂ CoB ₈ H ₁₁] in CD ₃ CN	-4.69	Cyclopentadienide
	-3.10	
	-2.10	Carborane CH
	-3.20	
XIII, X[9-(η-C ₅ H ₅)-7,8,9-C ₂ CoB ₈ H ₁₁] in CDCl ₃	+2.86 ^b	H bridge
	-5.32 ^b	
	-2.74 ^b	Cyclopentadienide
	-4.24 ^b	
XIV, X[9-(η-C ₅ H ₅)-7,8,9-C ₂ CoB ₈ H ₁₁] in CDCl ₃	+2.59 ^b	Carborane CH
	+13.14 ^b	

^a Value obtained in (CD₃)₂CO solution. ^b Shifts obtained at 251 MHz.

The spectrum of II also contained an area 1 singlet at -6.2 ppm assigned to the boron atom carrying the pyridine substituent. The structure of II has been unambiguously determined by an X-ray diffraction study,³⁰ and on the basis of the spectral data described

(30) M. R. Churchill and K. Gold, *J. Chem. Soc., Chem. Commun.*, 901 (1972); *Inorg. Chem.*, **12**, 1157 (1973).

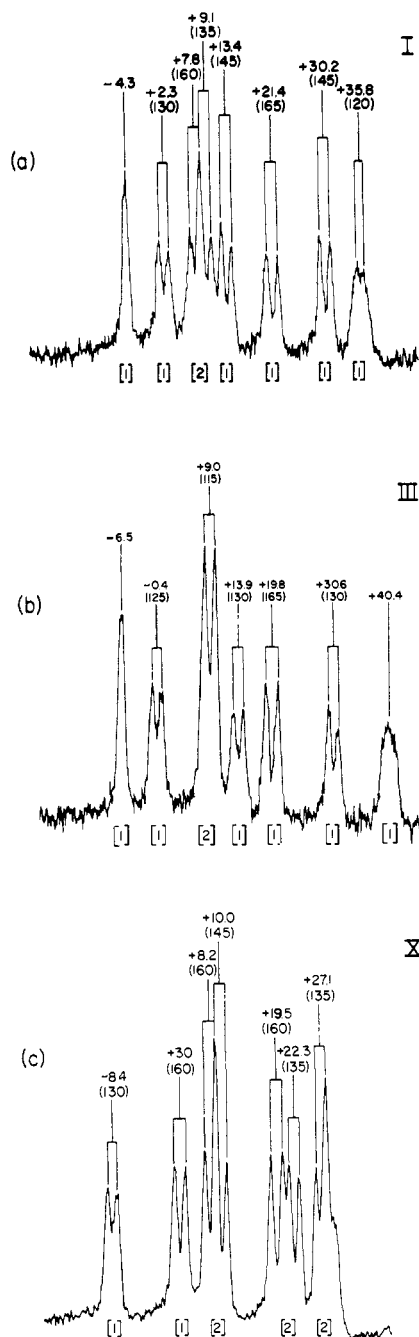


Figure 1. The 80.5-MHz ^{11}B nmr spectra of (a) I in CH_2Cl_2 , (b) III in $(\text{CH}_3)_2\text{CO}$, and (c) X in CH_3CN . All shifts are quoted in ppm relative to $\text{BF}_3 \cdot \text{OEt}_2$ and splittings are given in Hz.

above we assign an analogous structure to I (Figure 3) except that $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ has been replaced by $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$. This structure grossly resembles that proposed³¹ for $9\text{-C}_5\text{H}_5\text{N-7,8-C}_2\text{B}_9\text{H}_{11}$ except that a $\{\text{BH}\}^{2+}$ group in the open pentagonal face has been replaced by $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ or $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$. The additional bridge hydrogen atom in II was not located by the X-ray study. However, it seems most probable that this proton is located in the open face of the metallocarborane. Further, since CHB or CHC bridge protons are unprecedented,³² a reasonable loca-

(31) D. C. Young, D. V. Howe, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 859 (1969).

(32) E. Groszek, J. B. Leach, G. T. F. Wong, C. Ungermann, and T. Onak, *Inorg. Chem.*, **10**, 2770 (1971).

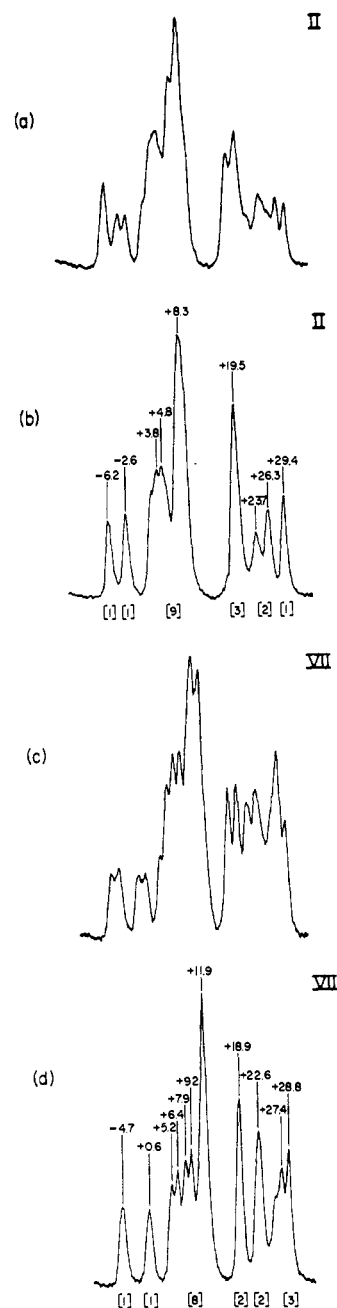


Figure 2. The 80.5-MHz ^{11}B nmr spectra of (a) II in $(\text{CH}_3)_2\text{CO}$, (b) II in $(\text{CH}_3)_2\text{CO}$ with ^1H decoupling, (c) VII in CH_3CN , and (d) VII in CH_3CN with ^1H decoupling.

tion for this proton would be between boron atoms 10 and 11 in both I and II (Figure 3). In connection with this we noted that the high field resonance at +35.8 ppm in the 80.5-MHz ^{11}B nmr spectrum of I was broadened, possibly by additional coupling with the bridge proton. Accordingly the ^{11}B nmr spectrum of I was measured while irradiating at the frequency of the proton resonance observed at +11.1 ppm in the ^1H nmr spectrum; under these conditions the signal at +35.8 ppm in the ^{11}B nmr spectrum appeared as a well-resolved doublet. There was no apparent change in the other resonances in the ^{11}B nmr spectrum.

An alternative location for the bridge hydrogen would be between boron atom 10 and the cobalt atom. In view of Grimes' proposal¹² that high field ^1H nmr resonances (*i.e.*, more than *ca.* 5 ppm above TMS) may

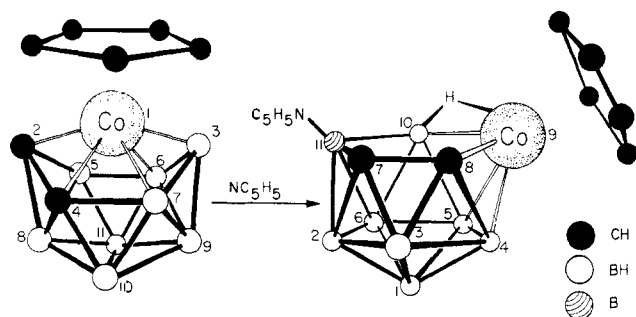


Figure 3. Formation of I from $X[(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ and pyridine. II is formed similarly from $X[1,2\text{-C}_2\text{B}_5\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_5\text{H}_{11}]$ and has $\text{C}_5\text{H}_5\text{N}^{2-}$ in place of C_5H_5^- . Only the enantiomers with lowest numbered carbon atoms are illustrated.

be associated with protons bridging boron and a transition metal, this latter location would seem more consistent with the ^1H nmr data. Some recent observations^{33,34} which relate high field ^1H nmr resonances with crystallographically located B-H-Mn and B-H-Co groups lend support to this argument.

A piperidine adduct, III, of $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ was also prepared in 87% yield. The 100-MHz ^1H nmr (Table I), 80.5-MHz ^{11}B nmr (Figure 1b), and mass spectra (cutoff at m/e 331 for the formula $\text{C}_{12}\text{H}_{26}\text{B}_8\text{NCo}$) of III all indicated that this adduct had a structure analogous to that of I except that the $\text{C}_5\text{H}_5\text{N}$ substituent has been replaced by $\text{C}_5\text{H}_{10}\text{NH}$.

The reaction of $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ with carbanions was also investigated. An ethereal solution of this complex reacted with *n*-butyllithium to give a red solution. After oxidation the starting material and a purple oil were obtained from the reaction mixture. The ^1H nmr, ^{11}B nmr, and mass spectral data indicated that the oil was $X[1-(\eta\text{-C}_4\text{H}_9\text{C}_5\text{H}_4)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ formed by butyl substitution of the C_5H_5^- ligand. Similar reactions were found to occur with $[3-(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$, $[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$, and $X[2-(\eta\text{-C}_5\text{H}_5)\text{-}1,6,2\text{-C}_2\text{CoB}_7\text{H}_9]$ possibly *via* a radical pathway in which the first step involves reduction of Co^{III} to Co^{II} with concomitant oxidation of C_4H_9^- to $\text{C}_4\text{H}_9\cdot$. However, the reaction did not appear to involve the metallocarbaborane polyhedron and will be described elsewhere. No reaction was observed with the carborane anions $\text{C}_2\text{B}_{10}\text{H}_{11}^-$ and $\text{CH}_3\text{C}_2\text{B}_{10}\text{H}_{10}^-$ presumably owing to steric hindrance by the C_5H_5^- ligand in $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$. In order to test this hypothesis the reaction of $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ with several amines was examined qualitatively in benzene solution. Both piperidine and diethylamine reacted rapidly on warming as evidenced by the color change from purple to the red color of the adducts. Pyridine also reacted on warming though not as rapidly as the two secondary amines. However, 2-methylpyridine reacted only slowly in warm benzene and triethylamine did not appear to react at all under similar conditions. Thus, since triethylamine and 2-

methylpyridine are stronger Lewis bases than diethylamine and pyridine, respectively, it would seem that the C_5H_5^- ligand does "shelter" the reactive boron atom from attack by amines or carbanions having large steric requirements. No reaction was apparent between BH_4^- and $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ or $X[1,2\text{-C}_2\text{B}_5\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_5\text{H}_{10}]^-$ in ethanol.

Adducts Containing Closo Metallocarbaborane Polyhedra. Both I and II were oxidized by FeCl_3 giving the compounds IV and V in 81 and 86% yields, respectively. The blue cationic complex IV was isolated as the PF_6^- salt and exhibited signals attributable to pyridine, cyclopentadienide, two nonequivalent carborane CH groups, and CH_2Cl_2 (one molecule of CH_2Cl_2 was found to solvate two molecules of IV but could be removed *in vacuo*) in the 100-MHz ^1H nmr spectrum. No signals were observed which could be assigned to a bridge proton. The 80.5-MHz ^{11}B nmr spectrum of IV (Figure 4b) was largely similar to that of $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ except that the highest field resonance had become a singlet and had shifted downfield by *ca.* 12 ppm. On the basis of these data we propose a closo structure for IV analogous to that proposed for $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ except that a terminal hydride ligand on boron atom 7 has been formally replaced by $\text{C}_5\text{H}_5\text{N}$ (Figure 5). Polar solvents such as acetone, acetonitrile, or ethanol decomposed IV in a few hours; the complex also decomposed slowly in moist air. It seemed likely that this reactivity was connected with the cationic character of IV; thus, in order to obtain a more stable complex, the piperidine adduct III was oxidized with FeCl_3 then deprotonated using K_2CO_3 to give the neutral complex VI in 34% yield. The mass spectrum of VI exhibited a cutoff at m/e 329 and an ion distribution within the parent peak array consistent with that calculated²⁹ for $\text{C}_{12}\text{H}_{21}\text{B}_8\text{NCo}$. The 100-MHz ^1H nmr spectrum (Table I) was in agreement with a formulation for VI analogous to that of IV except that the $\text{C}_5\text{H}_5\text{N}$ ligand had been replaced by $\text{C}_5\text{H}_{10}\text{N}^-$. However, the 80.5-MHz ^{11}B nmr spectrum of VI (Figure 4a) was unlike that of IV although a singlet of area 1 was observed and no molecular symmetry was apparent. We surmised that this difference might be due to the proximity of the free nitrogen lone pair on the piperidyl ligand to the metallocarbaborane polyhedron. If this were so, protonation of the lone pair should remove the discrepancy. Accordingly CF_3COOH was added to the sample solution of VI resulting in a color change from green to blue and the development of an ^{11}B nmr spectrum (Figure 4b) identical in appearance with that of IV. Thus it seems that VI is indeed structurally analogous to IV. As anticipated the neutral compound VI was less reactive than IV and remained unchanged in acetonitrile solution for several days.

The mass spectrum of V obtained by FeCl_3 oxidation of II exhibited a cutoff at m/e 393 and an ion distribution within the parent peak array consistent²⁹ with that calculated for $\text{C}_9\text{H}_{25}\text{B}_{17}\text{NCo}$. The 100-MHz ^1H nmr spectrum (Table I) indicated the presence of the pyridine ligand and the absence of a bridge proton. Signals assigned to four nonequivalent carborane CH groups and CH_2Cl_2 of solvation were also present. The 80.5-MHz ^{11}B nmr spectrum of V (Figure 4c) was complicated by the extensive overlap of resonances,

(33) J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 3042 (1973).

(34) An X-ray diffraction study (K. Callahan, A. L. Sims, and C. E. Strouse, private communication) of $[(\eta\text{-C}_5\text{H}_5)_2\text{C}_2\text{CoB}_7\text{H}_{11}]$ has established the proposed geometry but locates the carbon atoms in positions 5 and 6 to give $X[10-(\eta\text{-C}_5\text{H}_5)\text{-}5,6,10\text{-C}_2\text{CoB}_7\text{H}_{11}]$. A tentative location of the bridge hydrogens places one in a BHB bridge and the other in a BHCo bridge, in accord with the ^1H nmr shifts²⁹ of +4.2 and +18.3 ppm.

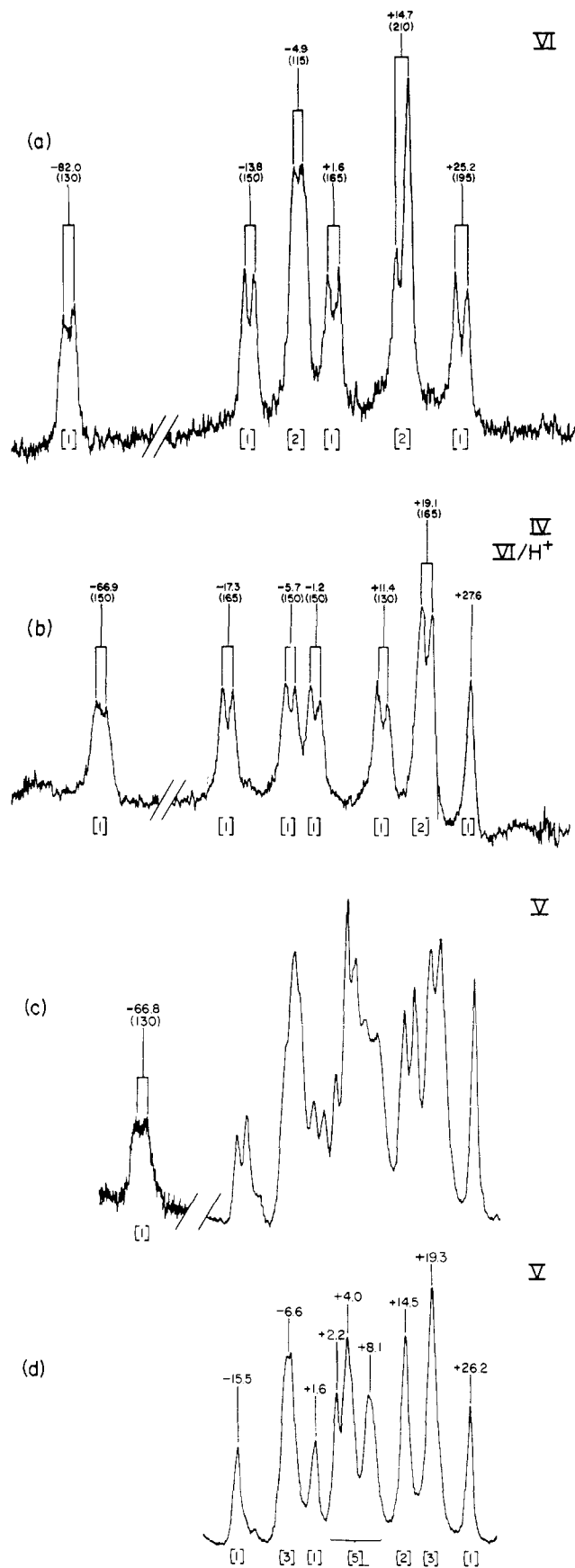


Figure 4. The 80.5-MHz ^{11}B nmr spectra of (a) VI in CDCl_2 ; (b) VI in $\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN-CF}_3\text{COOH}$, the spectrum of IV in $(\text{CH}_3)_2\text{CO}$ is identical in appearance with shifts, (splittings), and [areas] as follows: -68.3 (150) [1], -15.5 (150) [1], -5.3 (130) [1], -0.4 (130) [1], $+10.4$ (150) [1], $+20.0$ (150) [2], and $+28.2$ (singlet) [1]; (c) V in $(\text{CH}_3)_2\text{CO}$; and (d) V in $(\text{CH}_3)_2\text{CO}$ with ^1H decoupling.

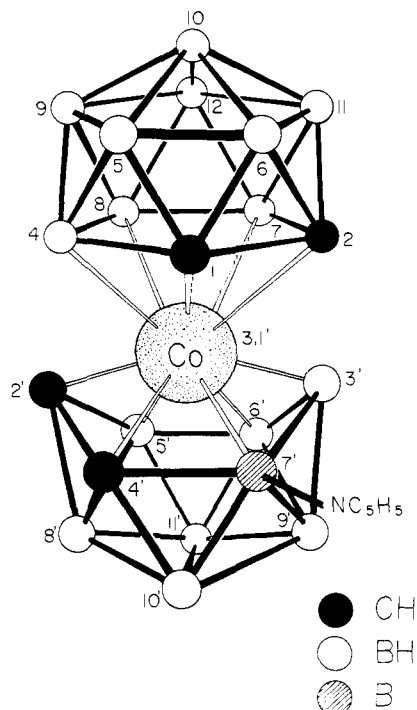


Figure 5. Proposed structure of IV with $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ in place of $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$, V, and of VI with $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ in place of $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ and $\text{C}_5\text{H}_5\text{N}$ in place of $\text{C}_5\text{H}_5\text{N}$. Only one enantiomer is illustrated.

although a singlet of area 1 was observed at high field along with a doublet of area 1 at -66.8 ppm. The spectrum was somewhat simplified by ^1H decoupling and bore a qualitative resemblance to the spectrum of $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_8\text{H}_{10}]^-$. Consequently we believe that V has a structure analogous to that proposed for IV except that the $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ fragment has been replaced by $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$.

Unsubstituted Nido Metalloboranes. The existence of the adducts I, II, and III along with their oxidation to the closo species IV, V, and VI reinforced our supposition that the formation of $X[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ and $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_8\text{H}_{10}]^-$ by polyhedral contraction proceeded *via* intermediates which contained the $X\{7,8,9\text{-C}_2\text{CoB}_8\text{H}_{11}\}$ moiety, these intermediates being structurally similar³⁵ to $\text{C}_2\text{B}_9\text{H}_{12}^-$ except that a $\{\text{BH}\}^{2+}$ fragment has been replaced by $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ or $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$. The data obtained from our studies of the pyridine adducts have allowed a more definitive characterization of these intermediates.

Degradation of $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_8\text{H}_{10}]^-$ by hydroxide ion in aqueous media afforded a red-brown solution from which the brown anion VII could be precipitated as its tetramethylammonium salt in 63% yield. The 100-MHz ^1H nmr spectrum of VII (Table I) contained signals attributable to tetramethylammonium, four nonequivalent carborane CH groups, and one signal attributable to a bridge proton. The only information relating to the structure of VII was provided by the 80.5-MHz ^{11}B nmr spectrum (Figure 2c), which was complicated by the extensive overlap of resonances. This spectrum was very similar in appearance to that of

(35) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 862 (1968).

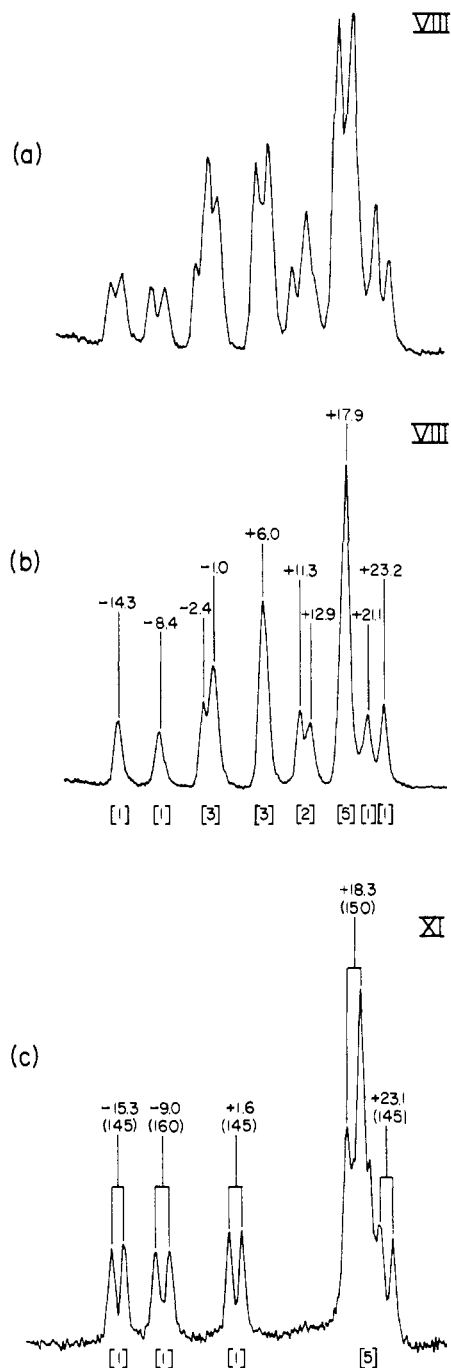


Figure 6. The 80.5-MHz ^{11}B nmr spectra of (a) VIII in CD_3CN , (b) VIII in CD_3CN with ^1H decoupling, and (c) XI in CH_2Cl_2 .

II except that the singlet at -6.2 ppm in the spectrum of II appeared as a doublet at -4.7 ppm in the spectrum of VII.

In view of this overall similarity we believe that II and VII are structurally analogous except that the terminal pyridine substituent in II is replaced by hydride in VII. Assuming Grimes' proposal concerning bridge hydrogen resonances (*vide supra*) is correct, the resonance at $+3.95$ ppm in the ^1H nmr spectrum of VII is indicative of a BHB bridge proton. Pyridine substitution of boron atom 11 would thus cause the bridge hydrogen to move to a BHC bridge location in II. In order to confirm that VII is an intermediate in the polyhedral contraction of $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]$, a sample of VII was oxidized using H_2O_2 in basic media to

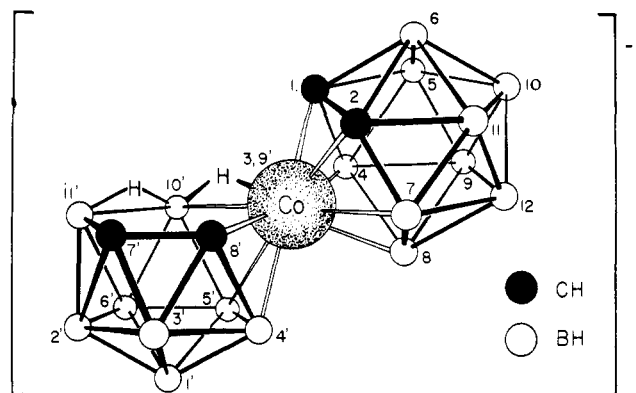


Figure 7. Proposed structure for VIII or XI with $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ in place of $\{(\pi\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$. Only one enantiomer is illustrated.

give a 78% yield of $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_9\text{H}_{10}]^-$.

We have previously compared VII with $\text{C}_2\text{B}_9\text{H}_{12}^-$; since $\text{C}_2\text{B}_9\text{H}_{13}$ may be obtained^{36,37} by protonation of $\text{C}_2\text{B}_9\text{H}_{12}^-$, we treated VII with HCl in methanol thus obtaining the mustard yellow compound VIII in 83% yield. The 100-MHz ^1H nmr spectrum of VIII (Table I) contained signals attributable to four nonequivalent carborane CH groups, tetramethylammonium, and two bridge protons. The 80.5-MHz ^{11}B nmr spectrum of VII (Figure 6a) indicated the absence of molecular symmetry and the infrared spectrum³⁸ contained no bands which could be assigned to a terminal Co-H moiety.

There are two possible structures for the nido 11-atom fragment in VIII. In the first the carbon atoms are assigned to positions 2 and 7 and the cobalt atom to position 11, thus leaving two B-B bonds in the open face to accommodate bridge protons. The second, more probable structure, is analogous to that proposed for VII except that an additional BHC bridge proton is present in the molecule. This latter structure is consistent with the presence of bridge hydrogen resonances at $+1.5$ and $+6.1$ ppm in the ^1H nmr spectrum of VIII. Recent crystallographic studies³⁴ also support a structure with both carbon atoms in the open face of the polyhedron (Figure 7). In order to establish that the protonation of VII is reversible a sample of VIII was dissolved in methanol containing potassium hydroxide. The ^{11}B nmr spectrum of this solution was like that of VII. Oxidation of VIII by H_2O_2 in basic media afforded $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ in 75% yield, confirming that the carbon atoms in VII do not separate on protonation.

Since the nido carborane $1,2\text{-C}_2\text{B}_9\text{H}_{13}$ eliminates hydrogen to give $2,3\text{-C}_2\text{B}_9\text{H}_{11}$ on heating,³⁹ the pyrolysis of VIII was investigated. At 150° in cyclooctane VIII eliminated hydrogen to give an 80% yield of the green compound IX. The 100-MHz ^1H nmr spectrum (Table I) of IX contained resonances attributable to tetramethylammonium and two types of nonequivalent

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

(37) D. V. Howe, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, *Inorg. Chem.*, **10**, 2516 (1971).

(38) See paragraph at end of paper regarding supplementary material.

(39) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **90**, 869 (1968).

carborane CH groups. The 80.5-MHz ^{11}B nmr spectrum (Figure 8) was simplified by ^1H decoupling and contained two sets of resonances of relative areas 2:4:2 and 1:1:4:2:1 whose shifts corresponded well with those of the $\{2,3,1\text{-C}_2\text{CoB}_9\text{H}_{10}\}$ and $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}$ moieties. Consequently, we believe that IX is an isomer of the previously reported²⁹ $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ in which the carbon atoms of the 11-atom polyhedron occupy positions 2 and 3, *i.e.*, $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',3'\text{-C}_2\text{B}_9\text{H}_{10}]^-$. In connection with this we have observed that, at 150° , both $X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_9\text{H}_{10}]^-$ and $X[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]^-$ may be converted to the corresponding isomers with carbon atoms at positions 2 and 3 in the 11-atom polyhedron.⁴⁰

Attempts to isolate the intermediate in the polyhedral contraction of $[3\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$ were of only limited success. Degradation of $[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$ by hydroxide ion in protic media afforded a red solution. Addition of tetramethylammonium chloride to this solution precipitated a red material, Xa. The ^1H and ^{11}B nmr spectra of this material indicated that it contained two compounds in the approximate proportions 1:2 (based on the integration of the two cyclopentadienyl resonances in the ^1H nmr spectrum). Attempts to separate the components of Xa by inert atmosphere chromatography were partly successful, but further reactions took place on the column and we were unable to obtain products of adequate purity by this means. If HCl was added to the reaction mixture instead of tetramethylammonium chloride a yellow material XIa was formed which could be extracted into dichloromethane. Again the ^1H and ^{11}B nmr spectra of XIa indicated the presence of two compounds in the approximate proportions 1:2. Attempts to separate the components of XIa by a variety of means were unsuccessful. Oxidation of XIa in basic media using H_2O_2 afforded $X[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ (*ca.* 45%) and $[(\eta\text{-C}_5\text{H}_5)\text{-C}_2\text{CoB}_7\text{H}_9]$ (compound IB in ref 29) (*ca.* 5%) while pyrolysis at 150° in cyclooctane afforded only⁶ $[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$.

Fortunately, pure samples of the major components of Xa and XIa could be prepared by an alternative route, although in low yield. Reduction of $X[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ using Zn-HCl in ethanol afforded the brown compound XI in 27% yield. The 251-MHz ^1H nmr spectrum of XI (Table I) contained resonances assigned to cyclopentadienide and two carborane CH groups. In addition two broad resonances attributable to bridge hydrogens were present. The mass spectrum exhibited a cutoff at m/e 246 consistent with the formula $\text{C}_7\text{H}_{15}\text{B}_8\text{Co}$, presumably resulting from the complete loss of H_2 within the spectrometer. Since temperatures of *ca.* 100° were necessary to volatilize XI, complete hydrogen elimination could occur thermally (*vide infra*). The 80.5-MHz ^{11}B nmr spectrum of XI (Figure 6c) contained four doublets of area 1 and a group of overlapping resonances of area 4. Comparison of this spectrum with that of VIII suggested that XI is structurally analogous to VIII except that a $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ moiety has been replaced by $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ (Figure 7). The compound XI was

(40) D. F. Dustin, W. J. Evans, C. J. Jones, R. J. Wiersema, and M. F. Hawthorne, manuscript in preparation.

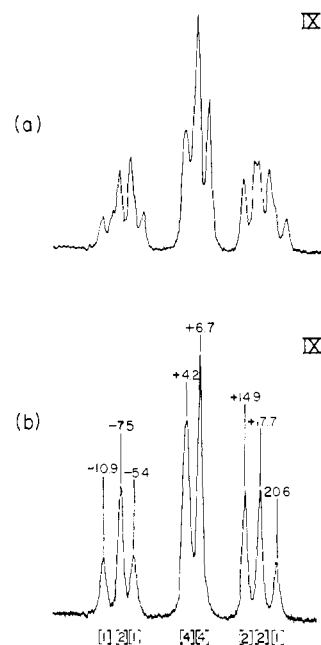


Figure 8. The 80.5-MHz ^{11}B nmr spectra of (a) IX in $(\text{CH}_3)_2\text{CO}$, and (b) IX in $(\text{CH}_3)_2\text{CO}$ with ^1H decoupling.

identified as the major component of the mixture XIa from the ^1H and ^{11}B nmr spectral data. Oxidation of XI using H_2O_2 in basic media afforded $X[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ in 81% yield. Pyrolysis of XI in cyclooctane at 150° afforded a 26% yield of $[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ while at 120° a mixture of this compound and $X[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ was formed. In both cases more than 100% production of hydrogen was found. Since the pyrolysis afforded a comparatively low yield of the closo metallocarborane and substantial decomposition took place, we believe that this additional hydrogen is produced in side reactions associated with decomposition of XI.

An aqueous methanolic solution of KOH dissolved XI to give a red solution from which the compound X could be precipitated in 58% yield by addition of tetramethylammonium chloride. The 100-MHz ^1H nmr spectrum (Table I) of X contained resonances due to tetramethylammonium, cyclopentadienide, and two nonequivalent carborane CH groups. In addition a broad resonance attributable to a bridge proton was observed. The 80.5-MHz ^{11}B nmr spectrum of X (Figure 1c) contained resonances from eight nonequivalent boron atoms and was quite similar to that of I. Accordingly we assign a structure to X which is analogous to that of I (Figure 3) except that the $\text{C}_5\text{H}_5\text{N}$ ligand has been replaced by hydride. The ^1H nmr resonance at +2.9 ppm in X would seem to indicate a BHB bridge as opposed to BHC as was proposed for I (*vide supra*). The compound X was identified as the major component of the mixture Xa by the ^1H and ^{11}B nmr spectral data. Oxidation of X using H_2O_2 in basic media afforded $X[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$ in 84% yield, thus confirming that X is an intermediate in the polyhedral contraction of $[3\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$.

Degradation of $[3\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$ or $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]^-$ in the presence of cobalt affords polymetallic species^{26,27} containing the

{1,2,3,6-C₂Co₂B₈H₁₀} fragment.^{41,42} These species presumably result from the initial removal of {BH}²⁺ from position 6 of the parent icosahedral metallocarborane, followed by complexation with cobalt ions. Since the degradation products VII and X are thought to have a cobalt atom in the open pentagonal face of the molecule, a rearrangement must take place in the absence of cobalt ions. A sample of [3-(η-C₅H₅)-1,2,3-C₂CoB₉H₁₁] was degraded as described previously²⁶ except that cobalt ions were not added until a reaction time of 24 hr had elapsed. After a further 3 hr at reflux the reaction mixture was treated with H₂O₂ and afforded a 62% yield of X[1-(η-C₅H₅)-2,4,1-C₂CoB₉H₁₁] but only 3% of the trimetallic species. Similarly degradation of [1,2-C₂B₉H₁₁-3,3'-Co-1',2'-C₂B₉H₁₁]⁻ in 30% aqueous NaOH for 6 hr at 95° afforded a 52% yield of X[1,2-C₂B₉H₁₁-3,1'-Co-2',4'-C₂B₉H₁₀]⁻ whereas a similar experiment in which cobalt ions were added after 3 hr gave a 48% yield.

These experiments demonstrate that if the immediate degradation product is not trapped by reaction with cobalt, a species is formed which is inert to reaction with cobalt. Since examples of metallocarboranes with adjacent cobalt atoms are known,⁴³ it seems unlikely that the formation of the C₂CoB₂ open-face would account for this inert behavior. A more likely cause is the protonation of the open face, even under basic conditions, the presence of a bridge hydrogen then preventing the reaction with cobalt. Such a protonation reaction will be very fast in the protic media used for degradation and the good yield (75%) of a polymetallic complex²⁶ indicates that protonation of the first formed C₂B₃ face is not occurring. Rather it seems that, in the absence of cobalt ions, the first intermediate rearranges to the geometry proposed for VII and X and then becomes protonated. To test the validity of this scheme samples of VII and X were placed in sealed bulbs with excess sodium hydride suspended in dry tetrahydrofuran. After a period of 5 days at room temperature VII afforded an 8.7% yield of hydrogen and X an 8.5% yield. These figures demonstrate that both these species can retain their bridge hydrogen atoms in strong base.

These observations are of interest since most of the cobaltacarboranes synthesized so far have carborane fragments whose structures correspond with those expected^{44,45} for nido and arachno boranes with the same number of vertices; one exception to this is the "canastide" ion.⁴¹ Here we have found that, although the "canastide" ion is stable when bonded to two cobalt ions, in the presence of only one cobalt ion a rearrangement occurs to produce the expected "decaborane-like" structure. However, it is not clear whether the driving force for this rearrangement is the attainment of a particular geometry for the C₂B₈ fragment or a preference for the metal ion to be located in the open face of a nido metallocarborane. It should be noted that, for iron- and nickel-containing metallocarboranes, examples have been found^{43,46} in which the carborane

(41) D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969).

(42) M. R. Churchill, A. H. Reis, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 4993 (1970).

(43) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 4565 (1973).

(44) R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971).

(45) R. W. Rudolph and W. R. Pretyes, *Inorg. Chem.*, **11**, 1974 (1972).

(46) R. R. Rietz and M. F. Hawthorne, unpublished work.

fragment does not adopt the geometry of the related⁴⁵ nido borane.

Infrared and Electronic Spectral Data. The infrared spectra³⁸ of the compounds described were largely unexceptional. All the compounds exhibited bands in the region 2500–2600 cm⁻¹ assigned to BH stretching vibrations. In addition the spectra of II, VII, VIII, IX, and X contained a band at ca. 950 cm⁻¹ attributable to (CH₃)₄N⁺ while the spectra of I, III, VI, X, and XI contained a band in the region 810–840 cm⁻¹ attributable to the presence of the C₅H₅⁻ ligand. In the case of IV this band was obscured by strong absorptions owing to the PF₆⁻ ion. No bands were observed in the spectra of VIII and XI which might arise from the presence of a terminal Co–H group. The infrared spectra of IV and V contained a sharp band at 1630 and 1625 cm⁻¹, respectively, which was unique to the closo species with the pyridine substituent.

The electronic spectra (Table II) of the closo com-

Table II. Electronic Spectral Data (CH₃CN Solution)

Compound	λ _{max} , mμ (ε)
I	440 (5215), 400 (6440), 260 sh (16,125)
II	470 sh (4950), 400 (6450), 270 (19,250), 235 sh (13,875)
III	510 sh (350), 420 sh (1065), 370 (2600), 295 (6220), 260 (12,600)
IV	600 (925), 340 sh (3760), 280 sh (9700), 250 (18,800)
IV ^a	605 (1025), 340 sh (4430), 280 sh (10,250), 250 (20,700)
V	630 (1160), 360 sh (5040), 260 (22,400)
VI	650 (1280), 460 (4750), 315 sh (8900), 250 (15,600)
VII	540 sh (470), 480 sh (805), 395 (3250), 310 sh (7800), 270 (16,600)
VIII	400 sh (1250), 265 (14,300)
IX	600 (285), 490 (455), 385 (9360), 300 sh (8120), 290 (15,370), 235 (13,250)
X	520 sh (460), 460 sh (675), 380 (2500), 275 sh (10,380), 245 (12,150)
XI ^a	380 sh (850), 275 (12,400), 245 (11,000)

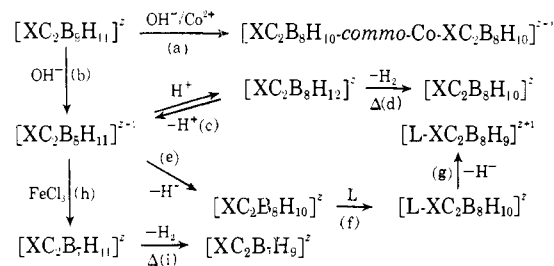
^a Spectrum measured in CH₂Cl₂ solution.

pounds IV, V, VI, and IX contained a band in the region 600–650 mμ and were green or blue in color. In contrast the spectra of the nido compounds I, II, III, VII, VIII, X, and XI contained no absorptions in the region 550–650 mμ and were red or brown in color. This marked color difference is in accord with the substantial structural differences between the proposed nido and closo geometries.

Conclusion

The reactions and compounds described here complete a reaction scheme (Scheme I) starting from the generalized heteroborane [XC₂B₉H₁₁][±], where X =

Scheme I



$\{\text{BH}\}^{2+}$ and $z = 0$, $\text{X} = \{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ and $z = 0$, or $\text{X} = \{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ and $z = -1$.

The cobalt insertion reaction (a) has been reported^{26,27} for the cobalt containing species while $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]^-$ may be prepared from $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ in one step—although only in 30–40% yield. The degradation, reversible protonation, and pyrolysis reactions (b, c, and d) are well known^{35,36,39} for the carboranes and are demonstrated here for the cobalt-carboranes. The oxidation, adduct formation, and further oxidation steps (e, f, and g) have been shown indirectly for the carboranes. Oxidation of $\text{C}_2\text{B}_9\text{H}_{12}^-$ using FeCl_3 in the presence of Lewis bases (e.g., pyridine or tetrahydrofuran) affords the nido ligand adducts directly.³¹ However, since $2,3\text{-C}_2\text{B}_9\text{H}_{11}$ reacts very readily³⁹ with Lewis bases, the initial formation of an unisolated closo carborane is not unlikely. Again the oxidation of nido ligand adducts has not been carried out directly, but substituted closo carboranes of analogous structure have been prepared by an electronically equivalent pathway.⁴⁷ The final reactions involving degradation of $[\text{XC}_2\text{B}_9\text{H}_{11}]^{z-1}$ with excess FeCl_3 to give $[\text{XC}_2\text{B}_7\text{H}_{11}]^z$, which can be pyrolyzed to give $[\text{XC}_2\text{B}_7\text{H}_9]^z$, have been described previously.^{29,48}

Thus it appears that $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ or $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ can replace $\{\text{BH}\}^{2+}$ in a polyhedral environment with retention of the major chemical features of the polyhedral framework. Some differences in reactivity are apparent, of which the most pronounced concerns the species $[\text{XC}_2\text{B}_9\text{H}_{11}]^{z-1}$. While $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ and $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ are readily deprotonated but not oxidized in air, both VII and X are not easily deprotonated but are readily oxidized. Thus it seems that the bridge hydrogen of $\text{C}_2\text{B}_9\text{H}_{12}^-$ is largely protic in nature while that in VII and X is more hydridic. The ability of $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}^{2+}$ to replace $\{\text{BH}\}^{2+}$ in a polyhedral environment is surprising in view of the chemical differences between these elements, and attempts to initiate similar reaction schemes using iron or nickel in place of cobalt have thus far been unsuccessful.²⁴ Wade has suggested⁴⁹ that $\{\text{Ru}(\text{CO})_3\}$ is electronically analogous to $\{\text{BH}\}$ and contributes three orbitals and two electrons to the polyhedral bonding of $[\text{Ru}_6(\text{CO})_{18}]^{2-}$, just as is proposed for $\{\text{BH}\}$ in $\text{B}_6\text{H}_6^{2-}$. Although transition metals were not considered in their discussion, Lipscomb and coworkers have pointed out⁵⁰ that a heteroatom contributing two electrons in an axially symmetric σ -orbital and a π -orbital pair might replace a $\{\text{BH}\}$ group in $\text{B}_{12}\text{H}_{12}^{2-}$. It is interesting, therefore, to note that the metal atom in $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}$ is formally isoelectronic with that in $\{\text{Ru}(\text{CO})_3\}$.⁵¹ Extension of this analogy between $\{\text{BH}\}$ and $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}$ would lead one to expect that $\{(\eta\text{-C}_5\text{H}_5)\text{Ni}\}$ might replace $\{\text{CH}\}$ in a polyhedral environment. Thus $[(\eta\text{-C}_5\text{H}_5)_2\text{Ni}_2\text{B}_{10}\text{H}_{10}]$ should exist as a stable heteroborane analog of $\text{C}_2\text{B}_{10}\text{H}_{12}$; this point is under investigation.

In a more general sense it is possible to envisage a number of factors which are important in determining whether or not a transition metal may replace a $\{\text{BH}\}$

group throughout a reaction sequence. (1) The metal must be in an oxidation state which is stable to a variety of reaction conditions when in the presence of the polyhedral residue and the other ligands on the metal. (2) While in this oxidation state the metal, in combination with the other ligands, must be able to satisfy the electronic requirements of the polyhedral framework. (3) The metal atom must be able to tolerate a variety of coordination numbers within the polyhedral framework. (4) The other ligands on the metal must be inert under the reaction conditions to which they may be exposed. (5) Criteria 1, 2, and 3 are concerned with the compatibility of the metal atom with the residue of the polyhedral framework. The existence of a reaction sequence further requires that, when the above requirements are met, the metal atom does not render the remainder of the polyhedral framework inert to chemical attack.

The failure of attempts⁵² to produce new metallocarboranes by degradation of $[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-M-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]^z$, where $\text{M} = \text{Ni}^{\text{IV}}$ and $z = 0$, $\text{M} = \text{Ni}^{\text{III}}$ and $z = -1$, and $\text{M} = \text{Fe}^{\text{III}}$ and $z = -1$, may be associated with requirements 1 and 2. The third requirement is amply demonstrated by the reaction scheme described earlier, in that the cobalt atom is bound to the polyhedral framework by four, five, or six atoms at various points in the scheme. The fourth requirement is exemplified by the pyrolysis reactions of VIII and XI. While the pyrolysis of VIII, containing the $\{1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}\}^+$ fragment, proceeds in high yield, the pyrolysis of XI which contains the $\{(\eta\text{-C}_5\text{H}_5)\text{Co}\}$ fragment proceeds in low yield and substantial decomposition is observed.

Clearly the foregoing discussion represents only a preliminary evaluation of metallocarborane chemistry. However, the concept of a metallocarborane as a transition metal complex containing a π -bonded carborane ligand is no longer adequate. The discovery⁴³ of metallocarboranes containing formal Co^{III} ions within bonding distance of one another demonstrates that the chemistry of metals may be significantly modified when in a polyhedral metallocarborane environment. Hopefully the need for a more sophisticated model for metallocarboranes will stimulate active interest in the role of the metal atom in this chemically unique class of compounds.

Experimental Section

Physical Measurements. The 100-MHz ^1H nmr spectra were recorded on Varian HA 100 spectrometer; 80.5-MHz ^{11}B and 251-MHz ^1H nmr data were recorded on an instrument designed and constructed by Professor F. A. L. Anet and Dr. C. H. Bradley of this department. Infrared spectra were recorded using a Perkin-Elmer Model 137 spectrophotometer and electronic spectra using a Beckman Model DB instrument. Mass spectra were obtained on an A.E.I. Model MS-9 spectrometer and elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. With the exception of cyclooctane which was purified by passage through a column of activated alumina, solvents used were reagent grade, as were other reagents used. Potassium hydroxide was obtained as pellets containing 85% KOH and hydrogen peroxide was 30% v/v in aqueous solution. The compounds $[3\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}1,2,3\text{-C}_2\text{CoB}_9\text{H}_{11}]$, $\text{K}[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_9\text{H}_{11}]$, $\text{X}[1\text{-}(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_9\text{H}_{10}]$, and $[(\text{CH}_3)_4\text{N}]\text{X}[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_9\text{H}_{10}]$ were prepared by reported^{22,26,29} procedures. All reactions other than oxidations were carried out in a nitrogen

(47) D. A. Owen and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 6002 (1969).

(48) J. Plešek and S. Hermanek, *Chem. Ind. (London)*, 1267 (1971).

(49) K. Wade, *J. Chem. Soc., Chem. Commun.*, 792 (1971).

(50) E. B. Moore, L. L. Lohr, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(51) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972).

(52) L. F. Warren, Ph.D. Dissertation, University of California, Riverside (1970).

atmosphere using solvents which had previously been saturated with nitrogen. All operations involving the compounds III, VII, VIII, X, and XI were carried out using Schlenk equipment and standard inert atmosphere procedures. While all the compounds described seemed stable to air in the solid state for short periods (minutes), solutions of III, VII, and X were oxidized by air. Moist air decomposed IV over a few days and acetone was found to react with VIII and XI. All the compounds except IX are best stored in a dry nitrogen atmosphere. Preparative thick-layer chromatography was carried out using silica gel plates F-254 obtained from EM Laboratories. Electronic spectra were obtained from solutions in spectrograde solvents which, where necessary, were saturated with nitrogen. Hydrogen evolution experiments were carried out using standard vacuum line techniques, reactions being carried out in sealed glass bulbs fitted with break seals. Volumes of noncondensable (-196°) gas were measured by means of a Sprengel pump. Previously characterized compounds formed in the oxidation and pyrolysis reactions were identified by their 80.5-MHz ^{11}B nmr spectra.

$X[9-(\eta\text{-C}_5\text{H}_5)\text{-}11\text{-C}_5\text{H}_5\text{N-}7,8,9\text{-C}_2\text{CoB}_8\text{H}_{10}]$, I. A solution of $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (0.5 g, 2.0 mmol) in benzene (40 ml) was treated with pyridine (0.25 ml, 3.1 mmol). The solution was stirred at room temperature for 3 hr during which time the purple color of the closo compound gave way to the red color of the adduct, and red crystals began to precipitate. Hexane (50 ml) was then added while the mixture was stirred for a further 30 min. The red product was isolated by filtration and recrystallized from dichloromethane–heptane (0.55 g, 85%), mp 224° . *Anal.* Calcd for $\text{C}_{12}\text{H}_{20}\text{B}_8\text{NCo}$: C, 44.53; H, 6.18; B, 26.72; N, 4.33; Co, 18.24. Found: C, 44.62; H, 6.39; B, 26.53; N, 4.00; Co, 18.19.

$[(\text{CH}_3)_4\text{N}]X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}11'\text{-C}_5\text{H}_5\text{N-}7',8'\text{-C}_2\text{B}_8\text{H}_{10}]$, II. A solution of $[(\text{CH}_3)_4\text{N}]X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_8\text{H}_{10}]$ (0.5 g, 1.3 mmol) in acetonitrile (2.5 ml) was treated with pyridine (0.5 ml, 6.2 mmol). The mixture was stirred for 3 hr at room temperature during which time the blue color of the starting material gave way to the red color of the adduct. Acetone (40 ml) was then added followed by a solution of $(\text{CH}_3)_4\text{NCl}$ (0.5 g, 4.5 mmol) in ethanol–water (60 ml of a 1:1 v/v mixture). Evaporation of the solvent under reduced pressure caused the product to precipitate; this material was isolated by filtration and washed with water followed by dichloromethane to give a brown powder (0.42 g, 70%). This material was purified by recrystallization from dichloromethane using a soxhlet extractor (this operation was carried out in a nitrogen atmosphere). Smaller quantities of this adduct could be recrystallized from dichloromethane–chloroform. *Anal.* Calcd for $\text{C}_{13}\text{H}_{38}\text{B}_{17}\text{N}_2\text{Co}$: C, 33.58; H, 8.18; B, 39.52; N, 6.03; Co, 12.70. Found: C, 33.50; H, 8.01; B, 39.75; N, 5.80; Co, 12.48.

$X[9-(\eta\text{-C}_5\text{H}_5)\text{-}11\text{-C}_5\text{H}_5\text{NH-}7,8,9\text{-C}_2\text{CoB}_8\text{H}_{10}]$, III. A solution of piperidine (0.1 g, 1.2 mmol) in benzene (10 ml) was added to a solution of $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (0.25 g, 1.0 mmol) in benzene (20 ml) and the mixture was stirred for 45 min. Hexane (50 ml) was then added over a period of 15 min to complete the precipitation of the red product (0.30 g, 87%) which was recrystallized from dichloromethane–hexane, mp $>200^{\circ}$ dec. *Anal.* Calcd for $\text{C}_{12}\text{H}_{28}\text{B}_8\text{NCo}$: C, 43.72; H, 7.89; B, 26.23; N, 4.25; Co, 17.91. Found: C, 43.91; H, 8.00; B, 26.18; N, 4.28; Co, 17.54.

$X[1-(\eta\text{-C}_5\text{H}_5)\text{-}7\text{-C}_5\text{H}_5\text{N-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}][\text{PF}_6]_2$, IV. A solution of FeCl_3 (20 ml of a solution containing 0.5 g of FeCl_3 in 30 ml of 1:1 v/v acetone–water) was added to a solution of I (0.25 g, 0.77 mmol) in acetone (25 ml) over a period of 5 min with stirring. After this time the solution was poured into water (200 ml) and a solution of KPF_6 (2.0 g) in water (20 ml) was added. The blue precipitate was then extracted into dichloromethane–ether (2 \times 150 ml of a 2:1 v/v mixture) and the extract was dried over MgSO_4 . The dried solution was evaporated under reduced pressure and more ether was added during the evaporation to precipitate the blue product (0.32 g, 81%). The product was purified by recrystallization from dichloromethane–chloroform then dichloromethane–ether. *Anal.* Calcd for $\text{C}_{12}\text{H}_{19}\text{B}_8\text{NCoPF}_6$: C, 30.81; H, 4.07; B, 18.49; N, 3.00; Co, 12.62. Found: C, 30.14, H, 4.34; B, 18.50; N, 3.61; Co, 12.83.

$X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}7'\text{-C}_5\text{H}_5\text{N-}2',4'\text{-C}_2\text{B}_8\text{H}_{10}]$, V. A solution of FeCl_3 (20 ml of a solution of 0.5 g of FeCl_3 in 30 ml of 1:1 v/v acetone–water) was added to a solution of II (0.5 g, 1.1 mmol) in acetone–water (30 ml of a 2:1 v/v mixture). The combined solutions were stirred for 10 min during which time the color changed from red to deep green. The reaction mixture was then poured into water (100 ml) and the product was extracted into dichloromethane (2 \times 100 ml). The combined extracts were dried over MgSO_4 and filtered; addition of hexane to the filtrate followed by evaporation

of the dichloromethane caused the green product to precipitate (0.40 g, 86%). The product was recrystallized from dichloromethane–hexane as a dichloromethane solvate, mp 159° . *Anal.* Calcd for $\text{C}_9\text{H}_{22}\text{BNCo}\cdot 0.5\text{CH}_2\text{Cl}_2$: C, 26.38; H, 6.02; B, 42.49; N, 3.24; Cl, 8.22; Co, 13.65. Found: C, 26.45; H, 6.19; B, 42.70; N, 3.48; Cl, 8.55; Co, 13.32.

$X[1-(\eta\text{-C}_5\text{H}_5)\text{-}7\text{-C}_5\text{H}_5\text{N-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$, VI. A solution of FeCl_3 (25 ml of a solution containing 0.5 g of FeCl_3 in 30 ml of 1:1 v/v acetone–water) was added to a solution of III (0.25 g, 0.75 mmol) in acetone (30 ml) and the mixture was stirred for 5 min. After this time the solution was poured into aqueous K_2CO_3 (200 ml of a 1% w/v solution). The green product was extracted into ether (2 \times 200 ml), and the combined extracts were dried over MgSO_4 . After filtration the ether extract was evaporated to dryness and the green residue was redissolved in acetonitrile, the solution was filtered and the green product was precipitated by slow addition of water (85 mg, 34%). The compound was purified by recrystallization from dichloromethane–heptane, mp 151° dec. *Anal.* Calcd for $\text{C}_{12}\text{H}_{20}\text{B}_8\text{NCo}$: C, 43.98; H, 7.33; B, 26.39; N, 4.28; Co, 18.02. Found: C, 43.60; H, 7.71; B, 26.02; N, 4.58; Co, 18.44.

$[(\text{CH}_3)_4\text{N}]X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}7',8'\text{-C}_2\text{B}_8\text{H}_{10}]$, VII. A solution of $\text{K}[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,3'\text{-Co-}1',2'\text{-C}_2\text{B}_8\text{H}_{10}]$ (1.0 g, 2.8 mmol) in aqueous potassium hydroxide (100 ml of a solution containing 30 g, 0.55 mmol, of KOH) was heated to 95° for 6 hr. After this time tetramethylammonium chloride (1.5 g in 50 ml of water) was added and the resulting precipitate was isolated by filtration then washed with water. This brown solid was redissolved in acetone; addition of water and evaporation of most of the acetone precipitated the product (0.81 g, 64%) which was recrystallized from acetone–water. *Anal.* Calcd for $\text{C}_{12}\text{H}_{18}\text{B}_{17}\text{N}_2\text{Co}$: C, 31.26; H, 9.99; B, 39.86; N, 6.08; Co, 12.81. Found: C, 31.55; H, 10.06; B, 40.05; N, 6.19; Co, 12.49.

Oxidation of VII. A sample of VII (100 mg, 0.22 mmol) was dissolved in acetone (5 ml) to which an aqueous methanolic solution of KOH (0.25 g, 4.6 mmol, of KOH in 30 ml of 5:1 v/v water–methanol) was added. Hydrogen peroxide (1 ml) was then added, the mixture was stirred for 5 min and filtered, and the blue product (65 mg, 75%), which was identified as $[(\text{CH}_3)_4\text{N}]X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_8\text{H}_{10}]$, was dried *in vacuo* and recrystallized from dichloromethane–chloroform.

$[(\text{CH}_3)_4\text{N}]X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,9'\text{-Co-}7',8'\text{-C}_2\text{B}_8\text{H}_{10}]$, VIII. Hydrochloric acid (2 ml of 11 *N* aqueous HCl) was added to a suspension of VII (0.5 g, 1.1 mmol) in methanol (50 ml) and the mixture was warmed to dissolve all the starting material. Slow addition of water (50 ml) followed by evaporation of some of the methanol under reduced pressure precipitated the mustard colored product (0.35 g, 83%) which was recrystallized from methanol–water containing 1% by volume 1 *N* HCl. *Anal.* Calcd for $\text{C}_8\text{H}_5\text{B}_7\text{NCo}$: C, 24.77; H, 9.03; B, 47.37; N, 3.61; Co, 15.22. Found: C, 24.52; H, 8.77; B, 47.17; N, 3.87; Co, 15.08.

Oxidation of VIII. A sample of VIII (100 mg, 0.26 mmol) was dissolved in methanol (10 ml) and aqueous KOH (0.5 g, 9.2 mmol, of KOH in 20 ml of H_2O) added. Careful addition of hydrogen peroxide (1 ml) to the solution, which was stirred for 5 min, afforded a blue precipitate (75 mg, 75%). This was isolated by filtration, dried, and recrystallized from dichloromethane–chloroform. This material was identified as $[(\text{CH}_3)_4\text{N}]X[1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',4'\text{-C}_2\text{B}_8\text{H}_{10}]$.

Pyrolysis of VIII. Preparation of $[(\text{CH}_3)_4\text{N}][1,2\text{-C}_2\text{B}_9\text{H}_{11}\text{-}3,1'\text{-Co-}2',3'\text{-C}_2\text{B}_8\text{H}_{10}]$, IX. A sample of VIII (100 mg, 0.26 mmol) was suspended in cyclooctane (20 ml) and the mixture was heated to reflux for 3 hr with stirring. After this time the product was collected by filtration and washed with chloroform then redissolved in dichloromethane–acetonitrile (9:1, v/v). This solution was eluted through a 2 \times 3-cm silica gel column and the solvent was removed under reduced pressure. The green solid thus obtained was recrystallized from dichloromethane–chloroform (80 mg, 80%). *Anal.* Calcd for $\text{C}_8\text{H}_5\text{B}_7\text{NCo}$: C, 24.90; H, 8.56; B, 47.61; N, 3.63; Co, 15.30. Found: C, 24.54; H, 8.55; B, 47.21; N, 3.55; Co, 14.82.

In a separate reaction using a sealed bulb VIII (132 mg, 0.34 mmol) and cyclooctane (5 ml) were heated to 160° for 3 hr. The reaction afforded IX (110 mg, 81%) and a noncondensable gas presumed to be hydrogen (0.33 mmol, 97%).

$X[9-(\eta\text{-C}_5\text{H}_5)\text{-}7,8,9\text{-C}_2\text{CoB}_8\text{H}_{10}]$, XI. To a suspension of $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (0.5 g, 2.1 mmol) in acidified ethanol (50 ml of ethanol containing 6 ml of 11 *N* aqueous HCl), zinc dust (1.0 g) was added over a period of 15 min with shaking. After this

time dichloromethane and heptane were added (100 ml of a 3:1 v/v mixture) followed by water (300 ml). The brown solution forming the lower organic phase of the mixture was run out and passed through a column of packed dry MgSO_4 (an $8.0 \times 3.5\text{-cm}$ column was used) and the product eluted with dichloromethane–heptane (3:1 v/v mixture) until the first gray band reached the base of the MgSO_4 column. Evaporation of the dichloromethane from the eluted light brown solution precipitated the product (0.135 g, 27%) which was recrystallized from dichloromethane–heptane, mp 128° dec. *Anal.* Calcd for $\text{C}_7\text{H}_{17}\text{B}_8\text{Co}$: C, 34.09; H, 6.90; B, 35.06; Co, 23.94. Found: C, 34.24; H, 7.14; B, 34.60; Co, 24.07. Further elution afforded more of the product (up to 190 mg) along with impurities. Further purification of this material could be effected by the following procedure. A sample of the impure material (ca. 100 mg) was dissolved in dichloromethane (ca. 5 ml) and the resulting solution was adsorbed on alumina (ca. 20 ml of activity I acidic aluminum oxide). While in this state the metallocarborane was subject to immediate oxidation on exposure to air. The mixture was washed with dichloromethane until the washings were colorless; then hydrochloric acid (ca. 3 ml of 11 N HCl) was added and the solid was thoroughly mixed until it became a uniform mustard color. The purified compound could then be eluted off the alumina with dichloromethane; addition of heptane and evaporation of dichloromethane caused the purified product to precipitate.

Oxidation of XI. A sample of XI (50 mg, 0.2 mmol) was dissolved in methanol (5 ml) and aqueous potassium hydroxide (0.3 g, 5.5 mmol of KOH in 10 ml of H_2O) was added followed by hydrogen peroxide (0.5 ml). The mixture was stirred for 5 min and water (30 ml) was added, and the products were extracted into dichloromethane (2×30 ml). The dichloromethane solution was dried over MgSO_4 , filtered, and, after addition of hexane, evaporated to precipitate the product (40 mg, 81%) which was identified as $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$.

Pyrolysis of XI. A sample of XI (50 mg, 0.2 mmol) was suspended in cyclooctane and the mixture was heated to reflux for 3 hr. After this time the solvent was removed under reduced pressure, and the products were separated by preparative thick-layer chromatography on silica gel with dichloromethane–hexane eluent. The major product eluted as a purple band which was separated and extracted into dichloromethane; addition of hexane and evaporation of the solution afforded $[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (13 mg, 26%). Trace amounts of other materials separated but these were not obtained in sufficient quantity for characterization.

Two pyrolysis experiments were carried out in sealed bulbs; in the first, XI (72 mg, 0.29 mmol) and cyclooctane (5 ml) were heated to 160° for 3 hr to give $[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (20 mg, 28%)

and a noncondensable gas (0.40 mmol, 137%). In the second experiment XI (61 mg, 0.25 mmol) and cyclooctane (5 ml) were heated to 120° for 30 min to give $[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,3,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (11 mg, 18%) and $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (2.5 mg, 4%), which were separated by preparative thick-layer chromatography, along with a noncondensable gas (0.31 mmol, 123%).

$[(\text{CH}_3)_4\text{N}]X[9-(\eta\text{-C}_5\text{H}_5)\text{-}7,8,9\text{-C}_2\text{CoB}_8\text{H}_{11}]$, **X**. A sample of XI (0.1 g, 0.41 mmol) was dissolved in an aqueous methanolic solution of potassium hydroxide (1.0 g, 18.5 mmol, of KOH in 25 ml of 4:1 v/v water–methanol) and the mixture was filtered into an aqueous solution of tetramethylammonium chloride (1.0 g in 20 ml of water). The resulting precipitate was isolated by filtration, washed with water, dried *in vacuo*, and recrystallized from dichloromethane–chloroform to give the red crystalline product (75 mg, 58%). *Anal.* Calcd for $\text{C}_{11}\text{H}_{28}\text{B}_8\text{NCo}$: C, 41.33; H, 8.77; B, 27.05; N, 4.38; Co, 18.47. Found: C, 41.10; H, 8.72; B, 26.74; N, 4.24; Co, 18.14.

Oxidation of X. A sample of X (50 mg, 0.16 mmol) was dissolved in acetone (5 ml); aqueous potassium hydroxide (0.1 g, 1.9 mmol, of KOH in 20 ml of H_2O) was then added followed by hydrogen peroxide (0.5 ml) and the mixture was stirred for 5 min. The mixture was then extracted with dichloromethane (2×20 ml), and the extract was dried over MgSO_4 . After filtration hexane was added to the extract, evaporation of the dichloromethane caused $X[1-(\eta\text{-C}_5\text{H}_5)\text{-}2,4,1\text{-C}_2\text{CoB}_8\text{H}_{10}]$ (32 mg, 84%) to precipitate.

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Supplementary Material Available. A listing of infrared spectral data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105×148 mm, $\frac{1}{20\times}$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-7633.