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# The Structures and Reactivities of *Closo*- and *Nido*-carboranes

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The structures, methods of synthesis, and chemical properties of *closo*- and *nido*-carboranes are discussed and certain general features of the chemical reactions of carboranes are indicated.
The bibliography includes 228 references.

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## I. INTRODUCTION

Among organic derivatives of the elements, the class of organoboron compounds (carboranes)—compounds having the structure of regular polyhedra or their fragments [1] and consisting of boron and carbon atoms or the atoms of other elements†—shows very great promise.

The most complete compilation of data on the chemistry of carboranes has been published in Grimes' monograph [2] (up to 1970) and in Williams' review [3] (up to 1968). Lipscomb's monograph [4] deals with problems of the theory of the structures and chemical bonding in boron hydrides and carboranes. The latest advances in the chemistry of carboranes have been described systematically in annual reviews [5-8]. Furthermore, individual stages in the development of this field of chemistry were dealt with in a number of early reviews [9-15]. Certain special problems of the chemistry of carboranes are considered in other publications [16-25].

Bearing in mind the considerable interest shown by many investigators in modern problems of the chemistry of organic derivatives of the elements, in particular in the chemistry of carboranes, which is developing vigorously, we thought it useful to supplement and to attempt to survey the available literature data. The main aim of the present review is a consideration of the general characteristics of the chemical reactions of *closo*-, *nido*-, and *arachno*-carboranes, the methods of synthesis, structures, and chemical properties of each representative of these classes of compounds being quoted for reference and illustration.

According to Williams [3], the first information about the existence of carboranes was obtained by Landesman in 1953, who detected by mass-spectrometry ions derived from compounds having the compositions $C_2B_3H_x$, $C_2B_4H_y$, and $C_2B_5H_z$ amongst the pyrolysis products of a mixture of diborane and acetylene, their overall yield with respect to the amount of diborane which reacted being less than 1%. Later, Keilin obtained the same mixture (in a yield of about 2%) from pentaborane(9) and acetylene in an electric discharge. The lower limit to the number of hydrogen atoms, $C_2B_4H_{y\geq 6}$ and $C_2B_5H_{Z\geq 7}$, was established on the basis of mass-spectrometric data and it was concluded that the compounds have a closed structure. In 1956 Good repeated this investigation and isolated compounds having the compositions $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$. According to mass-spectrometric, $^{11}B$ NMR, and $^1H$ NMR data, the only possible structure for $C_2B_5H_5$ proved to be that of a trigonal bipyramid. Octahedral and pentagonal bipyramidal structures were proposed respectively for $C_2B_4H_6$ and $C_2B_5H_7$. These data were published at the beginning of the 1960s. [26,27] Good and Williams suggested that the compounds obtained be called carboranes. Subsequently, this name was extended also to other compounds whose molecules consist of closed polyhedra or their fragments and contain boron and carbon atoms.

Reports of the synthesis of yet another representative of the family of carboranes—$C_2B_{10}H_{12}$ and its *C*-derivatives obtained from decaborane(14) ($B_{10}H_{14}$) or its complexes with Lewis bases ($B_{10}H_{12}L_2$) and compounds of the acetylene series—were published in 1962-1963. Thermal isomerisation (450-500°C) of the 1,2-isomer yielded the 1,7-isomer [28] and at a higher temperature also the 1,12-isomer of carborane(12). [29]

Carboranes with 9,8,7, and 6 boron atoms in the polyhedron were obtained by the degradation of 1,2- and 1,7-$C_2B_{10}H_{12}$. [30-32] The compound $Me_2C_2B_6H_6$ was isolated by Williams and Gerhart from the products of the reaction of hexaborane(10) with dimethylacetylene [33]. Thus systematic studies yielded all the representatives of the homologous series of *closo*-carboranes having the general formula $C_2B_nH_{n+2}$. *closo*-Carboranes containing one and three carbon atoms in the molecule have now been also synthesised.

Reports of the synthesis of a representative of *nido*-carboranes ($C_2B_4H_8$), i.e. carboranes with an open structure, appeared at the beginning of the 1960s. [34] *nido*-Carboranes containing up to four carbon atoms in the molecule are now known.

$C_2B_7H_{13}$, the first representative of *arachno*-carboranes, was reported in 1966. [35] The second *arachno*-carborane ($C_2B_8H_{14}$) became known comparatively recently [36].

† Compounds containing in the molecule nitrogen, phosphorus, arsenic, sulphur, germanium, silicon, etc. atoms as well as transition metal atoms have been obtained. In the present review the chemistry of heteroboranes, heterocarboranes, metalloboranes, and metallocarboranes is not considered, but the general features of the chemistry of carboranes can be extended also to these classes of compounds.

## II. CLASSIFICATION AND NOMENCLATURE. THE NATURE OF BONDING IN CARBORANES

In accordance with Williams' suggestion [1], carboranes are classified as follows: *closo*-carboranes $C_0-_2B_nH_{n+2}$, *nido*-carboranes $C_0-_4B_nH_{n+4}$, and *arachno*-carboranes $C_0-_6B_nH_{n+6}$; the case with $C_0$ corresponds to boron hydride (boranes).

### 1. Nomenclature

According to the recommendations by the Commission on Nomenclature of the American Chemical Society [37], the names of these compounds are devised in accordance with the following rules: initially the location of the carbon atoms in the molecule is indicated, then the number of carbon atoms is stated, and a prefix is added characterising the type of structure (*closo*- or *nido*-); next follows a Greek numeral corresponding to the total number of atoms in the molecule and the ending borane is added; finally the number of hydrogen atoms is indicated in brackets.

For anions, the method of forming the name is on the whole the same, but the number of hydrogen atoms is stated at the beginning, the ending borane is replaced by borate, and the charge of the anion is indicated in brackets. For example, the compound 1,10-$C_2B_8H_{10}$ is called 1,10-dicarba-*closo*-decaborane(10), 7,8-$C_2B_9H_{13}$ is 7,8-dicarba-*nido*-undecaborane(13), and 7,8-$C_2B_9H_{12}^-$ is dodecahydro-7,8-dicarba-*nido*-undecaborate(1-).

The fundamental principles of the numbering of atoms in boron hydride and carborane molecules are as follows. In *closo*-carboranes atoms located in planes perpendicular to the highest-order symmetry axis are numbered clockwise in succession starting with the topmost atom. For *nido*-carboranes, one employs their planar projection and the structure is considered from the side opposite to that of the open face. The numbering is also clockwise and begins with the atoms closest to the centre of the projection. The numbering must be such that carbon atoms and those of other elements have the minimum numbers (Fig. 1)

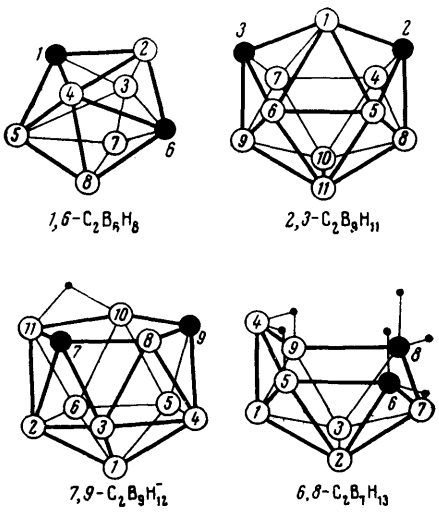



Figure 1.

### 2. Isoelectronic Series

In the chemistry of carboranes it is convenient to distinguish isoelectronic series [3], i.e. series of compounds whose molecules have the same geometrical and electronic structures, differing from one another in the CH/$BH^-$ or CH/$BH_2$ ratios of the numbers of different units, $BH^-$ or $BH_2$ being equivalent to the CH structural unit. As an example, one may quote the series $B_6H_{10}$, $CB_5H_9$, $C_2B_4H_8$, $C_3B_3H_7$, $C_4B_2H_6$ or $B_6H_8$‡, $CB_5H_7$, and $C_2B_4H_6$ (Figs. 2 and 3).

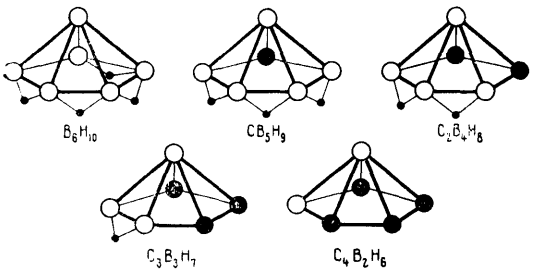



Figure 2.

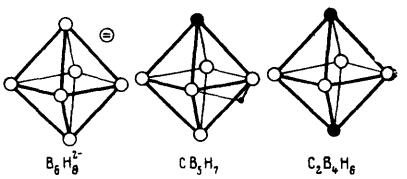



Figure 3.

For *closo*-compounds, the CH/$BH^-$ series can be represented as follows in a general form: $B_{n+2}H_{n+2}^{2-}$, $CB_{n+1}H_{n+2}^-$, and $C_2B_nH_{n+2}$. If this electronic series is extended by yet another CH unit, we obtain the family $C_3B_{n-1}H_{n+2}^+$. A compound of this type must have a positive charge (+1), but the abstraction of a proton should make the molecule neutral as a whole ($C_3B_{n-1}H_{n+1}$). A compound of this type has been obtained ($C_3B_5H_7$); [39] it belongs to the isoelectronic series $C_3B_5H_8^+$, $C_2B_6H_8$, ($CB_7H_8^-$), and $B_8H_8^{2-}$ (Fig. 4).

The following series may be quoted as an example of a CH/$BH^-$ isoelectronic series of compounds with an open structure: $C_2B_8H_{12}$§, $CB_9H_{12}$¶, and $B_{10}H_{12}^{2-}$ (Fig. 5).

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‡ $B_6H_8$ has not been obtained, but $B_6H_6^{2-}$ does exist. Formally, protonation of the latter should yield $B_6H_8$, analogously to the reaction $B_{10}H_{10}^{2-} + 2H^{2+} \rightarrow B_{10}H_{12}$. [38]

§ Obtained for the isomer $C_2B_8H_{12}$. [40,41]

¶ A $C$-$\overset{+}{N}R_3$-substituted derivative of this carborane ($R_3NCB_9H_{11}$) has been obtained; the molecule is neutral as a result of the presence of the cationic fragment $R_3\overset{+}{N}$. [35]

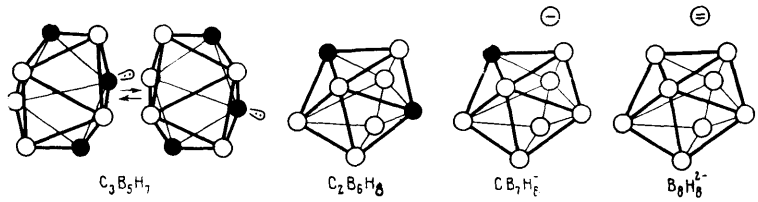



Figure 4.

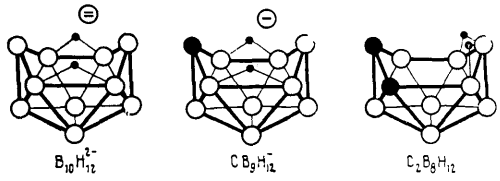



Figure 5.

The above isoelectronic series can be significantly extended by employing the atoms of other elements as the structural units of the polyhedral molecules, such as those of aluminium, gallium, zinc, germanium, tin, lead, nitrogen, phosphorus, sulphur, arsenic, and others.

Since the isoelectronic compounds have corresponding structures, it follows that carbon and other atoms are involved in the formation of the system of bonding orbitals in the same way as boron atoms, i.e. all the principles governing the formation of chemical bonds proposed for boron hydrides[4] apply to them. When transition metal atoms are considered as structural units, account must be taken of the specific character of their bonds with the carborane ligand. Transition metal complexes with carborane ligands have been examined in detail in Hawthorne's reviews[19,21-23].

## 3. The Three-centre Bond and the Influence of the Carbon Atom on Electron Distribution in Carboranes

The characteristics of the structure and chemical bonding in boron hydrides and carboranes have been explained by postulating the formation of a two-electron chemical bond between three atoms (a three-centre bond). In the non-excited state there are two electrons in the three-centre bonding orbital. In boron hydride and carborane molecules all the atomic orbitals of each atom are involved in the formation of a chemical bond and all the resulting bonding orbitals are filled with electrons. Three different types of three-centre bonds can be formed: the central B–B–B bond, the open B–B–B bond, and the open B–H–B bond.

In the central B–B–B bond each atom provides one hybridised atomic orbital, and the orbitals overlap in such a way that the maximum electron density is in the centre of the triangle (Fig. 6*a*). In the open B–B–B bond the central atom provides a *p* orbital and the other two supply hybridised atomic orbitals, their overlapping being of the type shown in Fig. 6*b*. In the open B–H–B bond the central hydrogen atom provides the *s* orbital for the formation of the bond and the two boron atoms provide their hybridised atomic orbitals (Fig. 6*c*). In case *a* 2/3 of an electron formally corresponds to each atom forming the three-centre bond, and in cases *b* and *c* there is one electron per central atom, while the other two atoms each have half an electron. The principles governing the calculation and description of the bonding in boron hydrides and carboranes have been described in detail in Lipscomb's monograph[4].

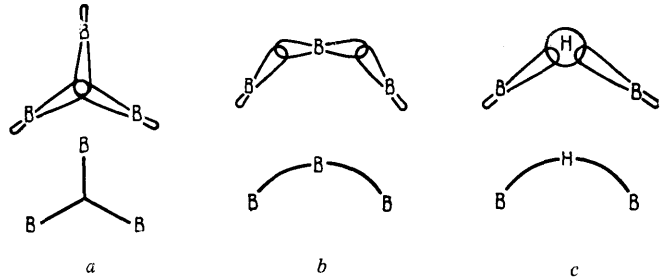



Figure 6.

When highly symmetrical $B_nH_n^{2-}$ anions and certain carboranes were considered, it proved convenient to describe these structures on the hypothesis that molecular orbitals delocalised over the entire molecule are present[43-46].

Using the Edmiston–Ruedenberg method, Lipscomb and coworkers recently determined the degree of localisation of the orbitals for a series of carboranes and introduced the concept of fractional three-centre bonds, i.e. essentially of specifically delocalised three-centre bonds embracing more than three atoms of the molecule[47-51]. It was shown that the valence structures of boron hydrides can be described without resorting to open three-centre B–B–B bonds[50,52]. For example, Fig. 7 illustrates the valence structure of decaborane[53], used until 1971 and proposed by Laws et al.[51] On the other hand, valence structures involving open three-centre B–C–B bonds were suggested for some of the carboranes investigated[50].

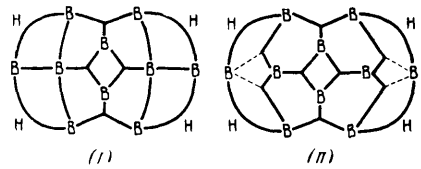



Figure 7.

Fig. 8 presents the valence structure proposed recently for the compounds 1,2-$C_2B_4H_6$,[50] 1,6-$C_2B_4H_6$,[50] 2,3-$C_2B_4H_8$,[49] and 2,4-$C_2B_5H_7$.[47,48]

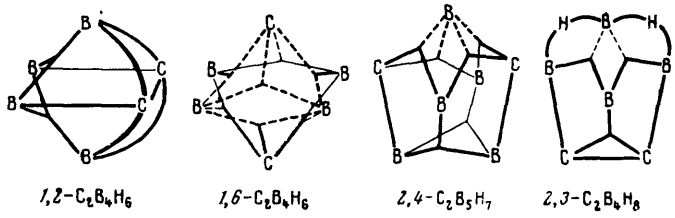



Figure 8.

Having surveyed the available data, Lipscomb and coworkers[50] formulated several additional conclusions the essential features of which are as follows:

(1) there exist unique valence structures for many boranes and carboranes ($B_2H_6$, $B_4H_{10}$, $B_5H_{11}$, $B_6H_{10}$, 1,2-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 2,3-$C_2B_4H_8$, etc.);

(2) the concept of fractional three-centre bonds can be successfully applied to certain boron hydrides and carboranes;

(3) for the description of boron hydrides, it is not obligatory to resort to the concept of the open B–B–B three-centre bond;

(4) in contrast to boron hydrides, the employment of the concept of the open three-centre bond in order to describe the valence structure is useful for only some carboranes.

Since the carbon atoms in carboranes are involved in the formation of three-centre and two-centre bonds, like boron atoms, and bearing in mind that the charge of the carbon nucleus is greater by unity than that of the boron nucleus, the appearance of an excess positive charge on the carbon atoms (at least in relation to the boron atoms equivalent in the structural sense) may be expected. The polyhedral species $B_nH_n^{2-}$ have a 2- charge and in a symmetrical structure, for example the icosahedral structure, the charge is distributed uniformly among all the boron atoms. The replacement of two BH structural units by two CH units leads to a molecule which is neutral as a whole. Two "superfluous" electrons remain (in $B_nH_n^{2-}$), but, instead of being localised, are distributed over the entire molecule. As a result, the carbon atoms bear a considerable positive charge.

Certain chemical properties of carboranes and of the functional groups linked to carbon atoms are due to the excess positive charge on the carbon atoms. This is manifested by the acidity of the hydrogen atoms in the C–H bonds, by the cleavage of the C–C and C–element bonds with substituents in certain functional derivatives of carboranes, by the $^{13}C$ NMR spectra, and by other physicochemical properties. This factor can also account for the electron-accepting effect of the corresponding carboranyl group in the carboranes investigated.

The presence of a positive charge on the carbon atom leads to the "withdrawal" of the electron densities from the neighbouring boron atoms, and these atoms of the carborane nucleus are in fact involved in nucleophilic reactions, while electrophilic reactions involve the boron atoms most remote from carbon[44,45].

The general ideas concerning the chemical reactions and their possible mechanisms are discussed in Section VI.

## III. THE SYNTHESIS, STRUCTURE, AND PROPERTIES OF *CLOSO*-CARBORANES

### Dicarba-*closo*-pentaborane(5) ($C_2B_3H_5$)

Of the three possible isomers of the first representative of *closo*-carboranes, two are known—1,2- and 1,5-$C_2B_3H_5$ (Fig. 9). According to a molecular orbital calculation, the thermodynamic stability of the $C_2B_3H_5$ carborane isomers decreases in the sequence 1,5->1,2->2,3-.[53] Among these isomers, 1,5-$C_2B_3H_5$ is the most readily available and has been most thoroughly investigated. For example, 1,2-$C_2B_3H_5$ was obtained by Grimes[54,55] in the form of the *CB*-dimethyl derivative in a mixture with other carboranes by the reaction of acetylene and diborane in an electric discharge. The structure with the methyl groups in the 2- and 3-positions has been proposed for this compound on the basis of $^{11}B$ NMR, $^1H$ NMR, infrared and mass-spectrometric data.

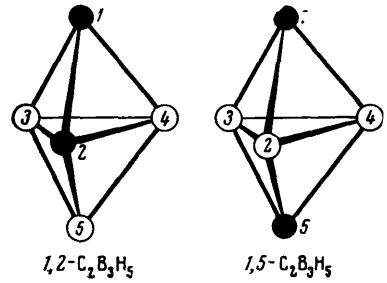



Figure 9.

The 1,5-$C_2B_3H_5$ isomer was detected in the pyrolysis products of a mixture of acetylene and diborane[3]. It is also formed, in a mixture with other carboranes, by the reaction of pentaborane(9) with acetylene in an electric discharge[26]. Methods have been developed for the synthesis of the lowest carboranes in high yields[56–58]. The interaction of pentaborane(9) and acetylene in a stream at 500–600°C using hydrogen as the carrier gas leads to a 70% yield of a mixture of the lower carboranes containing about 40% of 1,5-$C_2B_3H_5$.[56] Pyrolysis of 2,3-$C_2B_4H_8$ at 450–460°C for 10 s gives a 100% yield (25–30% conversion) of a mixture of the same carboranes containing 40% of 1,5-$C_2B_3H_5$.[57,58] The structure of the carborane was established on the basis of $^{11}B$ NMR, $^1H$ NMR, infrared and mass-spectrometric data[26]. The exact molecular structure of 1,5-$C_2B_3H_5$ was determined by electron diffraction[59].

1,5-$C_2B_3H_5$ is resistant to the action of air, water, carbon dioxide, and acetone at room temperature. Also at room temperature, the carborane mixed with $B_2D_6$ exchanges the hydrogen atoms linked to boron for deuterium[26]. The chemical stability of this compound can be explained by its high electronic symmetry. The breakdown of the symmetry following the introduction of polar substituents results in a decrease of stability[60]. For example, the adduct of 1,5-$C_2B_3H_5$ with triethylamine and the product of the halogenation of the carborane are stable only at a low temperature (−78°C). With increase of temperature, the compounds decompose. On the other

hand, derivatives of the carborane with non-polar substituents are stable. When, 1,5-$C_2B_3H_5$ is heated to 350°C in sealed tubes for 9 h, it dimerises with formation of a B–B bond between two $(C_2B_3H_4)_2$ bipyramids. The formation of a small amount of the trimer $C_2B_3H_4(C_2B_3H_3)C_2B_3H_4$ has also been suggested. The reaction of 1,5-$C_2B_3H_5$ with methylacetylene leads to an interesting result. *B*-(*cis*-prop-1-enyl)-1,5-dicarba-*closo*-pentaborane ($C_2B_3H_4$. .$C_3H_5$)—the product of the addition of the *closo*-carborane to the acetylene derivative—is formed in 20% yield after 24 h at 165°C.[60] At 300°C, 1,5-$C_2B_3H_5$ interacts with diborane to form 3,6-$C_2B_6H_{10}$ in a yield less than 5%.[61]

Monocarba-*closo*-hexaborane(7) ($CB_5H_7$)

This compound is obtained in the decomposition of 1-methylpentaborane(9) in an electric discharge[62]. Another method of synthesis involves the pyrolysis of alkylpentaboranes(9).[63] According to $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data, $CB_5H_7$ has an octahedral structure (Fig. 10). It is of interest to note that the bridging hydrogen atom is not localised between two boron atoms, but executes tautomeric transitions with $\Delta G = 14$ and 12 kcal mole$^{-1}$ for $CB_5H_7$ and $CH_3CB_5H_6$ respectively[63]. This is reflected in the $^{11}B$ NMR spectra, which contain three doublets with 1 : 2 : 2 intensity ratios at −30°C, while at 110°C the spectrum consists of two doublets with a 1 : 4 intensity ratio in consequence of the rapid transitions of the bridging hydrogen atom between the boron atoms in the 2-, 3-, 4-, and 5-positions, i.e. the boron atoms in these positions are indistinguishable by the above method. It is suggested that the tautomeric transitions take place via a transition state with a bridging hydrogen atom between the boron atoms in the 3- and 6-positions[63]. When acted upon by bases, the $CB_5H_7$ molecule splits off the bridging hydrogen atom with formation of the anion $CB_5H_6^-$.[64]

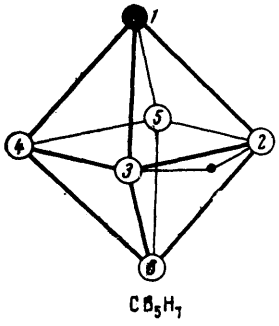



Figure 10.

Dicarba-*closo*-hexaborane(6) ($C_2B_4H_6$)

Both possible isomers of dicarba-*closo*-hexaborane with the carbon atoms in the 1,2- and 1,6-positions have been obtained (Fig.11). It is formed in a mixture with other carboranes by the reaction of acetylene with pentaborane in an electric discharge[65]. The analogous interaction of acetylene with diborane leads to a mixture of products containing 1,6-$C_2B_4H_6$.[54,55] The best method for the synthesis of a mixture of $C_2B_4H_6$ isomers on a preparative scale involves the decomposition of $C_2B_4H_8$ by ultraviolet radiation[66]. The yields of the 1,2- and 1,6-isomers in this reaction reach 15 and 20% respectively, with the simultaneous formation of 15% of 1,5-$C_2B_3H_5$. 1,2-$C_2B_4H_6$ is formed in a low yield (3–5%) in the pyrolysis of $C_2B_4H_8$ at 450°C in the course of 0.5 s; the yield of the 1,6-isomer in this reaction is about 20%.[57]

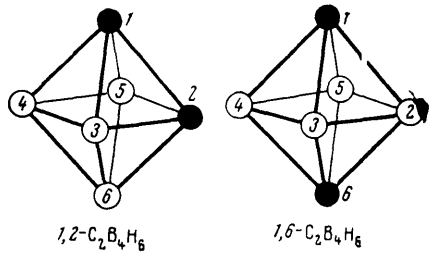



Figure 11.

An octahedral structure has been proposed for 1,2- and 1,6-$C_2B_4H_6$ on the basis of NMR, infrared spectroscopic, and mass-spectrometric data (Fig. 11).[27] The exact molecular structure of 1,6-$C_2B_4H_6$ in the gas phase was determined by electron diffraction[59,67]. The 1,2-$C_2B_4H_6$ [68] and 2-Cl-1,6-$C_2B_4H_5$ [69] structures were investigated by microwave spectroscopy. The results led the authors[69] to the conclusion that there is no additional interaction between the chlorine atom and the carborane nucleus, i.e. the contribution of B–Cl $\pi$ bonding in 2-Cl-1,6-$C_2B_4H_5$ is almost zero.

The 1,6-isomer is thermodynamically more stable than the 1,2-isomer by 15 kcal mole$^{-1}$ [70,71] and at 250°C the latter is converted quantitatively into 1,6-$C_2B_4H_6$.[72] Certain chemical properties of only one of the isomers (1,6-$C_2B_4H_6$) have been studied. The carborane is stable at room temperature in air and does not react with water or acetylene; it exchanges with $B_2D_6$ the hydrogen atoms bound to boron[27]. The reaction of 1,6-$C_2B_4H_6$ with a threefold excess of trimethylamine at room temperature in the course of eleven days leads to the formation of 5-$Me_3N^+$. .(2,4-$C_2B_4H_6$)$^-$. The base introduces an additional electron pair into the nucleus of the *closo*-carborane and converts it into a *nido*-carborane derivative 2,4-$C_2B_4H_8$.[73] The dilithio-derivative $LiCB_4H_4CLi$ is formed slowly by the reaction 1,6-$C_2B_4H_6$ with BuLi in ether at room temperature; the dilithio-derivative reacts with MeI to form a *CC*-dimethyl derivative and treatment with one equivalent of MeI and then with bromine yields $MeCB_4H_4CBr$. The interaction with electrophilic agents proceeds via the boron atoms. Thus bromination in the presence of $AlBr_3$ gives rise to 2-Br-1,6-$C_2B_4H_5$,[74] while iodination in the presence of $Al_2I_6$ leads to the formation of 2-I-1,6-$C_2B_4H_5$.[75] Iodocarborane reacts with trimethylamine to form the quaternary ammonium salt $[Me_3N^+C_2B_4H_5]I^-$, which suggests the mobility of the I atom in the B–I bond.

Treatment of 1,6-$C_2B_4H_6$ with sodionaphthalene followed by the addition of $CoCl_2$ and $NaC_5H_5$ and oxidation with air led to a mixture of products, from which 1,7,2,4-$(CoC_5H_5)_2$. .$C_2B_3H_5$ was isolated in 3% yield[76]. This complex is formally a derivative of the tetra-anion $C_2B_3H_5^{4-}$.

Dicarba-*closo*-heptaborane(7) ($C_2B_5H_7$)

In this case four isomers are possible of which only two (2,3- and 2,4-$C_2B_5H_7$) have been obtained (Fig. 12). The 2,3-isomer has been isolated in a yield of about 1.5% as the *CC*-dimethyl derivative from a mixture with other carboranes formed by the reaction of $B_8H_{12}$ with dimethylacetylene. The structure of the compound has been determined by NMR and infrared spectroscopy [40].

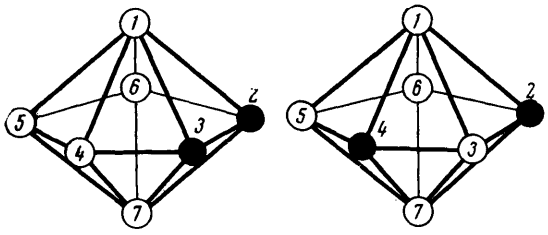



Figure 12.

The 2,4-$C_2B_5H_7$ isomer is more readily available and has been studied in greater detail. It was obtained for the first time by the reaction of $B_5H_9$ with acetylene in an electric discharge [26,27]. It is formed in 40% yield on pyrolysis of $C_2B_4H_8$ at 450°C for 10 s. Pyrolysis for 8 h above 300°C leads to a single volatile reaction product—2,4-$C_2B_5H_7$, in a yield reaching 38%. [57,58,77] This carborane is also formed together with other products from a mixture of diborane and acetylene in an electric discharge [54,55]. A structure has been proposed for 2,4-$C_2B_5H_7$ on the basis of NMR, infrared and mass-spectrometric data [77]. Subsequently the pentagonal bipyramidal structure was confirmed by microwave spectroscopy [78]. The study of the vibrational spectra of 2,4-$C_2B_5H_7$ and two other lower carboranes (1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$) led to the assignment of all the line frequencies, to the determination of the integral line intensities, and to the calculation of the polarisation constants [79].

The 2,4-$C_2B_5H_7$ isomer reacts with BuLi in ether to form the dilithio-derivative. *C*-Methyl, *CC*-dimethyl, *C*-bromo-, and *C*-trimethylsilyl derivatives of 2,4-$C_2B_5H_7$ were obtained from the lithio-derivatives. When the carborane is treated with alcoholic alkali, it undergoes total degradation [80]. Electrophilic reactions involve the boron atom in the 5-position. For example, bromination in the presence of $AlBr_3$ leads to 5-Br-2,4-$C_2B_5H_7$ [80] and chlorination yields 5-Cl-2,4-$C_2B_5H_7$. [81] A mixture of all the isomers (1-, 3-, and 5-$ClC_2B_5H_6$) is formed under the conditions of radical chlorination.

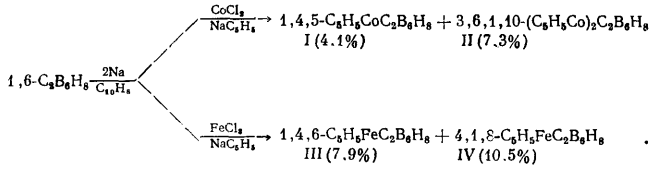
The hydrogen atoms linked to $B_{(3)}$, $B_{(5)}$, and $B_{(6)}$ are involved in isotope exchange with $B_2D_6$ at room temperature, and on heating to 100°C the hydrogen atoms at $B_{(1)}$ and $B_{(7)}$ are also exchanged [82].

When a solution of 2,4-$C_2B_5H_7$ in tetrahydrofuran (THF) is treated with sodionaphthalene and then with $CoCl_2$ and $NaC_5H_5$ and oxidised by air, a mixture of compounds is formed, eight of which have been isolated [83]. Two of these are derivatives of the dianion $C_2B_5H_7^{2-}$ and the tetraanion $C_2B_5H_7^{4-}$. In addition there are the mononuclear and dinuclear complexes $(C_5H_5)Co(C_2B_4H_6)$, $[(C_5H_5)Co]_2(C_2B_4H_6)$, $(C_5H_5)Co(C_2B_6H_8)$, and $[(C_5H_5)Co]_2(C_2B_6H_8)$, which are the products of the disproportionation of the polyhedral carborane ligand $C_2B_5H_7$. The mechanism of the disproportionation reaction has not been established.

Treatment of the reaction mixture obtained by reducing $C_2B_5H_7$ with $FeCl_2$ and $NaC_5H_5$ followed by oxidation leads to the preferential formation of 5-[(2)-2,4-$C_2B_5H_6$]-1,2,4-$C_5H_5Fe^{III}C_2B_4H_5$ and a small amount of 1,2,4-$C_5H_5Fe^{II}HC_2B_4H_6$ and 5-R-1,2,4-$C_5H_5Fe^{III}C_2B_4H_5$, where R = $C_{10}H_7H$ (traces). It is interesting to note that analogous iron complexes with a carborane ligand are formed directly from 2,4-$C_2B_5H_7$ and $Fe(CO)_5$ when they are heated in the gas phase. 1,2,4-$(CO)_3Fe^{III}C_2B_4H_6$ and 5,1,7-$(CO)_3Fe^{III}C_2B_5H_7$ were isolated [84].

Dicarba-*closo*-octaborane(8) ($C_2B_6H_8$)

Six structural isomers are possible. However, only the 1,6-$C_2B_6H_8$ isomer has so far been obtained. It was first isolated in a yield of about 12% as the *CC*-dimethyl derivative by the reaction of hexaborane(10) with dimethylacetylene [33]. The authors proposed a dodecahedral structure (Fig. 13) as the most likely. Hawthorne and coworkers synthesised this isomer in a mixture with other carboranes by the pyrolysis of $C_2B_7H_{13}$; the yield of 1,6-$C_2B_6H_8$ reaches 30%. [31,32,85] A method of synthesis based on the pyrolysis of $C_2B_5H_7$ in the presence of $B_2H_6$ has also been proposed [86]. The cleavage of 1,6-$C_2B_6H_8$ by $Me_4NBH_4$ on heating in diglyme with subsequent treatment by dry HCl leads to a mixture of the monocarba-*nido*-boranes $CB_5H_9$, 1-$MeCB_5H_8$, and 3-$MeCB_5H_8$. [87] The reduction of 1,6-$C_2B_6H_8$ with sodionaphthalene in THF followed by treatment with transition metal salts and $NaC_5H_5$ led to a series of transition metal $\pi$ complexes with the carborane ligands $C_2B_6$: [88]




The reaction constants for the carboranyl group have been determined using *C*-(fluorophenyl)derivatives of 1,6-dicarba-*closo*-octaborane: $\sigma_i = +0.08$ and $\sigma_R^\circ = -0.02$. [89]

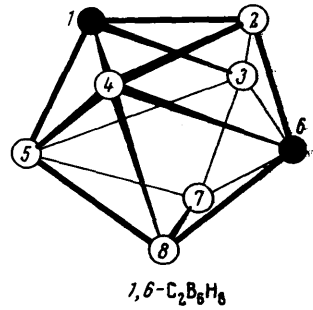
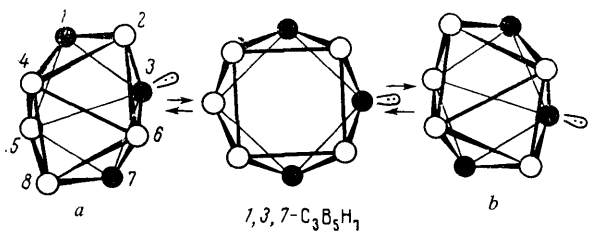



Figure 13.

Tricarba-*closo*-octaborane(7) ($C_3B_5H_7$)

$C_3B_5H_7$ is rightly regarded as one of the most interesting and unusual carboranes and is an example of tricarba-*closo*-boranes—compounds which, according to the isoelectronic principle, should be either positively charged or should exist in the form of neutral molecules with an overal zero charge as a result of the abstraction of a single proton from the carbon atom. Two carbon atoms differ from the third, at which there is a free electron pair.

The carborane $C_3B_5H_7$ was obtained by the pyrolysis of $\mu$-$SiH_3$- or 4-$SiH_3$-2,3-$C_2B_4H_7$ in 15–20% yields [39]. According to $^{11}B$ NMR and $^1H$ NMR data, rapid transitions between structures *a* and *b* (Fig. 14) and time-averaged NMR spectra are observed. Thus the $^{11}B$ NMR spectrum contains three doublets with the intensity ratios 2 : 2 : 1 and the $^1H$ NMR spectrum contains three quartets due to the protons bound to boron and the signal due to the proton in the C–H bond with the relative intensity ratio 5 : 2. $C_3B_5H_7$ is stable in air and withstands heating to 250°C. On heating to 450°C, partial degradation takes place quantitatively, and 2,4-$C_2B_5H_7$ is formed. The fate of the carbon atom split off was not determined.



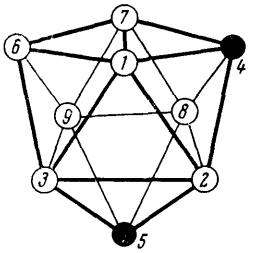

1,3,7-$C_3B_5H_7$

Figure 14.

Dicarba-*closo*-nonaborane(9) ($C_2B_7H_9$)

Six isomers are possible, but the only one known is 4,5-$C_2B_7H_9$ (Fig. 15), which is obtained by the pyrolysis of $C_2B_7H_{13}$ in a yield of about 7% [32,85] together with other carboranes. The yield of $C_2B_7H_9$ increases in the pyrolysis of the sodium salt of $C_2B_7H_{13}$. [85] 4,5-$C_2B_7H_9$ is also formed in a yield of 30% as a result of the slow reaction of 1,6-$C_2B_6H_8$ with $B_2H_6$ at room temperature [90]. The structure of the compound, proposed on the basis of infrared spectroscopic and NMR data [32,85], has been confirmed by the X-ray diffraction analysis of 4,5-$Me_2C_2B_7H_7$. [91]

As expected, electrophilic substitution of 4,5-$C_2B_7H_9$ involves the boron atom in the 6-position, it being most remote from the carbon atoms. 6-Me, 6-Et-, and 6-Br-4,5-$C_2B_7H_8$ have been obtained. The product of exhaustive bromination at 100°C is the tetrabromo-derivative [92] and not the pentabromide. The reduction of 4,5-$C_2B_7H_9$ by sodium in THF followed by treatment with $CoCl_2$ and $NaC_5H_5$ and oxidation by air leads to the formation of the three complexes 2,3,10-$C_5H_5CoC_2B_7H_9$ (I), 4,1,8-$C_5H_5CoC_2B_6H_8$ (II), and 1,2,3,6-$(C_5H_5Co)_2C_2B_8H_{10}$ (III). Compound (II) is the cobalt analogue of the iron–carborane complex 4,1,8-$C_5H_5FeC_2B_6H_8$. The complexes (I) and (III) are derivatives of the dianion $C_2B_7H_9^{2-}$ and the tetra-anion $C_2B_8H_{10}^{4-}$. $\sigma_i = 0.09$ and $\sigma_R^\circ = -0.05$ for the 4,4,5-$C_2B_7H_8$ group were determined using *C*-(fluorophenyl) derivatives. The authors believe that $\sigma_R^\circ$ for this group is higher than the corresponding constant for other carboranes [89].



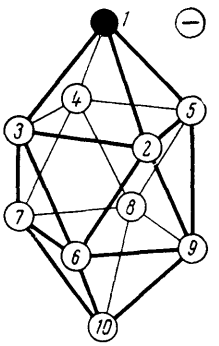

4,5-$C_2B_7H_9$

Figure 15.

Decahydromonocarba-*closo*-decaborate (1-) ($CB_9H_{10}^-$)

Two isomers are possible. One of them, 1-$CB_9H_{10}^-$ (Fig. 16), was obtained by the following reaction [93,42]:

$$Na_2B_{10}H_{13}CN \xrightarrow{2H^+} CB_{10}H_{12}NH_3 \xrightarrow[NaOH,\ H_2O]{Me_2SO_4} CB_{10}H_{12}NMe_2 \rightarrow$$
$$\xrightarrow[Na,\ THF]{} CB_{10}H_{13}^- + 2\text{-}CB_{10}H_{11}^-$$
$$\xrightarrow{310^\circ} 1\text{-}CB_9H_{10}^- + CB_{11}H_{12}^-.$$




1-$CB_9H_{10}^-$

Figure 16.

The electrochemical oxidation of $Et_4N^+CB_9H_{10}^-$ in acetonitrile involves dimerisation with formation of $(Et_4N^+)_2B_{18}C_2H_{18}^{2-}$. According to $^{11}B$ NMR data, the compound has a dimeric structure with a $\sigma$ bond between the boron atoms in the 10- and 10′-positions [94]. Chlorination of $CB_9H_{10}^-$ in aqueous solution at room temperature yields $CB_9H_5Cl_5^-$. According to $^{11}B$ NMR data, the chlorination involves boron atoms remote from carbon. The chlorination of the dimer with formation of the *B*-octachloro-derivative proceeds similarly [94].

Dicarba-*closo*-decaborane(10) ($C_2B_8H_{10}$)

Of the seven possible isomers, three have been obtained: 1,2-, 1,6-, and 1,10-$C_2B_8H_{10}$ (Fig. 17). The 1,2-isomer can be synthesised in a nearly quantitative yield by the pyrolysis of 5,6-$C_2B_8H_{12}$ [95] or its sodium salt at 120–200°C *in vacuo*.[96] 1,2-$C_2B_8H_{10}$ is also one of the products of the thermal decomposition of $C_2B_7H_{11}$.[40] The structure of the carborane was established by infrared spectroscopy and NMR.[95,96] Among chemical properties, its capacity for involvement in oxidation and reduction reactions is noteworthy. When it is treated with sodium in THF, a dianion is formed and protonation of the latter gives 5,6-$C_2B_8H_{12}$ in 30% yield [96]:

$$1,2\text{-}C_2B_8H_{10} \xrightarrow{2e} (C_2B_8H_{10})^{2-} \xrightarrow{2H^+} 5,6\text{-}C_2B_8H_{12}.$$

The 1,6-$C_2B_8H_{10}$ isomer is formed on pyrolysis of $C_2B_7H_{13}$. When this reaction is carried out in the presence of diborane, the yield of 1,6-$C_2B_8H_{10}$ increases to 41%. About 8% of 1,7-$C_2B_{10}H_{12}$ is formed similarly. Other carboranes were not isolated [32,85]. When $B_2H_6$ is allowed to react with sodium salt of $C_2B_7H_{12}^-$ and $C_2B_7H_{13}$ in an ethereal solution, the yield of the isomer reaches 75–80%.[97]

Rapid pyrolysis of 5,6-$C_2B_8H_{12}$ at 500°C *in vacuo* gives a mixture of the two isomers 1,6-$C_2B_8H_{10}$ and 1,10-$C_2B_8H_{10}$.[96] Structures were proposed for 1,6- and 1,10-$C_2B_8H_{10}$ on the basis of infrared spectroscopic and NMR data [32,85] and have been confirmed by X-ray diffraction of 1,6-$Me_2$-1,6-$C_2B_8H_8$.[98] Among the three isomers of *closo*-$C_2B_8H_{10}$, the 1,10-isomer is the most stable. The 1,2- and 1,6-isomers are wholly converted into the 1,10-isomer on heating to 300°C. Among chemical properties, mention should be made of the fairly high acidity of the C–H protons, which are readily split off under the influence of strong bases ($pK_a$ = 27.3 for the 1,10 isomer [99]). Interaction of 1,6- and 1,10-$C_2B_8H_{10}$ with BuLi results in the formation of the dilithio-derivative, from which various *C*-substituted carboranes were obtained [100–102]. Treatment of 1,6-$C_2B_8H_{10}$ with aqueous-alcoholic alkali leads to partial degradation of the carborane with elimination of the boron atom in the 2-position and the formation of $C_2B_7H_{12}^-$. The reaction with piperidine proceeds similarly.

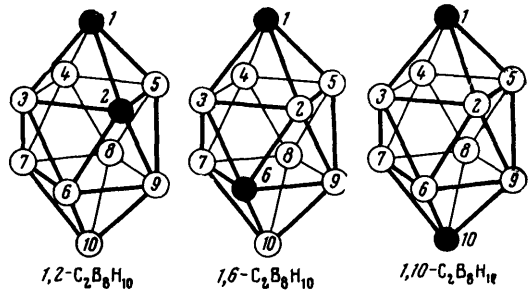



Figure 17.

Under the influence of acids, the 1,6-isomer decomposes to boric acid, and the reaction of 1,6-$C_2B_8H_{10}$ with diborane yields 1,7-$C_2B_{10}H_{12}$. The 1,10-$C_2B_8H_{10}$ isomer is resistant to the action of both acids and alkalis. Photochemical chlorination of 1,10-$MeC_2B_8H_8$ results in the formation of 1,10-$(CCl_3)_2C_2B_8Cl_8$.[100] The dianions derived from 1,6- and 1,10-$C_2B_8H_{10}$ form a wide range of complexes with transition metals [98,103].

$\sigma_i$ = +0.10 and +0.05 and $\sigma_R^\circ$ = −0.02 and −0.01 have been determined for the 1,6-$C_2B_8H_9$ and 1,10-$C_2B_8H_9$ carbonyl groups. The results indicate a weak electron-accepting effect of these groups. The latter is enhanced on passing from a pentacoordinate to a hexacoordinate carbon atom ($\sigma_R^-$ = +0.19 for the 1-1,7-$C_2B_{10}H_{11}$ group). When the carbon atoms are remote from one another, as in $C_2B_{10}H_{12}$, $\sigma_R^\circ$ diminishes [104].

Undecahydromonocarba-*closo*-undecaborate(1-) ($CB_{10}H_{11}^-$)

Five isomers are possible, of which only one, 2-carba-*closo*-undecaborate(1-), is known at present [42,93] (Fig. 18) The $^{11}B$ NMR spectrum of this isomer at 80.5 MHz consists of three doublets with the relative intensities 1 : 5 : 4. The authors suggest that the carbon atom is in the 2-position, the structure undergoing a rapid rearrangement via the *dsd* mechanism to an equivalent structure (Fig. 18). For this reason, the boron atoms in the 1-, 4-, 5-, and 8-positions and also in the 3-, 6-, 7-, 10-, and 11-positions are indistinguishable in the $^{11}B$ NMR spectra, while the atom in the 9-position gives rise to a signal with a relative intensity of unity [94]. It is noteworthy that another mechanism has been proposed for the isomerisation of 2-$CB_{10}H_{11}^-$ to account for the observed spectrum and has been used by Tolpin and Lipscomb [105] for $B_{11}H_{11}^{2-}$ (Fig. 19). If the "opening–closure" of the structure of 2-$CB_{10}H_{11}^-$ involves the atoms in the 1-, 4-, 5-, and 8-positions adjoining the carbon atom in the 2-position, the $^{11}B$ NMR spectrum should also show three doublets with the intensity ratios 1 : 5 : 4, referring to the boron atoms in the 9-position, the 3-, 7-, 6-, 10-, and 11-positions, and the 1-, 4-, 5-, and 8-positions respectively.

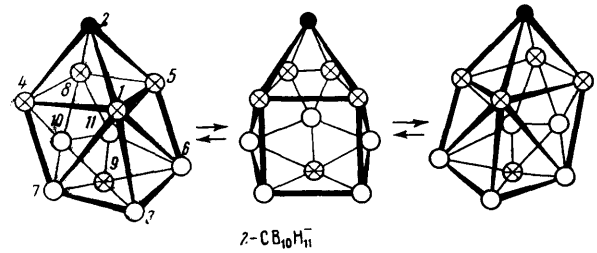



Figure 18.

Dicarba-*closo*-undecaborane(11) ($C_2B_9H_{11}$)

Of the 20 possible isomers of this carborane, only one (2,3-$C_2B_9H_{11}$) is known (Fig. 20); it is formed on pyrolysis of $C_2B_9H_{13}$ at 100°C in a yield of about 22%. Under the same conditions, the yield of the *CC*-dimethyl derivative from the corresponding dicarbaundecaborate reaches 75%.[32,106] A structure was proposed for $C_2B_9H_{11}$ on the basis of $^{11}B$ NMR and $^1H$ NMR data and the formation of the optically inactive $C_2B_9H_{10}Ph$ from the optically active

anion $C_2B_9H_{11}Ph^-$ (this shows that the plane of symmetry passes through the carbon atoms [107]). It was subsequently confirmed by X-ray diffraction [108].

Oxidation of 2,3-$C_2B_9H_{11}$ by iron(III) salts or $H_2Cr_2O_7$ in aqueous solutions results in partial decomposition of the initial carborane with formation of $C_2B_7H_{13}$. [32,109] Treatment of 2,3-$C_2B_9H_{11}$ in benzene at 0°C with chromic acid leads to the "oxidative hydroxylation" product 4,5-$(OH)_2$-2,3-$C_2B_9H_9$. [110]

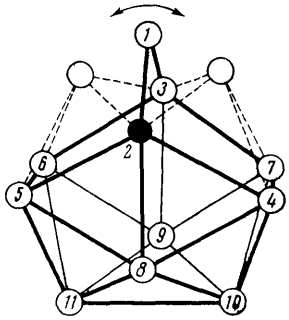


Figure 19.

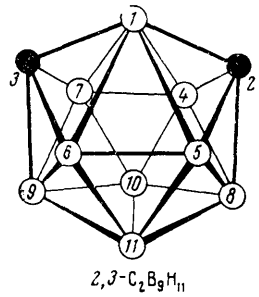



Figure 20.

Nucleophilic agents react with $C_2B_9H_{11}$ to form adducts of the type $C_2B_9H_{11}L$. [106,111,112] The interaction of 2,3-$C_2B_9H_{11}$ with a number of Lewis bases (L) leads to the opening of the *closo*-carborane structure and the formation of 10-L-7,9-$C_2B_9H_{11}^-$. $Bu^-$, $Me^-$, $H^-$, malonic acid derivatives, and the carboranyl anions $C_2B_8H_9^-$ and $C_2B_{10}H_{11}^-$ have been used as L. [111] However, the reaction with other Lewis bases, such as $EtO^-$, $PPh_3$, and $NMe_3$, results in the formation of a 3-substituted derivative 3-L-7,9-$C_2B_9H_{11}$. [112] The formation of 10-substituted dicarbaundecaborate anions in one case and of 3-substituted derivatives in the other may be associated, according to the authors [112], with the fact that, on being attacked by L, the boron atom in the 1-position in $C_2B_9H_{11}$ moves in one case to the side opposite to that from which the Lewis base attacks, with formation of the isomer 10-L-7,9-$C_2B_9H_{11}$, while in the other case the boron atom moves in the opposite direction and 3-L-7,9-$C_2B_9H_{11}$ is formed (Fig. 21). However, we believe that this explanation is inadequate (see Section VI).

2,3-$C_2B_9H_{11}$ interacts with two equivalents of sodium in THF, the second equivalent adding on only in the presence of naphthalene and treatment of the reaction mixture with $CoCl_2$ and $NaC_5H_5$ followed by oxidation with air results in the formation of a mixture of complexes [88]. $\sigma_i = +0.12$ and $\sigma_R^\circ = +0.01$ for the 2-$C_2B_9H_{10}$ carbonyl group [114,115].

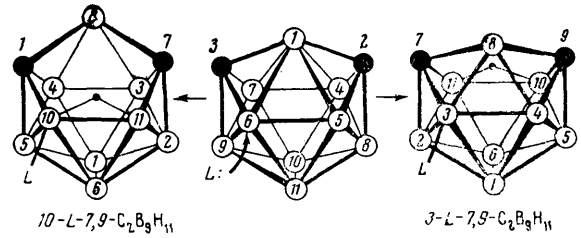



Figure 21.

Dodecahydromonocarba-*closo*-dodecaborate(1-) ($CB_{11}H_{12}^-$)

The only possible isomer $CB_{11}H_{12}^-$ (Fig. 22) is formed together with $CB_9H_{10}^-$ from cyanodecaborane [93,42]. A structure was proposed for the carborane on the basis of the $^{11}B$ NMR spectrum, which contains three doublets with the relative intensities 1 : 5 : 5. The carborane is not oxidised at the anode in acetonitrile up to a potential of 2.4 V. [94]

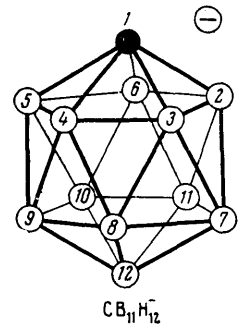



Figure 22.

Dicarba-*closo*-dodecaborane(12) ($C_2B_{10}H_{12}$)

All three possible isomers, 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$, are known (Fig. 23). Since there are very numerous data for the properties of the $C_2B_{10}H_{12}$ isomers, we shall consider only their most general properties. More detailed information can be found in a number of reviews [2,3,15,113].

The thermodynamic stability of the carborane(12) isomers varies in the series $o > m \sim p$.

$$1,2\text{-}C_2B_{10}H_{12} \xrightarrow{450^\circ} 1,7\text{-}C_2B_{10}H_{12}. \quad (1)$$

$$1,7\text{-}C_2B_{10}H_{12} \underset{}{\overset{600^\circ}{\rightleftarrows}} 1,12\text{-}C_2B_{10}H_{12} \quad . \quad (2)$$

At a high temperature an equilibrium mixture of the *m*- and *p*-isomers is formed [116] [Eqn. (2)]. Under the influence of strong bases, protons are readily abstracted at room temperature from the carbon atoms with formation of the corresponding carboranyl anions.

The p*K*a, determined by various methods for the *o*-, *m*-, and *p*-isomers, are respectively 19, 24, and 26 (Kashin et al. [117]) and 23.3, 22.9, and 30 (Petrov et al. [118]). Hawthorne and coworkers showed that treatment with alkalis under severe conditions results in the cleavage of the *o*- and *m*-carborane nuclei with formation of 1,2- and 1,7-$C_2B_9H_{12}^-$. [30,119] 1,12-$C_2B_{10}H_{12}$ undergoes a similar cleavage in low yield to 2,9-$C_2B_9H_{12}$ only in a 20% KOH solution in boiling propanediol. Protonation of this anion leads to the non-polar compound 2,9-$C_2B_9H_{13}$. [120]

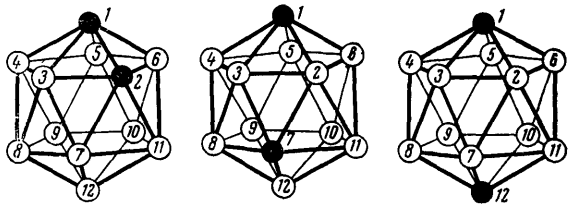



Figure 23.

The stability of the carborane(12) isomers varies in the sequence $o < m < p$. The interaction of derivatives containing one or two alkali metal and alkaline earth metal atoms with electrophilic agents leads to *C*-derivatives. Electrophilic substitution takes place at the boron atoms most remote from the carbon atoms. Substitution in 1,2-$C_2B_{10}H_{12}$ takes place primarily in the 9(12)-position; the 1,7-isomer is substituted in the 9(10)-position and the 1,12-isomer in the 2-position, the only one possible. The ease and rates of electrophilic reactions of the three carborane isomers also vary in the sequence $o > m > p$.

The oxidation of the $C_2B_{10}H_{12}$ isomers by $KMnO_4$ in an acid medium leads to the formation of all the possible *B*-hydroxy-derivatives [121]. Reduction with sodium in liquid ammonia or THF leads to dianions [122] and the oxidation of the dianion obtained from 1,12-carborane(12) gives rise to 1,7-carborane(12), while the oxidation of the dianions derived from 1,7- and 1,2-carboranes(12) leads to the formation of 1,2-carborane(12). [123,124] Treatment of the dianions with $CoCl_2$ or other transition metal salts and $NaC_5H_5$ results in the formation of complexes where the metal atom constitutes the thirteenth vertex of the polyhedron [125,126]. Protonation of the dianions leads to the dicarbadodecaborate(1-) monoanions. The structures of some of these have been determined by X-ray diffraction [127,128]. The molecular structures of *o*-, *m*-, and *p*-$C_2B_{10}H_{12}$ have been determined by electron diffraction [129]. $\sigma i = +0.295$ and $+0.213$, and $\sigma_R^0 = +0.004$ and $-0.036$ have been found for the fluorophenyl derivatives of the corresponding 1,2- and 1,7-carborane isomers respectively [114].

## IV. THE SYNTHESIS, STRUCTURE, AND PROPERTIES OF *NIDO*- AND *ARACHNO*-CARBORANES

### 1. *NIDO*-CARBORANES

#### Dicarbo-*nido*-pentaborane(7) ($C_2B_3H_7$)

Three isomers of $C_2B_3H_7$ are possible. The only one of these obtained, 1,2-$C_2B_3H_7$, was isolated after the reaction of the tetraborane(10) $B_4H_{10}$ with acetylene in the gas phase at 50°C. Its structure (Fig. 24) is based on $^{11}B$ and $^1H$ NMR data [130]. The carborane is stable in the gas phase at 50°C, but decomposes at 100°C. In the liquid state polymerisation with formation of $(C_2B_3H_7)_X$ takes place at temperatures as low as 25°C. The polymerisation is greatly accelerated in the presence of HCl, polar solvents, and other polar substances. In dilute non-polar solutions this compound is comparatively stable. The schemes quoted below illustrate its chemical properties [131]:

$$C_2B_3H_7 + C_2H_2 \xrightarrow{50^\circ} C_4B_2H_6 + \text{solid residue}.$$

To determine the characteristics of the formation of $C_4B_2H_6$, the reaction of $C_2B_3H_7$ with acetylenic compounds labelled with deuterium and $^{13}C$ was investigated. It was shown that the alkyne is inserted preferentially in the C–B bond and to a lesser extent in the C–C bond [132].

$$C_2B_3H_7 + C_2H_4 \xrightarrow{90^\circ} BEt_3 + B_2H_2Et_4;$$
$$C_2B_3H_7 + BMe_3 \rightarrow B_2H_6 + H_2 + \text{solid residue};$$
$$C_2B_3H_7 + NEt_3 \rightarrow C_2B_3H_7 \cdot NEt_3;$$
$$C_2B_3H_7 + NaH \rightarrow \text{polymerisation};$$
$$C_2B_3H_7 + Br_2 \rightarrow Br_2C_2B_3H_7 \xrightarrow{Br_2} BBr_3 + HBr + \text{solid residue}.$$

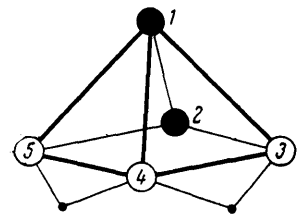


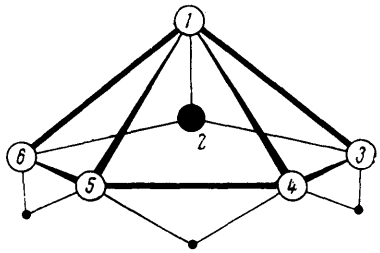

Figure 24.

1,2-$C_2B_3H_7$ reacts with iron pentacarbonyl to form a $\pi$ complex [131]. The reaction of $(\pi\text{-}C_2B_3H_7)Co(\pi\text{-}C_5H_5)$, an analogue of $(\pi\text{-}C_2B_3H_7)Fe(CO)_3$, with sodium hydride, followed by treatment with $CoCl_2$ and $NaC_5H_5$, results in the formation of a complex of the type $[(\pi\text{-}C_5H_5)Co]_2.(\pi\text{-}C_2B_3H_5)$, which is an example of a dinuclear complex with three parallel planar ligands [76].

#### Monocarba-*nido*-hexaborane(9) ($CB_5H_9$)

Of the two possible isomers of this carborane, only the 2-$CB_5H_9$ isomer with the carbon atom at the base of a pentagonal pyramid is known (Fig. 25). This compound is

one of the products of the pyrolysis of methylpentaborane[63]. 2-Et-2-$CB_5H_8$ is formed in 3.3% yield by the reaction of pentaborane with lithium methylacetylide[133]. Methyl derivatives of 2-$CB_5H_8$ are also formed as side products in the synthesis of 2,3-$C_2B_4H_8$.[134] The fully alkylated monocarba-*nido*-hexaborane(9) ($MeCB_5H_3Me_5$) is a side product in the reaction of acetylene with tetraethyldiborane[135,136]. The structure of $CB_5H_9$, proposed on the basis of $^{11}B$ NMR data[137,138], was confirmed by microwave spectroscopy[139]. Pyrolysis of $CB_5H_9$ at 250°C for 3.5 days leads to 1,7-$C_2B_{10}H_{12}$ and $C_2B_7H_{13}$.[140] This method of synthesis of the higher carboranes from the lower carboranes is of definite theoretical interest†.



2-$CB_5H_9$

Figure 25.

Dicarba-*nido*-hexaborane(8) ($C_2B_4H_8$)

Three isomers of this carborane are possible, two of which have been obtained (Fig. 26). A derivative of 2,4-$C_2B_4H_8$ has been synthesised, namely the ammonium inner salt $C_2B_4H_7^-N^+Me_3$ (see p.647).[73] The second isomer 2,3-$C_2B_4H_8$ can be synthesised and is well known. It is formed in a yield of about 40% in the pyrolysis of a mixture of pentaborane(9) and acetylene at 235°C for 40 h.[72] The structure of the carborane, proposed on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data[34,72,141], was confirmed by the X-ray diffraction of its *CC*-dimethyl-derivative[142,143]. The vibrational spectra of the unsubstituted and *C*-methyl-substituted carboranes have been published and discussed[144]. Pyrolysis of 2,3-$C_2B_4H_8$ leads to a mixture of the lowere *closo*-carboranes, the process being the most convenient method for the synthesis of the *closo*-carboranes $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$.[57,58,77] The electrophilic halogenation of 2,3-$C_2B_4H_8$ and its *C*-methyl derivatives involves the boron atoms adjoining the carbon atoms at the base of the molecule[145,146]. This mode of reaction is inconsistent with the charges calculated by the SCF method, according to which electrophilic reactions should involve the boron atom in the 1-position. To account for the above course of reaction, Marynick and Lipscomb[49] carried out a comparative assessment of the bonding orbitals in the molecule and demonstrated the considerable role of the orbitals of the skeleton in the reaction (see Section VI).

† Rietz and Hawthorne[140] suggest that 1,2-$C_2B_{10}H_{12}$ can be obtained from 2,3-$C_2B_4H_8$ and $B_6H_{10}$ and that the composition of the products formed from $B_6H_{10}$, $C_3B_3H_7$, and $C_4B_2H_6$ should be investigated.

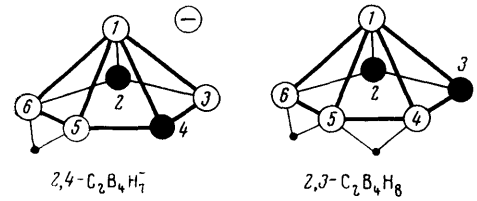



Figure 26.

Isotope exchange between 2,3-$C_2B_4H_8$ on the one hand, and $D_2$ and $B_2D_6$ on the other has been studied and various deuterio-derivatives of this carborane have been obtained[147]. When an ethereal solution of $C_2B_4H_8$ is treated with sodium hydride, the product is dicarba-*nido*-hexaborate(1-) anion ($C_2B_4H_7^-$),[148] which reacts with alkyl halide derivatives of silicon, germanium, boron, lead, tin, and also with chlorosilane and chlorogermane to give the corresponding bridged derivatives, in which the atom of the element is linked by a three-centre bond with two boron atoms of the carborane[149,151]. The interaction of $SiH_2Cl_2$ with two equivalents of $C_2B_4H_7^-$ in THF at 0°C leads to a 70% yield of a compound with two carborane ligands bound to the $SiH_2$ group by two three-centre bonds—$\mu\mu'$-$SiH_2(C_2B_4H_7)_2$ (Fig. 27).[151,152] The compounds obtained with an $MR_3$ or $MR_2$ bridge group containing non-transition elements are good examples illustrating the possibility of the formation of a non-classical chemical bond not only by boron atoms but also by a number of non-electron-deficient elements, including carbon (see Section VI).

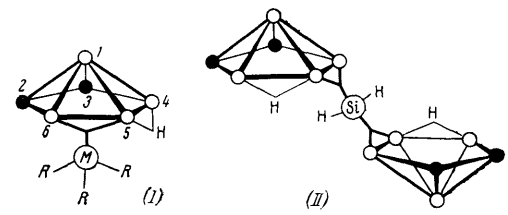


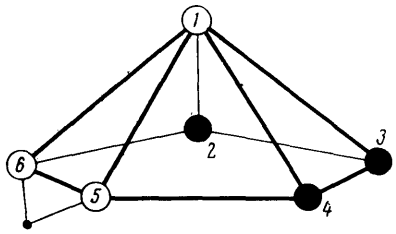

Figure 27.

The reaction of $Na^+C_2B_4H_7^-$ with $(\pi\text{-}C_5H_5)Fe(CO)_2I$ initially leads to a complex in which iron is bounded by a three-centre bond to the carborane ligand, namely $\mu$-[$(\pi\text{-}C_5H_5)$.$Fe(CO)_2$]$C_2H_4B_7$; this compound can be converted in 90% yield into the $\pi$ complexes $(\pi\text{-}C_5H_5)Fe^{II}(\pi\text{-}C_2B_4H_7)$ and $(\pi\text{-}C_5H_5)Fe^{III}(\pi\text{-}C_2B_4H_6)$.[84,153] The interaction of $Na^+$.$C_2B_4H_7^-$ with $NaC_5H_5$ and $CoCl_2$ in THF with subsequent oxidation by air leads to 1,7,2,3-$(C_5H_5Co)_2C_2B_3H_5$.[76] The reaction of 2,3-$C_2B_4H_8$ with an excess of $Fe(CO)_5$ at 240°C also leads to $\pi$ complexes of the transition metal with carborane ligands. 1,2,3-$(CO)_3FeC_2B_4H_6$ and 1,2,3-$(CO)_3FeC_2B_3H_7$ were obtained by this reaction[84,154]

Tricarba-*nido*-hexaborane(7) ($C_3B_3H_7$)

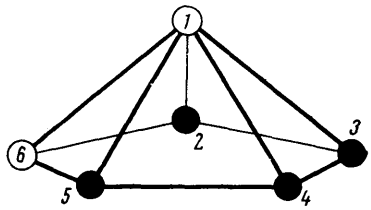
Of the four possible isomers, only one (2,3,4-$C_3B_3H_7$) has been obtained (Fig. 28). *C*-Methyl derivatives of this carborane are formed at 50°C in the gas-phase reaction

between tetraborane(10) ($B_4H_{10}$) with acetylene. The yields of the methyl derivatives 2-$MeC_3B_3H_6$ and 2,3- and 2,4-$Me_2C_3B_3H_5$ are respectively 3.3, 6.5, and 5.3%.[155,156] The interaction of $B_4H_{10}$ with $C_2H_2$ is a first-order reaction with respect to $B_4H_{10}$ and a zero-order reaction with respect to acetylene. The proposed reaction mechanism involves the formation of $B_4H_8$ in the first, slowest stage, and this compound then interacts rapidly with acetylene, giving a solid polymeric residue $(C_2BH_4)_x$ (80%) and a mixture of volatile products, in which 4-$MeCB_5H_8$, 2,3-$C_2B_4H_8$, and 2,3,4-$C_3B_3H_7$ are also present in an overall yield of 2%.[156] In many studies the mechanism of the formation of tricarbohexaborane (7) and its methyl derivatives was studied using $C_2D_2$.[156,157] When 2,4-$Me_2C_3B_3H_5$ and other $C_3B_3H_7$ derivatives are treated with strong bases, a proton is abstracted from the bridging position with formation of the corresponding anions. Treatment of these anions with DCl leads to $\mu$-D-derivatives of $C_3B_3H_7$.[157,158] Treatment of the anion 2-$MeC_3B_3H_5^-$ with pentacarbonylmanganese bromide leads to an adduct, where Mn is linked to a $\sigma$ bond to the boron atom of the carborane ligand according to the authors[153]. When the adduct is heated, two equivalents of CO are evolved and 2Me-1,2,3,4-$(CO)_3MnC_3B_3H_5$ is formed. Heating of 2-$MeC_3B_3H_6$ and 2,3-$Me_2C_3B_3H_6$ with $Mn_2(CO)_{10}$ in the gas phase leads to similar complexes[158].




2,3,4,-$C_3B_3H_7$

**Figure 28.**




2,3,4,5-$C_4B_2H_6$

**Figure 29.**

Tetracarba-*nido*-hexacarborane(6) ($C_4B_2H_6$)

This compound completes the family of the *nido*-carboranes $C_nB_6-nH_{10}-n$ having the structure of a pentagonal pyramid. Of the three possible isomers, only one has been obtained, in which all the carbon atoms are located at the base of the pyramid (Fig. 29). The fully alkylated carborane was synthesised according to the scheme[159]

$$NaR_3BC \equiv CR + ClBR_2 \rightarrow R_2BRC = CRBR_2 \rightarrow C_4B_2R_6.$$

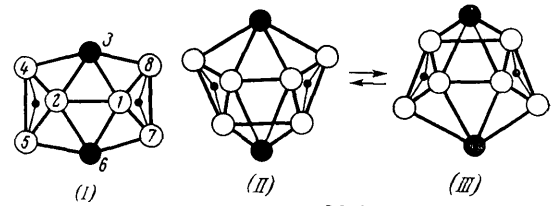
The unsubstituted carborane $C_4B_2H_6$ was obtained by the pyrolysis of 1,2-tetramethylenediborane[63]. The carborane is also formed in 5–10% yield in the reaction of $C_2B_3H_7$ with $C_2H_2$.[131,132] Its structure was established by $^{11}B$ NMR, $^1H$ NMR, infrared[63,159,160] and microwave[161] spectroscopy. According to the authors[161], $C_4B_2H_6$ can be regarded as an analogue of the $\pi$ complexes of the cyclopentadienyl anion in which one of the carbon atoms at the base and the transition metal atom have been replaced by two boron atoms, but this similarity is extremely formal.

Dicarba-*nido*-octaborane(10) ($C_2B_6H_{10}$)

Of the seven possible isomers, only one (3,6-$C_2B_6H_{10}$) has been obtained (Fig. 30). Its yield in the reaction of $C_2B_3H_5$ with diborane is less than 5%:

$$C_2B_3H_5 + {}^3/_2B_2H_6 \xrightarrow{300^\circ} C_2B_6H_{10} + 4H_2.$$

It is suggested that, under the reaction conditions, $B_3H_7$ is formed from $B_2H_6$ and reacts with $C_2B_3H_5$ to give $C_2B_6H_{10}$.[61] The low yield of this carborane is probably due to its instability. Thus in the liquid state 3,6-$C_2B_6H_{10}$ decomposes with formation of mainly $C_2B_6H_8$ and $C_2B_5H_7$. 3,6-$C_2B_6H_{10}$ is the first carborane isoelectronic with $B_8H_{12}$. The structure (I) of the compound was established on the basis of $^{11}B$ and $^1H$ NMR data. The authors[61] also do not rule out the possibility of tautomeric transitions between the equivalent structures (II) and (III) (Fig. 30). They also quote the interatomic distances in the molecule[61].




(I) (II) (III)

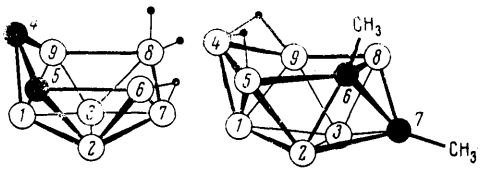
3,6-$C_2B_6H_{10}$

**Figure 30.**

Dicarba-*nido*-nonaborane(11) ($C_2B_7H_{11}$)

This carborane can have 25 isomers depending on the position of the carbon atoms in the molecule. The reaction of octaborane(12) ($B_8H_{12}$) with acetylenic compounds gives an approximately 65% yield of a mixture of two *nido*-carboranes with seven and eight boron atoms in the molecule[40,162]. The unsubstituted carborane $C_2B_7H_{11}$ is interesting because, according to $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data, one of the boron atoms, in the 8-position, is linked by $\sigma$ bonds to two hydrogen atoms, i.e. this compound is the first example of a carborane containing the $BH_2$ group (Fig. 31).[161] It is striking that the *CC*-dimethyl derivative of this carborane, obtained by the

reaction of $B_8H_{12}$ with dimethylacetylene, has a structure different from that of the unsubstituted $C_2B_7H_{11}$ (Fig. 31), which is shown clearly by the $^{11}B$ and $^1H$ NMR spectra[161]. X-Ray diffraction[163] confirmed the structure proposed for $Me_2C_2B_7H_9$ on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopy[40]. The structural differences and the greater stability of the *CC*-dimethyl derivative of $C_2B_7H_{11}$ have been explained by the steric or electronic influence of the methyl groups[162].

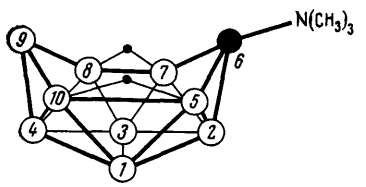



4,5-$C_2B_7H_{11}$ 6,7-$(CH_3)_2$-$C_2B_7H_9$

**Figure 31.**

Monocarba-*nido*-decaborane(13) ($C_1B_9H_{13}$)

Four isomers of $C_1B_9H_{13}$ are possible, of which only the 6-$CB_9H_{13}$ isomer, obtained in the form of the derivative $B_9H_{11}CNMe_3$, is known (Fig. 32). The structure of this carborane was established on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data[42].




6-$N(CH_3)_3$-$CB_9H_{11}$

**Figure 32.**

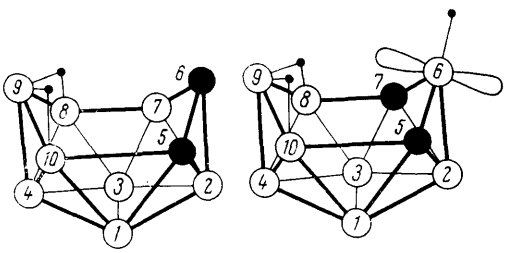
acid medium at 20°C in the course of 4 h.[95] As already mentioned, heating of the 5,6-isomer in *N*-ethylpiperidine-borane yields 1,2-$C_2B_8H_{10}$.[95] Certain other reactions of 5,6-$C_2B_8H_{12}$ have been described[99]:

$$5,6\text{-}C_{12}B_8H_{12} \xrightarrow[\text{vacuum}]{500^\circ} 1,6\text{-} + 1,10\text{-}C_2B_8H_{10};$$

$$5,6\text{-}C_2B_8H_{11}^- \xrightarrow{120\text{–}200^\circ} 1,2\text{-}C_2B_8H_{10} + C_2B_8H_{10}^{2-} + H_2;$$

$$5,6\text{-}C_2B_8H_{12} + 2e \rightarrow C_2B_8H_{12}^{2-} \xrightarrow{200^\circ} 5,7\text{-}C_2B_8H_{10}^{2-} \xrightarrow{H_3O^+} C_2B_7H_{13}.$$

The interaction of 5,6-$C_2B_8H_{12}$ with $EtO^-$ gives a low yield of a new compound of the class of *arachno*-carboranes—6,9-$C_2B_8H_{14}$.[36] Another isomer, 5,7-$C_2B_8H_{12}$ (Fig. 33), was obtained by the reaction of $C_2B_7H_{12}^-$ with diborane[41]. According to the authors[41], the boron atom in the 6-position in this compound is *sp*-hybridised, one *p* orbital remaining free. In the interaction with trimethylamine this orbital and the orbital with the electron pair of the nitrogen atom form the B—N bond. When $C_2B_8H_{12}NMe_3$ is heated to 150°C, *closo*-1,6-$C_2B_8H_{10}$ is formed and treatment with anhydrous HCl in $CH_2Cl_2$ at 80°C gives rise to the initial carborane—5,7-$C_2B_8H_{12}$. Furthermore, treatment with an excess of HCl results in the substitution of the hydrogen atom in the 6-position by chlorine and the formation of 6-Cl-5,7-$C_2B_8H_{11}$, the carborane containing, like the unsubstituted compound, a free *p* orbital. Pyrolysis of the chlorocarborane *in vacuo* leads to *closo*-Cl-1,6-$C_2B_8H_9$ and treatment with $D_2O$ yields $C_2B_7H_{11}D_2$, deuterium being linked to carbon atoms[41].

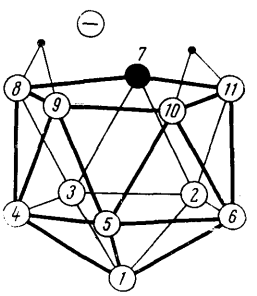


5,6-$C_2B_8H_{12}$ 5,7-$C_2B_8H_{12}$

**Figure 33.**

Dicarba-*nido*-decaborane(12) ($C_2B_8H_{12}$)

Of the sixteen possible isomers of $C_2B_8H_{12}$, two have been obtained: 5,6- and 5,7-$C_2B_8H_{12}$ (Fig. 33). As already mentioned, the 5,6-$C_2B_8H_{12}$ isomer is the main product of the reaction of octaborane(12) ($B_8H_{12}$) with acetylene. The *CC*-dimethylderivative is obtained by the analogous reaction with dimethylacetylene. A structure has been proposed for the carboranes on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data and also the fact that the decomposition of the *CC*-dimethyl derivative in propionic acid on a palladium catalyst results in the formation of n-butane[40,162]. 5,6-$C_2B_8H_{12}$ is also formed in 90% yield in the oxidation of 7,8-$C_2B_9H_{12}$ by $Fe^{3+}$ in an



7-$CB_{10}H_{13}^-$

**Figure 34.**

Monocarba-*nido*-undecaborane(14) ($C_1B_{10}H_{14}$)

Among the three possible isomers, the derivatives of only one isomer, with the carbon atom in the open face, have been obtained (Fig. 34). The anion derived from this carborane ($CB_{10}H_{13}^-$) can be obtained either from cyanodecaborane [42,93] or by the reaction of decaborane with alkyl isocyanides [42,93,164-167]. Among the chemical properties of $C_{10}H_{13}^-$, electrophilic halogenation reactions have been mentioned. The reaction with $Br_2$ leads to mono- and di-bromo-derivatives. At 0°C chlorine decomposes this anion. The reaction with iodine does not occur even in the presence of catalysts. In electrophilic halogenation reactions $R_3NCB_{10}H_{12}$ is less reactive [167]; for example, bromination takes place only in the presence of $AlCl_3$. Numerous *C*- and *B*-derivatives of $CB_{10}H_{13}^-$ have been described [42]. $\pi$ Complexes with transition metals have been obtained from $CB_{10}H_{11}^{3-}$ and $H_3NCB_{10}H_{10}^{2-}$. [42]

Dicarba-*nido*-undecaborane(13) ($C_2B_9H_{13}$)

Of the nine possible isomers, two compounds with the carbon atoms in the open face and the isomer with the carbon atoms in the 2,9-positions have been synthesised [120] (Fig. 35). 7,8-, 7,9-, and 2,9-$C_2B_9H_{13}$ are obtained on protonation of the corresponding dicarbaundecaborate anions, which are synthesised by the alkaline cleavage of 1,2- 1,7-, and 1,12-$C_2B_{10}H_{12}$. Structures have been proposed for the carboranes and their anions on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data [30, 31,32,106,119,120]. The 7,9-isomer is much less stable than the 7,8-isomer [32].

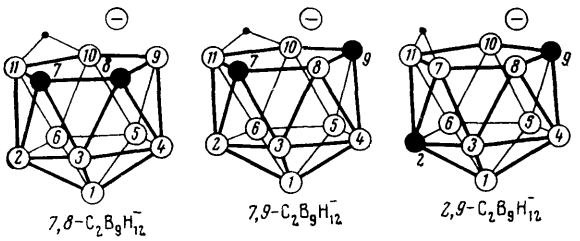



Figure 35.

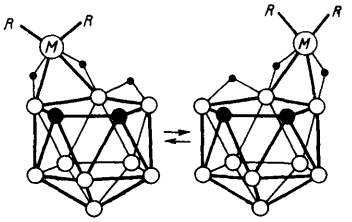



Figure 36.

The thermal decomposition of these carboranes, leading to *closo*-2,3-$C_2B_9H_{11}$, has already been mentioned [31,32]. The interaction of 7,8-$C_2B_9H_{13}$ with trialkylaluminium and trialkylgallium leads to $R_2Al.C_2B_9H_{12}$ and the corresponding gallium derivatives [168]. According to $^{11}B$ and $^1H$ NMR, the $AlMe_2$ group undergoes tautomeric transitions between two equivalent positions (Fig. 36). [169] X-Ray diffraction confirmed the conclusion that the $AlMe_2$ group is in the "bridging" position [170]. Heating of *nido*-$B_9C_2H_{12}MR_2$ (M = Al or Ga) in benzene leads to *closo*-1,2,3-$RMC_2B_9H_{11}$. On heating to 450°C, these compounds isomerise to a metallocarborane with the carbon atoms in the *m*-positions.

The reactions of both *nido*- and *closo*-metallocarboranes with $TiCl_4$ result in the formation of catalysts resembling Ziegler catalysts, in the presence of which ethylene polymerises at 25°C and 1 atm. [168] 7,8-$C_2B_9H_{13}$ can be titrated as a strong monobasic acid [30,32] and under the influence of strong bases the second bridge proton is also abstracted [119].

The structure of dicarba-*nido*-undecaborate(1-) anions was determined on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data. The hydrogen atom in the bridge position in 7,8-$C_2B_9H_{12}$ undergoes rapid tautomeric transitions between the 9,10- and 10,11-positions. In 7,9-$C_2B_9H_{12}$ the bridge hydrogen atom is linked to the atoms in the 10- and 11-positions. The isotope exchange involving 7,8- and 7,9-$C_2B_9H_{12}^-$ and their derivatives has also been studied [171]. Comparison of the spectra of various 7,8-$C_2B_9H_{12}$ derivatives led to the assignment of the peaks in the $^{11}B$ NMR spectrum of this anion [171,172]. 7,9-$C_2B_9H_{12}$ is thermodynamically more stable than the 7,8-isomer and on heating to 300°C the latter is converted into the former [119,173].

The electrophilic substitution reactions of 7,8-$C_2B_9H_{12}^-$ take place at the open face with formation of 9-substituted derivatives of 7,8-$C_2B_9H_{11}^-$. For example, iodination with $I_2$ in an aqueous ethanol solution yields 9-I-7,8-$C_2B_9H_{11}^-$. The oxidative substitution reaction leads to the 9- and 10-substituted derivatives of the 7,8-isomer [174,175]. Alkylation of 7,9-$C_2B_9H_{11}^{2-}$ yields 10-Alk-7,9-$C_2B_9H_{11}^-$ (Fig. 37). [176]

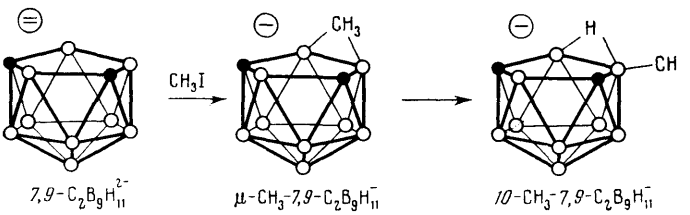
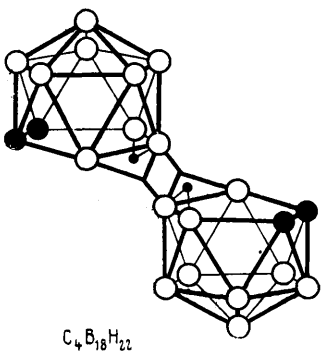



Figure 37.

Oxidation of 7,9-$C_2B_9H_{12}^-$ with chromic acid results in the formation of $C_2B_7H_{13}$ in a high yield [177]. Cautious oxidation of 7,8-$C_2B_9H_{12}^-$ in an acid medium at −15°C with $K_2Cr_2O_7$ leads to the stable carborane $C_4B_{18}H_{22}$. $^{11}B$ NMR, $^1H$ NMR, and infrared and ultraviolet spectroscopic data indicate a structure in which two $C_2B_9H_{11}$ fragments are joined by two three-centre bonds (Fig. 38). [178] As already mentioned, the oxidation of 7,8-$C_2B_9H_{12}^-$ by iron(III) salts in an acid medium leads to 5,6-$C_2B_8H_{12}$. [95] Numerous transition metal complexes were obtained with the dicarbollide ions $C_2B_9H_{11}^{2-}$. [2,19-23,179] The interaction of 7,8-$C_2B_9H_{11}^{2-}$ with $GeI_2$, $SnCl_2$, and $Pb(OAc)_2$ leads to heteroanalogues of tricarba-*closo*-dodecaborane(11). [180] $^{119}Sn$ Mössbauer spectroscopic data for 3-Sn-1,2-$C_2B_9H_{11}$ have

shown that the outer electronic shell of the tin(II) atom is of the $5s^2$ type [181]. The analogous germanium compound was obtained from 7,9-$C_2B_9H_{11}^{2-}$. The reaction of 7,9-$C_2B_9H_{11}^{2-}$ with $SnCl_2$ results in the formation of 2,3-$C_2B_9H_{11}$. 3-Sn-1,7-$C_2B_9H_9$ is formed as an intermediate [112]:

$$7,9\text{-}C_2B_9H_{11}^{2-} + SnCl_2 \rightarrow (3\text{-Sn-}1,7\text{-}C_2B_9H_{11}) \rightarrow 2,3\text{-}C_2B_9H_{11}.$$



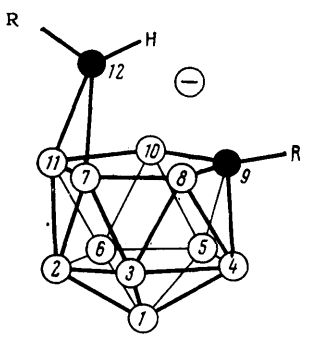
$C_4B_{18}H_{22}$

**Figure 38.**

The interaction of the dicarbollide ions with $RBCl_2$ leads to the restoration of the icosahedral structure, involving the formation of 3-R-$C_2B_{10}H_{11}$. [182-185] $\sigma_i$ and $\sigma_R^o$ have been determined for 7,8- and 7,9-$C_2B_9H_{12}^-$ and the corresponding dicarbollide ions [114,186]. Zakharkin et al. [186] believe that the second negative charge in $C_2B_9H_{11}^{2-}$ is located mainly at the boron atoms not in the open face.

Dicarbarba-*nido*-dodecaborane(14) ($C_2B_{10}H_{14}$)

The neutral compound have not been obtained. The anions of the corresponding *nido*-carboranes are formed when the dianions $(C_2B_{10}H_{12})^{2-}$ obtained from 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ are protonated [187]. The structure of one of the $C_2B_{10}H_{13}^-$ isomers, based on X-ray diffraction data, is presented in Fig. 39. [127,128]




$R_2C_2B_{10}H_{11}^-$
(R=$CH_3$,$C_6H_5$)

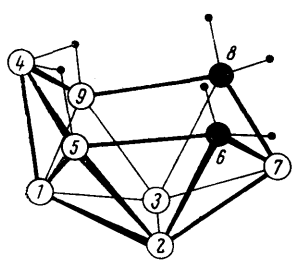
**Figure 39.**

## 2. *ARACHNO*-CARBORANES

*arachno*-Carboranes have the general formula $C_{0-6}B_nH_{n+6}$. This class of carboranes has been least thoroughly investigated. Only two *arachno*-carboranes have been obtained hitherto. They have an open structure, like *nido*-carboranes, and differ only by the number of hydrogen atoms in the open face. The most objective feature characterising *closo*, *nido*-, and *arachno*-carboranes is the electronic structure of compounds of these classes (see Section V).

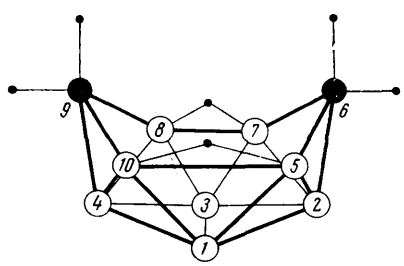
Dicarba-*arachno*-nonaborane(13) ($C_2B_7H_{13}$)

$C_2B_7H_{13}$ can have nineteen isomers. As already mentioned, the only one obtained (6,8-$C_2B_7H_{13}$) is formed as a result of the oxidation of $C_2B_9H_{11}$ in aqueous solution [32,35] or by the oxidation of 7,9-$C_2B_9H_{12}^-$ with chromic acid [177]. The structure of $C_2B_7H_{13}$ (Fig. 40) was established on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data and also the study of the chemical properties of this carborane [32,35]. X-Ray diffraction data have been published for *CC*-$Me_2C_2B_7H_{11}$. [188] As already stated, thermal decomposition leads to a mixture of the *closo*-carboranes $C_2B_6H_8$, $C_2B_7H_9$, and $C_2B_8H_{10}$. [32,85] Interaction with strong bases leads to the abstraction of two "axial" protons from the carbon atoms with formation of $C_2B_7H_{11}^{2-}$, whose treatment with $D^+$ yields $C_2B_7H_{11}D_2$. [32] The interaction of $C_2B_7H_{11}^{2-}$ with $CoCl_2$ leads to the formation of $\pi$ complexes containing two $C_2B_7H_9^{2-}$ carborane ligands with carbon atoms in the 1,6- or 6,9-positions, depending on the reaction conditions. The 1,10-isomer has been obtained by thermal isomerisation [189]. The reactions of $C_2B_7H_{11}^{2-}$ with $Mn(CO)_5Br$, $Mn_2(CO)_{10}$, and $Mn(CO)_2Cl$ in THF lead to 1,4,6-$(CO)_3MnC_2B_6H_8^-$. [190]




6,8-$C_2B_7H_{13}$

**Figure 40.**




6,9-$C_2B_8H_{14}$

**Figure 41.**

6,9-Dicarba-*arachno*-decaborane(14) ($C_2B_8H_{14}$)

As already mentioned, this carborane is formed when 5,6-$C_2B_8H_{12}$ is acted upon by $EtO^-$. Its structure has been proposed on the basis of $^{11}B$ NMR, $^1H$ NMR, and infrared spectroscopic data (Fig. 41).[36]

## V. THE CHARACTERISTIC FEATURES OF THE VARIATION OF THE PHYSICOCHEMICAL PROPERTIES OF CARBORANES

The experimental data on the properties of *closo*-, *nido*- and *arachno*-carboranes which have accumulated can be treated in general terms and make it possible to discover a relation between their structure and the variation of their physicochemical and chemical properties in the light of the characteristics of the three-centre bonds in these compounds. The Table lists certain physicochemical parameters of carboranes, such as the interatomic distances $l$, the C–H bond stretching vibration wavenumbers $\nu$(C–H), the chemical shifts of the C–B bond protons $\tau$, and the coordination numbers (C.N.) of the carbon and boron atoms. When the interatomic distances in carboranes and other similar structures are compared, a striking feature is the greater distances between the atoms of the molecular skeleton compared with the bond lengths in classical organic and organoboron compounds. For example, the C–C distance in 1,2-$C_2B_{10}H_{12}$ is 1.65 Å,[129] which greatly exceeds $l_{C-C}$ for the $\sigma$ bond in organic compounds of different types ($l_{C-C} \leq 1.55$ Å).[194] The B–C distance in the same carborane is of the order of 1.71 Å [129] and in the 1,7-isomer it is 1.73 Å, while in trimethylboron the C–B bond length is 1.578 Å.[195] The greater C–C and B–C interatomic distances in carboranes undoubtedly reflect the specific nature of the bonds in these compounds. Evidently the increase of the C–C and B–C interatomic distances is associated with the deficiency of electrons and the specific features of the three-centre bond. In contrast to the bonds in the skeleton, where in the general case two-centre bonds also do not coincide with the straight line joining the two atoms, the external C–H and B–H bonds as well as the bonds with the substituents are ordinary $\sigma$ bonds. As a result of this, comparison of the characteristics of these bonds with the behaviour familiar in organic chemistry and the chemistry of organic derivatives of the elements can yield useful information about the state of the atoms constituting the molecular skeleton. In organic compounds the C–H and C–Me bond lengths are known to depend on the hybrid state of the carbon atoms, amounting to 1.09 and 1.54 Å ($sp^3$), 1.07 and 1.49–1.53 Å ($sp^2$), and 1.06 and 1.46 Å ($sp$) respectively. The C–H and C–Me bond lengths in *closo*-carboranes are of the order of 1.1 and 1.53 Å, the corresponding values in *nido*-carboranes being 1.07 and 1.51 Å respectively. Comparison of these results (see Table) indicates the predominant $sp^3$ hybridisation of the carbon atoms in the majority of *closo*-carboranes‡ and $sp^2$ hybridisation in *nido*-carboranes. The shorter C–Me and particularly C–Hal bond lengths are in many cases apparently associated with the appreciable electron-accepting properties of the carbonyl groups. For example, the C–I bond length in 1,12-$I_2$-1,12-$C_2B_{10}H_{11}$ is 2.082 Å,[196] while in MeI it amounts to 2.132 Å;[194] on the other hand, in $CF_3I$ the bond length is 2.101 Å.[197]

‡ In many cases, for example in the 1,6-$C_2B_8H_{10}$ molecule, carbon atoms are apparently in the $sp^2$ hybrid state.

Bearing in mind the $\sigma$ bonding with the substituent, the state of the boron atoms in the polyhedron can be inferred also from the properties of the substituents linked to the polyhedron (H, halogen, alkyl, etc.); however, the lack of adequate experimental data still precludes such a comparison. Molecular orbital calculations indicate $sp^3$ or $sp^2$ hybridisation[4,24], while in the theory of three-centre orbitals an $sp^3$ hybrid state of the boron atoms is postulated[4]. Despite the insufficiency of experimental data, certain conclusions about the characteristics of the state of the boron atoms can be reached from a formal comparison of the coordination number with the possible distribution of electron density among the atoms of the polyhedron. Thus it is easy to note a tendency towards an increase of the distance between the atoms of the polyhedron with increase of the coordination number. An interesting approach to this problem was proposed by Wade in relation to the borane anions $B_nH_n^{2-}$. On the basis of the fact that the bond in *closo*-structures is formed by the $(n+1)$th electron pair [198], the author determined the formal number of electrons corresponding to each edge of the polyhedron, i.e. the "bond order" between the atoms as a function of $n$ and the number of adjacent atoms ($x_1$ and $x_2$)§:

$$\text{"bond order"} = \frac{(n+1)(x_1+x_2)}{nx_1x_2}.$$

He attributed the decrease of the interatomic distance with decrease of the coordination number to the increase of the "bond order". Since the observed decrease of the interatomic distance is greater than expected, Wade concluded that in the given molecule the electronic charge is distributed non-uniformly, being higher on atoms with a lower coordination number than on atoms with a higher coordination number [199].

Evidently the absence of a direct relation between the interatomic distances and the coordination number can be explained if one considers the distribution of the $(n+1)$th electron pair over the localised bonding orbitals rather than over the atoms of the polyhedron. Each atom supplies three atomic orbitals for the formation of the bonds in the nucleus, i.e. is involved in the formation of three bonding orbitals, and the number of electrons joining the central atom to its $x$ neighbours is six. Thus the formal number of electrons corresponding to the given atom will decrease with increase of the coordination number. The higher thermodynamic stability of the isomer of the given carborane in which the carbon atoms have a smaller coordination number¶ can be attributed to the fact that in these isomers the excess positive charge on the carbon atoms (see Section II) is more compensated compared with the isomers in which the carbon atoms have higher coordination numbers.

With increase of the number of atoms $n$ forming the polyhedron (in consequence of the decrease of the quantity $n + 1/n$—the average number of electron pairs at each atom of the polyhedral molecule), there is an increase of the excess positive charge on the atoms of the polyhedron, including the carbon atoms with identical coordination numbers, which is manifested in the properties of the C–H bonds (see Table).

§ $x$ = C.N. – 1, i.e. the outer $\sigma$ bond is disregarded.

¶ In all the known unsubstituted carboranes the carbon atoms occupy the positions with the minimum coordination numbers. If several isomers of the given carborane are known, then the isomers in which the carbon atoms have a higher coordination number are converted into isomers with a smaller number coordination number[3], for example 1,6-$C_2B_8H_{10}$ → 1,10-$C_2B_8H_{10}$.[32]

In his study of the relation between the individual classes of carboranes, boron hydrides, and related structures, Wade noted that $n$-atomic molecules with *closo*-, *nido*-, and *arachno*-structures have respectively $n + 1$, $n + 2$, and $n + 3$ electron pairs binding together the molecular skeleton. The addition of an electron pair to the *closo*-structure $B_nH_n^{2-}$ leads to the *nido*-structure $B_nH_n^{4-}$ with a rearrangement of the skeleton and the formation of a fragment of the next polyhedron with one vertex missing[198]. Having combined with two electrons, the molecules of *closo*-carboranes are converted to the electronic analogues of *nido*-carboranes, corresponding to the *nido*-structures of derivatives of carborane dianions, and having combined with four electrons they are converted into analogues of *arachno*-carboranes. The addition of one proton per unit negative charge gives rise to structural analogues of *nido*- and *arachno*-carboranes[200]. For example:

$$2,3\text{-}C_2B_9H_{11} \xrightarrow{2e} C_2B_9H_{11}^{2-} \xrightarrow{H^+} 7,9\text{-}C_2B_9H_{12}^-\ ,$$
$$1,2\text{-}C_2B_8H_{10} \xrightarrow{2e} C_2B_8H_{10}^{2-} \xrightarrow{2H^+} 5,6\text{-}C_2B_8H_{12}\ .$$

Characteristics of carboranes.

| Carborane | C.N.* C B | (C.N. of C)** $l_{C-R}$, Å (R = H, Me) | $l_{C-C}$, Å | (C.N. of C) $l_{C-B}$, Å (C.N. of B)** | (C.N. of B) $l_{B-B}$, Å (C.N. of B)** | $^1$H NMR spectrum*** $\tau_{C-H}$, p.p.m. | i.r.(Raman) spectrum $\nu_{C-H}$, cm$^{-1}$ | $\sigma_i$; $\sigma_R^\circ$ | References**** |
|---|---|---|---|---|---|---|---|---|---|
| *closo*-1,5-$C_2B_3H_5$ | 4<br>5 | 1.071 | — | (4) 1.556(5) | (5) 1.853 (5) | 5.35 | 3165 (3152) | — | 26[bc], 59[a], 79[c] |
| 1,2-$C_2B_4H_6$ | 5<br>5 | 1.10 | 1.540 | (5) 1.605—1.627 (5) | (5) 1.721;1.752 (5) | — | — | — | 27[bc], 68[a] |
| 1,6-$C_2B_4H_6$ | 5<br>5 | 1.103; 1.11 | — | (5) 1.633;1.635 (5) | (5) 1.720;1.725 (5) | 7.63 | 3107 (3118) | — | 27[bc], 59[a], 67[a], 79[c] |
| 2,4-$C_2B_5H_7$ | 5<br>5;6 | 1.09 | — | C(2)–B(3) 1.606<br>C(2)–B(6) 1.502 | (5) 1.650 (5)<br>(5) 1.650—1.894 (6) | —<br>4.3 | 3110 (3096) | — | 77[bc], 78[a], 79[c] |
| 1,7-$C_2B_6H_8$ | 5;6<br>5 | — | — | — | — | 5.2 | 3080 | +0.08<br>−0.02 | 32[bc], 85[bc]<br>191[a], 89[d] |
| 1,7-$Me_2C_2B_6H_6$ | 5;6 | 1.521 | — | (5) 1.500 (5)<br>(5) 1.595—1.697(6) | (5) 1.696—1.806 (6)<br>(6) 1.842—1.920 (6) | 7.84 | 2930 | — | |
| 4,5-$C_2B_7H_9$ | 5<br>5;6 | — | — | — | — | 4.4 | 3075 | +0.09<br>−0.05 | 32[bc], 85[bc], 91[a], 89[d] |
| 4,5-$Me_2C_2B_7H_7$ | 5<br>5;6 | 1.53 | — | (5) 1.61(6) | (5) 1.72(6)<br>(6) 1.77—2.01 (6) | 7.5 | 2935 | — | |
| 1,6-$C_2B_8H_{10}$ | 5;6<br>5;6 | — | — | — | — | (5)4.8;(6)8.1 | 3120,3070 | +0.10<br>−0.02 | 32[bc], 85[bc], 98[a], 104[d] |
| 1,6-$Me_2C_2B_8H_8$ | 5;6<br>5;6 | (5) 1.505;<br>(6) 1.527 | — | (5) 1.588—1.611(6)<br>(6) 1.632(5)<br>(6) 1.750—1.777 (6) | (5) 1.681—1.696 (5)<br>(6) 1.780—1.861(6) | (5)7.2;(6)8.7 | 3005,2960 | — | |
| 2,3-$C_2B_9H_{11}$ | 5<br>6;7 | — | — | — | — | 4.2 | 3060 | +0,12<br>−0.01 | 32[bc] 108[a],<br>114[d] 115[d] |
| 2,3-$Me_2C_2B_9H_9$ | 5<br>6;7 | 1.52 | — | (5)1.60—1.70(6)<br>(5)1.67(*l*) | (6)~1.80(6)<br>6) 2.05(*l*) | — | 2885 | — | |
| 1,2-$C_2B_{10}H_{12}$ | 6<br>6 | 1.15 | 1.65 | (6)~1.711(6) | (6) 1.793(6) | 6.5 | 3080 | +0.295<br>+0.004 | 129[a], 192[b], 114[d] |
| 1,7-$C_2B_{10}H_{12}$ | 6<br>6 | 1.15 | — | (6)~1.726(6) | (6) 1.805 (6) | 7.15 | 3071 | +0.213<br>−0.036 | 129[a], 192[b], |
| 1,12-$C_2B_{10}H_{12}$ | 6<br>6 | 1.15 | — | (6) 1.710 (6) | (6) 1.772—1.792 (6) | 7.32 | 3067 | — | 129[a], 192[b] |
| *nido*-2-$CB_9H_9$ | 4<br>5; 6 | — | — | (4) 1.530 (5)<br>(4) 1.713 (6) | (5) 1.759—1.782 (6)<br>(6) 1.781—1 830 (6) | 4 62 | — | — | 137[a], 138[b], 139[b] |
| 2,3-$C_2B_4H_8$ | 4<br>5;6 | 1.04 | 1.418 | (4) 1.509 (5)<br>(4) 1.748 (6) | — | — | 3040,3032 (3044,3032) | — | 34[b], 77[b], 144[c], 142[a] 143[a] |
| 2,3-$Me_2C_2B_4H_6$ | 4<br>5;6 | 1.506 | 1.432 | (4) 1.520 (5)<br>(4) 1.762 (6) | (5) 1.768 (6)<br>(6) 1.705 (6) | 7.97 | 2980,2954, 2922 (2960,2927, 2869) | — | 34[b] |
| 2,3,4,5-$C_4B_2H_6$ | 4<br>4;6 | — | C(2)–C(3) 1.436<br>C(3)–C(4) 1.424 | (4) 1.541 (4)<br>(4) 1.703 (4) | (4) 1.886 (2) | 4.24<br>5.38 | 2950 | — | 63[bc], 159[bc], 160[bc] 161[a] |
| 3,6-$C_2B_6H_{10}$ | 4<br>4;6 | — | — | (5) 1.617 (5)<br>(5) 1.697 (6) | (5) 1.704 (6)<br>(6) 1.721 (6) | — | 2975,2965 2878,2865 | — | 61[ac] |
| 4,5-$C_2B_7H_{11}$ | 4;5<br>5;6 | — | — | — | — | 7.19;8,05 | 3048,2982 | — | 162[bc], 163[a] |

Table (continued).

| Carborane | C.N.* C B | (C.N. of C)** $l_{C-R}$, Å (R = H,Me) | $l_{C-C}$, Å | (C.N. of C) $l_{C-B}$, Å (C.N. of B)** | (C.N. of B) $l_{B-B}$, Å (C.N. of B)** | $^1$H NMR spectrum*** $\tau_{C-H}$, p.p.m. | i.r.(Raman) spectrum $\nu_{C-H}$, cm$^{-1}$ | $\sigma_I$; $\sigma_R^0$ | References**** |
|---|---|---|---|---|---|---|---|---|---|
| 6,7-$Me_2C_2B_7H_9$ | 5<br>5;6 | 1.47—1.53 | 1.55 | (5) 1.60—1.75 (5)<br>(5) 1.60—1.65 (6) | (5) ~1.80 (6)<br>(6) 1.69—1.81 (6) | 7.68;8.72 | 2965.2935 | — | 162bc, 163a |
| 9,12-$C_2B_{10}H_{13}^-$ | 4;5<br>5;6 | — | — | — | — | 7.48;6.79 (doublet)<br>7.19 (doublet) | — | — | 187b, 128a, 193b |
| 9,12-$Me_2C_2B_{10}H_{11}^-$ | 4;5<br>5;6 | (5) 1.520; (4) 1.518<br>C(12)—H 0.957 | — | (4) 1.642(6)<br>(5) 1.625 (5)<br>(5) 1.670 (6) | (5) 1.72—1.867(6)<br>(6) 1.757—1.847 (6) | 6.45(quartet)<br>8.32 (singlet);<br>8.67(doublet) | — | — | |
| *arachno*-6,8-$C_2B_7H_{13}$ | 5<br>5;6 | — | — | — | — | 9.9; 10.77 | 3055.2910 | — | 32bc |
| 6,8-$Me_2C_2B_7H_{11}$ | 5<br>5;6 | C—H 0.98<br>C—Me 1.527 | — | (5) 1.700 (5)<br>(5) 1.671—1.714 (6) | (5) 1.732 (6)<br>(6) 1.710—1.826 (6) | 8.7; 10.73 | 2925 | — | 188a |

*The coordination numbers (C.N.) of carbon atoms (upper figures) and boron atoms (lower figures) are quoted.

**The coordination numbers of the atoms in the skeleton for which the interatomic distances are quoted are indicated in brackets.

***$\tau = 10 - \delta$; the coordination numbers of the corresponding carbon atoms are indicated in brackets for 1,6-$C_2B_8H_{10}$.

****a—interatomic distances; b—$^1$H NMR data; c—infrared and Raman spectroscopic data; d—reaction constants.

## VI. THE POSSIBLE MECHANISMS OF THE CHEMICAL REACTIONS OF CARBORANES

The nature of the chemical bond in carboranes and boron hydrides is manifested not only in the characteristics of their structure but naturally also in the nature of their chemical reactions, such as reduction, oxidation, and interaction with nucleophilic and electrophilic agents. We shall attempt to consider the reactions involving localised three-centre as well as two-centre bonds.

### 1. Reduction of Carboranes

One of the most general and interesting reactions of carboranes, mainly *closo*-carboranes, is their ability to combine with electrons when acted upon by alkali metals. The addition of electrons to *closo*-structure with $n$-atoms in the polyhedron is accompanied by a rearrangement of the carborane molecule, the resulting anions being isolated in the form of transition metal complexes or protonation products with the metal atom inserted at the missing vertex of the polyhedron with $n + 1$ atoms.

In the light of ideas concerning three-centre bonds, the addition of two electrons can be formally represented as follows. The electrons can add on successively to the three-centre bond with formation of a two-centre bond and an atomic orbital with an electron pair. At the intermediate stages of their transfer electrons can be accommodated at a non-bonding orbital, if such is present, or at the nearest antibonding orbital (Fig. 42). Next, the system of bonding orbitals probably rearranges with formation of two two-centre orbitals, from the atomic orbital with the electron pair and a second three-centre orbital. Thus two three-centre orbitals are formally rearranged

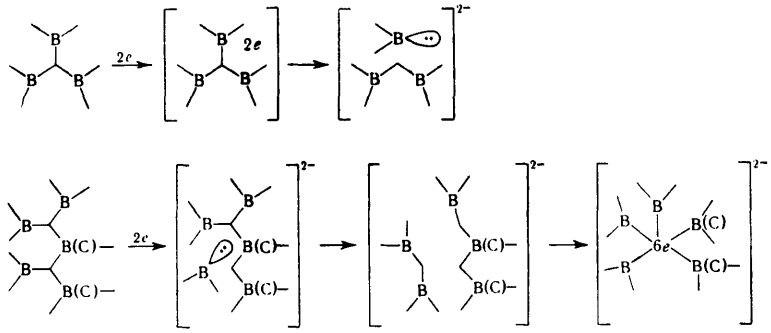


Figure 42.

into three two-centre orbitals, and the electron pair is located in the resulting additional bonding orbital. The bonding two-centre orbitals formed are probably to some extent delocalised, i.e. there is a possibility of the formation of (three) bonding five-centre orbitals, made up of the atomic orbitals of the atoms in the open face (Fig. 42). The last structure in Fig. 42 does not reflect the real directions of the atomic orbitals but merely the possibility of the formation of bonding orbitals common to the atoms in the open face (by analogy with Hawthorne's ideas concerning the nature of the bond in transition metal complexes with the carborane ligands $C_2B_9H_{11}^{2-}$ and in the dicarbollide ions themselves [179]).

The scheme in Fig. 42 illustrates the proposed mechanism of the addition of electrons to the *closo*-carborane molecule (a fragment of the possible valence structure is indicated). Two of the five atoms are carbon atoms. The scheme shows that the addition of electrons is accompanied by the opening of the structure, with formation of a pentagonal face. The possibility of the opening of the carborane nucleus with formation of a hexagonal face is illustrated by the scheme in Fig. 43. [201] Similarly to the scheme in Fig. 42, two of the six atoms are carbon atoms. It is noteworthy that the addition of electrons to the carborane molecule must involve primarily the immediate environment of the carbon atoms (the site with the lowest electron density) and in the resulting anions the carbon atoms must be located in the open face—the site with the maximum electron density. Accordingly, electrophilic reactions, for example protonation and interaction with transition metal salts (formation of metallocarboranes), proceed at the open face containing at least one carbon atom.

Substituents in the carborane nucleus may play an important role in determining the sites of addition of electrons. Depending on the nature of the substituent and its location in the polyhedron, the attack by electrons can take place at three-centre bonds other than in the unsubstituted carboranes. Furthermore, polarisation of the three-centre bond itself under the influence of the substituent can lead to the opening of the three-centre bond and hence of the polyhedral molecule in different directions, i.e. to the formation of an atomic orbital with an electron pair at different atoms of the polyhedron. All these factors lead to different sets of dynamic structures [201].

The addition of electrons must be accompanied by a considerable increase in the energy of the bonding orbitals of the carborane nucleus and the corresponding decrease of the energy of the antibonding orbitals. This must facilitate the corresponding rearrangements of the molecular skeleton. The rearrangements can lead either to a superposition of the physicochemical characteristics of the individual isomers or, when they are sufficiently rapid, to an averaging of the spectroscopic physicochemical parameters of the dianions in solutions [201].

The high reactivity of the dianions is shown also by the ease of occurrence of various chemical reactions, such as disproportionation, interaction with various electrophilic agents, with the solvent, etc. Thus, when electrons add to $2,4\text{-}C_2B_5H_7$, with subsequent treatment by $CoCl_2$ and $NaC_5H_5$ and then oxidation by air, a mixture of compounds is formed, eight of which have been isolated [83]. When the dianions are treated with transition metal salts, the resulting complexes have different structures [88], probably owing to the different electronic structures of the transition

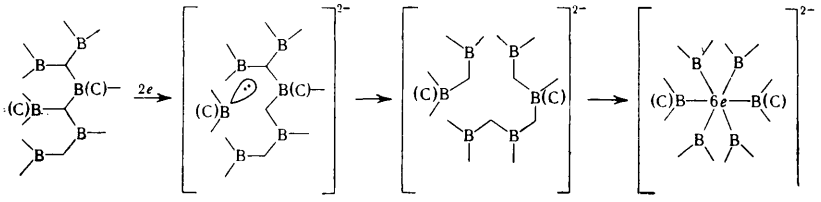


Figure 43.

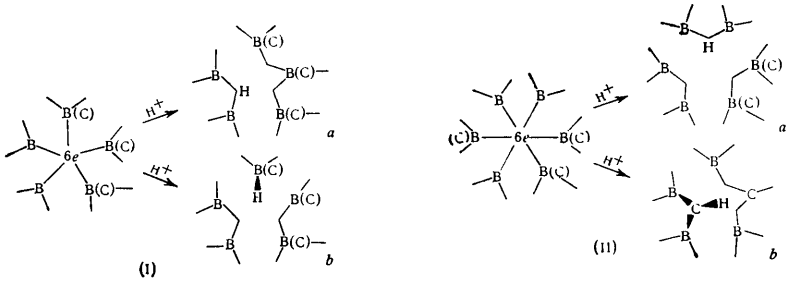


Figure 44.

metal atoms, for example cobalt(III) and iron(III), and the consequent stabilisation of various dynamic structures of the dianions. On formation of complexes with transition metals, the given electronic system of the dianion is fixed to a greater or smaller extent and it is possible to isolate complexes having a definite structure.

The structure of the dianions is also fixed on protonation. However, it is not always identical with the structure of the corresponding carborane ligands in transition metal complexes. On interaction of the bonding orbitals in the open face with a proton, the electron pairs are localised. Two versions of such localisation are possible. In the first a system of two two-centre orbitals and a three-centre B–H–B bond is formed as a result of the protonation of the dianion. (The formation of a B–H–C bond and even more so a C–H–C bond in the final structure is unlikely in view of the excess positive charge on the carbon atoms relative to the boron atoms in the open face.) The initial pentagonal or hexagonal face of the dianion is then fixed. In the second version the system of bonding orbitals in the open face is disturbed owing to the localisation of electrons at one of the atoms with formation of a C–H or B–H σ bond. For understandable reasons, the formation of a C–H σ bond is preferable (localisation of an electron pair at the given atom). The carbon atom thus forms two σ bonds with two substituents. The remaining four electrons are accommodated at two two-centre orbitals. In the case of a hexagonal face one may then expect its narrowing, since the four electrons in the two two-centre orbitals cannot bind a system of six atoms (Fig. 44). The protonation of $R_2C_2B_{10}H_{10}^{2-}$, leading to the monoanion $R_2C_2B_{10}H_{11}^{-}$, one of the isomers of which has a structure (Fig. 39) where one of the carbon atoms is linked by σ bonds to R and H and is located above the plane of the open pentagonal face [127,128], may serve as an example.

Scheme Ia in Fig. 44 occurs in the protonation of, for example, the dicarbollide ions $C_2B_9H_{11}^{2-}$ (the fragments of the possible valence structures are indicated in the Figure). The protonation of the dianion with formation of a monoanion having the structure IB is not so far known. Scheme II can describe the protonation of $C_2B_8H_{10}^{2-}$ derived from 1,2-$C_2B_8H_{10}$ (II*a*) and of $C_2B_{10}H_{12}^{2-}$ derived from 1,2-$C_2B_{10}H_{10}R_2$ (II*b*). The II*b* fragment was taken from Tolpin and Lipscomb [127].

Similarly to the formation of dianions (Figs. 42 and 43), one may expect the addition of not only two but also of four and more electrons to carborane molecules with the corresponding structural rearrangements. If one begins with a carborane containing $n$ atoms in the polyhedron, the tetra-anions should give rise to a molecule isoelectronic with *arachno*-carboranes having a structure representing a fragment of a polyhedron with two vertices more than in the initial *closo*-carborane, i.e. $n + 2$, while in the case of hexa-anions the resulting structure should have three vertices more, i.e. $n + 3$, and so on. Indeed, complexes have been obtained with cobalt(III) in which the carborane ligands can be regarded as tetra-anions and hexa-anions: $C_2B_6H_8^{4-}$, $C_2B_8H_{10}^{4-}$, $C_2B_7H_9^{6-}$, etc. [83,88,202]

## 2. Oxidation of Carboranes

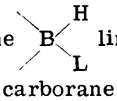
Molecules with the closed structure of the isoelectronic series $B_nH_n^{2-}$, $CB_{n-1}H_n^{-}$, and $C_2B_{n-2}H$ can not only combine with two electrons, but theoretically can also give up two electrons. Indeed the system of bonding orbitals in the skeleton of these molecules includes three two-centre and $n - 2$ three-centre bonds, which follows from the solution of the equations †

$$2x + 2y = 2n + 2 \text{ (electron balance)},$$
$$3n = 2x + 3y \text{ (orbital balance)},$$
$$x = 3,\ y = n - 2,$$

where $n$ is the number of atoms in the polyhedron, $x$ the number of two-centre orbitals, and $y$ the number of three-centre orbitals. After the removal of two electrons, three two-centre bonds can rearrange to two three-centre bonds with retention of the structure as a whole or, if possible, with increase of molecular symmetry. Thus, in principle, it is possible to obtain, for example, the species $C_2B_nH_{n+2}^{2+}$ or the corresponding derivatives $C_2B_nH_{n+1}^{+}$ and $C_2B_nH_n^{0}$—their deprotonation products. Isoelectronic analogues of such systems are known in the series of boron hydrides, for example $B_4Cl_4$ (tetrahedron), [203-205] $B_8Cl_8$ (dodecahedron), [206-209] and $B_9Cl_9H$. [210] The last two compounds are isoelectronic with $C_2B_6H_8^{2+}$ and $C_2B_7H_9^{2+}$ respectively.

The oxidation of the dianions to neutral *closo*-carboranes can be treated formally as a process which is the reverse of the addition of electrons (Figs. 42 and 43) and which leads to the closure of the open structure of the dianion. The oxidant interacts with the bonding two-electron five- or six-centre orbitals, but, in contrast to the usual electrophilic agents, does not fix the possible structures of the dianion, forming a bond with the carborane ligand and resulting in the closure of the *nido*-structure and to a *closo*-structure as a result of electron transfer from the dianion [211]. The formation of particular isomers of *closo*-carboranes may be determined both by the existence of dynamic structures and, mainly, by the mode of closure of the pentagonal and hexagonal faces of the dianions, i.e. by the energy of the transition state whose structure is probably close to that of the dianion–oxidant transition complex.

## 3. Reactions of Carboranes with Nucleophilic Agents

The mechanism of the interaction of carboranes with nucleophilic agents resembles in the first stage the interaction with an electron pair. The nucleophilic agent interacts with a three-centre orbital, with formation of a two-centre orbital and a boron–nucleophilic agent σ bond (Fig. 45). As a result, the *closo*-structure opens at the site of attack by the nucleophilic agent, as in electron addition, and an open face is formed. Depending on the nature of the carborane and the attacking nucleophilic species, the  linkage may be retained in the residual part of the carborane molecule, or the boron atom may be eliminated after the addition of a second molecule of the nucleophilic agent. For example, the reaction of 1,6-$C_2B_4H_6$ with $Me_3N$ leads to the opening of the *closo*-carborane molecule [73]. The sequence of the electronic and structural rearrangements of the molecule in this reaction

† This set of equations is a special case of the set of Lipscomb's equations put forward to describe boron hydrides and other compounds in terms of the topological theory [4].

can be represented by the scheme in Fig. 46. The electron pair of the nitrogen atom interacts with the three-centre $C_{(1)}-B_{(2)}-B_{(3)}$ orbital to form the $Me_3N-B_{(2)}$ σ bond. The $B_{(2)}-H$, $B_{(2)}-B_{(5)}$, and $B_{(4)}-B_{(5)}-B_{(6)}$ bond orbitals then rearrange in such a way that the molecule is opened still more, and a pentagonal pyramid is formed, the hydrogen atom linked by a σ bond to the $B_{(2)}$ atom migrating to the bridge position.

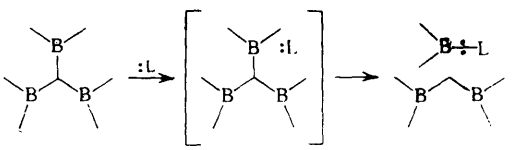


Figure 45.

Another example is provided by the reaction of $C_2B_9H_{11}$ with Lewis bases. The nucleophilic agent L interacts with a three-centre orbital, for example between the $B_{(1)}$, $C_{(3)}$, and $B_{(6)}$ atoms, as a result of which a $B_{(6)}-L$ σ bond is formed and the structure opens. The hydrogen atom linked to $B_{(6)}$ in the initial carborane moves to the bridge position in the product (Fig. 47). According to this scheme, the formation of the 3-isomer for certain L as a result of the opening of the $C_2B_9H_{11}$ structure on the side of the attacking L species [112] is unlikely. The 10-L-7,9-$C_2B_9H_{11}$ isomer is probably formed initially and is converted into 3-L-7,9-$C_2B_9H_{11}$ as a result of the migration of the $B_{(8)}$ atom.

The cleavage of 1,2-(1,7)-$C_2B_{10}H_{12}$ with alkali [119] is illustrated by the scheme in Fig. 48. The mechanisms of the cleavage of $R_2C_2B_{10}H_{10}$ by other nucleophilic agents, such as BuLi, RMgX, piperidine, etc., are similar [212-214]. The intermediate $C_2B_{10}H_{12}R^-$ is an electronic analogue of the dicarbadodecaborate monoanion $C_2B_{10}H_{13}^-$ formed on protonation of the dianion $C_2B_{10}H_{12}^{2-}$. The mechanism of the formation of $C_2B_7H_{13}$ in the cleavage of 1,6-$C_2B_8H_{10}$ with alkali can be represented similarly [100]. Apart from the addition of OH and the elimination of a boron atom, there is in this case a reduction stage, i.e. the transfer of two electrons to the molecule with formation of an *arachno*-carborane.

The general characteristics of the interaction of nucleophilic agents with a three-centre bond are probably manifested not only for *closo*-carboranes but also for *nido*-carboranes having an open B–H–B three-centre bond. Naturally reactions involving the closed B–B–B bonds of the nucleus are also possible. The reactions involving B–H–B bonds must begin, like the reactions involving the three-centre B–B–B bond, with the supply of electrons to the energetically lowest unfilled B–H–B orbital and a subsequent rearrangement of the resulting system via schemes I and II (Fig. 49). Reactions such as the addition of electrons to diborane with formation of $B_2H_6^{2-}$ [215] and the elimination of the bridge hydrogen atom from *nido*-carboranes and boron hydrides by bases or alkali metals proceed similarly. The reactions of carboranes with open three-centre B–C–B bonds (for example, 1,2-$C_2B_4H_6$) [50] can be described by similar schemes. As in reactions involving a closed three-centre bond, in this case the interaction with nucleophilic agents (or electron addition) must evidently be accompanied by the opening of the carborane molecule and the ligand must apparently form a bond with a boron atom. Subsequently, in the interaction with a second ligand molecule, the boron atom may be eliminated.

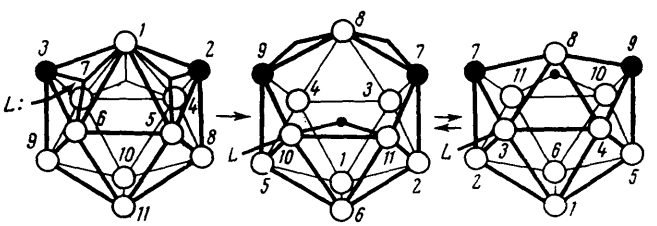


Figure 47.

## 4. Reactions of Carboranes with Electrophilic Agents

In considering the reactions of carboranes with electrophilic agents, it is logical to treat them as reactions involving two-centre bonds. Indeed there are atoms in carboranes with free electrons, i.e. not involved in the formation of a bond, and the vacant orbital of the electrophilic agent E (which is present or formed in the course of the reaction) interacts with a bonding two-centre orbital (possibly with an antibonding orbital in the transition state, as suggested, for example, by Nefedov et al. [216]); this

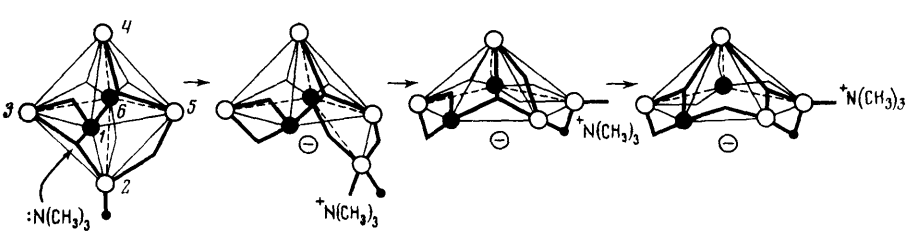


Figure 46.

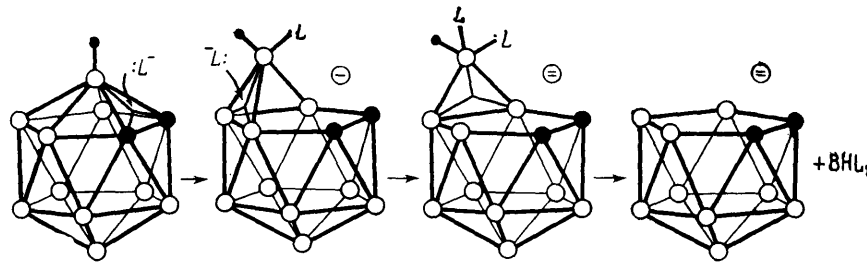


Figure 48.

involves the formation of a three-centre orbital. The possible versions of the three-centre bond formed are presented in Fig. 50 (I)‡.

The nature of the intermediate complex of the carborane with the electrophilic agent and the type of the three-centre bond formed depend on the distribution of electron density among the bonds, the bond polarisabilities, and the characteristics of E, i.e. ultimately on the energy of the orbitals of the reactants and the transition state. On formation of a three-centre bond, the reaction can proceed in several ways.

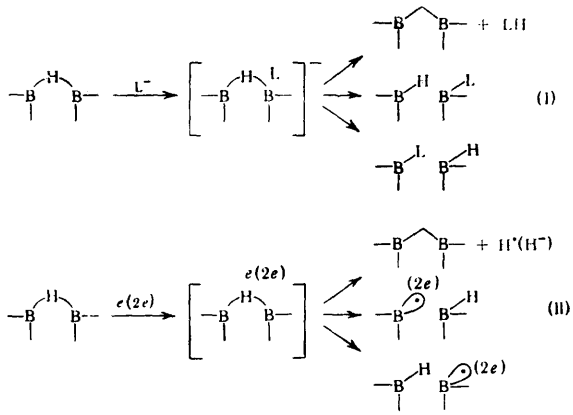


Figure 49.

1. The removal of a proton ($H^+$) and the formation of substitution products, as, for example, in Fig. 50 (II). The possibility of the formation of isomeric substitution products follows from this scheme. Indeed, depending on the reaction conditions and the nature of the catalyst, the ratio of the isomers formed in the halogenation of carborane(12) varies[217]. In many cases electrophilic substitution leads to a unique product, for example alkylation and halogenation of $4,5\text{-}C_2B_7H_9$ lead to $6\text{-}E\text{-}4,5\text{-}C_2B_7H_9$ (E = Me, Et, or Br).[92] In the series of boron hydrides protonation of $B_{10}H_{10}^{2-}$ leads to the formation of $B_{10}H_{12}$ containing three-centre B–H–B bonds involving the boron atoms at the vertices, which in an acid medium take part in the isotope exchange of hydrogen atoms for deuterium atoms[38]. Deuterium exchange involving $1,2\text{-}C_2B_{10}H_{12}$ in an acid medium leads to the substitution of the hydrogen atoms at all the boron atoms[218].

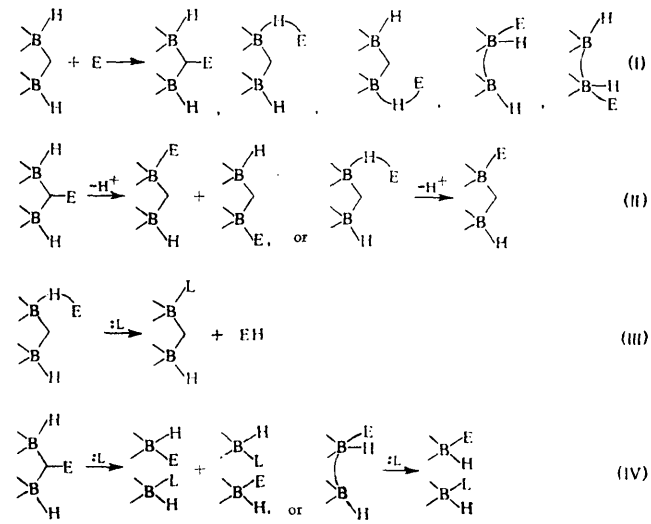


Figure 50.

2. The rupture of a three-centre B–H–E bond, possibly under the influence of the nucleophilic agent (see the interaction of three-centre bonds with nucleophilic agents), with formation of an E–H bond and a vacant orbital at the B atom, which interacts rapidly with an electron donor (when a nucleophilic agent is involved in the process, simultaneously with formation of an E–H bond), as shown, for example, in Fig. 50 (III). The oxidative hydroxylation of carboranes formally proceeds via a similar mechanism[110,121].

3. The rupture of a three-centre B–B–E bond. This stage can also be initiated by the nucleophilic agent [Fig. 50 (IV)]. The *closo*-structure is then of course opened

‡ The generally accepted notation for three-centre bonds is used. For bonds of the open type, such representation can be inconsistent in certain cases with the geometrical structure, i.e. in the transition state the B–H–E bond may prove to be linear.

with formation of B–E and B–L bonds. The opening of the $B_{10}H_{12}^{2-}$ structure in the series of boron hydrides takes place in this way in the interaction with $Et_2S$ in an acid medium, resulting in the formation of $B_{10}H_{12}(SEt_2)_2$.[219] The reaction of 1,6-$C_2B_8H_{10}$ with hydrochloric acid does not stop at any intermediate stage and the opening is accompanied by the breakdown of the structure; boric acid is formed[100]. The breakdown of carboranes in an acid medium in the presence of a palladium catalyst and the oxidative degradation of carboranes, for example of 2,3-$C_2B_9H_{11}$ to $C_2B_7H_{13}$ [32] or of 7,8-$C_2B_9H_{12}^-$ to 5,6-$C_2B_8H_{12}$,[95] can probably be included among reactions of this type.

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In conclusion we must note that there may be an alternative to the proposed reaction mechanisms, i.e. in principle, nucleophilic reactions, including the addition of electrons to two-centre bonds and electrophilic reactions involving three-centre bonds, can proceed via the following mechanisms.

1. As already mentioned, the interaction with nucleophilic agents begins with the accommodation of electrons in the nearest orbital (the energetically lowest unoccupied orbital), which is a non-bonding or weakly antibonding orbital in a three-centre bond and an antibonding orbital in a two-centre bond (Fig. 51). It is easily seen that in the general case the reaction involving a three-centre bond is energetically preferable ($E^0_{ABC} < E^*_{AB}$). However, in many cases the two-centre bond is weak, i.e. the energy of the bonding orbital is enhanced and that of the antibonding orbital is reduced. For example, electrons add to *C*-halogenocarboranes(12) at the C–halogen bond with formation of a halide ion and $\geq C^-$: after hydrolysis, the unsubstituted carborane is formed[201]. The reaction of *B*-halogenocarboranes involves both the boron–halogen bond and the three-centre bonds in the nucleus. The former process leads to unsubstituted carboranes and the latter to the dianion of the halogenocarborane, the oxidation of which leads to a mixture of the possible isomers of the halogenocarborane[201].

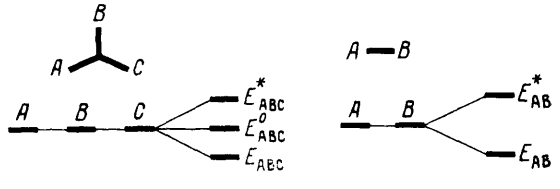



Figure 51.

2. The reactions of electrophilic agents via three-centre bonds can be, in principle, represented by the scheme in Fig. 52:[220,221] the carborane structure is opened with formation of a vacant orbital at one of the atoms, this being followed by rapid interaction of the latter with the nucleophilic agent and the formation of a B–E bond. We believe this mechanism to be unlikely, although it can account for certain reactions, for example the degradation of the carborane nucleus.

Comparison of the foregoing considerations with data from other chemical fields suggests that the interactions of electrophilic agents with two-centre bonds, particularly σ bonds, with formation of three-centre bonds are of a general type. For example, electrophilic reactions of compounds containing an "electron-deficient" atom (B, Be, Al, Ga, etc.), carbenes, and other similar compounds or 'onium compounds, including carbonium ions, proceed in this way. For example, Olah and coworkers have been successfully developing the concept of the intermediate formation of three-centre C–E–C and C–E–H bonds in organic chemistry (here E = $R^+$, $NO_2^+$, $H^+$, etc.).[222–228]

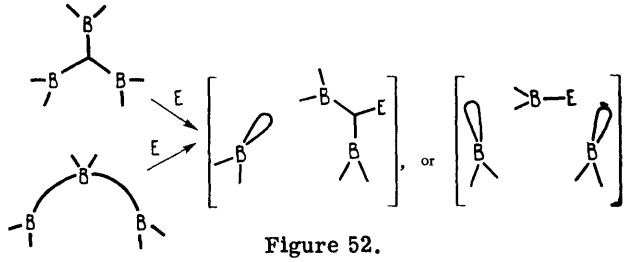



Figure 52.

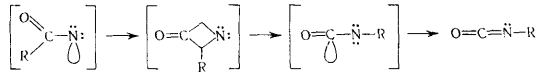
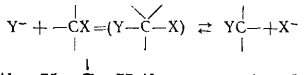


Figure 53.

The concept of the intermediate formation of three-centre bonds can be used successfully in describing certain intermediate stages in electrophilic substitution reactions of aromatic compounds. Such bonds are undoubtedly formed in many rearrangements involving a carbonium ion or an atom with a vacant atomic orbital (sextet rearrangements) (Fig. 53). Thus, three-centre bonds, which are so characteristic of "electron-deficient" compounds (Group III elements) are characteristic also of compounds formed by Group IV–VII elements. This applies in the first place to the intermediates and transition states in such reactions when the element can form a vacant orbital. We may note that three-centre bonds have been successfully invoked to described many inert gas compounds. For example, in the linear $XeF_2$ molecule the atoms are joined by a three-centre bond of the open type: Xe (the central atom) supplies the 5*p* orbital containing an electron pair and the two fluorine atoms each provide a 2*p* orbital containing one electron. The four electrons are accommodated in the bonding and non-bonding orbitals. All synchronous reactions involving three (and more) centres probably also proceed via an intermediate state in which three-centre (and many-centre) orbitals are formed. For example, in the $S_N2$ reactions



the formation of the Y–C–X three-centre bond may be expected in the transition state, two electrons being accommodated in the bonding orbital and two in the non-bonding three-centre orbital.

We believe that consideration of the reactions of carboranes, boron hydrides, and related compounds with nucleophilic and electrophilic agents in the light of ideas concerning three-centre and two-centre bonds permits a prediction of the possible modes of the reactions and leads to a better understanding of their mechanisms.

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