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 a 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 common examples of closo-carboranes are:

1. $\text{C}_2\text{B}_{10}\text{H}_{12}$: In $\text{C}_2\text{B}_{10}\text{H}_{12}$, $n = 12$; 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 $\text{C}_2\text{B}_{10}\text{H}_{12}$, confirming this as a closo kind. Three isomers (ortho-, meta- and para-) are possible.

![Figure 19. Structure and isomerism in $\text{C}_2\text{B}_{10}\text{H}_{12}$ (dicarba-closo-dodecaborane).](image)

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2. \( \text{C}_2\text{B}_3\text{H}_5 \): In \( \text{C}_2\text{B}_3\text{H}_5 \), \( n = 5 \); 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 \( \text{C}_2\text{B}_3\text{H}_5 \), confirming this as closo kind. Three isomers are possible which given below.

\[
\begin{align*}
\text{I} & : \quad \begin{array}{c}
\text{C} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{C}
\end{array} \\
\text{II} & : \quad \begin{array}{c}
\text{C} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{C}
\end{array} \\
\text{III} & : \quad \begin{array}{c}
\text{C} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{C}
\end{array}
\end{align*}
\]

\( (1, 5) \) \quad \( (1, 2) \) \quad \( (2, 3) \)

Figure 20. Structure and isomerism in \( \text{C}_2\text{B}_3\text{H}_5 \).

\[ \textbf{Nido-(Nestlike) Carboranes} \]

These are nest-like geometries and can assumed as the derivatives of closed triangular polyhedral structures in which one vertices 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. \( \text{C}_2\text{B}_9\text{H}_{13} \): In \( \text{C}_2\text{B}_9\text{H}_{13} \), \( n = 11 \); 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 \( \text{C}_2\text{B}_9\text{H}_{13} \), confirming this as nido kind. The structure of some the possible isomers that can be obtained experimentally are given below.

\[
\begin{align*}
\text{I} & : \quad \begin{array}{c}
\text{C} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{C}
\end{array} \\
\text{II} & : \quad \begin{array}{c}
\text{C} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{C}
\end{array} \\
\text{III} & : \quad \begin{array}{c}
\text{C} \\
\text{B} \\
\text{B} \\
\text{B} \\
\text{C}
\end{array}
\end{align*}
\]

\( (2, 3) \) \quad \( (7, 8) \) \quad \( (7, 9) \)

Figure 21. Structure and isomerism in \( \text{C}_2\text{B}_9\text{H}_{13} \).
2. C2B\textsubscript{4}H\textsubscript{8}: In C2B\textsubscript{4}H\textsubscript{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 C2B\textsubscript{4}H\textsubscript{8}, confirming this as a nido kind. The structure of some the possible isomers that can be obtained experimentally are given below.

![Figure 22. Structure and isomerism in C2B\textsubscript{4}H\textsubscript{8}](image)

**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 4\( n \)+6 skeletal electrons) involved in multicentre bonding in arachno-carboranes; where \( n \) represents the total number of B and C atoms. Some of common examples of arachno-carboranes are:

1. C2B\textsubscript{6}H\textsubscript{12}: In C2B\textsubscript{6}H\textsubscript{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 C2B\textsubscript{6}H\textsubscript{12}, confirming this as an arachno kind. The structure of some the possible isomers that can be obtained experimentally are given below.

![Figure 23. Structure and isomerism in C2B\textsubscript{6}H\textsubscript{12}](image)
2. C\textsubscript{2}B\textsubscript{1}H\textsubscript{13}: In C\textsubscript{2}B\textsubscript{1}H\textsubscript{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\textsubscript{2}B\textsubscript{1}H\textsubscript{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\textsubscript{2}B\textsubscript{1}H\textsubscript{13}.

\[
\begin{align*}
\text{Skeletal electron pairs} & \quad \text{Closo} & \quad \text{Nido} & \quad \text{Arachno} \\
6 & \quad n = 5 & \quad C_2B_3H_5 & \quad n = 4 & \quad C_4H_4 & \quad n = 3 & \quad C_3H_6 & \quad C_3H_5^- \\
7 & \quad n = 6 & \quad C_2B_4H_6 & \quad n = 5 & \quad C_2B_3H_7, B_2H_9, C_3H_5 & \quad n = 4 & \quad B_4H_{10} & \quad C_4H_4^{2-}
\end{align*}
\]

Figure 25. continued on next page...
Figure 25. continued on next page...
Some hypho-carboranes (C$_2$B$_{n-2}$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 conjunctocarbones.

Figure 25. Structural relationship between closo, nido, and arachno carboranes.
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