

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

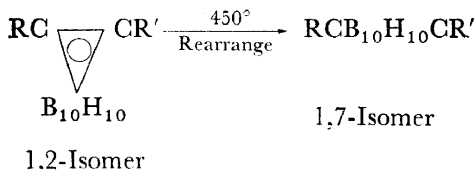
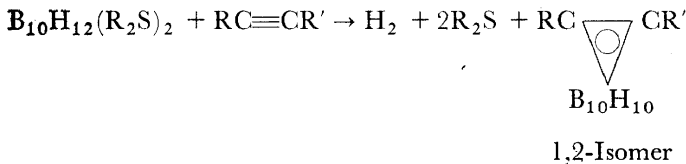
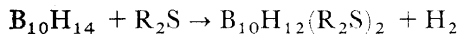
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In 1965¹ the first examples of bonding between a transition metal and the two isomeric dicarbollide ions, $B_9C_2H_{11}^{2-}$ were reported. The latter ions are eleven-particle icosahedral fragments which accept the transition metal in such a manner 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 ferrocene² 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 this chemistry and emphasize more recent results obtained with the isomeric (3)-1,2- and (3)-1,7-dicarbollide ions and the newly discovered $B_7C_2H_9^{2-}$ (ref. 3) and $B_6C_2H_8^{2-}$ (ref. 4) ligands which also form polyhedral species by the incorporation of transition metals.

BACKGROUND REVIEW

The carborane ligands described in this paper are all derived from the isomeric 1,2- and 1,7-dicarboclosododecaborane(12) species⁵. The latter compounds are easily prepared from an alkyne and a $B_{10}H_{12}$ (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. The rearrangement of the 1,2- to the 1,7- $B_{10}C_2H_{12}$ system proceeds smoothly⁶ at elevated temperatures and is somewhat dependent upon the nature of the substituents attached to carbon. *Figure 1* presents the icosahedral structure⁷ and the numbering system⁸ associated with the 1,2- and 1,7- $B_{10}C_2H_{12}$ isomers. Although the

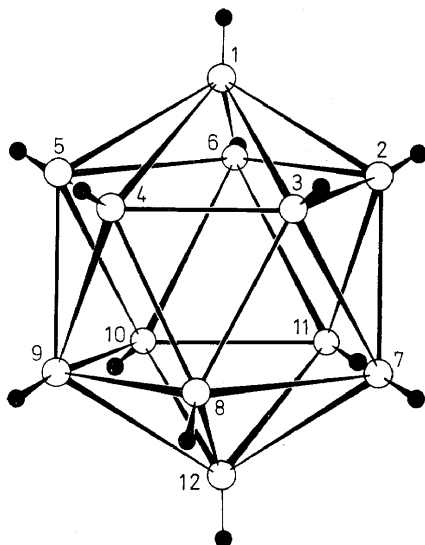
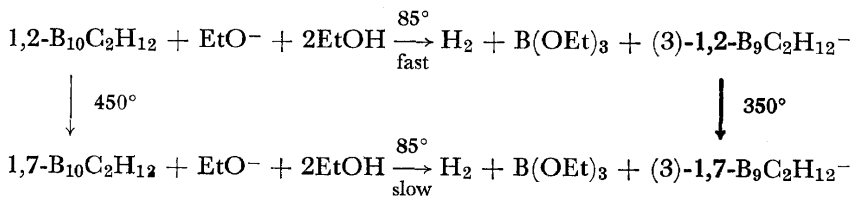


Figure 1. The icosahedral structure and accepted numbering system

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^{9,10}. 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. The thermal rearrangement of the (3)-1,2- $B_9C_2H_{12}^-$ system to its (3)-1,7-isomer is observed¹⁰ at temperatures near 350°. A rationale of the lability 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 state¹² 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 most likely 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 formulae¹². The twelfth hydrogen atom required by the empirical formulae $B_9C_2H_{12}^-$ 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.

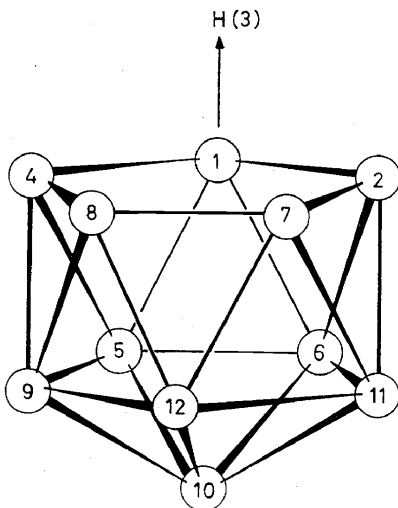
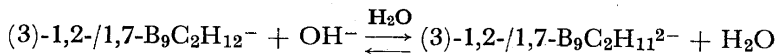


Figure 2. Framework of the $B_9C_2H_{12}^-$ ions

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. Similarly, the (3)-1,2- and

(3)-1,7- $B_9C_2H_{12}^-$ + NaH $\xrightarrow{\text{THF}}$ H_2 + Na + (3)-1,2-/1,7- $B_9C_2H_{11}^{2-}$
 (3)-1,7- $B_9C_2H_{11}^{2-}$ ions appear to be present in very concentrated (5–10 N) aqueous hydroxide ion solutions containing the corresponding $B_9C_2H_{12}^-$ ion¹³. Indirect chemical evidence for this equilibrium will be presented at



a later point in this paper.

The results of x-ray crystallographic studies¹⁴ carried out with a variety of metal complexes of the (3)-1,2- $B_9C_2H_{11}^{2-}$ ion coupled with simplified molecular orbital theory suggests that the (3)-1,2- and (3)-1,7- $B_9C_2H_{11}^{2-}$ ions resemble the simplified structures presented in *Figure 3*. In these drawings, the 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

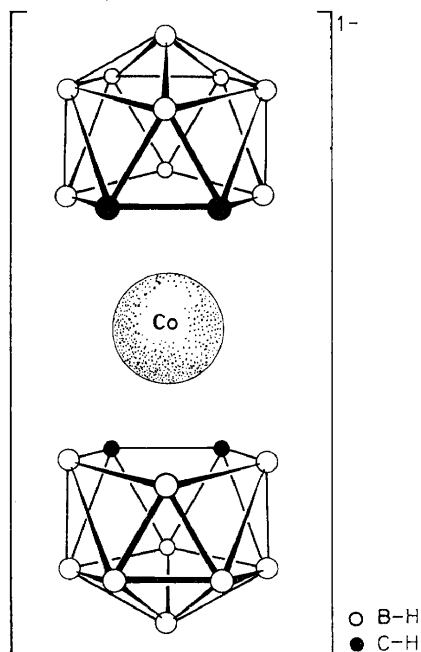


Figure 4. Simplified structure of the $[\pi-(3)-1,2-B_9C_2H_{11}]_2Co^-$ ion

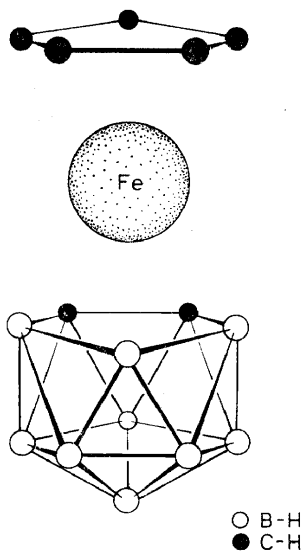


Figure 5. Simplified structure of $[\pi-(3)-1,2-B_9C_2H_{11}]Fe[\pi-C_5H_5]$

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 possible¹³ to prepare complexes of iron,

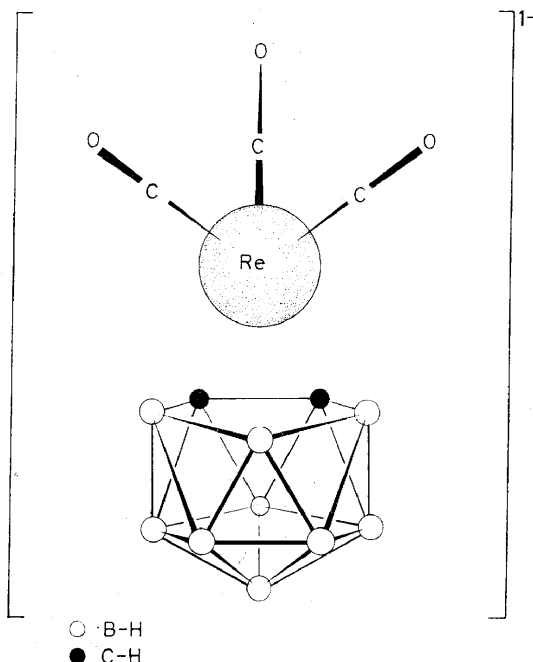


Figure 6. Simplified structure of the $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Re(CO)}_3^-$ ion

cobalt, nickel, etc. in 80–90 per cent yield by reacting the metal halide with strongly basic aqueous solutions of the (3)-1,2- and (3)-1,7- $\text{B}_9\text{C}_2\text{H}_{12}^-$ ions. In these cases, it appears as though the dinegative ligand anions are generated according to the equilibrium presented above and that these dianions scavenge metal ions more effectively than does hydroxide ion.

RECENT DEVELOPMENTS IN (3)-1, 2-DICARBOLLIDE CHEMISTRY

The aqueous preparative method employed in the preparation of certain (3)-1,2- and (3)-1,7- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ complexes has been applied to copper(II)¹⁵. A bright blue anion results which may be converted to a less stable brick-red complex by a reversible single electron oxidation reaction¹⁵. Elemental analyses suggested that the blue complex formally contained two (3)-1,2-dicarbollide ligands and copper(II). The brick-red complex could therefore be considered to be a similar complex of copper with the formal oxidation state +3. Single crystal x-ray diffraction studies¹⁶ have confirmed these compositions and at the same time uncovered an unusual structural feature; unsymmetrical bonding of copper to the two coplanar ligands. *Figure 7* presents the simplified structure of the two copper complexes which have essentially the same geometry. Each of the two ligands are seen to have “slipped” by 0.6 Å with respect to the metal nucleus and to have done so while remaining coplanar. Wing¹⁶ has rationalized these structures by suggesting that the shorter B–Cu interactions arise from a somewhat localized bonding which resembles that seen in π -allylic complexes. Although

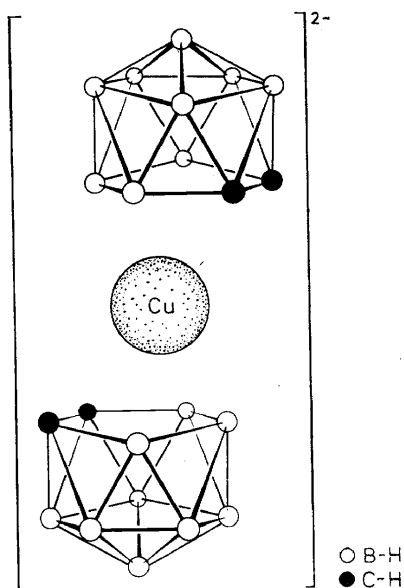
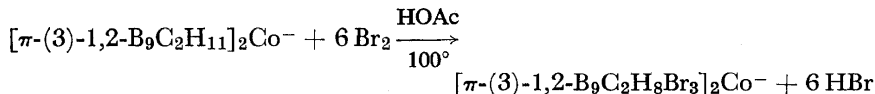


Figure 7. Simplified structure of copper(II) "slipped-sandwich" complex

the answer to this question is not presently available, the interesting fact remains that copper does form "sandwich" bonded derivatives in this series of complexes while no π -cyclopentadienyl copper complex is now known.

The chemical reactivity of representative (3)-1,2-dicarbollyl transition metal complexes has become a subject of investigation. While the results of this study are not wholly definitive at this time, it may be accurately stated that there is little resemblance between the reactivity of π -cyclopentadienyl derivatives and the corresponding π -(3)-1,2-dicarbollyl complexes.

Bromination of the $[\pi$ -(3)-1,2- $B_9C_2H_{11}]_2Co^-$ ion in glacial acetic acid at 100° resulted in the formation of a hexabromo derivative¹⁵ in good yield. The structure of the hexabromo derivative has been determined by x-ray



diffraction studies¹⁷ and is presented in simplified form in *Figure 8*. The bromide atom positions in the hexabromo derivative suggests that the substitution reaction is controlled by the +I effect of the two carbon atoms present in each ligand. Thus, one finds substitution at the two positions furthest removed from the two carbon atoms plus one of the two boron atoms which are only slightly closer to the two carbon atoms. Such a substitution pattern is not greatly different than that expected for the parent 1,2-dicarbacosododecaborane(12) molecule¹⁸ if one assumes that in the complex the two carbon atoms bear partial positive charges and that the

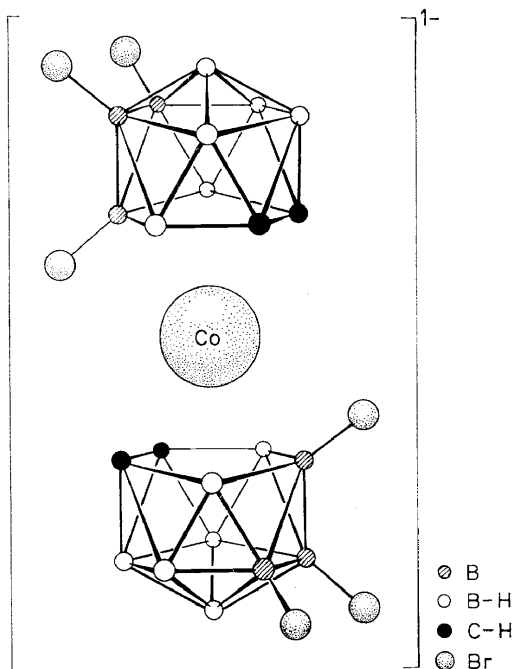
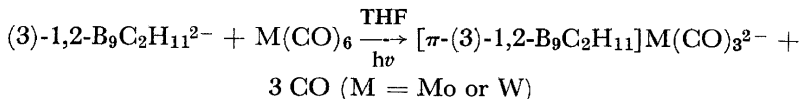


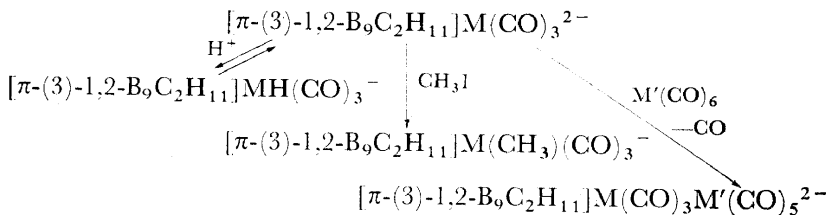
Figure 8. Simplified structure of the $[\pi-(3)-1,2-B_9C_2H_8Br_3]_2Co^-$ ion

cobalt atom does not greatly perturb the charge distribution generated by the two carbon atoms. It is interesting, however, that the two unique bromine atoms in the brominated species are located on boron atoms which are nearest neighbours to the metal atom.

Continued work in the area of (3)-1,2-dicarbollide derivatives of the transition metal carbonyls has led to the discovery of the (3)1,2-dicarbollyl analogues of $\pi-C_5H_5M(CO)_3^-$ ions¹⁹ where $M = Mo$ and W and the subsequent conversion of these complexes to binuclear metal carbonyl derivatives. The initial research in this area resulted in the preparation of the $[\pi-(3)-1,2-B_9C_2H_{11}]M(CO)_3^{2-}$ series by photochemical means¹⁵. Irradiation of tetrahydrofuran solutions of metal hexacarbonyl and the



(3)-1,2-dicarbollide ion with an unfiltered mercury source led to the smooth evolution of CO and the production of the anionic complexes in high yield. The nucleophilic character of the $[\pi-(3)-1,2-B_9C_2H_{11}]M(CO)_3^{2-}$ ions was illustrated¹⁵ by their reaction with protons, methyl iodide and an additional mole of $M(CO)_6$. The binuclear complexes have been produced with all these combinations of Mo and W. These species are moderately stable and their existence has no recorded counterpart in π -cyclopentadienyl chemistry. The structure of $[\pi-(3)-1,2-B_9C_2H_{11}]Mo(CO)_3W(CO)_5^{2-}$ was determined by x-ray diffraction studies²⁰ and is presented in Figure 9. The structures



M = Mo or W

M' = Mo or W

of the $[\pi-(3)-1,2-B_9C_2H_{11}]M(CO)_3^-$ ions are most likely identical to that of the rhenium carbonyl derivative, $[\pi-(3)-1,2-B_9C_2H_{11}]Re(CO)_3^-$ presented in Figure 6.

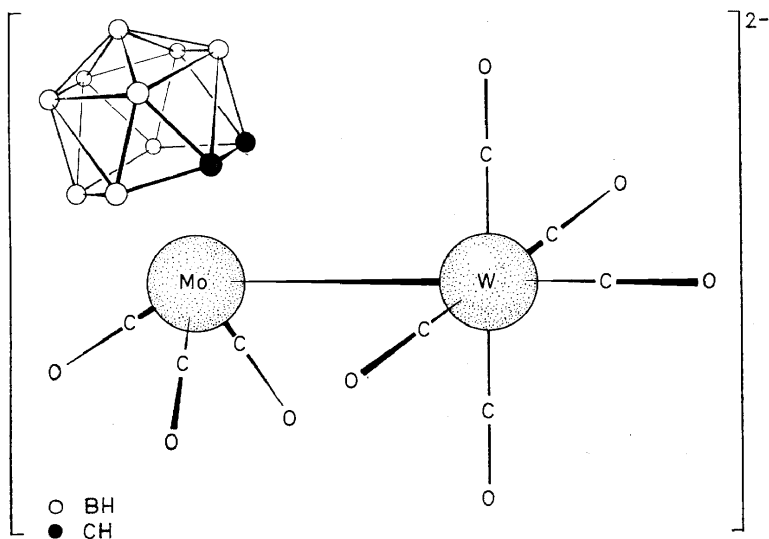


Figure 9. Simplified structure of the $[\pi-(3)-1,2-B_9C_2H_{11}]Mo(CO)_3W(CO)_5^{2-}$ ion

TRANSITION METAL DERIVATIVES OF THE $B_7C_2H_9^{2-}$ ION

The recently described²¹ nido-carborane, $B_7C_2H_{13}$, and its C-substituted derivatives are easily prepared by the chromic acid oxidation of the corresponding closo-carborane^{22,24}, $B_9C_2H_{11}$ or $(3)-1,7-B_9C_2H_{12}^-$ ion. Figure 10 presents the structure^{21,23,24} of the C,C'-dimethyl derivative of $B_7C_2H_{13}$. The $B_7C_2H_{13}$ nido-carborane system is extremely interesting due to the presence of methylene carbon atoms in the periphery of the open face of this species. Chemical evidence, presented elsewhere^{21,24} proved that the polar hydrogen atoms attached to the two carbon atoms were highly acidic and the C-substituents were always in equatorial positions. In addition, under more basic conditions, the bridge hydrogen atoms could be exchanged with deuterium oxide. Thus, four potentially acidic hydrogen atoms are present in all known $B_7C_2H_{13}$ derivatives. It was therefore of interest to study the reaction of $B_7C_2H_{13}$ and its C-substituted derivatives with strong bases

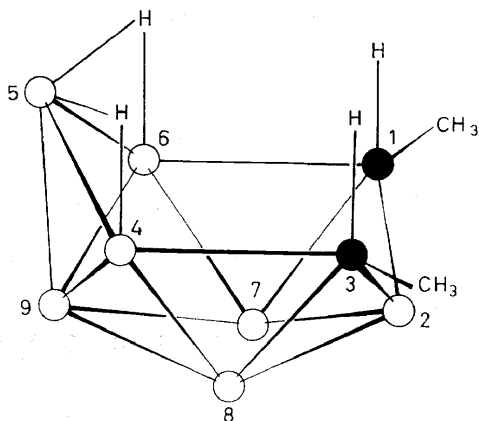
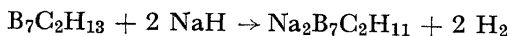


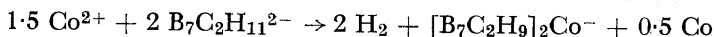
Figure 10. Structure of 1,2-dimethyl derivative of $B_7C_2H_{13}$ with terminal B—H hydrogen atoms removed

and to examine the reactions of the resulting anions with transition metal ions. This would appear to present a reasonable approach to a new series of polyhedral transition metal derivatives which have the gross geometry of the known $B_{10}H_{10}^{2-}$ ion (ref. 25) and $B_8C_2H_{10}$ (ref. 24, 26) closo-carboranes (bicapped Archimedean antiprism).

The reaction of $B_7C_2H_{13}$ and its C-substituted derivatives with sodium hydride in diethyl ether produced two moles of hydrogen and the as yet, unisolated $B_7C_2H_{11}^{2-}$ ion³. Subsequent reaction of the $B_7C_2H_{11}^{2-}$ ion with



cobalt(II) chloride led to the formation of two additional moles of hydrogen, cobalt metal and the new complex $[B_7C_2H_9]_2Co^-$. The cobalt complex was isolated and characterized as its tetramethylammonium or cesium salt³.



Similar results were obtained with a variety of C-substituted $B_7C_2H_{11}^{2-}$ ions when employed as starting materials.

Figure 11 presents the 60 Mc/sec 1H n.m.r. spectrum of the parent cobalt complex as the tetramethylammonium salt. The sharp singlet at high field represents the twelve protons associated with the $(CH_3)_4N^+$ cation. The two broad singlets which appear at low field are assigned to carborane

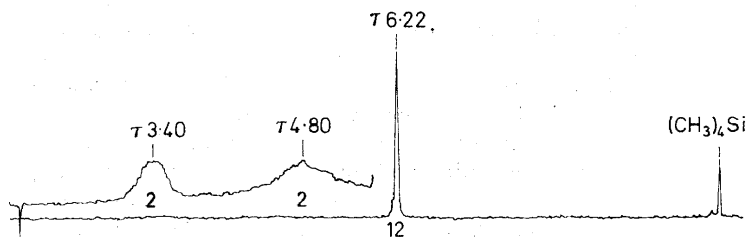


Figure 11. The 60 Mc/sec 1H n.m.r. spectrum of the $[\pi-B_7C_2H_9]_2Co^-$ ion

C—H resonances which arise from the presence of two non-equivalent carbon atom environments in each $B_7C_2H_9^{2-}$ ligand.

The 32 Mc/sec ^{11}B n.m.r. spectrum of $[B_7C_2H_9]_2Co^-$ is presented in Figure 12. Seven distinct ^{11}B resonances (doublets) are readily discerned.

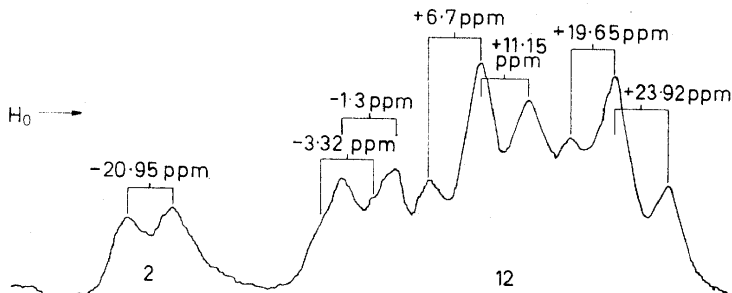


Figure 12. The 32 Mc/sec ^{11}B n.m.r. spectrum of the $[\pi-B_7C_2H_9]_2Co^-$ ion relative to $BF_3 \cdot O(C_2H_5)_2$

Thus, the seven boron atoms present in each ligand are non-identical although both of the $B_7C_2H_9^{2-}$ ligands attached to cobalt(III) are identical to one another. These n.m.r. data serve to point out the low symmetry of the $[B_7C_2H_9]_2Co^-$ ion. Since the bicapped Archimedean anti-prism is known to represent the structure of the stable $B_{10}H_{10}^{2-}$ and $B_8C_2H_{10}$ carboranes, it was attractive to attempt to rationalize the partial structure formally produced from each $B_7C_2H_9^{2-}$ ligand and the cobalt(III) ion in terms of this geometry. In addition, one could be guided by the following facts. (1) The ^{11}B n.m.r. spectrum contained a low-field doublet which ordinarily suggests²⁵ the presence of an apical BH group of low coordination number. (2) One would expect the two carbon atoms of each ligand to be separated and not to reside in a nearest-neighbour relationship. (3) The two carbon atoms of each ligand would most likely be found within bonding distance of the metal ion, as in the (3)-1,2-dicarbollyl complexes discussed above. On this basis, the anti-isomer structure shown in Figure 13 was tentatively assigned to the parent $[B_7C_2H_9]_2Co^-$ ion. This structure was recently confirmed²⁷ by single crystal x-ray diffraction studies carried out by Templeton, Zalkin and St. Clair.

The reaction of the cyclopentadienide ion with $Co(II)$ in the presence of the $B_7C_2H_{11}^{2-}$ ion led to the formation of a mixed complex $(C_5H_5)Co(B_7C_2H_9)$ having no formal charge³. This complex was easily sublimed and characterized by high-resolution mass spectrometry as well as by elemental analysis.

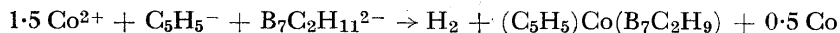


Figure 14 presents the 60 Mc/sec 1H n.m.r. spectrum of the mixed complex and one discerns the presence of a cyclopentadienyl singlet of area 5 and two broad singlets, each of unit area, which correspond to the two dissimilar carborane C—H resonances.

The 32 Mc/sec ^{11}B n.m.r. spectrum shown in Figure 15 contains seven discrete doublets, one of which arises at low-field. The interpretation of this

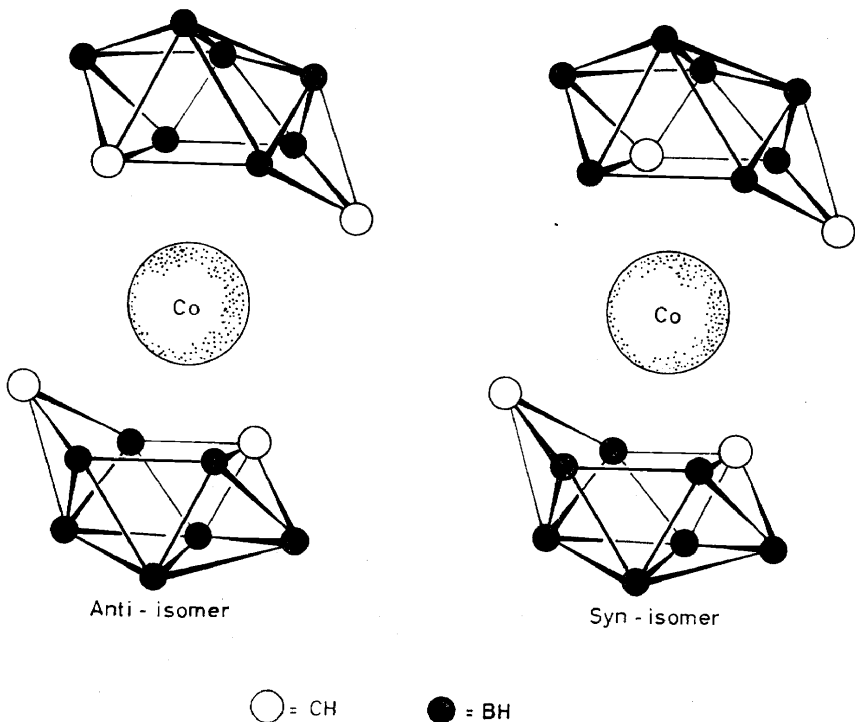


Figure 13. Simplified structures of isomeric $[\pi\text{-B}_7\text{C}_2\text{H}_5]_2\text{Co}^-$ ions. Actual structure was shown to be that of the anti-isomer

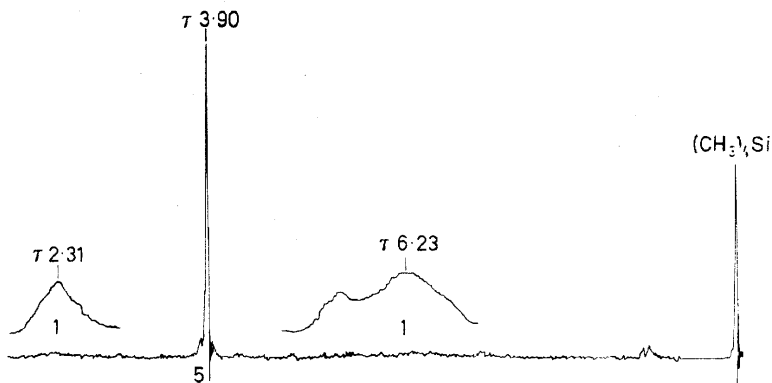


Figure 14. The 60 Mc/sec ^1H n.m.r. spectrum of $[\pi\text{-B}_7\text{C}_2\text{H}_9]\text{Co} [\pi\text{-C}_5\text{H}_5]$. The shoulder on the low field side of the high field C—H resonance is attributed to an impurity which was subsequently removed.

data coupled with the ^1H n.m.r. data follows the same arguments employed in the case of the $[\text{B}_7\text{C}_2\text{H}_9]_2\text{Co}^-$ ion and leads to the proposed structure of the mixed complex shown in Figure 16.

It thus appears as though a second broad family of polyhedral transition metal-carborane complexes are capable of existence and a great deal of

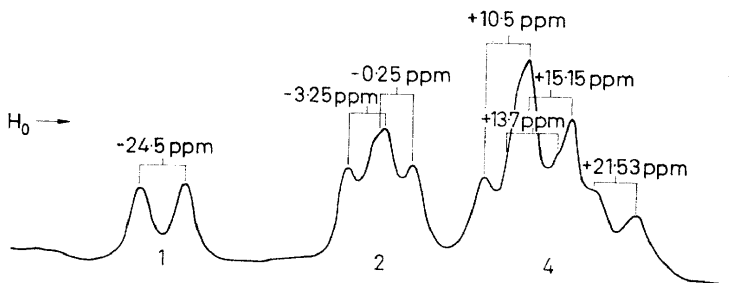


Figure 15. The 32 Mc/sec ^{11}B n.m.r. spectrum of $[\pi\text{-B}_7\text{C}_2\text{H}_9]\text{Co} [\pi\text{-C}_5\text{H}_5]$ relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

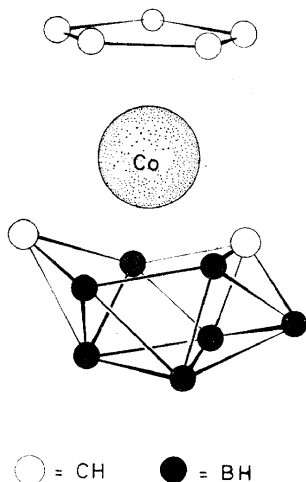
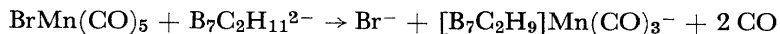


Figure 16. Simplified drawing of the proposed $[\pi\text{-B}_7\text{C}_2\text{H}_9]\text{Co} [\pi\text{-C}_5\text{H}_5]$ structure

further work is in progress which employs the $\text{B}_7\text{C}_2\text{H}_9^{2-}$ ligand and a variety of transition metal ions.

TRANSITION METAL DERIVATIVES OF THE $\text{B}_6\text{C}_2\text{H}_8^{2-}$ ION

Following the discovery of the $[\text{B}_7\text{C}_2\text{H}_9]\text{Co}^-$ and $(\text{C}_5\text{H}_5)\text{Co}[\text{B}_7\text{C}_2\text{H}_9]$ systems described above, attempts were made to prepare the $[\text{B}_7\text{C}_2\text{H}_9]\text{Mn}(\text{CO})_3^-$ ion which would be analogous to the $(3)\text{-1,2-B}_9\text{C}_2\text{H}_{11}\text{Mn}(\text{CO})_3^-$ ion described above. Accordingly, the $\text{B}_7\text{C}_2\text{H}_{11}^{2-}$ ion was allowed to react



with $\text{BrMn}(\text{CO})_5$ in diethyl ether solution⁴. Examination of the reaction products proved that the major product was a moderately stable anion which contained carborane and manganese carbonyl fragments. Elemental analyses, molecular weight data and equivalent weight determinations suggested that the product ion was not the expected $[\text{B}_7\text{C}_2\text{H}_9]\text{Mn}(\text{CO})_3^-$ ion, but a similar species derived from a B_6 carborane. The ^{11}B n.m.r. spectrum confirmed the formulation $[\text{B}_6\text{C}_2\text{H}_8]\text{Mn}(\text{CO})_3^-$.

Figure 17 presents the 60 Mc/sec ^1H n.m.r. spectrum of the isolated ion as the tetramethylammonium salt. A single carborane C—H resonance is observed and strongly suggests that the carborane carbon atoms are in equivalent environments.

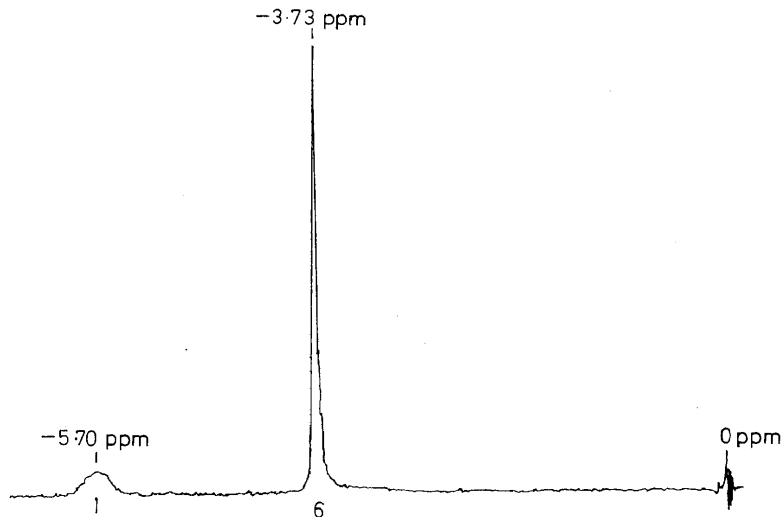


Figure 17. The 60 Mc/sec ^1H n.m.r. spectrum of the $[\pi\text{-B}_6\text{C}_2\text{H}_8] \text{Mn}(\text{CO})_3^-$ ion

The 32 Mc/sec ^{11}B n.m.r. spectrum shown in Figure 18 is quite simple and may be broken down into a 1:2:2:1 population. The low-field doublet again suggests²⁵ the presence of an apical BH group of low coordination number. The tricapped trigonal prism has recently been assigned to the geometry of the $\text{B}_7\text{C}_2\text{H}_9$ carborane^{24,26}. The equivalence of the two carborane carbon atoms and the 1:2:2:1 boron atom population immediately suggests

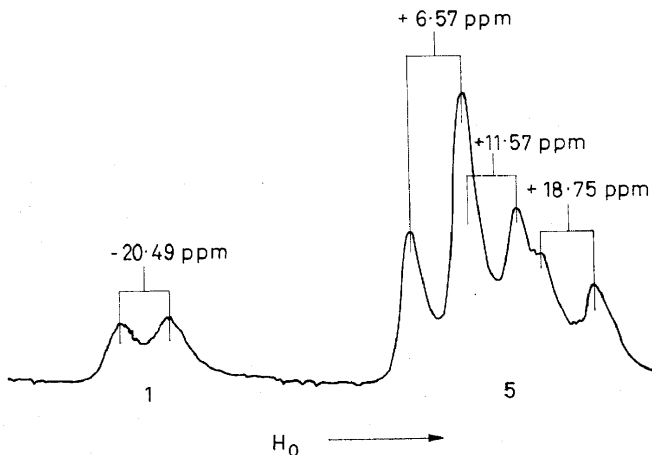


Figure 18. The 32 Mc/sec ^{11}B n.m.r. spectrum of the $[\pi\text{-B}_6\text{C}_2\text{H}_8] \text{Mn}(\text{CO})_3^-$ ion relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

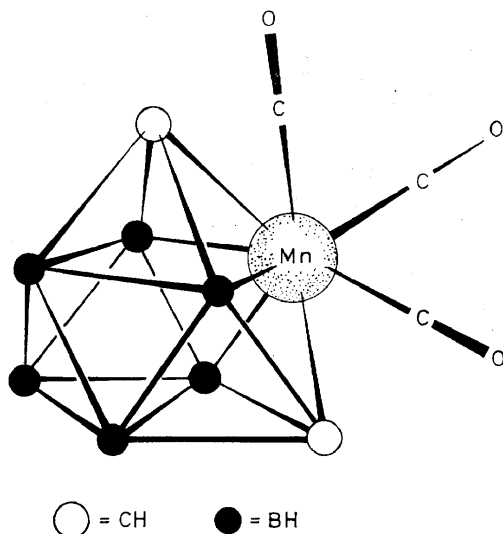


Figure 19. Simplified drawing of the proposed structure of the $[\pi\text{-B}_6\text{C}_2\text{H}_8]\text{Mn}(\text{CO})_3^-$ ion

the tricapped trigonal prism structure presented in Figure 19. Further work with this third series of polyhedral ions is in progress. The fate of the boron atom removed from the $\text{B}_7\text{C}_2\text{H}_{11}^{2-}$ precursor has not, as yet, been determined.

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