Subject	Chemistry
Paper No and Title	11. Inorganic Chemistry –III (Metal π-Complexes and Metal Clusters)
Module No and Title	Module19 and Nomenclature and classification of higher boranes
Module Tag	CHE_P11_M19

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

TABLE OF CONTENTS

1. Learning Outcomes

After studying this module, you shall be able to:

- Learn about naming of boranes (neutral, ionic, open boron frameworks, non-bridging substituents and carboranes)
- Identify different classes of boranes
- Understand unusual stoichiometries and fascinating structures

2. Introduction

Boranes

Of the elements in group 13 (III A), boron is a non-metal and other elements are primarily metallic in their properties. The chemistry of boron is quite different from that of the elements in this group. The tendency of boron to form covalent bonds has more similarity with carbon and silicon than with other group 13 elements. Boron occurs naturally as *borax* $Na_2B_4O_5(OH)_4.8H_2O$ and as *kernite* $Na_2B_4O_5(OH)_4.2H_2O$. Boron exists in several allotropic forms. Boron has two stable isotopes, $_5B^{11}$ (80.4% abundance) and $_5B^{10}$ (19.6%), of which $_5B^{10}$ has a very high neutron absorption cross section. The $_5B^{11}$ formed after neutron absorption by $_5B^{10}$ upon nuclear decay emits high energy particles $_3Li^7$ and $_2He^4$ which can kill cancerous tissues. This use of boron compounds in the treatment of cancerous tumors is called boron neutron capture therapy (BNCT). Boron compounds find use in the preparation of the glazes and borosilicate glasses. Metal rich borides are extremely hard and find applications as turbine blades, combustion chamber liners and rocket nozzles

Systematic borane chemistry began in 1912 with the pioneering work of Alfred Stock and his research group. The initial work involved the reaction of magnesium boride/ magnesium diboride (MgB_2) with acids by which a mixture of boranes was obtained. Since then, better routes have been developed for synthesis of boranes which involve thermolysis /cracking of diborane (B_2H_6) under varied conditions, often in the presence of hydrogen. Boron forms many hydrides like carbon and oxygen containing minerals with complex structures (Borates) like silicon. In addition to simple hydrides, boron forms various neutral and anionic polymeric boron-hydrogen compounds having cage-like structures consisting of maximum 12 B atoms. These extensive series of volatile compounds are called molecular hydrides/boranes by analogy with alkanes (hydrocarbons). Boranes can be classified into mainly three classes such as *closo*, *nido* and *arachno* based on their structural features.

3. Nomenclature

3.1 Neutral and ionic boranes

Boranes exist both as neutral and ionic species.

Neutral boranes are named as follows:

a) The Latin prefixes mono-, di-, tri-, etc. are used before "borane" to indicate the number of boron atoms in the compound.

b) The number of hydrogen atoms in the molecule is indicated by enclosing the appropriate Arabic numeral in parentheses directly following the name.

For example:

BH_3 borane (3)
B_2H_6 diborane (6)
B_3H_7 triborane (7)
B_4H_{10} tetraborane (l0)
B_5H_9 pentaborane (9)
B_5H_{11} pentaborane (11).
B_6H_{10} hexaborane (10)
$B_{10}H_{14}$ decaborane (14)
$B_{10}H_{16}$ decaborane (16)
$B_{20}H_{16}$ icosaborane (16)

These names are given on the molecular formulae rather than on the structures. In practice, it is permissible to drop the numerical designation of the number of hydrogen atoms in borane (3).

Names for anions end in "ate" rather than "ane" and specify both the number of H and B atoms and the charge. For example: $B_5H_8^-$ is octahydropentaborate (1−).

1. $Na[B_2H_7]$ sodium heptahydrodiborate(1 -)
2. $Na_2[B_2(C_6H_5)_6]$ sodium hexaphenyldiborate(2 -)
3. $Ca[B_3H_8]_2$ calcium octahydrotriborate(1 -)
4. $Na[B_9H_{14}]$ sodium tetradecahydrononaborate(1-)
5. $Na_2[B_{10}C1_{10}]$ sodium decachlorodecaborate(2-)
6. $Na_2[B_{10}H_{10}]$ sodium decahydrodecaborate(2-)
7. $Na[B_{10}H_9NH_3]$ sodium amminenonahydrodecaborate(1-)
8. $B_{10}H_8(NH_3)_2$ diammineoctahydrodecaboron
9. $[B_{10}H_7(NH_3)_3]^+$ triammineheptahydrodecaboron(1+) ion
10. $[B_{10}H_8(COOH)_2]^{2-}$ dicarboxyoctahydrodecaborate(2-) ion
11. $Na_2B_4O_7$ sodium heptaoxotetraborate(2-) or sodium tetraborate

Prefixes, such as *nido* or *closo* for open and closed boron frameworks may be used when required for clarity as:

1. $Na_2[B_{10}H_{10}]$ sodium decahydro-*closo*-decaborate(2-)
2. $Na_2[B_{10}H_{12}]$ sodium dodecahydro-*nido*-decaborate(2-)
3. $Na[B_{10}H_{13}]$ sodium tridecahydro-*nido*-decaborate(1-)
4. $Na_2[B_{10}H_{14}]$ sodium tetradecahydro-*nido*-decaborate(2-)
5. $Na[B_{10}H_{15}]$ sodium pentadecahydro-*nido*-decaborate(1-)
6. $[B_{12}H_{12}]^{2-}$ dodecahydro-*closo*-dodecaborate(2-) ion
7. $[B_{12}H_{11}Cl]^{2-}$ chloroundecahydro-*closo*-dodecaborate(2-)ion
8. $[B_{12}H_{11}NH_3]^-$ ammineundecahydro-*closo*-dodecaborate(1-)ion
9 $B_{12}H_{10}(NH_3)_2$ diamminedecahydro-*closo*-dodecaboron

3.2 Numbering of positions in open framework

For numbering purposes, the open boron frameworks are viewed as plane projections from opposite side of the open portion of the framework. The boron atoms are numbered by zones with the interior atoms of the projection being numbered first followed by the peripheral atoms. Each zone of atoms is numbered clockwise. In more complex cases numbering in each zone is started at an arbitrary twelve o'clock position selected by as many as necessary of the following criteria taken in order:

(a) The molecule is oriented so that the twelve o'clock position lies in a symmetry plane containing only a few atoms e.g. B_2H_6 (Figure 1), B_4H_{10} (Figure 2) and B_5H_9 (Figure 3).

(b) The molecule is oriented so that the twelve o'clock position will be in the portion of this symmetry plane containing the greater number of atoms e.g. B_5H_{11} (Figure 4), B_6H_{10} (Figure 5), $B_9H_{13}L$ (Figure 6), $B_{11}H_{13}L$ (Figure 7).

(c) The molecule is oriented so that the twelve o'clock position lies opposite the greater number of bridge hydrogens e.g. B_8H_{12} (Figure 8), B_9H_{15} (Figure 9).

For boranes with skeletal replacement, the numbering is based on a parent boron skeleton with all boron-boron bonds equivalent. Lowest numbering for heteroatoms takes priority over (c).

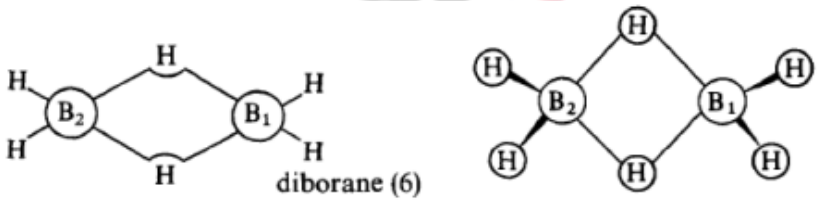


Figure 1.B_2H_6

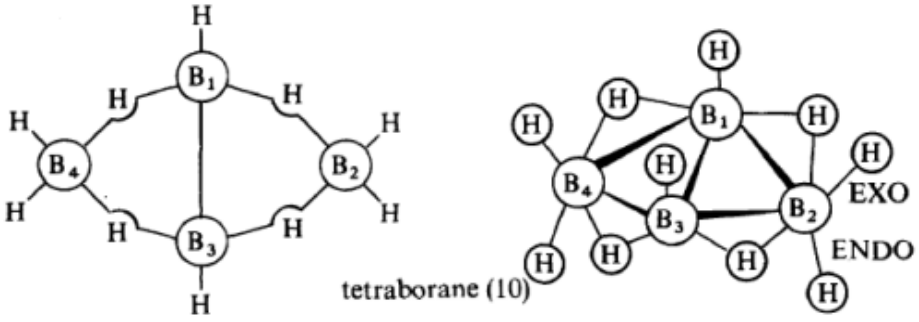


Figure 2.B_4H_{10}

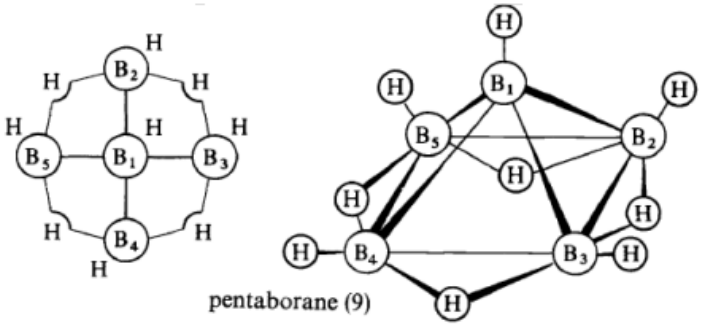


Figure 3. B_5H_9

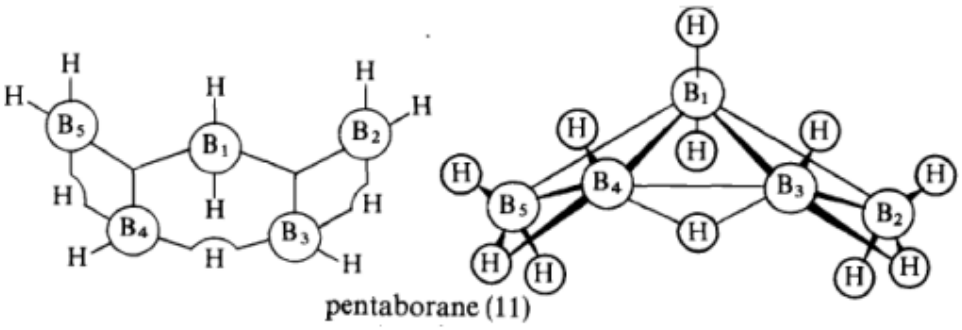


Figure 4. B_5H_{11}

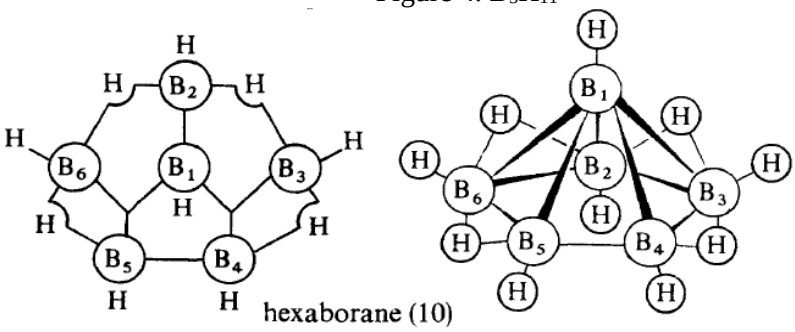


Figure 5. B_6H_{10}

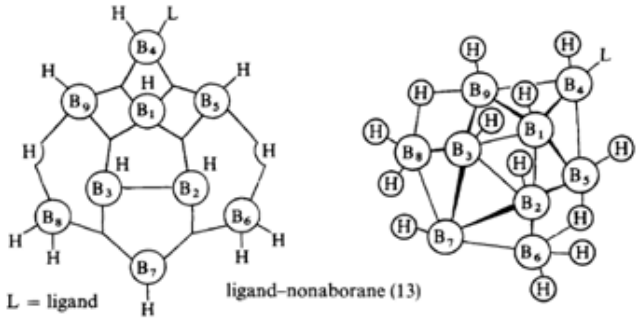


Figure 6. $B_9H_{13}L$

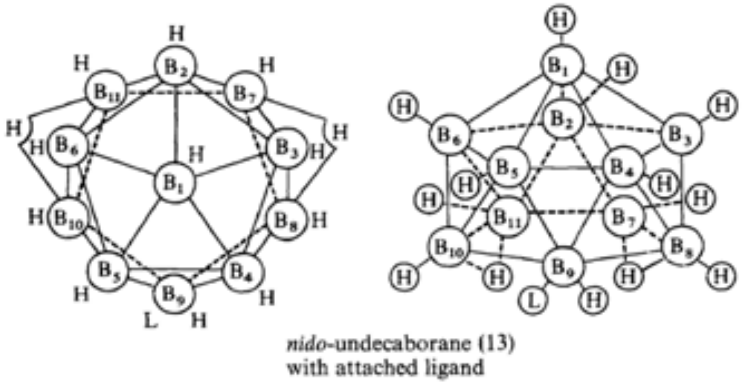


Figure 7. $B_{11}H_{13}L$

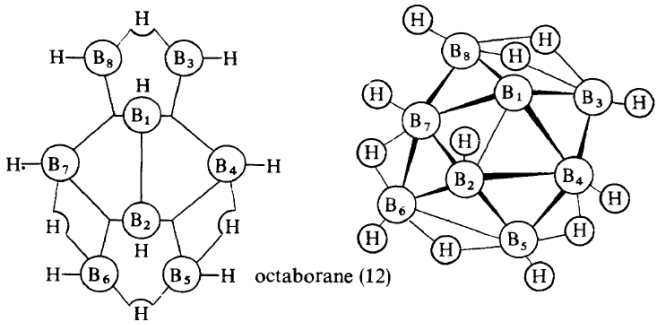


Figure 8. B_8H_{12}

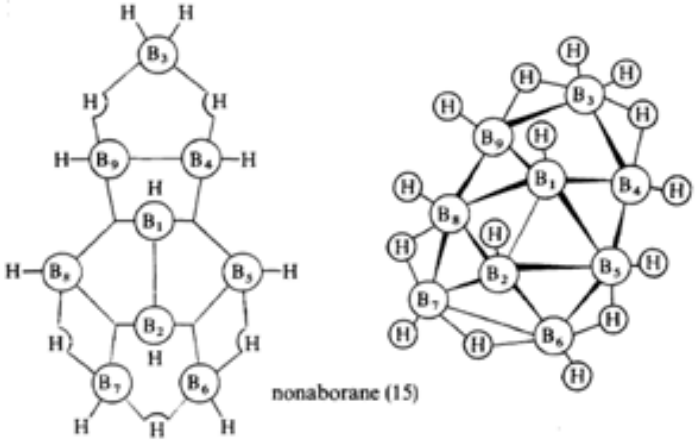
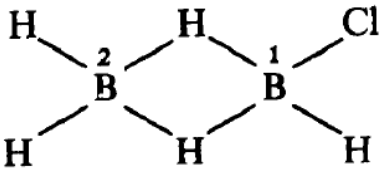


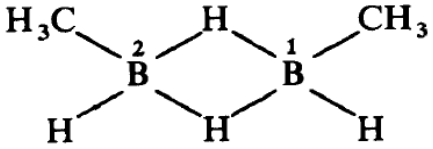
Figure 9.B_9H_{15}

3.3 Naming of non-bridging substituents:

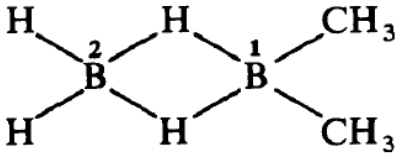
The appropriate prefix is directly attached to the name of the parent compound and is numbered corresponding to the boron atom to which the substituent is attached, the number being as low as possible. Examples:

1. 

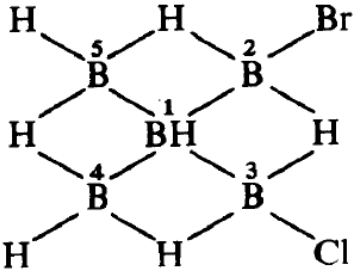
1-chlorodiborane (6)

2. 

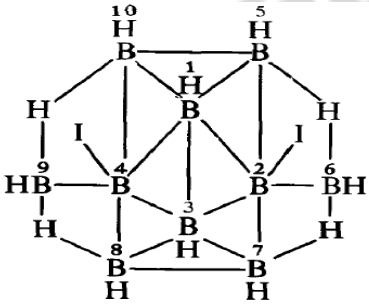
1,2-dimethyldiborane (6)

3. 

1,1-dimethyldiborane (6)

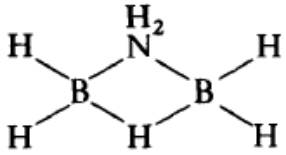
4. 

2-bromo-3-chloropentaborane (9)

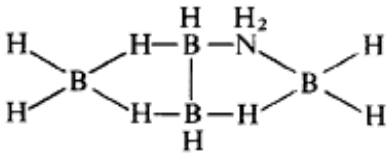
5. 

2,4-diidodecaborane (14)

Substituents for hydrogen atoms in bridge positions are designated by use of the symbol 'μ' as a prefix to the name of the substituent1. If it is necessary to distinguish between bridge positions, the bridge positions are indicated by designating the numbers of the boron atoms across which bridging occurs followed by a hyphen. The lowest possible numbers are used to designate points of bridging as is done for substituents. Examples:

1. 

μ-aminodiborane (6)

2. 

1,2-μ-aminotetraborane (10)

3.4 Boranes with skeletal replacement (carboranes)

The names of the general classes of compounds in which one or more boron atoms in a network have been replaced by a hetero atom are formed by an adaptation of organic replacement

nomenclature as carbaboranes, azaboranes, phosphaboranes, thiaboranes, etc. In this adaptation, a boron atom is replaced by another atom irrespective of valence for example, $B_{10}C_2H_{12}$ is very stable, has many known derivatives, and is named dicarbadodecaborane, as the dicarba replacement derivative of the unknown $B_{12}H_{12}$ which is isoelectronic with and is in this respect a replacement derivative of the very stable $[B_{12}H_{12}]^{2-}$ anion. The heteroatom is directly bonded with boron.

The positions of the hetero atoms in the cage or network are indicated by the lowest possible numbers consistent with the numbering of the parent polyborane. Since the number of bridge hydrogens in nido heteroboranes is different from that in the parent polyboranes. only the symmetry of the boron skeleton of the parent polyborane is considered in numbering. For this purpose all boron—boron bond lengths are to be considered equivalent.

Examples:

1. $B_3C_2H_5$	dicarba-closo-pentaborane(5)
2. $B_4C_2H_6$	l,2-dicarba-closo-hexaborane(6)
3. $B_4C_2H_6$	1,6-dicarba-closo-hexaborane(6)
4. B_5CH_7	carba-closo-hexaborane(7)
5. $B_4C_2H_8$	2,3-dicarba-nido-hexaborane(8)
6. $B_3C_3H_7$	1,2,3-tricarba-nido-hexaborane(7)
7. $B_5C_2H_7$,	dicarba-closo-heptaborane(7)
8. $B_6C_2H_8$	dicarba-closo-octaborane(8)
9. $B_8C_2H_{10}$	dicarba-closo-decaborane(10)
10.$B_9C_2H_{13}$	7,8-dicarba-nido-undecaborane(13)
11. $B_{10}C_2H_{12}$	l,2-dicarba-closo-dodecaborane(12)
	1,7 -dicarba-closo-dodecaborane(12) isomers
	1,12-dicarba-closo-dodecaborane(12)
12. $B_{11}PH_{12}$	phospha-closo-dodecaborane(12)
13. $B_{10}CPH_{11}$	1-phospha-2-carba-closo-dodecaborane (11)
14. $B_{10}SH_{12}$	7-thia-nido-undecaborane(12)

4.1 Classification of boranes

Boranes can be classified into five structural categories:

1. *Closo*-boranes (from Greek: cage like): They have complete closed polyhedral structure with trigonal faces (football like structure). General formula of closo borane is $B_nH_n^{2-}$.

2. *Nido*-boranes (from Latin: nest like): They have non-closed structures in which the B_n cluster occupies n corners on an (n + 1)-cornered polyhedron. General formula of nido borane is B_nH_{n+4}/ $B_nH_n^{4-}$ (2n+4)

3. *Arachno*-boranes (from Greek: spider's web like): They have even more open cluster in which the B atoms occupy n contiguous corners of an (n + 2)-cornered polyhedron. General formula of arachno borane is B_nH_{n+6}/ $B_nH_n^{6-}$ (2n+6)

4. *Hypho*-boranes (from Greek: net like): They have the most open clusters in which the B atoms occupy n corners on an (n + 3)-cornered polyhedron. General formula of hypo borane is $B_nH_n^{8-}$

5. *Conjuncto*-boranes (from Latin: join together): They have structures formed by linking two or more of the preceding type of cluster together. General formula of nido borane is $B_nH_n^{10-}$

For example:
The formulas of boranes can be related to these formulas by formally subtracting H^+ ions from the formula to make the number of B and H atoms equal. For example, to classify $B_9H_{I4}^-$ it can formally be considered to be related to $B_9H_9^{6-}$.

$$B_9H_{I4}^- - H^+ = B_9H_9^{6-}$$

The classification for this borane is therefore *arachno.*

Table. 1 Formulas of Boranes and Carboranes

Type	Borane	Example	Carborane	Example
Closo	$B_nH_n^{2-}$	$B_{12}H_{12}^{2-}$	$C_2B_{n-2}H_n$	$C_2B_{10}H_{12}$
Nido	B_nH_{n+4}[a]	$B_{10}H_{14}$	$C_2B_{n-2}H_{n+2}$	$C_2B_8H_{12}$
Arachno	B_nH_{n+6}[b]	B_9H_{15}	$C_2B_{n-2}H_{n+4}$	$C_2B_7H_{13}$

(Note- [a]*Nido* borane may also have formulas $B_nH_{n+3}^-$ and $B_nH_{n+2}^{2-}$; [b]*Arachno* borane may also have formulas $B_nH_{n+5}^-$ and $B_nH_{n+4}^{2-}$)

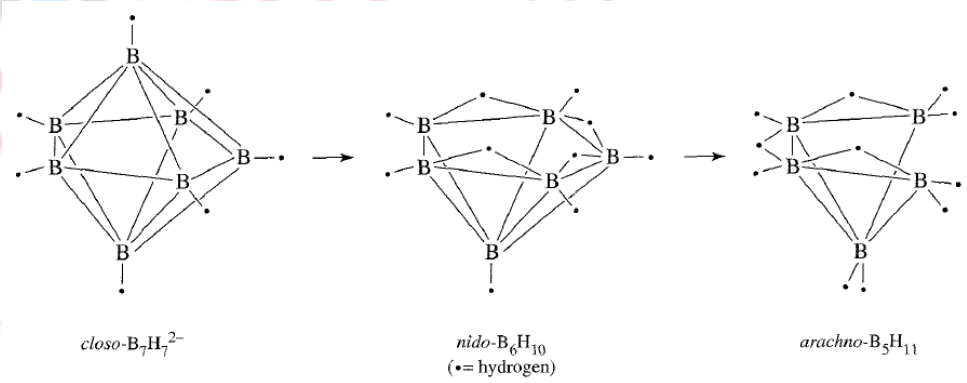


Figure.10 Structures of *closo*, *nido*, and *arachno* boranes

5. Summary

- Hydrides of boron are called boranes.
- Boranes can be classified into *closo, nido, arachno, hypho* and *conjuncto* boranes.
- *Closo, nido, arachno, hypho* and *conjuncto* boranes have general formula $B_nH_n^{2-}$, $B_nH_n^{4-}$, $B_nH_n^{6-}$, $B_nH_n^{8-}$, $B_nH_n^{10-}$ respectively.
- The formulas of boranes can be related to these formulas by formally subtracting H^+ ions from the formula to make the number of B and H atoms equal.
- For example, to classify $B_9H_{14}^-$ it can formally be considered to be related to $B_9H_9^{6-}$.
  $B_9H_{14}^- - H^+ = B_9H_9^{6-}$

  The classification for this borane is therefore *arachno.*
- $B_{10}C_2H_{12}$ is very stable, has many known derivatives, and is named dicarbadodecaborane, as the dicarba replacement derivative of the unknown $B_{12}H_{12}$ which is isoelectronic with and is in this respect a replacement derivative of the very stable $[B_{12}H_{12}]^{2-}$ anion.