

# Polyhedral Boranes and Wade's Rules

Massachusetts Institute of Technology

# Outline

- 1 Polyhedral Boranes
- 2 Wade's Rules
- 3 Heteroboranes
- 4 Molecular Orbital Picture

# Polyhedral Boranes

## An Important Class of Electron-Deficient Borane Compounds

### Hydroborane Clusters

- 1 Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme
- 2 In a cluster atoms form a cage-like structure
- 3 There are a great number of known neutral and anionic hydroborane clusters
- 4 These structures are often described as being polyhedral or deltahedral
- 5 A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron

# Polyhedral Boranes

## An Important Class of Electron-Deficient Borane Compounds

### Hydroborane Clusters

- 1 Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme
- 2 In a cluster atoms form a cage-like structure
- 3 There are a great number of known neutral and anionic hydroborane clusters
- 4 These structures are often described as being polyhedral or deltahedral
- 5 A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron

# Polyhedral Boranes

## An Important Class of Electron-Deficient Borane Compounds

### Hydroborane Clusters

- 1 Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme
- 2 In a cluster atoms form a cage-like structure
- 3 There are a great number of known neutral and anionic hydroborane clusters
- 4 These structures are often described as being polyhedral or deltahedral
- 5 A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron

# Polyhedral Boranes

## An Important Class of Electron-Deficient Borane Compounds

### Hydroborane Clusters

- 1 Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme
- 2 In a cluster atoms form a cage-like structure
- 3 There are a great number of known neutral and anionic hydroborane clusters
- 4 These structures are often described as being polyhedral or deltahedral
- 5 A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron

# Polyhedral Boranes

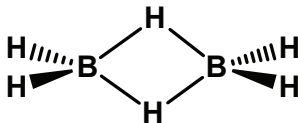
## An Important Class of Electron-Deficient Borane Compounds

### Hydroborane Clusters

- 1 Electron-deficient species possess fewer valence electrons than are required for a localized bonding scheme
- 2 In a cluster atoms form a cage-like structure
- 3 There are a great number of known neutral and anionic hydroborane clusters
- 4 These structures are often described as being polyhedral or deltahedral
- 5 A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron

# $B_2H_6$

## The Simplest Hydroborane

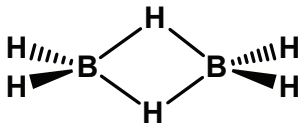


- This is an electron-deficient compound held together by two 3c-2e bonds.
- Higher boranes are prepared by pyrolysis of  $B_2H_6$  in the vapor phase.



# $B_2H_6$

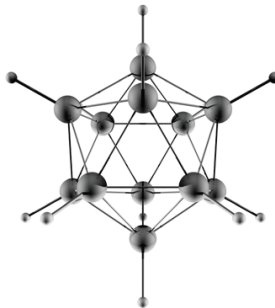
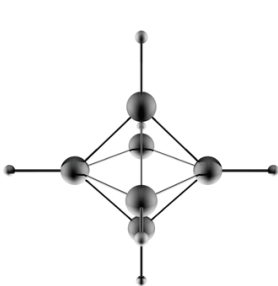
## The Simplest Hydroborane



- This is an electron-deficient compound held together by two 3c-2e bonds.
- Higher boranes are prepared by pyrolysis of  $B_2H_6$  in the vapor phase.

# $[B_6H_6]^{2-}$ and $[B_{12}H_{12}]^{2-}$

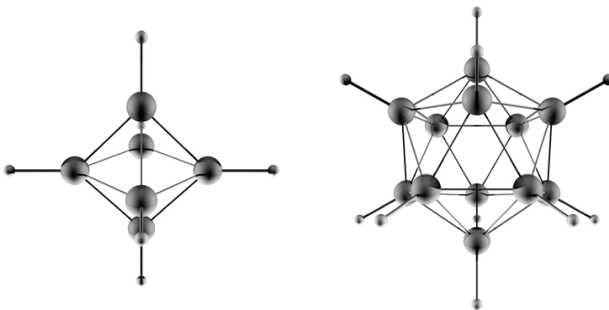
Selected Examples of Polyhedral Boranes



- What are the point groups of these two anions?

# $[B_6H_6]^{2-}$ and $[B_{12}H_{12}]^{2-}$

Selected Examples of Polyhedral Boranes



- What are the point groups of these two anions?

# Deltahedral Cages With Five to Twelve Vertices

Can Be Used to Rationalize Borane Cluster Structures



$n = 5$   
Trigonal  
bipyramid



$n = 6$   
Octahedron



$n = 7$   
Pentagonal  
bipyramid



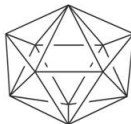
$n = 8$   
Dodecahedron



$n = 9$   
Tricapped  
trigonal prism



$n = 10$   
Bicapped  
square-antiprism



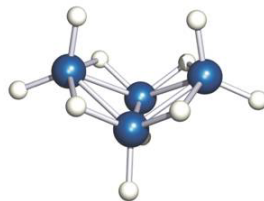
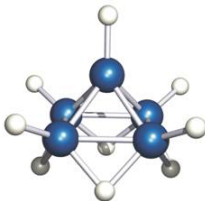
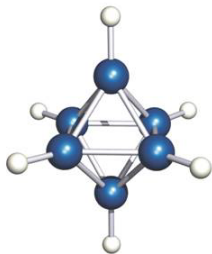
$n = 11$   
Octadecahedron



$n = 12$   
Icosahedron

# Naming Polyhedral Boranes

*Closo*, *Nido*, *Arachno*...



(a)



*closo*

Remove one  
vertex  
→



*nido*

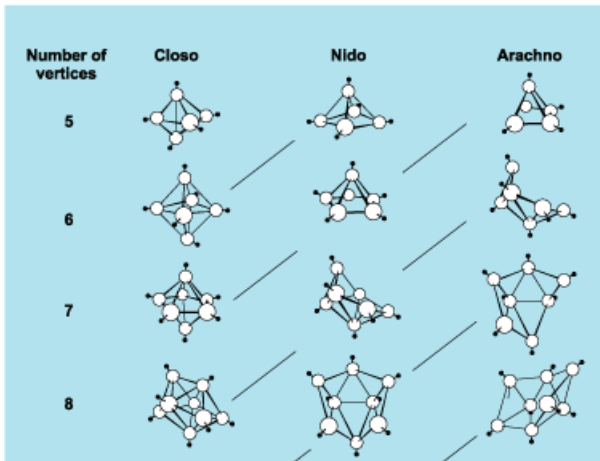
Remove one  
vertex  
→



*arachno*

# Families of Polyhedral Boranes

The *Closo* Structures Are The Parent Structures



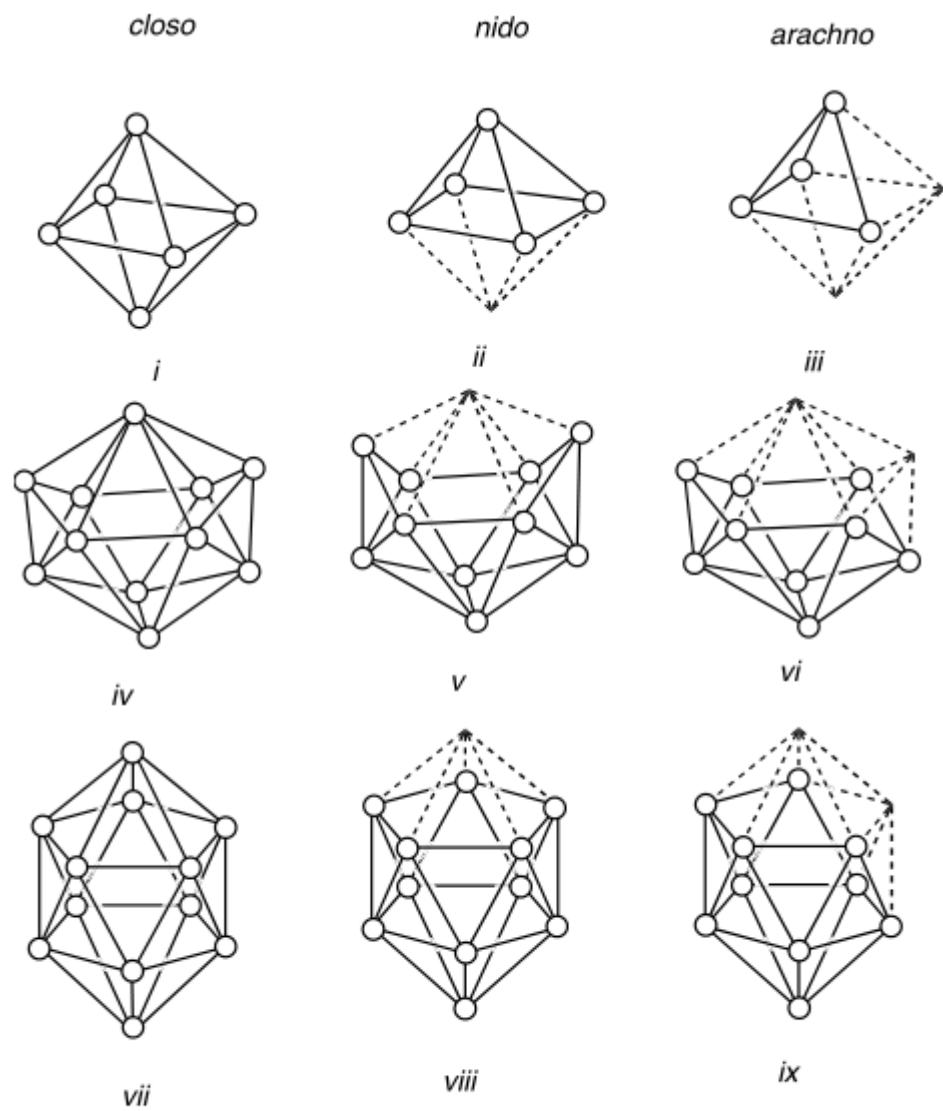


Fig. 1. Some idealized deltahedra and deltahedral fragments. The dashed lines delineate the positions of missing vertices.

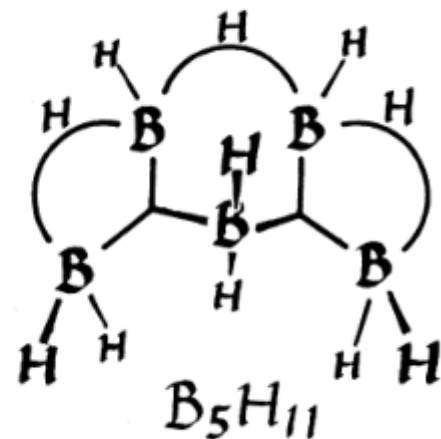
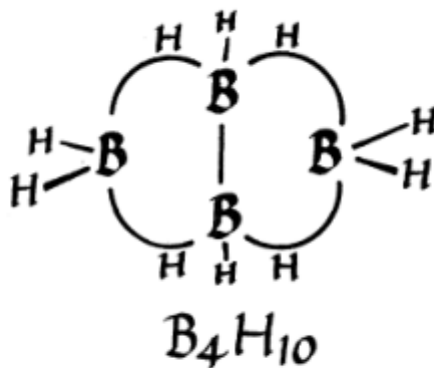
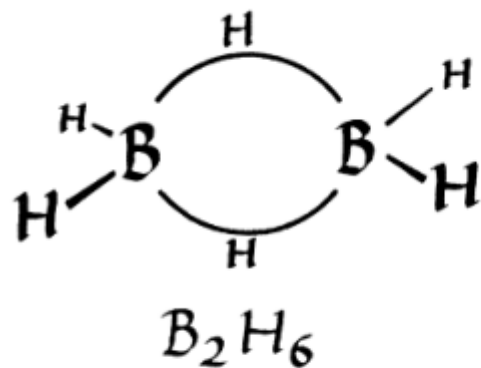
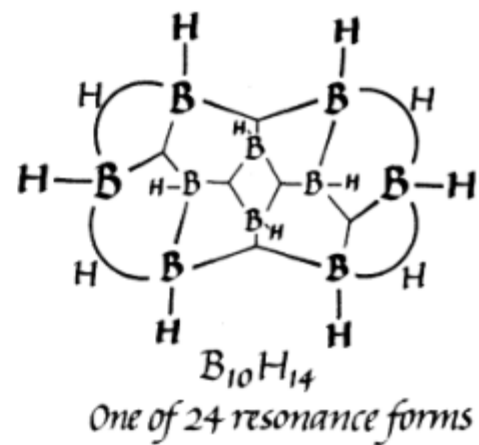
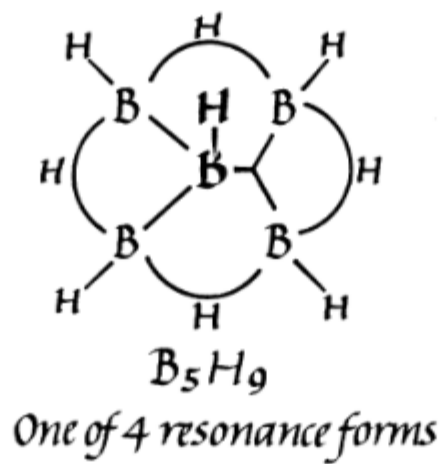
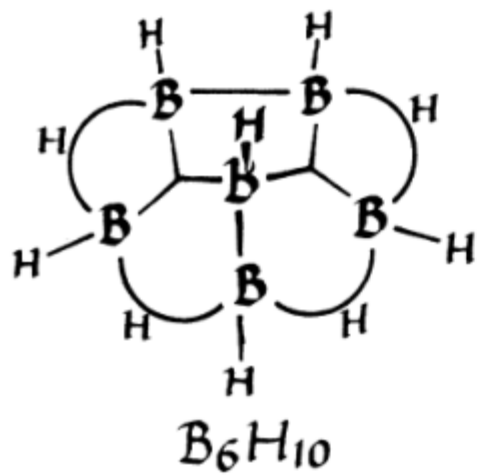


Fig. 11 (left). Bonds in  $B_2H_6$ , according to three-center bond theory. Fig. 12 (center). Bonds in  $B_4H_{10}$ . Fig. 13 (right). Bonds in  $B_5H_{11}$ .





# Wade's Rules

## A Classification Scheme For Polyhedral Borane Clusters



- Classification of structural types can often be done more conveniently on the basis of valence electron counts.
- Most classification schemes are based on a set of rules formulated by Prof. Kenneth Wade, FRS, in 1971.

# Wade's Rules

## A Classification Scheme For Polyhedral Borane Clusters



- Classification of structural types can often be done more conveniently on the basis of valence electron counts.
- Most classification schemes are based on a set of rules formulated by Prof. Kenneth Wade, FRS, in 1971.

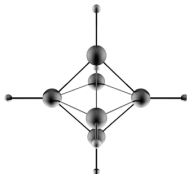
# Wade's Rules

## A Classification Scheme For Polyhedral Borane Clusters

- In a *closo* polyhedral borane structure:
- The number of pairs of framework bonding electrons is determined by subtracting one B-H bonding pair per boron.
- The  $n+1$  remaining framework electron pairs may be used in boron-boron bonding or in bonds between boron and other hydrogen atoms.

# Example: $[B_6H_6]^{2-}$

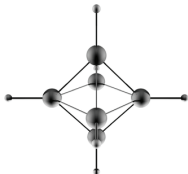
## Understanding Wade's Rules



- Number of valence electrons =  $6(3) + 6(1) + 2 = 26$  or 13 pairs of electrons.
- Six pairs of electrons are involved in bonding to terminal hydrogens (one per boron).
- Therefore seven  $(n + 1)$  pairs of electrons are involved in framework bonding, where  $n =$  number of boron atoms in cluster.

# Example: $[B_6H_6]^{2-}$

## Understanding Wade's Rules



- Number of valence electrons =  $6(3) + 6(1) + 2 = 26$  or 13 pairs of electrons.
- Six pairs of electrons are involved in bonding to terminal hydrogens (one per boron).
- Therefore seven  $(n + 1)$  pairs of electrons are involved in framework bonding, where  $n =$  number of boron atoms in cluster.

# Tabular Summary of Wade's Rules

## Classification and Electron Count of Boron Hydrides

Type	Formula	Skeletal Electron Pairs
<i>Closo</i>	$[\text{B}_n\text{H}_n]^{2-}$	$n + 1$
<i>Nido</i>	$\text{B}_n\text{H}_{n+4}$	$n + 2$
<i>Arachno</i>	$\text{B}_n\text{H}_{n+6}$	$n + 3$
<i>Hypso</i>	$\text{B}_n\text{H}_{n+8}$	$n + 4$
<i>Klado</i>	$\text{B}_n\text{H}_{n+10}$	$n + 5$

- *Closo* comes from the Greek for cage, *Nido* the Latin for nest, *Arachno* the Greek for spider, *Hypso* the Greek for net, and *Klado* the Greek for branch.

# Tabular Summary of Wade's Rules

## Classification and Electron Count of Boron Hydrides

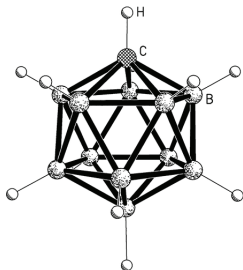
Type	Formula	Skeletal Electron Pairs
<i>Closo</i>	$[B_nH_n]^{2-}$	$n + 1$
<i>Nido</i>	$B_nH_{n+4}$	$n + 2$
<i>Arachno</i>	$B_nH_{n+6}$	$n + 3$
<i>Hypso</i>	$B_nH_{n+8}$	$n + 4$
<i>Klado</i>	$B_nH_{n+10}$	$n + 5$

- *Closo* comes from the Greek for cage, *Nido* the Latin for nest, *Arachno* the Greek for spider, *Hypso* the Greek for net, and *Klado* the Greek for branch.



# Heteroboranes

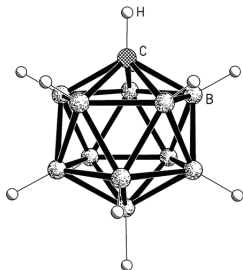
## Inclusion of Other Atoms in the Hydroborane Cage



- Many derivatives of boranes containing other main group atoms are also known.
- These heteroboranes may be classified by formally converting the heteroatom to a  $BH_x$  group having the same number of valence electrons.

# Heteroboranes

## Inclusion of Other Atoms in the Hydroborane Cage



- Many derivatives of boranes containing other main group atoms are also known.
- These heteroboranes may be classified by formally converting the heteroatom to a  $BH_x$  group having the same number of valence electrons.

# Considering Other Atoms in the Context of Wade's Rules

## Classification of Heteroborane Clusters

Heteroatom	Replace With
C, Si, Ge, Sn	BH
N, P, As	BH <sub>2</sub>
S, Se	BH <sub>3</sub>

- These represent the most common main group heteroatoms incorporated into hydroborane clusters.

# Considering Other Atoms in the Context of Wade's Rules

## Classification of Heteroborane Clusters

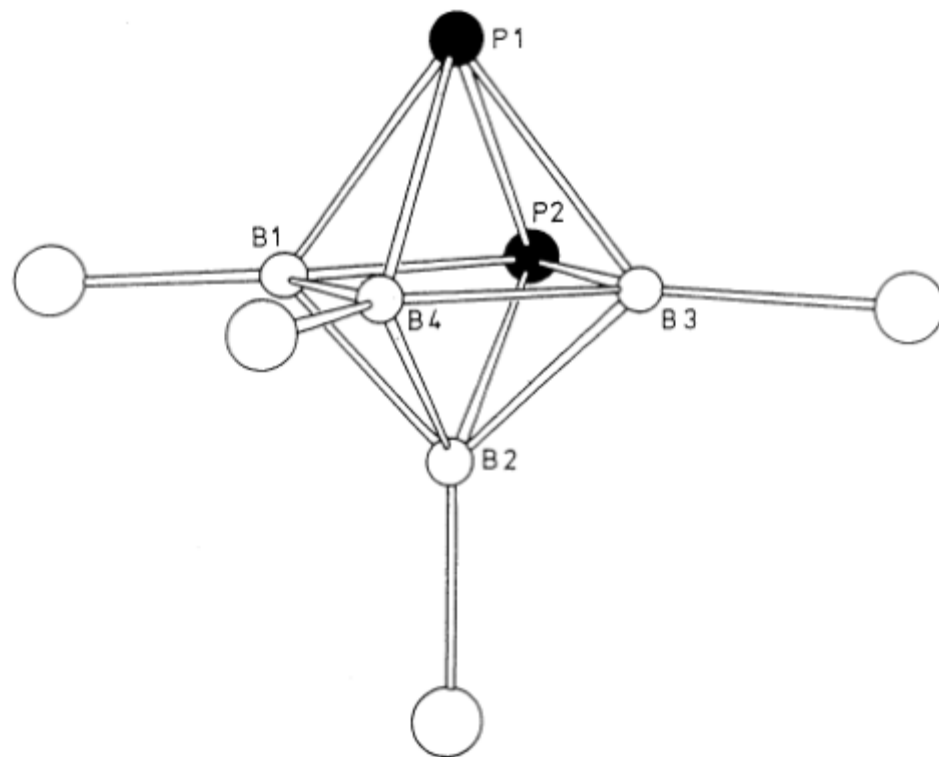
Heteroatom	Replace With
C, Si, Ge, Sn	BH
N, P, As	BH <sub>2</sub>
S, Se	BH <sub>3</sub>

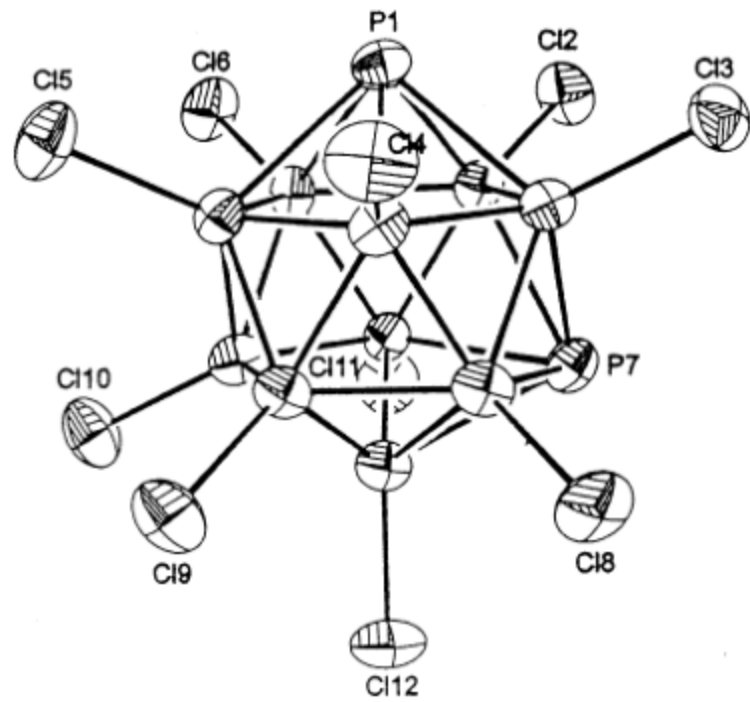
- These represent the most common main group heteroatoms incorporated into hydroborane clusters.

# Examples

## Understanding Wade's Rules

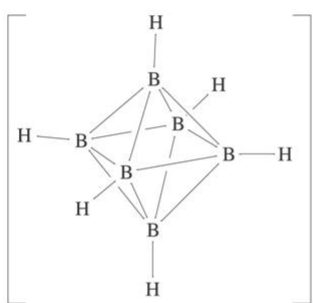
- Classify the following polyhedral heteroboranes according to their valence electron count:
- $C_2B_7H_{13}$
- $SB_9H_{11}$
- $CPB_{10}H_{11}$



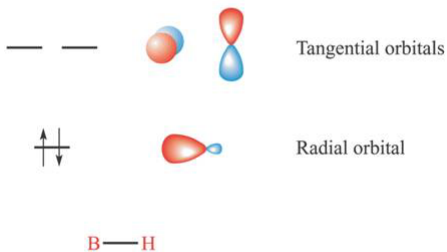


# Bonding in $[B_6H_6]^{2-}$

## Frontier Orbitals for Each BH Unit



$2-$   $E_{MO}$  ↑





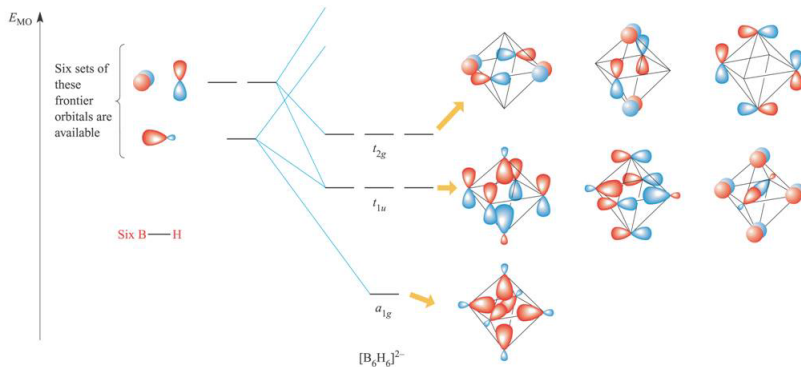
# Bonding in $[B_6H_6]^{2-}$

## Frontier Orbitals for Each BH Unit

- Choose z-axis to point to center of polyhedron
- Consider  $s$  and  $p_z$  to form two  $sp$  hybrid orbitals: one bonds to H  $1s$  and the other points into center of cluster.
- The  $p_x$  and  $p_y$  orbitals on boron are unhybridized and are called tangential orbitals.
- The six hybrids not used in bonding to hydrogen and the unhybridized  $2p$  orbitals of the borons remain to participate in bonding with the  $B_6$  core.

# Bonding in $[B_6H_6]^{2-}$

## Radial and Tangential Bonding Molecular Orbitals



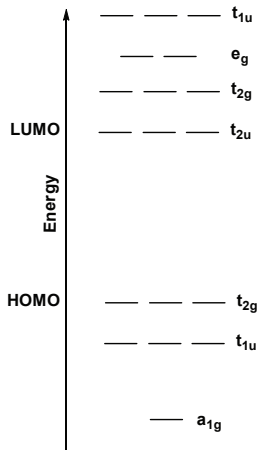
# Bonding in $[B_6H_6]^{2-}$

## Radial and Tangential Bonding Molecular Orbitals

- When the six B-H units come together, a total of 18 ( $6 \times 3$ ) atomic orbitals combine to form 18 molecular orbitals.
- There are seven orbitals with net bonding character delocalized over the skeleton.
- All of the bonding orbitals are filled ( $n + 1$  framework bonding pairs), so seven pairs of electrons are used to hold the cluster together. The bonding cannot be interpreted using a localized electron model.
- There is a considerable energy gap between the bonding MOs and the remaining largely antibonding MOs, contributing to the stability of the cluster.

# Bonding in $[B_6H_6]^{2-}$

## Full Molecular Orbital Diagram



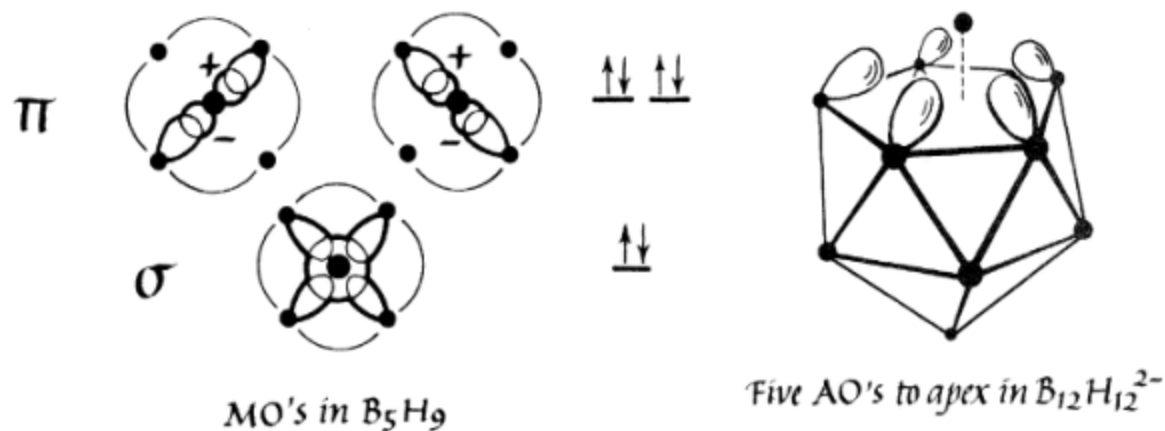


Fig. 17 (left). Symmetry molecular orbitals (*MO's*) in the boron framework of  $B_5H_9$ . The  $\sigma$  molecular orbital is a five-centered one, and each of the  $\pi$  components is actually an open three-center bond. Fig. 18 (right). A situation with five atomic orbitals (*AO's*) containing four electrons produced when a neutral BH unit is removed from the apex of  $B_{12}H_{12}^{2-}$  or  $C_2B_{10}H_{12}$ . These five atomic orbitals form a  $\sigma$  (bonding),  $\pi$  (bonding), and  $\delta$  (antibonding) set of five molecular orbitals, like those in the  $\pi$  electron system of  $C_5H_5$ .

# *ACCOUNTS OF CHEMICAL RESEARCH*

VOLUME 6

NUMBER 8

AUGUST, 1973

## **Three-Center Bonds in Electron-Deficient Compounds. The Localized Molecular Orbital Approach**

William N. Lipscomb

*Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138*

*Received December 18, 1972*

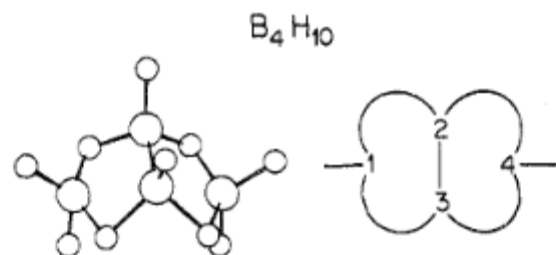
Having more valence atomic orbitals than valence electrons, electron-deficient compounds present ambiguities in the use of the paired electron bond. Molecular orbitals, at least of stable neutral compounds, are filled usually with a substantial energy gap to the lowest unoccupied excited orbital. However, molecular orbitals based upon the molecular symmetry group are delocalized. Moreover, they are not readily transferable to chemically closely related molecules.

Here, we seek a middle ground: nearly transferable multicenter bonds. We derive localized molecular orbitals (LMO's) objectively from accurate self-consistent field (SCF) molecular orbital (MO) theory. We explore the limits of transferability of these LMO's in the boranes, carboranes, and their related ionic species. Finally, we only begin to ask how these LMO's restrict the compositions, geometries, and reaction pathways in this area of chemistry.

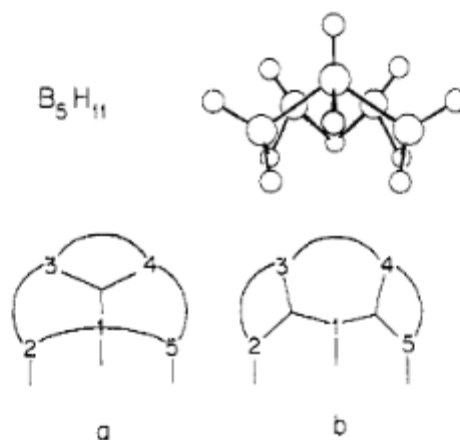
### Localized Molecular Orbitals

Recent studies have considerably narrowed the gaps between resonance descriptions of these molecules<sup>1,2</sup> and molecular orbital results.<sup>3,4</sup> Extended Hückel theory, developed in this laboratory,<sup>4,5</sup> has been related<sup>6,7,8</sup> to rigorously defined SCF theory<sup>9,10</sup> of complex molecules. Leaving aside the severe limitations of SCF theory when electron correlation<sup>11</sup> is important, we note that it yields good approximations to electron density and to properties derived from one-electron operators,<sup>12-14</sup> like the dipole moment and nmr shielding constants.

Here, we start with symmetry MO's. Their conversion to localized chemical bonds is achieved by mixing MO's of different symmetries. For example, con-

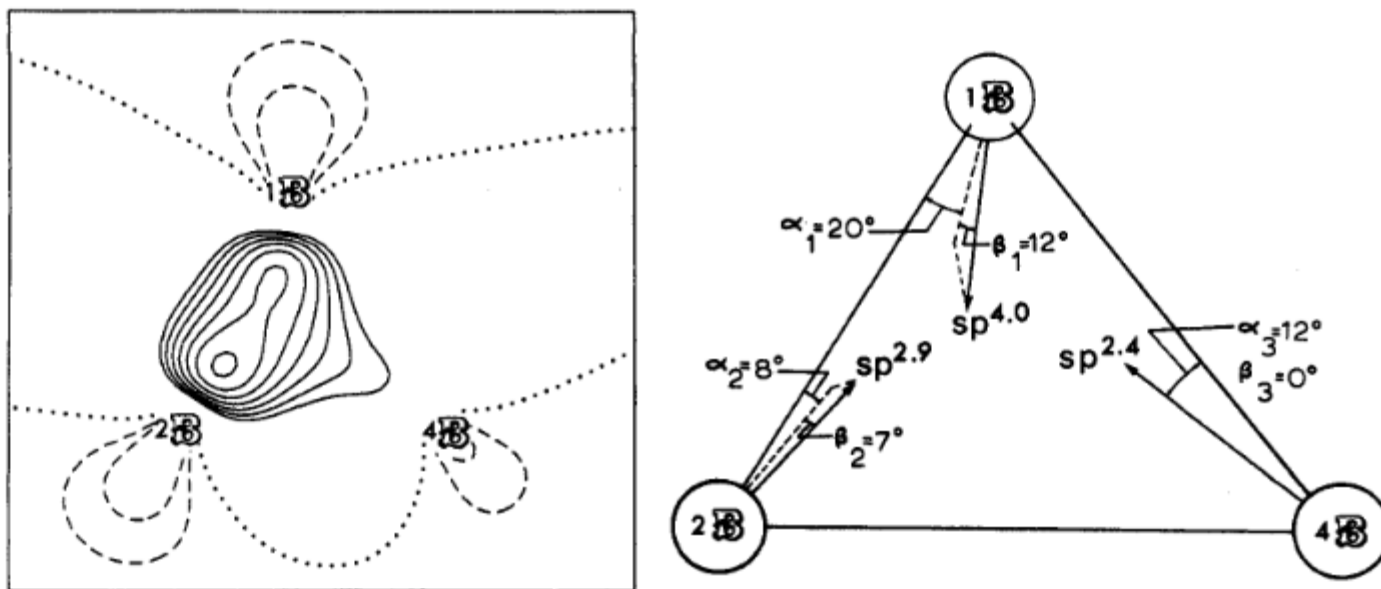


**Figure 3.** Geometrical and localized valence structure of  $B_4H_{10}$ . One terminal hydrogen is omitted from each boron (or, later, carbon) atom. The extra terminal H is indicated by a straight line, and the bridge hydrogen by a curved line.



**Figure 4.**  $B_5H_{11}$ . Structure a, with an open three-center B(2)-B(1)-B(5) bond, is not favored by the localization, which yields central three-center bonds idealized in structure b.





**Figure 5.** (a) One of the two localized three-center orbitals in the boron framework of  $B_5H_{11}$ . The electron density is obtained by squaring this function. (b) Hybrids resulting from the localization procedure.



**Figure 6.**  $B_6H_{10}$ , which localizes uniquely.

# 3D Aromaticity

Such a localized orbital can be imagined to exist in every triangular face of  $B_nH_n^{2-}$ . In the present approach, the adjacent localized orbitals in the same  $B_nH_n^{2-}$  ion are assumed to interact with each other, as in the case of  $p_\pi$  orbitals of carbon atoms in an unsaturated hydrocarbon. This assumption leads to a delocalized MO energy scheme of the  $B_nH_n^{2-}$  ion. Each MO of  $B_nH_n^{2-}$  can hence be expressed as a linear combination of the three-center BBB bonding orbitals. This three-center bond formalism actually leads to the same pattern of MO energy levels as does the LCAO method.<sup>12</sup>

On this basis, the MO calculation can be carried out in a manner entirely analogous to the original Hückel method for treating conjugated hydrocarbons, setting up an  $N \times N$  matrix  $A$ , where  $N$  is the number of triangular faces of a polyhedral borane considered. The  $n$ th column and  $n$ th row of the matrix are each put into a 1:1 correspondence with the  $n$ th face of the polyhedron. Diagonal matrix elements are given the value  $\alpha$  (Hückel Coulomb integral), and off-diagonal matrix elements, which correspond to faces with an edge in common, the value  $\beta$  (Hückel resonance integral). All other matrix elements are set equal to zero.

A secular equation of this polyhedral borane is then expressed as

**Table I.** Resonance Energies of Polyhedral Boranes

Species	Molecular shape	Number of faces	Resonance energy ( $\beta$ )	Number of valence structures <sup>a</sup>
$B_4H_4$	I	4	0.000	1
$B_5H_5^{2-}$	II	6	0.000	2
$B_6H_6^{2-}$	III <sup>b</sup>	8	0.844	32
$B_7H_7^{2-}$	IV <sup>c</sup>	10	0.938	20
$B_8H_8^{2-}$	V <sup>c</sup>	12	0.798	8 <sup>h</sup>
$B_9H_9^{2-}$	VI <sup>d</sup>	14	0.813	16
$B_{10}H_{10}^{2-}$	VII <sup>e</sup>	16	1.145	72
$B_{11}H_{11}^{2-}$	VIII <sup>f</sup>	18	1.000	16 <sup>h</sup>
$B_{12}H_{12}^{2-}$	IX <sup>g</sup>	20	1.763	132 <sup>h</sup>

<sup>a</sup> Reference 18. <sup>b</sup> R. Schaeffer, D. Johnson, and G. S. Smith, *Inorg. Chem.*, **4**, 917 (1965). <sup>c</sup> F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *ibid.*, **6**, 1271 (1967). <sup>d</sup> L. J. Guggenberger, *ibid.*, **7**, 2260 (1968). <sup>e</sup> R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 1779 (1962). <sup>f</sup> F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966). <sup>g</sup> J. A. Wunderlich and W. N. Lipscomb, *J. Am. Chem. Soc.*, **82**, 4427 (1960). <sup>h</sup> R. N. Camp, I. R. Epstein, and W. N. Lipscomb, unpublished work.