

<b>Subject</b>	<b>Chemistry</b>
<b>Paper No and Title</b>	<b>11: Inorganic Chemistry –III (Metal <math>\pi</math>-Complexes and Metal Clusters)</b>
<b>Module No and Title</b>	<b>Module23:Structure and bonding of carboranes</b>
<b>Module Tag</b>	<b>CHE_P11_M23</b>

<b>Principal Investigator</b>		<b>Co- Principal Investigator and Technical Coordinator</b>
<b>Prof A.K.Bakhshi</b> Sir Shankar Lal Professor, Department of Chemistry University of Delhi		<b>Dr Vimal Rarh</b> Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi  <i>Specialised in : e-Learning and Educational Technologies</i>
<b>Paper Coordinator</b>	<b>Content Writer</b>	<b>Reviewer</b>
<b>Prof. Ranjit K. Verma</b> Professor Department Of chemistry Magadh University, Bodh Gaya, Bihar	Dr.(Mrs.) Neeraj Sharma Professor, Deptt. of Chemistry, Himachal Pradesh University	<b>Prof. B. S. Garg</b> Professor emeritus Dept. of Chemistry University of Delhi
<b>Anchor Institute : SGTB Khalsa College, University of Delhi</b>		

## TABLE OF CONTENTS

1. Learning Outcomes
2. Introduction
3. Structure of carboranes
  - 3.1 Structural aspects
  - 3.2 Illustrations
4. Bonding in carboranes
5. Summary

 **Pathshala**  
पाठशाला  
A Gateway to All Post Graduate Courses

## 1. Learning Outcomes

After studying this module, you shall be able to

- Know about carboranes
- Know about types of carboranes
- Learn about various methods of preparation of carboranes

## 2. Introduction

Carboranes have been known for more than half century but interested primarily theoreticians in their structure and bonding and small groups of industrial researchers who recognized their potential for creating extremely heat-stable polymers. Carboranes are polyhedral boron-carbon molecules or clusters stabilized by electron-delocalized covalent bonding in skeletal framework. The characteristic feature of carboranes is the presence of one or more carbon atoms in electron delocalized boron cluster framework. As the skeletal carbon and boron atoms are involved in delocalized bonding, each typically having five or six neighbors including hydrogen or other attached substituents, these molecules are non-classical and their structure cannot be described in terms of usual organic bond diagrams in which a connecting line between two atoms explicitly indicates an electron pair. In structures, which are described connecting lines show the polyhedral geometry only and do not in general, represent electron pairs. The range of composition in carborane cages extends from boron rich clusters such as  $C_2B_{10}H_{12}$  and  $CB_{11}H_{12}^-$  having as many as six skeletal carbon atoms but those with high boron content are dominant. Consequently, in most theoretical treatments of structure and bonding, carboranes are treated as polyhedral boranes in which one or more skeletal boron atoms are replaced by carbon. The basic principles of bonding in boron clusters are well understood after decades of study and in recent years, the advent of density functional theory (DFT) and other powerful computational tools has led to major advances in correlation of electronic structures with geometry, reactivity, bond strength, NMR shifts, coupling constants, vibrational frequencies and other properties.

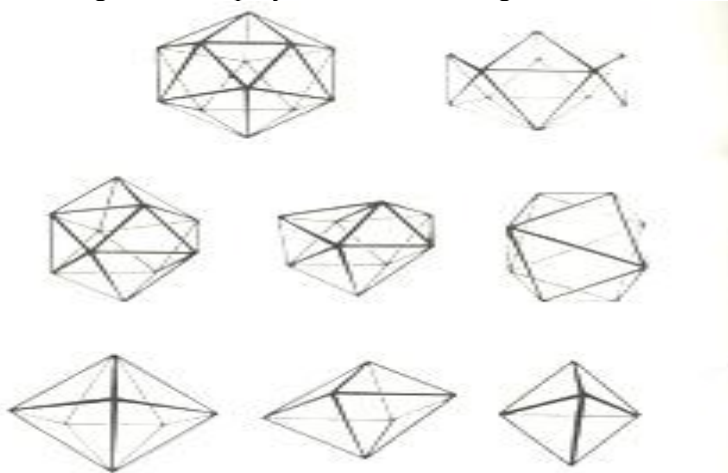
## 3. Structure of Carboranes

### 3.1 Structural aspects

A carborane is a cluster composed of boron, carbon and hydrogen atoms. Like many of the related boranes, these clusters are polyhedra and are similarly classified as *closo*-, *nido*-, *arachno*-, *hypho*-, etc. based on whether they represent a complete (*closo*-) polyhedron, or a polyhedron that is missing one (*nido*-), two (*arachno*-), or more vertices. The number of valence electrons in carbon atom is equal to those of boron atom plus a hydrogen atom. Hence BH unit can be substituted by carbon in carboranes.

The carboranes are classified as follows:

1. *Closo*-structures are adopted by borane anions  $B_nH_n^{2-}$  ( $n=6 \rightarrow 12$ ), carboranes  $C_2B_{n-2}H_n$  ( $n=5 \rightarrow 12$ ), and related isoelectronic species. Their  $n$  skeletal boron (or carbon) atoms define the vertices of the triangular-faced polyhedra shown in Fig. 1.



**Fig.1** Polyhedra that form the basis for the structures of *closo*-borane anions  $B_nH_n^{2-}$  and carboranes  $C_2B_{n-2}H_n$ .

The same polyhedra serve as the basis for the structures of *nido* and *arachno* compounds, too, although for these boranes and carboranes the polyhedra are incomplete.

2. *Nido* structures are adopted by neutral boranes  $B_nH_{n+4}$ , carboranes  $CB_{n-1}H_{n+3}$ ,  $C_2B_{n-2}H_{n+2}$ ,  $C_3B_{n-3}H_{n+1}$  and  $C_4B_{n-4}H_n$ , and related ionic species, whose  $n$  skeletal boron (or carbon) atoms occupy all but one of the vertices of the appropriate  $(n+1)$ -vertex polyhedron.

3. *Arachno* structures are adopted by boranes  $B_nH_{n+6}$  and isoelectronic carboranes  $C_2B_{n-2}H_{n+4}$ , etc. Their  $n$  skeletal atoms define all but 2 of the vertices of the appropriate  $(n+2)$  vertex polyhedron. The formulas of typical *closo*- *nido*- and *arachno*-boranes and -carboranes are listed in Table-1.

**Table. 1**  
 Typical. *closo*-, *nido*-, and *arachno*- Boranes and Carboranes.

No. of skeletal bod pairs	No. of polyhedron vertices	Fundamental polyhedron (symmetry)	<i>closo</i> species $B_nH_n^{2-}$	<i>nido</i> species $B_nH_n^{4-}$	<i>arachno</i> species $B_nH_n^{6-}$
6	5	Trigonal bipyramid ( $D_{3h}$ )	$C_2B_3H_5$	-	$B_3H_6^-$
7	6	Octahedron ( $O_h$ )	$B_6H_6^{2-}$ $CB_5H_7$ $C_2B_4H_6$	$B_5H_9$ $C_2B_8H_7$	$B_4H_{10}$ -
8	7	Pentagonal bipyramid ( $D_{5h}$ )	$B_7H_7^{2-}$ $C_3B_5H_7$	$B_4H_{10}; B_6H_{11}$ $C_xB_{5-x}H_{10-x}$ ( $X - 1 - 4$ )	$+B_5H_{11}$ -
9	8	Dodecahedral ( $D_{2d}$ )	$B_8H_8^{2-}$ $C_2B_6H_8$ $C_3B_5H_7$	- - -	$B_6H_{12}$
10	9	Tricapped trigonal Prism ( $D_{3h}$ )	$B_9H_9^{2-}$ $C_2B_7H_9$	$B_8H_{12}$ $C_2B_2H_{10}$	
11	10	Bicapped Archilnedean antiprism ( $D_{4d}$ )	$B_{10}H_{10}^{2-}$ $CB_3H_{10}^{2-}$ $C_2B_5H_{10}$	$B_8H_{12}^-$ $C_2B_7H_{11}$ -	$B_8H_{14}$ - -
12	11	Octadecahedron ( $C_{2d}$ )	$B_{11}H_{11}^{2-}$ $CB_{10}H_{11}$ $C_2B_2H_{11}$	$B_{10}H_{14}$ $CB_9H_{13}$ $C_2B_8H_{12}$	$B_9H_{15}$ $C_2B_7H_{13}$ -
13	12	Icosahedron ( $I_h$ )	$B_{12}H_{12}^{2-}$ $B_{11}H_{12}^-$ $C_2B_{10}H_{12}$	$CB_{10}H_{13}$ $B_{10}H_{15}^-$ $C_2B_9H_{11}^{2-}$ $C_4B_7H_{11}$	$B_{10}H_{15}^-$ $B_{10}H_{14}^-$ -

a For the cation  $Bv_6H_{11}^+$ .

b The compound  $C_4H_4B_6$  leg not a *nido*-carborane, but has an adamantane-type structure

4. *Hypho*-Carboranes ( $C_2B_{n-2}H_{n+6}$ ): three vertices are missing from parent *closo* carborane.
5. *Conjuncto*-Carboranes (from Latin: join together): *conjuncto* carboranes are formed by joining two or more preceding types.

The positions of the hydrogen atoms in boranes and carboranes are worth noting. In *closo*-borane anions  $B_nH_n^{2-}$ , the  $n$  BH units are aligned so that the B-H bonds point radially outward away from the centres of the  $B_n$  polyhedral and are referred to as *exo*-B-H bonds. The CH units of isoelectronic *closo*-carboranes  $CB_{n-1}H_n^-$  or  $C_2B_{n-2}H_n$  are similarly orientated. When anions  $B_nH_n^{2-}$  and  $CB_{n-1}H_n^-$  are protonated to form  $B_nH_{n+1}^-$  and  $CB_{n-1}H_{n+1}$ , the extra hydrogen atom apparently occupies a bridging position either between two boron atoms (over an edge of the  $n$ -cornered polyhedron) or for three atoms (over a polyhedron face). On the basis of microwave spectroscopic study to be in or over one  $B_3$  octahedral face, which is bounded by longer B-B bonds than the others.

### Illustrations

1. *Closo*-Carboranes ( $C_2B_{n-2}H_n$ ): e.g. 1,6-dicarba-*closo*-hexaborane  $C_2B_4H_6$  has regular octahedron structure where four boron atoms are present in one plane and two carbon atoms are present above and below the plane containing boron atoms. It has closed symmetrical structure.

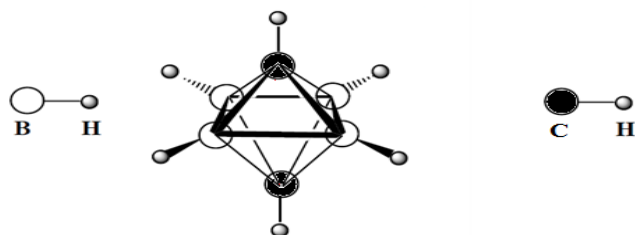
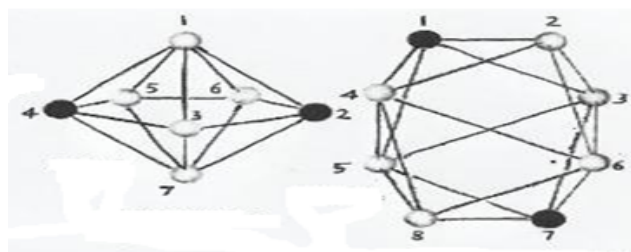
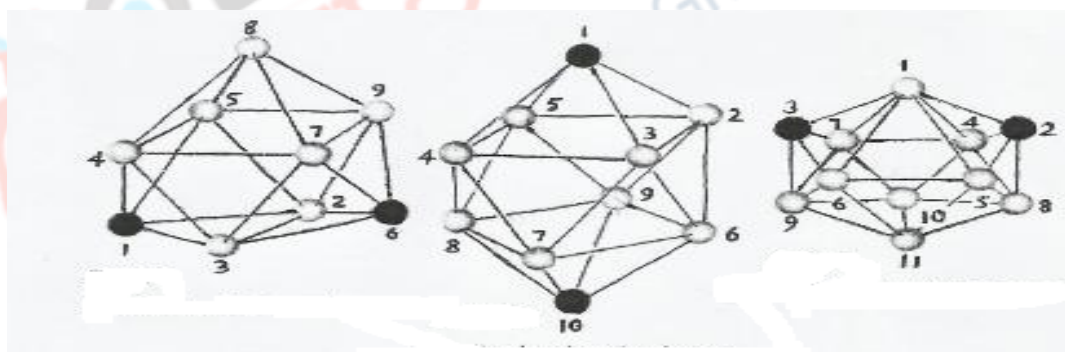


Fig.2. Structure of  $C_2B_4H_6$  (all vertices are occupied).



$C_2B_5H_7$   $C_2B_6H_8$   
2,4-dicarpa-*closo*-heptaborane 1,7-dicarpa-*closo*-octaborane

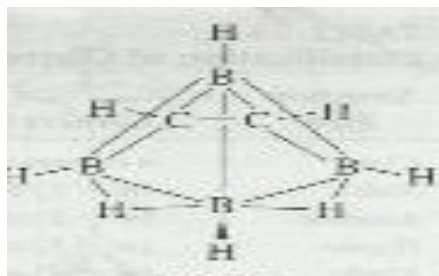


$C_2B_7H_9$   $C_2B_8H_{10}$   $C_2B_9H_{11}$   
1,6-dicarpa-*closo*-nonaborane 1,10-dicarpa-*closo*-decaborane 2,3-dicarpa-*closo*-undecaborane

Fig.3. Dicarba-*closo*-borane skeletons with from 7 to 11 cage atoms

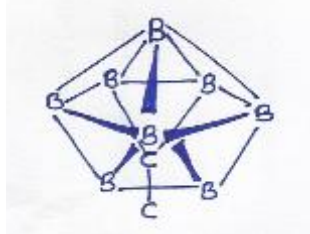
2.Nido-Carboranes ( $C_2B_{n-2}H_{n+2}$ ): e.g. in  $C_2B_4H_8$  only four vertices( $n-2$ ) are occupied by boron atoms of regular six cornered octahedron (with  $n$  vertices) and two by boron atoms.





**Fig.4 .** Structure of  $C_2B_4H_8$  (one vertex is missing).

3. *Arachno*-carboranes ( $C_2B_{n-2}H_{n+4}$ ): e.g ,  $C_2B_8H_{10}^{4-}$



**Fig.5** Structure of  $C_2B_8H_{10}^{4-}$  (two vertices are missing)

#### 4. Bonding in Carboranes

##### WADE-MINGO RULES (polyhedral skeleton electron pair theory)

In order to rationalize the structure of carboranes, a scheme of skeletal electron counting was developed to which the following rules are applicable:

**Step-1 :** First, the number of skeletal electrons are calculated as sum of the following contributions.

- Each B-H bond contributes 2 electrons.
- Each C-H bond contributes 3 electrons.
- Each additional hydrogen contributes 1 electron.
- Finally the anionic charge on the cluster is to be added to above contributions.

i.e. skeletal electron count =  $2(B-H) + 3(C-H) + 1(\text{additional H}) + \text{anionic charge on cluster}$

**Step-2 :** Calculate the number of pairs of electrons

$$\text{No. of electron pairs} = \frac{\text{Skeletal electron count}}{2}$$

**Step-3 :** Let the number of vertices ( no. of B and C atoms) is given by 'n'. Then by comparing the number of electron pairs with number of vertices(n) , the cluster's structure can be identified as follows

No. of electron pairs	Type of borane
n+1	Closo
n+2	Nido
n+3	Arachno
n+4	Hypo

**Closo-carboranes:** These have a completely closed triangular polyhedral structure in which all the vertices of the triangular polyhedral structure are occupied by boron and some carbon atoms. There are (n+1) electron pairs present in multicentre bonding orbitals of skeletal structure (cage or framework) of *closo*-carborane (n is the total number of B and carbon atoms) e.g.  $C_2B_{10}H_{12}$ . In  $C_2B_{10}H_{12}$ , n= 12. According to Wade's rule the two CH units, contribute  $2 \times 3 = 6$  electrons and ten BH units contribute  $10 \times 2 = 20$  electrons to the bonding molecular orbitals or the skeletal structure. Thus there are 13 electron pairs (n+1=13) present in the multicentre bonding orbitals of  $C_2B_{10}H_{12}$ .

**Nido-Carboranes:** These carboranes may be assumed to be derived from the *closo* triangular polyhedral structure of a *closo*-carborane by removal of one of the vertices of the polyhedron. The resulting nido (nest like) skeletal structure has (n+2) electron pairs in its multicentre bonding orbitals. In *nido*- $C_2B_4H_8$ , (n= 2 + 4 =6), the two CH units contribute  $2 \times 3 = 6$  electrons, the four BH units contribute  $4 \times 2 = 8$  electrons and the two extra hydrogens contribute 2 electrons to bonding orbitals of the skeletal structure of *nido*-2,3  $C_2B_4H_8$ . Thus, there are 8 electron pairs (n+2 =8) in the multicentre bonding orbitals of the skeletal structure of the carborane.

**Arachno-Carborane:** The structure of this type of carboranes may be assumed to have been derived from *nido*-structures by the removal of the vertices of these structures. There are (n+3) electron pairs in the multicentre orbitals of carboranes. eg.  $C_2B_7H_{13}$ .

#### Important features of Bonding

1. The triangular-faced polyhedra shown in Fig.1 form the basis for the structures of boranes and carboranes.
2. The skeletal boron or carbon atoms occupy all, all but one, or all but two of the vertices of the appropriate polyhedron in *closo*, *nido* or *arachno* compounds, respectively.
3. Each skeletal boron or carbon atom has a hydrogen atom (or some other singly bonded ligand) terminally attached to it by a bond radiating outward (exo) away from the center of the polyhedron to which a pair of electrons is allocated.
4. The remaining valence shell electrons (b pairs) are regarded as skeletal bonding electrons.
5. Each skeletal boron or carbon is considered to provide three atomic orbitals for skeletal bonding.
6. The symmetries of the polyhedra are such as to generate (n+1) skeletal bonding molecular orbitals from these atomic orbitals, (where n= number of polyhedron vertices [n=(b-1)]).
7. Compounds with **a** skeletal atoms and **b** skeletal bond pairs adopt *closo* structures if  $b=(a+1)$ , *nido* structures if  $b=(a+2)$  and *arachno* structures if  $b=(a+3)$ .



## 5. Summary

- Carboranes are compounds with the basic structural unit containing a number of C and B atoms arranged on the vertices of a triangular polyhedron.
- The structures of carboranes are closely related to those of the isoelectronic boranes.  
 $BH=B^{\ominus}=C$ ;  $BH_2=BH^{\ominus}=BL=CH$
- Structure of carboranes can be predicted with the help of Wade-Mingo rules.
- The C and B atoms in *closo*-structures are numbered in such a manner that the top vertex is given 1 and the remaining vertices are numbered in clockwise direction.

 **Pathshala**  
पाठशाला  
A Gateway to All Post Graduate Courses