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Metallocarboranes That Exhibit Novel Chemical Features

A virtually unlimited variety of structural and dynamic features are observed in metallocarborane chemistry.

M. Frederick Hawthorne and Gary B. Dunks

In 1964 it was reported (*1*) that icosahedral 1,2-dicarba-*closo*-dodecaborane-12 (hereafter referred to as 1,2-$B_{10}C_2H_{12}$) and its carbon-substituted derivatives, formed in the reaction of an acetylene with $B_{10}H_{14}$ in the presence of a ligand catalyst, could be degraded with base to form anions having the general formula $B_9C_2H_{10}R_2^-$ (where R stands for hydrogen, alkyl, or aryl). Later work (*2*) proved that the more thermodynamically stable 1,7-dicarba-*closo*-dodecaborane-12 (1,7-$B_{10}C_2H_{12}$), a carbon atom position isomer of 1,2-$B_{10}C_2H_{12}$ formed by thermal rearrangement (*3*) of the 1,2- isomer, was degraded under similar conditions to yield an isomeric $B_9C_2H_{12}^-$ ion. Both reactions proceed by the formal extraction of a BH^{2+} vertex from the corresponding isomeric $B_{10}C_2H_{12}$ icosahedral carboranes followed by proton addition to the resulting $B_9C_2H_{11}^{2-}$ ion. The removed vertex proved to be one of two equivalent 3- or 6-BH vertices located as nearest neighbors of the two CH vertices of both $B_{10}C_2H_{12}$ isomers (Fig. 1). At the time, it was suspected that the twelfth, or one "extra," hydrogen atom present in the isomeric $B_9C_2H_{12}^-$ ions was bonded to the open pentagonal face of the icosahedral fragment formed by BH^{2+} removal. The mode of such bonding has probably been established (*4*) by ^1H and ^{11}B nuclear magnetic resonance and selective deuteration experiments. Thus, the "extra" hydrogen atom (Fig. 1) is present in one (1,7- isomer) or two equivalent (1,2- isomer) B-H-B bridge positions accompanied by rapid equilibration in the latter isomer.

With these results, the stage was set for the discovery of an entirely new class of extremely stable organometallic complexes, now known as metallocarboranes. The ligands present in these new complexes were formed by the removal of the "extra" B-H-B bridge hydrogen atom from the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions as a proton, thus producing a new type of ligand, the ions (3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$, respectively [where (3) indicates the vacant position in the icosahedron]. Each $B_9C_2H_{11}^{2-}$ ligand is capable of donating six delocalized electrons to a transition metal electron acceptor as in the well-known case of ferrocene, $(\pi\text{-}C_5H_5)_2Fe$, which has two similarly disposed $C_5H_5^-$ ligands. The first report of this new transition metal bonding scheme appeared in 1965 (*5*), and the general scope of metallocarborane chemistry is still expanding at a rapid rate. The initial research developed syntheses of the transition metal complexes $[(B_9C_2H_{11})_2M^n]^{n-4}$ (Fig. 2), where $n-4$ denotes the charge of the complex and M represents a transition metal ion such as formal Fe(II), Fe(III), Co(II), or Co(III) complexed with a pair of (3)-1,2- or (3)-1,7-$B_9C_2H_{11}^{2-}$ ions (*6*), hereafter termed "dicarbollide ions."

An early x-ray diffraction study (*7*) proved that the iron atom in [(3)-1,2-$B_9C_2H_{11}$]$(C_5H_5)Fe^{III}$ was symmetrically located between the open face of the (3)-1,2-$B_9C_2H_{11}^{2-}$ ligand and the π-bonding face of the $C_5H_5^-$ ligand, thus completing the icosahedron. Many other structural studies with a variety of transition metal dicarbollide ion complexes have proved this to be the general mode of ligand to metal bonding. Facial "sandwich" bonding of the $B_9C_2H_{11}^{2-}$ ligand with transition metal moieties such as $M(CO)_3$ metal carbonyl and $M(\pi\text{-}C_5H_5)$ metal cyclopentadienide units suggests that the metal bonding orbitals of the $B_9C_2H_{11}^{2-}$ ligands (*6*, *8*) closely resemble those found in the simple metallocenes de-

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rived solely from $C_5H_5^-$ as in ferrocene, $(\pi\text{-}C_5H_5)_2Fe$ (*9*). Thus, the six electrons donated to the metal acceptor are most likely delocalized in five sp^3-like atomic orbitals (Fig. 3) pointing toward the empty icosahedral vertex of the $B_9C_2H_{11}^{2-}$ ions. Such an orbital set, if we ignore the reduction of symmetry due to the presence of two carbon atoms, would present bonding A, E_1, and antibonding E_2 molecular orbitals. Whatever the precise details of bonding may be, it is fair to say that the chemistry of the dicarbollide ions closely parallels that of the $C_5H_5^-$ ion in terms of bonding to transition metals (*6, 10*) and both series of metal complexes exhibit remarkable thermal stability, but characteristically different chemical reactions.

A logical extension of the principle of incorporating transition metal or main group elements in polyhedral surfaces has led to the discovery of icosahedral complexes containing a transition metal complexed with $B_{10}CH_{11}^{3-}$ (*11*), $B_9CPH_{10}^{2-}$ (*12*), and $B_{10}SH_{10}^{2-}$ (*13*) ligands, all of which are approximately isomorphous with the dicarbollide ions. Furthermore, the discovery of metallocarboranes, among others, containing ligands such as $B_8C_2H_{10}^{2-}$ (*14*), $B_7C_2H_9^{2-}$ (*15*), and $B_6C_2H_8^{2-}$ and $B_6C_2H_8^{4-}$ (*16*) has further extended this area of chemistry.

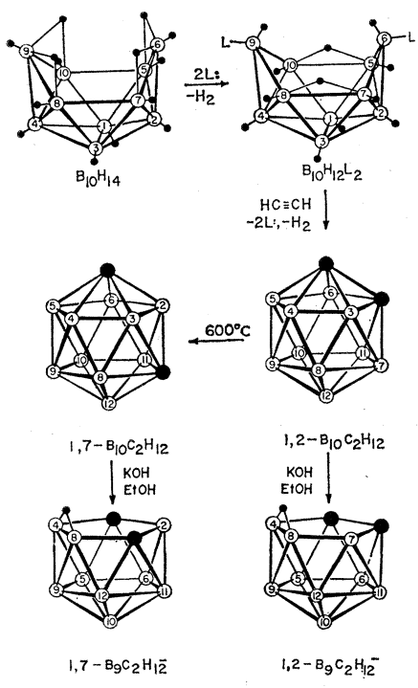


Fig. 1. Schematic conversion of $B_{10}H_{14}$ to the isomeric $B_9C_2H_{12}^-$ ions. The "extra" hydrogen atom of the 1,7-$B_9C_2H_{12}^-$ ion is in a static bridge position between B(4) and B(8), whereas in the 1,2-$B_9C_2H_{12}^-$ ion it is in rapid equilibrium between the B(4)-B(8) (as depicted) and the B(7)-B(8) positions. Terminal hydrogen atoms have been omitted from the carborane species for clarity. Filled circles, CH; open circles, BH; L, ligand; EtOH, ethyl alcohol; KOH, potassium hydroxide; HC ≡ CH, acetylene.

Table 1. Bis-(3)-1,2-dicarbollide complexes of the 3*d* transition metals.

	Symmetrical sandwich
d^3	Cr(III)
d^5	Fe(III)
d^6	Fe(II), Co(III), Ni(IV),* Pd(IV)*
d^7	Co(II),† Ni(III), Pd(III)
	Slipped sandwich
d^8	Cu(III), Ni(II), Pd(II), Au(III)
d^9	Cu(II), Au(II)

* Ni(IV) and Pd(IV) exhibit another type of distortion (Fig. 5). † Structure not experimentally confirmed.

The scope of metallocarborane chemistry appears limitless, and it is impossible to present an exhaustive review of the significant contributions made in this area by other groups or a prognostication of future discoveries in the allotted space. We have therefore chosen to discuss in this article aspects of metallocarborane chemistry which appear to be unusually novel from the viewpoints of synthesis, structure, and molecular dynamics which were developed in our laboratory. Excellent comprehensive reviews of the subject of metallocarboranes have recently appeared (*17*).

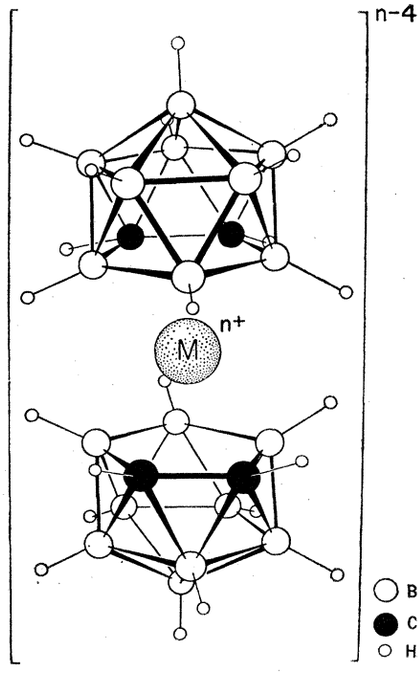


Fig. 2. Symmetrical sandwich structure of the bis-(3)-1,2-dicarbollyl transition metal complexes (*30*).

Structural Oddities and Molecular Rearrangements

In this section we describe phenomena related to molecular structure and bonding as well as thermal polyhedral rearrangements and a metallocarborane system that displays rapid and reversible rearrangement at room temperature.

As pointed out above, the most generally observed mode of metal to ligand bonding in the transition metal derivatives of the dicarbollide ions is that shown in Fig. 2, with nearly equidistant metal-boron and metal-carbon contacts. However, this generalization rests on the fact that the most widely known dicarbollide complexes of all types have been formed with transition metals that contribute six or fewer *d* electrons to bonding, such as d^3 Cr(III) (*18*), d^5 Fe(III) (*6*), and d^6 Co(III) (*6*).

The discovery of the bis-(3)-1,2-dicarbollide complexes of nickel, palladium, copper, and gold (*6, 19–21*) provided examples of d^6, d^7, d^8, and d^9 (Table 1) transition metal electron

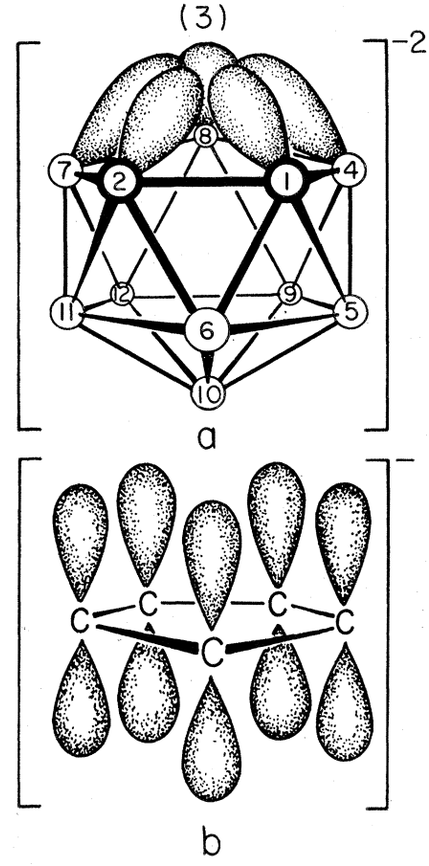


Fig. 3. Schematic representation of the sp^3-like bonding orbitals in the (3)-1,2-$B_9C_2H_{11}^{2-}$ ion (a) compared to the *p* bonding orbitals of the $C_5H_5^-$ ion (b). (Light circles) BH, (heavy circles) CH, (3) open position left by the removal of a boron atom.

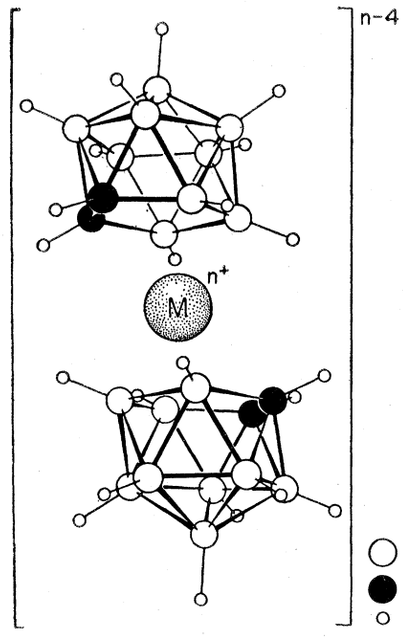


Fig. 4 (left). "Slipped" sandwich structure of the bis-(3)-1,2-dicarbollyl complexes of d^8 and d^9 transition metals (*22, 23*).

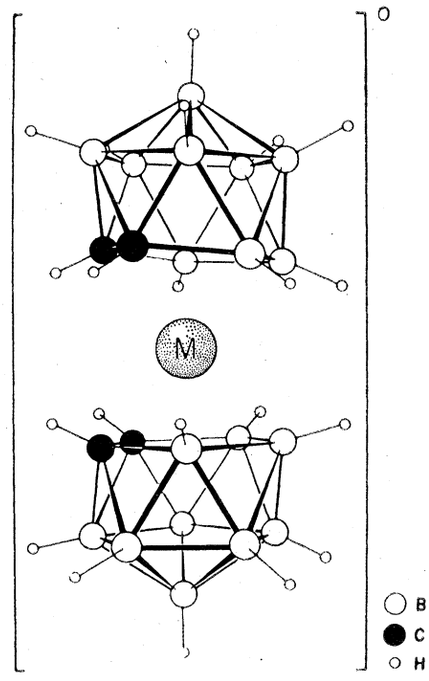


Fig. 5 (right). "Cisoid" sandwich structure of the bis-(3)-1,2-dicarbollyl Ni(IV) and Pd(IV) complexes (*28*).

configurations, the latter three for the first time.

X-ray diffraction studies of the bis-(3)-1,2-dicarbollide complexes of formal Cu(II) (d^9) and Cu(III) (d^8) by Wing (*22, 23*) revealed that the two coplanar faces of the dicarbollide ligand were parallel in both cases, but the two ligands had "slipped" with respect to the copper nucleus. This slippage placed the copper nucleus closer to the three boron atoms of the pentagonal ligand face than to the two carbon atoms (Fig. 4), with Cu-B and Cu-C distances of 2.20 and 2.57 angstroms, respectively, in the case of the Cu(II) derivative, and with corresponding distances of 2.11 and 2.52 angstroms in the case of the Cu(III) derivative. Additional x-ray diffraction studies by Wing (*23*), coupled with spectroscopic data gathered in our laboratory (*19–21*), gave excellent support for the structural assignments presented for the d^8 and d^9 complexes in Table 1. The d^7 Ni(III) complex was examined by Stucky (*24*) and found to be isomorphous with the corresponding d^6 Co(III) complex of known symmetrical sandwich structure (*6, 25*). Earlier, this same bonding mode was established for the d^5 [(3)-1,2-$B_9C_2H_{11}$]$(C_5H_5)Fe^{III}$ complex (*7*). Consequently, it may be assumed that the data presented in Table 1 are essentially correct. Two explanations have been offered to explain "slipped" sandwich bonding (*20, 22, 23*) in the d^8 and d^9 complexes. Both explanations are based on the relatively large number of d electrons available from the metal for bonding, and differ more in language than concept. Warren and Hawthorne (*20*) considered the fact that the E_1-like molecular orbitals of each ligand were filled and interacted with an empty $nd_{z^2}(n+1)s$ hybrid acceptor orbital which, for reasons of symmetry, could only interact with one E_1-like orbital and then only in a noncentroidal manner. In addition, we suggested that only one of the empty E_2-like ligand orbitals could interact with a filled nd_{yz} metal orbital, and, again, this interaction could not be centroidal. These two suggested noncentroidal orbital interactions are similar to those previously proposed (*26*) for noncentroidal bonding of d^{10} Ag(I) in its benzene complex. The second explanation of "slipped" sandwich bonding was suggested by Wing (*22, 23*), who drew attention to the similarity of the observed bonding interactions to those seen in π-allylic complexes, in which only three ligand carbon atoms are π-bonded to the transition metal. In the case at hand, the three facial boron atoms of the (3)-1,2-$B_9C_2H_{11}^{2-}$ ligand would play the role of the π-allylic carbon atoms.

The "slipped" sandwich bonding seen in the electron-rich (3)-1,2-dicarbollide complexes is unprecedented in the known transition metal chemistry of the cyclopentadienide ligand to which it bears a close formal resemblance. Electron-rich derivatives of $C_5H_5^-$ are either very unstable or known as σ-bonded complexes, as in $C_5H_5Cu^IP(C_2H_5)_3$ (*27*). The problem posed by "slipped" sandwich bonding awaits a thorough theoretical study.

The formal d^6 Ni(IV) (*6, 19, 20*) and Pd(IV) (*20, 21*) (3)-1,2-dicarbollide complexes shown in Table 1 present an entirely different set of structural formulations. An x-ray diffraction study of the parent Ni(IV) derivative (*28*) proved that the (3)-1,2-dicarbollide ligand in this and the isomorphous Pd(IV) derivative was distorted, not "slipped," and that the carbon atoms were eclipsed (Fig. 5). The nature of the ligand distortion was such as to bring the carbon atoms

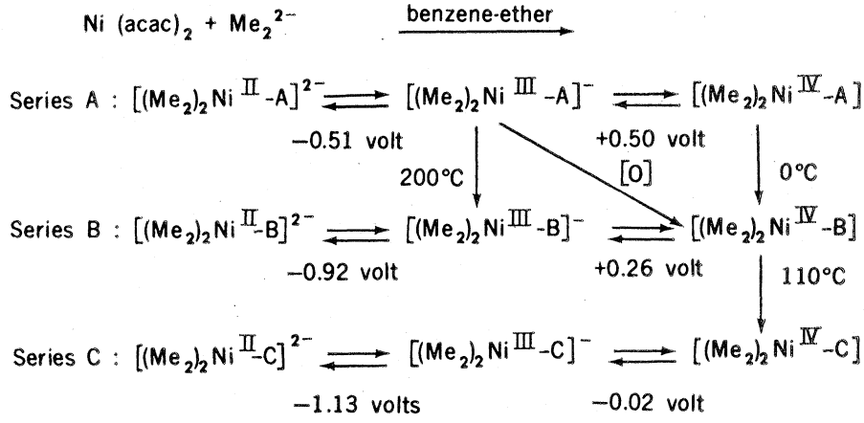
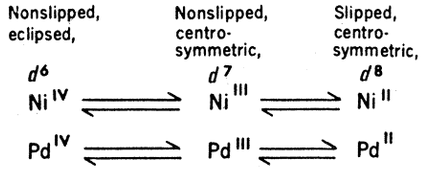


Fig. 6. Reaction and rearrangement sequence showing the electrochemistry of the bis-[1,2-dimethyl-(3)-1,2-dicarbollyl]nickel system. Me_2^{2-}, $B_9H_9C_2(CH_3)_2^{2-}$; acac, $(CH_3COCHCOCH_3)^-$.

closer to the center of an imagined icosahedron and, at the same time, produce Ni-C contacts of 2.07 Å and Ni-B contacts of 2.10 Å. This resulted in a dihedral angle of about 6° between the B_3C_2 bonding facial planes of the two ligands. These data, when combined with the structural observations presented in Table 1, provide the following relationship between the structure and the formal metal *d* electron configuration for the nickel and palladium complexes having six, seven, and eight *d* electrons. As indicated, reversible electron transfer reactions were observed between the stable oxidation states of the nickel and palladium complexes.



While the d^6 dicarbollide derivatives of nickel and palladium have many unusual properties (*21*), the most intriguing chemistry of these complexes is seen in their derivatives, which bear methyl groups at all four available carbon atoms (*21*). For simplicity, an abbreviated designation of these compounds will be employed (*29*).

Reaction of Ni(II) acetylacetonate, $Ni(acac)_2$, with the 1,2-dimethyl-(3)-1,2-dicarbollide ion (*21*) produces a yellow $[(Me_2)_2Ni^{II}]^{2-}$ complex (*29*), which was reversibly oxidized to a

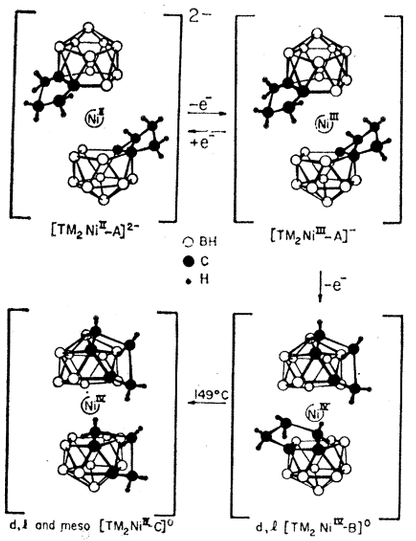


Fig. 7. Reaction sequence and stereochemistry of the bis-(μ-1,2-trimethylene-1,2-dicarbollyl)nickel system. The [μ-1,2-$(CH_2)_3$-1,2-$B_9C_2H_9$]$^{2-}$ ligand is represented by TM.

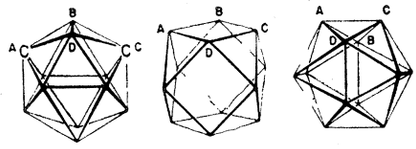


Fig. 8. The "diamond-square-diamond" (dsd) polyhedral rearrangement mechanism proposed by Lipscomb (*32*).

$[(Me_2)_2Ni^{III}]^-$ complex. Further oxidation of this Ni(III) species provided a neutral $(Me_2)_2Ni^{IV}$ derivative. The latter oxidation step was irreversible, since reduction of the Ni(IV) derivative did not regenerate the originally formed $[(Me_2)_2Ni^{III}]^-$ ion. Evidence for other rearrangements was obtained, and it became obvious that the structural mobility of this system was unprecedented in metallocarborane chemistry (*21*). A subsequent chemical and spectroscopic investigation of all the related derivatives, coupled with an x-ray diffraction study (*30*) of the rearranged $(Me_2)_2Ni^{IV}$ complex first observed, provided a rational picture of the molecular rearrangements that occur in the C-tetramethyl derivatives of nickel dicarbollide complexes. Three isomeric series of these nickel complexes exist, and have been designated series A, series B, and series C. Figure 6 outlines the nature of the rearrangements that were observed with the nickel derivative, and their corresponding electrochemistry (*31*). Spectroscopic and chemical studies carried out with the corresponding $[(Me_2)_2Pd^{III}]^-$ and its oxidation and rearrangement products disclosed a series of rearrangements virtually identical to those found with the nickel system, except that the B-series isomers could not be isolated in the palladium system. The driving forces for rearrangement in the sequence $(Me_2)_2Ni^{IV}A \rightarrow (Me_2)_2Ni^{IV}B \rightarrow (Me_2)_2Ni^{IV}C$ are most probably the great steric repulsions introduced by the four eclipsed methyl groups in $(Me_2)_2Ni^{IV}A$ and the less important steric repulsions introduced when *d,l*-$[(Me_2)_2Ni^{IV}B]$ forms meso or *d,l*-$[(Me_2)_2Ni^{IV}C]$. Similarly, the μ-trimethylene complex (Fig. 7) (*31*)—which is limited to 1,2- to 1,6- rearrangements since the trimethylene bridge between the (3)-1,2-dicarbollyl carbon atoms allows only rearrangements which retain the dicarbollyl carbon atoms as nearest neighbors—undergoes a sequence of reversible oxi-

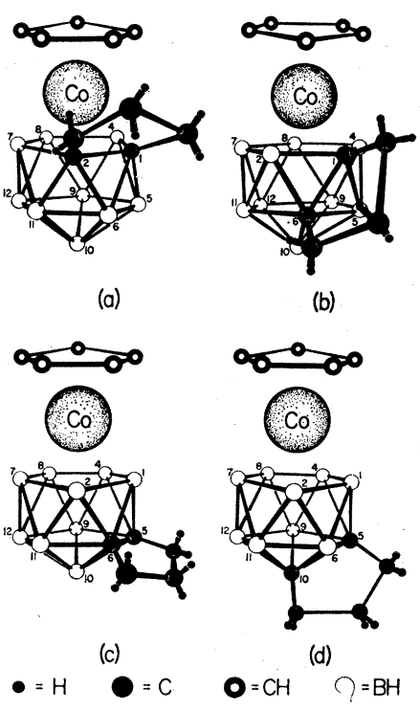


Fig. 9. The proposed structures of the μ-trimethylene isomers, produced from (a) [(3)-μ-1,2-$(CH_2)_3$-1,2-$B_9C_2H_9$]$(C_5H_5)Co^{III}$, are: (b) 1,6; (c) 5,6; and (d) 5,10.

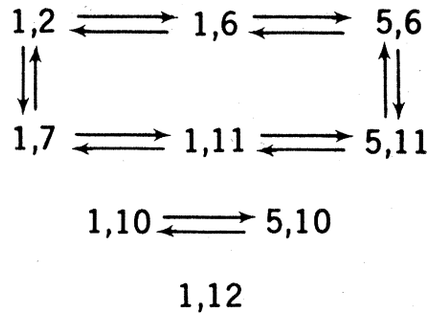


Fig. 10. Limits of polyhedral rearrangements available through the dsd mechanism.

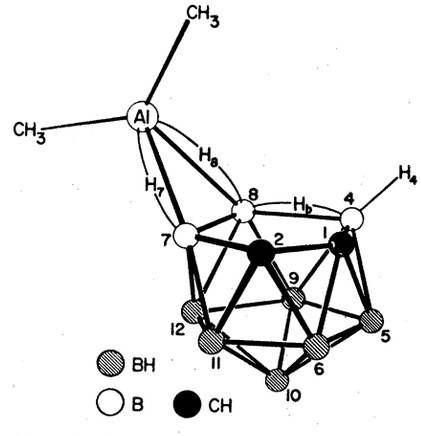


Fig. 11. Structure of $B_9[Al(CH_3)_2]C_2H_{12}$ determined by x-ray diffraction (*39*) and nuclear magnetic resonance (*37*). In the enantiomeric form H_4 becomes a bridging hydrogen.

dations and irreversible thermal rearrangements (*31*). The ease with which these two systems rearrange is reflected in the measured thermodynamic activation parameters and rate data (*31*). Values of the enthalpy and entropy of activation, $\Delta H\ddagger$ and $\Delta S\ddagger$, ranged from 19 kilocalories per mole with three entropy units to 35 kilocalories per mole with 22 entropy units, respectively.

Lipscomb (*32*) has reviewed known and hypothetical polyhedral rearrangements which do, or conceivably could, occur in the polyhedral borane anion and carborane series. A general rearrangement mechanism which he proposed was the "diamond-square-diamond" (dsd) mechanism, in which adjacent atoms lose their nearest neighbor relationship and a non-nearest neighbor atomic pair gain this relationship (Fig. 8) during the rearrangement process. In the case of icosahedral systems, such as the nickel or palladium (3)-1,2-dicarbollide complexes, a cuboctahedral transition state or intermediate is suggested (Fig. 8) which is fully compatible with the 1,2- to 1,6- polyhedral rearrangements observed in the present instance. An alternative polyhedral rearrangement process, which invokes rotation of triangular B_2C faces, has been proposed by Muetterties and Knoth (*33*). This mechanism is equally compatible with the observed rearrangement. Regardless of which mechanism one chooses to accept, the fact remains that the rearrangement of $(Me_2)_2Ni^{IV}A$ to $(Me_2)_2Ni^{IV}B$ is an exceedingly facile, sterically accelerated polyhedral rearrangement (*31*) since the similar polyhedral rearrangement of 1,2-$B_{10}C_2H_{12}$ to 1,7-$B_{10}C_2H_{12}$ is characterized (*34*) by a high $\Delta H\ddagger$ (62 kcal/mole) and a small and positive $\Delta S\ddagger$.

The observation of icosahedral rearrangements in the nickel and palladium dicarbollyl complexes described above suggested that a study of the thermal isomerization of related dicarbollyl complexes would be of interest if carried to the extreme limit of isomerization in the vapor phase at high temperatures. The complexes [(3)-1,2-$B_9C_2H_{11}$]$(C_5H_5)Co^{III}$, [(3)-1,2-$(CH_3)_2$-1,2-$B_9C_2H_9$]$(C_5H_5)Co^{III}$, and [(3)-μ-1,2-$(CH_2)_3$-1,2-$B_9C_2H_9$](C_5H_5)-Co^{III} were chosen for this purpose (*35*) because of their high thermal stability and ready availability. As in the case of the related nickel dicarbollyl system (*21*), the [(3)-1,2-μ-$(CH_2)_3$-1,2-$B_9C_2H_9$] $(C_5H_5)Co^{III}$ (Fig. 9), could

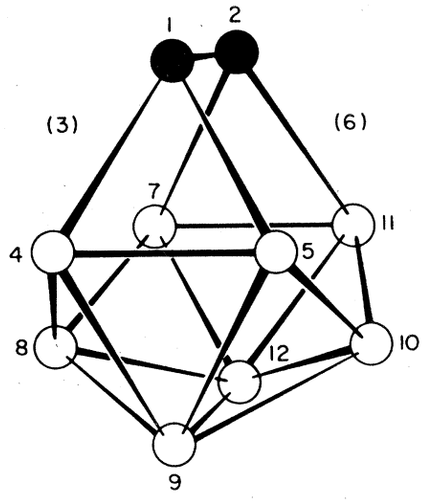


Fig. 12. Structure of the π-bonding bidentate (3,6)-1,2-dicarbacanastide ion. (Filled circles) CH, (open circles) BH.

only give 1,2- to 1,6- rearrangements. The [(3)-1,2-$(CH_3)_2$-$B_9C_2H_9$](C_5H_5)-Co^{III} and [(3)-1,2-$B_9C_2H_{11}$](C_5H_5)-Co^{III} derivatives allow free movement of all dicarbollyl carbon atoms to produce nine possible isomers, and the former derivative was closely related to both the unsubstituted and μ-trimethylene derivatives.

Experiments were performed in which each of the three derivatives was slowly sublimed in vacuo through a hot zone (400° to 500°C) and rapidly condensed in a cold zone. Under the conditions used in these and subsequent experiments it was impossible to strictly relate the observed distributions of rearranged products to kinetic or thermodynamic control. However, this fact did not mitigate the ultimate usefulness of the study since we were principally concerned with the appearance of totally new isomers of the dicarbollide ligand in the complexes, regardless of their relative thermodynamic stabilities. Initial experiments with the 1,2- unsubstituted and 1,2-dimethyl derivatives proved that four isomers were produced upon pyrolysis at 400° to 500°C. The μ-1,2-trimethylene derivative was rearranged to a single isomer, which was subsequently shown to be the μ-1,6-trimethylene isomer (Fig. 9b). A comparison of the ^{11}B and ^1H nuclear magnetic resonance spectra of the μ-1,6-trimethylene isomer with the spectra of the isomers obtained from the rearrangement of the 1,2- unsubstituted and 1,2-dimethyl derivatives identified the corresponding 1,6- isomers in both series. Furthermore, the 1,7- and 1,11-isomers of the latter two series were identified by direct synthesis (1,7- isomers) and nuclear magnetic resonance coupled with other criteria (1,11- isomers).

In the final series of experiments, the μ-1,6-trimethylene and the 1,11-unsubstituted complexes were examined at 600° to 700°C by using the same experimental method. At these higher temperatures two additional isomers of the unsubstituted complex (1,12- and 1,10-) and two additional isomers of the μ-trimethylene complex (5,6- and 5,10-) were obtained (Fig. 9). The 5,11-, 5,10-, and 5,6- isomers of these dicarbollyl complexes are the only examples of metallocarboranes that have no carbon atoms within bonding distance of the metal atom.

The dsd polyhedral rearrangement mechanism (*32*) in its strictest form does not allow the formation of 1,10-, 5,10-, or 1,12- isomers from the corresponding 1,2- isomer (*32*) (Fig. 10). On the other hand, rotation of trigonal polyhedral faces, alone or coupled with a dsd-like rearrangement, allows the interconversion of all the observed isomers. The obvious conclusion is that the simplified dsd mechanism is not strictly applicable to the case at hand or to the known rearrangement of 1,7-$B_{10}C_2H_{12}$ to 1,12-$B_{10}C_2H_{12}$ (*32, 36*). Further research is required to elucidate the true nature of these and related polyhedral rearrangements.

Although most of the research described in this article involves transition metal complexes of the dicarbollide ions, extremely interesting stereochemically nonrigid complexes of aluminum and gallium have been discovered (*37*). The reactions leading to these new species rest on the fact that the (3)-1,2-$B_9C_2H_{12}^-$ ion is easily protonated to yield its conjugate acid, (3)-1,2-$B_9C_2H_{13}$ (*1*). The latter material is a strong monoprotic acid which regenerates the (3)-1,2-$B_9C_2H_{12}^-$ ion on neutralization. The reaction of R_3M (R is CH_3 or C_2H_5 when M is aluminum, or R is C_2H_5 when M is gallium) with (3)-1,2-$B_9C_2H_{13}$ proceeded in two discrete steps (*37*).

$$MR_3 + B_9C_2H_{13} \rightarrow B_9(MR_2)C_2H_{12} + RH$$
$$B_9(MR_2)C_2H_{12} \rightarrow B_9(MR)C_2H_{11} + RH$$

A determination of the structure of $B_9(AlC_2H_5)C_2H_{11}$ by x-ray diffraction (*38*) proved this compound to be nearly identical to icosahedral 1,2-$B_{10}C_2H_{12}$, with an $Al(C_2H_5)$ group replacing a BH group at the 3-vertex (Fig. 1). Polyhedral rearrangement (*37*) of this derivative at 350°C in vacuo produced the compound corre-

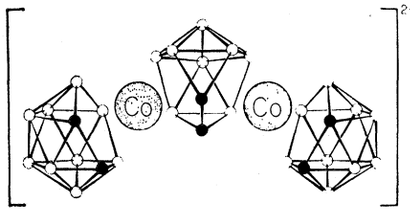


Fig. 13. Structure of the $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})Co^{III}(B_9C_2H_{11})]^{2-}$ complex (*42*). (Open circles) BH, (filled circles) CH.

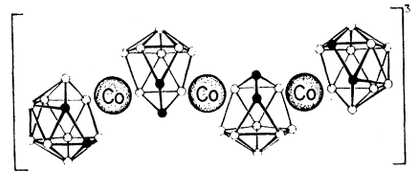


Fig. 14. Structure of the $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})CO^{III}\ (B_8C_2H_{10})CO^{III}\ (B_9C_2H_{11})]^{3-}$ complex (*44*). (Open circles) BH, (filled circles) CH.

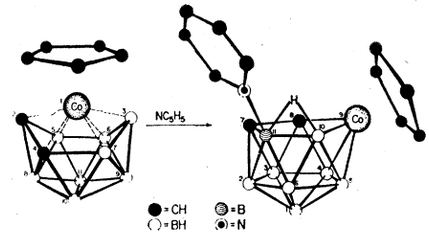


Fig. 15. Reaction sequence leading to $[(B_8C_2H_{10})Co^{III}(C_5H_5)]NC_5H_5$ (*46*).

sponding to the 1,7-$B_{10}C_2H_{12}$ derivative.

The intermediate containing two methyl groups attached to aluminum, $B_9[Al(CH_3)_2]C_2H_{12}$, proved to be much more novel with respect to structural dynamics (*37*, *39*). An x-ray diffraction study (*39*) revealed the heavy atom skeleton shown in Fig. 11, with the $Al(CH_3)_2$ group attached to the icosahedral fragment by external bonds. However, for this compound at room temperature, the ^{11}B nuclear magnetic resonance spectrum at 80 megahertz was not in agreement with the structure seen in the x-ray diffraction study (*39*), since all nine boron atoms were found in unique positions in the crystal and the spectrum appeared to be time-averaged between enantiomorphic forms (endo and exo CH_3-Al groups) of the determined structure. Consequently, the ^{11}B and ^1H nuclear magnetic resonance spectra of this peculiar species were examined at a low temperature, and characteristic coalescence temperatures were observed in both types of spectra at $-22°$ and $-75°C$, respectively. The results of these low-temperature nuclear magnetic resonance studies proved that, indeed, enantiomorphic forms could be "frozen" and observed spectroscopically. The free energy of activation $\Delta F‡$ (10.6 ± 0.5 kcal/mole) and first-order rate constant for their interconversion were calculated (*37*) from these nuclear magnetic resonance data.

Degradation of Transition Metal Complexes

A π-bonding bidentate ligand, $B_8C_2H_{10}^{4-}$. The (3)-1,2-$B_9C_2H_{11}^{2-}$ ligand may be generated from (3)-1,2-$B_9C_2H_{12}^{-}$ in hot aqueous base. The addition of transition metal halides (*6*) to such solutions provided a useful synthesis route to several bis-(3)-1,2-dicarbollide complexes. The long reaction times under these reaction conditions led to the formation of an unexpected product containing the π-bonding bidentate ligand $B_8C_2H_{10}^{4-}$ (Fig. 12) (*40*), which was given the trivial name (3,6)-1,2-dicarbacanastide ion (*41*). The isolated complex was formulated as $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})Co^{III}(B_9C_2H_{11})]^{2-}$ (*40*) and its structure (Fig. 13) confirmed by single crystal x-ray diffraction studies (*42*). Conceptually, the (3,6)-1,2-dicarbacanastide ion may be produced from 1,2-$B_{10}C_2H_{12}$ by removal of BH^{2+} groups from the 3 and 6 positions of the icosahedral carborane. The actual reaction sequence that leads to the $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})Co^{III}(B_9C_2H_{11})]^{2-}$ ion may proceed as shown in the following equations and pass through an unobserved intermediate, $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})]^{3-}$.

$$B_9C_2H_{12}^- + OH^- \rightleftharpoons B_9C_2H_{11}^{2-} + H_2O$$

$$4B_9C_2H_{11}^{2-} + 3Co(OH)_2 \rightarrow 2[(B_9C_2H_{11})_2Co]^- + 6OH^- + Co$$

$$[(B_9C_2H_{11})_2Co]^- + 2OH^- + H_2O \rightarrow [(B_9C_2H_{11})Co(B_8C_2H_{10})]^{3-} + H_2 + B(OH)_3$$

$$[(B_9C_2H_{11})Co(B_8C_2H_{10})]^{3-} + Co(OH)_2 + B_9C_2H_{11}^{2-} \rightarrow [(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})]^{3-} + 2OH^-$$

$$2[(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})]^{3-} + Co(OH)_2 \rightarrow 2[(B_9C_2H_{11})Co(B_8C_2H_{10})Co(B_9C_2H_{11})]^{2-} + 2OH^- + Co$$

The product ion may be formally considered to contain two π-bonded Co(III) ions with the (3,6)-1,2-dicarbacanastide ligand playing the role of a central "double-barreled" π-bonding ligand.

A detailed examination of the crude reaction mixtures which contained $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})Co^{III}(B_9C_2H_{11})]^{2-}$ afforded an even more interesting product (*43*), $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})\ Co^{III}\ (B_8C_2H_{10})\ Co^{III}\ (B_9C_2H_{11})]^{3-}$, whose structure (Fig. 14) was confirmed by x-ray diffraction studies (*44*). This product was obtained in very low yield and could have arisen by the reaction of two $[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})]^{3-}$ ions with Co(II) ion, followed by oxidation of the initially formed $\{[(B_9C_2H_{11})Co^{III}(B_8C_2H_{10})]_2Co^{II}\}^{4-}$ ion by Co(II) ion, to form the observed product and cobalt metal.

The two (3,6)-1,2-dicarbacanastide complexes described above are characterized by simple electrochemical oxidation-reduction potentials (*43*). In the absence of more complicated electrochemical reactions, it may be inferred that the cobalt entities present in these complexes extend electron delocalization throughout the entire ion and do not function as independent oxidation-reduction sites.

Polyhedral contraction. Recent studies (*45*) have shown that degradation of $[(3)\text{-}1,2\text{-}B_9C_2H_{11}](C_5H_5)Co^{III}$ and $[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$ with aqueous hydroxide ion followed by hydrogen peroxide oxidation affords $(B_8C_2H_{10})(C_5H_5)Co^{III}$ and $[(B_8C_2H_{10})((3)\text{-}1,2\text{-}B_9C_2H_{11})Co^{III}]^-$, respectively. These new complexes formally contain a $B_8C_2H_{10}^{2-}$ ligand, which may arise by oxidation and closure of a species containing an open $B_8C_2H_{10}^{4-}$ ligand. Both of these new complexes adduct 1 mole of pyridine to form open complexes with the pyridine molecule attached to the $B_8C_2H_{10}^{2-}$ ligand. The structure of one such pyridine adduct has been determined by x-ray diffraction studies (*46*). The reaction sequence leading to the formation of the pyridine adduct of known structure is presented in Fig. 15. Additional degradation-oxidation reactions have been discovered (*45*) which give stepwise removal of BH^{2+} from metallocarboranes, and this general sequence has been termed "polyhedral contraction."

Polyhedral Expansion

As illustrated above, reactions are known which systematically reduce the size of carborane ligands and polyhedral metallocarboranes. We have also discovered a general reaction sequence which allows us to build up a polyhedral metallocarborane by the stepwise addition of transition metal vertices, and we have designated this process as "polyhedral expansion" (*14*). The basis of polyhedral expansion is the fact that polyhedral carboranes and metallocarboranes have accessible unfilled molecular orbitals, which may acquire one or more electrons from a reducing agent such as an alkali metal. If such reductions are effected, the possibility exists that the closed polyhedral structure will become opened by Jahn-Teller or other distortions and be available for bonding to a transition metal as a ligand. The implications of this synthesis route are manifold and need not be strictly limited to carboranes and metallocarboranes as starting materials, since polyhedral transition metal clusters might be found to undergo similar reduction and expansion reactions.

Supraicosahedral cobalt complexes derived from 1,2-$B_{10}C_2H_{12}$. The direct reduction of the icosahedral 1,2-$B_{10}C_2H_{12}$ carborane has been accomplished with alkali metals (*3*, *47*).

$$1,2\text{-}B_{10}C_2H_{12} + 2Na \rightarrow 2Na^+ + B_{10}C_2H_{12}^{2-}$$

The electrons are accepted and the resulting $B_{10}C_2H_{12}^{2-}$ ion will revert to the carborane starting material on oxidation. The structure of the $B_{10}C_2H_{12}^{2-}$ ion produced by this means has not been described although it may very well be an opened or highly distorted icosahedron. Nonetheless, the $B_{10}C_2H_{12}^{2-}$ ion serves as an efficient ligand in a series of isomeric cobalt complexes (*48*) having the composition $(B_{10}C_2H_{12})(C_5H_5)Co^{III}$ and $[(B_{10}C_2H_{12})_2Co^{III}]^-$. The reaction sequence employed in the synthesis of these complexes involves the reaction of $C_5H_5^-$ with Co(II) and the $B_{10}C_2H_{12}^{2-}$ ion formed from 1,2-$B_{10}C_2H_{12}$ and sodium metal in tetrahydrofuran. The $[(B_{10}C_2H_{12})_2Co^{III}]^-$ complex was formed as a by-product.

$$2C_5H_5^- + 3Co^{2+} + 2B_{10}C_2H_{12}^{2-} \rightarrow 2(B_{10}C_2H_{12})(C_5H_5)Co^{III} + Co$$

$$4B_{10}C_2H_{12}^{2-} + 3Co^{2+} \rightarrow 2[(B_{10}C_2H_{12})_2Co^{III}]^- + Co$$

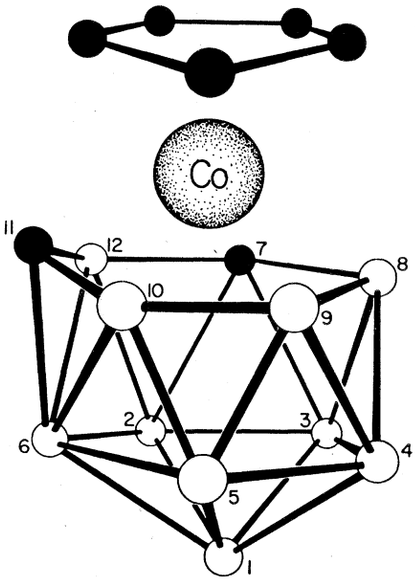


Fig. 16. Proposed structure of $(B_{10}C_2H_{12})(C_5H_5)Co^{III}$. (Filled circles) CH, (open circles) BH.

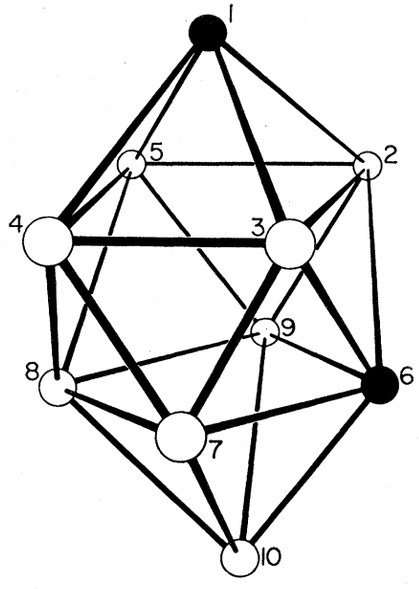


Fig. 17. Structure of 1,6-$B_8C_2H_{10}$ carborane. (Filled circles) CH, (open circles) BH.

In addition to the $B_{10}C_2H_{12}^{2-}$ complexes, a small amount of the known $[(3)\text{-}1,2\text{-}B_9C_2H_{11}](C_5H_5)Co^{III}$ complex was isolated and shown to be a hydrolysis product of $(B_{10}C_2H_{12})(C_5H_5)Co^{III}$.

While the structure of the uncomplexed $B_{10}C_2H_{12}^{2-}$ ligand is not known, ^{11}B and ^1H nuclear magnetic resonance studies have provided a rationale for the structure of the complexed ligand. Figure 16 represents the proposed structure of the $(B_{10}C_2H_{12})(C_5H_5)Co^{III}$ complex initially isolated from the reaction mixture. It has been experimentally demonstrated that the pictured complex thermally rearranges to two other isomers in a sequential manner.

The evidence available, including preliminary x-ray diffraction results (*49*), strongly suggest that the formal Co(III) ion present in these new complexes occupies a vertex position in a 13-vertex polyhedral array (Fig. 16). This being the case, the icosahedron no longer represents the largest known polyhedron possible among the metallocarboranes.

Polyhedral expansion products from 1,6-$B_8C_2H_{10}$. The 1,6-$B_8C_2H_{10}$ carborane (Fig. 17) (*50*) reacted with two equivalents of sodium naphthalide ($Np^{\bullet-}$) to produce a $B_8C_2H_{10}^{2-}$ ligand, which was subsequently treated with Co(II) and $C_5H_5^-$. The reaction product, $(B_8C_2H_{10})(C_5H_5)Co^{III}$ was structurally characterized by ^{11}B and ^1H nuclear magnetic resonance spectra (*14*). The most probable structure is shown in Fig. 18. The gross polyhedral configuration of this species is the same as that found in previously described $B_9C_2H_{11}$ carborane (*51*) and the $B_{11}H_{11}^{2-}$ ion (*52*).

$$1,6\text{-}B_8C_2H_{10} + 2Np^{\bullet-} \rightarrow B_8C_2H_{10}^{2-} + 2Np$$

$$2C_5H_5^- + 3Co^{2+} + 2B_8C_2H_{10}^{2-} \rightarrow 2(B_8C_2H_{10})(C_5H_5)Co^{III} + Co$$

We have demonstrated (*53*) that the metallocarborane described above, $(B_8C_2H_{10})(C_5H_5)Co^{III}$, reacts with two or more $Np^{\bullet-}$ ions to produce metal-containing anions, which will function as ligands in a further application of the polyhedral expansion reaction. The principal product formed when these ligands are reacted with Co(II) and $C_5H_5^-$ is a bimetallic species, $[(C_5H_5)Co^{III}]_2B_8C_2H_{10}$. A minor product, believed to be a trimetallic species $[(C_5H_5)Co^{III}]_3B_8C_2H_{10}$, was also produced. Figure 19 presents a proposed structure of the bimetallic compound, based on nuclear magnetic resonance spectra. The proposed structure is similar to that of the dicarbacanastide complex discussed above (Fig. 13).

This example of the addition of a second metal vertex to a metallocarborane lends considerable support to the concept of using carborane frameworks as templates for the construction of clusters which contain several transition metal vertices.

Polyhedral expansion of 1,6-$B_6C_2H_8$. The first *closo*-carborane to be examined in the polyhedral expansion reaction was 1,6-$B_6C_2H_8$ (*54*) (Fig. 20). Reaction of the carborane with sodium amalgam followed by the usual addition of Co(II) and $C_5H_5^-$ produced two derivatives of the $B_6C_2H_8^{2-}$ ligand (*16, 55*) and small amounts of a third product derived from another ligand, $B_6C_2H_8^{4-}$. The first-named species were formulated as $(B_6C_2H_8)(C_5H_5)Co^{III}$ and $[(B_6C_2H_8)_2Co^{III}]^-$. The low symmetry exhibited by both of these products in their ^{11}B and ^1H nuclear magnetic resonance spectra suggested that the same carborane ligand was common to both. Since the known (*56*) $[(B_6C_2H_8)Mn^I(CO)_3]^-$ ion has been shown to have a tricapped trigonal prism as the parent polyhedron, we adopted that overall geometry in the present examples. The complexed $B_6C_2H_8^{2-}$ ligand produced by electron addition to 1,6-$B_6C_2H_8$ has the proposed structure shown in Fig. 21.

A side product formed in this reaction, $(C_5H_5)Co^{III}(B_6C_2H_8)Co^{III}(C_5H_5)$, contained the π-bidentate ligand $B_6C_2H_8^{4-}$ (*16*). The structure originally proposed from ^{11}B and ^1H nuclear magnetic resonance spectral data (*16*) has been shown to be incorrect (*57*). The structure deduced from x-ray diffraction data is presented in Fig. 22 (*57*).

Electrophilic Substitution of Metallocarboranes

Electrophilic substitution in polyhedral carborane systems occurs at the boron atom or atoms on which the highest ground-state electron density resides (*58*). These are the boron atoms located farthest from the polyhedral carbon atoms (*59*). Electrophilic substitution reactions carried out on complexed carborane ligands provide no exception and will be discussed in this section.

The reaction of $Rb[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co^{III}]^-$ with excess bromine in glacial acetic acid produced the $[(8,9,12\text{-}Br_3\text{-}1,2\text{-}B_9C_2H_8)_2Co^{III}]^-$ ion (*6*).

$$[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co^{III}]^- + 6Br_2 \rightarrow [(8,9,12\text{-}Br_3\text{-}1,2\text{-}B_9C_2H_8)_2Co^{III}]^- + 6HBr$$

The observed structure, depicted in Fig. 23 (*25*), illustrated that indeed complexed carborane ligands undergo substitution at those boron atoms farthest from the polyhedral carbon atoms. A polarographic examination of the brominated product gave two reversible reduction waves, which suggests that the reduction proceeds in two steps to the corresponding d^8 formal Co(I) species. The resulting high formal charge (3−) on the reduced complex is possibly stabilized by an electron-withdrawing effect of the bromine substituents (*6*).

Treatment of $K[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co^{III}]$ with carbon disulfide in the presence of aluminum chloride and hydrogen chloride produced the unique complex $((3)\text{-}1,2\text{-}B_9C_2H_{10})_2Co^{III}S_2C^{\oplus}H$, in which the opposed dicarbollyl ligands are bridged by a $-SC^{\oplus}HS-$ moiety (Fig. 24) (*60*).

$$[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co^{III}]^- + CS_2 + H^+ \xrightarrow{AlCl_3} [((3)\text{-}1,2\text{-}B_9C_2H_{10})_2Co^{III}S_2C^{\oplus}H] + H_2$$

Interestingly, this complex contains an electron-deficient carbon stabilized by the nonbonding electron pairs of its neighboring sulfur atoms. A similarly bridged complex has been prepared by using acetic acid–acetic anhydride as the

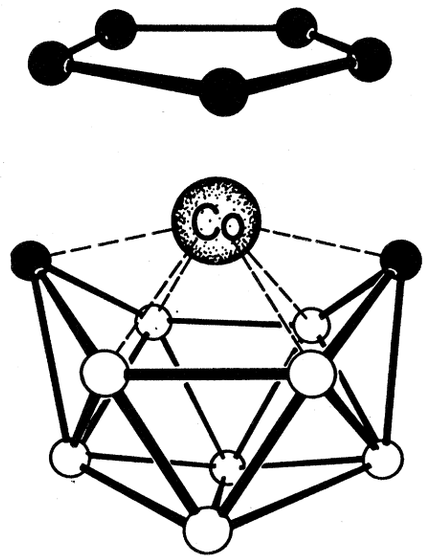


Fig. 18. Proposed structure of $(B_9C_2H_{10})(C_5H_5)Co^{III}$. (Filled circles) CH, (open circles) BH.

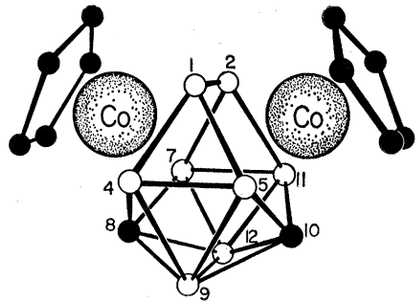


Fig. 19. Proposed structure of $[(C_5H_5)Co^{III}]_2B_8C_2H_{10}$, which includes the (3,6)-8,10-dicarbacanastide ligand. (Filled circles) CH, (open circles) BH.

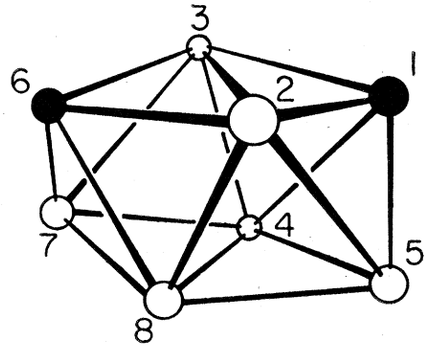
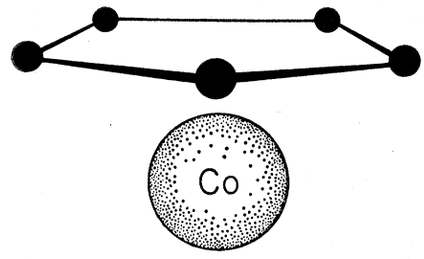


Fig. 20. Structure of 1,6-$B_6C_2H_8$ carborane. (Filled circles) CH, (open circles) BH.



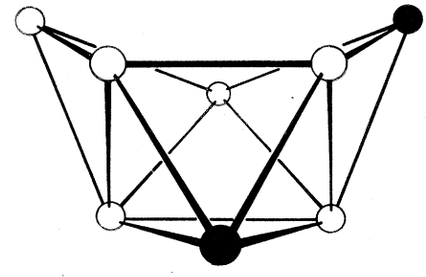


Fig. 21. Proposed structure of $(B_6C_2H_8)(C_5H_5)Co^{III}$. (Filled circles) CH, (open circles) BH.

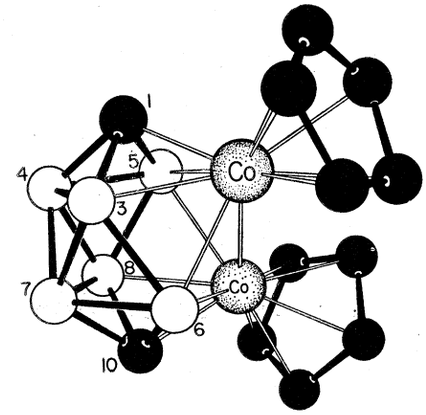


Fig. 22. Structure of $(C_5H_5)Co^{III}(B_6C_2H_8)Co^{III}(C_5H_5)$ (*57*). (Filled circles) CH, (open circles) BH.

electrophilic reagent in which -O-C$^{\oplus}$-(CH_3)O- is the bridging moiety (*61*). The mechanism of these apparent electrophilic substitution reactions may involve a protonated intermediate. A proton placed in close proximity to hydridic hydrogen atoms suggests the possibility of the addition of a neutral donor ligand (L) with the attendant loss of a molecule of hydrogen—thus, the formal replacement of $:H^-$ with neutral :L (*62*). This protonation reaction is demonstrated when $[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{II}]^{2-}$ is protonated with strong acid to yield $[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{II}H]^-$ (*62*), which in turn reacts with diethyl sulfide to produce $[((3)\text{-}1,2\text{-}B_9C_2H_{11})\text{-}Fe^{II}((3)\text{-}1,2\text{-}B_9C_2H_{10}S(C_2H_5)_2)]^-$ (Fig. 25) (*62*).

$$[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{II}H]^- + R_2S \rightarrow H_2 + [((3)\text{-}1,2\text{-}B_9C_2H_{11})Fe^{II}((3)\text{-}1,2\text{-}B_9C_2H_{10}SR_2)]$$

where R stands for C_2H_5. In another bridged complex ion, formulated as $[((3)\text{-}1,2\text{-}B_9C_2H_{10})_2Co^{III}C_6H_4R]^-$ (R is H or CH_3), the bridging moiety is a phenyl ring bound to the opposing carborane ligands through ortho carbon atoms (Fig. 26) (*63*). This compound arises from the decomposition of $R\text{-}C_6H_4N_2^{\oplus}[((3)\text{-}1,2\text{-}B_9C_2H_{11})_2Co^{III}]$ (R is H or CH_3), presumably by a free-radical mechanism (*63*).

Finally, a series of reactions was carried out to determine whether the 1,6-$B_7C_2H_9^{2-}$ dicarbazapyl ligand or the $C_5H_5^-$ cyclopentadienyl ligand was more reactive toward electrophilic substitution in the mixed complex $(1,6\text{-}B_7C_2H_9)(C_5H_5)Co^{III}$ (Fig. 27) (*15*, *64*). In both Friedel-Crafts acylation and bromination it was found that reaction occurred at the dicarbazapyl ligand (*65*).

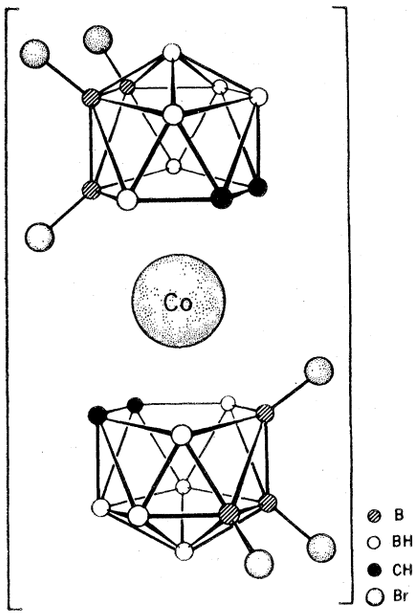


Fig. 23. Structure of $[(8,9,12\text{-}Br_3\text{-}(3)\text{-}1,2\text{-}B_9C_2H_8)_2Co^{III}]^-$ (*25*).

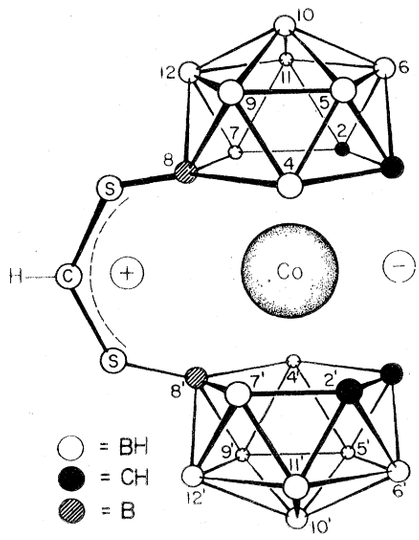


Fig. 24. Structure of $((3)\text{-}1,2\text{-}B_9C_2H_{10})_2Co^{III}S_2C^{\oplus}H$ (*60*).

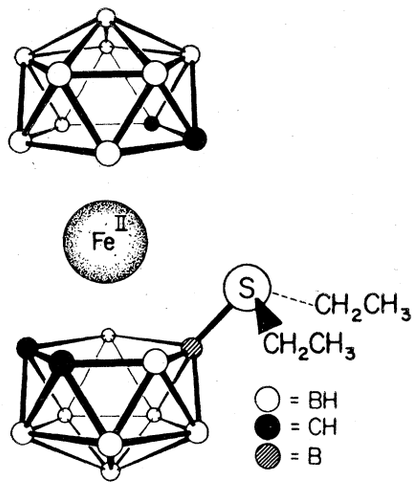


Fig. 25. Proposed structure of $[((3)\text{-}1,2\text{-}B_9C_2H_{11})Fe^{II}((3)\text{-}1,2\text{-}B_9C_2H_{10}S(C_2H_5)_2)]$ ion.

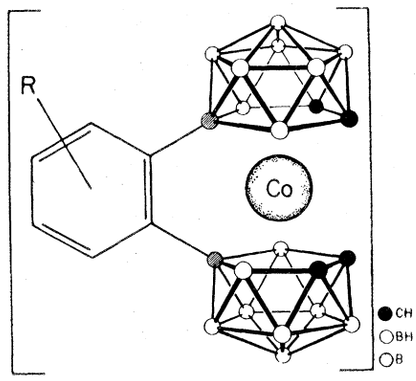


Fig. 26. Proposed structure of $[((3)\text{-}1,2\text{-}B_9C_2H_{10})_2Co^{III}C_6H_4R]^-$ (R is H or CH_3).

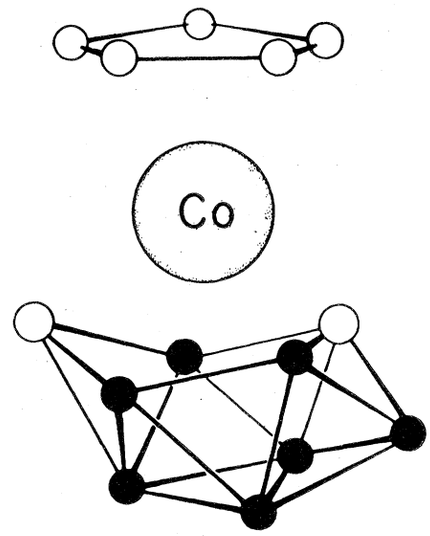


Fig. 27. Proposed structure of $(1,6\text{-}B_7C_2H_9)(C_5H_5)Co^{III}$ based on the confirmed structure of $[(1,6\text{-}B_7C_2H_9)_2Co^{III}]^-$ (*64*). (Filled circles) BH, (open circles) CH.

Summary

Among the myriad transition metal and main group complexes of ligands derived from carboranes, some exhibit unique structural variations and novel dynamic behavior.

Three structural types are known for the bis-dicarbollyl transition metal complexes, which differ only in *d* electronic configuration. These are typified by the bis-dicarbollylnickel system, in which the "slipped" sandwich d^8, the "symmetrical" sandwich d^7, and the "cisoid" sandwich d^6 complexes are observed. These structures can be interconverted by using appropriate redox reactions.

The fluxional behavior of certain carborane species is exemplified by the $B_9[Al(CH_3)_2]C_2H_{12}$ complex, in which the $Al(CH_3)_2$ moiety is rapidly equilibrating in solution between bridging positions on the open face of the $B_9C_2H_{12}$ icosahedral fragment.

Synthetic techniques have been developed which facilitate both enlargement and reduction of the size of the polyhedral starting material, and provide unprecedented versatility in the preparation of new transition metal complexes. Significantly, these reactions have produced bimetallic and 13-vertex polyhedral species unattainable by other means.

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Citation Analysis as a Tool in Journal Evaluation

Journals can be ranked by frequency and impact of citations for science policy studies.

Eugene Garfield

As a communications system, the network of journals that play a paramount role in the exchange of scientific and technical information is little understood. Periodically since 1927, when Gross and Gross published their study (*1*) of references in 1 year's issues of the *Journal of the American Chemical Society*, pieces of the network have been illuminated by the work of Bradford (*2*), Allen (*3*), Gross and Woodford (*4*), Hooker (*5*), Henkle (*6*), Fussler (*7*), Brown (*8*), and others (*9*). Nevertheless, there is still no map of the journal network as a whole. To date, studies of the network and of the interrelation of its components have been limited in the number of journals, the areas of scientific study, and the periods of time their authors were able to consider. Such shortcomings have not been due to any lack of purpose, insight, or energy on the part of investigators, but to the practical difficulty of compiling and manipulating manually the enormous amount of necessary data.

A solution to this problem of data is available in the data base used to produce the *Science Citation Index* (SCI) (*10*). The coverage of the SCI is international and multidisciplinary; it has grown from 600 journals in 1964 to 2400 journals in 1972, and now includes the world's most important sci-

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