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PERSPECTIVES IN METALLOCARBORANE CHEMISTRY

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Introduction

The original synthesis of metallocarboranes [1], Fig. 1, was effected by

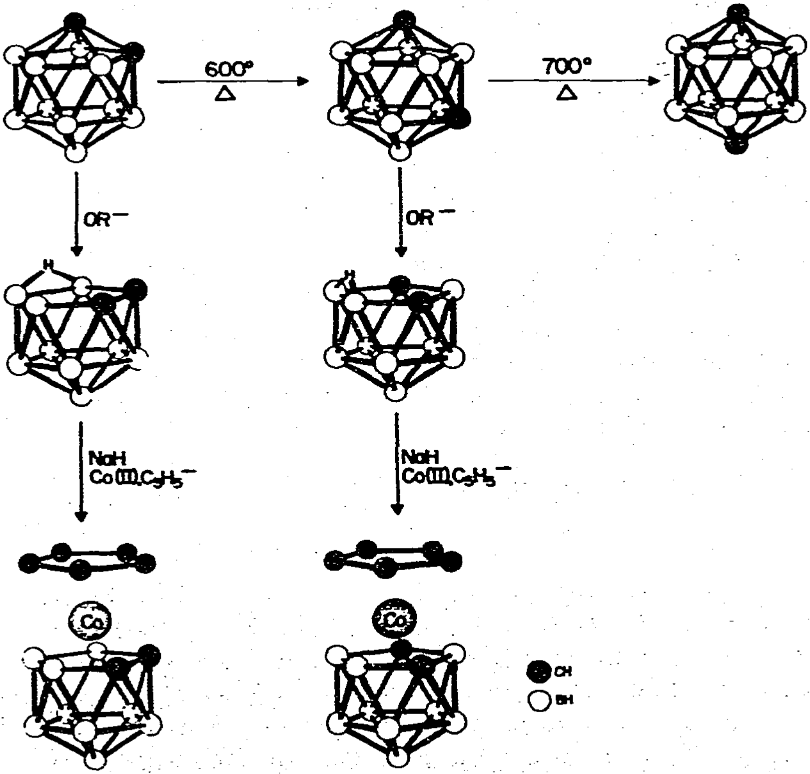

Fig. 1. Top: Thermal isomerization of 1,2-$C_2B_{10}H_{12}$ to the 1,7- and 1,12-isomers. Center: Base degradation of 1,2- and 1,7-$C_2B_{10}H_{12}$ to the 7,8- and 7,9-$C_2B_9H_{12}^-$ isomers. The bridging hydrogen in the 7,8-isomer is shown in one of the two equivalent bridge positions. Bottom: Synthesis of $C_5H_5CoC_2B_9H_{11}$ isomers from the degraded ions.

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* Contribution number 3439.

deprotonation of *nido* carborane anions* (eqn. 1) in a manner similar to that employed to prepare ferrocene [2] (eqn. 2).

$$C_2B_9H_{12}^- + NaH \rightarrow C_2B_9H_{11}^{2-} \xrightarrow[(2)\ [O]]{(1)\ \frac{1}{2}Fe^{II}} \tfrac{1}{2}Fe(C_2B_9H_{11})_2^- \qquad (1)$$

$$C_5H_6 + NaH \rightarrow C_5H_5^- \xrightarrow{\frac{1}{2}Fe^{II}} \tfrac{1}{2}(C_5H_5)_2Fe \qquad (2)$$

Since the $C_5H_5^-$ and $C_2B_9H_{11}^{2-}$ ions are isoelectronic, in that six electrons are available for donation to a metal ion, it was originally believed that similarities in physical and chemical behavior of ferrocene and the metallocarboranes would be found. The observation [1] that the ferracarborane preferentially existed in the tripositive oxidation state of the metal, rather than as Fe^{II} in ferrocene, was the first of many subsequent examples of the unique behavior of metallocarboranes.

Synthesis by degradation

Although the first metallocarborane syntheses were performed in nonaqueous solvent systems, some of these compounds could also be prepared in strong aqueous base [3] (eqn. 3). It is believed that a small concentration of

$$C_2B_9H_{12}^- + OH^- \rightarrow C_2B_9H_{11}^{2-} \xrightarrow[(2)\ [O]]{(1)\ \frac{1}{2}Fe^{II}} \tfrac{1}{2}Fe(C_2B_9H_{11})_2^- \qquad (3)$$

$C_2B_9H_{11}^{2-}$ is present in this solvent system at equilibrium, and complexation of the dianion drives the reaction to completion. Yields similar to those obtained in nonaqueous solvents are generally obtained, with greater experimental convenience. Unfortunately, not all metallocarboranes may successfully be prepared in aqueous systems.

The preparation of mixed ligand complexes may be effected by the inclusion of a third component, usually $C_5H_5^-$, in the reaction mixture [4]. Yields of the mixed ligand product, however, were generally poor, for side products included large quantities of the symmetrical complexes (eqn. 4).

$$C_5H_5^- + C_2B_9H_{11}^{2-} + Fe^{II} \xrightarrow{[O]} (C_5H_5)FeC_2B_9H_{11} + (C_5H_5)_2Fe + (C_2B_9H_{11})_2Fe^- \qquad (4)$$

Subsequent workers [5, 6] have found that much higher yields of these mixed species may be obtained by modification of the reaction conditions. Most conveniently, it has been discovered that prior degradation of the carborane cage to the $C_2B_9H_{12}^-$ ion is often not necessary; instead, the combination of $C_2B_{10}H_{12}$, C_5H_6, and a metal halide (M = Co, Fe) in strong alcoholic base affords the mixed ligand complexes $(C_5H_5)MC_2B_9H_{11}$ in good yield [5]. An improved high-yield preparation of the cobalt complex from the potassium salt, $K^+C_2B_9H_{12}^-$, has also been recently reported [6].

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* *Closo*-carboranes and -metallocarboranes are closed triangular polyhedra. *Nido* species have structures formed by removal of a vertex of high connectivity from a *closo* skeleton. *Commo* compounds involve the sharing of an atom, generally a metal, between two polyhedra.

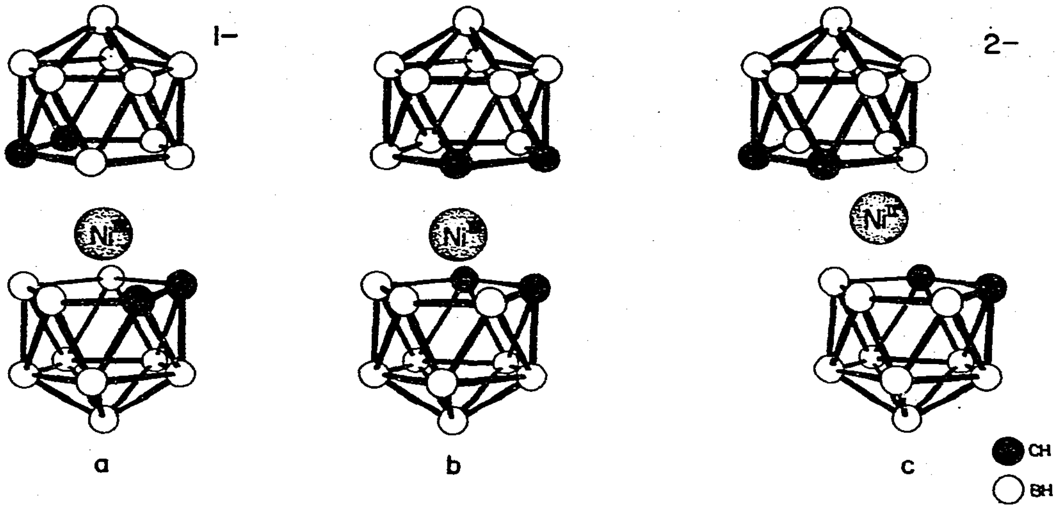

Fig. 2. (a) Symmetrical sandwich structure of $[(1,2\text{-}C_2B_9H_{11})_2Ni^{III}]^-$ ion. (b) *Cisoid* sandwich structure of $(1,2\text{-}C_2B_9H_{11})Ni^{IV}$. (c) Slipped sandwich structure of $[(1,2\text{-}C_2B_9H_{11})_2Ni^{II}]^{2-}$.

Structures of twelve-vertex metallocarboranes

The structures of these twelve-vertex metallocarboranes depend on the number of *d* electrons present on the metal atom [7]. Those complexes which involve metals of d^5, d^6 and d^7 electronic configurations, such as Fe^{III}, Co^{III} and Ni^{III}, exhibit a symmetrical sandwich geometry (Fig. 2a) in which the metal atom is nearly equidistant from five other atoms, and the overall structure can be described as a distorted icosahedron. Complexes in which two carbon atoms are located in positions adjacent to the metal generally adopt a *transoid* configuration in which the carbon atoms in the two icosahedra are as far away from each other as possible, but a *cisoid* arrangement has been found in $(C_2B_9H_{11})_2Ni$ (Fig. 2b).

When the number of *d* electrons on the metal atom increases above seven, as, for example in the case of d^8 Ni^{II}, a distortion from symmetrical sandwich geometry is observed. Instead of being equally bonded to three boron atoms and two carbon atoms, the metal occupies a position closer to the boron atoms than to the carbon atoms. Additional distortions are observed in complexes of the $1,7\text{-}C_2B_9H_{11}{}^{2-}$ moiety. This "slipped sandwich" configuration (Fig. 2c) has been demonstrated for complexes of Cu^{III}, Cu^{II}, Ni^{II} and Au^{III}. Two explanations of this distortion have been offered; one treats these complexes as analogs of organometallic π-allyl compounds [8], while the other suggests that the observed slip distortion is due to restricted orbital overlap [9], also observed in benzene-silver complexes.

Rearrangements of metallocarboranes

Thermal migration of polyhedral carbon atoms in carboranes was established in $C_2B_{10}H_{12}$ shortly after the report of its synthesis [10]. This intramolecular isomerization involves the thermal rearrangement of the molecule to lower-energy isomers in which the CH vertices in the polyhedron move to sites more distant from each other, and is explained by electrostatic repulsion of the partially positively charged carbon atoms. Similar migrations of polyhedral carbon atoms in metallocarboranes were first detected in the *C,C'*-dimethyl substituted Ni^{IV} complex, $[(CH_3)_2C_2B_9H_9]_2Ni$ [11]. This system is of high interest, for there are important structural alterations which are produced by the change of formal oxidation state of the metal. These latter changes are independent of carbon atom substitution, however. The Ni^{II}—Ni^{III}—Ni^{IV} transformation, which is electrochemically reversible, involves structural change from "slipped sandwich" Ni^{II} to symmetrical sandwich Ni^{III} to distorted *cisoid* Ni^{IV}. In the *C,C'*-dimethyl substituted complexes, additional isomerism was found to occur (Fig. 3), and crystallographic investigations determined that carbon atom migration was the reason for this behavior.

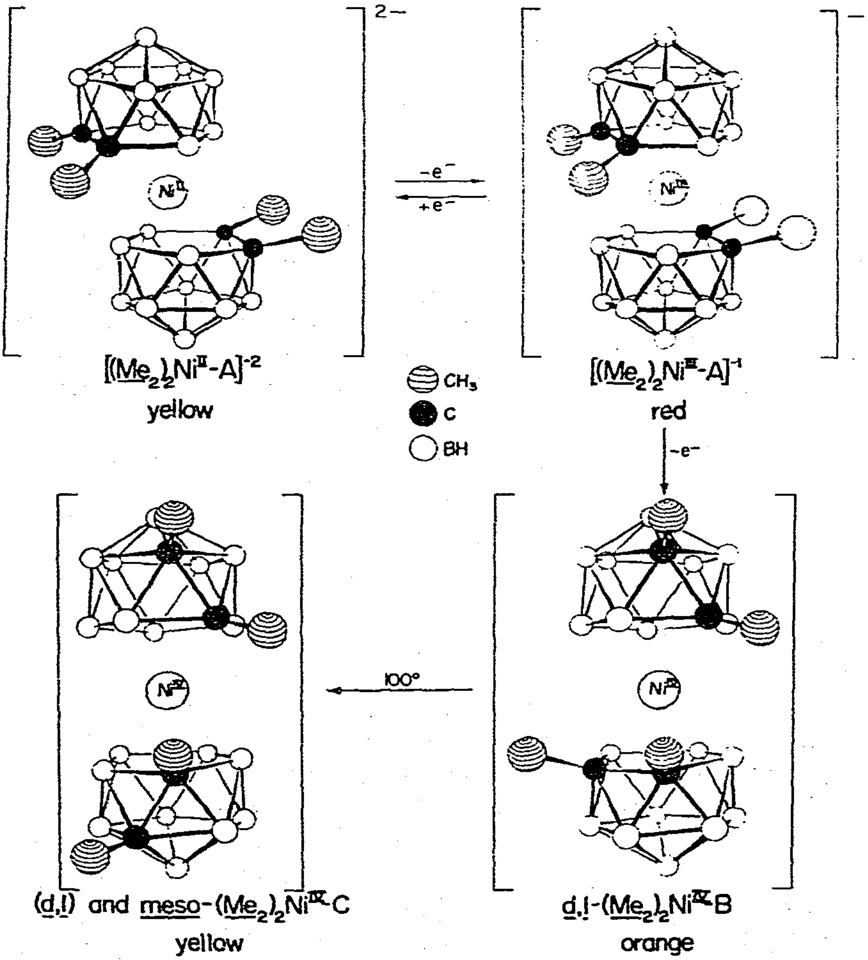

Fig. 3. Structural changes observed upon redox and polyhedral rearrangement in the 1,2-$(CH_3)_2$-1,2-$C_2B_9H_9Ni^{n-}$ system ($n = 0, 1, 2$).

The first product isolated from the reaction of 1,2-$(CH_3)_2$-1,2-$C_2B_9H_9^{2-}$ with Ni^{II} was the symmetrical sandwich [12] Ni^{III} complex in which the carbon atoms on the two cages are located in a *trans* disposition with respect to the metal. Oxidation to the Ni^{IV} complex would produce a near *cisoid* arrangement of the carbon atoms and their associated methyl groups, and apparently there is sufficient steric strain brought about by the close approach of these methyl groups that a polyhedral rearrangement ensued. The resulting oxidation product has one polyhedral cage in which the two carbon atoms remain in adjacent positions and bonded to the nickel atom; the second cage has undergone rearrangement in which one of the carbon atoms has exchanged positions with a boron atom [13]. This exchange occurs with a boron atom previously separated from the nickel vertex, and in the product the nickel is coordinated to four boron atoms and one carbon atom in the rearranged cage, and there is less steric crowding. A second thermal rearrangement also occurs in which the first cage undergoes a similar isomerization to produce another $[(CH_3)_2C_2B_9H_9]_2Ni$ species in which the nickel is bonded to two B_4C rings. These rearrangements occur at extremely low temperatures when compared to the rearrangement of the parent 1,2-$C_2B_{10}H_{12}$, and it was originally speculated that the influence of the metal could be responsible for the decrease in activation energy. The observation [11] that elevated temperatures were necessary to produce similar rearrangements in unsubstituted $(C_2B_9H_{11})_2Ni$ indicated the important role of steric interactions in the rearrangement process.

Similar polyhedral rearrangements occur in other metallocarboranes. For example, all the possible positional isomers of the $C_5H_5CoC_2B_9H_{11}$ system have been prepared [14], although it was necessary to force the carbon atoms to remain adjacent in some cases by use of a *C,C'*-trimethylene group to interconnect the polyhedral carbon vertices. Thermal rearrangements of nonicosahedral metallocarboranes have recently been intensively investigated [15], and polyhedral rearrangments in general have been reviewed [16].

Synthesis of lower metallocarboranes

Deprotonation of other carborane anions is effective in the preparation of metallocarboranes. The $C_2B_7H_{11}^{2-}$ ion, prepared from $C_2B_7H_{13}$, was found to react with Co^{II} to afford metallocarboranes of the $C_2B_7H_9^{2-}$ ion [17] (eqn. 5).

$$2\,C_2B_7H_{13} + 4\,NaH \rightarrow C_2B_7H_{11}^{2-} \xrightarrow{3/2\,Co^{II}} (C_2B_7H_9)_2Co^- + \tfrac{1}{2}Co^0 + H_2 \qquad (5)$$

Again in this system, mixed ligand complexes could be prepared by the inclusion of cyclopentadienide ion in the reaction mixture (eqn. 6).

$$C_2B_7H_{11}^{2-} + C_5H_5^- + Co^{II} \rightarrow C_5H_5CoC_2B_7H_9 + (C_5H_5)_2Co + (C_2B_7H_9)_2Co^- + H_2 \qquad (6)$$

The existence of polymetallocarboranes was demonstrated upon study of the colored residues ensuing from an aqueous preparation of $(C_2B_9H_{11})_2Co^-$. Two compounds were separated which were determined to be bi- [18, 19] and tri-cobalt species [20], respectively (Fig. 4), and which contained terminal $C_2B_9H_{11}$ groups and new bidentate carborane ligands of the formula $C_2B_8H_{10}^{4-}$

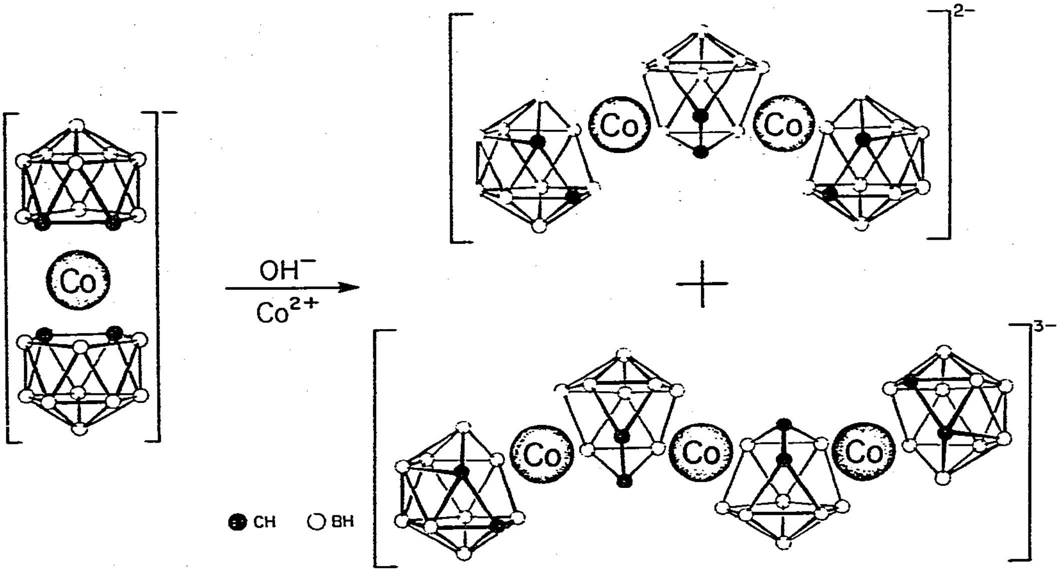

Fig. 4. Degradation of $(1,2\text{-}C_2B_9H_{11})_2Co^-$ to bi- and trimetallic metallocarboranes.

which bridged between the metals. It was proposed [18] that in the presence of strong base, the initially formed $(C_2B_9H_{11})_2Co^-$ complex was further degraded, eliminating another boron vertex from the polyhedron to form the proposed intermediate $\{C_2B_9H_{11}CoC_2B_8H_{10}\}$, which could either react with Co^{II} and $C_2B_9H_{11}{}^{2-}$ to form the bimetallic complex, or react with Co^{II} and another partially degraded $\{C_2B_9H_{11}CoC_2B_8H_{10}\}$ moiety to produce the tricobalt species. The existence of the $C_2B_9H_{11}{}^{2-}$ ion in strongly basic solutions of $(C_2B_9H_{11})_2Co^-$ was indicated by the isolation [18] of $(C_2B_9H_{11})_2Ni$ when Ni^{II} was added to such a solution.

When basic solutions of $(C_2B_9H_{11})_2Co^-$ or of $(C_5H_5)CoC_2B_9H_{11}$ were heated in the absence of additional Co^{II}, and the resulting reaction mixtures oxidized, high yields of new metallocarboranes containing degraded, yet fully closed, lower homologous polyhedra were obtained [21]. An example of this reaction is shown in eqn. 7 and depicted in Fig. 5. This type of reaction, which involves

$$(C_5H_5)CoC_2B_9H_{11} \xrightarrow[(2)\ H_2O_2]{(1)\ OR^-;\ -B(OR)_3} (C_5H_5)CoC_2B_8H_{10} \tag{7}$$

the degradative removal of a BH vertex, followed by oxidation of the intermediate *nido* metallocarborane to a *closo* complex, has been termed “polyhedral contraction”. Both mixed-sandwich metallocarboranes and *commo* metallocarboranes exhibit this reaction, although it is apparently limited to cobalt-containing species. Decomposition generally results when polyhedral contraction reactions are attempted on metallocarboranes containing metals other than cobalt.

Polyhedral contraction is not solely effective on twelve-vertex metallocarboranes, but may be carried out on smaller species as well [21]. Thus the

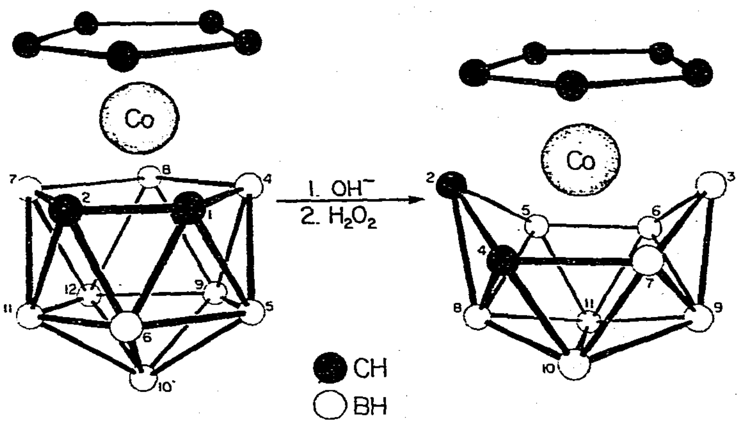

Fig. 5. Polyhedral contraction of $C_5H_5Co(1,2\text{-}C_2B_9H_{11})$ to $C_5H_5Co(2,4\text{-}C_2B_8H_{10})$.

oxidative degradation of $(C_5H_5)CoC_2B_8H_{10}$, prepared as in eqn. 7 by polyhedral contraction of $(C_5H_5)CoC_2B_9H_{11}$, afforded the *nido* complex $(C_5H_5)CoC_2B_7H_{11}$ which, upon pyrolysis, produced the lower *closo* species $(C_5H_5)CoC_2B_7H_9$ (eqn. 8).

$$(C_5H_5)CoC_2B_8H_{10} \xrightarrow[\text{EtOH}]{\text{FeCl}_3} (C_5H_5)CoC_2B_7H_{11} \xrightarrow[-H_2]{\Delta} (C_5H_5)CoC_2B_7H_9 \qquad (8)$$

Attempted polyhedral contraction of the thirteen-vertex metallocarborane $(C_5H_5)CoC_2B_{10}H_{12}$ (vide infra) to one of the isomeric $(C_5H_5)CoC_2B_9H_{11}$ compounds resulted instead in the extrusion of three boron vertices and one carbon vertex, to produce the ionic complex $(C_5H_5)CoCB_7H_8^-$ [22]. This "polyhedral supercontraction" is the only known example of the removal of a polyhedral carbon vertex from a metallocarborane without complete degradation of the polyhedron.

Polyhedral expansion

One of the most important new areas in metallocarborane chemistry involves what might be considered the reverse of polyhedral contraction, and has been termed "polyhedral expansion". This method of synthesizing metallocarboranes originates from the "aromaticity" of carboranes and the delocalized bonding present in these compounds. The presence of low-lying unfilled molecular orbitals in carboranes suggested that they would be susceptible to reduction, and that disruption of the closed structures to produce opened products could be a consequence. Such open structures could accomodate metal atoms in a manner similar to that previously discussed in the synthesis of metal complexes from opened carborane dianions.

The first successful application of the polyhedral expansion reaction involved the reduction of the eight-vertex closed carborane $C_2B_6H_8$, followed by reaction with Co^{II} and $C_5H_5^-$. Obtained in low yields were two products, formulated as $(C_5H_5)CoC_2B_6H_8$ and $(C_5H_5)_2Co_2C_2B_6H_8$ [23]. The latter species, an unexpected bimetallic complex, had apparently arisen through a double polyhedral expansion (eqn. 9).

$$C_2B_6H_8 \xrightarrow{2Na} C_2B_6H_8^{2-} \xrightarrow[C_5H_5]{Co^{II}} (C_5H_5)Co^{II}C_2B_6H_8^{-} \xrightarrow{2Na}$$

$$(C_5H_5)CoC_2B_6H_8^{3-} \xrightarrow[C_5H_5^-]{Co^{II}} (C_5H_5)_2Co_2C_2B_6H_8^{-} \xrightarrow{[O]} (C_5H_5)_2Co_2C_2B_6H_8 \qquad (9)$$

This promising new method of metallocarborane synthesis was rapidly investigated, employing other carboranes and other metals, and numerous new species were isolated and characterized. Among the more interesting compounds which resulted were the first thirteen-vertex metallocarboranes, formed [24] by the polyhedral expansion of the twelve-vertex starting material, 1,2-$C_2B_{10}H_{12}$ (eqn. 10).

$$C_2B_{10}H_{12} \xrightarrow{2Na^+C_{10}H_8^-} C_2B_{10}H_{12}^{2-} \xrightarrow[C_5H_5^-,\ [O]]{Co^{II}} (C_5H_5)CoC_2B_{10}H_{12} \qquad (10)$$

The red-colored product originally isolated from this preparation was found to undergo thermal isomerization at a surprisingly low temperature. At 60° it produced an orange isomer, while at 80° a red-orange complex isomeric with the previous two compounds could be isolated. The structures of these isomers and the rearrangement process is depicted in Fig. 6 [25].

As portended by the isolation of a bimetallocarborane in the synthesis of $(C_5H_5)CoC_2B_6H_8$, subsequent work has indicated that metallocarboranes may also undergo polyhedral expansion to produce bimetallocarboranes. The 2,3-isomer of $(C_5H_5)CoC_2B_8H_{10}$ may be prepared by the polyhedral expansion of 1,6-$C_2B_8H_{10}$ in the presence of $C_5H_5^-$ and Co^{II} [26]. This substance has a structure isomeric with the $(C_5H_5)CoC_2B_8H_{10}$ prepared by polyhedral contraction [21] of $(C_5H_5)CoC_2B_9H_{11}$ discussed earlier. When 2,3-$(C_5H_5)CoC_2B_8H_{10}$ is reduced by three equivalents of sodium naphthalide (one equivalent to reduce Co^{III} to Co^{II} and the other two equivalents to produce the metallocarborane dianion), and then treated with $C_5H_5^-$ and Co^{II}, a new bimetallocarborane is produced which has the formula $(C_5H_5)_2Co_2C_2B_8H_{10}$ [27]. The polyhedral expansion of

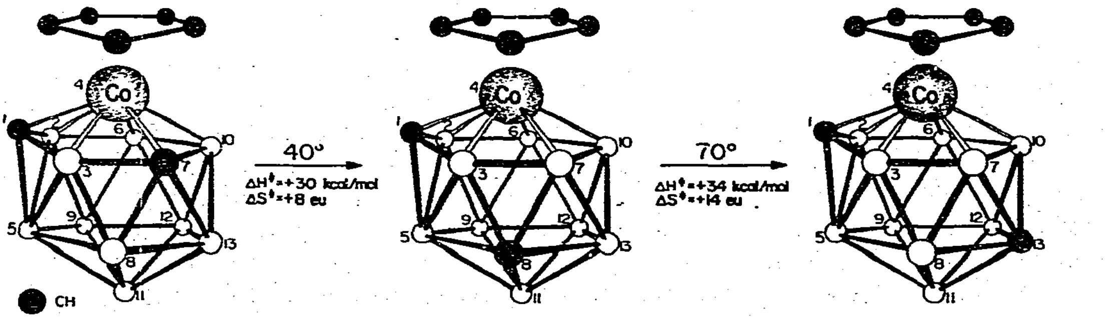

Fig. 6. Rearrangement temperatures, thermochemical parameters, and structural changes in the polyhedral isomerizations of the thirteen-vertex $C_5H_5CoC_2B_{10}H_{12}$ complexes.

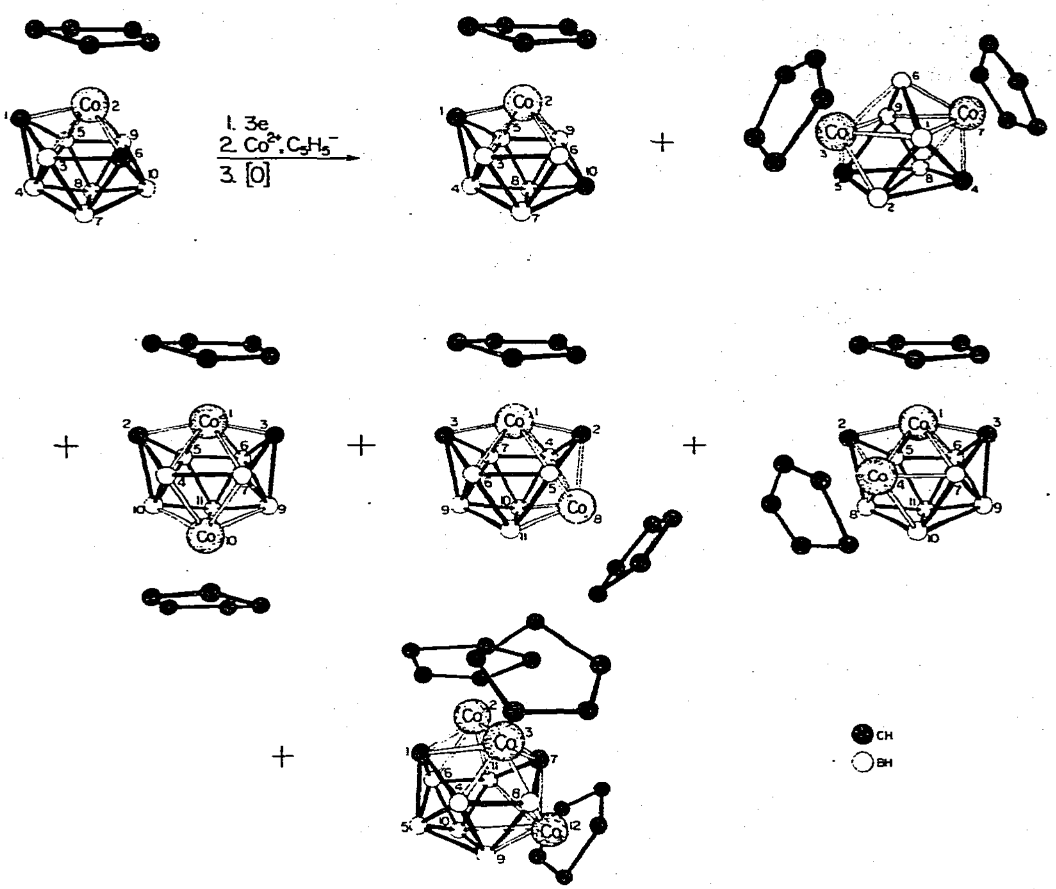

Fig. 7. Starting materials and products from the polyhedral expansion of $C_5H_5Co(1,6\text{-}C_2B_7H_9)$.

2,1,6-$(C_5H_5)CoC_2B_7H_9$ with cobalt(II) and cyclopentadienide ion afforded a number of products (Fig. 7), one of which was a trimetallocarborane [28] formulated as $(C_5H_5)_3Co_3C_2B_7H_9$.

The polyhedral expansion of 4,5-$C_2B_7H_9$ in the presence of Fe^{II} and $C_5H_5^-$ (eqn. 11) afforded three unexpected products [29]. Two of these species had only six boron atoms and were formulated as $(C_5H_5)FeC_2B_6H_8$ and $(C_5H_5)_2Fe_2C_2B_6H_8$. The third product, $(C_5H_5)FeC_2B_8H_{10}$, has one boron atom greater than the number in the starting carborane. No significant amounts of the expected

$$4,5\text{-}C_2B_7H_9 \xrightarrow[(2)\ Fe^{II},\ C_5H_5^-,\ [O]]{(1)\ 2e^-}$$

$$(C_5H_5)FeC_2B_6H_8 + (C_5H_5)_2Fe_2C_2B_6H_8 + (C_5H_5)FeC_2B_8H_{10} \qquad (11)$$

product, $(C_5H_5)FeC_2B_7H_9$, were detected.

The biferracarborane prepared in eqn. 11 was observed to exist in paramagnetic and diamagnetic forms, and a crystallographic study of the diamagnetic species [29] showed it to have a geometry (Fig. 8) different from that previous-

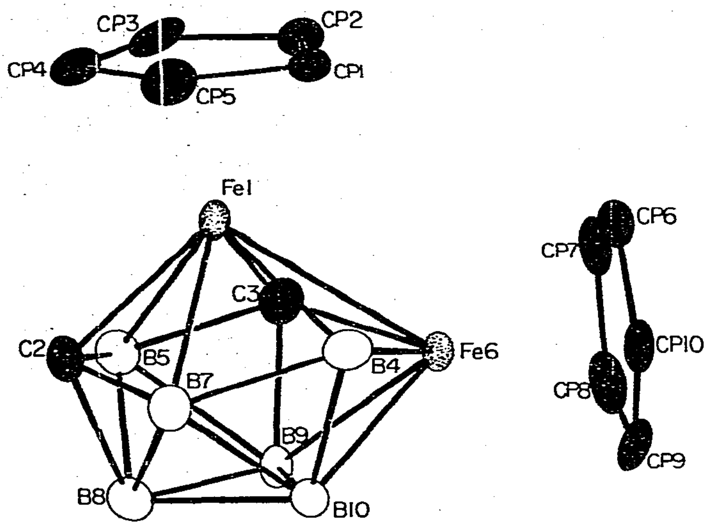

Fig. 8. Novel ten-vertex geometry of diamagnetic $(C_5H_5)_2Fe_2C_2B_6H_8$, prepared by polyhedral expansion of $4,5\text{-}C_2B_7H_9$.

ly observed in ten-vertex borane, carborane and metallocarborane polyhedra. This geometrical change may be due to its electron deficiency; $(C_5H_5)_2$-$Fe_2C_2B_6H_8$ has two fewer electrons than the isoelectronic and geometrically similar series of $B_{10}H_{10}^{2-}$, $C_2B_8H_{10}$ and $(C_5H_5)CoC_2B_7H_9$.

Polyhedral expansion has also been used to produce even larger metallocarboranes. Expansion of the thirteen-vertex $(C_5H_5)CoC_2B_{10}H_{12}$ produced a novel fourteen-vertex species $(C_5H_5)_2Co_2C_2B_{10}H_{12}$, the structure of which is unknown but proposed [30] to be that depicted in Fig. 9.

Polyhedral expansion is not restricted to the introduction of cyclopentadienyl cobalt vertices, as was exemplified earlier in the discussion of the biferra-

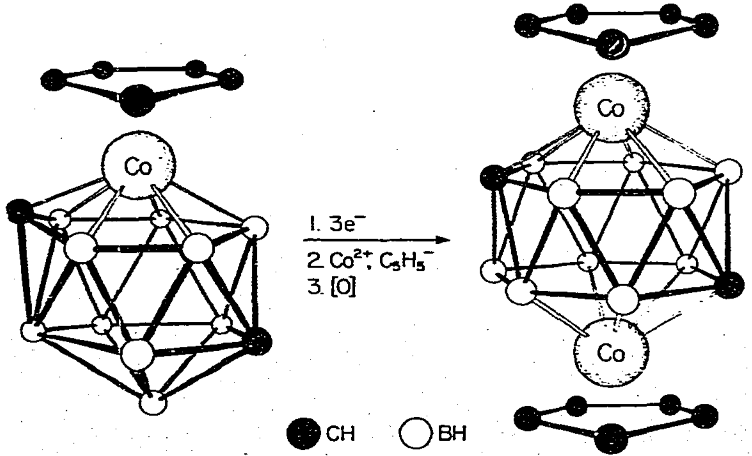

Fig. 9. Synthesis of a fourteen-vertex bimetallocarborane by polyhedral expansion of a thirteen-vertex monometallic complex.

carborane $(C_5H_5)_2Fe_2C_2B_6H_8$. Molybdenum and tungsten carbonyl derivatives have been prepared by the in situ photolysis of solutions of $M(CO)_6$ (M = Mo, W) and $C_2B_{10}H_{12}^{2-}$ [25]. A mixed cobalt—nickel metallocarborane was prepared [31] by the polyhedral expansion of the $(C_5H_5)CoCB_7H_8^-$ ion, itself the result of polyhedral supercontraction mentioned previously. The first titanacarborane was recently prepared [32a] by the reaction of $TiCl_4$ and $C_2B_{10}H_{12}^{2-}$. The resulting complex $(C_2B_{10}H_{12})_2Ti^{2-}$ contains formal Ti^{II} and has a fourteen-electron configuration. Its structure [32b], surprisingly, is quite similar to the eighteen-electron mixed ligand complex $(C_5H_5)CoC_2B_{10}H_{12}$.

Polyhedral subrogation

The earliest polymetallocarboranes were prepared by the degradation, in strong base, of previously formed metallocarboranes in the presence of excess metal ion. This reaction method has been termed "polyhedral subrogation", and has been expanded into a useful preparative method for the preparation of bimetallocarboranes containing similar or different transition metal vertices. Reaction of the thirteen-vertex monometallocarborane $(C_5H_5)CoC_2B_{10}H_{12}$ with base in the presence of Fe^{II} and $C_5H_5^-$ proceeds in good yield to produce a new thirteen-vertex complex [33] formulated as $(C_5H_5)_2CoFeC_2B_9H_{11}$ (eqn. 12 and

$$(C_5H_5)CoC_2B_{10}H_{12} \xrightarrow[C_5H_5^-]{OH^-,\ Fe^{II}} (C_5H_5)_2CoFeC_2B_9H_{11} + B(OH)_3 \qquad (12)$$

Fig. 10). The scope and limitations of this reaction are still being determined, but it is an attractive alternative to the successive application of polyhedral expansion and contraction reactions in the synthesis of metallocarboranes.

Recent advances

An unexpected and potentially valuable new route to polymetallocarboranes was discovered during study of the thermal rearrangements of monometallo-

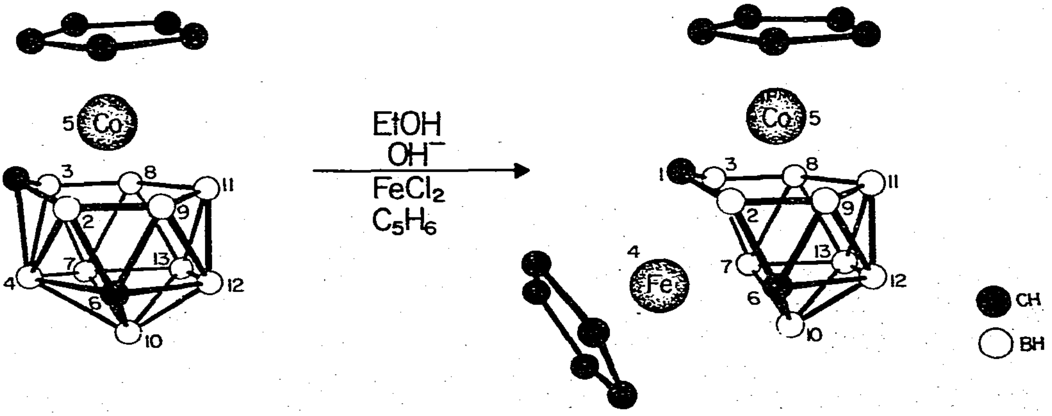

Fig. 10. Polyhedral subrogation of $C_5H_5Co(1,6\text{-}C_2B_{10}H_{12})$ with Fe^{II} to produce a thirteen-vertex cobaltaferracarborane.

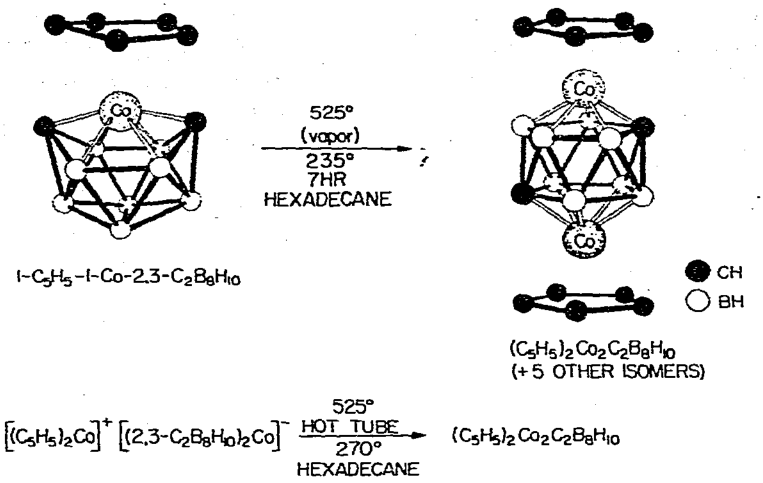

Fig. 11. Thermal metal transfer as a synthetic route to bimetallocarboranes.

carboranes [34]. The 2,3-isomer of $(C_5H_5)CoC_2B_8H_{10}$ was found to give a mixture of products when sublimed through a tube heated to 525°. Among the products was a number of isomeric compounds of the formula $(C_5H_5)_2Co_2C_2B_8H_{10}$ (Fig. 11). Yields of these bimetallic products up to 32%, based on consumed starting materials, were obtained when the reaction was carried out in hexadecane solution at 235°; six isomeric species were obtained. Even more surprising was the discovery that similar products were formed during pyrolysis of the cobalticinium salt of the *commo* metallocarborane (eqn. 13). Yields comparable to

$$(C_5H_5)_2Co^+(C_2B_8H_{10})_2Co^- \xrightarrow[270^\circ,\ \text{in solution}]{525^\circ,\ \text{in vacuo}} (C_5H_5)_2Co_2C_2B_8H_{10} \qquad (13)$$

those found for the neutral species were realized. The driving force for this reaction may be in the attainment of an icosahedral geometry in the products; nevertheless, this is the first example of the facile synthesis of a bimetallocarborane of larger size by pyrolysis of a monometallocarborane, and it is as well the first example of the preparation of a neutral species from pyrolysis of a *commo* complex. The large number of isomeric products arising in this reaction reflects the energy-rich environment in which they were prepared, and indicates that a wealth of new compounds and structures may be forthcoming from a study of the high-temperature behavior of metallocarboranes and their appropriate salts.

Until very recently, the metallocarboranes that had been prepared had only a limited set of other ligands connected to the metal vertex. Primarily the compounds contained either two carborane ligands (*commo* compounds) or were mixed species involving one polyhedral cage and a capping ligand such as cyclopentadienide, although several carbonyl compounds have been reported. These capping ligands were normally chosen on the basis of experimental convenience, and little effort had been expended towards the preparation of metallocarboranes containing other diverse ligands bonded to the metal. The preparation of some new phosphine-substituted metallocarboranes has recently been reported [35]

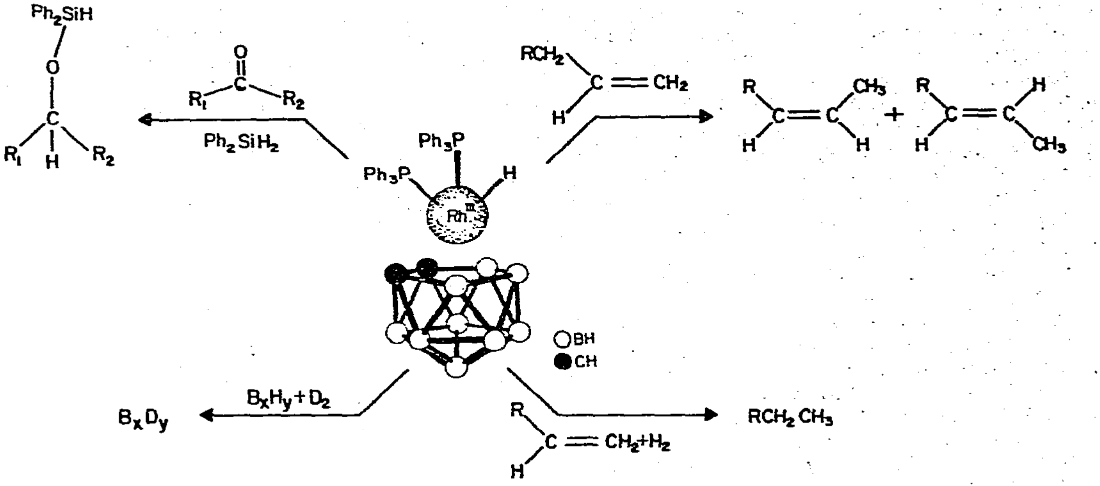

Fig. 12. Structure and catalytic properties of the hydridometallocarborane $(Ph_3P)_2HRh(1,2\text{-}C_2B_9H_{11})$.

however, and these species have proven to be of great interest due to their catalytic properties (Fig. 12).

The reaction of the *nido* monoanion $C_2B_9H_{12}^-$ with certain rhodium or iridium complexes, such as $[(C_6H_5)_3P]_3RhCl$ in methanolic solution, resulted in the isolation, in 80-90% yields, of compounds formulated as $HM[(C_6H_5)_3P]_2$-$C_2B_9H_{11}$(M = Rh, Ir)[35]. Infrared and ^{1}H NMR spectra unambiguously indicated the presence of a metal—hydrogen interaction. Both the rhodium and iridium complexes catalyze the isomerization of terminal olefins, and under a hydrogen atmosphere they catalyze olefinic hydrogenation. They function as effective catalysts for the hydrosilylation of ketones, and are highly active in promoting deuterium exchange at terminal BH vertices [36] in a wide variety of boranes, carboranes and metallocarboranes.

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