Translated from *Uspekhi Khimii*, **43**, 1207-1240 (1974) U.D.C. 547.401;547.401

Metallocarboranes

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A systematic account is given of the literature data on metallocarboranes. Particular attention is devoted to methods of their synthesis and their structures. The characteristic differences between metallocarboranes with π-linked carboranyl ligands and their π-cyclopentadienyl analogues are considered.
The bibliography includes 134 references.

CONTENTS

I. Introduction 551
II. Nomenclature 551
III. π-Complexes based on products of partial degradation of carboranes 551
IV. Metallocarboranes obtained by the polyhedral expansion reaction 566
V. Carborane derivatives of non-transition metals 569

I. INTRODUCTION

A new field in the chemistry of organic derivatives of the elements arose recently and has been developing vigorously—the chemistry of polyhedral carboranes. One of the most interesting properties of compounds of this class is the ability of carboranes or products of their partial degradation to react with derivatives of transition or non-transition metals to form metallocarboranes containing metal atoms at one or several vertices of the molecule. As a rule, transition metals combine with the carborane fragment in π-type complexes, as happens in their classical cyclopentadienyl derivatives. The bond between non-transition metals and the carbon and boron atoms of the polyhedron is described in terms of many-centre bonds, the main principles of which have been described in Lipscomb's monograph[1] on boron hydrides. The vigorous development of the chemistry of metallocarboranes, particularly in recent years, led us to write the present review, since the reviews in the literature are obsolete[2-4] or deal with selected studies by individual groups of workers[5-8].

In the present review the data have been arranged systematically in terms of types of metallocarboranes. The dicarbollyl complexes of transition metals, the largest class of metallocarboranes, are discussed first. Problems associated with metallocarboranes based on π-mono- and π-hetero-carbollyl ligands isoelectronic with the π-dicarbollyl ligand are considered next. This is followed by an examination of metallocarboranes containing a transition metal (in the vast majority of cases cobalt) and π-linked ligands comprising lower carboranes. The next section deals with metallocarboranes obtained by the polyhedral expansion reaction. Metallocarboranes containing a non-transition metal in the polyhedral molecule are considered in the last section.

Particular attention has been devoted in this review to the methods of synthesis and the structures of metallocarboranes and their most interesting physicochemical characteristics are described. The review embraces all studies in 1965–1972 (and partly in 1973).

II. NOMENCLATURE

The nomenclature in the field of metallocarboranes constitutes a fairly complex problem in view of the wide variety of carborane systems behaving as ligands and the continuous appearance of new derivatives the names of which do not fit within the framework of the IUPAC rules[9]. Therefore, together with the adopted nomenclature, we shall employ the trivial nomenclature widely used in the literature, which greatly simplifies the discussion of the problem and is to a large extent consistent with the literature data. The advantage of this approach to the problem consists also in a considerable abbreviation of the names of the compounds under consideration. For example, instead of the IUPAC name "caesium 3,3′-*commo*-bis(nonahydro-1,2-dicarba-3-chroma-*closo*-dodecaborate) we shall call the compound $[(B_9C_2H_{11})_2Cr]^-Cs^+$, the "caesium salt of bis(dicarbollyl)chromium". We may note that in the IUPAC nomenclature the terms "*commo*" and "*closo*" denote a closed polyhedral system and the term "*nido*" denotes structures containing open planes or B–H–B bridging linkages. The presence of carbon atoms in the polyhedron is designated by the term "*carba*" and their number is given by the prefixes mono-, di-, etc. The number of boron atoms is designated respectively by monobora, dibora, etc. One of the most widely investigated ions employed as a π-ligand, $B_9C_2H_{11}^{2-}$, has been called "dicarbollide" and the isoelectronic ions $B_{10}CH_{11}^{3-}$, $B_9CPH_{10}^{2-}$, and $B_9CAsH_{10}^{2-}$ have been called "carbollide", "phosphacarbollide", and "arsacarbollide" respectively. The numerals before the π-ligand formula denote the position of the carbon atoms or those of carbon and an element (phosphorus, arsenic) in the carborane moiety. For example, the carbon atoms in $1,2\text{-}B_9C_2H_{11}^{2-}$ are in the 1- and 2-positions of the dicarbollyl ligand and in $1,7\text{-}B_9CPH_{10}^{2-}$ the carbon atom is in the 1-position and the phosphorus atom in the 7-position of the phosphacarbollyl ligand. The number in brackets before the name of the ligand denotes the position occupied by the metal in the polyhedron.

III. π-COMPLEXES BASED ON PRODUCTS OF PARTIAL DEGRADATION OF CARBORANES

1. Dicarbollyl Complexes of Transition Metals

Icosahedral carboranes $B_{10}H_{10}C_2H_2$ interact with nucleophilic agents such as alkali metal alkoxides[10-12] and amines[13,14]. This results in the removal of the boron atom from the 3-position in *o*- and *m*-carborane rings and in the formation

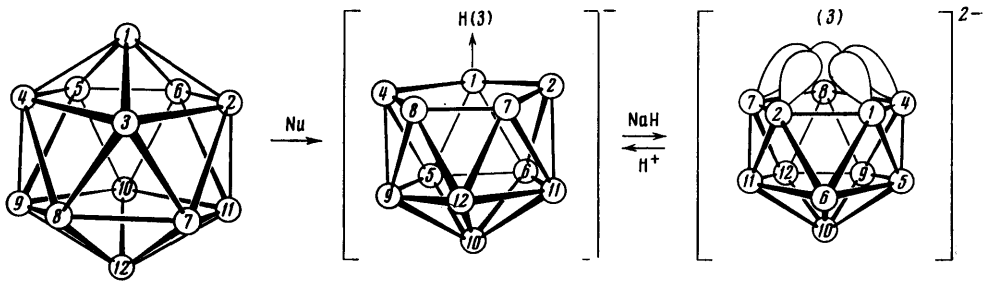


Figure 1.

of dicarbaundecaborate anions $B_9C_2H_{12}^-$. As shown for the first time by Hawthorne and coworkers[15,16], dicarbaundecaborate anions are acids which split off a proton on treatment with sodium hydride and give rise to the dicarbollide ion $B_9C_2H_{11}^{2-}$. The pK_a of the dicarbaundecaborate anion has been determined[17,18] and amounts to 21.3. Butyllithium has been used in some cases to generate the dicarbollide ion[19]. It has been shown that in a strongly alkaline medium there is an equilibrium between the dicarbaundecaborate and dicarbollide ions[16]; this has been used to obtain transition metal complexes in an aqueous medium. The (3)-1,2-$B_9C_2H_{11}^{2-}$ and (3)-1,7-$B_9C_2H_{11}^{2-}$ ions are isoelectronic with the hypothetical ion $B_{11}H_{11}^{4-}$. A structural scheme for the synthesis of dicarbollide ions is presented below (Fig. 1). Fig. 1 shows that the dicarbollide ion is a fragment of an icosahedron and consists of nine BH and two CH units. In the (3)-1,2-$B_9C_2H_{11}^{2-}$ ion the carbon atoms adjoin one another and in the (3)-1,7-$B_9C_2H_{11}^{2-}$ ion they are separated by a boron atom. According to the quantum-mechanical description of the dicarbollide ion[16], five atomic orbitals, largely sp^3-hybridised, are directed from the five atoms in the pentagonal B_3C_2 plane to the vacant position at the apex; six electrons are distributed in these orbitals. The combination of these atomic orbitals leads to one strongly bonding a_1-orbital, two degenerate bonding e_1-orbitals, and two strongly anti-bonding e_2-orbitals. Six electrons occupy the a_1- and both e_1-orbitals. In the reaction of the dicarbollide ion with transition metal salts dicarbollide complexes of the general type $(\pi\text{-}B_9C_2H_{11})_2M$ are formed. On the other hand, when the reaction is carried out in the presence of the cyclopentadienide ion, complexes of the type $[(\pi\text{-}C_5H_5)M\ (\pi\text{-}B_9C_2H_{11})]$ in some cases are formed. We shall examine the dicarbollyl complexes in terms of groups of transition metals.

A. The Iron Group

In the iron group (Fe, Ru, Os) the dicarbonyl complexes have been obtained for iron only. They were the first examples of metallocarboranes in which the transition metal is linked by a π-bond to the carborane moiety[15,20]. Hawthorn and coworkers[15,16] found that the 1,2-dicarbollide ion reacts with iron(II) chloride in tetrahydrofuran (THF) to form the bis(dicarbollyl)iron dianion $[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{II}]^{2-}$ in which the iron atom is in the +2 formal oxidation state (FOS). This ion is readily oxidised by atmospheric oxygen to $[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{III}]^-$ — an analogue of the ferrocinium ion. The structures of the dicarbollyliron complexes are presented in Fig. 2.

A detailed method for their synthesis in an aqueous medium has been published[21]. Iron(II) complexes are mainly obtained by the reduction of the corresponding iron(III) complexes with sodium amalgam:

$$1.2\text{-}B_9C_2H_{11}^{2-} + FeCl_2 \rightarrow [(\pi\text{-}1,\ 2\text{-}B_9C_2H_{11})_2Fe^{II}]^{2-} \underset{Na/Hg}{\overset{O_2}{\rightleftarrows}} [(\pi\text{-}1,\ 2\text{-}B_9C_2H_{11})_2Fe^{III}]^- .$$

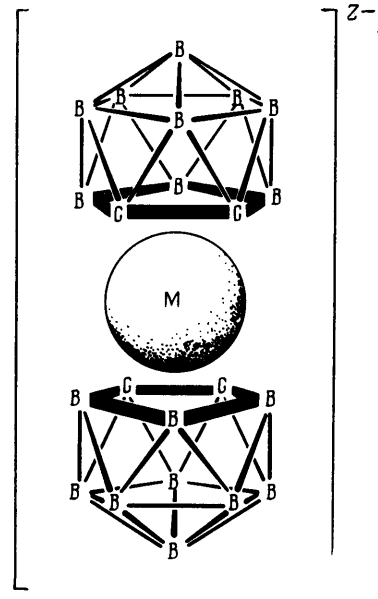


Figure 2.

Complexes based on *CC'*-dimethyl- and *C*-phenyl-1,2-dicarbollide ions have been obtained[16]. A method for the synthesis of dicarbollyliron complexes via the dithallium derivative of 1,2-dicarbollide was proposed recently[22]. The bis(dicarbollyl)iron(III) ion is resistant to the reaction of strong acids and alkalies and is thermally stable up to 300°C, but the corresponding *CC'*-dimethyl- and *C*-phenyl derivatives decompose in an aqueous alkaline solution on boiling via the mechanism

$$[(\pi\text{-}1,2\text{-}B_9C_2H_9Me_2)_2Fe]^- + OH^- + 2H_2O \rightarrow 2[1,2\text{-}B_9C_2H_{10}Me_2]^- + Fe(OH)_2.$$

Like ferrocene, the iron(II) complexes have the d^6 configuration and are diamagnetic, while the iron(III) complexes are paramagnetic. When a mixture of $C_5H_5^-$ and $1,2\text{-}B_9C_2H_{11}^{2-}$ ions was treated with iron(II) chloride in THF, low yields of π-cyclopentadienyl-π-dicarbollyliron complexes with the iron atom in the +2 or +3 formal oxidation state were obtained:

$$C_5H_5^- + 1,2\text{-}B_9C_2H_{11}^{2-} + FeCl_2 \rightarrow [(\pi\text{-}C_5H_5)\,Fe\,(1,2\text{-}B_9C_2H_{11})]^- \underset{Na/Hg}{\overset{[O]}{\rightleftarrows}}$$
$$\rightleftarrows (\pi\text{-}C_5H_5)\,Fe\,(1,2\text{-}B_9C_2H_{11})\ .$$

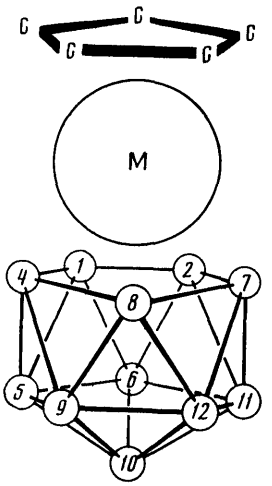


Figure 3.

A convenient method for the synthesis of the neutral complex $(\pi\text{-}C_5H_5)Fe(1,2\text{-}B_9C_2H_{11})$ in methanol with a yield in excess of 50% was proposed recently[23]. The structure of the π-cyclopentadienyl-π-dicarbollyliron(III) was determined[24] and the sandwich type of binding in this complex was confirmed (Fig. 3). It is interesting that the distances from the iron atom to the carbon atoms of the cyclopentadienyl ring and to the carbon and boron atoms in the pentagonal plane of the dicarbollyl ligand are the same, amounting to approximately 2.07 Å. The ESR spectra of all the dicarbollyliron(III) complexes showed the presence of an unpaired electron[25]. The experimental effective magnetic moments of the iron(III) complexes[26] were found to agree well with the values calculated theoretically[27]. Studies on the Mössbauer spectra of the complexes

$$[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{III}]^-,\ (\pi\text{-}C_5H_5)\,Fe^{III}\pi\text{-}1,2\text{-}B_9C_2H_{11}]$$
$$[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{II}]^{2-}\ \text{and}\ [(\pi\text{-}C_5H_5)\,Fe^{II}\,(\pi\text{-}1,2\text{-}B_9C_2H_{11})]^-$$

showed[28,29] that their quadrupole splitting parameters are analogous to the values for the corresponding biscyclopentadienyl derivatives, although they are somewhat higher. The reason for this is the higher s-electron density at the iron atom in the dicarbollyl complexes than in the cyclopentadienyl complexes, which suggests a more effective withdrawal of d electrons through π-bonding from the metal in the former case.

In C-substituted derivatives the bis-(1,2-dicarbollyl)-iron(II)$^{2-}$ residue exhibits powerful electron-donating properties both via the inductive mechanism ($\sigma_i = -0.27 - -0.43$) and via the conjugative mechanism ($\sigma_R = -0.15 - -0.22$), the properties being more pronounced than those of the ferrocenyl group[30]. The ^1H and ^{11}B NMR spectra and the oxidation-reduction potentials of dicarbollyliron complexes have been published[16]. The latter are presented in Table 1.

The reduction potentials of π-(3)-1,2-dicarbollyliron(III) complexes in 50% aqueous acetone.

Compound	$E_{1/2}$ for $M^{III} + e^- \rightarrow M^{II}$, mV	Compound	$E_{1/2}$ for $M^{III} + e^- \rightarrow M^{II}$, mV
$Me_4N[(1,2\text{-}B_9C_2H_{11})_2Fe]$	−0.424	$Me_4N[(1,2\text{-}B_9C_2H_{10}Ph)_2Fe]$	−0.464
$Me_4N[(1,2\text{-}B_9C_2H_9Me_2)_2Fe]$	−0.538	$(C_5H_5)Fe(1,2\text{-}B_9C_2H_{11})$	−0.080

One should note the higher thermal stability and the higher resistance to the action of acids and bases of the dicarbollyliron complexes compared with their cyclopentadienyl analogues—ferrocene and the ferrocenium ion. In contrast to ferrocene, the dicarbollyliron(II) complexes are rapidly oxidised to iron(III) complexes, which are more stable in this case.

When the 1,2-dicarbollide ion was treated with an excess of iron pentacarbonyl, a dimeric carbonyl product with π-dicarbollyl ligands was obtained[31]:

$$1,2\text{-}B_9C_2H_{11}^{2-} + Fe(CO)_5 \xrightarrow[70^\circ]{THF} \{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe_2(CO)_4\}^{2-}\ .$$

In the solid state the complex in the form of the tetramethylammonium salt decomposes slowly in air, while in solution in acetone or acetonitrile the decomposition is rapid. The *trans*-structure proposed initially for the dimer[31] was not confirmed and it was shown that, like $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, the μ-carbonylbis-[π(3)-1,2-dicarbollyl]-iron] dianion has the *cis*-configuration[32].

The chemistry of dicarbollyliron complexes has been little investigated. It has been established that in a strongly acid medium (concentrated HCl, $HClO_4$–CH_3OH), the complex $[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{II}]^{2-}$, which is an analogue of ferrocene, is protonated[33], but the ^1H NMR spectrum of $[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Fe^{II}H]^{2-}$ in a high field does not show the hydrogen signal characteristic of the protonated form of ferrocene $(C_5H_5)_2FeH^+$. The appearance in the infrared spectrum of $[(1,2\text{-}B_9C_2H_{11})_2FeH]^-$ of a band at 1835 cm^{-1} can equally indicate both the presence of an Fe–H bond and of B–H–B bridging linkages. For this reason, the available data do not allow a choice between these two alternative schemes[33]. It has been shown that the protonated form of bis-(1,2-dicarbollyl)iron(II) reacts smoothly with dialkyl sulphides, the reaction being accompanied by the evolution of hydrogen and the formation of *B*-substituted products[33]:

$$R_2S + [HFe^{II}(1,2\text{-}B_9C_2H_{11})_2]^- \rightarrow H_2 + [Fe^{II}(1,2\text{-}B_9C_2H_{11})(1,2\text{-}B_9C_2H_{10}SR_2)]^-\ .$$

The latter are readily oxidised with formation of neutral stable paramagnetic iron(III) complexes. The reverse reduction process is also possible:

$$[Fe^{II}(1,2\text{-}B_9C_2H_{11})(1,2\text{-}B_9C_2H_{10}SR_2)]^- \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} [Fe^{III}(1,2\text{-}B_9C_2H_{11})(1,2\text{-}B_9C_2H_{10}SR_2)]^0\ .$$

When hydrogen chloride was passed into a suspension of $[(1,2\text{-}B_9C_2H_{11})_2Fe^{III}]^-Cs^+$ in diethyl sulphide, a very low yield of the disubstituted complex $Fe^{II}(1,2\text{-}B_9C_2H_{10}SEt_2)_2$ was isolated together with the monosubstituted product. Chemical oxidation of the disubstituted complex led to the first example of cationic bis(dicarbollyl)metal complexes,

namely $[(1,2\text{-}B_9C_2H_{10}SEt_2)_2Fe^{III}]^+$.[33] The substitution mechanism at the boron atom of the dicarbollyl ligand is regarded as acid-catalysed nucleophilic substitution in which the proton removes the most hydridic hydrogen atom of the ligand with subsequent attack by the nucleophile at this position. The structure of the boron-substituted complexes, an example of which is presented in Fig. 4, was established on the basis of ^1H and ^{11}B NMR data.

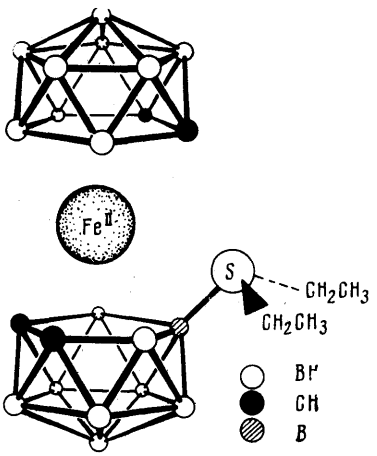


Figure 4.

When hydrogen chloride is passed into suspension of $[(1,2\text{-}B_9C_2H_{11})_2Fe^{III}]^-K^+$ in CS_2 in the presence of $AlCl_3$, a bridge-type dicarbollyl complex with an electron-deficient carbon atom is formed[34]:

$$[(1,2\text{-}B_9C_2H_{11})_2Fe]^- + CS_2 + H^+ \rightarrow \begin{matrix} 1,2\text{-}B_9C_2H_{10}S \\ Fe \\ 1,2\text{-}B_9C_2H_{10}S \end{matrix} \!\!>\!\!^{+}CH \ .$$

B. The Cobalt Group

In the cobalt group (Co, Rh, Ir) dicarbollyl complexes are known for cobalt only. The reaction of the 1,2-dicarbollide ion with cobalt chloride gives a high yield of the bis-(1,2-dicarbollyl)cobalt anion with the cobalt atom in the +3 formal oxidation state[16,35], the anion being an analogue of the cobalticinium ion:

$$2\,(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + 1,5\text{-}CoCl_3 \rightarrow \{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co\}^- + 3Cl^- + 0.5Co^0 \ .$$

A complex with the ion (3)-1,7-$B_9C_2H_{11}^{2-}$ – $\{[\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]_2CO\}^-$ was obtained analogously. When $CoCl_2$ interacts with a mixture of $C_5H_5^-$ and 1,2- or 1,7-$B_9C_2H_{11}^{2-}$ ions, neutral π-cyclopentadienyl-π-(3)-dicarbollylcobalt complexes are formed[16,35].

Improved methods for the synthesis of (π-C_5H_5)Co(π-1,2-$B_9C_2H_{11}$) complexes were proposed recently[23,36]. Dicarbollylcobalt complexes can be obtained via the dithallium dicarbollide[22]. X-Ray diffraction analysis of the caesium salt of bis-[(3)-1,7-dicarbollyl]cobalt(III)[37] confirmed that the structure presented in Fig. 2 is general. A series of π-cyclopentadienyl-π-C-substituted 1,2-dicarbollylcobalt complexes have been obtained[16,38], among which the greatest interest attaches to $(C_5H_5)Co^{III}[B_9C_2H_{10}\cdot(CH_2OH)]$. When CrO_3 was allowed to react with this complex, the *C*-formyl and *C*-carboxy-derivatives were synthesised[38]. The greater ease of the oxidation of the CH_2OH group to CHO compared with the oxidation of the latter to COOH is unusual in this case. The acid chloride was obtained from the acid; it enters into the Friedel–Crafts reaction with benzene in the presence of $AlCl_3$, giving a ketone:

$$(C_5H_5)Co[B_9C_2H_{10}(COCl)] + C_6H_6 \xrightarrow{AlCl_3} (C_5H_5)Co[B_9C_2H_{10}(COC_6H_5)] \ .$$

The pK_a for the acid $(C_5H_5)Co[B_9C_2H_{10}(COOH)]$ in 50% ethanol is 3.54.[38]

It is impossible to isolate dicarbollylcobalt(II) complexes. This suggests that the cobalt(II) complexes formed initially are rapidly oxidised by cobalt chloride with formation of very stable bis(dicarbollyl)cobalt(III) salts with the d^6 configuration. However, the existence of cobalt(II) complexes is supported by the oxidation-reduction potentials obtained by polarographic and cyclic volt-amperometric methods, which indicate the occurrence of one-electron reduction of bis(dicarbollyl)cobalt(III) and its *C*-substituted derivatives, i.e. the transition $d^6 \rightarrow d^7$ or $M^{III} + e^- \rightarrow M^{II}$.

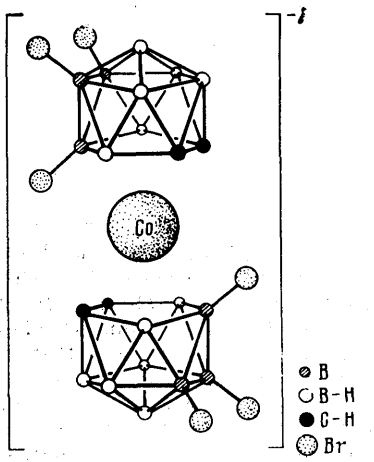


Figure 5.

In the case of an unsubstituted complex, the reversible one-electron M^{III} oxidation wave is observed at +1.57 mV, which led to the hypothesis that a dicarbollyl complex with a cobalt atom in the +4 formal oxidation state exists[16]. A careful electrochemical study of dicarbollylcobalt complexes led to the conclusion that the dicarbollyl ligand stabilises the metal in both the highest and the lowest oxidation states and for the complexes (π-C_5H_5)Co(π-1,2-$B_9C_2H_{11}$) and $[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$ the $M^{III} + e^- \rightarrow M^I$ transition is observed at −2.11 and −2.24 mV respectively together with $M^{III} + e^- \rightarrow M^{II}$.[39]

Bromination of the rubidium salt of $[(1,2\text{-}B_9C_2H_{11})_2Co]^-$ in acetic acid gave the hexabromo-derivative[16], where there are three halogen atoms in each π-ligand according to X-ray diffraction data[40] (Fig. 5). This compound is

interesting in the sense that its two one-electron reduction waves corresponding to the processes

$$Co^{III} + e^- \xrightarrow{-0.48\ mV} Co^{II} \text{ and } Co^{II} + e^- \xrightarrow{-1.58\ mV} Co^{I},$$

are displaced to the region of highly positive potentials and clearly confirm the possibility of the existence of π-bonded cobalt d^8-complexes[16].

The 1,2-dicarbollide ion reacts with dicobalt octacarbonyl to form π-dicarbollyldicarbonylcobalt, which is readily oxidised[30]:

$$2(1,2\text{-}B_9C_2H_{11}^{2-}) + Co_2(CO)_8 \rightarrow 2\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co(CO)_3\}^- + 4CO.$$

In the synthesis of dicarbollyl complexes in a highly alkaline medium there is a possibility of further degradation of the dicarbollyl ligand in the complex with elimination of the BH unit. In this case the product is the bidentate π-bonding ligand $B_8C_2H_{10}^{4-}$, which has been called the (3,6)-1,2-dicarbanastide ion, whose interaction with an excess of the transition metal salt and the π-ligands leads to two- and three-metal derivatives. Thus in a highly alkaline medium $[(1,2\text{-}B_9C_2H_{11})_2Co]^-$ is converted by $CoCl_2$ and $1,2\text{-}B_9C_2H_{11}^{2-}$ ions into

$\{[(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co[(3,6)\text{-}1,2\text{-}B_8C_2H_{10}]Co[(3)\text{-}1,2\text{-}B_9C_2H_{11}]\}^{2-}$ (Fig.6)

and $[\{[(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co[(3,6)\text{-}1,2\text{-}B_8C_2H_{10}]\}_2Co]^{3-}$ (Fig.7) [41-44].

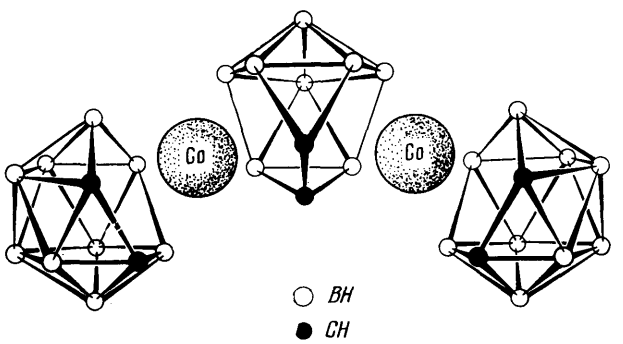


Figure 6.

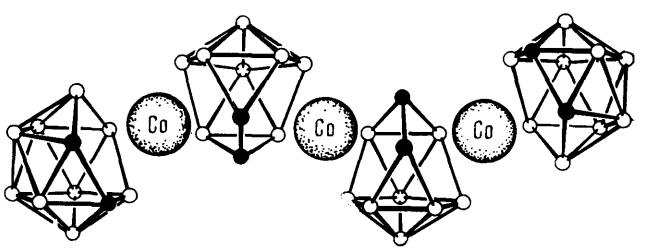


Figure 7.

$(C_5H_5)Co(1,2\text{-}B_9C_2H_{11})$ reacts with $CoCl_2$ and $C_5H_5^-$ in the presence of alcoholic alkali to form $[(C_5H_5)Co]_2[(3,6)\text{-}B_8C_2H_{10}]$ (Fig. 8) and $\{(C_5H_5)Co[(3,6)\text{-}1,2\text{-}B_8C_2H_{10}]\}_2Co$ (Fig. 9).[36] The ^{11}B NMR spectra of the $\eta[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co\}^-$ ion and of its *B*-deuteriated and *B*-halogenated derivatives have been recorded[45] at 70.6 MHz and the signals in the spectrum have been assigned to the corresponding boron atoms in the ligand. On the basis of the ^{59}Co NQR spectra of $Cs(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Co$, Harris[46] concluded that the π-dicarbollyl and π-cyclopentadienyl groups are almost indistinguishable as regards binding to Co^{III} and Fe^{II} and the boron atoms in the dicarbollyl ligand have an electron-donating capacity close to that of carbon atoms. However, subsequently this view was revised[28].

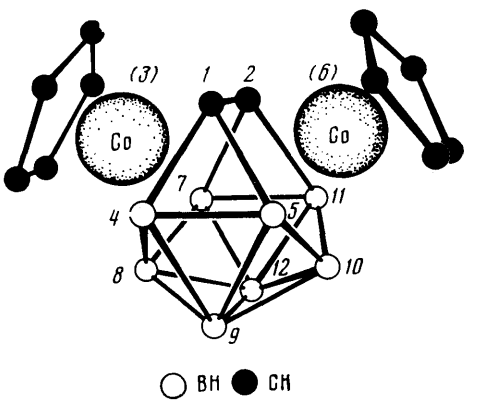


Figure 8.

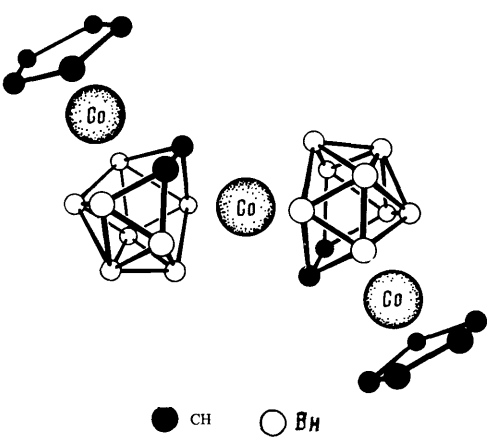


Figure 9.

As a substituent linked via the carbon atoms of the ligand, bis(dicarbollyl)cobalt is a weak electron acceptor via the inductive mechanism ($\sigma_i = -0.01 - 0.06$) and a moderately strong donor via the conjugative mechanism ($\sigma_R = -0.07 - -0.12$)[30]. The replacement of one dicarbollyl group by a cyclopentadienyl group increases the inductive electron-accepting capacity of the complex ($\sigma_i = 0.21$) but hardly alters the resonance electron-donating component ($\sigma_R - -0.10$). The ability of the bis(dicarbollyl) complex to enter into conjugation with π-substituents has been confirmed by the electronic spectra of bis-(*C*-alkenyldicarbollyl)cobalt[47].

In their attempts to alkylate bis(dicarbollyl)cobalt(III) under the conditions of the Friedel–Crafts reaction, Francis and Hawthorne[41,48] observed an interesting reaction involving the formation of a bridge-type derivative of the dicarbollyl complex with an electron-deficient carbon atom. When hydrogen chloride is passed into a suspension of bis(dicarbollyl)cobalt and $AlCl_3$ in CS_2, the –S–CH–S– bridge linked to the boron atoms of the ligands is formed between dicarbollyl ligands:

$$[(1,2\text{-}B_9C_2H_{11})_2Co]^- + CS_2 + H^+ \rightarrow \begin{matrix} 1,2\text{-}B_9C_2H_{10}S \\ Co^- \quad CH^+ \\ 1,2\text{-}B_9C_2H_{10}S \end{matrix} \quad \text{(Fig. 10)}\ ^{49}$$

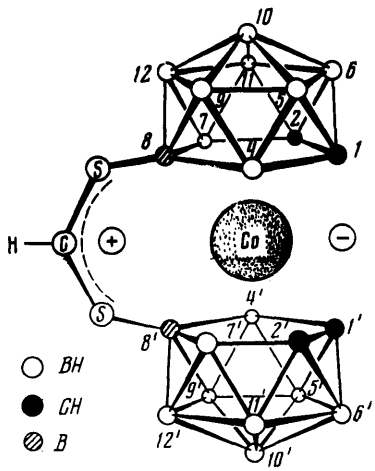


Figure 10.

The complex $(1,7\text{-}B_9C_2H_{10})_2CoS_2CH$ was obtained similarly from $\{[(3)\text{-}1,7\text{-}B_9C_2H_{11}]_2Co\}^-$. A bridge with an electron-deficient carbon atom is formed also in an acetic acid–acetic anhydride mixture in the presence of $HClO_4$ as a catalyst:

$$[(1,2\text{-}B_9C_2H_{11})_2Co]^- + MeCOOH \rightarrow (1,2\text{-}B_9C_2H_{11})Co(1,2\text{-}B_9C_2H_{10}OOCMe) \xrightarrow{H^+} \rightarrow (1,2\text{-}B_9C_2H_{10})_2CoO_2CMe\ .$$

The carbonium ionic centres in $(1,2\text{-}B_9C_2H_{10})_2CoS_2CH$ and $(1,2\text{-}B_9C_2H_{10})_2CoO_2CMe$ are relatively inactive with respect to protic solvents, probably owing to the proximity of the negative charges of the heteroatoms. A solution of $NaBH_4$ in ethanol reduces $(1,2\text{-}B_9C_2H_{10})CoS_2CH$ to $[(1,2\text{-}B_9C_2H_{10})_2CoS_2CH_2]^-$ in quantitative yield. Aqueous ethanol hydrolyses the bridge-type derivatives:

$$(1,2\text{-}B_9C_2H_{10})_2CoS_2CH \xrightarrow[70°]{EtOH} \{[1,2\text{-}B_9C_2H_{10}(SH)]_2Co\}^-\ ,$$

$$(1,2\text{-}B_9C_2H_{10})_2CoO_2Me \xrightarrow[70°]{EtOH} \{[1,2\text{-}B_9C_2H_{10}(OH)]_2Co\}^-\ .$$

Like bis(dicarbollyl)iron(II), bis(dicarbollyl)cobalt(III) enters into an acid-catalysed nucleophilic substitution reaction in diethyl sulphide, leading to a neutral product[33]:

$$[(1,2\text{-}B_9C_2H_{11})_2Co]^- + HCl + Et_2S \rightarrow Co(1,2\text{-}B_9C_2H_{11})[1,2\text{-}B_9C_2H_{10}SEt_2]\ .$$

When an aqueous solution of $K(1,2\text{-}B_9C_2H_{11})_2Co$ is treated with phenyldiazonium tetrafluoroborate, cation exchange and the formation of the phenyl diazonium salt of bis(dicarbollyl)cobalt$(PhN_2)^+[(1,2\text{-}B_9C_2H_{11})Co]^-$ are observed[50] instead of the expected formation of coupling or arylation products. At room temperature the salt is insoluble in benzene but on heating above 60°C it dissolves completely with liberation of a gas and the formation of biphenyl and a coupling product the structure of which is illustrated in Fig. 11. Decomposition of the phenyldiazonium salt in toluene and of the tolyldiazonium salt in benzene yielded coupling products containing the tolyl and phenyl groups respectively and methylbiphenyl, i.e. the aryl group from the diazonium cation does not enter into the composition of the complex. The reaction scheme in Fig. 12 was put forward on the basis of these products.

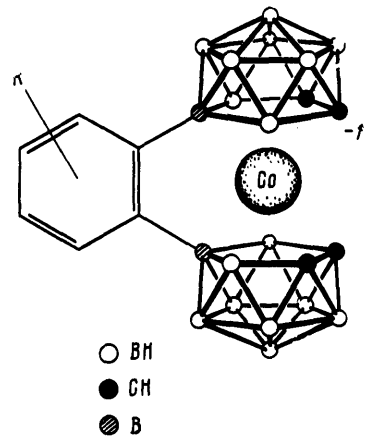


Figure 11.

The complexes $(\pi\text{-}C_5H_5)Co(\pi\text{-}1,2\text{-}B_9C_2H_{11})$ and $[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^-$ served as the starting materials for the synthesis of new metallocarboranes containing one and two boron atoms less than in the initial metallocarboranes[51,52]. The reaction has been called the "polyhedral contraction reaction". In general its equation is

$$[LCo(B_nC_2H_{n+3})]^z \xrightarrow[2.\ -2e^-]{1.\ -BH^{+}} [LCo(B_{n-1}C_2H_{n+1})]^{\beta},$$

where $z = 0$ for $L = C_5H_5^-$ and $z = -1$ for $L = (3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-}$.

The base-catalysed degradation of the complexes with subsequent oxidation of the products by hydrogen peroxide gives rise to a new metallocarborane containing the π-(1)-2,4-$B_6C_2H_{10}^{2-}$ ion as one of the ligands (Fig. 13):

$$(\pi\text{-}C_5H_5)Co(\pi\text{-}1,2\text{-}B_9C_2H_{11}) \xrightarrow[2.\ H_2O_2]{1.\ OH^-} (\pi\text{-}C_5H_5)Co[\pi\text{-}(1)\text{-}2,4\text{-}B_6C_2H_{10}]\ ,$$

$$[(\pi\text{-}1,2\text{-}B_9C_2H_{11})_2Co]^- \xrightarrow[2.\ H_2O_2]{1.\ OH^-} \{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co\text{-}[\pi\text{-}(1)\text{-}2,4\text{-}B_6C_2H_{10}]\}^-\ .$$

The last complex forms with pyridine an inner salt having the composition $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co[\pi\text{-}(1)\text{-}2,4\text{-}B_6C_2H_{10}\cdot C_5H_5N]$,[51] in which the 'onium nitrogen atom is linked to the boron atom of the π-(1)-2,4-$B_6C_2H_{10}$ ligand according to X-ray diffraction analysis[53,54]. Oxidation of complexes containing the (1)-2,4-$B_6C_2H_{10}$ ligand by iron(III) chloride in boiling ethanol results in their further degradation. In the case of the cyclopentadienyl-containing complex, a *nido*-metallocarborane is formed as the main product under these conditions. Like the neutral *nido*-carboranes $B_6C_2H_{12}$,[55–57] the *nido*-metallocarborane $(C_5H_5)Co(B_7C_2H_{11})$ slowly splits off hydrogen on heating to

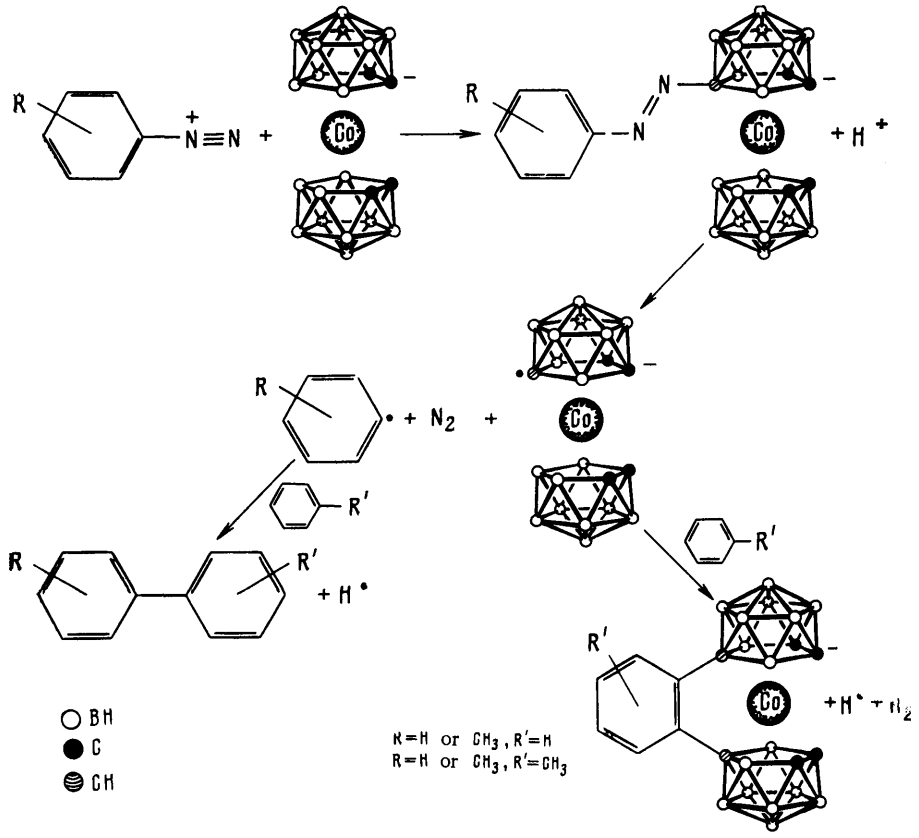


Figure 12.

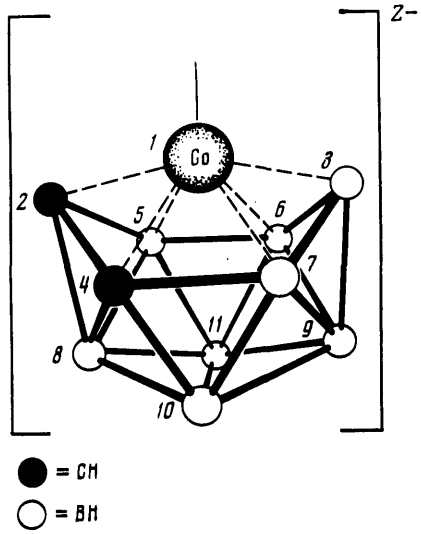


Figure 13.

70°C and is converted into a *closo*-metallocarborane with the π-(2)-6,7-$B_7C_2H_9$ ligand. However, at 70°C the π-(2)-6,7-$B_7C_2H_9$ ligand in the complex rearranges to π-(2)-1,6-$B_7C_2H_9$. Further rearrangement to the 1,10-isomer requires a temperature of 150°C.

The above sequence of reactions is illustrated schematically in Fig. 14. The complex $\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co.[\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9]\}^-$ was obtained similarly from $\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Co[\pi\text{-}(1)\text{-}2,4\text{-}B_6C_2H_{10}]\}^-$ (Fig. 15).

An interesting property of π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt and its *CC'*-dimethyl derivative is the ability to undergo a gas-phase rearrangement at 400–700°C with formation of isomeric complexes differing in the distribution of carbon atoms in the dicarbollyl ligand [58] (Fig. 16). In none of the isomers obtained do the carbon atoms in the ligand retain adjacent positions. Therefore the driving force of the rearrangement in the isomerisation of metallocarboranes as well as carboranes [4] is presumably the mutual repulsion of the carbon atoms, which are the most electropositive centres in the molecule.

C. The Nickel Group

In the nickel group (Ni, Pd, Pt) the dicarbollyl derivatives of all the metals are known. The paramagnetic complex $[(1,2\text{-}B_9C_2H_{11})_2Ni^{II}]^{2-}$ with the d^9 configuration, which is extremely readily oxidised to the nickel(III) complex with the d^7 configuration, was obtained by the reaction of the (3)-1,2-dicarbollide ion with nickel(II) salts in THF or in a highly alkaline medium [16,59]. Oxidation of the nickel(III) complex by iron(III) chloride leads to the neutral diamagnetic complex $(1,2\text{-}B_9C_2H_{11})_2Ni^{IV}$ with the d^6 configuration. Nickel complexes with the (3)-1,7-$B_9C_2H_{11}^{3-}$ ligand in which the nickel atom is in the +2, +3, and +4 formal oxidation states were obtained similarly [16].

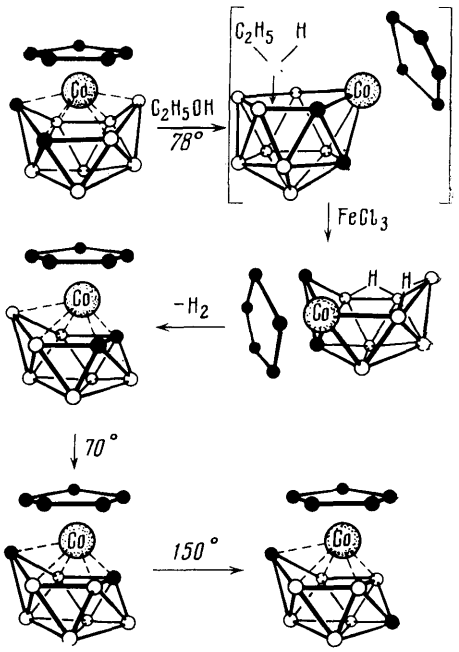


Figure 14.

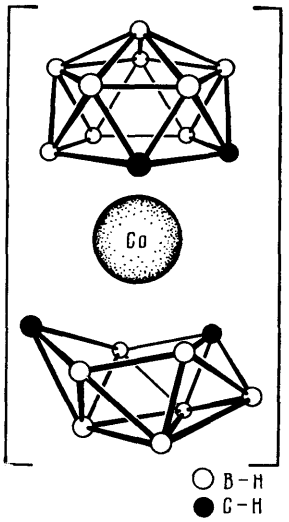


Figure 15.

Dicarbollylnickel complexes have characteristic structural features which depend on the formal oxidation state of the metal. The nickel(II) complexes have a distorted sandwich structure with the ligands displaced relative to one another in opposite directions (Fig. 17).[60] The nickel(III) complexes have the normal sandwich structure (Fig. 2), while a cisoid sandwich configuration, in which both carbon atoms of each ligand are located on the same side of the molecule, is characteristic of nickel(IV) (Fig. 18).[61] This gives rise to an appreciable dipole moment in $(1,2\text{-}B_9C_2H_{11})_2Ni^{IV}$, amounting, for example, to 6.16 D in cyclohexane. Owing to the high positive charge on the metal atom (+4), bis(dicarbollyl)nickel(IV) is a powerful-electron accepting substituent (σ_i = 0.50–0.65).[30] Complexes with *C*-methyl- and *C*-phenyl-1,2-dicarbollyl ligands have been obtained[62]. In this case enantiomers exist, so that three isomers are possible: the *meso*-isomer and the (±)-recemate. This was confirmed by the ^{19}F NMR spectra of *p*- and *m*-fluorophenyl-substituted nickel(IV) complexes, which contain two fluorine signals corresponding to the *meso*-form and the (±)-racemate.[30]

The complex $(1,2\text{-}B_9C_2H_{11})_2Ni^{IV}$ is readily reduced to $[(1,2\text{-}B_9C_2H_{11})_2Ni^{III}]^-$ by "hard" Lewis bases with some degradation of the complex[61]. An interesting property of

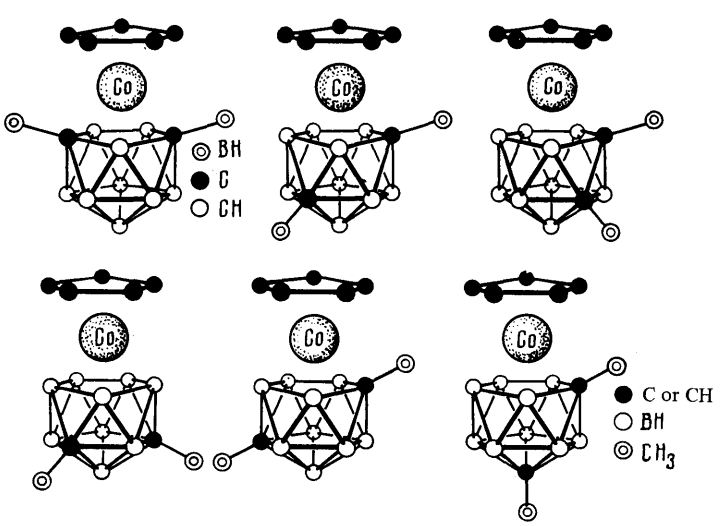


Figure 16.

$(1,2\text{-}B_9C_2H_{11})_2Ni^{IV}$ is the considerable acidity of the C–H bond in the dicarbollyl ligand, which was shown by the ease of deuterium exchange with D_2O in an alkaline medium, while in acid solutions (D_2SO_4 in DOAc) the deuterium exchange is slow and involves only the B–H bonds of the ligand. "Soft" Lewis bases, for example Cl^-, Br^-, and SCN^-, react with $(1,2\text{-}B_9C_2H_{11})_2Ni^{IV}$ to give 1 : 1 adducts, which can be isolated in a crystalline form. Similar adducts have been obtained with condensed aromatic hydrocarbons—pyrene naphthalene, and phenanthrene—and aromatic *n*-bases such as dimethylaniline [61].

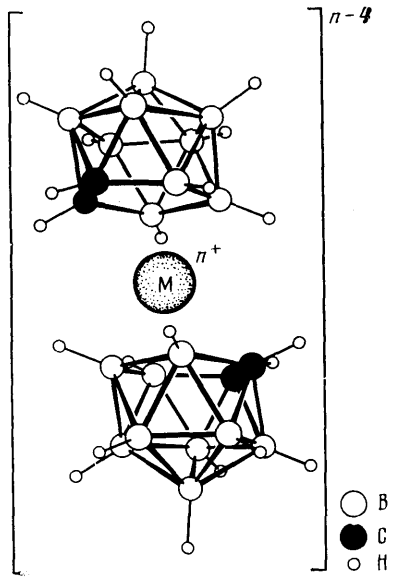


Figure 17.

Molecular rearrangements characteristic of metallocarboranes can be observed in *CC'*-disubstituted dicarbollylnickel complexes. There is a possibility of three isomeric series of compounds [62-64]: series A—compounds with adjacent carbon atoms on the binding surfaces of both ligands; series B—compounds with adjacent carbon atoms in both ligands but in one of the ligands one carbon atom is displaced to the interior of the ligand so that its binding plane contains four boron atoms and one carbon atom; series C—compounds with adjacent carbon atoms in both ligands and with (B_4C) binding surfaces. The conversions of series A compounds into series B and C compounds are irreversible. The reaction sequences and the electrochemical characteristics of the reactions of the bis-(*CC'*-dimethyldicarbollyl)nickel system are presented below:

$$Ni(acac)_2 + 2[(3)\text{-}1,2\text{-}B_9C_2H_9Me_2]^{2-}\dagger \rightarrow$$

Series A

$$\rightarrow [(Me_2Cb)_2Ni^{II}\text{—}A]^{2-} \underset{-0.55\,mV}{\rightleftharpoons} [(Me_2Cb)_2Ni^{III}\text{—}A]^- \xrightarrow[\downarrow 200^\circ]{[O]}$$

Series B

$$[(Me_2Cb)_2Ni^{II}\text{—}B]^{2-} \underset{-1.02\,mV}{\rightleftharpoons} [(Me_2Cb)_2Ni^{III}\text{—}B]^- \underset{+0.15\,mV}{\rightleftharpoons} [(Me_2Cb)_2Ni^{IV}\text{—}B]^0 \downarrow 100^\circ$$

Series C

$$[(Me_2Cb)_2Ni^{II}\text{—}C]^{2-} \underset{-1.19\,mV}{\rightleftharpoons} [(Me_2Cb)_2Ni^{III}\text{—}C]^- \underset{-0.10\,mV}{\rightleftharpoons} [(Me_2Cb)_2Ni^{IV}\text{—}C]^0 .$$

† $Me_2Cb \equiv [(3)\text{-}1,2\text{-}B_9C_2H_9Me_2]$.

Fig. 19 illustrates the structure of bis-*CC'*-dimethyl-1,2-dicarbollylnickel(IV) with one isomerised ligand.

Unsubstituted bis-(1,2-dicarbollyl)nickel(IV) is converted into the series B and C compounds in gas-phase isomerisation at 300–400°C. [62]

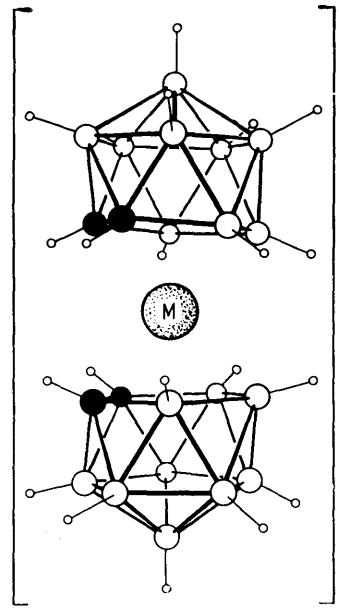


Figure 18.

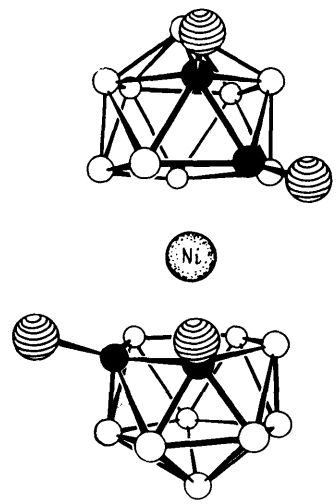


Figure 19.

A neutral mixed nickel(III) complex was obtained in a low yield by the reaction of $NiBr_2$ with $C_5H_5^-$ and $1,2\text{-}B_9C_2H_{11}^{2-}$ ions in THF [65]:

$$C_5H_5^- + 1,2\text{-}B_9C_2H_{11}^{2-} + NiBr_2 \rightarrow [(\pi\text{-}C_5H_5)Ni(\pi\text{-}1,2\text{-}B_9C_2H_{11})]^- \xrightarrow{[O]}$$

$$\rightarrow (\pi\text{-}C_5H_5)Ni(\pi\text{-}1,2\text{-}B_9C_2H_{11}) .$$

The cyclopentadienyl and dicarbollyl complexes of nickel exhibit many characteristic differences. Whereas the dicyclopentadienylnickel complex with the d^6 configuration, i.e. $(C_5H_5)_2Ni^{2+}$, has sometimes not been isolated, bis(dicarbollyl)nickel(IV) is an entirely stable crystalline compound. From this standpoint, the electrochemical reactions (the $E_{1/2}$ values) of the nickel complexes are of interest[65]:

$M^{IV} + e^- \rightarrow M^{III}$ and $M^{III} + e^- \rightarrow M^{II}$.

$(C_5H_5)_2Ni$ + 0.77 mV	−0.09 mV
$(C_5H_5)Ni(B_9C_2H_{11})$ + 0.46 mV	−0.52 mV
$(B_9C_2H_{11})_2Ni$ + 0.18 mV	−0.56 mV

The wave corresponding to the oxidation of nickel to the quadrivalent state in the dicyclopentadienylnickel complex could be observed only at −40°C; above 0°C, this complex decomposes rapidly. In the d^6 state π-cyclopentadienyl-π-dicarbollylnickel(VI) is more stable and decomposes much more slowly than $(C_5H_5)_2Ni^{2+}$, but it could not be isolated. The higher stability of the dicarbollylnickel complexes has been explained by the higher negative charge of the dicarbollyl ligand (2- compared with 1- for the cyclopentadienyl ligand), which leads to a less effective positive charge of the nickel atom in the d^6 electronic state[65].

When palladium acetylacetonate is added to an excess of 1,2-dicarbollide ions, an unstable diamagnetic d^8-complex $[(1,2\text{-}B_9C_2H_{11})_2Pd^{II}]^{2+}$, extremely sensitive to air, is formed[66]. Its solutions decompose on standing in several hours, but, on rapid oxidation of the palladium(II) complex, an electrically neutral d^6-complex is formed in high yield:

$$[(1,2\text{-}B_9C_2H_{11})_2Pd]^{2-} \xrightarrow[CH_2Cl_2]{I_2} (1,2\text{-}B_9C_2H_{11})Pd .$$

When equimolar amounts of the palladium(II) and palladium(IV) complexes are mixed, $[(1,2\text{-}B_9C_2H_{11})_2Pd]^-$ is formed quantitatively[66]. It has been shown that palladium complexes have structures completely identical to those of the corresponding nickel complexes discussed above[62,66]. Chemically they also have much in common. For example, the neutral complex $(1,2\text{-}B_9C_2H_{11})_2Pd^{IV}$ is a strong Lewis acid and forms crystalline adducts with π- and n-bases[62]. Like the nickel complexes, the bis-(*CC'*-dimethyl-1,2-dicarbollyl)palladium system undergoes rearrangements leading to a change in the positions of the carbon atoms in the ligands[62]:

$$Pd(acac)_2 + 2[(3)\text{-}1,2\text{-}B_9C_2H_9Me_2]^{2-} \rightarrow$$

Series A

$$\rightarrow [(Me_2Cb)_2Pd^{II}\text{—}A]^{2-} \underset{-0.44\,mV}{\rightleftharpoons} [(Me_2Cb)_2Pd^{III}\text{—}A]^- \xrightarrow{[O]}$$

Series C

$$[(Me_2Cb)_2Pd^{II}\text{—}C]^{2-} \underset{-0.71\,mV}{\rightleftharpoons} [(MeCb)_2Pd^{III}\text{—}C]^- \underset{-0.47\,mV}{\rightleftharpoons} [(Me_2Cb)_2Pd^{IV}\text{—}C]^0 .$$

Mixed neutral complexes have been synthesised (yield 10%) by the reaction of the π-tetraphenylcyclobutadienylpalladium(II) dichloride dimer with the (3)-1,2-dicarbollide ion and its dimethyl derivative[16]:

$$(\pi\text{-}C_4Ph_4PdCl_2)_2 + 2[(3)\text{-}1,2\text{-}B_9C_2H_{11}]^{2-} \rightarrow 2(\pi\text{-}C_4Ph_4)Pd[\pi\text{-}1,2\text{-}B_9C_2H_{11}] .$$

A dicarbollide derivative of platinum was obtained by the reaction of cyclo-octa-1,5-dieneplatinum dichloride with the 1,2-dicarbollide ion[62]:

$$(1,5\text{-}C_8H_{12})PtCl_2 + (3)\text{—}1,2\text{-}B_9C_2H_{11}^{2-} \rightarrow (1,5\text{-}C_8H_{12})Pt[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}] .$$

A fundamentally new method of synthesising the dicarbollide complexes of nickel, palladium, and platinum was proposed by Stone and coworkers[22], who found that 1,8-$B_9C_2H_{11}$ (Tebbe et al.[67]) undergoes the polyhedral expansion reaction on treatment with $Ni(1,5\text{-}C_8H_{12})_2$, $(1,5\text{-}C_8H_{12})Ni(PEt_3)_2$, $Pd(t\text{-}BuNC)_2$, $Pt(PEt_3)_3$, or $Pt(PMe_2Ph)_3$, yielding respectively $(1,5\text{-}C_8H_{12})Ni(1,7\text{-}B_9C_2H_{11})$, $(Et_3P)_2Ni(1,7\text{-}B_9C_2H_{11})$, $(t\text{-}BuNC)_2Pd(1,7\text{-}B_9C_2H_{11})$, $(Et_3P)_2Pd(1,7\text{-}B_9C_2H_{11})$, and $(PhMe_2P)_2Pr(1,7\text{-}B_9C_2H_{11})$. The (3)-$1,7\text{-}B_9C_2H_{11}^{2-}$ ion then behaves as the dicarbollyl ligand. The reaction of 1,8-dicarba-*closo*-undecaborane(II) with bis(cyclo-octa-1,5-diene)nickel is illustrated schematically in Fig. 20.[22]

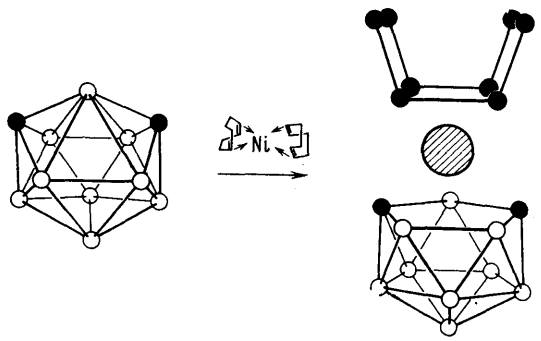


Figure 20.

D. The Copper Group

The dicarbollyl derivatives of all the metals of the copper group (Cu, Ag, Au) are known.

The addition of $CuSO_4$ in a highly alkaline medium to the 1,2-dicarbollide ion yields the paramagnetic d^9-complex $[(1,2\text{-}B_9C_2H_{11})_2Cu^{II}]^{2-}$, which is unstable in air and is readily converted into the diamagnetic d^8-complex $(1,2\text{-}B_9C_2H_{11})_2Cu^{III}$:[16,66]

$$CuSO_4 + 1,2\text{-}B_9C_2H_{11}^{2-} \rightarrow [(1,2\text{-}B_9C_2H_{11})_2Cu^{II}]^{2-} \underset{Na/Hg}{\overset{O_2}{\rightleftharpoons}} [(1,2\text{-}B_9C_2H_{11})_2Cu^{III}]^- .$$

The reaction of $AuCl_3$ with a large excess of 1,2-dicarbollide ions in dimethoxyethane with subsequent oxidation by aqueous hydrogen peroxide yields the stable complex $(1,2\text{-}B_9C_2H_9)_2Au^{III}$-.[66] The salt is diamagnetic and can be reduced to the paramagnetic complex $[(1,2\text{-}B_9C_2H_9)_2Au^{II}]^{2-}$:

$$AuCl_3 + 1,2\text{-}B_9C_2H_{11}^{2-} \rightarrow [(1,2\text{-}B_9C_2H_{11})_2Au^{II}]^{2-} \underset{Na/Hg}{\overset{O_2}{\rightleftharpoons}} [(1,2\text{-}B_9C_2H_{11})_2Au^{III}]^- .$$

The attempts to obtain analogous bis(dicarbollyl) systems for silver were unsuccessful[66], but subsequently[68] the possibility of the existence of such complexes was briefly reported. It has been suggested that the (3)-1,2-dicarbollide ion be used for the qualitative detection of copper in aqueous solutions[69,70].

According to data for the polarographic reduction of the dicarbollyl complexes of copper and gold, the existence of the d^{10}-complexes is possible, since the polarograms show, together with the process $M^{III} + e^- \rightarrow M^{II}$, one-electron reduction waves corresponding to the process $M^{II} + e^- \rightarrow M^I$ (M = Cu or Au).

It is interesting that the most stable states of the copper and gold complexes are those in which the metal atom is in

the +3 formal oxidation state, i.e. the bivalent metal complexes are very powerful reducing agents [66].

An X-ray diffraction study of the bis(dicarbollyl) complexes of copper(II) and copper(III) showed [71,72] that they have a distorted sandwich structure analogous to those of the nickel(II) and palladium(II) complexes. Thus examination of the structures of complexes with electronic configurations ranging from d^5 to d^9 has shown that the d^5-, d^6-, and d^7-complexes have a symmetrical sandwich structure, while the d^8- and d^9-complexes have a distorted sandwich structure. Wing [66,71,72] explains the presence of such structures by π-allyl bonding in which six boron atoms enter into the first coordination sphere of the metal (three atoms from each dicarbollyl ligand).

E. The Chromium Group

The dicarbollyl complexes of all the metals in the chromium group (Cr, Mo, W) have been obtained. The reaction of $CrCl_3$ with the (3)-1,2- or (3)-1,7-$B_9C_2H_{11}^{2-}$ ions in THF leads to paramagnetic bis(dicarbollyl)chromium in which the metal atom is in the +3 formal oxidation state. In contrast to the isoelectronic chromocenium salts, which are readily hydrolysed in aqueous solutions [74], $[(\pi\text{-}B_9C_2H_{11})_2Cr]^-$ salts are stable in air and are not decomposed by hot concentrated H_2SO_4. However, these complexes decompose in a hot alkaline solution, regenerating the dicarbollide ion in a quantitative yield [73]. Neutral π-cyclopentadienyl-π-1,2-dicarbollylchromium has been obtained by the reaction of $CrCl_3$ with the $C_5H_5^-$ and 1,2-$B_9C_2H_{11}^{2-}$ ions. According to Clair et al., [75] bis-(1,2-dicarbollyl)chromium has a regular sandwich structure.

Chromium, molybdenum and tungsten hexacarbonyls react with the 1,2-dicarbollide ion in THF on ultraviolet irradiation with displacement of three carbon monoxide molecules and the formation of π-dicarbollylmetal tricarbonyl complexes [16,31]:

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + M(CO)_6 \xrightarrow[-3CO]{h\nu} \{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]M(CO)_3\}^{2-} \quad (M = Cr, Mo, W)\ .$$

The complexes are isoelectronic with the complexes $(C_5H_5)M(CO)_3^-$ and enter into protonation and alkylation reactions [16]:

$$[(1,2\text{-}B_9C_2H_{11})Mo(CO)_3]^{2-} \xrightarrow{HCl} [(1,2\text{-}B_9C_2H_{11})Mo(CO)_3H]^-\ ,$$

$$[(1,2\text{-}B_9C_2H_{11})W(CO)_3]^{2-} \xrightarrow{MeI} [(1,2\text{-}B_9C_2H_{11})W(CO)_3Me]^-\ .$$

The reactions of the 1,2-dicarbollide ion with two moles of $M(CO)_6$ and the reactions of $M(CO)_6$ with $(1,2\text{-}B_9C_2H_{11})M(CO)_3^{2-}$ (M = W or Mo) lead to the same dinuclear products with the empirical formula $(B_9C_2H_{11})M_2(CO)_x^{2-}$ (x = 7 or 8). [16] Fig. 21 presents the structure of such a dinuclear complex obtained by the reaction

$$\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mo(CO)_3\}^{2-} + W(CO)_6 \rightarrow \{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mo(CO)_3W(CO)_5\}^{2-}\ .$$

F. The Manganese Group

Bromomanganese pentacarbonyl and bromorhenium pentacarbonyl react rapidly with the 1,2-dicarbollide ion at room temperature with liberation of one mole of carbon monoxide. On heating, a further two moles of carbon monoxide are evolved and a π-dicarbollylmetal tricarbonyl anion is formed [16,76]:

$$1,2\text{-}B_9C_2H_{11}^{2-} + BrM(CO)_5 \xrightarrow[-CO]{90^\circ} [(\sigma\text{-}1,2\text{-}B_9C_2H_{11})M(CO)_5]^- \xrightarrow[-2CO]{70^\circ}$$

$$\rightarrow [(\pi\text{-}1,2\text{-}B_9C_2H_{11})M(CO)_3]^- \quad (M = Mn, Re)\ .$$

An X-ray diffraction analysis of the rhenium derivative has been carried out [77]. The closeness of the C–Re and B–Re distances (Fig. 22), which are 2.31 and 2.35 A respectively, is noteworthy.

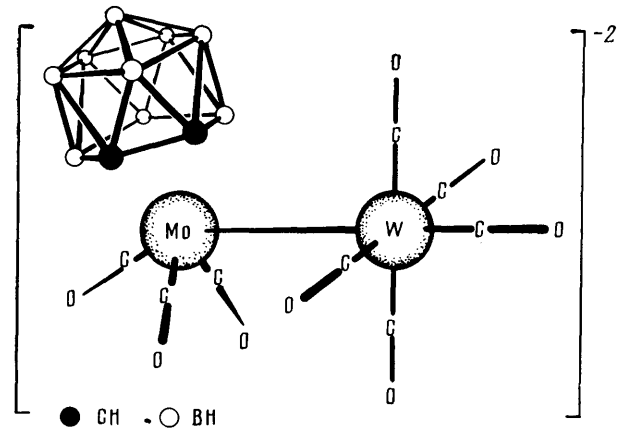


Figure 21.

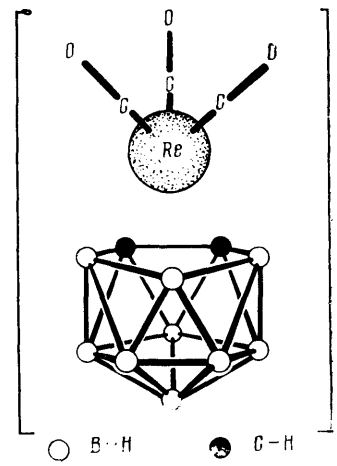


Figure 22.

When $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}(Mn)(CO)_3]^-$ is acted upon by triphenylphosphine under ultraviolet irradiation in THF for 12 h at 60°C, one carbonyl group is substituted by the triphenylphosphine group [78]:

$$[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Mn(CO)_3]^- + PPh_3 \xrightarrow{h\nu} [(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})Mn(CO)_2PPh_3]^-\ .$$

2. Mono- and Hetero-Carbollyl Complexes of Transition Metals

The monocarbollide ion $B_{10}CH_{11}^{3-}$ is readily formed *in situ* on deamination and deprotonation of the carborane $B_{10}H_{12}CNMe_3$ by metallic sodium in THF [79]. This reaction proceeds more readily and with a higher yield in the

presence of naphthalene[80]. Two general methods have been proposed for the synthesis of π-complexes[81-83].

1. By adding butyl-lithium or sodium hydride to a mixture of $B_{10}H_{12}CNH_2R$ or a salt of $B_{10}H_{12}CH^-$ and the metal halide in THF or by adding the metal halide to the trisodium salt $Na_3B_{10}CH_{11}$ obtained directly.

2. By the interaction in a highly alkaline medium between $B_{10}H_{12}CNH_2R$ or a salt of $B_{10}H_{12}CH^-$ and the metal halide. This method gives high yields for nickel and cobalt.

Both methods have been used to synthesise the bis-(π-carbollyl) complexes of iron, cobalt, nickel, chromium, and manganese. Fig. 23 presents the general type of the structure of the λ-complexes obtained from the $B_{10}CH_{11}^{3-}$ and $B_{10}CH_{10}NH_2R^{2-}$ ions.

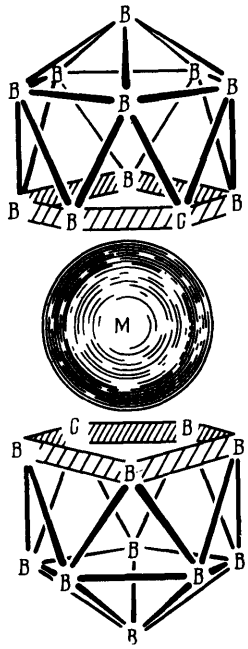


Figure 23.

The π-monocarbollyl ligand stabilises a high oxidation state of the metal to an even greater extent than the π-dicarbollyl ligand. Whereas the synthesis of $(1,2\text{-}B_9C_2H_{11})_2Ni^{IV}$ requires the oxidation of the nickel(III) complex by iodine or iron(III) chloride, $[(B_{10}CH_{11})_2Ni^{IV}]^{2-}$ and $(B_{10}CH_{10}NH_2R)_2Ni^{IV}$ are formed directly during isolation in air. Moreover, the diamagnetic complex $[(B_{10}CH_{11})_2Co]^{3-}$, which contains cobalt in the +3 formal oxidation state, is oxidised by cerium(IV) ions to the paramagnetic complex $[(B_{10}CH_{11})_2Co]^{2-}$ in which the cobalt atom is in the +4 formal oxidation state.

In the monocarbollyl complexes isolated directly from the reaction mixture, manganese is in the +4 formal oxidation state and iron, cobalt, and chromium are in the +3 formal oxidation state. All the complexes obtained, with the exception of that of manganese, are stable in air and do not decompose in acid media.

The complexes obtained from $B_{10}H_{12}CNH_3$ are of interest from the standpoint of reactions involving the amino-group. For example, $(B_{10}H_{10}CNH_3)_3Ni$ reacts with nitric acid and dimethyl sulphate to form $[(B_{10}H_{10}COH)_2Ni]^{2-}$ and $(B_{10}H_{10}CNHMe_2)_2Ni$ respectively[82,83].

Muetterties and coworkers[84] synthesised metallocarboranes with a monocarbollyl ligand starting with the $B_{10}H_{13}^-$ ion and Group VI metal carbonyls (ultraviolet irradiation). The $[(B_{10}H_{10}COH)M(CO)_4]^-$ anions formed initially react with sodium hydride to form the dianions $[(B_{10}H_{10}COH)NCO(CO)_3]^{2-}$, whose structure is illustrated in Fig. 24 for the molybdenum derivative as an example. Both types of compounds are decomposed quantitatively by bases with the removal of a carbon atom from the icosahedral skeleton and the formation of complexes belonging to the class of *nido*-metalloboranes.

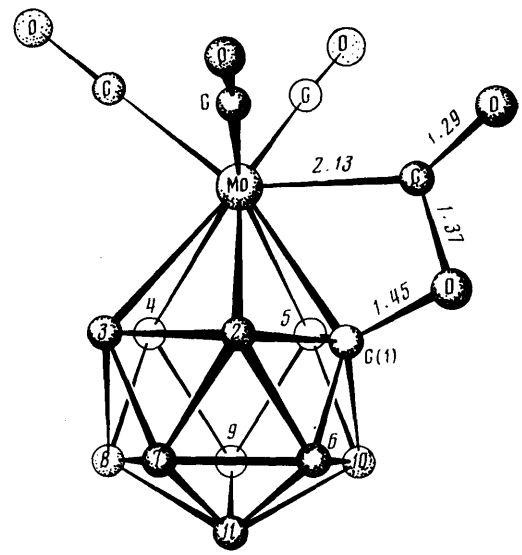


Figure 24.

Like carboranes(10) ($B_{10}H_{10}C_2H_2$), when acted upon by piperidine, 1,2- and 1,7-phosphacarboranes and 1,2- and 1,7-arsacarboranes give rise to the phospha- and arsa-carbaundecaborate anions, whose deprotonation generates heterocarbollide ions[85] isoelectronic with the dicarbollide ion and capable of behaving as π-ligands in transition metal complexes:

$$B_{10}H_{10}CHE \xrightarrow{C_5H_{10}NH} B_9H_{10}CHE^- \xrightarrow{NaH} B_9H_9CHE^{2-} \quad (E = P, As)\ .$$

A characteristic feature of the heterocarbaundecaborate anions is the presence of phosphorus or arsenic atoms which can be alkylated; the compounds then become neutral. Their deprotonation leads to heterocarbollide ions with a single negative charge[85,86]:

$$B_9H_{10}CHE^- + MeI \rightarrow B_9H_{10}CHEMe \xrightarrow{NaH} B_9H_9CHEMe^- \quad (E = P, As)\ .$$

When the 1,2- and 1,7-$B_9H_9CHP^{2-}$ ions are acted upon by iron(II) chloride in THF solution, salts of $[(1,2\text{-}B_9H_9CHP)_2Fe^{II}]^{2-}$ and $[(1,7\text{-}B_9H_9CHP)_2Fe^{II}]^{2-}$ are formed

respectively[85,86]. Treatment of $[(1,7\text{-}B_9H_9CHP)_2Fe]^{2-}$ with methyl iodide leads to the neutral compound $(1,7\text{-}B_9H_9CHPMe)_2Fe$, which is identical with the complex obtained from $1,7\text{-}B_9H_9CHPMe^-$ and $FeCl_2$ (Little et al.[86]):

$$[(1,7\text{-}B_9H_9CHP)_2Fe]^{2-} + MeI \rightarrow (1,7\text{-}B_9H_9CHPMe)_2Fe \leftarrow 1,7\text{-}B_9H_9CHPMe^- + FeCl_2 \ .$$

This complex exists as a mixture of isomers (the shaded circles in Fig. 25 indicate the possible positions of the carbon atoms).

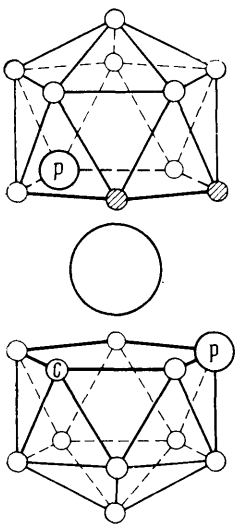


Figure 25.

In contrast to the bis(dicarbollyl) and bis(monocarbollyl) complexes of iron, bis(phosphacarbollyl)iron(II) is not oxidised by air in aqueous solution, although oxidation with cerium(IV) ions gives a small yield of the paramagnetic complex $[(1,7\text{-}B_9H_9CHP)_2Fe^{III}]^-$.[86]

The neutral complex $(\pi\text{-}C_5H_5)Fe(\pi\text{-}1,7\text{-}B_9H_9CHPMe)$ has been obtained by the interaction of the $C_5H_5^-$ and $1,7\text{-}B_9H_9CHPMe^-$ ions and $FeCl_2$. The reactions of 1,2- and $1,7\text{-}B_9H_9CHPMe^-$ ions with $CoCl_2$ give rise to bis(phosphacarbollyl) complexes in which the metal atom is in the +2 formal oxidation state and does not exhibit a tendency towards oxidation. In contrast, the reactions of the 1,2- and $1,7\text{-}B_9H_9CHP^{2-}$ ions with $CoCl_2$ lead to complexes in which the cobalt atom is in the +3 formal oxidation state.

The dianion $1,7\text{-}B_9H_9CHP^{2-}$ reacts with $NiCl_2$ to form bis-(1,7-phosphacarbollyl)nickel in which the nickel is in the +2 formal oxidation state.[85] The mixed complexes $(1,7\text{-}B_9H_9CHPMe)Mn(SO)_3$ and $[(1,7\text{-}B_9H_9CHP)Mn(CO)_3]^-$ have been obtained[86]. The substitution of one carbonyl group by a triphenylphosphine group in $[(1,7\text{-}B_9H_9CHP)Mn.(CO)_3]^-$ takes place readily on ultraviolet irradiation[78].

The reaction of triphenylcyclopropenylnickel carbonyl bromide with $1,7\text{-}B_9H_9CHPMe^-$ in THF gave a mixed nickel complex in 40% yield[87]:

$$[C_3Ph_3NiBr(CO)]_2 + 1,7\text{-}B_9H_9CHPMe^- \rightarrow C_3Ph_3Ni(1,7\text{-}B_9H_9CHPMe) \ .$$

The interaction of allylmagnesium chloride and $1,7\text{-}B_9H_9CHPMe^-$ with $NiCl_2$ results in the formation of a π-allyl complex[87]:

$$CH_2\text{-}CHCH_2MgCl + 1,7\text{-}B_9H_9CHPMe^- + NiCl_2 \rightarrow (C_3H_5)Ni(1,7\text{-}B_9H_9CHPMe) \ .$$

π-Methylallyl-π-phosphacarbollylnickel has been obtained similarly. When nitric oxide was passed through a solution of $1,7\text{-}B_9H_9CHPMe^-$ and $NiCl_2$ in THF, a nitrosyl complex was isolated in a low yield:

$$NO + 1,7\text{-}B_9H_9CHPMe^- + NiCl_2 \rightarrow (NO)Ni(1,7\text{-}B_9H_9CHPMe) \ .$$

The arsacarbollide ion reacts with transition metals like the phosphacarbollide ion. This is illustrated by the synthesis of π-cyclopentadienyl-π-1,2-arsacarbollylcobalt with the metal atom in the +3 formal oxidation state[88]:

$$C_5H_5^- + 1,2\text{-}B_9H_9CHAs^{3-} + CoCl_2 \rightarrow (C_5H_5)Co(1,2\text{-}B_9H_9CHAs) \ .$$

Arsacarbollyl complexes of manganese and iron have been obtained[88]. Under the conditions of the photochemical reaction, bis-(1,7-heterocarbollyl)iron(II) reacts with Group VI metal hexacarbonyls to form complicated complexes[89]:

$$[(1,7\text{-}B_9H_9CHE)_2Fe]^{2-} + M(CO)_6 \xrightarrow{h\nu} \{[1,7\text{-}B_9H_9CHEM(CO)_5]_2Fe\}^{2-} \quad (M = Cr, Mo, W) \ .$$

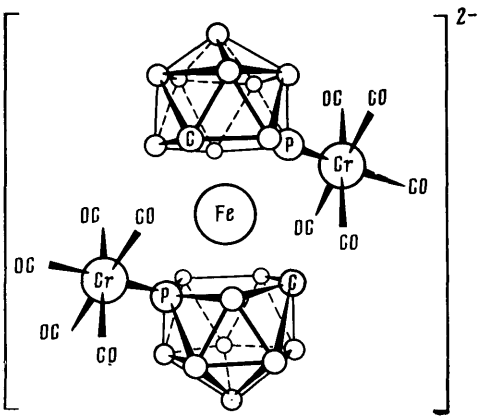


Figure 26.

In these complexes the heterocarbollyl ligand is π-bonded to the iron atom and σ-bonded via the phosphorus or arsenic atom to the Group VI metal atom. The structure of the $\{[1,7\text{-}B_9H_9CHP.Cr(CO)_5]_2Fe\}^{2-}$ ion is illustrated in Fig. 26.

3. Complexes Based on the π-$B_7C_2H_9$ Ligands

The axial hydrogen atoms of the methine groups in 1,3-dicarba-*nido*-nonaborane(13) ($1,3\text{-}B_7C_2H_{13}$) are acidic and when the carborane is treated with sodium hydride one mole of H_2 is evolved with formation of the dianion $B_7C_2H_{11}^{2-}$.[90,91] The reaction of anhydrous $CoCl_2$ with $B_7C_2H_{11}^{2-}$ leads to additional liberation of H_2 and the formation of a complex with the metal atom in the +3 formal oxidation state. It is suggested that five atomic orbitals, in which six electrons are located, originate from the five atoms of the ligand (they are predominantly sp^3-hybridised). The ligand is illustrated schematically in Fig. 27.

The name dicarbazapide given to the $B_7C_2H_9^{2-}$ ligand originates from the Greek work "zapato" (nine)‡. In the synthesis of bis(dicarbazapyl)cobalt products with different positions of the carbon atoms in the ligand are obtained depending on the reaction conditions[91]:

$$2\,(1,3\text{-}B_7C_2H_{11})^{2-} + 1.5\,Co^{2+} \xrightarrow{70^\circ} \{[\pi\text{-}(2)\text{-}1,6\text{-}B_7C_2H_9]_2\,Co\}^- + 0.5\,Co^0 + 2H_2\,,$$

$$2\,(1,3\text{-}B_7C_2H_{11})^{2-} + 1.5Co^{2+} \xrightarrow{25^\circ} \{[\pi\text{-}(2)\text{-}6,7\text{-}B_7C_2H_9]_2Co\}^- + 0.5Co^0 + 2H_2\,.$$

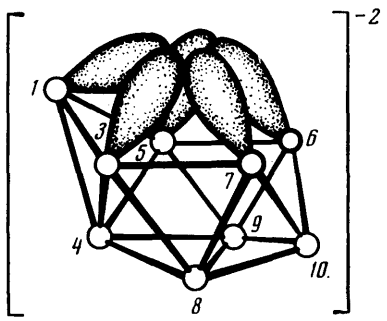


Figure 27.

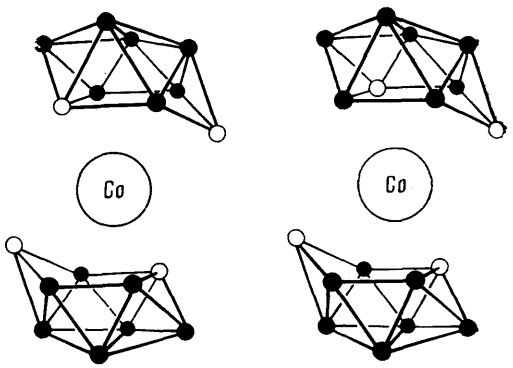


Figure 28.

At 70°C the product is a complex in which the carbon atoms are located in the 1- and 6- or 7-positions according to X-ray diffraction[92]. There is a possibility of the existence of *syn*- and *anti*-isomers (Fig. 28), but there is no information about the formation of more than one isomer. An isomer with the carbon atoms in the 6- and 7-positions is formed at room temperature (Fig. 29). A third isomer in which the carbon atoms are in the 1- and 10-positions has been obtained by heating $Cs(1,6\text{-}B_7C_2H_9)_2Co$ at 315°C for 24 h.[91,93]

‡ "Zapato" is a Spanish noun describing a shoe which resembles the shape of the $B_7C_2H_9^{2-}$ dianion[91] (Ed. of Translation).

The reaction of the $B_7C_2H_{11}^{2-}$ and $C_5H_5^-$ ions with $CoCl_2$ leads to $(\pi\text{-}C_5H_5)Co(\pi\text{-}1,6\text{-}B_7C_2H_9)$. No data have been obtained concerning the formation of the 6,7-isomer. Like the symmetrical complex, π-cyclopentadienyl-π-1,6-dicarbazapylcobalt isomerises on prolonged heating at 315°C with formation of the 1,10-isomer (Fig. 30).

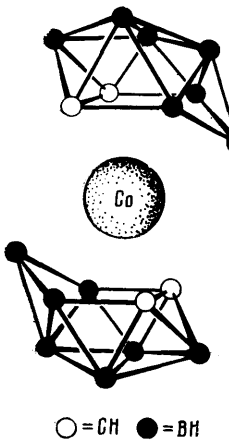


Figure 29.

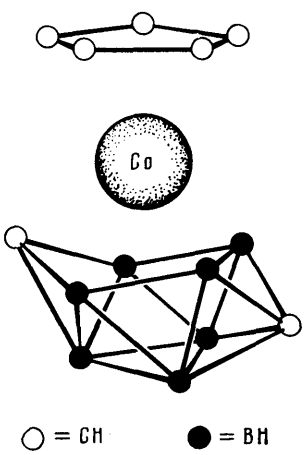


Figure 30.

Acetylation of π-cyclopentadienyl-π-1,6-dicarbazapylcobalt under the conditions of the Friedel–Crafts reaction yielded an acetyl derivative substituted at the boron atom[94]. An attempt to rearrange the compound with the 1,6-carborane structure to the 1,10-structure was unsuccessful. When the acetyl derivative is treated with $LiAlH_4$, the corresponding carbinol is not formed but the carbonyl group disappears. When $(C_5H_5)Co(1,6\text{-}B_7C_2H_9)$ is brominated in CCl_4 at room temperature, the *b*-dibromo-derivative is formed together with an insignificant amount of the *b*-tribromo-product. The bromine atoms are probably bonded to the boron atoms in the 8- and 10-positions in the ligand[94].

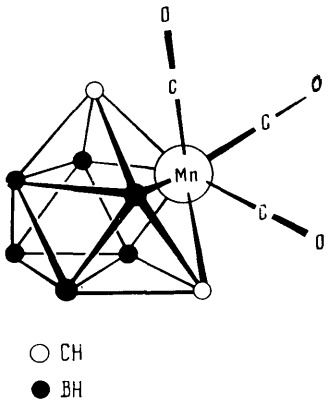


Figure 31.

An attempt was made to synthesise carbonyl derivatives of manganese with the π-$B_7C_2H_9$ ligand by treating $B_7C_2H_{11}^{2-}$ in boiling THF with bromomanganese pentacarbonyl[95,96]. However, the product was a complex with the π-$B_6C_2H_8$ ligand for which the structure presented in Fig. 31 was proposed.

4. π-Complexes Based on the Lowest Carboranes

Certain *nido*-carboranes or their deprotonation products react with transition metal derivatives to form π-complexes in which the π-carborane ligand is regarded as isoelectronic with the π-cyclopentadienyl ligand.

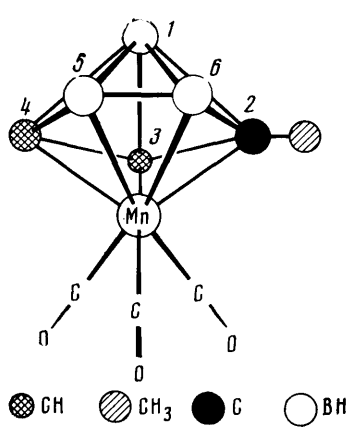


Figure 32.

2-Methyltricarbahexaborane(7) reacts with manganese carbonyl at 175–200°C in a sealed tube and gives rise to a quantitative yield of the isoelectronic analogue (π-2-$MeC_3B_3H_5$)$Mn(CO)_3$ (whose structure is illustrated in Fig. 32) of the known metallocene (π-C_5H_5)$Mn(CO)_3$:[97]

$$MeC_3B_3H_6 + \frac{1}{2}\,Mn_2(CO)_{10} \rightarrow (\pi\text{-}MeC_3B_3H_5)\,Mn(CO)_3 + \frac{1}{2}\,H_2\ .$$

Another method of synthesising this complex uses the reaction of sodium tricarbahexaborate with bromomanganese pentacarbonyl[98]. A σ-derivative is then formed as an intermediate and on heating is converted into a π-complex:

$$NaMeC_3B_3H_5 + BrMn(CO)_5 \xrightarrow[\text{fast}]{25^\circ} (\sigma\text{-}MeC_3B_3H_5)\,Mn(CO)_5 \xrightarrow[\text{slow}]{100^\circ} (\pi\text{-}MeC_3B_3H_5)\,Mn(CO)_3\ .$$

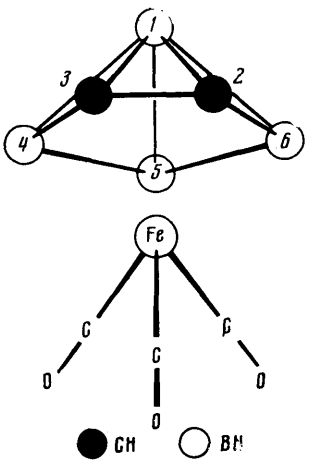


Figure 33.

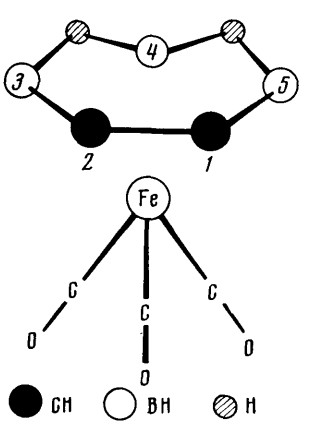


Figure 34.

The interaction of 2,3-dicarbahexaborane(8) ($C_2B_4H_8$) with iron pentacarbonyl at 240°C results in the formation of two π-complexes[99]: (π-$B_4C_2H_6$)$Fe(CO)_3$ (Fig. 33) and (π-$B_3C_2H_7$)$Fe(CO)_3$ (Fig. 34). The second complex is also formed in the reaction between dicarba-*nido*-pentaborane(7) with iron pentacarbonyl under ultraviolet irradiation[100]. The iron complexes obtained are isoelectronic with the $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ cation and the π-$B_4C_2H_6$ and π-$B_3C_2H_7$ ligands have two negative charges.

Another pathway to the synthesis of π-carborane complexes of iron consists of the reaction of sodium dicarbahexaborate with cyclopentadienyliron dicarbonyl iodide and

subsequent photochemical decomposition of the μ-iron complex[101]:

$$NaC_2B_4H_7 + (\pi\text{-}C_5H_5)\,Fe(CO)_2I \xrightarrow{25^\circ} \mu\text{-}[(\pi\text{-}C_5H_5)\,Fe(CO)_2]_2C_2B_4H_7 \xrightarrow{h\nu} (\pi\text{-}C_5H_5)\,Fe^{II}(\pi\text{-}B_4C_2H_7) + (\pi\text{-}C_5H_5)\,Fe^{III}(\pi\text{-}B_4C_2H_6)\,.$$

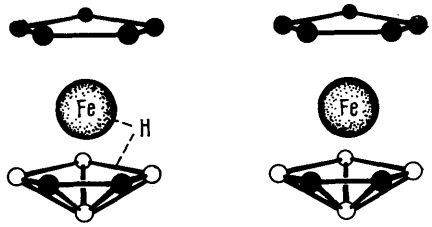


Figure 35.

The structures of both complexes have been deduced on the basis of ^{11}B NMR spectra and are presented in Fig. 35.

IV. METALLOCARBORANES OBTAINED BY THE POLYHEDRAL EXPANSION REACTION

The method of synthesis of metallocarboranes by the reduction of *closo*-carboranes has been called the polyhedral expansion reaction, since the resulting metallocarboranes have the structure of a polyhedron in which the number of vertices is greater by unity than in the initial carborane. The polyhedral expansion reaction has been largely applied to carboranes of the general type $B_nH_nC_2H_2$.

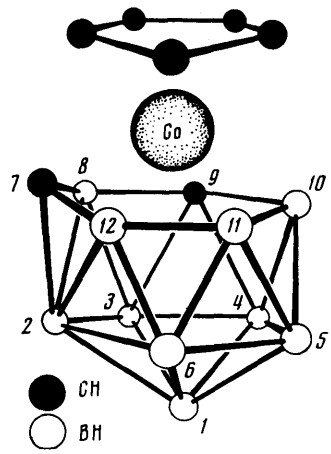


Figure 36.

The carborane 1,2-$B_{10}H_{10}C_2H_2$ is reduced by two moles of naphthalenesodium in THF to the dianion $B_{10}H_{10}C_2H_2^{2-}$,[102-103] which reacts with sodium cyclopentadienide and with $FeCl_2$ or $CoCl_2$ to form π-cyclopentadienyl-π-dodecahydrocarba-*nido*-dodecaboratoiron(III) or the corresponding cobalt(III) complex respectively[104,105]:

$$C_5H_5^- + B_{10}H_{10}C_2H_2^{2-} + MCl_2 \rightarrow [(\pi\text{-}C_5H_5)\,M^{II}(\pi\text{-}B_{10}C_2H_{12})]^- \xrightarrow{-e^-} \rightarrow (\pi\text{-}C_5H_5)\,M^{III}(\pi\text{-}B_{10}C_2H_{12}) \quad (M = Fe, Co)\,.$$

The iron(III) complex is paramagnetic (the effective magnetic moment is 2.12 Bohr magnetons) and is readily reduced by $NaBH_4$ to the iron(II) complex[105].

The red cobalt(III) complex, obtained directly from the reaction mixture, rearranges on boiling in hexane into an orange cobalt(III) complex, which is in turn converted on boiling in benzene into a red-orange cobalt(III) complex. X-Ray diffraction analysis[106] of the red complex (π-C_5H_5)Co^{III} (π-$B_{10}H_{10}C_2H_2$) showed that it exists in the form of a pair of enantiomers with the carbon atoms in the 7- and 9-positions or 7- and 11-positions (Fig. 36).

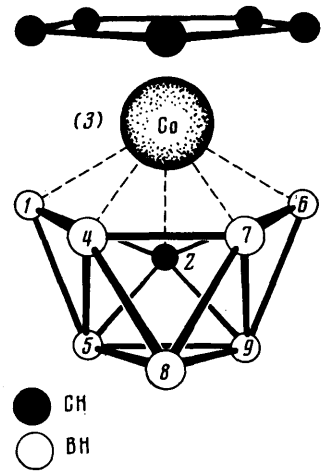


Figure 37.

In the orange isomer the carbon atoms occupy the 6- and 7-positions and in the red-orange isomer the 5- and 7-positions[107]. Alkaline degradation of the orange complex (π-C_5H_5)Co^{III} (π-$B_{10}C_2H_{12}$) leads to a new metallocarborane—π-cyclopentadienyl-π-octahydro-2-carba-*nido*-octaboratocobalt [(π-C_5H_5)Co^{III} (π-2-B_7CH_8)]$^-$,[107,108] for which the structure illustrated in Fig. 37 was proposed.

The reaction of the dianion $B_{10}C_2H_{12}^{2-}$ with cobalt(II), iron(II), and nickel(II) salts proceeds in accordance with the equation

$$2\,B_{10}C_2H_{12}^{2-} + M^{n+} \rightarrow [(\pi\text{-}B_{10}C_2H_{12})_2\,M]^{n-4} \quad (n = 2,3)\,.$$

and leads to bis-(π-dodecahydrodicarba-*nido*-dodecaborate) complexes (Fig. 38)[105,109].

The reaction of the dianion $B_{10}C_2H_{12}^{2-}$ with molybdenum and tungsten hexacarbonyls under ultraviolet irradiation leads to carboranylmetal tricarbonyl units[105]:

$$B_{10}C_2H_{12}^{2-} + M(CO)_6 \xrightarrow[-CO]{h\nu} [(\pi\text{-}B_{10}C_2H_{12})\,M(CO)_3]^{2-} \quad (M = Mo, W)$$

Zakharkin and Kalinin[109,110] found that the iron(III), cobalt(III) and nickel(II) complexes obtained from the dianions of carborane(10) and its *C*-substituted derivatives are readily oxidised by $CuCl_2$ with formation of carboranes. A characteristic feature of these complexes is the

ease of their rearrangements associated with a change in the relative positions of the carbon atoms in the π-carborane ligand. While oxidation of the complexes obtained directly by the reaction leads to the initial carborane 1,2-$B_{10}C_2H_{12}$ and its derivatives, oxidation of the rearranged complexes yields the 1,7- and 1,12-$B_{10}C_2H_{12}$ carboranes and their derivatives. This method has been recommended by the authors for the low-temperature isomerisation of 1,2-$B_{10}C_2H_{12}$ carboranes to 1,7-$B_{10}C_2H_{12}$ carboranes. In the $(B_{10}C_2H_{12})_2M^{n-4}$ complexes reversible transitions from the *closo*- to the *nido*-structure are observed in the ligands:

$$closo\text{-}B_{10}C_2H_{12} \underset{CuCl_2(-4e^-)}{\overset{+2e^-+MX_n}{\rightleftharpoons}} nido\text{-}(B_{10}C_2H_{12})_2\ M^{n-4}\ .$$

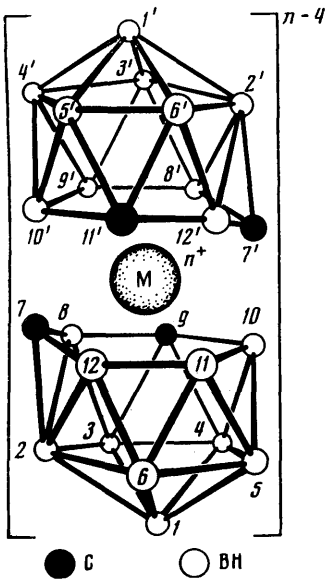


Figure 38.

The oxidation of the complexes $(B_{10}C_2H_{12})_2M^{n-4}$ has also been investigated by Brattsev and Stanko[111], but their results require additional confirmation.

The polyhedral expansion reaction applied to the carborane 1,8-$B_9C_2H_{11}$ leads to a metallocarborane containing the π-(3)-1,7-dicarbollyl ligand (see Section III, 1).

Polyhedral expansion of the carborane 1,6-$B_8C_2H_{10}$ using naphthalenesodium, sodium cyclopentadienide, and $CoCl_2$ leads to two main products[112]: $(\pi\text{-}B_8C_2H_{10})Co^{III}(\pi\text{-}C_5H_5)$ (Fig. 39) and $[(\pi\text{-}B_8C_2H_{10})_2Co^{III}]^-$. Next, on treatment of π-cyclopentadienyl-π-decahydrodicarba-*nido*-decaboratocobalt with naphthalenesodium and subsequent addition of sodium cyclopentadienide and $CoCl_2$, a two-metal carborane complex was obtained[113]:

$$C_5H_5CoB_8C_2H_{10} \xrightarrow[\text{THF, } 50^\circ]{\substack{1.\ 3(Na^+C_{10}H_8^-),\\ 2.\ Na^+C_5H_5^-\\ 3.\ CoCl_2}} C_5H_5CoB_8C_2H_{10}CoC_5H_5\ .$$

A structure with a bidentate π-linked $B_8C_2H_{10}$ ligand (dicarbacanastide), which, in contrast to the ligand considered previously (Fig. 7), contains carbon atoms in the 8- and 10-positions (Fig. 40), was proposed for the complex[113].

Treatment of the carborane 1,7-$B_6C_2H_8$ with two equivalents of naphthalenesodium in THF and subsequent addition of sodium cyclopentadienide and $CoCl_2$ lead to the formation, together with the normal product $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}B_6C_2H_8)$ (Fig. 41), of the two-metal complex[114]

$(C_5H_5)_2Co_2B_6C_2H_8$[114].

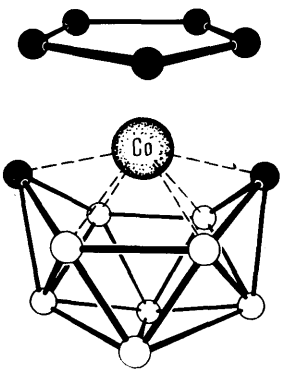


Figure 39.

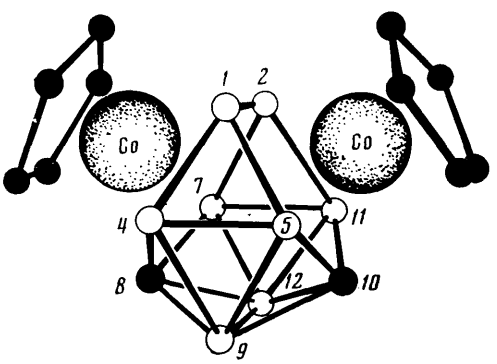


Figure 40.

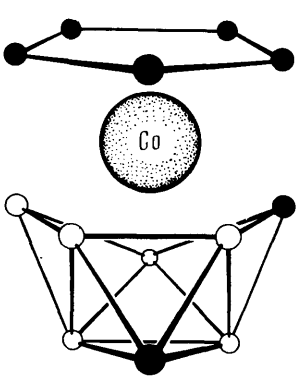


Figure 41.

The complex was shown to have an unusual structure with the two cobalt atoms occupying adjoining vertices of the polyhedron (Fig. 42).[7,8] The structure quoted by Dunks and Hawthorne[114] is incorrect.

Interesting results were obtained by Miller and Grimes when they applied the polyhedral expansion reaction to the carborane 2,4-$B_5C_2H_7$.[115] Its treatment with two moles of naphthalenesodium gave the dianion $B_5C_2H_7^{2-}$ whose interaction with sodium cyclopentadienide and $CoCl_2$ and subsequent oxidation by atmospheric oxygen leads to the formation of more than twenty neutral metallocarboranes, eight of which have been isolated and characterised. The structures proposed for these complexes are illustrated in Fig. 43. All the complexes are formally derivatives of the ligands $B_4C_2H_6^{2-}$, $B_4C_2H_6^{4-}$, $B_5C_2H_7^{2-}$, $B_5C_2H_7^{4-}$, $B_6C_2H_8^{2-}$, and $B_6C_2H_8^{4-}$.

The authors considered the possible mechanism of the formation of the metallocarboranes and proposed the following reaction sequence[115]: (1) the formation of the $B_5C_2H_7^{2-}$ dianion from $B_5C_2H_7$ and naphthalenesodium; (2) the formation of the $(\pi\text{-}B_5C_2H_7)Co^{II}(\pi\text{-}C_5H_5)^-$ anion from $CoCl_2$, NaC_5H_5, and $B_5C_2H_7^{2-}$; (3) the reaction of the $(\pi\text{-}B_5C_2H_7)Co^{II}(C_5H_5)^-$ ion with $B_5C_2H_7^{2-}$ via electron transfer (a) and alkaline degradation (b) mechanisms leading to the formation of the open-chain metallocarborane anions $(\pi\text{-}B_5C_2H_7)Co^{II}(\pi\text{-}C_5H_5)^{3-}$ and $(\pi\text{-}B_4C_2H_6)Co^{II}(\pi\text{-}C_5H_5)^{3-}$ respectively; (4) the insertion of the Co^{2+} ion in

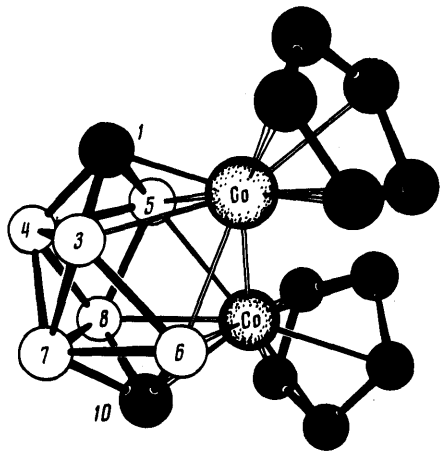


Figure 42.

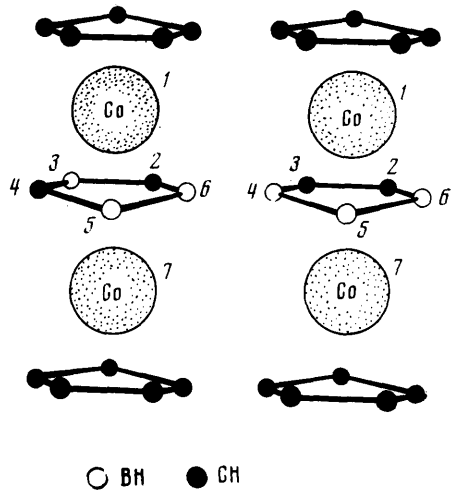


Figure 44.

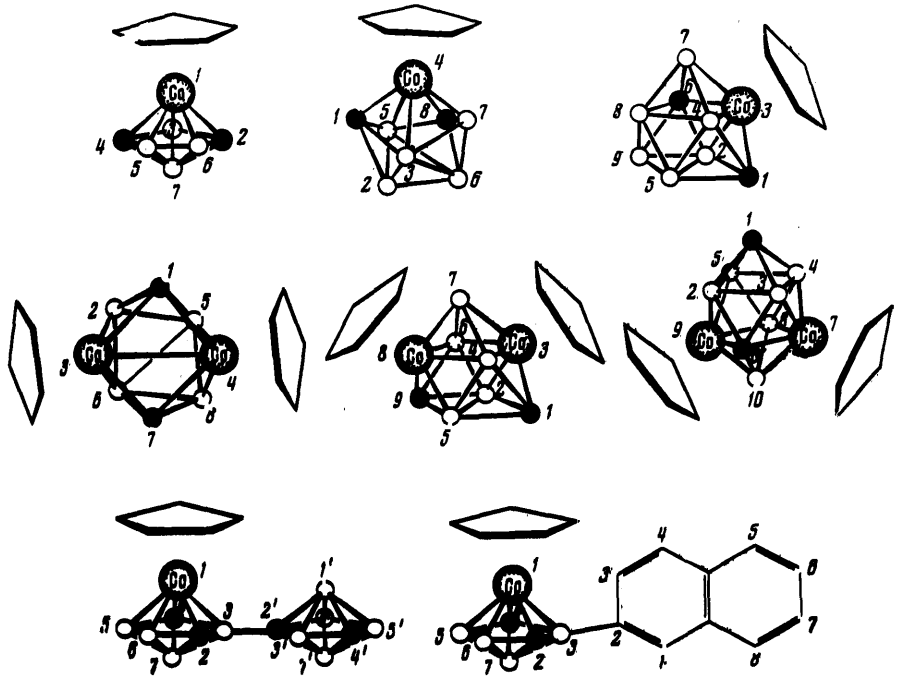


Figure 43.

certain open-chain metallocarborane ions with formation of two-metal units; (5) oxidation by air of the cobalt(II) ions formed in stages (2), (3), and (4) to the neutral cobalt(III) metallocarboranes $(\pi\text{-}B_{n-2}C_2H_n)Co^{III}(\pi\text{-}C_5H_5)$ and $(\pi\text{-}B_{n-2}C_2H_n)Co_2(\pi\text{-}C_2H_5)$; (6) side reactions associated with the deprotonation of the carborane units and the formation of their σ-bonded derivatives.

Nor can one rule out the possibility of the disproportionation of the $B_5C_2H_7^{2-}$ anion to $B_4C_2H_6^{2-}$, $B_6C_2H_8^{2-}$, and other units before the stage in which the metal is inserted into the *nido*-carborane system[115]. All the π-carborane ligands discussed above had a three-dimensional structure. Grimes and coworkers[116] were the first to obtain π-complexes with planar π-ligands. By treating the carborane 1,6-$B_4C_2H_6$ with naphthalenesodium and the subsequent reaction of the dianion $B_4C_2H_6^{2-}$ with $C_5H_5^-Na^+$ and $CoCl_2$, the dinuclear complex $[(\pi\text{-}1,7)\text{-}2,4\text{-}B_3C_2H_5]Co_2(\pi\text{-}C_5H_5)_2$ was obtained; its structure is shown in Fig. 44.

The isomeric complex $[(\pi\text{-}1,7\text{-})\text{-}2,3\text{-}B_3C_2H_5]Co_2(\pi\text{-}C_5H_5)_2$ was synthesised by the reaction of sodium dicarba-*nido*-hexaborate $NaB_4C_2H_7$ with C_5H_5Na and $CoCl_2$ (Fig. 44).[116] Both complexes obtained are formally derivatives of the $B_3C_2H_5^{4-}$ ligand. The π-carborane complexes are structurally similar to the complex $[Ni(C_5H_5)_3]^+$.[117] However, in contrast to the $[Ni_2(C_5H_5)_3]^+$ system, which is readily converted into nickelocene under the influence of moisture, the $(B_3C_2H_5)Co_2(C_5H_5)_2$ systems are resistant to the action of water, atmospheric oxygen, and solvents.

V. CARBORANE DERIVATIVES OF NON-TRANSITION METALS

The possibility of the formal substitution of the BH vertices in the polyhedral carborane structures by isoelectronic units is clearly illustrated, for example, by the isoelectronic series of compounds $B_{12}H_{12}^{2-}$, $B_{11}CH_{12}^-$, and $B_{10}C_2H_{12}$, from which it follows that the BH unit is isoelectronic with the CH^+ unit.[4] By analogy, Be is isoelectronic with the BH unit and therefore one might expect the existence of the neutral compound $BeB_9C_2H_{11}$.

Using the familiar reaction whereby the dicarbollide ion is built up with the aid of phenylboron dichloride to the icosahedral carborane structure[118], Popp and Hawthorne[119,120] attempted to build up the dicarbollide ion with beryllium chloride:

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{3-} + BeCl_2 \rightarrow (3)\text{-}BeCl - 1,2\text{-}B_9C_2H_{11}^- .$$

but they were unable to obtain a berylcarborane by this reaction.

The $B_9C_2H_{13}$ carborane, which may be regarded as a diprotonated dicarbollide ion, was used to synthesise a berylcarborane. Its reaction with metal alkyls should result in the formation of an alkane on protolysis of the metal–carbon bond and the metal should be inserted in the open face of the icosahedral fragment. For dialkylberyllium, the presence of electron-donating solvents is necessary to stabilise the product. Accordingly, dimethylberylliumdiether and diethylberyllium-diether were used for the synthesis[119,120]:

$$(3)\text{-}1,2\text{-}B_9C_2H_{13} + BeR_2 \cdot 2(OEt_2) \xrightarrow{\text{benzene/ether}} 2RH + (3)\text{-}Be\text{-}1,2\text{-}B_9C_2H_{11} \cdot OEt_2 .$$

The product is very sensitive to moisture and on hydrolysis yields the (3)-1,2-$B_9C_2H_{12}^-$ ion.

When the reaction was carried out with diethylberyllium containing only one-third of the required amount of ether, an insoluble polymeric product consisting of [(3)-Be-1,2-$B_9C_2H_{11}$]n units with icosahedral geometry, linked by Be–H–B bridges, was obtained. When the ether adduct of the berylcarborane is treated with trimethylamine, the complex (3)-[$BeNMe_3$]-1,2-$B_9C_2H_{11}$, whose structure is illustrated in Fig. 45, is formed.

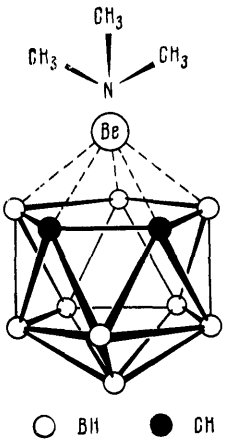


Figure 45.

Mikhailov and Potapova obtained an aluminacarborane in the form of an adduct with two THF molecules by the reaction of the 1,2-dicarbollide ion with ethylaluminium dichloride in THF[121]:

$$1,2\text{-}B_9C_2H_{11}^{3-} + EtAlCl_2 \xrightarrow{THF} (3)\text{-}EtAl - 1,2\text{-}B_9C_2H_{11} \cdot 2THF.$$

This compound was the first example of metallocarboranes containing a non-transition metal in the polyhedron. Subsequently the ability of the carborane $B_9C_2H_{13}$ to undergo protolysis at the metal–carbon bond was used to synthesise alumina- and galla-carboranes[122,123]. When equimolar amounts of trialkylaluminium and $B_9C_2H_{13}$ were mixed and heated at 50°C for 1 h, 7,8-μ-dialkylalumina-1,2-dicarba-*nido*-undecaborane(13) was formed:

$$(3)\text{-}1,2\text{-}B_9C_2H_{13} + R_3Al \rightarrow (3)\text{-}AlR_2\text{-}1,2\text{-}B_9C_2H_{13} + RH .$$

According to X-ray diffraction[124,125], the aluminium atom in $B_9C_2H_{12}AlR_2$ deviates from the open face of the icosahedral fragment and the angle between the $B_{(7)}$–Al–$B_{(8)}$ and $B_{(7)}$–$B_{(8)}$–$B_{(4)}$–$C_{(1)}$–$C_{(2)}$ planes is 130° (Fig. 46). It is suggested that the aluminium atom is linked to the $B_{(7)}$ and $B_{(8)}$ atoms by two bridging hydrogen bonds. A low-temperature study of the ^{11}B NMR spectra established[123] the occurrence of a tautomeric process involving the exchange of the bridge positions between the dialkylaluminium fragment and the proton H_b, as shown in Fig. 46. At low temperatures the ^1H NMR spectra reveal the splitting of the signal corresponding to the Me_2Al group, which indicates the *endo*- and *exo*-locations of the methyl groups relative to the open face[123]. The gallium derivative was obtained similarly:

$$(3)\text{-}1,2\text{-}B_9C_2H_{13} + Et_3Ga \rightarrow (3)\text{-}GaEt_2\text{-}1,2\text{-}B_9C_2H_{13} + C_2H_6 .$$

When 7,8-μ-dialkylalumina-1,2-dicarba-*nido*-undecaborane(13) is heated in benzene, 3-alkyl-3-alumina-1,2-dicarba-*closo*-dodecaborane(12) is formed:

$$(3)\text{-}AlR_2\text{—}1,2\text{-}B_9C_2H_{12} \xrightarrow[25\ h]{77^\circ} (3)\text{-}RAl - 1,2\text{-}B_9C_2H_{11} + RH\ .$$

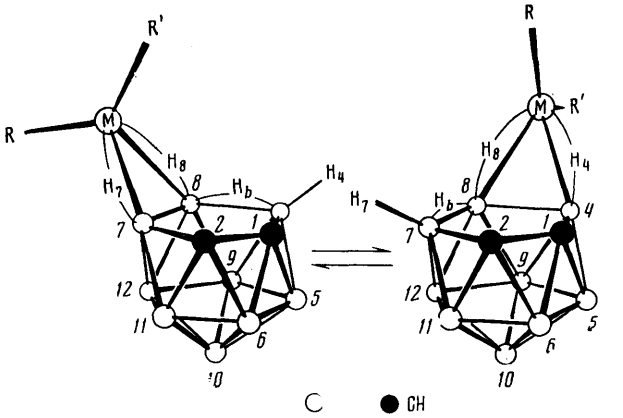


Figure 46.

It has been established that the monoethylaluminium derivative has the closed icosahedral structure with an EtAl unit [122,126]. This compound forms with THF the adduct obtained previously by Mikhailov and Potapova.

Heating the diethylgallium derivative also leads to the formation of a closed structure:

$$(3)\text{-}1,2\text{-}B_9C_2H_{12}GaEt_2 \xrightarrow{77^\circ} (3)\text{-}GaEt - 1,2\text{-}B_9C_2H_{11} + C_2H_6\ .$$

At 410°C 3-ethyl-3-alumina-1,2-carborane undergoes thermal isomerisation in the gas phase forming 3-ethyl-3-alumina-1,7-carborane [123]:

$$(3)\text{-}AlEt - 1,2\text{-}B_9C_2H_{11} \xrightarrow{410^\circ} (3)\text{-}AlEt - 1,7\text{-}B_9C_2H_{11}\ .$$

The selective formation of the 1,7-isomer in the isomerisation process resembles the behaviour of the carborane $1,2\text{-}B_{10}C_2H_{12}$, which rearranges to $1,7\text{-}B_{10}C_2H_{12}$ at 400–500°C, [4] but its behaviour differs from that of other metallocarboranes, particularly $Ni[(3)\text{-}1,2\text{-}B_9C_2H_9Me_2]_2$ and $Pd[(3)\text{-}1,2\text{-}B_9C_2H_9Me_2]_2$, [62,63] for which rearrangements leading to a 1,6- disposition of the carbon atoms are characteristic.

Alumina- and galla-carboranes are sensitive to the action of moisture and are readily hydrolysed with formation of the $(3)\text{-}1,2\text{-}B_9C_2H_{12}$ ion. Their reaction in benzene with anhydrous HCl gives a quantitative yield of $(3)\text{-}1,2\text{-}B_9C_2H_{13}$. An interesting property of the compounds $B_9C_2H_{12}AlEt_2$ and $B_9C_2H_{11}AlEt_2$ is their ability to form with $TiCl_4$ complexes whose solutions polymerise ethylene like the Ziegler–Nata catalysts [123].

The dicarbollide ion interacts with bivalent Group IVB metal salts, forming a product resulting from the insertion of the metal in the open face of the dicarbollide [127,132]:

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + MX_2 \rightarrow (3)\text{-}M\text{-}1,2\text{-}B_9C_2H_{11} \quad (Me{=}Ge, Sn, Pb)\ .$$

The metallocarboranes obtained are stable in air, but are hydrolysed in acid and alkaline media to the anions $B_9C_2H_{12}^-$.

A similar reaction involving the building up of 1,2- and 1,7-phosphacarbollide and 1,2- and 1,7-arsacarbollide ions with the aid of GeI_2 leads to phospha- and arsa-germacarboranes containing three heteroatoms in the icosahedral structure [129]:

$$\begin{aligned} &1,2\text{-}B_9H_9CH\ni^{2-} + GeI_2 \rightarrow 1,2,3\text{-}GeB_9H_9CHE, \\ &1,7\text{-}B_9H_9CH\ni^{2-} + GeI_2 \rightarrow 1,2,7\text{-}GeB_9H_9CHE. \end{aligned} \qquad (E = P,\ As)$$

When the monocarbollide ion was built up with trichloromethylgermane, a germacarborane was obtained [130]:

$$Na_3B_{10}H_{10}CH + MeGeCl_3 \rightarrow B_{10}H_{10}CHGeMe - 1.2\ .$$

The gas-phase reaction of trimethylgallium or trimethylindium with 1,3-dicarba-*nido*-hexaborane(8) yields 1-methyl-1-galla- or 1-methyl-1-inda-2,4-dicarba-*closo*-heptaborane(7): [131,132]

$$B_4C_2H_8 + GaMe_3 \xrightarrow{215^\circ} MeGaB_4C_2H_6;\ B_4C_2H_8 + InMe_3 \xrightarrow{95-110^\circ} MeInB_4C_2H_6\ .$$

The structure of the gallacarborane is illustrated in Fig. 47. The indacarborane probably has a similar structure.

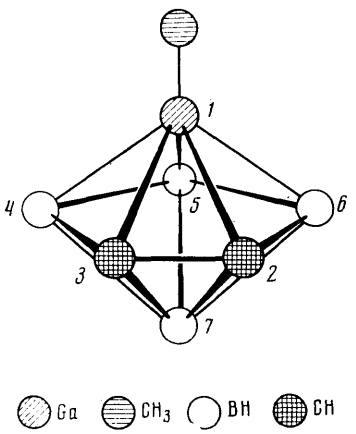


Figure 47.

After the manuscript had been sent to the editors, a number of papers on metallocarboranes were published. Certain early investigations have been summarised in Snaith and Wade's review [133]. The polyhedral expansion reaction has been developed further. Hawthorne and coworkers [134] described in detail the application of this reaction to the $1,7\text{-}C_2B_6H_8$, $4,5\text{-}C_2B_7H_9$, $1,6\text{-}C_2B_8H_{10}$, $1,10\text{-}C_2B_8H_{10}$, and $1,8\text{-}C_2B_9H_{11}$ systems. Using $CoCl_2$ and NaC_5H_5, metallocarboranes of the following types were obtained: $C_5H_5CoC_2B_nH_{n+2}$, $(C_5H_5Co)_2C_2B_nH_{n+2}$, and $C_5H_5CoC_2B_nH_{n+1}(C_2B_nH_{n+1})$. The formation of the mixed ferracarboranes from the $1,7\text{-}C_2B_6H_8^{2-}$ and $1,6\text{-}C_2B_8H_{10}^{2-}$ dianions, NaC_5H_5, and $FeCl_2$ has been described [134].

The application of the polyhedral expansion reaction to metallocarboranes yielded interesting results. The reduction of the complex $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}1,6\text{-}C_6B_7H_9)$ by naphthalenesodium in THF and its subsequent reaction with NaC_5H_5 and $FeCl_2$ led to the formation of the bimetallocarborane $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_2B_7H_9)Fe(\pi\text{-}C_5H_5)$ in which there is one paramagnetic and one diamagnetic centre [135].

The cobaltaferracarborane $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}C_2B_9H_{11})Fe^{III}(\pi\text{-}C_5H_5)$ was obtained by the alkaline degradation of the complex $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}C_2B_{10}H_{12})$ in the presence of $FeCl_2$ and C_5H_6.[135]

The reaction of the reduced form of $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}1,6\text{-}C_2B_7H_9)$ with NaC_5H_5 and $CoCl_2$ leads to the formation of $(C_5H_5Co)_2C_2B_7H_9$ and $(C_5H_5CO)_3C_2B_7H_9$.[136] It is suggested that the last complex has an icosahedral structure with the cobalt atoms at three vertices. The reaction of the reduced complex $[Me_4N](\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)$ with NaC_5H_5 and $NiBr_2$ yielded the two-metal monocarbon metallocarborane $(\pi\text{-}C_5H_5)Co^{III}(\pi\text{-}CB_7H_8)Ni^{IV}(\pi\text{-}C_5H_5)$.[137]

Salentine and Hawthorne[137] quote tentative structures for metallocarboranes. The study of the chemical properties of certain metallocarboranes has been continued[138]. Hawthorne and coworkers[139] attempted to classify metallocarboranes in terms of the total number of electrons involved in the formation of the polyhedra. The $2n + 14$, $2n + 16$, and $2n + 26$ electron rules are valid for *closo*-polyhedral heteroboranes containing one transition metal at the vertex, for *nido*-polyhedra of this type, and for *closo*-polyhedra with two transition metals at the vertices respectively. A series of X-ray diffraction studies have been made on metallocarboranes, confirming the structures proposed previously: $(B_6C_2H_8)Mn(CO)_3$,[140] $(B_3C_2H_7)Fe(CO)_3$,[141] and $(B_9C_2H_{11})_2Ni$.[142]

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