Tetrahedron. Vol. 30, pp. 1795 to 1806. Pergamon Press 1974. Printed in Great Britain

POLYHEDRAL REARRANGEMENTS INVOLVING FIVE- AND SIX-COORDINATE CARBON

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(Received 18 January 1974)

Abstract—Polyhedral carboranes and metallocarboranes characteristically contain C atoms having coordination numbers of 5 and 6 within the polyhedral surface. Thermal carbon and metal atom migration reactions are observed in these species and we here report results obtained with polyhedra containing 10, 11, 12 and 13 vertices. Thermodynamic activation parameters have been measured for several representative rearrangement reactions and their mechanistic significance is discussed. General rules which appear to govern carbon and metal atom migration reactions are advanced.

INTRODUCTION

Carboranes, treated here as a family of electron deficient compounds, may be defined as species in which an isoelectronic substitution of $:CH^+$ for $:BH$ (three atomic orbitals, two electrons) has been conceptually accomplished in an otherwise viable borane structure. In this paper the resonance stabilized polyhedral borane dianion series, $B_nH_n^{2-}$, where n = 6 through 12, will be considered to be the parent borane species in which such $:BH$ substitutions occur to yield the uncharged carborane series $C_2B_nH_{n+2}$. Furthermore, isoelectronic substitution of $:BH$ by other heteroatoms, notably transition metals, are now well documented and lead to a second type of heteroatom borane. Combination of $:CH^+$ and transition metal substitution for $:BH$ vertices yields the polyhedral metallocarboranes. To generate examples of isoelectronic substitution one may utilize recently advanced electron counting schemes[1] for metal cluster compounds and arrive at the following representative variety of groups demonstrated to replace $:BH$ in polyhedral borane dianions (Table 1).

Since it is easily shown that an n-vertex polyhedron requires n + 1 electron pairs[1,2] for skeletal bonding, appropriate combination of the groups shown in Table 1 and adjustment of the formal oxidation state of the transition metal will lead to a variety of heteroatom polyhedral boranes which satisfy the n + 1 electron pair rule. Consequently, polyhedral CH vertices are found in a profusion of electronic and steric environments and, even more importantly, these CH vertices commonly occur in situations which make them nearest neighbors to four or five polyhedral vertices. Thus, such *carbon atoms* are 5- and 6-coordinate, respectively. Fig 1 illustrates the 10, 11, 12 and 13 vertex polyhedral geometries which will be treated here along with their polyhedral numbering systems.[3]

Table 1 illustrates the point that the isoelectronic substitution of $:CH^+$ for $:BH$ formally amounts to placing a carbonium ion-like C atom in a highly electron delocalized environment. This is not to say that such electron deficient C atoms are carbonium ions in the sense of the physical organic chemist, since solvolysis and other processes associated with "normal" carbonium ions are not observed in carborane chemistry. Nonetheless, physical measurements such as dipole moment determinations[4] and IR spectral observations of the high frequency C–H stretching mode[5] are clearly consistent with the presence of polyhedral C atoms which bear a net positive charge. A large amount of chemical reaction data[6] has also been amassed to further support this view. In short, the sequestering of formal $:CH^+$ by a borane framework is unique in chemistry and no simple analogies exist.

The polyhedral nature of the carboranes and the associated high coordination number of their resident C atoms may at first sight appear absurd. However, the lines connecting neighboring framework atoms (Fig 1) are not bonds in the Lewis sense, but simply serve to establish the molecular geometry. Lipscomb *et al.* have gone to great lengths to rationalize the bonding situation present in carboranes and related species.[7] In their studies they correctly treated polyhedral bonding in terms of delocalized molecular orbitals and the overall chemical properties of the $C_2B_nH_{n+2}$ carboranes were adequately predicted or rationalized by these calculations. Although "resonance energies" cannot be experimentally determined, as is possible in the case of the classical cyclohexatriene-benzene system, accurate molecular orbital calculations[7] do suggest enhanced stabilization of the carboranes with respect to their constituent elements and it is thus not surprising to find much of aromatic hydrocarbon chemistry closely paralleled by carborane chemis-

Table 1. Polyhedral substitution series

Vertex	Atomic orbitals for skeletal bonds	Electrons for skeletal bonds	Non-bonding electrons
BH	3	2	0
CH$^+$	3	2	0
CH	3	3	0
π-C_5H_5Fe	3	1	6
π-C_5H_5Co	3	2	6
π-C_5H_5Ni	3	3	6
$(CO)_3Mn$	3	1	6
$(CO)_3W$	3	0	6

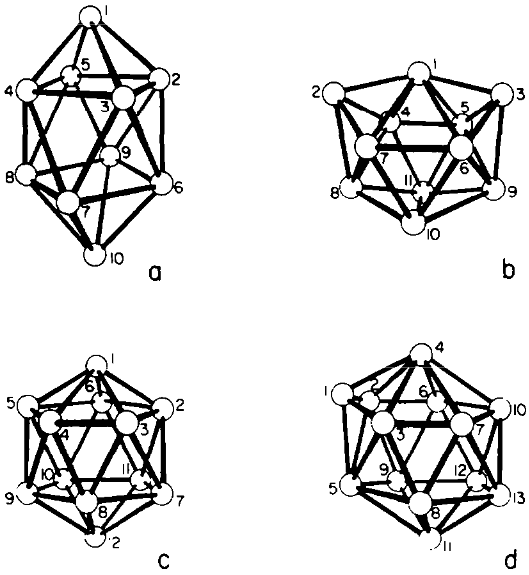

Fig 1. Idealized geometries and numbering systems of 10-, 11-, 12- and 13-atom closed polyhedra.

try (electrophilic substitution, electron addition and C-metalation reactions, for example).

One rather general reaction of the polyhedral heteroatom boranes which dramatizes their inherent kinetic stability with respect to retention of their gross geometry is polyhedral rearrangement. In examples of this reaction type, CH or other heteroatom vertices migrate over the polyhedral surface and, in so doing, generate a series of heteroatom positional isomers. The first documentation of this sort of rearrangement was provided[8] in 1963 and involved the thermal transformation of $1,2\text{-}C_2B_{10}H_{12}$ to $1,7\text{-}C_2B_{10}H_{12}$, the thermodynamically favored icosahedral isomer, at temperatures near 400°. In the reactant and product, both C atoms are 6-coordinate. The driving force ascribed to this rearrangement was the mutual coulombic repulsion of the two nearest neighbor C atoms present in the $1,2\text{-}C_2B_{10}H_{12}$ icosahedral surface. At this point in time mechanistic considerations were advanced and Lipscomb proposed[9] the "diamond-square-diamond" mechanism (dsd) depicted in Fig 2. In this mechanism a cuboctahedron was proposed as a transition state geometry. While this mechanism is extremely attractive and involves only small atomic motion, it could not explain the rearrangement of $1,7\text{-}C_2B_{10}H_{12}$ to its 1,12-isomer near 700°[10] since no combination of successive "dsd" rearrangements was compatible with the observed transformation. Three alternative mechanisms were proposed. One involved the mutual rotation of pentagonal pyramid caps (Fig 3a). The second mechanism proposed[11] involved the suggestion that triangular faces could rotate without great disruption of the total polyhedron (Fig 3b). The third mechanism assumed that the cuboctahedron was a thermally accessible, high-energy intermediate in

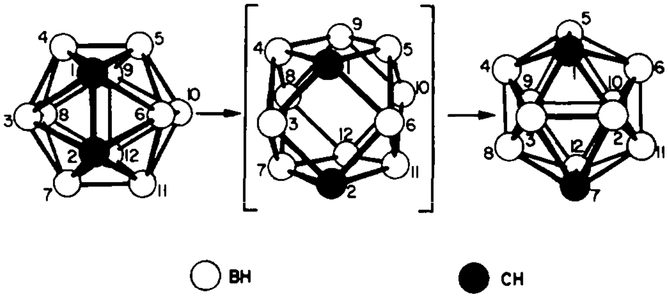

Fig 2. Isomerization of $1,2\text{-}C_2B_{10}H_{12}$ to $1,7\text{-}C_2B_{10}H_{12}$ by the diamond-square-diamond (dsd) mechanism.

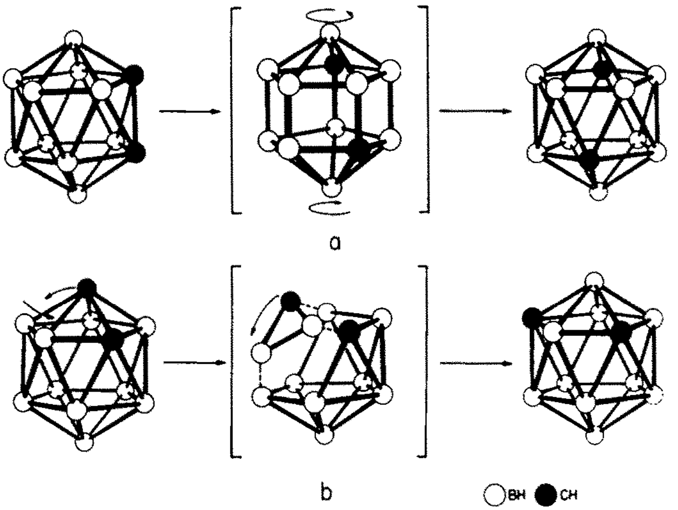

Fig 3. (a) Isomerization of 1,2-$C_2B_{10}H_{12}$ to 1,12-$C_2B_{10}H_{12}$ by the rotation of pentagonal pyramid cap mechanism. (b) Isomerization of 1,2-$C_2B_{10}H_{12}$ to 1,7-$C_2B_{10}H_{12}$ by the rotation of triangular face mechanism.

which triangular faces could rotate and the normal "dsd" rearrangement occur as well. As will be shown below, the true mechanism(s) of these and many other polyhedral rearrangements has yet to be established. The problem is such that no simple series of experiments can distinguish between the above proposed reaction mechanisms. One fact is clear, however: regardless of the pathways available to these isomerization reactions, the thermodynamically preferred isomers of the $C_2B_{10}H_{12}$ system are those in which the C atoms are as far removed from one another as possible. Thus the predicted[9,11] and observed[8,10] ordering of stability is 1,2- < 1,7- < 1,12-$C_2B_{10}H_{12}$. Typical enthalpies of activation[12] for the rearrangements described above are of the order of 60 kcal/mol with entropies of activation of the order of 7 e.u.

While coulombic considerations undoubtedly provide the driving force for icosahedral (and other) rearrangements, steric repulsion of neighboring substituted polyhedral C atoms must also be of importance as shown by Salinger and Frye.[12] These authors attached bulky diphenylmethylsilyl groups to both C atoms of 1,2-$C_2B_{10}H_{12}$ and obtained the corresponding 1,7-isomer at temperatures as low as 280°. Their estimated ΔH^{*} and ΔS^{*} were 45 kcal/mol and -1 e.u., respectively.

With these data available, it is apparent that both coulombic C atom repulsion and steric interactions will provide driving forces for the rearrangement when the migrating heteroatoms occupy positions of identical coordination number in the reactant and product. A third factor must now be introduced which often determines the cause of thermal polyhedral rearrangements in nonicosahedral systems: C atom coordination number.

The discovery of 1,6-$C_2B_8H_{10}$ (Fig 1a) and its thermal rearrangement to the more stable 1,10-$C_2B_8H_{10}$ involves two superimposed contributions to the driving force for rearrangement. Further C atom separation occurs, lessening coulombic repulsion, and perhaps most importantly, the C atom originally present in the 6-coordinate 6-position moves to the 10-position in which carbon displays a coordination number of 5. Thus, both the 1- and 10-C atoms have the lowest possible coordination number commensurate with the bicapped Archimedean antiprismatic geometry of the $C_2B_8H_{10}$ polyhedron. Later work by Rietz, *et al.*[13] demonstrated that the 1,2-$C_2B_8H_{10}$ isomer readily rearranged to the 1,6-isomer, presumably due to coulombic C atom repulsion. As in the case of the icosahedral rearrangements described above, no mechanistic conclusions can be drawn from these data.

One reasonable rationale of the apparent preference of C atoms for polyhedral positions of low coordination number is based on the fact that the highly electronegative C atoms have much less diffuse *s* and *p* atomic orbitals available for skeletal bonding than do B atoms. Consequently, any reduction in the number of neighbor atom orbitals which must be shared will enhance the effective overlap of those neighboring skeletal orbitals which remain and thus lower the energy of the resulting bonding molecular orbital.

Whereas only those heteroatom boranes which contain carbon have been discussed thus far, we present below additional data encompassing the recently observed rearrangement of C atoms in polyhedral metallocarboranes.

Polyhedral rearrangements of metallocarboranes

Twelve-atom polyhedra. For the $C_2B_{10}H_{12}$ system, which has two heteroatoms in an icosahedral geometry, there are only three possible geometrical isomers: 1,2-, 1,7- and 1,12- (Fig 1c); the vertices in this geometry are all formally 6-coordinate and equivalent, the isomeric differences resulting solely from changes in C atom separations. The replacement of a BH vertex by an isoelectronic transition metal vertex such as π-$C_5H_5Co^{2+}$ complicates matters; for the π-$C_5H_5CoC_2B_9H_{11}$ series of compounds, which contains three heteroatoms (two C, one Co) in an icosahedral geometry, there are nine possible isomers. All of these isomeric complexes have been prepared, either by direct synthesis or by thermally induced polyhedral rearrangement of other isomers, and have been completely characterized;[14] the isomeric structures and details of the rearrangements are shown in Fig 4.

The thermal isomerization studies on the π-$C_5H_5CoC_2B_9H_{11}$ system were performed by passing the metallocarboranes, in the gas phase, through an evacuated chamber held at a constant high (400–700°) temperature. A consequence of these non-equilibrium conditions is that the product distribution primarily reflects kinetic accessibility rather than thermodynamic stability of the isomers.

As shown in Fig 4a carbon vertices which were vicinal in the starting material rearranged to form isomers in which the C atoms were no longer adjacent. Motion of the C atoms away from the Co atom was also apparent, although higher temperatures were necessary to produce reasonable quantities of the species so formed. The driving force to produce isomers having nonvicinal C atoms was found to be so large that it was necessary to link the polyhedral C atoms with a trimethylene bridge before thermal rearrangement in order to produce isomers which had adjacent C atoms nonvicinal to the Co atom (Fig 4b). Because of the nonequilibrium conditions employed, it was not possible to determine whether, in a thermodynamic sense, a C atom prefers to migrate away from a vicinal C atom or away from an adjacent Co vertex.

Physical studies on the isolated $C_5H_5CoC_2B_9H_{11}$ isomers indicated that both the formal Co(III)–Co(II) reduction potentials and the visible spectra showed direct correlations with the location of the heteroatoms in the polyhedron. Reduction potentials were found to vary from −1·03 to −1·80 V *vs* sce (saturated calomel electrode), and λ_{max} from 430 to 381 nm, depending upon the relative orientations of the C atoms with respect to the Co atom. Isomers with two C's adjacent to Co exhibited $E_{p/2}$ between −1·0 and −1·25 V and λ_{max} at 430–414 nm, while those isomers with one C adjacent to Co showed values of −1·33 to −1·45 V and 414–402 nm. The isomers which had only B atoms vicinal to Co exhibited $E_{p/2}$ values between −1·75

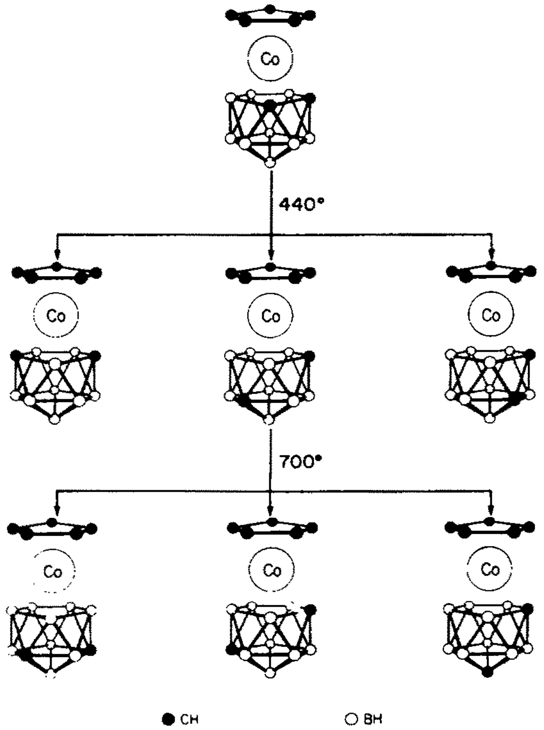

Fig 4. (a) Isomers produced by the thermal polyhedral rearrangement of C_5H_5Co-1,2-$C_2B_9H_{11}$.

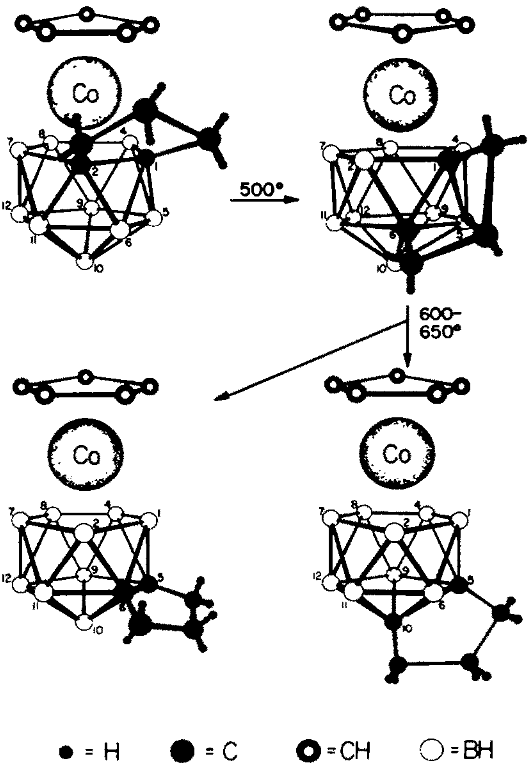

Fig 4. (b) Isomers produced by the thermal polyhedral rearrangement of C_5H_5Co-1,2-μ-$(CH_2)_3$-1,2-$C_2B_9H_9$.

and −1·80 V and λ_{max} between 386 and 381 nm. These data indicate that more electron density is donated to the metal as the number of vicinal C vertices is decreased and is in agreement with the assignment of greater positive charge residing on the C atoms than on the B atoms.

This first investigation of the rearrangements of metallocarborane polyhedra indicated that similar processes occur in both carboranes and metallocarboranes: the migration of positive C atoms away from each other. Further rearrangement of carbons away from adjacent Co vertices also appears to be operative in these systems, although the work did not show such a rearrangement to be thermodynamically favored. Recent work in our laboratory has shown that the monocarbon metallocarborane $C_5H_5NiCB_{10}H_{11}$, isoelectronic with $C_2B_{10}H_{12}$, may be isolated in three isomeric forms. The thermally least stable isomer has vicinal C and Ni atoms, and migration of C away from the metal vertex occurs during thermal polyhedral isomerization.[15] Structures of the three isomers are depicted in Fig 5.

An unusual type of polyhedral rearrangement in which C atoms migrate away from an adjacent metal vertex yet remain vicinal to another C was observed in the $\{[C_2B_9H_9(CH_3)_2]_2Ni\}^{n-}$ system (n = 0 − 2), and is schematically presented in Scheme 1.[16,17] Three isomeric series, designated A, B, and C, have been isolated and shown to have different C atom locations in their polyhedra. Compounds within each series differ in formal charge on the Ni and in gross structure but retain the same polyhedral C atom positioning. The structures of some of these species are shown in Fig 6. The important structural feature seen here is the *cisoid*, nearly eclipsed C atoms observed in the formal Ni(IV) complexes. The steric crowding produced by this arrangement precluded isolation of the series A isomer of $[C_2B_9H_9(CH_3)_2]_2Ni(IV)$; instead, this compound underwent a remarkably facile C atom migration at 0° to produce the series B isomer in which one of the C–CH_3 vertices had moved away from the metal and away from the C–CH_3 groups on the adjacent polyhedron. Similar C atom migration on the second cage produced the two series C isomers.

A rough measure of the importance of steric effects in this rearrangement can be obtained by comparison of the corresponding C,C-dimethyl and unsubstituted compounds; isomerization of the former was rapid at 0°, while $(1,2\text{-}C_2B_9H_{11})_2Ni(IV)$

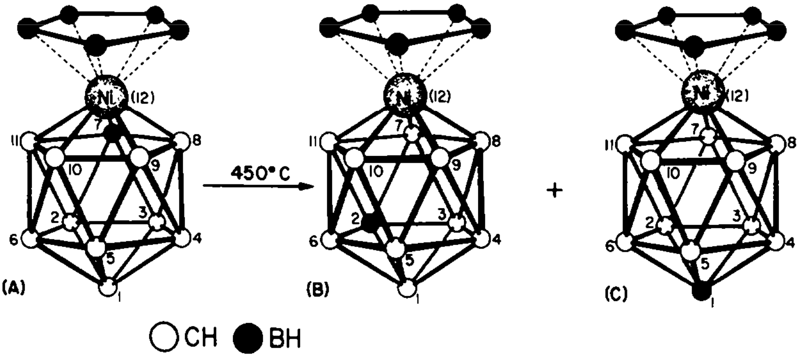

Fig 5. Thermal rearrangement of $\pi\text{-}C_5H_5NiCB_{10}H_{11}$.

SCHEME 1. Reaction sequence and electrochemistry of the *bis*(1,2-dimethyl-1,2-dicarbollyl)nickel system

$$\begin{tikzcd}
 & \mathrm{Ni(acac)_2} + Me_2^- \arrow[r, "\text{benzene-ether}"] & & \\
\text{Series A:} & {[(Me_2)_2\mathrm{Ni^{II}}\text{–A}]^-} \arrow[r, shift left] & {[(Me_2)_2\mathrm{Ni^{III}}\text{–A}]^-} \arrow[l, shift left, "-0{\cdot}51\text{v}"] \arrow[r, shift left] \arrow[d, "200^\circ"'] \arrow[dr, "{[0]}"] & {[(Me_2)_2\mathrm{Ni^{IV}}\text{–A}]} \arrow[l, shift left, "+0{\cdot}50\text{v}"] \arrow[d, "0^\circ"] \\
\text{Series B:} & {[(Me_2)_2\mathrm{Ni^{II}}\text{–B}]^-} \arrow[r, shift left] & {[(Me_2)_2\mathrm{Ni^{III}}\text{–B}]^-} \arrow[l, shift left, "-0{\cdot}92\text{v}"] \arrow[r, shift left] & {[(Me_2)_2\mathrm{Ni^{IV}}\text{–B}]} \arrow[l, shift left, "+0{\cdot}26\text{v}"] \arrow[d, "110^\circ"] \\
\text{Series C:} & {[(Me_2)_2\mathrm{Ni^{II}}\text{–C}]^-} \arrow[r, shift left] & {[(Me_2)_2\mathrm{Ni^{III}}\text{–C}]^-} \arrow[l, shift left, "-1{\cdot}13\text{v}"] \arrow[r, shift left] & {[(Me_2)_2\mathrm{Ni^{IV}}\text{–C}]} \arrow[l, shift left, "-0.02\text{v}"]
\end{tikzcd}$$

$Me_2^- = C_2B_9H_9(CH_3)_2^-$; acac = $(CH_3COCHCOCH_3)^-$

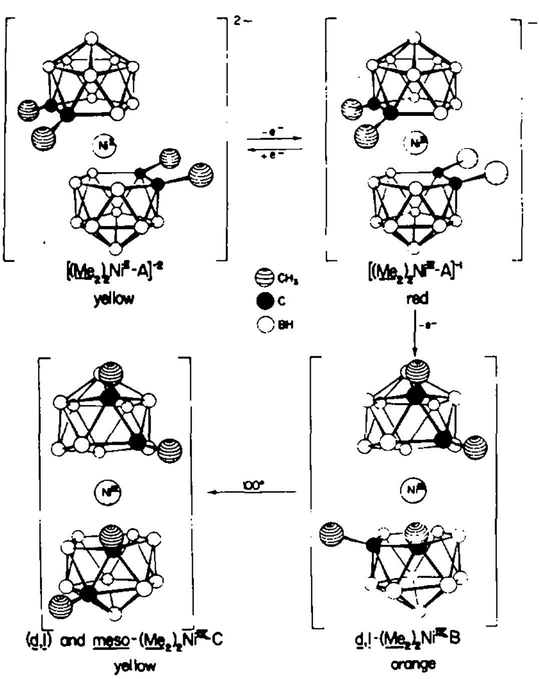

Fig 6. Structures observed in the $[1,2\text{-}(CH_3)_2\text{-}1,2\text{-}C_2B_9H_9]_2Ni$ system.

was found to rearrange only when heated to 300° *in vacuo*. Further evidence was found in the rearrangement of the anionic Ni(III) complex, in which the two pairs of C atoms are *trans*;[18] C atom migration corresponding to isomerization from series A to series B occurred at a reasonable rate only at 200°. These data indicate that steric acceleration is the causative factor in the low-energy polyhedral rearrangements observed in the C,C-dimethyl compounds.

The presence of four heteroatoms in a 12-vertex (icosahedral) borane allows the existence of 37 isomeric species. Metallocarboranes of this type, such as $[(\pi\text{-}C_5H_5)_2Co]_2C_2B_8H_{10}$ have recently been synthesized[19] and a preliminary examination of thermal rearrangements was undertaken; the results are depicted in Fig 7.[20] Two distinct types of rearrangements were detected in this system. The metal-metal bonded isomer was found to isomerize at 250° to produce an isomer with nonadjacent metal vertices. The identical product was formed upon heating a different $[C_5H_5Co]_2C_2B_8H_{10}$ isomer with nonvicinal metals and adjacent C atoms. The latter rearrangement is another example of migration of polyhedral carbons to nonvicinal positions. The former isomerization is of a type not previously encountered and involves thermal migration of a metal vertex. Because no change in coordination number is attained in icosahedral rearrangements, the driving force for this isomerization is probably coulombic repulsion between the two metal atoms.[20] Relief from strain caused by the adjacent metal vertices in the starting material can be ruled out as a causative factor, for no unusual distortions were observed in the crystal structure of this material.[21]

Thirteen-atom polyhedra. The first 13-vertex closed polyhedral compound to be synthesized was $(\pi\text{-}C_5H_5)CoC_2B_{10}H_{12}$[22,23]; the isoelectronic species $B_{13}H_{13}^{2-}$, $CB_{12}H_{13}^-$ and $C_2B_{11}H_{13}$ are as yet unreported.

The red species $4\text{-}(\pi\text{-}C_5H_5)\text{-}4\text{-}Co\text{-}1,6\text{-}C_2B_{10}H_{12}$ was found to be fluxional in solution at room temperature; the compound exhibits an ^{11}B NMR spectrum showing more molecular symmetry than that determined crystallographically,[23] but at low temperatures (−80°) it was found possible to slow the interconversion sufficiently to obtain the ^{11}B NMR spectrum of the "frozen" molecule. The rearrangement which occurs is an interconversion between optical isomers (C atoms at positions 1 and 6 or 1 and 7), and may proceed through a dsd-type intermediate, as shown in Fig 8.

This 13-vertex cobaltacarborane also undergoes a series of smooth C atom migrations in a temperature range which allowed their kinetic and thermodynamic parameters to be determined.[24] This information, along with the structures of the rearrangement products, are presented in Fig 9.

The gross geometry observed[23] for the first member of this series (and assumed for the other members) presents some new variables for consideration in the polyhedral rearrangements of icosahedral carboranes or metallocarboranes: vertices of different coordination number in a low symmetry structure apparently result in a lower resonance energy and a decreased barrier to polyhedral rearrangement.

As indicated in Fig 9, vertices of different coordination number occur in this closed 13-particle polyhedron; position 1 is formally 5-coordinate, while vertices 4 and 5 are formally 7-coordinate. A crystallographic study[23] has shown that the least stable isomer has C atoms at positions 1 and 6 (or 7) (5- and 6-coordinate positions, respectively, which are also adjacent to the Co atom at high-coordinate position 4) but the C atoms are nonvicinal. During the polyhedral rearrangements in this system (Fig 9), the C atom at the low-coordinate position 1 remains in place, while the second C atom, at a 6-coordinate position, migrates over the polyhedral surface to other 6-coordinate positions more remote from the other C atom and the Co atom as well. These observations indicate that C atoms prefer sites of lower coordination number and suggest that, in instances in which C atoms are in sites of different coordination number, the C atom at the higher coordinate vertex will preferentially migrate.

The first step in this 13-vertex polyhedral rearrangement may also be significant in the determination of preferential atomic motion; little change in C–C distance is effected in this first rearrangement,

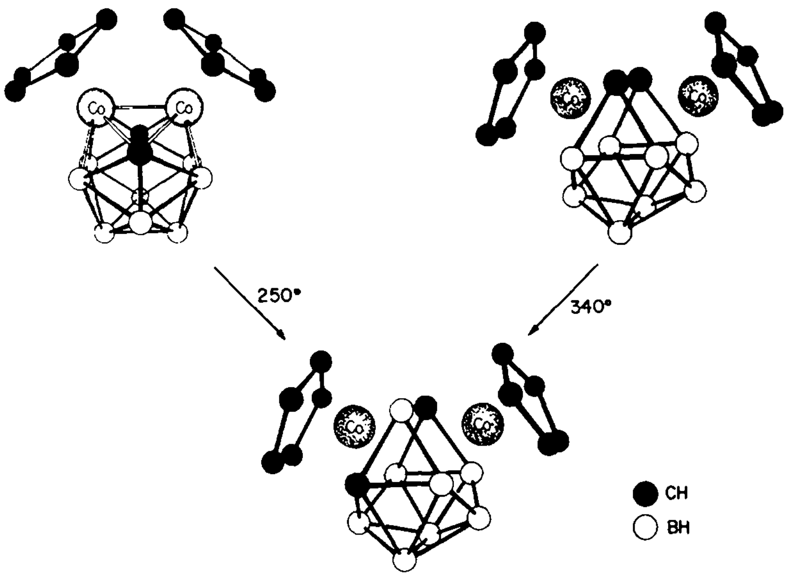

Fig 7. Thermal rearrangements of isomeric $(\pi\text{-}C_5H_5)_2Co_2C_2B_8H_{10}$ compounds.

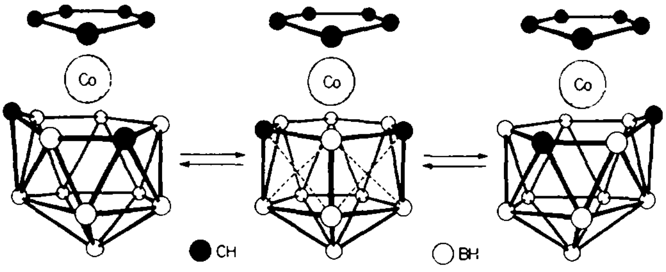

Fig 8. Schematic representation of racemization of $4\text{-}(\pi\text{-}C_5H_5)\text{-}4\text{-}Co\text{-}1,6\text{-}C_2B_{10}H_{12}$ through a dsd intermediate.

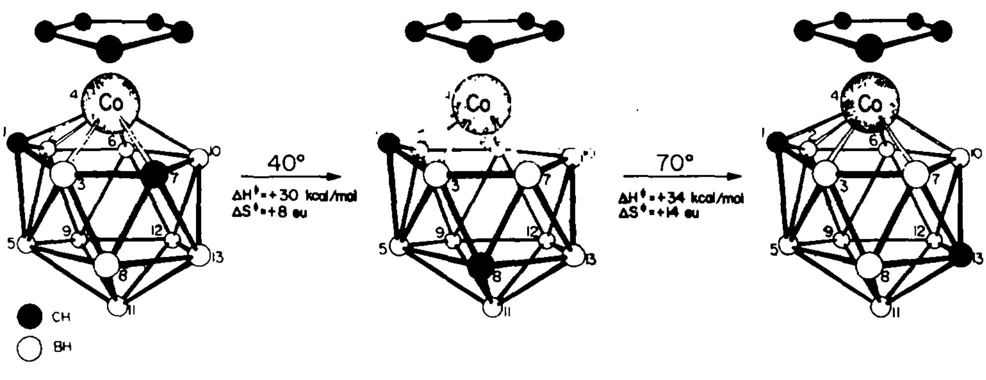

Fig 9. Thermal polyhedral rearrangements of the $\pi\text{-}C_5H_5CoC_2B_{10}H_{12}$ system.

while the migration of the C to position 8 gives greater separation from the Co. The second step increases both C–C and Co–Co distances.

In the case of icosahedral geometry it was observed that replacement of a BH vertex by a C_5H_5Co vertex lowered the barrier to polyhedral rearrangement; $C_5H_5CoC_2B_9H_{11}$ was found to rearrange at temperatures lower than those necessary to produce similar isomerization in 1,2-$C_2B_{10}H_{12}$. However, both these rearrangements occur at temperatures at which the collection of kinetic data is inconvenient, and no precise measurement of the effect of this type of replacement on kinetic and thermodynamic properties has been available in the past. In the case of the 13-atom polyhedron, however, such a comparison has recently become available.

The synthesis of compounds of the formula $(C_5H_5Co)_2C_2B_9H_{11}$ has recently been reported,[25] and three isomeric complexes have been detected, one of which thermally rearranges to the other. The structures of these species proposed on the basis of the known structure[23] of the monometallic analog and on spectral data are shown in Fig 10, along with the relevant thermodynamic parameters of the polyhedral rearrangement.[25] It can be seen by comparison with Fig 9 that the replacement of a BH vertex by a C_5H_5Co in this 13-atom geometry has slightly increased the activation energy for rearrangement. Comparing these results with those observed in the icosahedral compounds, it appears that the replacement of one BH vertex by C_5H_5Co lowers the activation energy for rearrangement (compare $C_2B_{10}H_{12}$ with $C_5H_5CoC_2B_9H_{11}$), but the incorporation of a second metal vertex has a small effect in the opposite direction. Geometrical differences in the compounds compared could, however, have an influence on this behavior, and only a study of the rearrangements of icosahedral bimetallic complexes can definitively indicate the effect of a second metal vertex. Such work is currently in progress.

Eleven-atom polyhedra. Closed polyhedra with eleven vertices are represented in the borane and carborane series by $B_{11}H_{11}^{2-}$, $CB_{10}H_{11}^-$ and $C_2B_9H_{11}$. The structure of the latter has been shown[26] to have octadecahedral C_{2v} symmetry and a unique 7-coordinate B atom, and the structures of the isoelectronic anions are presumed to be similar. Recent work has indicated that the anionic species undergo facile molecular rearrangements[27,28] and these systems are currently under intensive examination. The $C_2B_9H_{11}$ species has been found to exist in only one isomeric form, in which the C atoms occupy 5-coordinate positions. In view of the results presented in this paper, it is probable that the preference of C atoms for low-coordinate positions precludes thermal isomerization of this compound.

An 11-vertex cobaltacarborane in which one of the C atoms is at a 6-coordinate vertex has been synthesized, however,[29a] and found to rearrange to an isomeric species[29b] in which the C atoms occupy low-coordinate vertices. This isomerization and its thermodynamic parameters[24] are shown in Fig 11.

The C atoms are adjacent in the 2,4-isomer, 1-C_5H_5-1-Co-2, 4-$C_2B_8H_{10}$, and in the polyhedral rearrangement shown in Fig 11 they move apart. This motion is consistent with the previously described results on carboranes and metallocarboranes, in that coulombic repulsions between the two positive carbon centers are thought to provide a driving force for isomerization. The desire of polyhedral C to occupy a low-coordinate position is also indicated in this rearrangement, however; the C atom at the 5-coordinate position 2 of the polyhedron does not thermally migrate, while the 6-coordinate carbon originally at position 4 rearranges to the low-coordinate position 3. It also appears that the C atoms prefer low-coordinate positions even if these sites are adjacent to the metal vertex. The polyhedral rearrangement shown in Fig 11 may also be effected photochemically;[30] details of this unusual transformation will be presented elsewhere.

Thermal rearrangements of bimetallic 11-vertex

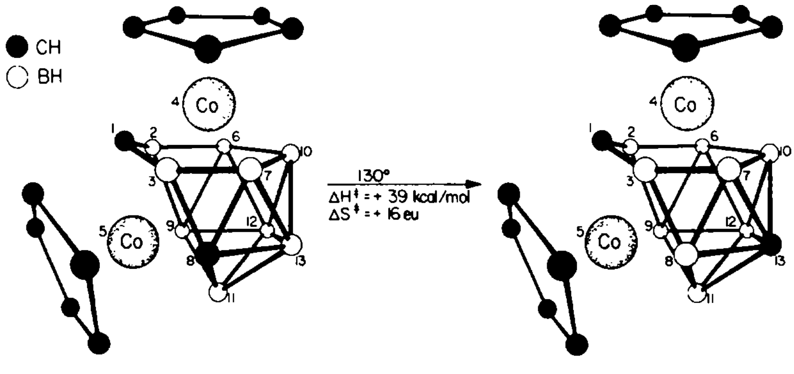

Fig 10. Thermal polyhedral rearrangement of the $(\pi\text{-}C_5H_5)_2Co_2C_2B_9H_{11}$ system.

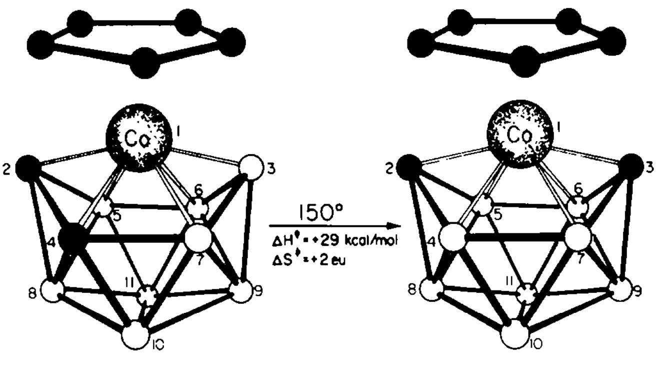

Fig 11. Polyhedral rearrangement of the π-$C_5H_5CoC_2B_8H_{10}$ system.

metallocarboranes have recently been reported,[20] and are depicted in Fig 12. The first isomerization is similar to that shown in Fig 11 and discussed above, and involves migration of a C atom to a site of lower coordination number. The second rearrangement is another example of migration of a polyhedral Co vertex from a position adjacent to Co to a position in which the metals are nonvicinal.

Ten-atom polyhedra. Examples of 10-atom polyhedra having bicapped Archimedean antiprismatic geometries are known in boranes, carboranes and metallocarboranes. Thermodynamic parameters for the rearrangements of a exopolyhedrally substituted 10-vertex borane and of a carborane have been determined and are shown in Fig 13. The rearrangement of the polyhedral borane 2,3-$B_{10}H_8[N(CH_3)_3]_2$, specifically to the 1,6-isomer, indicates that it is possible to proceed through a dsd intermediate. This facile rearrangement has been rationalized by the invocation of nonbonding repulsions of the vicinal substituents.[11] The rearrangements of the $C_2B_8H_{10}$[13,31] carboranes once again shows the effect of repulsive forces between the two positive C centers and also the preference of C to achieve a lower coordination number.

Polyhedral rearrangements of $C_5H_5CoC_2B_7H_9$ metallocarboranes have recently been investigated,[24] and the isomerizations studied kinetically. These results are shown in Fig 14. Carbon atom migration was observed to result in preferential movement to low-coordinate positions; isomerization to a higher-coordinate location more distant from the metal was not seen in this system. A lowering of the activation energy to polyhedral rearrangement by the replacement of a BH vertex by a C_5H_5Co vertex becomes evident when one compares the thermodynamic parameters in Figs 13 and 14.

Two isomeric 10-vertex metallocarboranes of the general formula $[(\pi\text{-}C_5H_5)Co]_2C_2B_6H_8$ have been prepared to date. One isomer, prepared by the polyhedral expansion of $C_2B_6H_8$,[19a] was found to have a Co–Co bond.[32] Polyhedral rearrangement of this compound occurred at 280° to afford the second isomer in which the metals are nonadjacent.[20] This reaction sequence is depicted in Fig 15, and is another example of migration of metals in bimetallic metallocarboranes to nonvicinal apices.

CONCLUSIONS

Carbon atoms which are incorporated into polyhedral borane geometries exhibit properties consistent with their description as sequestered carbonium ions. In many carboranes and metallocarborane compounds, two of these positive C

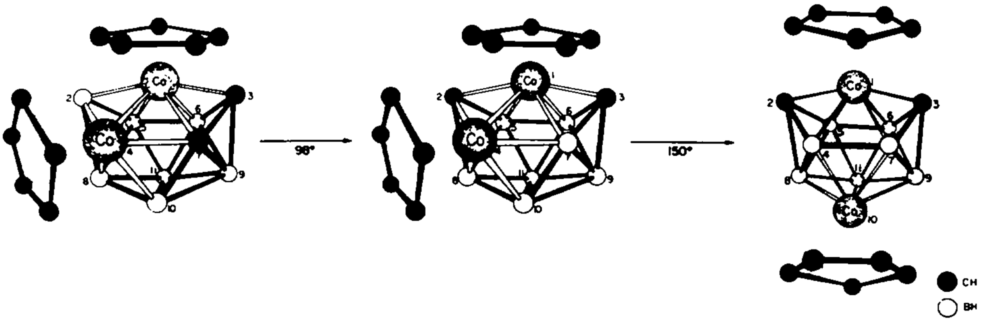

Fig 12. Thermal rearrangements in the $(\pi\text{-}C_5H_5)_2CoC_2B_7H_9$ system.

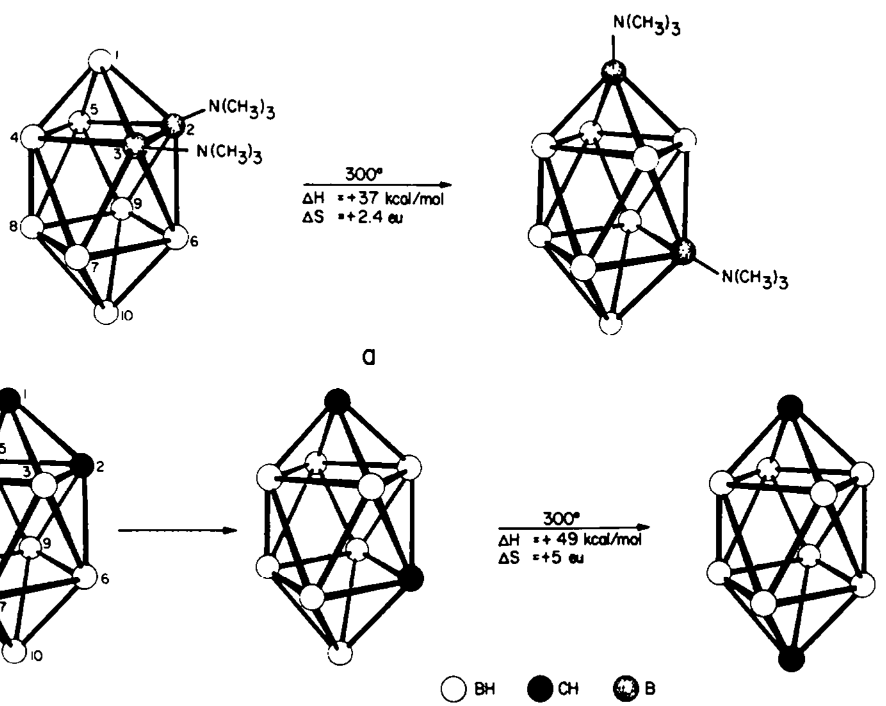

Fig 13. Rearrangements of 10-atom polyhedra. (a) 2,3-$[(CH_3)_3N]$-$B_{10}H_8$ to 1,6-$[(CH_3)_3N]_2$-$B_{10}H_8$. (b) 1,2-$C_2B_8H_{10}$ to 1,6-$C_2B_8H_{10}$ to 1,10-$C_2B_8H_{10}$.

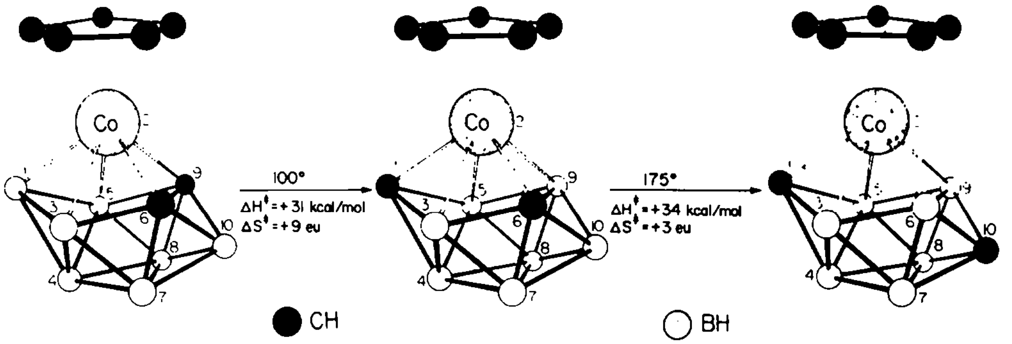

Fig 14. Polyhedral rearrangements in the π-$C_5H_5CoC_2B_7H_9$ system.

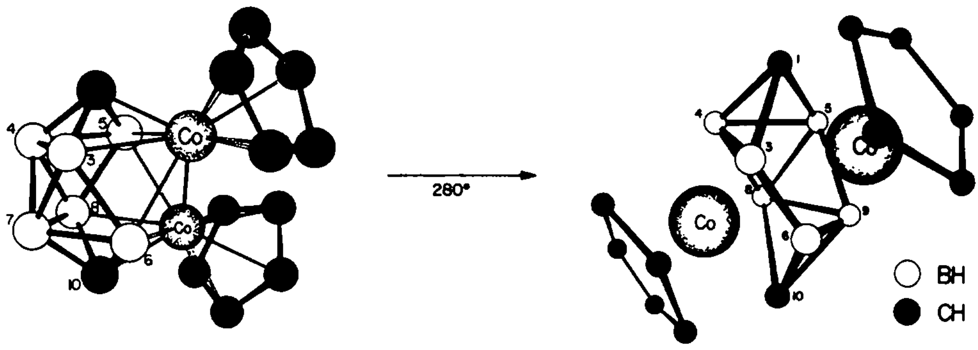

Fig 15. Thermal metal migration in the polyhedral rearrangement of 2,9-(π-C_5H_5)$_2$-2,9-Co_2-1,10-$C_2B_8H_{10}$.

atoms occupy adjacent polyhedral vertices, and the large coulombic repulsive force generated by such positioning results in a tendency for the C atoms to migrate away from each other in a polyhedral rearrangement.

Such intramolecular isomerizations are characterized by a large enthalpy term ($\Delta H^{*} =$ 20–65 kcal/mol) and a generally small entropy of activation, as seen in the examples presented. The large enthalpy term implies significant changes in bonding in the transition state, and all of the proposed polyhedral rearrangement mechanisms reflect this requirement in distortions from low-energy triangulated faces to square or rectangular-faced high-energy intermediates or transition states in the isomerization. Because there exist no conclusive data which support any one of the proposed mechanisms over the others, the available data must be examined for details of polyhedral rearrangements not related to mechanistic interpretations.

Our approach to the study of polyhedral heteroatom migrations has been to characterize the chemical consequences in terms of preferred heteroatom coordination, the various heteroatom effects on the activation energies for isomerization, and the effects of heteroatom positions on the physical properties of metallocarboranes.

The following general rules of heteroatom migration have thus been developed for carboranes and metallocarboranes:

(1) In polyhedra in which all vertices have equal coordination numbers, the heteroatoms will thermally migrate away from each other to minimize any electrostatic repulsions between them;*

(2) In polyhedra which possess vertices of different coordination numbers, carbon atoms will thermally migrate to low-coordinate positions and transition metals will prefer to occupy high-coordinate vertices.† The preferred low coordination number of carbon atoms and the preferred high coordination number of metal atoms takes precedence over heteroatom separation.

(3) In general, the reduction potential of a metal in a metallocarborane will become more negative as the number of C atoms vicinal to the metal decreases; there is a concomitant increase in the energy of the long-wavelength electronic absorption.

(4) Steric effects, such as large substituents on polyhedral C atoms, decrease the activation energy to rearrangement, but do not appear to affect the preceding rules.

Acknowledgment—This work was supported, in part, by the Office of Naval Research, the Army Research Office (Durham), and the National Science Foundation, to whom we express our appreciation.

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*The reverse of thermal heteroatom migration has been observed upon chemical reduction.[33]

†To our knowledge, only one known metallocarborane has a metal atom in low-coordinate vertex: 4-(π-C_5H_5)-4-Fe-1, 8-$C_2B_6H_8$.[19a] The thermal behavior of this novel species is under investigation.

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