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# Cobalt Complexes of Carbaboranes

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The results of studies on the chemical behaviour and methods of synthesis of cobalt complexes of carbaboranes are surveyed and described systematically. The methods of synthesis are classified and the applications of each method are considered. A systematic account is given of methods for the identification of cobalt complexes of carbaboranes. The chemical properties of such complexes are determined by the structure and properties of the carbaborane ligand. The electronic configuration of the cobalt atom in different cobalt complexes of carbaboranes varies within wide limits ($d^8$–$d^5$). The review deals with studies in the period 1965-1978 and partially in 1979.
There are 229 references.

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## I. INTRODUCTION

Polyhedral π-complexes of metals belonging to the Cu, Cr, Mn, Fe, Co, and Ni subgroups, based on the highest and lowest carbaboranes, are now known. Preparative methods have been developed for their synthesis and their properties are being vigorously investigated. The principal achievements in this field have been described in a number of reviews[1-11]. Exhaustive information about the period from 1965 to 1972 is presented in the review of Zakharkin and Kalinin[12]. The aim of the present publication is to isolate cobalt complexes from the overall wide variety of polyhedral and transition metal π-complexes as the most typical representatives of compounds of this class which have attracted the attention of investigators.

## II. GENERAL CHARACTERISTICS OF THE COMPLEXES

Carborane π-complexes of iron and cobalt having the general formula $[(B_9C_2H_{11})_2M]^{z-}$ (M = Fe or Co, $z = 2$ or 1), the formal analogues of compounds of the type of ferrocene and the cobaltocenium cation, were synthesised for the first time in 1965. In these complexes the iron and cobalt atoms are coordinated to the dicarbollide dianion[13,14]. The results of X-ray diffraction studies on metal complexes of carbaboranes[15,16], $^{11}B$ and $^1H$ NMR and NQR data[17] for these compounds, as well as their magnetic, electronic[18] and electrochemical properties agree with the hypothesis of the sandwich nature of the metal–ligand bond in these π-complexes. The possibility of the existence of metal complexes of carbaboranes follows from the quantum-mechanical description of the dicarbollide ion[19,20]. The calculation is based on the hypothesis of the formation by the five atomic orbitals of the open pentagonal $B_3C_2$ surface of three bonding and two antibonding molecular orbitals[19,20]. The filling of the bonding molecular orbitals with six electrons makes the dicarbollide ion an isoelectronic and isostructural analogue of the Cp anion (Cp = $C_5H_5$) (see also Zakharkin and Kalinin[12]).

Apart from compounds of the type $[(B_nC_2H_{n+2})_2Co]^-$, Cp-containing complexes having the general formula $(\eta^5\text{-CpCo})_mB_nC_2H_{n+2}$ ($m = 1$–4; $n = 3$–10) are also known at the present time.

One of the qualitative features of the stability of metal complexes of carbaboranes is the validity of the empirical rule concerning the number of electrons required for the formation of the π-complex with participation of bonds in the ligand. It has been shown[21] that this number is given by the formula $2k + 14$, where $k$ is the number of vertices in the polyhedron of the metal carbaborane complex. For example, in $CpCo.B_3C_2H_{11}$ ($m = 1$, $n = 9$; 12 vertices) there are altogether 60 electrons, which include five electrons from the Cp ligand, 9 electrons from the cobalt atom, 11 electrons from the 11 hydrogen atoms, 27 electrons from the 9 boron atoms, and 8 electrons from the 2 carbon atoms. The formation of all the CH and BH bonds requires 22 electrons, while the remaining 38 electrons are involved in the formation of bonds in the π-complex and their number can be calculated from the empirical formula $2k + 14$ ($k = 12$).[21] For bimetallic carbaborane complexes $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$, the formula $2k + 26$ is used[21].

The stability of the complexes and their chemical properties depend on the formal degree of oxidation (f.d.o.) of the metal and the overall charge of the π-complex. Complexes whose overall charge is smaller and whose metal atom has the usual f.d.o. are more stable. On the other hand, a high molecular charge of the π-complex and an uncharacteristic f.d.o. of the metal reduce the stability of the compound[21] (see also Section IV). The molecular geometry of the cobalt complex of a carbaborane also influences its stability. The most stable compounds are those whose polyhedron is an icosahedron[22]. In dicobalt complexes of carbaboranes the direct Co–Co interaction stabilises the system[23], but, at an elevated temperature, compounds in the polyhedron of which cobalt atoms do not occupy neighbouring vertices are more stable. Such a disposition of cobalt atoms does not interfere with the more vigorous vibration of the Cp rings[23].

There exists the view[21] that a complex of the type $CpCo.B_nC_2H_{n+2}$ can be regarded as a heterocarbaborane in which the BH fragment has been replaced by the isoelectronic CpCo fragment. It is suggested that, like the BH fragment, the CpCo group supplies three orbitals and two electrons of the binding process[21,24]. To a first approximation, this concept explains satisfactorily and predicts certain chemical and physicochemical properties of cobalt complexes of carbaboranes, particularly the existence of a number of analogies in the chemistry of cobalt complexes of carbaboranes and of

carbaboranes themselves[25]. An example may be provided by the polyhedral expansion and contraction, polyhedral rearrangement, and electrophilic bromination reactions. However, bearing in mind the specific formalism underlying this concept, one must use it with caution in discussing the chemical and physicochemical properties of cobalt complexes of carbaboranes. In the first place we may note that symmetrical complexes of the type $[(B_mC_2N_{n+2})_2Co]^-$, which do not contain the CpCo fragment, also have a number of properties resembling those of carbaboranes and asymmetric cobalt complexes of carbaboranes of the type $CpCoB_nC_2H_{n+2}$. These concern the involvement of the above compounds in the same polyhedral contraction (see Section III), polyhedral rearrangement, and electrophilic bromination (see Section IV) reactions.

Furthermore, the study of the $^{11}B$ and $^{13}C$ NMR of halogen-substituted cobalt complexes of carbaboranes $\{[(1,2\text{-}B_9C_2H_{11})_2.Co]^-$, $[(9\text{-}Br\text{-}1,2\text{-}B_9C_2H_{10})_2Co]^-$, and $[(9,12\text{-}Br_2\text{-}1,2\text{-}B_9C_2H_9)_2Co]^-\}$ established that the nature of the change in electron density following the introduction of the halogen is the same for the cobalt complexes of carbaboranes and icosahedral boranes and carbaboranes[26]. The most intense deshielding is observed at boron or carbon atoms occupying the opposite vertices relative to the halogen-substituted boron atoms. The carbon atoms in the complex $[(9,12\text{-}Br_2\text{-}1,2\text{-}B_9C_2H_9)_2Co]^-$ are deshielded to the greatest extent, while the $B_{(5)}$ and $B_{(11)}$ atoms, closest to the substituted $B_{(9)}$ and $B_{(12)}$ atoms, are deshielded to a smaller extent[26]. Furthermore, it has been shown for $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ by infrared spectroscopy that the coordination of the dicarbollyl ligand to the cobalt atom does not abolish the capacity of the CH group for the formation of a hydrogen bond[27]. Next, a study of the photoelectron spectra of bis(dicarbollyl)cobalt derivatives containing a bridging ligand in the 8- and 8′-positions [−S−S, −S−, −S−$\overset{+}{S}$(Me)−, −S−$\overset{+}{C}$H−S−, −$\overset{+}{S}$(Me)−, and −$\overset{+}{O}$(Me)−] showed that, firstly, within the carbaborane ligand in each derivative there is a uniform distribution of charge density over the boron atoms and, secondly, the presence of a bridging atom more electronegative than boron (S, $\overset{+}{S}$, $\overset{+}{O}$) causes a shift of electron density both from the two carbaborane ligands and from the central cobalt(III) atom[28]. All these findings show that the nature of the bond within the polyhedral ligand apparently does not undergo profound and fundamental changes as a result of coordination; this entails the retention of the properties of carbaboranes in their cobalt complexes. Furthermore, whereas the presence of the negative charge in $[(B_nC_2H_{n+2})_2.Co]^-$ gives rise to certain anomalies, neutral complexes of the type $CpCoB_nC_2H_{n+2}$ are even closer in their properties to the corresponding carbaboranes. The chemical and physicochemical properties of cobalt complexes of carbaboranes therefore in general still depend largely on the structure and properties of the carbaborane fragments involved in the complex.

However, this does not imply that the role of the metal in the carbaborane complexes is insignificant. The possibility, in principle, of the existence of a metal complex of a carbaborane and its stability depend on the nature of the metal atom. In the Fe, Co, Ni series the cobalt atom, which has the stable $d^6$ electronic state, forms diamagnetic complexes which either have a low molecular charge $\{[(B_nC_2H_{n+2})_2Co]^-\}$ or are altogether uncharged $(CpCoB_nC_2H_{n+2})$. At the same time, as a result of its high molecular charge, the complex $[(1,2\text{-}B_9C_2H_{11})_2Fe^{II}]^{2-}$ is readily oxidised [Fe(II) → Fe(III)] and is converted into the paramagnetic complex $[(1,2\text{-}B_9C_2H_{11})_2Fe^{III}]^-$. Iron ($d^5$ electronic configuration) is an effective oxidant, which to a large extent determines the properties of the paramagnetic complex. (For nickel complexes, see Zakharkin and Kalinin[12].) One may also not that, as a result of coordination, there is a partial redistribution of electron density within the carbaborane ligand in the metal complexes.

The electron-donating influence of the *C*-substituted dianion $(B_9C_2H_{11})^{2-}$ is a combination of the inductive effect (+*I*) and the conjugation effect (+*R*).[29] The direction of the inductive effect in the coordinated dicarbollyl ligand changes (−*I*), while the nature of the conjugation effect remains the same (+*R*).[29,30] The replacement of the dicarbollyl ligand in the complex $[Co(B_9C_2H_{11})_2]^-$ by the cyclopentadienyl ligand enhances the electron-accepting properties of the residual *C*-substituted dicarbollyl group[29]. Comparison of the constants $\sigma_i$ and $\sigma_R^0$, calculated by Taft's method, shows that the $B_9C_2H_{11}CoC_5H_4$ group is a stronger accepter than the $C_5H_5CoB_9C_2H_{10}$ group.

The study of the $^{11}B$ and $^{13}C$ NMR of the paramagnetic complexes $CpMB_nC_2H_{n+2}$ [$n = 6$–$9$, M = Cr(III), Fe(III), Ni(III), or Co(II)] showed that, firstly, there is a redistribution of the unpaired electron density from the non-bonding orbitals of the central metal atom to the molecular orbitals of the carbaborane ligand and, secondly, the unpaired electrons interact not only with atoms linked to the central metal atom, but also with the more remote boron atoms[31]. In cobalt complexes of carbaboranes containing two cobalt atoms one may expect even more profound changes in electron density distribution, particularly in those cases where a Co–Co bond is present in the complex. An increase in the number of cobalt atoms in polyhedral π-complexes should therefore apparently entail changes in properties such that the new compounds will resemble to a decreasing extent their parent compounds (carbaboranes) and the properties will probably approach those of the usual cluster compounds of cobalt. During this transition, one may expect the appearance of compounds of a new type, with unique properties different from those of carbaboranes and clusters.

Theoretically[32,33] it is possible to predict the molecular geometries on the basis of the overall number of valence electrons in the polyhedron. At the same time the structure can be established and the cobalt complexes of carbaboranes identified by comparing the ultraviolet, infrared, NMR and mass spectra as well as the oxidation-reduction potentials. The ultraviolet spectra of cobalt complexes of *closo*-carbaboranes† are known to contain a band in the range 600–650 nm (green and blue complexes), while complexes with a *nido*-structure do not absorb in this region and they are red or brown[35]. Furthermore, the isomers of cobalt complexes of carbaboranes differing in the number of carbon atoms in the open pentagonal surface coordinated to the cobalt atom also exhibit differences in their ultraviolet spectra. In the isomer sequence *a* → *b* → *c* → *d* (Fig. 1 for R = H), the number of carbon atoms diminishes from two to zero and at the same time $\lambda_{max}$ for the band referred to the *d*–*d* transition undergoes a hypsochromic shift in the ultraviolet spectra of the complexes[6]. Analogous behaviour has been observed in the ultraviolet spectra of the isomers 1,2,4-, 1,2,3-, and $10,2,3\text{-}(\eta^5\text{-Cp})Co(Me_2B_8C_2H_8)$.[36] We may also note that complexes of the type $(CpCo)_2B_nC_2H_{n+2}$ ($n = 6$–$8$), which differ in the presence or absence of the Co–Co bond, also have characteristic absorption bands in the ultraviolet spectra[37].

The infrared spectra of cobalt complexes of carbaboranes having the general formula $(LCoB_nC_2H_{n+2})^z$ (L = Cp, $z = 0$; L = $B_nC_2H_{n+2}$, $z = -1$) retain all the principal characteristic

† For the nomenclature of the complexes, see Ref. 34 and the reviews by Zakharkin and Kalinin[12] and Grimes[193].

frequencies of the carbaboranes[35,38] and cyclopentadienyl ligands[39] and, on substitution in these ligands, the infrared spectra of the complexes exhibit the same changes as those of the substituted carbaboranes[38] and cyclopentadienylcobalt complexes[39]. The formation of the metal–dicarbollyl bond in $[Co(B_9C_2H_{11})_2]^-$ is characterised by a very intense polarised line in the Raman spectrum at 180–300 $cm^{-1}$, which has been assigned to the metal–dicarbollyl stretch[40].

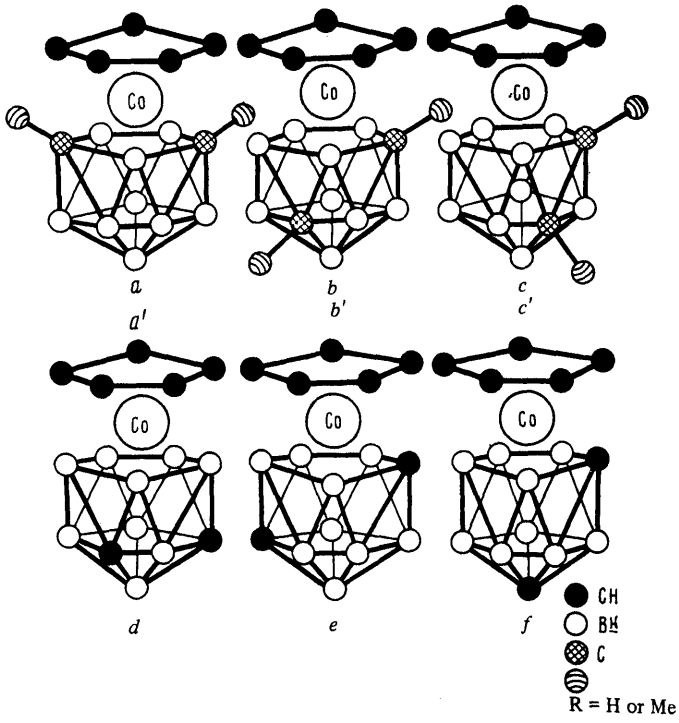



**Figure 1.** Postulated structures of the isomers (*a*–*f*) formed in the thermal gas-phase rearrangement of 3,1,2-($\eta^5$-Cp)Co.(1,2-$R_2B_9C_2H_9$): R = H (*a*–*c*) or $CH_3$ (*a'*–*c'*).

The use of triple resonance to observe the proton spectra with simultaneous suppression of signals due to $^{11}B$ and $^1H$ nuclei permits unambiguous assignments of the resonance lines[41]. Thus parameters of the $^1H$ [41] and $^{11}B$ [42–44] NMR spectra such as the chemical shift, the integral intensity, and the spin–spin splitting constant as well as the spin–lattice relaxation times $T_1$ of the $^{11}B$ and $^1H$ nuclei[45] are used successfully for the standard identification of metal complexes of carbaboranes.

Furthermore, substitution in the carbaborane ligand in $CpCo(HCB_9H_9Cr)$ leads to an alteration of the chemical shift of the protons in the Cp ring[46]. With increase of the number of bromine atoms in $CpCoB_9C_2H_{11-n}Br_n$ ($n = 1$–3), the signal of the protons of the Cp ring shifts downfield[47]. (For a description of the influence of the structure of cobalt complexes of carbaboranes on the reduction potential, see Section IV.) However, the most reliable results in the determination of the polyhedral structures were obtained by diffraction methods. X-Ray diffraction analysis of Cs[Co.$(B_9C_2H_{11})_2$] [15] yields the general type of structure of bisdicarbollylcobalt complexes. Figs.2 [48] and 3 [49] illustrate derivatives of the bisdicarbollylcobaltate anion. In both cases substitution takes place at the boron atoms. The cobalt atom in the structure of the anion $[Co(B_7C_2H_9)_2]^-$ (Fig.4) is located between the pentagonal $B_3C_2$ surfaces where the position (6 or 9) of one of the carbon atoms has not been rigorously established[16].

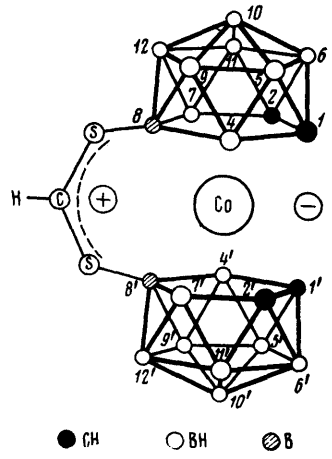



**Figure 2.** The structure of $[3,3'\text{-}Co(1,2\text{-}B_9C_2H_{10})_2]S_2C^+H$.[48]

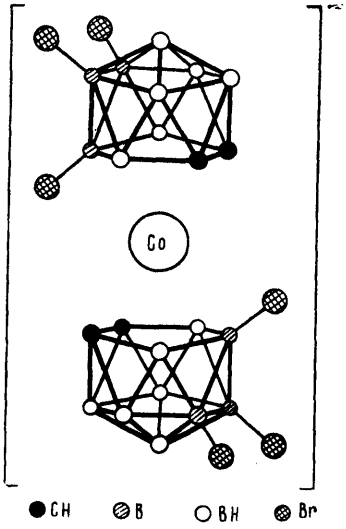



**Figure 3.** The structure of the $[Co(B_9C_2H_8Br_3)_2]^-$ ion[49].

The carbon atom in the $[3,4\text{-}(\eta^5\text{-}Cp)CoB_7CH_8]^-$ polyhedron (Fig.5) has a low coordination number (5),[50] which agrees with the general postulate, according to which the carbon atom in the polyhedron of the carbaborane in its metal occupies mainly a vertex with a low coordination number[51,52]. The cobalt atom in $(CpCoB_7CH_8)^-$ is coordinated to five boron atoms, where three Co–B distances are 2.15–2.18 Å while two are 1.97 and 1.98 Å.[50]

Figs. 6 and 7 present the structures of two *nido*-complexes 8,6,7-($\eta^5$-Cp)$CoB_7C_2H_{11}$ [53] and (1,2-$B_9C_2H_{11}$-3,11'-Co-9'-$C_5H_5N$-7',8'-$B_8C_2H_{10}$)$^-$.[54,55] The $CpCoB_7C_2H_{11}$ molecule has a geometry similar to that of decaborane with three heteroatoms (C,C,Co) in the open first surface. Two hydrogen atoms [$H_{(1)}$ and $H_{(2)}$] occupy bridging positions[53]. The carbaborane ligand $B_8C_2H_{10}$ in $(B_9C_2H_{11}CoB_8C_2H_{10}Py)^-$ has an open six-atom surface $C_{(7')}B_{(2')}B_{(6')}B_{(10')}B_{(9')}C_{(8')}$, four atoms of the surface being involved in coordination to the cobalt atom[54,55]. The pyridine fragment is linked to the boron atom. The position of the extra hydrogen has not been established.

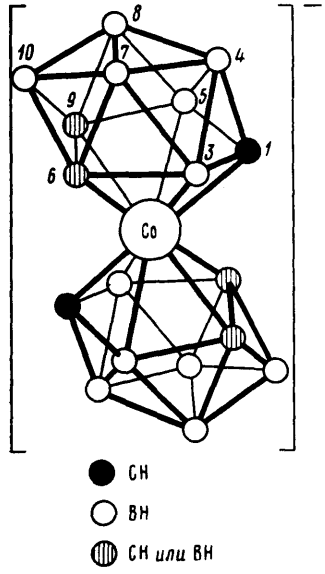



**Figure 4.** The structure of the $[Co(B_7C_2H_9)_2]^-$ ion[16].

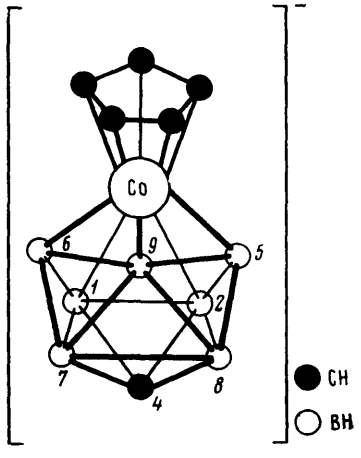



**Figure 5.** The structure of the $[CpCoB_7CH_8]^-$ ion[50].

The structure of 2,9,1,10-($\eta^5$-CpCo)$_2B_6C_2H_8$ is a distorted square antiprism (Fig. 8), while the 2,3,1,7-($\eta^5$-CpCo)$_2B_8C_2H_{10}$ molecule is a distorted icosahedron (Fig. 9). In both polyhedra the cobalt atoms occupy neighbouring vertices and the Co–Co bond length is 2.489 Å [24,52] and 2.389 Å [56] respectively.

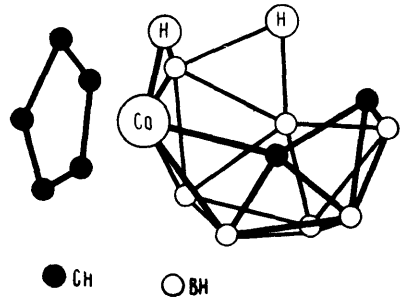



**Figure 6.** The structure of $CpCoB_7C_2H_{11}$.[53]

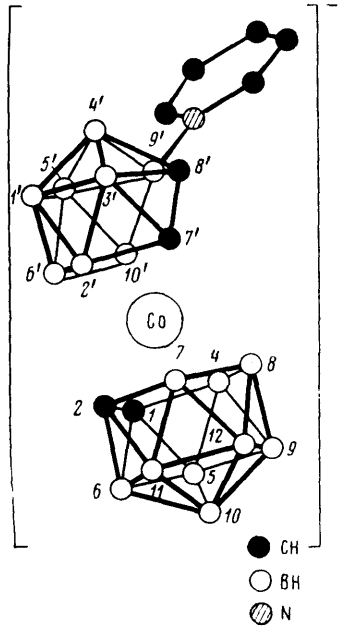



**Figure 7.** The structure of $[B_9C_2H_{11}Co(B_8C_2H_{10}C_5H_5N)]^-$.[54,55] (The bridging hydrogen atom is not represented.)

The carbaborane ligands in the complex [($\eta^5$-Cp)$Co_2$.$(B_8C_2H_{10})_2$]$^-$ are non-equivalent and there is no Co–Co bond (Fig. 10). One of the carbaborane ligands is bidentate[44].

Figs. 11 [57,58] and 12 [58,59] illustrate di- and tri-cobalt complexes of carbaboranes, which are derived from the bidentate dicarbacanastide anion $(B_8C_2H_{10})^{4-}$. The Fe–Co bond is present in the ($\eta^5$-Cp)$CoFe(Me_4B_8C_4H_8)$ complex. The molecule has the form of two pentagonal bipyramids joined by the common vertex, which is occupied by the iron atom. The B–H fragment is the vertex of two trigonal pyramids, whose bases consit of the trigonal planes of the two pentagonal

bipyramids. The system is interesting because it contains two electrons less than would be expected according to the number of vertices in the polyhedron[60,63].

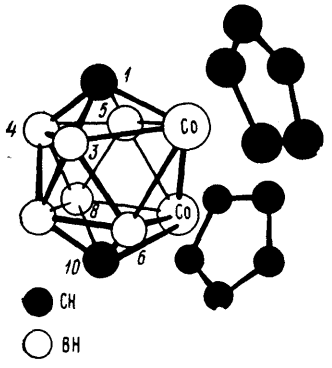



**Figure 8.** The structure of $(CpCo)_2B_6C_2H_8$.[24,52]

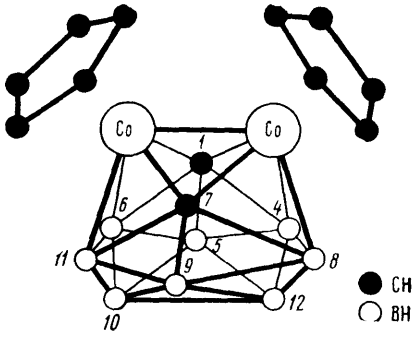



**Figure 9.** The structure of $(CpCo)_2B_8C_2H_{10}$.[56]

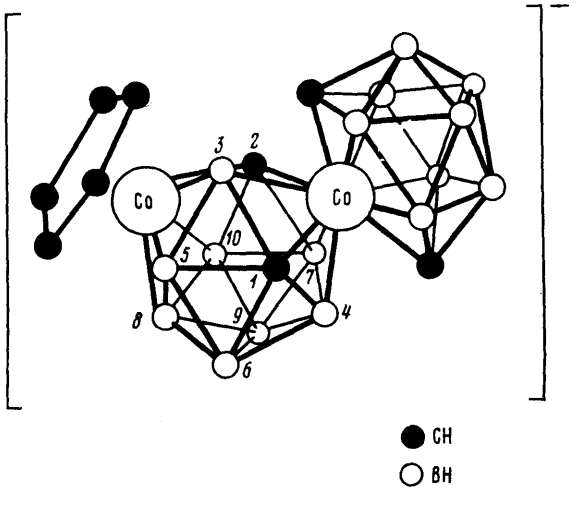



**Figure 10.** The structure of the $(CpCoB_8C_2H_{10}CoB_8C_2H_{10})^-$ ion[44].

## III. SYNTHESIS OF COBALT COMPLEXES OF CARBABORANES

The existing methods for the synthesis of cobalt complexes of carbaboranes can be largely divided into three groups. These include in the first place a series of methods based on the combination of the products of the partial degradation of carbaboranes and (or) their cobalt complexes. The "direct" synthesis, where the starting materials are *nido*- and *arachno*-carbaboranes and cobalt complexes of carbaboranes[20,61,62,64], as well as the polyhedral contraction method, based on the use of cobalt complexes of carbaboranes, should be assigned to this series. Next we may note the polyhedral expansion reaction which includes the reduction of polyhedral *closo*-carbaboranes and (or) cobalt complexes of carbaboranes by sodionaphthalene with subsequent reduction of the resulting anions by $CoCl_2$ and CpNa. These reactions lead to the formation of cobalt complexes of carbaboranes[4,52,65,66] and (or) di- and tri-cobalt carbaborane complexes[67–70] respectively, the new polyhedron containing one vertex more than the initial polyhedron. The third method involves the "direct" synthesis of cobalt complexes of carbaboranes from carbaboranes in the gas phase. We shall examine each method in detail.

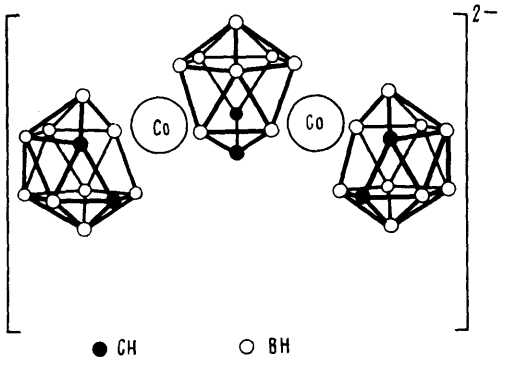



**Figure 11.** The structure of the $(B_9C_2H_{11}CoB_8C_2H_{10}CoB_9C_2H_{11})^{2-}$ ion[57].

### 1. The "Direct" Synthesis of Polyhedral Cobalt Complexes of *closo*-Carbaboranes from *nido*- and *arachno*-Carbaboranes

The method can be represented by the following general sequence of reactions:

$$B_{10}C_2H_{12-n}R_n \xrightarrow{Nu} (B_9C_2H_{12-n}R_n)^- \quad , \qquad (1)$$

$$(B_9C_2H_{12-n}R_n)^- \underset{H^+}{\overset{Nu'}{\rightleftarrows}} (B_9C_2H_{11-n}R_n)^{2-} \quad , \qquad (2)$$

$$(B_9C_2H_{11-n}R_n)^{2-} + Co^{2+} \rightarrow [(B_9C_2H_{11-n}R_n)_2Co]^- \quad . \qquad (3)$$

Attack by strong nucleophiles (Nu are alkali metal alkoxides[71,72], ammonia[73], dialkylamines[73], trialkylamines[74], piperidines[75–78], and hydrazines[79–83]) on the electropositive boron atom[38,84,85] leads to the formation of an anion with an open pentagonal surface over which the hydrogen atom is located. Studies of $^{11}B$ and $^{13}C$ NMR spectra of the isomers of the dicarba-*nido*-dodecahydroundecaborate(1-) anion showed that the bond between the "extra" hydrogen atom and

the boron atoms is of the bridge type. In the case of $(1,2\text{-}B_9C_2H_{12})^-$ it can be regarded as a three-centre bridge bond or as the product of the dynamic process $B_{(8)}\text{–}H\text{–}B_{(4)} \rightleftharpoons B_{(8)}\text{–}H\text{–}B_{(7)}$. The existence of the $B_{(8)}\text{–}H\text{–}B_{(4)}$ bridge has been postulated in the isomer $(1,7\text{-}B_9C_2H_{12})$.[86] Being an acid ($pK_a = 21.3$,[87,88] R = H), the anion $(B_9C_2H_{12-n}R_n)^-$ readily reacts with nucleophiles (Nu′ = Na,[13] NaH,[13,89] or n-BuLi [90]) with formation of the dianion $(B_9C_2H_{11-n}R_n)^{2-}$. In an aqueous medium NaOH is used as the nucleophile[20,91]. The coordination of the dicarbollide dianions to cobalt ions leads to the formation of the symmetrical polyhedron $[(B_9C_2H_{11-n}R_n)_2Co]^-$, which is an isoelectronic analogue of the cobaltocenium cation. In the presence of the Cp anion, the neutral complex CpCo.$B_9C_2H_{11-n}R_n$ is formed. $[3,1,2\text{-}B_9C_2H_{11}Co(CO)_2]^-$, an analogue of the corresponding Cp derivative of cobalt, has been obtained by treating $Co_2(CO)_8$ with the dicarbollide dianion $(B_9C_2H_{11})^{2-}$.[92]

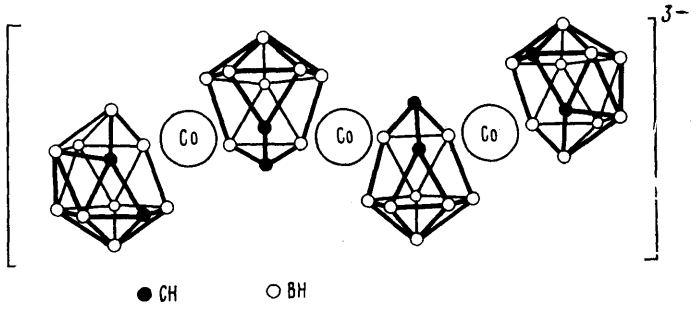



**Figure 12.** The structure of the $[(B_9C_2H_{11}CoB_8C_2H_{10})_2Co]^{3-}$ ion[59].

Table 1 presents the carbollyl and dicarbollyl sandwich π-complexes of cobalt obtained by the "direct" method. Columns 4 and 5 list respectively the initial carbaborane and the nucleophile (Nu) acting on the former. Next, Table 1 lists the anion formed or its salt (column 6), the reagent reacting with it (column 7), and the polyanion or its salt (column 8) produced by this interaction. Column 9 lists the cobalt compounds reacting with an anion or polyanion to form a π-complex.

The choice of the nucleophile for the first two stages depends on the nature of the carbaborane and the strength of the R–carbaborane bond[38]. The synthesis is carried out in aqueous and alcoholic media or in an absolute complex-forming solvent [tetrahydrofuran (THF), ether, and dimethoxyethane (DME)][20].

The "direct" synthesis under consideration has acquired particular importance when its single-stage version was developed: the anion $(B_9C_2H_{12})^-$ (obtained *in situ* by the alkaline methanolysis of the *o*-carbaborane $B_{10}C_2H_{12}$) $CoCl_2.6H_2O$, and $C_5H_6$ were added in the presence of an excess of KOH.[64] The yield of $(\eta^5\text{-Cp})CoB_9C_2H_{11}$ was 72%. The authors note[64] that the optimum yield of the asymmetric complex is attained when methanol is used as the solvent. $(\eta^5\text{-Cp})Co.(2,3\text{-}B_8C_2H_{10})$ was obtained similarly[64].

The method of synthesis of the bis(dicarbazapyl)cobaltate ion $[(B_7C_2H_9)_2Co]^-$ [2,2′-*commo*-bisnonahydridodicarba-2-cobalta-*closo*-decaborate (Ed.of Translation)] differs somewhat from that described above[16,61,62]. The initial compound is also a *nido*-carbaborane (Fig.13), which is converted under the influence of sodium hydride into the dianion $(1,3\text{-}B_7C_2H_{11})^{2-}$ (Fig.14). Next, the anion $(1,3\text{-}B_7C_2H_{11})^{2-}$ is made to react with anhydrous $CoCl_2$, which immediately leads to the formation of the polyhedral *closo*-complex $[(B_7C_2H_9)_2Co]^-$. Two moles of hydrogen are evolved in the reaction. The hydrogen is probably formed as a result of the elimination of two bridging hydrogen atoms from the *nido*-carbaborane anion (Fig.14). The structure of the bis(dicarbazapyl)cobaltate anion[16] is illustrated in Fig.4.

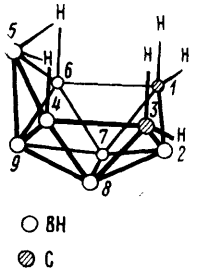



**Figure 13.** The structure of 1,3-dicarba-*nido*-nonaborane-(13).[38]

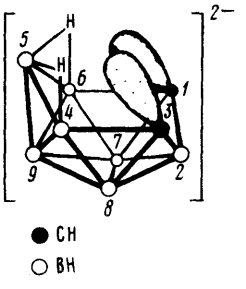



**Figure 14.** The postulated structure of the 1,3-dicarba-*nido*-undecahydroborate(2-) ion.

## 2. The "Direct" Synthesis of Polyhedral Dicobalt Complexes of Carbaboranes from Cobalt Complexes of Carbaboranes

It had been established previously that the "direct" synthesis of cobalt complexes of carbaboranes is accompanied in many instances by the formation of di- and tri-cobalt complexes of carbaboranes[58,64,109,110]. The alkaline degradation of $1,2\text{-}B_{10}C_2H_{12}$ led to the isolation of polyhedral cobalt complexes—derivatives of the bifunctional ligand $(B_8C_2H_{10})^{4-}$.[58,109]. The structures of the resulting bimetallic complex $(1,2\text{-}B_9C_2H_{11}\text{-}3,3'\text{-Co-}1',2'\text{-}B_8C_2H_{10}\text{-}6',3''\text{-Co-}1'',2''\text{-}B_9C_2H_{11})^{2-}$ (Fig.11) and the trimetallic complex $\{[(3,1,2\text{-}B_9C_2H_{11})Co.(3,6,1,2\text{-}B_8C_2H_{10})]_2Co\}^{3-}$ (Fig.12) were established by X-ray diffraction[57,59]. It has been suggested[58] that the formation

**Table 1.** Cobalt complexes of carbaboranes obtained by the "direct"method and the reagents used in the synthesis.

| | Compound | T.p. | Yield, % | Initial carbaborane | Nucleophile | Anion or its salt | Reagent | Polyanion or its salt | Cobalt cpd. | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $NMe_4[3,1,2\text{-}B_9C_2H_{11})_2Co]$ | — | 86 | $1.2\text{-}B_{10}C_2H_{12}$ | MeOH, MeOK | $HNaMe_3(1.2\text{-}B_9C_2H_{12})$ | NaOH, $H_2O$ | $(1.2\text{-}B_9C_2H_{11})^{2-}$ | $CoCl_2$ | 91 |
| 2 | $Cs[3,1,2\text{-}B_9C_2H_{11})_2Co]$ | >300 | 72 | $B_{10}C_2H_{12}$ | MeOH, MeOK | $HNMe_3(1.2\text{-}B_9C_2H_{12})$ | Na or NaH | $Na_2(3,1,2\text{-}B_9C_2H_{11})$ | $CoCl_2$ | 14,20 |
| 3 | $Cs[(3,1,2\text{-}B_9C_2H_{11})_2Co]$ | — | 79 | — | — | $HNMe_3(1.2\text{-}B_9C_2H_{12})$ | 40% NaOH in water | $(3,1,2\text{-}B_9C_2H_{11})^{2-}$ | $CoCl_2\times\times 6H_2O$ | 20 |
| 4 | $Cs[(3,1,7\text{-}B_9C_2H_{11})_2Co]$ | >350 | 80 | — | — | $HNMe_3(1.7\text{-}B_9C_2H_{12})$ | NaH | $Na_2(1.7\text{-}B_9C_2H_{11})$ | $CoCl_2$ | 20 |
| 5 | $Cs[(3,1,7\text{-}B_9C_2H_{11})_2Co]$ | — | 90 | — | — | $HNMe_3(1.7\text{-}B_9C_2H_{12})$ | 50% NaOH in water | $(3,1,7\text{-}B_9C_2H_{11})^{2-}$ | $CoCl_2\times\times 6H_2O$ | 20 |
| 6 | $NMe_4[(3,1,2\text{-}PhB_9C_2H_{10})_2Co]$ | 290—293 | 70 | $1.2\text{-}PhB_{10}C_2H_{11}$ | MeOH, MeOK | $HNMe_3(3,1,2\text{-}PhB_9C_2H_{11})$ | NaH | $Na_2(1.2\text{-}PhB_9C_2H_{10})$ | $CoCl_2$ | 14,20 |
| 7 | $NMe_4[(3,1,2\text{-}6\text{-}PhB_9C_2H_{10})_2Co]$ | 275—277 | 62 | $1.2\text{-}3\text{-}PhB_{10}C_2H_{11}$ | EtOH, KOH | $HNMe_3[(Ph)B_9C_2H_{11}]$ | NaH | $(1.2\text{-}6\text{-}PhB_9C_2H_{10})^{2-}$ | $CoCl_2$ | 93 |
| 8 | $NMe_4[(3,1,2\text{-}Me_2B_9C_2H_9)_2Co]$ | 273—275 | 63 | $Me_2B_{10}C_2H_{10}$ | MeOH, MeOK | $NHMe_3(1.2\text{-}Me_2B_9C_2H_{10})$ | Na or NaH | $Na_2(1.2\text{-}Me_2B_9C_2H_9)$ | $CoCl_2$ | 14,20 |
| 9 | $NMe_4[(3,1,2\text{-}\mu\text{-}1,2\text{-}(CH_2)_3B_9C_2H_9)_2Co]$ | — | 46 | $(CH_2)_3B_{10}C_2H_{10}$ | EtOH, KOH | $K[(CH_2)_3B_9C_2H_{10}]$ | n-BuLi | — | $CoCl_2$ | 94 |
| 10 | $NMe_4[(3,1,2\text{-}1,2\text{-}(CH=\!=CH_2)_2B_9C_2H_9)_2Co]$ | 273 | 51 | $1.2\text{-}1.2\text{-}(CH=CH_2)_2B_{10}C_2H_{10}$ | EtOH, KOH | $NHMe_3\text{-}1.2\text{-}1.2(CH=\!=CH_2)_2B_9C_2H_{10})$ | NaH | $[1.2\text{-}1.2\text{-}(CH=CH_2)_2B_9C_2H_9]^{2-}$ | $CoCl_2$ | 30 |
| 11 | $AsPh_4[(3,1,2\text{-}1,2\text{-}(3'\text{-cyclo-}C_3H_4)B_9C_2H_9)_2Co]$ | 203—204 | 53 | $1.2\text{-}1.2\text{-}(3'\text{-cyclo-}C_3H_4)B_{10}C_2H_{10}$ | EtOH, KOH | $HNMe_3[1,2\text{-}1,2\text{-}(3'\text{-cyclo-}C_3H_4)B_9C_2H_{10}]$ | NaOH | $[1,2\text{-}1,2\text{-}(3'\text{-cyclo-}C_3H_4)B_9C_2H_9]^{2-}$ | $CoCl_2$ | 30 |
| 12 | $NMe_4[3,1,2\text{-}1,2\text{-}(1,4\text{-dihydro-benzo})B_9C_2H_9]_2Co$ | 125 | 30 | $1,2\text{-}1,2\text{-}(1,4\text{-dihydro-benzo})B_{10}C_2H_{10}$ | KOH | $HNMe_3[1,2\text{-}1,2\text{-}(1,4\text{-dihydrobenzo})B_9C_2H_{10}]$ | NaH | $Na_2[1,2\text{-}1,2\text{-}(1,4\text{-dihydro-benzo})B_9C_2H_9]$ | $CoCl_2$ | 95 |
| 13 | $NMe_4[(3,1,2\text{-}1,2(benzo)B_9C_2H_9)_2Co]$ | >300 | 50 | — | — | $[1,2\text{-}1,2(benzo)B_9C_2H_{10}]^-$ | NaH | $[3,1,2\text{-}1,2\text{-}(benzo)B_9C_2H_9]^{2-}$ | $CoCl_2$ | 95 |
| 14 | $B_9C_2H_{11}CoC_5H_5$ | 247—248 | 72 | $B_{10}C_2H_{12}$ | MeOH, | $(B_9C_2H_{12})^-$ | Na or NaH | $(B_9C_2H_{11})^{2-}$ | $CoCl_2$ | 14 |
| 15 | $3,1,2\text{-}B_9C_2H_{11}CoC_5H_5$ | 246—248 | 15 | — | MeOK | $HNMe_3(3,1,2\text{-}B_9C_2H_{12})$ | NaH,Na | $Na_2(3,1,2\text{-}B_9C_2H_{11})$ | $CoCl_2$ | 20 |
| 16 | $[3,1,2\text{-}1\text{-}(CH_2OH)B_9C_2H_{10}]CoC_5H_5$ | 208—209 | 58 | — | — | $K[(CH_2OH)B_9C_2H_{11}]$ | KOH, | *in situ* | $CoCl_2$ | 46 |
| 17 | $[3,1,2\text{-}1\text{-}(CH_2OH)B_9C_2H_{10}]CoC_5H_5$ | 208—210 | 13 | — | — | $K[(CH_2OH)B_9C_2H_{11}]$ | EtOH | $Tl_2[(CH_2OH)B_9C_2H_{10}]$ | $CoCl_2$ | 46 |
| 18 | $[3,1,2\text{-}1\text{-}(CH_2CN)B_9C_2H_{10}]CoC_5H_5$ | 233—235 | 9 | — | — | $K[(CH_2CN)B_9C_2H_{11}]$ | TlOH | $Tl_2[(CH_2CN)B_9C_2H_{10}]$ | $CoCl_2$ | 46 |
| 19 | $[3,1,2\text{-}6\text{-}(CH_2=\!=CH)B_9C_2H_{10}]CoC_5H_5$ | 191—192 | 60 | $3\text{-}CH_2=CHB_{10}C_2H_{11}$ | $C_5H_{10}NH$ | — | KOH, MeOH | $K(6\text{-}CH_2=CHB_9C_2H_{10})$ | $CoCl_2$ | 96 |
| 20 | $(3,1,2\text{-}6\text{-}NH_2B_9C_2H_{10})CoC_5H_5$ | 245—246 | 80 | $3\ NH_2B_{10}C_2H_{11}$ | $C_5H_{10}NH$ | — | KOH, MeOH | $K(6\text{-}NH_2B_9C_2H_{10})$ | $CoCl_2$ | 96 |
| 21 | $(3,1,2\text{-}9\text{-}ClB_9C_2H_{10})CoC_5H_5$ | 193—194 | 65 | $9\text{-}ClB_{10}C_2H_{11}$ | KOH, EtOH | — | KOH, MeOH | $K(9\text{-}ClB_9C_2H_{10})$ | $CoCl_2$ | 96 |
| 22 | $(3,1,2\text{-}9\text{-}IB_9C_2H_{10})CoC_5H_5$ | 191—192 | 70 | — | — | — | KOH, MeOH | $K(9\text{-}IB_9C_2H_{10})$ | $CoCl_2$ | 96 |
| 23 | $[3,1,2\text{-}1\text{-}Me\text{-}2\text{-}(COOMe)B_9C_2H_9]CoC_5H_5$ | 219—220 | 30 | — | — | $K[(Me)(COOMe)B_9C_2H_{10}]$ | TlOH | $Tl[(Me)(COOMe)B_9C_2H_9]$ | $CoCl_2$ | 46 |
| 24 | $[3,1,2\text{-}1\text{-}Me\text{-}2\text{-}(CF=\!=CFCF_3)B_9C_2H_9]CoC_5H_5$ | 146.5—148.5 | 3.9 | — | — | $K[(Me)(CF=CFCF_3)B_9C_2H_{10}]$ | TlOH | $Tl_2[(Me)(CF=\!=CFCF_3)B_9C_2H_9]$ | $CoCl_2$ | 46 |
| 25 | $NMe_4[3,1,2\text{-}B_9C_2H_{11}Co(CO)_2]$ | — | 17.6 | — | — | $HNMe_3(3,1,2\text{-}B_9C_2H_{12})$ | NaH | — | $Co_2(CO)_8$ | 92 |
| 26 | $NMe_4[(2,6,7\text{-}B_7C_2H_9)_2Co]$ | 235 | 64.5 | $B_7C_2H_{13}$ | NaH | $Na_2(1,3\text{-}B_7C_2H_{11})$ | — | — | $CoCl_2$ | 61,62 |
| 27 | $NMe_4[(2,1,6\text{-}B_7C_2H_9)_2Co]$ | 240 | 53 | $B_7C_2H_{13}$ | NaH | $Na_2(1.3\text{-}B_7C_2H_{11})$ | — | — | $CoCl_2$ | 61,62 |
| 28 | $(2,1,6\text{-}B_7C_2H_9)CoC_5H_5$ | 158—159 | 36 | $B_7C_2H_{13}$ | NaH | $Na_2(1.3\text{-}B_7C_2H_{11})$ | — | — | $CoCl_2$ | 61,62 |
| 29 | $[(2,3\text{-}Me_2B_4C_2H_4)_2CoH]$ * | — | 34 | $Me_2B_4C_2H_6$ | NaH | $Na(2.3\text{-}Me_2B_4C_2H_5)$ | — | — | $CoCl_2$ | 97,98 |
| 30 | $(NMe_4)_3[(B_{10}H_{10}CH)_2Co]$ | — | — | $B_{10}H_{12}CNMe_3$ | Na | $HNMe_3(B_{10}H_{12}CH)$ | n-BuLi | — | $CoCl_2$ | 99,101 |
| 31 | $Cs_3\cdot H_2O[(B_{10}H_{10}CH)_2Co]$ | — | 60 | $B_{10}H_{12}CNMe_3$ | Na | $HNMe_3(B_{10}H_{12}CH)$ | 50% NaOH in water | — | $CoCl_2\times\times 6H_2O$ | 99,101 |
| 32 | $(NMe_4)_3[(B_{10}H_{10}CH)_2Co]$ | — | — | $B_{10}H_{12}CNMe_3$ | Na | — | — | $Na_3(B_{10}H_{10}CH)$ | $CoCl_2$ | 100 |
| 33 | $(NMe_4)_3[(B_{10}H_{10}CNH_2Et)_2Co]$ | — | — | $B_{10}H_{12}CNH_2Et$ | base in water | — | — | — | $CoCl_2\times\times 6H_2O$ | 100 |
| 34 | $(NMe_4)_2[(B_{10}H_{10}CNH_2)Co(B_{10}H_{10}CNH_3)]$ | — | — | $B_{10}H_{12}CNH_3$ | 50% NaOH in water | — | — | — | $CoCl_2\times\times 6H_2O$ | 99,100 |
| 35 | $NMe_4[(7\text{-}B_{10}H_{10}CH)CoC_5H_5]$ | >300 | 85 | — | — | $Cs(B_{10}H_{10}CH_3)$ | KOH, EtOH | — | $CoCl_2$ | 102 |
| 36 | $B_9H_9CHCoC_5H_5$ | — | 55 | — | — | $NMe_4(6\text{-}B_9CH_{12})$ | KOH, EtOH | $(B_9CH_{11})^{2-}$ | $CoCl_2\times\times 6H_2O$ | 103 |
| 37 | $NMe_4[(1,2\text{-}B_9H_9CHP)_2Co]$ | — | 13 | — | — | $C_5H_{10}NH_2(7,8\text{-}B_9H_{10}CHP)$ | $NEt_3$ | — | $CoCl_2$ | 104 |
| 38 | $NMe_4[(3,1,7\text{-}B_9H_9CHP)_2Co]$ | — | — | $1,7\text{-}B_{10}H_{10}CHP$ | $C_5H_{10}NH$ | $C_5H_{10}NH_2(1.7\text{-}B_9H_{10}CHP)$ | NaH | — | $CoCl_2$ | 105 |
| 39 | $NMe_4[3,1,7\text{-}B_9H_9CHP)_2Co]$ | — | 77 | — | — | $HNMe_3(1,7\text{-}B_9H_{10}CHP)$ | $NMe_3$ | — | $CoCl_2$ | 104 |
| 40 | $(1,2\text{-}B_9H_9CHPMe)_2Co$ | 276—278 | 29 | $7,8\text{-}B_9H_{10}CHPMe$ | $NEt_3$ | — | — | — | $CoCl_2$ | 104, 105 |
| 41 | $(1,7\text{-}B_9H_9CHPMe)_2Co$ ** | 278—279 | 30 | $7,9\text{-}B_9H_{10}CHPMe$ | NaH | — | — | — | $CoCl_2$ | 104, 105 |
| 42 | $(1,7\text{-}B_9H_9CHPMe)_2Co$ ** | 232—234 | 29 | $7,9\text{-}B_9H_{10}CHPMe$ | NaH | — | — | — | $CoCl_2$ | 104, 105 |
| 43 | $(7,8\text{-}B_9H_9CHAs)CoC_5H_5$ | 250—251 | — | $1,2\text{-}B_{10}H_{10}CHAs$ | $C_5H_{10}NH_2$ | $C_5H_{10}NH_2(7,8\text{-}B_9H_{10}CHAs)$ | $NEt_3$ | — | $CoCl_2$ | 106 |
| 44 | $Cs[(B_{10}H_{10}S)_2Co]$ | — | — | $B_{10}H_{12}S$ | n-BuLi | — | — | — | $CoCl_2$ | 107, 108 |
| 45 | $Cs[(B_{10}H_{10}S)_2Co]$ | — | — | $B_{10}H_{12}S$ | 50% NaOH in water | — | — | — | $CoCl_2\times\times 6H_2O$ | 107, 108 |
| 46 | $[Co(C_5H_5)_2][(B_{10}H_{10}S)_2Co]$ | 287—287.5 | — | $B_{10}H_{12}S$ | n-BuLi | — | — | — | $CoCl_2$ | 107 |
| 47 | $(B_{10}H_{10}S)CoC_5H_5$ | 267.6—268.5 | — | $B_{10}H_{12}S$ | n-BuLi | — | — | — | $CoCl_2$ | 107 |
| 48 | $(B_{10}H_{10}S)Co(PEt_3)_2$ | — | — | $B_{10}H_{12}S$ | n-BuLi | — | — | — | $CoCl_2\times(PEt_3)_2$ | 107 |

*The carbaborane $Me_4B_8C_4H_8$ is also formed as a side product.
**Optically active compound.

of these polyhedral complexes is a result of the partial dehydration of $[(B_9C_2H_{11})_2Co]^-$, formed during the reaction, which gives rise to $[(B_9C_2H_{11})Co(B_8C_2H_{10})]^{3-}$. The interaction of the latter with $Co^{2+}$ and $(B_9C_2H_{11})^{2-}$ results in the

formation of a bimetallic complex, while the reaction of these two anions with $Co^{2+}$ leads to the formation of a trimetallic complex.

Probably the same principle underlies the formation of $3,6,1,2$-$(\eta^5$-$CpCo)_2B_6C_2H_9CH_2OH$ in the alkaline cleavage and 1-hydroxymethyl-*o*-carbaborane $B_{10}C_2H_{11}CH_2OH$ by treatment with $OH^-$ in absolute alcohol and after subsequent addition of $C_5H_6$ and $CoCl_2$ in the presence of an excess of KOH; the compound was obtained in 73% yield[111].

Alkaline alcoholysis of cobalt complexes of carbaboranes with subsequent interaction of the resulting anions with $M^{2+}$ ($M = Co$ or Fe) and $C_5H_6$ is used nowadays as a preparative method for the synthesis of di- and tri-cobalt complexes of carbaboranes[64,70,112].

The reaction of $4,1,8$-$(\eta^5$-$Cp)CoB_{10}C_2H_{12}$ with KOH in EtOH and then with $CoCl_2$ and $C_5H_6$ yielded $4,5,1,8$-$(\eta^5$-$CpCo)_2B_9C_2H_{11}$. The corresponding dimethyl derivative was obtained analogously from $4,1,8$-$(\eta^5$-$Cp)Co(B_{10}C_2H_{10}$-$1,8$-$Me_2)$. The compounds were isolated in 43–58% yield[112]. The same method makes it possible to obtain bimetallic carbaborane heterocomplexes by carrying out the reaction in the presence of $FeCl_2$. Thus, $4,5,1,8$-$(\eta^5$-$Cp)_2$-4-Co-5-Fe-$B_9C_2H_{11}$ and its dimethyl derivative were isolated and characterised[112]. Furthermore, $CpCo(B_9C_2H_{11})FeCp$ was obtained from CpCo.$(6,7$-$B_{10}C_2H_{12})$ in EtOH by treatment with KOH and then with an excess of $FeCl_2$ and $C_5H_6$.[113] The tricobalt carbaborane complex $\{[(\eta^5$-$Cp)CoB_9C_2H_{11}]_2Co\}^-$ was isolated by treating $4,1,8$-$(\eta^5$-$Cp)CoB_{10}C_2H_{12}$ in ethanol with KOH and by subsequent reaction with $CoCl_2$ in the absence of $C_5H_6$.[112] The cobalt carbaborane complex $CpCoB_9C_2H_{11}$ is the starting material for the synthesis of $3,6,1,2$-$(\eta^5$-$CpCo)_2B_8C_2H_{10}$. The reaction is carried out in MeOH and the yield is 57%.[64] The synthesis of $[2,11,1$-$(\eta^5$-$CpCo)_2B_9C_2H_{10}]$ by the reaction of $Cp_2Co$ with $(1$-$B_9CH_{10})^-$ in the presence of sodium amalgam is of interest[114].

The presence of bridging hydrogen atoms with acid properties in the *nido*-complex $(\eta^5$-$Cp)CoB_3C_2H_7$ is responsible for its reaction with NaH. Deprotonation gives rise to the anion $(CpCoB_3C_2H_6)^-$, which interacts with $CoCl_2$ and $RC_5H_4Na$ ($R = H$,[62,102] Me, Et, or $SiMe_3$ [116]) in THF, which gives a moderate yield of the "three-layer" sandwich complex $1$-$(\eta^5$-$Cp)$-7-$(\eta^5$-$C_5H_4R)$-1-Co-7-Co-$2,3$-$B_3C_2H_5$.[70,115,116] The *nido,closo*-complex $[(Me_2B_3C_2H_5)Co(Me_2B_4C_2H_4)]^-$ reacts with $CoCl_2$ and NaCp to give a low yield of the neutral complex $(\eta^5$-$Cp)Co(Me_2B_3C_2H_5)CoH(Me_2B_3C_2H_5)$.[98]

In conclusion we may note that the above method is synthetically simple, can be used on a preparative scale, and as a rule does not give rise to a complex mixture of reaction products. Its disadvantage is a fairly limited set of initial carbaboranes employed.

### 3. The Polyhedral Contraction Method

The method includes a stage with partial degradation of the cobalt complex of the carbaborane (removal of the $BH^{2+}$ species) and the subsequent oxidation stage. Cobalt complexes of carbaboranes whose molecules contain one vertex more than the initial cobalt carbaborane complex are obtained by this method[110,117,118]. In a general form the reaction is

$$(LCoB_nC_2H_{n+2})^z \xrightarrow[2)\ -2e]{1)\ -BH^{2+}} (LCoB_{n-1}C_2H_{n+1})^z,$$

$$L=Cp,\ z=0;\ L=B_nC_2H_{n+2},\ z=-1.$$

The nucleophiles employed are KOH and EtOH and the oxidants are $H_2O_2$ and $FeCl_3$. It has been suggested that the polyhedral contraction reaction proceeds via the intermediate formation of *nido*-complexes[35,53]. Indeed, when the *closo*-complex $[3,3$-$Co(1,2$-$B_9C_2H_{11})_2]^-$ is treated with KOH in an aqueous medium, the product is the *nido*-complex $(1,2$-$B_9C_2H_{11}$-$3,9'$-Co-$7',8'$-$B_8C_2H_{11})^-$ in 63% yield. The oxidation of the latter with $H_2O_2$ in an alkaline medium gives the *closo*-complex $(1,2$-$B_9C_2H_{11}$-$3,1'$-Co-$2',4'$-$B_8C_2H_{10})^-$.[35] Furthermore, $CpCoB_8C_2H_{10}$ is converted in the presence of EtOH and $FeCl_3$ into the *nido*-complex $CpCoB_7C_2H_{11}$, which can be dehydrogenated to the *closo*-complex $CpCoB_7C_2H_9$.[53] The study of the intermediates in the polyhedral contraction reaction of $3,1,2$-$(\eta^5$-$Cp)CoB_9C_2H_{11}$ is also consistent with the above hypothesis[35].

The polyhedral contraction of $3,1,2$-$(\eta^5$-$Cp)CoB_9C_2H_{11}$ leads to the formation of the normal reaction product $1,2,4$-$(\eta^5$-$Cp)CoB_8C_2H_{10}$ (63%) and the cobalt carbaborane complex $2,6,7$-$(\eta^5$-$Cp)CoB_7C_2H_9$.[117,118] The initial compound reacts with KOH in an ethylene glycol–ethanol–water mixture and the resulting red solution is then treated with $H_2O_2$. The hypothesis of the $1,2,4$-$(\eta^5$-$Cp)CoB_8C_2H_{10}$ structure is based on $^1H$ and $^{11}B$ NMR data[118] and certain structural analogies[54]. The compound retains the *closo*-geometry of the initial metal carbaborane complex and is its lowest homologue. Under the conditions of the polyhedral contraction reaction, the symmetrical complex $[3,3$-$(1,2$-$B_9C_2H_{11})_2Co]^-$ forms only the lowest homologues $(1,2$-$B_9C_2H_{11}$-$3,1'$-Co-$2',4'$-$B_8C_2H_{10})^-$.[118]

The conversion into the next metal carbaborane complex homologue ($B_7$) is achieved by refluxing $(1,2$-$B_9C_2H_{11}$-$3,1'$-Co-$2',4'$-$B_8C_2H_{10})^-$ in ethanol in the presence of $FeCl_2$.[118] The compound obtained (11% yield) has the structure $(1,2$-$B_9C_2H_{11}$-$3,2'$-Co-$1',6'$-$B_7C_2H_9)^-$. If the polyhedral complex $1,2,4$-$(\eta^5$-$Cp)CoB_8C_2H_{10}$ undergoes the polyhedral contraction reaction, the resulting cobalt carbaborane complex $CpCo.B_7C_2H_{11}$ does not retain the *closo*-geometry of the initial polyhedron[118]. The $^1H$ NMR spectrum of this compound contains two broad signals to a high field of the tetramethylsilane signal, indicating the presence of non-terminal hydrogen atoms[54,119]. It has therefore been suggested that the resulting complex has the *nido*-structure. The reaction led to the isolation also of a small amount (2%) of $6,7$-$(\eta^5$-$Cp).CoB_7C_2H_9$—the usual product of the polyhedral contraction reaction. On treatment of $3,1,7$-$(\eta^5$-$Cp)CoB_9C_2H_{11}$ and $1,2,3$-$(\eta^5$-$Cp)CoB_8C_2H_{10}$ with bases, only cobalt hydroxide is formed[118]. The complex is probably decomposed in this case more rapidly than boron is eliminated from the polyhedron of the cobalt complex of the carbaborane. On treatment of $(\eta^5$-$Cp)CoB_{10}C_2H_{12}$ with an ethanol solution of KOH, the product is (in 60% yield) the polyhedral complex $(\eta^5$-$Cp)Co.(2$-$B_7CH_8)$.[120] If $(\eta^5$-$Cp)CoB_{10}C_2H_{11}Me$ is used as the starting material, then $(\eta^5$-$Cp)Co(2$-$B_7CH_8)$ and the corresponding *C*-methyl derivative are isolated[120,121].

### 4. The Polyhedral Expansion Method

(*a*) *The polyhedral expansion of carbaboranes.* In contrast to the first method ("direct" synthesis), which is based on the use of the initial *nido*- and *arachno*-carbaboranes, the polyhedral expansion reaction is based on the comparatively readily available *closo*-carbaboranes $B_nC_2H_{n+2}$ ($n = 4$–$10$). Like aromatic benzenoid systems, *closo*-carbaboranes readily combine with two electrons, using for this purpose the nonbonding and the lowest-lying antibonding molecular orbitals. This was demonstrated first for $1,2$-$B_{10}C_2H_{12}$:[122]

$$1,2\text{-}B_{10}C_2H_{12} + 2e \rightarrow (1,2\text{-}B_{10}C_2H_{12})^{2-}.$$

As a result of the Jahn–Teller effect or other distortions, the *closo*-carbaborane struture is opened. The dianion

formed exhibits the properties of a complex-forming ligand capable of reacting with the transition metal[3].

The reduction of the carbaborane 1,7-$B_9C_2H_8$#[38] with sodionaphthalene constituted experimental confirmation of the concept of polyhedral expansion[52,123]:

$$1,7\text{-}B_6C_2H_8 + Na \xrightarrow[THF]{C_{10}H_8} Na_2B_6C_2H_8 \quad .$$

When the reduction product is treated with an excess of sodium cyclopentadienide in the presence of an excess of $CoCl_2$, 1,4,5-($\eta^5$-Cp)$CoB_6C_2H_8$ is formed[52,123]. The compound contains one vertex more than the initial $B_6C_2H_8$ and is a typical product of the polyhedral expansion reaction. Another compound obtained in this reaction was the bimetallic complex 2,9,1,10-($\eta^5$-CpCo)$_2B_6C_2H_8$,[52,123] whose structure was established by X-ray diffraction[52] (see Fig.8). This complex is obtained as a result of the polyhedral expansion reaction of a cobalt carbaborane complex—in the present instance of the 1,4,5-($\eta^5$-Cp)$CoB_6C_2H_8$ formed (for further details, see below). We may add that the polyhedral expansion reaction of 1,7-$B_6C_2H_8$, carried out in the absence of CpNa, gives rise to the symmetrical complex $(Ph_4As)^+$(4,5-$B_6C_2H_8$-1,1'-Co-4',5'-$B_6C_2H_8$)$^-$.[52] The carbaborane 4,5-$B_7C_2H_9$ enters into the polyhedral expansion reaction[52]:

$$4,5\text{-}B_7C_2H_9 + 2e \rightarrow (B_7C_2H_9)^{2-}$$
$$(B_7C_2H_9)^{2-} \xrightarrow{Co^{2+};\ Cp^-} 2,3,10\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9 + 4,6\text{-}(\eta^5\text{-Cp})CoB_6C_2H_8 \quad .$$

Under the conditions of the polyhedral expansion reaction, both isomers (1,6- and 1,10-) of the carbaborane $B_8C_2H_{10}$ [38] give rise to symmetrical and asymmetric polyhedral π-complexes of cobalt[52,65]:

$$1,6\text{-}B_8C_2H_{10} \xrightarrow{2e} (B_8C_2H_{10})^{2-} \xrightarrow{Co^{2+};\ Cp^-} 1,2,3\text{-}(\eta^5\text{-Cp})CoB_8C_2H_{10} +$$
$$+ (CpCo)_2B_8C_2H_{10} + [(B_8C_2H_{10})_2Co]^- + 1,6\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9 +$$
$$+ [\eta\text{-}(\sigma\text{-}B_8C_2H_9)B_8C_2H_9]Co(\eta^5\text{-Cp}) \quad .$$

At room temperature the main reaction product (44%) is 1,2,3-($\eta^5$-Cp)$CoB_8C_2H_{10}$. The reaction of the isomer 1,10-$B_8C_2H_{10}$ is also not unambiguous. Together with 1,2,3-($\eta^5$-Cp)$CoB_8C_2H_{10}$ (44%), a large number of side products were isolated: $CpCoB_7C_2H_9$ (4%), $CpCoB_9C_2H_{11}$ (2%), $(CpCo)_2$.$B_8C_2H_{10}$ (two isomers—1 and 0.2%), and $CpCo(B_8C_2H_9$-$B_8C_2H_9)$ (4%). When the polyhedral expansion reaction of the carbaborane 1,6-$B_8C_2H_{10}$ is carried out at −80 °C, mainly three bimetallic complexes are formed, two of which are isomers of $(CpCo)_2B_8C_2H_{10}$ and the third is $[(\eta^5\text{-Cp})Co_2$.$(B_8C_2H_{10})_2]^-$.[44] The amount of the normal polyhedral expansion reaction product, which is 1,2,3-($\eta^5$-Cp)$CoB_8C_2H_{10}$ is greatly reduced compared with the conditions[52] examined above.

Under the conditions of the polyhedral expansion reaction, the carbaborane 2,3-$B_9C_2H_{11}$ gives rise to the two isomers 2,4- and 2,9-($\eta^5$-Cp)$CoB_9C_2H_{11}$.[52] The reaction products were also found to contain the polyhedral π-complexes 2,3-($\eta^5$-Cp)$CoB_8C_2H_{10}$, 1,6- and 3,10-($\eta^5$-Cp)$CoB_7C_2H_9$, and $(CpCo)_2B_8C_2H_{10}$. It has been suggested[74] that the above compounds are formed as a result of the decomposition of the initial carbaborane 2,3-$B_9C_2H_{11}$. The 13-vertex polyhedra (7,9-$B_{10}C_2H_{12}$-13,13'-Co-7',9'-$B_{10}C_2H_{12}$)$^-$ and 13,7,9-($\eta^5$-Cp).$CoB_{10}C_2H_{12}$ (Fig.15c) have been obtained by the reduction of the carbaborane 1,2-$B_{10}C_2H_{12}$ with sodionaphthalene in THF [122,124] followed by the interaction of the resulting dianion with an excess of CpNa and $CoCl_2$;[125,126] the structure of the second compound was determined by X-ray diffraction[127,128].

The side products of the polyhedral expansion reaction of 1,2-$B_{10}C_2H_{12}$ are[125,126] 7,8-($\eta^5$-Cp)$CoB_9C_2H_{11}$ (1%) and the zwitter-ion ($\eta^5$-$C_2H_5$)Co($\eta^5$-$C_5H_4B_9C_2H_{11}$). The latter compound is a cobaltocenium derivative in which the C-substituted anion $(B_9C_2H_{11})^-$ plays the role of a substituent and an anion simultaneously (Fig.16).[129] The "extra" hydrogen atom in the anion $(1,2\text{-}B_9C_2H_{11})^-$ is located over the pentagonal surface, is linked to all the atoms of the latter, and is displaced closer to the $B_{(8)}$ atom (Fig.16). The distances of the hydrogen atom from each atom in the surface are smaller than the coresponding van der Waals B–H and C–H radii[129].

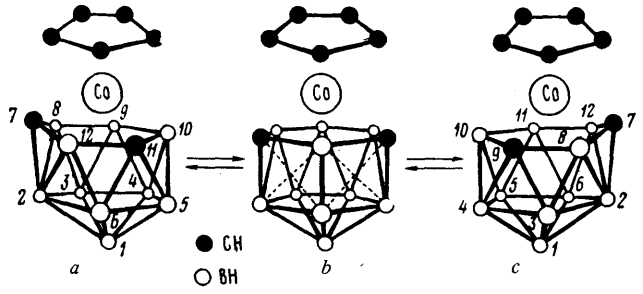



**Figure 15.** The postulated mechanism of the interaction of the 7,9- and 7,11-enantiomers of ($\eta^5$-Cp)$CoB_{10}C_2H_{12}$.

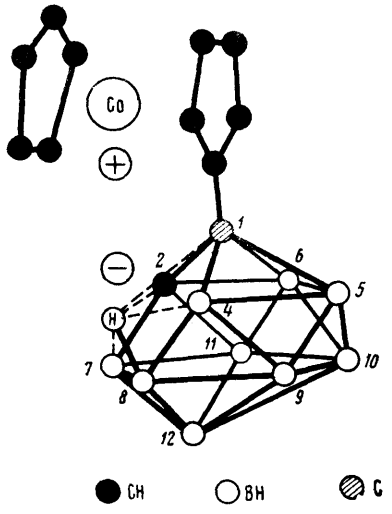



**Figure 16.** The structure of the zwitter-ion ($\eta^5$-Cp)Co($\eta^5$-$C_5H_4B_9C_2H_{11}$) (H is a bridging atom)[129].

The formation of $[(B_{10}H_{10}C_2RR')_2Co]^-$ (R = R' = H or Me; R = H, R' = Me or Ph) from the corresponding dianions $(B_{10}H_{10}C_2RR')^{2-}$ is accompanied by the partial oxidation of the initial dianions to the carbaboranes and of the resulting complexes $[(B_{10}H_{10}C_2RR')_2Co]^-$ to the isomeric $B_{10}$ carbaboranes. The ease of oxidation of the dianions depends on the reduction potential of the carbaborane $B_{10}H_{10}C_2RR'$. The

# In previous reviews[3,4] this carbaborane is represented as the 1,6-isomer, which conflicts with the X-ray diffraction study of the *C,C'*-dimethyl analogue[56].

easier the reduction of the carbaborane, the easier the oxidation of its dianion[130]. Thus the dianion $[B_{10}H_{10}C_2HPh]^{2-}$ has been converted under the conditions into the corresponding monoanion $[(B_{10}H_{10}C_2HPh)_2Co]^-$, whereas in the case of $(B_{10}H_{10}C_2Ph_2)^{2-}$ it was possible to isolate only $B_{10}H_{10}C_2Ph_2$.[130] $E_{1/2}$ is known to be −1.95 and −1.14 V respectively for $B_{10}H_{10}C_2HPh$ and $B_{10}H_{10}C_2Ph_2$.

The use of the lowest carbaboranes, particularly $B_5C_2H_7$, under the conditions of the polyhedral expansion reaction, has led to somewhat unexpected results[66]. The formation of twenty compounds, among which $(\eta^5\text{-Cp})CoB_4C_2H_6$ is present in the greatest amount (20–25%), has been observed. Monocobalt carbaborane complexes $(\eta^5\text{-Cp})CoB_nC_2H_{n+2}$ ($n = 5$, 6) and dicobalt carbaborane complexes $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$ ($n = 4$, 5, 6), as well as the substituted compounds ($\eta^5$-Cp).Co[$\eta^5$-($\sigma$-$B_5C_2H_6$)$B_4C_2H_5$] and ($\eta^5$-Cp)Co[$\eta^5$-($\sigma$-$C_{10}H_7$)$B_4C_2H_5$] have been isolated. The remaining compounds have not been characterised. The product of the polyhedral expansion reaction of 2,4-$B_5C_2H_7$, carried out in the absence of CpNa, is $[Co(2,4\text{-}B_4C_2H_6)_2]^-$ in a very low yield[70].

Under the conditions of the polyhedral expansion reaction, the *nido*-carbaborane 2,3-$B_4C_2H_8$ is largely converted into $(\eta^5\text{-CpCo})_2B_3C_2H_5$ and $(\eta^5\text{-Cp}_6)CoB_3C_2H_5$.[70] The carbaborane 1,6-$B_4C_2H_6$ also does not give rise to the normal polyhedral expansion reaction product and yields 2,4-CpCo.$B_3C_2H_5$CpCoB$_4C_2H_5$-$C_{10}H_7$ and 1,7,2,4-$(CpCo)_2B_3C_2H_5$.[70,115] The latter compound belongs to the new class of "three-layer" sandwich complexes. Under the conditions of the polyhedral expansion reaction, cobalt complexes of carbaboranes have not been obtained at all from the carbaborane 1,5-$B_3C_2H_5$.[70] These findings show that the polyhedral expansion reaction is less typical for the lowest carbaboranes. However, one should note that the change in reaction conditions (time, temperature, etc.) can apparently lead to other results.

(*b*) *The polyhedral expansion reaction of cobalt complexes of carbaboranes.* Like *closo*-carbaboranes, cobalt complexes of carbaboranes are involved in the polyhedral expansion reaction[4]. In a general form, the reaction is as follows:

$$CpCoB_nC_2H_{n+2} \xrightarrow[3)\ [O]]{1)\ 3e;\ 2)\ M'Cl_2;\ CpNa} (Cp)_2CoM'B_nC_2H_{n+2}$$
$$M' = Co \text{ or } Fe.$$

The reduction proceeds formally in two stages: (1) reduction of the metal: Co(III) → Co(II); (2) two-electron reduction of the carbaborane fragment with formation of the anion of the cobalt complex of the *nido*-carbaborane. The subsequent reaction of CpNa with $M'Cl_2$ ($M' = Co$ or Fe) gives a mixture of the di- and tri-cobalt complexes of carbaboranes, which is then oxidised in air. The new compound has one or two vertices more than the initial cobalt carbaborane complex. The reaction time and temperature depend on the initial cobalt carbaborane complex[69].

The first examples of the polyhedral expansion reaction of cobalt carbaborane complexes were examined for the complexes $CpCoB_8C_2H_{10}$ [67] and 2,1,6-$CpCoB_7C_2H_9$.[68] The principal advances in this field have been described by Evans and Hawthorne[69]. Under the conditions of the polyhedral expansion reaction, the complex 2,1,6-$CpCoB_7C_2H_9$ gives rise to a mixture of $(CpCo)_2B_7C_2H_9$ isomers and the trimetallic complex $(CpCo)_3B_7C_2H_9$. The isomers 1,10,2,3-$(CpCo)_2B_7C_2H_9$, 1,8,2,3-$(CpCo)_2B_7C_2H_9$§, and 1,4,2,3-$(CpCo)_2B_7C_2H_9$ were identified by $^1H$ and $^{11}B$ NMR. This reaction is accompanied by the polyhedral rearrangement of the initial 2,1,6-$CpCoB_7C_2H_9$, which leads to 3,2,10-CpCo.$B_7C_2H_9$. In addition, 1,9,4,5-$(CpCo)_2B_5C_2H_7$ was detected in the reaction products[69].

The products of the polyhedral expansion reaction of 1,2,3-$CpCoB_8C_2H_{10}$ are 2,3,1,7-$(CpCo)_2B_8C_2H_{10}$ (Fig. 9), whose structure has been established by X-ray diffraction[56], and $[(2,3\text{-}B_8C_2H_{10})_2Co]^-$. Under these conditions, the isomer 1,2,4-$CpCoB_8C_2H_{10}$ gives rise to three compounds, one of which is 3,4,1,2-$(CpCo)_2B_8C_2H_{10}$.[69]

Together with the normal products of the polyhedral expansion reaction of the complex 3,1,2-$CpCoB_9C_2H_{11}$, which consist of the isomers $(CpCo)_2B_9C_2H_{11}$ and [3,3-Co(1,2-$B_9C_2H_{11})_2]^-$, 2,1,7-$CpCoB_9C_2H_{11}$ was also isolated[69].

The isomers 1,14,2,10- and 1,14,2,9-$(CpCo)_2B_{10}C_2H_{12}$ with a 14-vertex polyhedron were obtained under the conditions of the polyhedral expansion reaction of two $CpCoB_{10}C_2H_{12}$ isomers[43]. The reduction of 2,1,6-$CpCoB_7C_2H_9$ and subsequent treatment with an excess of CpNa and $FeCl_2$ lead to a paramagnetic compound, whose reduction with $NaBH_4$ yielded the diamagnetic complex $[CpCo^{III}(B_7C_2H_9)Fe^{III}Cp]$.[113]

The polyhedral expansion reaction of $[CpCoB_7CH_8]^-$ in the presence of $NiBr_2.2C_2H_4(OMe)_2$ leads to the formation of four $[CpCo^{III}(B_7CH_8)Ni^{IV}Cp]$ isomers[131]. However, the only product of the analogous reaction of 2,1-$CpCoB_{10}CH_{11}$ was the naphthalene complex 2,1-$(\eta^6\text{-}C_{10}H_8)CoB_{10}CH_{11}$.[132]

Thus the polyhedral expansion reaction is applicable mainly to the intermediate and higher homologues of carbaboranes and their cobalt complexes. The method makes it possible to obtain a large series of mono-, di-, and tri-cobalt carbaborane complexes as well as dimetallic heterocomplexes of carbaboranes. The possibility of synthesising polymetallic carbaborane complexes by this method is probably problematical. The method is synthetically simple and the initial compounds are readily available, but it often gives rise to a complex mixture of products.

## 5. The Gas-Phase Synthesis of Cobalt Complexes of Carbaboranes

The direct synthesis of metal complexes of carbaboranes in the gas phase is carried out in a special reactor at an elevated temperature. The initial compounds are the lower carbaborane homologues $B_nC_2H_{n+2}$ ($n = 3$–5) and $CpCo(CO)_2$.[133]

In the presence of $CpCo(CO)_2$ at 230 °C, the carbaborane 1,5-$B_3C_2H_5$ yields $(\eta^5\text{-Cp})CoB_3C_2H_5$ (10%) and two isomers of the dicobalt carbaborane complex: 1,7,2,4- and 1,2,3,5-$(\eta^5\text{-CpCo})_2B_3C_2H_5$. 1,2,4-$(\eta^5\text{-Cp})CoB_4C_2H_6$ (70%) and a small amount (5%) of the eight-vertex polyhedron 3,5,1,7-$(\eta^5\text{-}CpCo)_2B_4C_2H_6$ were obtained from the carbaborane 1,6-$B_4C_2H_6$ at 270–280 °C. In the presence of $CpCo(CO)_2$ at 260 °C, a mixture of products, consisting of the cobalt carbaborane complexes $(\eta^5\text{-Cp})CoB_5C_2H_7$ and $(\eta^5\text{-Cp})CoB_4C_2H_6$, two isomers of the dicobalt carbaborane complex $(\eta^5\text{-CpCo})_2B_5C_2H_7$, and two isomers of the tricobalt carbaborane complex $(\eta^5\text{-CpCo})_3B_5C_2H_7$, was obtained from the carbaborane 2,4-$B_5C_2H_7$. The trimetallic carbaborane complex {($\eta^5$-Cp)Co.(2,3-$Me_2B_4C_2H_4$)[$Fe(CO)_3$]$_2$} is formed when 1,2,3-($\eta^5$-Cp)Co.(2,3-$Me_2B_4C_2H_4$) (structure established by Weiss and Bryan[134]) interacts with an excess of $Fe(CO)_5$ at 125 °C.[135]

Thus the method examined is at present the only preparative procedure for the synthesis of the lowest homologues of cobalt carbaborane complexes. However, under the reaction conditions, the initial carbaborane and its newly formed cobalt complex undergo a polyhedral rearrangement, which leads to a complex mixture of products and hinders their isolation.

§ This is possibly the 1,2,3,8-isomer.

The thermolysis of cobalt complexes of carbaboranes can also be regarded as one of the methods for the synthesis of such complexes. The method is used to synthesise various isomers of cobalt complexes of carbaboranes which cannot be obtained by other methods or for the synthesis of di- and tri-cobalt complexes of carbaboranes from the corresponding monocobalt complexes. The first type of synthesis has already been examined in Section IV. We shall consider separately only the elegant solution of the problem of the synthesis of 1-($\eta^5$-Cp)-7-($\eta^5$-$C_5H_4R$)-1-Co-7-Co-2,4-$B_3C_2H_5$ from 1-($\eta^5$-Cp)-7-($\eta^5$-$C_5H_4R$)-1-Co-7-Co-2,3-$B_3C_2H_5$.[116] Whereas the direct reaction of $[(\eta^5\text{-Cp})CoB_3C_2H_6]^-$ with $CoCl_2$ and $NaC_5H_4R$ can be used to synthesise the 1,7,2,3-isomer, in the case of the 1,7,2,4-isomer the polyhedral rearrangement method is the only possible procedure.

Six isomers of the dimetallic carbaborane complex ($\eta^5$-$CpCo)_2B_8C_2H_{10}$ were obtained on heating ($\eta^5$-Cp)$CoB_8C_2H_{10}$ at 235 °C in hexadecane for 7 h; 2,9,1,12-($\eta^5$-$CpCo)_2B_8C_2H_{10}$, in which the cobalt atoms are located in the *para*-positions of the $Co_2B_8C_2H_{10}$ icosahedron, was isolated from the mixture of isomers[136]. The gas-phase thermolysis of the cobalticenium salt $[(\eta^5\text{-Cp})_2Co]^+[Co(B_8C_2H_{10})_2]^-$ at 525 °C and in hexadecane at 270 °C gives rise to five ($\eta^5$-$CpCo)_2B_8C_2H_{10}$ isomers[136].

In conclusion one should note that the anionic complexes of carbaboranes are usually isolated as ammonium or alkali metal salts. The synthesis of $[(B_{10}H_{10}S)_2Co]^-[(\eta^5\text{-Cp})_2Co]^+$, where the cobalticenium ion plays the role of the cation, has also been described[107].

## IV. THE PROPERTIES OF POLYHEDRAL π-COMPLEXES OF COBALT

### 1. Intramolecular Rearrangements in the π-Complexes

The absence of symmetry elements from the carbaborane ligand leads to the optical isomerism of the polyhedral π-complexes of cobalt. In particular, the complexes $[(B_9H_9CHP.CH_3)_2Co]^-$,[104] 1,2,4-($\eta^5$-Cp)$CoB_8C_2H_{10}$,[118] and 7,9-($\eta^5$-Cp)$CoB_{10}C_2H_{12}$ (Fig.15c)[127] are optically active. The pure enantiomers have not been isolated[104,118,127], but the form of the $^{11}B$ NMR spectrum of $CpCoB_{10}C_2H_{12}$ at −90 °C indicates unambiguously the presence of two asymmetric 7,9- and 7,11-isomers (Figs.15a and 15c).[127,128] Below −30 °C, their interconversions can be observed.

The proposed mechanism of the optical rotation of the enantiomers[126] is illustrated in Fig.15. The phenomenon of the polyhedral rearrangement is well known in the carbaborane chemistry[38]. Cobalt complexes of carbaboranes, whose properties are largely determined by the presence of the carbaborane fragment in the molecule, also undergo a polyhedral rearrangement. However, with increase of the number of CoCp fragments in the molecule of the cobalt carbaborane complex, the properties of the latter begin to differ appreciably from those of the carbaborane analogues (see Section I). Indeed, although the occurrence of the isomerisation reaction 2,3,8,1,6-($\eta^5$-$CpCo)_3B_5C_2H_7$ → 2,3,4,1,10-($\eta^5$$CpCo)_3B_5C_2H_7$ has been established in principle (Fig.17), on heating 2,3,8,1,6-($\eta^5$-$CpCo)_3B_5C_2H_7$ mainly decomposes and gives rise to equimolar amounts of 1,8,5,6- and 1,7,5,6-($\eta^5$-$CpCo)_2B_5C_2H_7$.[23] The polyhedral rearrangement of cobalt complexes of carbaboranes was first observed for $Cs[(B_7C_2H_9)_2Co]$ and its asymmetric derivative $CpCoB_7C_2H_9$.[137] The isomers formed are a result of the migration of the carbon atom via the carbaborane fragment. Subsequently it was shown[25,37] that the migration of both the carbon and the cobalt atoms is possible in the isomerisation of cobalt complexes of carbaboranes.

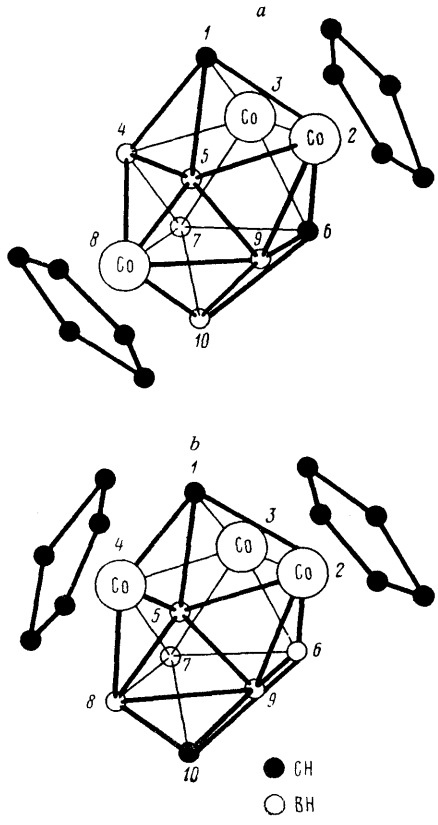



**Figure 17.** The postulated structures of 2,3,8,1,6-($\eta^5$-$CpCo)_3B_5C_2H_7$ (*a*) and 2,3,4,1,10-($\eta^5$-$CpCo)_3B_5C_2H_7$ (*b*) (one of the Cp ligands is not represented).

(*a*) *Polyhedral rearrangement of cobalt complexes of carbaboranes.* The presence of the cobalt atom in the polyhedron of a cobalt carbaborane complex facilitates the polyhedral rearrangement of the latter compared with the carbaborane itself[22]. Among polyhedral π-complexes the crystal of the 12-atom ($\eta^5$-Cp)$CoB_3C_2H_{11}$ polyhedron has the highest energy barrier to the polyhedral rearrangement, which is believed[22] to indicate a high resonance stabilisation of the icosahedron. Non-icosahedral cobalt complexes of carbaboranes of the type ($\eta^5$-Cp)$CoB_nC_2H_{n+2}$ ($n = 6$, 7, 8, and 10) have similar activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$, so that it is believed[22] that the polyhedral rearrangements of these complexes have similar mechanisms.

According to an empirical rule governing the polyhedral rearrangement of non-icosahedral systems of the type ($\eta^5$-Cp)$CoB_nC_2H_{n+2}$ ($n = 6$, 7, 8, and 10),[22] (1) the coordination number of the cobalt atom, which is high in the polyhedron of the cobalt complex of the carbaborane, does not change in the rearrangement, (2) as a result of the rearrangement there is no mutual approach of the carbon atoms

of the polyhedron, (3) the coordination number of the carbon atom decreases in the course of the rearrangement, and (4) the distance between the carbon and cobalt atom increases. In the latter case the postulates indicated in (2) and (3) must hold. With certain limitations, this rule is applicable also to the lowest homologues of cobalt complexes of carbaboranes ($n = 3$, 4, 5) where partes (2) and (3) mainly hold, while part (4) frequently simply cannot be fulfilled[23].

We shall consider specific examples of the isomerisation of cobalt complexes of carbaboranes. The polyhedral rearrangement of the 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ icosahedron[138] and its *C*-alkyl derivatives[139] proceeds in accordance with the empirical rule[22]. In the gas phase (at 400–700 °C) 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ gives rise to six new isomers in 87–93% yields (Figs.1*a*–1*f* for R = H). If 3,1,2-($\eta^5$-Cp)Co(1,2-$Me_2B_9C_2H_9$) is sublimed in a hot tube at 400–500 °C, three isomers are formed (Figs.1*a'*–1*c'* for R = Me).[139] At the same time, the rearrangement of 3,1,2-($\eta^5$-Cp)Co[1,2-$(CH_2)_3B_9C_2H_9$] (Fig.18*a*) at 500 °C led to the isolation of only one isomer (Fig.18*b*) in which both carbon atoms are in the *ortho*-positions[139]. The presence of the trimethylene bridge precludes the second part of the empirical rule.

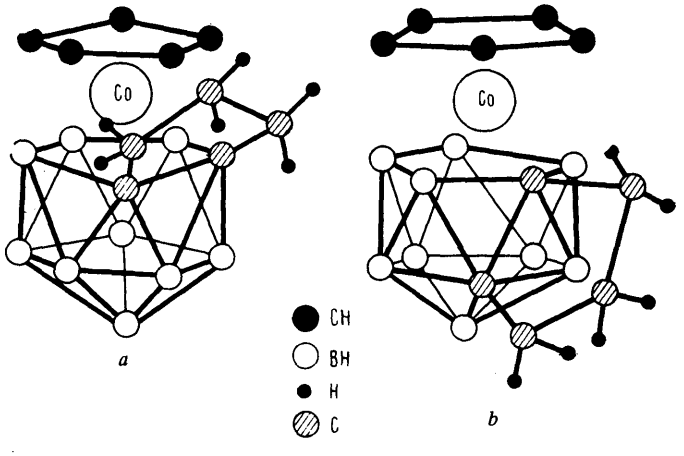



**Figure 18.** The postulated stuctures of the isomers 3,1,2-($\eta^5$-Cp)Co[1,2-$(CH_2)_3B_9C_2H_9$] (*a*) and 3,1,6-($\eta^5$-Cp)Co[1,6-$(CH_2)_3B_9C_2H_9$] (*b*).

In order to explain the mechanism of the polyhedral rearrangements under consideration, one must assume that the rearrangement follows the *dsd* (*diamond–square–diamond*) scheme proposed by Lipscomb[140] with the simultaneous rotation of the triangular $B_2C$ plane [12,141]. The 4,1,7-($\eta^5$-Cp)$CoB_{10}C_2H_{12}$ non-icosahedral system readily isomerises in solution. On heating at 40 °C, the 4,1,8-isomer is formed, while at 70 °C, the 4,1,13-isomer has been isolated[22]. The identification of the 1,8- and 1,13-isomers has not been confirmed by X-ray diffraction.

Heating of 1,2,4-($\eta^5$-Cp)$CoB_8C_2H_{10}$ [Fig.19 (I, R = H)][32] and its *C*-substituted derivative 1,2,4-($\eta^5$-Cp)Co(2,4-$Me_2B_8C_2H_8$) [Fig.19, (I, R = Me)][36] in solution is also accompanied by a polyhedral rearrangement. In the first case the 1,2,3-isomer [Fig.19, (III, R = H)] was isolated in 94% yield[22]. On heating (2,4-$B_8C_2H_{10}$-1,3'-Co-1',2'-$B_9C_2H_{11}$)$^-$ the only product is also (2,3-$B_8C_2H_{10}$-1,3'-Co-1',2'-$B_9C_2H_{11}$)$^-$.[22] In the case of 1,2,4-($\eta^5$-Cp)Co(2,4-$Me_2B_8C_2H_8$) [Fig.19, (I, R = Me)] a mixture of two isomers is formed[36]. It is believed that in this instance the isomerisation proceeds in steps (1,2,4 → 10,2,3 → 1,2,3) via the intermediate formation of the least stable isomers 10,2,3-($\eta^5$-Cp)Co.(2,3,-$Me_2B_8C_2H_8$)[Fig.19,(II, R = Me)]. The transition 1,2,4-($\eta^5$-Cp)Co(2,4-$Me_2B_8C_2H_8$) → 10,2,3-($\eta^5$-Cp).Co(2,3-$Me_2B_8C_2H_8$)[Fig.19, (I) → (II), R = Me] is accompanied by a decrease of the coordination number of cobalt and an increase of the distance between the carbon atoms in the open $B_4C_2$ hexagonal surface of the $CoB_8C_2$ polyhedron. The latter factor promotes the stabilisation of the high positive charge on the cobalt atom by the carbaborane ligand (see Section II). In the course of the further isomerisation (10,2,3 → 1,2,3) [Fig.19, (II) → (III), R = Me] the coordination number of the cobalt atom increases, which agrees with the first part of the empirical rule. However, the fourth part breaks down, since the open hexagonal surface of the 1,2,3-($\eta^5$-Cp)Co(2,3-$Me_2B_8C_2H_8$) isomer now contains two carbon atoms[36]. We may note that mass-spectrometric, ultraviolet spectroscopic, NMR, and oxidation-reduction potential data have been used for the identification of the isomers.

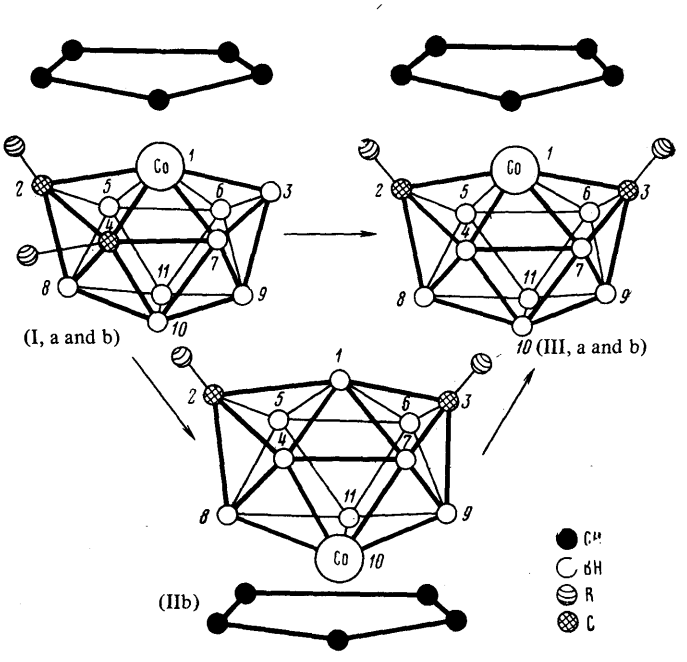



**Figure 19.** The polyhedral rearrangement of 1,2,4-($\eta^5$-Cp)Co(2,4-$R_2B_8C_2H_8$) ( R = H or $CH_3$).

Five isomers (2,6,9- 2,1,6-, 2,1,7-, 2,1,10-, and 2,3,10-) of the cobalt carbaborane complex ($\eta^5$-Cp)$CoB_7C_2H_9$ are known, the complex 2,1,10-($\eta^5$-Cp)$CoB_7C_2H_9$ having the highest thermal stability[22,62]. On heating in solution[22,118] or in the gas phase[62,137], each isomer is converted into the 2,1,10-isomer (Fig.20). The gas-phase rearrangement of the symmetrical complex [(2,1,6-$B_7C_2H_9$)$_2$Co]$^-Cs^+$ proceeds analogously[62,137]. The isomerisation of 2,4,5-($\eta^5$-Cp)$CoB_6C_2H_8$ also takes place in conformity with the empirical rule. When the complex is heated in cyclooctane at 150 °C, 2,4,6-($\eta^5$-Cp)$CoB_6C_2H_8$ is

formed[22]. Theoretically[22] the complex 3,1,7-($\eta^5$-Cp)$CoB_5C_2H_7$ (assumed structure) can be converted into the 3,1,8-isomer, since in this case the carbon atom migrates from the open surface of the polyhedron, which decreases the number of Co–C interactions. However, the complex 3,1,7-($\eta^5$-Cp).$CoB_5C_2H_7$, which is stable up to 250 °C, does not isomerise at 340 °C, disproportionating with formation of 2,4-$B_5C_2H_7$, ($\eta^5$-CpCo)$_3B_5C_2H_7$, and ($\eta^5$-CpCo)$_3B_5C_2H_7$ (traces)[23].

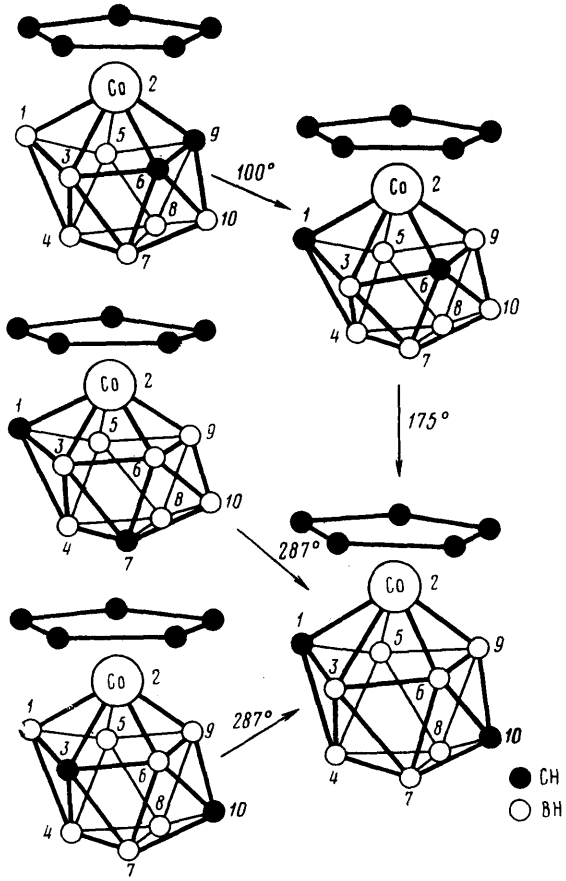



**Figure 20.** The poyhedral rearrangement of ($\eta^5$-Cp)Co.$B_7C_2H_9$.

The polyhedral rearrangement of 1,2,3-($\eta^5$-Cp)$CoB_4C_2H_6$ and its methyl derivative 1,2,3-($\eta^5$-Cp)Co(2-Me$B_4C_2H_5$) (whose structure has been established) takes place in accordance with the empirical rule (the distance between the carbon atoms increases) and leads to the formation of the corresponding 1,2,4-isomers and a small amount of 1,7,2,4-($\eta^5$-CpCo)$_2B_3C_2H_5$.[23]

Among the three possible isomers of the $CoB_3C_2$ system, only 1,2,4-($\eta^5$-Cp)$CoB_3C_2H_5$ is known, its carbon atoms being located at non-neighbouring vertices[23]. Such carbaboranes and their metal complexes have the highest thermal stabilities. In conformity with these findings, heat treatment of 1,2,4-($\eta^5$-Cp)$CoB_3C_2H_5$ in the gas phase is accompanied solely by the decomposition of the initial compound and the formation of the $CoB_4C_2$, $Co_2B_3C_2$, and $Co_2B_4C_2$ systems[23].

*(b) Polyhedral rearrangement of dicobalt complexes of carbaboranes.* The prsence of a second CpCo group in the polyhedron greatly facilitates the isomerisation of the complex. In the course of the rearrangement complexes containing the Co–Co bond are formed as a rule. In these compounds the cobalt and carbon atoms have smaller coordination numbers than in the initial complexes. Furthermore, the initial distances between the carbon atoms can also be retained. Polyhedra with the Co–Co bond are formed at a lower temperature than the final product of the polyhedral rearrangement.

On heating 4,5,1,8-($\eta^5$-CpCo)$_2B_9C_2H_{11}$ at 150 °C in cyclooctane, the isomer 4,5,1,13-($\eta^5$-CpCo)$_2B_9C_2H_{11}$ is formed. In contrast to the initial isomer, in the new isomer both Cp ligands are equivalent. The polyhedral rearrangement of 4,5,1,8-($\eta^5$-CpCo)$_2$(1,8-Me$_2B_9C_2H_9$) proceeds analogously. After the isomerisation, the two Me groups are also equivalent[112]. The hypothesis concerning the structure of the isomer was based on infrared and ultraviolet spectroscopic and NMR data.

The isomers 2,3,1,7-($\eta^5$-CpCo)$_2B_8C_2H_{10}$ [50] and 3,6,1,2-($\eta^5$-CpCo)$_2B_8C_2H_{10}$ [59] (whose structures have been established) isomerise at 250° and 330 °C respectively to 2,4,1,8-($\eta^5$-CpCo)$_2B_8C_2H_{10}$.[25,37] The CpCo fragment and the carbon atom migrate in the former and latter case respectively. The coordination number remains unchanged in the course of the isomerisation.

The 1,4,2,3-($\eta^5$-CpCo)$_2B_7C_2H_9$ polydehdron, containing the Co–Co bond, is formed on isomerisation of 1,6,2,4-($\eta^5$-CpCo)$_2B_7C_2H_9$ and 1,8,2,3-($\eta^5$-CpCo)$_2B_7C_2H_9$. In the course of the 1,6,2,4 → 1,4,2,3 rearrangement the Co–Co bond is retained and the coordination number of the carbon atom decreases. The Co–Co bond appears as a result of the process 1,8,2,3 → 1,4,2,3, Further isomerisation of the 1,4,2,3-isomer gives rise to the 1,10,2,3-($\eta^5$-CpCo)$_2B_7C_2H_9$ polyhedron from which the Co–Co bond disappears. The reaction is accompanied by the formation of ($\eta^5$-CpCo)$_3B_7C_2H_9$.[25,37]

The polyhedral rearrangement of 2,6,1,10-($\eta^5$-CpCo)$_2B_6C_2H_8$ (whose structure has been established[24]) gives rise to 2,7,1,10-($\eta^5$-CpCo)$_2B_6C_2H_8$. The compound was identified on the basis of NMR and ultraviolet spectroscopic data. The Co–Co bond disappears as a result of the migration of the CpCo group. The coordination number of cobalt does not change under these conditions[25,37].

The isomerisation 1,8,5,6-($\eta^5$-CpCo)$_2B_5C_2H_7$ → 1,7,5,6-($\eta^5$-CpCo)$_2B_5C_2H_7$ is an exothermic process, i.e. the conversion of the red 1,8,5,6-isomer, in which the cobalt atoms occupy non-neighbouring vertices, into the green 1,7,5,6-isomer, containing the Co–Co bond, is accompanied by the evolution of heat. In addition, it has been shown that at 340 °C equilibrium is established between these isomers[23]. The structure of the isomers has been determined on the basis of a set of spectroscopic data[23] and has been confirmed by X-ray diffraction[142].

Only the single isomer 3,5,1,7-($\eta^5$-CpCo)$_2B_4C_2H_6$ is known for the $Co_2B_4C_2$ system; its structure has been determined by $^1$H and $^{11}$B NMR. Its conversion into 3,5,2,8-($\eta^5$-CpCo)$_2$.$B_4C_2H_6$ is theoretically possible, since this would entail a decrease of the number of direct Co–C interactions from four to two. However, the isomerisation products were not detected below the decomposition temperature (340 °C).[23]

At 300 °C 1,7,2,3-($\eta^5$-CpCo)$_2B_3C_2H_5$ is converted into 1,7,2,4-($\eta^5$-CpCo)$_2B_3C_2H_5$. There is no Co–Co bond in either compound[102,129]. The structure of the complexes has been established[115,143]. The latter compound does not isomerise up to its decomposition temperature (~400 °C). The rearrangement of the methyl-substituted 1,7,2,3-isomer proceeds similarly. When the isomerisation of 1,7,2,3-($\eta^5$-CpCo)$_2B_3C_2H_5$ was carried out at a lower temperature, the 1,2,4,5- and

1,2,3,5-isomers were also isolated; they both contain the Co–Co bond (the structure was postulated on the basis of $^{11}B$ NMR data). It has been suggested that the isomerisation of the 1,7,2,3-isomer proceeds in accordance with the scheme 1,7,2,3→1,2,4,5→1,2,3,5→1,7,2,4 (Fig.21). In the first stage the *ortho*-positions of the carbon atoms are retained, but the coordination number of the cobalt atom decreases. The formation of the 1,2,3,5-polyhedron is accompanied by an increase of the distance between the carbon atoms and the migration of the CpCo fragment gives rise to the 1,7,2,4-isomer in which there is no Co–Co interaction and the cobalt atoms have the initial coordination numbers[23].

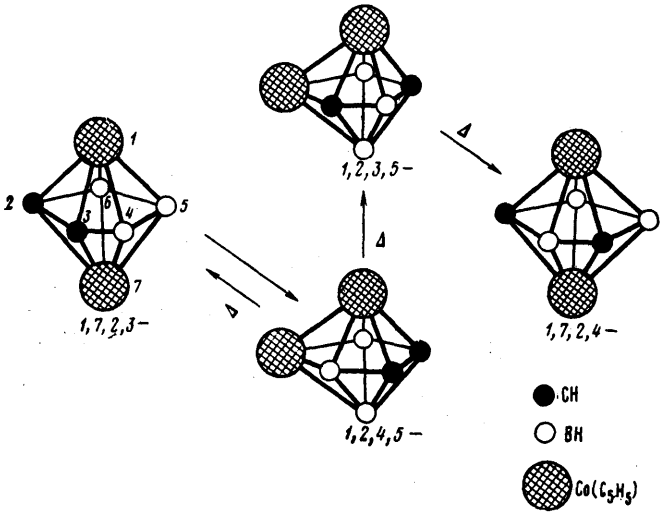



**Figure 21.** The polyhedral rearrangement of 1,7,2,3-$(\eta^5$-$CpCo)_2B_3C_2H_5$.

corresponding derivatives (V) (Fig.22). Their structure was established by infrared spectroscopy, NMR, and mass spectrometry.

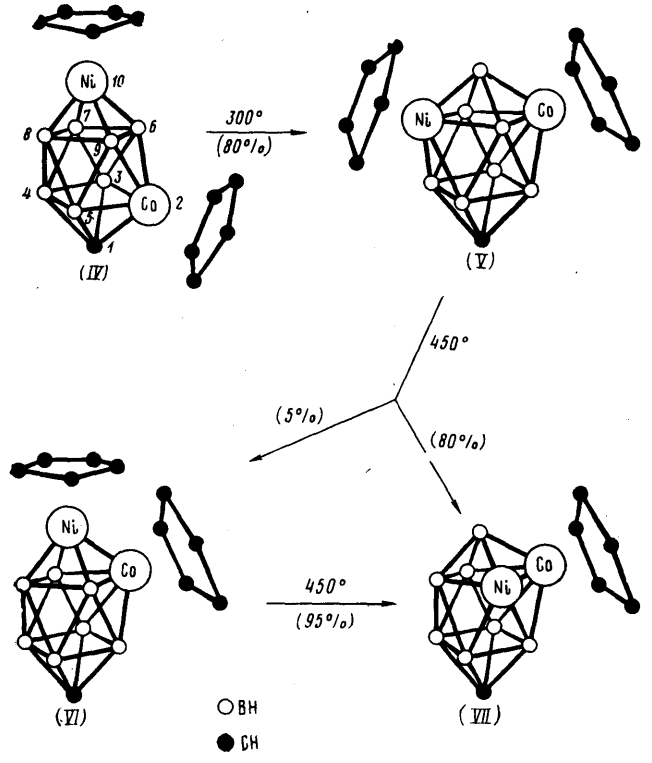



**Figure 22.** The polyhedral rearrangement of $(\eta^5$-$Cp)^2Co.NiB_7CH_8$ [in (VII) the Cp ligand at the nickel atom is not represented].

Thus the presence of two cobalt atoms in the polyhedron does not by itself introduce fundamental changes into the properties of the complexes, but a new tendency is clearly shown. Firstly, the ability of the polyhedron to undergo a rearrangement depends on the possibility of the formation of complexes with a Co–Co bond in the course of the isomerisation. Secondly, complexes with a Co–Co bond always isomerise. In those cases where compounds with a Co–Co bond were not detected in the course of the polyhedral rearrangement, the reaction was carried out at a high temperature. Possibly the use of milder conditions will permit the isolation of these intermediate complexes.

(c) *Polyhedral rearrangement of bimetallic heterocomplexes of carbaboranes.* It has been suggested that the Co(III)–Fe(III) derivatives, which are electron-deficient systems, decompose under the conditions of the polyhedral rearrangement[21]. Indeed, 4,5,1,8-$(\eta^5$-$Cp)_2CoFeB_9C_2H_{11}$ decomposes on heating and does not give rise to isomerisational products[112]. The bimetallic carbaborane complexes $(\eta^5$-$Cp)_2CoNiB_7CH_8$ readily undergo the polyhedral rearrangement. The isomerisation gives rise to polyhedra with a Co–Ni bond [Fig.22, (IV)–(VII)][132]. The bromo-derivatives (IV) (Fig.22) $(\eta^5$-$Cp)_2CoNiB_7CH_{8-n}Br_n$ ($n=1$, 2) gives rise only to the

The ability of cobalt π-complexes of carbaboranes to isomerise in boiling solvents complicates their analysis and purification.

## 2. The Oxidation-Reduction Properties of Cobalt Complexes of Carbaboranes

(a) *Electrochemical properties.* The electronic configuration of the cobalt atom in monocobalt complexes of carbaboranes can vary within wide limits ($d^8 \rightarrow d^5$) (Table 2).[91,144] However, complexes containing cobalt in the formal +3 oxidation state ($d^6$) have been isolated mainly in a chemically pure form. At the same time, oxidation of the yellow-orange diamagnetic compound $[(B_{10}H_{10}CH)_2Co]^{3-}$ gives rise to the black paramagnetic complex $[(B_{10}H_{10}CH)_2Co]^{2-}$, containing cobalt in the $d^5$ state[99,101].

The cobalt atom has the $d^7$ electronic configuration in the complex $(B_9C_9CHPCH_3)_2Co$.[104] The existence of the complex $[(B_9C_9CHPCH_3)_2Co]^+$ ($d^8$) has been demonstrated electrochemically, but it has not been isolated[104]. It followed from the foregoing that, although polyhedral ligands are capable of stabilising the highest and lowest oxidation states of the

cobalt atom, a particular oxidation state of cobalt is preferred for each. The nature of the change in the electrochemical behaviour of cobalt complexes of carbaboranes within a single homologous series is still unknown. However, a clear relation has been established between the reduction potential of the cobalt carbaborane complex and the structure of its isomers. The closer the carbon atom in the polyhedron to the cobalt atom, the easier the reduction of the complex. The isomer containing two carbon atoms in the cobalt coordination plane has the lowest reduction potential compared with other isomers of the given cobalt carbaborane complex (see Nos. 15—17, 21, 22, 23, and 24 in Table 2). This is because the carbon in the polyhedron of the cobalt carbaborane complex is an electron deficient centre and reduces the electron density on the cobalt atom, which facilitates its reduction[99,139]. This property has been used to determine the structures of the isomers of cobalt complexes of carbaboranes[22,36,139].

There exists an analogy between the nature of the influence of substituents on the electrochemical properties of cobalt complexes of carbaboranes and their carbaborane parent compounds[145]. Methyl and phenyl groups at the carbon atom of the dicarbollyl ligand lower the reduction potential of the complex (see Nos. 9, 10, and 11 in Table 2). The presence of three bromine atoms in the polyhedron greatly facilitates the reduction of the complex (No. 12 in Table 2). It is believed that the formal high negative charge of the complex (-3), formed in the $d^6 \rightarrow d^7 \rightarrow d^8$ reduction process, is stabilised as a result of the electron-accepting properties of the bromine atoms[20].

**Table 2.** The potentials of oxidation-reduction processes (relative to the saturated calomel electrode).

| No. | Compound | Method* | $M^{IV}+e \rightarrow M^{III}$ $d^5 \rightarrow d^6$ | $M^{III}+e \rightarrow M^{II}$ $d^6 \rightarrow d^7$ | $M^{II}+e \rightarrow M^{I}$ $d^7 \rightarrow d^8$ | References |
|---|---|---|---|---|---|---|
| 1 | $NEt_4[(1,2\text{-}B_9C_2H_{11})_2Co]$ | P (*c*) | — | −1.36 | −2.24 | 144 |
| 2 | $NEt_4[(1,2\text{-}B_9C_2H_{11})_2Co]$ | P (*d*) | — | −1.37 | −2.37 | 144 |
| 3 | $Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$ | P (*a*) | — | −1.42 | — | 14,20 |
| 4 | $Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$ | CVA (*b*) | +1.57 | −1.46 | — | 20 |
| 5 | $[(1,2\text{-}B_9C_2H_{11})_2Co]^-$ | CVA (*b*) | +0.70 | −1.53 | — | 58 |
| 6 | $NEt_4[1,7\text{-}B_9C_2H_{11})_2Co]$ | P (*c*) | — | −1.14 | −2.52 | 144 |
| 7 | $NEt_4[1,7\text{-}B_9C_2H_{11})_2Co]$ | P (*d*) | — | −1.21 | −2.70 | 144 |
| 8 | $Cs[(1,7\text{-}B_9C_2H_{11})_2Co]$ | CVA (*b*) | irrevers. | −1.17 | — | 20 |
| 9 | $NMe_4[1,2\text{-}Me_2B_9C_2H_9)_2Co]$ | P (*a*) | — | −1.16 | — | 14,20 |
| 10 | $NMe_4[1,2\text{-}Me_2B_9C_2H_9)_2Co]$ | CVA (*b*) | irrevers. | −1.13 | — | 20 |
| 11 | $NMe_4[(1,2\text{-}PhB_9C_2H_{10})_2Co]$ | P (*a*) | — | −1.28 | — | 14,20 |
| 12 | $NMe_4[(1,2\text{-}Br_2B_9C_2H_9)_2Co]$ | CVA (*b*) | irrevers. | −0.48 | −1.58 | 20 |
| 13 | $(1,2\text{-}B_9H_9CHPMe)_2Co$ | CVA (*b*) | — | +0.43 | −0.78 | 104 |
| 14 | $(1,7\text{-}B_9H_9CHPMe)_2Co$ (m.p. = 278—279°) | CVA (*b*) | — | +0,41 | −0.74 | 104 |
| 15 | $4,1,7\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$ | CVA (*b*) | — | −0.72 | −0.74 | 22 |
| 16 | $4,1,8\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$ | CVA (*b*) | — | −1.15 | — | 22 |
| 17 | $4,1,13\text{-}(\eta^5\text{-Cp})CoB_{10}C_2H_{12}$ | CVA (*b*) | — | −1.16 | — | 22 |
| 18 | $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ | P (*c*) | — | −1.21 | −2.11 | 144 |
| 19 | $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ | P (*d*) | — | −1.19 | −2.21 | 144 |
| 20 | $3,1,2\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11}$ | CVA (*b*) | irrevers. | −1.25 | — | 20 |
| 21 | $2,1,6\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9$ | CVA (*b*) | — | −1.03 | — | 22 |
| 22 | $2,1,7\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9$ | CVA (*b*) | — | −1.33 | — | 22 |
| 23 | $2,4,5\text{-}(\eta^5\text{-Cp})CoB_6C_2H_8$ | CVA (*b*) | — | −0.84 | — | 22 |
| 24 | $2,4,6\text{-}(\eta^5\text{-Cp})CoB_6C_2H_8$ | CVA (*b*) | — | −1.11 | — | 22 |
| 25 | $(NMe_4)_2(B_9C_2H_{11}CoB_9C_2H_{10}CoB_9C_2H_{11})$ | P (*c*) | — | −1.48 | −2.36 | 144 |
| 26 | $(NMe_4)_2(B_9C_2H_{11}CoB_9C_2H_{10}CoB_9C_2H_{11})$ | P (*d*) | — | −1.49 | −2.43 | 144 |
| 27 | $(NMe_4)_2(B_9C_2H_{11}CoB_9C_2H_{10}CoB_9C_2H_{11})$ | CVA (*b*) | +1.57 | −1.46 | — | 58 |
| 28 | $(NMe_4)_2[(B_9C_2H_{11}CoB_9C_2H_{10})_2Co]$ | CVA (*b*) | +1.07 | −1.36 | — | 58 |

*P = polarographic method; CVA = cyclic voltamperometric method. The measurements were performed under the following conditions: *a*) in 0.10 M $LiClO_4$ in 50% aqueous acetone as the supporting electrolyte; *b*) in 0.10 M $Et_4NClO_4$ in acetonitrile as the supporting electrolyte; *c*) in 0.10 M n-$Bu_4PF_6$ in acetonitrile as the supporting electrolyte; *d*) in 0.15 M n-$Bu_4NPF_6$ in dimethoxyethane as the supporting electrolyte.

Unsuccessful attempts have been made to carry out the reversible reduction of the complexes $[(B_{10}H_{10}S)_2Co]^-$ [107] and $[(B_9H_9CHP)_2Co]^-$.[104] However, it is not clear whether this is a property of the above π-complexes or is a consequence of the chosen experimental conditions. The reduction of the isomers of $(\eta^5\text{-Cp})Co^{III}(Me_2B_8C_2H_8)$ is a two-stage two-electron process. The first wave corresponds to the Co(III) → Co(II) transition and the second corresponds to the addition of a second electron and the formation of the anion $[CpCo^{II}.(Me_2B_8C_2H_8)]^{2-}$. For the 1,2,4- and 10,2,3-isomers, both stages are reversible: $E_{1/2} = -0.83$ and −1.64 V in the former case and $E_{1/2} = -1.23$ and −1.57 V in the latter. The second stage in the reduction of $1,2,3\text{-}(\eta^5\text{-Cp})Co(2,3\text{-}M_3B_8C_2H_8)$ takes place irreversibly ($E_{1/2} = -0.75$ and −1.66 V).[36]

The complex $2,1\text{-}(\eta^6\text{-}C_{10}H_8)CoB_{10}CH_{11}$, containing the coordinated neutral arene ligand $C_{10}H_8$, is also reduced in two stages. The reversible reduction observed at −0.62 V is attributed to the Co(III) → Co(II) transition. As −1.31 V a quasi-reversible process is observed and is regarded as the reduction of the naphthalene ligand $C_{10}H_8$.[132]

The reduction and oxidation of cobalt complexes of carbaboranes containing two or three metal atoms as a rule proceeds in a reversible one-electron stage (Table 3). The reduction of cluster compounds of transition metals takes place similarly[146]. Probably[112] in this case the high degree of electron delocalisation determines the behaviour of the group of metal atoms within the polyhedron as a single metallic centre.

The reduction potentials of di- and tri-cobalt complexes of carbaboranes also depend on the isomeric structure of the complex. The same relations as those mentioned above for monocobalt complexes of carbaboranes have been observed[112] (see Nos. 2—4, 5, and 6, in Table 3).

**Table 3.** The reduction and oxidation potentials of di- and tri-metal complexes of carbaboranes.

| No. | Compound | Reduction ($E_{p/2}$, V) | Oxidation ($E_{p/2}$, V) | Refs. |
|---|---|---|---|---|
| 1 | $1,14,2,10\text{-}(\eta^5\text{-CpCo})_2B_{10}C_2H_{12}$ | −1.10 | +1.17 | 43 |
| 2 | $4,5,1,3\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{11}$ | −0.85 | +0.77 | 112 |
| 3 | $4,5,1,8\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{11}$ | −0.92 | +0.97 | 112 |
| 4 | $4,5,1,13\text{-}(\eta^5\text{-CpCo})_2B_9C_2H_{11}$ | −1.25 | +0.83 | 112 |
| 5 | $4,5,1,8\text{-}(\eta^5\text{-CpCo})_2(1,8\text{-}Me_2B_9C_2H_9)$ | −0.91 | +0.92 | 112 |
| 6 | $4,5,1,13\text{-}(\eta^5\text{-CpCo})_2(1,13\text{-}Me_2B_9C_2H_9)$ | −1.25 | +0.87 | 112 |
| 7 | $2,7,1,10\text{-}(\eta^5\text{-CpCo})_2B_8C_2H_8$ | −1.50 | +1.37 | 25 |
| 8 | $\{[(\eta^5\text{-Cp})CoB_9C_2H_{11}]_2Co\}^-$ | −0.84 | +0.86 | 112 |
| 9 | $4,5,1,8\text{-}(\eta^5\text{-Cp})_2\text{-}4Co\text{-}5Fe\text{-}B_9C_2H_{11}$ | −0.42 | +0.90 | 112 |
| 10 | $4,5,1,8\text{-}(\eta^5\text{-Cp})_2\text{-}4Co\text{-}5Fe\text{-}(1,8\text{-}Me_2B_9C_2H_9)$ | −0.47 | +0.92 | 112 |

It is known[112] that the oxidation and reduction of bimetallic heterocomplexes of carbaboranes containing iron and cobalt atoms proceed in a single reversible one-electron stage (Nos. 9 and 10 in Table 3). In this case there is an analogy with the electrochemical behaviour of $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$ ($n = 5$ to 10).[43,112] On the other hand, according to cyclic voltamperometric data, the $(\eta^5\text{-Cp})_2CoNiB_7CH_8$ isomers are reduced in a single reversible one-electron stage, while their oxidation is irreversible. The reduction of $(\eta^5\text{-Cp})_2Co^{III}Ni^{IV}.B_7CH_8$ gives rise to a complex containing $Co^{III}$ and $Ni^{III}$, but it has not been isolated.

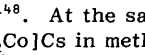
(*b*) *The effect of reducing and oxidising agents.* When $[(B_9C_2H_{11})_2Co]^-$ is acted upon by n-BuLi, the product is an analogue of cobaltocene—the complexes $[(B_9C_2H_{11})_2Co]^{2-}$,

which is unstable in air[14]. Paramagnetic complexes of the type $CpCo^{III}(B_nC_2H_{n+2})Fe^{III}Cp$ ($n=7$, 9) are reduced by $NaBH_4$, which yields diamagnetic compounds of the type $[CpCo(B_nC_2H_{n+2})FeCp]^-$.[113]

It has been established that $CpCoB_9C_2H_{11}$ is stable in oxidising media such as in solution of $CrO_3$ in $CH_3COOH$, or acetone in the presence of $H_2SO_4$, or an alkaline solution of $KMnO_4$.[46] At the same time, on treatment with $CuCl_2$ and other oxidants the complexes $[(B_{10}H_{10}C_2RR')_2Co]^-$ are converted quantitatively into *o*-carbaboranes of the type $o$-$B_{10}H_{10}C_2RR'$ (R = R' = H or Me; R = H, R' = Me or Ph).[130]

### 3. Chemical Properties of Cobalt Complexes of Carbaboranes

There is an analogy between the chemical behaviour of cobalt complexes of carbaboranes and carbaboranes themselves, although under the reaction conditions the cobalt atom or the Cp ligand are not reaction centres (polyhedral expansion reaction, polyhedral rearrangement, bromination, etc.). Reactions of cobalt complexes of carbaboranes are known in which the nature of the products is determined by the presence of the CoCp fragment in the polyhedral molecule. These are metallation, acetylation, and nitration reactions. As far as is allowed by the available structural data, we shall endeavour to compare the chemical properties of cobalt complexes of carbaboranes, carbaboranes, and Cp sandwich complexes of cobalt. Aqueous alkaline solutions of cobaltocenium salts are known to be stable under radiolysis conditions[147]. The complex $[(1,2\text{-}B_9C_2H_{11})_2Co]^-$ is also stable in the water–nitrobenzene system under irradiation from a $^{60}Co$ $\gamma$-source[148]. At the same time the radiolysis of $[(1,2\text{-}B_9C_2H_{11})_2Co]Cs$ in methanol[149] or the nitrobenzene–bromoform mixture[150] leads to the formation of the corresponding bis-(dicarbollyl)cobalt(III) derivative in which the substituent



(>CHOH or –CBr=CBr–) occupies a bridging position between the two dicarbollyl ligands.

The reaction of 1,2,4-($\eta^5$-Cp)$CoB_8C_2H_{10}$ with (*trans*-PhCH=CHPh)$Pt(PEt_3)_2$ in toluene at 20 °C leads to 1-($\eta^5$-Cp)Co-8-$(PEt_3)_2$Pt-2,7-$B_8C_2H_{10}$ (Fig.23), which is regarded as a compound resulting from the inclusion of the $(Et_3P)_2Pt$ fragment in the carbaborane ring[151]. Another bimetallic carbaborane heterocomplex $(C_8H_{12})NiC_2B_8H_{10}CoCp$ is formed when 1,2,4-($\eta^5$-Cp)$CoB_8C_2H_{10}$ is treated with $(1,5\text{-}C_8H_{12})_2Ni$.[151] We may note that the carbaborane 2,3-$Me_2$-2,3-$B_9C_2H_9$ also reacts with the analogous zerovalent nickel and platinum complexes to form *closo*-carbaborane complexes of nickel and platinum[151].

In aqueous THF solution in the presence of acid the complex (*C,C'*-$Me_2B_4C_2H_2)_2CoH$ is almost quantitatively converted into $(Me_2B_3C_2H_5)CoH(Me_2B_4C_2H_4)$.[98] The latter compound contains two B–H–B fragments and a Co–H fragment. NMR studies failed to demonstrate the occurrence of exchange between B–H–B and Co–H, although the authors[98] do not rule out the possibility of such an exchange at a very low rate. It is of interest that, under the influence of NaH or KOH, $[(Me_2B_3C_2H_5).Co(Me_2B_4C_2H_4)]^-$ is obtained from $(Me_2B_3C_2H_5)CoH(Me_2B_4C_2H_4)$, the proton being split off from the cobalt atom, while the B–H–B fragments are retained. We may note that this process is reversible[98].

The symmetric and asymmetric *closo*-complexes having the general formula $[(2,4\text{-}B_8C_2H_{10})CoL]^{z-}$ (L = 1,2-$B_9C_2H_{11}$, $z=-1$; L = Cp, $z=0$) are converted into complexes with the *nido*-structure of the type $[(B_8C_2H_{10}.Nu)CoL]^z$ (Nu = pyridine, piperidine, or ethanol) on interaction with Lewis bases[35, 53,117,118] The structure of (1,2-$B_9C_2H_{11}$-3,11'-Co-9'-$C_5H_5N$-7',8'-$B_8C_2H_{10})^-$ has been established by NMR [35,117] and X-ray diffraction[54,55] (Fig. 7).

It is believed[35] that the structure of the $CoB_8C_2H_{10}.Nu$ fragment in the *nido*-complexes ($\eta^5$-Cp)$CoB_8C_2H_{10}$.Nu (Nu = $C_5H_5N$ or $C_5H_{10}NH$), obtained by treating 1,2,4-($\eta^5$-Cp).$.CoB_8C_2H_{10}$ with pyridine or piperidine, is analogous to that discussed above. However, there is no unanimous view concerning the structure of ($\eta^5$-Cp)$CoB_8C_2H_{10}$.EtOH.[53,118]

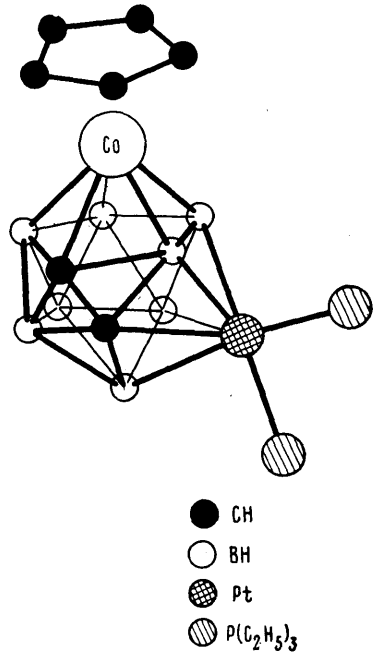



**Figure 23.** The structure of 1-($\eta^5$-Cp)Co-8-$(PEt_3)_2$Pt-2,7-$B_8C_2H_{10}$.[151]

The hydrogen atoms attached to the boron atoms in 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ and 1,2,4-($\eta^5$-Cp)$CoB_8C_2H_{10}$ are exchanged for deuterium in the presence of $(PPh_3)_3RuHCl$. The exchange apparently proceeds via a stage involving the oxidative addition of the terminal BH bond of the complex to the catalyst[152].

The moderate acidity of the hydrogen atom in the C–H bond of the carbaborane $B_{10}C_2H_{12}$ is responsible for the ready formation of the *C*-lithio-derivative in the reaction of the carbaborane with n-BuLi. The reaction of the carbaborane with RMgBr proceeds similarly[38]. The reaction of organometallic compounds (RLi, RMgBr) with an isoelectronic analogue of the complex $CpCoB_9C_2H_{11}$—the cobalticenium cation—gives rise to the products of addition to the Cp ring, i.e. $CpCoC_5H_5R$. There has been only one mention of the formation of the substituted cobalticenium $[RC_5H_4CoCp]^+$ in this reaction, but hitherto this finding has not been confirmed experimentally[153]. We shall now turn to cobalt complexes of carbaboranes. The reaction n-BuLi with 1,2,4-($\eta^5$-Cp)$CoB_8C_2H_{10}$ in ether leads to the alkylation of the complex in the Cp ligand and the formation of 1,2,4-($\eta^5$-$C_5H_4Bu$).$.CoB_8C_2H_{10}$.[35] RLi (R = n-Bu or C≡CPh) [154] and ArMgBr (Ar = Ph, *m*-$FC_6H_4$, or *p*-$FC_6H_4$) [155] in THF also react with 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$. The reaction of 3,6,1,2-($\eta^5$-CpCo)$_2$.

.$B_8C_2H_{10}$ with RLi (R = Bu or Ph) in THF leads to the substitution of the hydrogen atom in one of the Cp ligands by an R-group with formation of 3-($\eta^5$-CpCo)-6-($\eta^5$-$C_5H_4$RCo)-1,2-$B_8C_2H_{10}$ (R = Bu or Ph).[156]

It is believed[35,154-156] that the reduction process Co(III) → Co(II) takes place in the course of the reaction and the radical $C_4H_9^{\cdot}$ is formed, which leads to the alkylation of the Cp ring. On the other hand, on treatment of 3,1,2-($\eta^5$-Cp).$CoB_9C_2H_{11}$ with BuLi (molar ratio 1:1) in ether, the main product is the *C*-lithio-derivative 3,1,2-($\eta^5$-Cp)Co(1-$LiB_9C_2H_{10}$). For a reactant ratio of 2:1, the product is 3,1,2-($\eta^5$-Cp)Co(1,2-$Li_2B_9C_2H_9$). The compounds have been isolated in the form of carboxylic acids. 3,1,2-($\eta^5$-$C_5H_4$Bu)$CoB_9C_2H_{11}$ is formed in a small amount as a side product[154].

Instances of the electrophilic substitution of hydrogen atoms in the polyhedral ligand of a cobalt carbaborane complex are known. Substitution takes place at the boron atoms most remote from the carbon atoms, which results in an enhancement of their electron density[157,158]. When [(1,2-$B_9C_2H_{11})_2Co]^-$ is treated with an excess of bromine in glacial acetic acid, the bromo-derivative [(8,9,12-$Br_3$-1,2-$B_9C_2H_8)_2$.$Co]^-$, illustrated in Fig.3, is formed[20]. Its structure was established by X-ray diffraction[49]. The asymmetric complex 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ is also brominated under analogous conditions[47]. It has been established that the bromination of 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ with bromine in $CH_2Cl_2$ in the presence of $AlCl_3$ takes place in steps. Depending on the amount of bromine, mono-, di-, or tri-bromo-derivatives of 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ are formed. The authors suggest[47] that initially substitution takes place at the boron atom in the 8-position and then successively in the 9- and 12-positions. 3,1,2-($\eta^5$-Cp)Co(1-$MeB_9C_2H_{10-n}Br_n$) (n = 1, 2) has been obtained similarly[47]. On bromination of the complex CpCo(1,6-$B_7C_2H_9$),[62] substitution takes place also at the boron atom[159]. On treatment with an excess of bromine in $CCl_4$, CpCo.$(B_7C_2H_7Br_2)$ is formed.

Bimetallic carbaborane heterocomplexes, particularly isomers IV and V of the complex $(\eta^5\text{-Cp})_2CoNiB_7CH_8$, are also brominated successfully (Fig.22). Bromination is achieved with one or two moles of bromine in $CCl_4$, which yields respectively mono- and di-bromo-derivatives[132]. In all the instances examined, there is no substitution in the Cp ligand. We may note that cobaltocene is oxidised by bromine to the cobalticenium ion[160].

Thus cobalt complexes of carbaboranes behave analogously to carbaboranes under the conditions of electrophilic bromination[38]. In addition, bromination of the π-complexes takes place also in glacial acetic acid, while carbaboranes are inert under these conditions.

Another electrophilic substitution reaction, the Friedel–Crafts acetylation, also leads to the formation of B-substituted complexes only.

Acetylation of ($\eta^5$-Cp)Co(1,6-$B_7C_2H_9$) gives a 72% yield of ($\eta^5$-Cp)Co(8-$CH_3CO$-$B_7C_2H_8$). The acetyl derivative readily gives rise to the corresponding 2,4-dinitrophenylhydrazone, but is not converted into the corresponding carbinol in the presence of $LiAlH_4$.[159] The complex ($\eta^5$-Cp)Co(1,10-$B_7C_2H_9$) is inert under the conditions corresponding to the acylation of the 1,6-isomer. This is apparently a consequence of a more symmetrical distribution of electron density in the ligand of the 1,10-isomer.

The acetylation of 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ does not proceed as smoothly as in the case of ($\eta^5$-Cp)Co(1,6-$B_7C_2H_9$).[161] The reaction is carried out in an atmosphere of nitrogen by treatment with $CH_3COCl$ and $AlCl_3$. As in bromination, substitution takes place at the $B_{(8)}$ atom, which is most remote from the electron-deficient carbon atoms and therefore has the highest electron density. The structure of 3,1,2-($\eta^5$-Cp)Co(8-$CH_3COB_9C_2H_{10}$) has been established by X-ray diffraction[161]. However, 3,1,2-($\eta^5$-Cp)Co(8-$CH_3COB_9C_2H_{10}$) is formed in a small amount and is not the only reaction product. At the same time, 3,1,2-($\eta^5$-Cp)Co(8-$RB_9C_2H_{10}$), where R = Cl, OH, or $OCOCH_3$, have been isolated[161]. Acetylation of 3,1,2-($\eta^5$-Cp)Co(1-$PhB_9C_2H_{10}$) with a mixture of $CH_3COCl$ and $AlCl_3$ in dichloroethane at 45–55 °C leads only to the oxidation of the B–H bond and the formation of the B-hydroxy-derivative[162]. We may note that, among the known cyclopentadienyl π-complexes of cobalt, acetylation is undergone only by ($\eta^5$-Cp)Co($\eta^4$-$C_4H_4$), with substitution at a carbon atom of the $C_4H_4$ ligand (yield approximately 10%).[163]

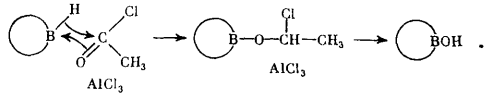
When 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ is refluxed in benzene with an excess of $AlCl_3$, the B-substituted derivative 3,1,2-($\eta^5$-Cp)Co(8-$ClB_9C_2H_{10}$) is formed[161].

The B–H bond in 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ is oxidised more readily than in the *o*-carbaborane. The oxidation takes place under the influence of $CrO_3$ in $(CH_3CO)_2O$ or $CH_3COOH$ in the presence of $H_2SO_4$ [162] and of the nitrating mixture ($HNO_3:H_2SO_4 = 1:3$) [162] and also in Friedel–Crafts acetylation[161,162]. In the first case the *B*-acetoxy and *B,B*-diacetoxy-derivatives are formed together with 3,2,1-($\eta^5$-Cp)Co(8-$HOB_9C_2H_{10}$).[162] The reaction with the nitrating mixture gives the nitrate 3,2,1-($\eta^5$-Cp)Co(8-$O_2NOB_9C_2H_{10}$).[162]

The nitration of 3,2,1-($\eta^5$-$C_5H_4Ph$)$CoB_9C_2H_{11}$ and 3,2,1-($\eta^5$-Cp)Co(1-$PhB_9C_2H_{10}$) gives two series of compounds. On the one hand, the *para*-nitro-derivatives 3,2,1-($\eta^5$-$C_5H_4C_6H_4NO_2$-*p*)$CoB_9C_2H_{11}$ and 3,2,1-($\eta^5$-Cp)Co(1-*p*-$NO_2C_6H_4B_9C_2H_{10}$) are formed, and, on the other, the products are the corresponding $B_{(8)}$ derivatives 3,2,1-($\eta^5$-$C_5H_4C_6H_4NO_2$-*p*)Co(8-$O_2NOB_9C_2H_{10}$) and 3,2,1-($\eta^5$-Cp)Co(1-*p*-$NO_2C_6H_4$-8-$O_2NOB_9C_2H_9$).[162] It is believed that the *B*-hydroxy-derivative is formed initially and is then converted into the nitrate.

The formation of the *B*-hydroxy- and *B*-acetoxy-derivatives 3,2,1-($\eta^5$-Cp)Co(8-$RB_9C_2H_{10}$) (R = OH or $OCOCH_3$ from 3,2,1-($\eta^5$-Cp)$CoB_9C_2H_{11}$ under the conditions of the acetylation reaction (treatment with $CH_3COCl + AlCl_3$) is fairly unexpected[161,162], since the $CH_3COCl + AlCl_3$ mixture does not have very pronounced oxidising properties. Furthermore, the reaction of $CH_3COCl$ and $AlCl_3$ with 3,2,1-($\eta^5$-Cp)Co(1-$PhB_9C_2H_{10}$) in dichloroethane also led to the formation of the *B*-hydroxy-derivative 3,2,1-($\eta^5$-Cp)Co(1-Ph-8-$HOB_9C_2H_9$) instead of the expected acetylation in the benzene ring[162]. 3,2,1-($\eta^5$-Cp)Co(1-Me-8-$HOB_9C_2H_9$) has been obtained similarly[162].

It is believed that the formation of the *B*-hydroxy-derivatives must be regarded as a hydride shift reaction:



This hypothesis agrees well with the idea that there is enhanced electron density at the $B_{(8)}$ atom and with known experimental facts (the formation of $B_{(8)}$ derivatives alone).

The enhanced hydride mobility of the hydrogen atoms linked to boron atoms facilitates the hydrogen–halogen exchange in reactions of alkyl halides with 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ compared with the carbaboranes $B_{10}C_2H_{12}$. On treatment of 3,1,2-($\eta^5$-Cp)$CoB_9C_2H_{11}$ with RX (R = Me, Et, or iso-Br; X = I or Br), both alkylation and exchange halogenation in the carbaborane ring takes place. The reaction leads to the formation of the *B*-alkyl-*B*-halogeno-derivatives $CpCoB_9C_2H_{11}$:[164]

$$3,1,2\text{-}(\eta^5\text{-Cp})\,CoB_9C_2H_{11} + RX \xrightarrow[20^\circ]{AlCl_3} (\eta^5\text{-Cp})\,CoB_9C_2H_{11-n-m}R_nX_m \quad n = 3, 4;\ m = 1, 2.$$

There exists another series of reactions of dicarbollylcobalt complexes in which substitution takes place only at the $B_{(8)}$ atom. All these reactions are carried out in the presence of acids. On treatment of $[3,3\text{-}Co(1,2\text{-}B_9C_2H_{11})_2]^-$ with diethyl sulphide in a strongly acid medium, a neutral compound is formed[165]:

$$[3,3\text{-Co}(1,2\text{-}B_9C_2H_{11})_2]^- + HCl + Et_2S \rightarrow 1,2\text{-}B_9C_2H_{11}\text{-}3,3'\text{-Co-}8'\text{-}SEt_2\text{-}1',2'\text{-}B_9C_2H_{10} + H_2.$$

Treatment of $[3,3\text{-Co-}(1,2\text{-}B_9C_2H_{11})_2]^-$ with carbon disulphide in the presence of $AlCl_3$ and HCl yields the compounds $\{[3,3\text{-Co-}(1,2\text{-}B_9C_2H_{10})_2]^-S_2C^+H\}$, in which two dicarbollyl groups are linked by the $[SC^+(H)S]$ bridge[166]. The 1,7-isomer reacts similarly[166]; the structure of the resulting compound is illustrated in Fig. 2.[48,167]

The electron-deficient carbon atom in the complexes formed is stabilised by the free electron pair of the sulphur atom. The compound in which the $[OC^+(CH_3)O]$ fragment is a bridge between dicarbollyl groups has been isolated by treating $[3,3\text{-Co}(1,2\text{-}B_9C_2H_{11})_2]^-$ with the $CH_3COOH$–$(CH_3CO)_2O$ mixture in the presence of catalytic amounts of $HClO_4$.[147] It has been suggested[165] that a protonated complex is formed in the course of the reaction and is then subjected to nucleophilic attack by a neutral molecule ($Et_2S$ or $CS_2$), which results in the formation of the corresponding $B_{(8)}$ derivative and evolution of molecular hydrogen[165,166]. The protonated complex hypothesis agrees satisfactorily with the hypothesis of the hydride properties of the hydrogen at the boron atom in the 8-position[162].

The carbonium centres in the complexes $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-.O_2C\overset{+}{C}H_3\}$ and $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-S_2\overset{+}{C}H\}$ are inert towards protic solvents. This is probably a consequence of the partial delocalisation of the positive charges of the neighbouring heteroatoms and the proximity of the negative charge. The interaction with $NaBH_4$ is rapid and gives a good yield[166]:

$$\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-S_2C^+H\} + NaBH_4 \rightarrow [(1,2\text{-}B_9C_2H_{10})_2CoS_2CH_2]^-.$$

The hydrolysis of $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-O_2C^+CH_3\}$ and the analogous sulphur-containing derivatives leads to the formation of a diol and a dithiol respectively[166]. Furthermore, the corresponding thiolothioformyl derivative was isolated in the hydrolysis of $\{[(1,2\text{-}B_9C_2H_{10})_2Co]^-S_2C^+H\}$.[166]

The reaction of $[3,3\text{-Co}(1,2\text{-}B_9C_2H_{11})_2]^-$ with $S_2Cl_2$ in $CH_2Cl_2$ leads to $[8,8\text{-S}(B_9C_2H_{10})_2Co]^-$ after alkaline methanolysis[168]. This reaction has no analogies in the chemistry of carbaboranes. The sulphur atom in the complex is highly reactive and is readily alkylated with formation of 8,8-RS.$(B_9C_2H_{10})_2Co$, R = alkyl[168].

In the presence of diazonium salts $[(7,8\text{-}B_9C_2H_{11})_2Co]^-$ gives rise to the complex $RC_6H_4N_2.[(7,8\text{-}B_9C_2H_{11})Co]$. On heating, this compound is converted into the *B*-substituted derivative in which the phenylene unit occupies a bridging position between the two dicarbollyl groups[169].

The reaction of the dicarbollyl complex 3,2,1-($\eta^5$-Cp).$CoB_9C_2H_{11}$ with $PhBCl_2$ is interesting[170]: there is a complete analogy with the chemical behaviour of cobaltocene. In both cases the addition of the Ph(Cl)B fragment to the Cp ligand is accompanied by the heterolysis of the B–Cl bond and a ring expansion reaction, which leads to the formation of a six-electron borinate ion involved in a $\pi$-type coordination[153]:

$$3,2,1\text{-}(\eta^5\text{-Cp})CoB_9C_2H_{11} + PhBCl_2 \rightarrow 3,2,1\text{-}(\eta^6\text{-}C_6H_5B\text{—Ph})CoB_9C_2H_{11}.$$

3,2,1-($\eta^5$-Cp)$CoB_9C_2H_{11}$ is initially reduced with sodionaphthalene in THF, whereupon, after the addition of an excess of $PhBCl_2$ and exposure of the reaction product to air, a derivative of the borinate ion is obtained in 17% yield[170]. When $CpCoB_9H_9CHCCH(OH)R$ is treated with $LiAlH_4$ and $H_2AlCl$, the CHOH group is reduced and $CpCoB_9H_9CHCCH_2R$ is formed[171].

The oxidation of 3,1,2-($\eta^5$-Cp)$CoB_9H_9CHCCH_2OH$ with chromium trioxide in acetone in the presence of $H_2SO_4$ yields 3,1,2-($\eta^5$-Cp)$CoB_9H_9CHCCHO$. The oxidation of the $CH_2OH$ group to CHO then takes place more readily than the oxidation of the aldehyde group to the carboxy-group[46]. Under the influence of $CrO_3$ in an acid medium, the complex $(\eta^5\text{-CpCo})_2$.$B_8H_8CHCCH_2OH$ yields the corresponding aldehyde. Further oxidation of $(\eta^5\text{-CpCo})_2B_8H_8CH_8CCHO$ is difficult apparently owing to pronounced steric hindrance[111].

The aldehyde and ketone groups in 3,1,2-($\eta^5$-Cp)Co.$B_9H_9CHCR$ (R = CHO [46] or $COCH_3$ [161]) form the corresponding hydrazones on reaction with 2,4-dinitrophenylhydrazine. On treatment of 3,1,2-($\eta^5$-Cp)$CoB_9H_9CHCCHO$ with $C_2H_5ONa$ or $t\text{-}C_4H_9ONa$, the CHO group is split off with formation of $CpCoB_9H_9C_2H_2$, while the reactions with Grignard reagents take place stereoselectively and leads to diastereoisomeric secondary alcohols[171]. The Clemmensen reduction of 3,1,2-($\eta^5$-Cp)$CoB_9H_9CHCCOCH_3$ gives rise to an ethyl-substituted complex[161]. The carboxylic acid 3,1,2-($\eta^5$-Cp)$CoB_9H_9CHC$.$COOH$ ($pK_a = 3.54$) is converted into the methyl ester by treatment with diazomethane or into the acid chloride by reaction with $PCl_5$.[46] The acid chloride 3,1,2-($\eta^5$-Cp)Co.$B_9C_9CHCCOCl$ does not hydrolyse and undergoes very slowly the Friedel–Crafts reaction with benzene. The passivity of the COCl group is also regarded as a consequence of steric factors[46]. Treatment of the *B*-hydroxy-derivative 3,1,2-($\eta^5$-Cp)Co(8-$HOB_9C_2H_{10}$) with acetic anhydride or $CH_3COCl$ leads to the corresponding *B*-acetoxy-derivative 3,1,2-($\eta^5$-Cp)Co(8-$CH_3OCOB_9C_2H_{10}$).[161,162] The amino- ($pK_a$ = 6.04) and vinyl groups in 3,1,2-($\eta^5$-Cp)Co(6-$RB_9C_2H_{10}$), where $R = NH_2$ or $CH=CH_2$, exhibit a reduced reactivity compared with the corresponding carbaborane derivatives[96]. The nitro-derivatives 3,1,2-($\eta^5$-Cp)$CoB_9H_9CHCC_6H_4NO_2$ and 3,1,2-($\eta^5$-$C_5H_4C_6H_4NO_2$)$CoB_9C_2H_{11}$ are reduced to the corresponding substituted anilines on treatment with tin and HCl in an alcoholic solution[162].

Thus it follows from the examples presented that the chemical behaviour of the functional groups in the polyhedral ligand in a cobalt carbaborane complex differs little from the usual chemical reactions of these groups.

In conclusion of the discussion of the chemical properties of cobalt complexes of carbaboranes, we may mention that the properties of the complex $[(\eta^5\text{-Cp})Co(7\text{-}B_{10}CH_{11})]^-$ differ significantly from those of the compounds considered here. The complex is chemically inert and is stable for 90 h at 100 °C in KOH and EtOH solutions. It does not undergo polyhedral expansion and contraction reactions. The anion $[(\eta^5\text{-Cp})Co(7\text{-}B_{10}CH_{11})]^-$ is not converted into a neutral complex containing Co(IV) on treatment with oxidants ($KMnO_4$, $FeCl_3$, or the $Ce^{4+}$ ion).[102]

## V. POLYHEDRAL COBALT COMPLEXES OF *NIDO*-CARBABORANES

The *nido*-complexes of cobalt are obtained by the polyhedral contraction reaction[35,118] (see Section III) or by treating with nucleophiles (pyridine, piperidine, and ethanol) *closo*-complexes of the type $[(B_8C_2H_{10}CoL)]^z$, where L = 1,2-$B_9C_2H_{11}$ with $z = -1$ or L = Cp with $z = 0$ [35,53,117,118] (for further details, see Section IV).

When polyhedral cobalt *nido*-carbaborane complexes $[(B_8C_2H_{10}NC_5H_5)CoL]^z$ [35,117] or $CpCoB_7C_2H_{11}$ (Fig. 6) are oxidised[118] with iron(III) chloride, a non-terminal hydrogen atom is split off and the closed system of the cobalt *closo*-carbaborane complex is formed:

$$[(7,8\text{-}B_8C_2H_{10}\cdot NC_5H_5)CoL]^z \xrightarrow{FeCl_3} [(2,4\text{-}B_8C_2H_9NC_5H_5)CoL]^{z+1}$$
$$L = C_5H_5,\ z = 0;\ L = 1,2\text{-}B_9C_2H_{11},\ z = -1$$
$$CpCoB_7C_2H_{11} \xrightarrow{FeCl_3} CpCo(6,7\text{-}B_7C_2H_9).$$

The $[1,2,4\text{-}(\eta^5\text{-Cp})Co(7\text{-}C_6H_5NB_8C_2H_9)]^+$ formed is precipitated by $PF_6$ anions. The compound is decomposed in polar solvents[35]. A more stable neutral *closo*-complex $(\eta^5\text{-Cp}).CoB_8C_2H_9C_5H_{10}$ is obtained in 34% yield by oxidising $(\eta^5\text{-Cp}).CoB_8C_2H_{10}.NHC_5H_{10}$ and iron(III) chloride and by subsequent treatment with $K_2CO_3$.[35]

Like the anion $(B_9C_2H_{12})^-$, the cobalt *nido*-carbaborane complex $(1,2\text{-}B_9C_2H_{11}\text{-}3,9'\text{-}Co\text{-}7',8'\text{-}B_8C_2H_{11})^-$ is protonated in the presence of HCl and converted into the complex $(1,2\text{-}B_3C_2H_{11}\text{-}3,9'\text{-}Co\text{-}7',8'\text{-}B_8C_2H_{12})^-$ having the *nido*-structure[35]. The oxidation of the latter with hydrogen peroxide in an alkaline medium gives rise to $(1,2\text{-}B_9C_2H_{11}\text{-}3,1'\text{-}Co\text{-}2',4'\text{-}B_8C_2H_{11})^-$ (yield 75%).[35]

The main product of the reaction between $(\eta^5\text{-Cp})CoB_8C_2H_{10}$ (VIII) and EtOH in the presence of $FeCl_3$ is $2,1,10\text{-}(\eta^5\text{-Cp})Co.B_7C_2H_9$ (IX). It has been suggested[53] that the reaction proceeds via the intermediate formation of the *nido*-complex $8,6,7\text{-}(\eta^5\text{-Cp})CoB_7C_2H_{11}$ (X), which is converted into $3,2,1\text{-}(\eta^5\text{-Cp})CoB_7C_2H_9$ (XI) after dehydrogenation. The thermal rearrangement of the latter gives the final *closo*-complex (XI).[53]

On refluxing in cyclooctane (at approximately 150 °C) complexes with the *nido*-structure can also be converted into cobalt complexes of *closo*-carbaboranes[53,118]:

$$CpCoB_7C_2H_{11} \xrightarrow{\Delta} CpCo(1,10\text{-}B_7C_2H_9)$$

$$(1,2\text{-}B_9C_2H_{11}\text{-}3,9'\text{-}Co\text{-}7',8'\text{-}B_8C_2H_{12})^- \xrightarrow{\Delta} (1,2\text{-}B_9C_2H_{11}\text{-}3,1'\text{-}Co\text{-}2',3'\text{-}B_8C_2H_{10})^-.$$

Thus cobalt complexes of *nido*-carbaboranes usually have the properties of carbaboranes with the *nido*-structure[38].

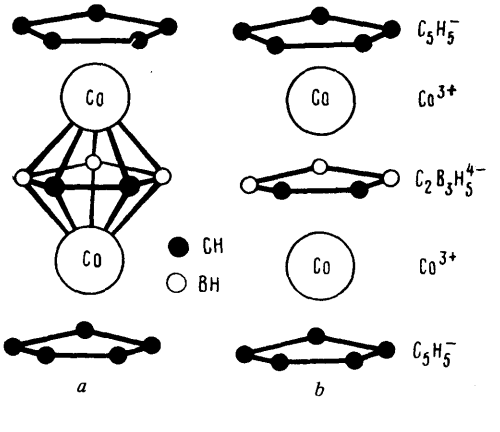



**Figure 24.** Schematic illustration of two different descriptions of the type of bond in the "three-layer" sandwich compound $(\eta^5\text{-CpCo})_2B_3C_2H_5$.

## VI. CARBABORANE-CONTAINING THREE-LAYER SANDWICH STRUCTURES

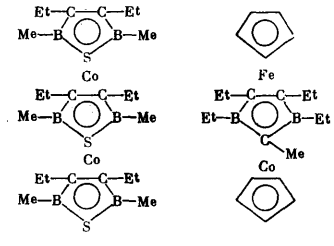
The complex $(\eta^5\text{-CpCo})_2B_3C_2H_5$ is the lowest homologue among the known polyhedral dicobalt complexes of carbaboranes having the general formula $(\eta^5\text{-CpCo})_2B_nC_2H_{n+2}$ ($n = 3$–$10$). The compound exists in the form of four isomers, two of which [1,7,2,3- and 1,7,2,4-$(\eta^5\text{-CpCo})_2B_3C_2H_5$] contain cobalt atoms in the *para*-position with respect to the carbaborane fragment (Fig.24). In the non-Soviet literature compounds of this type are referred to as "triple-decker sandwich structures"; we shall refer to them as three-layer sandwich structures. There exist two equivalent but different qualitative descriptions of the type of binding in these compounds[116,143]. They can be regarded as dicobalt complexes of carbaboranes existing as a result of strong and highly localised covalent interactions (Fig.24*a*). Here the central $Co_2B_3C_2$ fragment contains 16 valence electrons, in agreement with the empirical rule[21,172]. The other alternative description of the binding is based on the formal subdivision of the molecule into three planar ring systems ($C_5H_5^-$, $B_3C_2H_5^{4-}$, and $C_5H_5^-$) and two $Co^{3+}$ ions (Fig.24*b*).

The structures of $1,7,2,3\text{-}(\eta^5\text{-CpCo})_2(3\text{-}MeB_3C_2H_4)$ [115] and $1,7,2,4\text{-}(\eta^5\text{-CpCo})_2(2\text{-}MeB_3C_2H_4)$ have been determined[143]. All the three rings in the complexes are planar but not parallel. The C–C distances in the carbaborane ligand in the 1,7,2,3- and 1,7,2,4-isomers are 1.44 and 1.52 Å respectively.

The results of the study of the $^1H$ and $^{11}N$ NMR of the two isomers show that the electron density in the $B_3C_2H_5$ ligand of the 1,7,2,4-isomer is delocalised over the ring, while in the 1,7,2,3-isomer it is localised mainly at the C–C bond[116]. The presence of substituents in the $B_3C_2H_5$ ligand alters the positions of the chemical shifts for all three rings. Substitution of the Cp ring influences mainly the electron density in the central $B_3C_2H_5$ ligand[116]. The red complex $1,7,2,3\text{-}(CpCo)_2B_3C_2H_5$ absorbs in the ultraviolet at 776 nm, while the green complex $1,7,2,4\text{-}(CpCo)_2B_3C_2H_5$ absorbs in the region of 555 μm.[116] The thermal stability of the 1,7,2,3-isomer is lowest. At 200 °C it is converted into the 1,2,3,5-, 1,2,4,5-, and 1,7,2,4-isomers[23]. The isomers of $(CpCo)_2B_3C_2H_5$ are diamagnetic, resistant to oxidation in the solid state, and do not react with water[115,143].

The isomer $1,7,2,4\text{-}(CpCo)_2B_3C_2H_5$ has been obtained by oxidising the products of the reaction of CpNa and an excess of $CoCl_2$ with the carbaborane $1,6\text{-}B_4C_2H_6$ subjected to preliminary treatment with sodionaphthalene[70,115]. Another isomer and its C-substituted derivatives have been obtained by the reaction of $(RB_4C_2H_6)^-$ with CpNa and $CoCl_2$ followed by oxidation (R = H, Me,[70,115] Ph, or $SiMe_3$ [116]). The 1,7,2,3-isomer or its Cp-substituted derivative $CpCoB_3C_2H_5Co(C_5H_4R)$ (R = H, Me, Et, or $SiMe_3$) has been obtained by the reaction of $[(\eta^5\text{-Cp})CoB_3C_2H_6]^-$ with an excess of $CoCl_2$ and $RC_5H_4Na$ in THF.[70,115,116] The three-layer sandwich structure $1,7,2,3\text{-}(\eta^5\text{-CpCo})_2(\mu\text{-}2,3\text{-}1,3\text{-}C_3H_4B_3C_2H_3)$ is also known[173]. The reaction of $CpCo(CO)_2$ with $(C,C'\text{-}Me_2B_4C_2H_4)_2CoH$ in THF on irradiation or on refluxing in the absence of irradiation yields $1,2,4,5\text{-}(\eta^5\text{-CpCo})_2(Me_2B_3C_2H_3)$ and $(\eta^5\text{-Cp})Co.(Me_2B_3C_2H_3)CoH(Me_2B_3C_2H_5)Co(\eta^5\text{-Cp})$,[98] while the reaction of $CpCo(CO)_2$ with $(Me_2B_4C_2H_4)_2FeH_2$ results in the formation of $1,7,2,3\text{-}(\eta^5\text{-Cp})Co(Me_2B_3C_2H_3)Fe(CO)_3$.[63] In the reactions considered three-layer sandwich structures are formed in low yields (≤5%) and are mixed with other cobalt complexes of carbaboranes[70,98,115,173]. The compounds are isolated by chromatographic methods on silicone gel. The interaction of $Co_2(CO)_8$ with thiaborolene gives rise to the formation of a three-layer sandwich structure (XII) in which the thiadiborolene ligand plays the role of both a μ-ligand and an η-ligand[174]. The Lewis acid 1,3-diborolene reacts with $Co_2(CO)_8$ to form $[\eta\text{-}R_4(Me)B_2C_3]Co(CO)_2$.[175] The interaction of 1,3-diborolene with $CpCo(CO)_2$ in the presence of $[CpFe(CO)_2]_2$ gives rise to the formation of compound (XIII).[175] Compounds (XII) and (XIII) have high thermal stability and are resistent

to oxidation:



(XII) (XIII)

## VII. COBALT σ-COMPLEXES OF CARBABORANES

As a result of the marked electron-deficient properties $B_{10}C_2H_{12}$, the σ-complex $\{[(B_{10}C_2H_{10})_2]_2Co\}^{2-}$ does not contain the usual stabilising ligands (CO or $PR_3$). A cobalt complex is formed when 2,2′-ligand dilithiobiscarbaborane is treated with anhydrous $CoCl_2$.[176,177]

The coordination sphere of the cobalt atom consists of four Co–Co σ-bonds and the Co–H–B bridge bond. In the carbaborane icosahedra there is a tetrahedral arrangement around the cobalt atom[178]. Under the influence of oxidants and reductants, the cobalt in $\{[(B_{10}C_2H_{10})_2]_2Co\}^-$ readily undergoes a change in its formal oxidation state from +3 to +1.[176,177] The complex $(HC_2B_{10}C_2H_{11})Co_2(CO)_6$, obtained from $Co_2(CO)_8$ and $HC{\equiv}CB_{10}C_2H_{11}$, is also known[179]. It does not contain a direct cobalt-carbaborane σ-bond, but is an interesting example of carbaborane-containing acetylenic cobalt complexes[180].

## VIII. COBALT-CONTAINING BORANES

Like the cobalt complexes of carbaboranes, the known cobalt complexes of boranes can be regarded as borane derivatives in the polyhedra of which the BH vertex has been replaced by the CpCo group. Fig.25 illustrates the molecular structure of 2-($\eta^5$-cyclopentadienyl)-2-cobalt-*nido*-$\eta^3$-pentaborane(9).[181] The cobalt atom is located between the Cp and $B_4H_8$ fragments, the latter behaving as a three-electron-donating ligand in relation to cobalt[181]. The complex ($\eta^5$-Cp).Co(5-$B_9H_{13}$), the dicobalt borane complex 1,2-($\eta^5$-CpCo)$_2B_4H_6$, and its substituted derivatives 1,2-($\eta^5$-CpCo)$_2$-(3-cyclo-$C_5H_9B_4H_{15}$), 1,2-($\eta^5$-CpCo)$_2$(4-cyclo-$C_5H_9B_4H_5$), and ($\eta^5$-Cp.Co)$_2$(σ-4-$C_5H_9B_4H_5$) are also known[173].

The crystal and molecular structures of ($\eta^5$-Cp)Co(5-$B_9H_{13}$) have been determined by X-ray diffraction[182]. The complex has the *nido*-structure and contains four bridge bonds, among which three are of the B–H type and one is of the B–H–Co type. The $B_4$ surface of the borane ligand is almost parallel to the plane of the Cp-ring.

The above compounds are resistant to the action of air and water. The complex 2-($\eta^5$-Cp)Co$B_4H_8$ undergoes a polyhedral rearrangement at 200 °C, the cobalt atom migrating to the 1-position[173]. A mixture of complexes has been obtained by adding an excess of $CoCl_2$ and CpNa in THF to a solution of $Na^+[B_5H_8]^-$ at −196 °C; it was then separated by thin-layer chromatography and silica gel. (CpCo)$_2$(3-cyclo-$C_5H_9B_4H_5$) and (CpCo)$_2$(4-cyclo-$C_5H_9B_4H_5$) are apparently formed when the Cp anion is hydrogenated by the hydroborate anion $(B_5H_8)^-$.[173,183] Apart from the compounds enumerated above, ($\eta^5$-CpCo)$_3B_3H_5$, ($\eta^5$-CpCo)$_3B_4H_4$, and ($\eta^5$-CpCo)$_4B_4H_4$ were later isolated in lower yields from the products of the reaction of $Na^+[B_5H_8]^-$ with $CoCl_2$ and CpNa.[173,184] The crystal and molecular structures of 1,2,3-($\eta^5$-CpCo)$_3B_3H_5$ and 1,2,3-($\eta^5$-CpCo)$_3B_4H_4$ gave been determined by X-ray diffraction[185]. Under the conditions of the gas-phase method, not only the complexes described above[183,184] but also clusters containing five boron atoms, ($\eta^5$-CpCo)$_3B_5H_5$ and ($\eta^5$-CpCo)$_3B_5H_4C_5H_5$,[186] have been obtained from pentaborane(9), cyclopentadiene, and cobalt.

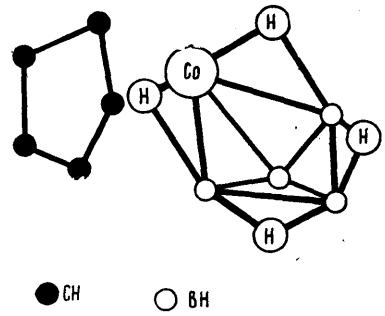



**Figure 25.** The structure of 2-($\eta^5$-cyclopentadienyl)-2-cobalta-*nido*-pentaborane(9).[181]

The symmetrical cobalt borane complex $[(B_{10}H_{12})_2Co]^{2-}$ is formed when the labile $Zn(B_{10}H_{12}).(C_4H_8O)_2$ [187] is acted upon by anhydrous $CoCl_2$ in acetone[188]. The salt $[N(CH_3)_4]_2.[(B_{10}H_{12})_2Co]$ is sparingly soluble in water, is more soluble in alcohol, and is very readily soluble in acetonitrile, acetone, and DMF.

The interaction of $Co_2(CO)_8$ with $NaB_{10}H_{13}$ [188] or $Na_2(B_{18}H_{20})$ [189,190] in THF yielded carbonyl derivatives of cobalt borane complexes $[N(CH_3)_4][(B_{10}H_{12})Co(CO)_3]$ (yield 55%) and $[N(CH_3)_4][(B_{18}H_{20})Co(CO)_3]$ (yield 20%) respectively. The complex $[N(CH_3)_4]_2[Co(B_{10}H_{12})_2]$ catalyses the condensation of nitriles with acetylenes, which leads to the formation of alkylpyridines[191]. The cobalt-containing derivatives of phosphadecaborane ($\eta^5$-Cp)Co(7-$B_{10}H_{10}$PR) and [($\eta^5$-Cp)Co(7-$B_{10}H_{10}$P)]$^-$ (R = Me, Et, n-Pr, or Ph) have been obtained in 15–35% yield by the reaction of 7-$B_{10}H_{12}$PR with $CoCl_2$ and $C_5H_6$ in the presence of an excess of KOH in anhydrous EtOH. The alkylation of [($\eta^5$-Cp)Co(7-$B_{10}H_{10}$P)]$^-$ with RI (R = Me, Et, or n-Pr) gives a high yield of ($\eta^5$-Cp)Co(7-$B_{10}H_{10}$PR). A hypothesis concerning their structure was put forward on the basis of $^{11}B$ and $^1H$ NMR and ultraviolet spectroscopic data[192].

During the preparation of this review for the press, a while series of communications devoted to the development of theoretical ideas about the structure and nature of the bonds in metal carbaborane complexes as well as new methods of synthesis and new compounds were published. A review[193] discusses the nature of the bonds in metal complexes of carbaboranes, their structure, and nomenclature, as well as general problems of the synthesis of such complexes. It includes tabes with data on known complexes; the methods of synthesis of principal metal carbaborane complexes are described. Another review[194] discusses advances in the chemistry of metal carbaborane complexes during the last ten years. These reviews[193,194] include exhaustive information about studies on the chemistry of metal complexes of carbaboranes published up to 1974 inclusive. The bibliography for 1950–1976, reflecting the results of electrochemical research into transition metal complexes, including cobalt complexes of carbaboranes, is presented in another review[195].

The topology of the bonds in polyhedral boranes, carbaboranes, and metal complexes of carbaboranes is discussed from the standpoint of graph theory in a paper by King and Rouvray[196]. Wade's empirical rule[196,197] is used widely in the study of the principal characteristics of various types of rearrangements in carbaboranes and their metal complexes[198] and in the discussion of the structures of cobalt complexes of carbaboranes[199–203]. The *closo*-complexes 1,8,2,3-$(\eta^5\text{-Cp})_2$-1-Fe-8-Co-$B_7C_2H_9$ [199] and $(\eta^5\text{-CpCo})_4B_4H_4$,[200] whose structures have been determined by X-ray diffraction, contain fewer electrons than would be expected from Wade's rule. It is believed[204] that such electron deficiency leads either to partial filling of the *d* orbitals of the transition metal or to the formation of the so-called M–M "extra bond" and the consequent distortion of the geometry of the polyhedron (see, for example, Stanko et al.[199]). The presence of five 12-vertex clusters, containing twenty eight electrons and having both *nido*- and *closo*-structures, also constitutes a deviation from Wade's rule[201,202,205]. The causes of these deviations are also discussed by Nishimura[206].

The structures of the zwitter-ions 5-$[(\eta^5\text{-Cp})\text{Co}(\eta^5\text{-}C_5H_4)$-2,3-$Me_2B_4C_2H_3]\text{Co}(2,3\text{-}Me_2B_3C_2H_5)$ [209] and $(\eta^5\text{-Cp})\text{Co}(\eta^5\text{-}C_5H_4)$-$Me_4B_8C_4H_8$,[210] the mixed cluster 2,3,10-$(\eta^5\text{-Cp})_2$-2-Ni-3-Co-$B_7CH_8$,[211] the cluster $(\eta^5\text{-CpCo})_2(Me_4B_6C_4H_6)$,[203] the isostructural analogue of one of the isomers of the corresponding unsubstituted complex[205], the pentasubstituted compound 8,1,2,3,7-$(\eta^5\text{-Cp})\text{Co}(12\text{-}C_2H_5O\text{-}1,2,3,7\text{-}Me_4B_7C_4H_6)$,[201] the polyhedron $(NMe_4)[(\eta^5\text{-CpCo})_2B_9CH_{10}]$,[209] the three-layer sandwich compound 1,7,2,3-$(\eta^5\text{-CpCo})_2[(\mu\text{-}2,3)$-1,3-$C_3H_4B_3C_2H_3]$, whose planar bicyclic ligand $(B_3C_5H_7)^{4-}$ is isoelectronic with the pentalenide anion $(C_8H_7)^-$,[210] and the metal *closo*-carbaborane complex 1,2-$(\eta^5\text{-CpCo})_2B_4H_6$, in which the Co–Co distance amounts to 2.577 Å and is a maximum for compounds of this kind[211], have been determined by X-ray diffraction.

The gas-phase reaction is used widely for the direct synthesis of cobalt complexes of boranes and carbaboranes. 1-$(\eta^5\text{-Cp})CoB_5H_9$ and 2-$(\eta^5\text{-Cp})CoB_3H_{13}$,[212] $(\eta^5\text{-Cp})\text{Co}(Me_2$-$SnB_4C_2H_4)$,[213] 1,7,2,5-$(\eta^5\text{-CpCo})_2(2,5\text{-}Me_2\text{-}B_5C_2H_5)$, and others[214] have been obtained. In the last instance[214] the synthesis was carried out without the preliminary formation of the carbaborane ligand, metallic cobalt or $CpCo(CO)_2$, pentaborane(9), and but-2-yne may be used as the starting materials. $CpCo(CO)_2$ is being used with increasing fequency as the starting material. The reaction is carried out under ultraviolet irradiation[205] or with heating[218]. The isomeric compounds $(\eta^5\text{-Cp})\text{Co}(Me_4B_6C_4H_6)$ and $(\eta^5\text{-Cp})\text{Co}(Me_4B_7C_4H_7)$ [205] as well as the isomeric compounds 2-[1,3,5-(2′,4′-$B_5C_2H_6$)-1,8,5,6-$(\eta^5\text{-CpCo})_2B_5C_2H_6$] [218] have been obtained in this way.

The method based on the use of the products of the partial degradation of polyhedral carbaboranes and boranes under the influence of nucleophiles continues to be developed[219]. The π-complex $[1,2\text{-}(\eta^5\text{-Cp})CoB_9CH_{10}]^-$ [220] and new cobalt heteroborane complexes containing arsenic[221,222], antimony[222], selenium, and tellurium[223] have also been obtained by this method. $(Me_2B_4C_2H_4)_2FeH_2$ [204] and 2-$(\eta^5\text{-Cp})CoB_4H_8$ [224] have been used as starting materials.

The range of applications of the polyhedral expansion reaction has been increased. The reaction has been carried out for $Me_4B_8C_4H_8$ [205] and the nickel borane complex [*nido*-$(\eta^5$-Cp)$NiB_{10}H_{12}]^-$.[225]

The oxidative coupling reaction, examined previously[98], has been studied in relation to new examples. The synthesis of $(\eta^5\text{-Cp})\text{Co}[(R)(Me_4)B_7C_4H_6]$ (R = H [205] or $C_2H_5O$ [204]) has been achieved by the interaction of $[(Me_2B_4C_2H_4)\text{CoH}.(Me_2B_3C_2H_3)]^-$ [205] or $(Me_2B_4C_2H_4)_2FeH_2$ [204] with $CoCl_2$ in the presence of a cyclopentadienylating agent. The complex $(\eta^5\text{-Cp})CoB_7C_4H_{11}$ and three isomers of the complex $(\eta^5\text{-CpCo})_2B_6C_4H_{10}$ are formed on treating *closo*-1,2,3-$(\eta^5$-Cp)$CoB_4C_2H_6$ or *nido*-1,2,3-$(\eta^5\text{-CpCo})B_3C_2H_7$ with a KOH solution in ethanol.

The tetramethyl derivative $(\eta^5\text{-CpCo})_2(Me_4B_6C_4H_6)$, which is a structural analogue of one of the isomers of the complex $(\eta^5\text{-CpCo})_2B_6C_4H_{10}$, was obtained as the only reaction product under analogous conditions from the corresponding C,C′-dimethyl-substituted cobalt complexes of carbaboranes[205]. The mechanism of the reaction and the causes responsible for it have been discussed[202,205].

The chemistry of the dicarbollylcobalt complex has been enriched by new reactions. When 3,1,2-$(\eta^5\text{-Cp})CoB_9C_2H_{11}$ reacts with sulphur in benzene in the presence of $AlCl_3$, a mixture of mercapto-isomers 3,1,2-$(\eta^5\text{-Cp})\text{Co}(n\text{-HS-}B_9C_2H_{10})$, where n = 8 or 9, is formed. The symmetrical complex gives rise to the S-bridged compound $Cs[Co(3,1,2\text{-}B_9C_2H_{10})_2\text{-}8,8'\text{-S}]$ under these conditions. In the absence of sulphur the final reaction product is the complex $Cs[Co(3,1,2\text{-}B_9C_2H_{10})_2\text{-}8,8'\text{-}(1,2\text{-}C_6H_4)]$ with the phenylene unit in the bridge position[221]. The substitution of the hydrogen at the boron atom in the 8-position, which has enhanced electron density, and the formation of complexes with substituents in the bridge position have been observed also in the reaction of $[Co.(B_9C_2H_{11})_2]^-$ with $NaNO_2$, RCHO (R = H or Me), $SeO_2$, or Te in $H_2SO_4$. Nitrogen-, selenium-, and tellurium-containing complexes are readily alkylated by treatment with $Me_2SO_4$, forming $[Co(B_9C_2H_{10})_2\text{-}8,8'\text{-X}]$, where X = NHMe, $NMe_2$, $Se^+Me$, or $Te^+Me$.[222] The oxidation-reduction properties of "thre-layer" sandwich compounds of the type $(CpCo)_2B_3C_2H_5$ have been investigated by electrochemical methods[228].

Like boranes, cobalt complexes 2-$(\eta^5\text{-Cp})CoB_4H_8$ are deprotonated by sodium hydride and interact with acetylene. In the latter case the product is a carbaborane system, in particular 1,2,3-$(\eta^5\text{-Cp})CoB_5C_2H_7$. The reaction with higher alkynes RC≡CR′ gives rise to "addition products" of the type $CpCoB_4H_8.RC_2R'$, which are regarded as intermediates[219]. Ultraviolet irradiation of 2-$(\eta^5\text{-Cp})CoB_4H_8$ in the presence of $Fe(CO)_5$ gives rise to the mixed cluster 1,2,3-$(\eta^5\text{-Cp})_2Co_2.(CO)_4FeB_3H_3$.[219]

Liquid chromatography has been used successfully for the separation and identification of cobalt π-complexes of carbaboranes[223].

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