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Thermal Isomerization Studies of Small Metallocarboranes. Cage Rearrangement Equilibria and Reversible Cobalt Atom Migrations

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Received August 2, 1974

Abstract: The vapor phase thermal behavior of six-, seven-, and eight-vertex monocobaltacarboranes, seven-, eight-, and nine-vertex dicobaltacarboranes, and a ten-vertex tricobaltacarborane was examined. In addition to phenomena of types previously observed in metallocarborane studies, e.g., intramolecular migration of metal and carbon atoms, and intermolecular transfer of cobalt and boron, several processes novel to metallocarborane chemistry were found, including the conversion of a neutral cobaltacarborane to a carborane via thermal ejection of cobalt, the migration of cobalt from a 5- to a 4-coordinate polyhedral vertex, and two examples of cage rearrangement equilibria involving reversible metal–metal cleavage. The isomerization of 1,7,2,3-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ to the 1,7,2,4 species via the isolable 1,2,4,5 and 1,2,3,5 intermediates was examined, and a mechanism has been proposed for the sequence. The equilibrium constant for the reversible rearrangement of 1,7,5,6- to 1,8,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ was determined as a function of temperature. The results obtained are discussed and evaluated in conjunction with previously reported work on the isomerization of large cobaltacarborane systems.

The rearrangement of polyhedral carboranes and metallocarboranes has received much attention from experimentalists and theoreticians.[1-6] Although the basic phenomenon involved—cooperative movement of atoms in the surface of a triangulated polyhedral cage—is almost unknown outside of boron chemistry, within this area it occurs with such facility and regularity that an understanding of it is a fundamental aspect of boron cage chemistry. Previous work on cage rearrangements has dealt with systems of large or intermediate size, especially those of icosahedral (12-vertex) geometry. The only reported small carborane rearrangement in the polyhedral $C_2B_{n-2}H_n$ series is that of octahedral 1,2- to 1,6-$C_2B_4H_6$.[7] In the metallocarborane field, Hawthorne et al. have examined the thermal isomerization of several monocobalt 9- to 13-vertex[4,5] and dicobalt 10- to 12-vertex[6] cages and noted several trends which we shall discuss later in this paper. Despite the isolation of many smaller metallocarboranes in recent years,[8] their thermal rearrangements have not previously been investigated.

In the course of our work on small metallocarboranes and metalloboranes having as few as five cage atoms,[9-11] we have noted numerous instances of thermal isomerization and/or disproportionation and accordingly initiated detailed studies of several selected cobaltacarborane systems having one to three metal atoms. The results are, in part, in accord with expectations based on studies of larger sys-

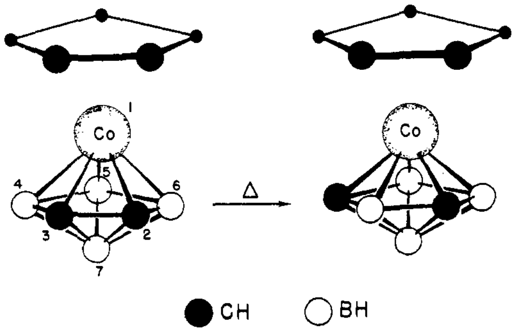

Figure 1. Thermal rearrangement of 1,2,3-(η-C_5H_5)$CoC_2B_4H_6$ to 1,2,4-(η-C_5H_5)$CoC_2B_4H_6$.

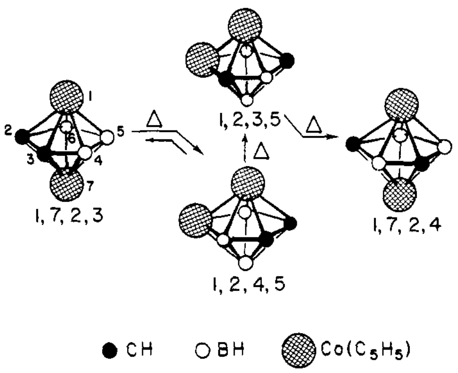

Figure 2. The principal rearrangement sequence for (η-C_5H_5)$_2Co_2C_2B_3H_5$ isomers.

tems,[4-6] but in other respects differ significantly from earlier work and supply some new insights into the factors controlling cage rearrangement processes.

Results and Discussion

General Approach and Scope. All experiments were conducted in the vapor phase in sealed Pyrex tubes without solvent, utilizing electrically neutral, air-stable, crystalline η-cyclopentadienylcobaltacarboranes, all of which were originally prepared in our laboratory. The systems examined were monocobalt species of six, seven, and eight vertices, dicobalt cages of seven, eight, and nine vertices, and a tricobalt ten-vertex system.

Six-Vertex Cages. Pyrolysis of 1,2,4-(η-C_5H_5)$CoC_2B_3H_5$. Three isomers are possible in a CoC_2B_3 octahedral system, only one of which, 1,2,4-(η-C_5H_5)$CoC_2B_3H_5$,[10] contains nonadjacent framework carbon atoms. Since the higher thermal stability of carborane and metallocarborane isomers having nonadjacent carbons compared to those with adjacent carbons is well established, it was considered unlikely that 1,2,4-(η-C_5H_5)$CoC_2B_3H_5$ would isomerize to the unknown 1,2,3 or 1,2,6 systems, both of which would have adjacent carbons. Consequently, the thermolysis of 1,2,4-(η-C_5H_5)$CoC_2B_3H_5$ was expected to result in formation of di- and possibly tricobalt metallocarboranes, polymerization, and decomposition, rather than cage rearrangement. This was in fact observed, the predominant metallocarborane products of pyrolysis at 250° being CoC_2B_4, $Co_2C_2B_3$, and $Co_2C_2B_4$ cage systems. In addition to the expected thermal metal transfer[12] evidenced by the dicobalt products, boron transfer also occurred, giving 4-boron species. Spectroscopic evidence for monomethylated metallocarboranes was also obtained, the methyl groups presumably forming from decomposition of the original metallocarborane. The relatively low thermal stability of this octahedral cobaltacarborane, as compared with larger homologs, is indicated by the substantial degradation at 250°.

Seven-Vertex Monocobalt Cages. Rearrangement of 1,2,3-(η-C_5H_5)$CoC_2B_4H_6$. The structure of 1,2,3-(η-C_5H_5)$CoC_2B_4H_6$[13] (Figure 1) has been confirmed in an X-ray diffraction study[14] of the *C,C'*-dimethyl derivative. The parent compound exhibits high thermal stability, but at 400° isomerized almost quantitatively to 1,2,4-(η-C_5H_5)$CoC_2B_4H_6$, a species previously obtained[15] in the sodium naphthalide-metal ion treatment of 2,4-$C_2B_5H_7$. Although traces of 1,7,2,4-(η-C_5H_5)$_2Co_2C_2B_3H_5$ were produced, no other monocobalt isomers were found. Analogous results were obtained in the pyrolysis of the *C*-methyl derivative, 2-CH_3-1,2,3-(η-C_5H_5)$CoC_2B_4H_5$. Since the 1,2,3 and 1,2,4 isomers are the only possible pentagonal bipyramidal CoC_2B_4 systems having the metal in an apical (five-coordinate) vertex and both cage carbons in equatorial (four-coordinate) vertices, these findings are in conformity with previous observations[5] that (1) framework carbon atoms tend to favor low-coordinate vertices, (2) cobalt atoms prefer high-coordinate positions, and (3) the carbon atoms tend to separate from one another. It should be emphasized that these empirical rules describe trends and do not prohibit structures containing high-coordinate carbon and/or low-coordinate metal atoms; indeed, the isolation of several such species as stable compounds is described elsewhere in this paper.

Seven-Vertex Dicobalt Cages. Rearrangement of 1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_5$. X-Ray studies of their *C*-methyl derivatives have established the structures of 1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_5$[16a] and its 1,7,2,4 isomer[16b] (Figure 2), which we have described[13,16a] as triple-decked metallocene analogs since the central ring in each case is formally $C_2B_3H_5^{4-}$, isoelectronic with $C_5H_5^-$. Pyrolysis of the 1,7,2,3 parent compound or the *C*-methyl-substituted species above 300° yields respectively 1,7,2,4-(η-C_5H_5)$_2Co_2C_2B_3H_5$ or its *C*-methyl derivative. Since this conversion in net effect results in the separation of the cage carbons while leaving the cobalt and carbon atoms in their favored five-coordinate and four-coordinate polyhedral vertices, respectively, it is in accord with the empirical rules outlined earlier. The 1,7,2,4 isomer (previously obtained[13] from the reduction of 1,6-$C_2B_4H_6$ with sodium naphthalide followed by treatment with $CoCl_2$ and NaC_5H_5) does not undergo further rearrangement below its decomposition temperature (~400°).

In order to gain further insight into this isomerization, the rearrangement of 1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_5$ was conducted at 200–250°, a temperature range barely sufficient to effect slow conversion. Under these relatively mild conditions, two additional (η-C_5H_5)$_2Co_2C_2B_3H_5$ species were isolated as intermediates, and a close examination of the thermal behavior of these individual species established that the main route is that shown in Figure 2 (evidence that other pathways may also be operative to a minor extent is given in the Experimental Section). As the diagram indicates, the 1,7,2,3 → 1,2,4,5 conversion is slightly reversible (the implications of this are discussed later in connection with the (η-C_5H_5)$_2Co_2C_2B_5H_7$ system).

The structure of the previously reported[10] 1,2,3,5 isomer was deduced from ^1H and ^{11}B NMR spectra and other considerations such as the method of preparation. The NMR spectra of the new 1,2,4,5 isomer, given in the Experimental Section, indicate the presence of a mirror plane which generates equivalent cage CH groups and a pair of equivalent BH units; the (η-C_5H_5)Co moieties are nonequivalent and hence lie on the mirror plane, as does the unique boron. Two possible structures, 1,2,3,6 and 1,2,4,5, have the required symmetry, but the 1,2,4,5 geometry is strongly indicated on the grounds that the very low-field[17] ^{11}B NMR signal of area 2 correlates with low-coordinate boron atoms[15,18] adjacent to both cobalts; this effect is particularly evident in comparison with the ^{11}B spectrum of the 1,2,3,5 isomer, a uniquely defined structure[19] which contains only one such boron atom. A further indication of the 1,2,4,5 geometry is the reversibility of the 1,7,2,3 → 1,2,4,5 conversion, which strongly suggests that the cage carbons remain adjacent in the new isomer.

The isolation of the 1,2,4,5 and 1,2,3,5 species as stable intermediates is particularly interesting, since their formation from the 1,7,2,3 isomer requires the migration of cobalt from a "favored" five-coordinate vertex to a supposedly unfavorable four-coordinate equatorial vertex. There is little doubt that the placement of cobalt in a low-coordinate vertex is normally energetically unfavorable (for example, as was discussed above, no such monocobalt $(\eta\text{-}C_5H_5)CoC_2B_4H_6$ species has been detected). Clearly, this tendency is offset in 1,2,4,5- and 1,2,3,5-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ by other factors which not only permit one cobalt to occupy an equatorial vertex but also allow an apical-equatorial migration. We have suggested in an earlier paper[10] that the 1,2,3,5 isomer and its iron analog, 1,2,3,5-$(CO)_6Fe_2C_2B_3H_5$ (both of which were produced in the gas-phase polyhedral expansion of 1,5-$C_2B_3H_5$) are stabilized by the direct metal-metal interactions in these systems. This proposal is supported by the present studies of the $(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ rearrangement, and further evidence of the importance of cobalt-cobalt bonding as a determinant of thermal stability is given by the $(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ system described later in this paper.

Although detailed kinetic studies have not been undertaken, the sequence outlined in Figure 2 allows some deductions about the mechanism by which these interconversions take place. Perhaps the simplest a priori possibility is the diamond-square-diamond, or dsd, rearrangement proposed by Lipscomb[1] for the isomerization of triangulated boron polyhedra. In this mechanism, a diamond-shaped array of atoms (two adjacent triangles) is stretched along the short diagonal to give a square, which is then compressed along the other diagonal to form a new diamond array. Application of the dsd mechanism to 1,7,2,3-$(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ does not give a particularly satisfactory accounting of the observed rearrangement. While successive dsd operations are capable of interconverting the four species in Figure 2 (and indeed can, in principle, produce all geometrically possible isomers[1]), a dsd pathway in this system entails several objections: (1) it can account for the observed sequence only if several additional, but unknown, intermediate isomers are postulated, i.e., none of the three transformations shown can occur directly in a single dsd cycle; (2) intermediates having unfavorable features, such as apex (five-coordinate) carbons, two equatorial metals, or both, are required; and (3) the sequence in Figure 2 is much more selective than expected for a simple dsd mechanism, which might be expected to produce additional transformations beyond those actually observed.

These objections do not, in themselves, rule out a simple dsd mechanism but they do render it less attractive. A more appealing pathway involves the rotation of triangular groups on the polyhedral surface, a mechanism originally proposed by Muetterties and Knoth[2] for icosahedral cage rearrangements. It seems to us significant that each conversion in Figure 2 can occur via a single triangle rotation; for example, a one-third rotation of triangle Co(7)-B(4)-B(5) in the starting material yields the 1,2,4,5 species, rotation of a B_2C triangle in the 1,2,4,5 isomer can produce the 1,2,3,5, and rotation of a CoB_2 triangle in the latter compound yields the 1,7,2,4 final product. In contrast to the dsd route, none of these conversions requires more than one step.[20] Moreover, the observed sequence can be accounted for in terms of a rotating triangle mechanism if several restrictions are applied: (1) carbon may not move from an equatorial into an apex (high-coordinate) position; (2) carbon atoms once separated cannot return to adjacent vertices; (3) rotation of B_2C or B_2Co triangles is preferred; (4) cobalt will tend to adopt an apex location, provided rules 1-3 are followed. The rotating triangle mechanism with these constraints is in agreement with our results, and in fact uniquely yields the observed sequence with one exception: the original 1,7,2,3 isomer, under the proposed rules, could yield the 1,2,3,4 and 1,2,3,6 isomers, which have not been observed. However, if either species were formed, under the above rules it could convert only to the known 1,2,3,5 or 1,2,4,5 species; if this were to take place rapidly, such an intermediate might well not be detected.

The proposed restrictions (1), (2), and (4) are closely related to empirical rules set forth by Hawthorne et al.[5] for the rearrangement of monocobalt metallocarboranes of six to ten boron atoms. However, while these workers also suggested that cobalt would not migrate from a high- to a low-coordinate vertex, such movement obviously does occur in the present system. An additional trend noted by the Hawthorne group, the tendency of cobalt and carbon to separate, seems at best weak in the $(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ rearrangements since the number of Co-C links in the four isomers is four, two, three and four, respectively. We emphasize that the Hawthorne proposals were limited to systems of six to ten boron atoms and thus no discrepancy with our observations is indicated; the differences however, are interesting and will be further discussed below.

With respect to the proposed rotating triangle rearrangement mechanism, it may be noted that calculations based on triangle rotations in a cuboctahedral intermediate have been applied with some success to the isomerization of halogenated 1,2- and 1,7-$C_2B_{10}H_{12}$ derivatives,[21,22] in contrast to the dsd mechanism which cannot in itself account for the observed product distributions.

Irrespective of the detailed mechanism, the observed sequence of the $(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ rearrangement is readily explained. The principal driving force is the separation of cage carbon atoms, which converts the 1,7,2,3 to the 1,7,2,4 isomer. However, the 1,7,2,3 → 1,7,2,4 250° conversion may not occur except via intermediates in which one cobalt occupies an equatorial vertex. The activation energy for the migration of cobalt to an equatorial location, as in the 1,2,4,5 isomer, is lowered by the stabilizing effect of cobalt-cobalt bonding. Thus, the existence of the 1,2,4,5 species in equilibrium with the 1,7,2,3 compound at elevated temperature provides a ready pathway to the 1,7,2,4 species.

Eight-Vertex Monocobalt Cages. Disproportionation of 3,1,7-$(\eta\text{-}C_5H_5)CoC_2B_5H_7$. The $(\eta\text{-}C_5H_5)CoC_2B_5H_7$ system is known in only one isomeric form, with no evidence of any other isomers having been detected in any experiments. The 3,1,7 isomer was originally obtained in low yield in the polyhedral expansion of 2,4-$C_2B_5H_7$ with sodium in tetrahydrofuran,[15] but a much better synthesis is the reaction of $(\eta\text{-}C_5H_5)Co(CO)_2$ with $C_2B_5H_7$ in the vapor phase.[10] The structure of 3,1,7-$(\eta\text{-}C_5H_5)CoC_2B_5H_7$ (Figure 3a) has not been confirmed in an X-ray study, but a unique assignment[15] can be made from the ^{11}B and ^1H NMR spectra provided that (1) cobalt is assumed to occupy a five-coordinate vertex in the dodecahedral framework, and (2) one accepts the previously invoked correlation[15,18] between very

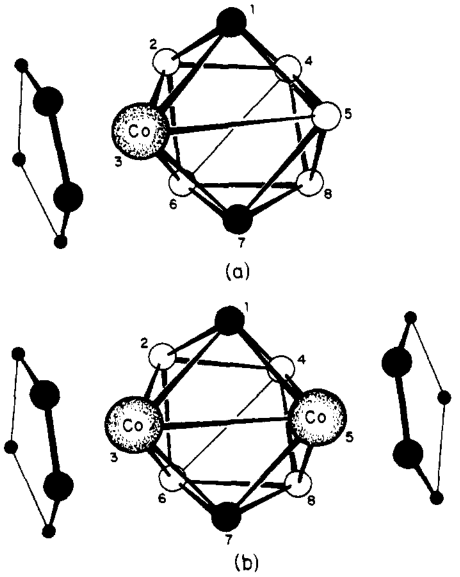

Figure 3. Proposed structures of eight-vertex cobaltacarboranes: (a) 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$, (b) 3,5,1,7-(η-C_5H_5)$_2Co_2C_2B_4H_6$.

low field ^{11}B NMR signals and boron atoms occupying four-coordinate vertices adjacent to cobalt. The spectra reveal that the molecule is totally asymmetric, and the ^{11}B resonance at δ −56.5 ppm (relative to BF_3 etherate) is assigned to a four-coordinate BH group adjacent to the metal atom; thus the other two four-coordinate members linked to the metal must be nonequivalent CH groups, and the structure is 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$. Disregarding enantiomers, no other gross geometry is possible based on a dodecahedral eight-vertex cage and consistent with the above assumptions.

The compound is thermally stable below 250°; at 340° it undergoes disproportionation in which a (η-C_5H_5)Co moiety is transferred from one substrate molecule to another, releasing the carborane 2,4-$C_2B_5H_7$ and forming a pair of dicobalt (η-C_5H_5)$_2Co_2C_2B_5H_7$ isomers (discussed below), plus traces of tricobalt species and some solid residue. Although the intermolecular thermal transfer of cobalt from (η-C_5H_5)$CoC_2B_8H_{10}$ to yield several dicobalt species has been reported,[12] to our knowledge the isolation of a carborane from the disproportionation of a neutral metallocarborane is novel.

The absence of any evidence for other isomers of (η-C_5H_5)$CoC_2B_5H_7$ (or its isostructural analog[23] 3,1,7-$(CO)_3FeC_2B_5H_7$) is significant, since previous work on monocobalt metallocarboranes of 9–12 vertices suggested that cobalt and carbon atoms tend to separate.[5] Application of this principle (rule d in ref 5), with the restrictions given,[5] suggests that 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$ should rearrange to the 3,1,8 isomer, thereby severing one of the cobalt–carbon links. The fact that no such rearrangement occurs even at high temperatures means that either this metallocarborane does not exhibit the drive for cobalt–carbon separation which has been observed in larger cobaltacarboranes, or else the structure is actually 3,1,8-(η-C_5H_5)$CoC_2B_5H_7$; if the latter were true, the failure to rearrange would be explainable on the basis that the carbon–carbon and carbon–cobalt distances were already maximized and no driving force for isomerization would exist. While not absolutely ruling out the possibility that the compound is the 3,1,8 isomer, we feel that this is improbable since the presence of two four-coordinate BH groups adjacent to cobalt would be expected to produce two very low field ^{11}B NMR resonances (vide supra) instead of the unique signal actually observed. Thus, it appears that 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$ does not exhibit a tendency for separation of carbon from cobalt. Further discussion of this finding appears in the concluding section.

Eight-Vertex Dicobalt Cages. Pyrolysis of 3,5,1,7-(η-C_5H_5)$_2Co_2C_2B_4H_6$. As is the case with the monocobalt eight-atom system discussed in the previous section, only one dicobalt eight-vertex isomer has been isolated.[10,15] The proposed structure (Figure 3b)[15] based primarily on ^{11}B and ^1H NMR spectra, contains metal atoms at vertices 3 and 5 and carbons at 1 and 7. This geometry is consistent with the symmetry requirements imposed by the NMR data[15] and contains equivalent four-coordinate BH groups, each adjacent to one cobalt atom. The alternative 3,5,2,8 structure (inadvertently overlooked in our earlier report[15]) also satisfies the data, except that such a molecule would have low-coordinate borons adjacent to *two* cobalts, which would be expected to produce ^{11}B NMR signals at extremely low field;[10,15] the actual resonance at −56 ppm is nearly identical with that observed for the monocobalt species (η-C_5H_5)$CoC_2B_5H_7$, and hence favors the 3,5,1,7 geometry in which each low-coordinate boron is adjacent to only one cobalt atom.

The pyrolysis of 3,5,1,7-(η-C_5H_5)$_2Co_2C_2B_4H_6$ at 340° gave results similar to that of the monocobalt eight-vertex system, in that no rearrangement to other isomers was observed. Considerable boron and cobalt transfer took place, evidenced by the formation of CoC_2B_4, $Co_2C_2B_5$, $Co_2C_2B_4$, $Co_2C_2B_6$, and $Co_3C_2B_5$ cages. In addition, a new compound whose mass spectrum corresponded to (η-C_5H_5)$_3Co_3C_2B_4H_6$ was isolated in a quantity too small for further characterization. The fact that rearrangement to the unknown 3,5,2,8-(η-C_5H_5)$_2Co_2C_2B_4H_6$, which would have reduced the number of direct Co–C links from four to two, did not occur parallels the thermal behavior of 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$. As in the latter case, we interpret the absence of isomerization to mean that no isomer of higher thermal stability exists; however, the possibility that kinetic factors (e.g., the lack of a suitable pathway) are responsible cannot be altogether excluded.

Nine-Vertex Dicobalt Cages. Reversible Rearrangement of (η-C_5H_5)$_2Co_2C_2B_5H_7$ Isomers. Two (η-C_5H_5)$_2$-$Co_2C_2B_5H_7$ species are known: the red 1,8,5,6 isomer was obtained in the polyhedral expansion of 2,4-$C_2B_5H_7$ via sodium naphthalide reduction,[15] and the 1,8,5,6 and green 1,7,5,6 species were both produced in the vapor phase reaction of 2,4-$C_2B_5H_7$ with (η-C_5H_5)$Co(CO)_2$.[10] For convenience we shall refer to the 1,8,5,6 and 1,7,5,6 compounds as isomer A and isomer B, respectively. The proposed structures,[23a] shown in Figure 4, are based on ^{11}B NMR, ^1H NMR, infrared, electronic, and mass spectra. Since the cobalt atoms in B are adjacent while those in A are not, it was assumed that a rearrangement of B to A would occur at elevated temperature. While isomerization of B was indeed observed, it was unexpectedly found that the conversion is not quantitative and that an equilibrium is established between A and B (Figure 4). The equilibrium constant K_{eq} = [B]/[A] was measured as 1.00 ± 0.05 at 340°, in separate experiments starting with pure samples of B and A, respectively. Determination of K_{eq} at several temperatures from 240 to 340° gave an extrapolated value of K_{eq} = 6 ± 1 at 25°. The calculated value of ΔH for the A → B rearrangement is −2 ± 1 kcal, so that the rearrangement involving migration of the cobalt atoms toward each other is slightly, but clearly, exothermic. Thus, the isomer with adjacent cobalts, B, is more stable at room temperature than at higher temperatures, with respect to conversion to A.

This rearrangement is the first known example of a mea-

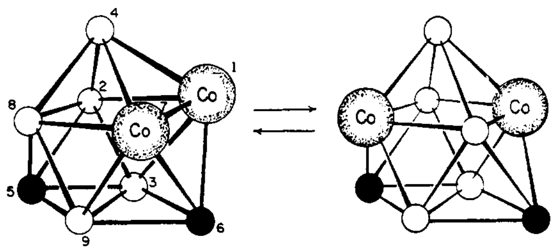

Figure 4. Reversible rearrangement of 1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ (left) and 1,8,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ (right). Cyclopentadienyl rings are omitted from the drawings.

surable equilibrium between closo-metallocarborane isomers. In all previously reported thermal isomerizations, the conversions were stated or implied to be irreversible; in most cases, in fact, we believe that the observed metallocarborane conversions do occur essentially quantitatively and that measurable equilibria such as that involving A and B may be comparatively rare. However, these observations suggest that the factors controlling the relative stabilities of metalloboron cage isomers may be more complex than formerly thought, particularly in systems containing more than one metal atom. Clearly, in isomers A and B there are forces operating in opposite directions, which are in a delicate state of balance. While the data needed for a sophisticated discussion are not available, a tentative suggestion is that the direct cobalt-cobalt interaction in B tends to be stabilized electronically, possibly by a bond order higher than the average bond order for adjacent framework atoms in the molecule; on the other hand, steric crowding of the cyclopentadienyl groups in B would tend to provide a driving force for separation of the metals. Such a steric factor would be more important at higher temperatures, in which thermal motion of the C_5H_5 rings is greater. These suggestions are in accord with the observed decrease in the relative concentration of isomer B with increasing temperature.

An indication that equilibria involving reversible metal-metal cleavage in metallocarboranes are not restricted to $(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ is given by the $(\eta\text{-}C_5H_5)_2Co_2C_2B_3H_5$ system discussed above. Although a value of K_{eq} has not been determined, the conversion of the 1,7,2,3 to the 1,2,4,5 isomer is clearly reversible since pyrolysis of the latter species generates a small (~10%) yield of the 1,7,2,3 isomer (the major product, as described earlier, is the 1,2,3,5 system). In this instance the reversible cobalt migration is even more remarkable than in the $(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$ system, since it involves movement between four- and five-coordinate vertices on the seven-atom polyhedral cage.

Ten-Vertex Tricobalt Cages. Rearrangement of 2,3,8,1,6-$(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$. The tricobalt isomers 2,3,8,1,6- and 2,3,4,1,10-$(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ (Figure 5) were obtained in the reaction of $(\eta\text{-}C_5H_5)Co(CO)_2$ with 2,4-$C_2B_5H_7$ in the vapor phase[10] and were structurally characterized from NMR, infrared, and mass spectra with particular reliance on the detailed fine structure of the C-H proton signals in the 100-MHz ^1H NMR spectra. While X-ray confirmation is still pending, the structural assignments based on NMR arguments[10] are reasonably certain. The pyrolysis of the 2,3,8,1,6 isomer at 300° resulted primarily in loss of cobalt from the cage, giving an approximately equimolar mixture of 1,8,5,6- and 1,7,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7$; since the equilibrium constant for interconversion of the latter species under these conditions is near unity (see previous section), the composition of this product mixture gives no information on the nature of the dicobalt isomer initially formed in the pyrolysis. In addition to the dicobalt species, a trace of the 2,3,4,1,10 tricobalt isomer was also obtained. The rearrangement is in the direction expected; the number of Co-C bonds decreases, and the movement of the five-coordinate CH group to a four-coordinate vertex is in accord with other metallocarborane rearrangements as discussed above. It should also be noted that the conversion of 2,3,8,1,6 to the 2,3,4,1,10 isomer increases the number of direct Co-Co bonds, indicating once again that the formation of metal-metal links is not thermally inhibited and may in certain circumstances be a positive stabilizing factor.

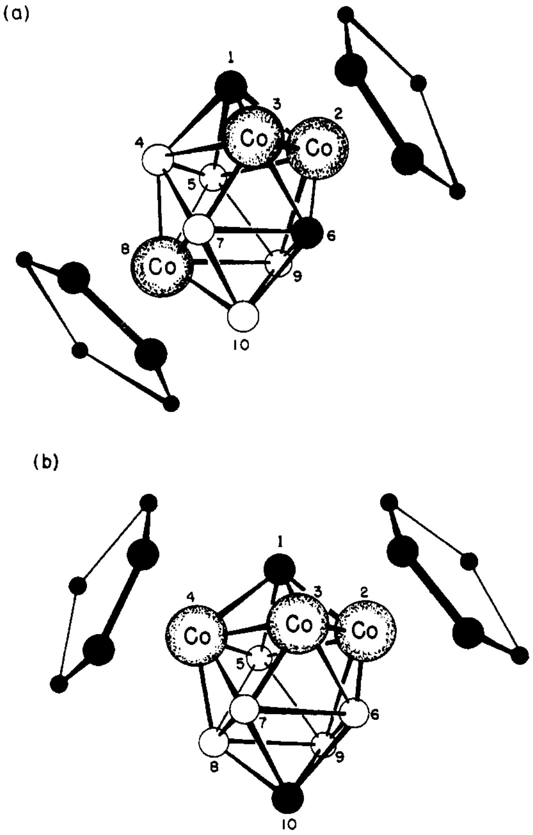

Figure 5. Proposed structures of 2,3,8,1,6-$(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ (a) and 2,3,4,1,10-$(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ (b). One cyclopentadienyl ring has been omitted from each drawing.

The thermal stabilities of the two tricobalt isomers provide an interesting comparison with the icosahedral tricobalt system 2,3,5,1,7-$(\eta\text{-}C_5H_5)_3Co_3C_2B_7H_9$,[24] the only other previously reported metallocarborane having more than two metal atoms. The latter compound is unstable in solution at room temperature, decomposing to a dicobalt species over a period of days;[24] in contrast, the $(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7$ species are unchanged in or out of solution at 25°, and temperatures above 250° are required to effect degradation of either compound at a significant rate. It is conceivable that the higher cobalt-boron ratio in the smaller systems contributes to their stability, a suggestion which is possibly related to the well-known cohesion of metal cluster systems such as $RCCo_3(CO)_9$ and $(C_2H_5)_2C_2Co_4(CO)_{10}$ toward thermal and oxidative degradation.

Conclusions

The principal findings with respect to the thermal behavior of the cobaltacarboranes studied are given in Table I. It is clear from the foregoing discussion that detailed evaluation of the results requires, for most purposes, consideration of each system individually. However, some general tendencies may be noted. In most cases, particularly those in

Table I. Summary of Major Processes in Cobaltacarborane Pyrolyses

Cage system	No. of vertices	Intramolecular rearrangements obsd	Groups involved in intermolecular transfer
CoC_2B_3	6	None	$(C_5H_5)Co$, BH
CoC_2B_4	7	1,2,3 → 1,2,4	$(C_5H_5)Co$, BH
CoC_2B_5	8	None	$(C_5H_5)Co$
$Co_2C_2B_3$	7	1,7,2,3 ⇄ 1,2,4,5 → 1,2,3,5 → 1,7,2,4	None detected
$Co_2C_2B_4$	8	None	$(C_5H_5)Co$, BH
$Co_2C_2B_5$	9	1,7,5,6 ⇄ 1,8,5,6	$(C_5H_5)Co$
$Co_3C_2B_5$	10	2,3,8,1,6 → 2,3,4,1,10[a]	$(C_5H_5)Co$

[a] Trace.

which the original compound is not expected to be the most stable isomer, a mechanism exists which allows its rearrangement to the more stable form. Usually, this occurs at a temperature too low to permit extensive decomposition. When the temperature is raised to the point at which degradation occurs, the transfer of cobalt and occasionally boron is observed, except in the remarkable case of 1,7,2,4-$(\eta$-$C_5H_5)_2Co_2C_2B_3H_5$ for which we could find no evidence of such an effect. The high temperatures required for degradation and thermal transfer in most of these compounds attest to their generally high thermal stability which is comparable to that of their larger cobaltacarborane homologs.[4-6]

Some useful comparisons may be made with the empirical rules cited by Hawthorne et al.[5] for the thermal rearrangements of cobaltacarboranes having six to ten boron atoms (rules a, b, and c had been noted earlier in studies of carboranes and metallocarboranes): (a) the cobalt atom will migrate to the highest-coordinate vertex and remain there; (b) the carbon atoms will not decrease their mutual separation; (c) the carbons will migrate irreversibly to the lowest-coordinate vertices; and (d) the carbons will tend to migrate away from the cobalt provided rules b and c are adhered to. In our work involving systems of three to five boron atoms and one to three cobalts, these trends are generally followed where applicable, with some notable exceptions. Thus, rule a is violated in the rearrangement of 1,7,2,3-$(\eta$-$C_5H_5)_2Co_2C_2B_3H_5$ to the 1,2,4,5, 1,2,3,5, and 1,7,2,4 isomers, in which cobalt moves from a five- to a four-coordinate location and then returns to a five-coordinate position. Rules b and c are followed in all instances insofar as isolable species are concerned; this is as expected since the drive of carbon atoms to separate from each other and to prefer low-coordinate vertices is firmly established in carborane as well as metallocarborane chemistry. Rule d is difficult to evaluate in the small cages, since the separation of carbon from cobalt atoms is in many cases hindered by the compact geometry and by the constraints of rules a-c. However, in the isomerization of the $(\eta$-$C_5H_5)_2Co_2C_2B_3H_5$ system this effect does not appear significant, and in the pyrolysis of the $(\eta$-$C_5H_5)CoC_2B_5H_7$ and $(\eta$-$C_5H_5)_2Co_2C_2B_4H_6$ cages, where migration of carbon away from cobalt might be expected, it is not observed. We are inclined to view rule d as a marginal effect which is easily overridden in smaller cages by other structural or thermodynamic factors. In the larger systems for which it was proposed,[5] the cobalt-carbon separation tendency does, however, seem to play a significant role.

Aside from the comparisons with larger cages, this study produced two kinds of thermal behavior not previously noted in metallocarborane chemistry: elimination of a metal from a neutral monometallocarborane to generate a carborane, and two cases of rearrangement equilibria between metallocarborane isomers entailing reversible metal-metal bond cleavage. The metal ejection, which occurred with 3,1,7-$(\eta$-$C_5H_5)CoC_2B_5H_7$, can be accounted for in terms of the particularly high stability of the carborane product, $C_2B_5H_7$, which permits it to survive the ~300° temperatures required for disproportionation. The implications of isomerization equilibria in dimetallocarboranes have been discussed earlier in this paper, but we reiterate the prediction that this type of phenomenon will be encountered in other reactions as metallocarborane chemistry develops.

The cumulative import of all studies thus far on the cobaltacarboranes would seem to be that the factors governing the chemistry and cage rearrangements in the various systems are of sufficient complexity and subtlety that few generalizations can be expected to hold for the entire family. This is especially obvious in the observed equilibrium between 1,8,5,6- and 1,7,5,6-$(\eta$-$C_5H_5)_2Co_2C_2B_5H_7$, where factors operating in opposite directions with respect to cobalt-cobalt bonding are evident, and rules designed to predict the "most stable" isomer can be formulated only as a function of temperature. The situation is reminiscent of the $C_2B_{n-2}H_n$ polyhedral carborane series, the smaller members of which exhibit a chemistry notably different from their larger homologs.[3] In the metallocarboranes, the higher metal/boron ratio in the smaller cages is an additional factor likely to affect the chemistry, as in the higher stability of the 10-vertex vs. the 12-vertex tricobalt species mentioned earlier.

Finally, we wish to point out that observations regarding relative thermal stabilities of metallocarborane isomers are not necessarily relevant to the identification of new species obtained under mild conditions. For example, in the synthesis of metallocarboranes via reductive cage opening in solution followed by metal ion insertion[18] (polyhedral expansion), a procedure normally conducted at room temperature or below, the geometry of the metallocarborane products must be largely influenced by the manner in which the original carborane cage opens; indeed, many species prepared via this route[15,18] do not reflect at all the thermal isomerization trends discussed above. Consequently, the patterns of metal or carbon atom migrations in polyhedra at high temperatures cannot be used as structural arguments in assigning the geometry of metallocarboranes formed under low-energy conditions.

Experimental Section

Materials. The cobaltacarboranes used in this study were prepared as described in recent papers.[10,13,15] Thin layer and preparative layer chromatography of product mixtures were conducted on precoated plates of silica gel F-254 purchased from Brinckmann Instruments, Inc. Solvents were reagent grade and used as received.

Spectra. Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained either on a Varian HA-100 spectrometer or a JEOL PS-100P pulse Fourier transform instrument. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6E spectrometer, infrared spectra were obtained on a Beckman IR-8 instrument, and electronic spectra were obtained on a Cary 14 spectrophotometer.

General Procedure. Reactions were conducted in evacuated, sealed Pyrex bulbs that had been dried by flaming or evacuating overnight at 10^{-6} Torr. The bulbs were of sufficient volume to maintain samples entirely in the vapor phase at the reaction temperature. In most cases, the progress of the reaction was followed visually by observing the vapor and condensed phases. After cooling, the bulbs were reattached to the vacuum line and checked for noncondensables and other materials volatile at room temperature. Except where noted, no significant amounts of room temperature volatile species or insoluble residues were formed. The bulbs were filled with N_2 and the solution extracted with CH_2Cl_2 and filtered in air. The solutions were evaporated to give metallocarborane product mixtures which were separated by preparative layer chromatography (PLC). Known compounds were identified from their thin layer chromatographic (TLC) behavior, color, and/or infrared or mass spectra. All new compounds reported herein were characterized from ^{11}B and ^{1}H NMR, uv-visible, infrared, and mass spectra. Identification of even trace quantities of known products was conveniently facilitated by spotting the product together with a known sample on the same TLC plate and developing simultaneously. The colors and representative R_f values are as follows (Cp = η-C_5H_5). Samples developed in hexanes: 1,2,3-$CpCoC_2B_4H_6$, 0.10, yellow-orange; 1,2,4-$CpCoC_2B_4H_6$, 0.36, yellow; 3,5,1,7-$Cp_2Co_2C_2B_4H_6$, 0.27, brown; 2-CH_3-1,2,3-$CpCoC_2B_4H_5$, 0.15, yellow-orange; 2-CH_3-1,2,4-$CpCoC_2B_4H_5$, 0.43, yellow; 1,2,4-$CpCoC_2B_3H_5$, 0.74, red. Developed in 50% benzene in hexanes: 1,7,2,3-$Cp_2Co_2C_2B_3H_5$, 0.21, red-brown; 1,2,4,5-$Cp_2Co_2C_2B_3H_5$, 0.67, green with bluish tinge; 1,2,3,5-$Cp_2Co_2C_2B_3H_5$, 0.70, green with yellowish tinge; 1,7,2,4-$Cp_2Co_2C_2B_3H_5$, 0.46, brownish green. Developed in 35% benzene in hexanes: 3,1,7-$CpCoC_2B_5H_7$, 0.91, red; 1,8,5,6-$Cp_2Co_2C_2B_5H_7$, 0.81, red; 1,7,5,6-$Cp_2Co_2C_2B_5H_7$, 0.66, green; 2,3,8,1,6-$Cp_3Co_3C_2B_5H_7$, 0.48, brown; 2,3,4,1,10-$Cp_3Co_3C_2B_5H_7$, 0.25, violet-brown.

Pyrolysis of 1,2,4-(η-C_5H_5)$CoC_2B_3H_5$. A 4.0-mg (0.022 mmol) sample of 1,2,4-(η-C_5H_5)$CoC_2B_3H_5$ was heated at 150, 200, and finally 250° for 18 hr to give 0.022 mmol of noncondensables, a dark insoluble residue, and 0.6 mg of metallocarboranes. TLC analysis indicated that the major component was starting material with at least six other compounds present. The mass spectrum of the mixture contained peaks corresponding to $C_5H_5CoC_2B_4H_6$, $(C_5H_5)_2Co_2C_2B_3H_5$, and $(C_5H_5)_2Co_2C_2B_4H_6$ and their monomethyl derivatives, as well as starting material.

Pyrolysis of 1,2,3-(η-C_5H_5)$CoC_2B_4H_6$. A 21.7-mg (0.109 mmol) sample of 1,2,3-(η-C_5H_5)$CoC_2B_4H_6$ was heated for 75 min at 400° to give 20.8 mg of product, identified as 1,2,4-(η-C_5H_5)$CoC_2B_4H_6$; only a trace of other material was indicated on TLC. In another experiment, 10.8 mg (0.055 mmol) of the compound was heated at 410° for 26 hr to give 0.050 mmol of noncondensables and 8.1 mg of metallocarboranes. PLC of the latter gave 6.3 mg of starting material and 0.3 mg of a mixture which was shown on mass spectroscopic analysis to contain $(C_5H_5)_2Co_2C_2B_3H_5$, $(C_5H_5CoC_2B_4H_5)_2$, and unidentified species.

Pyrolysis of 2-CH_3-1,2,3-(η-C_5H_5)$CoC_2B_4H_5$. A 37.0-mg (0.174 mmol) sample of 2-CH_3-1,2,3-(η-C_5H_5)$CoC_2B_4H_5$ was heated for 90 min at 400° to give 0.02 mmol of noncondensables, a slight brownish deposit, and 35.2 mg of metallocarboranes. The mass spectrum of this mixture indicated the presence of $CH_3(C_5H_5)CoC_2B_4H_5$, $CH_3(C_5H_5)_2Co_2C_2B_3H_4$, and $[CH_3(C_5H_5)CoC_2B_4H_4]_2$. PLC separation afforded 32.7 mg (88% yield) of 2-CH_3-1,2,4-(η-C_5H_5)$CoC_2B_4H_5$, characterized from the following data: ^{11}B NMR (CCl_4) doublets at δ −6.1 ppm rel to $BF_3 \cdot O(C_2H_5)_2$, J = 168 Hz, area 3, and −2.9, J = 159 Hz, area 1; ^{1}H NMR (CCl_4) singlets at δ −1.79 ppm rel to $(CH_3)_4Si$ (CH_3 resonance), −3.70 (cage CH), −4.72 (C_5H_5), area ratio 3:1:5 approximately; ir (CCl_4 vs. CCl_4, cm^{-1}): 3940 w, 3120 w, 3055 w, 2955 m, 2920 m, 2860 m, 2565 vs, 1824 w, 1760 w, 1683 w, 1443 m, 1414 m, 1371 w, 1266 w, 1160 m, 1101 m, 1070 m, 1005 m, 956 w, 937 w, 890 w, 866 m, 828 s, 704 s, 668 w, 601 w; mass spectrum, intense parent group with B_4 pattern and cutoff at *m/e* 212, corresponding to the $^{12}C_8{}^{59}Co{}^{11}B_4{}^{1}H_{13}{}^{+}$ parent ion.

Pyrolysis of 1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_5$. A 61.9-mg (0.200 mmol) sample of 1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_5$ was heated for 70 min at 225° to give 61 mg of metallocarboranes. PLC separation gave 55.2 mg of starting material, 0.3 mg of 1,2,3,5-(η-C_5H_5)$_2Co_2C_2B_3H_5$, 0.3 mg of 1,7,2,4-(η-C_5H_5)$_2Co_2C_2B_3H_5$, and 1.1 mg of the new compound 1,2,4,5-(η-C_5H_5)$_2Co_2C_2B_3H_5$. This species was characterized from the following data:[25] ^{11}B NMR ($CDCl_3$) doublets at δ −44.7, J = 151 Hz, area 2, and −11.4, J = 149 Hz, area 1. ^{1}H NMR ($CDCl_3$) singlets at δ −5.16 (cage CH), area 2, −4.88 (C_5H_5), area 5, −4.56 (C_5H_5), area 5; ir (CH_2Cl_2 vs. CH_2Cl_2, cm^{-1}) 3940 w, 3100 w, 2520 vs, 1235 m, 1200 m, 1114 m, 1000 m, 942 w, 865 w, 827 w, 807 s, 620 w; uv-visible (CH_3CN, λ_{max}, μm (log ϵ)) 790 (2.08 (sh)), 590 (2.81), 425 (3.10 (sh)), 317 (4.00), 271 (4.22); mass spectrum, intense cutoff at *m/e* 310 corresponding to the $^{12}C_{12}{}^{59}Co_2{}^{11}B_3{}^{1}H_{15}{}^{+}$ parent peak, and a B_3 pattern in the parent region. The mass spectra of the four known isomers of (η-C_5H_5)$_2Co_2C_2B_3H_5$ are nearly identical.

The uv-visible spectrum of 1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_5$ has not previously been reported. In CH_3CN solution the bands are 776 (2.59), 525 (2.81 (sh)), 407 (3.50), and 314 (4.50). Spectra of the 1,7,2,4 and 1,2,3,5 isomers are given in ref 10.

Pyrolysis of 1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_5$ for longer periods gave varying amounts of the 1,2,4,5, 1,2,3,5, and 1,7,2,4 isomers. Thus, in reactions of (a) 49.4 mg at 225 ° for 12 hr, (b) 44.6 mg at 200° for 12 hr, and (c) 17.2 mg at 200° for 142 hr, the following yields (mg) of the 1,7,2,3, 1,2,4,5, 1,2,3,5, and 1,7,2,4 isomers were obtained: experiment a, 36.2, 3.6, 5.5, and 0.7; experiment b, 40.1, 0.4, 0.2, 0.1; experiment c, 9.3, 0.8, 2.8, and 0.6.

Pyrolysis of 1,2,4,5- and 1,2,3,5-(η-C_5H_5)$_2Co_2C_2B_3H_5$. A sample of 1,2,4,5-(η-C_5H_5)$_2Co_2C_2B_3H_5$ (2.0 mg) was heated at 225° for 70 min to give 1.0 mg of starting material, 0.1 mg of the 1,7,2,3 isomer, and 0.3 mg of the 1,2,3,5 isomer. Pyrolysis of a 2.2-mg sample of 1,2,3,5-(η-C_5H_5)$_2Co_2C_2B_3H_5$ at 225° for 70 min gave 1.7 mg of the 1,2,3,5 and 0.1 mg of the 1,7,2,4 isomer. No other isomers were detectable by TLC or PLC in either case.

Pyrolysis of 1,7,2,4-(η-C_5H_5)$_2Co_2C_2B_3H_5$. Except for slight material loss, the 1,7,2,4 isomer was unchanged on heating at 225° for 22 hr and at 340° for 16 hr. On heating at 400° for 3 hr, a sample of 6.3 mg gave 4.6 mg of metallocarborane products and a dark insoluble nonvolatile residue. PLC separation gave 0.2 mg of 1,2,3,5-(η-C_5H_5)$_2Co_2C_2B_3H_5$,[26] 3.0 mg of starting material, and bands of 0.3 and 0.2 mg whose mass spectra indicated the presence of a $[(C_5H_5)_2Co_2C_2B_3H_4]_2$ species and chlorinated derivatives of $(C_5H_5)_2Co_2C_2B_3H_5$, the latter probably originating from traces of CH_2Cl_2.

Pyrolysis of 2-CH_3-1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_4$. A 13.9-mg sample of 2-CH_3-1,7,2,3-(η-C_5H_5)$_2Co_2C_2B_3H_4$ was heated at 300° for 6 hr to give 0.3 mg of unidentified material (possibly the 1,2,3,5 isomer) and 10.4 mg (75% yield) of 2-CH_3-1,7,2,4-(η-C_5H_5)$_2Co_2C_2B_3H_4$. The spectroscopic data on this compound are as follows: ^{11}B NMR ($CHCl_3$) doublets at δ −19.9, J = 121 Hz, area 2, and −12.8, J = 135 Hz, area 1; ^{1}H NMR ($CDCl_3$) singlets at δ −1.97 (CH_3), −2.38 (cage CH), −4.43 (C_5H_5), area ratio 3:1:10; ir (CH_2Cl_2 vs. CH_2Cl_2, cm^{-1}) 3015 w, 3010 w, 2910 m, 2855 m, 2500 vs, 1816 w, 1747 w, 1663 w, 1410 m, 1122 m, 1111 m, 1027 m, 1008 m, 946 m, 854 m, 832 m, 804 s, 793 s; mass spectrum, intense parent group with B_3 pattern and cutoff at at *m/e* 324, corresponding to the $^{12}C_{13}{}^{59}Co_2{}^{11}B_3{}^{1}H_{17}{}^{+}$ parent ion.

Pyrolysis of 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$. A 23-mg (0.110 mmol) sample of 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$ was pyrolyzed for 24 hr at 340° to give 0.039 mmol of noncondensables (Toepler pumped), 0.042 mmol of 2,4-$C_2B_5H_7$ (identified from its ir and mass spectra), 15.5 mg of metallocarboranes, and a dark insoluble residue. PLC separation of the metallocarborane mixture gave 1.0 mg of starting material, 4.1 mg of 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$, 4.0 mg of 1,7,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$, 3.9 mg of 2,3,8,1,6-(η-C_5H_5)$_3Co_3C_2B_5H_7$, and 0.3 mg of 2,3,4,1,10-(η-C_5H_5)$_3Co_3C_2B_5H_7$. In an experiment under milder conditions designed to check for rearrangement isomers, a 5-mg (0.025 mmol) sample was heated at 150, 200, and 250° with no evidence of reaction, and finally at 300° for 22 hr to give volatiles containing 2,4-$C_2B_5H_7$, and a mixture of metallocarboranes. PLC separation of the latter gave 3.2 mg (0.015 mmol) of starting material, 0.2 mg of 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$, and 0.2 mg of 1,7,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$.

A recently obtained ^{11}B NMR spectrum of 3,1,7-(η-C_5H_5)$CoC_2B_5H_7$, recorded on a pulse Fourier transform instrument, is superior to that reported earlier[15] (the compound was previously numbered 4,1,8) and exhibits doublets at δ −56.6 (J = 171 Hz), −13.0 (156), +1.6 (166), +10.4 (166), and +15.6 (164).

Pyrolysis of 3,5,1,7-(η-C_5H_5)$_2Co_2C_2B_4H_6$. A sample of 7.8 mg (0.024 mmol) of 3,5,1,7-(η-C_5H_5)$_2Co_2C_2B_4H_6$ was heated at 340° for 19 hr to give 0.027 mmol of noncondensables, 2.2 mg of 1,2,4-(η-C_5H_5)$CoC_2B_4H_6$, 1.5 mg of starting material, 0.1 mg of a fraction whose mass spectrum contained peaks corresponding to $(C_5H_5)_2Co_2C_2B_5H_7$, $(C_5H_5)_2Co_2C_2B_6H_8$, and $[(C_5H_5)CoC_2B_4H_5]_2$, 0.2 mg of a fraction whose mass spectrum correspond to $(C_5H_5)_3Co_3C_2B_4H_6$ (but could not be characterized due to insufficient sample), and 1.5 mg of a fraction whose mass spectrum exhibited peaks corresponding to $(C_5H_5)_2Co_2C_2B_3H_5$ and $(C_5H_5)_3Co_3C_2B_5H_7$. TLC analysis of the latter fraction in a slightly different solvent mixture identified it as a mixture of the known species[10] 1,7,2,4-$(C_5H_5)_2Co_2C_2B_3H_5$ and 2,3,8,1,6-$(C_5H_5)_3Co_3C_2B_5H_7$.

Pyrolysis of (η-C_5H_5)$_2Co_2C_2B_5H_7$ Isomers. A 6-mg sample of 1,8,5,6-(η-C_5H_5)$_2Co_2C_2B_5H_7$ was heated at 150, 200, 250, and finally at 300° for 6.5 hr to give 6.0 mg of metallocarboranes, which on PLC separation gave 2.7 mg of starting material, 2.7 mg of 1,7,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_7$, and 0.3 mg of 2,3,8,1,6-(C_5H_5)$_3$$Co_3C_2B_5H_7$. In a separate experiment, 2.7 mg of the 1,7,5,6 isomer was heated at 300° for 4 hr to give 2.3 mg of metallocarboranes, which on TLC analysis was shown to consist of equal amounts of the 1,7,5,6 and 1,8,5,6 isomers and a trace of 2,3,8,1,6-(η-C_5H_5)$_3$$Co_3C_2B_5H_7$. Precise measurement of the mole ratio of 1,8,5,6- to 1,7,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_7$ by integration of the ^{11}B NMR resonances[27] at δ −116 and −80 in the spectrum of the product mixture, gave a value of 1.00:1.08.

Several additional experiments were conducted to determine the isomerization equilibrium constant. Pure samples of the 1,8,5,6 and 1,7,5,6 isomers were pyrolyzed separately for 20 min at 340°, yielding ^{11}B NMR-measured isomer ratios (1,8,5,6/1,7,5,6) of 1.01 and 1.01, respectively. Pure samples of each isomer were also heated at 240° for 196 hr, giving respective isomer ratios of 1.30 and 1.39. Values of K_{eq} and $\Delta H°$ calculated from these data are given in the main section.

Pyrolysis of 2,3,8,1,6-(η-C_5H_5)$_3$$Co_3C_2B_5H_7$. A 4-mg sample of 2,3,8,1,6-(η-C_5H_5)$_3$$Co_3C_2B_5H_7$ was heated at 300° for 10 hr to give a very slight residue and 3.1 mg of metallocarboranes, which on PLC separation gave 0.1 mg each of 1,7,5,6- and 1,8,5,6-(η-C_5H_5)$_2$$Co_2C_2B_5H_7$, 2.3 mg of starting material, and <0.1 mg of 2,3,4,1,10-(η-C_5H_5)$_3$$Co_3C_2B_5H_7$.

Acknowledgments. The pulse Fourier transform ^{11}B and ^{1}H NMR spectra obtained in this work were recorded on an instrument purchased in part from a Departmental instrument grant from the National Science Foundation. This work was supported in part by the Office of Naval Research.

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(20) A triangle rotation in a pentagonal bipyramid can be accomplished *in effect* by two successive dsd operations, which would necessarily involve a pentagonal bipyramidal intermediate. However, triangle rotations are not required to proceed in this way, and might well occur via an open-cage intermediate or transition state in which the carbon atoms can avoid unfavorable coordination sites.

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(25) The isolation and characterization of metallocarborane samples as small as 1 mg or less have become routine, thanks to TLC and PLC techniques combined with the extreme sensitivity of Fourier transform NMR spectroscopy, which can generate signals of high signal/noise ratio on micromole-size samples.

(26) The formation of the 1,2,3,5 isomer during the high-temperature degradation of the 1,7,2,4 species might be indicative of an equilibrium between these species, since the 1,2,3,5 → 1,7,2,4 conversion at lower temperatures is well established. However, at the lower temperatures (340° and below) there is no evidence for such an equilibrium. Due to the complexity of the 400° reaction in which extensive decomposition occurs, the significance of the formation of the 1,2,3,5 isomer cannot be determined.

(27) The spectra employed for area integrations had signal/noise ratios of at least 50:1. The possibility of error in peak area measurements due to saturation effects was minimized by the use of sufficiently long time between pulses (60 msec) to permit virtually complete relaxation, since $T_1 \approx$ 2-5 msec. Since the area ratios utilized involve borons in comparable environments in both isomers, and the areas are proportional to the degree of relaxation, any saturation effect would affect both isomers similarly and thus, in any event, leave the area ratios unchanged. However, we are grateful to a referee for raising this important point.