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Metallocarbaboranes. Structural Studies in Recent Years

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Structural studies on metallocarbaboranes (MCB) are surveyed and modern theoretical ideas about the electronic structure of cluster and particularly polyhedral MCB systems are discussed. The characteristic features of the geometry of the polyhedra in specific MCB are examined in connection with the specific features of their electronic structure.
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I. INTRODUCTION

Metallocarbaboranes (MCB) constitute a large class of polyhedral compounds which contain, together with boron and carbon atoms, also several metal atoms in the polyhedron. These compounds, which occupy an intermediate position at the junction between organoelemental and organometallic chemistry, have become in recent years the objects of vigorous research. As frequently happens, the results obtained in this boundary field of science are not only of independent importance but to a large extent they have enriched the ideas which have arisen in adjacent disciplines and have frequently stimulated their development. Such a stimulating role in relation to the chemistry of cluster compounds was played at one time by MCB, which became, as early as the middle of the 1960's, one of the first examples of metal-containing polyhedral systems. The studies in this field have made it possible to combine successfully the researches into the complex and unexpected reactions and far-reaching thermal rearrangements with the synthesis of a large number of extremely stable compounds which are promising from the practical standpoint.

The specific features of MCB are determined in the first place by their unusual polyhedral structures, which are distinguished by an usually wide variety and frequently by their aesthetic perfection. It is therefore natural that in the investigation of these compounds structural studies (these are carried out almost exclusively by X-ray diffraction) occupy in a certain sense a central position, because, on the one hand, they provide the necessary information without which it would be impossible to plan and achieve the synthesis of MCB and, on the other hand, they serve as a basis for the development and improvement of theoretical ideas about their structure.

The following figures reveal the rate of growth of the number of structural studies on MCB in recent years. Thus the exhaustive review by Grimes,[1] which covers the literature up to 1975, quotes a list of more than 400 compounds synthesised by that time, of which only 46 have been subjected to structural studies; at the beginning of 1981, 95 X-ray

diffraction studies on MCB had been performed and during the last 1.5–2 years a further 25 studies concerned with this field have been published.

As a result of the wide variety of the structures of MCB, in many of these studies not only was the structure of the newly synthesised compound established but also new types of polyhedra, unusual modes of coordination of the metal atoms, or hitherto unknown motifs in the disposition of the atoms in the polyhedron were discovered. Although less than 20 years have elapsed since the synthesis of the first MCB by Hawthorne and co-workers[2] in 1965, definite theoretical ideas have already been formulated, which, while they do not always possess an adequate predictive power, at any rate make it possible to generalise and arrange systematically the experimental data accumulated at the present time. Here we have in view the rules for the evaluation of the numbers of skeletal electrons (i.e. the electrons responsible for the bonding in the polyhedron), sometimes referred to as Wade's rules, or the "$2n + 2$" rules.[3] The important role of these rules for the elucidation of the structures of cluster compounds in general and the wide variety of polyhedral boron derivatives in particular has been examined in a number of studies (see, for example, Refs. 3–7). The essential features of Wade's ideas are briefly described in this review in order to employ them subsequently in considering the MCB structures.

II. MODERN IDEAS ABOUT THE ELECTRONIC STRUCTURE OF METALLOCARBABORANES

The ideas underlying the "$2n + 2$" rule have been described in a most logical and readily understood form in the book of King and Rouvray,[5] who consider the structure of cluster systems from the standpoint of the topology of the polyhedron. According to their description, each boron or carbon atom (for simplicity, we shall consider initially a purely carbaborane polyhedron) in an n-vertex polyhedron have an outer atomic orbital (AO), which is used to form the exopolyhedral bond, two tangential orbitals directed along the tangent to the envelope of the polyhedron, and one internal orbital directed towards the centre of the polyhedron (the inner and outer orbitals can be regarded, for example, as two sp-hybrid orbitals). When a cluster is formed, the exopolyhedral orbitals (n orbitals) are not involved and the interaction of $2n$ tangential AO leads to n bonding and n antibonding cluster orbitals.[5] It remains to explain what happens to the n inner orbitals.

In comparing "superaromatic" three-dimensional clusters with planar aromatic systems (here a comparison is made of the sp^2-hybrid orbitals involved in the formation of the σ-bonds of the aromatic ring with the tangential orbitals and of the unhybridised p orbitals with the inner orbitals of the cluster atoms), King and Rouvray[5] emphasise the important topological difference between these two types of aromatic systems. The planar systems are characterised by cyclic graphs C in which each atom is linked to only two neighbours, while the so-called complete graphs K_n, in which each atom is assumed to be bound to all the remaining atoms, are characteristic of the cluster polyhedra. This topological difference is responsible for the different forms of the quantum-chemical equations—for example, the different matrices of the linear equations in the simple Hückel method (only the non-diagonal elements in these matrices, which correspond to pairs of atoms between which there is a chemical bond, are known to be non-zero). The solution of these equations shows that, in contrast to planar molecules, for example, those of benzene (where the interaction of six "inner" p orbitals gives rise to three bonding and three antibonding π orbitals), in the three-dimensional systems the interaction of the n inner orbitals leads to only one non-bonding cluster orbital and $n - 1$ antibonding orbitals.

Thus the total number of the bonding MO in an n-vertex cluster is $n + 1$ (n orbitals formed by the tengential AO and one formed by the inner AO). This approach provides a clear explanation of the experimental rule[3] according to which the most stable carbaboranes, with the maximum delocalisation of electron density, have $2n + 2$ skeletal electrons, which are responsible for the bonding in the polyhedron. Such polyhedra have only triangular faces; they are referred to as *closo*(closed)-polyhedra or deltahedra.

When one of the vertices of the *closo*-polyhedron is removed, one (open) (non-triangular) face arises in the latter. The resulting polyhedron can be regarded as a combination of two complete graphs, one of which includes only inner vertices i.e. those not located on the "open" face, and the other only the boundary vertices (belonging to the "open" face). The interaction of the inner orbitals of the atoms belonging to each graph results in the formation of one additional bonding orbital in each instance. Thus the total number of binding orbitals formed by the interaction of both tangential and inner orbitals in such instances is $n + 2$, where n is the number of vertices of the polyhedron. Such polyhedra with one "open" face are referred to as *nido*-polyhedra (from the Greek "nido"—nest). The so-called *arachno*-structures (from the Greek "arachne"—cobweb) with $2n + 6$ skeletal electrons can be obtained by the removal of two vertices from *closo*-systems.

Thus the opening of the polyhedron, namely the formation of *nido*- and *arachno*-systems, corresponds to an excess of skeletal electrons (relative to $2n + 2$). A deficiency of skeletal electrons can also affect the character of the cluster polyhedron, leading to the formation of extremely unusual structures in which one or several triangular faces have over their centres additional vertices (caps). These polyhedra can also be formally classified as *closo*-systems, because they contain only triangular faces. However, in contrast to the polyhedra representing "normal" $2n + 2$ electron clusters, polyhedra with additional vertices can be subdivided into two smaller *closo*-polyhedra (for example, along the planes of the faces over which the caps are centred). Certain "super-electron-deficient" systems of this kind will be discussed below.

Table 1. The numbers of electrons supplied to the MCB polyhedron by various groups.

Group	No. of electrons	Group	No. of electrons
BH	3—1=2	$Fe(CO)_3$	8+6—12=2
CH	4—1=3	CoCp	9+5—12=2
PMe	5—1=4	$RhH(PPh_3)_2$	9+1+4—12=2
$Re(CO)_3$	7+6—12=1	$NiC_2B_9H_{11}$	10+4—12=2
FeCp *	8+5—12=1	$Pt(PPh_3)_2$	10+4—12=2
$CoC_2B_9H_{11}$	9+4—12=1	NiCp	10+5—12=3
$Rh(PPh_3)_2$	9+4—12=1	$AuC_2B_9H_{11}$	11+4—12=3

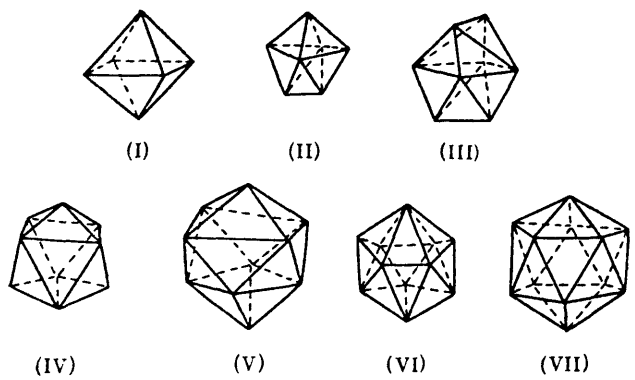
*Here and henceforth Cp = cyclopentadienyl.

In conclusion of this Section, one may indicate how the numbers of skeletal electrons in specific, particularly polyhedral, MCB systems should be evaluated (Table 1). It is

evident from the foregoing that the BH and CH groups each supply three orbitals and correspondingly two and three electrons to the polyhedron. When a transition metal atom is incorporated in the polyhedron, it is assumed that, of the nine of its orbitals, it employs three for bonding in the polyhedron, while the remaining six are used to form bonds with external ligands. It is assumed that the electrons of the metal and the ligands fill in the first place the orbital not involved in the bonding within the polyhedron, i.e. the six outer orbitals. The ML_n group therefore supplies to the polyhedron x electrons of the metal and k electrons of the n ligands, while 12 electrons are distributed among the exopolyhedral orbitals. Thus, overall, the group ML_n supplies $x + k - 12$ skeletal electrons to the polyhedron. For example the $Fe(CO)_3$, CoCp, $Pt(PR_3)_2$, etc. groups function, like the BH group, as donors of two electrons, while the NiCp group, like the CH group, supplies three electrons to the polyhedron.

III. THE STRUCTURES OF METALLOCARBABORANES

We shall now proceed directly to the discussion of the structures of the MCB. The ideal *closo*-polyhedra characteristic of the $B_nH_n^{2-}$ ions and carbaboranes with $n = 6 - 12$ are presented below (Table 2).

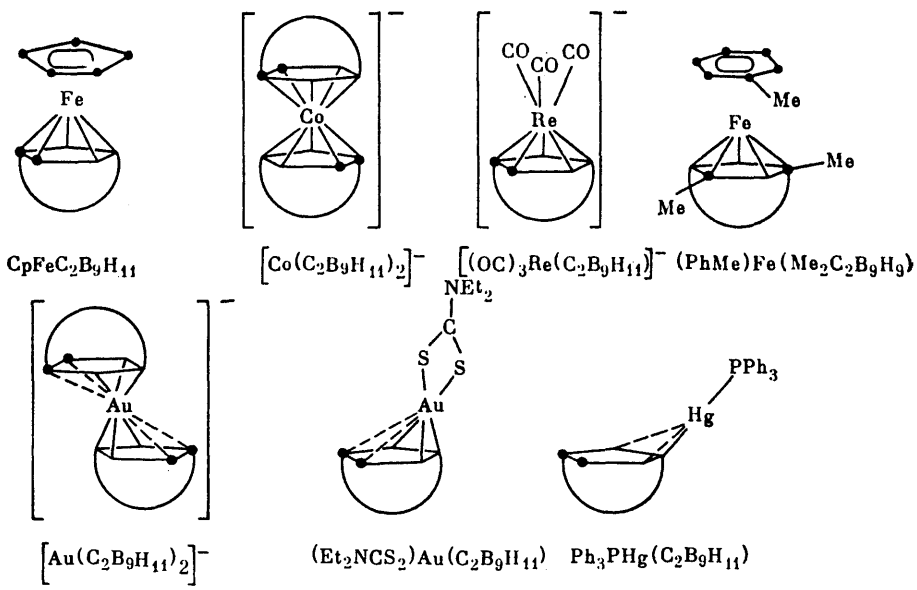


The polyhedra of the MCB and carbaboranes having the same number of vertices are usually analogous, although the introduction of a metal atom normally reduces the symmetry of the polyhedron relative to the corresponding carbaboranes. In a number of instances new skeletons, without analogues in the structural chemistry of boranes and carbaboranes, have been discovered in MCB: however, for their description it is frequently also convenient to begin with the *closo*-systems listed in Table 2.

Table 2. *closo*-Polyhedra characteristic of the $B_nH_n^{2-}$ ions and the carbaboranes $C_2B_{n-2}H_n$.

No.	Ion	Polyhedron	Symmetry group	No. of vertices	No. of edges	No. of faces
(I)	$B_6H_6^{2-}$	Octahedron	O_h	6	12	8
(II)	$B_7H_7^{2-}$	Pentagonal bipyramid	D_{5h}	7	15	10
(III)	$B_8H_8^{2-}$	Dodecahedron	D_{2d}	8	18	12
(IV)	$B_9H_9^{2-}$	Three-cap trigonal prism	D_{3h}	9	21	14
(V)	$B_{10}H_{10}^{2-}$	Two-cap square antiprism	D_{4d}	10	24	16
(VI)	$B_{11}H_{11}^{2-}$	Octadecahedron	C_{2v}	11	27	18
(VII)	$B_{12}H_{12}^{2-}$	Eicosahedron	I_h	12	30	20

We shall next consider MCB structures with different numbers n of vertices in the polyhedron; only the most characteristic and typical examples, and not all the structures investigated, are quoted for each value of n. A more complete idea about the MCB structures can be obtained from a number of previous reviews.[1,8-15]



$CpFeC_2B_9H_{11}$ $[Co(C_2B_9H_{11})_2]^-$ $[(OC)_3Re(C_2B_9H_{11})]^-$ $(PhMe)Fe(Me_2C_2B_9H_9)$

$[Au(C_2B_9H_{11})_2]^-$ $(Et_2NCS_2)Au(C_2B_9H_{11})$ $Ph_3PHg(C_2B_9H_{11})$

Figure 1. 12-Vertex MCB;[16-23] for simplicity, the *nido*-eicosahedral fragments are represented by half-circles.

1. The Highest (12- and 13-Vertex) Metallocarbaboranes

The most extensive and most widely investigated class of MCB comprises the eicosahedral 12-vertex MCB (Fig.1)†. The first MCB whose structure has been investigated, namely $CpFeC_2B_9H_{11}$, which has a sandwich structure, belongs to this class.[16] Its iron atom is symetrically coordinated to the cyclopentadienyl ligand and to the "open" pentagonal C_2B_3 face of the dicarbollide $(C_2B_9H_{11})^{2-}$ ligand; the Fe–C and Fe–B distances are identical within the limits of the accuracy of the measurement and amount to 2.04 Å.

Subsequently a large number of 12-vertex MCB, incorporating the metals of almost all the Groups in the Periodic System, were synthesised; more than 40 of these have been studied by X-ray diffraction. Almost all the 12-vertex metallocarbaboranes have a more or less strongly distorted eicosahedral structure and, in contrast to the iron derivatives menticned above, in most cases are diamagnetic complexes satisfying Wade's rule. As an example, one may quote two MCB investigated in the form of caesium salts—the anions $[Co(C_2B_9H_{11})_2]^-$ [17] and $[(OC)_3Re(C_2B_9H_{11})]^-$,[18] which belong to the class of MCB known for the longest time, and also the π-arene complex of bivalent iron $(MePh)Fe(Me_2C_2B_9H_9)$ synthesised several years ago.[19] A fully symmetrical coordination of the metal atom to the π-dicarbollide ligand was observed in these compounds. However, such symmetrical coordination is by no means always observed in the 12-vertex MCB. Thus, on passing from the d^6 and d^7 complexes of iron(II), cobalt(III), and rhenium(I), etc. to the d^8 complexes of palladium(II), platinum(II), and gold(III) and further to the d^{10} derivatives of mercury(II), considerable distortion of the symmetrical coordination is observed, being reflected in a shift of the metal atom towards the B atoms of the "open" face and in the breakdown of its planarity, which promotes a shift of carbon atoms away from the metal atom and a shortening of the C–C bond in the *ortho*-dicarbollide ligand. Such distortion of the coordination of the carbaborane ligand can be called the "shift" distortion and in the case of the *ortho*-dicarbollide ligand the "pseudo-π-allyl" distortion.

For example, the difference between the Au–B and Au–C distances in the anion $[Au(C_2B_9H_{11})_2]^-$ [20] reaches approximately 0.5 Å, the angle of inflection in the "open" face along the B...B line is 13.6°, and the C–C bond is shortened to 1.46 Å. As a result of the further "opening" of the MCB polyhedron on passing to the mercury derivative $Ph_3PHg(C_2B_9H_{11})$,[21] the metal atom is bound to only one B atom in the "open" face (the Hg–B distance is 2.20 Å), while the binding to its neighbours in the face assumes the character of weak interaction (with Hg...B distances of 2.50 and 2.53 Å). Finally, the thallium complex can be regarded as the double salt $[R_4P]^+Tl^+[C_2B_9H_{11}]^{2-}$ rather than the phosphonium slat of the thallium-carbaborane anion (Tl...B = 2.664–2.744 Å and Tl...C = 2.915 Å[22]).

It must be emphasised that the above distortions of the *closo*-structure are observed under conditions where the "$2n + 2$" rule formally holds and are independent of whether or not the 18-electron rule holds for the coordination of the metal atom. This is indicated by the structural data for the two gold complexes presented in Fig.1, namely $[(Et_2NCS_2)_2Au]^+[(Au(C_2B_9H_{11})_2]^-$ [20] and $(Et_2NCS_2).Au(C_2B_9H_{11})$,[23] in which identical pseudo-π-allyl distortions are observed, although in the former the Au atom has a 20-electron shell whereas in the latter it has an 18-electron shell. The only structural investigation of the platinacarbaborane $Pt(C_2B_9H_{11})_2$, incorporating the Pt atom in the +4 oxidation state, carried out hitherto[24] has shown that the distortions in the polyhedron are determined evidently solely by its electronic configuration and not by the presence in it of a specific metal atom. Indeed, in the d^6 complex indicated the platinum atom is included in two eicosahedra which are actually symmetrical: the average Pt–C and Pt–B distances are 2.24 and 2.20 Å respectively.

The nature of the "shift" distortions in the symmetrical coordination of the metal in the 12-vertex MCB has been studied in two investigations,[25,26] in which calculations were carried out for the interaction of the $Pt(PH_3)_2$ fragment with the borate anion $B_{11}H_{11}^{2-}$ and its carbaborane analogues by the extended Hückel method (Fig.2). The calculation showed that the character of the coordination of the metal atom as well as the orientation of the PtP_2 group relative to the ligand are determined by the interaction between the highest occupied molecular orbital (HOMO) in this group (i.e. the hybridised d_{xz}-p_x orbital localised in the plane of the Pt–P bonds) and the lowest unoccupied MO (LUMO) of the ligand. In the borate anion $B_{11}H_{11}^{2-}$ two electrons are located at the doubly degenerate $5e_1$ level. As a result of the replacement of one or two B atoms in the "open" face by C atoms, the degeneracy is removed and the location of the nodal plane of the LUMO depends on the positions of the carbon atoms in the carbaborane ligand. The optimum overlap of the HOMO of the metal and the LUMO of the ligand occurs for the orientation in which their nodal planes coincide.

The HOMO nodal plane of the $Pt(PH_3)_2$ fragment is perpendicular to the PtP_2 plane and the ML_2 fragment should therefore be at right angles to the symmetry plane of the $CB_{10}H_{11}$ (I) and *ortho*-$C_2B_9H_{11}$ (III) ligands (Fig.2) and parallel to this plane in the case of the *meta*-$C_2B_9H_{11}$ (II) ligand. Such orientation does actually obtain in the three palladium and platinum complexes whose structures have been investigated: $(Me_3CNC)_2Pd(1\text{-}Me_3NCB_{10}H_{10})$,[27] $(PhMe_2P)_2Pt(2,5\text{-}Me_2C_2B_9H_9)$,[28] and $(Et_3P)_2Pt(3,4\text{-}C_2B_9H_{11})$.[25]

Fig.2 illustrates yet another, perhaps even more important conclusion reached in the above studies.[25,26] Calculation has shown that the LUMO of the carbaborane ligand is localised at the B atoms to a much greater extent than at the C atoms. This factor explains qualitatively the "shift" distortions of the MCB eicosahedra observed for the 12-vertex complexes of metals with the d^8–d^{10} electron configuration.

The most realistic prospects, at the present time, for the practical application of the MCB are also associated with the largest and most thoroughly investigated class of MCB, namely the 12-vertex complexes. Several years ago a structural study was made[29] on the rhodium hydride complex $(Ph_3P)_2PhH(C_2B_9H_{11})$—an effective homogeneous catalyst for the hydrogenation of olefins. A study of the catalytic properties of this complex established that the rate of the hydrogenation reaction diminishes after the addition of free triphenylphosphine to the reaction mixture. The authors[29] suggested that the catalytic hydrogenation reaction takes place with participation of a coordination-unsaturated metal atom and that the first, rate-limiting stage of the catalytic process involves the elimination of the Ph_3P ligand.

These ideas were used for the specific synthesis of a new rhodiacarbaborane complex with a still higher catalytic activity. In the new compound $(Ph_3P)HRhC_2B_9H_{10}C_4H_7$), whose structure has also been studied,[30] the rhodium atom is involved in η^2-type coordination to the double bond of the butenyl substituent of the dicarbollide ligand (Fig.3). The η^2-coordinated double bond, activated by the interaction with the rhodium atom, is hydrogenated in the first place

†The carbon atoms in Fig.1 and also in some of the subsequent figures are designated by filled circles.

under the conditions of the hydrogenation reaction. Subsequently the metal atom becomes coordination-unsaturated, which in fact determines the catalytic properties of the complex. Indeed the complex described proved to be one of the most effective catalysts for the homogeneous hydrogenation of olefins known at the present time. The related alkene-substituted carbaborane rhodium hydride complex $(PH_3P)_2HRhC_2B_9H_9C_8H_{14}$), with an unsaturated exopolyhedral nine-membered ring, whose double bond is coordinated to the metal atom (Fig. 3), exhibits a somewhat smaller catalytic activity.[31]

Yet another rhodium complex showing a catalytic activity, namely $(Ph_3P)_2HRhC_2B_{10}H_{12}$ (Fig. 4),[32] belongs to the group of the very few structurally characterised 13-vertex MCB.

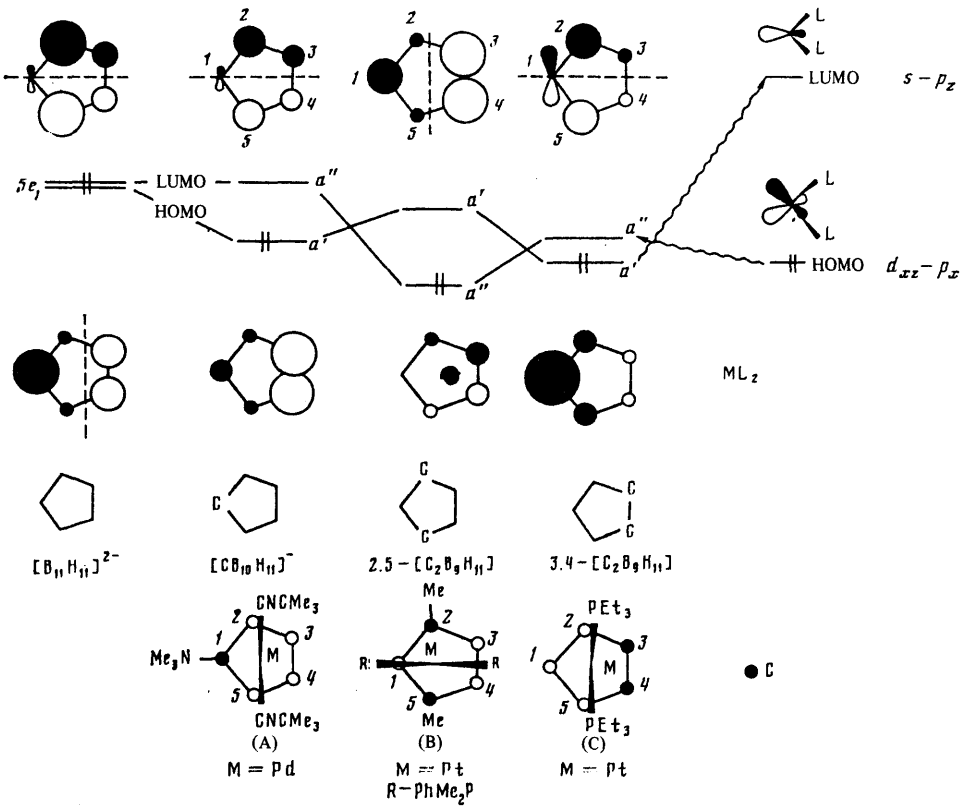
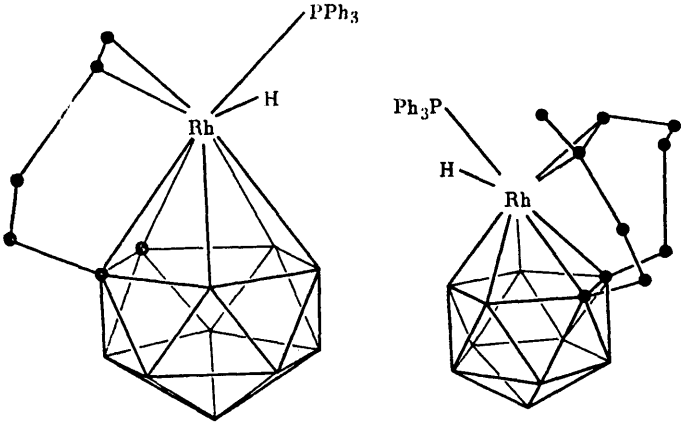


Figure 2. Comparison of the results of theoretical[25,26] and experimental[25,27,28] studies of the geometrical features of the molecules of 12-vertex MCB.

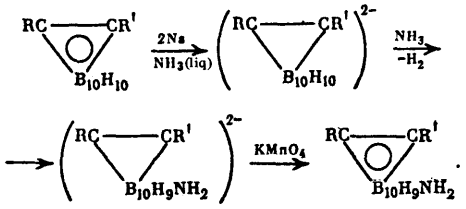
These complexes contain the so-called docosahedral polyhedron in which, in contrast to the eicosahedron, the "open" pentagonal face coordinating the metal atom has been replaced by a hexagonal face. Structural studies on the 13-vertex complexes of cobalt, i.e. $CpCoC_2B_{10}H_{12}$,[33] and titanium, i.e. $[Me_4N]_2[Ti(Me_2C_2B_{10}H_{10})_2]$,[34] with a docosahedral structure are important for the understanding of the mechanisms of certain reactions of the series of *o*- and *m*-carbaborane derivatives.



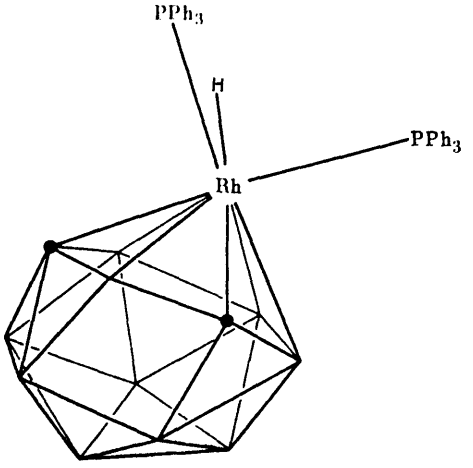
$(Ph_3P)HRhC_2B_9H_{10}C_4H_7$ $(Ph_3P)HRhC_2B_9H_9C_8H_{14}$

Figure 3. The structures of 12-vertex alkenerhodium hydride complexes—catalysts of the homogeneous hydrogenation of olefins.[30,31]

In 1967 Soviet workers proposed an effective method of synthesis of B-substituted derivatives of *o*-carbaborane by treating with nucleophiles the products of the reduction of *o*- and *m*-carbaborane derivatives with a solution of sodium in liquid ammonia (see Kalinin's review[35]). It is suggested that this process proceeds via the intermediate stage of dicarbadodecaborate(14) dianions:



The dicarbadodecaborate anion is also formed on reduction of *o*-carbaborane by metallic sodium in THF in the presence of catalytic amounts of naphthalene. The introduction of transition metal salts ($CoCl_2$ and $TiCl_4$) into the reaction mixture made it possible to isolate the derivatives of the dicarbadodecaborate anion in a pure form and to investigate their structure.[33,34] It may be hoped that detailed studies of the 13-vertex MCB will lead in the future to the possibility for a more detailed investigation of the mechanism of this reaction, which is exceptionally important for the chemistry of *o*- and *m*-carbaboranes and also will make it possible to explain the preferential formation of only some of the isomers of its final complex which are possible in principle.



$(Ph_3P)_2HRhC_2B_{10}H_{12}$

Figure 4. The structure of $(Ph_3P)_2RhH(C_2B_{10}H_{12})$.[32]

2. 11-Vertex MCB

The geometry of the octahedron is characteristic of 11-vertex *closo*-MCB (Fig.5). Many 11-vertex MCB, whose structures have been investigated, for example, the cobaltacarbaborane $CpCoC_2B_8H_9Br$ which we have studied,[36] can be regarded as resulting from the coordination of the metal atom to the non-planar hexagonal "open" face of the boron–carbon skeleton, which resembles a basket and is well-known in the chemistry of boron as the decaborane-14 ($B_{10}H_{14}$) skeleton. In contrast to the eicosahedron, in which each vertex has five nearest neighbours in the polyhedron, in the octadecahedron with pentacoordination (here and henceforth the coordination number C.N. is understood as the number of nearest neighbours in the polyhedron) there are two tetracoordinate and one hexacoordinate vertices. Numerous studies of the structures of MCB with polyhedra having non-isotypical vertices and also investigation of the thermal rearrangements in these systems[9] have shown that the isomers in which the carbon atoms occupy the vertices with the lowest C.N. and the metal atoms occupy those with the highest C.N. are as a rule thermodynamically most stable. A good illustration of this finding is provided by the structure of the bimetallic 11-vertex MCB $Cp_2FeCoC_2B_7H_9$ in the octadecahedral polyhedron of which two carbon atoms occupy tetracoordinate vertices and the iron and cobalt atoms occupy respectively hexacoordinate and pentacoordinate vertices. In this molecule there are 23 skeletal electrons instead of the 24 expected for *closo*-MCB, which causes, according to the authors of the structural study,[37] certain geometrical distortions (differences between the lengths of chemically equivalent B–B bonds amounting to approximately 0.10 Å have been observed), which leads to the loss of a plane of

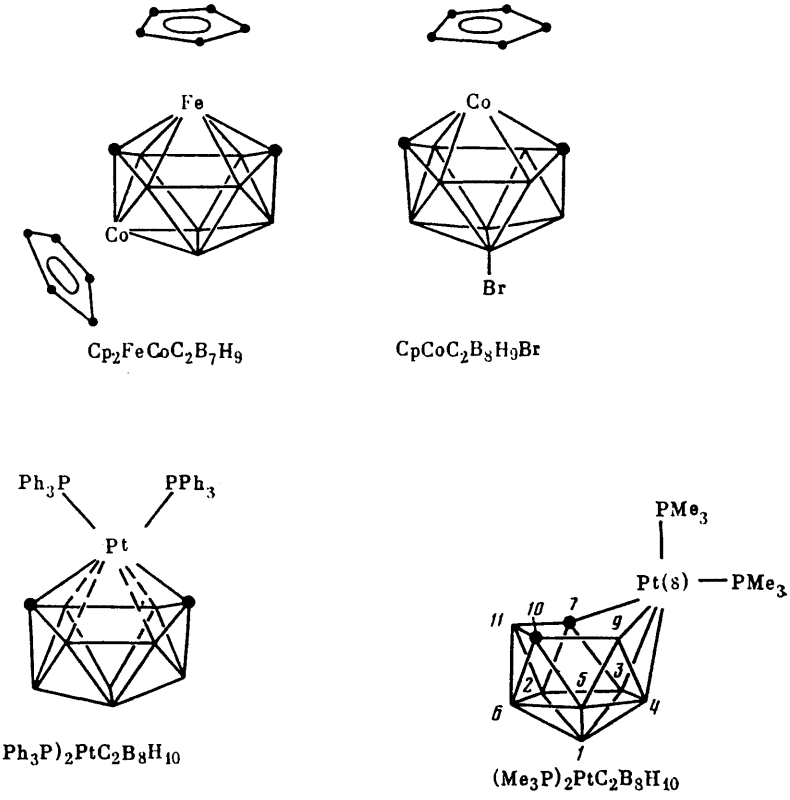
symmetry by the $FeCoC_2B_7$ polyhedron. However, it is noteworthy that the lack of one electron does not affect the geometry of the iron cyclopentadienyldicarbollyl complex $CpFeC_2B_9H_{11}$.[16]

The difference between the C.N. of the atoms in the polyhedron influences the lengths of the bonds in which they are involved. This difference makes it possible, for example, to account for the significant (up to approximately 0.3 Å) difference between the Co–C and Co–B distances in $CpCoC_2B_8H_9Br$. On the other hand, the increase of the Pt–B distance to 2.60–2.66 Å compared with the Pt–C bond, which is 2.17 Å long in the complex $(Ph_3P)_2PtC_2B_8H_{10}$,[38] can be hardly accounted for solely by the influence of the difference between the C.N. of the B and C atoms. This becomes even more evident in relation to another 11-vertex platinacarbaborane, namely $(Me_3P)_2PtC_2B_8H_{10}$.[39] Although this complex contains 24 skeletal electrons, it has in fact a *nido*-eicosahedral structure and not an octadecahedral structure, but its polyhedron can in fact be regarded as a highly distorted octadecahedron in which the metal atom is very markedly displaced relative to the symmetry plane of the polyhedron. As a result, the distances from the platinum atom to the most remote boron and carbon atoms in the "formally open face" of the octadecahedron (3.10 and 2.82 Å) altogether do not correspond to a valence interaction.

Although the 11-vertex MCB have been investigated in much less detail than the 12-vertex compounds, the few examples examined have already shown that here too the same rule apparently holds as for the eicosahedral MCB: the incorporation of a metal atom with a d^8 configuration leads to the "loosening" of the polyhedron and sometimes, as, for example, in the last platinacarbaborane considered above,[39] also to a decrease of its symmetry. It will be shown below that this rule holds likewise for the lowest MCB.

3. 10-Vertex MCB

The 10-vertex *nido*-carbaboranes, having the decaborane-14 skeleton, which have been investigated in fair detail, are structurally very close to the 11-vertex MCB with an octadecahedral polyhedron. Like each of the BH groups, the



$Cp_2FeCoC_2B_7H_9$ $CpCoC_2B_8H_9Br$

$(Ph_3P)_2PtC_2B_8H_{10}$ $(Me_3P)_2PtC_2B_8H_{10}$

Figure 5. 11-Vertex MCB.[36–39]

CpCo group in the cobaltacarbaborane $CpCo(C_2B_7H_{11})$[40] (Fig.6) behaves, as usual, as the donor of two electrons, while the two CH groups supply three electrons each to the polyhedron; the bridging hydride atoms, whose location has been objectively identified in a structural study,[40] serve as a source of further two electrons. Overall, the complex contains 24 skeletal electrons and has the structure of a 10-vertex *nido*-polyhedron.

Whereas the metal atom in the cobalt complex occupies, as was to be expected, a high-coordination site in the "open" face, in the nickel derivative $(Et_3P)_2Ni(Me_2C_2B_7H_9)$[41] and the platinum derivative $(Ph_3P)_2Pt(CB_8H_{12})$[42] with an analogous skeleton the metal atom occupies a low-coordination site. The coordination of the metal atom in this low-coordination site in the "open" face constitutes a model in a certain sense (assuming that the metal atom is coordinated to the centres of the edges of the polyhedron) of the square-planar environment characteristic of the usual nickel(II) and platinum(II) complexes.

The second low-coordination site in the "open" face of 10-vertex *nido*-complexes of nickel and platinum is occupied by a carbon atom, which, together with the exopolyhedral ligand (the Me group in the nickel complex and the hydrogen atom in the platinum compound), turned "to the outside" of the polyhedron, contains also the so-called "axial" hydrogen atom directed towards the centre of the "open " face. The question arises how one should take into account this carbon atom in calculating the number of skeletal electrons. If both its substituents are regarded as exopolyhedral, then the given carbon atom should serve as a donor of two (4−2 = 2) electrons. In this case the 10-vertex *nido*-polyhedron contains 22 skeletal electrons, i.e. two electrons less than would be necessary to satisfy Wade's "2*n* + 4" rule. This discrepancy is entirely reasonable because, according to Wade's rule, each atom employs three orbitals for the bonding in the polyhedron (see above), while the above discussion assumes that the C(9) and C(6) atoms in the nickel and platinum complexes respectively employ only two orbitals for the bonding in the polyhedron. If, on the other hand, it is assumed that the H_{ax} atom is not an exo-substituent in the full sense of the term and is involved in the bonding within the polyhedron (for example, in the weak interaction with the neighbouring, in relation to the carbon atom, boron atoms in the "open" face), then in this instance both electrons of the $C-H_{ax}$ bond can be classified as the skeletal electrons of the complex. Thus the total number of skeletal electrons

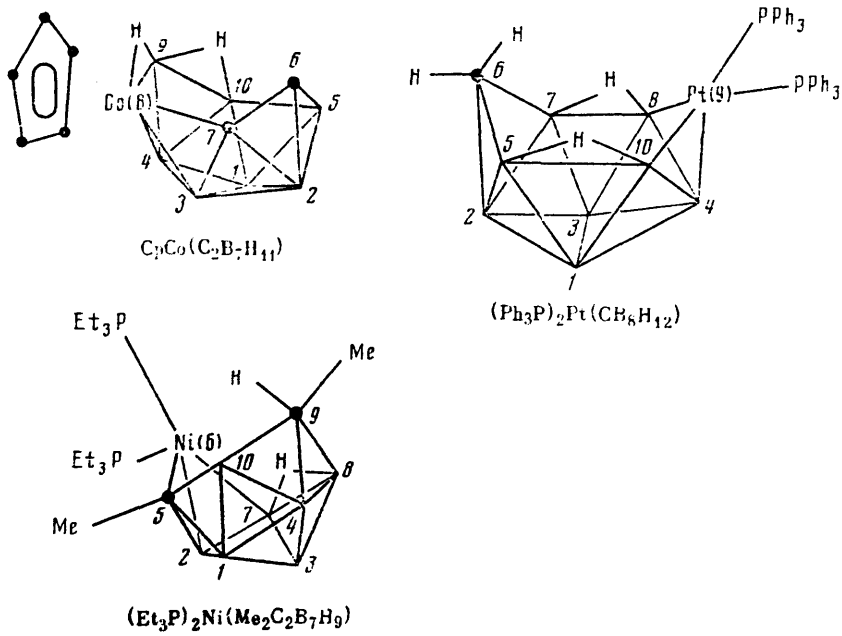


Figure 6. 10-Vertex *nido*-MCB.[40–42]

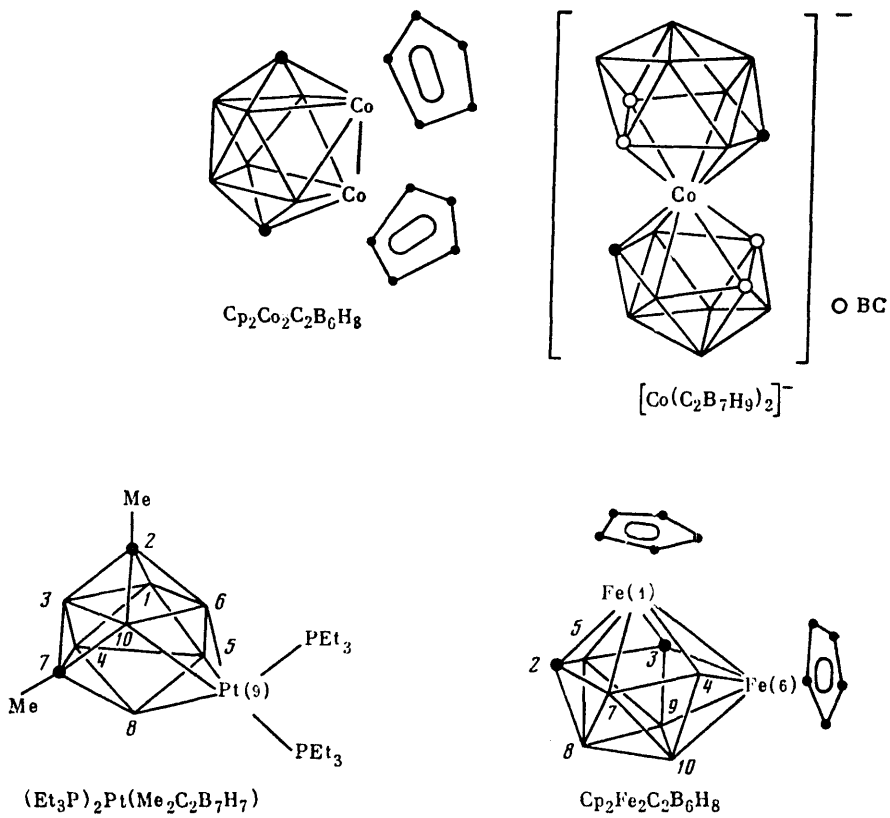


Figure 7. 10-Vertex *closo*-MCB.[43–46]

in the nickel and platinum derivatives under discussion is 24 and is consistent with the *nido*-geometry of the 10-vertex complex.

The "basic" polyhedron in 10-vertex *closo*-MCB is the so-called two-cap square antiprism centred with respect to the faces of both bases (Fig. 7). Polyhedra having this structure have been found in structural studies on cobaltacarbaboranes—the bimetallic complex $Cp_2Co_2C_2B_6H_8$ [43] and a *commo*-MCB—the $[Co(C_2B_7H_9)_2]^-$ anion#.[44] It is striking that the metal atoms in both compounds occupy vertices in the "equatorial" belt of the antiprism, whiole the low-coordination positions in the "caps" are occupied preferentially by carbon atoms.

As in the MCB with a larger number of vertices discussed above, the 10-vertex cobaltacarbaboranes (with a d^6 configuration of the metal atom) have a fairly symmetrical structure. On the other hand, in the platinacarbaborane $(Et_3P)_2Pt(Me_2C_2B_7H_7)$[45] ($d^8$ configuration), which, like its cobalt analogues, satisfies Wade's rule, appreciable distortions of the polyhedron are observed. They are expressed in the formation of a tetragonal open face C(7)B(8)Pt(9)B(10), which arises as a result of the dissociation of one of the "equatorial" bonds [Pt(9)...C(7) bonds 2.83 Å long] in a two-cap square antiprism.

In discussing the structure of 10-vertex MCB, one must not fail to mention the structure of the very interesting bimetallic iron complex $Cp_2Fe_2C_2B_6H_8$.[46] The geometry of the diamagnetic molecule can be described only approximately as one corresponding to a two-cap square antiprism. For the purpose of this description, one must imagine that one "equatorial" bond C(3)–B(4) in the antiprism has been broken and one of the "caps" [Fe(6)] is linked directly to the metal atom in the "equatorial" belt remote from it [the Fe(6)–Fe(1) bond 2.571 Å long].

Such structural anomalies are evidently due to the insufficiency of skeletal electrons for the construction of a 10-vertex *closo*-system. In the given complex there are 20 (instead of 22) electrons, which is the reason for their unusual structure. Although formally this compound belongs to the class of 10-vertex *closo*-MCB (with all the faces triangular), in fact it does not have the geometry characteristic of these systems. Furthermore, its polyhedron can be regarded as a three-cap trigonal prism [with the C(3)B(5)B(9) and B(4)B(7)B(10) bases and the Fe(1), Fe(6), and B(8) "caps"] having one additional vertex at C(2), which corresponds to 9-vertex *closo*-MCB (20 electrons).

A number of interesting 10-vertex MCB and metalloborane complexes have been described by Crook and co-workers,[47–50] who investigated the reactions of the iridium complex *trans*-$[Ir(CO)Cl(PPh_3)_2]$ with the *closo*-$B_{10}H_{10}^{2-}$ borate dianion in

#According to the IUPAC nomenclature, the term *commo*-MCB is given to complexes in which the polyhedra are linked together via a common metal atom.

methanol. In the course of the formation of two of the products investigated, namely $(MeCOO)(Ph_3P)HIrCB_8H_7 \cdot (PPh_2)$[47] and $IrC(OH)B_8H_6(OMe)(C_6H_4PPh_2)(PPh_3)$[48] (Fig. 8), a carbon atom from the solvent as well as the metal atom was inserted in the borane skeleton during the reaction, which resulted in the formation of 10-vertex iridacarbaboranes. The first of these complexes has 22 skeletal electrons (in calculating the number of electrons one must take into account the Zwitter-ionic character of the molecule—the positive charge of the P atom linked to the B atom and the negative charge on the polyhedral skeleton) and possesses the geometry of a fairly symmetrical (the Ir^{III} atom has the d^6 configuration) two-cap square antiprism, which is characteristic of 10-vertex *closo*-MCB.

The second complex investigated contains two skeletal electrons less, because, firstly, it has no hydride ligand and, secondly, its polyhedron does not carry a negative charge. The Ir(7)...B(9) distance in this complex is fairly large (2.82 Å) and the authors[48] characterised it as a *nido*-MCB and the Ir(7)B(8)B(9)C(10) face is regarded as open. Furthermore, the similarity of the polyhedra of this iridacarbaborane and the bimetallic iron complex discussed above is striking. The similarity appears entirely reasonable because both complexes are, as it were, "superelectron-deficient" (see above) 10-vertex classical systems and each has 20 skeletal electrons. As in the iron derivative, in the polyhedron of the iridium complex there is one "additional" vertex, which in this instance is occupied by the B(3) boron atom. It must also be emphasised that the purely boron hydride complex $(Ph_3P)(Ph_2PC_6H_4)HIrB_9H_8$, obtained by the reaction of $IrCl(PPh_3)_3$ with $B_9H_{12}^-$, which is isoelectronic with the above compounds, has an analogous structure, which has been characterised[49] (Fig. 8).

The reaction involving the formation of iridium complexes, mentioned above, has an interesting feature: in these processes the *ortho*-boration of one of the benzene rings of the Ph_3P ligand takes place simultaneously with the insertion of the metal atom in the borane polyhedron. It has been found that similar processes play an important role in the chemistry of MCB and metalloboranes containing triphenylphosphine ligands. Thus, apart from the products mentioned above, the octahedra of the metalloborane $(OC)_3(Ph_3P) \cdot (Ph_2PC_6H_4)_2Ir_2B_4H_2$,[50] in which the metal atoms occupy two neighbouring vertices, have been isolated and structurally characterised in the reaction of $Ir(CO)Cl(PPh_3)_2$ with *closo*-$B_{10}H_{10}^{2-}$, apart from the products mentioned above. Here the benzene rings of the two phosphine ligands at one of the metal atoms have undergone *ortho*-boration. The authors[49,50] suggest that the *ortho*-boration process is not simply a concomitant reaction, involving the elimination of hydrogen atoms in the formation of C–B bonds in the polyhedral skeleton already present, but constitutes an important stage involving the insertion of the metal atom into the polyhedron. In their view the CH group in the benzene ring can serve during the reaction as a source of an additional electron pair, which is supplied to the borane polyhedron and initiates its decomposition.

Incidentally, this view can be open to a definite objection, particularly if one takes into account the results obtained in a structural study[51] of the products of the thermal rearrangement of the 10-vertex *nido*-platinacarbaborane $(Ph_3P)_2 \cdot Pt(CB_8H_{12})$ discussed above (Fig. 6). When this complex is heated, two moles of H_2 are evolved and bonds are formed between the *ortho*-carbon atoms of two benzene rings in different Ph_3P groups and the boron atoms in the 8- and 10-positions.

Thus the *ortho*-boration of the benzene rings of the triphenylphosphine ligands need not necessarily be accompanied by rearrangements in the polyhedral skeleton. It may be that the specific features of the reaction are associated with the enforced geometrical proximity in the C–H (benzene ring) and B–H (carbaborane ligand) bonds, which are characterised by the opposite polarisations of the hydrogen atoms.

4. 9-Vertex MCB

As a rule, 9-vertex MCB consist of a polyhedron having the form of a three-cap trigonal prism. Such geometry is characteristic of, for example, the MCB anion $[CpCoCB_7H_8]^-$, whose structure has been investigated[52] using its caesium salt (Fig. 9). Here the carbon atom occupies a low-coordination position in one of the "caps", while the cobalt atom is located at one of the vertices of the base. The differences between the Co–B(5) and Co–B(6) distances (on average

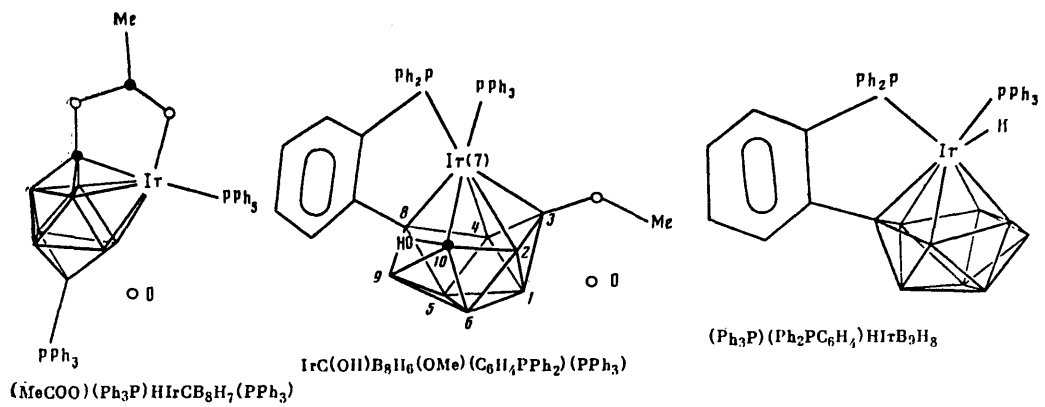
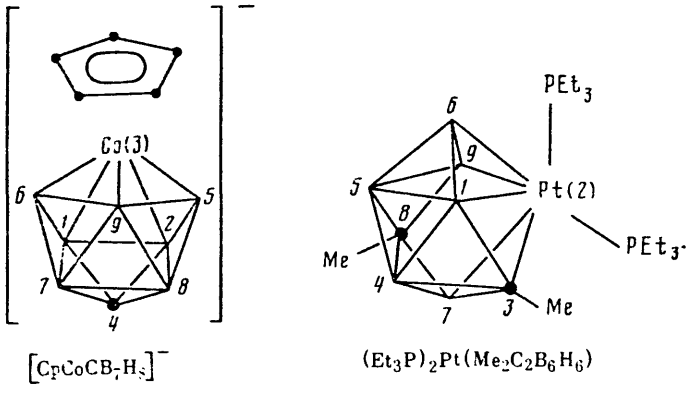


Figure 8. Borane and carbaborane complexes of iridium.[47–49]

1.98 Å) and between the Co–B(1), Co–B(2), and Co–B(9) distances (on average 2.16 Å) can be explained by the lower C.N. of the B(5) and B(6) atoms in the "caps" of the polyhedron.



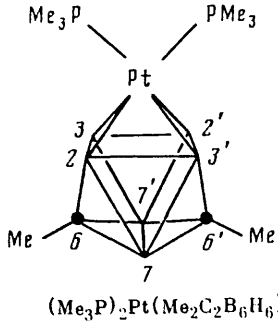


Figure 9. 9-Vertex MCB.[52–54]

Two 9-vertex platinacarbaboranes with analogous compositions, namely $(Et_3P)_2Pt(Me_2C_2B_6H_6)$[53] and $(Me_3P)_2.Pt(Me_2C_2B_6H_6)$,[54] have appreciably different structures. In the first compound, where the platinum atom occupies one of the vertices in the base of the prism, as in the platinum(II) complexes discussed above, appreciable distortions of the polyhedron are observed: the platinum atom forms two short Pt(2)–B(6) (2.17 Å) and Pt(2)–C(3) (2.18 Å) bonds (which, together with the PEt_3 ligands, build up its environment to a square) and three long bonds with the boron atoms in the 1-, 7-, and 9-positions having an average length of 2.48 Å. The B(7)...B(9) distance in the base of the prism does not correspond to the formation of a bond and the Pt(2)B(7)C(8).B(9) face is "open".

On the other hand, the polyhedron ot the triphenylphosphine derivative of platinum is actually symmetrical: four Pt–B bonds are 2.19–2.24 Å long. Thus this complex infringes the rule, mentioned above, concerning the appearance of appreciable distortions in the polyhedron following the introduction of an atom with a d^8 configuration. The only anomaly in the structure consists, in this instance only, in the location of the metal atom at a low-coordination vertex of the polyhedron.

5. 8-Vertex MCB

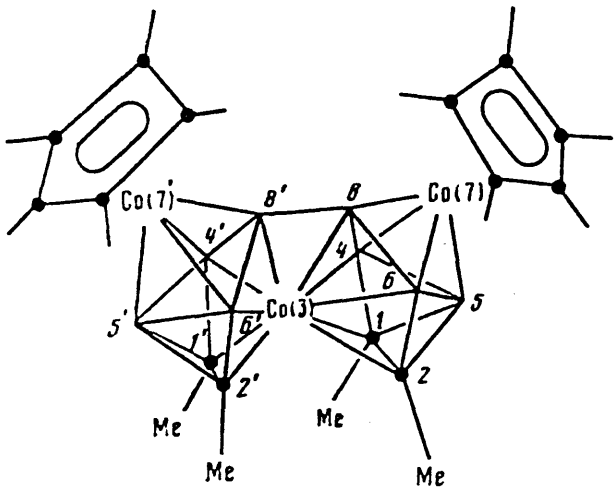
The 8-vertex *closo*-MCB should have the structure of a dodecahedron with triangular faces according to the general scheme (Table 2). This very interesting polyhedron can be regarded as a combination of two distorted tetrahedra (it is sometimes referred to as a "Siamese" polyhedron. Indeed, in order to obtain this polyhedron, it is necessary to extend one tetrahedron and to compress the other along the $\bar{4}$ symmetry axis and then insert one in the other.

In the cobaltacarbaborane $(C_5Me_5)_2Co_3Me_4C_4B_8H_7$ [55] the two dodecahedral fragments are combined not only via the carbon metal atom in a *commo*-type arrangement but also via a B–B bond 1.758 Å long, which is exopolyhedral in relation to both MCB skeletons (Fig. 10). Both crystallographically independent dodecahedra have virtually identical geometries and a fairly symmetrical structure: the breakdowns in symmetry are evidently associated with the different radii and C.N. of the atoms forming part of the polyhedron. The molecule as a whole has an approximate symmetry plane perpendicular to the B(8)–B(8′) bond. The absence of a second possible mirror plane is associated with the small but significant rotation of the dodecahedral fragments relative to one another as a result of which the C(1)...C(1′) distance is shorter by approximately 0.1 Å than the C(2)...C(2′) distance. This rotation has been attributed[55] to the influence of the additional H atom [apart from the terminal H atoms at the B(4), B(5), and B(6) atoms], which was not detected in the structural study and which is apparently located in the vicinity of the Co(3), B(6), B(8), B(6′), and B(8′) atoms.

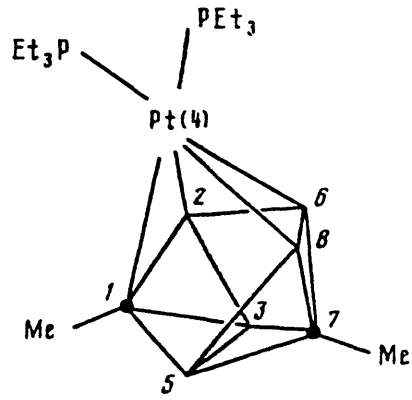
The only 8-vertex MCB with an isolated polyhedron, whose structure has been investigated hitherto, namely $(Et_3P)_2.Pt(Me_2C_2B_5H_5)$,[56] is a platinum(II) derivative and its polyhedron is highly distorted as was to be expected. The coordination of the platinum atom can be regarded as of the "square-planar" type [involving the P atoms in the centres of the B(2)–B(6) and B(6)–B(8) edges]. On the other hand, the formation of a bond along any of the two diagonals of the "open" Pt(4)C(1)B(5)B(8) face [Pt(4)...B(5) = 3.105 Å; C(1)...B(8) = 2.896 Å] would have led to a *closo*-dodecahedral structure.

Although the number of structural studies of 8-vertex MCB has been extremely small, the dodecahedral borate dianion $B_8H_8^{2-}$ has been known for a fairly long time.[57] The dodecahedral metalloboranes $Cp_4Co_4B_4H_4$ [58] and $Cp_4Ni_4B_4H_4$ [59] have been obtained recently and their structures characterised (Fig. 10). These compounds are interesting because they have a symmetrical *closo*-structure, although the former has two electrons less and the latter two electrons more than required by Wade's rule. It is natural therefore that the studies of these structures were immediately followed by a whole series of theoretical investigations in which attempts were made to account for the causes responsible for the breakdown of the "2n + 2" rule for the dodecahedron.

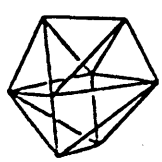
It has been noted in the study of Wade and co-workers[60] that the HOMO and the LUMO of the cluster system having the dodecahedral structure are non-degenerate, in contrast to the frontier orbitals of almost all the remaining *closo*-polyhedra. Therefore, although the introduction of two additional electrons into the dodecahedral system or conversely the removal of an electron pair leads to some loosening of the bond in the polyhedron, nevertheless it does not cause appreciable distortions in the latter. On the other hand, a change in the number of skeletal electron pairs in the majority of other *closo*-systems with degenerate frontier orbitals would have led to the appearance of an unstable paramagentic complex, which is distorted as a consequence of the Jahn–Teller effect. This qualitative study has been



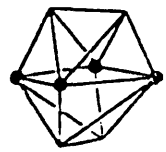
$(C_5Me_5)_2Co_3Me_4C_4B_8H_7$



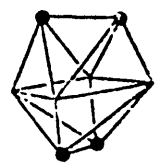
$(Et_3P)_2Pt(Me_2C_2B_5H_5)$



$B_8H_8^{2-}$



$Cp_4Co_4B_4H_4$



$Cp_4Ni_4B_4H_4$

Figure 10. MCB and metalloboranes with 8-vertex polyhedra.[55-59]

confirmed by quantum-chemical calculations for dodecahedral borane and metalloborane systems by the extended Hückel method.[61] The calculation not only justified the stability of the dodecahedral systems not satisfying Wade's rule but also made it possible to explain why the metal atoms in the nickel dodecahedron with an "electron excess" occupy the vertices of an extended tetrahedron or why those in the cobalt complex with an "electron deficiency" are located at the vertices of a compressed tetrahedron.

6. Small (7- and 6-Vertex) MCB

Among the small MCB, the compounds with a 7-vertex polyhedron, having the geometry of a pentagonal bipyramid have been studied in greatest detail. The metal atom in such polyhedra usually occupies a high coordination apical site, as happens, for example in the cobaltacarbaborane $CpCo(Me_2C_2B_4H_4)$[62] (Fig.11), which can serve as an example of a complex with a symmetrical structure typical for 7-vertex MCB. The cobalt atom is located at the high-coordination apical site and is linked symmetrically to the atoms in the equatorial plane (Co–C = 2.031 Å; Co–B = 2.092 Å); the carbon atoms occupy the neighbouring vertices in this plane and the length of the C–C bond (1.461 Å) is close to that found in the dodecahedral fragments of the cobaltacarbaborane $(C_5Me_5)_2Co_3Me_4C_4B_8H_7$ (on average 1.448 Å[55]), mentioned above, and are much shorter than in the analogous eicosahedral systems. This difference is evidently associated with the differences between the C.N. of the carbon atoms in the dodecahedron and the pentagonal bipyramid (C.N. = 4), on the one hand, and in the eicosahedron (C.N. = 5), on the other.

Having examined the structure of a symmetrical cobaltacarbaborane (with the d^6 configuration), we shall now turn to the discussion of the structure of the analogous platinum(II) derivative (with the d^8 configuration). As in all the derivatives of d^8 metals examined above, significant distortions of the geometry of the polyhedron were observed in this instance. The distortions in the 7-vertex MCB have the character of a "shift" deformation analogous to those observed for the eicosahedral MCB. Thus the platinum atom in the complex $(Et_3P)_2Pt(Me_2C_2B_4H_6)$[63] is much closer to the boron atoms (the average Pt–B distance is 2.21 Å) than for the carbon atoms (the average Pt–C distance is 2.855 Å); the angle of inflection of the "open" face along the B...B line,

which tends to shift the carbon atoms away from the metal atom, is 21.4° [in the corresponding 12-vertex complex $(Et_3P)_2PtC_2B_9H_{11}$ [28] the average Pt...C distance is 2.572 Å and the ange of inflection of the "open" face is 9.1°].

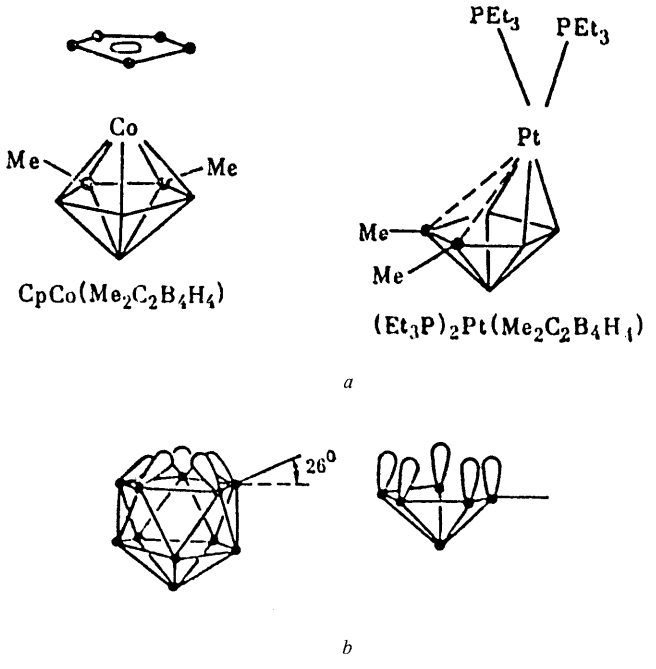


Figure 11. *a*) 7-Vertex MCB;[62,63] *b*) the orientation of the "lobes" of the frontier orbitals of *nido*-carbaborane ligands.[64]

Comparison of these geometrical parameters shows that, although the "shift" distortions in the 7- and 12-vertex polyhedra are of the same type, in the case of the small MCB they are more distinct. This difference is linked directly to the different directions of the exopolyhedral bond in the eicosahedron and in the pentagonal bipyramid. Indeed, in the eicosahedron the exopolyhedral bond emerges from the plane of the pentagonal face in the direction of the vertex centred above it (the angle between the direction of this bond and the plane of the face is 26°), while in the pentagonal bipyramid the exopolyhderal bond is in the equatorial plane. Calculations by the extended Hückel method[64] have shown that this difference leads to different orientations of the "lobes" of the frontier orbitals of the carbaborane ligand: in the eicosahedral fragment the long axes of the "lobes" form a much smaller angle with the plane of the "open" face than in the pentagonal bipyramidal fragment (Fig.11). Bearing in mind that the "shift" distortions in the coordination of the dicarbollide ligand are caused by the preferential localisation of the frontier orbitals at the boron atoms, it becomes understandable why the different orientation of the "lobes" of the orbitals in the pentagonal bipyramid requires a more significant shift of the metal atom in the direction of the boron atoms to achieve a more effective overlap. Such orientation in the orbitals also explains the weaker bonding of the metal atom in the 7-vertex polyhedra compared with the 12-vertex polyhedra, which leads to different barriers to the rotation of the PtP_2 fragment relative to the carbaborane ligand.

Thus two singlets are observed in the ^{31}P NMR spectrum of the platinum dicarbollide complex even at room temperature, while in the spectrum of the pentagonal bipyramidal complex this splitting of the signal is observed only when the temperature is reduced.[63]

A whole series of structural studies on 7-vertex MCB have been undertaken to investigate the unusual chemical properties of derivatives of their hydride *commo*-MCB $(Me_2C_2B_4H_4)_2FeH_2$ (Fig.12). The hydride hydrogen atoms could not be located in a study[65] of the structure of the initial complex. These atoms are apparently disordered and are alternately centred above the four FeB_2 faces of the two pentagonal bipyramidal polyhedra. The presence of the hydrogen atoms is responsible for the appreciable mutual inclination of the pentagonal faces (the dihedral angle is 7.8°), which leads to the appearance of the energetically unfavourable short intramolecular contact Me...Me = 3.53 Å.

Each polyhedron of the complex $(Me_2C_2B_4H_4)_2FeH_2$ contains $2n + 2$ skeletal electrons and satisfies Wade's rule. This can be readily demonstrated by taking into account the fact that the "neutral" carbaborane ligand $Me_2C_2B_4H_4$ serves as a donor of four electrons, while the hydride hydrogen atoms can be regarded, for simplicity, as bound only to the metal atom (in this case the iron atom contributes two electrons to the polyhedron).

For an alternative description of the bonding in the complex under discussion, one can resort, as in the case of other MCB systems with giant polyhedra, to the topological model of a superaromatic cluster proposed by Slovokhotov and Struchkov.[66] In this model the total number of skeletal electrons and the number of vertices in both giant polyhedra are evaluated and the atoms belonging to the two skeletons are taken into account only in the determination of the number of electrons and are not included in the total number of vertices. In the *commo*-complex considered each MCB group serves as a rule as a donor of two electrons and the MCB groups each contribute three electrons to the polyhedron; on the other hand, the presence of the iron atom in this system leads in essence to a decrease of the number of skeletal electrons (the contribution of the iron atom is $8 + 2 - 12 = -2$). Thus the total number of electrons in the complex $(Me_2C_2B_4H_4)_2FeH_2$ is 26, which corresponds to 12 (without taking into account the iron atom) vertices of the polyhedron.

The specific features of the chemical behaviour of the complex $(Me_2C_2B_4H_4)_2FeH_2$ are associated with its ability to lose readily the hydride hydrogen atoms and to combine with metal-containing groups. This result in the formation of compounds in the molecules of which two carbaborane ligands are combined not only via the common central metal atom but also via yet another, additional atom occupying the position of a "cap" in relation to one of the triangular faces in each polyhedron. Such compounds can be called "wedged" *commo*-MCB.

Thus the interaction of the initial iron hydride complex with $CpCo(CO)_2$ and $Co(PEt_3)_4$ leads to the formation of mixed bimetallic MCB having the compositions $CpCoFe(Me_4C_4B_8H_8)$[67] and $(Et_3P)_2CoFe(Me_4C_4B_8H_8)$,[68] which have been investigated by X-ray diffraction. In the study of the electronic structures of these compounds it is convenient to employ the topological model of joined polyhedral systems.[66] In the cyclopentadienylcobalt complex, which incorporates, apart from the CpCo group, four CMe groups, eight BH groups, and the iron atom, there are 26 electrons corresponding to 12 "outer" (disregarding the iron atom and the "additional" BH group) vertices of the joined polyhedron. As a consequence of the replacement of the Cp ligand in the phosphine complex by two Et_3P groups, the number of skeletal electrons

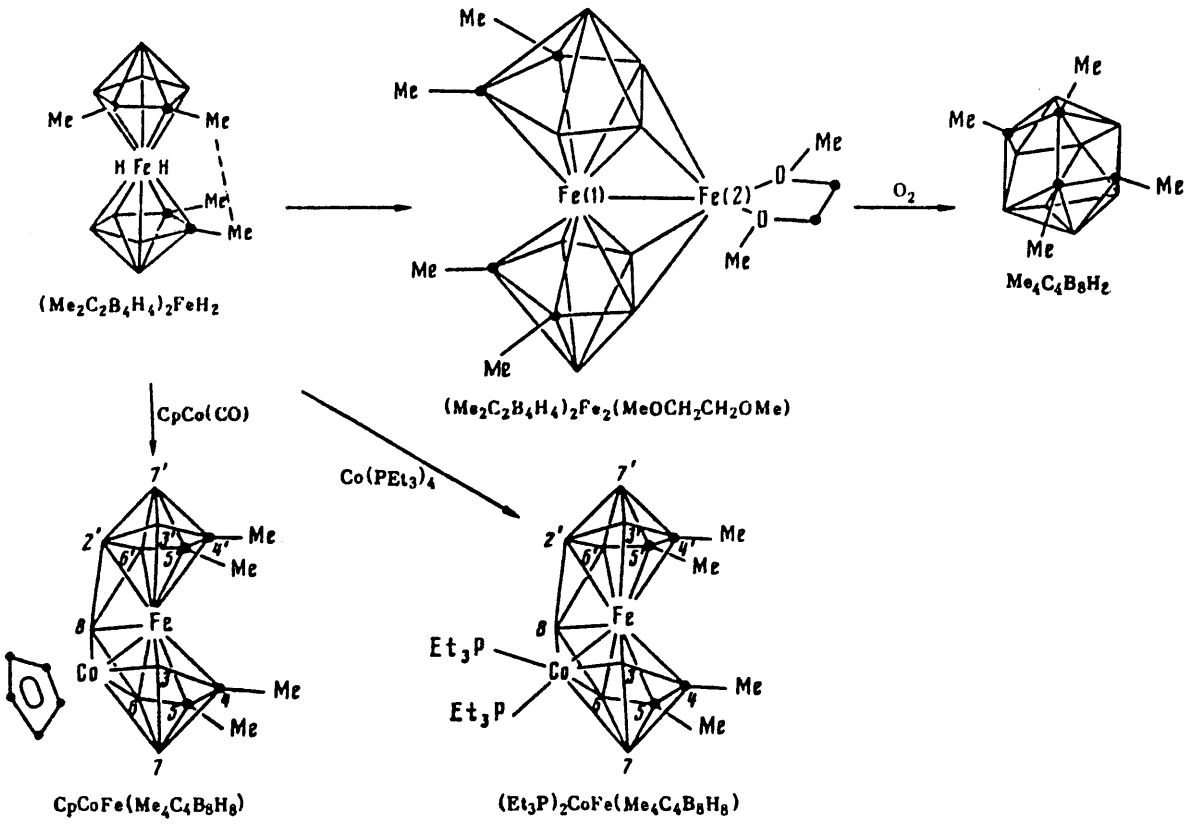


Figure 12. The structure of $(Me_2C_2B_4H_4)_2FeH_2$ and its reaction products.[65,67,68,71,72]

should be one less. This difference in the atomic structure influences in the given instance also the geometrical characteristics: almost all the bonds involving the cobalt atom and the boron atom located at the "additional" vertex in the phosphine complex are longer (on average by 0.08–0.10 Å) than the corresponding distances in the cyclopentadienyl derivative.

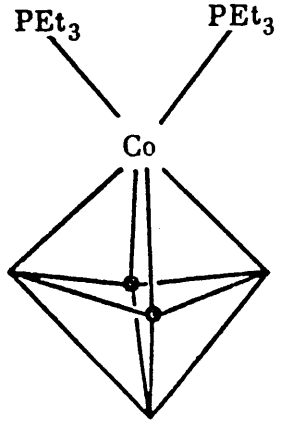
This explanation of the difference between bond lengths in the complexes described appears somewhat more correct than the remark by Barket et al[68] concerning the difference between the polyhedral radii of the cobalt(II) (in the Et_3P complex) and cobalt(III) (in the Cp derivative) atoms. Naturally the "deficit" of electron density (−1e) in such cluster systems is not localised solely at the metal atom but is distributed to a greater or lesser degree throughout the polyhedron. Precisely as a consequence of such delocalisation, not only the bond involving the Co atom but also others (for example, the edges connecting the additional BH group to the Fe and B atoms) are lengthened in the polyhedron of the phosphine complex.

An interesting feature of the iron and cobalt complexes is the asymmetric disposition of the "additional" BH group relative to the coordination planes of the carbaborane and MCB ligands, which is expressed by greatly increased (by approximately 0.3 Å) B(8)–B(2′) and B(8)–B(6′) distances compared with the B(8)–B(6) bond. This provided the authors[69] with a basis for the hypothesis that the "additional" BH group is linked only to the polyhedron containing the cobalt atom and that the relatively short distances to the boron atoms in the other polyhedral fragment are determined solely by the geometrical requirements—the repulsion of the Me groups to the "opposite" side of the polyhedron. In this case the "wedged" complexes can be represented as the usual *commo* MCB in which the 7- and 8-vertex polyhedra are combined via the common iron atom.

However, this view was disproved in a study[70] where a quantum-chemical calculation was carried out on the "wedged" metalloboranes and MCB by the extended Hückel method. The calculations showed that in the model borate anion $[Fe(BH)(B_6H_6)_2]^{4-}$ a symmetrical disposition of the "additional" boron atom relative to the coordinating faces of the *nido*-borane ligands corresponds to an energy minimum and the overlap of the frontier orbitals of each ligand with those of the "additional" BH group is equally important for the bonding in the polyhedron. It has been shown by the methods of perturbation theory that the introduction of the CoCp group instead of one of the BH groups of the borane ligand alters the character of the frontier orbitals of this ligand, which creates more favourable conditions for the overlap with the orbitals of the "additional" BH group. However, such substitution cannot lead to the complete dissociation of the bond between this group and the second, frequently borane, fragment.

The structure of a MCB of the "wedged" type, which constitutes an intermediate in the "oxidative cross-linking" of the ligands in the initial hydride complex $(Me_4C_2B_4H_4)_2FeH_2$, has also been investigated (Fig.12). This process, which proceeds readily in the presence of oxidants and leads to the formation of the tetracarbon carbaborane $Me_2C_4B_8H_8$, has been studied in detail.[71,72] The investigation of mixtures of the complexes $(R_2C_2B_4H_4)_2FeH_2$ with various alkyl radicals R

established that the "cross-linking" of the carbaborane groups does not entail the intermolecular exchange of ligands. In the presence of oxygen or rather oxidants, the "cross-linking" process in the tetrahydrofuran or dimethoxyethane solutions of the hydride complexes takes place almost instantaneously. However, in an inert atmosphere these solutions can persist for a short time (several hours) and the colour changes from dark-red to violet only gradually. The introduction of even trace amounts of oxidants into such a solution induces the instantaneous formation of the tetracarbon carbaborane $R_4C_4B_8H_8$.



$(Et_3P)_2CoC_2B_3H_5$

Figure 13. The structure of $(Et_3P)_2CoC_2B_3H_5$.[77]

The crystals of the intermediate in the "cross-linking" process isolated from the violet solution proved, however, to be fairly stable in air and were investigated by X-ray diffraction.[72] It was found that the molecule of the bimetallic complex $(Me_2C_2B_4H_4)_2Fe_2(MeOCH_2CH_2OMe)$ (Fig.12) contains one of the iron atoms at the "additional" vertex of the "wedged" *commo*-MCB. In contrast to the compounds examined above, the "additional" vertex in this complex [the Fe(2) atom] is located symmetrically relative to the two identical carbaborane ligands. Although the Fe(1)–Fe(2) distance in this structure (2.414 Å) is appreciably smaller than the lengths of the analogous bonds in the other MCB polyhedra (see above, for example), the authors[72] conclude that there is no direct Fe–Fe interaction on the basis of the results of magnetic measurements and the EPR spectra of this paramagnetic complex. Bearing in mind the short Fe–Fe distance, this conclusion appears to us extremely controversial. Thus the electronic structure of this unusual complex, which does not satisfy any of the rules for the evaluation of the number of skeletal electrons employed above, is not as yet entirely clear.

In conclusion of the discussion of the 7-vertex MCB, we may mention bimetallic monopolyhedral pentagonal-bipyramidal complexes. Such compounds, for example, the cobaltacarborane $Cp_2Co_2MeC_2B_3H_4$,[73] can be regarded, on the one hand, as the usual *closo*-MCB systems satisfying the "2*n* + 2" rule and, on the other hand, they can be formally treated as "three-decker" sandwiches made up of the Co^{3+} cations and the $C_5H_5^-$ and $C_2B_3H_5^{4-}$ anions, because these molecules contain a planar carborane face to which two metal atoms are coordinated simultaneously. Although this treatment proved to be extremely useful and stimulated to a considerable extent very interesting studies on the synthesis[74,75] of "multidecker" systems as well as their theoretical investigation,[76] the cluster model of delocalised interactions is undoubtedly more important for the description of the nature of the bonding in MCB of this kind. This is indicated, in particular, also by the stability of such complexes, which distinguishes them from the unstable purely cyclopentadienyl "multidecker" derivatives.

The results of the first structural investigation of the 6-vertex octahedral MCB complex $(Et_3P)_2CoC_2B_3H_5$ were not published until 1980.[77] This complex (Fig.13) belongs to the class of the paramagnetic *closo*-MCB, mentioned above, which contain one skeletal electron less than is required by the "2*n* + 2" rule. As mentioned above, it is as yet not entirely clear how this anomaly in the electronic structure influences the geometry of the polyhedron. One can only note that appreciable differences between the Co–C (2.112 Å) and Co–B (1.955 Å) distances as well as appreciable deviations from planarity in the equatorial belt of the octahedron (the angle of inflection along the B...B line is 19°) are observed in the given structure

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In a brief review, it is naturally impossible to dwell on a whole series of other aspects of the structural chemistry of the MCB. We disregarded many structures of *closo*- and *nido*-MCB, did not consider at all complexes with the *arachno*-structure, and did not discuss the extensive class of tetracarbon MCB, which is being vigorously investigated. All these questions undoubtedly merit additional consideration. Here we concentrated attention on compounds with *closo*-polyhedra containing between six and twelve vertices.

In conclusion of the discussion of these compounds, it must be emphasised yet again that the entire wide variety of these structures can be classified and interpreted on the basis of the rules for the counting of skeletal electrons widely employed in cluster chemistry. The overall geometry of the MCB molecules obeys these rules fairly rigorously.

On the other hand, small and sometimes also not very small distortions in the geometry of the polyhedra depend to a large extent on the nature of the metal and primarily on its electronic configuration. Thus, as the *d* sublevels of the metal atoms in the series of transition and post-transition elements are filled, geometrical distortions arise in the MCB systems and become increasingly more marked, being expressed by a decrease of symmetry and a loosening of the polyhedron. Analysis[78] of structural data on the cyclopentadienyl derivatives of post-transition elements has shown that this trend, namely the enhancement of coordination distortions as the *d* sublevels of the metal atoms are filled, is extremely general: it is manifested in complexes of transition and post-transition elements with both planar aromatic and polyhedral "superaromatic" ligands.

Yet another comment may be made on this subject. In all the MCB complexes of bivalent platinum mentioned above, the distortions of the polyhedron lead to a disposition of the strongest bonds involving the metal atom which imitates the square planar coordination characteristic of the usual classical platinum(II) complexes. In considering this question in a wider sense, one may stress that symmetrical MCB *closo*-polyhedra are observed only for metals with the electronic configuration for which an octahedral environment is typical (Fe^{II}, Fe^{III}, Co^{III}, Pt^{IV}, etc.). The introduction into the

carbaborane polyhedron of metals having a less symmetrical coordination [tetragonally distorted octahedral (Cu^{II}), square planar (Pt^{II}, Pd^{II}), and linear (Hg^{II})] leads as a rule to a considerable loosening and (or) decrease of the symmetry of the polyhedron.

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