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Structural Rearrangements in Carbaboranes and Related Compounds

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The rearrangements of polyhedral boron compounds are described systematically and classified. The fundamental characteristics of various types of rearrangements are examined and the relation between them and the electronic structure and symmetry of the molecules is established.
The bibliography includes 191 references.

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I. INTRODUCTION

Rearrangements of atoms and of the molecular skeleton are characteristic of polyhedral boron compounds, particularly carbaboranes. They can take place under both thermal and chemical influences. This review presents a systematic arrangement of studies in this field in order to discover the relation between the chemical properties and the electronic structures of molecules and to establish on this basis the general characteristics of the rearrangement of polyhedral boron compounds†. Data published up to 1978 are used in the review.

From the entire multiplicity of the rearrangements of cyclic and open-chain polyhedral molecules and ions, it is possible to isolate two main groups: (a) rearrangements in which the initial and final molecules (ions) have structures based on the same polyhedron; (b) rearrangement involving a change in the type of polyhedron. The rearrangement of the first type (thermal rearrangements) are characterised by the fact that they are caused by thermal excitation and proceed without a change in the number of electrons between the initial and final systems. The rearrangements initiated by electromagnetic radiation, for example, ultraviolet light, and chemically initiated thermal rearrangements also take place without a change in the type of polynedron. Rearrangements of the second type are characterised by a change in the total number of electrons in the atoms of the skeleton. Depending on whether the rearrangement takes place owing to an increase of the number of electrons in the system or their decrease, it is possible to distinguish reductive and oxidative rearrangements respectively. Reductive rearrangements involve the opening of the polyhedral molecule following the appearance of additional external σ bonds. On the other hand, oxidative rearrangements lead to the closure of the polyhedral molecule or ion.

When the mechanisms of thermally initiated (i.e. without the involvement of chemical reagents) rearrangements of polyhedral compounds are considered, different versions of the so-called *dsd* mechanism (diamond–square–diamond) are most widely used (Fig. 1). This mechanism was proposed by Lipscomb, who used it to account for the rearrangement of virtually all closed polyhedral systems[3]. The second mechanism discussed in the literature is based on the hypothesis that different fragments of the polyhedral molecule can rotate in both the ground and transition states[4-7]. The third type of possible mechanisms, involving *closo*-compounds, is based on the hypothesis that the molecule is opened in the transition state to give a fragment of the next polyhedron and is then reclosed but in a different direction[5,8], while in the case of *nido*-compounds the polyhedral molecule is closed with subsequent opening[9-12]. The lack of adequate experimental data on this problem permits in most cases only a theoretical consideration of various mechanisms of the thermal rearrangements. We believe that the limitations due to the symmetry of the occupied and vacant boundary molecular orbitals can serve as a criterion for the selection of the most probable pathways in the rearrangements (see Section III).

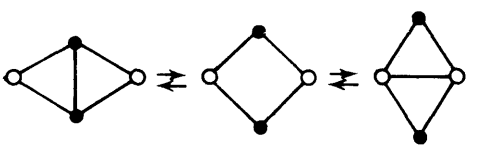


Figure 1. Model of the *dsd* (*diamond-square-diamond*) mechanism.

The rule governing the relation between the type of structure, the class of compound, and the number of electrons binding the skeleton of an n-atomic molecule, which was discovered by Wade, plays an important role in determining the direction of the reductive and oxidative rearrangements: the $n + 1$, $n + 2$, and $n + 3$ electron pairs characterise the *closo*-, *nido*-, and *arachno*-structures. The addition of two electrons to a closed n-atomic polyhedral molecule should lead to its opening with formation

† This review constitutes a stage in the systematic analysis of studies in the chemistry of carbaboranes and other polyhedral boron compounds (this is a development of our previous communications[1,2]).

of the *nido*-structure of a fragment of the next $(n + 1)$-atomic polyhedron; the addition of the next electron pair gives rise to the *arachno*-structure of an n-atomic fragment of the $(n + 2)$-atomic polyhedron, etc.[13] Taking into account the importance of the above features of the chemistry of polyhedral boron compounds, we shall refer to them as the *"Wade rule"*.

As will be shown below (see Sections II and III), a change in the number of electrons and in the general case in the number of orbitals occupied by electrons in the transition stage constitutes the driving force also of a number of thermal rearrangements, including those of closed polyhedral systems. On the other hand, reductive rearrangements are associated with the accommodation of additional electrons in the lowest unoccupied molecular orbitals (LUMO), while oxidative rearrangements involve the removal of electrons from the highest occupied molecular orbitals (HOMO) of the initial molecule. The rearrangement proper proceeds as a spontaneous process or as a process with a low activation energy and in the latter case constitutes in essence a thermal process. Using a particular classification one must therefore bear in mind the limits of its applicability. Although the proposed classification is partly conventional, particularly when the individual stages of the rearrangements are considered, we nevertheless believe that it is useful when the process as a whole is considered.

II. GENERAL CHARACTERISTICS OF THE REARRANGEMENTS OF POLYHEDRAL BORON COMPOUNDS

In many chemical reactions of carbaboranes and other polyhedral boron compounds the decisive role of the characteristic features of the chemical bonds involving the atoms in these compounds is manifested. Analysis of literature data on the structures and reactivities of polyhedral boron compounds enabled us to isolate the following most significant features which determine the feasibility, direction, and mechanism of the rearrangements.

1. The presence of a reactive dynamic electronic system linking the atoms of the molecular skeleton, in the absence of a σ skeleton characteristic of classical carbon compounds.
2. The dependence of the configurational stability of polyhedral molecules on the symmetry of the boundary HOMO and LUMO and the energy gap between them and the consequent relation between the type of the resulting structure of the polyhedral molecule and the number of electrons binding the molecular skeleton (Wade's rule).
3. The reactions of polyhedral compounds with electrophiles involving HOMO and the reactions with nucleophiles involving LUMO.
4. The equal participation of boron and carbon atoms as well as other hetero-atoms in the electronic structure of the skeleton of the polyhedral molecule and the consequent appearance of an excess charge on the heteroatoms (for example, a positive charge on the carbon atoms in carbaboranes) and polarisation of the entire electronic system binding the atoms of the skeleton.

1. THE CHEMICAL BOND IN POLYHEDRAL BORON COMPOUNDS

Two main approaches have now been developed, permitting a description of the valence and electronic structures of the molecules of polyhedral boron compounds: the topological approach[14-17] and quantum-chemical calculations based mainly on the molecular orbital method in various approximations[14,18-29].

The topological approach is based on the idea that a strong two-electron bond may be formed between three atoms, i.e. a three-centre bond[30]. This concept was introduced because polyhedral systems cannot be described solely in terms of two-centre bonds, since in these compounds each boron atom supplies only two electrons for three atomic orbitals involved in the formation of the bonds of the skeleton. In order to describe the polyhedral molecule within the framework of the topological approach, equations are derived for electron balance, charge balance, orbital balance, and hydrogen atom balance. Their solution yields the number of three-centre and two-centre bonds characterising the given system. Next, using a series of topological limitations, topologically allowed valance structures are selected from all the possible combinations. Bearing in mind that formally 2/3 of the electronic charge corresponds to each atom on formation of a closed three-centre bond, a single charge corresponds to each atom on formation of a two-centre bond, etc., the method makes it possible to assess, together with the possible valence structures, also the charge distribution among the atoms of the polyhedral molecule. The topological approach is used to describe the chemical reactions of polyhedral compounds[31,32] and rearrangements[32,33] too. However, we believe that in the given instance the formalism of this method does not permit an understanding of the essential features of the transformations taking place and it is necessary to impose additional boundary conditions on the possible directions and mechanisms of the chemical reactions (see below).

The quantum-chemical calculations for the description of the electronic structures of polyhedral compounds are based on the molecular orbital method, which, being the most general procedure for the description of the chemical bond, makes it possible to obtain quantitative parameters characterising the given molecule. The molecular orbital method is used for the calculations on the ground states, for the determination of the possible directions of the reactions in particular rearrangements, and for the estimation of the stabilities of the intermediate compounds[10,34,35] (for example, in the rearrangement of 1,2-$C_2B_4H_6$ to the 1,6-isomer[36]).

Using the criteria governing the localisation of molecular orbitals proposed in the literature[37-40], Lipscomb and coworkers determined the localised valence structures of many boron hydrides and carbaboranes[23,24,28,29,41-44]. The valence structures obtained by the localisation of molecular orbitals agree on the whole with the topologically allowed structures when one considers in the latter case the set of possible structures taking into account the symmetry of the molecule. The majority of the molecules for which calculations have been made within the framework of the localisation criteria contain atoms whose bonds have minimal electron populations. The concept of a *fractional* three-centre bond was therefore introduced[41] and in the general case the concept of a fractional bond[28]. In order to represent the extent to which the bond is fractional (its population), together with valence bonds represented by continuous lines the following conventional representations have been introduced:

dashed line with an arrow	(·····→)	0.15 - 0.25 e;
continuous arrow	(——→)	0.25 - 0.35 e;
dashed line	(·····)	0.35 - 0.5 e;
continuous line	(——)	0.5 e.

Bonds with populations $< 0.15\ e$ are excluded from consideration[28]. Fig. 2 presents as an example the localised valence structures of 2,4-$C_2B_5H_7$,[24,41,43] 2,3-$C_2B_4H_8$,[24,41,44] $C_2B_7H_{13}$, 7,8-$C_2B_9H_{12}^-$, and $C_2B_{10}H_{13}^-$.[28] The hypothesis that fractional bonds are formed by localised molecular orbitals can apparently be also interpreted from the standpoint of delocalised three- and two-centre bonds, and they can be considered as delocalised (multicentre) bonds.

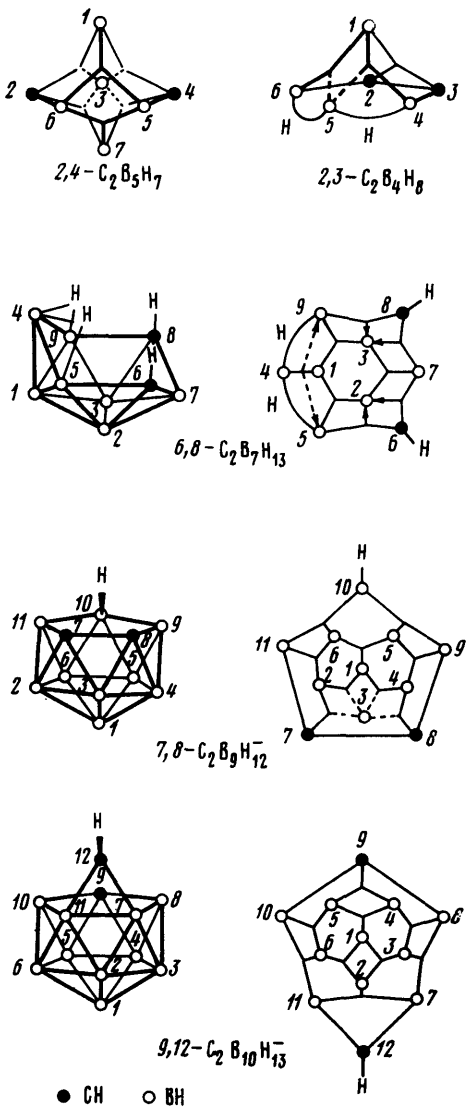


Figure 2. The valence structures of certain carbaboranes.

Since each valence line originating from an atom is usually associated with an atomic orbital, the notation used for fractional bonds requires some explanation. In this instance the "valence line" does not designate a localised atomic orbital but represents the direction of highest electron density in space. For localised two- and three-centre bonds, these concepts are identical. Within the framework of the valence bond method, fractional three-centre bonds can be described by resonance structures (Fig. 3).[41] The ideas concerning rapid electronic exchange processes and the combinatorial treatment of electron transfer in "electron deficient" polyhedral molecules have features in common with these concepts[45].

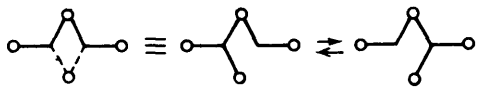


Figure 3. Representation of fractional three-centre bonds in terms of the valence bond method.

In polyhedral boron compounds localised two-centre bonds in general need not be normal σ bonds, since, owing to the geometrical characteristics of the molecular structure, they may not have axial symmetry, whereupon, like π bonds or "banana" type bonds, they should possess increased energy. This should in turn facilitate reactions with electrophiles involving such bonds and should lead to the formation of a three-centre bond (Fig. 4*a*).[2]

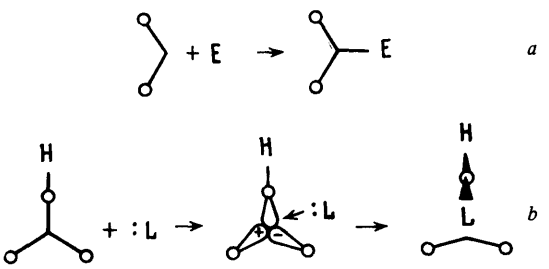


Figure 4. Models of the interaction of valence fragments of polyhedral boron compounds: *a*) formation of a two-centre bond with electrophiles; *b*) formation of a three-centre bond with nucleophiles.

Bonds of the second type, localised three-centre bonds, are characterised by three localised molecular orbitals, one of which is bonding and has low energy and the other two are antibonding. Depending on the symmetry and nature of the atoms forming the bond, one of the antibonding orbitals may have a very low position and its energy may approach that of a non-bonding level. Hence follows the high reactivity of the three-centre bond in relation to nucleophiles and reductants (Fig. 4*b*).[2]

Bonds of the third type in polyhedral compounds, delocalised (many-centre) bonds, are in general characterised by the presence of a high-energy HOMO and a low-energy LUMO. This should be manifested by a tendency of these bonds to undergo both electrophilic and nucleophilic reactions.

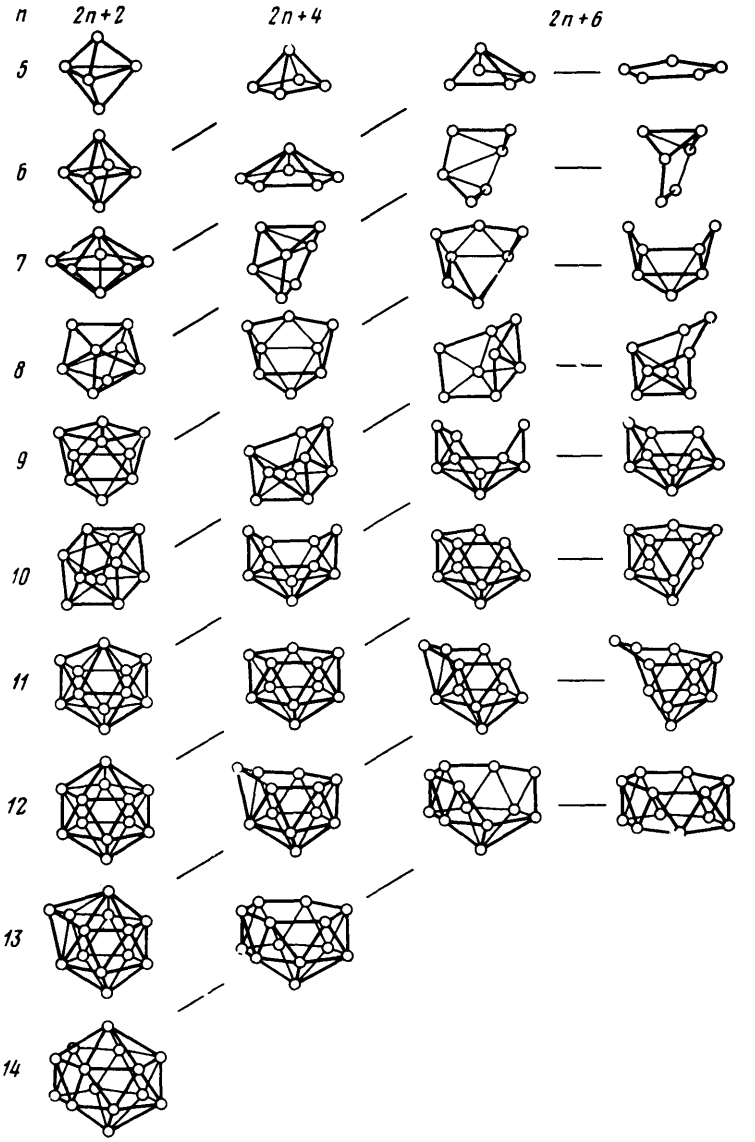


Figure 5. Relation between the type of structure of polyhedral boron compounds and their electronic structure (illustration of the Wade rule).

Thus chemical bonding in polyhedral boron compounds is characterised by a system of highly reactive two-, three-, and many-centre bonds. On the other hand, in the compounds under consideration there is no additional electronic system strongly binding the atoms of the molecular skeleton, in contrast to classical organic, particularly aromatic compounds where there exists, in terms of the σ–π approximation, a relatively inactive σ-skeleton imparting stability to the molecule in many reactions, in addition to the active π-electron system. Structural rearrangements of the molecular skeleton can therefore occur in polyhedral boron compounds during chemical reactions and thermal or electronic (under the influence of radiation) excitation.

2. RELATION BETWEEN THE NUMBER OF ELECTRONS AND THE STRUCTURE OF POLYHEDRAL COMPOUNDS

The direction of the rearrangements and the nature of the compounds formed are determined by the electronic structure of the polyhedral molecules and ions. Wade's rule, which establishes the relation between the number of electrons (or the number of electron pairs) participating in the binding of the atoms in the molecular skeleton and the type of structure, plays an important role in the understanding of the reductive and oxidative rearrangements of carbaboranes and other polyhedral boron compounds [13]. Rudolph and Pretzer [46] examined this relation in detail and confirmed by molecular orbital calculation the validity of

this rule: in particular they found that, when $n = 5$ for a system of $2n + 2 = 12$ electrons, there is a potential energy minimum corresponding to the *closo*-structure—a trigonal bipyramid, for a system with a $2n + 4 = 14$ electrons the minimum corresponds to the *nido*-structure—a tetragonal pyramid, and for a system with $2n + 6 = 16$ electrons, the minimum corresponds to the *arachno*-structure—a pentagonal fragment of a pentagonal bipyramid (Fig. 5). The authors[46] give an excellent illustration of this rule for the structural relation governing various polyhedral compounds[47]. This scheme (see Fig. 5) was supplemented by the present authors by the structures of closed polyhedra with 13 and 14 vertices and their fragments as well as certain alternative structures of *arachno*-compounds corresponding to the structures of borane and carbaborane ligands in transition metal complexes and, when $n = 9$, to the structure of the *arachno*-carbaborane $C_2B_7H_{13}$ (the first column in Fig. 5). This scheme does not include certain derivatives of boron hydrides and metalloboranes where bonds are formally formed by $2n$ electrons, for example in B_4Cl_4 (tetrahedron)[48-50], B_8Cl_8 (square antiprism)[51-54], B_9Cl_8H or $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$,[56] and $(\eta^5\text{-}C_5H_5)_3Co_3B_5H_5$.[57] As a possible structure of the above metalloboranes, Miller and Grimes[56] and Hall et al.[57] proposed $n - 1$ *closo*-polyhedra, where the "superfluous" BH or $Co(\eta^5\text{-}C_5H_5)$ structural unit is located above one of the triangular faces.

Among polyhedral boron compounds, there are examples of compounds which do not formally fit within the framework of the relations noted by Wade. We shall consider for example, the *arachno*-carbaboranes $C_2B_7H_{13}$[58,59] and $C_2B_8H_{14}$.[60,61] In these compounds the number of electrons binding the atoms of the molecular skeleton is the same as in the *closo*-carbaboranes $C_2B_7H_9$ and $C_2B_8H_{10}$ respectively. However, in the latter all the $3n$ atomic orbitals are involved in the construction of the molecular orbitals of the skeleton, while in *arachno*-carbaboranes only $3n - 2$ orbitals are involved, since two atomic orbitals, one from each carbon atom, form the C–H σ bond and for this reason there are two CH_2 structural units. Similarly in the series of the *nido*-carbaboranes $C_2B_7H_{11}$ has the BH_2 structural unit[62], i.e. $3n - 1$ atomic orbitals participate in the formation of the bonds of the skeleton; although the number of electrons binding the atoms of the skeleton is $2n + 2$, i.e. corresponds to the *closo*-structure, the compound is a *nido*-carbaborane and has an open structure.

Thus, when Wade's rule is applied to molecules in the ground state, account must be taken not only of the number of electrons binding the atoms in the skeleton but also of the total number of electrons in the $3n$-atomic orbitals of the n-atomic polyhedral molecule‡. In the more general case, including the excited states of the molecule, it is necessary to consider the number of occupied molecular orbitals made up of $3n$-atomic orbitals and not the number of electrons: the $n + 1$, $n + 2$, and $n + 3$ occupied orbitals will characterise the *closo*-, *nido*-, and *arachno*-structures respectively.

‡ $3n$ atomic orbitals are considered, and not the total number $4n$, because one orbital of each atom is involved in the formation of an outer σ bond and does not affect the nature of the structure.

3. REARRANGEMENTS INITIATED BY ELECTROPHILES AND NUCLEOPHILES

A graphical representation of localised two- and three-centre bonds can be conveniently employed for a clear description of reactions of polyhedral boron compounds with electrophiles and nucleophiles[2]. As already mentioned, chemical reactions with electrophiles E can proceed via two-centre or many-centre bonds (Figs. 4*a* and 6). In the latter case the reaction should lead to the localisation of the electron pair and the formation of either a three-centre bond BEB or a two-centre bond B–E or C–E with the electrophile. The reaction via a two-centre bond involves the intermediate formation of a three-centre bond BEB[2]. The strength of the latter is determined by the nature of the electrophile, the possibility of additional stabilisation as a result of the overlap of the electrophile orbitals, not involved in the formation of the bond, with the orbitals of the molecular skeleton, and finally, the symmetry of the three-centre bond[63,64]. Three-centre bonds BHB are quite stable. BEB bonds, where E = SiR_3, GeR_3, etc, are less stable and isomerise on heating in such a way that the electrophile moves to the terminal position relative to the boron atom (a B–E σ bond is formed), although the corresponding compounds with a bridge position of the electrophile E may be isolated and characterised, for example, μ-Me_3Si-2,3-$C_2B_4H_7$.[65-68] When E = Alk, compounds with a bridging alkyl group, for example μ-Alk-7,9-$C_2B_9H_{11}^-$ are stable only below 0°C, isomerising at room temperature to 10-Alk-7,9-$C_2B_9H_{11}^-$ in a few minutes[63,64]. Analogous compounds with an asymmetric alkyl bridge group, for example, in the 7,8-isomer (μ-Alk-7,8-$C_2B_9H_{11}^-$) are unstable even at low temperatures if they are formed at all.[12,69]

If the boron atoms forming a three-centre bond with the electrophile are non-equivalent, the BEB bond should be polarised in the direction ensuring the compensation of this non-equivalence. As a result of this, the three-centre bond is cleaved in such a way that the electrophile appears at the boron atom with the higher positive charge (in the initial state) (Fig. 6*a*). The directing effect in the rearrangement of the three-centre bond is static and to some extent resembles that in the directing effect in addition to the double bond in olefins.

There are several pathways leading to the transformation of a compound with a bridge group (Fig. 6). Pathways *b* and *c* (Fig. 6)§, leading to the formation of substitution products, were discussed in our earlier communication[2]. Pathways *d*, *e*, and *f* correspond to the oxidation of the system, i.e. to the closure of the polyhedron in the case of *nido*-compounds. Pathway *g* involves a rearrangement of the system, consisting in the migration of the boron atom with the substituent to the site of the missing vertex of the polyhedron with formation of a new isomer of the *nido*-carbaborane. As a result, the substituent passes to the terminal position and the hydrogen atom, previously in the terminal position, migrates to the bridge position. This mode of reaction was observed in the interaction of dicarbollide ions $C_2B_9H_{11}^{2-}$ with alkyl halides[12,63]. The driving force of this rearrangement is apparently electron transfer from the bonding orbital of the skeleton (B–Alk–B) to the B–Alkσ bond, oriented axially, i.e. involves in

§ Pathway *b* is in principle unlikely, since it requires the abstraction of a hydride hydrogen atom in the form of a proton.

essence the oxidation of the system and, in conformity with the Wade rule, the closure of the molecule into an octadecahedron. There are two σ-linked groups at the migrating boron atom in the transition state and stabilisation takes place as a result of further migration of the atom and the supply of electrons from the B–H σ bond to the bonding BHB orbital of the molecular skeleton. The molecule is then again opened and a fragment of an icosahedron with an equatorial orientation of the substituent is formed (Fig. 7).[12] The transition state in the given rearrangement can be stabilised, in principle, also as a result of the ejection of H^- or E^- (Alk^-) (Figs. 6*d*, 6*e*, and 6*f*) and in this instance the structure of the closed polyhedron is fixed (see also Section V, subsection 2).

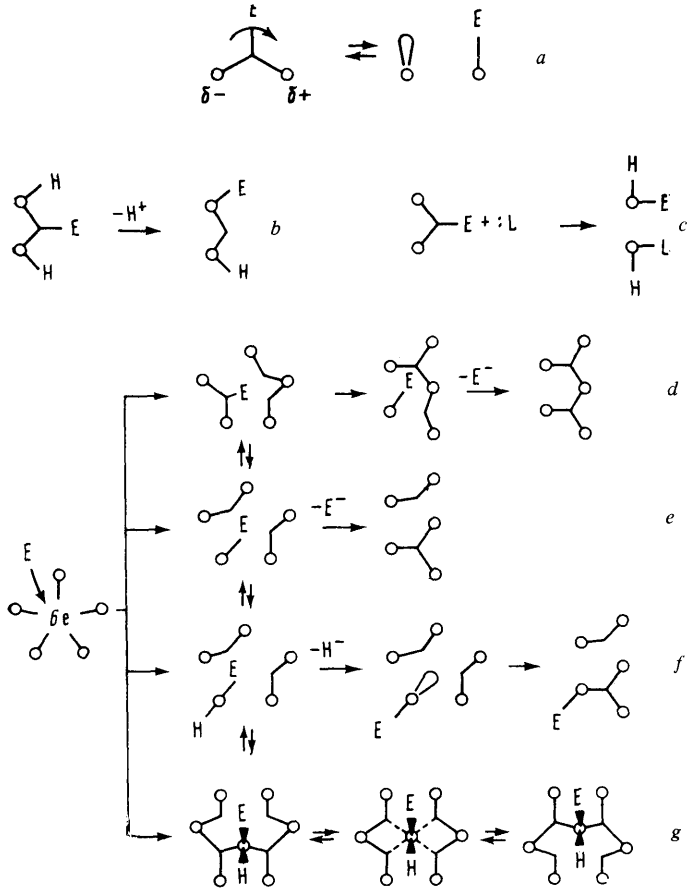


Figure 6. Possible rearrangements of bonds in systems with three- and many-centre bonds on interaction of two- and many-centre (five-centre) bonds with electrophiles.

The interaction of carbaboranes and other polyhedral compounds of boron with nucleophiles L and the reductants among them should proceed, as mentioned above, via three-centre and many-centre bonds having in the general case the lowest vacant orbitals. The attack by the nucleophile is on the three-centre bond and leads to its dissociation in such a way that L is oriented axially and H equatorially relative to the open face produced (Fig. 4*b*)¶. The stabilisation of the system requires the supply of electrons to orbitals linking the atoms of the molecular skeleton. This condition is fulfilled either on ejection of a proton from the boron atom forming a bond with the nucleophile and the involvement of the liberated electron pair in the binding of the atoms of the skeleton or after a rearrangement similar to that discussed above for the reaction of dicarbollide ions with alkyl halides. As a result electrons of the B–H σ bond (L) are used for the binding of the atoms of the skeleton, i.e. a BHB bridge bond is formed.

The characteristics found for the rearrangements initiated by electrophiles and nucleophiles show that, like the oxidative and reductive rearrangements, they proceed with a change in the number of electrons and in the general case in the number of orbitals binding the atoms of the skeleton of the molecule or ion in the transition state. We suggest that the thermal rearrangements of closed polyhedral systems can also proceed via a transition state in which the number of orbitals occupied by electrons changes (increases). As will be shown below, this is equivalent to the supply of additional electrons to the vacant orbitals. Thus, in the course of such thermal rearrangements, one may expect the opening of the *closo*-structure to the *nido*-structure due to electron transfer to a vacant orbital closest as regards energy and subsequent reclosure of the polyhedron, but in another direction. The foregoing permits the conclusion that an essential condition for the above rearrangements is a change in the number of occupied molecular orbitals during the reaction.

III. QUANTUM-CHEMICAL CRITERIA OF THE REARRANGEMENTS

The quantum-chemical approach is the most general and promising when the rearrangements of polyhedral molecules are considered. The possibility of determining the potential energy surface for a given system enables one to characterise unambiguously and quantitatively all possible molecular transformations. The difficulty of calculations of this kind in practice suggests that it might be useful to determine semiquantitative or even qualitative but objective criteria characterising a given rearrangement. The prediction of the relative configurational stability, direction, and mechanism of the rearrangements can be based in many instances on the first- and second-order Jahn–Teller effects[70]. The first-order Jahn–Teller effect arises under the following conditions: when a molecule with a given symmetry has a degenerate electronic state, the corresponding configuration of atoms in the polyhedral molecule is unstable and the structure changes in such a way that the degeneracy is removed[71]. Rearrangements of the skeleton can be both static and dynamic, i.e. the degeneracy may be removed by the vibrational motions of the molecule. The second-order Jahn–Teller effect is manifested when there is no degeneracy in the ground state but the boundary molecular orbitals have similar energies[70]. In this case the symmetry

¶When the nucleophile approaches from the other side of the bond (from the side opposite to the direction of the corresponding atomic orbital), L and H have the opposite orientations: equatorial for L and axial for H.

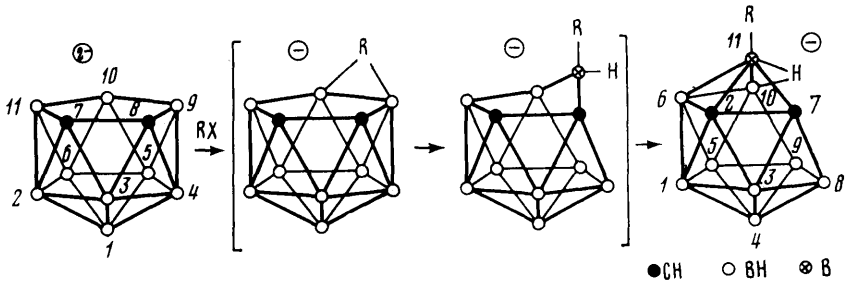


Figure 7. The proposed mechanism for the rearrangement of 7,8-dicarba-*nido*-undecaborate to the 2,7-isomer during the reaction of the dicarbollide ion with alkyl halides.

of the HOMO and LUMO and the energy gap between them determines the possibility of the rearrangement (makes it symmetry-allowed) and its ease in the particular direction.

It has been shown[72-74] that the energy change in the system following a small shift along a normal coordinate Q can be represented as follows:

$$E_0 - E_0' = \Delta E_0 = Q\left\langle \Psi_0 \left| \frac{\partial V}{\partial Q} \right| \Psi_0 \right\rangle + \frac{1}{2} Q^2 \left\langle \Psi_0 \left| \frac{\partial^2 V}{\partial Q^2} \right| \Psi_0 \right\rangle + Q^2 \sum_k \frac{\left[\left\langle \Psi_0 \left| \frac{\partial V}{\partial Q} \right| \Psi_k \right\rangle\right]^2}{E_0 - E_k}; \quad (1)$$

having assumed that the first term of the series characterising symmetrical shifts is zero, i.e. by considering only shifts which alter the initial molecular symmetry, the following expression was obtained[74]:

$$\Delta E_0 = \frac{1}{2} Q^2 \left\langle \Psi_0 \left| \frac{\partial^2 V}{\partial Q^2} \right| \Psi_0 \right\rangle + Q^2 \sum_k \frac{\left[\left\langle \Psi_0 \left| \frac{\partial V}{\partial Q} \right| \Psi_k \right\rangle\right]^2}{E_0 - E_k} = f_{00} Q^2 + f_{0k} Q^2, \quad (2)$$

where Ψ_0 and Ψ_k are the wave functions of the ground degenerate state with the energy E_0 and of the excited state with the energy E_k and V is the potential energy of the system corresponding to the nucleus–nucleus and nucleus–electrons interactions.

For any Q, we have $f_{00} > 0$, since it characterises the energy change averaged with respect to the initial optimised electron distribution. On the other hand, $f_{0k} < 0$, since $E_0 - E_k < 0$. Thus the stability of the given molecular configuration in relation to the rearrangement along the coordinate Q is determined by the relative values of f_{00} and f_{0k}:

(1) $f_{00} \gg f_{0k}$, $\Delta E_0 \gg 0$—system with the given symmetry is stable;

(2) $f_{00} \sim f_{0k}$, $\Delta E_0 \sim 0$—a rearrangement with a low activation energy is possible;

(3) $f_{00} \ll f_{0k}$, $\Delta E_0 \ll 0$—system is unstable and rearranges spontaneously to a system with another symmetry[74].

In a qualitative consideration of rearrangements it is not necessary to consider all the excited states and the treatment may be restricted to the one-electron transition between occupied and unoccupied boundary orbitals. These transitions can be observed experimentally in the ultraviolet and visible spectra. The smaller the energy gap and the closer the HOMO and LUMO levels, the greater the ease of the rearrangement. The initial configuration is regarded as unstable if the energy gap is < 4 eV.[74]

The choice of the possible direction of the rearrangements is restricted to the condition where the integral $\langle \Psi_0 | \partial V/\partial Q | \Psi_k \rangle$, which is included in the expression for f_{0k}, is not equal to zero. For this purpose, the representations of the given coordinate Q should be included in the products of the representations of the boundary molecular orbitals, and in the more general case of the orbital ψ_i, occupied in Ψ_0, and the orbital ψ_j, populated in Ψ_k.[74]

The Jahn–Teller effects can have important stereochemical manifestations in the chemistry of polyhedral boron compounds and can be used both for the explanation of the existing empirical rules, for example the Wade rule, and for the prediction of the possible mechanisms of the rearrangements of the skeleton of a polyhedral molecule[63].

It is possible to distinguish the following most characteristic manifestations of these effects.

1. The thermodynamic and kinetic stabilities of polyhedral boron compounds in relation to thermal rearrangements are determined by the energy gap ΔE between the boundary molecular orbitals, which, as already mentioned, may be estimated from spectroscopic data. For example, in the case of icosahedral carbaboranes(12) ΔE is large, which follows from the absence of absorption in the visible and ultraviolet spectra up to 200 nm, i.e. $\Delta E > 6$ eV, and the rearrangements of $C_2B_{10}H_{12}$ are observed only at temperatures of approximately 500°C and above. On the other hand, the spectra of the monoanions $C_2B_{10}H_{13}^-$ show absorption bands with a maximum at $\lambda = 260$ nm[75] and $\Delta E = 4.8$ eV; as a result of this, the rearrangements in the monoanions occur even at 100°C.[76,77] The dianions $C_2B_{10}H_{12}^{2-}$ derived from 1,2- and 1,7-$C_2B_{10}H_{12}$ absorb at $\lambda = 300$ nm, and those derived from 1,12-$C_2B_{10}H_{12}$ absorb at 335 nm,[75] to which correspond $\Delta E = 4.1$ and 3.7 eV respectively, and the rearrangements proceed readily at room temperature. The possible direction and type of the resulting isomers are then determined by other factors, including the symmetry of the boundary molecular orbitals.

When the mechanisms of thermal rearrangements are considered, it is striking that deformations which do not alter the initial molecular symmetry should be excluded from consideration. Otherwise, the first term of the expansion, which is positive by definition, must be again taken into account in Eqn. (1). Furthermore, the representation of a fully symmetrical deformation can be included only in the product of the deformations of boundary orbitals with identical symmetry. Thus fully symmetrical deformations will increase greatly the energy of the system. For example, in the rearrangements of icosahedral

carbaboranes $C_2B_{10}H_{12}$ the mechanisms involving a cubo-octahedral transition state appear unlikely on symmetry grounds, since the corresponding normal vibrations of a molecule with C_{2v} symmetry are fully symmetrical (see also Section V, subsection 2).

2. Any change in the number of orbitals occupied by electrons should lead to the destabilisation of the molecules or ions having a given symmetry. Indeed the atoms of the skeleton tend to assume a configuration such that all the electrons occupy bonding orbitals and the energy gap ΔE between the boundary orbitals is a maximum. For example, although the addition of electrons reduces the energy of the system on the whole, it destabilises the molecule or ion with the given symmetry relative to the zero non-bonding level, since the electrons are accommodated in antibonding molecular orbitals. The ease of rearrangements leading to a change in the initial symmetry and the accommodation of additional electrons at a bonding level is determined by the low value of ΔE between the antibonding orbital being filled and the nearest unfilled orbital and the occurrence of normal vibrational displacements with a suitable symmetry. In the borane anions $B_nH_n^{2-}$ ($n = 5,6,7,8,10,12$), the LUMO are degenerate[14,18], so that the rearrangements arising on increasing the number of electrons and the formation of $B_nH_n^{4-}$ may be caused by the first-order Jahn–Teller effect[46]. On passing the corresponding carbaboranes, for example, the $C_2B_nH_{n+2}$ series, the symmetry of the polyhedral molecule decreases, for example, from I_h in $B_{12}H_{12}^{2-}$ to C_{2v} in 1,2- and 1,7-$C_2B_{10}H_{12}$ or D_{5d} in 1,12-$C_2B_{10}H_{12}$. This should be accompanied by the splitting of the corresponding degenerate levels. However, the splitting is apparently not very great and the addition of electrons to carbaboranes and heteroboranes is also accompanied by a change in the initial structure owing to the second-order Jahn–Teller effect†. Here one should note that the degeneracy of the ground state is not in the general case a sufficient condition for the rearrangements (static deformations), as has been suggested, for example, by Rudolph and Pretzer[46] and Pearson[74]. In most cases the electronic degeneracy is converted into a vibronic degeneracy as a result of dynamic processes (see Bersuker[78], chapter VI). However, owing to the specific features of the reactions with nucleophiles and reductants via three-centre or many-centre bonds in polyhedral boron compounds, the addition of electrons should lead to the opening of the closed polyhedral molecule with formation of a tetragonal, pentagonal, or hexagonal face[2] (see also Sections II and IV).

3. The excitation of an electron to a vacant orbital is equivalent in terms of its stereochemical consequences to the addition of one or two electrons to the same orbital, and the symmetry of the molecule in the excited state should therefore be the same as that of the molecule which has combined with one or two electrons[79]. Thus, on excitation of electrons, there is a possibility of easy rearrangements of the atoms of the skeleton and the consequent formation of, for example, positional isomers depending on the positions of the substituents and heteroatoms in the polyhedral molecule. When the stereochemical results of the excitation or addition of electrons to a polyhedral molecule are compared, account must be taken of the lifetime of the excited state of the molecule. If the latter is short, the system may not attain the optimum configuration and the structure of the excited molecule may differ from that which has combined with the electrons.

4. The change in the symmetry of the polyhedral molecule or ion when the number of occupied orbitals is altered is determined by the symmetry of the possible soft deformations, i.e. the deformations of the boundary molecular orbitals. After the rearrangement, a molecule (ion), characterised by the correspondence of the number of occupied bonding orbitals with the number of electrons and by the maximum energy gap, is formed.

5. The decrease of molecular symmetry, i.e. the symmetry of the molecular orbitals, after the introduction of polar substituents at the atoms of the skeleton of the polyhedral molecule should lead, as already mentioned, to the splitting of the molecular orbital energy levels. Consequently, in the general case there is a possibility of the mutual approach of the HOMO and LUMO levels. In conformity with the second-order Jahn–Teller effect, this is manifested by the facilitation of the rearrangements of the corresponding molecules and by an increase of their reactivity. For example, the introduction of polar substituents in 1,5-$C_2B_3H_5$ destabilises the molecule to such an extent that the compounds prove to be unstable at room temperature[80].

The fundamental principles and rules of both thermal and reductive and oxidative rearrangements follow from the data discussed above: the Wade rule for rearrangements induced by a change in the number of electrons in the system, and the change in the number of molecular orbitals, binding the atoms of the molecular skeleton and occupied by electrons in the ground and transition states, for a series of thermal rearrangements.

IV. REDUCTIVE AND OXIDATIVE REARRANGEMENTS

According to the Wade rule, any change in the number of electrons without the alteration of the given set of molecular orbitals in conformity with the Jahn–Teller effects, should be accompanied by the destabilisation of the initial configuration and a change in the symmetry of the skeleton of the molecule or ion. When electrons are added, the molecule tends to undergo a rearrangement to achieve an increase in the number of bonding orbitals, and when electrons are removed, it tends to undergo a rearrangement involving a corresponding decrease. The Wade rule fully satisfies these requirements. For example, the addition of two electrons to an n-atomic polyhedral molecule with a *closo*-structure, i.e. having $n + 1$ electron pairs and the corresponding number of bonding orbitals, should lead to a *nido*-structure of the n-atomic fragment of an $(n + 1)$-atomic closed polyhedron having $n + 2$ pairs of bonding electrons distributed in $n + 2$ bonding orbitals.

1. REDUCTIVE REARRANGEMENTS

(a) The Addition of Electrons

The three-centre bonds between carbon and boron atoms in *closo*-carboaranes are the most polarised and therefore have the lowest unoccupied molecular orbitals. This determines the course of the reactions with nucleophiles, including reductants, formally at the boron atoms adjoining carbon atoms. The opening of a *closo*-structure to give a *nido*-structure after the addition of two electrons with formation of a pentagonal or hexagonal face may be

† If the LUMO remain degenerate in the given compounds, the rearrangement is again determined by the first-order Jahn–Teller effect.

accounted for by the rearrangement of the three-centre bonds to two-centre bonds in accordance with the schemes illustrated in Fig. 8.[2] The reduction is usually carried out with metallic sodium in liquid ammonia or tetrahydrofuran (THF). In the latter case electron-transferring agents, for example, naphthalene, are frequently used to achieve the addition of two electrons[81,82]. Electrochemical reduction of polyhedral molecules has also been described[83-87].

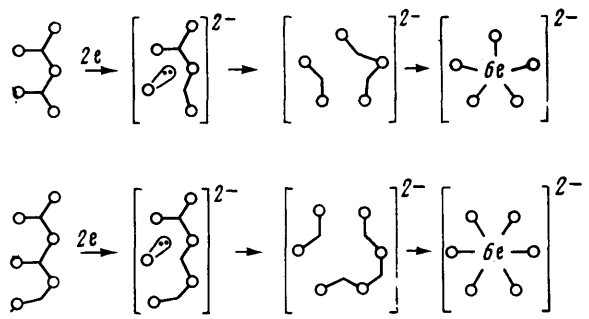


Figure 8. Models of the interaction of possible fragments of polyhedral molecules with reducing agents.

The complexity of the study of reactions involving the addition of electrons to polyhedral molecules consists in the fact that, owing to the one-electron multistage mechanism of this process, radical-anions are formed at an intermediate stage and this determines in many instances the course of cross-linking and disproportionation reactions. Furthermore, the dianions formed may not be individual species and may consist of sets of dynamic structures. Thus the energy barriers between different $C_2B_3H_5^{2-}$ isomers are very low and easy rearrangements of the atoms of the skeleton are therefore possible[10]. The interaction of the dianions with electrophiles is accompanied by the fixation of the open structure and it is possible to isolate individual compounds. Protonation of the dianions leads to the corresponding monoanions and uncharged *nido*-carbaboranes. Depending on the nature of the binding of the proton, the open face retains its structure completely on formation of the BHB bridge bond or partly contracts on formation of B–H or C–H bonds[2]. The above features are illustrated by the examples described below.

1,2-$C_2B_8H_{10}$. The addition of two electrons to 1,2-$C_2B_8H_{10}$ gives rise to a dianion whose protonation gave the *nido*-carbaborane 5,6-$C_2B_8H_{12}$ (Fig. 9) in 30% yield[88]. The reduction of *nido*-5,6-$C_2B_8H_{12}$ with sodium amalgam in ethanol leads, in conformity with the Wade rule, to the *arachno*-carbaborane 6,9-$C_2B_8H_{14}$ in 26% yield. The formation of the 6,9-isomer in this reaction can be explained by the migration of the $C_{(6)}$ atom (Fig. 9).[61]

$C_2B_{10}H_{12}$. The dianions of all the carbaborane(12) isomers and many of their *C*- and *B*-derivatives have now been investigated. The results of the early theoretical calculations suggested that the addition of electrons to $C_2B_{10}H_{12}$ may not be accompanied by a significant change in the icosahedral structure[14,34]. It was therefore postulated that the opening of the icosahedral molecule does not occur in the stage involving the addition of electrons to the molecule, but during the protonation of the dianions formed[14]. However, experimental ^{11}B NMR, infrared spectroscopic, and ultraviolet spectroscopic data indicate a significant change in the icosahedral structure of $C_2B_{10}H_{12}$ molecules when electrons are added to them. The ^{11}B NMR spectra of the dianions derived from *o*-, *m*- and *p*-$C_2B_{10}H_{12}$ and their various derivatives, recorded at 32.1 MHz by a double resonance technique, are characterised by a set of broad lines over a wide frequency range and differ fundamentally from the spectra of the initial carbaboranes(12)[75,89]. The *nido*-structure of $C_2B_{10}H_{12}^{2-}$ is also indicated by the infrared spectra of the dianions in THF solution where there are two signals in the range 2400–2600 cm^{-1} due to the stretching vibrations of two types of B–H bonds, apparently located in the open face and in the closed part of the polyhedron. The ultraviolet spectra of the dianions $C_2B_{10}H_{12}^{2-}$ derived from 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ contain absorption bands with maxima at 298 ± 10, 295 ± 10, and 335 nm respectively. This distinguishes them from the initial icosahedral carbaboranes, which do not absorb in the visible and ultraviolet (up to 200 nm) spectra[75].

On the basis of these data, we suggest that the dianions $C_2B_{10}H_{12}^{2-}$ have a structure of the molecular skeleton similar to that of the corresponding carbaborane ligands in transition metal complexes (Fig. 10) and are characterised by rapid dynamic rearrangements of the molecular skeleton[75,89].

The chemical properties of the dianions derived from 1,2- and 1,7-$C_2B_{10}H_{12}$ indicate specific differences between their structures. Thus protonation of these dianions under identical conditions gives rise to mixtures differing in the ratio of the isomeric monoanions[75,89]. Oxidation of the complexes of the corresponding dianions by cobalt(III) also leads to neutral carbaboranes(12) with different yields and different mixture compositions[89,90]. The nature of the

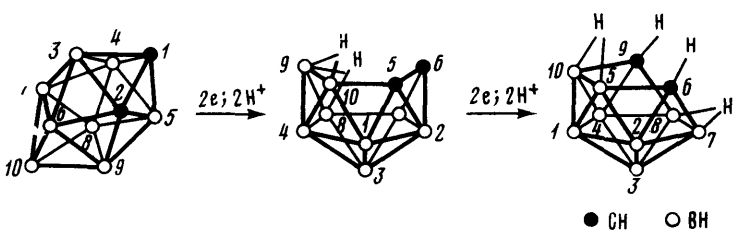


Figure 9. The opening of *closo*-1,2-$C_2B_8H_{10}$ to give *nido*-5,6-$C_2B_8H_{12}$ and *arachno*-6,9-$C_2B_8H_{14}$ on reduction and subsequent protonation.

structural differences between the dianions cannot be determined exactly by experimental methods. Presumably they are associated with the different positions of carbon atoms in the open face: for example, 1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ give rise to the dianions 7,9-$C_2B_{10}H_{12}^{2-}$ and 7,10-$C_2B_{10}H_{12}^{2-}$ respectively. The structure in which only one carbon atom is on the open face has been suggested for the dianion derived from 1,12-$C_2B_{10}H_{12}$ (Fig. 10).[11]

It is noteworthy that the dianions obtained from 1,2- and 1,7-$C_2B_{10}H_{12}$ have similar spectroscopic characteristics. Furthermore, oxidation of these dianions leads to the same product—1,2-$C_2B_{10}H_{12}$. Some workers used these data as the basis for the hypothesis that the dianions from 1,2- and 1,7-$C_2B_{10}H_{12}$ are identical[77,83,91,92]. However, the foregoing considerations, the non-characteristic nature of the spectroscopic characteristics examined, and the possibility of the formation of *o*-carbaborane(12) on closure of the fragment of a 13-vertex polyhedron with an arbitrary distribution of carbon atoms in the open face[11,75] led us to the conclusion that this view is erroneous.

(b) Electrochemical Reduction

$C_2B_9H_{11}$. The electrochemical reduction of *closo*-2,3-$(CH_3)_2$-2,3-$C_2B_9H_9$ and its *B*-hydroxy- and *B*-alkoxy-derivatives proceeds in stages. The first stage leads to the formation of radical-anions. For 2,3-$(CH_3)_2$-$C_2B_9H_9$ and its *B*-hydroxy-derivatives, this process is electrochemically irreversible, which is attributed to the possibility of the occurrence of a chemical reaction or a change in the carbaborane molecule. For B-alkoxy-derivatives of carbaborane(11), the addition of two electrons in stages is observed, the first stage being reversible. The radical-anions formed are stable in this case. Analogous stable radical-anions are formed when the corresponding carbaboranes are acted upon by sodium in THF. Both electrochemical and chemical (Na in THF) addition of an electron to the radical-anions leads to the formation of derivatives of 7,9-$C_2B_9H_{11}^{2-}$ dianions[87].

$C_2B_{10}H_{12}$. In contrast to the multistage reduction of $C_2B_9H_{11}$ derivatives discussed above, a single two-electron wave is observed in the electrochemical reduction of icosahedral *o*-carbaboranes[83-86].

(c) Transition Metal Complexes of the Dianions

The fixation of the structure of the dianion and the overall stabilisation of the carbaborane ligand take place also when transition metal complexes are formed. The addition of electrons from sodium to polyhedral molecules with a *closo*-structure and subsequent treatment with transition metal salts and $C_5H_5^-Na^+$ constitute one of the main methods for the synthesis of metallocarbaboranes, metalloheteroboranes, and metalloboranes (the polyhedral expansion method[81,82,93-97]). The method involving the direct insertion of a transition metal atom in the polyhedral molecule without preliminary reduction of the latter[98-102] is in essence analogous to the polyhedral expansion method, since in this case electrons are also transferred to the polyhedral molecule, but this time from the transition metal atom‡ and the reduction and complex formation stages are thus combined. Since the number of atoms constituting the molecular skeleton changes in these reactions (increases), we shall describe only the fundamental principles without considering in detail all the available literature data concerning the synthesis of metal-containing molecules and ions (see the relevant reviews[103-106]). The rearrangements of polyhedral molecules in polyhedral expansion reactions are fully consistent with the Wade rule, i.e. complexes having the structure of the next polyhedron are formed as a result. The metal atom then occupies the vertex with the highest coordination number. As a result of the addition of electrons, the initial polyhedral molecule rearranges and becomes a ligand in the complex. The structure of the ligand corresponds to the structure of a fragment of the next polyhedron (the Wade rule) and in carbaborane ligands the carbon atoms are located in the open face. This reflects the mode of addition of electrons

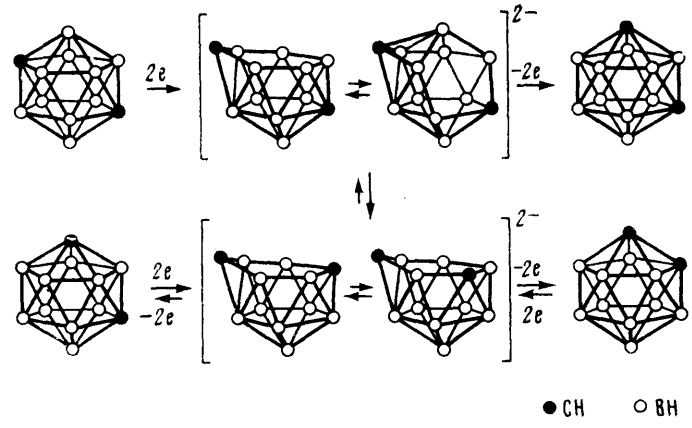


Figure 10. The possible modes of opening of icosahedral carbaboranes following the addition of electrons and rearrangement of the resulting dianions.

‡ For example, the following transition metal complexes are used as reagents: $Fe(CO)_5$, $(C_5H_5)Co(CO)_2$, $(C_2H_4)Ni(PPh_3)_2$, (*trans*-stilbene)$Pt(PMe_3)_2$, etc.

and the stability of the corresponding dianions in which the carbon atoms are in the open face.

Successive application of the polyhedral expansion method yielded metallocarbaboranes containing two and three transition metal atoms, i.e. formally the initial n-atomic molecule with a *closo*-structure, which ultimately combines with three pairs of electrons, is converted into an n-atomic fragment of the $(n + 3)$-atomic polyhedron and the sites of the three missing vertices are occupied by the transition metal atoms (Fig. 11*a*). The hitherto unknown structures of polyhedra with 13 and 14 vertices were also obtained by the polyhedral expansion reaction of the icosahedral carbaborane (Figs. 11*b* and 11*c* [95]).

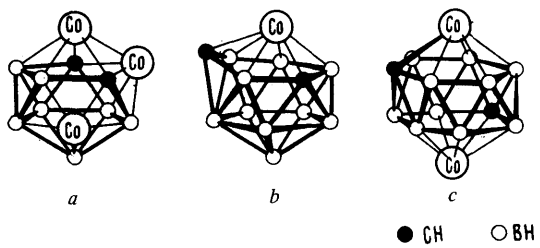


Figure 11. The structures of metallocarbaboranes obtained by the polyhedral expansion method: *a*) 1,2,8,3,6-$(\eta^5\text{-}C_5H_5)_3Co_3C_2B_7H_9$; *b*) 1,2,4-$(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$; *c*) 1,14,2,10-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_{10}H_{12}$ (suggested structure of one of the isomers). The ligands C_5H_5 are not shown in the Figure.

By reducing the carbaboranes $Me_4C_4B_8H_8$ with $NaC_{10}H_8$ and subsequent treatment with NaC_5H_5 and $FeCl_2$, Grimes and coworkers [97] obtained several $(\eta^5\text{-}C_5H_5)_2Fe_2Me_4C_4B_8H_8$ isomers. X-Ray diffraction analysis established that two out of the four isomers isolated have the structure of 14-vertex fragments of 15-vertex closed polyhedra with an open tetragonal or pentagonal face [the *nido*-structure of a $(2n + 4)$-electron polyhedron] (Fig. 12). Nevertheless, the authors [97] believe that 14 atoms of the molecular skeleton are linked by 30 electrons, i.e. belong to the type of $(2n + 2)$-electron polyhedra, which should have a *closo*-structure according to the Wade rule.

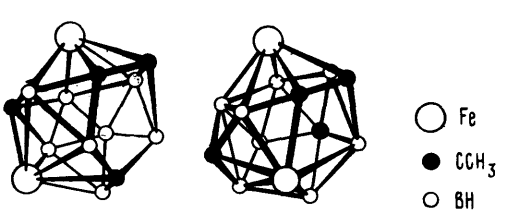


Figure 12. The structures of 15-vertex *nido*-metallocarbaboranes. The ligands C_5H_5 are not shown in the Figure.

Hawthorne and coworkers [107] examined the problem of the application of the Wade rule to metallocarbaboranes. Taking into account the tendency of the transition metal atom to complete its outer electron shell, i.e. to have 18 electrons in the latter, and also the fact that six ligand electrons participate in the coordination of the ligand to the transition metal, the "magic numbers" determining the type of structure and class of metallocarbaboranes were also derived. For complexes with a single transition metal atom and a single carbaborane ligand, $2n + 14$ electrons characterise *closo*-compounds and $2n + 16$ electrons characterise *nido*-compounds. For the metal : ligand = 1 : 2 ratio, the corresponding numbers are $2n + 12$ for a *closo*-structure, $2n + 14$ for *closo*- and *nido*-structures, and $2n + 16$ for a *nido*-structure. For the ratio 2 : 1, a polyhedral *closo*-molecule is characterised by $2n + 26$ electrons [107].

In his study of the structure of transition metal complexes with dicarbollide ions, Wegner [108] noted that the molecules have an icosahedral structure for metals with a $d^5 - d^7$ electronic configuration and a significantly distorted (open) structure for $d^8 - d^9$ metals. The transition from a d^6 configuration to d^7, d^8, and d^9 configurations is equivalent to the addition of one, two, and three electrons respectively. Thus the opening of an icosahedral *closo*-structure takes place directly in the reduction of the polyhedral system and not in the protonation stage [108].

(d) The Addition of Nucleophiles

Reductive rearrangements (opening) of closed polyhedral molecules as a result of the addition of nucleophiles should include, as already noted, several stages apart from the addition of electrons (see also the footnote in Section II, subsection 3): the ejection of a proton from the boron atom with which the nucleophile has formed a bond, and reorientation of the resulting atomic orbital with an electron pair; another more probable reaction pathway involves a rearrangement of the polyhedral molecule and the supply of electrons from the B–H bond to the orbitals of the skeleton as a result of the formation of a BHB bridge bond. If the compound formed is unstable, for example, because the carbon atoms are not located in the open face, stabilisation may be achieved due to further rearrangements (see Section V, subsection II).

$C_2B_4H_6$. The addition of nucleophiles, for example, Me_3N, Me_3P, or H^-, to *closo*-1,6-$C_2B_4H_6$ leads to the opening of the molecule and the formation of *nido*-5-Me_3N-2,4-$C_2B_4H_6$, 5-Me_3P-2,4-$C_2B_4H_6$, and 2,4-$C_2B_4H_7^-$ respectively (Fig. 13*a*). [109–111]

$C_2B_9H_{11}$. The interaction of 2,3-$C_2B_9H_{11}$ with a wide range of nucleophiles L proceeds with formation of 10-L-7,9-$C_2B_9H_{11}^-$ [112–114] (Fig. 13*b*). The suggested formation of 3-L-7,9-$C_2B_9H_{11}^-$ was disproved [115,116].

The opening of closed polyhedral metallocarbaboranes on treatment with nucleophiles has been observed in many instances [117–119].

2. OXIDATIVE REARRANGEMENTS

The oxidative rearrangements of *nido*-carbaboranes may be described in terms of schemes which are the opposite of those for the addition of electrons. The oxidant E interacts with the highest occupied two-centre or delocalised five- or six-centre orbital and a two-centre B–E or C–E bond or a three-centre BEB bond is formed. The opening of the latter and the formation of a B–E or C–E bond lead

to partial closure of the *nido*-structure. Electron transfer to the oxidant completes the closure of the structure (Figs. 6*d*, 6*e*, and 6*f*). Evidently the mode of oxidative rearrangements is determined by the direction of electrophilic attack and may not take place along the same coordinate as the reverse process involving the opening of the structure under the influence of a reductant or a nucleophile.

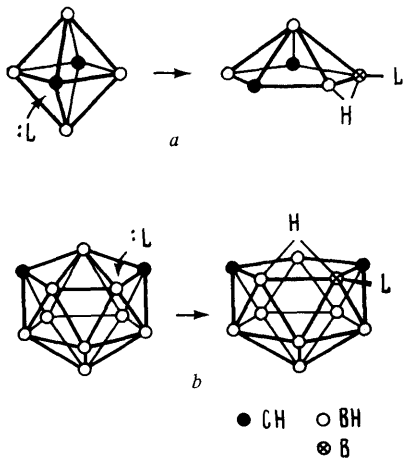


Figure 13. The opening of *closo*-carbaboranes on interaction with nucleophiles: *a*) 1,6-$C_2B_4H_6$; *b*) 2,3-$C_2B_9H_{11}$.

Many transformations of neutral *nido*-carbaboranes into *closo*-carbaboranes on pyrolysis may be classified as oxidative rearrangements. Such a reaction is used in the synthesis of all the lower and medium carbaboranes $C_2B_nH_{n+2}$:

$$C_2B_9H_{13} \xrightarrow{-H_2} C_2B_9H_{11}\ ^{58,\,120},$$
$$C_2B_8H_{12} \xrightarrow{-H_2} C_2B_8H_{10}\ ^{62,\,88,\,121-120},$$
$$C_2B_7H_{13} \xrightarrow{-H_2} C_2B_7H_9\ (+\ C_2B_6H_8 + C_2B_8H_{10})\ ^{58,\,124},$$
$$C_2B_4H_8 \xrightarrow{-H_2} C_2B_4H_6\ (+\ C_2B_3H_5 + C_2B_5H_7)\ ^{125-127}.$$

Owing to the radical mechanism of the pyrolysis, reactions involving the disproportionation or cross-linking of the polyhedral molecules frequently occur. Intramolecular oxidation (closure) also takes place when a halide anion is eliminated from (B)-Hal-$C_2B_{10}H_{11}^{2-}$ [128]:

$$(C_2H_{10}H_{11}X)^{2-} \rightarrow C_2B_{10}H_{11}^{-} + X^{-}.$$

Depending on the distribution of electron density in the open face of the polyhedral molecule, reactions with electrophiles can proceed in different ways and the oxidative rearrangement can lead to different products.

Examples of the oxidative rearrangements of open polyhedral compounds are the closure of thioboranes on oxidation and pyrolysis [129]:

$$arachno\text{-}6\text{-}SB_9H_{12}^{-} \xrightarrow{-2e,\,[O]} nido\text{-}6\text{-}SB_9H_{11} \xrightarrow{-H_2\,(t^\circ)} closo\text{-}1\text{-}SB_9H_9,$$

the formation of *closo*-2,3-$C_2B_9H_{11}$ on oxidation of *nido*-7,9-$C_2B_9H_{11}^{2-}$ with stannous chloride [114]:

$$nido\text{-}7,9\text{-}C_2B_9H_{11}^{2-} \xrightarrow{-2e\,(SnCl_4)} closo\text{-}2,3\text{-}C_2B_9H_{11},$$

and oxidative rearrangements of carbaborane(12) dianions and their derivatives.

A characteristic feature of the oxidative rearrangements of the dianions $C_2B_{10}H_{11}^{2-}$ is that they lead to isomers of the icosahedral carbaborane(12), which are in general different from the initial isomers. For example, the oxidation of the dianions of both 1,2- and 1,7-$C_2B_{10}H_{12}$ leads exclusively to 1,2-$C_2B_{10}H_{12}$, [83] while the dianion derived from 1,12-$C_2B_{10}H_{12}$ yields only 1,7-$C_2B_{10}H_{12}$. [130,131] The oxidation of the dianions derived from a series of *C*-derivatives of *p*-carbaborane yields also derivatives of the *o*-isomer together with those of the *m*-isomer, depending on the type and number of substituents [11,75,132,133]. The direction of the rearrangements is greatly influenced by substituents in the carbaborane ring. The oxidative rearrangement of the dianion obtained from 2-Hal-1,12-$C_2B_{10}H_{11}$ leads to a mixture of the two possible isomers of (B)-Hal-1,7-$C_2B_{10}H_{11}$ and unsubstituted 1,12- and 1,7-$C_2B_{10}H_{12}$. Mainly 10-Hal- and 3-NH_2-$C_2B_{10}H_{12}$ are formed together with 1,2- and 1,7-$C_2B_{10}H_{12}$ from 9-Hal-1,7-$C_2B_{10}H_{11}$ under analogous conditions [130]. In many instances the influence of the substituent is so great that the direction of the rearrangement changes; for example, derivatives of the 1,7-isomer are formed together with those of 1,2-$C_2B_{10}H_{12}$ in the oxidation of the dianion obtained from 1-CH_2Hal-1,2-$C_2B_{10}H_{11}$. [134]

Thus the set of experimental data shows that the substituent influences the direction not only of oxidative but also of reductive rearrangements and the occurrence of the rearrangements in the dianions themselves.

Oxidative rearrangements of *nido*-metallocarbaboranes lead to the closure of the polyhedron, as expected [135].

V. THERMAL REARRANGEMENTS

1. REARRANGEMENT OF CLOSED POLYHEDRAL SYSTEMS

The rearrangements of closed polyhedral molecules take place over a wide temperature range. For example, the anions $B_2H_6^{2-}$, $B_{11}H_{11}^{2-}$, and $CB_{11}H_{11}^{-}$ rearrange so fast that the characteristics of the ^{11}B NMR spectra of these species in solution at room temperature and below are averaged out. On the other hand, 1,7-$C_2B_{10}H_{12}$ isomerises to 1,12-$C_2B_{10}H_{12}$ only above 500°C. We have already noted that many thermal rearrangements involve electron transfer between occupied and unoccupied boundary molecular orbitals, which determines the course of the given reaction. In this case the excitation of the electron is apparently associated with an appreciable mutual approach of the HOMO and LUMO levels on deformation of the molecule as a result of the vibrational motion or collision of the molecules. In the limiting case in the transition state there is a possibility of degeneracy of the electronic state of the molecule. Since, according to the Jahn–Teller effect, the excitation of the electron is stereochemically equivalent to the addition of one or two electrons, the deformed molecule may be stabilised to a greater or lesser extent in the open state. The possibility of easy structural rearrangements of an excited molecule and the closure of the polyhedron in a direction which is not the same as that of its opening lead to the isomerisation of the initial molecule. The alternative model of the mechanism of thermal rearrangements is based on the familiar ideas concerning the occurrence of synchronous (concerted) reactions. In the absence of symmetry-dependent prohibitions the energy of the system varies smoothly along the reaction coordinate and does not require the mutual approach of the HOMO and LUMO energy levels.

Evidently, among all the possible deformations of the initial molecule leading to the final product, those which are consistent with molecular symmetry, are minimal, and have the lowest force constants will actually occur. Thus, when the mechanisms of thermal rearrangements are considered, it is useful to employ the second-order Jahn–Teller effect, which imposes certain symmetry-dependent limitations on "soft" deformations. In conformity with this effect, the deformation should not be fully symmetrical and its representation should be included in the product of the representations of boundary molecular orbitals (see Section III).

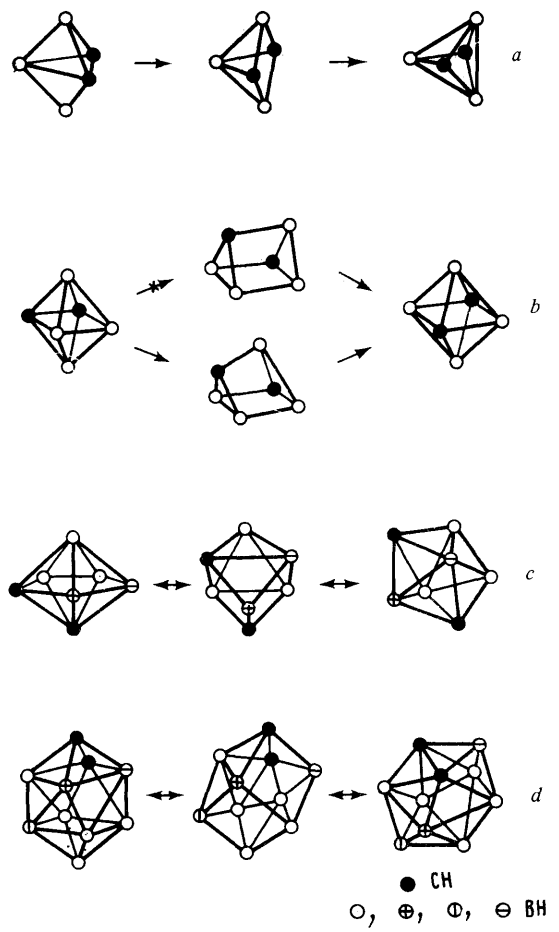


Figure 14. The proposed mechanisms for the thermal rearrangements of *closo*-carbaboranes with different structures: *a*) trigonal bipyramid; *b*) octahedron; *c*) pentagonal bipyramid; *d*) square antiprism with two vertices. In order to represent the rearrangements with greater clarity, the boron atoms in structures *c* and *d* are marked in different ways.

When the system attains equilibrium, the thermodynamically most stable isomer predominates. In the series of carbaboranes the tendency determining the direction of the rearrangement is the endeavour by carbon atoms to occupy positions in which their excess positive charge is compensated to the maximum extent and the molecule has the highest symmetry. This determines the high stability of isomers in which carbon atoms are furthest apart and have the minimum possible coordination number[2,136].

Trigonal bipyramid $C_2B_3H_5$. Dicarba-*closo*-pentaborane(5) has the structure of a trigonal bipyramid. In this structure there is a possibility of three isomers depending on the positions of the carbon atoms in the molecule. According to molecular orbital calculations, the thermodynamic stabilities of the isomers decrease in the sequence 1,5- > 1,2- > 2,3-$C_2B_3H_5$.[20] Only the two isomers 1,5- and 1,2-$C_2B_3H_5$ are known and the latter has been obtained only as the 2,3-dimethyl derivative, 2,3-Me_3-1,2-$C_2B_3H_5$, which does not rearrange to the 1,5-isomer and this served as the basis for the hypothesis that it is stabilised by the presence of methyl substituents[3,137]. The fact that 1,5-$C_2B_3H_5$ is formed in the reaction of diborane or pentaborane(9) with acetylene or in the pyrolysis of the *nido*-carbaborane 2,3-$C_2B_4H_8$, in which the carbon atoms occupy adjacent positions, indicates the intermediate formation of the $C_2B_3H_5$ isomers with carbon atoms in adjacent positions, i.e. 1,2- and (or) 2,3-$C_2B_3H_5$. Under reaction conditions, they rapidly isomerise to the thermodynamically more stable 1,5-isomer[137].

The mechanism of the rearrangements in the systems considered has not been investigated. A possible mechanism involves the rearrangement of the rhomboid fragment, made up of two trigonal faces, to a square, this being followed by the closure of the structure and the reformation of a rhomboid fragment in which the carbon atoms are separated by boron atoms—a *dsd* mechanism (Fig. 14*a*).[3]

Octahedron. $C_2B_4H_6$. An example of a rearrangement of an octahedral molecule is provided by the isomerisation of 1,2-$C_2B_4H_6$ to the 1,6-isomer, which occurs at 250°C.[138] Calculations show that the 1,6-isomer is more stable than the 1,2-isomer by 15 kcal mole^{-1},[139] which agrees with the direction of isomerisation. Lipscomb and coworkers[36] established by molecular orbital calculations that the rearrangement proceeds via the intermediate formation of a compound having the structure of a distorted trigonal prism (Fig. 14*b*). Mechanisms based on the formation in the transition state of a molecule with the structure of a non-distorted trigonal prism or on the opening of the *closo*-molecule to give a *nido*-structure, i.e. a pentagonal pyramid, are ruled out, since they require high activation energies[35,36].

Pentagonal bipyramid. $C_2B_5H_7$. Of the four possible $C_2B_5H_7$ isomers, two have been obtained so far: 2,3-$C_2B_5H_7$[62,122] and 2,4-$C_2B_5H_7$.[125] Rearrangements of this type of polyhedron have not been observed in the series of unsubstituted carbaboranes, although the 2,4-isomer should apparently be more stable. Lipscomb[3] proposed a two-stage mechanism for the possible rearrangement of the 2,3-isomer to 2,4-$C_2B_5H_7$, involving successive application of the *dsd* model (Fig. 14*c*) (see also subsection 3 of this Section).

Dodecahedron. $B_8H_8^{2-}$, $C_3B_5H_7$, and $C_2B_6H_8$. It has been noted that polyhedral systems of this type can readily undergo structural rearrangements of the atoms of the skeleton[140]. The influence of solvents, counterions, and temperature on the nature of the dynamic processes in the system has been investigated by ^{11}B NMR for the anion

$B_8H_8^{2-}$.[141] In solvents of low polarity at a temperature below 10°C the ^{11}B NMR spectrum has three signals with relative intensities of 2 : 4 : 2. On passing to highly polar solvents or on raising the temperature, the spectrum is gradually transformed and at 46°C in 1,2-dimethoxyethane it contains only signal. According to the authors [141,142], these data show that $B_8H_8^{2-}$ in solution has the structure of a trigonal prism with two vertices (solvents of low polarity, low temperature) or a square antiprism (polar solvents, elevated temperature) and not a dodecahedron (Fig. 15*a*). We believe that this interpretation of spectroscopic data is insufficiently justified. For example, the authors' assumption[141] that a change of temperature can lead to a complete conversion of one polyhedral form into another under the conditions of equilibrium between the suggested structures of a trigonal prism with two vertices and a square antiprism is incomprehensible. There is no doubt that rapid rearrangements of the polyhedral molecule (dynamic processes) are characteristic of the given system.

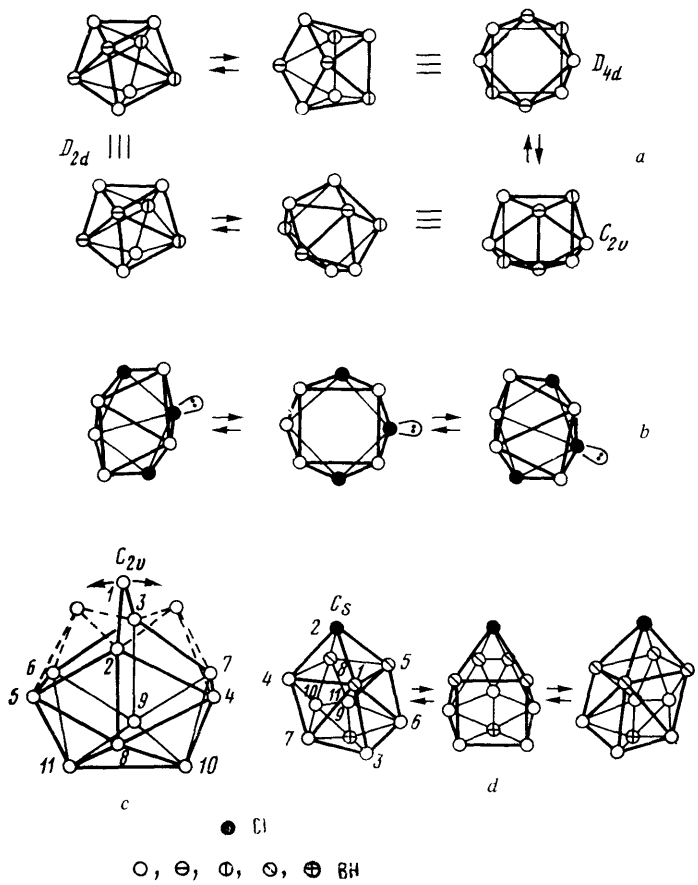


Figure 15. The proposed mechanisms for the dynamic rearrangements of certain closed polyhedral compounds: a) $B_8H_8^{2-}$; b) $C_3B_5H_7$; c) $B_{11}H_{11}^{2-}$; d) $CB_{10}H_{11}^{-}$. To achieve a greater clarity in the representation of the rearrangements, the boron atoms in structures *a* and *d* are marked in different ways.

$C_3B_5H_7$. Tricarba-*closo*-octaborane(7) is a second example of the occurrence of rapid rearrangements of the skeleton of an eight-atom polyhedral molecule. The ^{11}B NMR spectrum of this compound contains three signals with relative intensities 2 : 2 : 1, while the ^1H NMR spectrum consists of three quartets, due to protons linked to the boron atoms, and [a single] signal originating from the proton in the C–H bond with relative [H–B/H–C] intensities of 5 : 2. In order to account for the spectroscopic data, the authors[143] postulate the occurrence of dynamic rearrangements of the molecule with a dodecahedral structure via a transition state having the structure of a square antiprism (Fig. 15*b*).

One may assume that such easy rearrangements in the compounds considered are caused either by the degeneracy of the ground molecular state or by the low value of the energy gap between HOMO and LUMO and, in conformity with the Jahn–Teller effects, the configurational instability of the molecules.

$C_2B_6H_8$. Only one isomer (1,7-$C_2B_6H_8$) of dicarba-*closo*-octaborane(8) has been obtained. According to X-ray diffraction data, it has the structure of a dodecahedron (D_{2d} symmetry). Although the ^{11}B NMR spectrum of 1,7-$C_2B_6H_8$ has only two signals with relative intensities of 4 : 2, the authors[58,142] suggest that this compound undergoes dynamic rearrangements of its molecular skeleton and that the presence of the signal with a relative intensity of 4 is due to a random superposition of two signals having relative intensities of 2 : 2.

Square antiprism with two vertices. $C_2B_8H_{10}$. Of the seven possible isomers of dicarba-*closo*-decaborane(10), only three are known at the present time: 1,2-, 1,6- and 1,10-$C_2B_8H_{10}$. As was to be expected, the stabilities of these isomers increase in the sequence 1,2- < 1,6- < 1,10-$C_2B_8H_{10}$. The compounds 1,2- and 1,6-$C_2B_8H_{10}$ wholly isomerise to the 1,10-isomer on heating to 300°C.[58,88] The mechanism proposed for the rearrangements is based on the *dsd* model and requires several consecutive stages (Fig. 14*d*).[3]

Octadecahedron. $B_{11}H_{11}^{2-}$, $CB_{10}H_{11}^{-}$, and $C_2B_9H_{11}$. As for the dodecahedron, the rearrangement of polyhedral compounds having the structure of an octahedron proceed very readily.

$B_{11}H_{11}^{2-}$. The ^{11}B NMR spectrum of *closo*-undecaborate(2-) contains only one signal[144] and its nature is independent of the solvent employed and the temperature[145]. A decrease of temperature causes only a broadening of the signal in the spectrum, apparently due to the increased viscosity of the solution. Analogous data were obtained for $B_{11}H_7Br_4^{2-}$. The ^{11}B NMR spectrum of this compound has two signals with relative intensities of 4 : 7, caused by substituted and unsubstituted boron atoms. Tolpin and Lipscomb[145] explained the results on the hypothesis that these ion rapidly rearrange in solution via a transition state with the structure of an 11-vertex fragment of an icosahedron (Fig. 15*c*).

$CH_{10}H_{11}^{-}$. Another mechanism of the rearrangement of molecules having an octadecahedral structure has been proposed[146] in a study of monocarba-*closo*-undecaborate(1-). This mechanism is based on the *dsd* model. The ^{11}B NMR spectrum of this compound is characterised by three signals with relative intensities of 1 : 5 : 4, which can be explained by a rapid rearrangement (Fig. 15*d*). As

a result, the boron atoms in the 1-, 4-, 5-, and 8-positions and those in the 3-, 6-, 7-,10-, and 11-positions are indistinguishable in their spectral effects, while the B(9) atom gives rise to a single-intensity signal[146]. It is noteworthy that both mechanisms considered yield equally satisfactory explanations of the observed ^{11}B NMR spectra of $B_{11}H_{11}^{2-}$ and $CB_{10}H_{11}^{-}$.

As in $B_8H_8^{2-}$, the dynamic processes in $CB_{10}H_{11}^{-}$ and $B_{11}H_{11}^{2-}$ are apparently caused by the degeneracy of the ground state or the proximity of the boundary orbitals of the molecule. The lack of data for the energies and symmetries of the molecular orbitals of these compounds makes it impossible at the present time to give preference to one of the two mechanisms proposed for the rearrangements. However, if the deformation leading to the opening of $B_{11}H_{11}^{2-}$ (C_{2v}) and $CB_{10}H_{11}^{-}$ (C_S) has B_2 and A'' symmetry respectively, then the deformation characterising the *dsd* model does not correspond to any of the normal vibrations of the molecules under consideration. On the assumption that the excitation energy required for the rearrangement of the molecule is distributed among the normal vibrational degrees of freedom and that the deformation in the direction of the soft vibrational mode leads to rearrangement, this nevertheless enables us to consider the "opening-closure" mechanism to be more probable for the rearrangements of $B_{11}H_{11}^{2-}$ and $CB_{10}H_{11}^{-}$.[63]

2,3-$C_2B_9H_{11}$. 2,3-Dicarba-*closo*-undecaborane(11) is the only one of the twenty possible isomers obtained at the present time and is theoretically the most stable. This carbaborane is formed from both 7,9-$C_2B_9H_{13}$ and 7,8-$C_2B_9H_{13}$ in which the carbon atoms are in adjacent positions[58]. In the latter case the carbon atoms in the $C_2B_9H_{11}$ formed in the first stage should also apparently be in adjacent positions and the structure is possibly 2,4-$C_2B_9H_{11}$. Its rapid isomerisation to the 2,3-isomer is consistent with the ease of the rearrangements of octadecahedral molecules.

Icosahedron. $C_2B_{10}H_{12}$ and $CHPB_{10}H_{10}$. Numerous studies have been devoted to the thermal rearrangements of carbaboranes(12) and their derivatives. It has been established that the thermodynamic stability of $C_2B_{10}H_{12}$ isomers increases in the sequence 1,2- < 1,7- < 1,12-$C_2B_{10}H_{12}$, and that at approximately 450° C the *o*-isomer isomerises wholly to the *m*-isomer.[147-151] The *p*-isomer is formed at a higher temperature (approximately 600° C and above)[152] and equilibrium is established between the *m*- and *p*-carbaboranes(12)[153]:

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

$$1,7\text{-}C_2B_{10}H_{12} \underset{}{\overset{600^\circ}{\rightleftharpoons}} 1,12\text{-}C_2B_{10}H_{12}.$$

The introduction of bulky substituents into the icosahedral molecule led to a considerable facilitation of the rearrangements in many instances[154].

As a result of systematic studies on the rearrangement of carbaborane(12) isomers their B-halogeno-derivatives, and other icosahedral heteroboranes, six different mechanisms have been suggested to account for the formation of the products of the rearrangement (Fig. 16). The mechanism involving a cubo-octahedral transition state (Fig. 16*a*) explains the formation of 1,7-$C_2B_{10}H_{12}$ from the 1;2-isomer, but cannot account for the formation of 1,12-$C_2B_{10}H_{12}$.[3,34,155,156] The mechanism which is also based on a cubo-octahedral transition state but is modified by the assumption that the trigonal faces in the latter can rotate (Fig. 16*b*) explains the formation of 1,12-$C_2B_{10}H_{12}$ and the composition of the isomer mixture formed in the rearrangements of 9-Br-1,2-$C_2B_{10}H_{11}$[157] and 9-Cl-1,7-$C_2B_{10}H_{11}$.[158] In another modification of the *dsd* mechanism the rotation of tetragonal faces in the transition state is postulated (Fig. 16*c*).

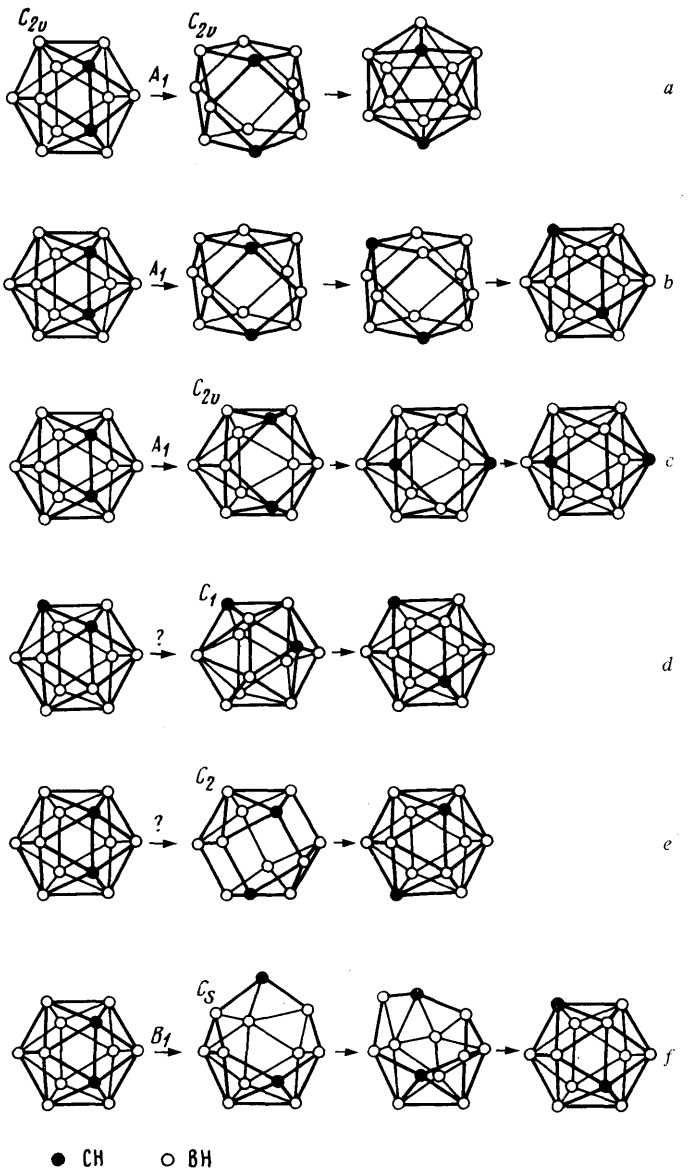


Figure 16. The mechanisms proposed for the rearrangements of icosahedral carbaboranes.

This mechanism has been proposed as one capable of explaining the rearrangements in the series of phosphacarbaboranes[5]. The last two mechanisms involve the rotation of trigonal faces (Fig. 16*d*) and pentagonal pyramidal fragments (Fig. 16*e*) in the ground icosahedral state[6,7]. These mechanisms also explain the formation of 1,12-$C_2B_{10}H_{12}$ and preference is given to the mechanism based on the rotation of pentagonal pyramids in the rearrangement of *B*-halogenophosphacarbaboranes[5]. Thus, according to the

authors[5], the mechanism of the rearrangements of icosahedral molecules should change on passing from the carbaborane system $C_2B_{10}H_{12}$ to the heterocarbaborane system $CHPB_{10}H_{10}$.

Wong and Lipscomb[5] proposed a mechanism for the rearrangements of icosahedral molecules which differs fundamentally from that considered above. It involves the opening of the icosahedral *closo*-structure to give a *nido*-structure which is a fragment of a 13-vertex polyhedron; the reverse closure of the polyhedron in other directions leads to the formation of different isomeric products (Fig. 16*f*). Since this mechanism predicted the occurrence of certain isomers whose formation in the series of phosphacarbaboranes had not been observed experimentally, the authors[5] gave preference to the mechanism involving the rotation of pentagonal pyramidal fragments. However, it is evident that, without the imposition of boundary conditions, the "opening-closure" mechanism, being one of the most general, will predict the formation of all possible isomers.

It was already noted above that the mechanisms involving a cubo-octahedral transition state do not meet the requirements of the symmetry of "soft" deformations. Indeed, if the molecules of 1,2- and 1,7-$C_2B_{10}H_{12}$ with C_{2v} symmetry are considered, the deformation leading to a cubo-octahedral transition state has the A_1 symmetry, i.e. is fully symmetrical (Figs. 16*a*, 16*b*, and 16*c*). On the basis of the symmetry I_h of a regular icosahedron ($B_{12}H_{12}^{2-}$), one can also conclude that this mechanism as well as the mechanism based on the rotation of pentagonal fragments are unlikely, since the direct product of the representations of the boundary orbitals of $B_{12}H_{12}^{2-}$ having the G_u symmetry for HOMO and G_g symmetry for LUMO[14,18] is equal to $A_u + F_{1u} + F_{2u} + G_u + H_u$, i.e. includes only representations which are antisymmetric relative to the inversion operation. On the other hand, the deformations considered are symmetrical relative to inversion (Figs. 16*a* and 16*e*) and their representations cannot therefore be included in the above product. The mechanisms involving the rotation of individual fragments of the icosahedral molecule (Figs. 16*d* and 16*e*) are also unlikely, since in the molecules with the given symmetry there are no normal vibrations corresponding to the required deformations. Furthermore, the mechanisms considered above require large displacements of many atoms. On the other hand, the deformation leading to the opening of the molecule (Fig. 16*f*) has the B_1 symmetry, if one begins with the C_{2v} symmetry for 1,2- and 1,7-$C_2B_{10}H_{12}$, and is minimal.

2. REARRANGEMENTS OF OPEN POLYHEDRAL MOLECULES

As already mentioned, the structures of *nido*-compounds are n-vertex fragments of an $(n+1)$-vertex closed polyhedron and are characterised by the presence of a tetragonal, pentagonal, or hexagonal face. Neutral polyhedral *nido*-compounds are also characterised by the presence of hydrogen bridge atoms§ in the open face, which determines their thermal instability—*nido*-carbaboranes decompose on heating with evolution of hydrogen and give rise to *closo*-carbaboranes (see Section IV, subsection II).

Thermal rearrangements of *nido*-carbaboranes have been observed only for the corresponding anions. Among the possible conformers, those with the maximum possible number of atoms in the open face are stable on thermal isomerisation. The relative thermodynamic stabilities of isomers with different positions of the heteroatoms in the molecule are determined, as already mentioned, by the possibility of compensating their excess charge. Accordingly, in the thermodynamically more stable *nido*-carbaboranes the carbon atoms are as a rule located in the open face.

Tetragonal pyramid. $C_2B_3H_7$. A distinctive feature of the familiar 1,2-$C_2B_3H_7$ isomer of dicarba-*nido*-pentaborane(7) is that only one carbon atom is located in the open face of the molecule and the second occupies a vertex position (Fig. 17*a*).[159] The stability of this particular isomer can be accounted for by the presence of two hydrogen bridge atoms. If both carbon atoms were in the open tetragonal face, then, in view of the necessity for the formation under these conditions of a CHB bridge, the excess positive charge on the carbon atom would have increased and not decreased. On the other hand, the formation of the BH_2 or CH_2 group is unfavourable in view of the principle governing the stability of polyhedral compounds¶. For this reason, only the 1,2-isomer of the neutral *nido*-carbaborane $C_2B_3H_7$ exists[10]. According to molecular orbital calculation, the dianion $C_2B_3H_5^{2-}$ should also have the structure of a tetragonal pyramid and the stability of the isomers should then vary in the sequence 2,4- > 2,3- > 1,2-$C_2B_3H_5^{2-}$ according to general principles. Calculation shows that the rearrangement of one isomer to another takes place as a result of the migration of an atom from the open face to the site of the missing vertex of the octahedron. This mechanism is symmetry-allowed and energetically more favourable than the *sds* (*square–diamond–square*) mechanism, which is also symmetry-allowed[10].

Pentagonal pyramid. $C_2B_4H_8$. Although two of the three possible isomers of dicarba-*nido*-hexaborane(8), with neighbouring or non-neighbouring carbon atoms in the open pentagonal face, are known (the 2,3- and 2,4-isomers†) (Fig. 17*b*), there are no literature data for the rearrangement of one isomer to the other. At the same time rearrangements of substituted carbaboranes with retention of the positions of the carbon atoms have been observed[65,110,111]:

$$5\text{-}Me_3N\text{-}2,4\text{-}C_2B_4H_6 \rightarrow 3\text{-}Me_3N\text{-}2,4\text{-}C_2B_4H_6\ ,$$
$$4\text{-}R_3Si\text{-}2,3\text{-}C_2B_4H_7 \rightarrow 1\text{-}R_3Si\text{-}2,3\text{-}C_2B_4H_7\ .$$

Calculation showed that the stabilities of the isomeric dianions vary in the sequence 2,4- > 2,3- > 1,2-$C_2B_4H_6^{2-}$.[10]

$C_2B_6H_{10}$. The proposed structure of the known isomer of dicarba-*nido*-octaborane(10) (I) is presented in Fig. 17*c*. ^{11}B and ^1H NMR data are also consistent with the possibility of dynamic transitions between structures (II) and (II′) (Fig. 17*c*).[160]

§ In conformity with the isoelectronic principle, certain *nido*-compounds, for example, *nido*-carbaboranes $C_4B_{n-4}H_n$, are uncharged and have no hydrogen bridge atoms.

¶ Polyhedral systems where, as far as possible, all the $3n$ orbitals of the atoms in the skeleton are involved in the formation of bonds are distinguished by the highest stability.

† The 2,4-isomer is known only as the anion 2,4-$C_2B_4H_7^-$ or the inner trimethylammonium salt[109,110].

$C_2B_7H_{11}$. Dicarba-*nido*-nonaborane(11) is interesting because its structure is greatly influenced by substituents at the carbon atoms of the molecular skeleton. Thus the possible structure of the unsubstituted carbaborane $C_2B_7H_{11}$ (the known isomer) (Fig. 17*d*) is characterised, according to the authors[62], by the presence in the open hexagonal face of two carbon atoms in the *ortho*-positions with respect to one another, and of only one BHB bridge. According to ^{11}B NMR data, another "superfluous" hydrogen atom forms a σ bond with a boron atom, giving rise thereby to the BH_2 structural unit. When methyl substituents are attached to the carbon atoms, the molecule has the usual structure of a fragment of a square antiprism with two vertices according to X-ray diffraction data (Fig. 17*d*). The authors[62] explain the structural differences and the greatest stability of the dimethyl derivative of $C_2B_7H_{11}$ by the steric or electronic influence of methyl groups.

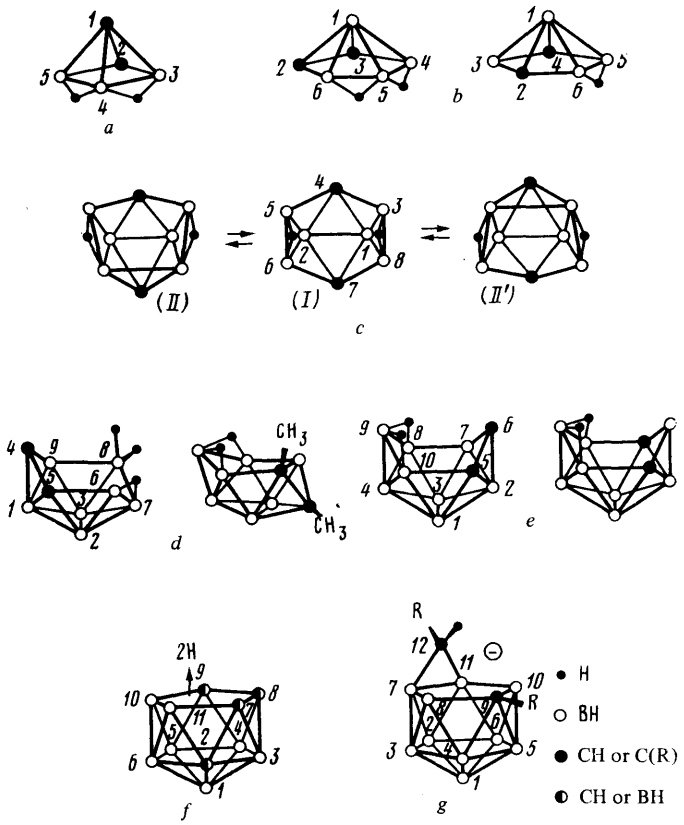


Figure 17. The structures of *nido*-carbaboranes: *a*) 1,2-$C_2B_3H_7$; *b*) 2,3-$C_2B_4H_8$ and 2,4-$C_2B_4H_7^-$; *c*) 4,7-$C_2B_6H_{10}$; *d*) 4,5-$C_2B_7H_{11}$ and 6,7-$Me_2C_2B_7H_9$; *e*) 5,6- and 5,7-$C_2B_8H_{12}$; *f*) 7,8-, 7,9-, 2,7-, 2,8- and 2,9-$C_2B_9H_{13}$; *g*) 9,12-$R_2C_2B_{10}H_{11}^-$ (R = Me or Ph).

$C_2B_8H_{12}$. Two isomers of dicarba-*nido*-decaborane(12) are known—with the carbon atoms in the open face occupying neighbouring positions (5,6-$C_2B_8H_{12}$)[62,122] and separated by one boron atom (5,7-$C_2B_8H_{12}$)[123] (Fig. 17*e*). Thermal rearrangements of $C_2B_8H_{12}$ isomers or their derivatives have not been noted.

$C_2B_9H_{13}$. Five isomers of dicarba-*nido*-undecaborane(13) are known at the present time: 7,8-, 7,9-‡, 2,9-, 2,8-, and 2,7-$C_2B_9H_{13}$ (Fig. 17*f*). These *nido*-carbaboranes are formed on protonation of the corresponding dicarba-*nido*-undecaborates(1-). The first three isomers are obtained on alkaline cleavage of 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$[161-163] and the last two are obtained as a result of chemically initiated thermal rearrangements occurring in the alkylation of 7,8- and 7,9-dicarbollide ions by alkyl halides[12,63,64,69].

Carrett and Hawthorne[164] achieved the thermal isomerisation of 7,8-$C_2B_9H_{12}^-$ to the 7,9-isomer:

$$7,8\text{-}C_2B_9H_{12}^- \xrightarrow{300^\circ} 7,9\text{-}C_2B_9H_{12}^-.$$

The rearrangements of dicarba-*nido*-undecaborates occur much more readily when their electronic structure is altered during the chemical reaction. Thus the rearrangement of the 7,8-isomer to the 2,7-isomer in the alkylation of 7,8-$C_2B_9H_{11}^{2-}$ is so fast that the intermediate Alk-7,8-$C_2B_9H_{11}^-$ cannot be detected even below 0°C:[12,69]

$$7,8\text{-}C_2B_9H_{11}^{2-} \xrightarrow{RX} (R\text{-}7,8\text{-}C_2B_9H_{11}^-) \rightarrow 11\text{-}R\text{-}2,7\text{-}C_2B_9H_{11}^-.$$

The structure of 11-R-2,7-$C_2B_9H_{11}^-$ has been demonstrated, together with other methods, by a complete X-ray diffraction investigation of the corresponding protonated derivative 11-Me-2,7-$C_2B_9H_{12}$.[165] The intermediate product μ-Alk-7,9-$C_2B_9H_{11}^-$ of the alkylation of 7,9-$C_2B_9H_{11}^{2-}$ is relatively more stable and has been detected, but not isolated because it rearranges rapidly above 0°C:[64]

$$7,9\text{-}C_2B_9H_{11}^{2-} \xrightarrow{RX} \mu\text{-}R\text{-}7,9\text{-}C_2B_9H_{11}^- \rightleftarrows \underset{\substack{+H^+\uparrow\downarrow-H^+}}{(7\text{-}R\text{-}2,8\text{-}C_2B_9H_{11}^-)} \xrightarrow{-H^+} (7\text{-}R\text{-}2,8\text{-}C_2B_9H_{10}^{2-}) \rightarrow$$
$$\rightarrow 10\text{-}R\text{-}7,9\text{-}C_2B_9H_{10}^{2-} \xrightarrow{+H^+} 10\text{-}R\text{-}7,9\text{-}C_2B_9H_{11}^-.$$

In the 2,7- and 2,8-isomers of *B*-alkyldicarba-*nido*-undecaborate(1-) only one carbon atom is located in the open face; the other is in the closed part of the polyhedron, and this is the reason for the low stability of these isomers. The direction and rate of the rearrangements of the 2,7- and 2,8-$C_2B_9H_{13}$ derivatives are determined by the tendency to remove both carbon atoms to the open face and the substituent by the equatorial position when the process is stereospecific[63]. Thus 11-Me-2,7-$C_2B_9H_{12}$ is relatively resistant to rearrangements; the monoanion 11-Me-2,7-$C_2B_9H_{11}^-$ rearranges in solution at room temperature to 8-Me-7,9-$C_2B_9H_{11}^-$, while the dicarbollide ion 11-Me-2,7-$C_2B_9H_{10}^{2-}$ is converted in solution below −30°C (liquid ammonia) into 9-Me-7,8-$C_2B_9H_{10}^{2-}$, yielding 9-Me-7,8-$C_2B_9H_{11}^-$ after protonation (Fig. 18).[12,69] Among the 2,8-isomers, only the compound 7-Alk-2,8-$C_2B_9H_{12}$ is relatively resistant to rearrangements. When a proton is abstracted, the above equilibrium between μ-Alk-7,9- and 7-Alk-2,8-$C_2B_9H_{11}^-$ is displaced towards μ-Alk-7,9-$C_2B_9H_{11}^-$, but the rearrangement as a whole proceeds towards 10-Alk-7,9-$C_2B_9H_{11}^-$. We suggest that the final product is formed as a result of the abstraction of a proton from 7-Alk-2,8-$C_2B_9H_{11}^-$ by a solvent molecule or by a second reactant molecule; as in the isomerisation of 11-Alk-2,7-$C_2B_9H_{11}^-$ to 9-Alk-7,8-$C_2B_9H_{11}^-$ (Fig. 18), the dianion

‡ The *nido*-carbaborane 7,9-$C_2B_9H_{13}$ is unstable, because two BHB bonds cannot be formed in the open face, and it has been characterised only in the form of a salt of the corresponding monoanion 7,9-$C_2B_9H_{12}^-$.[161]

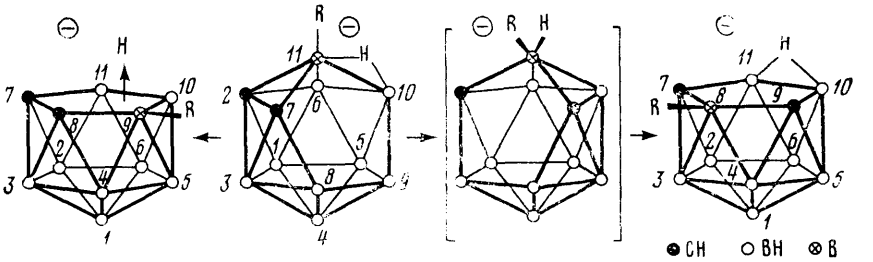


Figure 18. The possible modes of rearrangement of 11-R-2,7-$C_2B_9H_{11}^-$ (R = alkyl).

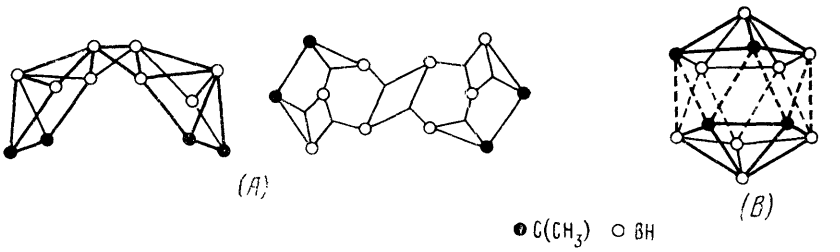


Figure 19. Structures proposed for the isomers of the four-carbon carbaborane $Me_4C_4B_8H_8$.

7-Alk-2,8-$C_2B_9H_{10}^{2-}$ rearranges to 10-Alk-7,9-$C_2B_9H_{10}^{2-}$. On protonation, the latter gives rise to 10-Alk-7,9-$C_2B_9H_{11}^-$.[63]

The rearrangements of 7,8- and 7,9-isomers to 2,7- and 2,8-dicarba-*nido*-undecaborates(1-), discussed above, are facilitated in reactions with electrophiles by the breakdown of the delocalisation of the electrons in the open face of dicarbollide ions and the axial orientation of the substituent on formation of a "π-complexes" and then a "σ-complex".[12] It is possible to distinguish two stages in these reactions: the first involving the addition of the electrophile to the dicarbollide ion (activation of the system) and the second involving a thermal rearrangement of the resulting dicarba-*nido*-undecaborate with an axially oriented alkyl group. Chemical activation is apparently energetically comparable to thermal activation and the rearrangements considered therefore proceed on the whole at lower temperatures.

$C_2B_{10}H_{14}$ derivatives. Owing to their low stability, neutral isomers of the *nido*-carbaborane $C_2B_{10}H_{14}$ have not been obtained. The anions of this carbaborane are relatively stable: the dianions, formed after the addition of two electrons to isomers of *closo*-$C_2B_{10}H_{12}$, and the monoanions obtained on protonation of the dianions. It was noted above that the dianions $C_2B_{10}H_{12}^{2-}$ are apparently not individual species, consisting of sets of dynamic structures based on the open structure of a fragment of a 13-vertex polyhedron. The rearrangements of the dianions are determined, on the one hand, by dynamic processes involving a change in the position of the vertex raised over the plane of the open face, as, for example, in the cobalt complex of the carbaborane ligand $C_2B_{10}H_{12}^{2-}$ (Fig. 20*e*)[166] and, on the other hand, they are determined by the migration of one of the atoms in the open face to the site of the missing vertex of the polyhedron. This type of rearrangement explains the transitions between different sets of dynamic structures, for example, in the isomerisation of the dianions obtained from *o*-, *m*-, and *p*-carbaboranes(12) and their derivatives (Fig. 10). A process with "closure-opening" of the polyhedral system is also possible.

Protonation of the dianions $C_2B_{10}H_{12}^{2-}$ and their derivatives leads to the fixation of the open face and the monoanions can be isolated as individual compounds. On heating to 100°C, one of the isomers isolated is converted quantitatively into the other[76,77]. Depending on the direction of electrophilic attack by the proton, the open structure of the dianion should be retained in its entirety, if the proton occupies a BHB bridge position, or closed to a greater or lesser extent on formation of a B–H or C–H σ bond[2]. The latter process takes place as a result of the transfer of an electron pair from the orbital binding the atoms of the molecular skeleton to an outer σ bond. This type of closure has been demonstrated by an X-ray diffraction study of one of the isomers C,C'-Me_2- and C,C'-Ph_2-$C_2B_{10}H_{11}^-$, which are characterised by the presence of the $C\begin{smallmatrix}R\\H\end{smallmatrix}$ structural unit (Fig. 17*g*).[167,168]

The closure of the structure of the dianion also occurs under the influence of other electrophiles. For example, the alkylation of the aminated dianions derived from 1,2-$C_2B_{10}H_{12}$ proceeds at the boron atom, and, when the latter migrates together with the substituent in the transition state, a hydride ion is evidently ejected (oxidised) from the boron atom with the alkyl group; the molecule undergoes closure to *closo*-2-NH_2-6-Alk-1,7-$C_2B_{10}H_{10}$.[169-172] This mode of reaction is apparently due to the increased hydride mobility of the hydrogen atom linked to the migrating boron atom attached to the substituent.

$Me_4C_4B_8H_8$. The synthesis of the stable four-carbon carbaborane $Me_4C_4B_8H_8$, isoelectronic with the $C_2B_{10}H_{12}^{2-}$ dianions, is of considerable interest in both theory and

practice[173-175]. In solutions $Me_4C_4B_8H_8$ exists in two equilibrium isomeric forms A and B:

$$A \rightleftarrows B,\ K = [B]/[A] = 0.5.$$

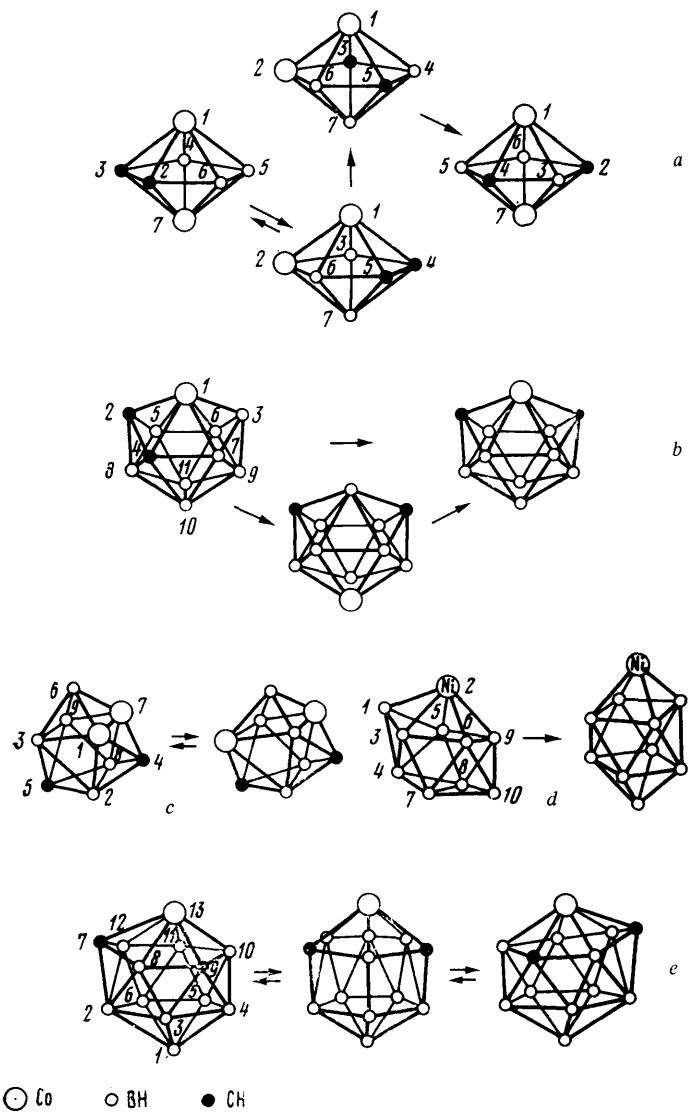


Figure 20. Thermal rearrangements of certain metallocarbaboranes: *a*) $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$; *b*) $(\eta^5\text{-}C_5H_5)CoC_2.B_8H_{10}$; *c*) $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$; *d*) $(\eta^5\text{-}C_5H_5)NiB_9H_9^-$; *e*) $(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$. The ligands C_5H_5 are not shown in the Figure.

When the solvent is removed, the equilibrium is wholly displaced towards isomer A. The ^{11}B NMR spectrum of isomer A is characterised by four signals of equal intensity distributed over a wide frequency range. The ^1H NMR spectrum has two signals due to the protons of the methyl groups and these are also of equal intensity. The proposed geometrical and valence structure of isomer A is presented in Fig. 19.[174] Compound B is characterised by a more compact ^{11}B NMR spectrum, in which there are two signals with relative intensities of 6 : 2. The ^1H NMR spectrum of this isomer contains, like that of isomer A, two signals, which merge at 40°C into a single narrow signal. On the basis of these data, the authors[173-175] proposed for isomer B the structure of a somewhat distorted icosahedron, having assumed the possibility of the rotation of the pentagonal pyramidal fragments in order to account for the spectroscopic data (Fig. 19). Above we already discussed this mechanism of the rearrangement of icosahedral molecules in terms of the correspondence between the symmetry of "soft" deformations and the symmetry of molecular orbitals and concluded that it is unlikely (Section V, subsection 1). The Wade rule suggests that a *nido*-structure of the fragment of a 13-vertex polyhedron with four carbon atoms in the open face is more likely for the isomers of $Me_4C_4B_8H_8$. Here account must also be taken of the possibility of some deformation of the open face of the molecule, associated, for example, with its narrowing. As a result of such deformation, the excess charge on the carbon atoms might be compensated to a greater extent. The interconversions of the isomers of $Me_4C_4B_8H_8$ can proceed either via a transition state having a structure close to that of the icosahedron, or as a result of consecutive migrations of the atoms in the open face to the sites of the missing vertex of the polyhedron.

3. REARRANGEMENTS OF METALLOCARBABORANES AND METALLOBORANES

The thermal rearrangements of metallocarbaboranes and metalloboranes have many features which are not characteristic of, for example, carbaboranes and are therefore considered separately in this review.

In their studies of the rearrangements of metallocarbaboranes containing between six and ten boron atoms and between one and three cobalt atoms Hawthorne and coworkers[176-178] derived the following empirical rules defining the direction of the rearrangements:

(a) the cobalt atom migrates to the vertex with the maximum coordination number and subsequently remains in this position;

(b) the carbon atoms in the skeleton do not approach one another;

(c) carbon migrates irreversibly to the vertex with the minimum coordination number;

(d) a carbon atom tends to migrate away from a cobalt atom if rules (b) and (c) hold.

Grimes and coworkers[179-181] fully confirmed the validity of these rules for metallocarbaboranes containing between three and five boron atoms, noting at the same time a number of features. Thus, during the rearrangement of 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ there is successive formation of 1,2,4,5- and 1,2,3,5-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, in which the cobalt atom occupies the position with the smallest coordination number (C.N.) and the rearrangement occurs only at a higher temperature, as a result of which the cobalt atom again occupies the position with the maximum coordination number (Fig. 20*a*).[179] The intermediate formation of the metallocarbaborane isomer in which cobalt has the smallest coordination number was also noted in the isomerisation of 1-$(\eta^5\text{-}C_5H_5)$-1-Co-2,4-$Me_2C_2B_8H_8$ (Fig. 20*b*).[180] These examples show that many rearrangements of metallocarbaboranes proceed via a series of stages. The problem of the mechanism of the rearrangements has not been discussed in most studies owing to the insufficiency

of experimental data. A mechanism based on the *dsd* model is possible. For the rearrangement of 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (Fig. 20*a*), Miller and Grimes [179] give preference to the mechanism involving the rotation of the trigonal faces of the polyhedron, noting correctly that this process, instead of being synchronous, may be a result of several consecutive stages, for example two *dsd* stages or, what is more probable, may occur via an open polyhedral intermediate [179]. A tendency of cobalt atoms to form Co–Co bonds was also noted, but in many instances it is compensated by the effect involving the repulsion of the cyclopentadienyl ligands. This in fact explains attainment of equilibrium between the two isomers of $(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$ (Fig. 20*c*). [179,181]

An interesting rearrangement has been observed for the nickel–borane complex $(\eta^5\text{-}C_5H_5)NiB_9H_9$. In solution after brief heating to 150°C or irradiation with ultraviolet light the complex, in which the nickel atom occupies the position with the highest coordination number, undergoes quantitative isomerisation to a complex with four-coordinated nickel (Fig. 20*d*). [182] Thus, together with the features noted above, there is apparently a tendency towards the formation of a more symmetrical structure as a result of the rearrangement, in which there is a possibility of a greater delocalisation of electrons.

An interesting example of the configurational instability of a metallocarbaborane molecule is the 13-vertex cobaltcarbaborane 13,7,9-$(\eta^5\text{-}C_5H_5)CoC_2B_{10}H_{12}$; in its solution there are rapid dynamic rearrangements between two enantiomers (Fig. 20*e*), which is manifested by the averaging of the NMR spectra of this compound. With decrease of temperature, the rate of the transitions diminishes and at −90°C the ^{11}B NMR spectrum indicates the absence of symmetry elements. The mechanism of the rearrangement is based on the *dsd* model and involves successive or synchronous formation of two tetragonal faces in the transition state (Fig. 20*e*). [166] The position of the above equilibrium is significantly influenced by substituents. Thus the introduction of a methyl group at one of the carbon atoms shifts the equilibrium towards the isomer in which the unsubstituted carbon atom occupies the position with the smallest coordination number [176].

In general, when the mechanisms of the rearrangements of metallocarbaboranes and metalloboranes are discussed, it is important to take into account the symmetry of the molecule, as for other polyhedral systems.

VI. CONCLUSION

In our discussion of the rearrangements of polyhedral molecules, we endeavoured in the first place to represent the characteristic features of the chemical behaviour of the compounds as the characteristic properties of carbaboranes, boron hydrides, and heteroborates, i.e. we tried to consider them as manifestations of the characteristics of the electronic structures of polyhedral boron compounds. The theoretical models which we employed, such as the model involving electrophilic reactions via two-centre bonds and nucleophilic reactions via three-centre bonds, can be useful only if one clearly realises the limits of their applicability. The latter depend in their turn on the validity in each specific case of concepts such as those of localised two-, three-, and many-centre bonds. Their energetic characteristics are also important. We believe that in a qualitative treatment the models employed are fully justified.

The presence of symmetry elements in the molecules and ions of polyhedral boron compounds and hence the symmetry of the electronic Hamiltonian permit a significant simplification of the selection of the possible directions and mechanisms of many of their reactions and in the first place their thermal rearrangements. In many cases it is sufficient for this purpose to consider the symmetry of the initial molecule and the symmetry of the deformation characterising the given mechanism of the rearrangement. In the more general case it is necessary to know the symmetry of the molecular orbitals, their energies, populations, as well as the types of the normal displacements possible in the given molecule or ion.

In general the use of fundamental concepts, such as the occurrence of the reactions as a result of the interaction of the bonding and antibonding orbitals of the reactants and the decisive role of the energy and symmetry of the boundary orbitals of the reactants and the transition state in determining the direction of the reaction, appear to be most promising in a qualitative discussion of the chemical properties of polyhedral boron compounds.

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During the preparation of this review for the press, certain fundamentally important reports devoted to the structures and rearrangements of polyhedral boron compounds were published. Here mention should be made in the first place of the papers by Lipscomb and coworkers [183–185]. Continuing their fundamental studies, the authors carried out quantum-chemical calculations (by the PRDDO method) on the closed borane anions $B_nH_n^{2-}$ and carbaboranes $C_{2n}B_nH_{n-2}$ and found that they have localised valence structures, which can be represented by fractional bonds [183]. A topological analysis has been carried out and preliminary calculations have been made for the structures of closed boron hydrides containing between 13 and 24 atoms in the polyhedron and the possible methods of synthesis of such polyhedral compounds have been classified [184]. In order to investigate the rearrangements of polyhedral boron compounds, calculations have been made on the configurational behaviour of the anion $B_{11}H_{11}^{2-}$. [185] Grimes and coworkers [186–189] continued their studies on the four-carbon carbaborane $Me_4C_4B_8H_8$ and transition metal complexes of polyhedral compounds. An X-ray diffraction study has been made of one of the isomers of $Me_4C_4B_8H_8$ [186] and a number of complexes based on it, and their structural rearrangements have been investigated [187,188]. X-Ray diffraction analysis also made it possible to demonstrate that one of the boron atoms in the complex $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, formally containing $2n$ electrons binding the atoms of the molecular skeleton, is located above the plane [189]. Mikhailov and coworkers achieved the rearrangement of icosahedral carbaboranes under the influence of γ-radiation [90]. Photoinitiated rearrangements of nickel dicarbollide complexes have also been observed [191].

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