RECENT DEVELOPMENTS IN THE CHEMISTRY OF POLYHEDRAL COMPLEXES DERIVED FROM METALS AND CARBORANES

M. F. HAWTHORNE

*Department of Chemistry, The University of California,
Los Angeles, California 90024, USA*

ABSTRACT

The formation of icosahedral carboranes, their degradation to dicarbollide ions, and formation of metallocarboranes from these ions are briefly reviewed. The bis(dicarbollyl) cobalt(III) anion reacts with cobalt hydroxide to produce bi- and tri-metallic polyhedral complexes incorporating the $(3\ 6)$-$1,2$-$B_8C_2H_{10}^{4-}$ ion and possessing novel structures. The strong acid (3)-$1,2$-$B_9C_2H_{13}$ reacts with $R_3M(R = \text{alkyl}, M = \text{Al or Ga})$ in two steps, first to give a dialkylmetal-substituted carborane, (3)-$1,2$-$B_9C_2H_{12}MR_2$. X-Ray diffraction and variable temperature n.m.r. (250 MHz ^{1}H and 80 MHz ^{11}B) show this carborane is bonded by B—H—Al bridge bonds and undergoes rapid tautomeric re-arrangement at room temperature. It reacts further to form a monoalkylmetal-substituted carborane, (3)-$1,2$-$B_9C_2H_{11}MR$. This compound rearranges at 400°C to afford (3)-$1,7$-$B_9C_2H_{11}MR$. Thermal rearrangement also occurs in $(\pi$-$C_5H_5)\,Co[\pi$-(3)-$1,2$-$B_9C_2H_{11}]$; six new isomers which result from migration of carbon atoms over the polyhedron have been isolated and characterized. Products from the thermal rearrangement of $(\pi$-$C_5H_5)Co[\pi$-(3)-$1,2$-$B_9C_2H_9(CH_3)_2]$ and $(\pi$-$C_5H_5)Co[\pi$-(3)-$1,2$-$B_9C_2H_9(CH_2)_3]$ are also reported. Structural elucidation and mechanistic implications of these rearrangements are discussed. Several closed polyhedral carboranes undergo an apparent reductive opening to afford dianions which, upon subsequent reaction with $CoCl_2$ and $C_5H_5^-$, form new closed polyhedra which incorporate the metal; these derivatives have the overall geometry of the next highest homologue of the known polyhedral species. Complexes formed in this manner from $1,6$-$B_6C_2H_8$, $1,6$-$B_8C_2H_{10}$, and $1,2$-$B_{10}C_2H_{12}$ are reported. The red 13-atom polyhedral complex $(\pi$-$C_5H_5)Co(7,8$-$B_{10}C_2H_{12})$ undergoes thermal rearrange-ment to two new isomers, orange and red-orange, which probably differ only in positions of the carbons in the polyhedron.
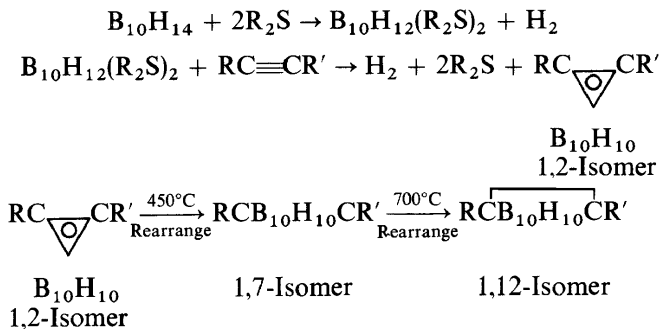

In 1965[1] the first examples of bonding between a transition metal and the two isomeric dicarbollide ions, $B_9C_2H_{11}^{2-}$ were reported. The latter ions are eleven-particle icosahedral fragments which accept the transition metal in such a manner as to complete the icosahedron. The interaction of the metal with the carborane fragment may be described as similar to the π-bonding found in ferrocene[2] and related species. The early work in this area has been

summarized elsewhere. Consequently, this paper will include only a brief summary of the essential features of the chemistry and emphasize more recent results.
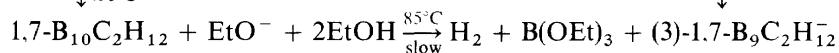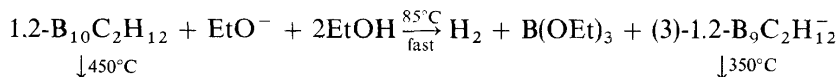
ICOSAHEDRAL CARBORANES AND THE DICARBOLLIDE IONS

The carborane ligands described in this paper are all derived from the isomeric 1,2- and 1,7-dicarba-*closo*-dodecaborane(12) species[3]. The latter compounds are easily prepared from an alkyne and a $B_{10}H_{12}(\text{ligand})_2$ species which, in turn, is obtained from decaborane-14 and a neutral ligand such as acetonitrile or a dialkyl sulphide. The R and R' groups attached to the alkyne system may be a combination of hydrogen, alkyl, aryl or substituted alkyl groups.

$$B_{10}H_{14} + 2R_2S \rightarrow B_{10}H_{12}(R_2S)_2 + H_2$$

$$B_{10}H_{12}(R_2S)_2 + RC\equiv CR' \rightarrow H_2 + 2R_2S + RC\underset{\bigtriangledown}{}CR'$$

$$\begin{array}{c} B_{10}H_{10} \\ \text{1,2-Isomer} \end{array}$$

$$RC\underset{\bigtriangledown}{}CR' \xrightarrow[\text{Rearrange}]{450°C} RCB_{10}H_{10}CR' \xrightarrow[\text{Rearrange}]{700°C} R\overline{CB_{10}H_{10}C}R'$$

$$\begin{array}{ccc} B_{10}H_{10} & \text{1,7-Isomer} & \text{1,12-Isomer} \\ \text{1,2-Isomer} & & \end{array}$$

The rearrangement of the 1,2- to the 1,7-$B_{10}C_2H_{12}$ system proceeds smoothly[4] at elevated temperatures and is somewhat dependent upon the nature of the substituents attached to carbon. *Figure 1* presents the icosahedral structure[5]
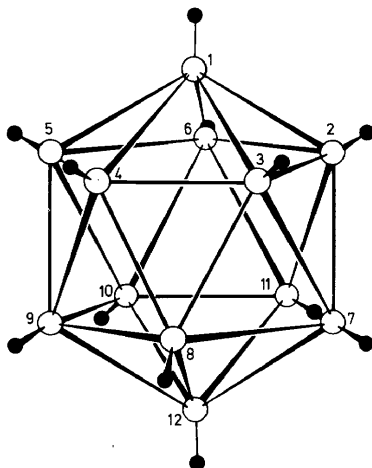
and .he numbering system[6] associated with the 1,2- and 1,7-$B_{10}C_2H_{12}$ isomers. Although the icosahedral carboranes are greatly stabilized by electron delocalization and undergo the reactions typical of aromatic organic species, they are rather easily attacked by bases such as ethanolic ethoxide ion[7, 8]. The 1,2- and 1,7-$B_{10}C_2H_{12}$ carboranes and their C-substituted derivatives form the correspondingly substituted (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions, respectively.

$$1.2\text{-}B_{10}C_2H_{12} + EtO^- + 2EtOH \xrightarrow[\text{fast}]{85^\circ C} H_2 + B(OEt)_3 + (3)\text{-}1.2\text{-}B_9C_2H_{12}^-$$

$$\downarrow 450^\circ C \qquad\qquad\qquad\qquad\qquad\qquad \downarrow 350^\circ C$$

$$1.7\text{-}B_{10}C_2H_{12} + EtO^- + 2EtOH \xrightarrow[\text{slow}]{85^\circ C} H_2 + B(OEt)_3 + (3)\text{-}1.7\text{-}B_9C_2H_{12}^-$$

The thermal rearrangement of the (3)-1,2-$B_9C_2H_{12}^-$ system to its (3)-1,7-isomer is observed[8] at temperatures near 350°C. A rationale of the lability
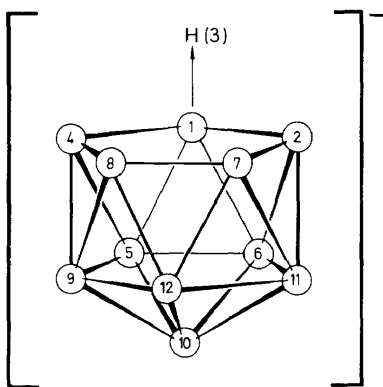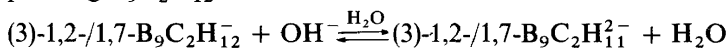

Figure 2. Framework of the $B_9C_2H_{12}^-$ ions

of the icosahedral carboranes to base may be derived from the fact that the carbon atoms present in the icosahedral carboranes bear partial positive charges in the ground state[9, 10] and thereby activate the two equivalent boron atoms which are nearest neighbours for nucleophilic attack. The rather general rearrangement of 1,2- to 1,7-isomers is probably a manifestation of the mutual coulombic repulsion of the two carbon atoms. *Figure 2* presents a schematic drawing of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions which were generated in both instances by the removal of the BH unit at vertex 3. The removal of this boron atom is denoted by the prefix (3)- in all formulae[10]. The twelfth hydrogen atom required by the empirical formula $B_9C_2H_{12}^-$ has not been observed spectroscopically. It is a reasonable assumption that this 'extra' hydrogen is in rapid motion about the periphery of the open pentagonal face of the ion. A more novel situation, depicted in *Figure 2*, places the 'extra' hydrogen atom in the centre of the pentagonal face. Such a model requires that the hydrogen atom be bonded to the pentagonal face by virtue of a six-centre molecular orbital.

Chemical evidence related to the character of the 'extra' hydrogen atom present in the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions was obtained from the observed reaction of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions with strong bases[1a, 1b] such as sodium hydride in tetrahydrofuran to produce the (3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$ ions, respectively.

$$(3)\text{-}1,2\text{-}/1,7\text{-}B_9C_2H_{12}^- + NaH \xrightarrow{THF} H_2 + Na^+ + (3)\text{-}1,2\text{-}/1,7\text{-}B_9C_2H_{11}^{2-}$$
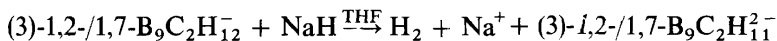
Similarly, the (3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$ ions appear to be present in very concentrated (5–10N) aqueous hydroxide ion solutions containing the corresponding $B_9C_2H_{12}^-$ ion[11].

$$(3)\text{-}1,2\text{-}/1,7\text{-}B_9C_2H_{12}^- + OH^- \underset{H_2O}{\rightleftharpoons} (3)\text{-}1,2\text{-}/1,7\text{-}B_9C_2H_{11}^{2-} + H_2O$$

The results of x-ray crystallographic studies[12] carried out with a variety of metal complexes of the (3)-1,2-$B_9H_2H_{11}^{2-}$ ion coupled with simplified molecular orbital theory suggests that the (3)-1,2- and (3)-1,7-$B_9C_2H_{21}^{2-}$ ions resemble the simplified structure presented in *Figure 3*. In this drawing, the
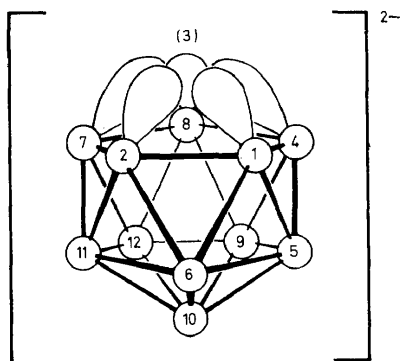
Figure 3. Framework of the $B_9C_2H_{11}^{2-}$ ions showing sp^3 orbitals at the open face

five sp^3 (assumed hybridization) orbitals associated with the atoms of the pentagonal face are directed toward the empty vertex at position 3. Electron balance and molecular orbital arguments place six electrons in these five atomic orbitals. Such an arrangement allows the generation of three bonding and two anti-bonding molecular orbitals reminiscent of the cyclopentadienide ion[2]. Consequently, the experimental test of this proposed similarity led to the initial discovery of a new class of carborane derivative in which the transition metal completes one or two icosahedra and at the same time resembles the transition metal present in π-bonded cyclopentadienyl derivatives. The preparative methods employed in the synthesis of these new derivatives are illustrated by the following representative equations. Each
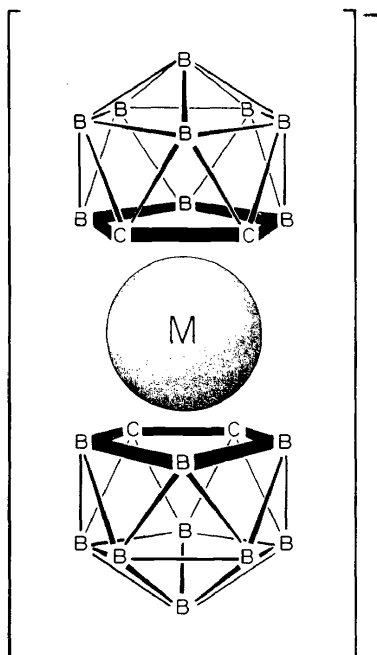
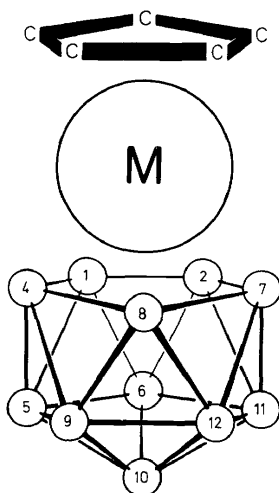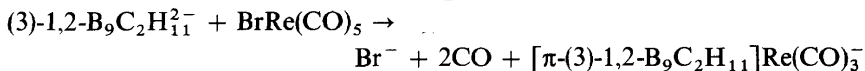*Figure 4.* Simplified structure of $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2M$ complexes

Figure 5. Simplified structure of $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]M[\pi\text{-}C_5H_5]$ complexes

551

of these reactions was carried out in tetrahydrofuran solution and the products isolated in good yield.

$$2(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + Fe^{2+} \rightarrow [\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe^{2-}$$

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + C_5H_5^- + Fe^{2+} \rightarrow [\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Fe[\pi\text{-}C_5H_5]^-$$

$$\downarrow_{-e^-} \qquad\qquad \uparrow_{+e^-}$$

$$[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Fe[\pi\text{-}C_5H_5]$$

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + BrRe(CO)_5 \rightarrow$$

$$Br^- + 2CO + [\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Re(CO)_3^-$$
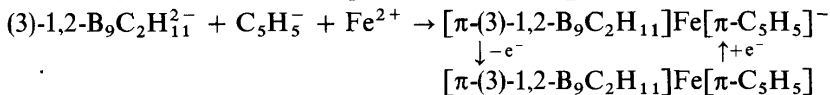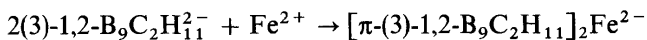
The experimentally determined structures of these three representative systems[12] are presented in *Figures 4, 5* and *6*. In each case the (3)-1, 2-$B_9C_2H_{11}^{2-}$ ligand is symmetrically bonded to the metal as in the corresponding π-cyclopentadienyl derivatives. In fact, the related bond distances between metal and ligand cannot be distinguished in the two cases!
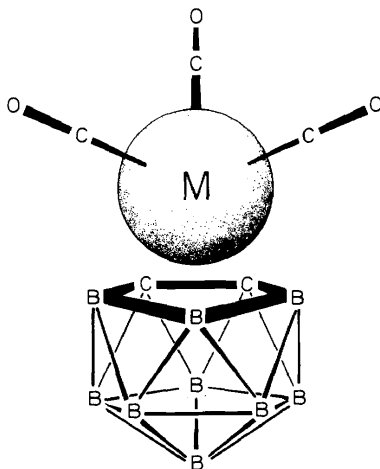
Figure 6. Simplified structure of $[\pi\text{-}(3)\text{-}B_9C_2H_{11}]M(CO)_3$ complexes

Additional research in this area has led to the preparation of the very stable (3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{2-}$ derivatives[1b] of formal cobalt(III) analogous to the two iron systems presented above. Many other metals are capable of forming complexes of this type and include chromium, palladium and nickel. Finally, it has proved possible[11] to prepare complexes of iron, cobalt, nickel, etc. in 80–90 per cent yield by reacting the metal halide with strong basic aqueous solutions of the (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions. In these cases, it appears as though the di-negative ligand anions are generated according to the equilibrium presented above and that these dianions scavenge metal ions more effectively than does hydroxide ion.

POLYMETAL POLYHEDRAL COMPLEXES

Some time ago it was observed that the preparation of certain (3)-1,2-dicarbollide metal complexes often produced coloured byproducts when these preparations were carried out in aqueous media. Subsequent work revealed that these unknown species resulted from the reaction of the normal (3)-1,2-dicarbollide complexes with bases and added Co^{2+} ion in the presence of protonic solvents such as ethanol or water. Proceeding in this manner and using the $[\pi\text{-(3)-1,2-}B_9C_2H_{11}]_2Co^-$ ion as a model, it proved possible to isolate a very stable, bright red dianion[13] having the apparent composition

○ B
● C
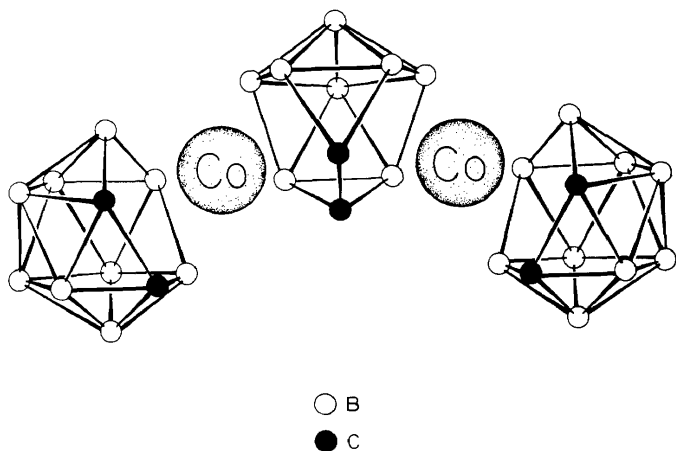
Figure 7. Simplified structure of $[\pi\text{-(3)-}B_9C_2H_{11}Co]_2B_8C_2H_{10}^{2-}$

$B_{26}C_6H_{32}Co_2^{2-}$. The ^{11}B n.m.r. spectrum of this ion was complex, but the ^1H n.m.r. spectrum revealed two types of carborane CH units present in a 2:1 ratio. A recently completed x-ray diffraction study[14] has confirmed the structure shown in *Figure 7*. The central, bifunctional ligand in this unusual structure might be considered to be a 'double-barrelled' π-bonding ligand which functions in much the same manner as the (3)-1,2-dicarbollide ion does. The formation of this unusual ligand must arise through base degradation of the (3)-1,2-dicarbollyl complex resulting in the formal loss of a BH^{2+} unit. The intermediate is then captured by Co^{2+} and a (3)-1,2-dicarbollide ion present in solution. Other capture processes are equally possible. We have suggested that the $B_8C_2H_{10}^{4-}$ ligand shown in *Figure 8* resembles a basket, and we have accordingly given it the trivial name (3,6)-1,2-dicarbacanastide ion derived from the Spanish noun meaning basket, 'canasta.' The prefix numerals have the same meaning as those employed in the trivial dicarbollide nomenclature.
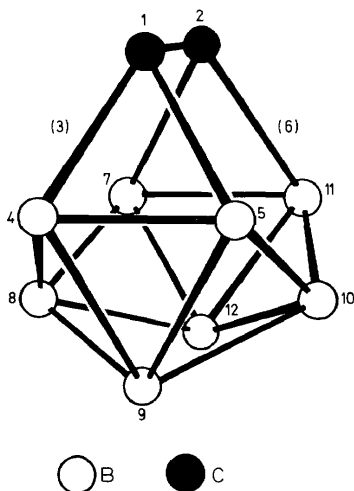
553

Figure 8. Simplified drawing of the (3,6)-1,2-dicarbacanastide ion having −4 charge

Further work with the aqueous base degradation reaction of $[(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co^-$ ion has led to the isolation of a second complex which contains three formal Co^{3+} ions, two (3,6)-1,2-dicarbacanastide ions and a pair of (3)-1,2-dicarbollide ions which function as chain-capping groups[15a, 15b]. This interesting structure is shown in *Figure 9*.
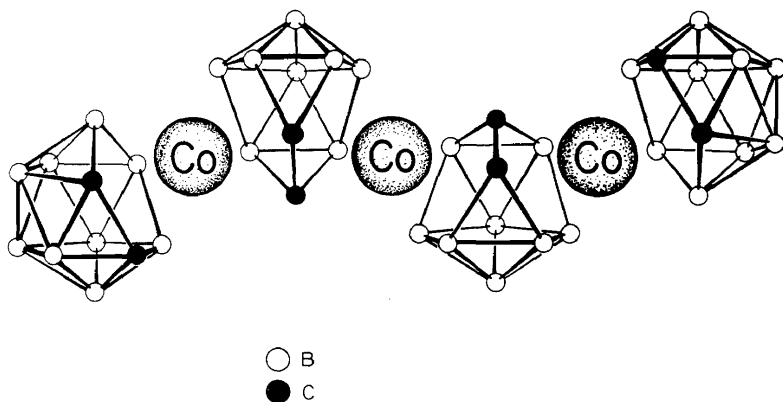

Figure 9. Simplified drawing of $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}Co\text{-}\pi\text{-}(3,6)\text{-}1.2\text{-}B_8C_2H_{10}]_2Co^{3-}$

ALUMINIUM DERIVATIVES OF THE DICARBOLLIDE IONS

In 1968 Mikhailov and Potapova[16] briefly reported the preparation of an aluminium derivative of the (3)-1,2-dicarbollide ion which was not structurally characterized. Their reaction sequence involved ethylaluminium dichloride, the (3)-1,2-dicarbollide ion and tetrahydrofuran solvent. The product obtained contained two molecules of tetrahydrofuran which were presumably complexed to an aluminium atom located at an icosahedral vertex.

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + Cl_2AlC_2H_5 \xrightarrow[-40^{\circ}C]{THF} 2Cl^- + B_9C_2H_{11}AlC_2H_5 \cdot 2THF$$
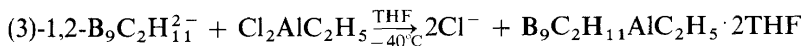
Our approach to this problem[17-19] was somewhat different in that it involved the reaction of the acidic $(3)\text{-}1,2\text{-}B_9C_2H_{13}$ species[20] with trialkyl-aluminium and gallium derivatives with identical results in both cases. The $(3)\text{-}1,2\text{-}B_9C_2H_{13}$ reactant was conveniently generated by the acidification of the $(3)\text{-}1,2\text{-}B_9C_2H_{12}^-$ ion under anhydrous conditions.

$$(3)\text{-}1,2\text{-}B_9C_2H_{12}^- + HCl \xrightarrow{Et_2O} (3)\text{-}1,2\text{-}B_9C_2H_{13} + Cl^-$$
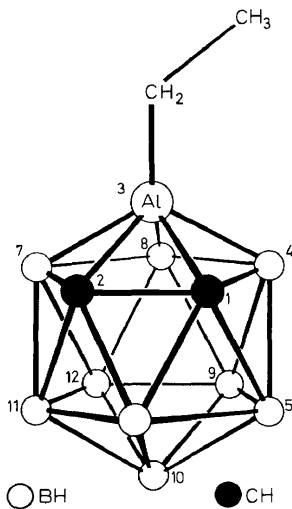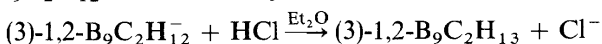
Figure 10. Simplified drawing of $\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}Al(C_2H_5)$

Subsequent reaction with the trialkylaluminium or gallium derivative in benzene solution proceeded in two distinct steps, each step involving the protolysis of an alkyl carbon–metal bond.

$$B_9C_2H_{13} + AlR_3 \rightarrow R_2AlB_9C_2H_{12} + RH$$

$$R_2AlB_9C_2H_{12} \rightarrow RAlB_9C_2H_{11} + RH$$
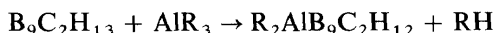
The product, $C_2H_5AlB_9C_2H_{11}$, was shown by x-ray crystallographic studies[17] to be the icosahedral species shown in Figure 10 which could be

555

converted to the tetrahydrofuran complex of Mikhailov and Potapova[16] by recrystallization from that solvent.

X-Ray diffraction studies of $(CH_3)_2AlB_9C_2H_{12}$[18] led to the discovery of a structure which appeared to have the aluminium atom bonded to the (3)-1,2-dicarbollide ion by B—H—Al bridge bonds as shown in *Figure 11*. This contention was supported[19] by [11]B n.m.r. studies at 80 MHz and proton n.m.r. studies at 250 MHz. The observed spectra were seen to be temperature
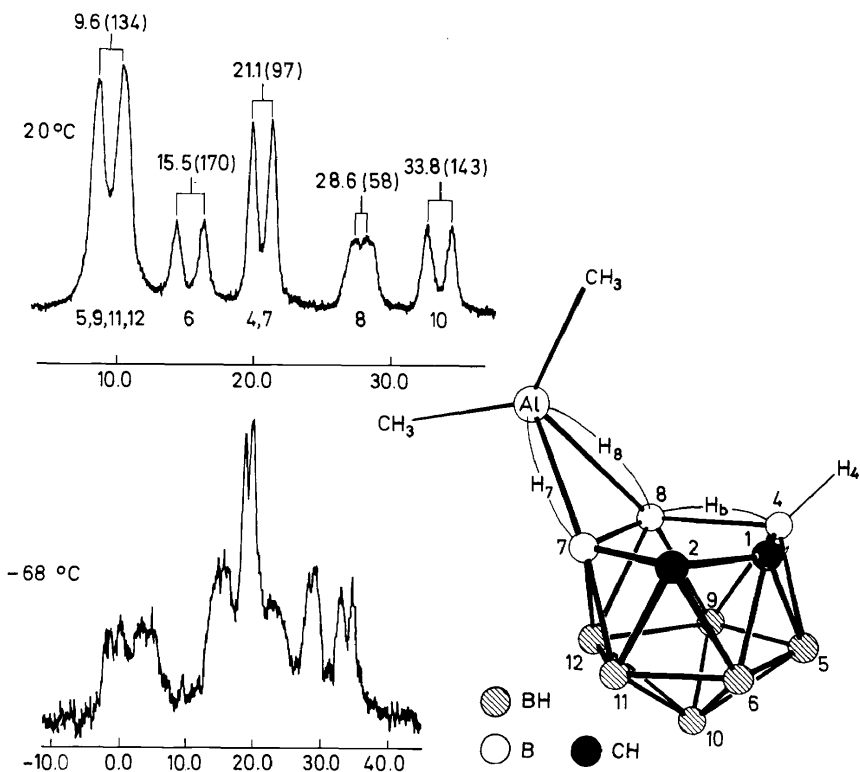
Figure 11. Structure of the (3)-1,2-$B_9C_2H_{12}Al(CH_3)_2$ complex and its [11]B n.m.r. spectrum at 20°C and −68°C. Structure shown represents one tautomer frozen at −68°C

dependent and in agreement with the proposed structure at −20°C or lower (*Figure 11*). At room temperature, the n.m.r. data supported the rapid tautomeric rearrangement illustrated in *Figure 12* in which the H-atoms labelled H_b and H_8 retained their bridge-bonded identities. The estimated activation energy for this process amounted to approximately 10 kcal/mole.

Thermal rearrangements of the (3)-1,2-$C_2H_5AlB_9C_2H_{11}$ derivative at 400°C in the vapour phase[19] produced a new icosahedral structure in which the carbon atoms remained closest neighbours of the aluminium atom, but occupied 1,7 positions with respect to one another (*Figure 10*).
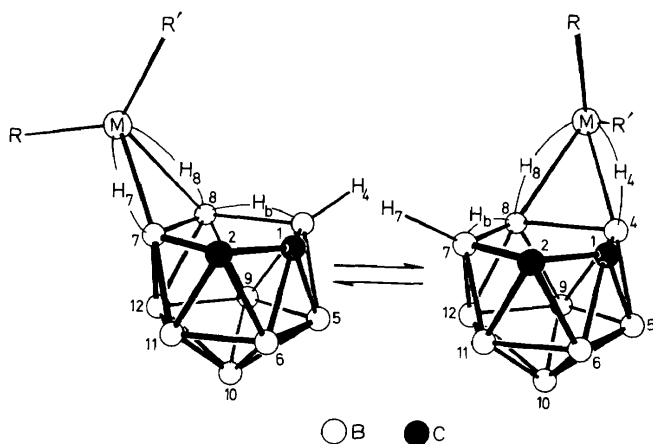
556

Figure 12. Tautomeric (3)-1,2-B$_9$C$_2$H$_{11}$Al(CH$_3$)$_2$ structures. H-atoms H$_b$ and H$_8$ retain their identities during tautomerization

THERMAL POLYHEDRAL REARRANGEMENTS OF
(π-C$_5$H$_5$)Co[π-(3)-1,2-B$_9$C$_2$H$_{11}$]

Rearrangement[21] of π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III), **1a** (*Figure 13*), in the vapour phase at elevated temperatures (400–700°C) led to excellent yields (87–93%) of six new isomers, **1b–1g** (*Figures 14* and *15*). The complexes, isolated by preparative thin-layer chromatography, result from the migration of the carbon atoms of the dicarbollyl ligand over the polyhedral surface. The isomers **1b–1d** are formed at 400–500°C; **1e–1g**, at 600–700°C.
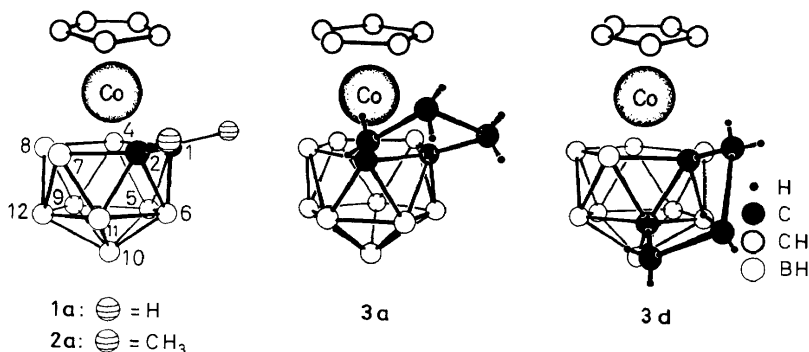
Figure 13. Proposed structures of π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III), **1a**, π-cyclopentadienyl-π-(3)-1,2-dimethyl-1,2-dicarbollylcobalt(III), **2a**, π-cyclopentadienyl-π-(3)-μ-1,2-trimethylene-1,2-dicarbollylcobalt(III), **3a**, and π-cyclopentadienyl-π-(3)-μ-1,6-tri-methylene-1,6-dicarbollylcobalt(III), **3d**

557

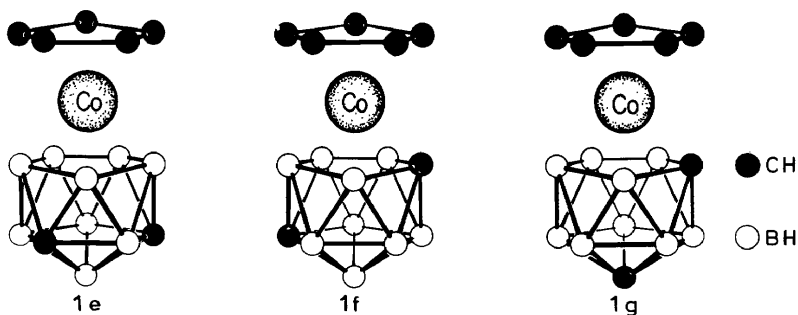*Figure 14.* Proposed structures of isomers **1e, 1f, 1g**, resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}B_9C_2H_{11})$ at 600–700°C

All seven isomers showed a mass spectral cut-off at $m/e = 258$ $[^{11}B_9{}^{12}C_7{}^1H_{16}{}^{59}Co^+]$, and the cyclic voltammograms exhibited reversible one-electron waves. Each ^1H n.m.r. spectrum (acetone-d_6) showed a sharp singlet in the 5.3–5.9 δ region (5H, cyclopentadienide C—H) and either one broad singlet (2H, dicarbollyl C—H) or two singlets (each 1H, dicarbollyl C—H) in the 2.3–3.9 δ region.

When $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9(CH_3)_2]$, **2a**, was sublimed through a hot tube (400–500°C) packed with quartz wool, **2b–2d** were obtained. Rearrangement of $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9(CH_2)_3]$, **3a**, at 500°C, on the other hand, gave only **3d**. The mass spectrum exhibited a cut-off at $m/e = 298$ $[^{11}B_9{}^{12}C_{10}{}^1H_{20}{}^{59}Co^+]$. Due to the presence of the trimethylene linkage in **3a**, the ligand carbon atoms are forced to remain in adjacent or *ortho* positions, thereby prohibiting any 1,7- or 1,11-rearrangements. There are at least 4 distinct resonances of area 1 in the 80.5 MHz ^{11}B spectrum of **3d**
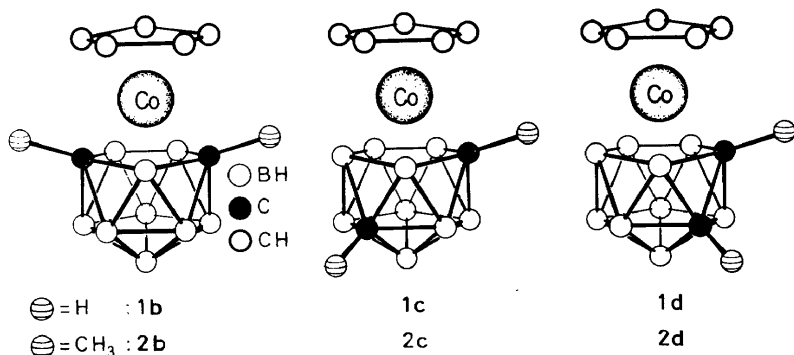

Figure 15. Proposed structures of isomers **1b, 1c, 1d, 2b, 2c,** and **2d** resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9R_2)(R = H, CH_3)$ at 400–500°C

(6 doublets in the ratio $1:3:1:1:1:2$, acetone-d_6); consequently, the complex is of C_1 symmetry and the most plausible structure is that of the 1,6-isomer shown in *Figure 13*. Isomer **1d**, also belongs to point group C_1 since the high-resolution [11]B spectrum revealed 9 unique B atoms. By correlation of R_f values of **1d**, **2d** and **3d**, the former two are assigned the structures in *Figure 15*.

The 80.5 MHz [11]B spectrum of **1c** also showed 9 different B atoms. Models indicate that the only possible structure is that of $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}1,11\text{-}B_9C_2H_{11}]$ (*Figure 15*).

The R_f values, infra-red and [1]H n.m.r. spectra of **1b** were identical with those of authentic $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$ synthesized from potassium (3)-1,7-dicarbadodecahydroundecaborate(-1). By correlation of R_f values, the structures of **2b** and **2c** follow.

[11]B spectra of **1e**, showed 6 types of B atoms in the ratio $2:1:2:1:2:1$, and in the 250 MHz [1]H n.m.r. spectra only one type of dicarbollyl C—H could be discerned. Of the two possible structures for **1e**, viz. $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}5,6\text{-}B_9C_2H_{11}]$ and $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}5,11\text{-}B_9C_2H_{11}]$, we prefer the latter (*Figure 14*), and **1e** is probably the first metallocarborane with *five B atoms* in the π-bonding face.
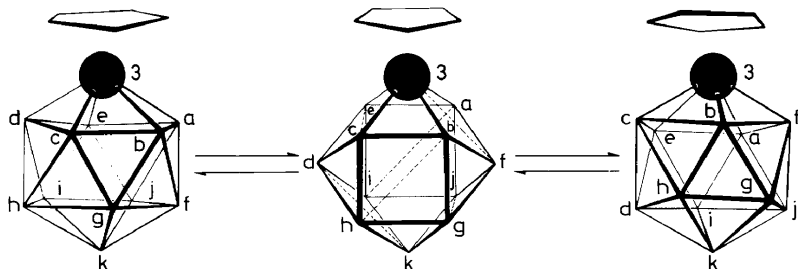

Figure 16. An example of Lipscomb's diamond-square-diamond isomerization using a cubocta-hedral intermediate or transition state. $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}B_9C_2H_{11})$ complexes

In the series $\mathbf{1a} \rightarrow \mathbf{1b} \rightarrow \mathbf{1c} \rightarrow \mathbf{1d} \rightarrow \mathbf{1e}$, as the number of carbon atoms in the metal-bonding face decreases $(2 \rightarrow 0)$, the complexes are reduced with greater difficulty and their λ_{max} values (*d–d* transitions) undergo a hypso-chromic shift (*Table 1*).

Based on the above correlations, the [11]B spectra (each shows 5 doublets in the ratio $2:2:2:2:1$), the $E_{p/2}$ and λ_{max} values for **1f** and **1g** (*Table 1*), the structures having the 1,12- and 1,10-skeletal arrangements (*Figure 14*) are assigned to **1f** and **1g**.

In principle, the possible interconversions of the isomeric $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}B_9C_2H_{11})$ complexes by Lipscomb's dsd[22] (diamond-square-diamond) mechanism (*Figure 16*) are as follows:

$$1,2 \rightleftharpoons 1,6 \rightleftharpoons 5,6$$
$$\Updownarrow \qquad\qquad \Updownarrow$$
$$1,7 \rightleftharpoons 1,11 \rightleftharpoons 5,11$$
$$1,10 \rightleftharpoons 5,10$$

Table 1

	1a 1,2-	1b 1,7-	1c 1,11-	1d 1,6-	1e 5,11-	1f 1,12-	1g 1,10-
Types of dicarbollyl CH	1	1	2	2	1	2	2
Types of borons—	6	6	9	9	6	5	5
relative ratio	2:2:2:1:1:1	2:2:2:1:1:1	1:1:1:1:1:1:1:1:1	1:1:1:1:1:1:1:1:1	2:2:2:1:1:1	2:2:2:2:1	2:2:2:2:1
$E_{p/2}$ vs. S.C.E.(V)	−1.22	−1.03	−1.33	−1.39	−1.75	−1.42	−1.44
λ_{max}, mμ(ε)	426(400)	414(298)	402(340)	404(290)	386(284)	408(350)	414(320)
Number of carbons in π-bonding face	2	2	1	1	0	(1)	(1)

Interestingly, the 1,10-, 5,10- and 1,12- complexes cannot be generated by this mechanism from the 1,2-isomer. On the other hand, all isomers can inter-convert by rotation of B_2C triangular faces.[23] Actually, the observed kinetically controlled isomeric interconversions may simultaneously employ both the dsd and the triangular face rotation processes.
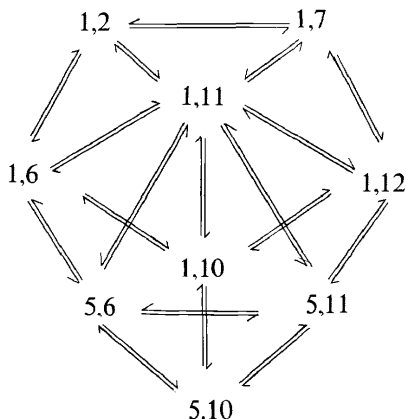
THE POLYHEDRAL EXPANSION REACTION

The availability of $1,6\text{-}B_6C_2H_8$ [24], $1,6\text{-}B_8C_2H_{10}$ [25] and the isomeric $B_{10}C_2H_{12}$ carboranes prompted us to consider the reactions which these carboranes might undergo with transition metal derivatives following the initial addition of electrons to the neutral carboranes. Successful reaction sequences of this sort would result in polyhedral metallocarborane derivatives which have the overall geometry of the next highest homologue of the known polyhedral series.

$$B_nC_2H_{n+2} + 2e^- \rightarrow B_nC_2H_{n+2}^{2-}$$
$$B_nC_2H_{n+2}^{2-} + Co^{2+} + C_5H_5^- \rightarrow (B_nC_2H_{n+2})Co(C_5H_5)^-$$

$$-e^- \diagup \text{oxidize}$$

$$(B_nC_2H_{n+2})Co(C_5H_5)$$
expanded polyhedron
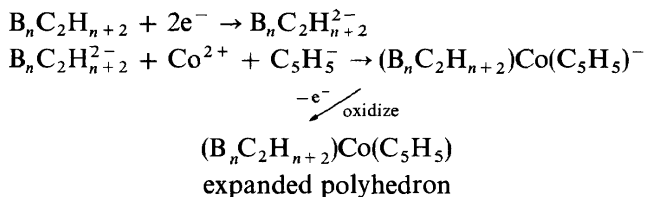
Treatment of $1,6\text{-}C_2B_6H_8$ [24] (*Figure 17*) with two equivalents of sodium amalgam in tetrahydrofuran at reduced temperature followed by the addition of excess anhydrous $CoCl_2$ produced in 3.9 per cent yield an anion which contained two $C_2B_6H_8^{2-}$ ions[26] in conjunction with formal cobalt(III). This anion was characterized as $[(C_2B_6H_8)_2Co(III)]^-$ and its ^{11}B and ^1H n.m.r. spectra were in agreement with the proposed structure shown in *Figure 18*.
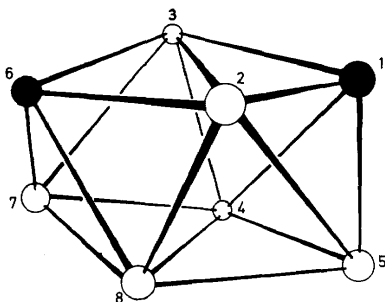
561

Figure 17. Simplified drawing of $1,6\text{-}B_6C_2H_8$

Treatment of $1,6\text{-}C_2B_6H_8$ with two equivalents of sodium naphthalide in tetrahydrofuran provided an alternate preparation of the ligand. Mixed complexes of formal cobalt(III) were isolated by column chromatography from the reaction of $1:5$ mixtures of the apparent $C_2B_6H_8^{2-}$ and $C_5H_5^-$ ions with anhydrous $CoCl_2$ in tetrahydrofuran. A red complex $(C_5H_5)Co(B_6C_2H_8)$ of formal cobalt(III) was prepared[26] in 4.1 per cent yield and was purified by sublimation. The ^{11}B and ^1H n.m.r. spectra of this compound agree with the proposed structure shown in *Figure 19*.

A green complex, $(C_5H_5)_2Co_2(B_6C_2H_8)$ was also obtained from the reaction[26] in 7.3 per cent yield. This represents the first member of a new
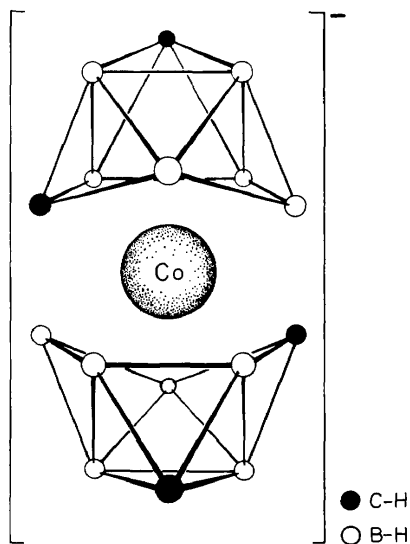

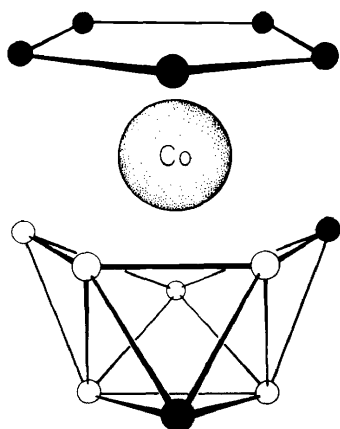*Figure 18.* Proposed structure of $[\pi\text{-}B_6C_2H_8]_2Co^-$ complex

562

Figure 19. Proposed structure of $[\pi\text{-}B_6C_2H_8]Co[\pi\text{-}C_5H_5]$ complex

bimetallic complex containing carborane ligands. The ^{11}B and ^1H n.m.r. spectra of this compound are in agreement with the proposed structure shown in *Figure 20*.

The extension of this synthetic method to 1,6-dicarba-*closo*-decaborane(10)[25], 1,6-$B_8C_2H_{10}$, (*Figure 21*) to give the $B_8C_2H_{10}^{2-}$ ion was examined next. Treatment of 1,6-$B_8C_2H_{10}$ in tetrahydrofuran at reflux with two equivalents of sodium naphthalide followed by the addition of a fourfold excess of $C_5H_5^-$ and an excess of $CoCl_2$ yielded a mixture of products[27]. A purple complex formulated as $(C_5H_5)Co(B_8C_2H_{10})$ was isolated by
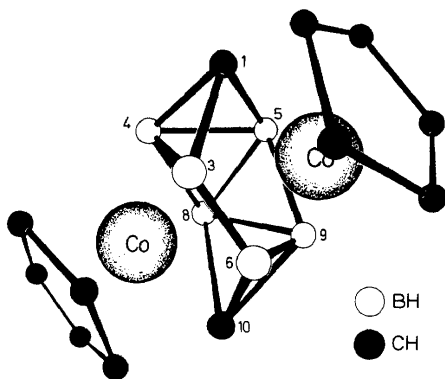
Figure 20. Proposed structure of $[\pi\text{-}C_5H_5Co]_2B_6C_2H_8$ complex
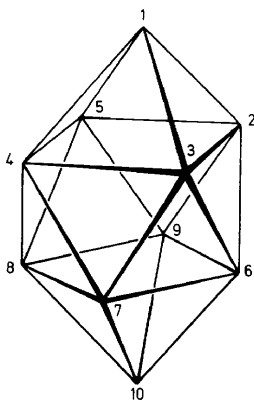
Figure 21. Simplified drawing of 1,6-$B_8C_2H_{10}$

column chromatography in 38 per cent yield. A structure (*Figure 22*) in which the cobalt completes an 11-member polyhedron with the carborane moiety is consistent with all n.m.r. data. This gross polyhedral geometry is seen in the $B_9C_2H_{11}$ carborane[28] and the isoelectronic $B_{11}H_{11}^{2-}$ ion[23].

The major product resulting from treatment of 1,6-$B_8C_2H_{10}$ with two equivalents of sodium in the presence of a catalytic amount of naphthalene followed by the addition of excess $CoCl_2$ was a green complex formulated as $(B_8C_2H_{10})_2Co^-$. This complex was isolated by column chromatography and recrystallized as its Cs^+ salt in 48 per cent yield. The n.m.r. data collected for this compound suggest that the structure of the $B_8C_2H_{10}^{2-}$ ligand present in $(B_8C_2H_{10})_2Co^-$ is identical to that present in $(C_5H_5)Co(B_8C_2H_{10})$.
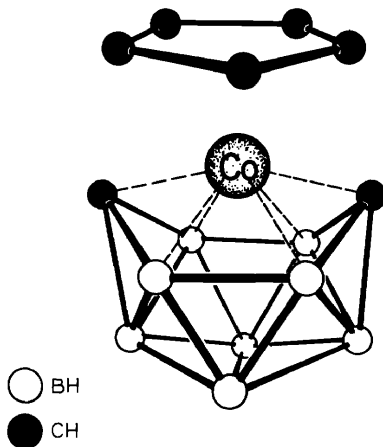

BH
CH

Figure 22. Proposed structure of $[\pi\text{-}C_5H_5]Co[\pi\text{-}B_8C_2H_{10}]$ complex

We now wish to report the probable formation of 13-atom polyhedral complexes[29] apparently generated with formal Co(III), π-bonded $C_5H_5^-$ and the $B_{10}C_2H_{12}^{2-}$ ion[30, 31, 32] formed by electron addition to $1,2\text{-}B_{10}C_2H_{12}$. The inclusion of the transition metal atom into the $B_{10}C_2H_{12}^{2-}$ ion presumably completes a 13-atom polyhedron (*Figure 23*). The $B_{10}C_2H_{12}^{2-}$ ion was produced by the reduction of $1,2\text{-}B_{10}C_2H_{12}$ at room temperature with 2 equivalents of sodium in tetrahydrofuran with a catalytic amount of
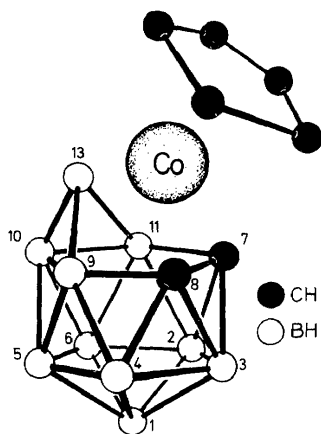
Figure 23. Proposed structure of $[\pi\text{-}C_5H_5]Co[\pi\text{-}7,8\text{-}B_{10}C_2H_{12}]$ complex

naphthalene. A threefold excess of $C_5H_5^-$ was added followed by excess $CoCl_2$. The products were separated by column chromatography and recrystallized from hexane–dichloromethane solutions. The major products included $(C_5H_5)Co(1,2\text{-}B_9C_2H_{11})$ (1 %), a complex formulated as $(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$ (50 %), and a mixture of complex anions which were isolated as their $(C_5H_5)_2Co^+$ and $(C_6H_5)_4As^+$ salts and formulated as $(B_{10}C_2H_{12})_2Co^-$ (12 %). The red $(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$ was found to undergo a thermal rearrangement to an orange isomer which subsequently undergoes further thermal rearrangement to a red-orange isomer. All isomers have an identical m.pt of 250–251°C, possibly due to the progressive thermal rearrangement in the solid phase.

The 60 MHz ^{1}H n.m.r. spectrum of red $(C_5H_5)Co(7,8\text{-}B_{10}C_2H_{12})$ exhibited a sharp peak of area 5 at τ 4.48 and a broad peak area 2 at τ 5.57 which were assigned to the cyclopentadienyl protons and the equivalent polyhedral C—H units respectively. The 80.5 MHz ^{11}B n.m.r. spectrum (*Figure 24*) consisted of doublets of area ratios $1:2:1:2:1:2:1$ which is consistent with a molecule containing 3 unique pairs and 4 unique boron atoms (*Figure 23*).

The 60 MHz ^{1}H n.m.r. of the orange isomer consisted of a sharp peak of area 5 at τ 4.48 and two broad peaks of area 1 at τ 5.10 and 7.08 which were

565

assigned to cyclopentadienyl protons and two types of polyhedral C—H units respectively. The 80.5 MHz ^{11}B n.m.r. spectrum contained doublets of area ratio 1:1:1:1:1:2:2:1 at ⬥−21.2 (140), −8.0 (138), −6.3 (149), −4.7 (140), +2.5 (170), +6.1 (170), +8.3 (161) and +12.8 (153), chemical shifts, [p.p.m., relative to $BF_3 \cdot O(C_2H_5)_2$ and coupling constants (Hz)].

The 60 MHz ^{1}H n.m.r. of the orange-red isomer consisted of a sharp peak of area 5 at τ 4.54 and two peaks of area 1 at τ 5.32 and 6.60 which were
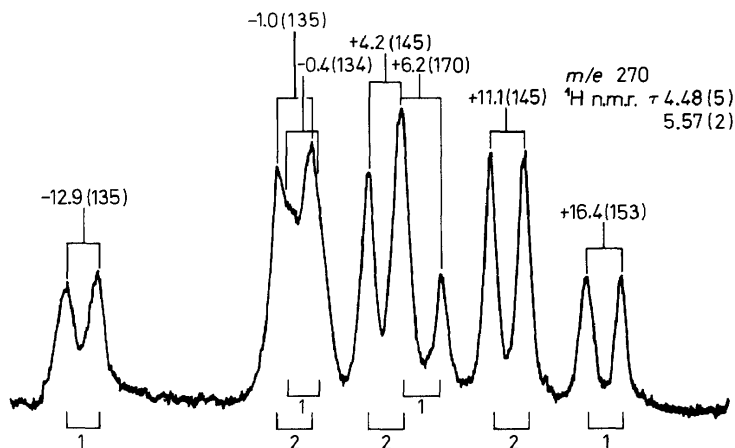

Figure 24. The ^{11}B n.m.r. spectrum of $[\pi\text{-}C_5H_5]Co[\pi\text{-}7,8\text{-}B_{10}C_2H_{12}]$ at 80.5 MHz

assigned to cyclopentadienyl protons and two types of polyhedral C—H units respectively. The 80.5 MHz ^{11}B n.m.r. consisted of ten doublets of equal area at −7.9 (145), −5.4 (169), −3.5 (145), −2.4 (161), +3.6 (145), +7.9 (145), +9.3 (169), +12.5 (145), +14.9 (145), and +16.9 (145).

The mass spectra of all three $(C_5H_5)Co(B_{10}C_2H_{12})$ isomers were virtually identical and exhibited sharp cut-offs at m/e 270 which correspond to the $^{11}B_{10}{}^{12}C_7{}^1H_{17}{}^{59}Co^+$ ion.

The data presented indicate that the orange and orange-red isomers of $(C_5H_5)Co(B_{10}C_2H_{12})$ are quite unsymmetrical, but probably retain the gross structure of the red isomer and (*Figure 23*) differ only in the position of the two carbon atoms in the polyhedral framework.

REFERENCES

[1] (a) M. F. Hawthorne, D. C. Young and P. A. Wegner, *J. Am. Chem. Soc.* **87**, 1818 (1965); (b) M. F. Hawthorne and T. D. A. Andrews, *Chem. Commun.* 443 (1965).
[2] W. Moffitt, *J. Am. Chem. Soc.* **76**, 3386 (1954).
[3] (a) T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak and J. W. Szymanski, *Inorg. Chem.* **2**, 1089 (1963); (b) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz and M. S. Cohen, *Inorg. Chem.* **2**, 1111 (1963).

[4] D. Grafstein and J. Dvorak, *Inorg. Chem.* **2**, 1128 (1963).

[5] (a) J. A. Potenza and W. N. Lipscomb, *J. Am. Chem. Soc.* **86**, 1874 (1964); (b) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.* **3**, 1673 (1963); (c) D. Voet and W. N. Lipscomb, *Inorg. Chem.* **3**, 1679 (1963)

[6] R. Adams, *Inorg. Chem.* **2**, 1087 (1963).

[7] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.* **86**, 1642 (1964).

[8] P. M. Garrett, F. N. Tebbe and M. F. Hawthorne, *J. Am. Chem. Soc.* **86**, 5016 (1964).

[9] W. N. Lipscomb, *Boron Hydrides*, W. A. Benjamin, Inc., New York, N.Y. (1963).

[10] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. A. Wegner, *J. Am. Chem. Soc.* **90**, 862 (1968).

[11] L. F. Warren, Jr. and M. F. Hawthorne, *J. Am. Chem. Soc.* **89**, 470 (1967).

[12] (a) A. Zalkin, T. E. Hopkins and D. H. Templeton, *Inorg. Chem.* **6**, 1911 (1967); (b) A. Zalkin, T. E. Hopkins and D. H. Templeton, *Inorg. Chem.* **5**, 1189 (1966); (c) A. Zalkin, D. H. Templeton and T. E. Hopkins, *J. Am. Chem. Soc.* **87**, 3899 (1965).

[13] J. N. Francis and M. F. Hawthorne, *J. Am. Chem. Soc.* **90**, 1663 (1968).

[14] D. St. Clair, A. Zalkin and D. H. Templeton, *Inorg. Chem.* **8**, 2080 (1969).

[15] (a) J. N. Francis and M. F. Hawthorne, *Inorg. Chem.* **10**, 863 (1971); (b) M. R. Churchill, A. H. Reis, J. N. Francis and M. F. Hawthorne, *J. Am. Chem. Soc.* **92**, 4993 (1970).

[16] B. M. Mikhailov and T. V. Potapova, *Izv. Akad. Nauk SSSR Ser. Khim.* **5**, 1153 (1968).

[17] D. A. Young, G. R. Willey, M. F. Hawthorne, M. R. Churchill and A. H. Reis, Jr., *J. Am. Chem. Soc.* **92**, 6663 (1970).

[18] M. R. Churchill, A. H. Reis, Jr., D. A. Young, G. R. Willey and M. F. Hawthorne, *Chem. Commun.* in press.

[19] D. A. Young, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.* in press.

[20] G. Popp and M. F. Hawthorne, *Inorg. Chem.* **10**, 391 (1971).

[21] M. K. Kaloustian, R. J. Wiersema and M. F. Hawthorne, *J. Am. Chem. Soc.* in press.

[22] W. N. Lipscomb, *Science* **153**, 373 (1966).

[23] E. L. Muetterties and W. H. Knoth, *Polyhedral Boranes*, Marcel Dekker, Inc., New York, N.Y. (1968).

[24] G. B. Dunks and M. F. Hawthorne, *Inorg. Chem.* **7**, 1038 (1968).

[25] F. N. Tebbe, P. M. Garrett, D. C. Young and M. F. Hawthorne, *J. Am. Chem. Soc.* **88**, 609 (1966).

[26] G. B. Dunks and M. F. Hawthorne, *J. Am. Chem. Soc.* **92**, 7213 (1970).

[27] W. J. Evans and M. F. Hawthorne, *J. Am. Chem. Soc.* in press.

[28] T. E. Berry, F. N. Tebbe and M. F. Hawthorne, *Tetrahedron Letters* **12**, 715 (1965).

[29] G. B. Dunks, M. M. McKown and M. F. Hawthorne, *J. Am. Chem. Soc.* **93**, 2541 (1971).

[30] D. Grafstein and J. Dvorak, *Inorg. Chem.* **2**, 1128 (1963).

[31] L. Zakharkin, V. Kalnin and L. Podvisotskaya, *Izv. Akad Nauk SSSR, Ser. Khim.* **10**, 2310 (1967).

[32] V. Stanko, Yu. V. Gol'typapin and V. Brattsev, *Zh. Obshch. Khim.* **39**, 1175 (1969).