NEW ROUTES TO, AND REACTIONS OF POLYHEDRAL TRANSITION METAL CARBORANE SPECIES

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ABSTRACT

While in the past few years many complexes of transition metals and carborane ligands have been described, synthetic routes then available were completely dependent on *nido-* or *arachno*-carborane derivatives containing nine, and seven boron atoms. In this paper we summarize two new methods which lead to transition metal complexes of carborane ligands. The first of these methods (Polyhedral Expansion) was based upon the formal two or four electron reduction of *closo*-$B_nC_2H_{n+2}$ carboranes to form effective ligands containing from six to ten boron atoms. In some cases bimetallic complexes were isolated and polyhedral isomerization reactions were observed in others. The second new method (Polyhedral Contraction) begins with a $B_9C_2H_{11}^{2-}$ ligand complex and leads to complexes of the $B_8C_2H_{10}^{2-}$ and $B_7C_2H_9^{2-}$ ligands by sequential removal of a formal BH^{2+} vertex followed by two-electron oxidation to form the next lowest metal complex of the homologous polyhedral series.

During the past several years a variety of transition metal complexes have been reported which contain ligands derived from the carborane family[1–6]. Those complexes which contain the $B_9C_2H_{11}^{2-}$ dicarbollide[1] ligand have been most extensively investigated due to the availability of the ligand from icosahedral $B_{10}C_2H_{12}$ carborane degradation[7], (*Figure 1*), and the ease with which the dicarbollide and structurally similar complexes are prepared. This paper describes new synthetic routes of wide applicability which provide polyhedral transition metal complexes of carborane derived ligands containing from six to ten boron atoms. This is now possible since representative members of the entire polyhedral $B_nC_2H_{n+2}$ carborane series are now known with $n = 3$ to 10[8]. The synthetic methods which will be outlined here employ two new tactics: electron addition to a polyhedral carborane followed by complexation of the product ion, and degradation of a pre-formed transition metal complex (formal removal of BH^{2+}) followed by oxidation. These methods have been named 'polyhedral expansion' and 'polyhedral contraction,' respectively, since the resulting polyhedral products contain at least one more or one less vertex than that present in the reactant[9, 10]. More than coincidentally, the geometry of the polyhedral product is that of the known

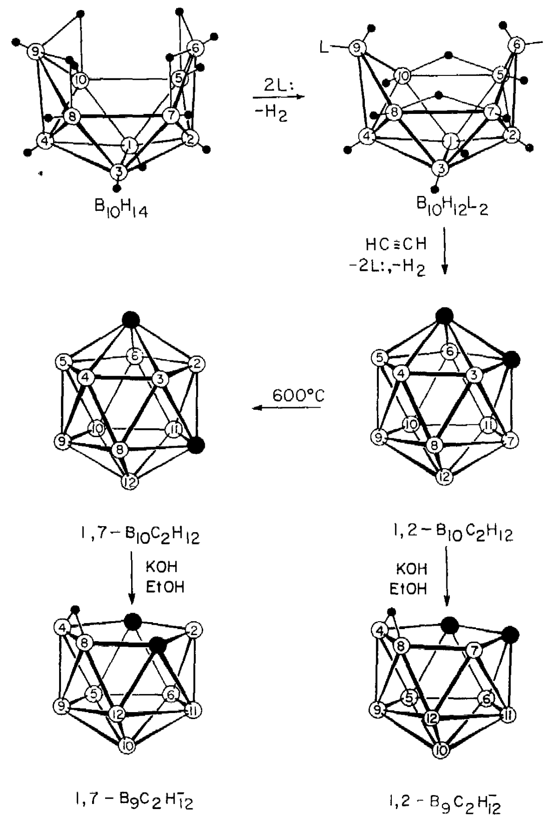

Figure 1. Schematic conversion of $B_{10}H_{14}$ to the isomeric $B_9C_2H_{12}^-$ ions. The 'extra' hydrogen atom of 1,7-$B_9C_2H_{12}^-$ is in a static bridge position between B(4) and B(8) while in the 1,2-$B_9C_2H_{12}^-$ ion it is in rapid equilibrium between the B(4)–B(8) (as depicted) and the B(7)–B(8) positions. Terminal hydrogen atoms have been omitted from the carborane species for clarity

carborane homologue which contains the same number of total vertices, counting each transition metal atom as one vertex.

THE POLYHEDRAL EXPANSION METHOD

Previously, carborane ligands prepared for complexation with transition metal moieties were generated by the removal of one or more protons from a *nido-* or *arachno*-carborane or carborane anion[1, 5]. This method was widely applied to the dicarbollide ion series in which

$$B_9C_2H_{13} \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} B_9C_2H_{12}^- \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} B_9C_2H_{11}^{2-}$$

the isomeric $B_9C_2H_{11}^{2-}$ ligands were formed[1] (*Figure 2*). Since *nido-* and *arachno*-carboranes containing fewer than nine boron atoms are not readily available (with the exception of *arachno*-$B_7C_2H_{13}$[11]), it was a desirable objective to develop a method of ligand formation which used the available $B_nC_2H_{n+2}$ *closo*-carboranes as starting materials. The strategic concept of the new synthetic method was based upon the assumed similarity of the

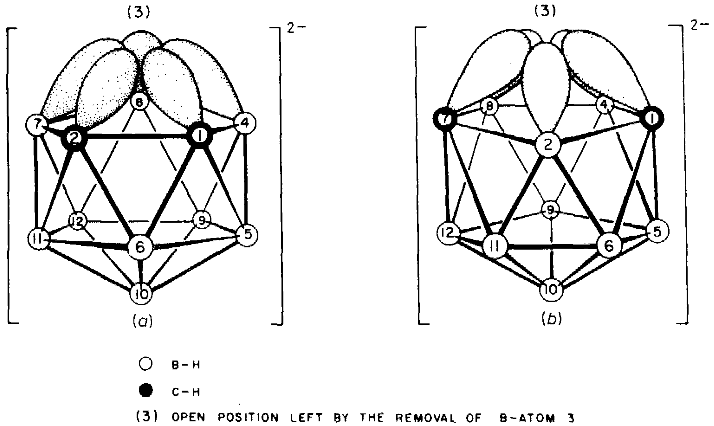

Figure 2. Schematic representation of the sp^3-like bonding orbitals in the (3)-1,2-$B_9C_2H_{11}^{2-}$ ion (*a*); and the (3)-1,7-$B_9C_2H_{11}^{2-}$ ion (*b*)

'aromaticity' of benzenoid hydrocarbons and the members of the $B_nC_2H_{n+2}$ carborane series. The former series of compounds readily accept electrons into their non-bonding and lowest-lying antibonding molecular orbitals[12] and it appeared likely that the *closo*-carboranes would behave similarly. In fact, Grafstein and Dvorak reported electron addition to the icosahedral

$$B_nC_2H_{n+2} + 2e^- \longrightarrow B_nC_2H_{n+2}^{2-}$$

1,2-$B_{10}C_2H_{12}$ carborane as early as 1963[13].

In order to test the polyhedral expansion concept experimentally, the known 1,6-$B_6C_2H_8$ carborane[8] (*Figure 3*) was subjected to reduction with

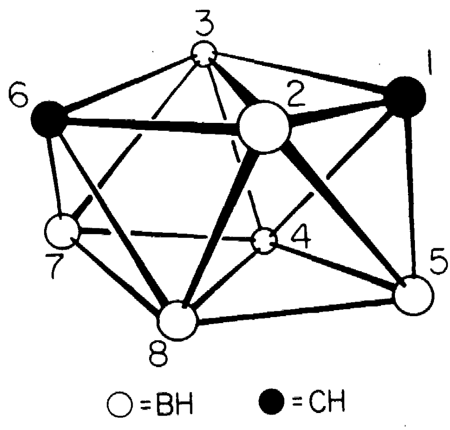

Figure 3. Structure of 1,6-$B_6C_2H_8$

two equivalents of sodium naphthalide in tetrahydrofuran. Electron addition

$$1,6\text{-}B_6C_2H_8 + 2Na \xrightarrow[THF]{C_{10}H_8} Na_2B_6C_2H_8$$

was observed[14]. The reduction product was then treated with sodium cyclopentadienide followed by excess $CoCl_2$. Two major products were isolated and characterized as

$$B_6C_2H_8^{2-} + 2C_5H_5^- + 3Co^{2+} \longrightarrow 2(B_6C_2H_8)Co^{III}(C_5H_5) + Co^0$$

$(B_6C_2H_8)Co^{III}(C_5H_5)$ (*Figure 4*) and $B_6C_2H_8[Co^{III}(C_5H_5)]_2$[14] (*Figure 5*). Nuclear magnetic resonance spectra suggested that $(B_6C_2H_8)Co^{III}(C_5H_5)$

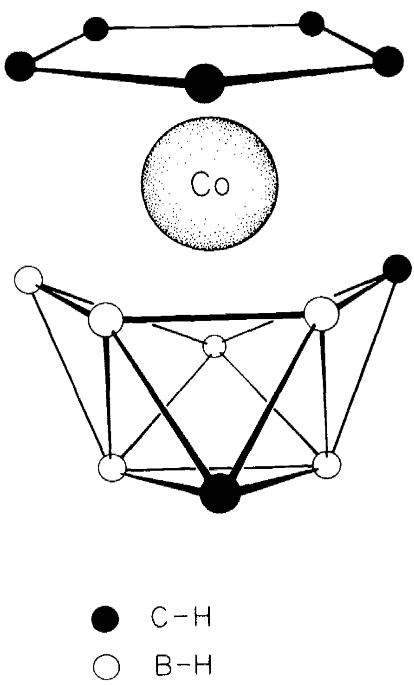

Figure 4. Proposed structure of $(B_6C_2H_8)Co^{III}(C_5H_5)$

was the expected polyhedral expansion product having the tricapped trigonal prism geometry of the known $1,6\text{-}B_7C_2H_9$ carborane[8]. The bimetallic product was assumed to have the bicapped Archimedean anti-prism structure of the known $B_8C_2H_{10}$ carboranes[8]. While initial n.m.r. data supported the latter assignment, the relative positions of the $Co^{III}(C_5H_5)$ vertices were impossible to define. Consequently, a single crystal x-ray diffraction study was carried out which proved the existence of a bicapped Archimedean anti-prism structure[15]. However, the two $Co^{III}(C_5H_5)$ vertices were found to be nearest neighbours, with one $Co^{III}(C_5H_5)$ in each of the equatorial belts

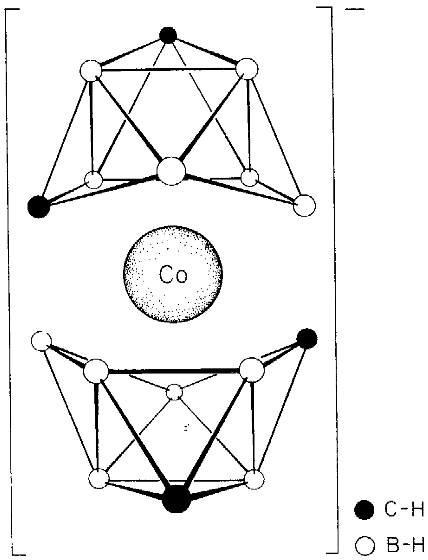

Figure 5. Proposed structure of $[(B_6C_2H_8)_2Co^{III}]^-$ ion

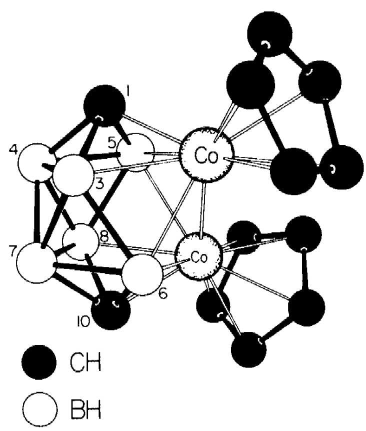

Figure 6. Structure of $(C_5H_5)Co^{III}(B_6C_2H_8)Co^{III}(C_5H_5)$

(*Figure 6*). A possible reaction sequence which leads to $(B_6C_2H_8)[Co^{III}$-$(C_5H_5)]_2$ is illustrated below:

$$1,6\text{-}B_6C_2H_8 + 2e^- \rightarrow B_6C_2H_8^{2-}$$

$$B_6C_2H_8^{2-} + Co^{2+} + C_5H_5^- \rightarrow [(B_6C_2H_8)Co^{II}(C_5H_5)]^-$$

$$[(B_6C_2H_8)Co^{II}(C_5H_5)]^- + 2e^- \rightarrow [(B_6C_2H_8)Co^{II}(C_5H_5)]^{3-}$$

$$[(B_6C_2H_8)Co^{II}(C_5H_5)]^{3-} + 2Co^{2+} + C_5H_5^- \rightarrow (C_5H_5)Co^{III}(B_6C_2H_8)Co^{III}\text{-}(C_5H_5) + Co^0$$

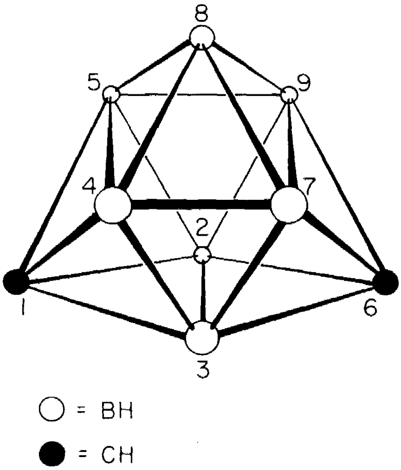

Figure 7. Structure of 1,6-$B_7C_2H_9$

The 1,6-$B_7C_2H_9$ carborane[8] (*Figure 7*) with a tricapped trigonal prism structure was next subjected to the polyhedral expansion reaction sequence[16]. Reduction of 1,6-$B_7C_2H_9$ proceeded in good order and $C_5H_5^-$ followed by $CoCl_2$ were then added. Two isomeric products previously obtained by

$$1,6\text{-}B_7C_2H_9 + 2e^- \rightarrow B_7C_2H_9^{2-}$$

$$2B_7C_2H_9^{2-} + 3Co^{2+} + 2C_5H_5^- \rightarrow (1,6\text{-}B_7C_2H_9)Co^{III}(C_5H_5) + (1,10\text{-}B_7C_2H_9)Co^{III}(C_5H_5) + Co^0$$

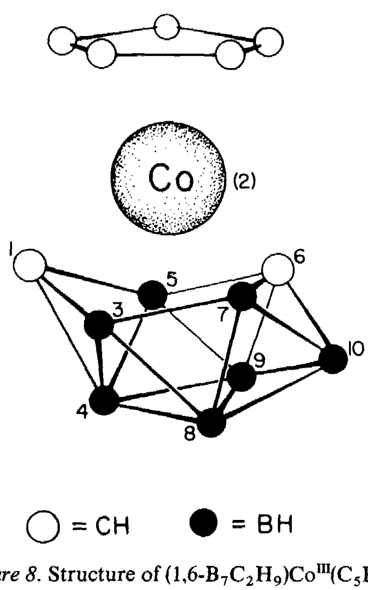

Figure 8. Structure of (1,6-$B_7C_2H_9$)Co^{III}(C_5H_5)

other means were isolated[5, 16]. These compounds were $(1,6\text{-}B_7C_2H_9)\text{-}Co^{III}(C_5H_5)$, (*Figure 8*), and $(1,10\text{-}B_7C_2H_9)Co^{III}(C_5H_5)$. The structures of these products are in agreement with the one-vertex homologous addition principle described above.

Both the 1,6- and 1,10-$B_8C_2H_{10}$ carboranes[8] of bicapped Archimedean anti-prism geometry (*Figure 9*) were subjected to the polyhedral expansion

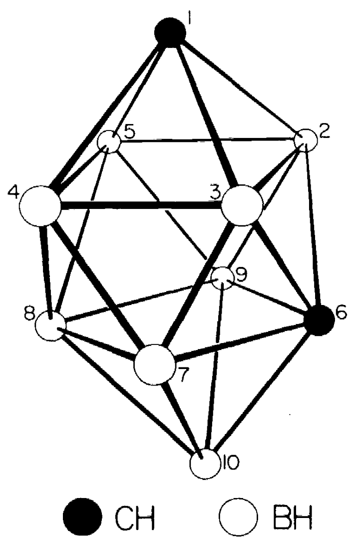

Figure 9. Structure of 1,6-$B_8C_2H_{10}$

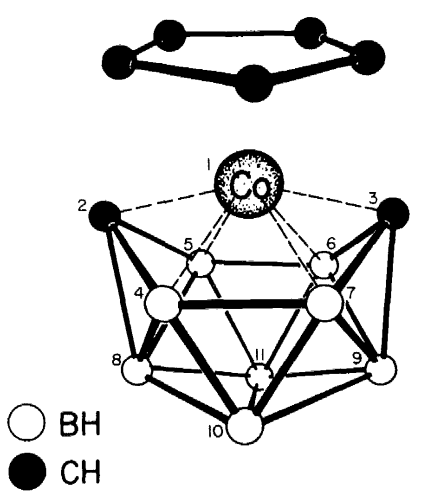

Figure 10. Proposed structure of $(2,3\text{-}B_8C_2H_{10})Co^{III}(C_5H_5)$

sequence using sodium naphthalide, $C_5H_5^-$ and $CoCl_2$ as before. In each

$$B_8C_2H_{10} + 2e^- \rightarrow B_8C_2H_{10}^{2-}$$

$$4B_8C_2H_{10}^{2-} + 3Co^{2+} \rightarrow 2[(B_8C_2H_{10})_2Co^{III}]^- + Co^0$$

$$2B_8C_2H_{10}^{2-} + 2C_5H_5^- + 3Co^{2+} \rightarrow 2(B_8C_2H_{10})Co^{III}(C_5H_5) + Co^0$$

case, two major products were obtained[9]. These products were characterized as $(2,3\text{-}B_8C_2H_{10})Co^{III}(C_5H_5)$, (*Figure 10*), and $[(2,3\text{-}B_8C_2H_{10})_2Co^{III}]^-$. Nuclear magnetic resonance spectra suggested that the 11-vertex structure seen in $2,3\text{-}B_9C_2H_{11}$, (*Figure 11*), was present in both compounds, with

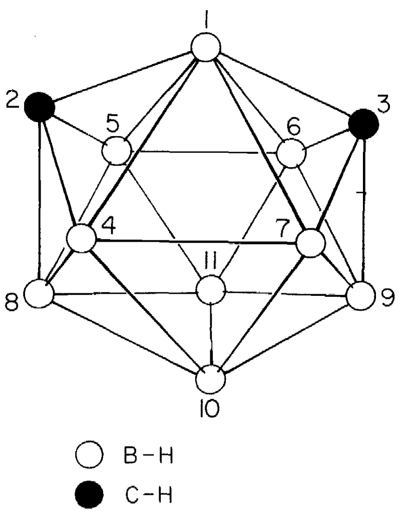

Figure 11. Structure of $2,3\text{-}B_9C_2H_{11}$

the cobalt atom playing the role of the unique 7-coordinate BH group found in the $2,3\text{-}B_9C_2H_{11}$ carborane structure[8]. Quite recently, we have demonstrated[17] that the metallocarborane described above, $(2,3\text{-}B_8C_2H_{10})Co^{III}$-$(C_5H_5)$, reacts with two or more equivalents of sodium naphthalide 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, $[(C_5H_5)Co^{III}]_2[(3,6)\text{-}8,10\text{-}B_8C_2H_{10}]$. A minor product, believed to be a trimetallic species $[(C_5H_5)Co^{III}]_3B_8C_2H_{10}$, was also produced. *Figure 12* presents the proposed structure of the bimetallic compound based upon nuclear magnetic resonance spectra. The proposed structure is similar to that of the dicarbacanastide complex prepared by other means[2].

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

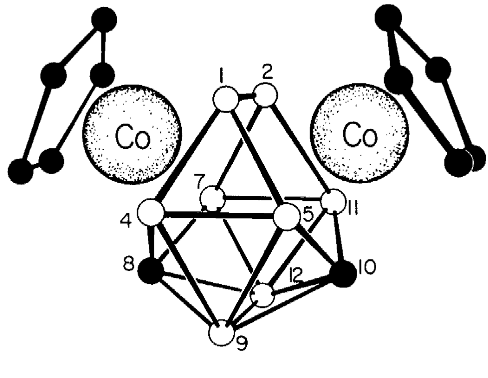

Figure 12. Proposed structure of $(C_5H_5)Co^{III}[(3,6)\text{-}8,10\text{-}B_8C_2H_{10}]Co^{III}(C_5H_5)$

several transition metal vertices. In addition, these synthetic routes 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.

Polyhedral expansion of 2,3-$B_9C_2H_{11}$ carborane (*Figure 11*), should lead to a transition metal complex containing a ligand in the $B_9C_2H_{11}^{2-}$ dicarbollide ion series[1]. Experimentally, this supposition is borne out since

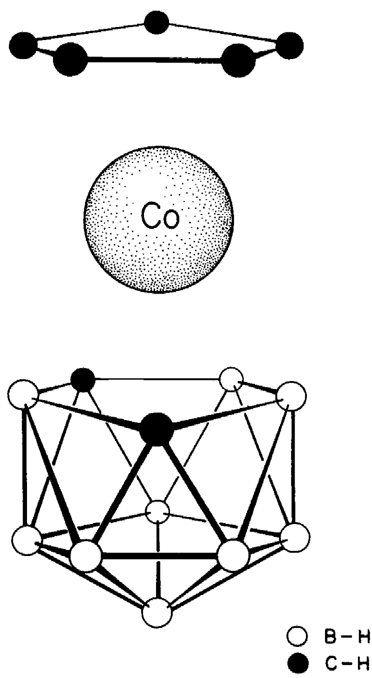

Figure 13. Structure of $(1,7\text{-}B_9C_2H_{11})Co^{III}(C_5H_5)$

$[1,7\text{-}B_9C_2H_{11}]Co^{III}(C_5H_5)$ is a major product of the expansion reaction using two equivalents of sodium, $C_5H_5^-$ and excess $CoCl_2$[16] (*Figure 13*). However, the reaction mixture produced polyhedral complexes which arose from the degradation of the B_9-carborane system. Among these products are found $(2,3\text{-}B_8C_2H_{10})Co^{III}(C_5H_5)$[9], $(1,10\text{-}B_7C_2H_9)Co^{III}(C_5H_5)$ and $(1,6\text{-}B_7C_2H_9)Co^{III}(C_5H_5)$[5] which were described above. The point in the synthesis sequence at which degradation occurs is not known at this time. However, since $[1,7\text{-}B_9C_2H_{11}]Co^{III}(C_5H_5)$ is known to be stable under the work-up conditions employed, it appears reasonable to assume that degradation occurs prior to this point.

REDUCTION AND POLYHEDRAL EXPANSION OF THE ICOSAHEDRAL $1,2\text{-}B_{10}C_2H_{12}$ CARBORANE

In 1963 Grafstein and Dvorak reported the reduction of the icosahedral $1,2\text{-}B_{10}C_2H_{12}$ with sodium metal in liquid ammonia solution[13]. Similar

$$\underset{B_{10}H_{10}}{R-C-CH} + 2Na \xrightarrow{NH_3} [Na_2(RC_2B_{10}H_{11})\ x\ NH_3]$$

$$[Na_2(RC_2B_{10}H_{11})\ x\ NH_3] \xrightarrow{H_2O} Na^+RC_2B_9H_{11}^-$$

reduction reactions have been observed with the 1,7- and $1,12\text{-}B_{10}C_2H_{12}$ isomers[18–20]. The resulting $B_{10}C_2H_{12}^{2-}$ ions have a unique chemistry of

$$1,2\text{-}, 1,7\text{-}, 1,12\text{-}B_{10}H_{10}C_2H_2 \underset{KMnO_4(NH_3)}{\overset{2Na(NH_3)}{\rightleftarrows}} B_{10}H_{10}C_2H_2^{2-}2Na^+ \qquad \text{(Refs. 18–20)}$$

$$o\text{-}B_{10}C_2H_{12} + 2Na \xrightarrow[C_{10}H_8]{THF} Na_2B_{10}C_2H_{12} \qquad \text{(Ref. 25)}$$

their own which will not be discussed at this time, except to say that the $B_{10}C_2H_{12}^{2-}$ ions may be protonated to yield $B_{10}C_2H_{13}^-$ ions[18–21] and oxidized to $B_{10}C_2H_{12}$[18–20] isomers with and without polyhedral rearrangement.

The icosahedron has been looked upon as the basic (and largest) building block of borane chemistry. Fragments of the icosahedron display the geometry of many of the lower boranes and the $B_{12}H_{12}^{2-}$[22], $B_{11}CH_{12}^-$[23] and $B_{10}C_2H_{12}$[24] species are the largest known regular polyhedral structures. We have attacked this assumed sacrosanct status of the icosahedron by use of the polyhedral expansion reaction.

The dianion formed by two-electron addition to $1,2\text{-}B_{10}C_2H_{12}$ (*Figure 14*) in tetrahydrofuran was treated with the normal expansion reagents; $C_5H_5^-$ and excess $CoCl_2$[25,26].

$$2Na_2B_{10}C_2H_{12} + 2NaC_5H_5 + 3CoCl_2 \xrightarrow[0°C]{THF} 2C_5H_5CoB_{10}C_2H_{12} + 6NaCl + Co^0$$

Product isolation afforded several complexes; $(1,2\text{-}B_9C_2H_{11})Co^{III}(C_5H_5)$, (1 per cent), $(7,8\text{-}B_{10}C_2H_{12})Co^{III}(C_5H_5)$, (50 per cent), (*Figure 15*) and

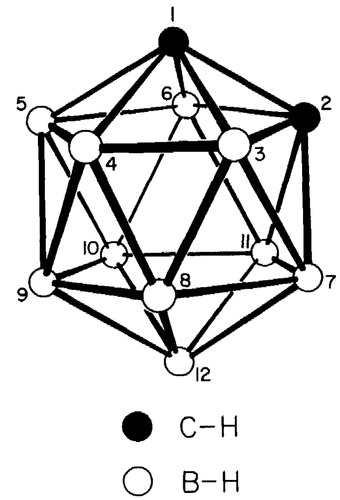

Figure 14. Structure of 1,2-$B_{10}C_2H_{12}$

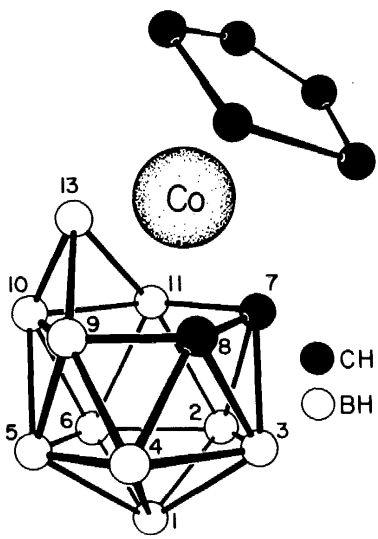

Figure 15. Proposed structure of (7,8-$B_{10}C_2H_{12}$)Co^{III}(C_5H_5)

[(7,8-$B_{10}C_2H_{12}$)$_2Co^{III}$]$^-$, (12 per cent), (*Figure 16*).

While the structure of the uncomplexed $B_{10}C_2H_{12}^{2-}$ ligand is not known, ^{11}B and ^{1}H nuclear magnetic resonance studies have provided a rationale for the structure of the uncomplexed ligand. *Figure 15* represents the proposed structure of the (7,8-$B_{10}C_2H_{12}$)(C_5H_5)Co^{III} complex initially isolated from the reaction mixture[24]. It has been experimentally demonstrated that the pictured complex thermally rearranges to two other isomers in a sequential manner[25].

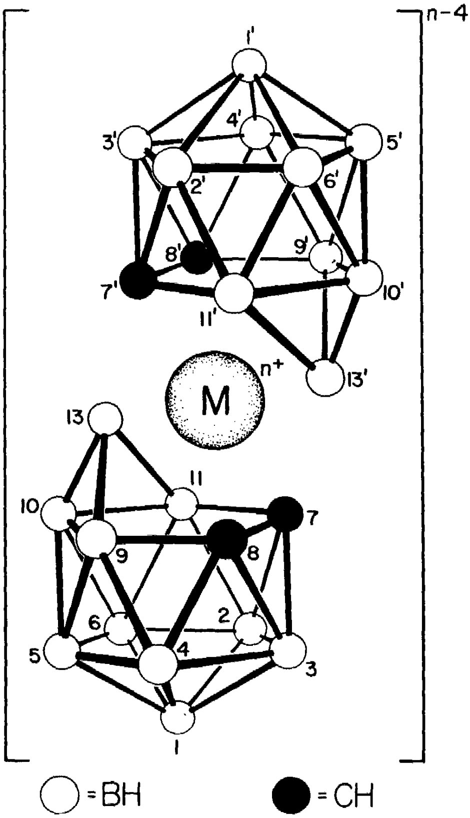

Figure 16. Proposed structure of $[(7,8\text{-}B_{10}C_2H_{12})_2Co^{III}]^-$

$$\underset{\text{red}}{(C_5H_5)Co^{III}(7,8\text{-}B_{10}C_2H_{12})} \xrightarrow{\Delta} \underset{\text{orange}}{(C_5H_5)Co^{III}(B_{10}C_2H_{12})} \xrightarrow{\Delta} \underset{\text{amber}}{(C_5H_5)Co^{III}(B_{10}C_2H_{12})}$$

The evidence available, including preliminary x-ray diffraction results[27] strongly suggest that the formal cobalt(III) ion present in these new complexes occupies a vertex position in a 13-vertex polyhedral array (*Figure 15*). This being the case, the icosahedron no longer represents the largest known polyhedron possible among the metallocarboranes.

THE POLYHEDRAL CONTRACTION METHOD

Unlike the reactions described above, in which the starting materials are carborane anions and *closo*-carboranes, polyhedral contraction involves reactions in which a metallocarborane is converted to its next lowest homologue by degradation and oxidation, according to the general equation:

$$[LCo^{III}(B_nC_2H_{n+2})]^z \xrightarrow[2)\ -2e^-]{1)\ -BH^{2+}} [LCo^{III}(B_{n-1}C_2H_{n+1})]^z$$

where L = $C_5H_5^-$, $z = 0$ and $n = 8$ or 9, or L = (3)-1,2-$B_9C_2H_{11}^{2-}$, $z = -1$ and $n = 8$ or 9[27,28]. This reaction affords a polyhedral metallocarborane with one less vertex than its precursor, specifically:

$$(1,2\text{-}B_9C_2H_{11})Co^{III}(C_5H_5) \xrightarrow[2)\ -2e^-]{1)\ -BH^{2+}} (2,4\text{-}B_8C_2H_{10})Co^{III}(C_5H_5) \qquad (\textit{Figure 17})$$

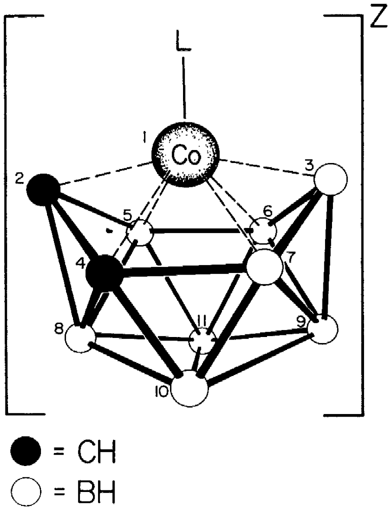

Figure 17. Proposed structure of (2,4-$B_8C_2H_{10}$)Co^{III}L; L = $B_9C_2H_{11}^{2-}$, $C_5H_5^-$

$$(2,4\text{-}B_8C_2H_{10})Co^{III}(C_5H_5) \xrightarrow[2)\ -2e^-]{1)\ -BH^{2+}} (6,7\text{-}B_7C_2H_9)Co^{III}(C_5H_5) \qquad (\textit{Figure 18})$$

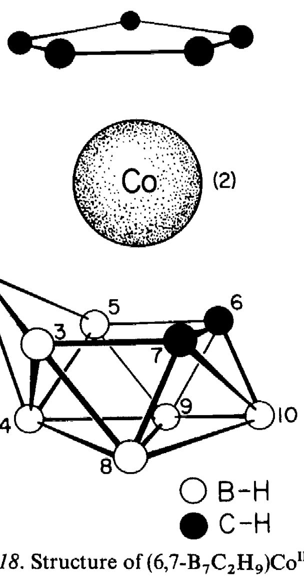

Figure 18. Structure of (6,7-$B_7C_2H_9$)Co^{III}(C_5H_5)

In addition to providing metallocarboranes containing two different carborane ligands, this reaction demonstrates that the metallocarborane polyhedron has a chemistry in its own right, over and above that of terminal B–H substitution[1, 29–31].

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