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Polyhedral Metallaboranes, Metallacarbaboranes, and Metallaheteroboranes with the η^5-C_5H_5Fe Fragment in the Polyhedron

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The literature data on the synthesis and properties of polyhedral boranes, carbaboranes, and heteroboranes with the η^5-C_5H_5Fe fragment in the polyhedron are surveyed and described systematically.
The bibliography includes 74 references.

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I. INTRODUCTION

One of the most important discoveries in chemistry during the last twenty years has been the synthesis of metallacarbaboranes—a new class of compounds with a polyhedral structure. The rigorous development of this field of chemistry has led to the preparation of an enormous number of compounds differing in their geometry, the number of vertices, and various combinations of boron and carbon atoms, a heteroatom (usually the atom of a Group II–VI non-transition element), and a transition metal atom. At the present time one can speak of the establishment of a new field of chemistry—the chemistry of polyhedral metallacarbaboranes and metallaboranes. The number of new metallacarbaborane structures is large and increases consistently every year, so that the reviews published in the literature in recent times have either become obsolete, or reflect only individual studies by certain groups of investigators,[1-4] or have been devoted to narrow specialist questions in the chemistry of metallacarbaboranes.[5-9] The present review deals with the structure, methods of synthesis, and certain reactions of polyhedral boranes, carbaboranes, and heteroboranes with the CpFe group† in the polyhedron. These compounds are a link between ferrocene, on the one hand, and *commo*-ferracarbaboranes, on the other. The structural and electronic analogies between ferracarbaboranes and ferrocene derivatives together with the specific features of the compounds themselves may be extremely attractive as objects of study from both theoretical and applied points of view.

The present review deals with the literature between 1965 and 1983.

II. THE NOMENCLATURE, STRUCTURE, AND TYPES OF BONDING IN POLYHEDRAL BORON-CONTAINING SYSTEMS WITH THE CpFe FRAGMENT IN THE POLYHEDRON

The compounds described cannot always be conveniently named in accordance with IUPAC rules.[10] For this reason, the trivial nomenclature adopted in the literature will also be used. In many cases, names will be omitted and will be replaced by graphical representations of the molecules and their overall formulae.

The structure of ferracarbaboranes, ferraboranes, and ferraheteroboranes with a CpFe fragment is described satisfactorily by the corresponding polyhedra and is determined both by the number of atoms in the polyhedral skeleton and by the type of these atoms. The types of bonding in polyhedral boron-containing systems have been discussed in a number of communications.[8,11-14] The qualitative description of the bonds in a metallacarbaborane polyhedron can be briefly formulated in terms of the following items:

1. All the electrons in the metallacarbaborane molecule are delocalised along the surface of the polyhedron.
2. Each atom in the polyhedron provides three atomic orbitals (AO) for polyhedral bonding. For the boron and carbon atoms and the atoms of other elements in the First Period, there remains one AO for bonding with another ligand (for example, a hydrogen, carbon, etc. atom). After being bound in the polyhedron, the transition metal atoms have six unoccupied AO, which are used for bonding with other ligands (C_5H_5, CO, PR_3, etc.) or are occupied by electrons not involved in bonding and localised at the metal atom.
3. The number of bonding molecular orbitals (MO) in the closed polyhedra (the *closo*-structure) with n vertices ($n \geq 5$) is $n + 1$. Consequently the number of skeletal electrons is $2n + 2$. The number of occupied MO is $n + 1$.
4. If the number of skeletal electrons in the polyhedron is greater than $2n + 2$, the latter acquires an open structure. When the number of electrons is $2n + 4$ we have the *nido*-structure (one vertex is lacking for the *closo*-structure). When the number of electrons is $2n + 6$, we have the *arachno*-structure (two vertices are lacking for the *closo*-structure). When the number of electrons is $2n + 8$, the *hypho*-structure obtains (three vertices are lacking for the *closo*-structure).
5. The *closo*-, *nido*-, *arachno*-, and *hypho*-metallacarbaboranes can be regarded as electronic analogues of the corresponding carbaboranes, boranes, and also carbaborane and borane anions.

Ferracarbaboranes and ferraboranes with the CpFe fragment in the polyhedron and having the *closo*- and

†Here and henceforth η^5-C_5H_5Fe = CpFe.

nido-structures are widely known. The *arachno*- and *hypho*-metallacarbaboranes have been obtained comparatively recently[6] and only a few examples are known. The theory underlying the qualitative treatment of bonding in polyhedral boron- and metal-containing systems has been called the theory of the counting of skeletal electron pairs (TCSEP). It is also known in the literature as Wade's rule. In the course of further development of the chemistry of metallacarbaboranes, compounds have been obtained with a structure which could not be predicted on the basis of the TCSEP.[15-17] In addition, *closo*-ferracarbaboranes with one or several CpFe subunits and a polyhedral skeleton do not have a negative charge for the d^5 electronic configuration of the iron atom. Thus the total number of skeletal electrons is less than the number necessary for the *closo*-structure, the number of the missing electrons being equal to the number of the CpFe subunits in the polyhedron. The theory of bonding in the given system was developed further in the review of O'Neill and Wade.[18]

III. GENERAL METHODS OF SYNTHESIS OF FERRACARBABORANES

Five main methods of synthesis of ferracarbaboranes, which are analogous to the general methods of synthesis of metallacarbaboranes, have been described in the literature:

1. Direct addition of the metal-containing group to the free boron-containing ligand, whereupon the ligand does not undergo structural changes.
2. Direct addition of the metal-containing group to the free boron-containing ligand in which the ligand undergoes marked structural changes.
3. Rearrangement or partial destruction of the metallacarbaborane with formation of a new complex.
4. Introduction of a boron atom into a metal complex with hydrocarbon ligands.
5. Introduction of a carbon atom into a metallaborane complex.

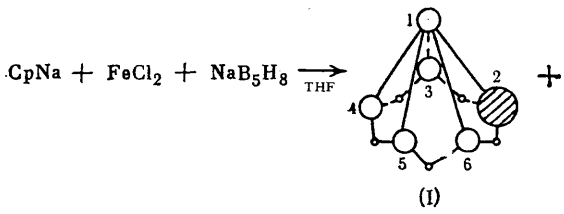
The first method of synthesis is very common. Numerous ferracarbaboranes with planar heterocyclic ligands, for example, borole, diborolin, thiadiborolin, borazine, etc. In addition, ferracarbaboranes with anionic carbaborane ligands, namely $C_2B_9H_{11}^{2-}$, $C_2B_{10}H_{12}^{2-}$, etc., have been obtained by this method. The second method of synthesis is also fairly widely known. One of the examples is the synthesis of ferracarbaboranes by the polyhedral expansion method. The third method of synthesis can be illustrated by various thermal rearrangements of the polyhedral skeleton and also by the polyhedral contraction reaction involving the ferracarbaborane nucleus. The fourth and fifth methods are so far known for only a limited number of examples, but they are undoubtedly promising and their development in the immediate future may be expected.

IV. COMPOUNDS HAVING (6-11)-VERTEX POLYHEDRAL STRUCTURES

In the systematic description of various polyhedral complexes containing both boron and iron, the latter will be considered in terms of increasing numbers of vertices in the polyhedron.

1. 6-Vertex Polyhedra

Only a limited number of examples of compounds of this type are known and all the ferracarbaboranes and ferraboranes obtained have the *nido*-structure. The ferraborane $CpFeB_5H_{10}$ (I) was obtained in a low yield together with other products on interaction of CpNa with $FeCl_2$ and NaB_5H_8 in THF at 25 °C:[19,20]

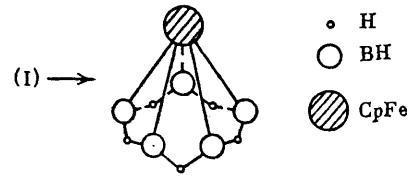


(I)

$$+ CpFeB_{10}H_{15} + Cp_2FeB_8H_8 .$$

○H ○BH ▨CpFe

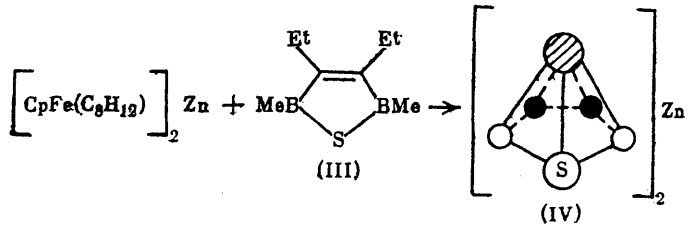
The structure of $Cp_2FeB_8H_8$ has not been established and the structure of $CpFeB_{10}H_{15}$ will be discussed below. On the basis of ^1H and ^{11}B NMR spectra, a pentagonal-pyramidal structure was assigned to complex (I). On heating in deuteriotoluene, the complex rearranges to the isomeric ferraborane (II), which is a structural analogue of ferrocene:



(II)

Like complex (I), the ferraborane (II) is a paramagnetic substance unstable in air.

On refluxing of the zinc salt of η^5-cyclopentadienyl-η^4-cycloocta-1,5-dienyliron in hexane with an excess of 3,4-diethyl-2,5-dimethylthiadiborolin (III), the zinc salt of the thiadiborolinyliron complex (IV) is obtained:[21]



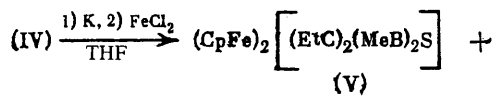
(III) (IV)

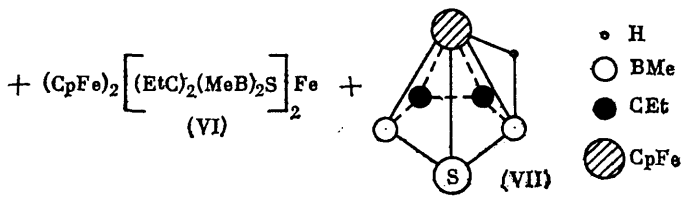
○ BMe ● CEt ▨ CpFe

Complex (IV) has 16 skeletal electrons, which are responsible for the *nido*-structure of its pentagonal pyramid#. The interaction of complex (IV) with potassium entails the replacement of the zinc cation by the potassium cation.

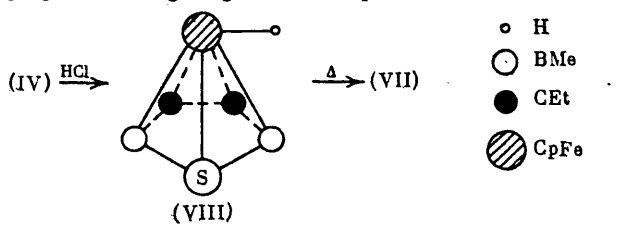
#Here and henceforth the number of skeletal electrons is calculated and its relation with the structure of the complexes considered established on the basis of the TCSEP.

The subsequent reaction with $FeCl_2$ in THF leads to the formation of a mixture of ferracarbaboranes:



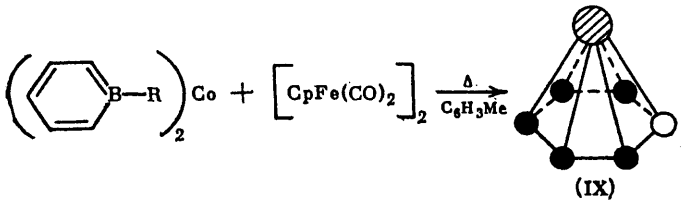


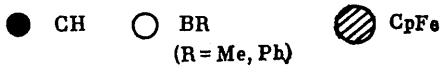
The structure of complexes (V) and (VI) will be examined below. Complex (VII), obtained in a very small amount, is isostructural with the initial complex (IV). Hydride hydrogen occupies the bridging position between the boron and iron atom, which has been demonstrated by ^{11}B NMR. Treatment of the zinc salt (IV) with dry HCl results in the formation of complex (VIII), containing a hydrogen atom linked to the Fe atom by a σ-bond. On heating of complex (VIII), the hydride hydrogen at the Fe atom passes to the bridging position, giving rise to complex (VII):



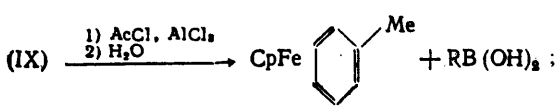
2. 7- and 8-Vertex Polydedra

The hexagonal-pyramidal derivatives of η^6-borarenyl-η^5-cyclopentadienyliron (IX) have been obtained by heating bis(η^6-borarenyl)-cobalt with $[CpFe(CO)_2]_2$ in mesitylene:[22]



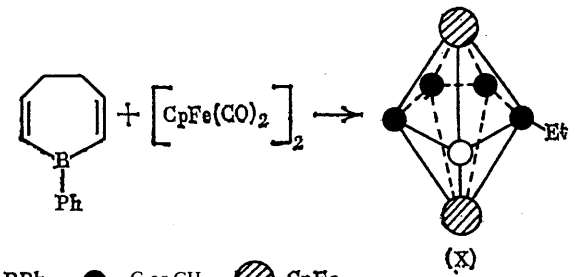


Complexes (IX) are crystalline substances stable in air. Their molecules contain 18 skeletal electrons and have the *nido*-structure. Oxidation of complex (IX) on treatment with Ce^{4+} leads to the removal of the boron atom from the polyhedral skeleton and to the formation of the methyl- or phenyl-ferrocenium cation in a high yield. Acylation of complex (IX) with acetyl chloride under the conditions of the Friedel-Crafts reaction entails the replacement of the BR fragment in the borarene ligand by the CMe fragment:



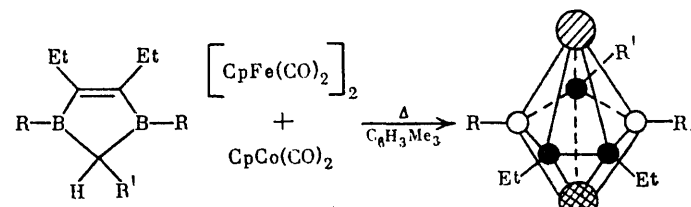
R=Me; Ph.

The above group of complexes is also of interest because it contains a large number of the so-called "multidecker sandwiches". Heating of 1-phenyl-4,5-dihydroborepin with $[CpFe(CO)_2]_2$ leads to the isomerisation of the boron-containing ligand and the formation of the diamagnetic complex (X), which is a triple-decker sandwich:[4]





Complex (X) contains 16 electrons and has the *closo*-structure, which has been demonstrated by X-ray diffraction (the Fe–Fe distance is 3.27 Å). When the alkyldiborolin (XIa) is heated with $[CpFe(CO)_2]_2$ and $CpCo(CO)_2$ at 180–200 °C in an inert atmosphere, the mixed diamagnetic complex (XIIa), containing Fe and Co atoms in the d^6 configuration, is formed in a low yield:[23]

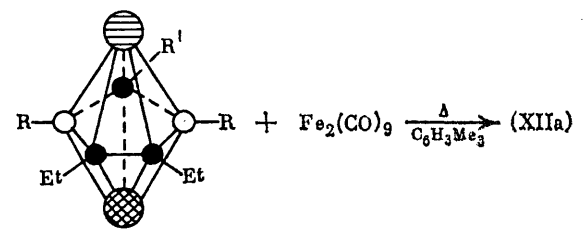


(XIa): R = Et, R' = Me
(XIb): R = Me, R' = H

(XIIa): R = Et, R' = Me
(XIIb): R = Me, R' = H



Complex (XIIa) is stable in air and can be sublimed *in vacuo* at 120 °C. Its *closo*-structure is due to the presence of 16 skeletal electrons. The synthesis of complex (XIIa) on heating the cobaltanickelacarbaborane (XIIIa) with iron nonacarbonyl in mesitylene has been described. Complex (XIIa) is then formed in a moderate yield (~10%) together with other metallocarbaboranes:[24]

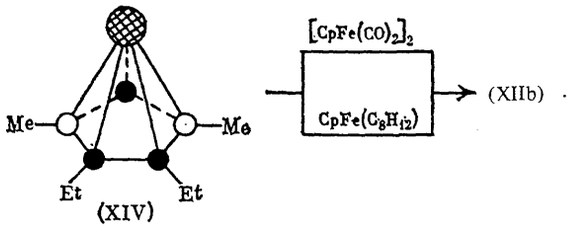


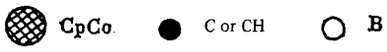
(XIIIa): R = Et, R' = Me
(XIIIb): R = Me, R' = H



Complex (XIIb) has been obtained in a moderate yield by the reaction of the cobaltacarbaborane (XIV) with organo-

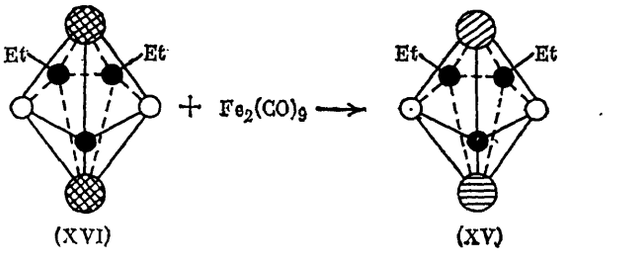
iron compounds:





The complex is formed in a very low yield together with other metallocarbaboranes when the cobaltacarbaborane (XIV) is reduced by potassium in THF, this being followed by reaction with $CpFe(CO)_2I$. Finally, complex (XIIb) has been obtained in a high yield by the reduction of the cobaltanickelcarbaborane (XIIIb) by potassium in THF and subsequent treatment with $FeCl_2$. It is believed[24] that complexes (XII, a and b) contain 30 valence electrons (in each case 6 π electrons of the Cp rings, 6 *d* electrons of the Fe atom, 8*d* electrons of the Co atom, and 4π electrons of the C_3B_2 ligand). Complex (XIIb) has the *closo*-structure, which has been demonstrated by X-ray diffraction (the bond distances are 3.104 Å for Fe–Co, 1.624 Å for Fe–C_3B_2, and 1.58 Å for Co–C_3B_2). On treatment with potassium in THF, complex (XIIb) is converted into a paramagnetic anion (31 valence electrons), while oxidation with $AgBF_4$ in ether results in the formation of the paramagnetic cation (29 valence electrons). According to EPR data, the maximum spin density in the anion is concentrated at the cobalt atom. On the basis of Mössbauer spectra, it is believed[24] that the structure of complex (XIIb) and its cation are related in the same way as the structures of ferrocene and the ferrocenium cation. The effective magnetic moments of the cation of complex (XIIb) (μ_{eff} = 2.10 μ_B), its temperature dependence, and the potentials of the anion $\rightleftharpoons$ neutral complex $\rightleftharpoons$ cation reversible transitions have been measured. The above communication[24] quotes data obtained by quantum-chemical calculations for complexes (XII, a and b) carried out using the extended Hückel method; the energies of all the 17 highest occupied MO, the types of the MO, and the contributions by the AO of the metals were determined. It follows from the calculated data that the CpFe fragment is linked to the C_3B_2 ring more strongly than the CpCo fragment. The EPR, Mössbauer, and electrochemical data are consistent with the main conclusions drawn from the quantum-chemical calculation.

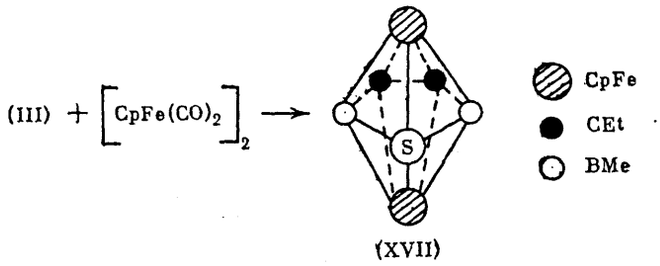
The dinuclear ferracarbaborane (XV), containing both the CpFe and $(CO)_3Fe$ fragments in the polyhedral skeleton, has been obtained by the reaction of the dinuclear nickelacarbaborane (XVI) with $Fe_2(CO)_9$:[24]



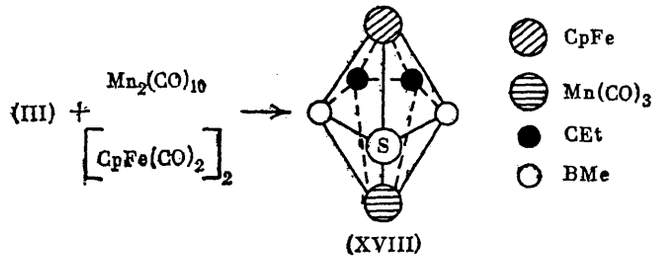


Complex (XV) is obtained in a mixture with other metallocarbaboranes, its maximum yield being obtained when the reaction is carried out in boiling mesitylene.

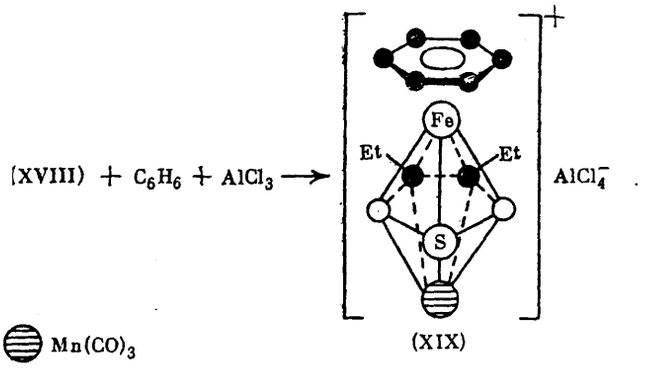
It is possible to obtain 7-vertex polyhedral ferracarbaboranes, containing an S atom in the polyhedron, by the reaction of thiadiborolin (III) with organic derivatives of transition metals (Fe, Co, Mn). The reaction with $[CpFe.(CO)_2]_2$ in boiling mesitylene affords a three-decker sandwich with two iron atoms—complex (XVII):[25]

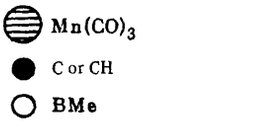


The structure of this complex, which is a diamagnetic crystalline substance stable in air but decomposing on treatment with inorganic acids, has been demonstrated by X-ray diffraction. The C_5H_5 and C_2B_2S rings are planar and have the transoid conformation, while the Fe–Fe distance is 3.236 Å. The interaction of the thiadiborolin (IV) with $[CpFe(CO)_2]_2$ and $Mn_2(CO)_{10}$ in boiling mesitylene leads to the formation of the diamagnetic complex (XVIII) with Fe and Mn atoms in the polyhedral skeleton:[26]



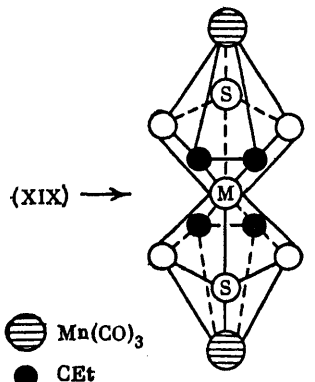
Complex (XVIII) is stable in air. Its *closo*-structure is determined by the presence of 16 skeletal electrons. Heating of complex (XVIII) in benzene in the presence of $AlCl_3$ results in the ready replacement of the Cp ligand by benzene:





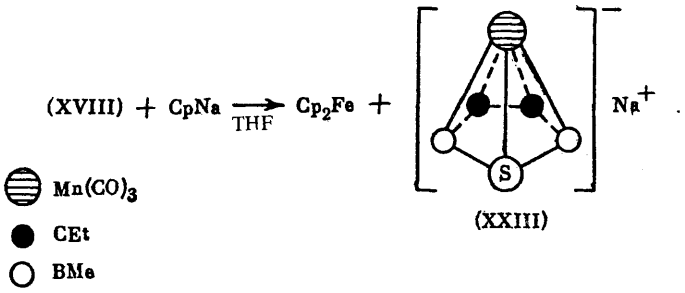
The cationic complex (XIX) formed under these conditions is extremely sensitive to hydrolysis. When it is heated *in vacuo*, a low yield of the mixed complex (XX), containing

3 metal atoms, is obtained:



(XX): M = Fe
(XXI): M = Co
(XXII): M = Ni

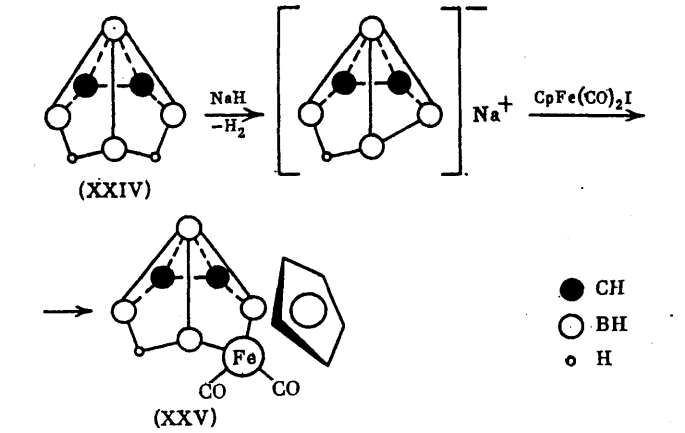
Another more general method of synthesis of complex (XX) and its structural analogues consists in treating complex (XVIII) with CpNa in THF.[27] This results in the removal of the CpFe fragment and the formation of the anionic complex (XXIII):



(XXIII)

Without being isolated, complex (XXIII) was made to react with transition metal chlorides of the type MCl_2 (M = Fe, Co or Ni) to form the trinuclear complexes (XX)–(XXII).

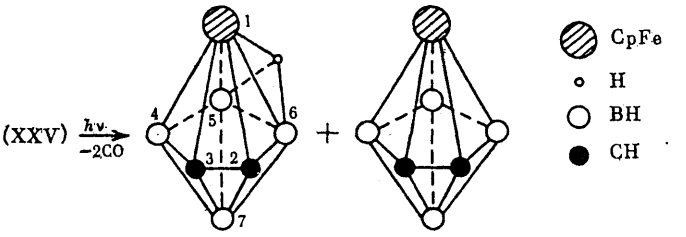
Another pathway leading to the synthesis of 7-vertex polyhedral *closo*-ferracarbaboranes involves the introduction of the CpFe fragment into the polyhedral skeleton of a *nido*-carbaborane. When the *nido*-carbaborane (XXIV) was treated with NaH in THF and then with $CpFe(CO)_2I$, the *nido*-carbaborane (XXV), which is sensitive to air and contains an Fe atom in a bridging position, was isolated in a satisfactory yield:[28,29]



(XXIV)

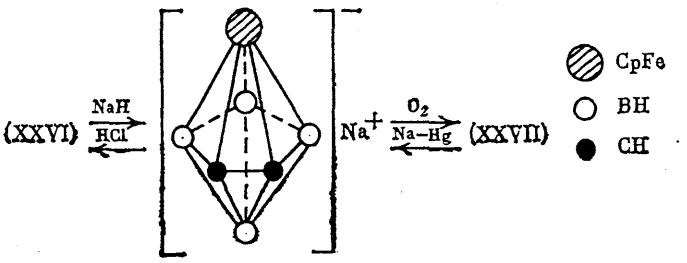
(XXV)

Irradiation of complex (XXV) with ultraviolet light leads to an almost quantitative yield of a mixture of the ferracarbaboranes (XXVI) and (XXVII):



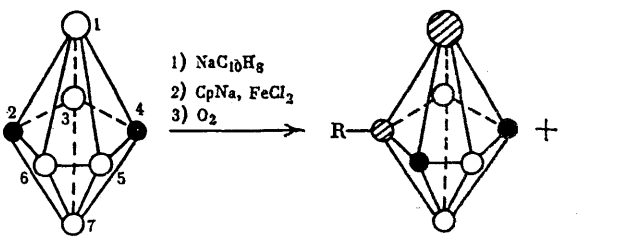
(XXVI) (XXVII)

Complex (XXVI) is diamagnetic (the Fe atom has the d^6 configuration) and contains 16 skeletal electrons, which determine its *closo*-structure, while complex (XXVII) is paramagnetic (μ_{eff} = 2.1 μ_B d^5 configuration of the Fe atom) and contains 15 skeletal electrons, i.e. is electron deficient. The reversible interconversion of the ferracarbaboranes (XXVI) and (XXVII) proceeds via the anionic complex (XXVIII) in accordance with the following mechanism:



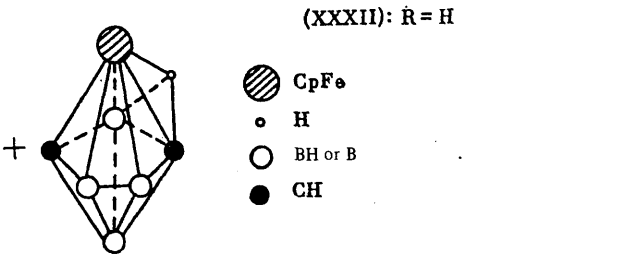
(XXVIII)

The substitution of the boron atom in the 1-position by the CpFe fragment and the formation of a mixture of the ferracarbaboranes (XXX)–(XXXIII) in a low yield via the mechanism



(XXIX)

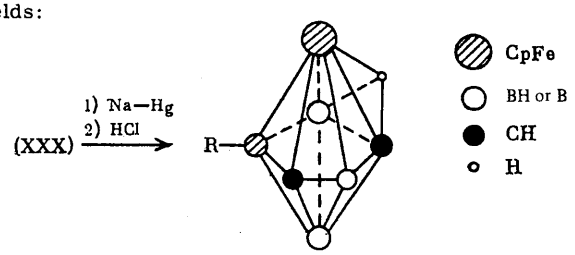
(XXX): R = 2′-(2′,4′-$C_2B_5H_6$)
(XXXI): R = $C_{10}H_7$
(XXXII): R = H



(XXXIII)

have been observed in the reaction of the *closo*-carbaborane 2,4-$C_2B_5H_7$ (XXIX) with sodionaphthalene and then with CpNa and $FeCl_2$.[29] Complexes (XXX)–(XXXII) are para-

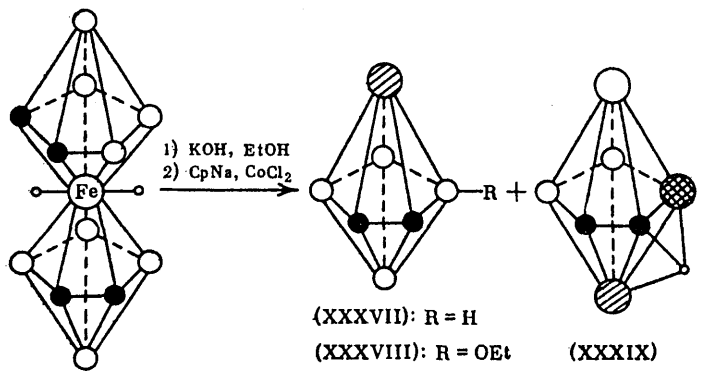
magnetic, while complex (XXXIII) is diamagnetic. Like the ferracarbaborane (XXVII), complex (XXX) is reduced by sodium amalgam to a diamagnetic derivative, whose protonation results in the formation of the diamagnetic complexes (XXXIV) and (XXXV) in overall quantitative yields:



(XXXIV): R = 2^1-(2^1,4^1-$C_2B_5H_6$)

(XXXV): R = H

Yet another method of synthesis of 7-vertex *closo*-ferracarbaboranes consists in the rearrangement of the *commo*-ferracarbaborane (XXXVI) on alkaline degradation and subsequent interaction with CpNa and $CoCl_2$.[30] The formation of a complex mixture of products, the main components of which were the ferracarbaboranes (XXXVII) and (XXXVIII), was then observed:



(XXXVII): R = H

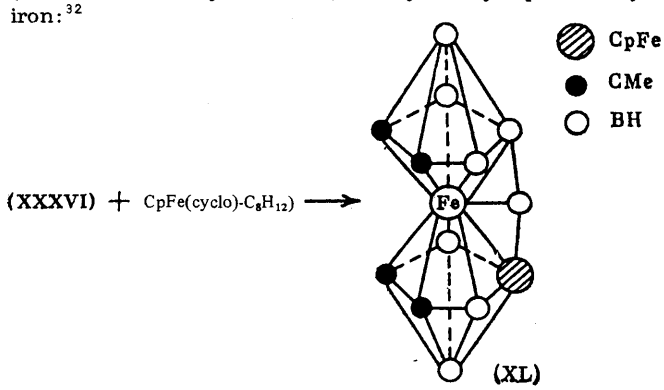
(XXXVIII): R = OEt (XXXIX)

(XXXVI)

CpFe CpCo CMe B or BH H

The ferracarbaboranes (XXXVII) and (XXXVIII) are paramagnetic, while the ferracobaltacarbaborane (XXXIX) is diamagnetic. Its structure was established by X-ray diffraction, from which it follows that it has the *closo*-structure. The Fe—Co distance is 2.56 Å.[31]

Only one example of an 8-vertex *closo*-ferracarbaborane with the CpFe fragment in the polyhedral skeleton is so far known. It was obtained from the *commo*-ferracarbaborane (XXXVI) and η^4-cyclo-octa-1,5-dienyl-η^5-cyclopentadienyl-iron:[32]

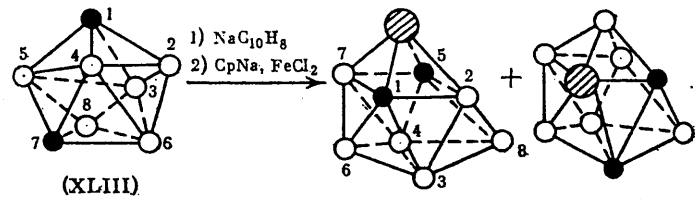


(XL)

Complex (XI) consists, as it were, of two polyhedra joined together, namely the upper 7-vertex and lower 8-vertex polyhedra respectively. According to the TCSEP, the upper polyhedron lacks one skeletal electron and the lower polyhedron lacks two such electrons. Such a deficiency of skeletal electrons leads to a marked distortion of the geometry of the ferracarbaborane molecule, expressed by the "sharing" of the BH fragment by the upper and lower clusters. If two electrons could be in some way introduced into the skeleton of complex (XL), then it is believed[32] that it would acquire the normal geometry. The upper polyhedron would still remain a pentagonal bipyramid, while the lower polyhedron would be converted into a dodecahedron. It has been suggested[32] that the metallacarbaboranes whose polyhedral skeleton lacks two and more electrons be called hyperelectron-deficient.

3. Complexes Having the Structure of (9—11)-Vertex Polyhedra

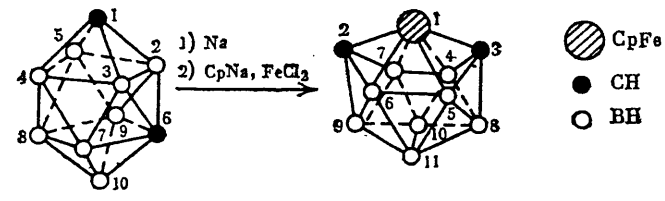
Two isomeric 9-vertex paramagnetic ferracarbaboranes (XLI) and (XLII), having the *closo*-structure and being represented by a three-cap trigonal prism, have been obtained by the polyhedral expansion of the *closo*-carbaborane 1,7-$C_2B_6H_8$ (XLIII):[33]



(XLIII) (XLI) (XLII)

CpFe CH BH

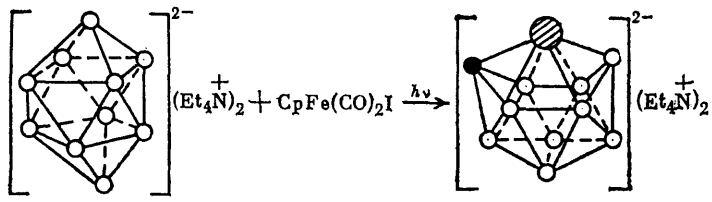
The polyhedral expansion of the *closo*-carbaborane 1,6-$C_2B_8H_{10}$ (XLIV) led to a satisfactory yield of the 11-vertex paramagnetic *closo*-ferracarbaborane (XLV):[33]



(XLIV) (XLV)

The ferracarbaboranes (XLI), (XLII), and (XLV) are readily reduced to the diamagnetic Fe(II)-forms by sodium amalgam. The dipole moments μ_{eff} have been measured[34] for the paramagnetic complexes (XLI), (XLII), and (XLV). Analysis of the EPR and ^{13}C and ^{11}B NMR spectra showed that the unpaired electron is localised not only at the Fe atom but also at the B and C atoms coordinating the metal atoms. The photochemical reaction of $(Et_4\overset{+}{N})_2B_{10}H_{10}^{2-}$ (XLVI) with $CpFe(CO)_2$ entails the polyhedral expansion of the borane skeleton with formation of the paramagnetic complex (XLVII), which is isostructural with complex

(XLV):[35]

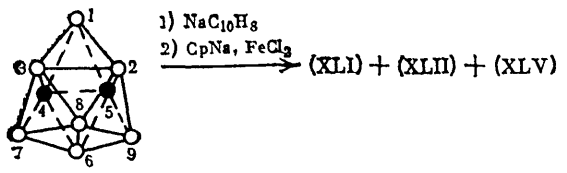


(XLVI) (XLVII)

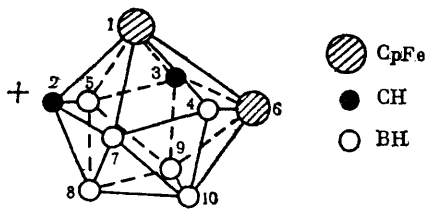
CpFe ● CH ○ BH

Complex (XLVII) has also been obtained on refluxing a solution of $K_2^+B_{10}H_{10}^{2-}$ and $CpFe(CO)_2I$ in 1,2-dimethoxyethane.

Structural distortions of the polyhedral skeleton in the electron-deficient dinuclear ferracarbaboranes is illustrated in relation to complex (XLVIII), which has been obtained, together with the ferracarbaboranes (XLI), (XLII) and (XLV), on polyhedral expansion of the *closo*-carbaborane $4,5\text{-}C_2B_7H_9$ (XLIX):[36]



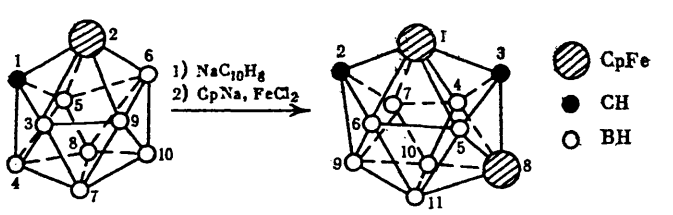
(XLIX)



(XLVIII)

The ferracarbaborane (XLVIII) is a paramagnetic substance (μ_{eff} = 3.05 μ_B), but it is converted in the course of a week at 20 °C into a diamagnetic isomeric form, which can be explained by the reorientation, over a period of time, of the spins of the unpaired electrons from parallel to antiparallel.[36] The structure of complex (XLVIII) was established by X-ray diffraction, from which it follows that it is a distorted two-cap Archimedes antiprism. It has one "superfluous" bond between the Fe atom at the vertex and the Fe atom in the nearest tetragonal belt. The Fe–Fe distance is 2.57 Å. The distortion of the geometry of this complex has also been discussed by Nishimura.[37]

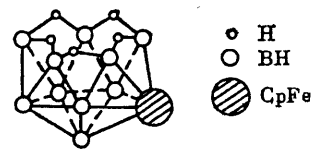
The polyhedral expansion of the *closo*-cobaltacarbaborane (L) results in the formation of the 11-vertex *closo*-ferracobaltacarbaborane (LI):[38]



(L) (LI)

Complex (LI) is a paramagnetic substance (μ_{eff} = 1.85 μ_B), whose *closo*-structure has been demonstrated by X-ray diffraction.[39]

The ferraborane (LII) having the structure of the 11-vertex *nido*-polyhedron, obtained from $B_5H_8^-Na^+$, $FeCl_2$ and CpNa in a mixture with other ferraboranes, is an icosahedron from which one vertex has been removed:[20]

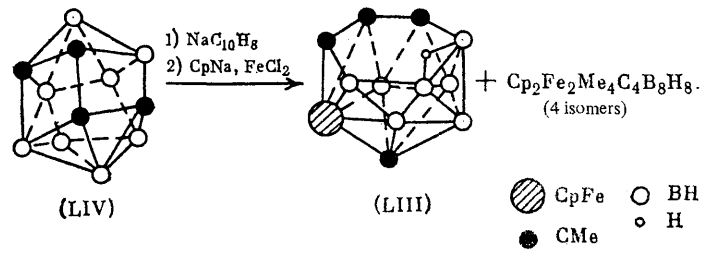


(LII)

Complex (LII) is diamagnetic, contains 26 skeletal electrons, and, in conformity with the TCSEP, has the *nido*-structure.

V. COMPOUNDS HAVING 12-VERTEX POLYHEDRAL STRUCTURES

The 12-vertex *closo*-polyhedra have the icosahedral structure, while the *nido*-polyhedra have the structure of an "open" icosahedron with an open hexagonal face. The *nido*-ferracarbaborane (LIII), having 12 vertices, has been obtained, together with other products, on polyhedral expansion of the four-carbon *nido*-carbaborane $C_4Me_4B_8H_8$ (LIV):[40]

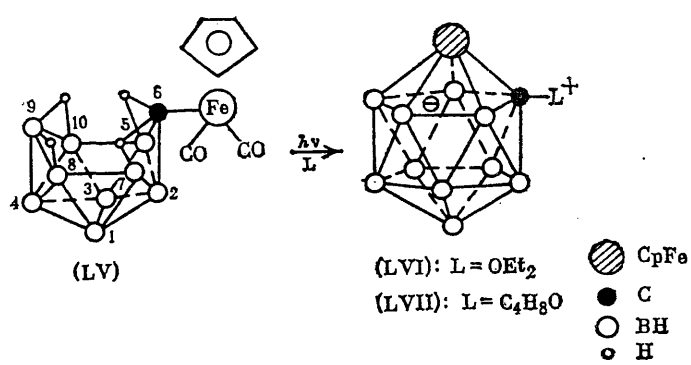


(LIV) (LIII)

CpFe ○ BH ○ H ● CMe

The structure of complex (LIII) has been established by X-ray diffraction. The distances between the Fe atom and the C and B atoms to which it is coordinated are in the range 2.051–2.168 Å. Complex (LIII) is diamagnetic and contains 28 skeletal electrons, which give rise to its *nido*-structure in conformity with the TCSEP. The structures of the remaining products of this reaction will be discussed below.

Irradiation of the σ-complex $B_{10}H_{13}$–σ-$Fe(CO)_2Cp$ (LV) with ultraviolet light in solution in ether or THF results in the "closure" of the polyhedral skeleton and the formation of a one-carbon ferracarbaborane (LVI) and (LXVII):[41]



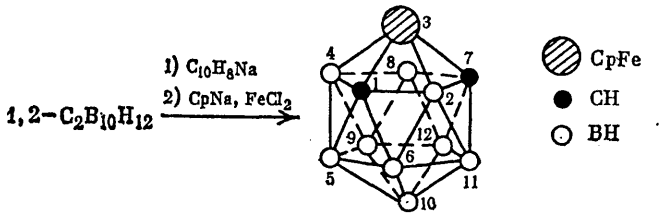
(LV)

(LVI): L = OEt_2
(LVII): L = C_4H_8O

CpFe ● C ○ BH ○ H

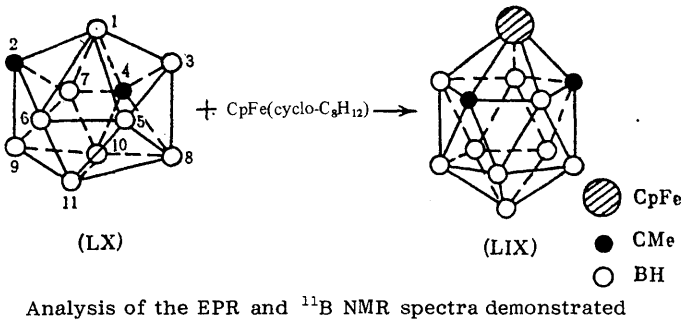
Complexes (LVI) and (LVII) each contain 25 skeletal electrons, i.e. one less than required by the TCSEP for the icosahedral *closo*-structure. Both complexes are isoelectronic with the ferrocenium cation. The *closo*-structure of complex (LVI) has been confirmed by X-ray diffraction.

The paramagnetic ferracarbaborane (LVIII), containing C atoms in the *meta*-positions relative to one another, has been obtained in a low yield together with other products on polyhedral expansion of *o*-carbaborane:[42]



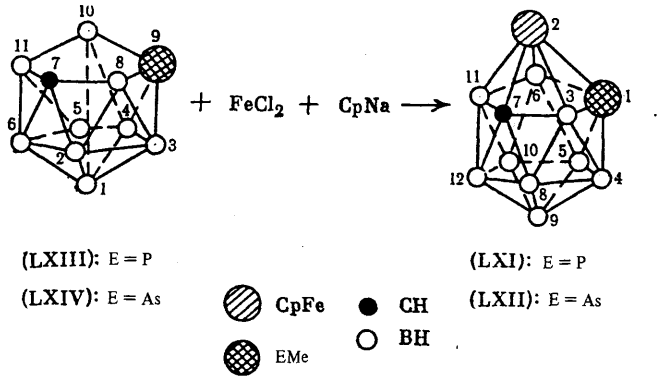
(LVIII)

Another method of synthesis of the 1,7-dimethylferracarbaborane (LIX), an analogue of complex (LVIII), based on the polyhedral expansion of the *closo*-carbaborane 2,3-Me_2-2,3-$C_2B_9H_9$ (LX) in its reaction with η^4-cyclo-octa-1,5-dienyl-η^5-cyclopentadienyliron, was discovered later:[43]



(LX) (LIX)

Analysis of the EPR and ^{11}B NMR spectra demonstrated the delocalisation of the spin density of the unpaired electron over the C(1), C(7), B(2), B(4), and B(8) atoms. The dipole moments μ_{eff} of complex (LVIII) have been measured.[44] The icosahedral ferraphosphacarbaborane (LXI)[35] and ferra-arsacarbaborane (LXII)[45] have been obtained by the reaction of the *nido*-phosphacarbaborane (LXIII) in THF and the *nido*-arsacarbaborane (LXIV) in Et_3N respectively with $FeCl_3$ and CpNa:



(LXIII): E = P
(LXIV): E = As
(LXI): E = P
(LXII): E = As

Both complexes, (LXI) and (LXII), are diamagnetic and each contains 26 skeletal electrons, which give rise to their *closo*-structures.

The polyhedral expansion of the 11-vertex *closo*-ferracarbaborane (XLV) results in the formation of the 12-vertex paramagnetic complex (LXV) containing two CpFe fragments:[46]

$$(XLV) \xrightarrow[2)\ [CpFeC_8H_8]^+]{1)\ NaC_{10}H_8} Cp_2Fe_2C_2B_8H_{10}$$

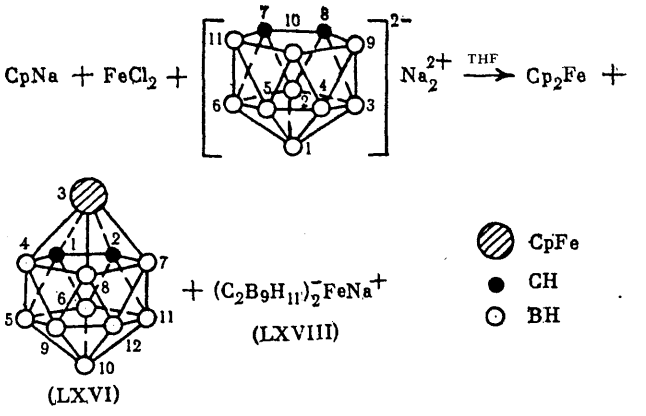
(LXV)

The structure of complex (LXV) has not been established. On standing for several days, it decomposes with reformation of the initial complex (XLV).

VI. THE MOST IMPORTANT 12-VERTEX *CLOSO*-FERRACARBABORANE—η^5-CYCLOPENTADIENYL-η^5-(3)-1,2-DICARBOLLYLIRON

1. Synthesis and Physical Properties

The ferracarbaborane investigated in greatest detail among the icosahedral complexes is η^5-cyclopentadienyl-η^5-(3)-1,2-dicarbollyliron (LXVI), which was first obtained in a moderate yield by the interaction of CpNa, $FeCl_2$, and 7,8-$C_2B_9H_{11}Na_2$ (LXVII) in THF:[47,48]



(LXVIII)

(LXVI)

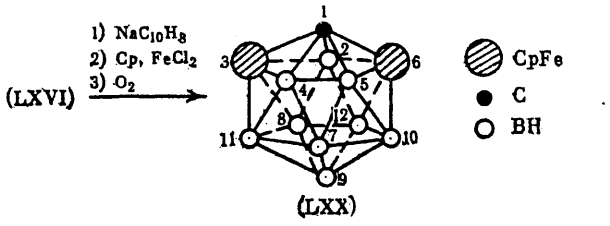
Ferrocene and the *commo*-ferracarbaborane (LXIII) is then formed together with compound (LXVI). A more convenient method of synthesis of compound (LXVI), based on the reaction of *o*-carbaborane, cyclopentadiene, and $FeCl_2$ with methanolic alkali and subsequent treatment of the reaction mixture with H_2O_2, has been proposed.[49] Compound (LXVI) is a purple paramagnetic substance and constitutes an electronic analogue of the ferrocenium cation, i.e. its Fe atom has the d^5 configuration. The structure of compound (LXVI) has been established.[50] The complex is a regular icosahedron in which the Fe atom is equidistant from the C and B atoms coordinating it, its distance from these atoms amounting to ~2.07 Å. It has 25 skeletal electrons, i.e. one less than is necessary for the 12-vertex *closo*-polyhedron—the icosahedron.

When compound (LXVI) is treated with sodium amalgam in acetonitrile, the diamagnetic monoanion [3-Cp-3,1,2-$FeC_2B_9H_{11}]^-$ (LXIX), isoelectronic with ferrocene (the Fe atom has the d^6 configuration), is formed.[47,48] Complex (LXIX) contains 26 skeletal electrons, which fully satisfies the TCSEP requirements for icosahedral *closo*-structures. The study of the kinetics of the oxidation of the Fe(III)-form of compound (LXVI) to the Fe(II)-form (LXIX) showed that the oxidation mechanism is analogous to that of the oxidation of ferrocene to the ferrocenium cation.[51] The EPR spectra of complex (LXVI) revealed the presence of an unpaired electron.[52] Analysis of the EPR and ^{11}B NMR spectra demonstrated the localisation of the spin density in complex (LXVI) at the B and C

atoms coordinating the Fe atom.[34] The experimental value of μ_{eff} for complex (LXVI)[34,53] proved to be close to the calculated value.[54] The study of the Mössbauer spectra of this compound showed that its quadrupolar splitting parameters are close to the corresponding values for the biscyclopentadienyl complexes, although they are somewhat higher than the latter.[55,56] The cause of this consists in the higher density of *s* electrons at the Fe atom than in the ferrocene–ferrocenium derivatives, indicating a more effective removal of *d* electrons from the Fe atom in compound (LXVI) owing to their involvement in π bonding with the ligands. Quantum-chemical calculation for the Fe(II)-form (LXIX) by the MO method with adjustment for self-consistency with respect to the atomic charges and atomic configurations showed that the Fe–$C_2B_9H_{11}$ interaction involves mainly the ligand σ orbitals, while the Fe–C_5H_5 interaction involves the π orbitals of the Cp ring.[57] Calculation of the total atomic charges showed that the maximum negative charge is present on the B(8) atom located symmetrically in the open C_2B_3 face of the dicarbollyl ligand, while the maximum positive charge is localised at the B(10) atom most remote from the Fe atom. In addition, it has been shown that the HOMO of complex (LXIX) has appreciable d_{z^2} character, as in ferrocene.

2. The Chemical Properties of η^5-Cyclopentadienyl-η^5-(3)-1,2-Dicarbolyliron and Its Derivatives

The chemical properties and reactivity of compound (LXVI) and its derivatives have been investigated in greatest detail compared with other ferracarbaboranes. On polyhedral expansion of the Fe(III)-form (LXVI), the dinuclear complex (LXX) was obtained in a very small amount together with 13-vertex ferracarbaboranes. The regular icosahedral structure was attributed to compound (LXX) on the basis of ^{11}B NMR spectra:[46]



(LXX)

Although both Fe atoms in complex (LXX) have the d^5 configuration, the complex is diamagnetic, which can be accounted for by the antiparallel orientation of the unpaired electron spins at the metal atoms. Complex (LXX) contains 24 skeletal electrons—two less than is required by the TCSEP for icosahedral *closo*-structures, which is characteristic of ferracarbaboranes containing several Fe atoms. The formation of complex (LXX) can be explained by the presence in the reaction medium of traces of NaOH under the influence of which complex (LXVI) undergoes initially alkaline degradation with removal of the B(6) atom from the polyhedral skeleton and its subsequent replacement by the CpFe fragment.

A detailed investigation of the chemical properties of compound (LXVI) and its derivatives has been undertaken by the authors of this review[58-68] and is considered below.

(a) Reactions of compound (LXVI) with electrophiles. In order to study the distribution of the relative electron density, the bromination of compound (LXVI)§ and of its bromo-derivatives was investigated.[58] It was shown that complex (LXVI) is brominated stepwise at the B atoms of the dicarbollyl ligand. In the absence of a catalyst, the first bromine atom enters the 8-position, while further bromination takes place only in the presence of $AlCl_3$ in the 9- and 12-positions:

$$(\text{LXVI}) \xrightarrow{Br_2} \underset{(\text{LXXI})}{CpFeC_2H_2B_9H_8\text{-}8\text{-}Br} \xrightarrow[AlCl_3]{1)\ Br_2} \underset{(\text{LXXII})}{CpFeC_2H_2B_9H_7\text{-}8,9\text{-}Br_2}$$

$$\xrightarrow[AlCl_3]{2)\ Br_2} \underset{(\text{LXXIII})}{CpFeC_2H_2B_9H_6\text{-}8,9,12\text{-}Br_3} .$$

The structure of the bromo-derivatives (LXXI)–(LXXIII) was demonstrated by ^{11}B NMR and also by specific synthesis from the bromo-derivatives (LXXIV) and (LXXV), where the bromine atoms are known to be in the 9- and 9- and 12-positions:

$$\underset{(\text{LXXIV})}{CpFeC_2H_2B_9H_8\text{-}9\text{-}Br} \xrightarrow{Br_2} (\text{LXXII}) ;$$

$$\underset{(\text{LXXV})}{CpFeC_2H_2B_9H_7\text{-}9,12\text{-}Br_2} \xrightarrow[AlCl_3]{Br_2} (\text{LXXIII}) .$$

The bromination of the 4-bromo-derivative (LXXVI) leads to the 4,8-dibromo-derivative (LXXVII):

$$\underset{(\text{LXXVI})}{CpFeC_2H_2B_9H_8\text{-}4\text{-}Br} \xrightarrow{Br_2} \underset{(\text{LXXVII})}{CpFeC_2H_2B_9H_7\text{-}4,8\text{-}Br_2} .$$

The presence of bromine atoms in compound (LXVI) makes it less reactive in electrophilic substitution reactions. It follows from the bromination data that the distribution of relative electron density in the dicarbollyl ligand of compound (LXVI) is as follows: B(8) > B(9), B(12) > B(4), B(5), B(6), B(10), B(11), C(1), C(2).

When compound (LXVI) is treated with thallium(III) trifluoroacetate in trifluoroacetic acid, the B–H bond is oxidised and the 8-trifluoroacetoxy-derivative (LXVIII) is formed:[59]

$$(\text{LXVI}) \xrightarrow[CF_3COOH]{Tl(OCOCF_3)_3} \underset{(\text{LXXVIII})}{CpFeC_2H_2B_9H_8\text{-}8\text{-}OCOCF_3} .$$

The structure of complex (LXXVIII) has been established by X-ray diffraction. Its methanolysis affords the 8-hydroxy-derivative (LXXIX):

$$(\text{LXXVIII}) \xrightarrow{H^+,\ MeOH} \underset{(\text{LXXIX})}{CpFeC_2H_2B_9H_8\text{-}8\text{-}OH} .$$

The oxidation of the B–H bond when compound (LXVI) is treated with $Tl(OCOCF_3)_3$ indicates an enhanced hydride mobility of the H atom at the B(8) atom.

Mercuration of compound (LXVI) by mercury(II) trifluoroacetate in the CF_3COOH–CH_2Cl_2 mixture yielded the 9-chloromercuri-derivative (LXXX):[60]

$$(\text{LXVI}) \xrightarrow[2)\ NaCl]{1)\ Hg(OCOCF_3)_2} \underset{(\text{LXXX})}{CpFeC_2H_2B_9H_8\text{-}9\text{-}HgCl} .$$

§ $CpFeC_2H_2B_9H_9$ and $CpFeHCB_9H_9CH$ are two ways of writing the formula of compound (LXVI) (d^5 configuration of the Fe atom).

When it is treated with bromine, the 9-bromo-derivative (LXXIV) is produced.

(b) Derivatives of compound (LXVI) substituted at a C atom of the dicarbollyl ligand. The synthesis of derivatives of compound (LXVI) substituted at a C atom of the dicarbollyl ligand and their subsequent reactions have been described.[61–63] These derivatives have been synthesised from the corresponding 1-substituted o-carbaboranes, cyclopentadiene, and $FeCl_2$ in methanolic alkali:

$$o\text{-}HCB_{10}H_{10}C\text{-}R + C_5H_6 + FeCl_2 \xrightarrow[2)\ H_2O_2]{1)\ KOH,\ MeOH} CpFeHCB_9H_9C\text{-}R;$$

$$R=CH_2OH,\ CH=CH_2,\ C(CH_3)=CH_2,\ C\equiv CH,\ CH_2OH.$$

In order to synthesise the acid (R = COOH), 7-COOH-7,8-$C_2B_9H_{11}K$ was used as the starting material. The proposed methods of synthesis of derivatives of compound (LXVI) with a functional group at a C atom of the dicarbollyl ligand make them readily available, which made it possible to investigate various reactions of 1-substituted ferracarbaboranes. Together with the usual properties of the carbaborane and cobaltacarbaboranes analogues, these reactions manifest specific features due to the presence of the ferracarbaborane nucleus. Various reactions of the hydroxymethyl derivative $CpFeHCB_9H_9CCH_2OH$, namely acylation, oxidation to the aldehyde, and replacement of the OH group by OR or Cl under the conditions of acid catalysis, have been investigated.[61] The solvolysis of the chloromethyl derivative $CpFeHCB_9H_9CCH_2Cl$, which demonstrated the ability of the $CpFe^{III}HCB_9H_9C$ group to stabilise as the intermediate species the carbonium ion centre linked to it, has been investigated. The synthesis of a ketone, secondary carbinols, and the diethyl acetal of an aldehyde derived from compound (LXVI) has been described. The ability of compound (LXVI) to form hydrogen bonds with basic solvents involving the C–H bonds of both ligands has been demonstrated by infrared spectroscopy[64] and the acid character of the C–H bonds of the dicarbollyl ligand in compound (LXVI) has been confirmed,[61] since they are metallated on treatment with butyl-lithium in ether. The ionisation constants of the acids $CpFeHCB_9H_9CCOOH$ in 50% ethanol (pK_a = 3.49) and $CpFeHCB_9H_9CCH_2COOH$ in 80% methylcellosolve (pK_a = 5.70) have been measured. The induction constant for the $CpFe^{III}HCB_9H_9C$ group (σ_i = 0.31) was calculated from the latter pK_a by Charton's method, from which it follows that the ferra(III)carbaboranyl group exhibits an appreciable electron-accepting effect.[61] The majority of the reactions of the 1-substituted derivatives of compound (LXVI) described can be used as preparative methods for their synthesis. The conversion of the Fe(III)-form into the Fe(II)-form of the 1-substituted derivatives of compound (LXVI) has been suggested[63] and consists in reduction by $NaBH_4$ in ethanol:

$$CpFeHCB_9H_9C\text{—}R \xrightarrow[2)\ CtX]{1)\ NaBH_4} [CpFe^{II}HCB_9H_9C\text{—}R]\,K_T;$$

$$R=CH_2OH,\ CH(OH)CH_3,\ CH=CH_2,\ C(CH_3)=CH_2,\ C\equiv CH;$$

$$Ct=Cs,\ Me_4N;$$

$$X=Cl,\ Br,\ I,\ NO_3.$$

The derivatives of the Fe(II)-form of compound (LXVI) are electronic analogues of ferrocene.

(c) Carbonium ions stabilised by the ferra(II)carbaboranyl group. The authors of the present review investigated the carbonium ion centre linked to the $CpFe^{II}HCB_9H_9C^-$ group[63,65] and found that the group stabilises the carbonium ion linked to it much more effectively than the ferrocenyl group. Since the positive charge on the carbon atom is balanced by the negative charge on the ferra(II)carbaboranyl group, the cation-containing molecule is electrically neutral and therefore exists in the form of zwitter-ions. Such zwitter-ions have been called[63,65] carbenium zwitter-ions. The protonation of the carbinols (LXXXI), (LXXXII), and (LXXXIII) by inorganic acids gave high yields of the primary carbenium zwitter-ion (LXXXIV) and the corresponding secondary zwitter-ions (LXXXV) and (LXXXVI) respectively:

$$[CpFe^{II}HCB_9H_9C\text{—}\underset{\displaystyle OH}{\underset{|}{C}}HR]^- \xrightarrow{H^+} CpFe^{II}HCB_9H_9C^-\text{—}C^+\!\!<^{R}_{H}.$$

(LXXXI): R=H
(LXXXII): R=Me
(LXXXIII): R=Ph

(LXXXIV): R=H
(LXXXV): R=Me
(LXXXVI): R=Ph

A convenient method of synthesis of the secondary and tertiary carbenium zwitter-ions, (LXXXV) and (LXXXVII) respectively, consists in the protonation of the corresponding olefins (LXXXVIII) and (LXXXIX):

$$[CpFe^{II}HCB_9H_9C\text{—}\underset{\displaystyle R}{\underset{|}{C}}=CH_2]^- \xrightarrow{H^+} CpFeHCB_9H_9\bar{C}\text{—}\overset{+}{C}\!\!<^{Me}_{R}.$$

(LXXXVIII): R=H
(LXXXIX): R=Me

(LXXXV): R=H
(LXXXVII): R=Me

The carbenium zwitter-ions (LXXXIV) and (LXXXVII) have been isolated in an individual form. They are diamagnetic, stable in air, and capable of being chromatographed on silica gel in moderately polar eluents. The relative stabilities on prolonged storage in air of the carbenium zwitter-ions increase in the sequence $\overset{+}{C}H_2 \ll \overset{+}{C}HMe \ll \overset{+}{C}HPh \cong \overset{+}{C}Me_2$. Conclusions about the structure and the probable mechanism of the stabilisation of the carbonium ion centre in such systems were reached from the X-ray diffraction analysis of the phenylcarbenium zwitter-ion (LXXXVI). The carbonium ion centre is stabilised by the strong iron-carbon interaction [the Fe–C^+ distance is 2.23 Å and the angle between the C(carbaborane)–C^+ bond and the C_2B_3 plane is 47°].

Furthermore, the C^+ atom has the sp^2-configuration and the C(carbaborane)–C^+ distance is 1.38 Å, from which follows the partial double bond character of the linkage between the C^+ atom and the carbon atom of the polyhedron. Thus the carbonium ion centre is stabilised in two ways—both by the electron-donating effect of the ligand with formation of a fulvene-like structure and with participation of the Fe atom.

Various reactions of the carbenium zwitter-ions have been investigated.[63,65] Despite their lower reactivity compared with organic carbonium ions and ferrocenyl carbonium ions, they combine with bases via the carbonium ion centre. The reactions of the primary and secondary zwitter-ions, (LXXIV) and (LXXXV) respectively, with electrically neutral Lewis bases lead to the formation of

adducts in the form of inner salts of type (XC):

$$(LXXXIV) \text{ or } (LXXXV) \xrightarrow{L} CpFe^{II}HCB_9H_9C\text{-}\underset{R}{\underset{|}{CH}}\text{-}\overset{+}{L}\ ;$$

(XC)

R=H or Me, L=PPh_3, NC_5H_5, SMe_2, N≡C—Me, N≡C—CH=CH_2.

The acid hydrolysis of the acetonitrilium inner salt (XC, R = H, L = N≡CMe) with simultaneous oxidation by H_2O_2 leads to the formation of the *N*-substituted acetamide $CpFeHCB_9H_9CCH_2NHCOMe$. The reaction of the tertiary zwitter-ion (LXXXVII) with pyridine leads to the adduct (XCI) and the olefin (LXXXIX) as the deprotonation product.

$$(LXXXVII) \xrightarrow{C_5H_5N} CpFe^{II}HCB_9H_9\bar{C}—CMe_2—\overset{+}{N}C_5H_5 + (LXXXIX).$$

The primary and secondary zwitter-ions, (LXXXIV) and (LXXXV) respectively, react with organolithium compounds, combining with the organic residue via the carbonium ion centre with formation of products of type (XCII):

$$(LXXXIV) \text{ or } (LXXXV) \xrightarrow[2)\ H_2O_2]{1)\ R'Li} CpFeHCB_9H_9C—CH\begin{matrix}R\\R'\end{matrix};$$

(XCII)

R=H or Me; R'=Bu, Ph, Bu—C≡C, Ph—C≡C, 1,2-$C_2B_{10}H_9$-1.

The reaction of the primary and secondary zwitter-ions with nucleophilic anions takes place similarly, affording products of type (XCIII):

$$(LXXXIV) \text{ or } (LXXXV) \xrightarrow[2)\ H_2O_2]{1)\ Nu^-} CpFeHCB_9H_9C—CH\begin{matrix}R\\Nu\end{matrix};$$

(XCIII)

R=H or Me; Nu=CN, iso-BuO, iso-BuS, PhO, PhS, CH_2NO_2.

On the other hand, cyanide and thiophenoxide anions do not add to the tertiary zwitter-ion (LXXXVII) and only the deprotonation of one of the methyl groups takes place with formation of the alkene (LXXXIX), which indicates an increased acidity of the H atoms of the methyl group in the tertiary and zwitter-ion. The primary and tertiary zwitter-ions, (LXXXIV) and (LXXXVII) respectively, abstract a hydride ion from $NaBH_4$, which leads to the quantitative formation of the methyl derivative (XCIV) and the isopropenyl derivative (XCV) respectively of complex (LXVI):

$$(LXXXIV) \text{ or } (LXXXVII) \xrightarrow[2)\ H_2O_2]{1)\ NaBH_4} CpFeHCB_9H_9C—CHR_2.$$

(XCIV): R=H
(XCV): R=Me

In contrast to this, when the primary zwitter-ion (LXXXIV) is treated with H_2AlCl in ether, the diethyloxonium inner salt (XCVI), which is extremely resistant to hydrolysis, is formed:

$$(LXXXIV) \xrightarrow{H_2AlCl,\ Et_2O} CpFe^{II}HCB_9H_9\bar{C}CH_2\overset{+}{O}Et_2.$$

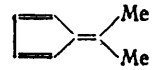
(XCVI)

In the absence of H_2AlCl, the cation (LXXXIV) does not react with ether even after prolonged heating. The more basic dimethoxyethane adds to the cationic centre of the primary zwitter-ion, giving rise to the inner salt (XCVII):

$$(LXXXIV) + MeOCH_2CH_2OMe \rightarrow CpFe^{II}HCB_9H_9\bar{C}\text{-}CH_2\overset{+}{\underset{|}{\underset{Me}{O}}}\text{-}CH_2CH_2OMe.$$

(XCVII)

The stabilisation of the carbonium ion centre linked to the $HCB_9H_9CHFe^{II}C_5H_4$ group has been investigated.[66] The isopropenyl derivative (XCVIII), containing a substituent in the Cp ring, has been obtained in order to synthesise this carbonium ion system from 6,6-dimethylfulvene, the 7,8-dicarbollide anion (LXVII), and $FeCl_2$ in the liquid ammonia–THF mixture:



$$+ (LXVII) + FeCl_2 \xrightarrow[2)\ H_2O_2]{1)\ NaNH_2} \rightarrow CH_2=\underset{|}{\underset{Me}{C}}—C_5H_4FeHCB_9H_9CH.$$

(XCVIII)

Complex (XCVIII) was reduced to the diamagnetic form (XCIX) with sodium tetrahydroborate:

$$(XCVIII) \xrightarrow[2)\ Me_4NBr]{1)\ NaBH_4} Me_4N[CH_2=\underset{|}{\underset{Me}{C}}—C_5H_4FeHCB_9H_9CH].$$

(XCIX)

The protonation of the alkene (XCIX) leads to the formation of a carbenium zwitter-ion (C), which was not isolated in an individual state owing to its high reactivity:

$$(XCIX) \xrightarrow{H^+} \{Me_2\overset{+}{C}C_5H_4Fe^{II}HCB_9H_9\bar{C}H\}.$$

(C)

In solution the cation (C) and the cationic component of (C) undergo a series of reactions. If the protonation is carried out in benzene, only the dimeric product (CI), which is a result of the addition of the cationic component of (C) to the double bond of the alkene (XCIX), is obtained:

$$(XCIX) \xrightarrow{H^+} \{(C)\} \xrightarrow[-H^+]{(XCIX),\ O_2} \rightarrow HCB_9H_9CHFeC_5H_4—CMe_2—CH=\underset{|}{\underset{Me}{C}}—C_5H_4FeHCB_9H_9CH.$$

(CI)

If its protonation is carried out in ether or dimethyl sulphide, then the inner salts (CII) and (CIII) are obtained together with the dimeric complex (CI):

$$(XCIX) \xrightarrow{H^+,L} L^+—CMe_2—C_5H_4Fe^{II}HCB_9H_9\bar{C}H + (CI).$$

(CII): L=OEt_2
(CIII): L=SMe_2

In the case of dimethyl sulphide, an appreciable amount of the inner salt having the dimeric structure (CIV) is formed in addition to complexes (CIII) and (CI):

$$HCB_9H_9CHFeC_5H_4—CMe_2—\underset{|}{\underset{{}^+SMe_2}{\overset{Me}{C}}}—C_5H_4Fe^{II}HCB_9H_9\bar{C}H.$$

(CIV)

It follows from these data that the carbonium ion centre is stabilised less effectively by the $HCB_9H_9CHFe^{II}C_5H_4$ group than by the $CpFe^{II}HCB_9H_9C$ group.

The greater stabilising capacity of the $CpFe^{II}HCB_9H_9\bar{C}$ group made it possible to obtain the stable vinyl cation (CV) and to isolate it for the first time in an individual state in the form of the zwitter-ion on protonation of the alkyne derivative (CVI):[66,68]

$$\underset{\text{(CVI)}}{[CpFe^{II}HCB_9H_9C{-}C{\equiv}CH]^-} \xrightarrow{H^+} \underset{\text{(CV)}}{CpFe^{II}HCB_9H_9\bar{C}{-}\overset{+}{C}{=}CH_2}.$$

The vinyl cation (CV) is diamagnetic and stable in air. it combines eith hydrogen halides via the vinyl cationic group to form tertiary carbenium zwitter-ions of type (CVII) in which the halogen atom is linked directly to the carbonium ion centre:

$$\text{(CV)} \xrightarrow{HX} CpFe^{II}HCB_9H_9\bar{C}{-}\overset{+}{C}\begin{matrix}Me\\X\end{matrix}.$$

(CVII): X=Cl, Br

When the vinyl cation (CV) is treated with nucleophiles, for example $NaBH_4$ or MeLi, only the deprotonation of the vinyl cationic group takes place with formation of the alkyne (CVI), while the products of the addition to the cationic centre, namely the alkenes (LXXXVIII) or (LXXXIX), are obtained in extremely small amounts. These data indicate the appreciable acidity of the hydrogen atoms in the vinyl cationic group.

The allyl cation system, stabilised by the $CpFe^{II}HCB_9H_9\bar{C}$ group, has also been investigated.[67] When the aldehyde (CVIII) is treated with β-styrylmagnesium bromide, the phenylallyl cation (CIX) is formed in the form of the zwitter-ion:

$$\underset{\text{(CVIII)}}{CpFeHCB_9H_9CCHO} \xrightarrow{PhCH{=}CHMgBr} \longrightarrow CpFe^{II}HCB_9H_9\bar{C}{-}CH{=}\overset{+}{C}H{=}CHPh.$$

(CIX)

The monosubstituted allyl cation (CX) was obtained analogously for the first time from the aldehyde (CVIII) and vinylmagnesium bromide:

$$\text{(CVIII)} \xrightarrow[2)\ H^+]{1)\ CH{=}CH_2MgBr} CpFe^{II}HCB_9H_9\bar{C}{-}CH{=}\overset{+}{C}H{=}CH_2.$$

(CX)

Both allyl cations, (CIX) and (CX), exhibit the dual reactivity characteristic of allyl cationic systems. The addition of the hydride ion entails the formation of the corresponding allyl derivative (CXI) and the *n*-propenyl derivative (CXII) of compound (XIVI):

$$\text{(CIX) or (CX)} \xrightarrow{NaBH_4} [CpFe^{II}HCB_9H_9C{-}CH_2{-}CH{=}CHR]^- + [CpFe^{II}HCB_9H_9C{-}CH{=}CH{-}CH_2R]^-.$$

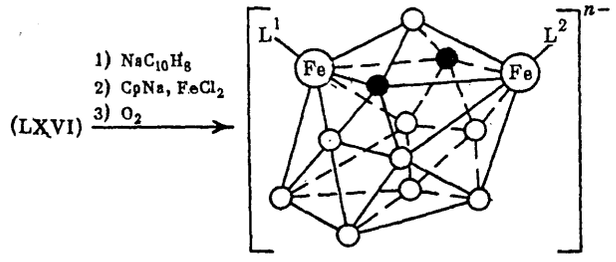
(CXII)

The stability of the carbonium ions stabilised by the ferra(II)carbaboranyl group have no analogy in the chemistry of both organic and organometallic carbonium ions. All the above features suggest that these are carbonium ions of a new type. Furthermore, the above reactions of the carbonium ions can be regarded as a convenient preparative method for the synthesis of various derivatives of compound (LXVI).

VII. COMPOUNDS HAVING 13- AND 14-VERTEX POLYHEDRAL STRUCTURES

1. 13-Vertex Polyhedral Ferracarbaboranes

The *nido*-ferracarbaboranes containing 13 vertices are so far unknown. The *closo*-polyhedron with 13 vertices is an icosahedron containing an additional vertex. Polyhedral expansion of compound (LXVI) yielded as the main product the diamagnetic dinuclear ferracarbaborane (CXIII).[60] The diemagnetic dinuclear complex (CXIV) was obtained in a much smaller amount at the same time:



(CXIII): $L^1 = L^2 = Cp$; $n = 0$

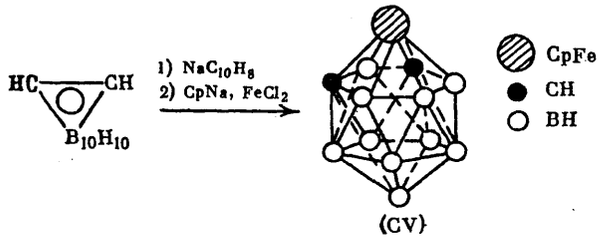
(CXIV): $L^1 = Cp$; $n = 1$

$L^2 = \eta^5$-1,2-$C_2B_9H_{11}$

● CH
○ BH

Preliminary X-ray diffraction analysis of complex (CXIII) demonstrated the absence of the Fe–Fe bond (3.2 Å). Structures have been attributed to complexes (CXIII) and (CXIV) on the basis of ^{11}B NMR spectra. Both Fe atoms in each complex have the d^5 configuration. Each complex has 26 skeletal electrons, i.e. according to the TCSEP they are electron-deficient. Their diamagnetism is due to the antiparallel orientation of the spins of the unpaired electrons, which arises in their conjugation with the π orbitals of the carbaborane ligand.

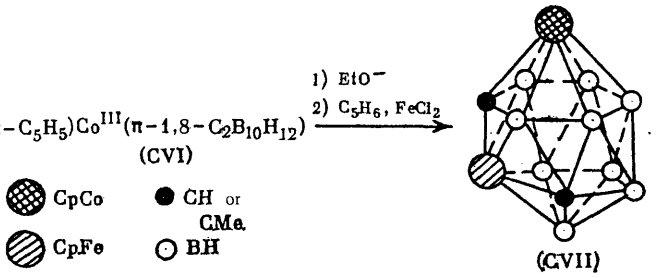
The main product of the polyhedral expansion reaction of o-carbaborane is complex (CV), which has the *closo*-structure:[42]



(CV)

The complex is paramagnetic and its reduction with $NaBH_4$ leads to a diamagnetic monoanion, which has been isolated in the form of the tetramethylammonium salt $[CpFe^{II}C_2B_{10}H_{12}]\cdot NMe_4$. The latter compound contains 28 skeletal electrons, which establish, according to the TCSEP, its *closo*-structure. The alkaline degradation of the 13-vertex *closo*-cobaltacarbaborane (CVI) entails the removal of the B(5) atom. The subsequent reaction with cyclopentadiene and $FeCl_2$ leads to the introduction of the CpFe fragment in the 5-position and the formation of the paramagnetic dinuclear *closo*-

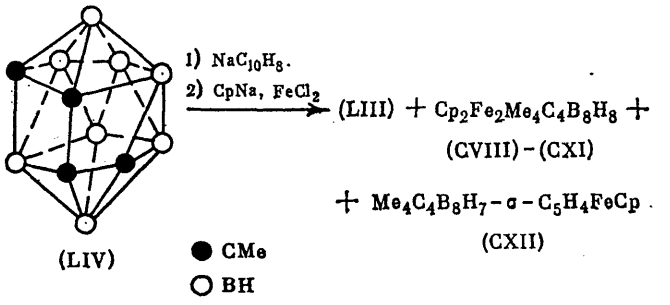
cobaltaferracarbaborane (CVII):[38,69]



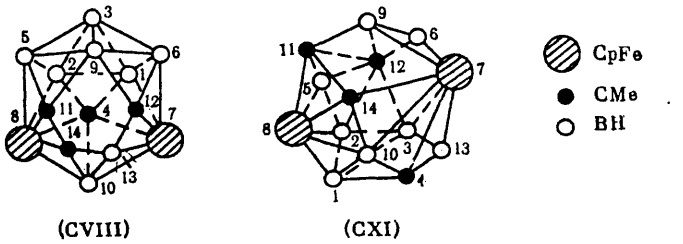
On treatment with $NaBH_4$, complex (CVII) is reduced to the diamagnetic monoanion [4-CpCo-5-CpFe^{II}-1,8-$C_2B_9H_{11}$]$^-$.

2. 14-Vertex Polyhedral Ferracarbaboranes

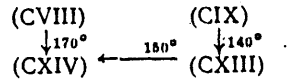
The 14-vertex *closo*-polyhedra can have structures of two types—those of a two-cap hexagonal antiprism and a six-cap cube. The 14-vertex *nido*-polyhedra can exist in several structures with a pentagonal or tetragonal open face. Polyhedral ferracarbaboranes with 14 vertices have been obtained comparatively recently and for this reason only a few examples are so far known. The polyhedral expansion of the four carbon *nido*-carbaborane (LIV) with subsequent addition of the CpFe fragment leads to the formation of a complex mixture of products containing 14-vertex dinuclear ferracarbaboranes:[40,70-73]



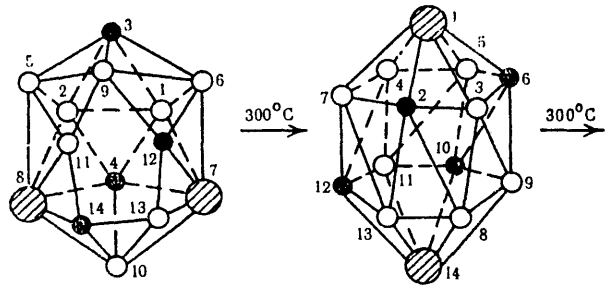
Compound (CXII) is a four-carbon carbaborane substituted at the B atom by the ferrocenyl group, which has been demonstrated by X-ray diffraction.[73] The dinuclear ferracarbaboranes (CVIII)–(CXI) have been obtained in the form of four diamagnetic isomers. The structures of complexes (CX) and (CXI) have not so far been established. Those of the isomers (CVIII) and (CIX) have been determined by X-ray diffraction.[70,71] Both complexes have the *nido*-structure with pentagonal B(9)–C(11)–C(14)–B(13)–B(12) [compound (CVIII)] and tetragonal Fe(7)–C(14)–C(11)–B(9) [compound (CIX)] openfaces. A mechanism has been proposed for the formation of several ferracarbaboranes of different structure from one four-carbon carbaborane, namely compound (LIV).[72]

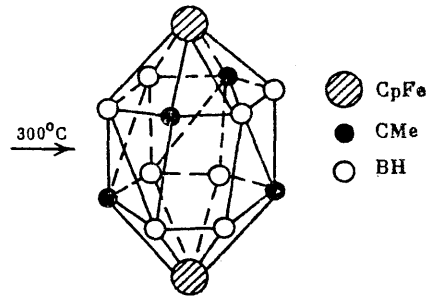


The ferracarbaboranes (CVIII) and (CIX) each contain 30 skeletal electrons and, according to the TCSEP, should have the *closo*-structure, which is not in fact observed. This can be accounted for by the presence of an appreciable potential barrier to the transition from the 14-vertex *nido*-systems to *closo*-systems.[71] On heating in nonane, the *nido*-ferracarbaboranes (CVIII) and (CIX) rearrange:



The structure of complex (CXIII) has not been established, while the diamagnetic complex (CXIV) has been characterised by X-ray diffraction.[71] The ferracarbaborane has the *nido*-structure with an open pentagonal face. On further heating, complex (CXIV) isomerises to the *closo*-polyhedron (CXV), which is also capable of undergoing thermal rearrangement to complex (CXVI):





Complexes (CXV) and (CXVI) are diamagnetic and each contains 30 skeletal electrons, which satisfies the TCSEP requirement for 14-vertex polyhedral *closo*-structures. The structures of complexes (CXV) and (CXVI) have been proposed on the basis of the analysis of their ^{11}B and ^{13}C NMR spectra.[71] Thus the isomeric ferracarbaboranes (CVIII), (CIX), and (CXIV) are a new class of metallacarbaboranes—metallacarbaboranes which have the *nido*-structure although the *closo*-structure is preferred. They have been called pseudo-*nido*-metallacarbaboranes.[71] The greater stability of the 14-vertex dinuclear ferracarbaboranes when the CpFe fragments in the polyhedral skeleton are separated from one another to the maximum extent as a consequence of the maximum overlap of the AO between individual vertices of the polyhedron has been justified theoretically.[74] It has been suggested that the pseudo-*nido*-ferracarbaboranes be regarded as precursors of the hitherto unknown polyhedral *closo*-metallacarbaboranes with 15 vertices.[71] Thus if a CpCo fragment coordinated to the atoms of the pentagonal open face could be introduced in some way into complexes (CVIII) and (CXIV),

one could obtain 15-vertex polyhedral *closo*-cobaltferracarbaborane of the type $CoFe_2C_4B_8$, satisfying the TCSEP requirements—32 skeletal electrons for 15 vertices.

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As can be seen from the data described above, the efforts of investigators of polyhedral ferracarbaboranes, ferraboranes, and ferraheteroboranes with the CpFe fragment in the skeleton have been largely concentrated on the development of methods for the synthesis of new polyhedral systems, while the chemistry of these interesting compounds remains, with a small exception, virtually uninvestigated. The study of the reaction of one of the ferracarbaboranes, namely η^5-cyclopentadienyl-η^5-(3)-1,2-dicarbollyliron, and of its derivatives yielded a number of interesting compounds with unusual properties. In view of the wide variety of ferracarbaborane systems, we are justified in assuming that these will be found to undergo new interesting chemical reactions.

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