

CHAPTER 10

Metal Clusters:

❖ Structure and Bonding in Higher Boranes

Boron hydrides or simply boranes are a class of compounds that have the generic formula B_xH_y . Though the boron does not react with hydrogen directly to form any of the boron hydrides, yet many of these compounds can easily be synthesized under special reaction conditions. However, because of the high affinity of boron for oxygen, these compounds readily oxidize on contact with air (lighter boranes even explode); and therefore, do not occur in nature. This class is derived from the borane (BH_3) itself, which exists only as a transient intermediate and dimerizes to form diborane (B_2H_6) immediately. The higher boranes are all consisted of boron clusters that are actually polyhedral in nature. Besides the neutral boranes, a large number of anionic boron hydrides also exist. The general formula for single-cluster boron hydrides is $B_nH_n^{2-}$, B_nH_{n+4} , B_nH_{n+6} , B_nH_{n+8} and B_nH_{n+10} (n is the number of boron atoms) for closo-, nido-, arachno-, hypho- and klado- type, respectively. There also exists a series of substituted neutral hypercloso-boranes that have the theoretical formulae of B_nH_n .

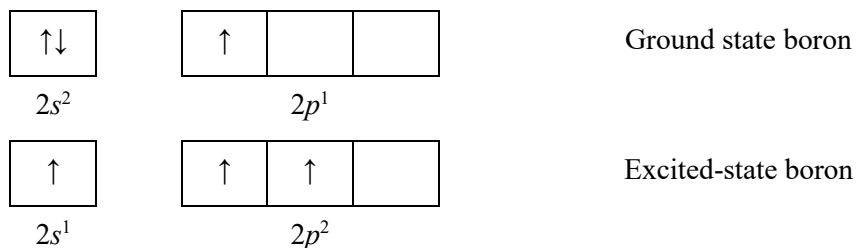
The naming of neutral boranes is done with a Greek prefix showing the number of boron atoms and the number of hydrogen atoms in brackets. In the naming of anions, the hydrogen count is specified first followed by the boron count and the overall charge in the bracket in the last. Furthermore, the prefix closo-nido- etc. can also be added. For example:

Formula	B_5H_9	B_4H_{10}	$B_6H_6^{2-}$
Name (IUPAC)	Pentaborane(9)	Tetraborane(10)	hexahydrido hexaborate(2-)
Type	Nido-	Arachno-	Closo-

Understandably many of the compounds have abbreviated common names. The prefix like closo-, nido are actually related to geometry and the number of framework electrons of a particular cluster. Now because the boron hydrides are electron-deficient compounds, the structure and bonding in higher boranes can be understood only after rationalizing the 3-center-2-electron bond involved.

➤ Valence Bond Treatment of Three-Centre Two-Electron Bond

The simplest example of boron hydride containing 3-center-2-electron bond is diborane; and therefore, the first orbital based approach we can use to study the diborane structure is valence bond theory. The B_2H_6 or diborane can be considered as a dimeric unit of two BH_3 molecules. Now, as all the three half-filled sp^3 hybrid orbitals of boron are already used to bind hydrogens, the dimerization seems to be impossible. However, the valence bond theory still suggests a mode of dimerization through sp^3 -hybridization. The electronic configuration of boron in its ground state and excited state are:



The mixing of one s and three p orbitals generate four sp^3 hybrid orbitals; three half-filled and one empty. Each boron atom in the diborane structure can use two of its sp^3 hybrid orbitals half-filled to bind two hydrogen atoms (terminal-H). The remaining two hybrid orbitals (one half-filled and one empty) are then used to bind bridging-H atoms as given below.

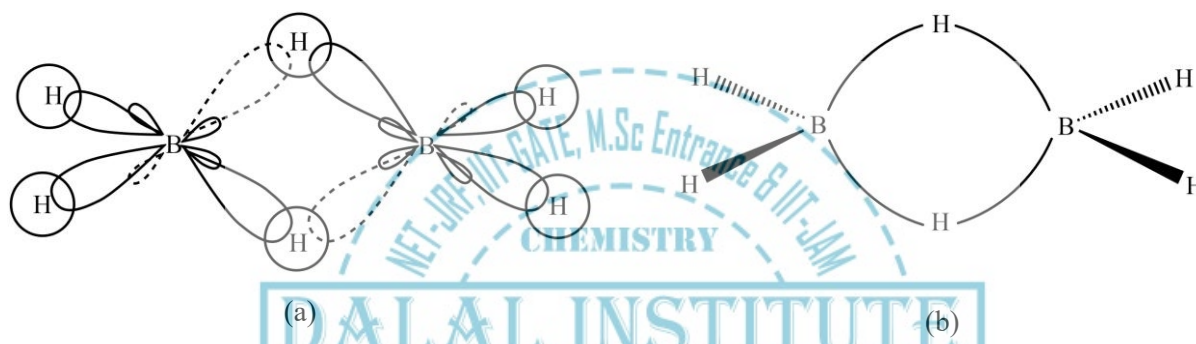
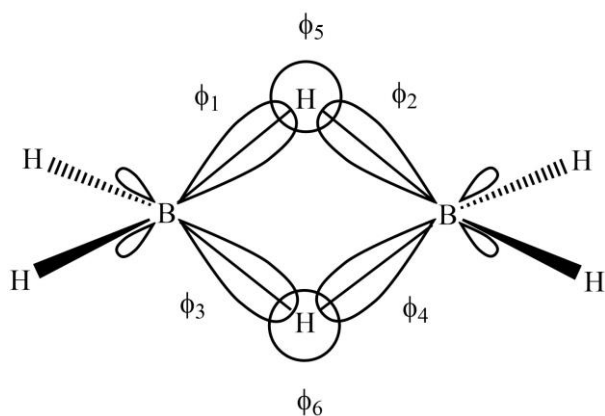


Figure 1. The (a) orbital overlap of hybrid atomic orbital of boron with hydrogens and (b) the resulting banana-shaped 3-center-2-electron bond.

It can be clearly seen that the valence electron in each bridging hydrogen must get delocalize over all three atoms (B–H–B) to bond to both of the B atoms simultaneously. This is pretty much contradictory for the valence bond theory, which likes to bound the valence electrons into regions of space that are localized between two participating nuclei only. Additionally, the molecular geometry of diborane cannot be explained using valence shell electron pair repulsion (VSEPR) theory as far as bridging hydrogens are concerned. According to VSEPR model, two bonds around each bridging hydrogen should be linear i.e. the B–H–B bond angle should be equal 180° with straight-line coordination around.

➤ **Molecular Orbital Treatment of Three-Centre Two-Electron Bond**

The rationalization of the 3-centre-2-electron bond is much more convincing from the molecular orbital approach, which considers the delocalization of electron density in bonding as a common phenomenon. Now because we only want to understand the nature of bonding involved in B–H–B bridges, we need to focus on just the part of the molecule. Before the formation of molecular orbitals, we need to identify the basis function required. Owing to the partial success of the valence bond theory in the rationalization of the 3-center-2-electron bond, we can make the use of four equivalent sp^3 hybrid orbitals and two s orbitals of hydrogen atoms to construct the symmetry adapted linear combinations (SALCs) of atomic orbitals.

Figure 2. Basis functions for the B–H–B portion in B₂H₆.

The reducible representation based upon four hybrid orbitals of borons and two 1s orbitals hydrogens in the B–H–B portion of diborane can be given as:

Table 1. The reducible representation based upon four hybrid orbitals of borons and two 1s orbitals hydrogens in the B–H–B portion of diborane.

D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ_{xy}	σ_{xz}	σ_{yz}	Irreducible components
Γ_H	2	0	0	2	0	2	2	0	$a_{1g} + b_{3u}$
Γ_B	4	0	0	0	0	4	0	0	$a_{1g} + b_{1g} + b_{2u} + b_{3u}$

The mathematical forms of the six normalized SALCs can be deduced through the projection operator theorem and are given by the equations (1) to (6) as:

$$\psi_{a_{1g}}(H) = \frac{1}{\sqrt{2}}(\phi_5 + \phi_6) \quad (1)$$

$$\psi_{b_{3u}}(H) = \frac{1}{\sqrt{2}}(\phi_5 - \phi_6) \quad (2)$$

$$\psi_{a_{1g}}(B) = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4) \quad (3)$$

$$\psi_{b_{1g}}(B) = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4) \quad (4)$$

$$\psi_{b_{2u}}(\text{B}) = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4) \quad (5)$$

$$\psi_{b_{3u}}(\text{B}) = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4) \quad (6)$$

The single-electron wave functions and corresponding molecular orbital shapes for B–H–B portion of diborane are shown in Figure 3. For simplicity, only the largest lobes of the four sp^3 hybrid orbitals are depicted. Nevertheless, the smaller lobes on the opposite side also have a good possibility to overlap, which makes the energies two nonbonding molecular orbitals unequal. The mixing of two SALCs of a_{1g} symmetry generates two molecular orbitals; one bonding and other antibonding shown by a_{1g} and a_{1g}^* , respectively. Similarly, the mixing of two SALCs of b_{3u} symmetry yields two molecular orbitals of b_{3u} and b_{3u}^* symmetry.

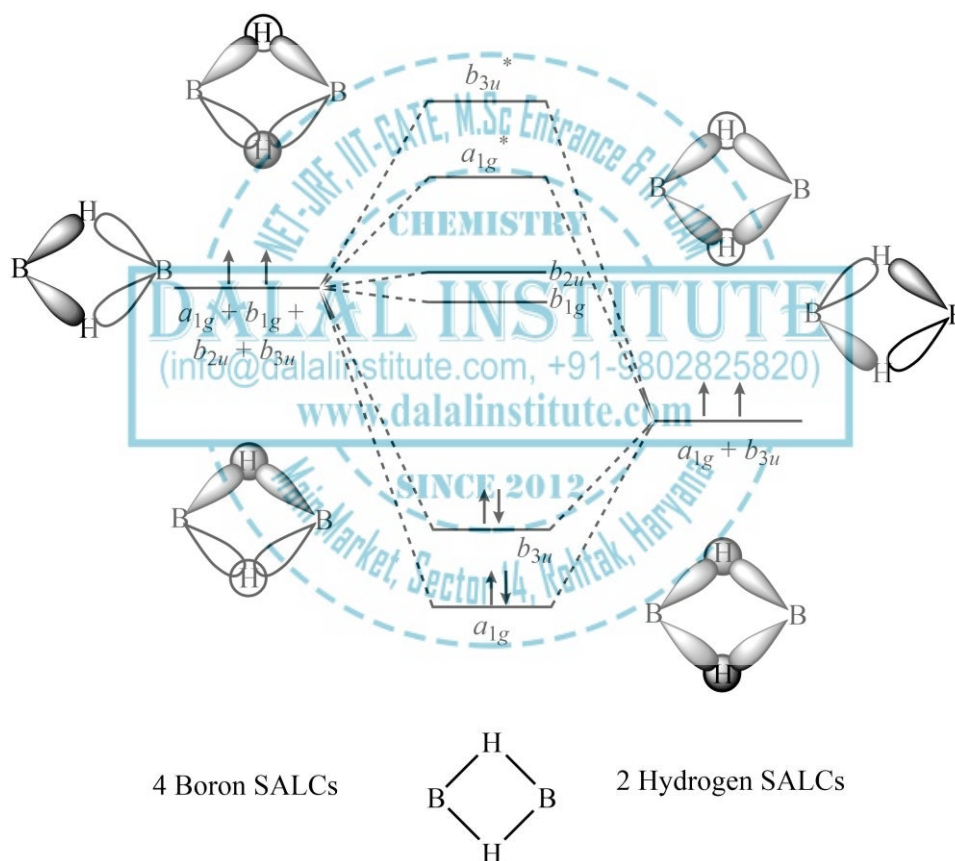


Figure 3. Partial one-electron molecular orbital energy level diagram for the B–H–B part of B_2H_6 .

The shapes of molecular orbital with a_{1g} and b_{3u} symmetry evidently show that the electron density present in them is actually delocalized over all three nuclei involved in B–H–B unit of diborane. A certain amount of direct B–B bonding in diborane is also present which helps to stabilize the molecule geometry; which is attributed to small-sized H-groups.

➤ **Classification of Bonds Present in Higher Boranes**

The explanation of overall bonding in higher boranes needs the calculation of electrons involved in the skeletal structure of B_n cluster and these electrons are generally referred as the “framework electrons”. Moreover, the B–H–B bridges are considered as part of the B_n framework while the terminal B–H are discarded. Though the electrons involved in the framework construction of B_n cluster are very much delocalized, yet the localized 3-centre 2-electron and 2-centre 2-electron orbital approach can be used to explain the main features of the boranes. Each B atom uses one electron in the normal 2-center-2-electron terminal B–H bond and the remaining two electrons are used in B_n framework. The structure of higher boranes may or may not have all of the following kinds of bonds i.e. they may possess few or all types.

1. Terminal B–H bond: This is a normal 2-center-2-electron covalent bond and is generally shown as B–H.



2. Direct B–B bond: This is a 2-center-2-electron bond and is able to connect two boron atoms. These bonds are generally represented as B–B.



3. Bridging or open B–H–B bond: This is a 3-center-2-electron bond and is able to connect two boron and one hydrogen atoms. These bonds are generally represented as B–H–B.



4. Closed B–B–B bond: This is a 3-center-2-electron bond and is able to connect three boron atoms that are at the corners of an equilateral triangle. These bonds are generally represented as B–B–B.



5. Open bridging B–B–B bond: This is a 3-center-2-electron bond and is able to connect three boron atoms to form a B–H–B like bridge found in diborane. These bonds are represented as B–B–B.



➤ **Geometry Prediction in Higher Boranes Using Lipscomb's Model Involving STYX Numbers**

The main initial approach to understand the structures of boranes and related species was Lipscomb's topological model involving STYX numbers and rules. W. N. Lipscomb was an American chemist who developed a method to find the key combinations of bonding profile that are actually possible for a specific boron hydride formula. Each boron atom in neutral boranes or hydroborate anions has at least one H attached by a normal 2-center-2-electron sigma bond; therefore, it can be assumed that one B–H bond is present per boron atom. Besides, Lipscomb also proposed that every other bond present in the cluster must belong to any of the following categories.

- i) 3-centre-2-electrons B–H–B bond, labeled as “S”.
- ii) Closed, open, or a mixture of both 3-centre 2-electrons B–B–B bond, labeled as “T”.
- iii) 2-center-2-electrons B–B bond, labeled as “Y”.
- iv) 2-center-2-electrons B–H terminal bond (simply no. of BH₂ groups), labeled as “X”.

The structure prediction of borane clusters using the Lipscomb model involves the three major components which are discussed in detail below.

1. The relationship between STYX code and valence electrons: The correlation between the boranes formula and the number and types of bonds in the cluster is given by simple equations of balance. These equations relate all kinds of sigma bonds to the number of valence electrons available.

i) *Three centers orbital balance:* The electron deficiency in a borane cluster can be removed only if one 3-center-2-electron bond is created by each boron atom. Thus, the sum of the number of 3-centre 2-electron B–H–B bonds and the number of 3-centre 2-electron B–B–B bonds must be equal the number of B–H units (n).

$$n = S + T \quad (7)$$

ii) *The hydrogen balance:* Supposing that one terminal hydrogen is attached to each boron atom, the number of hydrogen atoms leftover (m), must be distributed among bridges and additional B–H terminal bonds.

$$m = S + X \quad (8)$$

iii) *The electron balance:* Now, if each BH unit contributes one pair of electrons to the skeleton and each of the extra hydrogens gives one electron; the number of electron pairs contributed by additional hydrogens must be calculated by halving their number. All of these electron pairs must be participating in bonding; and therefore, the total number of bond pairs can be given as:

$$n + (m/2) = S + T + Y + X \quad (9)$$

From equation (7) and (8) we get

$$Y = \frac{1}{2}(S - X) \quad (10)$$

2. The calculation of various STYX possibilities: After knowing the correlation between various kinds of bonds with framework electron pairs in boron hydrides, we need to follow the following steps to write various STYX possibilities.

- Write down the general formula of given borane cluster in form like B_nH_{n+m} to fix the value of n and m .
- Calculate the number of B–H–B bridges which are represented by S . The value of S must lie within the range of $m/2$ to m . In other words, the value of S must satisfy the following condition.

$$\frac{m}{2} \leq S \leq m \quad (11)$$

The validation of the higher limit comes from the fact that m represents the total additional hydrogens out of which some are present in B–H–B bond and some are present in B–H terminal bond. Therefore, if all the additional hydrogens are present in B–H–B bond, the value of “ S ” at its maximum can just be equal to m . The validation of the lower limit can be derived equation (8) and equation (9) as:

$$n + (m/2) = (m - X) + T + Y + X \quad (12)$$

$$n = \left(\frac{m}{2}\right) + T + Y \quad (13)$$

From equation (7), we get

$$S + T = \left(\frac{m}{2}\right) + T + Y \quad (14)$$

$$S = \left(\frac{m}{2}\right) + Y \quad (15)$$

Thus, the value of S is always equal to or greater than $m/2$.

iii) For different values of S obtained in 2nd step, we have to calculate the equally possible solutions for the values of T , Y and X .

iv) There are many sets of STYX numbers for a given borane cluster and thus many possible topologies.

3. The shortlisting of STYX codes using empirical rules: In order to select the correct STYX code among several possibilities, empirical rules have been developed which follow as:

- The STYX number sets with negative value are not considered as they have no physical meaning.
- All boranes have at least a 2-fold symmetry, so it is assumed that any new hydride probably would have at least one plane, center, or two-fold axis of symmetry. Low symmetry seems to activate the center of reactivity.
- Only one terminal hydrogen and no bridging hydrogen may be attached to boron that is bound to five neighboring borons. This restricts B–H–B bridges and BH_2 groups to the open edges of boron frameworks.
- If a boron atom is bound to four other boron, it will probably not make use of more than one B–H–B bridge.
- A boron atom that is bound to only two other boron atoms will be involved in at least one B–H–B bridge.

The whole concept can be exemplified using the diborane structure. The general formula for diborane can be written in the form of B_2H_{2+4} ; which gives the values of n and m as 2 and 4, respectively. From equation (11), we get

$$\frac{4}{2} \leq S \leq 4 \quad (16)$$

The possible values of $S = 2, 3, 4$. By using $S = 2$ in equation (7), we get

$$2 = 2 + T \quad (17)$$

$$T = 0 \quad (18)$$

Similarly, putting $S = 2$ in equation (8), we get

$$4 = 2 + X \quad (19)$$

$$X = 2 \quad (20)$$

Now putting the values of T and X from equation (18) and equation (20) in equation (9), we get

$$2 + (4/2) = 2 + 0 + Y + 2 \quad (21)$$

$$Y = 0 \quad (22)$$

Similarly, by taking the value of S as 3 and 4, one can get two another set of possible STYX numbers as tabulated as given below.

Table 2. Three possible sets of STYX numbers for B_2H_6 .

Number of B–H–B bonds (S)	Number of B–B–B bonds (T)	Number of B–B bonds (Y)	Number of BH ₂ groups (X)
2	0	0	2
3	-1	1	1
4	-2	2	0

It can clearly be seen that out of three sets of STYX numbers, only the first one is physically reasonable since the latter two involve negative values. Besides, this also confirmed by the experimental geometrical structure of the diborane that the STYX number of 2002 is, of course, seems to be correct; because there are two B–H–B bridges, no three-center B–B–B bonds or two-center B–B bonds and two B–H terminal bonds in addition to those already considered i.e. two BH₂ groups. A similar procedure can be applied to find out the topological structures of other borane clusters like B_4H_{10} , B_5H_9 , $B_{10}H_{14}$.

➤ **Structure and Bonding Profile of Some Typical Higher Borane Clusters**

As we have already discussed the fundamentals of structure and bonding in higher borane systems, now we will implement those ideas to explain some typical examples.

1. Tetraborane-10 (B_4H_{10}): The bonding in B_4H_{10} can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

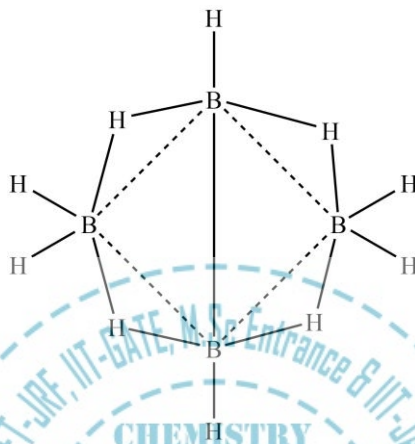


Figure 4. Planar view for the structure of B_4H_{10} .

It can be clearly seen that there are four B–H–B bridges, no closed or bridging B–B–B unit, one B–B bond and two terminal BH_2 groups. Hence, the overall STYX code for B_4H_{10} molecule is 4012. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 3. Nature and number of bonds (along with electrons required) present in B_4H_{10} .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 4 B atoms	Contribution from 10 H atoms
B–H–B	4	8	4	4
B–B–B	0	0	0	0
B–B	1	2	2	0
B–H	6	12	6	6

Hence, four 3-centre 2-electron and seven 2-centre 2-electron bonds require a total $4 \times 2 + 7 \times 2 = 22$ electrons. Four boron atoms have 12 valence electrons while 10 electrons are actually contributed by ten hydrogen groups that participating in both types of bonds.

2. Pentaborane-9 (B_5H_9): The pentaborane-9 (commonly called pentaborane) is an inorganic compound with the formula B_5H_9 , and is different from pentaborane-11 (B_5H_{11}). It is one of the most common cluster hydrides of boron, though it is a highly reactive compound. Owing to its high reactivity toward oxygen, it was once evaluated as rocket or jet fuel. Like many of the smaller boron hydrides, pentaborane is colorless, diamagnetic, and volatile. The bonding in B_5H_9 can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

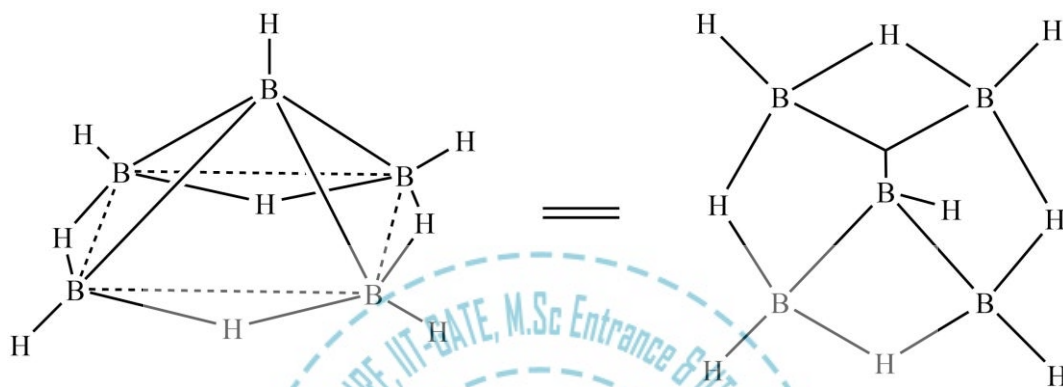


Figure 5. Structure of B_5H_9 .

Its structure is that of five atoms of boron arranged in a square pyramid. Each boron has a terminal hydride ligand and four hydrides span the edges of the base of the pyramid. It can be clearly seen that there are four B–H–B bridges, one closed or triply bridged B–B–B unit, two B–B bond and no terminal BH_2 groups. Hence, the overall STYX code B_5H_9 molecule is 4120. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 4. Nature and number of bonds (along with electrons required) present in B_5H_9 .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 5 B atoms	Contribution from 9 H atoms
B–H–B	4	8	4	4
B–B–B	1	2	2	0
B–B	2	4	4	0
B–H	5	10	5	5

Hence, five 3-centre 2-electron and seven 2-centre 2-electron bonds require a total $5 \times 2 + 7 \times 2 = 24$ electrons. Five boron atoms have 15 valence electrons while 9 electrons are actually contributed by nine hydrogen groups that are participating in both types of bonds.

3. Pentaborane-11 (B_5H_{11}): The pentaborane-11 is a compound with the general formula B_5H_{11} . It is a colorless liquid at room temperature with a boiling point of 63°C . The bonding in B_5H_{11} can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

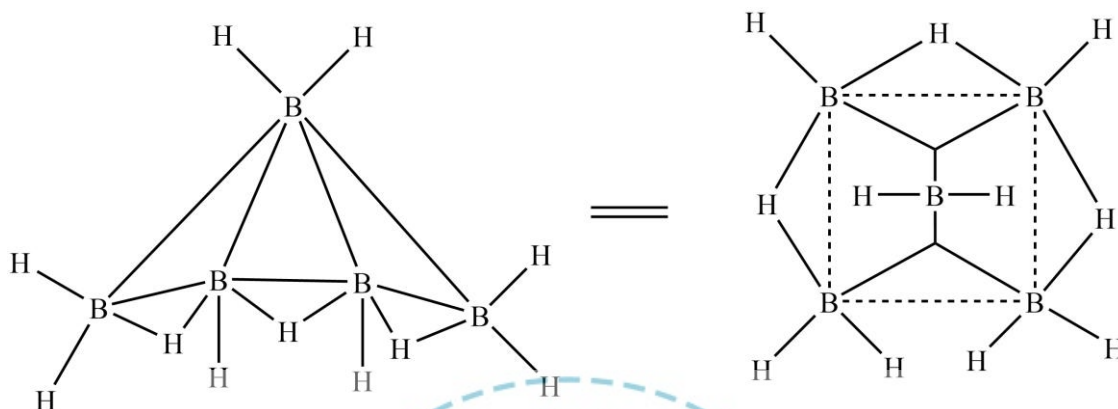


Figure 6. Structure of B_5H_{11} .

The pentaborane-11 is having unsymmetrical square-pyramidal and five boron atoms are present at the five corners of a square pyramid, just like in the case B_5H_9 molecule. Three out of five boron atoms have a terminal hydride ligand while two adjacent boron has two hydride group each, and four hydrides span the edges of the base of the pyramid. It can be clearly seen that there are three B–H–B bridges, two closed or triply bridged B–B–B unit, zero B–B bond and three-terminal BH_2 groups. Hence, the overall STYX code B_5H_{11} molecule is 3203. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 5. Nature and number of bonds (along with electrons required) present in B_5H_{11} .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 5 B atoms	Contribution from 11 H atoms
B–H–B	3	6	3	3
B–B–B	2	4	4	0
B–B	0	0	0	0
B–H	8	16	8	8

Hence, five 3-centre 2-electron and eight 2-centre 2-electron bonds require a total $5 \times 2 + 8 \times 2 = 26$ electrons. Five boron atoms have 15 valence electrons while 11 electrons are actually contributed by eleven hydrogen groups that are participating in both types of bonds.

4. Hexaborane-10 (B_6H_{10}): The bonding in B_6H_{10} can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.

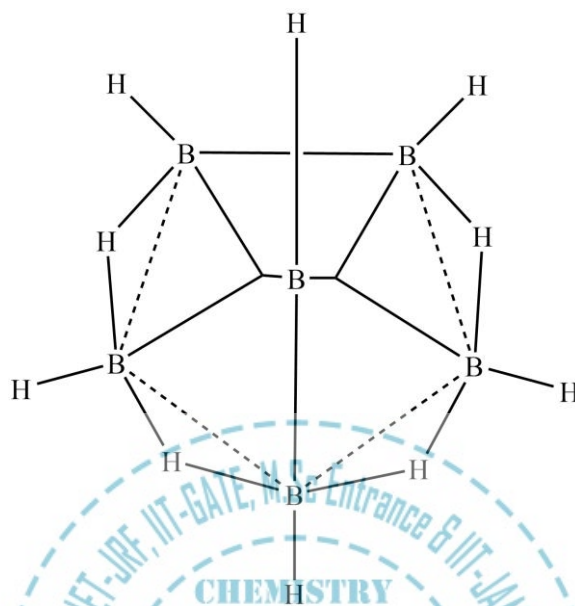


Figure 7. Structure of B_6H_{10} .

It can be clearly seen that there are four B–H–B bridges, two closed or triply bridged B–B–B unit, two B–B bond and no terminal BH_2 groups. Hence, the overall STYX code B_6H_{10} molecule is 4220. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 6. Nature and number of bonds (along with electrons required) present in B_6H_{10} .

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 6 B atoms	Contribution from 10 H atoms
B–H–B	4	8	4	4
B–B–B	2	4	4	0
B–B	2	4	4	0
B–H	6	12	6	6

Hence, six 3-centre 2-electron and eight 2-centre 2-electron bonds require a total $6 \times 2 + 8 \times 2 = 28$ electrons. Six boron atoms have 18 valence electrons while 10 electrons are actually contributed by ten hydrogen groups that are participating in both types of bonds.

5. Decaborane-14 ($B_{10}H_{14}$): The bonding in $B_{10}H_{14}$ can easily be explained by drawing the plane projections of its three-dimensional structure as shown below.



Figure 8. Structure of $B_{10}H_{14}$.

In decaborane, the B_{10} framework resembles an incomplete octadecahedron. Each boron has one radial hydride, and four boron atoms near the open part of the cluster feature extra hydrides. It can be clearly seen that there are four B-H-B bridges, six B-B-B unit (four B-B-B triple bridge bonds and two B-B-B bent bridge), two B-B bond and zero terminal BH_2 groups. Hence, the overall STYX code $B_{10}H_{14}$ molecule is 4620. Now considering the electron requirement of various kinds of bonds present, the individual contribution of boron and hydrogen atoms can easily be tabulated.

Table 7. Nature and number of bonds (along with electrons required) present in $B_{10}H_{14}$.

Nature of the Bond	Number of Bonds	Total electron required	Contribution from 10 B atoms	Contribution from 14 H atoms
B-H-B	4	8	4	4
B-B-B	6	12	12	0
B-B	2	4	4	0
B-H	10	20	10	10

Hence, ten 3-centre 2-electron and twelve 2-centre 2-electron bonds require a total $10 \times 2 + 12 \times 2 = 44$ electrons. Ten boron atoms have 30 valence electrons while 14 electrons are actually contributed by fourteen hydrogen groups which are participating in both types of bonds.

➤ **Structural Relationship Between Closo, Nido and Arachno Boranes**

The structural relationship between closo, nido and arachno boranes is shown by the diagonal connecting species having the same number of skeletal electron pairs. Hydrogen atoms are omitted for clarity.

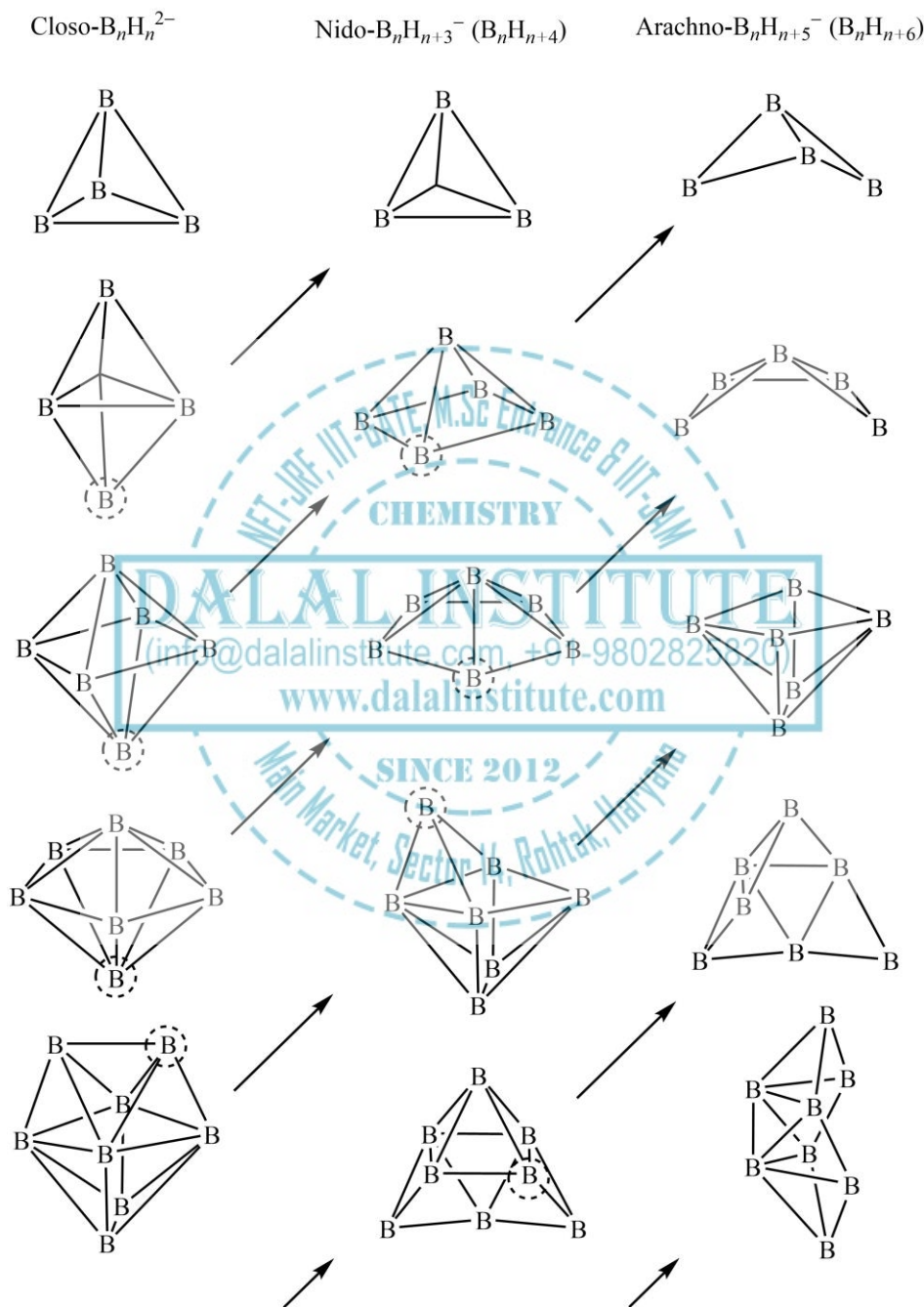


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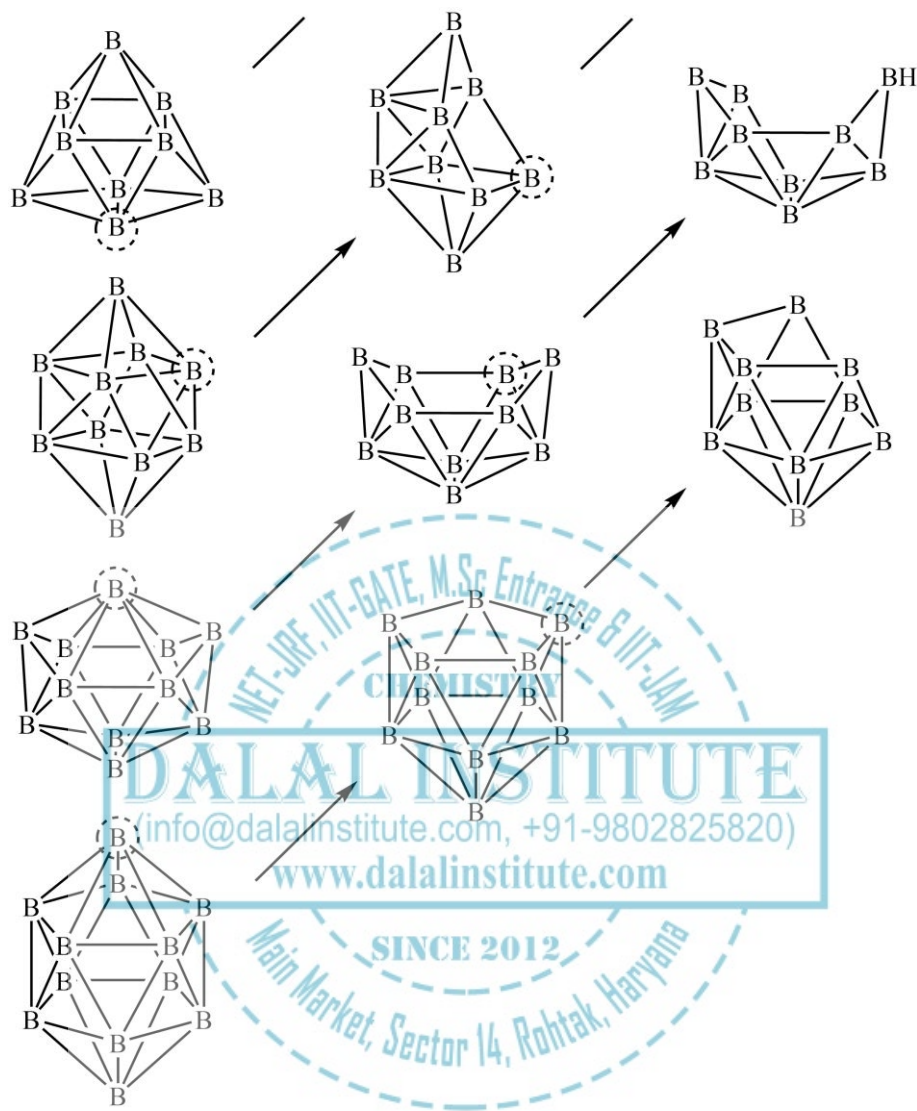


Figure 9. The structural relationship between closo, nido, and arachno boranes; the diagonal lines connect species that have the same number of skeletal electron pairs (SEP).

The structural relationships shown above explain various geometrical aspects of borane clusters; and provides a somewhat conceptual way to think about these systems. For instance, the structure of dodecahydro-closo-dodecaborate anion ($B_{12}H_{12}^{2-}$) is a regular icosahedron. Similarly, the structure of nido- $B_{10}H_{14}$ can easily be obtained just by removing a six-degree vertex from closo-decaborate ($B_{10}H_{10}^{2-}$) anion. The removal of one B–H unit and the addition of two H atoms converts nido- B_5H_9 into a butterfly-shaped arachno- B_4H_{10} borane. Nevertheless, it should also be noted that the interconversion of these structures may or may not be possible chemically; and the same statement can be made for their chemical formula.

❖ Wade's Rules

Though the Lipscomb's topological model involving STYX numbers and rules was good in the rationalization of structures of some of the boranes and related species, it was not enough to higher boranes and carbonyl clusters. Therefore, a more sophisticated and comprehensive method was needed. In 1971, a British chemist, Kenneth Wade, published a revolutionary paper in the field of cluster chemistry. The main outlines of this communication were later to be called as Wade's rules, which provided a straightforward and elegant explanation of the geometries of "electron-deficient" cluster compounds in terms of the number of skeletal electron pairs (SEPs) available. The main focus of this paper was on boranes, carboranes and low-valent transition-metal clusters; whose structures could not be explained by the normal 2-center-2-electron bond. After Wade's initial report, another British chemist, Michael Mingos, extended the principles of counting skeletal electron pairs to electron-precise and electron-rich clusters and gave a more generalized way of calculating the skeletal electron contribution of a wide range of transition-metal. Thereafter, the rules became known as the Wade-Mingos rules or, more formally, the polyhedral skeletal electron pair theory (PSEPT).

The structure prediction is based on different sets of rules ($4n$, $5n$, or $6n$), which are developed on the basis of the number of electrons present per vertex. The $4n$ rules are pretty much accurate in predicting the structures of clusters with 4 electrons per vertex, as is the case for many carboranes or boranes. The clusters following $4n$ rule are generally classified as closo-, nido-, arachno- or hypho-, depending on whether they represent a complete (closo-) deltahedron, or a deltahedron that is missing one (nido-), two (arachno-) or three (hypho-) vertices. However, if the count of electrons is near to 5 electrons per vertex, the structure changes occur and are governed by the $5n$ rules (based on 3-connected polyhedrons). Moreover, if the electron count is increased further, the clusters with $5n$ electron counts become very unstable, and the $6n$ rules find their role. The cluster compounds following $6n$ rule have structures that are dependent on rings.

➤ $4n$ Rule

The basis closo-polyhedra for the $4n$ rules are composed of triangular faces. The number of vertices in the cluster prediction and the corresponding basis polyhedron is given below.

Table 8. Base polyhedrons for structure prediction using $4n$ rule.

No. of Vertex	Polyhedron	No. of Vertex	Polyhedron
4	Tetrahedron	9	Tricapped trigonal prism
5	Trigonal bipyramid	10	Bicapped square antiprism
6	Octahedron	11	Octadecahedron
7	Pentagonal bipyramid	12	Icosahedron
8	D_{2d} (trigonal) dodecahedron		

Using the electron count, the predicted structure can be found. n is the number of vertices in the cluster. The $4n$ rules are enumerated in the following table.

Table 9. Electron count and predicted structure using $4n$ rule.

Electron count	Name	Predicted structure
$4n - 2$	Bicapped closo	$n - 2$ vertex closo polyhedron with 2 capped faces
$4n$	Capped closo	$n - 1$ vertex closo polyhedron with 1 face capped
$4n + 2$	Closo	Closo polyhedron with n vertices
$4n + 4$	Nido	$n + 1$ vertex closo polyhedron with 1 missing vertex
$4n + 6$	Arachno	$n + 2$ vertex closo polyhedron with 2 missing vertex
$4n + 8$	Hypso	$n + 3$ vertex closo polyhedron with 3 missing vertex
$4n + 10$	Klado	$n + 4$ vertex closo polyhedron with 4 missing vertex

The valence electrons are enumerated when the counting of electrons for each cluster is carried out. For each transition metal atom or ion present, ten electrons are subtracted from the total number of electrons. For example, in $\text{Rh}_6(\text{CO})_{16}$ the total number of electrons would be $6 \times 9 + 16 \times 2 - 6 \times 10 = 86 - 6 \times 10 = 26$. Therefore, the cluster is a closo polyhedron because $n = 6$, with $4n + 2 = 26$. When structure prediction is carried out, other postulates may be given as:

- i) For clusters that are comprised mainly of transition metals, any main group atoms are generally counted as ligands or interstitial atoms, and not vertices.
- ii) Larger atoms or more electropositive groups have the tendency to occupy vertices of higher connectivity; while the smaller or more electronegative atoms tend to fill vertices of low connectivity.
- iii) In some special boron hydride clusters, every boron connected to 3 or more vertices has one terminal H, while a boron connected to two other vertices has two terminal H. Any extra hydrogens left are placed in open-face positions to even out the coordination number of different vertices.
- iv) In some special cases of transition metal clusters, ligands are added to the metal centers to impart the metals a reasonable coordination numbers, and if any H atoms are present, they should be placed in bridging sites to even out the coordination numbers of different vertices.

Generally speaking, closo clusters with n vertices are n -vertex polyhedral structures. To find the nido-cluster structure, a closo cluster with $n + 1$ vertices is exploited as a starting point; if the cluster is consisted of small atoms, a vertex with high connectivity is removed; while if the cluster is consisted of large atoms, a vertex with low-connectivity is removed. To find the structure of arachno clusters, a closo polyhedron with $n+2$ vertices is exploited as the starting point, and a nido complex with $n+1$ vertex is created by the rule

discussed above. However, if the cluster is of small atoms, a second vertex which adjacent to the first is removed; and if the cluster is of large atoms mainly, the second vertex removed is not adjacent to the first one.

Examples: i) P_4 : Electron count = $4 \times$ number of valence electron of P = $4 \times 5 = 20$ electrons. Since $n = 4$, $4n + 4 = 20$, so the cluster is a nido borane. Starting from base polyhedron of $n + 1$ vertex, one vertex has to be removed. Here, starting from trigonal bipyramid and removing one axial vertex gives the tetrahedral cluster.

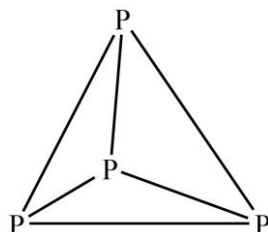


Figure 10. Structure of P_4 .

ii) S_4^{2+} : Electron count = $4 \times$ number of valence electron of S = $4 \times 6 - 2$ (for charge) = 22 electrons. Since $n = 4$, $4n + 6 = 22$, so the cluster is an arachno borane. Starting from base polyhedron of $n + 2$ vertex, two vertexes have to be removed. In this case, it will start from octahedron and then the removal of two non-adjacent vertexes will give square cluster.



Figure 11. Structure of S_4^{2+} .

iii) $B_5H_5^{4-}$: Electron count = $5 \times 3 + 1 \times 5 + 4 = 24$ electrons. Since $n = 5$, $4n + 4 = 24$, so the cluster is a nido borane. In this case, will start from octahedron and then the removal of one vertexes will give square pyramidal. The hydrogens have been omitted for clarity.

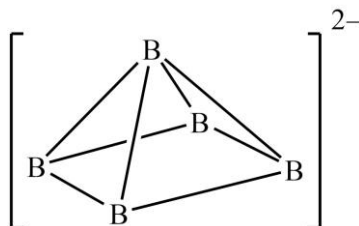


Figure 12. Structure of $B_5H_5^{4-}$.

iv) $\text{Os}_6(\text{CO})_{18}$: Electron count: $6 \times \text{Os} + 18 \times \text{CO} - 60$ (for 6 osmium atoms) $= 6 \times 8 + 18 \times 2 - 60 = 24$. Since $n = 6$, $4n = 24$, so the cluster is capped closo. Starting from a trigonal bipyramid, a face is capped. The carbonyls have been omitted for clarity.

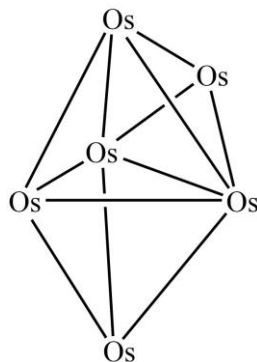


Figure 13. Structure of $\text{Os}_6(\text{CO})_{18}$.

v) $\text{C}_2\text{B}_5\text{H}_7$: Electron count $= 2 \times \text{C} + 5 \times \text{B} + 7 \times \text{H} = 2 \times 4 + 3 \times 5 + 7 \times 1 = 30$. Since n in this case is 7, $4n + 2 = 30$, the cluster is closo. The hydrogens have been omitted for clarity.



Figure 14. Structure of $\text{C}_2\text{B}_5\text{H}_7$.

The bookkeeping for deltahedral clusters is sometimes carried out by counting skeletal electrons pairs instead of the total number of electrons. The CH and BH units are considered as 3 and 2 electron donor, respectively. Additional hydrogen contributes 1 electron and charge is considered as it is. m is the sum of the number of boron and carbon atoms.

No. of e pair	$m - 1$	m	$m + 1$	$m + 2$	$m + 3$	$m + 4$	$m + 5$
Structure	Bicapped closo	Capped closo	Closo	Nido	Arachno	Hypno	Klado

For example, in $\text{C}_2\text{B}_7\text{H}_{13}$, m is 9, while electron pairs are $2 \times \text{CH} + 7 \times \text{BH} + 4 \times \text{H} = 6 + 14 + 4 = 24$ or 12 pairs. The number of framework electron pairs are $9 + 3 = 12$; hence the structure is arachno.

➤ **5n Rule**

If electrons per vertex are approaches 5, the $5n$ rule is used based on a different series of polyhedra known as the 3-connected polyhedra, in which each vertex is connected to 3 other vertices.

Table 10. Base polyhedrons for structure prediction using $5n$ rule.

No. of Vertex	Polyhedron	No. of Vertex	Polyhedron
4	Tetrahedron	14	Dual of triaugmented triangular
6	Trigonal prism	16	Square truncated trapezohedron
8	Cube	18	Dual of edge-contracted icosahedron
10	Pentagonal prism	20	Dodecahedron
12	D_{2d} pseudo-octahedron		

The $5n$ rules are as follows:

Table 11. Electron count and predicted structure using $5n$ rule.

Electron count	Predicted structure
$5n$	n -vertex 3-connected polyhedron
$5n + 1$	$n - 1$ vertex 3-connected polyhedron with one vertex inserted into an edge
$5n + 2$	$n - 2$ vertex 3-connected polyhedron with two vertexes inserted into an edge
$5n + k$	$n - k$ vertex 3-connected polyhedron with k vertex inserted into an edge

Examples: i) P_4S_3 : Electron count = $4 \times$ number of valence electron of P + $3 \times$ number of valence electrons of S = $4 \times 5 + 3 \times 6 = 38$ electrons. Since $n = 7$, $5n + 3 = 38$. Three vertices are inserted into edges.

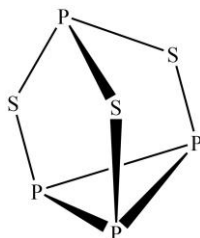


Figure 15. Structure of P_4S_3 .

ii) P_4O_6 : Electron count = $4 \times$ number of valence electron of P + $6 \times$ number of valence electrons of O = $4 \times 5 + 6 \times 6 = 56$ electrons. Since $n = 10$, $5n + 6 = 56$. Six vertices are inserted into edges.

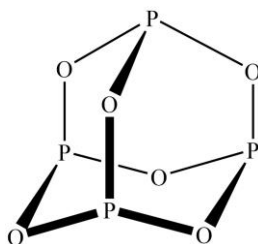


Figure 16. Structure of P_4O_6 .

➤ $6n$ Rule

If the electron count per vertex is about 6, a $6n$ rule is used for structure prediction. This is because structures based on $4n$ or $5n$ rules would become unstable if the number of electron approaches 6, and clusters tend to give structures governed by the $6n$ rules. The rules for the $6n$ structures are as follows:

Table 12. Electron count and predicted structure using $6n$ rule.

Electron count	Predicted structure
$6n - k$	n -membered ring with $k/2$ transannular bonds
$6n - 4$	n -membered ring with 2 transannular bonds
$6n - 2$	n -membered ring with 1 transannular bond
$6n$	n -membered ring
$6n + 2$	n -membered chain (n -membered ring with 1 broken bond)

Examples: i) S_8 : Electron count = $8 \times$ number of valence electron of S = 48 electrons. Since $n = 8$, $6n = 48$. Therefore, the cluster is an 8-membered ring.

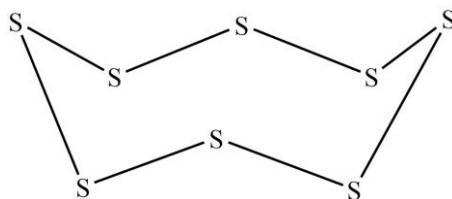


Figure 17. Structure of S_8 .

ii) C_6H_{14} : Electron count = $6 \times$ number of valence electron of C + $14 \times$ number of valence electrons of H = $6 \times 4 + 14 \times 1 = 38$ electrons. Since $n = 6$, $6n + 2 = 38$. Therefore, the cluster is a 6-membered chain.



Figure 18. Structure of C_6H_{14} .

It is also worth mentioning that Wade's rules not only rationalized the structures of a vast number of cluster compounds but they have also stimulated further research in cluster chemistry.

❖ Carboranes

Carboranes are the cluster composed of carbon, boron and hydrogen atoms; and just like boranes, can be classified as closo-, nido-, arachno-, hypho-, or -klado based on whether they represent a complete (closo) polyhedron, or a polyhedron that is missing one (nido-), two (arachno-), or more vertices. Carboranes are the most common examples of heteroboranes. The electronic structure of carboranes has been described by Wade-Mingos rules. Three main categories of carboranes are discussed below.

➤ Closo-(Closed) Carboranes

These are closed triangular polyhedral structures in which all the vertices of the triangular polyhedral geometries are occupied mainly by boron and some sites by carbon atoms. There are $n+1$ electron pairs (or $4n+2$ skeletal electrons) involved in multicentre bonding in closo-carborane; where n represents the total number of B and C atoms. Some of the common examples of closo-carboranes are:

1. $C_2B_{10}H_{12}$: 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 to the skeletal structure. Thus, there are 13 electron pairs ($n+1 = 13$) present in the multicentre bonding orbitals of $C_2B_{10}H_{12}$, confirming this as a closo kind. Three isomers (ortho-, meta- and para-) are possible.

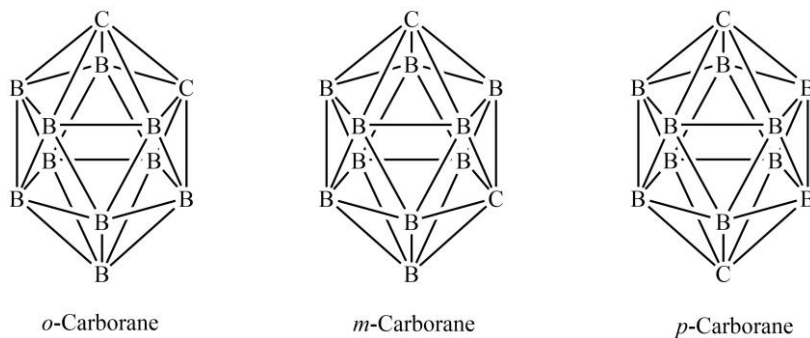


Figure 19. Structure and isomerism in $C_2B_{10}H_{12}$ (dicarba-closo-dodecaborane).

2. $C_2B_3H_5$: In $C_2B_3H_5$, $n = 5$; according to Wade's rule, the two CH units contribute $2 \times 3 = 6$ electrons and three BH units contribute $3 \times 2 = 6$ electrons to the bonding molecular orbitals or the skeletal structure. Thus there are 6 electron pairs ($n+1 = 6$) present in the multicentre bonding orbitals of $C_2B_3H_5$, confirming this as closo kind. Three isomers are possible which are given below.

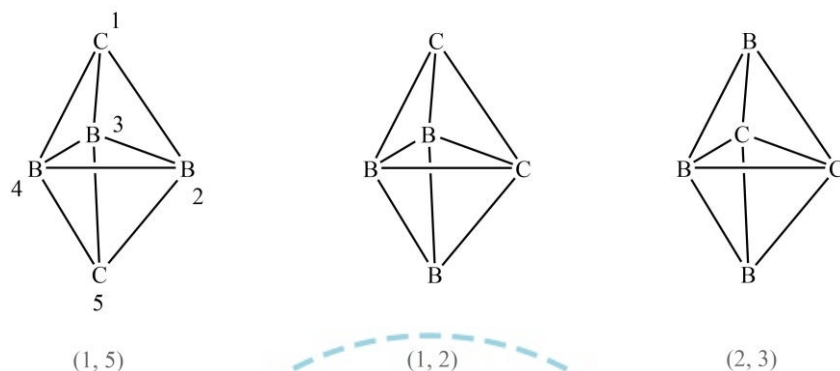


Figure 20. Structure and isomerism in $C_2B_3H_5$.

➤ **Nido-(Nestlike) Carboranes**

These are nest-like geometries and can be assumed as the derivatives of closed triangular polyhedral structures in which one vertex is removed. Most of the sites in these clusters are occupied by boron atoms while some sites by carbons. There are $n+2$ electron pairs (or $4n+4$ skeletal electrons) involved in multicentre bonding in nido-carboranes; where n represents the total number of B and C atoms. Common examples are:

1. $C_2B_9H_{13}$: In $C_2B_9H_{13}$, $n = 11$; and according to Wade's rule, the two CH units contribute $2 \times 3 = 6$ electrons, nine BH units contribute $9 \times 2 = 18$ electrons, and two additional hydrogens contribute $2 \times 1 = 2$ electrons to the bonding molecular orbitals or the skeletal structure. Thus there are total 26 electrons or 13 electron pairs ($n+2 = 13$) present in the multicentre bonding orbitals of $C_2B_9H_{13}$, confirming this as nido kind. The structure of some of the possible isomers that can be obtained experimentally are given below.

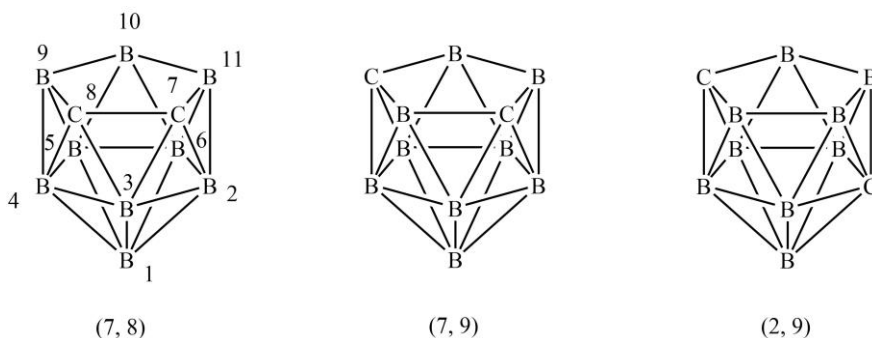


Figure 21. Structure and isomerism in $C_2B_9H_{13}$.

2. $C_2B_4H_8$: In $C_2B_4H_8$, $n = 6$; according to Wade's rule, the two CH units contribute $2 \times 3 = 6$ electrons and three BH units contribute $4 \times 2 = 8$ electrons and two additional hydrogens contribute $2 \times 1 = 2$ electrons to the bonding molecular orbitals or the skeletal structure. Thus there are total 16 electrons or 8 electron pairs ($n+2 = 8$) present in the multicentre bonding orbitals of $C_2B_4H_8$, confirming this as a nido kind. The structure of some of the possible isomers that can be obtained experimentally are given below.

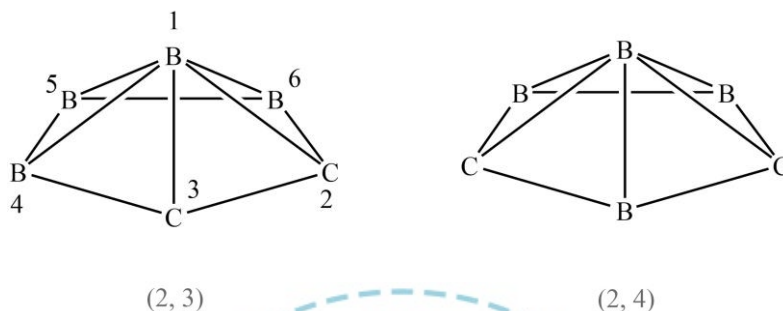


Figure 22. Structure and isomerism in $C_2B_4H_8$.

➤ **Arachno-(Weblike) Carboranes**

These are web-like geometries and can be assumed as the derivatives of closed triangular polyhedral structures in which two vertices are removed. Most of the sites in these clusters are occupied by boron atoms while some sites by carbons. There are $n+3$ electron pairs (or $4n+6$ skeletal electrons) involved in multicentre bonding in arachno-carboranes; where n represents the total number of B and C atoms. Some of the common examples of arachno-carboranes are:

1. $C_2B_6H_{12}$: In $C_2B_6H_{12}$, $n = 8$; according to Wade's rule, the two CH units contribute $2 \times 3 = 6$ electrons and six BH units contribute $6 \times 2 = 12$ electrons and four additional hydrogens contribute $4 \times 1 = 4$ electrons to the bonding molecular orbitals or the skeletal structure. Thus there are total 22 electrons or 11 electron pairs ($n+3 = 11$) present in the multicentre bonding orbitals of $C_2B_6H_{12}$, confirming this as an arachno kind. The structure of some of the possible isomers that can be obtained experimentally are given below.

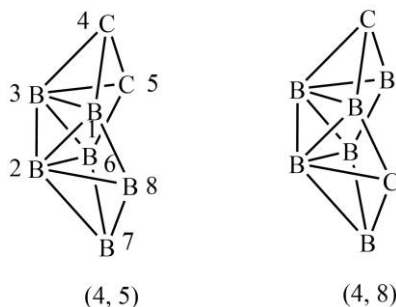


Figure 23. Structure and isomerism in $C_2B_6H_{12}$.

2. $C_2B_7H_{13}$: In $C_2B_7H_{13}$, $n = 9$; according to Wade's rule, the two CH units contribute $2 \times 3 = 6$ electrons and seven BH units contribute $7 \times 2 = 14$ electrons and four additional hydrogens contribute $4 \times 1 = 4$ electrons to the bonding molecular orbitals or the skeletal structure. Thus there are total 24 electrons or 12 electron pairs ($n+3 = 12$) present in the multicentre bonding orbitals of $C_2B_7H_{13}$, confirming this as an arachno-kind. The structure of some the possible isomers that can be obtained experimentally are given below.

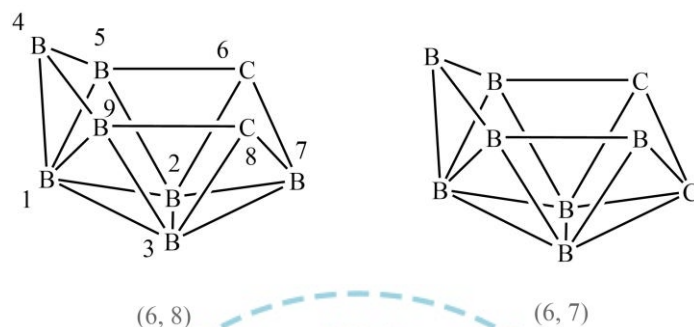


Figure 24. Structure and isomerism in $C_2B_7H_{13}$.

➤ **Structural Pattern Correlation Between Closo, Nido and Arachno Carboranes**

The structural pattern in closo, nido and arachno carboranes for different vertexes and skeletal electron pairs is very much important to to theoretical as well experimental analysis. Hs are omitted for clarity.

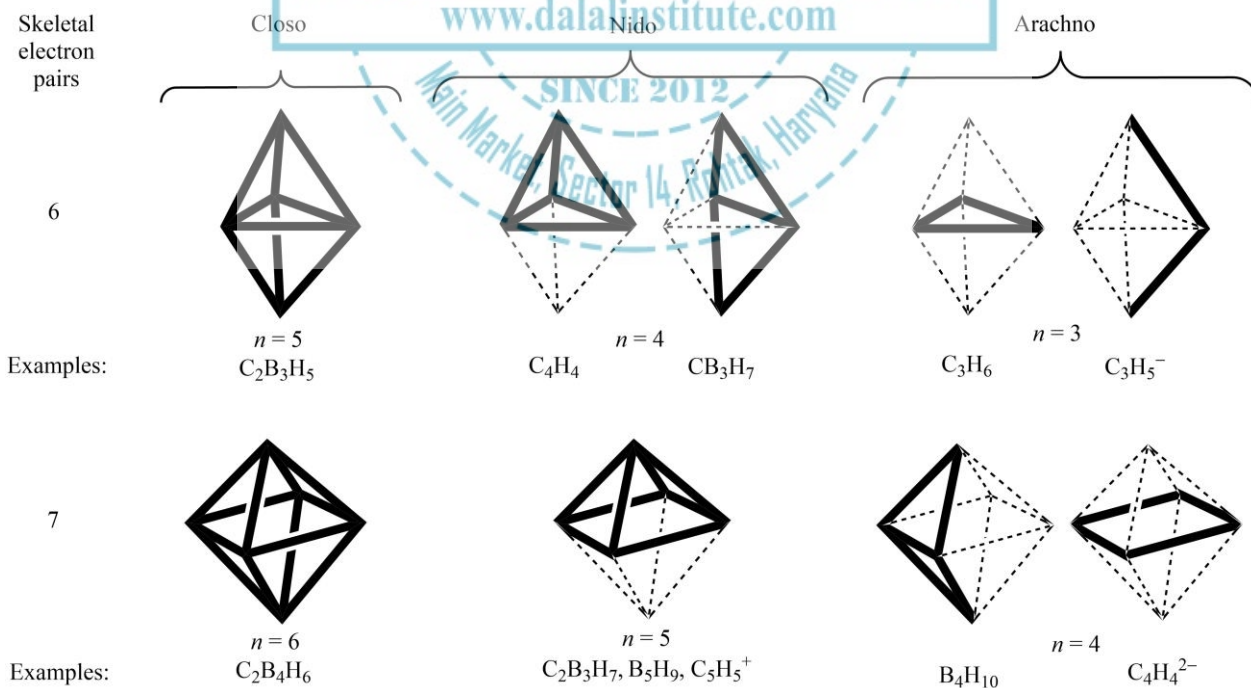


Figure 25. Continued on the next page...

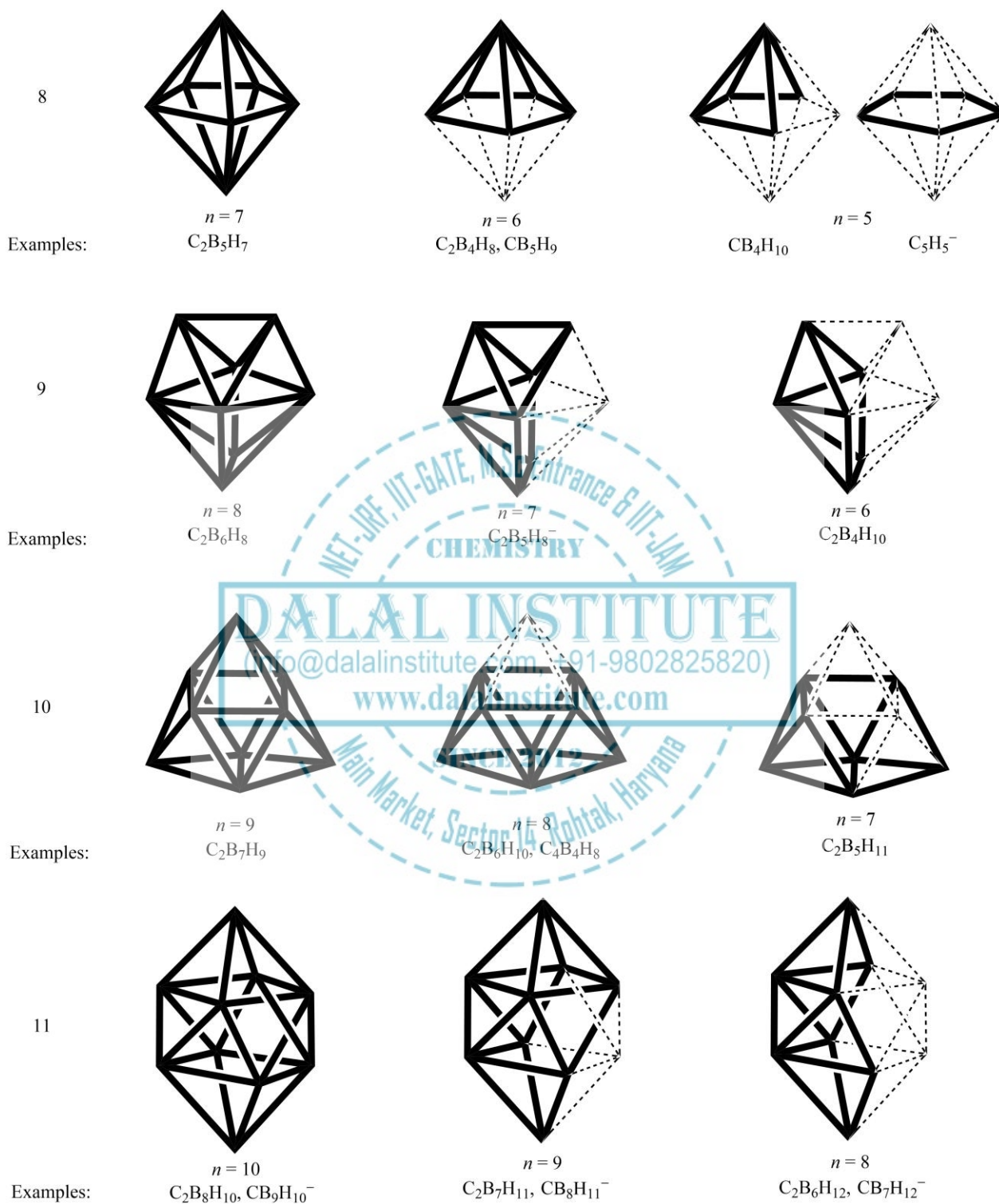


Figure 25. Continued on the next page...

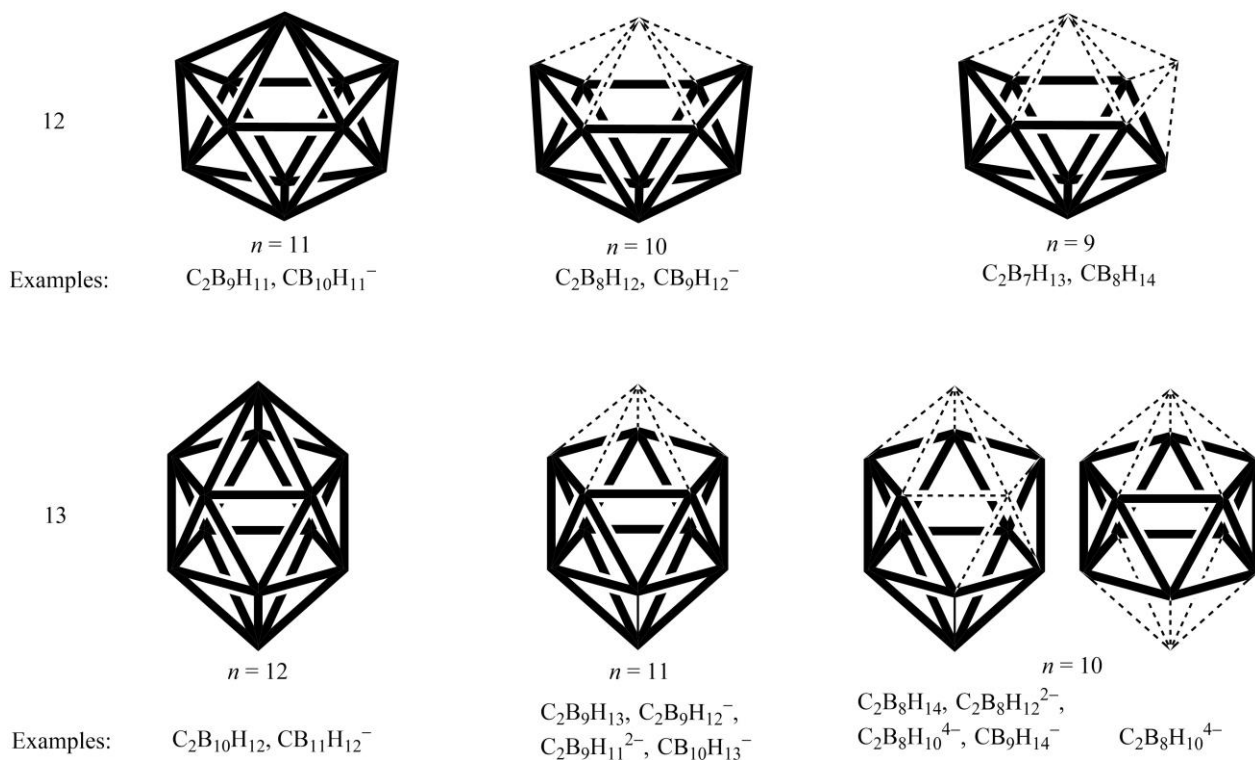


Figure 25. The structural relationship between closo, nido, and arachno carboranes.

Some hypoh-carboranes ($C_2B_{n-2}H_{n+6}$) also do exist in which three vertices from the parent deltahedron are missing. Furthermore, carboranes are also formed by joining two or more preceding types; called as conjuncto-carboranes.

❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters

Metal carbonyl clusters are the metal clusters (two or more metal centers directly bonded to each other) having carbonyl groups as the ligand species. The metal centers in these cluster geometries are actually present in low oxidation state (+1, 0, -1) that can be stabilized by carbonyl ligands. Metal carbonyl clusters are mainly formed by some end-group metal (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) of the *d*-block elements. The primary domain of carbonyl clusters is composed of neutral carbonyls, carbonyl anions, metal carbonyl hydrides. The carbonyl hydride clusters can be obtained from neutral carbonyls by replacing one of the CO groups with two H-groups; while carbonyl anions are derived by replacing CO with one H-atom and one negative charge, or with two negative charge. Metal carbonyl clusters can be classified into two types; low nuclearity carbonyl clusters (LNCC) and high nuclearity carbonyl clusters (HNCC), depending upon the number of metal centers involved in the skeletal framework. If the number of metal centers is in the range of 2–4, they are generally labeled as low nuclearity; while on the other hand, a metal-center number of 5 and

above makes them designable as high nuclearity carbonyl cluster system. Owing to the difference of electron counting scheme from high nuclearity carbonyl clusters, this section will exclusively deal with low nuclearity carbonyl clusters. The rationalization of bonding and structural profile of some important low nuclearity carbonyl clusters on the basis 18-electron scheme is discussed below.

➤ **Dinuclear Carbonyl Clusters:**

The structural framework of dinuclear metal carbonyl clusters is comprised of two metal centers connected by 1 metal-metal bond, and therefore, linear in geometry. The CO groups can be terminal, bridging or both. The most common examples of these are $\text{Co}_2(\text{CO})_8$, $\text{Fe}_2(\text{CO})_9$, $\text{Mn}_2\text{CO}_{10}$, $\text{Tc}_2\text{CO}_{10}$, and $\text{Re}_2\text{CO}_{10}$.

1. $\text{Co}_2(\text{CO})_8$: This cluster is known to exist in two isomers; the first one has a D_{3d} symmetry with one metal-metal bond with zero bridging carbonyl, the second one is of C_{2v} symmetry and has two bridging CO ligands along with one metal-metal bond. The 18-electron count for $\text{Co}_2(\text{CO})_8$ is $2 \times 9 + 8 \times 2 = 34$. Hence, one metal-bond (2 electrons) is needed to fulfill the requirement of two metal centers (36 electrons).



Figure 26. Structures and bonding in $\text{Co}_2(\text{CO})_8$.

2. $\text{Fe}_2(\text{CO})_9$: The structure of $\text{Fe}_2(\text{CO})_9$ exist with D_{3h} symmetry, and contains three bridging CO ligands and six terminal CO groups attached. The 18-electron count for $\text{Fe}_2(\text{CO})_9$ is $2 \times 8 + 9 \times 2 = 34$. Hence, one metal-bond (2 electrons) is needed to fulfill the requirement of two metal centers (36 electrons).

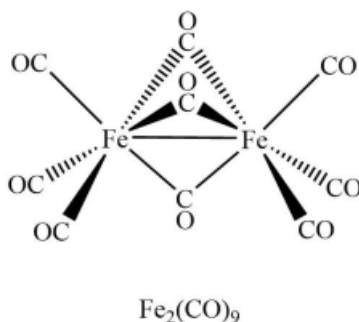
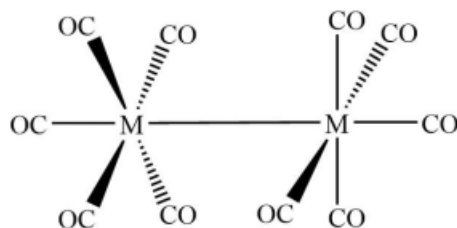


Figure 27. Structures and bonding in $\text{Fe}_2(\text{CO})_9$.

3. $M_2(CO)_{10}$: M_2CO_{10} ($M = Mn, Tc, Re$) exists with D_{4d} symmetry with one metal-metal bond and four CO ligands attached to each of the metal centre. The 18-electron count for M_2CO_{10} ($M = Mn, Tc, Re$) is $2 \times 7 + 10 \times 2 = 34$. Hence, one metal-bond (2 electrons) is needed to fulfill the requirement of two metal centers (36 electrons).



$M_2(CO)_{10}$
 $M = Mn, Tc, Re$

Figure 28. Structures and bonding in M_2CO_{10} ($M = Mn, Tc, Re$).

➤ Trinuclear Metal Carbonyls

The structural framework of trinuclear metal carbonyl clusters is comprised of three metal centers connected by three metal-metal bonds, and therefore, usually trigonal in geometry. The CO groups can be terminal, bridging or both. The most common examples of trinuclear carbonyl clusters are Fe_3CO_{12} , $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ systems.

1. Fe_3CO_{12} : $Fe_3(CO)_{12}$ is different, with two bridging CO ligands, resulting in C_{2v} symmetry. The 18-electron count for $Fe_3(CO)_{12}$ is $3 \times 8 + 12 \times 2 = 48$. Hence, three metal-metal bonds (6 electrons) are needed to fulfill the requirement of three metal centers (54 electrons).

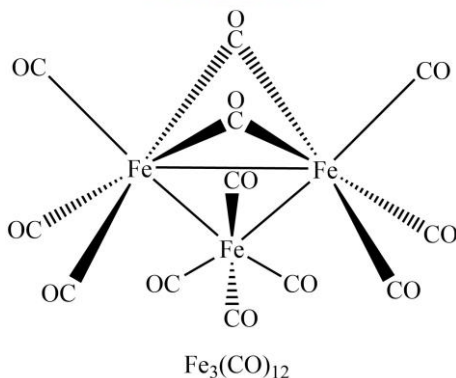


Figure 29. Structures and bonding in $Fe_3(CO)_{12}$.

2. $M_3(CO)_{12}$ ($M = Os, Ru$): For example, the $Ru_3(CO)_{12}$ cluster has D_{3h} symmetry, consisting of an equilateral triangle of Ru atoms, each of which has two axial and two equatorial CO ligands. $Os_3(CO)_{12}$ has the same structure. The 18-electron count for $M_3(CO)_{12}$ ($M = Os, Ru$) is $3 \times 8 + 12 \times 2 = 48$. Hence, three metal-metal bonds (6 electrons) are needed to fulfill the requirement of three metal centers (54 electrons).

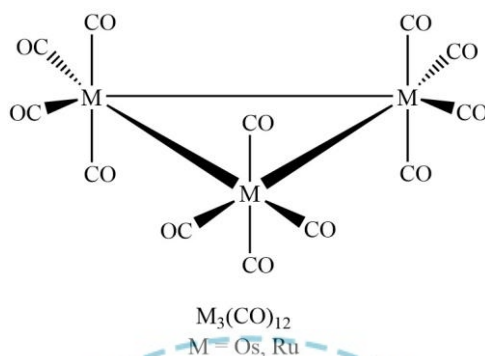


Figure 30. Structures and bonding in $M_3(CO)_{12}$ ($M = Os, Ru$).

➤ Tetranuclear Metal Carbonyls

The structural framework of tetranuclear metal carbonyl clusters is comprised of four metal centers connected by four to six metal-metal bonds, and therefore, usually tetrahedral in geometry. The CO groups can be terminal, bridging or both. The most common examples of tetranuclear carbonyl clusters are $Ir_4(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Re_4CO_{16}^{2-}$, $Ru_3(CO)_{12}$ and $Os_4(CO)_{16}$ systems.

1. $Ir_4(CO)_{12}$: The $Ir_4(CO)_{12}$ has perfect T_d symmetry with no bridging CO ligands groups. The 18-electron count for $Ir_4(CO)_{12}$ is $4 \times 9 + 12 \times 2 = 60$. Hence, six metal-metal bonds (12 electrons) are needed to fulfill the requirement of four metal centers (72 electrons).

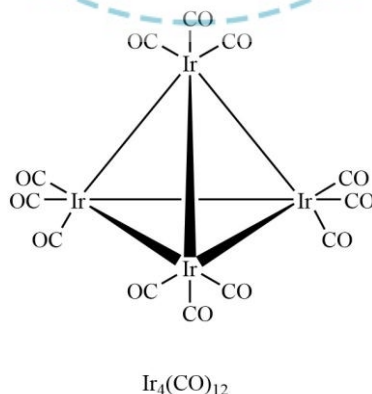


Figure 31. Structures and bonding in $Ir_4(CO)_{12}$.

2. M_4CO_{12} (M = Co, Rh): M_4CO_{12} (M = Co, Rh) is consisted of a tetrahedral M_4 core, but the molecular symmetry is C_{3v} . Three carbonyl ligands are bridging ligands and nine are terminal. The 18-electron count for $M_4(CO)_{12}$ (M = Co, Rh) is $4 \times 9 + 12 \times 2 = 60$. Hence, six metal-metal bonds (12 electrons) are needed to fulfill the requirement of four metal centers (72 electrons).

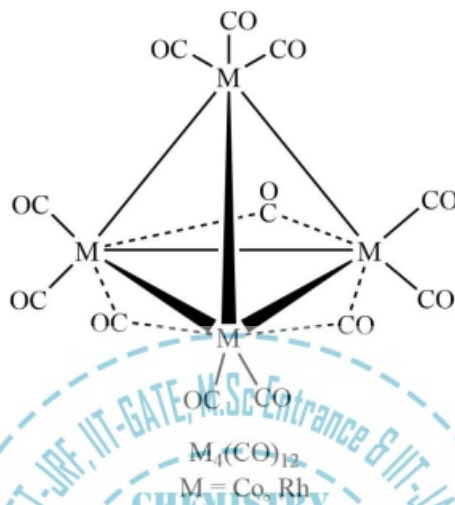


Figure 32. Structures and bonding in $M_4(CO)_{12}$ (M = Co, Rh).

3. $[Re_4(CO)_{16}]^{2-}$: $[Re_4(CO)_{16}]^{2-}$ has D_{2h} symmetry with no bridging carbonyl. The 18-electron count for $[Re_4(CO)_{16}]^{2-}$ is $4 \times 7 + 16 \times 2 + 2$ (charge) = 62. Hence, five metal-metal bonds (10 electrons) are needed to fulfill the requirement of four metal centres (72 electrons).

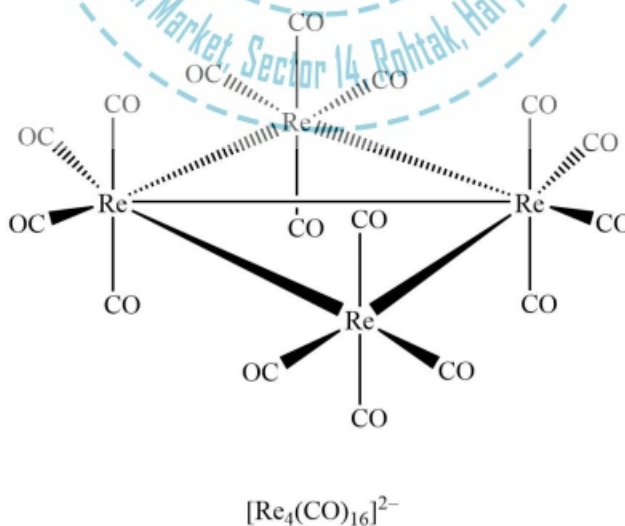


Figure 33. Structures and bonding in $[Re_4(CO)_{16}]^{2-}$.

4. $\text{Os}_4(\text{CO})_{16}$: The tetranuclear $\text{Os}_4(\text{CO})_{16}$ is analogous to cyclobutane with a puckered structure. The X-ray diffraction analysis of $\text{Os}_4(\text{CO})_{14}$ unveiled an irregular tetrahedral Os_4 skeleton with four weakly semi-bridging CO groups and four different Os–Os bond lengths. The 18-electron count for $\text{Os}_4(\text{CO})_{16}$ is $4 \times 8 + 16 \times 2 = 64$. Hence, four metal-metal bonds (8 electrons) are needed to fulfill the requirement of four metal centers (72 electrons).

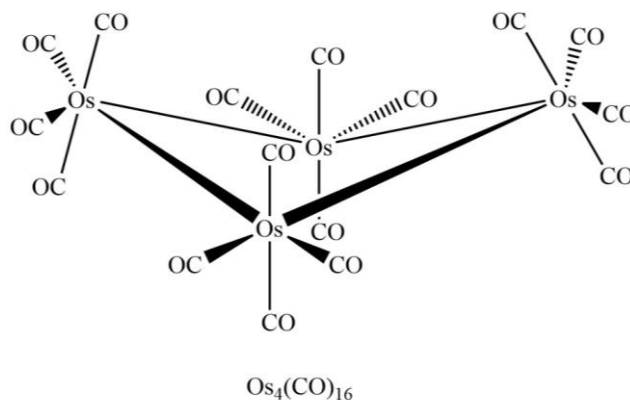


Figure 34. Structures and bonding in $\text{Os}_4(\text{CO})_{16}$.

It is worthy to note that the electron counting scheme in low nuclearity carbonyl clusters is the same as that is used in mononuclear metal carbonyl complexes.

❖ Total Electron Count (TEC)

The simple 18-electron rule has been proven of great significance in the case of structural rationalization of low nuclearity carbonyl clusters. However, if the number of metal centers per cluster is equal or greater than five; then the conventional approach is not significant, and does not provide any satisfactory results. For example, the 18-electron count for $\text{Rh}_6(\text{CO})_{16}$ is $6 \times 9 + 16 \times 2 = 86$; which means that eleven metal-metal bonds ($108 - 86 = 22$) are needed to fulfil the requirement of six metal centres. But the actual structure of $\text{Rh}_6(\text{CO})_{16}$ is consisted of an octahedral Rh_6 core with twelve metal-metal bonds. Moreover, simple 18-electron treatment for high nuclearity carbonyl clusters (HNCC) does not provide any information regarding the overall geometry. The situation also becomes more and more complex if some encapsulated heteroatom like carbon is also present. Therefore, because of the lacking of any rational solution for the electronic structure of high nuclearity carbonyl clusters, most of the efforts have been devoted to find a correlation between their structure and the number of electrons available for cluster binding. It is worthy to mention that high-nuclearity carbonyl clusters are also considered as electron-deficient compounds; which is obviously due to the inadequate number of electrons to allow the assignment of all bonds as 2-centre 2-electron in nature.

➤ **Isolobal Analogy Between $M(\text{CO})_3$ And BH Fragments**

A British chemist, Kenneth Wade, solved the unexplained problem of structure and bonding predictions in high nuclearity carbonyl clusters by developing a new scheme of electron counting, total electron count (TEC). This new proposal was actually the extension of his previously used scheme for boranes and carboranes, in which he had correlated the structure of boranes and their derivatives with the number of electrons involved in the skeletal framework. The idea behind this extension was that the $M(\text{CO})_3$ unit is actually isolobal with the BH unit. This can be better explained by taking the example of $\text{Ru}(\text{CO})_3$ fragment.

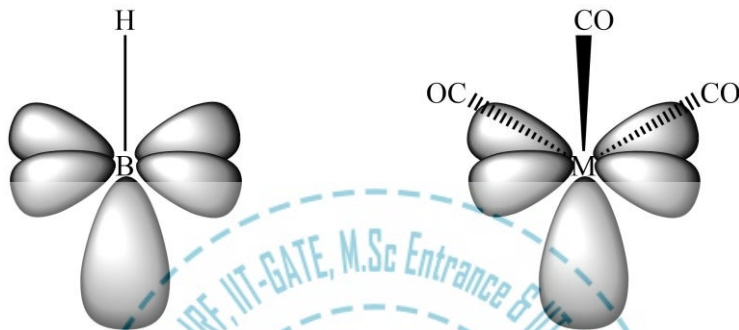


Figure 35. Structures and bonding in the isolobal pair of BH and $\text{Ru}(\text{CO})_3$.

The BH unit uses one of four valence orbitals of boron and two electrons, one from boron and one from hydrogen. Hence, the spare valence orbitals and corresponding electrons left on boron are three and two respectively. These spare orbitals and electrons are then used in cluster bonding. Similarly, the $\text{Ru}(\text{CO})_3$ unit uses six of nine valence orbitals of ruthenium and twelve electrons, six from ruthenium and six from three carbonyl ligands. Therefore, the spare valence orbitals and corresponding electrons left on ruthenium are three and two respectively.

Therefore, $3n$ valence orbitals and $2n$ electrons should be available in any B_nH_n cluster system. The overlap of $2n$ valence orbitals oriented towards the surface of the polyhedron generates n bonding and n antibonding molecular orbitals. The overlap of n valence orbitals oriented towards the core of the polyhedron generates 1 strongly bonding and $n-1$ weakly bonding, nonbonding or antibonding molecular orbitals. Thus we can say that a total of $n+1$ bonding molecular orbitals are generated in the process of cluster formation, and the number of electrons required to fill these bonding molecular orbitals is $2n+2$. However, in n BH units of B_nH_n cluster can supply only $2n$ electron, explain why $\text{B}_n\text{H}_n^{2-}$ or cluster is more stable than simple B_nH_n . The same argument holds true about $\text{Ru}_n(\text{CO})_{3n}$ cluster system, i.e. $2n+2$ electrons are needed to fill all the bonding molecular orbitals. Hence, $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ anion would be more stable than $\text{Ru}_6(\text{CO})_{18}$ cluster system.

➤ **Electron Counting Scheme for High Nuclearity Carbonyl Clusters**

The isolobal analogy of $M(\text{CO})_3$ fragment with B–H (or C–H) unit inspired Kenneth Wade to explore this field further; and he of course then came with a new set of rules for electron counting in high nuclearity carbonyl cluster systems. He suggested that the total electron count of these clusters can be correlated to

skeletal electron count participating in the cluster bonding in a similar way adopted in boranes or carboranes. The total electron count can be calculated by adding the following contributions:

- i) The number of valence electrons of all metal-centers.
- ii) Two electrons for each carbonyl group irrespective of the fact whether it is terminal or bridged.
- iii) One electron for each unit of negative charge.
- iv) The number of valence electrons of each hetero or interstitial atoms like carbon or nitrogen.

This total electron count then can be used to predict the structure and bonding of carbonyl cluster systems by extracting the skeletal electron count. Now, as we know that $2n+2$, $2n+4$, $2n+6$ skeletal electrons are required for closo, nido and arachno boranes, respectively; the same is true for metal carbonyl clusters. However, in addition to the 2 valence electrons to be used in the skeletal framework, each $M(CO)_3$ also contains 12 non-skeletal electrons. The theoretical basis of this claim comes from the fact that each $M-CO$ bond contains 4 electrons; 2 σ -electrons donated by CO ligand to the metal, and 2 π -electrons donated by the metal back to the lowest unoccupied antibonding molecular orbital of CO ligand. This gives a total electron count for closo polyhedron as $12n + 2(n+1)$. Hence, the predictions of structure and bonding in high nuclearity carbonyl cluster with n vertexes can be summed up only after considering these twelve non-skeletal electrons.

Table 9. Total electron count (TEC) and predicted structure.

Total electron count	Name	Predicted structure
$12n + 2(n - 1)$	Bicapped closo	$n - 2$ vertex closo polyhedron with 2 capped faces
$12n + 2n$	Capped closo	$n - 1$ vertex closo polyhedron with 1 face capped
$12n + 2(n + 1)$	Closo	Closo polyhedron with n vertices
$12n + 2(n + 2)$	Nido	$n + 1$ vertex closo polyhedron with 1 missing vertex
$12n + 2(n + 3)$	Arachno	$n + 2$ vertex closo polyhedron with 2 missing vertex
$12n + 2(n + 4)$	Hypho	$n + 3$ vertex closo polyhedron with 3 missing vertex
$12n + 2(n + 5)$	Klado	$n + 4$ vertex closo polyhedron with 4 missing vertex

It should also be noted that Wade's predictions based on total electron count are also applicable to low nuclearity carbonyl cluster systems in which the number of metal centers present is three or four. For example, the total electron count for $Ir_4(CO)_{12}$ is $4 \times Ir + 12 \times CO = 4 \times 9 + 12 \times 2 = 60$. Since $n = 4$, $12n + 2(n + 2) = 60$, so the cluster is nido. Starting from a trigonal bipyramid, a vertex is removed. Similarly, the total electron count for $Fe_3(CO)_{12}$ is $3 \times Fe + 12 \times CO = 3 \times 8 + 12 \times 2 = 48$. Since $n = 3$, $12n + 2(n + 3) = 48$, so the cluster is arachno. Therefore, the structure prediction Starts from a trigonal bipyramid, and then two axially opposite vertexes are removed.

➤ **Structure and Bonding Profile of Some Typical High Nuclearity Carbonyl Clusters Using TEC**

As we have already discussed the fundamentals of structure and bonding in high nuclearity carbonyl clusters systems, now we will implement those ideas to explain some typical examples.

1. $M_6(CO)_{16}$ ($M = Co, Rh$): The total electron count for $Rh_6(CO)_{16}$ is $6 \times Rh + 16 \times CO = 6 \times 9 + 16 \times 2 = 86$. Since $n = 6$, $12n + 2(n + 1) = 86$, so the cluster is closo. Therefore, the structure prediction starts from an idealized octahedron. The predicted structure for $Rh_6(CO)_{16}$ cluster system is shown below.

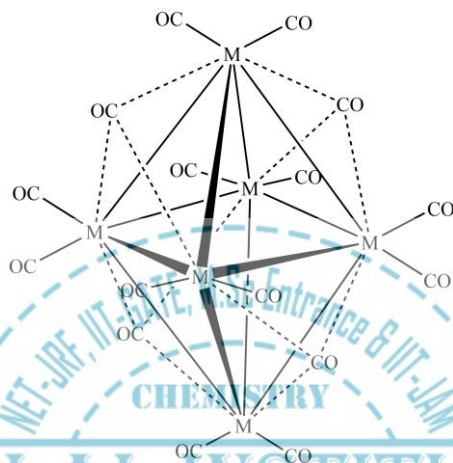


Figure 36. Structure of $M_6(CO)_{16}$ ($M = Co, Rh$).

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2. $Os_5(CO)_{16}$: The total electron count for $Os_5(CO)_{16}$ is $5 \times Os + 16 \times CO = 5 \times 8 + 16 \times 2 = 72$. Since $n = 5$, $12n + 2(n + 1) = 72$, so the cluster is closo. Therefore, the structure prediction starts from an idealized trigonal bipyramid. The predicted structure for $Os_5(CO)_{16}$ cluster system is shown below.

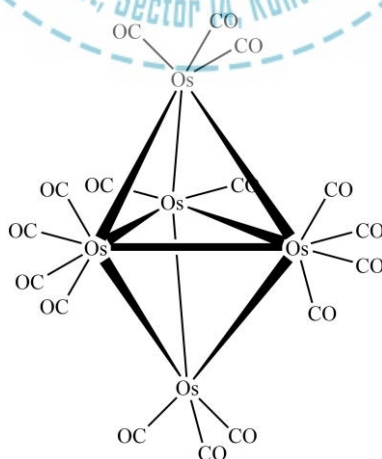


Figure 37. Structure of $Os_5(CO)_{16}$.

3. $[\text{Os}_6(\text{CO})_{18}]^{2-}$: The total electron count for $[\text{Os}_6(\text{CO})_{18}]^{2-}$ is $6 \times \text{Os} + 18 \times \text{CO} + 2$ (for negative charge) = $6 \times 8 + 18 \times 2 + 2 = 86$. Since $n = 6$, $12n + 2(n + 1) = 86$, so the cluster is closo. Therefore, the structure prediction starts from an idealized octahedron. The predicted structure for $[\text{Os}_6(\text{CO})_{18}]^{2-}$ cluster system is shown below.

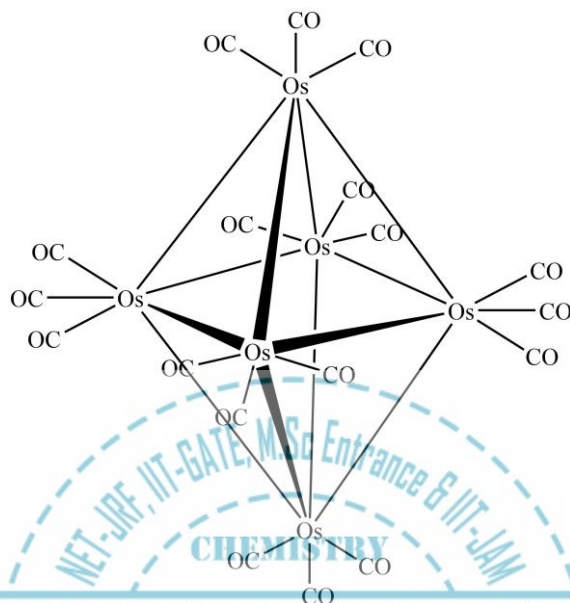


Figure 38. Structure of $[\text{Os}_6(\text{CO})_{18}]^{2-}$.

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4. $\text{Os}_5\text{C}(\text{CO})_{15}$: The total electron count for $\text{Os}_5\text{C}(\text{CO})_{15}$ is $5 \times \text{Os} + 15 \times \text{CO} + 1 \times \text{C} = 5 \times 8 + 15 \times 2 + 4 \times 1 = 74$. Since $n = 5$, $12n + 2(n + 2) = 74$, so the cluster is nido. Therefore, the structure prediction starts from an idealized octahedron, and then one vertex is removed. The predicted structure for $\text{Os}_5\text{C}(\text{CO})_{15}$ cluster system is shown below.

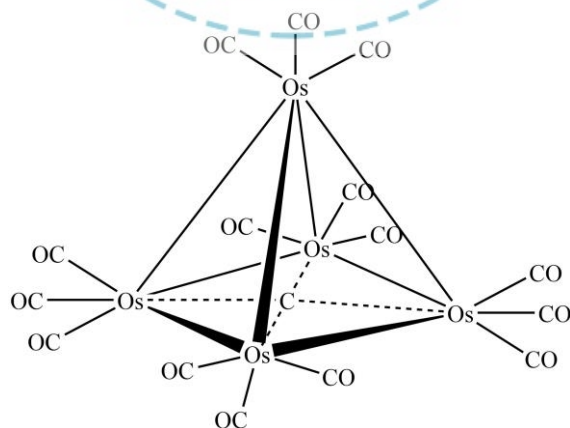


Figure 39. Structure of $\text{Os}_5\text{C}(\text{CO})_{15}$.

5. $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$: The total electron count for $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ is $6 \times \text{Ru} + 16 \times \text{CO} + 1 \times \text{N} + 1$ (for negative charge) = $6 \times 8 + 16 \times 2 + 1 \times 5 + 1 = 86$. Since $n = 6$, $12n + 2(n + 1) = 86$, so the cluster is closo. Therefore, the structure prediction starts from an idealized octahedron. The predicted structure for $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$ cluster system is shown below.

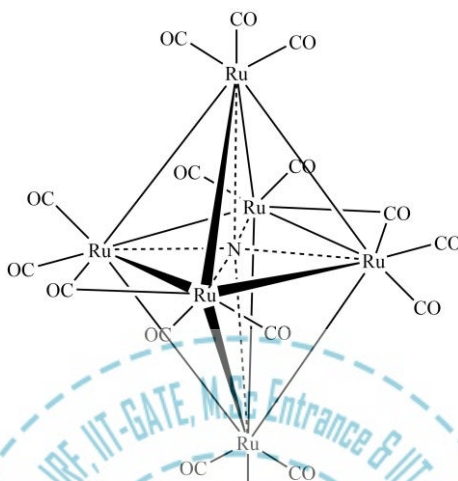


Figure 40. Structure of $[\text{Ru}_6\text{N}(\text{CO})_{16}]^-$.

6. $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$: The total electron count for $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ is $4 \times \text{Fe} + 12 \times \text{CO} + 1 \times \text{N} + 1$ (for negative charge) = $4 \times 8 + 12 \times 2 + 1 \times 5 + 1 = 62$. Since $n = 4$, $12n + 2(n + 3) = 62$, so the cluster is arachno. Therefore, the structure prediction starts from an idealized octahedron, then two adjacent vertexes are removed. The predicted structure for $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ cluster system is shown below.

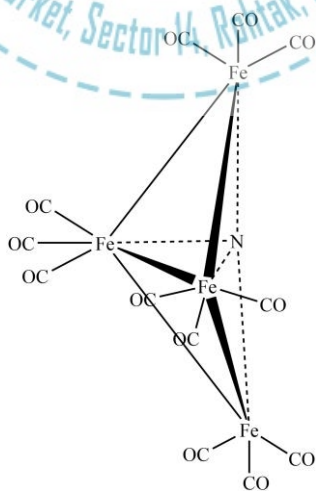


Figure 41. Structure of $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$.

➤ **Correlation Between TEC and SEP**

The implementation of the rules listed in 'Table 9' is more often carried out in reverse gear, i.e. 12 electrons for each metal center are subtracted from the total electron count. The number of electrons thus obtained is then divided by 2 to get skeletal electron pairs. The number of skeletal electron pairs (SEP) can be calculated using equation (23) as described below:

$$\text{SEP} = \frac{1}{2}(\text{TEC} - 12 \text{ electrons per metal center}) \quad (23)$$

Now the structure prediction of some common high nuclearity carbonyl cluster systems on the correlative basis of total electron count (TEC) and skeletal electron pairs (SEP) can be summed up as:

Table 10. Structure prediction of some common clusters on the correlative basis of TEC and SEP.

Carbonyl cluster	Total electron count (TEC)	Skeletal electron pairs (SEP)	Vertex in parent polyhedron	Predicted structure
$\text{Rh}_6(\text{CO})_{16}$	$(6 \times 9) + (16 \times 2) = 86$	$0.5 \times [86 - (6 \times 12)] = 7$	6	Closo
$\text{Os}_5(\text{CO})_{16}$	$(5 \times 8) + (16 \times 2) = 72$	$0.5 \times [72 - (5 \times 12)] = 6$	5	Closo
$\text{Os}_5\text{C}(\text{CO})_{15}$	$(5 \times 8) + (15 \times 2) + (4) = 74$	$0.5 \times [74 - (5 \times 12)] = 7$	5	Nido
$[\text{Fe}_4\text{C}(\text{CO})_{12}]^{2-}$	$(4 \times 8) + (12 \times 2) + (4) + (2) = 62$	$0.5 \times [62 - (4 \times 12)] = 7$	6	Arachno
$[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$	$(4 \times 8) + (12 \times 2) + (3) + (1) = 60$	$0.5 \times [60 - (4 \times 12)] = 6$	5	Nido
$[\text{Ru}_5\text{N}(\text{CO})_{14}]^-$	$(5 \times 8) + (14 \times 2) + (5) + (1) = 74$	$0.5 \times [74 - (5 \times 12)] = 7$	7	Nido
$[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$	$(4 \times 8) + (12 \times 2) + (5) + (1) = 62$	$0.5 \times [62 - (4 \times 12)] = 7$	6	Arachno

Finally, it should also be noted that the total electron counting scheme is applicable to most of the high nuclearity carbonyl cluster systems, yet the exceptions like $[\text{Ni}_5(\text{CO})_{12}]^{2-}$ do exist.

❖ Problems

- Q 1. Discuss the molecular orbital treatment of three-center two-electron bond in detail.
- Q 2. What are the STYX numbers? How would you use the Lipscomb's model to find out the STYX code for B_4H_{10} cluster system?
- Q 3. Draw and discuss the structure and bonding in B_5H_9 and B_5H_{11} .
- Q 4. How many B–H–B and B–B–B bonds are present in $B_{10}H_{14}$ cluster?
- Q 5. Discuss the structural relationship between closo, nido and arachno type boranes.
- Q 6. What are Wade's rules? How can we use these rules to predict the structures of $B_5H_5^{4-}$ and P_4 clusters?
- Q 7. What are carboranes? Explain with suitable examples.
- Q 8. Draw and discuss the structural pattern correlation between closo, nido and arachno type carboranes.
- Q 9. What are the low nuclearity carbonyl clusters? How do they differ from the high nuclearity ones?
- Q 10. How would you calculate the number of metal-metal bonds in $Fe_3(CO)_{12}$ and $Ir_4(CO)_{12}$?
- Q 11. Define total electron count (TEC).
- Q 12. Explain the electron counting scheme for high nuclearity carbonyl clusters in detail.
- Q 13. How would you explain the isolobal Analogy Between $Ru(CO)_3$ And BH units?
- Q 14. Using total electron count (TEC), explain the structure of $Rh_6(CO)_{16}$ and $Os_5C(CO)_{15}$.
- Q 15. Describe the correlation between total electron count (TEC) and skeletal electron pairs (SEP), and use same to predict the structures of $[Fe_4N(CO)_{12}]^-$ and $[H_3Ru_4(CO)_{12}]^-$.

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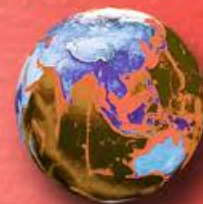
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