

half-time for the reverse reaction (relaxation) in the dark is about 90 min.

The optical rotatory dispersion Cotton effect trough at  $233\text{ m}\mu$  remains essentially unchanged, while the side-chain Cotton effect near  $335\text{ m}\mu$  decreases. These results indicate that the helical conformation of the polypeptide backbone is unaffected by the *cis-trans* photoisomerization.

In contrast, upon irradiation in trifluoroacetic acid at  $425\text{ m}\mu$ , the  $\lambda_{\text{max}}$  of the conjugate acid, the half-time for the partial conversion of the *trans* protonated azoaromatic side chains to photoequilibrium form containing *cis*-protonated configuration is only about 160 min. Unexpectedly, the half-time for the relaxation in the dark is much longer, 210 min. Also, the optical rotatory dispersion Cotton effect at  $425\text{ m}\mu$  for the *trans* form is replaced at somewhat lower wavelengths by Cotton effects that are of opposite sign and greater magnitudes. These observations are attributed to side-chain-side-chain interactions which tend to stabilize the extended *cis* form, once it is formed by irradiation.

### Conclusion

There is, today, much interest in the aspects of protein structure-function relationship. Specifically scientists are concerned with possible conformational altera-

tions which accompany interactions of biological macromolecules with other cellular constituents. Optical methods such as optical rotatory dispersion and circular dichroism spectra shed light on structural changes in biopolymers which are not primarily due to over-all change in helix content but rather to local conformations at particular sites. These may not affect any periodic or nonperiodic arrangement of peptide main chain bonds. Poly- $\alpha$ -amino acids with aromatic side chains provide an important model to study such delicate and subtle changes in conformation. Optical activity and circular dichroism are extremely sensitive to the environment and interactions of the aromatic side chains. We have discussed the difficulties in interpreting data for poly- $\alpha$ -amino acids where aromatic chromophoric effects overlap peptide group electronic transitions. Because of this, much remains uncertain for the specific analysis of poly- $\alpha$ -amino acid and protein conformations. However, these findings can be used as a powerful tool to yield information on side-chain structure-function relationships. Perhaps in the future we can obtain fascinating results on aromatic-side-chain effects in biopolymer structure by use of high-frequency nuclear magnetic resonance. Coupling patterns for *ortho* and *meta* protons should reveal specific interactions and orientations of the aromatic group with respect to the main chain.

## The Chemistry of the Polyhedral Species Derived from Transition Metals and Carboranes

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The first definitive research in boron hydride chemistry was conducted by Stock and his students who succeeded in preparing small quantities of several boron hydrides ( $\text{B}_2\text{H}_6$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_9$ ,  $\text{B}_5\text{H}_{11}$ ,  $\text{B}_6\text{H}_{10}$ , and  $\text{B}_{10}\text{H}_{14}$ ). This early work was necessarily carried out using the then newly developed vacuum-line technique. Later work by Schlesinger and his students at the University of Chicago led to improved preparative methods for the boron hydrides and uncovered many new reactions of these novel species. Throughout these early days little was known with regard to the structures of the boron hydrides. Consequently, the boron hydrides were regarded as unstable and highly reactive chemical oddities of unknown importance until X-ray and electron diffraction techniques elucidated their unusual structures and the unconventional multi-center bonding associated with these structures.

Following World War II, a high-energy fuel program was established under military auspices with the intent of producing large quantities of liquid boron hydride derivatives. The impetus which this program gave to boron hydride research culminated in the discovery

of the extraordinarily stable polyhedral borane ions<sup>1</sup> ( $\text{B}_n\text{H}_n^{2-}$ ,  $n = 10$  and  $12$ ) and the icosahedral  $\text{B}_{10}\text{C}_2\text{H}_{12}$  carboranes.<sup>1</sup> These highly symmetrical species are stabilized by three-dimensional electron delocalization, and they may be considered to be the aromatic members of the boron hydride series. These discoveries have since led to the characterization of the entire polyhedral ion and the corresponding isoelectronic carborane series ( $n = 6-12$  in  $\text{B}_n\text{H}_n^{2-}$  and  $\text{B}_{n-2}\text{C}_2\text{H}_n$ ).

While these developments are significant in themselves, more recent work<sup>2</sup> has opened up a new field of research which combines polyhedral carborane and transition metal chemistries in much the same way as the first metallocenes were fashioned from aromatic organic species and transition metal derivatives. Several families of polyhedral species are now known in

(1) See M. F. Hawthorne in "The Chemistry of Boron and its Compounds," E. L. Muetterties, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p 223, or E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Dekker Publishing Co., New York, N. Y., 1968, for recent reviews of this subject.

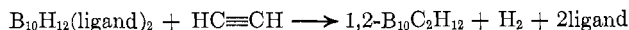
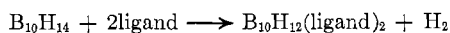
(2) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).

which a transition metal resides in the polyhedral surface. The remarkable stability exhibited by many of these materials suggests that they are stabilized by a degree of electron delocalization closely akin to that found in the  $B_nH_n^{2-}$  ions,<sup>1</sup> the carboranes,<sup>1</sup> and the more stable metallocenes. It is quite likely that species of this type will provide a new probe for the coordination chemist and for those interested in chemical bonding phenomena since rather unusual formal oxidation states of the common transition metals may be attained. In addition, many potential applications of a practical nature are apparent.

The original work conducted in this area of chemical synthesis involved the preparation of the  $B_9C_2H_{11}^{2-}$  ligand which,<sup>2,3</sup> as shown below, resembles the well-known  $\pi$ -bonding cyclopentadienide ion. The  $B_9C_2H_{11}^{2-}$  ion (or dicarbollide ion) is known in two isomeric forms, each of which constitutes an 11-particle icosahedral fragment capable of regenerating an icosahedral surface upon coordination of a transition metal at the open vertex. Later work has shown that bonding of this sort is not restricted to the  $B_9C_2H_{11}^{2-}$  ions and may be extended to the  $B_{10}CH_{11}^{3-}$ <sup>4</sup> and  $B_{10}SH_{10}^{2-}$ <sup>5</sup> icosahedral fragment ions and the  $B_7C_2H_9^{2-}$ <sup>6</sup> and  $B_6C_2H_8^{2-}$ <sup>7</sup> ions of totally different geometry. The chemistry of the  $B_9C_2H_{11}^{2-}$ ,  $B_7C_2H_9^{2-}$ , and  $B_6C_2H_8^{2-}$  derivatives will be emphasized in this article. Since these ligands are ultimately derived from two of the three isomeric  $B_{10}C_2H_{12}$  carboranes, the discussion begins with a brief review of pertinent icosahedral carborane chemistry.

### The Preparation and Selective Degradation of the 1,2- and 1,7- $B_{10}C_2H_{12}$ Carboranes

Two of the three isomeric  $B_{10}C_2H_{12}$  icosahedral carboranes were first reported in the unclassified literature in the early 1960's.<sup>8,9</sup> The preparation of these compounds and certain of their derivatives is based upon the reaction of an alkyne with  $B_{10}H_{12}(\text{ligand})_2$  intermediates<sup>8</sup> (ligand =  $R_2S$  or  $RCN$ ) to produce the 1,2 isomer of  $B_{10}C_2H_{12}$ ,<sup>8</sup> followed by thermal rearrangement of the initial product at 400–500° to the 1,7 isomer.<sup>9</sup> The icosahedral structure and numbering system<sup>10</sup> is depicted in Figure 1. The positions of the CH units are denoted by the prefix numbers.<sup>10</sup>



(3) (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. Andrews, *Chem. Commun.*, 443 (1965).

(4) (a) W. H. Knoth, *J. Am. Chem. Soc.*, **89**, 3343 (1967); (b) D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *ibid.*, **89**, 3342 (1967).

(5) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

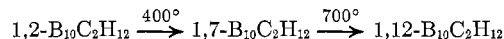
(6) M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967).

(7) M. F. Hawthorne and A. D. Pitts, *ibid.*, **89**, 7115 (1967).

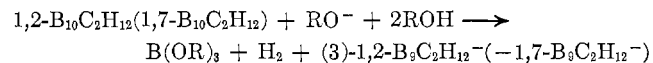
(8) (a) T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963); (b) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).

(9) D. Graffstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

(10) R. Adams, *ibid.*, **2**, 1087 (1963).



While the icosahedral carborane isomers and their derivatives enter into a variety of functional group reactions without disruption of the carborane nucleus,<sup>1</sup> the 1,2 and 1,7 isomers are susceptible to degradation with strong bases.<sup>11,12</sup> The products of these nearly quantitative degradation reactions have been characterized as 11-particle icosahedral fragments<sup>11,12</sup> having the composition  $B_9C_2H_{12}^-$ . The proposed heavy atom structures of these ions are depicted in Figure 2. The



precise position of the twelfth (or "extra") hydrogen atom is presently unknown although it most certainly takes up residence in the region of the open five-membered face of both isomeric ions. The removal of a  $BH^{2+}$  unit from the parent carboranes by bases may be rationalized in terms of nucleophilic attack at the most electron-deficient boron atoms in the icosahedral structures. These boron atoms are located<sup>13</sup> at the 3,6 and 3,2 positions in the 1,2- and 1,7- $B_{10}C_2H_{12}$  carboranes, respectively. The carbon atoms present in the icosahedral structures of the 1,2- and 1,7-carboranes provide centers of high positive charge which, in turn, activate the neighboring boron atoms

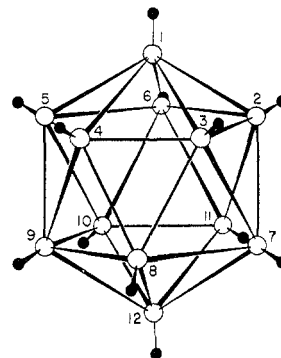


Figure 1. Icosahedral structure and numbering system employed for the  $B_{10}C_2H_{12}$  carboranes and derivatives.

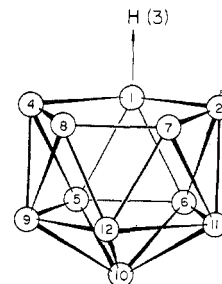


Figure 2. Simplified drawing of the isomeric  $B_9C_2H_{12}^-$  structures with B-H and C-H hydrogen atoms omitted.

(11) (a) R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964); (b) P. M. Garrett, F. N. Tebbe, and M. F. Hawthorne, *ibid.*, **86**, 5016 (1964).

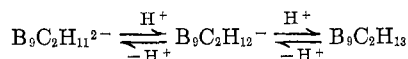
(12) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwein, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

(13) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc. New York, N. Y., 1963.

for attack by base. In this and previous presentations<sup>1,2</sup> of  $B_9C_2H_{12}^-$  chemistry we have, for consistency, defined the open vertex of the icosahedron as position 3. In this manner, the prefix numbers denoting carbon atom positions in the  $B_9C_2H_{12}^-$  ions remain 1,2 and 1,7 as in the parent carboranes. The prefix (3)- employed in formulas expresses the use of this arbitrary convention, *i.e.*, (3)-1,2- and (3)-1,7- $B_9C_2H_{12}^-$ .

### The Isomeric Dicarbollide Ions

Protonation of the (3)-1,2- and (3)-1,7- $B_9C_2H_{12}^-$  ions was found to produce an isomeric set of neutral  $B_9C_2H_{13}$  species<sup>11,14</sup> [(3)-1,2- and (3)-1,7- $B_9C_2H_{13}$ ] which are isoelectronic with the known  $B_{11}H_{13}^{2-}$  ion.<sup>15,16</sup> Both known isomers of  $B_9C_2H_{13}$  are very strong acids. Having established this point, it was reasonable to expect that the  $B_9C_2H_{11}^{2-}$  ions might exist. The latter ions would be extremely interesting if their structures approximated 11-particle icosahedral fragments since their open pentagonal faces would then most likely contain six delocalized electrons in five nearly equivalent  $sp^3$  atomic orbitals.<sup>1,2</sup> Such an array would closely resemble the cyclopentadienide ion, and five molecular orbitals,<sup>17</sup> which correspond to the  $A_1$ , the two  $E_1$ , and the two  $E_2$  molecular orbitals of that ion, should exist in the  $B_9C_2H_{11}^{2-}$  ions. This being the case, strong bonding to appropriate transition metal ions and the synthesis of "sandwich" species were anticipated. Consequently, it was most satisfying to find that both (3)-1,2- and (3)-1,7- $B_9C_2H_{12}^-$  and their C-substituted derivatives reacted with bases such as sodium metal or sodium hydride in ethereal solvents to produce hydrogen and the desired  $B_9C_2H_{11}^{2-}$  ions.<sup>2,3</sup> Protonation of the



dianions produced the corresponding monoanion in quantitative yield.<sup>2</sup> Further work proved that the  $B_9C_2H_{11}^{2-}$  ions could be generated in very concentrated aqueous hydroxide ion solution.<sup>18</sup>

Figure 3 illustrates the gross geometry of the  $B_9C_2H_{11}^{2-}$  ions and the probable disposition of the atomic orbitals associated with the open face.

Since the nomenclature employed throughout carborane chemistry was unwieldy, an attempt was made to adapt a trivial name for the isomeric  $B_9C_2H_{11}^{2-}$  ions. The Spanish noun "olla" describes a vessel having the rough shape of an 11-particle icosahedral fragment. Consequently, the presently unknown  $B_{11}H_{14}^{4-}$  ion became the "ollide ion" while the  $B_9C_2H_{11}^{2-}$  ions, being isoelectronic with the  $B_{11}H_{14}^{4-}$  ion, became the (3)-1,2- and (3)-1,7-dicarbollide ions.<sup>2</sup> Extension of this trivial nomenclature identifies the  $B_{10}CH_{11}^{3-}$  ion as (3)-1-carbollide ion.

(14) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).

(15) E. B. Moore, Jr., L. L. Lohr, Jr. and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(16) V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **1**, 734 (1962).

(17) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).

(18) L. F. Warren, Jr., and M. F. Hawthorne, *ibid.*, **89**, 470 (1967).

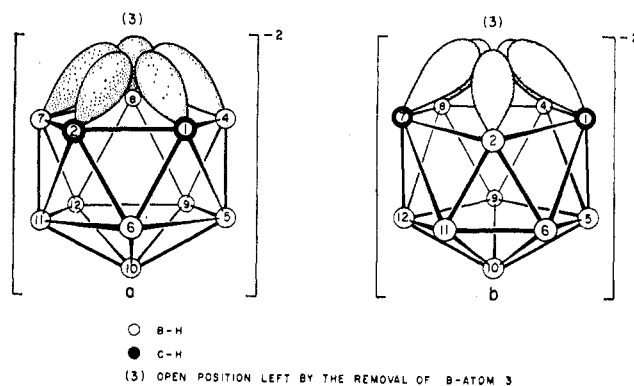
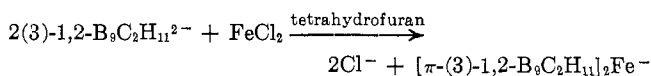


Figure 3. Proposed structures of the two isomeric  $B_9C_2H_{11}^{2-}$  (dicarbollide) ions.

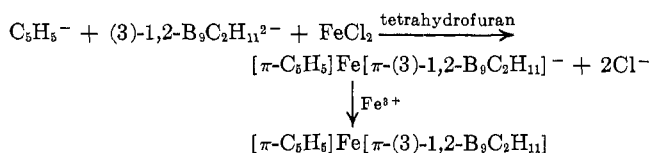
### Transition Metal Derivatives of the (3)-1,2- and (3)-1,7-Dicarbollide Ions

The first demonstration of a reaction in which a transition metal ion was inserted in the open face of a dicarbollide ion involved the reaction of ferrous chloride with the (3)-1,2- $B_9C_2H_{11}^{2-}$ ,<sup>2,3a</sup> ion. The reaction conditions were identical with those employed in the preparation of ferrocene. The resulting product was easily air oxidized to a complex which contained iron



in the formal oxidation state of 3+. Reduction of the  $Fe^{3+}$  derivative regenerated the  $Fe^{2+}$  species. The structure of the iron(III) complex was deduced<sup>2,19</sup> from <sup>11</sup>B nmr studies coupled with an X-ray diffraction study<sup>20</sup> of  $[\pi\text{-}C_5H_5]Fe[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$  to be discussed below. The  $Co^{2+}$  and  $Co^{3+}$  "sandwich" species were obtained from  $CoCl_2$  and the (3)-1,2-dicarbollide ion in an analogous fashion.<sup>2,3b</sup> Figure 4 presents the structure of the  $d^5$  iron system and the most probable structure of the corresponding  $d^6$  cobalt species. The structure of the  $d^7$   $Co^{2+}$  species has not yet been determined by X-ray diffraction studies or other methods. Attempts to incorporate the (3)-1,7- $B_9C_2H_{11}^{2-}$  ion in iron insertion reactions have as yet been unsuccessful. However, the complex  $[\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]_2Co^-$  was successfully prepared, and the "sandwich" structure shown in Figure 4 was confirmed<sup>21</sup> by X-ray diffraction studies, which could not distinguish the carbon atom positions.

The possibility of "sandwich" bonding of a  $C_5H_5^-$  and a (3)-1,2- $B_9C_2H_{11}^{2-}$  ion to the same iron or cobalt ion was examined, and  $[\pi\text{-}C_5H_5]Fe[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ ,<sup>19</sup> the corresponding iron species containing  $Fe^{2+}$ , and  $[\pi\text{-}C_5H_5]Co[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ <sup>3b</sup> were prepared. Fig-



(19) M. F. Hawthorne and R. L. Pilling, *ibid.*, **87**, 3987 (1965).

(20) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 8988 (1965).

(21) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **6**, 1911 (1967).

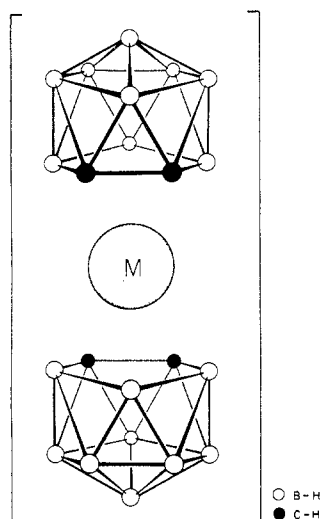


Figure 4. Generalized structure of the symmetrically bonded "π-sandwich" derivatives.

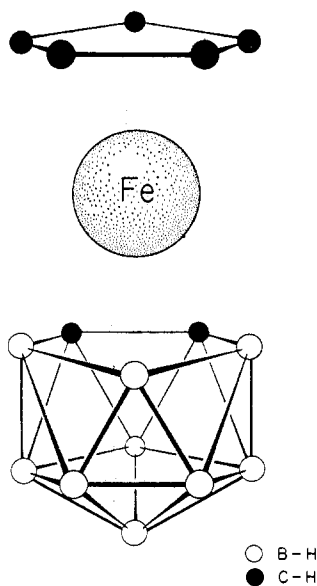


Figure 5. Structure of  $[\pi\text{-C}_5\text{H}_5]\text{Fe}[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]$ .

ure 5 depicts the structure of the  $d^5 \text{Fe}^{3+}$  mixed complex which resulted from an X-ray diffraction study.<sup>20</sup> Although, by way of example, only the unsubstituted derivatives of the iron and cobalt systems were discussed above, many C-substituted dicarbollide ions have been employed in similar reactions.<sup>2</sup>

The  $d^5 \text{Fe}^{3+}$  and  $d^6 \text{Co}^{3+}$  "sandwich" derivatives were found<sup>2</sup> to be surprisingly stable toward ordinary acids, bases, and oxidizing agents. Such stability undoubtedly reflects the presence of a high electron-delocalization energy.

Although the derivative chemistry of the various dicarbollide "sandwich" species has not yet been fully explored, one reaction, which is apparently an electrophilic substitution reaction, warrants discussion. Bromination<sup>2</sup> of  $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Co}^-$  in acetic acid solution at  $100^\circ$  results in the formation of a hexabromo derivative in high yield. X-Ray diffraction<sup>22</sup> studies

(22) The author wishes to thank Professor D. H. Templeton and Dr. A. Zalkin for this information received prior to publication.

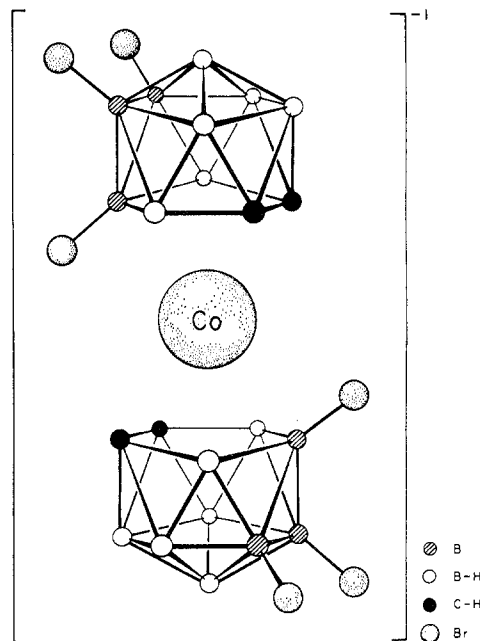
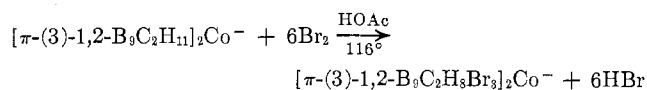
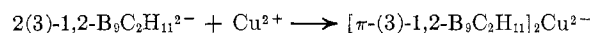


Figure 6. Structure of the  $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_8\text{Br}_3]_3\text{Co}^-$  ion.



proved that the hexabromocobalt complex has the structure shown in Figure 6. Electrochemical studies demonstrated that the hexabromo derivative containing formal  $\text{Co}^{3+}$  could be reduced in a two-step reversible process to the corresponding  $\text{Co}^+$  species.<sup>2</sup> This reduction is probably facilitated by the strong electron-attracting inductive effect of the bromine substituents. The positions of the bromine substitution (8, 8', 9, 9', 12, and 12') are as far removed from the carbon atoms in the ligand as possible. Furthermore, it seems likely that these positions establish the regions of highest electron density in the ground-state complex ion.

The reaction of the  $d^9 \text{Cu}^{2+}$  ion with aqueous  $(3)\text{-1,2-B}_9\text{C}_2\text{H}_{11}^{2-}$  led to the formation of a bright blue paramagnetic copper "sandwich." Chemical oxidation of this complex produced a red complex which was



shown by subsequent electrochemical studies<sup>2</sup> to be a formal  $d^8 \text{Cu}^{3+}$  sandwich. Cyclic voltammetry with the  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  complexes gave two reversible one-electron redox waves, incorporating a  $\text{Cu}^+$  species in the series. X-Ray diffraction studies of the  $d^9 \text{Cu}^{2+}$ <sup>23</sup> and  $d^8 \text{Cu}^{3+}$ <sup>24</sup> complex proved that both species were isostructural, having the "slipped sandwich" structure shown in Figure 7. These complexes are the first reported "sandwich" derivatives of copper. The unique slippage of the metal toward the three boron atoms in the open face of the ligand represents a displacement from the center line of  $0.6 \text{ \AA}$  for each ligand. Wing<sup>23,24</sup> has interpreted this structure as an

(23) R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).

(24) R. M. Wing, *ibid.*, **90**, 4828 (1968).

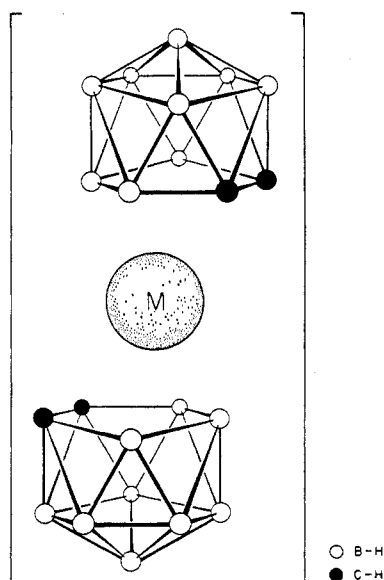


Figure 7. Generalized structure of the " $\pi$ -slipped sandwich" derivatives.

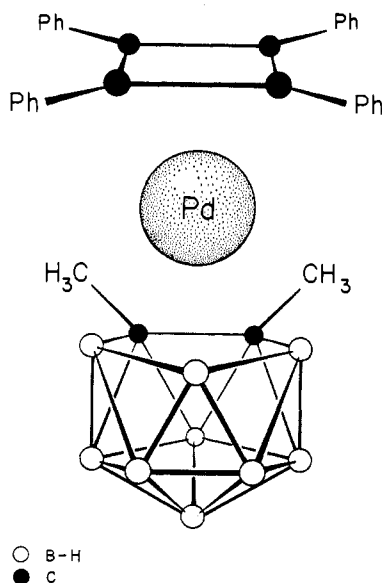


Figure 8. Structure of the  $[\pi\text{-C}_4(\text{C}_6\text{H}_5)_4]\text{Pd}[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_9(\text{CH}_3)]$  species.

analog of the many well known  $\pi$ -allylmetal complexes. An alternative scheme has been suggested.<sup>25</sup> Further studies have led to the preparation and characterization of gold,<sup>25</sup> palladium,<sup>25</sup> and nickel<sup>2,18</sup> complexes having a variety of oxidation states and "sandwich" structures,<sup>26</sup> some of which appear to be "slipped." In addition, a mixed complex containing tetraphenylcyclobutadiene and (3)-1,2-dicarbollide ligands has been reported.<sup>27</sup> This complex has the structure<sup>28</sup> shown in Figure 8.

Chromium complexes containing formal  $\text{Cr}^{3+}$  (two unpaired electrons) have been obtained,<sup>29</sup> and their

(25) L. F. Warren, Jr., and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 4823 (1968).

(26) Independent and unpublished work of R. M. Wing and G. D. Stucky, for which the author is indebted.

(27) P. A. Wegner and M. F. Hawthorne, *Chem. Commun.*, 861 (1966).

(28) We are indebted to Professor D. H. Templeton and Dr. A. Zalkin for the preliminary results of this investigation.

(29) H. Rühle and M. F. Hawthorne, *Inorg. Chem.*, in press.

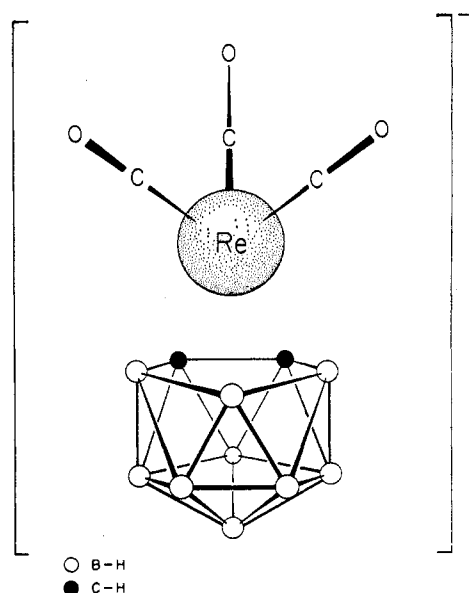
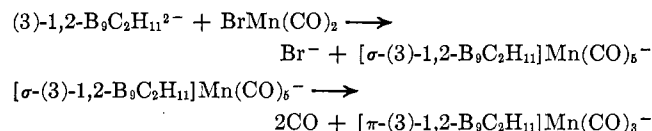


Figure 9. Structure of the  $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Re}(\text{CO})_3^-$  ion.

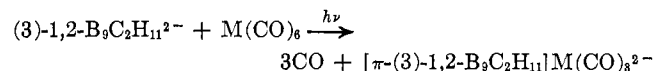
structure has been shown to be a symmetrically bonded sandwich<sup>30</sup> (Figure 4).

Since a large family of  $\pi$ -bonded organometallic compounds is derived from the metal carbonyls, efforts were made to synthesize several analogs which contained the (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$  ligand. The initial effort in this area was a study of the reactions of bromomanganese and bromorhenium pentacarbonyls<sup>31</sup> with (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$  and its C-substituted derivatives. In these reactions, bromide ion is rapidly formed followed by the slower evolution of carbon monoxide.



The  $\pi$ -bonded products of these reactions are remarkably stable toward air oxidation and hydrolysis. Their composition and structure are analogous to the known  $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$  species, as shown by an X-ray diffraction study with the rhenium product.<sup>32</sup> Figure 9 illustrates the structure of this ion.

The photochemical reaction of the (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$  ion with chromium, molybdenum, and tungsten hexacarbonyls led to the analogs of the  $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3^-$  ions ( $\text{M} = \text{Cr}, \text{Mo}, \text{and W}$ ).<sup>33</sup> The precise structures



of the tricarbonyl dianions have not yet been obtained by X-ray diffraction studies, but spectroscopic evidence suggests that they are isostructural with the manganese and rhenium tricarbonyl anions discussed above (Figure

(30) The author is indebted to Professor D. H. Templeton and Dr. A. Zalkin for these results received in advance of publication.

(31) M. F. Hawthorne and T. D. Andrews, *J. Am. Chem. Soc.*, **87**, 2496 (1965).

(32) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, **5**, 1189 (1966).

(33) (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); (b) E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allgem. Chem.*, **282**, 47 (1955).

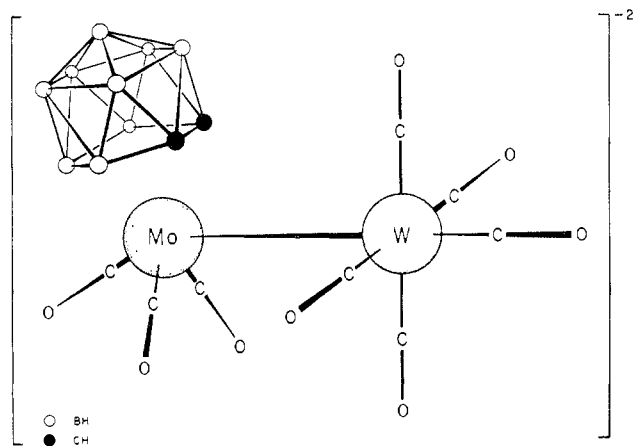


Figure 10. Probable structure of the dinuclear metal carbonyl,  $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3\text{W(CO)}_5^{2-}$ .

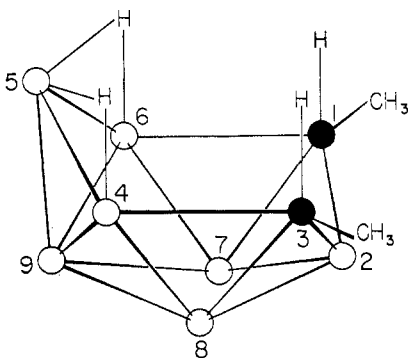
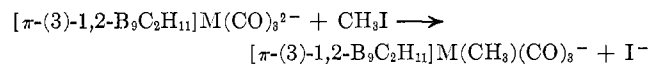
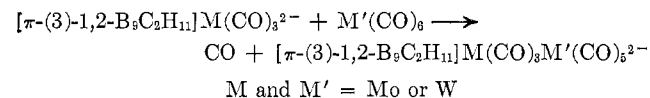


Figure 11. Structure of the C,C'-dimethyl derivative of  $\text{B}_7\text{C}_2\text{H}_{13}$ .

9). In addition, the molybdenum- and tungsten-containing products show<sup>2</sup> the known nucleophilic character<sup>33</sup> of the  $\pi\text{-C}_5\text{H}_5\text{M(CO)}_3^-$  (M = Cr, Mo, and W) systems.



In addition to the alkylation reaction shown above, these dianions are reversibly protonated<sup>2</sup> to form acidic metal hydride derivatives. Of more interest, perhaps,

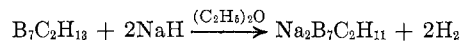


is the nucleophilic displacement of one CO ligand from the  $\text{M}'(\text{CO})_5$  species (M' = Mo or W) to produce<sup>2</sup> a novel series of dinuclear metal carbonyl derivatives. The latter ions have been briefly examined by X-ray diffraction methods, and the most reasonable structure is presented in Figure 10.<sup>34</sup>

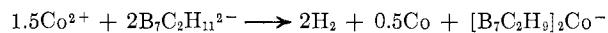
### Transition Metal Derivatives of the $\text{B}_7\text{C}_2\text{H}_9^{2-}$ and $\text{B}_6\text{C}_2\text{H}_8^{2-}$ Ligands

The  $\text{B}_7\text{C}_2\text{H}_{13}$  carborane system was recently described,<sup>35</sup> its structure was deduced from chemical

evidence<sup>35,36</sup> and confirmed by an X-ray diffraction study (Figure 11).<sup>37</sup> The most remarkable feature of the  $\text{B}_7\text{C}_2\text{H}_{13}$  carborane and its C-substituted derivatives is the high acidity of the axial hydrogen atoms<sup>35-37</sup> present in the methylene group. In addition, the B-H-B bridge hydrogen atoms are also available for ionization.<sup>35,36</sup> It was of interest, therefore, to remove as many protons from  $\text{B}_7\text{C}_2\text{H}_{13}$  as possible and to treat the resulting ion in the same fashion as the (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$  ion. The first step was accomplished with sodium hydride and led to the formation of the  $\text{B}_7\text{C}_2\text{H}_{11}^{2-}$  ion.<sup>6</sup> The latter ion has not, as yet, been isolated and characterized. Subsequent reaction of the



$\text{B}_7\text{C}_2\text{H}_{11}^{2-}$  ion with cobaltous chloride in diethyl ether furnished the first member of a new polyhedral complex ion<sup>6</sup> series which contains a transition metal combined with a carborane fragment. The insertion reaction was accompanied by a redox reaction, as shown, and



the product contained  $d^6 \text{Co}^{3+}$  and two  $\text{B}_7\text{C}_2\text{H}_9^{2-}$  ligands. Similar reactions have since been carried out with a variety of metals and the corresponding complexes characterized. A  $\text{Co}^{3+}$  complex was prepared in which a  $\pi\text{-C}_5\text{H}_5^-$  ligand was present in the same molecule<sup>6</sup> as the  $\text{B}_7\text{C}_2\text{H}_9^{2-}$  ligand. The  $^{11}\text{B}$  nmr spectra (32 Mcps) of all of the diamagnetic complexes contained a distinct low-field doublet, thought to represent a boron atom of low coordination number, and seven well-defined doublets in all. The  $^1\text{H}$  nmr spectra (60 Mcps) of these same complexes contained two resonances attributed to two types of carborane CH units. Thus, all evidence pointed to the fact that the  $\text{B}_7\text{C}_2\text{H}_{11}^{2-}$  ligand contained no equivalent atoms. Such a structure of the ligand was in agreement with the idea that the cobalt ion serves as a vertex (equatorial) in a bicapped Archimedean antiprism. In this manner, the cobalt ion would be bonded to five heavy atoms in each of the two attached ligands and play essentially the same role as the metal ion in the dicarbollide complexes. This was confirmed by an X-ray diffraction study,<sup>38</sup> and the structure of the  $[\text{B}_7\text{C}_2\text{H}_9]_2\text{Co}^-$  ion is shown in Figure 12. Figure 13 depicts the probable structure of the  $[\pi\text{-C}_5\text{H}_5]\text{Co}[\text{B}_7\text{C}_2\text{H}_9]$  species.

The initially formed  $[\pi\text{-C}_5\text{H}_5]\text{Co}[\text{B}_7\text{C}_2\text{H}_9]$  and  $[\text{B}_7\text{C}_2\text{H}_9]_2\text{Co}^-$  complexes have been thermally rearranged<sup>39</sup> (24 hr at  $310^\circ$ ) to produce a single new isomer in each case. The low-field doublet found in the  $^{11}\text{B}$  nmr spectra of the starting materials is not seen in the spectra of the products. This suggests that the boron atom present in the apical position of the initial com-

(36) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **90**, 869 (1968).

(37) D. Voet and W. N. Lipscomb, *Inorg. Chem.*, **6**, 113 (1967).

(38) The author wishes to thank Professor D. H. Templeton, Dr. A. Zalkin, and Mr. D. J. St. Clair for this information received prior to publication.

(39) T. A. George and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 1661 (1968).

(34) The author is indebted to R. M. Wing for these preliminary results obtained prior to publication.

(35) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 607 (1966).

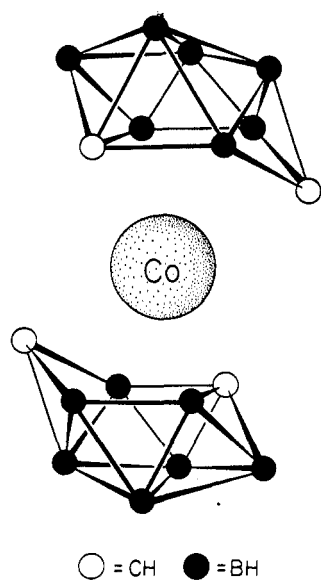


Figure 12. Structure of the  $[B_7C_2H_9]_2Co^-$  ion obtained from  $B_7C_2H_{11}^{2-}$  and  $Co^{2+}$ .

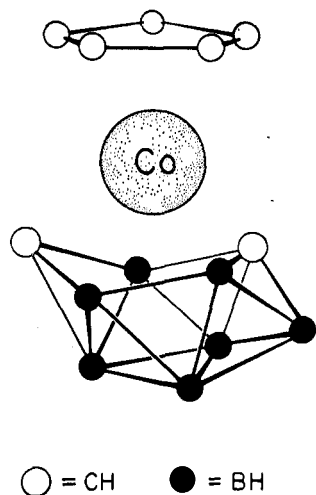


Figure 13. Proposed structure of  $[\pi-C_5H_5]Co[B_7C_2H_9]$  obtained from  $B_7C_2H_{11}^{2-}$ ,  $Co^{2+}$ , and  $C_5H_5^-$  ions.

plexes has been replaced by a carbon atom. The rearranged structures would then resemble those illustrated in Figures 14 and 15. An identical thermal rearrangement is observed<sup>36</sup> when 1,6- $B_8C_2H_{10}$  is converted to 1,10- $B_8C_2H_{10}$ .

The reaction of bromomanganese pentacarbonyl<sup>7</sup> with the  $B_7C_2H_{11}^{2-}$  ion resulted in the formation of bromide ion, CO, and an unidentified boron-containing species. In addition, a moderate yield of another new type of complex was obtained. This material has been formulated as the  $[B_6C_2H_8]Mn(CO)_3^-$  ion which contains a new  $B_6C_2H_8^{2-}$  ligand.<sup>7</sup> The  $^1H$  and  $^{11}B$  nmr spectra of this ion indicated two equivalent carborane protons (60 Mcps) and a 2:2:1:1 population of boron atoms (32 Mcps). On the basis of these results, the structure of this complex was formulated<sup>7</sup> as the tricapped trigonal prism shown in Figure 16. In this structure the  $Mn(CO)_3$  unit is also bonded to five heavy atoms.

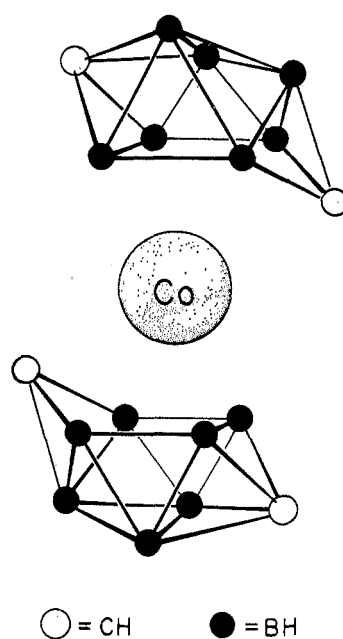


Figure 14. Proposed structure of  $[B_7C_2H_9]_2Co^-$  ion after thermal rearrangement.

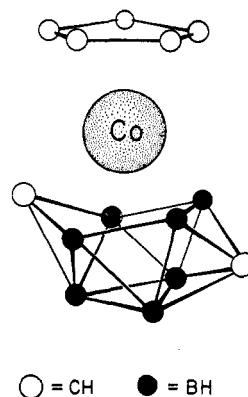


Figure 15. Proposed structure of  $[\pi-C_5H_5]Co[B_7C_2H_9]$  after thermal rearrangement.

Thus far, three series of polyhedral complexes have been obtained which have the gross polyhedral geometry of the known carboranes which would be formed by substituting a  $BH^{2+}$  for the metal ion. It will be very interesting to see if this series continues to expand. Further work is in progress and will be reported elsewhere.

### A Double-Barreled $\pi$ -Bonding Ligand

Some time ago it was observed that the preparation of certain (3)-1,2-dicarbollide metal complexes often produced colored by-products 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 protic solvents such as ethanol or water. Proceeding in this manner and using the  $[\pi-(3)-1,2-B_9C_2H_{11}]_2Co^-$  ion as a model, it proved possible to isolate a very

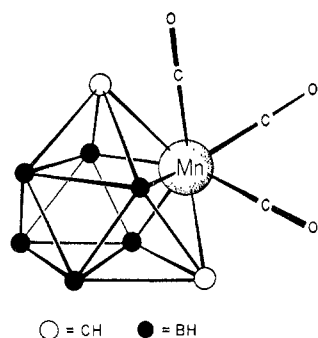


Figure 16. Proposed structure of the  $[B_5C_2H_8]Mn(CO)_3^-$  ion.

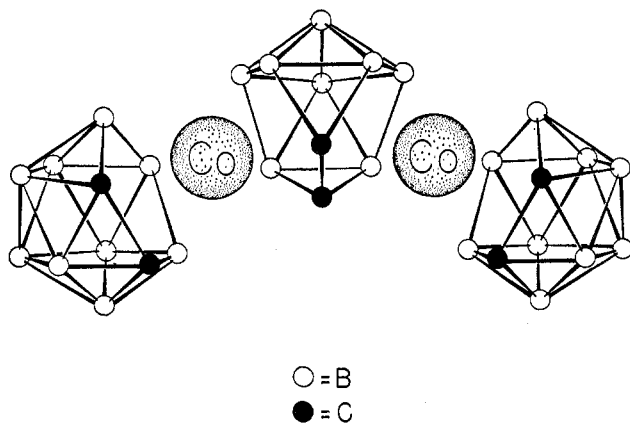


Figure 17. Double-barreled  $\pi$ -bonded complex containing cobalt and the (3,6)-1,2-dicarbacanastide ligand.

stable, bright red dianion<sup>40</sup> having the apparent composition  $B_{26}C_6H_{32}Co_2^{2-}$ . The  $^{11}B$  nmr spectrum of this ion was complex, but the  $^1H$  nmr spectrum revealed two types of carborane CH units present in a 2:1 ratio. A recently completed X-ray diffraction study<sup>38</sup> has confirmed the structure shown in Figure 17. The central, bifunctional ligand in this unusual structure

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

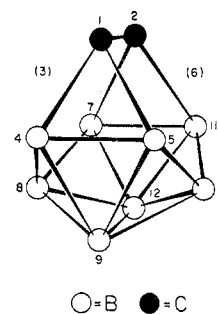


Figure 18. Simplified drawing of the (3,6)-1,2-dicarbacanastide ion having a charge of 4-.

might be considered to be a "double-barreled"  $\pi$ -bonding ligand which functions in much the same manner that 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  $B_5C_2H_{10}^{4-}$  ligand shown in Figure 18 resembles a basket, and we have accordingly given it<sup>40</sup> 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.

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