

Class - P.B.T. Sem II

Subject - Chemistry

Paper - CC-VI

Unit - IV

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Metal clusters - II

WADE RULE - A way of correlating the number of framework electrons with structure was first of all introduced with by Wade. It is a polyhedral skeletal electron pair theory. This rule may applied in the structure of boranes and carboranes. Form work for these structure may be determined through following formula

$$F = 3b + 4c + h + x - 2n$$

where b = the number of boron atoms

c = the number of carbon atoms

h = the number of hydrogen atoms.

x = the amount of negative

charge on the ion.

$n =$ the number of vertices
that is $b+c$.

RULE 1. — When the value of F is equal to the quantity $(2n+2)$, the substances should have a ~~cot~~ ~~cot~~ close structure i.e. the framework geometry is based on an n vertex triangulated regular polyhedron. This result is obtained for all of the boron dianion ($B_n H_n^{2-}$), for the carboranes anions ($C B_{n-1} H_n^-$) for neutral carboranes ($C_2 B_{n-2} H_n$).
For $B_6 H_6^{2-}$, the value of F is

$$F = 3 \times 6 + 4 \times 0 + 6 + 2 - 2 \times 6 \\ = 14.$$

Since the quantity $(2n+2)$ is also equal to 14, thus we have identified this ($B_6 H_6^{2-}$) as close structure. Similarly for the carborane $C_2 B_4 H_6$, we have

$$F = 3 \times 4 + 4 \times 2 + 6 + 0 - 2 \times 6 \\ = 14.$$

So, the structure of B_3H_6 is also a closo structure.

Rule - 2 — If we remove one boron atom from a vertex of a closo structure a nest or cup like structure is obtained. Such structures are known as nido structures to satisfy the valencies of the corresponding boron atoms extra hydrogen atoms are added. Thus the nido structures obey the framework electron formula $P = (2n+4)$. For example in the case of B_5H_9 , there are five B-H bonds which contributes two electrons each and four extra hydrogen atoms will contribute four electrons for a total of 14 ($2n+4$, $P=5$). The four H-atoms form bridges across the open edges of the nest. This corresponds to $7(n+2)$ electron pairs and the geometry will be derived from an octahedron ($n+1$) vertices. Thus

we can explain the square pyramid nido structure is derived from the close octahedron

Rule-3. - When the value of F is equal to the quantity $(2n+6)$ the compound have arachno structure. If we remove two vertex boron atoms then we get arachno structure. Therefore pentaborane(1) have formula $2n+6$ ($n=3$ electron pairs)

Wade rule for close, nido and arachno structures regarding $2n+2$, $2n+4$ and $2n+6$ may be justified as follow:

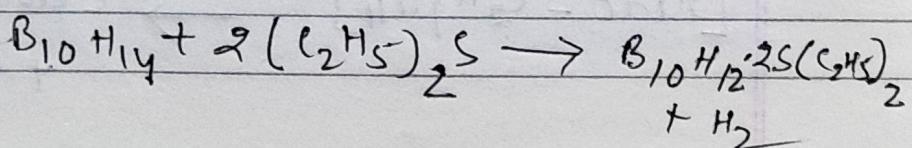
since for a regular delta-hedron having n -vertices, there will be $(n+1)$ molecular orbitals hence the number of electrons are $2n+2$ for close structure.

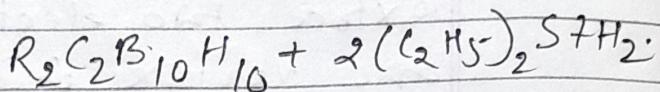
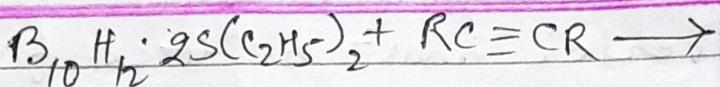
If two more electrons are added i.e $2n+4$, one bonding molecular orbital one vertex must be used for these extra two electrons. Therefore one

vertex must be used for these extra two electrons. therefore one vertex is removed and nido structure is obtained. this idea is extended for arachno structure the number of electrons become $(2n+6)$

CARBORANES — carbon atom is the isoelectronic with B^- or BH , similarly $C-H$ is isoelectronic with BH or BH_2 . The boron atom in a borane may be replaced by carbon atom since they retain isoelectronic system. Its best example is $[B_{12}H_{12}]^2$ and $C_2B_{10}H_{12}$. Thus $C_2B_{10}H_{12}$ is an example of carboranes. it may be synthesized as follow:

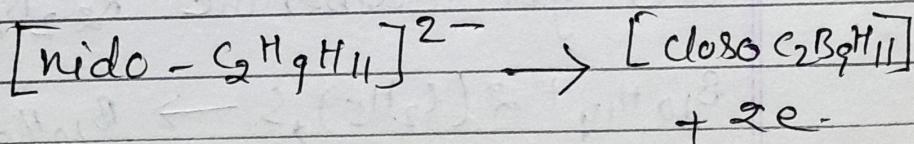
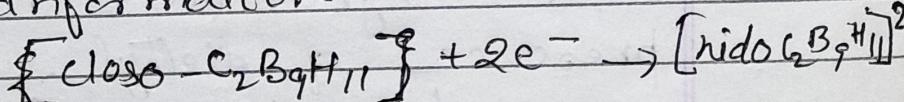
When decaborane(10) reacts with alkynes ($RC \equiv CR$) in the presence of diethyl sulphide we get carborane $R_2C_2B_{10}H_{16}$



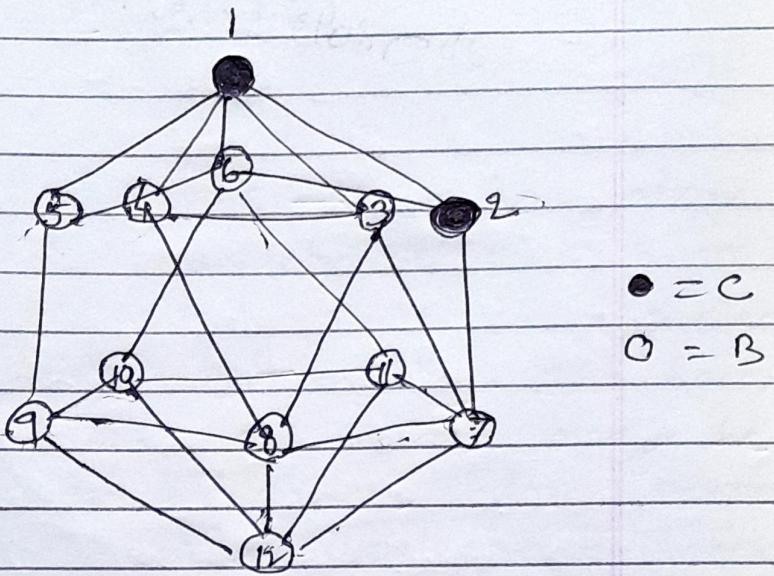


The product is known as ortho-carborane or 1,2-dicarba-closo-decaborane(12) which is iso-electronic and isostructural with $[\text{B}_{12}\text{H}_{12}]^{2-}$. It is stable to heat as well as to air but at high temperature (450°C and 620°C) it isomerizes to 1,7 (meta or neo-isomer) and the 1,12 (para isomer). (Fig-a)

Monocarboranes such as CB_5H_7 and CB_5H_9 obey the electronic rules or Wade rule for boranes and are known as closo, nido and arachno structures. When we apply the formula of the carboranes, each C-H bonds group should be regarded as donating three electrons the frame count. Some carboranes exhibit closo, nido transformation.



Metallocarboranes — Metallocarboranes are the compounds formed between metal atom and carborane species. For example — $[^2\text{C}_2\text{B}_9\text{H}_11\text{Mn}(\text{CO})_3]$



Structure of
1,2 dicarba - closo - dodecarane

(Fig - a)