(h^1-C_5H_5)HgBr and (h^1-C_5H_5)HgI may be treated similarly, for the same estimates can be made taking into account the larger size of the Br atoms hindering the packing, giving a slightly smaller intermolecular contribution and the contribution of ^{79}Br (50.5%) spin $^3/_2$ and ^{81}Br (49.5%) spin $^3/_2$ being slightly different from that of Cl (see Table I). The large size of the iodine atom in (h^1-C_5H_5)HgI is slightly offset by the fact that ^{127}I has a spin of $^5/_2$ which tends to increase its contribution to the second moment. In both cases the low value of the high-temperature second moment is thought due to the motion of the C_5H_5 rings in their approximate molecular planes.

Conclusions

The molecular motions detected in the present work are thought to be similar to those found in the case of the cyclooctatetraeneiron tricarbonyls,[3] where the C_8H_8 rings reorient in the solid state with simultaneous distortion and breaking of the metal–cyclooctatetraene bond. There may well be some bonding between the metal and the ligand during the motion, but it cannot be that observed in the static structure which is presumably the optimum bonding. The occurrence of bond breaking with reorientation in these compounds was unusual, being the only reported instance to date, and contrary to what one might intuitively expect in the solid at the relatively low temperatures at which it occurred. The cyclopentadienyl compounds investigated here represent an even more extreme example. In these compounds, not only must there be distortion of the rings as they "jump" between potential wells, but there must be a simultaneous change in the localized metal–carbon σ bond. As such, the result is of considerable interest and would seem to warrant further work on these systems as well as investigation of other potential examples.

For the series of compounds (h^1-C_5H_5)HgX (X = C_5H_5, Cl, Br, I), there is a general correspondence between the solid state results and those from high resolution nmr studies in solution. As the electronegativity of X is increased, the temperature of the transition increases. This implies that the activation energy for the process is increasing. It also implies that in the solid state, intramolecular forces contribute significantly to the barrier to reorientation. Two values for the activation energy in the solid state were obtained; one was obtained by least-squares fit of the experimental data using the BPP equation,[19] as modified by Smith.[20] This is an empirical relationship based on the change in the line width with temperature and usually yields values within 15% of those obtained by other methods. The second value for the activation energy was obtained by use of the Waugh estimate,[21] another empirical relationship, where $E = 37T$, where T is the temperature at the midpoint of the line-width transition. This very empirical formula usually yields values within 20% of those obtained from other methods. The E_a values for each compound are given in Table I. Although good fits were obtained using the BPP equation, the values from the Waugh estimate appear more "sensible." Measurement of the temperature dependence of T_1, the spin–lattice relaxation time, for these compounds will provide a much more direct method of obtaining values for the activation energy.

Acknowledgments. The authors acknowledge the National Research Council of Canada for financial support in the form of Operating Grants (C. A. F., R. G. G., and C. V. S.) and a Major Equipment Grant to purchase the nmr spectrometer (C. A. F.).

New 10- and 11-Atom Polyhedral Metallocarboranes Prepared by Polyhedral Contraction

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Abstract: The base degradation of [LCo(π-(3)-1,2-$B_9C_2H_{11}$)]^z followed by oxidation has been found to effect a polyhedral contraction to give [LCo(π-(1)-2,4-$B_8C_2H_{10}$)]^z, where L = $C_5H_5^-$ and z = 0 or L = (3)-1,2-$B_9C_2H_{11}^{2-}$ and z = −1. Further degradation of these complexes using $FeCl_3$ in ethanol gave [(π-C_5H_5)Co(π-$B_7C_2H_{11}$)] and [(π-(3)-1,2-$B_9C_2H_{11}$)Co(π-$B_7C_2H_9$)]$^-$. The former complex eliminates hydrogen at 150° to give [(π-C_5H_5)Co(π-(2)-1,10-$B_7C_2H_9$)].

Previously, metallocarborane complexes have been prepared by two general methods. The first involves deprotonation of a nido carborane which contains acidic hydrogen atoms followed by reaction of the resulting anion with a transition metal ion to give a metallocarborane.[1,2] The second, more general approach involves the direct reduction of a closo carborane to an anionic species using an alkali metal. Reaction of this anion with transition metal ions then gives the desired metallocarborane.[3–5] This second method has been

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[1] 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. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

[2] T. A. George and M. F. Hawthorne, *ibid.*, **91**, 5475 (1969).

[3] G. B. Dunks, Ph.D. Dissertation, University of California, Riverside, Calif., 1970.

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

[5] G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *ibid.*, **93**, 2541 (1971).

Table I. 100-MHz ^{1}H Nmr Spectral Data

Compound	Resonance[a]	Assignment
IA[b] $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$	-4.94	Cyclopentadienide
	-4.64	Carborane CH
IB[b] $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_9)]$	-5.22	Cyclopentadienide
	-5.20	Carborane CH
	-3.83	
II[c] $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$	-5.37	Cyclopentadienide
	-5.71	Carborane CH
	-4.16	
III[c] $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$	-3.11	Tetramethylammonium
	-2.77	Carborane CH
	-3.17	
	-4.13	
	-5.25	
V[b] $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$	-5.36	Cyclopentadienide
	-5.14	Carborane CH
	-6.20	
	$+4.19$	BHB bridge protons
	$+18.30$	
VI[d] $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$	-3.41	Tetramethylammonium
	-2.91	Carborane CH
	-3.35	
	-3.64	
	-7.03	
VII[c] $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$	-3.05	Tetramethylammonium
	-3.73	Carborane CH
	-6.55	
	-8.28	

[a] In ppm relative to tetramethylsilane (TMS). [b] Measured in $CDCl_3$ solution. [c] Measured in CD_3CN solution. [d] Measured in $(CD_3)_2Co$ solution.

named "Polyhedral Expansion"[4] since the product has a polyhedral structure containing one more vertex than the parent carborane.

We now wish to report some reactions in which a metallocarborane is converted to its next lowest homolog by degradation and oxidation according to the equation

$$[LCo(B_nC_2H_{n+2})]^z \xrightarrow[2.\ -2e^-]{1.\ -BH^{2+}} [LCo(B_{n-1}C_2H_{n+1})]^z$$

where L = $C_5H_5^-$, $z = 0$, and $n = 8$ or 9, or L = (3)-1,2-$B_9C_2H_{11}^{2-}$, $z = -1$, and $n = 8$ or 9. Since this reaction affords a polyhedral metallocarborane with one less vertex than its precursor we have named it "Polyhedral Contraction."

In addition to providing a route to commo metallocarboranes containing two different carborane ligands, this reaction demonstrates that the metallocarborane polyhedron has a chemistry in its own right,[6] over and above that of terminal B–H substitution.

Polyhedral Contraction of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$. Degradation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ by hydroxide ion in protic media at *ca.* 100° gave a red solution. Treatment of this solution with hydrogen peroxide produced a blue suspension from which the reaction products were extracted with chloromethane. Column chromatography of the dichloromethane extract afforded two major products, I and II, in 10 and 63% yield, respectively; I was further separated into two components, IA and IB in the proportions 5:1, by preparative thick layer chromatography. The purple complex II showed a cutoff at *m/e* 247 in the mass spectrum and an ion distribution within the parent peak array consistent with that calculated[7] for $C_7H_{15}B_8Co$. The 100-MHz ^{1}H nmr spectrum of II (Table I) indicated the presence of the cyclopentadienide ligand; the spectrum also contained two broad resonances assigned to nonequivalent carborane CH protons. No signals attributable to BHB bridge protons were observed to the high-field side of TMS.[6,8] The 80.5-MHz ^{11}B nmr spectrum (Figure 1) consisted of six doublets of area 1 and a signal of area 2, showing that the carbon and cobalt atoms are positioned in such a way as to destroy the symmetry of the metallocarborane moiety. On the basis of these data we propose an 11-atom closed polyhedral structure for II, analogous to that proposed for the previously reported[4] isomer of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_8C_2H_{10})]$. Further, on the basis of the known[9] structure of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(11)\text{-}7,8\text{-}B_8C_2H_{10}\cdot C_5H_5N)]^-$, derived[6] from the related complex $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})\text{-}Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]^-$ (*vide infra*), we assign the carbon atoms to positions 2 and 4 or 2 and 5 (Figure 2).[10] The com-

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(6) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *Chem. Commun.*, 900 (1972).

(7) Using an accelerating voltage of 10–12 eV we found that, for closo metallocarboranes, the ion distribution in the parent peak array was usually within *ca.* 5% of that calculated assuming normal isotopic abundances. In cases where other data suggested that the metallocarborane did not have a closo geometry, this generalization was no longer true.

(8) D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 93, 5687 (1971).

(9) M. R. Churchill and K. Gold, *Chem. Commun.*, 901 (1972).

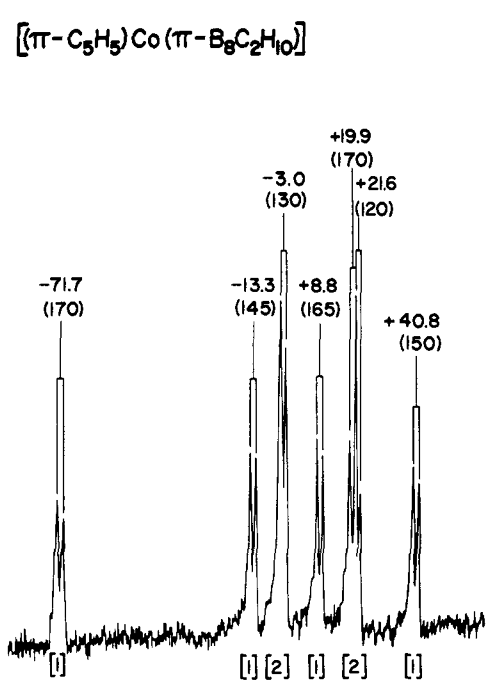

Figure 1. The 80.5-MHz ^{11}B nmr spectrum of II, measured in CD_3CN solution. Shifts are quoted in ppm with respect to $BF_3 \cdot O(C_2H_5)_2$.

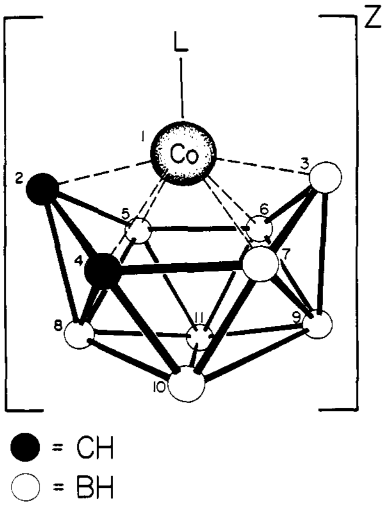

Figure 2. Proposed structure for II, L = $C_5H_5^-$ and $z = 0$, or III, L = (3)-1,2-$B_9C_2H_{11}^{2-}$ and $z = -1$. Only the enantiomer with carbon atoms in positions 2 and 4 is illustrated.

plex II can exist in two enantiomeric forms and, presumably, the reactions described herein produce a racemic mixture of both enantiomers. The pyridine adduct, [(π-(3)-1,2-$B_9C_2H_{11}$)-Co(π-(11)-7,8-$B_8C_2H_{10} \cdot C_5H_5N$)], was shown to be a racemic mixture by the structural study.[9]

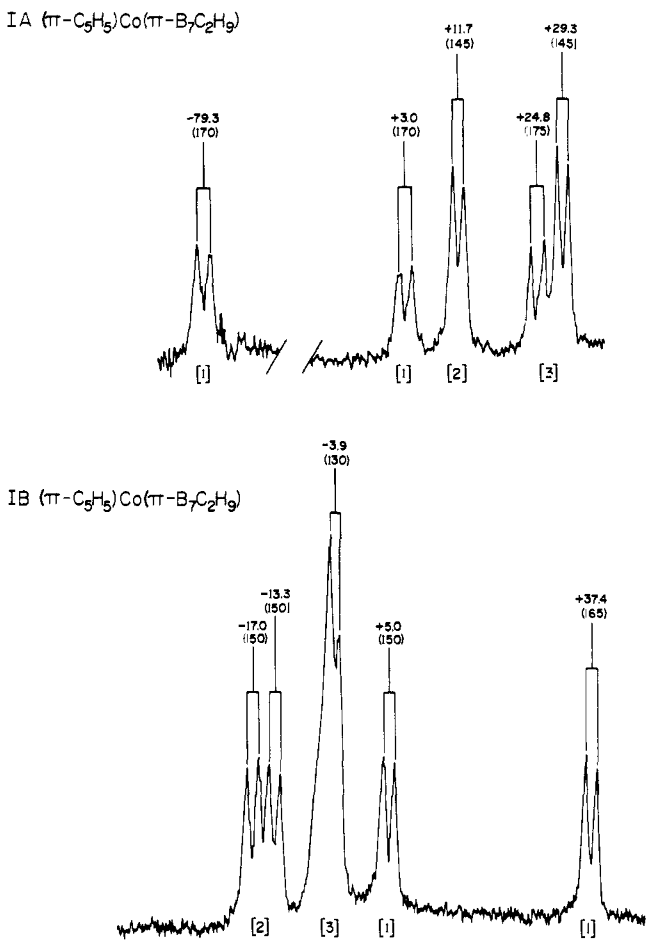

Figure 3. The 80.5-MHz ^{11}B nmr spectra of IA and IB measured in $CDCl_3$ and CH_2Cl_2 solutions, respectively.

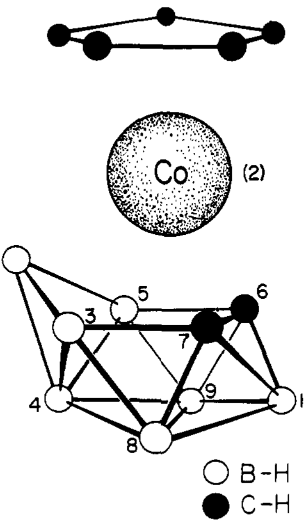

Figure 4. Proposed structure for IA and IV.

The yellow complexes IA and IB had similar mass spectra which showed a cutoff at *m/e* 235 and an ion distribution within the parent peak array consistent with that calculated for $C_7H_{14}B_7Co$. Both IA and IB exhibited resonances attributable to the cyclopentadienide ligand and carborane CH in their 100-MHz ^1H nmr spectra (Table I). The 80.5-MHz ^{11}B nmr spectrum of IA (Figure 3) contained five doublets of relative area 1 :1 :2 :1 :2, and could arise from an isomer of the previously reported[2] [(π-C_5H_5)Co(π-$B_7C_2H_9$)] in which the carbon atoms occupy equivalent positions on opposite sides of a plane of symmetry in the molecule (Figure 4). In refluxing hexane IA was quantitatively

(10) The compounds described herein are numbered according to the icosahedral system, *Inorg. Chem.*, 7, 1945 (1968), with metal atom vertices in parentheses. It should be noted that, owing to the inherent chirality of this numbering system, different enantiomers have different numbering. The formulas in this paper refer to the enantiomer with the lowest numbering for the carbon atoms, but are intended to represent a racemic mixture since no attempt was made to resolve the different enantiomers.

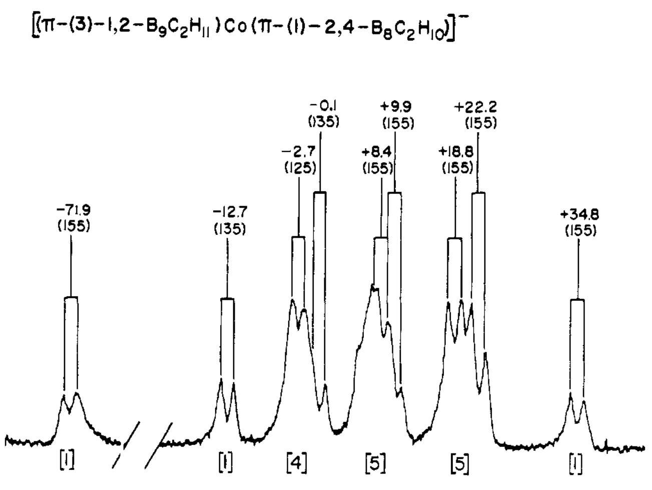

Figure 5. The 80.5-MHz ^{11}B nmr spectrum of III in CH_3CN solution.

converted to a red compound IC, and in refluxing xylene a yellow compound ID was also formed. IC and ID were readily separated using preparative thick layer chromatography and were identified as the previously reported[2] complexes $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ and $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$, respectively, by ^1H nmr, ^{11}B nmr and mass spectral measurements. In view of the facile rearrangement of IA to $[(\pi\text{-}C_5H_5)\text{-}Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$, we feel that the most likely location for the carbon atoms is positions 6 and 7 (Figure 4), since $[(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)_2Co]^-$ is formed[11] from $[(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)_2Co]^-$ under similar conditions[2] to those used to rearrange IA.

The rearrangement of IA to IC also appears to occur photochemically. These rearrangements are under further study in the hope of obtaining more information regarding the facile conversion of IA to $[(\pi\text{-}C_5H_5)\text{-}Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$.

The 80.5-MHz ^{11}B nmr spectrum of IB (Figure 3) consisted of four doublets of area 1 and a resonance of area 3 resulting from overlapping signals. Assuming IB is structurally analogous to IA, it would seem that the carbon atoms occupy positions which destroy the symmetry of the B_7C_2Co polyhedron. We have no further information concerning the location of the carbon atoms in IB, but it is possible to exclude the following isomers on the grounds of symmetry and the known spectra of the 1,6 and 1,10 isomers: 3,5; 8,9; 6,7; 1,6; 1,10; 1,4; 4,10. Unlike IA, IB did not undergo facile thermal rearrangements, and after 60 hr at reflux in cyclooctane the complex remained largely unchanged. Only 5–10% conversion to $[(\pi\text{-}C_5H_5)\text{-}Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ was found to have occurred, as measured by the relative areas and positions of the cyclopentadienyl resonances in the ^1H nmr spectrum.

Degradation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11})]$ did not occur under conditions similar to those used to degrade $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$. More forcing conditions resulted in some decomposition of the complex to give cobalt hydroxide.

Polyhedral Contraction of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$. Degradation of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$ by hydroxide ion in aqueous media at *ca.* 95° afforded a red solution which was oxidized by hydrogen peroxide. The reaction products were extracted into ether and, after removal of the solvent, were treated with aqueous tetramethylammonium chloride to precipitate a blue complex III in 85% yield. The 100-MHz ^1H nmr spectrum of III (Table I) indicated the presence of the tetramethylammonium cation and four nonequivalent carborane CH protons. The 80.5-MHz ^{11}B nmr spectrum (Figure 5) was complicated by the extensive overlap of resonances. However, the spectrum did contain a doublet of area 1 at *ca.* -72 ppm as did that of II. Further, the spectrum of III could be qualitatively reconstructed by superimposing the spectra of II and $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$. Thus we feel that II and III are structurally analogous except that II contains the $C_5H_5^-$ ligand whereas III contains the $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$ ligand (Figure 2). Reaction of III with pyridine affords a red adduct[6] whose structure has been unambiguously determined by X-ray methods.[9] The conversion of III to an adduct having this structure is easily accomplished by substituting boron atom 9 (or boron 11 depending on the enantiomer under consideration) and moving the cobalt atom from a symmetric position with respect to the B_4C_2 bonding face, to a position where it is bonded to only one carbon and three boron atoms. The hydrogen from the boron atom substituted with pyridine presumably moves to a BHB bridging position[6] during the reaction. Since this reaction scheme involves the minimum of atomic reorganization we feel that the proposed structure for III, and thus for II, is the most reasonable one consistent with the spectroscopic data.

Polyhedral Contraction of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$. Degradation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ was achieved using excess $FeCl_3$ in refluxing ethanol; the resulting solution was diluted with water and the products were extracted into dichloromethane. Column chromatography of the extract afforded a yellow complex IV in *ca.* 2% yield and a red complex V in 40% yield; further bands from the column afforded small quantities of intractable materials[12] which were not characterized. The compound IV was identified as IA or $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$ by ^1H nmr, ^{11}B nmr, and mass spectral measurements. The mass spectrum of V exhibited a cutoff at *m/e* 237 and an ion distribution within the parent peak array unlike that calculated for $C_7H_{14}B_7Co$ or $C_7H_{16}B_7Co$. However, the observed ion distribution could arise from a compound of formula $C_7H_{16}B_7Co$ which was undergoing loss of H_2 from the molecular ion. The 100-MHz ^1H nmr spectrum of V (Table I) contained signals attributable to the cyclopentadienyl ligand and two inequivalent carborane CH protons. In addition two broad resonances were observed at $+4.19$ and $+18.30$ ppm which we assign to BHB bridge protons.[6,8] The 80.5-MHz ^{11}B nmr spectrum of V (Figure 6) consisted of seven doublets of area 1, consistent with the formulation $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$. The spectrum also indicates that the carbon and cobalt atoms occupy positions which destroy the symmetry of the $\{B_7C_2Co\}$

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[11] D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **11**, 377 (1972).

[12] Similar materials could be obtained by further elution after the isolation of II (*vide supra*). In both cases, mass spectral data indicated that these materials were mixtures of compounds derived from $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_8C_2H_{10})]$ by substitution of alkoxy groups from the reaction medium. The compounds appeared to contain between one and five substituents but were not investigated further.

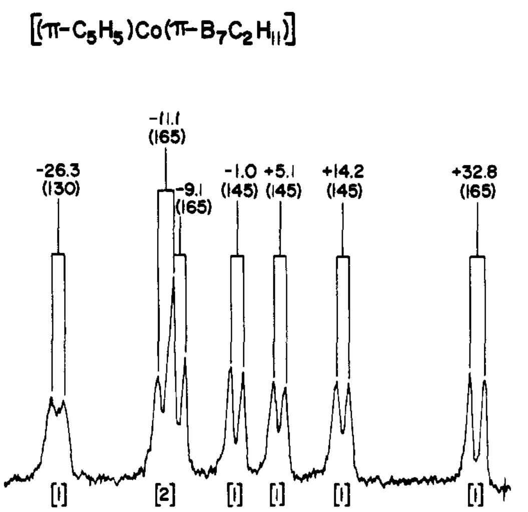

Figure 6. The 80.5-MHz ^{11}B nmr spectrum of V in CH_2Cl_2 solution.

framework. In view of the above data, we believe that V is a 10-atom nido metallocarborane having a structure similar to that found for $B_{10}H_{14}$ and proposed for $B_8C_2H_{12}$$^{13-17}$ (Figure 7). By analogy with 5,7-$B_8C_2H_{12}$ and 5,6-$B_8C_2H_{12}$ it seemed likely that V would eliminate hydrogen at elevated temperature.[16,17] This was found to be the case and, in refluxing cyclooctane (*ca.* 150°), a yellow complex was formed which was identified as $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ by ^1H nmr and ^{11}B nmr spectral measurements. At lower temperatures, in refluxing hexane, for example, this reaction did not proceed at a significant rate. However, in refluxing ethanol containing $FeCl_3$ traces of a yellow product were formed after 1 hr; thin layer chromatography indicated that this material was IV or $[(\pi\text{-}C_5H_5)\text{-}Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$. Thus it would appear that IV is formed from V under the reaction conditions used to prepare V. Further, since $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$ rearranges to $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ at 150° it seems probable that V eliminates hydrogen to give, in the first instance, $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$ which is then converted to the 1,10 isomer under the reaction conditions.

In the absence of an X-ray diffraction study it is impossible to make a definitive assignment of the cobalt and carbon atom positions in V. However, it is possible to rationalize the observed products of the above reactions in terms of one particular isomer. In refluxing ethanol the purple color of II is rapidly discharged giving rise to a brown solution containing intractable materials. Since II reacts with pyridine to give a red adduct of a nido metallocarborane[6,9] it seems likely that a similar process may occur in ethanol. The $\{B_8C_2Co\}$ polyhedron could open in one of two ways; the first pathway is that which occurs in the reaction with pyridine giving a complex in which cobalt is bonded to one carbon and three boron atoms.[6,9] The second pathway involves a motion of the cobalt atom from the B_4C_2 bonding face in the opposite sense, to a position where it is bonded to two carbon and two boron atoms. Assuming that the $FeCl_3$ degradation of this proposed intermediate removes a boron atom from the open face, as is found in the $FeCl_3$ degradation[17] of (3)-1,2-$B_9C_2H_{12}^-$, only a limited number of possibilities for the structure of V exist. Of these possibilities only one isomer could close directly to a closo metallocarborane with the symmetry required by the ^{11}B nmr spectrum of IV. Further, the expected product would be $[(\pi\text{-}C_5H_5)Co(\pi(2)\text{-}6,7\text{-}B_7C_2H_9)]$ as is found to be the case. This reaction scheme is illustrated in Figure 8 and requires that the carbon atoms occupy positions 2 and 6 in V, and that the cobalt atom occupy position 5 or 7 depending on the enantiomer under consideration.

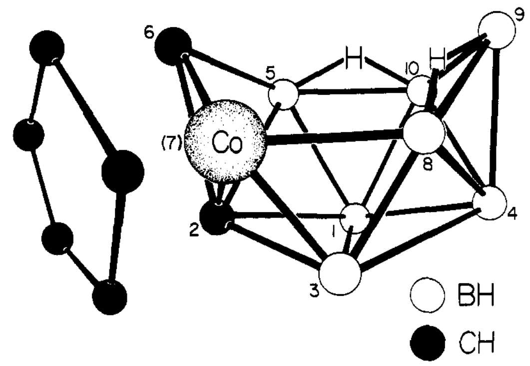

Figure 7. Proposed structure for V; only the enantiomer with the cobalt atom in position 7 is illustrated.

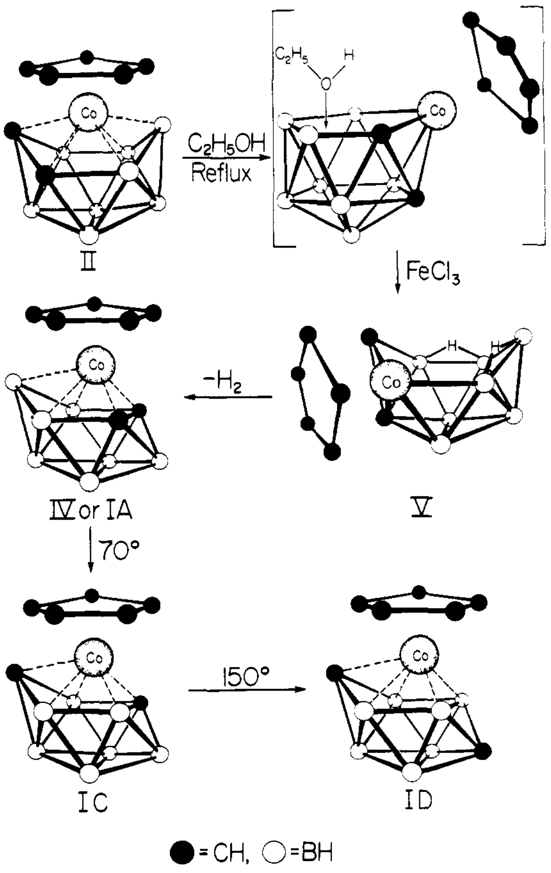

Figure 8. Reaction scheme for the degradation of II by $FeCl_3$ to give V, followed by elimination of H_2 from V to give $[(\pi\text{-}C_5H_5)\text{-}Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$.

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(13) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, 3, 436 (1950).

(14) C. M. Lucht, *J. Amer. Chem. Soc.*, 73, 2373 (1951).

(15) R. R. Rietz and R. Schaeffer, *ibid.*, 93, 1263 (1971).

(16) P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *ibid.*, **93**, 1265 (1971).

(17) J. Plesek and S. Heřmánek, private communication.

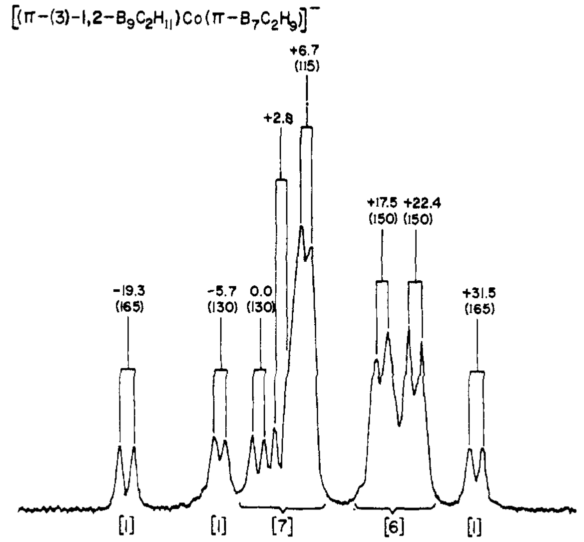

Figure 9. The 80.5-MHz ^{11}B nmr spectrum of VI in $(CD_3)_2CO$ solution.

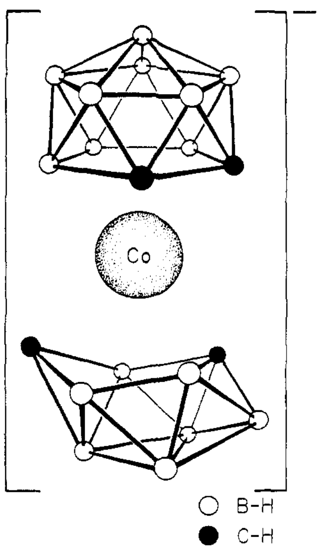

Figure 10. Proposed structure for VI; only one enantiomer of the $\{(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)Co\}$ fragment is illustrated.

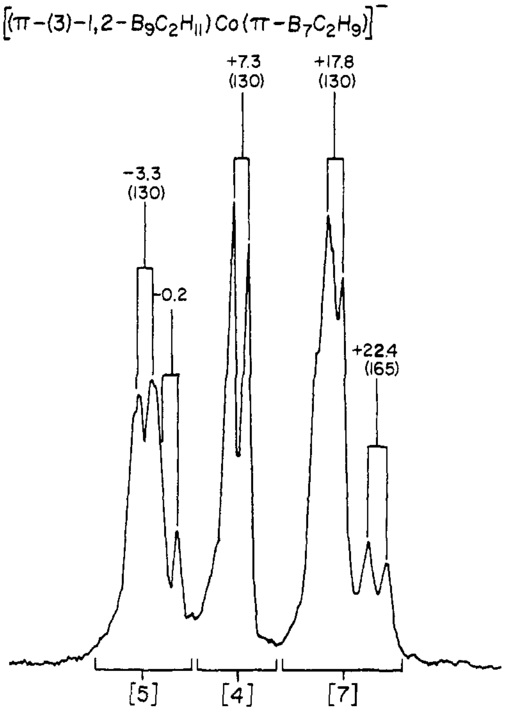

Figure 11. The 80.5-MHz ^{11}B nmr spectrum of VII in CD_3CN solution.

While this scheme is rather speculative it would appear to be consistent with the chemistry observed for these complexes. The location of the nonterminal hydrogens in V remains unknown; presumably they occupy B-H-B bridge positions in the open face of the $\{B_7C_2Co\}$ polyhedron, as is thought to be the case in $B_8C_2H_{12}$.[15-17] The observation of two BHB bridge resonances in the ^1H nmr spectrum suggests that these hydrogen atoms are not undergoing rapid tautomeric exchange.

Attempts to degrade the previously reported[4] $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,3\text{-}B_8C_2H_{10})]$ with $FeCl_3$ or hydroxide ion were unsuccessful. In strong base the formation of cobalt hydroxide was noted, as was observed for $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11})]$. Thus it would appear that, in these two compounds, hydroxide ion destroys the complex rather than remove a boron atom from the metallocarborane polyhedron.

Polyhedral Contraction of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$. The degradation of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]^-$ using $FeCl_3$ in refluxing ethanol afforded a mixture of compounds which were partially separated by column chromatography. The first major band to elute afforded the red complex VI in 11% yield. Further bands from the column did not afford pure compounds and were not investigated further. The 100-MHz ^1H nmr spectrum of VI (Table I) exhibited resonances attributable to the tetramethylammonium cation and to four nonequivalent carborane CH groups. However, no signals were observed on the high-field side of TMS which could be assigned to BHB bridge protons; thus it appeared that VI did not contain a nido metallocarborane polyhedron. The only information regarding the structure of VI was provided by the 80.5-MHz ^{11}B nmr spectrum (Figure 9) which contained signals whose areas and positions corresponded well with those expected for a commo metallocarborane containing the $(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$ and $(2)\text{-}1,6\text{-}B_7C_2H_9^{2-}$ *ligands. On the basis* of these data we formulate VI as $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ (Figure 10) in which 12- and 10-atom metallocarborane polyhedra are fused at the cobalt atom. In view of our observations concerning the formation of V from II, this formulation is not unreasonable. However, in the case of VI the reaction conditions are apparently sufficient to produce a closo metallocarborane moiety directly. At the reaction temperature (*ca.* 80°) the 1,6 isomer of the $\{B_7C_2H_9Co\}$ fragment would be formed[2] as is thought to be the case.

Since the complexes $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ and $[(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)_2Co]^-$ rearrange[2] to the corresponding 1,10 isomers at elevated temperature, the thermal rearrangement of VI to a complex whose ^{11}B nmr spectrum was consistent with the presence of the $\{(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9Co\}$ moiety would lend further support to our formulation of VI. Accordingly, a sample of VI was heated in refluxing anisole (154°) for

Table II. Infrared Spectral Data (Nujol Mull)

IA $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$	2580 (m), 2510 (s), 1410 (w), 1125 (w), 1070 (w), 1040 (w), 1005 (m), 950 (m), 915 (m), 835 (m), 805 (w)
IB $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_9)]$	2580 (m), 2520 (s), 1530 (m), 1410 (m), 1290 (w), 1240 (w), 1110 (w), 1100 (w), 1080 (w), 1070 (w), 1020 (m), 1010 (m), 980 (m), 965 (w), 940 (w), 890 (w), 855 (w), 835 (m), 810 (w), 800 (w), 765 (w)
II $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$	2610 (m), 2560 (s), 2520 (s), 1260 (w), 1075 (m), 1040 (m), 1005 (m), 965 (m), 950 (m), 930 (w), 895 (m), 870 (w), 840 (m), 800 (w), 745 (w), 695 (w)
III $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$	2560 (s), 2520 (s), 1470 (s), 1400 (w), 1260 (w), 1150 (w), 1100 (w), 1075 (m), 1020 (w), 1000 (w), 990 (w), 970 (w), 955 (w), 950 (m), 910 (w), 755 (w)
V $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$	2560 (s), 2510 (s), 1400 (m), 1310 (w), 1300 (w), 1220 (w), 1090 (w), 1075 (w), 1055 (w), 1025 (w), 1010 (m), 995 (m), 985 (m), 960 (w), 940 (w), 925 (w), 900 (w), 890 (w), 860 (w), 840 (m), 830 (m), 805 (w), 750 (m)
VI $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$	2560 (s), 1470 (s), 1200 (w), 1140 (w), 1100 (m), 1090 (m), 1070 (w), 1055 (w), 1020 (w), 985 (m), 950 (m), 895 (w), 880 (w), 840 (w), 780 (w), 688 (w)
VII $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$	2560 (s), 1480 (s), 1200 (w), 1130 (m), 1100 (m), 1075 (w), 1065 (w), 1050 (w), 1020 (w), 990 (m), 950 (m), 920 (w), 915 (w), 890 (w), 845 (w)

50 hr to give a fawn complex VII in 90% yield. The positions and areas of signals in the 80.5-MHz ^{11}B nmr spectrum (Figure 11) of VII corresponded well with those expected for a commo metallocarborane containing the $(3)\text{-}1,2\text{-}B_9C_2H_{11}{}^{2-}$ and $(2)\text{-}1,10\text{-}B_7C_2H_9{}^{2-}$ ligands. The 100-MHz ^1H nmr spectrum (Table I) contained signals attributable to the tetramethylammonium cation and to two nonequivalent carborane CH groups in the $B_7C_2H_9{}^{2-}$ ligand.[2] The signal at -3.73 ppm can be assigned to equivalent carborane CH groups in the $(3)\text{-}1,2\text{-}B_9C_2H_{11}{}^{2-}$ ligand. This equivalence is consistent with a more symmetric structure for the $B_7C_2H_9{}^{2-}$ ligand than was the case in VI. Thus we formulate VII as $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ having a structure similar to that of VI (Figure 10) except that the carbon atoms in the $B_7C_2H_9{}^{2-}$ ligand occupy positions 1 and 10 as anticipated.

Infrared and Electronic Spectral Data. The infrared spectra (Table II) of all the complexes described above exhibited bands in the region 2500–2600 cm^{-1} due to terminal B–H stretching vibrations. The spectra of IA, IB, II, and V contained a band of medium intensity in the region 810–840 cm^{-1} assigned to the $C_5H_5{}^-$ ligand. The spectra of III, VI, and VII contained a band at 950 cm^{-1} due to the presence of the tetramethylammonium cation. We were unable to detect bands in the region 1600–1900 cm^{-1} in the spectrum of V which might be assigned to BHB bridge groups. However, since bands of this type are usually very weak[18] this is not remarkable.

The electronic spectral data (Table III) did not provide information relating to the structures of the new complexes and, in the absence of a rigorous study of the electronic spectra of metallocarboranes, we have made no attempt to assign the bands in these spectra.

Table III. Electronic Spectral Data (Acetonitrile Solution)

Compound	λ_{max}, mμ	ϵ
IA		
$[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$	440	326
	315	4,360
	260	13,100
IB		
$[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_9)]$	390 sh	499
	290 sh	10,580
	260	23,650
	230 sh	10,200
II		
$[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$	565	635
	340	3,185
	280	13,080
	245	19,080
III		
$[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co\text{-}(\pi\text{-}(1)\text{-}2,4\text{-}B_8C,H_{10})]$	590	878
	345	4,760
	258	24,650
	230 sh	14,200
V		
$[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$	480	886
	360 sh	3,450
	270	26,500
VI		
$[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co\text{-}(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$	505	298
	375	2,980
	340	5,040
	285	21,000
VII		
$[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co\text{-}(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$	485	306
	345	7,600
	260	16,800
	230 sh	10,800

Electrochemical Data. The half-peak potentials for the new complexes and for $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,6\text{-}B_6C_2H_9)]$, IC, and $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$, ID, are given in Table IV, along with R_f values for the neutral complexes. All the complexes exhibited at least one reduction wave in the region 0 to -2 V, and in the case of III two waves were observed. A comparison of the reduction potentials for the two series of complexes II, IC, ID and III, VI, VII shows that the reduction potentials follow the same trend with variation of the nonicosahedral ligand. However, the reduction potentials of complexes containing the $(3)\text{-}1,2\text{-}B_9C_2H_{11}{}^{2-}$ ligand were significantly more negative than those of the corresponding complexes containing the $C_5H_5{}^-$ ligand. This is in accord with the previously reported[1] reduction potentials of -1.25 and -1.46 V for $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ and $Cs[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]$, respectively. A correlation between half-peak

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Table IV. Electrochemical Data and R_f Values

Compound	$E_{p/2}{}^a$	$R_f{}^b$
IA	−1.17	0.40
IB	−1.33	0.46
IC	−1.03	0.28
ID	−1.10	0.62
II	−0.81	0.16
III	−0.93, −1.70	
V	−0.87	0.15
VI	−1.29	
VII	−1.33	

[a] Measured in acetonitrile solution 0.1 *M* in $(C_2H_5)_4NClO_4$ using a Pt button electrode. Values are quoted in volts *vs.* the sce. [b] On ChromAR Sheet 1000 chromatographic medium with 9:1 hexane:dichloromethane eluent.

potential and the position of the long wavelength electronic spectral absorption has been made[19,20] for isomers of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_9C_2H_{11})]$. A similar situation exists for the four known isomers of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_9)]$. Thus increasingly negative reduction potentials in the order IC < ID < IA < IB correspond with decreasing wavelengths for the longest wavelength absorption in the electronic spectra[2] of these complexes (Tables III and IV).

Conclusion

The known chemistry of the metallocarboranes is almost entirely limited to terminal B–H subsitution[1,21–25] and thermal polyhedral rearrangement.[2,19,20,26] In this paper the chemistry of the metallocarboranes has been extended to include the polyhedral framework itself. In particular the concept of "Polyhedral Contraction," though not as general in application as that of "Polyhedral Expansion,"[4] has led to the synthesis of some new types of metallocarborane, namely nido metallocarboranes[6] and commo metallocarboranes containing two different polyhedra fused at the metal atom. Perhaps the most significant feature of this work is the demonstration that certain metallocarborane polyhedra exhibit a chemistry[6] which, in some respects, parallels that of the carboranes themselves.[15–17,27,28] Thus, in the systems studied so far,[6] it seems that the replacement of a {B–H} unit by $\{(\pi\text{-}C_5H_5)Co\}$ does not drastically change the chemistry of the polyhedral framework.

Experimental Section

Physical Measurements. The 100-MHz ^1H nmr spectra were obtained using a Varian HA-100 spectrometer. The 80.5-MHz ^{11}B nmr spectra were recorded using an instrument designed and constructed by Professor F. A. L. Anet and Dr. C. H. Bradley of this department. Infrared spectral data were obtained using a Perkin-Elmer Model 137 sodium chloride spectrophotometer and electronic spectra were recorded on a Beckman Model DB spectrometer. Electrochemical data were determined by previously described methods[29] and mass spectra were recorded using an Associated Electrical Industries Model MS-9 spectrometer. Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. Unless otherwise stated, reactions were carried out in a nitrogen atmosphere using reagent grade solvents which had been saturated with nitrogen. Electronic spectral measurements were made in spectrograde solvents. $K[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]$ and $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ were prepared using previously described methods.[1,24] Column chromatography was carried out using 60–200 mesh silica gel supplied by the J. T. Baker Chemical Co. Quantities were estimated by the volume of the dry powder. Preparative thick layer chromatography was carried out using ChromAR Sheet 1000 chromatographic medium.

Polyhedral Contraction of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$. (a) Preparation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ (II). $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})]$ (2.0 g, 7.8 mmol) was added to a mixture of ethylene glycol–ethanol–water (150 ml of a mixture in the proportions 100:40:10) containing potassium hydroxide (12.0 g, 210 mmol). The mixture was then heated to reflux for 25 hr, after which time the reaction mixture was quenched with water (500 ml) to give a red solution. Careful addition of hydrogen peroxide (10 ml of a 30% aqueous solution) resulted in the formation of a blue precipitate; this was extracted into dichloromethane (4 × 200 ml), and the combined extracts were dried over $MgSO_4$. After filtration the purple extract was stripped onto silica gel (*ca.* 60 ml) and mounted on a silica gel column (400 ml).

Elution with hexane–dichloromethane developed a yellow band containing IA and IB followed by a purple band containing II. The first band was collected and further purified as described in the next paragraph. The second, purple band containing the complex II was collected; evaporation of most of the solvent resulted in the precipitation of II (1.2 g, 63%) which was recrystallized from dichloromethane–hexane to give deep purple needles, mp 168°. *Anal.* Calcd for $C_7H_{15}B_8Co$: C, 34.37; H, 6.14; B, 35.35; Co, 24.14. Found: C, 34.40; H, 6.25; B, 35.09; Co, 23.91.

(b) Isolation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_9)]$ (IA and IB). The yellow solution obtained by chromatography as described in the previous paragraph was evaporated to dryness under reduced pressure at 40°. (Owing to the facile thermal rearrangement of IA it is necessary to keep the compound at temperatures below 40° throughout the purification.) The yellow residue contained IA and IB in the proportions 5:1 as measured by integration of the cyclopentadienyl resonances in the ^1H nmr spectrum of the mixture (total yield 170 mg, 10%). Separation of the components of this mixture was effected by preparative thick layer chromatography using hexane–dichloromethane eluent. R_f values for IA and IB are given in Table IV. The first band containing IB was extracted into dichloromethane, stripped to dryness under reduced pressure, and sublimed at 70° onto a water-cooled probe. The second band contained IA and was extracted into cold dichloromethane, evaporated to dryness under reduced pressure at room temperature, and then sublimed at 40° onto a water-cooled probe. *Anal.* Calcd for $C_7H_{14}B_7Co$: C, 36.11; H, 6.02; B, 32.50; Co, 25.37. Found (IA): C, 36.22; H, 6.13; B, 32.83. (IB, mp 91°): C, 35.70; H, 6.93; B, 32.03; Co, 25.09.

Polyhedral Contraction of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$. Preparation of $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ (III). $K[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]$ (2.0 g, 5.5 mmol) was added to a solution of potassium hydroxide (60 g, 1.05 mol) in water (200 ml) and the mixture heated to 95° for 6 hr with magnetic stirring. After this time the reaction mixture was quenched with water (600 ml) to give a red solution. Careful addition of hydrogen peroxide (12 ml of a 30% aqueous solution) produced a blue precipitate which was extracted into ether (3 × 300 ml). The combined ether extracts were evaporated at 40° under reduced pressure to give a blue oil; this was redissolved in water and the solution treated with aqueous tetramethylammonium chloride to precipitate the blue product. After filtration the product was dried *in vacuo* over P_2O_5 and then recrystallized from dichloromethane–chloroform as

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blue plates (1.8 g, 85%). *Anal.* Calcd for $C_8H_{33}NB_{17}Co$. C, 24.90; H, 8.56; N, 3.63; B, 47.61; Co, 15.30. Found: C, 24.70; H, 8.58; N, 3.82; B, 47.61; Co, 15.09.

Polyhedral Contraction of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$. Preparation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$, (V). $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ (1.0 g, 4.0 mmol) was dissolved in absolute ethanol (200 ml), ferric chloride (5.0 g, 31 mmol) was then added, and the mixture was heated to reflux for 45 min with stirring. After this time the reaction mixture was quenched with water (1000 ml), and the products were extracted into dichloromethane (3 × 300 ml). The combined extracts were dried over $MgSO_4$, filtered, and stripped onto silica gel (*ca.* 40 ml). This material was mounted on a silica gel column (400 ml), and the products were eluted with hexane–dichloromethane. The first band to elute was yellow and was purified in the manner described for IA above. This complex was identified as IA or $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9)]$ by ^1H nmr, ^{11}B nmr, and mass spectral measurements (20 mg, 2%). The second band to elute was red and, on evaporation of the solvent, afforded the red crystalline product (380 mg, 40%) which was recrystallized from dichloromethane–hexane, mp 123°. *Anal.* Calcd for $C_7H_{16}B_7Co$: C, 35.81; H, 6.82; B, 32.23; Co, 25.15. Found: C, 35.84; H, 7.06; B, 32.07; Co, 24.86.

Pyrolysis of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$. Formation of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$. A sample of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$ (V) (100 mg, 0.43 mmol) was added to cyclooctane (20 ml) and the mixture heated to reflux for 24 hr. After this time the bulk of the solvent was evaporated at reduced pressure, and the residual reaction products were separated using preparative thick layer chromatography with hexane–dichloromethane eluent. The first band to elute was yellow and contained $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ (84 mg, 85%) which was identified by ^1H nmr, ^{11}B nmr, and mass spectral measurements. Traces of a red material with an R_f value equal to that of $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ were also observed.

The above reaction was repeated using $[(\pi\text{-}C_5H_5)Co(\pi\text{-}B_7C_2H_{11})]$ (101 mg, 0.43 mmol) and cyclooctane (5 ml) which were placed in a tube with a break-seal. The tube was evacuated and sealed off on the vacuum line, then heated to 150° for 24 hr. After this time the tube was vented into the vacuum line, and the volume of noncondensable (−190°) gas formed was measured using a Sprengel pump (0.42 mmol, 98%). The residual material in the tube was treated in the manner described in the previous paragraph and afforded $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ (80 mg, 80%) and $[(\pi\text{-}C_5H_5)Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ (6 mg, 6%).

Polyhedral Contraction of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]^-$. Preparation of $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ (VI). A solution of $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(1)\text{-}2,4\text{-}B_8C_2H_{10})]$ (1.0 g, 2.6 mmol) and $FeCl_3$ (5.0 g, 31 mmol) in ethanol (100 ml) was heated to reflux for 3.5 hr. After this time the reaction mixture was poured into water (500 ml) and the resulting aqueous phase extracted with dichloromethane (2 × 200 ml). The dichloromethane was then evaporated under reduced pressure, and the resulting oil was redissolved in a little acetone–ethanol. A dilute aqueous solution of tetramethylammonium chloride was added and the mixture once again extracted with dichloromethane. The dichloromethane extract was stripped onto silica gel (*ca.* 40 ml) which was then mounted on a silica gel column (300 ml). Elution with dichloromethane developed a red band which was collected and stripped to dryness. The residue was redissolved in acetone and treated with a solution of tetramethylammonium chloride in aqueous ethanol. Evaporation of the acetone under reduced pressure precipitated the red product (110 mg, 11%) which was recrystallized from dichloromethane–chloroform. *Anal.* Calcd for $C_8H_{32}NB_{16}Co$: C, 25.68; H, 8.56; N, 3.75; B, 46.23; Co, 15.78. Found: C, 25.56; H, 8.41; N, 4.04; B, 46.52; Co, 15.58.

Thermal Rearrangement of $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]^-$ (VI). Preparation of $([CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,10\text{-}B_7C_2H_9)]$ (VII). A solution of $[(CH_3)_4N][(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Co(\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9)]$ (100 mg, 0.29 mmol) in anisole (20 ml) was heated to reflux for 50 hr. After this time the bulk of the solvent was evaporated under reduced pressure and the residue purified using preparative thick layer chromatography with dichloromethane eluent. Only one major band separated, and this was extracted into dichloromethane–acetonitrile which was then evaporated under reduced pressure. The residue was redissolved in acetone and treated with a solution of tetramethylammonium chloride in aqueous ethanol. Evaporation of the acetone precipitated the fawn product (90 mg, 90%) which was recrystallized from dichloromethane–chloroform. *Anal.* Calcd for $C_8H_{32}NB_{16}Co$: C, 25.68; H, 8.56; N, 3.75; B, 46.23; Co, 15.78. Found: C, 25.48; H, 8.55; N, 3.97; B, 45.93; Co, 15.49.

Acknowledgments. The authors are indebted to Dr. R. J. Wiersema for the ^{11}B nmr and electrochemical measurements and to Dr. G. B. Dunks for assistance with the hydrogen evolution experiment. We are grateful to Professor S. Hĕrmánek for information received prior to publication. The award of a NATO Fellowship (to C. J. J.) is gratefully acknowledged. This work was supported in part by the Office of Naval Research.

Ligand Protonation and Rates of Ligation with Nickel(II)

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Received March 24, 1972

Abstract: The rate constants have been determined for the reaction of a number of ligands and their protonated forms with $Ni(H_2O)_6^{2+}$ and $NiNTA(H_2O)_2^-$. These include imidazole and derivatives, bipyridine, phenanthroline and derivatives, cysteine and penicillamine, chelidamic acids, and pyridine-2-aldoxime. Varying effects of proton attachment to a ligand on its reactivity have been found. The lowered reactivity of hydroxy derivatives of pyridine and phenanthroline is ascribed to the predominance of the pyridone tautomer in solution and the results are assessed on this basis.

The complexing of nickel continues to be studied as representative of the behavior of labile octahedral complexes, and the general results so far obtained have been summarized.[1,2] We previously studied the kinetics of formation of mono complexes of nickel(II) with a variety of ligands including amino acids, peptides, and polyamino- and pyridinecarboxylates.[3] We drew attention to the unreactivity of the zwitterion

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