ment with the literature values[12] of -3.5 ppm (108 Hz) and 11.7 ppm (95 Hz) for $(CH_3)_3NBH_2N(CH_3)_2BH_3$.

Reaction of I-$1,5$-^{10}B with Dimethylamine. The solution resulting from the addition of 1.32 mmol of $^{10}B_2H_6$ to 0.705 mmol of $H^nB[N(CH_3)_2]_2$ in 0.3 ml of diethyl ether was freed of excess $^{10}B_2H_6$ by cooling to $-78°$ and pumping for 15 min. A 1.19-mmol sample of dimethylamine was then added and the boron-11 nmr spectrum was recorded within 5 min. The spectrum was rerun after periods of 22 min and 24 hr (Figure 8A–C). Product separation and characterization by infrared spectroscopy unequivocally identified the products as $[(CH_3)_2NBH_2]_2$ and $(CH_3)_2NHBH_2N(CH_3)_2BH_3$.

Low Temperature Nmr Study of the Reaction of I with Dimethylamine. A solution of I in 0.5 ml of diethyl ether was generated as detailed above from 0.671 mmol of $HB[N(CH_3)_2]_2$ and 0.798 mmol of diborane. After pumping off excess diborane, 0.623 mmol of dimethylamine was introduced and the system was warmed to $-78°$ and agitated at this temperature for 5 min. The sample was then transferred to the nmr probe which was maintained at $-50°$. The temperature was slowly increased from -50 to $25°$ and over a 60-min period; the nmr spectrum was scanned intermittently during the warming process.

Reaction of I with Sodium Hydride. A 0.101-g (0.792 mmol) sample of I and 2 ml of monoglyme were combined with 0.043 g (1.8 mmol) of oil-free sodium hydride in an nmr reaction vessel. The boron-11 nmr spectrum of the solution run immediately after mixing showed only starting materials. After 21 hr at room temperature, the reaction was complete. Assignment of nmr signals to $[(CH_3)_2NBH_2]_2$ and $Na(CH_3)_2N(BH_3)_2$ was confirmed by product isolation and identification by infrared spectroscopy.

Reaction of I-$1,5$-^{10}B with Sodium Hydride. A 0.5-ml mono-glyme solution of I-$1,5$-^{10}B prepared from 0.60 mmol of $H^nB[N(CH_3)_2]_2$ and 1.25 mmol of $^{10}B_2H_6$ was condensed into an nmr reaction vessel charged with 0.054 g (2.25 mmol) of oil-free sodium hydride. The boron-11 nmr spectrum recorded immediately afterwards showed only unreacted boron-10 labeled substrate. After 24 hr the nmr spectrum showed a quartet at 10.7 ppm, $J = 85$ Hz, characteristic of $Na(CH_3)_2N(BH_3)_2$,[18] but no boron-11 signal due to $[(CH_3)_2NBH_2]_2$. The triplet arising from an unidentified by-product, noted above, was also present in this spectrum.

The mass spectrum of I together with those of $[(CH_3)_2NBH_2]_2$ and μ-$(CH_3)_2NB_2H_5$ for comparison will appear following these pages in the microfilm edition of the journal. See paragraph at end of paper regarding supplementary material.

(18) P. C. Keller, *Inorg. Chem.*, 10, 2256 (1971).

Thermal Rearrangements of Nonicosahedral Cobaltacarboranes

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Abstract: The thermal rearrangements which isomerize the known isomers of nonicosahedral cobaltacarboranes of the type $(\eta\text{-}C_5H_5)CoC_2B_nH_{n+2}$, $n = 6, 7, 8$, and 10, are discussed. A summary of conclusions regarding these rearrangements is presented as a set of empirical rules which seem to govern the migration of heteroatoms during thermal isomerizations. Kinetic data of some representative rearrangements are also discussed.

The thermally induced migration of carbon atoms over the surfaces of polyhedral cobaltacarboranes is a well-established phenomenon.[1–5] However, only for the icosahedral complexes, $(\eta\text{-}C_5H_5)CoC_2B_9H_{11}$, and its carbon substituted derivatives have all possible isomers been isolated.[3] If the metal atom is used as a point of reference within the complex, the migration of carbon atoms produces nine possible isomers—all of which have been characterized.

We now wish to report a study of the thermal rearrangements of nonicosahedral cobaltacarboranes. Such a study is inherently limited, however, since all possible isomers of a given polyhedral geometry are not presently available either by direct synthesis or by other means. Nevertheless, an investigation of the rearrange-ments of the compounds which are presently known does reveal some basic principles which govern the manner in which the heteroatoms are distributed over the surface of a polyhedral metallocarborane. Although these principles will be invaluable in identifying isomers that may be synthesized in the future, the main objective of this work was to establish an understanding of the systematics which govern heteroatom migrations on polyhedral surfaces. The results are set forth as a list of empirical rules regarding the thermal rearrange-ments of polyhedral cobaltacarboranes. Subsequently, the investigation of carbon atom migration modes may be extended to include bi- and trimetallic systems.

Rearrangement of $(\eta\text{-}C_5H_5)CoC_2B_8H_{10}$. 1-$(\eta\text{-}C_5H_5)$-1-Co-2,4-$C_2B_8H_{10}$[6,7] rearranged to 1-$(\eta\text{-}C_5H_5)$-1-Co-

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

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

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

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

(5) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 1109 (1973).

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

(7) Numbers accompanying formulas refer to the positions of the heteroatoms within the *closo*-metallocarborane framework and to the location of the exopolyhedral substituents, if any. Lowest numbers consistent with the molecular geometry are given to carbon in accordance with the inverse periodic order adhered to by the IUPAC Inorganic Nomenclature Committee [see R. M. Adams, *Pure Appl. Chem.*, 30, 683 (1972)]. For example, in 1-$(\eta\text{-}C_5H_5)$-1-Co-2,4-$C_2B_8H_{10}$, cobalt occupies position 1 while carbon atoms are located at vertices 2 and 4. The cyclopentadienyl ring is π bonded to the cobalt.

Figure 1. (a) The thermal rearrangement of $1\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}Co\text{-}2,4\text{-}C_2B_8H_{10}$ to $1\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}Co\text{-}2,3\text{-}C_2B_8H_{10}$. (b) The thermal rearrangement of $[1,3'\text{-}Co(2,4\text{-}C_2B_8H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$ to $[1,3'\text{-}Co(2,3\text{-}C_2B_8H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$.

Figure 2. The thermal rearrangements of $(\eta\text{-}C_5H_5)CoC_2B_7H_9$.

$2,3\text{-}C_2B_8H_{10}{}^4$ in 94% yield over a period of 6 hr at 150° (Figure 1a). In a similar fashion, $[1,3'\text{-}Co(2,4\text{-}C_2B_8H_{10})(1',2'\text{-}C_2B_9H_{11})]^{-4}$ rearranged in 65% yield to $[1,3'\text{-}Co(2,3\text{-}C_2B_8H_{10})(1',2'\text{-}C_2B_9H_{11})]^{-8}$ over a period of 4 hr (Figure 1b). Some decomposition was observed during the course of the latter rearrangement which was carried out in the solid state at 150° using refluxing cyclooctane as a heat-transfer medium. Rearrangement in anisole solution at 155° was accompanied by a greater degree of decomposition possibly due to the more polar nature of the solvent. There are no additional isomers of $(\eta\text{-}C_5H_5)CoC_2B_8H_{10}$ known.

There are two important observations regarding these simple rearrangements of carbon atoms from the 2,4 isomer to the corresponding 2,3 isomer. First, as is the case with the neutral carboranes, the carbon atoms tend to migrate apart. In fact, there is no known instance in the thermal rearrangement of closo-metallo-carboranes where the carbon atoms move closer together since the driving force for these rearrrangements is due, in part, to the electrostatic repulsion between the formally electropositive carbon atoms.[9] Secondly, carbon atoms prefer to be located at low coordinate positions within the metallocarborane framework. The carbon atom initially at the six coordinate vertex 4 moved to the five coordinate vertex 3. This conclusion is further evidenced by the fact that the carbon atom at the five coordinate vertex 2 did not relocate, and once both carbon atoms achieved low coordinate positions, no further rearrangements were observed to take place at temperatures up to 235° in solution and 500° in a hot tube.

Rearrangements of $(\eta\text{-}C_5H_5)CoC_2B_7H_9$. As in the case of the $(\eta\text{-}C_5H_5)CoC_2B_8H_{10}$ systems described above, the thermal rearrangements observed with the 10-vertex cobaltacarboranes, $(\eta\text{-}C_5H_5)CoC_2B_7H_9$, resulted in the successive migration of carbon atoms to the vertices

having lower coordination number. Over a period of 4 hr in heptane solution at 100°, $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}6,9\text{-}C_2B_7H_9{}^{4,10}$ was quantitatively converted to $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,6\text{-}C_2B_7H_9{}^1$ (Figure 2). The 1,6 isomer was then further converted to $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,10\text{-}C_2B_7H_9{}^1$ in decane at 175°. The latter rearrangement has also been carried out in the solid state at 315°. The conversion of $[2,3'\text{-}Co(1,6\text{-}C_2B_7H_9)(1',2'\text{-}C_2B_9H_{11})]^-$ to $[2,3'\text{-}Co(1,10\text{-}C_2B_7H_9)(1',2'\text{-}C_2B_9H_{11})]^-$ has also been reported.[4]

$2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,7\text{-}C_2B_7H_9$ (compound IB in ref 4) rearranged to $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,10\text{-}C_2B_7H_9$ in hexadecane at 287° (Figure 2). The positions of the carbon atoms in the starting material have not as yet been unequivocally assigned, and the evidence for the 1,7 assignment is presented here. There is now sufficient precedent[11-13] for very low-field resonances (-40 to -80 ppm relative to $BF_3 \cdot O(C_2H_5)_2$) in the ^{11}B nmr spectra being attributable to low-coordinate boron atoms adjacent to a cobalt atom. Since no such resonance appeared in the nmr spectrum, we can assign a carbon atom to vertex number 1 with some confidence. There remain, then, only two possibilities for this isomer which are consistent with the molecular asymmetry as indicated by the nmr spectra: $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,3\text{-}C_2B_7H_9$ and $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,7\text{-}C_2B_7H_9$. The ^{11}B nmr studies of the paramagnetic cobalt(II) species derived from this compound indicate that the latter formulation is correct.[14]

The assignment of the carbon atoms to the 1,7 positions is further substantiated by electrochemical studies.

(10) The correctly numbered IUPAC formula for this isomer is $6\text{-}(\eta\text{-}C_5H_5)\text{-}6\text{-}Co\text{-}2,3\text{-}C_2B_7H_9$. For the sake of clarity in illustrating these rearrangements, we will number each isomer in the series in the same manner. It is misleading and confusing to have to employ two numbering orientations for two isomers of the same compound in order to adhere to the IUPAC rules. Trying to apply the rules of organic chemistry to metallocarboranes results in shortcomings of this kind which the icons of nomenclature fail to recognize.

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

(12) D. F. Dustin and M. F. Hawthorne, Inorg. Chem., 12, 1380 (1973).

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

(14) R. J. Wiersema, unpublished results.

(8) C. J. Jones, J. N. Francis, and M. F. Hawthorne, J. Amer. Chem. Soc., 95, 7633 (1973).

(9) R. Hoffman and W. N. Lipscomb, Inorg. Chem., 2, 231 (1963).

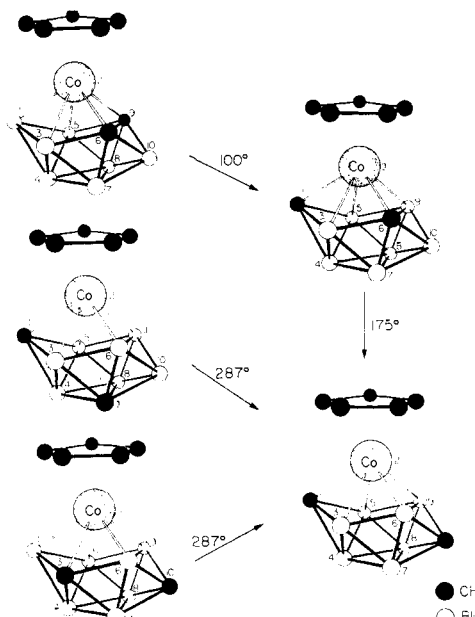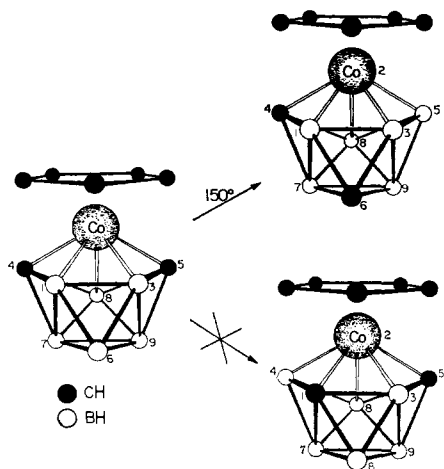Figure 3. The thermal rearrangement of $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}4,5\text{-}C_2B_6H_8$ to $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}4,6\text{-}C_2B_6H_8$.

Figure 4. The thermal rearrangements of $(\eta\text{-}C_5H_5)CoC_2B_{10}H_{12}$.

It has been observed that when a carbon atom moves out of a five-membered ring adjacent to the cobalt, the potential for reduction is lowered by 0.25–0.35 V.[3] A rationalization of this phenomenon is that a B_4C face is more effective than a B_3C_2 face in supplying electron density to the metal. As a result, the B_4C face better stabilizes higher oxidation states and the metal atom becomes more difficult to reduce.[15,16] A B_5 face is even more effective than a B_4C face in stabilizing high oxidation states. $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,6\text{-}C_2B_7H_9$ has a reduction potential ($E_{p/2}$ value determined by cyclic voltammetry) of -1.03 V. The hypothetical $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,3\text{-}C_2B_7H_9$ would be expected to have a similar value whereas $E_{p/2}$ for $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,7\text{-}C_2B_7H_9$ might be expected to be in the range of -1.30 to -1.40 V. The reduction for the proposed 1,7 isomer has, indeed, been reported to be -1.33 V.[4]

The polyhedral expansion of $4,5\text{-}C_2B_7H_9$ results in yet a fifth isomer of $(\eta\text{-}C_5H_5)CoC_2B_7H_9$ which was proposed to be $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}3,10\text{-}C_2B_7H_9$.[13,17] In 5 hr in hexadecane at 287°, the 3,10 isomer was converted in 85% yield to $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,10\text{-}C_2B_7H_9$. Clearly, the thermal rearrangements of the B_7 cobaltacarboranes are governed by the tendency of the carbon atoms to seek out low-coordinate vertices and/or to effect their mutual separation.

Rearrangement of $(\eta\text{-}C_5H_5)CoC_2B_6H_8$. Only two isomers of $(\eta\text{-}C_5H_5)CoC_2B_6H_8$ are known and we have recently found that one was converted to the other via a thermal rearrangement. After 5 hr at 150°, a sample of $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}4,5\text{-}C_2B_6H_8$[13] was converted in the solid state to an isomeric species identical with that prepared by the polyhedral expansion of $1,7\text{-}C_2B_6H_8$ (Figure 3). The structure of the rearranged isomer has been proposed to be $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}4,6\text{-}C_2B_6H_8$.[13,18] This same species has been prepared independently[11] by the polyhedral expansion of $2,4\text{-}C_2B_5H_7$ and the structure was proposed to be $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,5\text{-}C_2B_6H_8$ (compound III in ref 11; the numbering system used by the authors placed the carbon atoms at
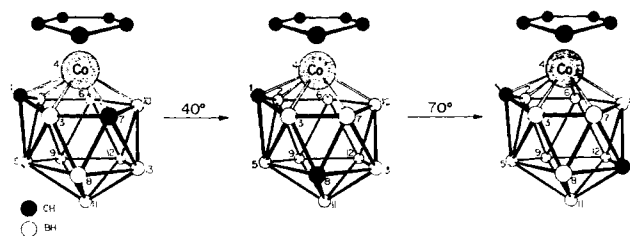
positions 1 and 6). In light of our observations regarding the rearrangements of cobaltacarboranes, we feel that this latter assignment is probably incorrect. In the 4,5 isomer, the carbon atoms are already at low-coordinate positions in the framework of the molecule. It is unlikely that a rearrangement moving a carbon atom to a position of higher coordination, no further from the cobalt atoms, and no further from the other carbon atom would take place. An examination of the $E_{p/2}$ values of $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}4,5\text{-}C_2B_6H_8$ and $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}4,6\text{-}C_2B_6H_8$, -0.84 and -1.11 V, respectively, further suggests that one carbon atom has been replaced by a boron atom in the five-membered face adjacent to the cobalt atom.

Miller and Grimes proposed the $2\text{-}(\eta\text{-}C_5H_5)\text{-}2\text{-}Co\text{-}1,5\text{-}C_2B_6H_8$ isomer on the basis that the preferred structure would have both carbon atoms bonded to the metal. In the past, we too have fallen into this trap[12] but have since concluded[19] that carbon atoms have no particular affinity for cobalt. In fact, as illustrated by all of the rearrangements described here, the driving force of the carbon atoms to separate themselves from cobalt interactions is nearly as great as their tendency to become separated from one another.

Rearrangements of $(\eta\text{-}C_5H_5)CoC_2B_{10}H_{12}$. The supericosahedral complex, $(\eta\text{-}C_5H_5)CoC_2B_{10}H_{12}$, undergoes two facile thermal rearrangements.[5] A single-crystal X-ray diffraction study[20] has shown that the structure of the thermally least stable isomer has carbon atoms located at positions 1 and 7 (Figure 4).[21] Subsequently, the complex has been shown to be fluxional in solution, rapidly interconverting between the 1,6 and 1,7 enantiomers. The structures of the remaining two isomers have not yet been reported.[22]

At 40° in dichloromethane, red $4\text{-}(\eta\text{-}C_5H_5)\text{-}4\text{-}Co\text{-}1,7\text{-}C_2B_{10}H_{12}$ was converted to a nonfluxional orange isomer which further rearranged to give a nonfluxional red-orange isomer in hexane at 70°. The 80.5-MHz [11]B nmr spectra of both the orange and red-orange isomers showed no low-field resonances; thus, it was concluded that the carbon atom initially located at the low-coordinate vertex 1 remained there, and the rearrangements involved only the carbon atom initially at vertex 7. The asymmetric nature of the nmr spectra of the orange and red-orange isomers ruled out the 1,5; 1,11; and 1,10 combinations. The 1,3 isomer was also eliminated as a possibility for the orange isomer since a

(15) W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 3342 (1967).

(16) W. H. Knoth, *Inorg. Chem.*, **10**, 598 (1971).

(17) The correct IUPAC name is $7\text{-}(\eta\text{-}C_5H_5)\text{-}7\text{-}Co\text{-}1,6\text{-}C_2B_7H_9$. See ref 9.

(18) The correct IUPAC name is $1\text{-}(\eta\text{-}C_5H_5)\text{-}1\text{-}Co\text{-}4,5\text{-}C_2B_6H_8$. See ref 9.

(19) K. P. Callahan, C. E. Strouse, A. L. Sims, and M. F. Hawthorne, *Inorg. Chem.*, in press.

(20) M. R. Churchill and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 1326 (1972).

(21) In the solid state, the complex exists as a mixture of the 1,6 and 1,7 enantiomers. For convenience, only one set of enantiomers will be referred to in the discussion.

(22) D. F. Dustin, Ph.D. Dissertation, University of California, Los Angeles, 1973.
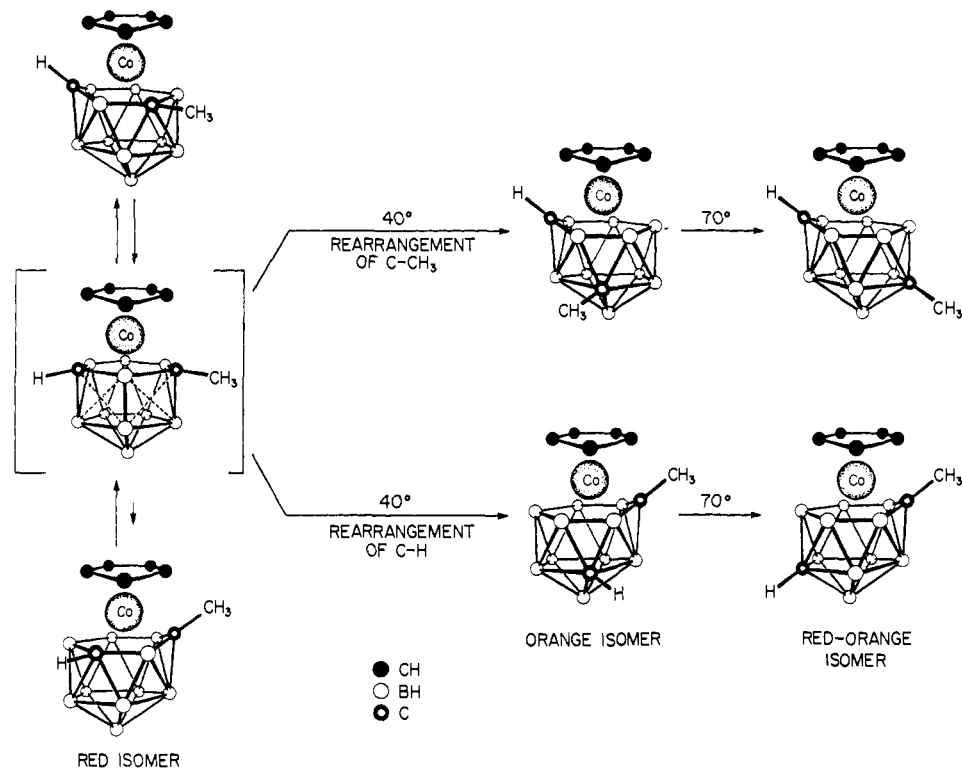
Figure 5. The proposed mechanism of the thermal rearrangements of $(\eta\text{-}C_5H_5)(CH_3)CoC_2B_{10}H_{11}$.

rearrangement from the 1,7 to the 1,3 isomer would involve the carbon atoms moving closer together.[23] Only the 1,8 and 1,13 possibilities remained for either isomer. Since a rearrangement from the 1,13 to the 1,8 locations would also involve carbon atoms moving closer together, it was concluded that the orange isomer had the carbon atoms located at positions 1 and 8 while the red-orange isomer had carbon atoms at positions 1 and 13.[23] The same progression of rearrangements would take place for the enantiomeric counterparts: 1,6 to 1,9 to 1,12. Virtually identical behavior was observed for the C,C'-dimethyl derivative, 4-(η-C_5H_5)-1,7-$(CH_3)_2$-4-Co-1,7-$C_2B_{10}H_{10}$.

The structural assignments given to the three isomers discussed above are consistent with the observed electrochemical data. The reduction potentials are -0.72, -1.15, and -1.16 V for the red, orange, and red-orange isomers, respectively. These values are in good agreement with the conclusion that the first rearrangement (red to orange) decreases the number of carbon atoms adjacent to the cobalt by one while the second rearrangement leaves the B_5C face intact.

A slightly different situation existed for the isomers of the monomethyl derivative, $(\eta\text{-}C_5H_5)(CH_3)CoC_2B_{10}H_{11}$, in that the red isomer was not fluxional. The rapid conversion of enantiomers observed with the unsubstituted and dimethyl derivatives had apparently been slowed down at room temperature and only one isomer was seen—probably the 7-methyl species due to possible steric interactions between 1-methyl protons and the cyclopentadienyl ring. At 40°, the red isomer rearranged to give an equimolar mixture of two different

orange isomers (both the 8-methyl and the 1-methyl species). The fact that both possible orange isomers were present in equal amounts (in contrast to the red isomers where only one was observed) suggested that the rearrangement from red to orange originated from some sort of intermediate or transition state such as that proposed[5] to exist between the two possible red isomers (Figure 5). Once the configuration of the intermediate was assumed, the rearrangement took place in one of two ways. Either polyhedral carbon atom could migrate away from the cobalt atom to the lower belt of boron atoms. When the normal geometry of the 13-vertex polyhedron was reattained, the two different orange isomers were generated. Each orange isomer then further rearranged to give a red-orange isomer.

Rearrangement Kinetics. Previous work in the area of polyhedral rearrangements has concentrated on compounds possessing icosahedral geometry. The available data for nonicosahedral systems have been limited to ten-atom polyhedra of the type $C_2B_8H_{10}$,[24] $B_{10}H_8[N(CH_3)_3]_2$,[25] and 2-(η-C_5H_5)-2-Co-1,6-$C_2B_7H_9$.[24] We have undertaken a study of the rearrangements of one additional ten-atom system as well as an 11- and a 13-atom metallocarborane. The kinetic data for these rearrangements are shown in Table I and the activation parameters are given in Table II. Table II also gives activation parameters for some additional polyhedral rearrangements.

A number of mechanisms for polyhedral rearrangements have been proposed and discussed[3,26] although

(23) Thermal migration of carbon atoms in metallocarboranes which does not result in greater carbon–carbon separation has only been achieved by linking the polyhedral carbon atoms with a trimethylene group (ref 3).

(24) Y. Ta-Ching, M.S. Thesis, University of California, Riverside, 1968.

(25) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 5434 (1964).

(26) (a) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, pp 55–72; (b) W. N. Lipscomb, *Science*, **153**, 373 (1966).

Table I. Kinetic Data for Selected
Nonicosahedral Rearrangements

Reaction	Temp, °C	$10^7 k$, sec^{-1}
2-(η-C$_5$H$_5$)-2-Co-6,9-C$_2$B$_7$H$_9$ →	80	478 ± 9
2-(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$	85	918 ± 14
	90	1660 ± 30
2-(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$ →	154	623
2-(η-C$_5$H$_5$)-2-Co-1,10-C$_2$B$_7$H$_9^a$	165	1940
	179	7680
1-(η-C$_5$H$_5$)-1-Co-2,4-C$_2$B$_8$H$_{10}$ →	97	326 ± 2
1-(η-C$_5$H$_5$)-1-Co-2,3-C$_2$B$_8$H$_{10}$	110	1330 ± 10
	117	2380 ± 10
4-(η-C$_5$H$_5$)-4-Co-1,7-C$_2$B$_{10}$H$_{12}$ →	35	2.30 ± 0.07
4-(η-C$_5$H$_5$)-4-Co-1,8-C$_2$B$_{10}$H$_{12}$	46	14.6 ± 1
	58	73.0 ± 5
4-(η-C$_5$H$_5$)-4-Co-1,8-C$_2$B$_{10}$H$_{12}$ →	66	1.87 ± 0.01
4-(η-C$_5$H$_5$)-4-Co-1,13-C$_2$B$_{10}$H$_{12}$	81	16.0 ± 0.05
	97	160 ± 5

a Reference 24.

Table II. Activation Parameters for Polyhedral Rearrangements

Compound	Rearrange-ment	$\Delta H^{\ddagger}$, kcal/ mol	$\Delta S^{\ddagger}$, eu	Ref
1,2-C$_2$B$_{10}$H$_{12}$	1,2 → 1,7	+62	+7	a
1,2-Bis(methyldiphenyl-silyl)carborane	1,2 → 1,7	+45	−1	a
(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$	1,6 → 1,10	+34	+3	24
1,6-C$_2$B$_8$H$_{10}$	1,6 → 1,10	+49	+5	24
1,6-(CH$_3$)$_2$-1,6-C$_2$B$_8$H$_8$	1,6 → 1,10	+50	+5	24
2,3-B$_{10}$H$_8$[N(CH$_3$)$_3$]$_2$	2,3 → 1,6	+37	+2	25
(η-C$_5$H$_5$)-2-Co-6,9-C$_2$B$_7$H$_9$	6,9 → 1,6	+31	+9	
(η-C$_5$H$_5$)-1-Co-2,4-C$_2$B$_8$H$_{10}$	2,4 → 2,3	+29	+2	
(η-C$_5$H$_5$)-Co-1,7-C$_2$B$_{10}$H$_{12}$	1,7 → 1,8	+30	+8	
(η-C$_5$H$_5$)-Co-1,8-C$_2$B$_{10}$H$_{12}$	1,8 → 1,13	+34	+14	

a R. M. Salinger and C. L. Frye, Inorg. Chem., 4, 1815 (1965).

we are in no position to state definitely which, if any, predominates in the cobaltacarborane rearrangements discussed here. We can, however, summarize the kinetic data with a few observations.

First, all of the cobaltacarborane rearrangements, with the exception of those for (η-C$_5$H$_5$)CoC$_2$B$_9$H$_{11}$, have nearly the same values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. This similarity suggests that the B$_6$, B$_7$, B$_8$, and B$_{10}$ systems may proceed via similar mechanisms. The 12-atom polyhedral complex, (η-C$_5$H$_5$)CoC$_2$B$_9$H$_{11}$, has a significantly higher barrier to rearrangement and this phenomenon is observed with other 12-atom systems such as B$_{12}$H$_{12}^{2-}$ and C$_2$B$_{10}$H$_{12}$. The mechanism of rearrangement for (η-C$_5$H$_5$)CoC$_2$B$_9$H$_{11}$ might very well be the same as that for the other cobaltacarboranes and the high activation energy of the 12-atom polyhedron could be due to the high resonance stabilization of icosahedral systems.

Secondly, for a given geometry, the cobaltacarborane undergoes a more facile rearrangement than does the neutral carborane of the same geometry. 2-(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$ rearranges much more easily than 1,6-C$_2$B$_8$H$_{10}$ and the rearrangements of (η-C$_5$H$_5$)CoC$_2$B$_9$H$_{11}$ take place at lower temperatures than those of C$_2$B$_{10}$-H$_{12}$.[27] Apparently, the inclusion of a cobalt atom into the polyhedral framework provides a lower energy pathway for the rearrangement. If two cobalt atoms were contained in a complex, the activation energy might be lowered even further. This last point is currently under investigation in this laboratory.

(27) D. Grafstein and J. Dvorak, Inorg. Chem., 2, 1128 (1963).

Conclusion

Several general trends are apparent from the studies of cobaltacarborane rearrangements. First, there is no evidence for the cobalt atom occupying a vertex other than that of highest coordination number. Second, the carbon atoms migrate to preferentially locate themselves at the vertices of lowest coordination number. Although the heteroatoms tend to relocate so as to increase their mutual separation, this tendency is mitigated by the affinity of carbon atoms for low-coordinate vertices and the cobalt for high-coordinate vertices. A summary of our observations may be expressed in terms of the following empirical rules governing the thermal rearrangements of the compounds (η-C$_5$H$_5$)CoC$_2$B$_n$H$_{n+2}$, n = 6–10. (a) The cobalt atom will occupy the vertex of highest polyhedral coordination number and remain there. (b) The carbon atoms will not decrease their mutual separation.[23] (c) Carbon atoms will migrate to vertices of lowest polyhedral coordination number. Once so located, they will migrate only to an alternate low-coordinate vertex. (d) Carbon atoms will tend to migrate away from the cobalt atom providing rules b and c are not violated.

All of the thermal rearrangements discussed here conform to these rules. One point which remains to be clarified is whether the heteroatoms will migrate to vertices of favorable coordination number even though such a rearrangement would involve a decrease in their mutual separation; e.g., would 1-(η-C$_5$H$_5$)-1-Co-2,10-C$_2$B$_8$H$_{10}$ rearrange to 1-(η-C$_5$H$_5$)-1-Co-2,3-C$_2$B$_8$H$_{10}$? Unfortunately, none of the cobaltacarboranes available at this time allow a test of this point. However, the attainment of vertices of favorable coordination number seems to dominate the migrations of carbon atoms, and this factor may prove to dominate the thermal rearrangements entirely.

Experimental Section

Materials. All rearrangements were carried out in nearly the same manner. Reagent grade solvents were used, and each reaction was performed under a nitrogen atmosphere. Starting materials were prepared by the reported procedures. The rearrangement products were identified by thin-layer chromatography and by their ^{1}H and ^{11}B nmr spectra. Baker "Analyzed Reagent" silica gel was used for column chromatography, and Mallinckrodt "Chromar 1000" was used for thick-layer chromatography. Silufol "UV$_{254}$" was used for thin-layer chromatography.

Rearrangement of 1-(η-C$_5$H$_5$)-1-Co-2,4-C$_2$B$_8$H$_{10}$. To a 100-ml round-bottom flask equipped with a condenser, nitrogen inlet, thermometer, and magnetic stirring bar was added 1.248 g of 1-(η-C$_5$H$_5$)-1-Co-2,4-C$_2$B$_8$H$_{10}$ and 50 ml of cyclooctane. The solution was heated at the reflux temperature for 6 hr. After cooling to room temperature, the solution was filtered affording 1.172 g of 1-(η-C$_5$H$_5$)-1-Co-2,3-C$_2$B$_8$H$_{10}$. The filtrate was chromatographed on silica gel with hexane yielding an additional 0.012 g of the product. The total yield was 1.184 g (95%).

Rearrangement of [1,3'-Co(2,4-C$_2$B$_8$H$_{10}$)(1',2'-C$_2$B$_9$H$_{11}$)]$^-$. A 0.200-g sample of [(CH$_3$)$_4$N][1,3'-Co-(2,4-C$_2$B$_8$H$_{10}$)(1',2'-C$_2$B$_9$H$_{11}$)] was suspended in 20 ml of cyclooctane and the mixture was heated at the reflux temperature for 4 hr. The crude product was isolated by filtration, washed with chloroform, and chromatographed on silica gel with 10% acetonitrile in dichloromethane. The solvent was evaporated from the green band and the resulting solid material was redissolved in an acetone–ethanol solution. The addition of aqueous tetramethylammonium chloride followed by evaporation of the acetone caused [(CH$_3$)$_4$N][1,3'-Co(2,3-C$_2$B$_8$H$_{10}$)-(1',2'-C$_2$B$_9$H$_{11}$)], 0.130 g (65% yield), to precipitate.

Rearrangement of 2-(η-C$_5$H$_5$)-2-Co-6,9-C$_2$B$_7$H$_9$. A 50-mg sample of 2-(η-C$_5$H$_5$)-2-Co-6,9-C$_2$B$_7$H$_9$ was added to 10 ml of heptane and the mixture was heated at the reflux temperature for 4 hr. The solvent was removed in vacuo and the product was isolated by sub-

limation at 80° onto a 0° cold finger; 46 mg (92%) of 2-(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$ was obtained.

Rearrangement of 2-(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$. A solution of 50 mg of 2-(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$ in 5 ml of decane was heated at the reflux temperature for 4 hr. Column chromatography of the reaction mixture on silica gel eluted with hexane afforded a yellow band. The solvent was removed and a yellow solid was sublimed at 70° to a 0° probe. 2-(η-C$_5$H$_5$)-2-Co-1,10-C$_2$B$_7$H$_9$, 38 mg (76%), was isolated.

Rearrangement of 2-(η-C$_5$H$_5$)-2-Co-1,7-C$_2$B$_7$H$_9$. A 40-mg sample of 2-(η-C$_5$H$_5$)-2-Co-1,7-C$_2$B$_7$H$_9$ was heated for 15 min in 5 ml of hexadecane at the reflux temperature. Column chromatography removed the hexadecane and the rearrangement product was eluted and further purified by thick-layer chromatography. The product was sublimed at 70° to a 0° cold finger yielding 20 mg (50%) of 2-(η-C$_5$H$_5$)-2-Co-1,10-C$_2$B$_7$H$_9$.

Rearrangement of 2-(η-C$_5$H$_5$)-2-Co-3,10-C$_2$B$_7$H$_9$. A 100-mg sample of 2-(η-C$_5$H$_5$)-2-Co-3,10-C$_2$B$_7$H$_9$ was heated in 7 ml of refluxing hexadecane for 5 hr. Column chromatography followed by sublimation at 70° to a −78° probe yielded 85 mg (85%) of 2-(η-C$_5$H$_5$)-2-Co-1,10-C$_2$B$_7$H$_9$.

Rearrangement of 2-(η-C$_5$H$_5$)-2-Co-4,5-C$_2$B$_6$H$_8$. A solid sample of 2-(η-C$_5$H$_5$)-2-Co-4,5-C$_2$B$_6$H$_8$ was placed in an nmr tube which was then immersed in cyclooctane at the reflux temperature for 5 hr. CDCl$_3$ was added to the tube, and the ^{1}H and ^{11}B nmr spectra identified the product as 2-(η-C$_5$H$_5$)-2-Co-4,6-C$_2$B$_6$H$_8$.

Rearrangement of 4-(η-C$_5$H$_5$)-4-Co-1,7-C$_2$B$_{10}$H$_{12}$. A 0.268-g sample of 4-(η-C$_5$H$_5$)-4-Co-1,7-C$_2$B$_{10}$H$_{12}$ was added to 20 ml of hexane and heated to the reflux temperature for 15 hr. The products were separated by column chromatography using silica gel eluted with hexane gradually enriched with dichloromethane. The bands that were separated were, in order of elution, 4-(η-C$_5$H$_5$)-4-Co-1,13-C$_2$B$_{10}$H$_{12}$ (trace), 4-(η-C$_5$H$_5$)-4-Co-1,8-C$_2$B$_{10}$H$_{12}$ (0.158 g, 60%), and 4-(η-C$_5$H$_5$)-4-Co-1,7-C$_2$B$_{10}$H$_{12}$ (0.101 g, 37%). If the rearrangement were performed in benzene at the reflux temperature for 24 hr, only one band, consisting of 4-(η-C$_5$H$_5$)-4-Co-1,13-C$_2$B$_{10}$H$_{12}$ (71%), was isolated.

Kinetic Methods. Kinetic runs at temperatures less than 60° were carried out in a constant temperature water bath. Others were carried out in an apparatus where a chamber containing the sample solution was suspended in a reservoir of refluxing liquid. A constant temperature of ±0.05° could be maintained within the sample chamber.

Kinetic data for the rearrangement of 2-(η-C$_5$H$_5$)-2-Co-6,9-C$_2$B$_7$H$_9$ to 2-(η-C$_5$H$_5$)-2-Co-1,6-C$_2$B$_7$H$_9$ were obtained by monitoring the increase in absorbance at 504 nm. In all other runs, aliquots were withdrawn from the samples at appropriate time intervals and injected into a high-pressure liquid chromatograph.[28] The absorbance of reactant and product was determined using a 280-nm uv detector and a strip-chart recorder. Individual peak areas were measured with a planimeter and, after corrections were made for differences in extinction coefficients at 280 nm, the concentration of each component was calculated. Plots of the log of the concentration of the reactants as a function of time gave first-order rate constants. Activation parameters were calculated from plots of ln k vs. $1/T$ using three temperatures for each reaction.

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Direct Insertion of Transition Metals into Polyhedral Carboranes. Structurally Novel Mono-, Di-, and Trimetallic Small Cage Systems

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Abstract: Metallocarboranes of iron, cobalt, and nickel have been prepared by the direct reaction of the small polyhedral carboranes 1,5-C$_2$B$_3$H$_5$, 1,6-C$_2$B$_4$H$_6$, or 2,4-C$_2$B$_5$H$_7$ with organometallic reagents in the gas phase or in solution, without the use of a prior cage-opening step. The novel six-vertex cages (CO)$_3$FeC$_2$B$_3$H$_5$ and (η-C$_5$H$_5$)-CoC$_2$B$_3$H$_5$, as well as the seven-vertex species (CO)$_6$Fe$_2$C$_2$B$_3$H$_5$ and (η-C$_5$H$_5$)$_2$Co$_2$C$_2$B$_3$H$_5$, were obtained from C$_2$B$_3$H$_5$ and Fe(CO)$_5$ or (η-C$_5$H$_5$)Co(CO)$_2$ in the gas phase at elevated temperatures. Reactions of these metal reagents or (π-C$_2$H$_4$)Ni[P(C$_6$H$_5$)$_3$]$_2$ with C$_2$B$_4$H$_6$ gave primarily seven-vertex monometallocarboranes containing an MC$_2$B$_4$ cage. The cobalt reagent and C$_2$B$_5$H$_7$ gave mono-, di-, and trimetallocarborane species, including two isomers of the novel (η-C$_5$H$_5$)$_3$Co$_3$C$_2$B$_5$H$_7$ system. Nickel and iron monometallocarboranes of seven or eight vertices were obtained from C$_2$B$_5$H$_7$ by analogous processes. The direct reaction of 1,2-C$_2$B$_{10}$H$_{12}$ and (η-C$_5$H$_5$)Co-(CO)$_2$ at 300° gave a mixture of cobaltacarboranes which were predominantly isomers of (η-C$_5$H$_5$)CoC$_2$B$_9$H$_{11}$. Molecular structures were assigned to the new compounds on the basis of ^{11}B and ^{1}H nmr spectra. Fine structure in the carborane CH ^{1}H nmr signals exhibited by several of the cobaltacarborane species was interpreted on the basis of H–C–B–H proton–proton coupling.

O f the many reported syntheses of metallocarboranes,[1] nearly all are variations on one or the other of two basic themes: (1) insertion of a metal atom into a neutral open-cage (nido) carborane, or (2) the opening of a closed polyhedral (closo) carborane framework to create a nido-carborane anion followed by the incorporation of a metal into the open face. The first method has been useful in limited applications, e.g., the synthesis of small metallocarboranes from nido-2,3-C$_2$B$_4$H$_8$,[2–6] but cannot be considered a truly

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