Polyatomic Complexes

The overarching name “polyatomic complexes” covers cage and cluster compounds, an is defined as complexes containing more than one metal atom.

Cages are complexes where there are no direct linkages between metal atoms.

Clusters are polymetallic complexes that contain direct metal-metal bonds. We will talk entirely about cluster complexes

Transition Metal Polyatomics

Transition metal polyatomics tend to follow the 18 e^- rule, and thus this can be useful in predicting structure.

This is called the Inert-Gas Shell approach.

It assumes that clusters are comprised of two major factors: metals and ligands.

4-Centred Clusters

Four-centred clusters tend to take on one of the three following geometries:

tetrahedron	butterfly	square planar
6 bonds	5 bonds	4 bonds
closo	*arachno* (O_h)	

5-Centred Clusters

As the number of centres increase, the number of possible arrangements of them increases exponentially. Luckily, the clusters adhere to a small subset of arrangements.

trigonal bipyramidal
9 bonds
closo

square planar
8 bonds
nido (O_h)

edge-bridged Td
8 bonds
nido

bridged butterfly
7 bonds

bow-tie
6 bonds

Hexanuclear Clusters

Hexanuclear clusters are often octahedral, and sometimes trigonal prisms.

octahedral
12 bonds (this is deceiving)
closo (O_h)

trigonal prism
9 bonds

Several of the other six-membered clusters are based on smaller geometries.

Hexanuclear Clusters (cont'd)

bicapped
tetrahedron
11 bonds

edge-sharing
bitetrahedron
11 bonds

edge-bridged
square pyramid
10 bonds

9 bonds

bicapped
butterflies
9 bonds

8 bonds

Restrictions

This method works well for transition metal clusters of 5 or less metals.

Exceptions occur:

- for 6-membered octahedral arrangements; these tend to follow Wade’s rules.
- for larger clusters; larger clusters adopt structures based on smaller clusters.
- for metal centres that typical disobey the 18 e^- rule.

Restrictions (cont'd)

The metal centres that typical disobey the 18 e^- rule also do not obey this predictive method:

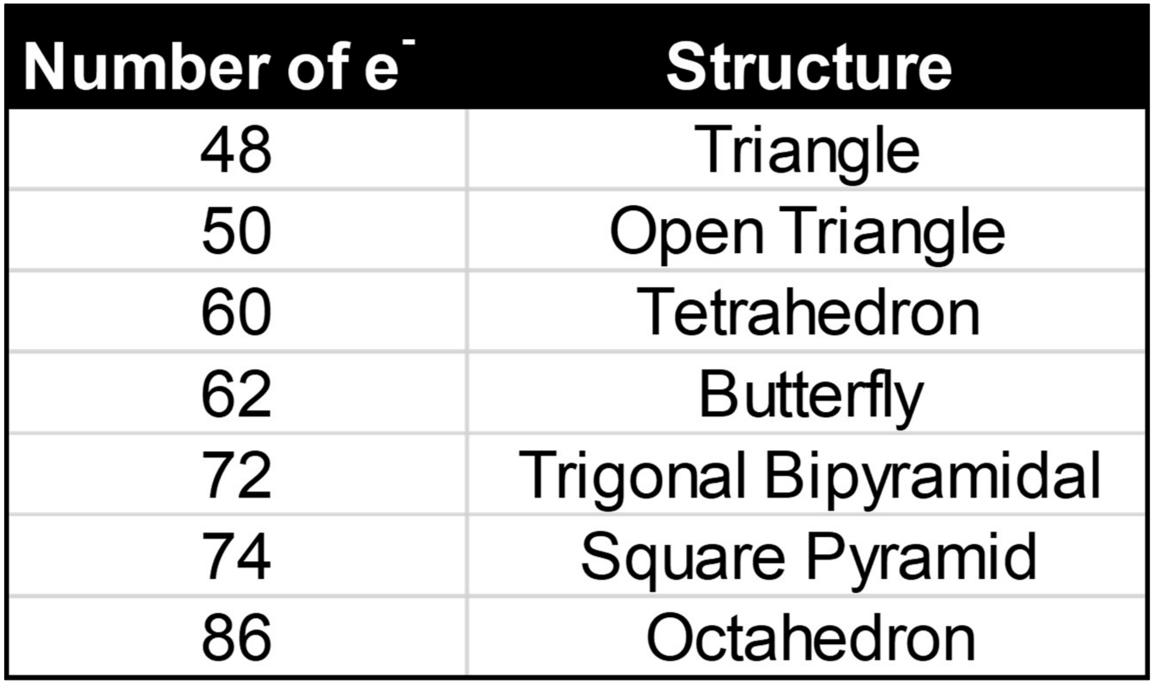
- d^8 centres prefer a 16 e^- arrangement due to a relatively high energy p_z metal orbital that tends to remain non-bonding.
- Heavy group 11 metals have a large s – p orbital gap and prefer 14 e^- species.
- Metals whose normal oxidation states and/or with π donor ligands don't follow the 18 e^- rule.

Low oxidation state metals with π acceptor ligands are the best candidates for this system, thus it is populated by metal carbonyls.

Magic Numbers

Because this system relies on the metals to require 18 e^-, there are specific numbers that predict different structures.

These are called the magic numbers:



Number of e^-	Structure
48	Triangle
50	Open Triangle
60	Tetrahedron
62	Butterfly
72	Trigonal Bipyramidal
74	Square Pyramid
86	Octahedron

Electron-Rich Systems

As system with “excess” electrons does not require the same number of M-M bonds.

With respect to the magic numbers, having 2 excess electrons opens one bond in the geometry:

Electron Poor Systems

In some cases, there is a greater electron deficiency than typical:

$H_2Os_3(CO)_{10}$

2 (H) + 24 (Os) + 20 (CO) = 46 e^-

This requires (3 x 18) 54 e^- to satisfy the Inert-Gas Shell of the osmium atoms. It has an 8 e^- deficit and thus requires four M-M bonds. The only way three metals can have 4 M-M bonds is to allow a (formal) double bond

Try predicting the structure of $H_4Re_4(CO)_{12}$.

An Example

For $Re_4(CO)_{16}^{2-}$:

Metal valence e^- = 4 x 7 (Re from group 7) = 28
Ligand valence e^- = 16 x 2 (CO is a Lewis base) = 32
negative 2 charge = 2
Total e^- = 62

Number of e^- for electron-precise structure = 4 x 18 = 72

So, there is a deficit of 10 e^-, or there needs to be 5 M-M bonds.

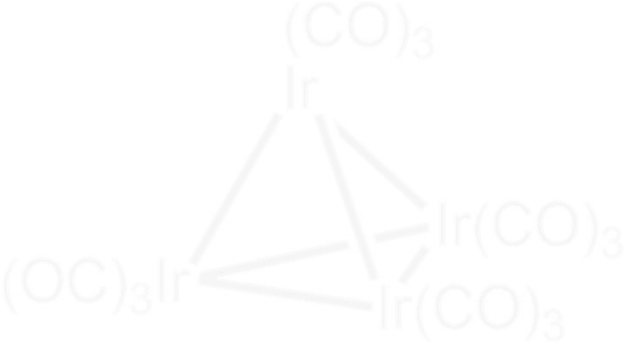
The structure with 4 centres and 5 M-M bonds is butterfly.

Synthesis of Metal Clusters

Transition metal clusters are necessarily low oxidation state metals with π-acceptor ligands. Thus they are often made in reducing environments in the presence of CO:

$$4\ IrCl_4 + 12\ CO + 8\ Cu\ (300\ atm,\ 200^{o}C) \rightarrow Ir_4(CO)_{12} + 8\ CuCl_2$$

$$4\ IrCl_4 + 20\ CO + 8\ H_2O\ (200\ atm,\ 60^{o}C) \rightarrow Ir_4(CO)_{12} + 16\ HCl + 8\ CO_2$$



Metal valence e^- = 4 x 9 (Ir) = 36

Ligand valence e^- = 12 x 2 (CO) = 24

no charge = 0

Total e^- = 60

Number of e^- for electron-precise structure = 4 x 18 = 72

needs 12 e^- = 6 bonds: tetrahedron

Thermal/Photochemical

Induced loss of carbonyls from 18 e^- species also results in condensation to clusters:

$$Co_2(CO)_8 \text{ (50°C)} \rightarrow Co_4(CO)_{12} \text{ (70°)} \rightarrow Co_6(CO)_{16}$$

$$Os_3(CO)_{12} + [Co(CO)_4]^- \text{ (h}\upsilon\text{)} \rightarrow [Os_3Co(CO)_{12}]^- + 4\ CO$$

The drawback to this technique is that less stable materials produce the bulk metal, losing all ligands:

$$Ni(CO)_4 \text{ (50°C)} \rightarrow Ni^0 + 4\ CO$$

$$Re_2(CO)_{10} \text{ (130°)} \rightarrow Re^0 + 10\ CO$$

Thermal Activation

Small clusters are often used to generate larger clusters by this method. Often a range of clusters is produced:

$$Os_3(CO)_{12}\ (210^{o}C) \rightarrow Os_6(CO)_{18} + Os_5(CO)_{16} + Os_7(CO)_{21} + Os_8(CO)_{25}$$

Metal valence e^- = 6 x 8 (Os) = 48

Ligand valence e^- = 18 x 2 (CO) = 36

no charge = 0

Total e^- = 84

Number of e- for electron-precise structure = 6 x 18 = 108

needs 24 e^- = 12 bonds: this thing

Clusters With Main Group Elements

If you remember, we counted e^- to understand metal clusters using the 18 e^- rule (Inert Gas Shell):

- Count the valent metal electrons as if the metal had a zero oxidation state.
- Count Lewis base ligands as 2 e^- donors (e.g. CO).
- Count covalent ligands as 1 e^- donors (e.g. Cl^-, H^-).
- Count Cp ligands as 5 e^- donors.
- Count η^6 arene ligands as 6 e^- donors.
- Add for negative charge, subtract for positive charge.

We can do this including main group fragments

- CH_2 donates 2 e^-, C donates 4 e^-, etc.

An Example with a Main Group Element

This method treats main group centres as ligands, and they donate electrons as makes sense.

For $Fe_5C(CO)_{15}$:

Metal valence e^- = 5 x 8 (Fe from group 8) = 40
Ligand valence e^- = 15 x 2 (CO is a Lewis base) = 30
= the naked carbon contributes 4 = 4
Total e^- = 74

Number of e^- for electron-precise structure = 5 x 18 = 90

There is a deficiency of 16 e^-. So 8 M-M bonds are needed.

Its either a square pyramid or an edge-capped tetrahedron.

$Fe_5C(CO)_{15}$

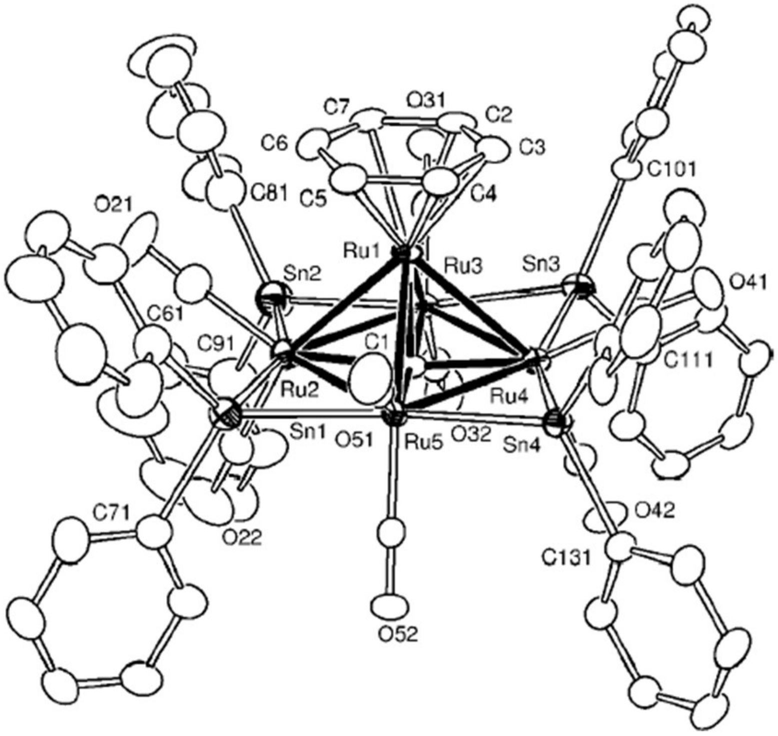
Notice that the carbon is not considered part of the over-all cluster and is actually interstitial. This is common for transition metal carbonyl clusters with main group elements.

A Main Group – T.M. Cluster

$Ru_5(CO)_8(SnPh_2)_4(C_6H_6)(m^5\text{-}C)$:

Ru:	5 x 8 =	40
CO:	8 x 2 =	16
$SnPh_2$:	4 x 2 =	8
C_6H_6:	1 x 6 =	6
C:	1 x 4 =	4
Total		74

Predicted: 5 x 18 = 90



So, there is a 16 e^- deficiency, calling for 8 bonds.

Either square pyramidal or edge-capped tetrahedron.

Adams, R. D.; Captain, B.; Fu , W.; Smith, M. D. Inorg. Chem., ***2002****, 41, 5593–5601.*

Synthesis of Main Group –TM Clusters

There are a myriad of ways to make main group – TM complexes, but they can be as simply as by a methathesis reaction:

$$BiCl_3 + 3\ [Ir(CO)_4]^- \rightarrow BiIr_3(CO)_9 + 3\ CO + 3\ Cl^-$$

Or insertion into an E-H bond:

$$Fe_3(CO)_{12} + RPH_2 \rightarrow H_2Fe_3(CO)_9(PR) + 3\ CO$$

Thermolysis or Photolysis

Thermolysis or photolysis can also induce clustering, in the same way it does in TM clusters:

This can also lead to interstitial elements:

Direct Reaction with the Element

Direct reaction of a transition metal cluster with the element can produce main group – TM clusters:

$$Co_2(CO)_8 + P_4 \rightarrow Co_3(CO)_9P + Co_2(CO)_6P_2 + Co(CO)_3P_3$$

Exception: Octahedral Structures

Octahedral structures systematically have two more electrons than would be predicted by the 18 e^- rule:

$Ru_6C(CO)_{17}$: 6 x 8 = 48
1 x 4 = 4
17 x 2 = 34
Total = 86

Predicted = 6 x 18 = 108

There is a deficit of 22 e^-, which is 11 M-M bonds. They actually form an octahedron (12 M-M bonds).

These structures are better predicted by PSEPT

Boranes

Boranes are a type of cluster compounds where the cluster is a geometric shape with some or all of the vertices occupied by a B-H group.

Boranes fall into 5 distinct classes, based on empirical formula:

$[B_xH_x]^{2-}$ are the closo-boranes: closed structure
$[B_xH_x]^{4-}$ are the nido-boranes: nest-like structure
$[B_xH_x]^{6-}$ are the arachno-boranes: spider-web-like structure

$[B_xH_x]^{8-}$ are the hypho-boranes: net-like structure
$[B_xH_x]^{10-}$ are the klado-boranes: branched structure

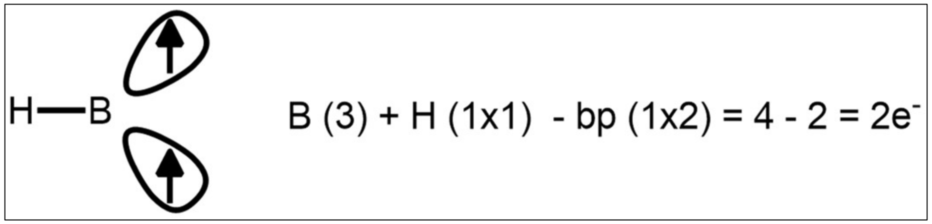
Boranes and their derivatives follow Wade’s rule, which is a simplification of PSEPT.

Wade’s Rule: Boranes

If the cluster is derived from a deltahedron (i.e., regular polygon with triangular faces) with “n” vertices, then there are n+1 bonding electron pairs. Thus, clusters can be assigned shape by their number of electron pairs.

This can be easily demonstrated using borane clusters.

- Each B-H unit donates two electrons for skeletal bonding.



B (3) + H (1x1) - bp (1x2) = 4 - 2 = 2e$^-$

- Each additional hydrogen in the cluster contributes one electron for skeletal bonding.
- There are additional electrons for each negative charge.

Bonding in PSEPT Clusters

PSEPT (polyhedral skeletal electron pair theory) clusters have each cluster nucleus contribute three orbitals to the cluster skeleton, for a total of 3n orbitals.

For PSEPT, “n” is the number of vertices in the parent deltahedron.

Of these orbitals, symmetry arguments have n+1 orbitals as bonding, n+1 as antibonding, and n-2 as non-bonding orbitals.

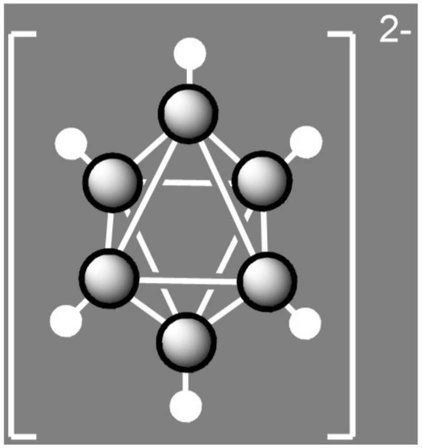
In comparison to the inert-gas shell model:

- the n+1 bonding orbitals are similar to the metal-metal bonds.
- the n-2 non-bonding orbitals are similar to the metal orbitals used for non-bonding pairs.

A good example is $B_6H_6^{2-}$.

$B_6H_6^{2-}$

Describe the cluster $[B_6H_6]^{2-}$:



B-H = 6 x 2 = 12

Charge = 2

Total = 14 (7 pairs)

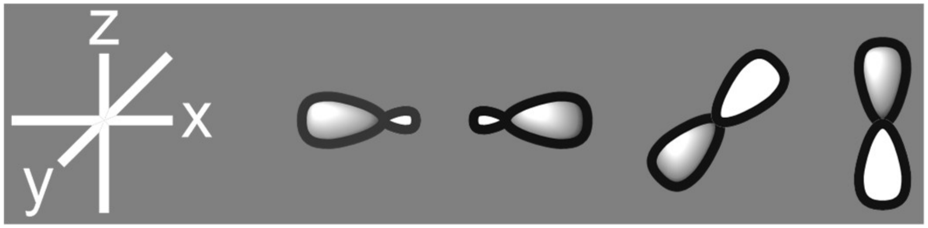
n+1 = 7, n = 6

This cluster has a parent octahedral structure, and is *closo.*

(6 borons)

Bonding in $B_6H_6^{2-}$

Symmetry-adapted orbitals for the borane octahedron are comprised of sp-hybridised centres, with two unmixed p orbitals:

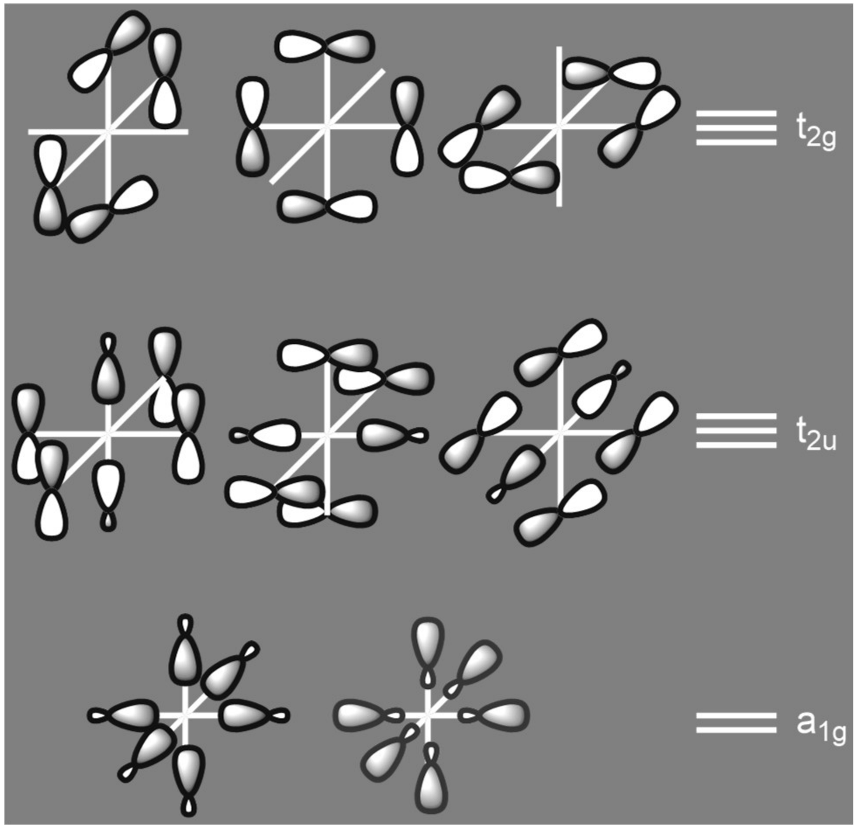


These can be mixed into eight bonding orbitals according to symmetry arguments.

Note that the fact that the nuclei are spherically arranged allows symmetry degeneracy that would normally not exist.

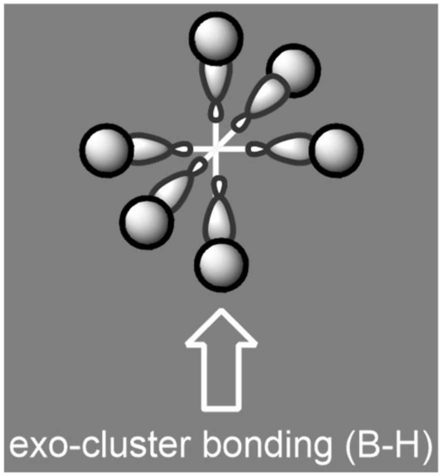
This limits PSEPT to deltahedra, and precludes many of the lower-symmetry cluster geometries allowed by the inert-gas shell arrangement.

Bonding SALCs



Bonding in $B_6H_6^{2-}$

The sp hybrid (red) is involved in exo-cluster bonding with the hydrogen atoms to give a bond order of 6 (1 per B-H bond):



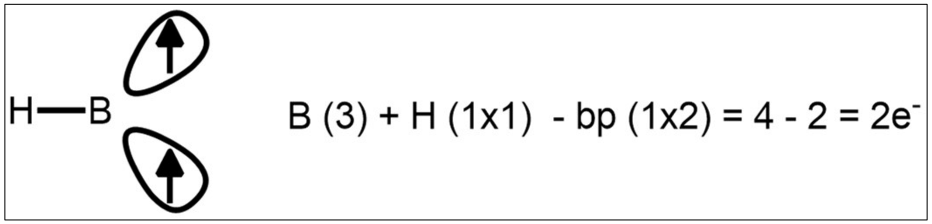
This leaves the remaining 7 orbitals (n+1) to form the skeletal orbitals for the polyhedron

Wade’s Rule: Boranes

If the cluster is derived from a deltahedron (i.e., regular polygon with triangular faces) with “n” vertices, then there are n+1 bonding electron pairs. Thus, clusters can be assigned shape by their number of electron pairs.

This can be easily demonstrated using borane clusters.

- Each B-H unit donates two electrons for skeletal bonding.



B (3) + H (1x1) - bp (1x2) = 4 - 2 = $2e^-$

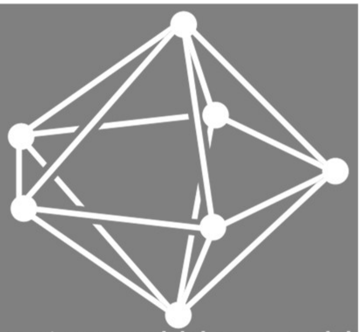
- Each additional hydrogen in the cluster contributes one electron for skeletal bonding.
- There are additional electrons for each negative charge.

Deltahedra

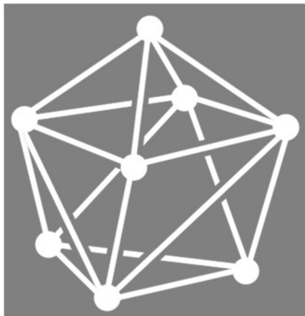
tertahedron
4 centres

trigonal bipyramid
5 centres

octahedron
6 centres

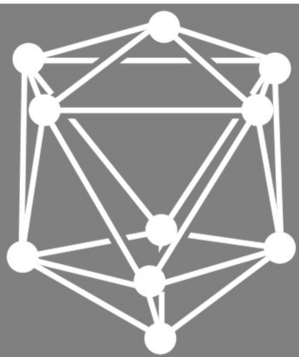


pentagonal bipryramid
7 centres



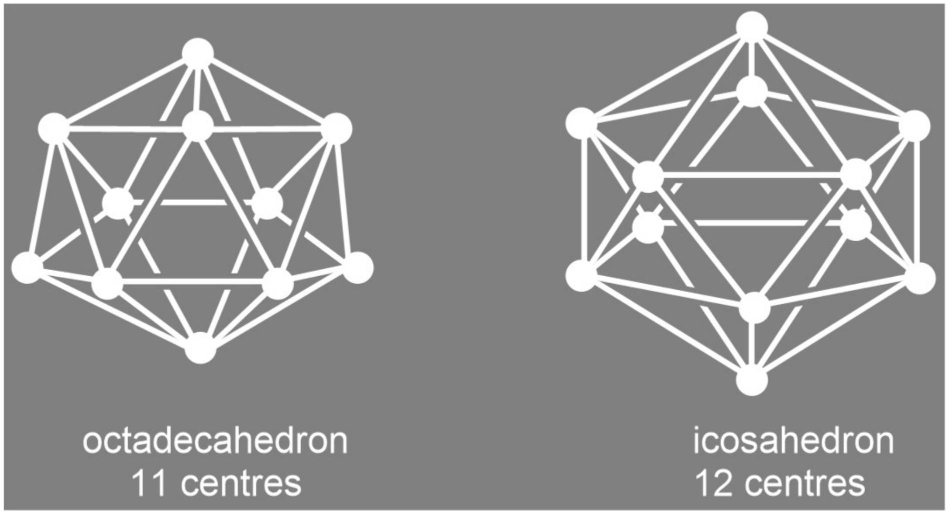
dodecahedron
8 centres

tricapped
trigonal prism
9 centres



bicapped archemedean
(square) antiprism
10 centres

Deltahedra (cont'd)

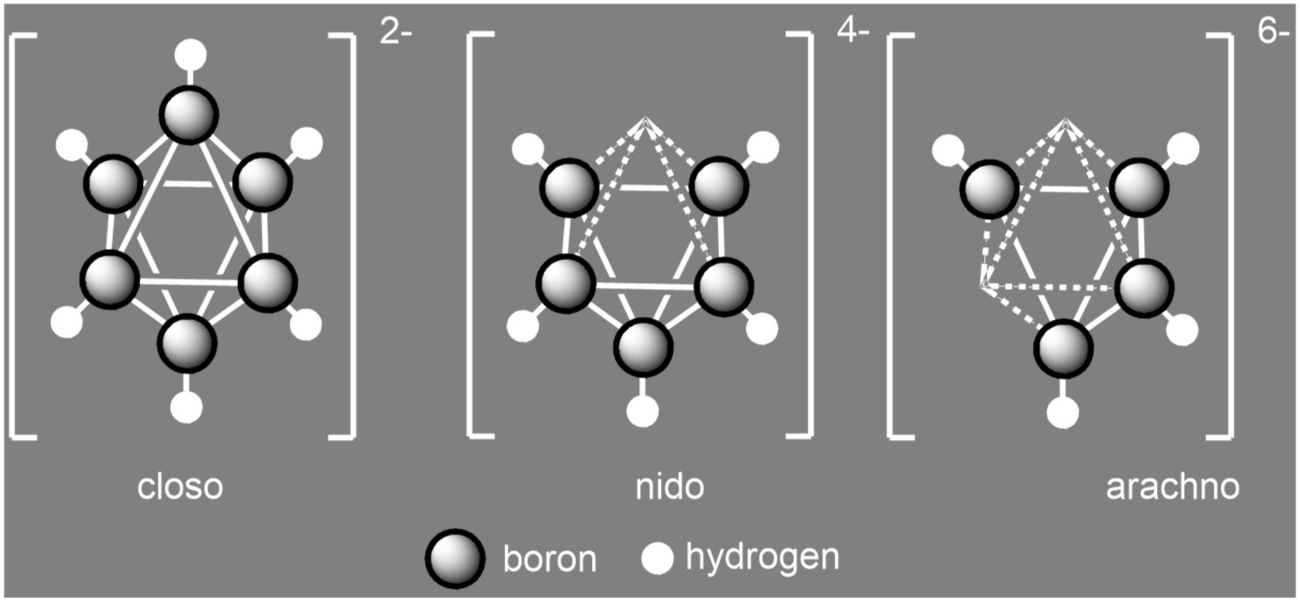


Deltahedra describe boranes (and carboranes) so well because these centres bond with three orbitals.

When transition metals bond with three orbitals as well, they mimic this structural type, and can be predicted by Wade's rule.

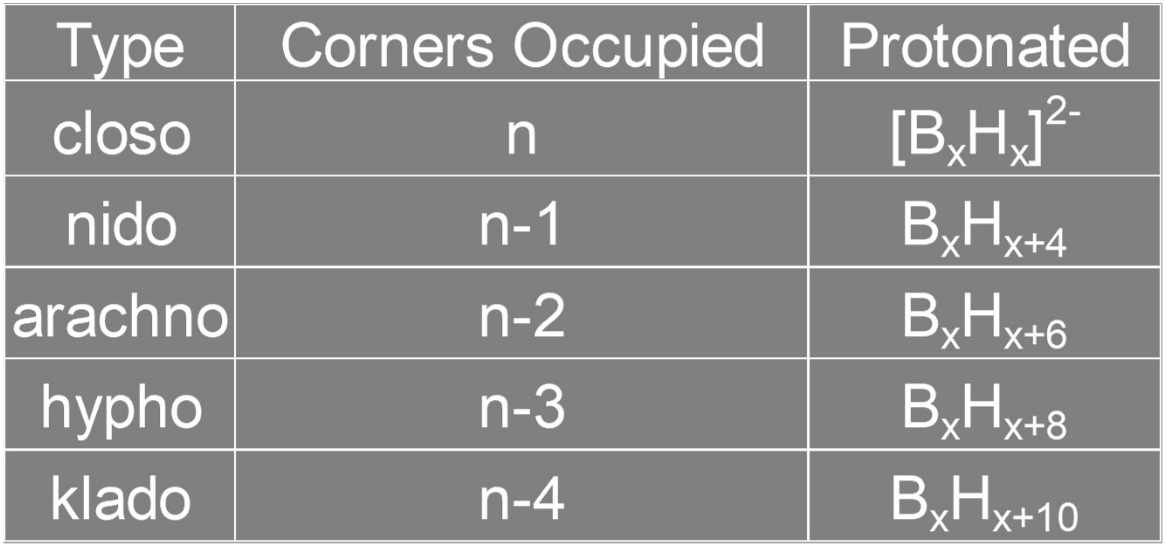
Boranes

These structures are differentiated by an increasing number of "missing corners" in the parent structure. For $B_6H_6^{2-}$:



Boranes

These are differentiated by their number of vertices and electron pairs in the structure. The below rules assume cluster with n vertices. The fully protonated form is shown to confuse you:

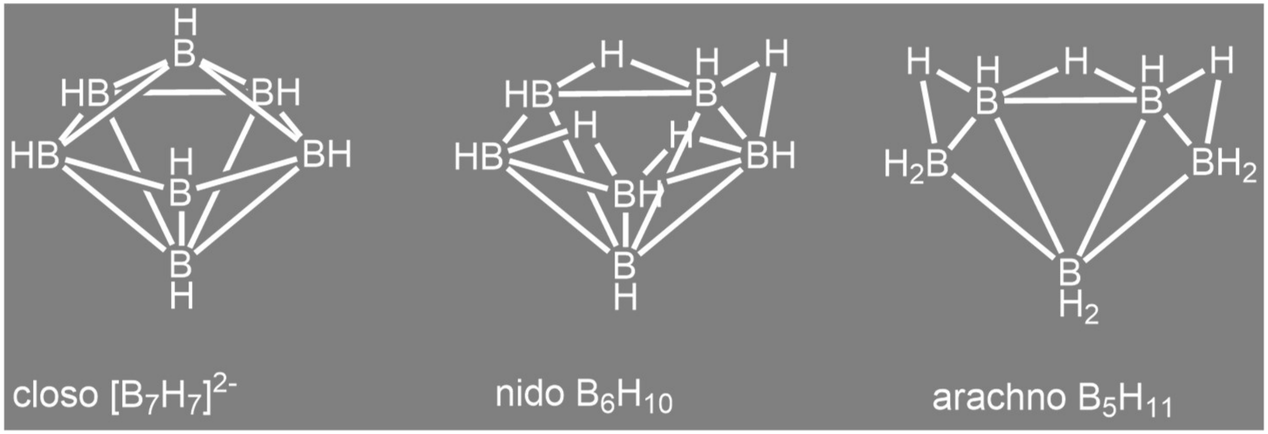


Type	Corners Occupied	Protonated
closo	n	$[B_xH_x]^{2-}$
nido	n-1	B_xH_{x+4}
arachno	n-2	B_xH_{x+6}
hypho	n-3	B_xH_{x+8}
klado	n-4	B_xH_{x+10}

These structures result from are Wade's rule. In the fully protonated species, there is always n+1 electron pairs.

It turns out that only the first three are stable on their own, hypho and klado are derivatives bonded to a larger molecule.

Structures from Wade's Rules



This series loses one boron to go from *closo* to *nido* and then one boron to go from *nido* to *arachno*. The remaining positions are hydrogen capped in a 3 centre, 2 electron (3c2e) bonding arrangement.

Boranes all have a positive ΔG, thus are less thermodynamically stable than pure B and H_2

This series occurs for the carboboranes as well.

Classification of Boranes

Boranes may carry a negative charge; consider it to be the loss of a proton:

Sometimes it is a little obscure to see the structural type right off, so a simple rule can be devised:

$$B_6H_{10} \rightarrow B_6H_6^{4-} + 4\ H^+ \ (\textit{nido})$$

Remove enough protons to make the numbers of H and B equal, the charge determines the class:

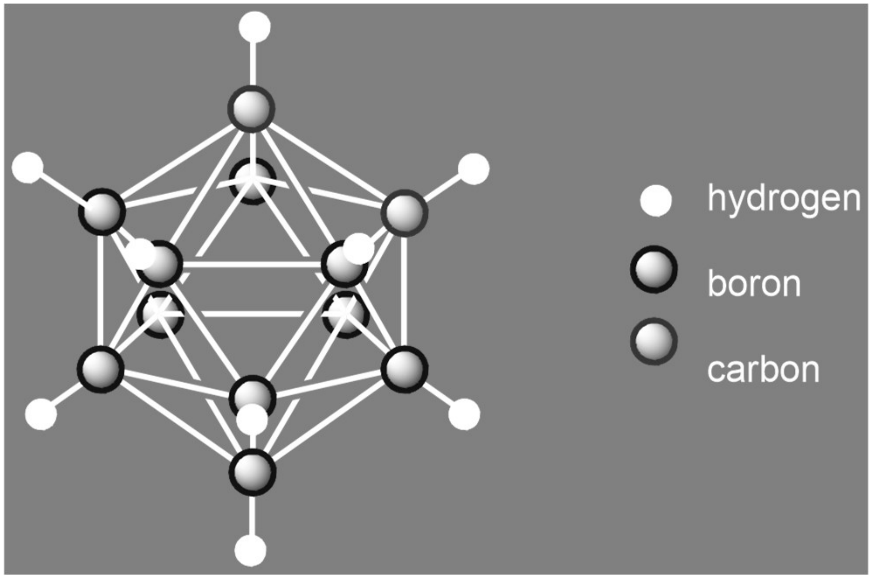
Closo	$B_xH_x^{2-}$
Nido	$B_xH_x^{4-}$
Arachno	$B_xH_x^{6-}$
Hypho	$B_xH_x^{8-}$
Klado	$B_xH_x^{10-}$

Carboboranes

Carboboranes are made from the reaction of boranes with acetylene, having the effect of replacing a B-H moiety with a (C-H)$^+$ moeity:

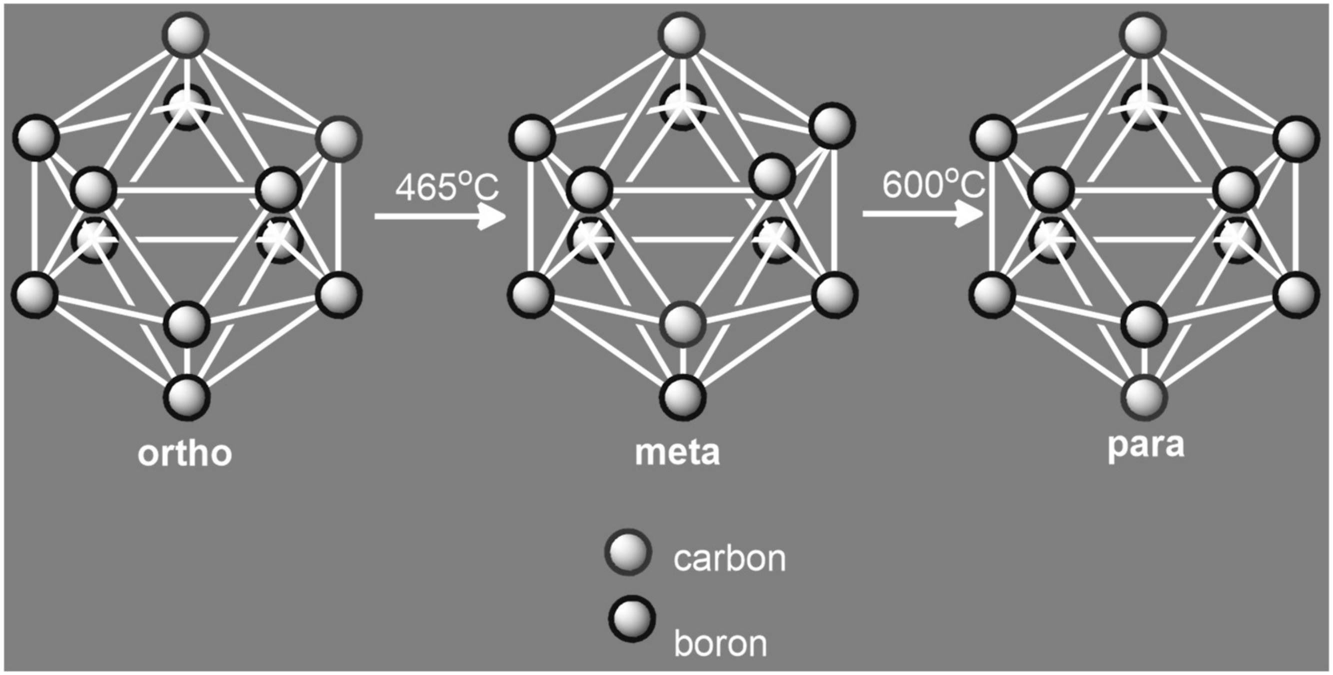
$$B_{10}H_{14}\ (\textit{nido}) + C_2H_2 \rightarrow C_2B_{10}H_{12}\ (\textit{closo}) + 2\ H_2$$

These obey Wade’s rule (but change the charge), and so the general formula shown above is for the *closo* structure.



Closo $C_2H_{10}H_{12}$

The position of the carbon in the structure is temperature dependant:



Note that each vertex actually bears a hydrogen atom, but they are left out because they are a pain to draw.

Structural Types of Carboboranes

The carboboranes can be classified like the boranes, and this classification is dependent on the electron count.

A carbon atom has one more electron in its valence shell than a boron atom, we can correct the electron count by substituting the "C" for a "BH", and then follow the rules for simple boranes:

- $C_2B_8H_{10}$ becomes $(BH)_2B_8H_{10}$, or $B_{10}H_{12}$.
- $B_{10}H_{12} \rightarrow B_{10}H_{10}^{2-} + 2H^+$ and is therefore *closo*.

- $C_2B_4H_8$ becomes $(BH)_2B_4H_8$, or B_6H_{10}.
- $B_6H_{10} \rightarrow B_6H_6^{4-} + 4H^+$ and is therefore *nido*.

Heteroatom Boranes

Clusters replacing a boron with one or more heteroatoms have been seen, and the chemistry is quite extensive.

These all obey Wade’s rule, and thus follow the electron count and structure of the simple boranes.

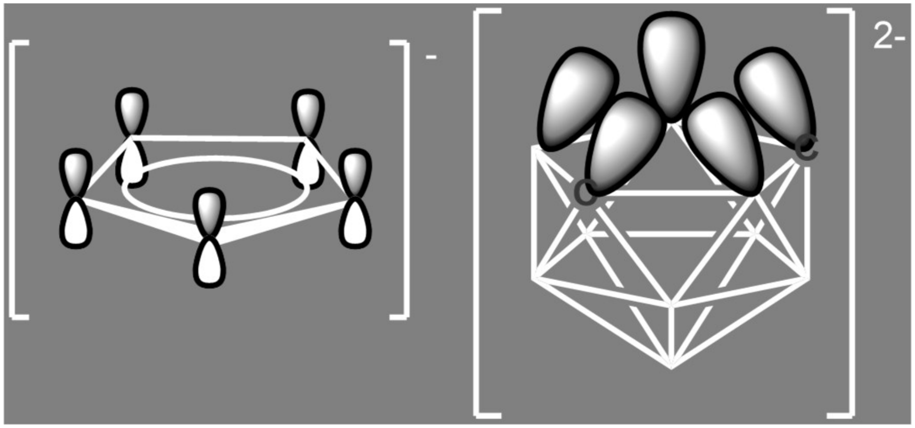
Counting electrons is relatively easy, when you consider the extra electrons each heteroatom provides:

Heteroatom	e^- config.	Replace With
C, Si, Ge, Sn, Pb	[B] + $1e^-$	BH
N, P, As	[B] + $2e^-$	BH_2
S, Se	[B] + $3e^-$	BH_3

Nido-$C_2B_9H_{11}^{2-}$

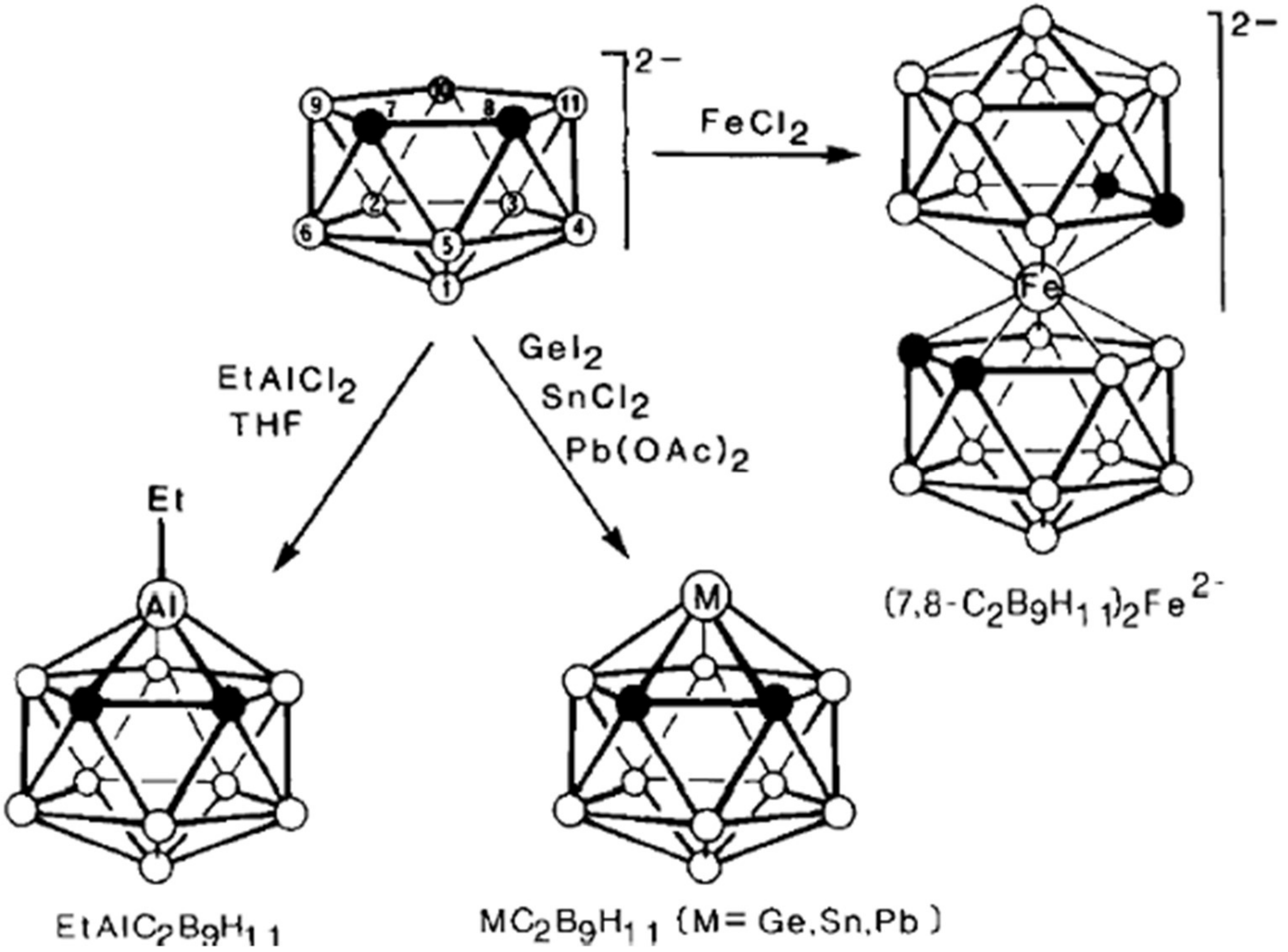
One of the interesting applications of carboranes is that they can be used as η^5 ligands in place of Cp.

They do share an orbital symmetry with Cp, and can be considered isolobal:



Using Nido-$C_2B_9H_{11}^{2-}$

Because of this similarity, it is possible to use this ligand in place of Cp:



Show this is *closo*

Inert Gas Shell vs. PSEPT

The 18 e^- rule considers the bonding in the cluster to follow valence-bond style two centre, two electron (2c2e) bonding.

This means that all of the bonds are localized on the vertices of the resulting polyhedra.

For clusters that approach a spherical distribution of metal atoms, the symmetry increases to such a degree that molecular orbitals change the bonding rules.

PSEPT can predict these structures more accurately. It is based on clusters that have regular dispersion of nuclei and all equilateral triangular faces (i.e., deltahedra).

Differences Between 18 e^- and PSEPT

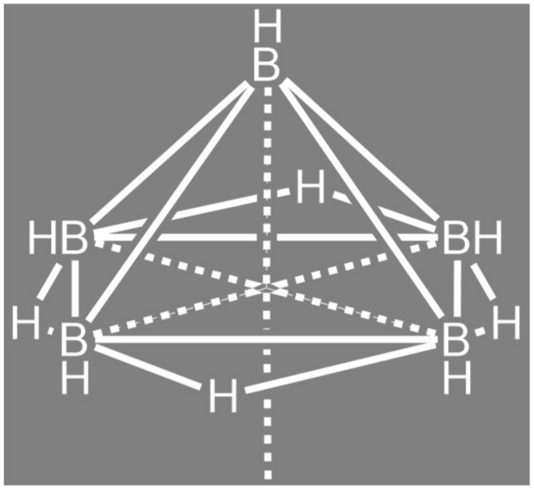
These two methods predict slightly different core electron counts, but often show an overlap in structures.

- The 18 e^- method (Inert-Gas Shell) is used mainly for small clusters of transition metals with carbonyls.
- It is also used when PSEPT predicts a structure with less vertices than metal atoms in the structure.
- Finally, it is used when the metal fragments (including ligands) in the cluster skeleton are contributing more than 2 electrons.

PSEPT is used when the clusters are all main group elements.

- It is also used for structures between 4 – 11 atoms, typically deltahedral arrangements, or modified deltahedrons (*nido, arachno*)

Try $[B_5H_8]^-$



Describe the cluster $[B_5H_8]^-$:

B-H = 5 x 2 = 10
H = 3 x 1 = 3
Charge = 1

Total =14 (7 pairs)

n+1 = 7, n = 6

This cluster has a parent octahedral structure, and is *nido.*

(5 borons)

Isolobality

The ability to make mixed transition metal fragments and main group fragments must be rational from a bonding standpoint.

The fact that these mix in cluster geometries can be predicted by PSEPT because there are similarities in:

- The number of contributed electrons
- The symmetry of the skeletal orbitals
- The energy of skeletal orbitals

Calculations of the frontier orbitals of different fragments can allow the prediction of unknown cluster compounds.

This leads to the idea of isolobal fragments; fragments that share orbital symmetry and energy.

Polyhedral Fragments: Transition Metals

PSEPT says: transition metal fragments contribute 9 MO:

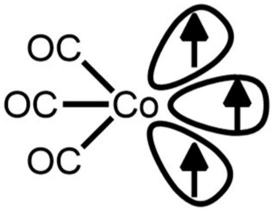
5 d + 3 p + 1 s

Three orbitals (6 e^-) act as non-bonding, so you can’t count those e^-. 3 orbitals (2 e^- each) are involved is “ex-cluster” bonding (i.e., are holding the fragment together, so you can’t count those either:

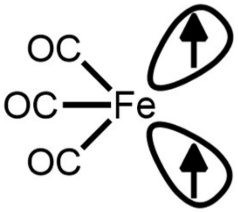
$x = v + n - 6 - 6$,　x is the # of donor e^-
$x = v + n - 12$　v is the valence e^- for the metal
n is the valence e^- for the ligand

You subtract the electrons that are doing something else.

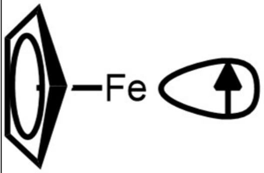
Fragment Donor e^-: Metals



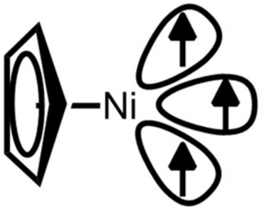
Co (9) + CO (3x2) - 12 = 15 -12 = $3e^-$



Fe (8) + CO (3x2) - 12 = 14 -12 = $2e^-$



Fe (7) + Cp (6) - 12 = 13 -12 = $1e^-$



Ni (9) + Cp (6) - 12 = 15 -12 = $3e^-$

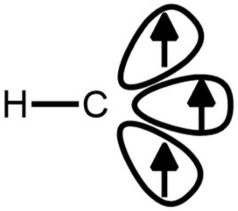
PSEPT in Main Group Elements

Like transition metals, the main group can be generalised with a rule for calculating the electrons the fragment will contribute to skeletal bonding.

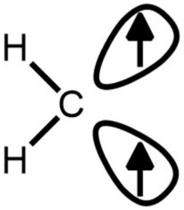
Like the transition metals, one orbital is participating in each ex-cluster bonding, but the d-orbitals are either non-existent or completely filled. Thus the equation becomes:

$x = v + n - 2b$, x is the # of donor e^-
v is the valence e^- for the element (main group only)
n is the valence e^- for the ligand
b is the number of ex-cluster bonds (or lone pairs)

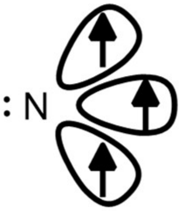
Fragment Donor e^-: Organics



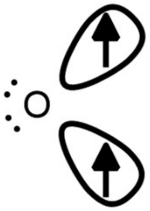
C (4) + H (1x1) - bp (1x2) = 5 - 2 = $3e^-$



C (4) + H (2x1) - bp (2x2) = 6 - 4 = $2e^-$



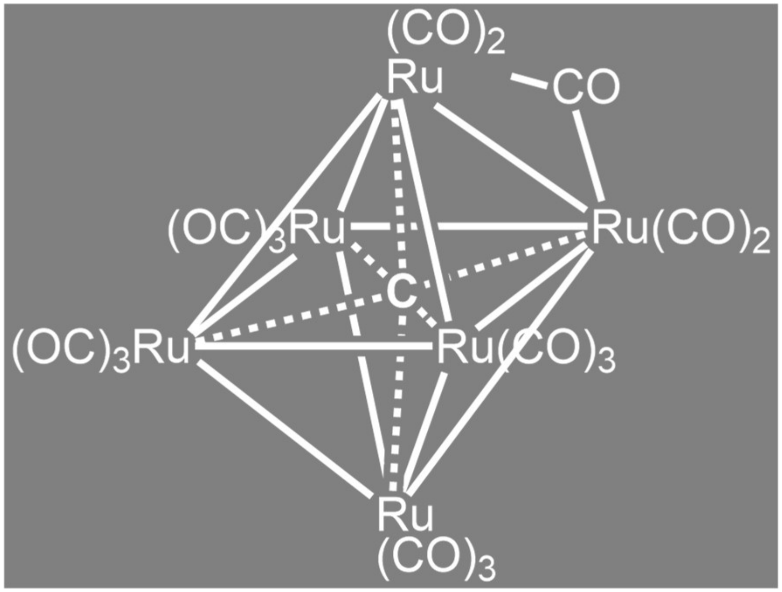
N (5) + 0 - lp (1x2) = 5 - 2 = $3e^-$



O (6) + 0 - lp (2x2) = 6 - 4= $2e^-$

PSEPT for a TM Octahedron

Using the PSEPT for the cluster $Ru_6(C)(CO)_{17}$:
$Ru(CO)_3$ x 4 + $Ru(CO)_2(\mu_2\text{-}CO)$ x 2



x = 8 (Ru) + 6 (3 CO) – 12
= 2
x = 8 (Ru) + 4 (2 CO) + 1 (μ_2-CO) – 12
= 1

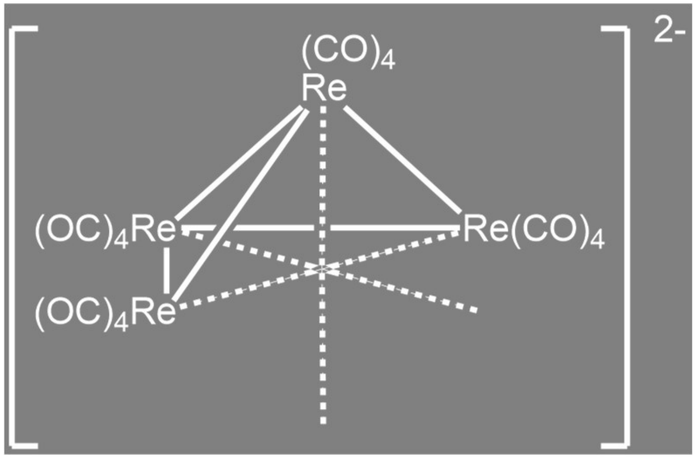
- 4 $Re(CO)_3$ contribute 8 e^-
- 2 $Re(CO)_2$ contribute 2 e^-
- the carbon contributes 4 e^-

totaling 14 electrons or 7 pair.

n+1 = 7, n = 6

This structure is based on the octahedron, and is *closo* (6 Ru).

$[Re_4(CO)_{16}]^{2-}$



We have seen a butterfly structure predicted using the Inert-Gas Shell Approach.

Using the PSEPT for the fragment $[Re(CO)_4]^{2-}$:

x = 7 (Re) + 8 (4 CO) – 12 = 3

Four $Re(CO)_4$ contribute 12 e^- and the negative charge contributes 2 e^-, totaling 14 electrons or 7 pair.

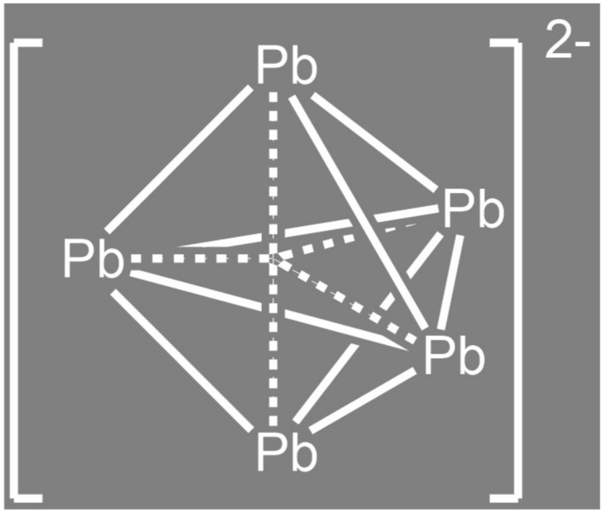
n+1 = 7, n = 6

This structure is based on the octahedron, and is *arachno* (4 Re).

Zintl Ions

Other groups rather than B-H in the main group can form clusters.

Pb_5^{2-} is an example of a Zintl ion:



x = 4 (Pb) + 0 (no ligands) – 2 (lp) = 2

Therefore 5 Pb contributes 10 e^-,
and the charge contributes 2 e^-,
for 12 e^- or 6 pairs.

n+1 = 6, n = 5

This is a trigonal bipyramidal *closo* cluster

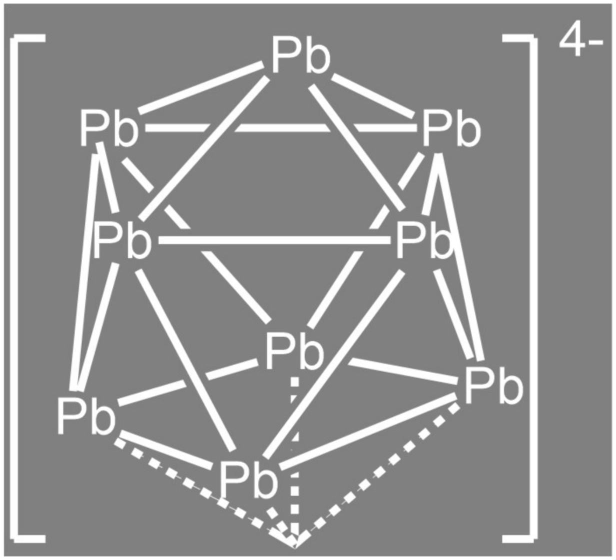
Another Example of a Zintl Ion

Pb_9^{4-} is an example of a Zintl ion:

$x = 4\ (Pb) + 0\ (no\ ligands) - 2\ (lp) = 2$

Therefore 9 Pb contributes 18 e^-,
and the charge contributes 4 e^-,
for 22 e^- or 11 pairs.

$n+1 = 11$, $n = 10$



This is a bicapped archimedean (square) antiprism *nido* cluster.

Zintl Ions

Zintl ions are clusters first found in solutions of main group metals (Sn, Pb, Sb, Bi) in liquid ammonia.

There structural characterization came about when intermetallic phases were dissolved in strongly Lewis basic solvents and the cations sequestered by complexing agents.

The main complexing agent is a cryptand, sometimes called 2,2,2-crypt:

Zintl Ions (cont'd)

Using of complexing cryptands prevented the highly reducing Zintyl phases from interaction with the cation, and thus several phases were isolated:

$$2\ KPb_{2.5} + 2\ 2,2,2\text{-crypt (en, } 50^{o}) \rightarrow (2,2,2\text{-crypt}K)_2Pb_5$$

Ternary intermetallic species gives rise to examples of mixed Zintl phases:

$$KTlSn_x + 2\ 2,2,2\text{-crypt} \rightarrow KTlSn_x + (\text{crypt}K)_3TlSn_8 + (\text{crypt}K)_3TlSn_9$$

In the above example, the stoichiometry isn't balanced because the reaction is not stoichiometric.

The cryptand encourages the dissolution of clusters, and the two predominant cluster compounds are given.

A mixed MG-TM Zintl

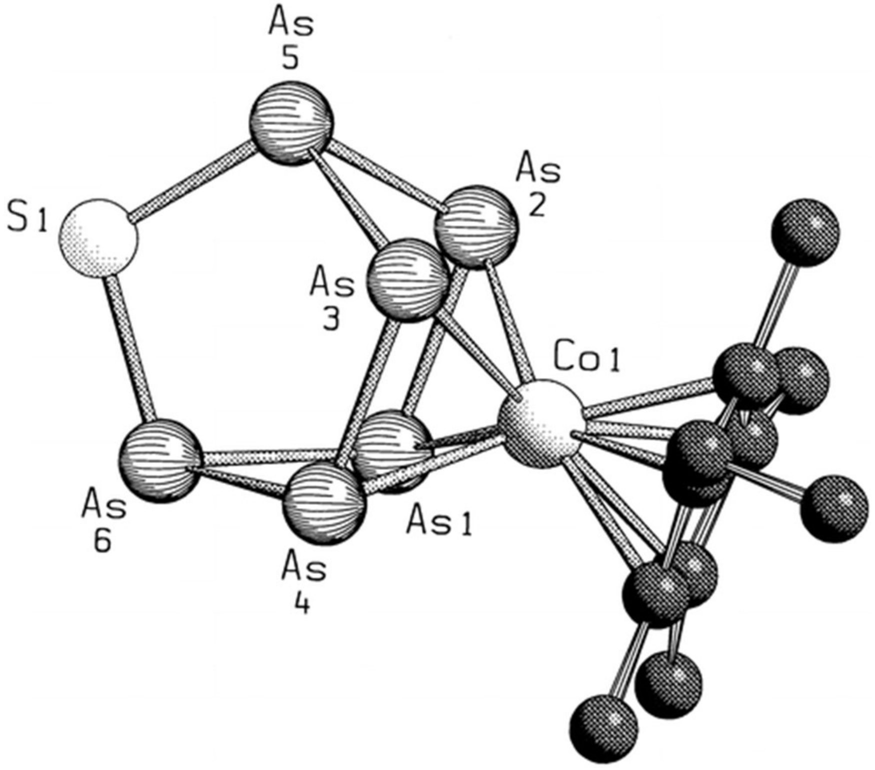
$(C_5Me_4Et)_2Co_2(CO)_2 + As_4S_4\bullet Cr(CO)_5 \rightarrow (C_5Me_4Et)Co(\eta^4\text{-}As_6S)$
(again, not stoichiometric)

For the CpCo fragment:
x = 9 + 5 –12 = 2

For the MG fragment:
As: 6 x 3 = 18
S: 1 x 2 = 2

Total is 22 e^-, 11 pr.
n = 10

This is a *arachno*, bicapped square antiprism
(8/10 cluster centres)

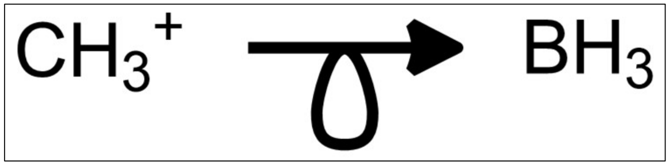


Brunner, H.; Leis, F.; Wachter, J.; Nuber, B. Organometallics ***1997****, 16(23), 4955.*

Isolobal Fragments

Sometimes, the fragments are not isostructural or isoelectronic, which are not necessities for fragments to be isolobal.

Isolobal fragments are typically denoted by an arrow with a lobe on it:



CH_3^+ BH_3

Isolobal Relationships

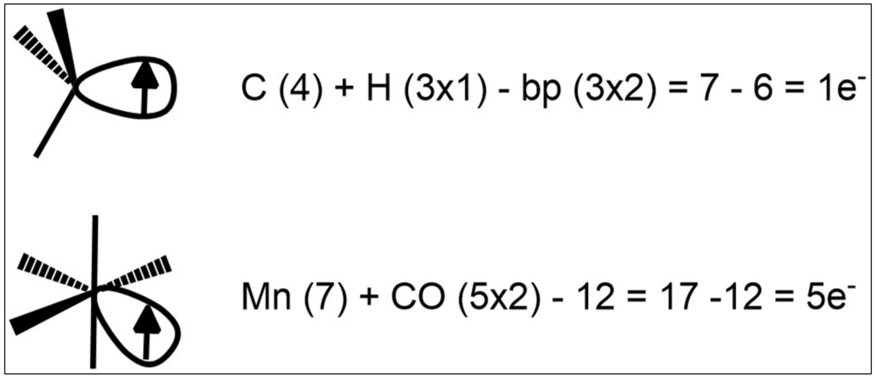
CH_3	**CH_2**	**CH**
H	$Fe(CO)_4$	$Co(CO)_3$
$Mn(CO)_5$	$Re(CO)_2Cp$	$NiCp$
$Fe(CO)_3Cp$	$Cr(CO)_5$	$Re(CO)_4$
$Mo(CO)_3Cp$	$TaMe(Cp)_2$	$Rh(h^6\text{-}C_6H_6)$

BH_3	**BH_2**	**BH**
$Co(CO)_5$	$Mn(CO)_4$	$Fe(CO)_3$
$Mn(CO)_2Cp$	$Fe(CO)Cp$	$ReCp$
CH_3^+	CH_2^+	CH^+

How is $Mn(CO)_5$ Related to CH_3

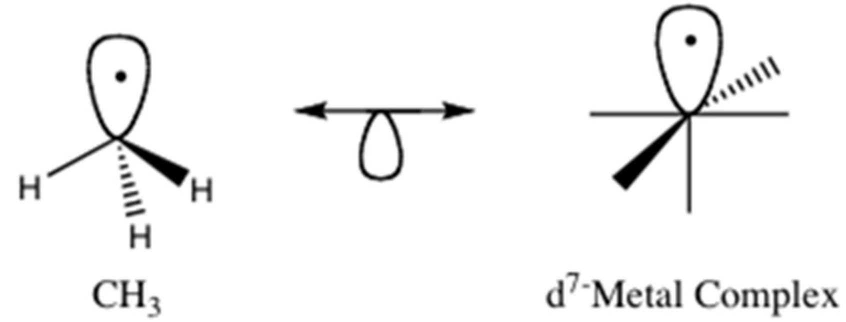
Isolobality is not determined like PSEPT vertex contribution, though there are similarities.

Fragments are isolobal if "if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar – not identical, but similar."



C (4) + H (3x1) - bp (3x2) = 7 - 6 = 1e^-

Mn (7) + CO (5x2) - 12 = 17 -12 = 5e^-



These are simpler to generate graphically, but there are algebraic relationships for them.

Elian, M.; Chen, M. M.-L.; Mingos, D. M. P.; Hoffmann, R.
Inorg. Chem. **1976**, *15*, 1148 – 1155

Calculations

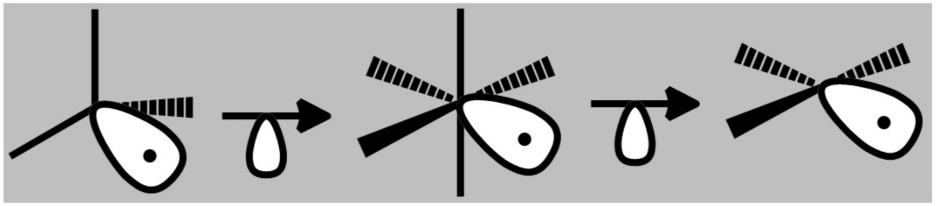
Main Group:	O_h metals	D_{4h}
8 - #e^- = x	18 - #e^- = x	16 - #e^- = x

If “x” is the same in these species, then they want the same number of electrons to fill their valence.

CH_2: 8 – C (4) – 2xH (2x1) = 8 – 6 = 2

$Mn(CO)_5$: 18 – Mn (7) – 5xCO (5x2) = 18 – 17 = 1

$PtCl(PMe_3)_2$: 16 – Pt (9) –Cl (2) – 2xPMe_3 (2x2) = 16 – 15 = 1



Calculations

Main Group: O_h metals D_{4h}

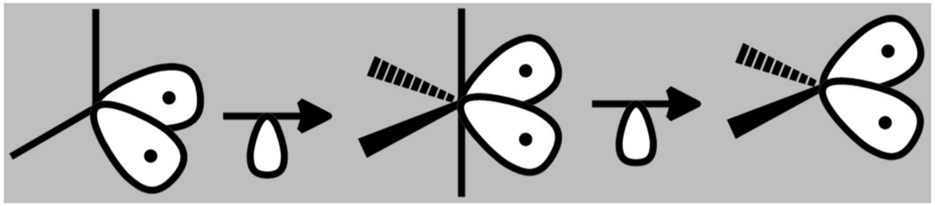
8 - #e^- = x 18 - #e^- = x 16 - #e^- = x

If “x” is the same in these species, then they want the same number of electrons to fill their valence.

CH_3: 8 – C (4) – 3xH (3x1) = 8 – 7 = 1

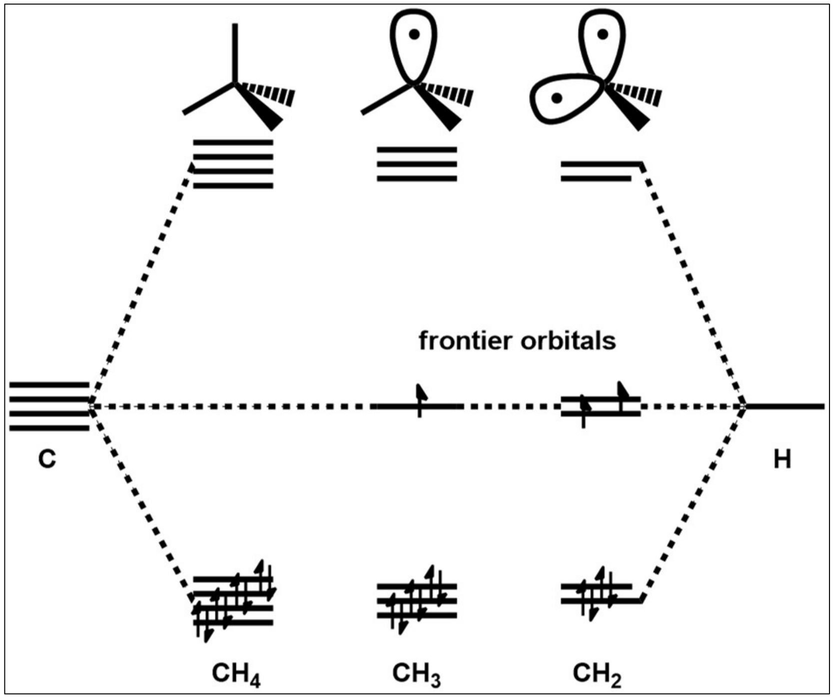
$Fe(CO)_4$: 18 – Fe (8) – 4xCO (4x2) = 18 – 16 = 2

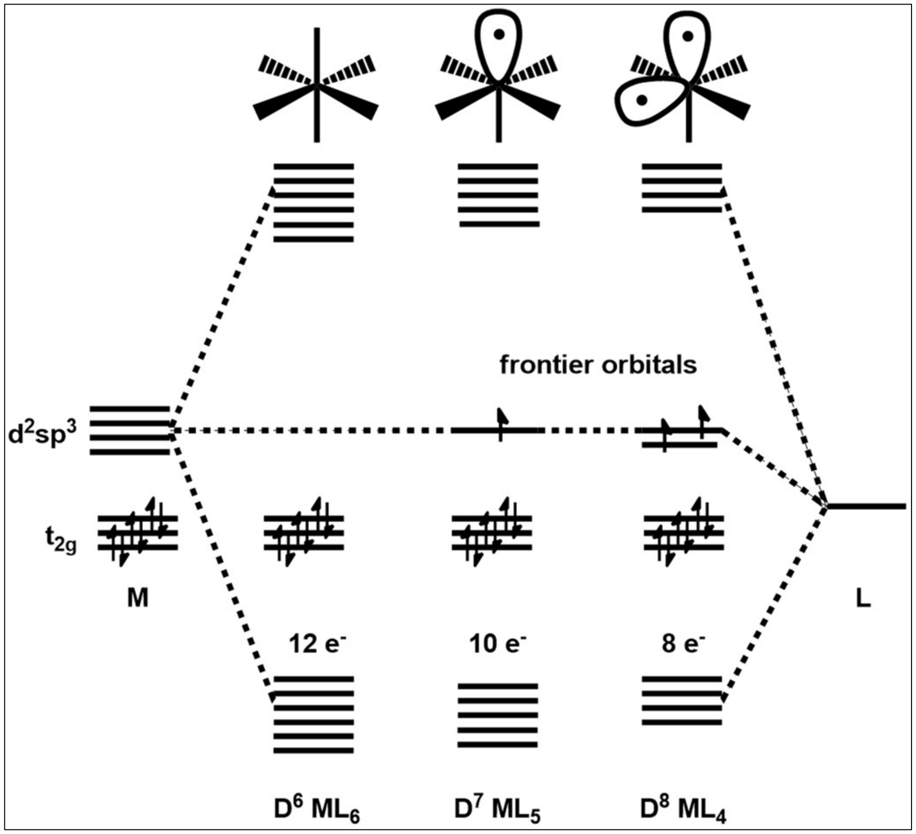
$Ni(NHC)_2$: 16 – Ni (10) – 2xNHC (2x2) = 16 – 14 = 2



MO Diagrams of Isolobality

For metal vertices that want to adhere to the 18 e$^-$ rule, the isolobal analogy states that they have equivalent bonding symmetries to main group fragments that want to adhere to the 8 e$^-$ rule…





Group 13 Compounds

There are three possible oxidation states for the group 13 compounds, represented by the basic formulae:

R_3M – where M is any metal in the group. This is by far the most common organometallic type for group 13.

$R_2M\text{-}MR_2$ – the homonuclear bond gives a formal oxidation state of two. This is specialized reactivity, and not common. It allows for a Lewis acid reactivity.

RM: – oxidation state one relies on (to first principles) the difference in energy between the *n*s and *n*p orbital energies. Since this energy difference becomes more pronounced as *n* increases, this is more common for the heavier group 13 compounds (In, Tl). It allows for a Lewis base reactivity.

Inert Pair Effect

The s orbital penetrates better to the nucleus, and thus these electrons are more tightly bound than the p electrons. As the principle quantum number is increased, this effect increases.

		Ionisation E (MJ/mol)		
	n	**1st**	**2nd**	**3rd**
Al	3	0.58	1.82	2.74
Tl	6	0.59	1.97	2.88

The n = 6 electrons are moving at speeds much closer to the speed of light, thus they behave as if they are massier than other electrons.

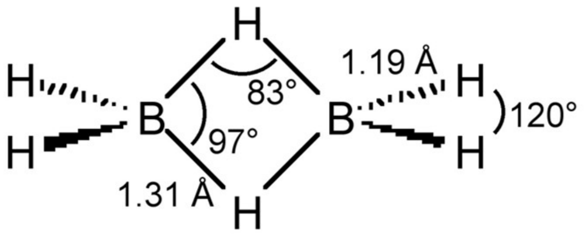
Due to their increased apparent mass, they are more attracted to the nucleus, and the 6s orbital contracts. The same can be said for the 6p electrons, but the nodal plane lessens the electron density at the nucleus.

Thus the 6p electrons are higher energy than the 6s electrons. The 6s pair appears inert.

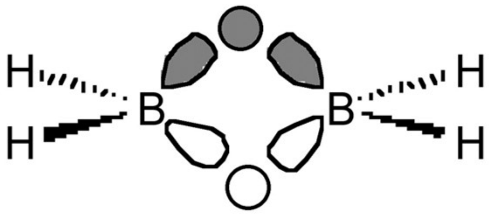
Boron

The chemistry of boron is controlled by two major factors:

- The charge density of boron is higher than the rest of the group, so its sigma bonds are more covalent in nature. It also is very polarizing, which changes its interaction with carbon.
- The diameter of boron is small, and so pi interactions (particularly hyperconjugation) are much more important



(a)



(b)

Homoleptic Alkyls

The homoleptic (all the same R group) alkyls for group 13 are typically monomeric in solution and in the gas phase, with the exception of aluminum.

The trialkyl compounds are typically made by metathesis:

$$BF_3.Et_2O + 3\ RMgX \rightarrow BR_3 + 3\ MgFX + Et_2O$$

$$AlCl_3 + 3\ MeLi \rightarrow AlMe_3 + 3\ LiCl$$

Industrial preparation of alkylboranes exploits the oxophilicity of aluminum:

$$B(OR)_3 + AlR_3 \rightarrow BR_3 + Al(OR)_3$$

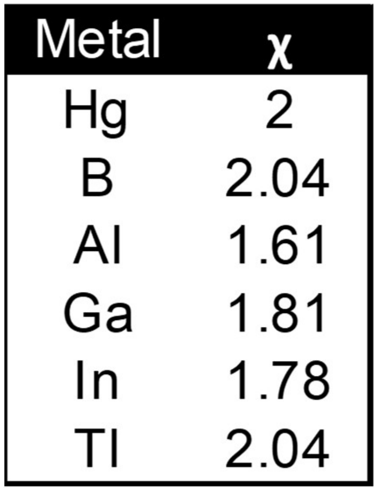
$$B_2O_3 + AlR_3 \rightarrow Al_2O_3 + BR_3$$

Transmetallation

Dialkyl mercury can be (and is) used to make alkyls of Al, Ga, and In, but can’t be used for B or Th:

$$2\,M + 3\,HgR_2 \rightarrow 2\,MR_3 + 3\,Hg$$

This is the most common method of making gallium and indium alkyls



Metal	χ
Hg	2
B	2.04
Al	1.61
Ga	1.81
In	1.78
Tl	2.04

Direct Reaction Of Sorts

AlR_3 can be made by direct reaction:

$$Al + 3/2\ H_2 + H_2C{=}CHR \rightarrow Al(CH_2CH_2R)_3$$

But this is actually a combination of direct reaction and 1,2-insertion (hydrometallation):

$Al + 3/2\ H_2 + 2\ AlEt_3 \rightarrow 3\ HAlEt_2$ “Vermehrung” (increase) step
$3\ Et_2AlH + 3\ H_2C{=}CH_2 \rightarrow 3\ AlEt_3$ “Anlagerung” (attachment) step

Hydrometallation is a common reaction for boron (hydroboration), aluminum, and gallium. The other metals in the group have too low a charge density.

Hydrometallation in Group 13

Hydrometallation goes through a transition state that uses a 3c2e bond:

It is an anti-Markovnikov addition, as the metal will shift to the less sterically congested side, adding the hydride to the higher branched side.

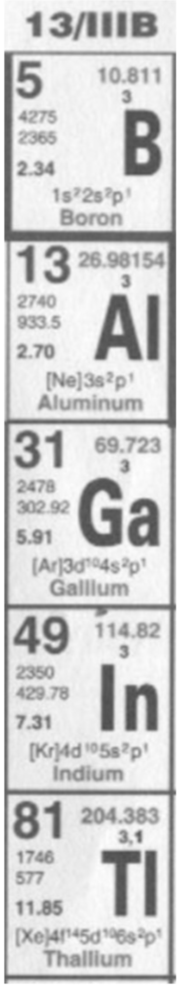
Anti-Markovnikov Regioselectivity

The regioselectivity of hydrometallation in group 13 gets worse down the group, thus hydroboration is the famous example in synthetic chemistry.

A possible explanation is that the orbitals involved are more extensive as *n* increases, making the bond distance longer.

Thus the boron is more responsive to the steric environment than the rest of group 13.

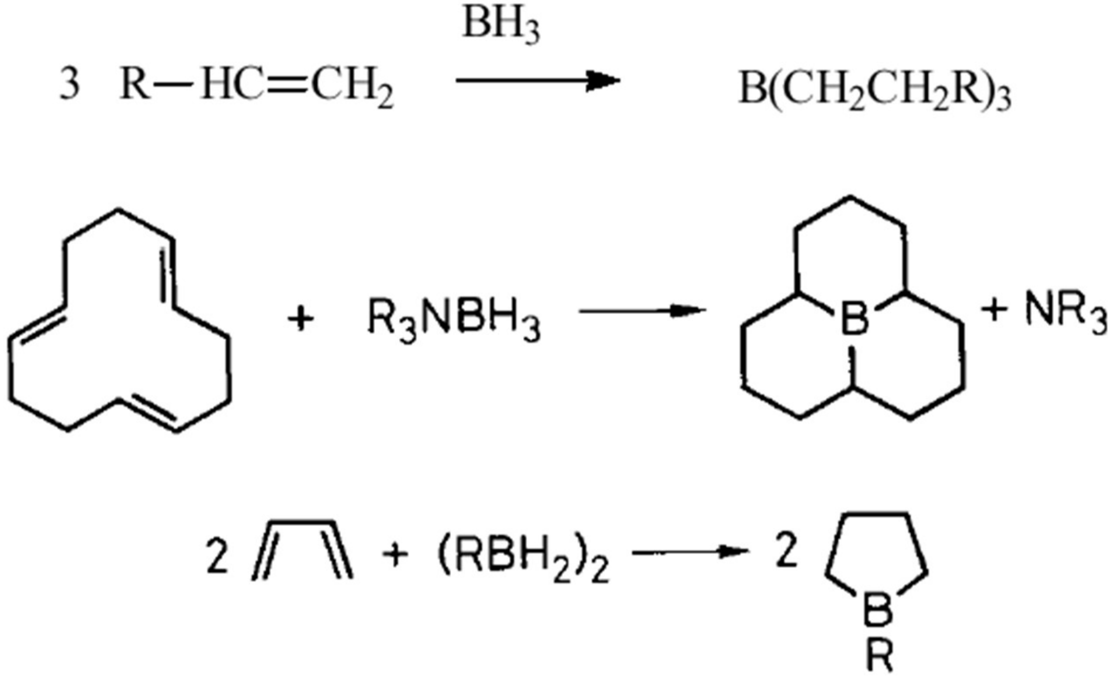
As well, hyperconjugation means that hydroboration is much less reversible than hydrometallation in the rest of the group. This is an important factor in organic chemistry for yields.



13/IIIB
5 10.811 3 4275 2365 2.34 **B** $1s^2 2s^2 p^1$ Boron
13 26.98154 3 2740 933.5 2.70 **Al** $[Ne]3s^2 p^1$ Aluminum
31 69.723 3 2478 302.92 5.91 **Ga** $[Ar]3d^{10} 4s^2 p^1$ Gallium
49 114.82 3 2350 429.78 7.31 **In** $[Kr]4d^{10} 5s^2 p^1$ Indium
81 204.383 3,1 1746 577 11.85 **Tl** $[Xe]4f^{14} 5d^{10} 6s^2 p^1$ Thallium

Boron and Hydrometallation

Some interesting boron organometallic compounds can be made by hydroboration:



$$3\ R{-}HC{=}CH_2 \xrightarrow{BH_3} B(CH_2CH_2R)_3$$

Hydroboration

Hydroboration is a versatile organic reaction:

Displacement: Reverse

The reverse of hydrometallation, elimination of an alkene is possible in hydrometallation:

$$M\text{-}CH_2CH_2R \rightarrow M\text{-}H + H_2C{=}CHR$$

This can be exploited synthetically since the metal (especially Al) will exchange alkene for less branched alkyls:

$$M\text{-}H + H_2C{=}CHR + H_2C{=}CH_2 \rightarrow M\text{-}CH_2CH_3 + H_2C{=}CHR$$

Given the choice, the metal will go to the lower branched system:

$$H_2C{=}CH_2 > H_2C{=}CHR > H_2C{=}CR_2$$

As a synthetic method, you would obviously use an excess of the alkene you want exchanged in.

Aluminium and Hydrometallation

Aluminium is the key example of alkene exchange and reverisble hydrometallation as a synthetic technique:

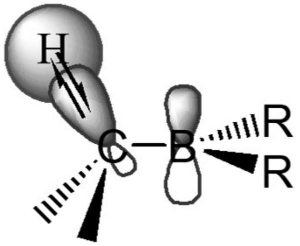
$$Al + 3/2\ H_2 + 3\ H_2C{=}CMe_2\ (100^oC,\ 200\ atm) \rightarrow {}^iBu_3Al$$

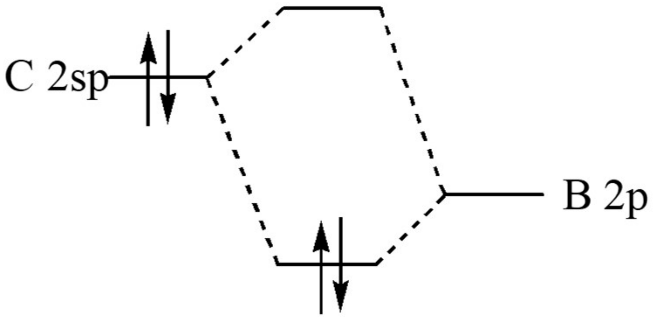
$${}^iBu_3Al + H_2C{=}CHMe \rightarrow {}^nPr_3Al + 3\ H_2C{=}CMe_2$$

$${}^nPr_3Al + 3\ H_2C{=}CH_2 \rightarrow Et_3Al + 3\ H_2C{=}CHMe$$

BR$_3$

R$_3$B is a monomer because of hyperconjugation. Boron's empty p orbital is close to the σ bonds in the α-carbon, due to its very small diameter. It stabilizes itself by forming a partial π bond:





The s bond is free to rotate, and this loss of stabilization is made up for by the hyperconjugation of the p orbital to the other s bonds on the carbon.

It can hyperconjugate to all three groups.

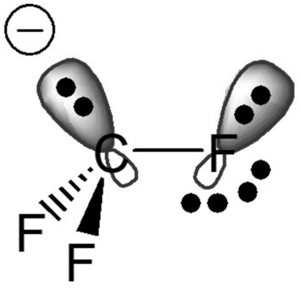
Small Radii

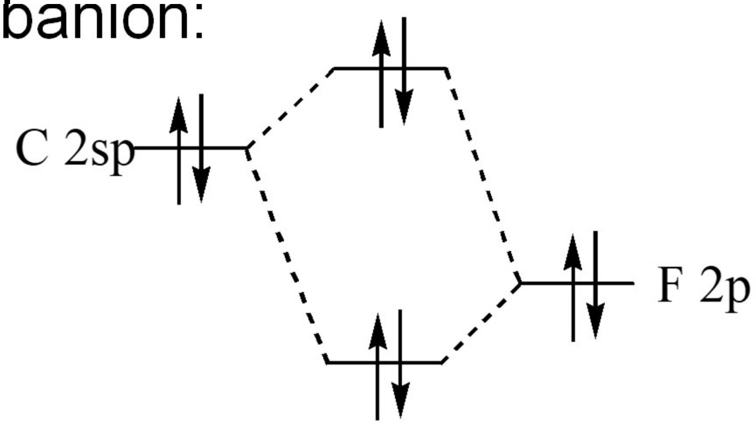
This same interaction is the reason why carbanions are less stable with small radii centres.

The carbanion can be thought of as an sp^3 hybridised centre with a lone pair. This lone pair is stabilised by electron withdrawing groups.

However, the closer these groups are to the carbon (i.e. the smaller their radii), the better the orbitals containing electron pairs can overlap with the electron pair on the carbanion.

Thus the less stable the carbanion:

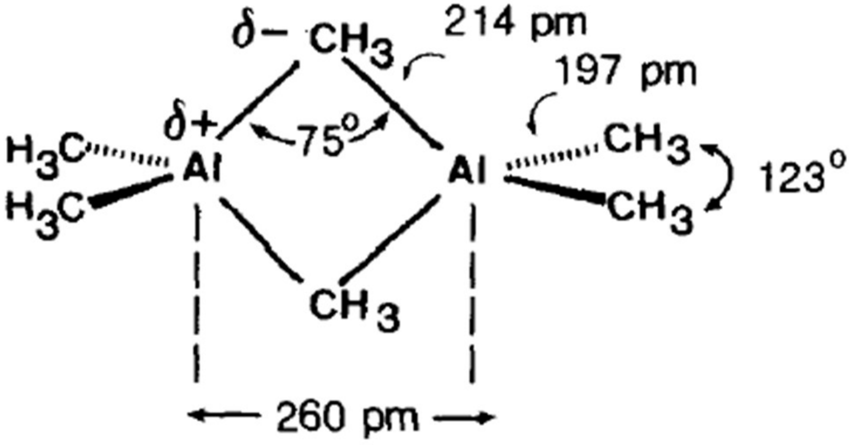




Al_2Me_6

The heavier members of the group exhibit less electrophilicity due to a decreasing charge density, and thus tend not to form 3c2e bonds

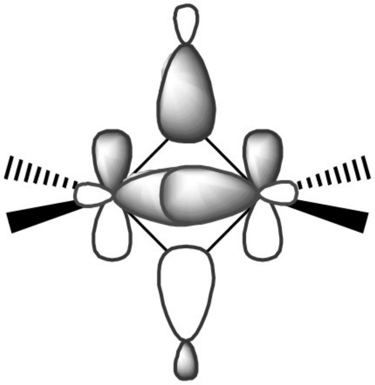
The exception is aluminium, which forms dimers in non-donor solvents:



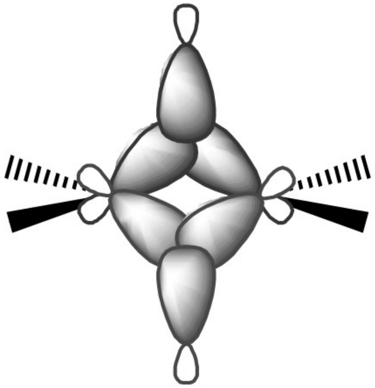
It retains its dimeric nature in the solid crystalline phase, but is a monomer in the gas phase and in donor solvents.

Al_2Me_6 (cont’d)

The closeness of the interatomic Al-Al distance (261 pm in the dimer, compared to 238 pm as a covalent bond) suggests that the geometry of aluminium is fluxional between the sp^2 and sp^3 hybridization:



Al with an sp^2 hybridization

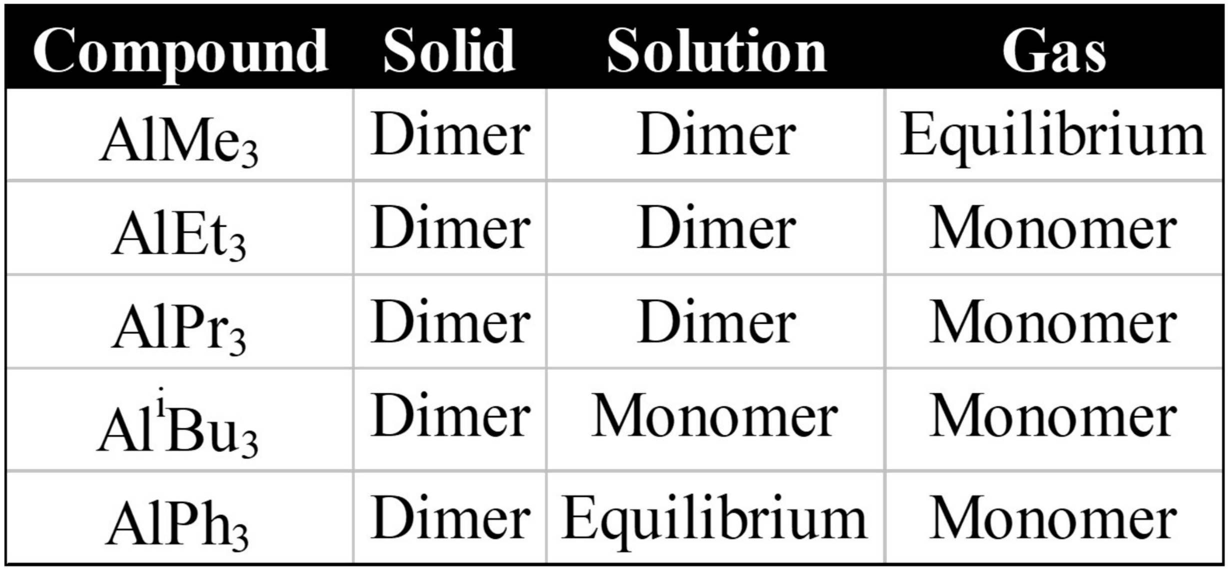


Al with an sp^3 hybridization

Notice that the bond to carbon goes from two 3c2e to one 2c2e bond and one 4c2e bond.

Aluminium Alkyls

On aluminium, the size of the R group affects how much aggregation there is. This is a steric crowding effect.



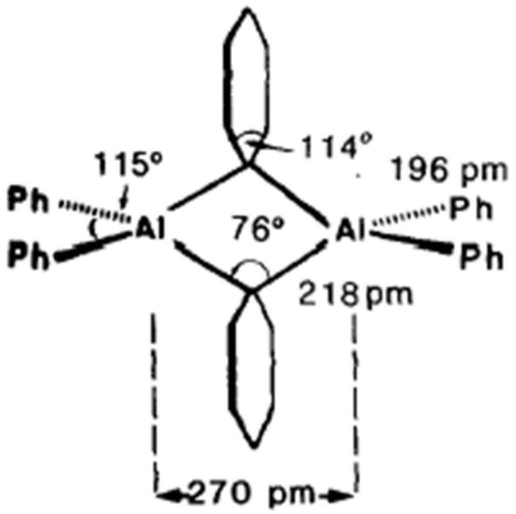
Compound	Solid	Solution	Gas
$AlMe_3$	Dimer	Dimer	Equilibrium
$AlEt_3$	Dimer	Dimer	Monomer
$AlPr_3$	Dimer	Dimer	Monomer
Al^iBu_3	Dimer	Monomer	Monomer
$AlPh_3$	Dimer	Equilibrium	Monomer

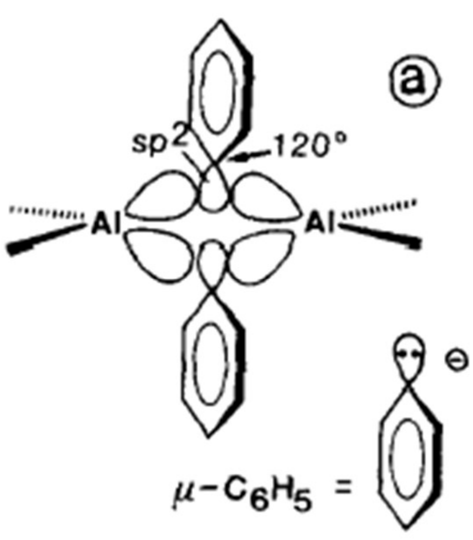
Interestingly, cryoscopic molecular weight determinations can determine the oligomerisation of the species in solution.

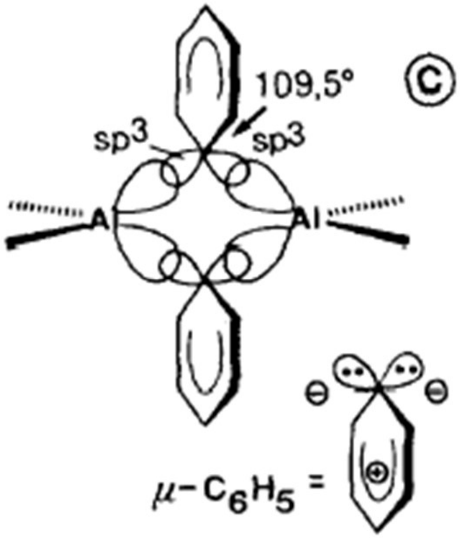
Al_2Ph_6

The internal angle of the phenyl ring and suggests that the bond between the ring and the two aluminium is fluxional between a 3c2e bond and a 3c4e bond.

The 3c4e bond destroy the aromaticity at the bonding carbon by incorporating the π-system p orbital in an sp^3 hybridization:







“Ate” Complexes

Lithium hydride is relatively insoluble and reacts slowly because of the very unreactive Li-H bond.

It is a polymer in the solid state and thus has solubility issues.

Activation of this material is possible by reacting it with MR_3, typically AlH_3 or BH_3:

$$LiH + MH_3 \rightarrow LiMH_4$$

The resulting material is soluble in a larger range of solvents, and is a more reactive hydride source.

The electropositive nature of the group 13 metal centre is the driving force behind complex formation.

Reducing Agents

Most hydrides are used as reducing agents. The most popular in order of reactivity are:

$NaBH_4$: The hydrogen bond is less polar in boron, so this is a less harsh hydride. It is possible to use it in alcohol solutions and even in water, if the reaction is fast. The sodium cation helps solubility in alcohols and water.

$LiAlH(O^tBu)_3$: This is an intermediate reducing agent that isn't as indiscriminate as $LiAlH_4$ but more reactive than $NaBH_4$. (.g. reacts with acid chlorides but not aldehydes)

$LiAlH_4$: very reactive with water and alcohol due to the more polar Al-H bond. This hydride is soluble in toluene, and ethers. It is much stronger.

Mixed Alkyl Halides of Group 13

The most common method of making mixed alkyl/halide compounds in group 13 is reproportionation:

$$2x\ MR_3 + (6-2x)\ MX_3 \rightarrow 6\ MR_xX_{3-x}\ (x = 1, 2)$$

This can be controlled by stoichiometry and conditions.

With many groups, a mixture of RMX_2 and R_2MX can result.

Subsequent reaction usually drives the system to stoichiometrically controlled point, but isolation of a pure product can be difficult.

Thus, there are better ways to go about this.

Reaction with HCl

The metal alkyls (particularly B, Al, Ga) react with one equivalent of hydrogen chloride to eliminate an alkane and form the monochloride:

$$MR_3 + HCl \rightarrow R_2MCl + RH$$

This reactivity is particularly labile and must be controlled (low T, introducing HCl slowly).

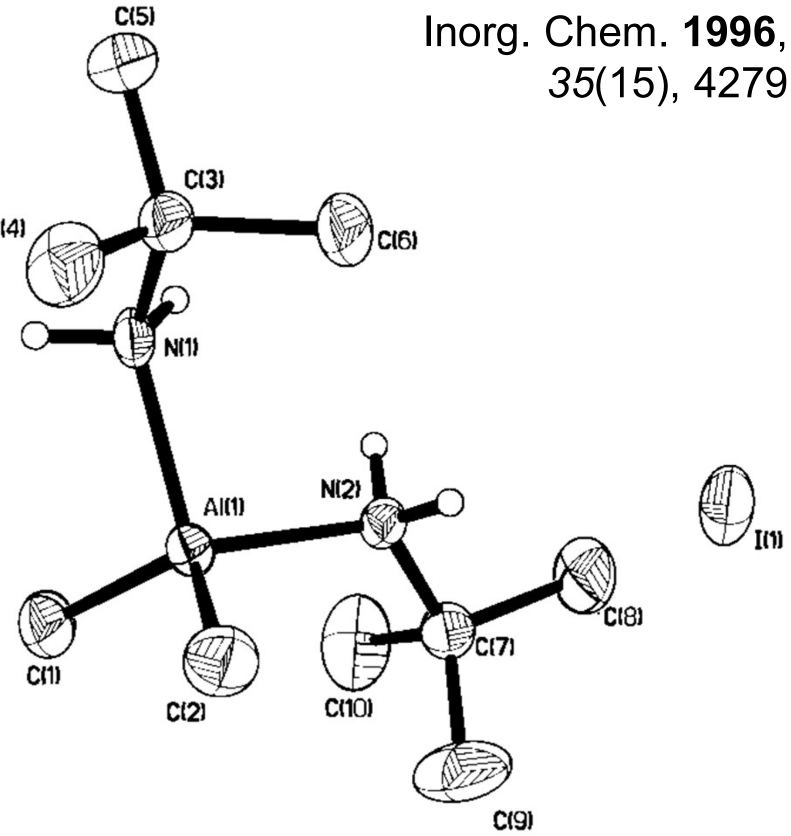
The second replacement can be more difficult (especially with boron) and results in mixed (R_2MCl, $RMCl_2$) systems.

Reaction with R'Cl

Aluminium and gallium can undergo an alkyl-haolgen exchange:

$$R_3Al + R'Cl \rightarrow R_2AlCl + R'R$$

The metals can be stabilised as dialkyl cations when R can be a stable anion.



Inorg. Chem. **1996**, *35*(15), 4279.

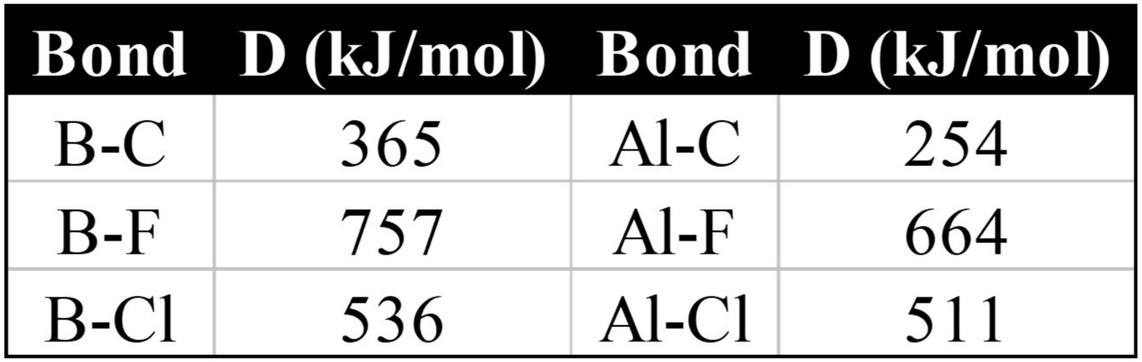
This reactivity requires a base to stabilise the aluminium cation, but demonstrates aluminium's fluxionality in solution.

This chemistry is similar for gallium, but not seen for boron because of the strength of B-C bonds.

Bond Strengths

Again, boron's small size and empty p orbital allows it to make very good hyperconjugated π bonds to carbon.

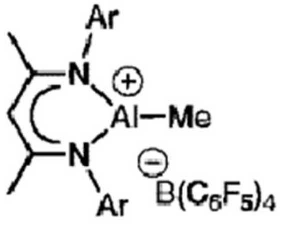
This gives it a strong enough bond that R_2B^+ is not in any significant concentration to allow reaction with R'Cl.



Bond	D (kJ/mol)	Bond	D (kJ/mol)
B-C	365	Al-C	254
B-F	757	Al-F	664
B-Cl	536	Al-Cl	511

Stabilization of Aluminium Cations

The stability of an aluminium cation requires either coordinative saturation (i.e. four groups around aluminium) as per the previous example, or by steric protection of the aluminium centre.



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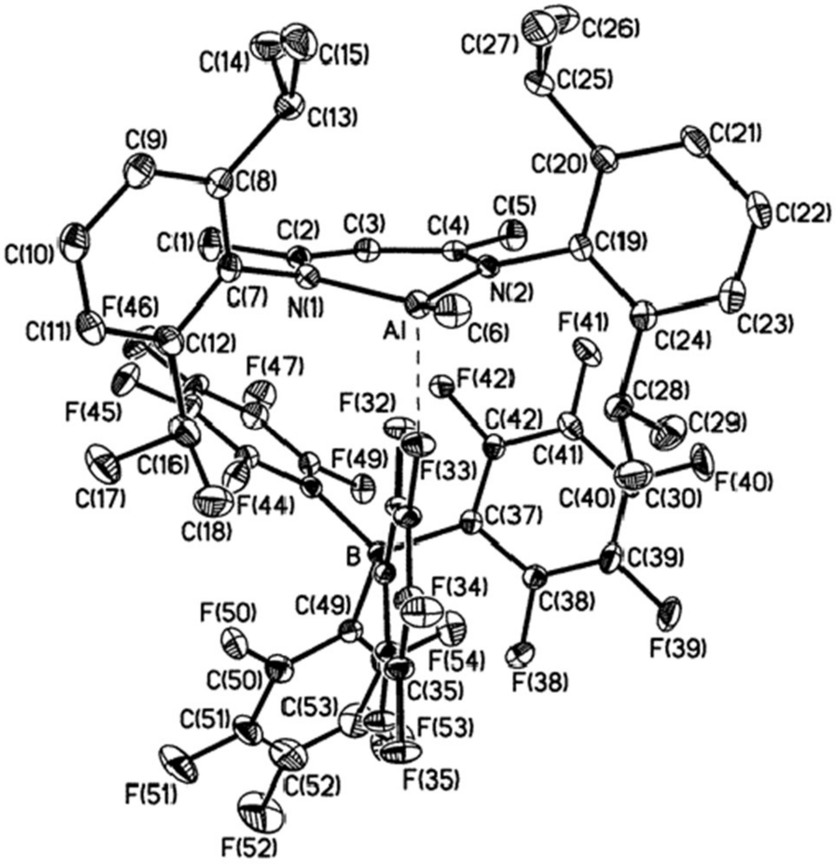


J. Am. Chem. Soc. **1999**, *121*(37), 8673.

Reactivity to I_2 by BR_3

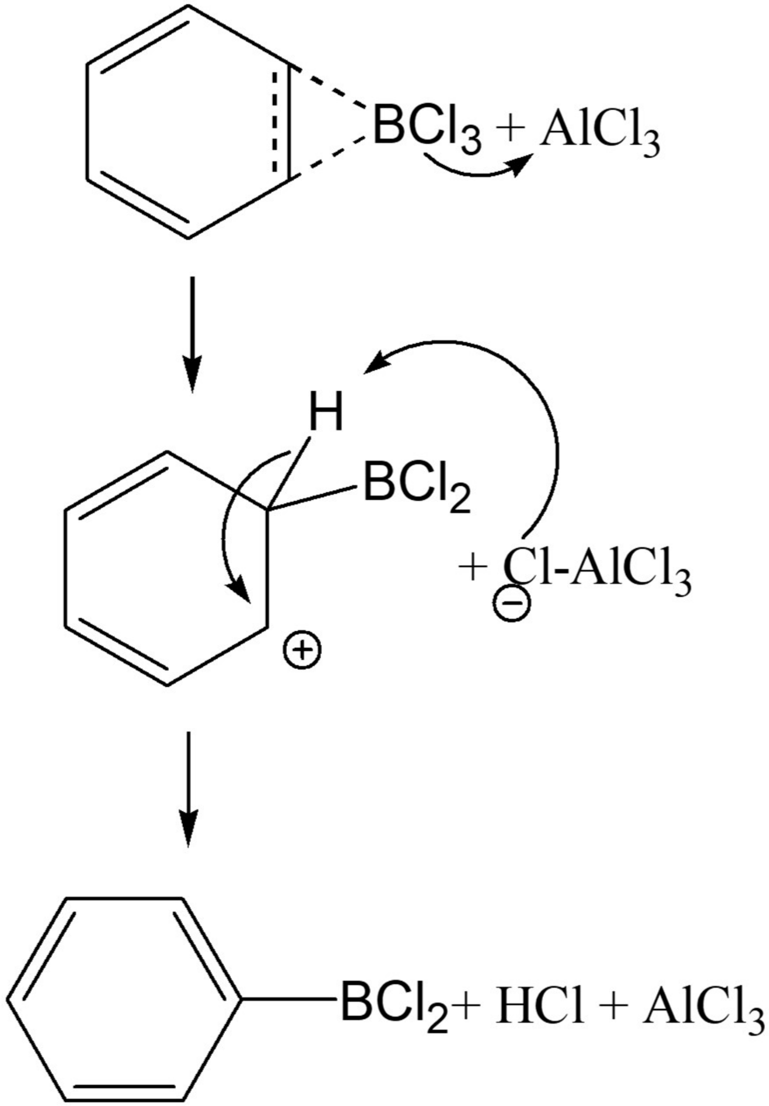
Alkyl boroiodides can be made from homoleptic alkylboranes by redox with diiodine:

$$I_2 + R_3B \rightarrow R_2BI + RI$$

The stable B-I bond and covalent C-I bond both contribute this specific reactivity:

- Boron's high charge density easily polarizes iodide's sp orbital for a good π hypercongugation
- Iodide's soft, extensive sp orbital overlaps well with boron
- The negligible difference in electronegativity of the C-I bond contributes to its stability

Friedel-Crafts Reaction



The Friedel-Crafts Reaction works only with BCl_2 to produce a boron alkyl:

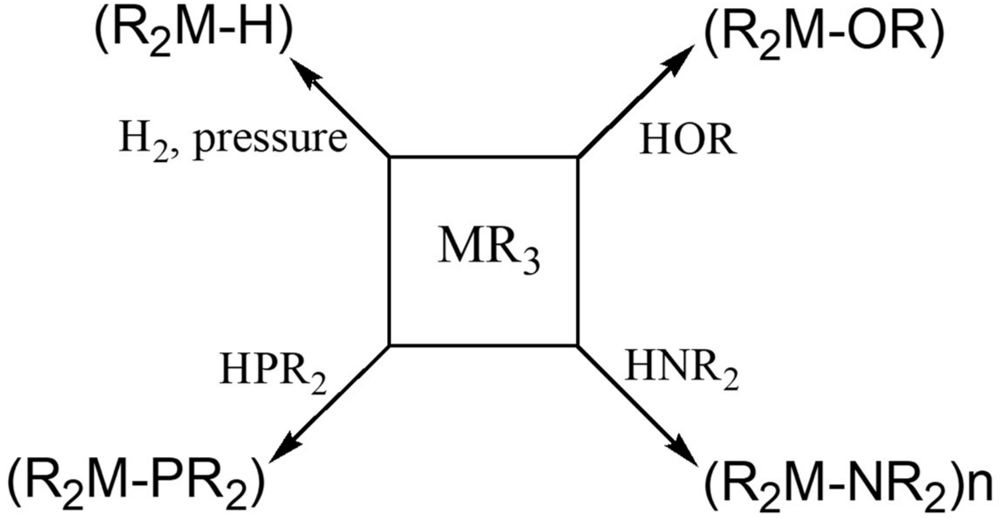
$ArH + BCl_3\ (AlCl_3) \rightarrow HCl + ArBCl_2$

The mechanism relies on aluminium being both electropositive enough to form a tetrahedral anion and big enough to accommodate 4 chloride in its coordination sphere.

Mixed Ligand Systems

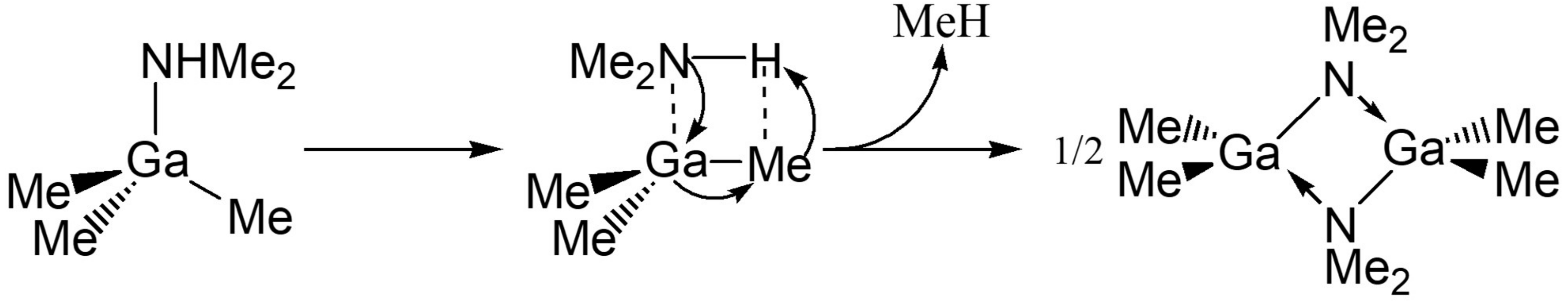
The homoleptic alkyl compounds of group 13 are highly reactive to proton-bearing species (including water).

Manipulating these compounds requires exclusion of oxygen and water, and the reactions are similar for Al, Ga, In:



Mixed Ligand Systems

These compounds require a four-coordinate intermediate, and thus is not common for boron:



Boron phosphides can be made by reaction with R_2BX:

$$R_2BX + HPR_2 + NEt_3 \rightarrow R_2B\text{-}PR_2 + NHEt_3^+X^-$$

This reaction with phosphorous is again due to boron’s polarizing power. Other mixed ligand systems of boron are made by metathesis.

Mixed Ligand Compounds

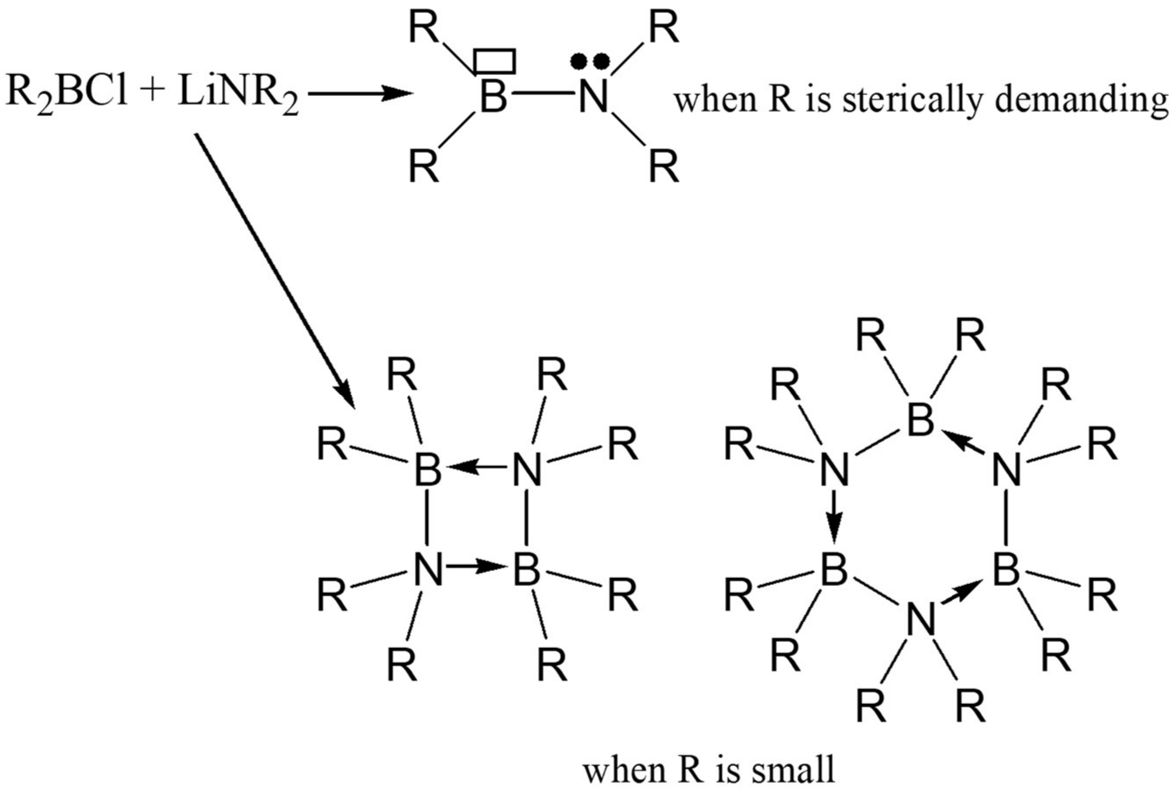
It is also common to make these through a metathesis reaction:

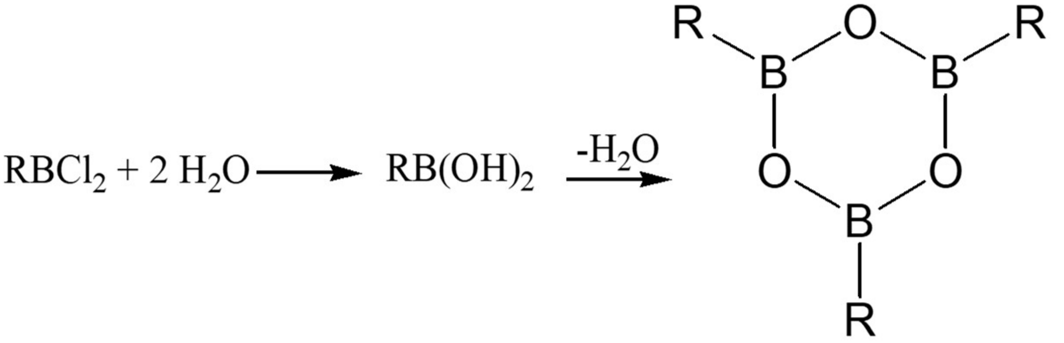
$$R_2AlCl + LiNMe_2 \rightarrow R_2Al\text{-}NMe_2 + LiCl$$

The mixed ligand compounds usually oligomerize.

Boron again sets itself apart with a tendency toward hyperconjugation and planar compounds, while the rest of the group tends toward three dimensional structures.

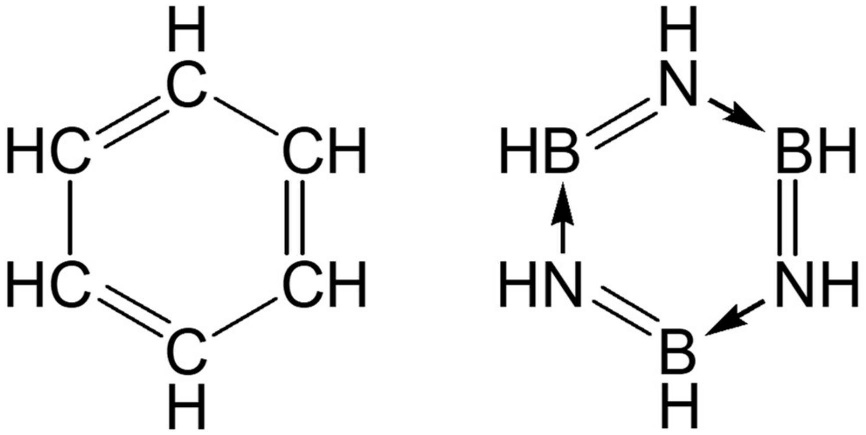
Boron Oxygen and Nitrogen





Borazine

Borazine is an analogue of benzene, made by $HBX_2 + H_3N$:



There is a net negative charge on the nitrogen and a net positive charge on the boron, which follows the electronegativity even though the dative bonds makes it appear that the charge difference might lie the other way.

This liquid is similar in many ways to benzene, and can be used to make other carbon analogues. It isn’t as strongly aromatic as benzene, so it shows less chemical resistance.

Oxygen and Nitrogen Compounds

For Al, Ga, : the oligomeriztion follows the Lewis acidity trend of the bridging compounds:

$$R_2N > RO > X$$

This is due to the fact that there are two 2c2e bonds, one dative bond from a lone pair.

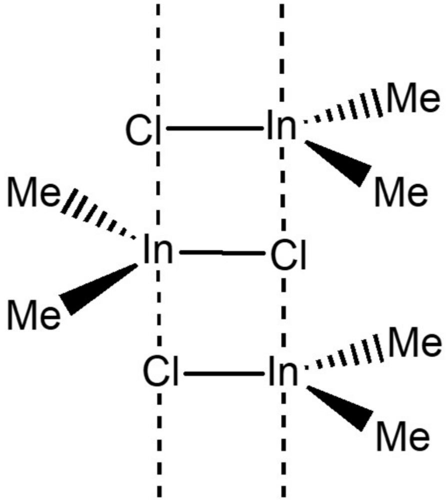
This is different than the trend for oligomerization with bridging alkyl groups, where the oligomerization is controlled by sterics.

Indium compounds tend to be polymeric.

Mixed Ligand Compounds of

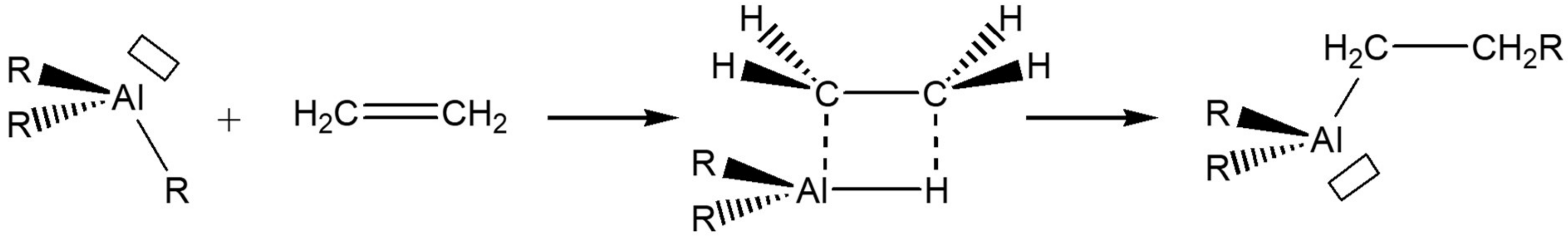
Due to the size of indium, it can easily form a trigonal bipyramidal geometry.

This allows it to form insoluble, low-reactivity polymers:



Reactions With Group 13

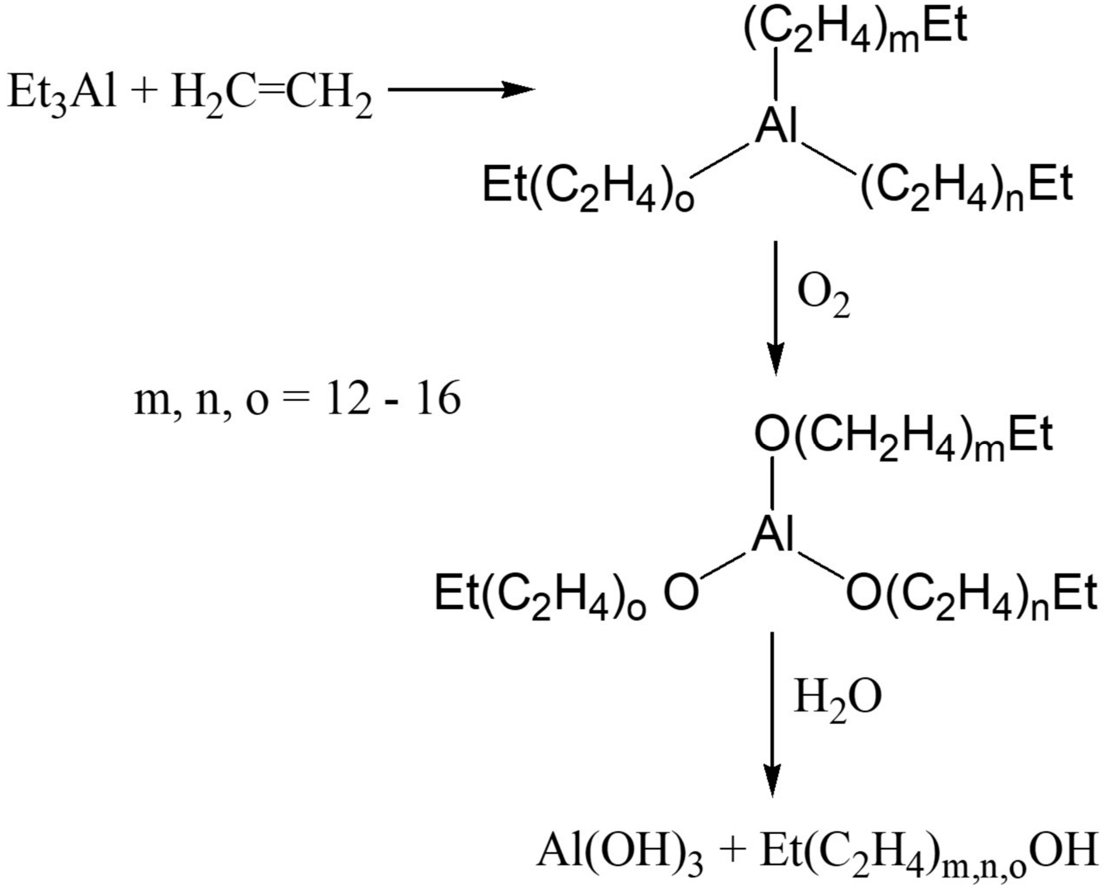
Carbometallation can be used to make longer-chain metal alkyl compounds of group 13, but its mainly used to make long-chain alcohols for detergents:



This requires a step of oxygen insertion, like we've seen in lithium chemistry:

$$AlR_3 + 3/2\ O_2 \rightarrow Al(OR)_3$$

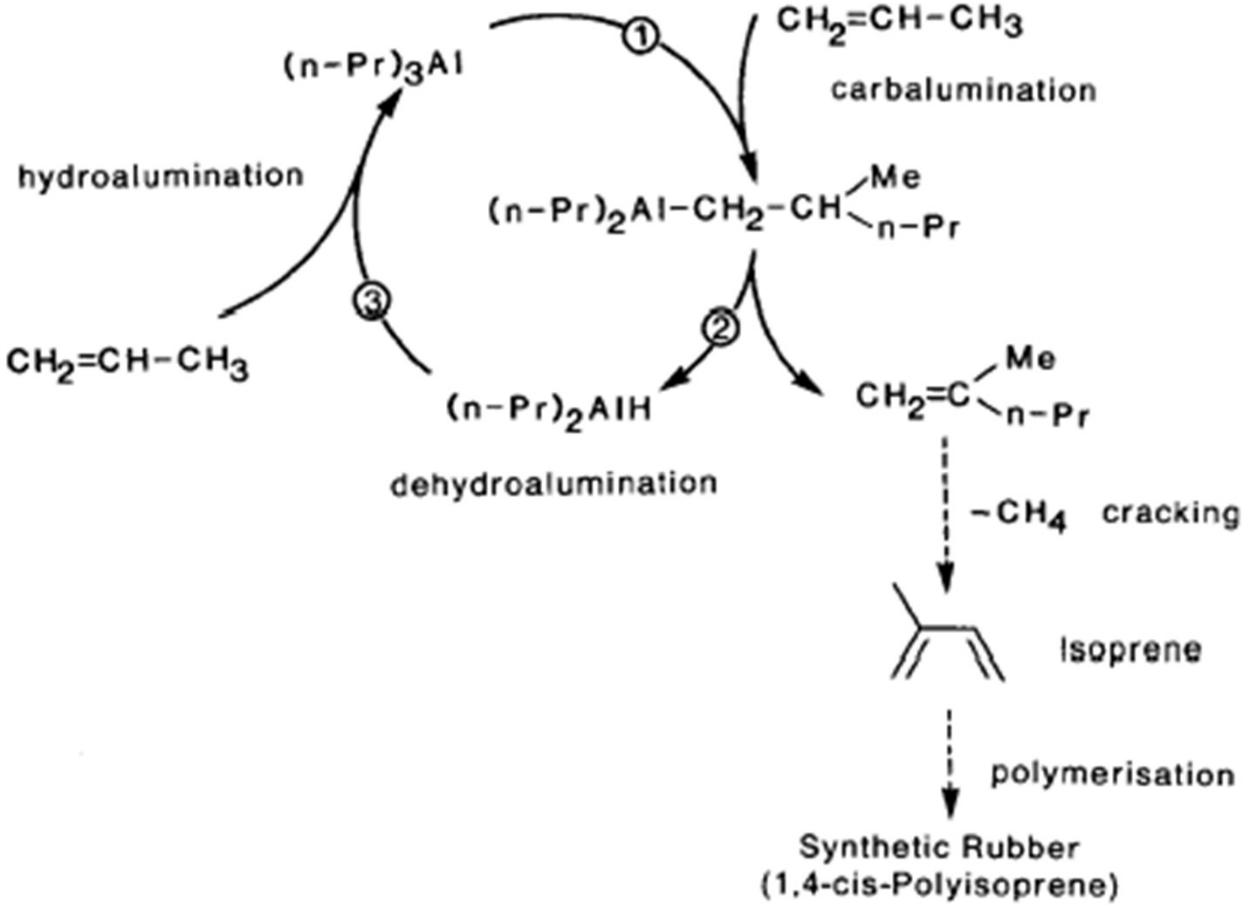
Soap-Making



m, n, o = 12 - 16

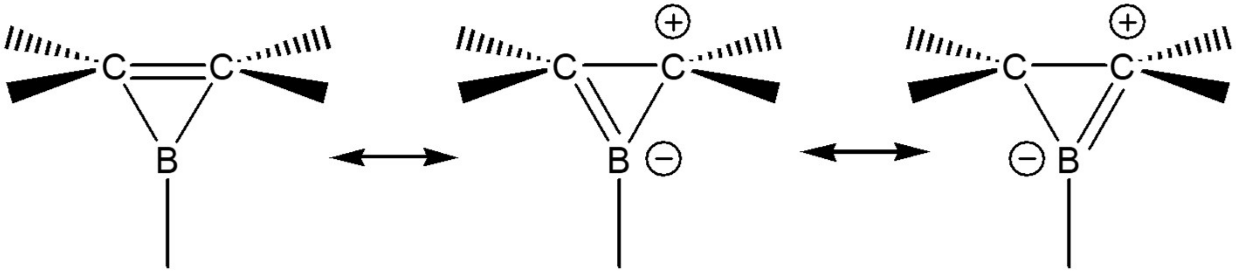
Isoprene Synthesis

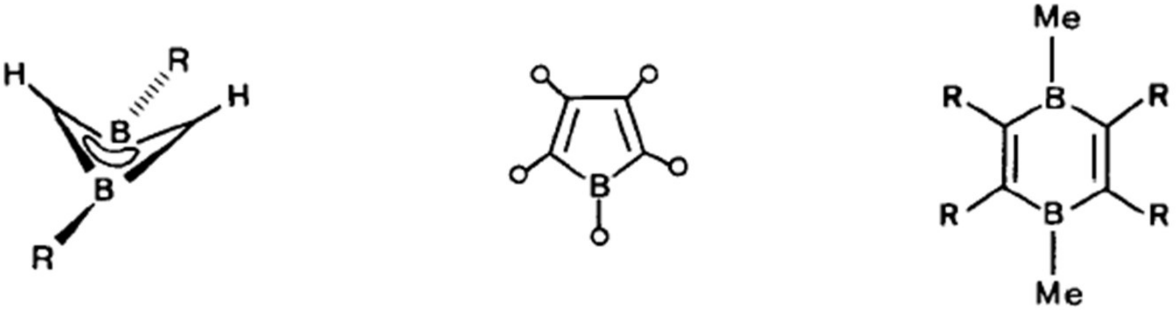
One of the main applications of 1,2-insertions at aluminium is the synthesis of isoprene, the monomer for polyisoprene (synthetic rubber):



Boracycles

Due to boron’s ability to participate in π systems, it has been incorporated in many aromatic compounds:





This penchant for hydride (3c2e) bridging and π system participation gives way to cluster chemistry: boranes and carboranes

Boranes

Boranes are a type of cluster compounds where the cluster is a geometric shape with some or all of the vertices occupied by a B-H group.

Boranes fall into 5 distinct classes, based on empirical formula:

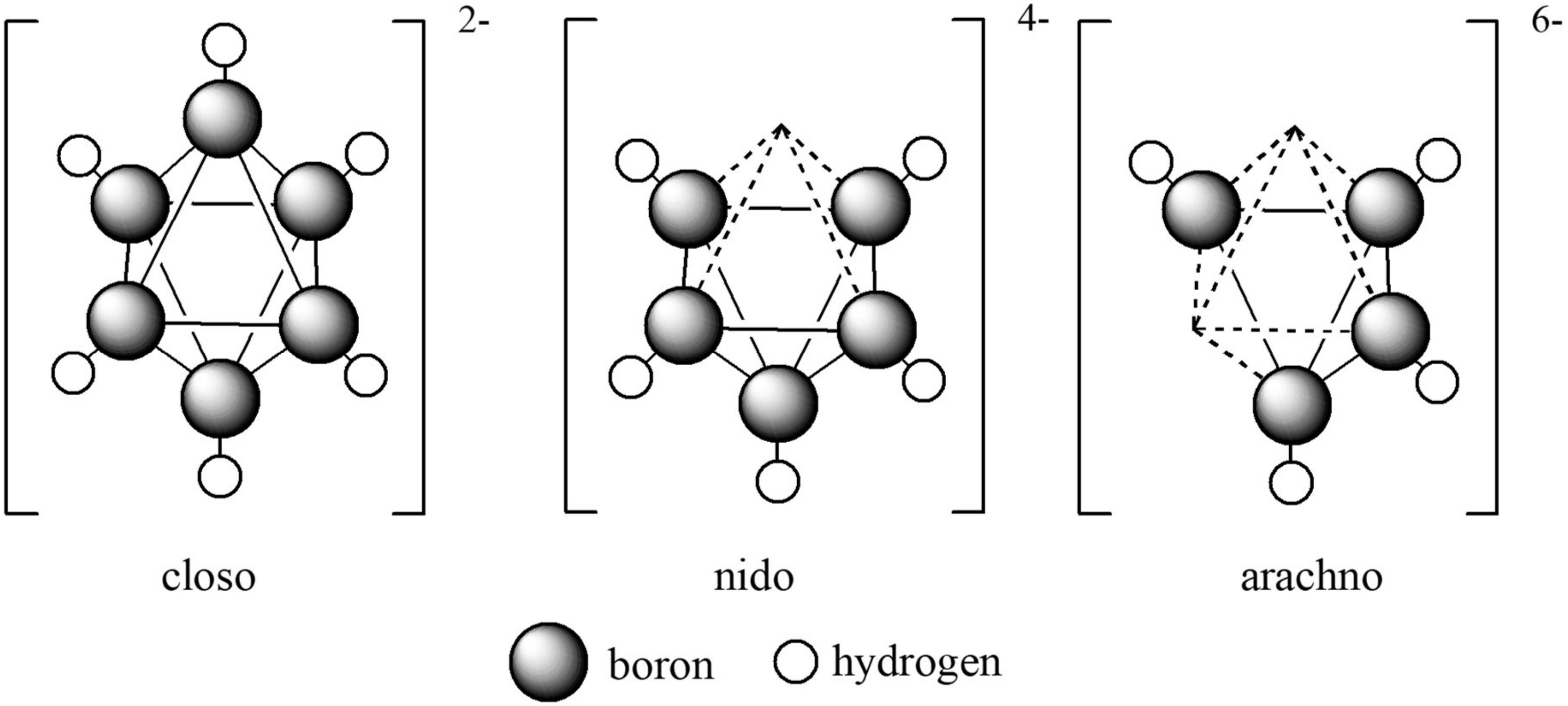
$[B_xH_x]^{2-}$ are the closo-boranes: closed structure
$[B_xH_x]^{4-}$ are the nido-boranes: nest-like structure
$[B_xH_x]^{6-}$ are the arachno-boranes: spider-web-like structure

$[B_xH_x]^{8-}$ are the hypho-boranes: net-like structure
$[B_xH_x]^{10-}$ are the klado-boranes: branched structure

Boranes and their derivatives follow Wade’s Rules.

Boranes

These structures are differentiated by an increasing number of "missing corners" in the parent structure. For $B_6H_6^{2-}$:



Boranes

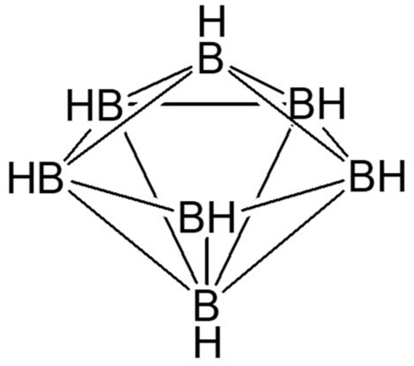
These are differentiated by their number of vertices and electron pairs in the structure. The below rules assume cluster with n vertices. The fully protonated form is shown to confuse you:

Type	Corners Occupied	Protonated
closo	n	$[B_xH_x]^{2-}$
nido	n-1	B_xH_{x+4}
arachno	n-2	B_xH_{x+6}
hypho	n-3	B_xH_{x+8}
klado	n-4	B_xH_{x+10}

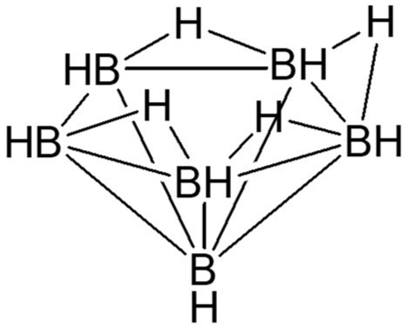
These are called Wade’s Rules. In the fully protonated species, there is always n+1 electron pairs.

It turns out that only the first three are stable on their own, hypho and klado are derivatives bonded to a larger molecule.

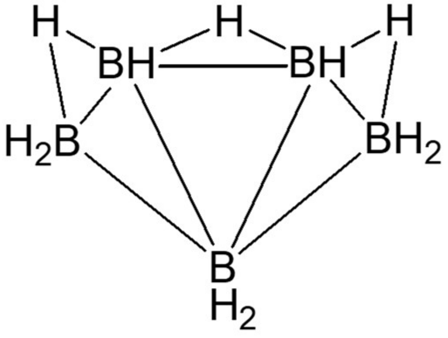
Structures from Wade’s Rules



closo $[B_7H_7]^{2-}$



nido B_6H_{10}



arachno B_5H_{11}

This series loses one boron to go from closo to nido and then one boron to go from nido to arachno. The remaining positions are hydrogen capped in a 3c2e bonding arrangement.

Boranes all have a positive ΔG, thus are less thermodynamically stable than pure B and H_2

This series occurs for the carboboranes as well

Classification of Boranes

Boranes may carry a negative charge; consider it to be the loss of a proton:

Sometimes it is a little obscure to see the structural type right off, so a simple rule can be devised:

$$B_6H_{10} \rightarrow B_6H_6^{4-} + 4\ H^+\ (\textit{nido})$$

Remove enough protons to make the numbers of H and B equal, the charge determines the class:

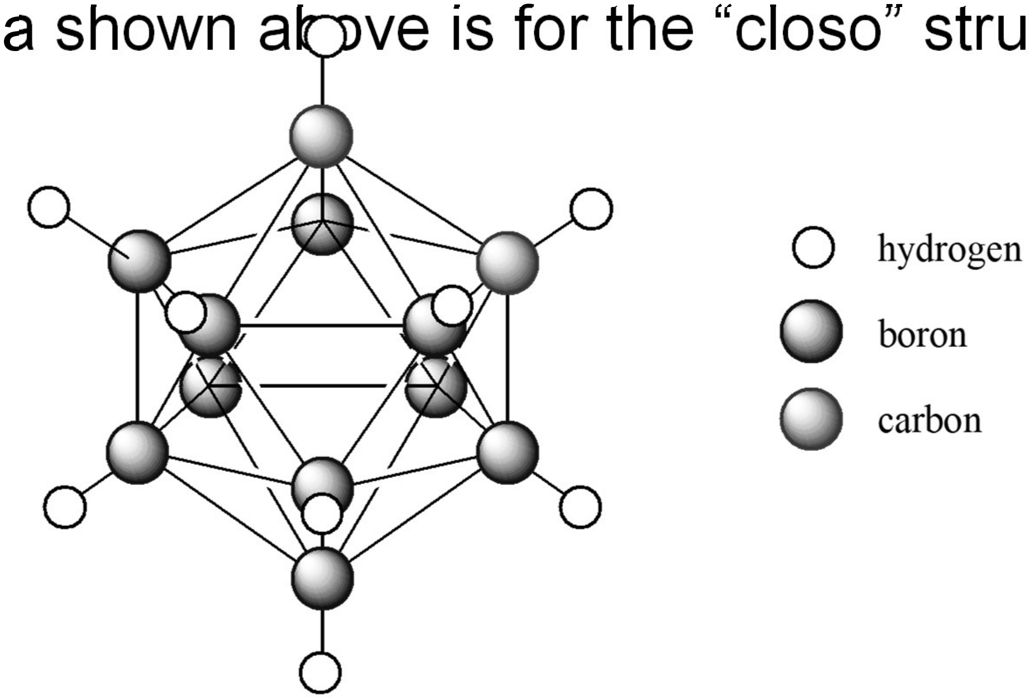
Closo	$B_xH_x^{2-}$
Nido	$B_xH_x^{4-}$
Arachno	$B_xH_x^{6-}$
Hypho	$B_xH_x^{8-}$
Klado	$B_xH_x^{10-}$

Carboboranes

Carboboranes are made from the reaction of boranes with acetylene, having the effect of replacing a B-H moiety with a (C-H)$^+$ moeity:

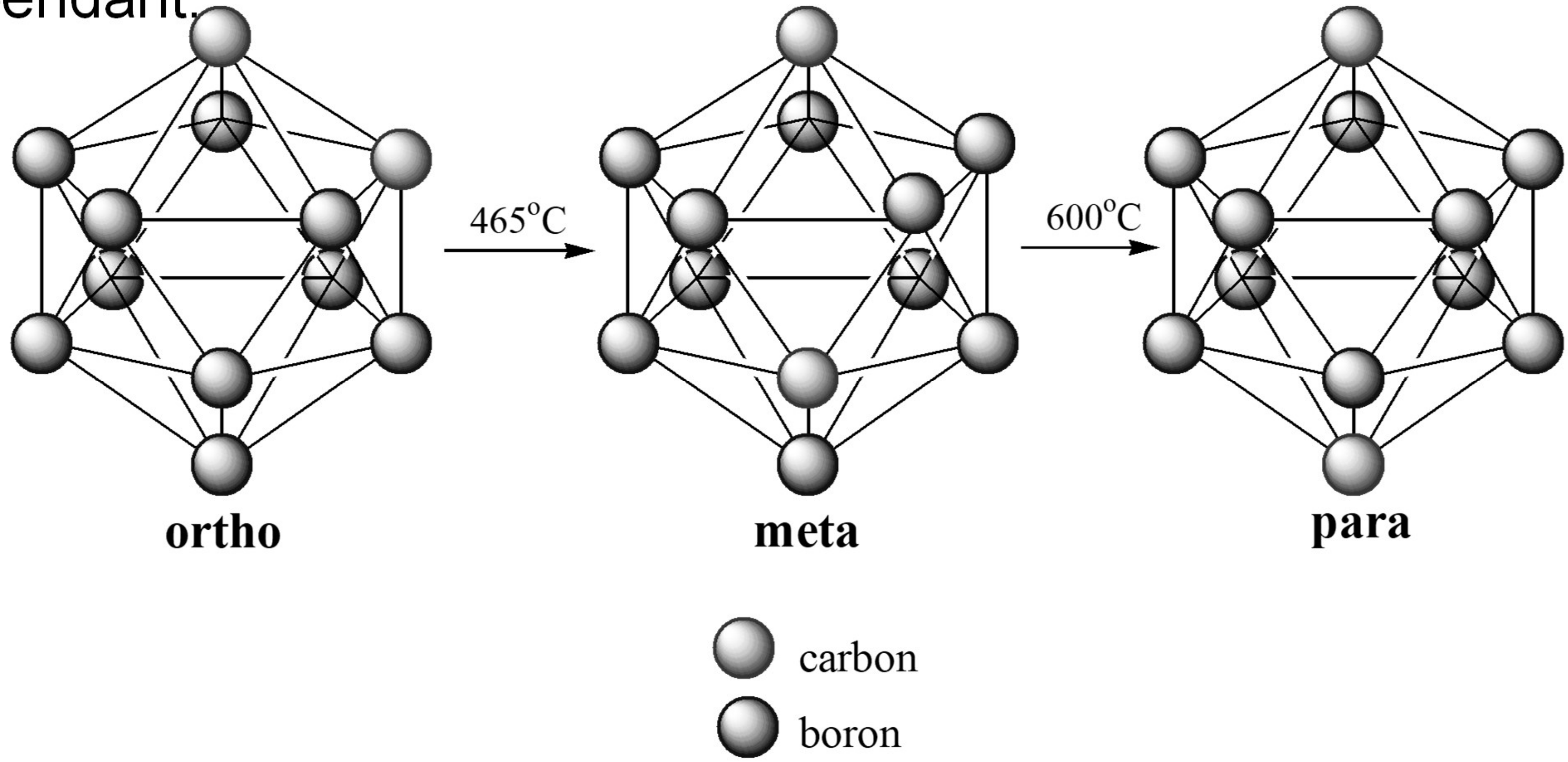
$$B_{10}H_{14}\ (\textit{nido}) + C_2H_2 \rightarrow C_2B_{10}H_{12}\ (\textit{closo}) + 2\ H_2$$

These obey Wade's Rules (but change the charge), and so the general formula shown above is for the "closo" structure.



Closo $C_2H_{10}H_{12}$

The position of the carbon in the structure is temperature dependant:



Note that each vertex actually bears a hydrogen atom, but they are left out because they are a pain to draw.

Structural Types of Carboboranes

The carboboranes can be classified like the boranes, and this classification is dependant on the electron count.

A carbon atom has one more electron in its valence shell than a boron atom, we can correct the electon count by substituting the C for a BH, and then follow the rules for simple boranes:

$C_2B_8H_{10}$ becomes $(BH)_2B_8H_{10}$, or $B_{10}H_{12}$.
$B_{10}H_{12} \rightarrow B_{10}H_{10}^{2-} + 2H^+$ and is therefore *closo*.

$C_2B_4H_8$ becomes $(BH)_2B_4H_8$, or B_6H_{10}.
$B_6H_{10} \rightarrow B_6H_6^{4-} + 4H^+$ and is therefore *nido*.

Heteroatom Boranes

Clusters replacing a boron with one or more heteroatoms have been seen, and the chemistry is quite extensive.

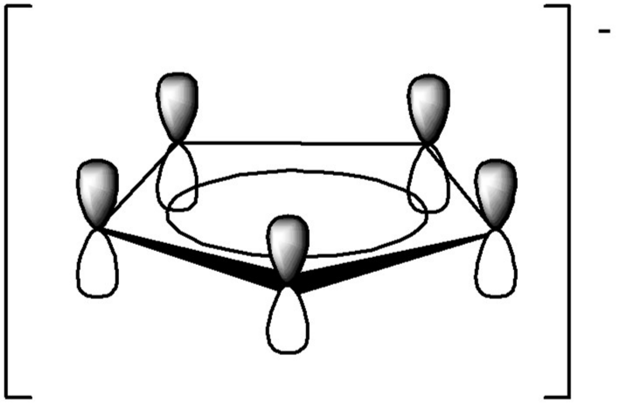
These all obey Wade's Rules, and thus follow the electron count and structure of the simple boranes.

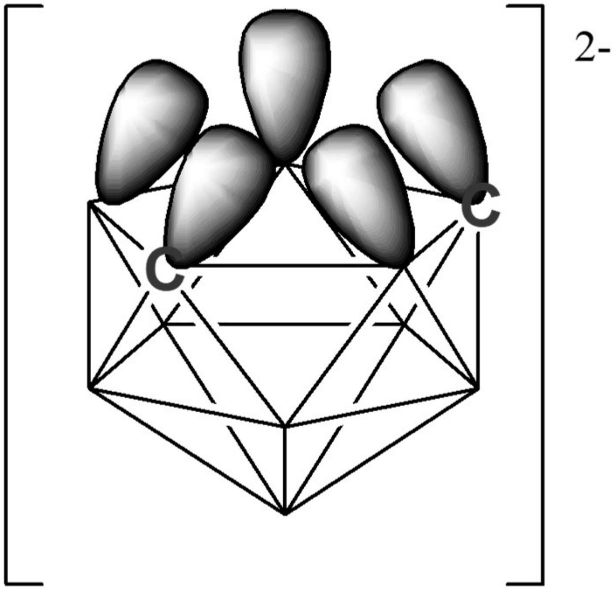
Counting electrons is relatively easy, when you consider the extra electrons each heteroatom provides:

Heteroatom	e^- config.	Replace With
C, Si, Ge, Sn, Pb	[B] + $1e^-$	BH
N, P, As	[B] + $2e^-$	BH_2
S, Se	[B] + $3e^-$	BH_3

Nido-$C_2B_9H_{11}^{2-}$

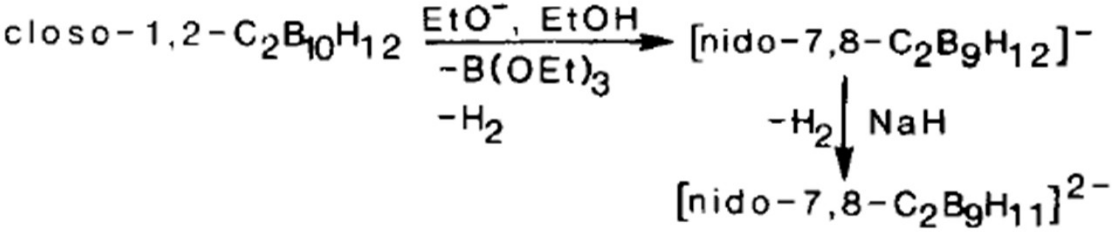
One of the interesting applications of carboranes is that they can be used as η^5 ligands in place of Cp. Note that these are not isoelectronic nor isolobal. They do share an orbital symmetry with Cp:



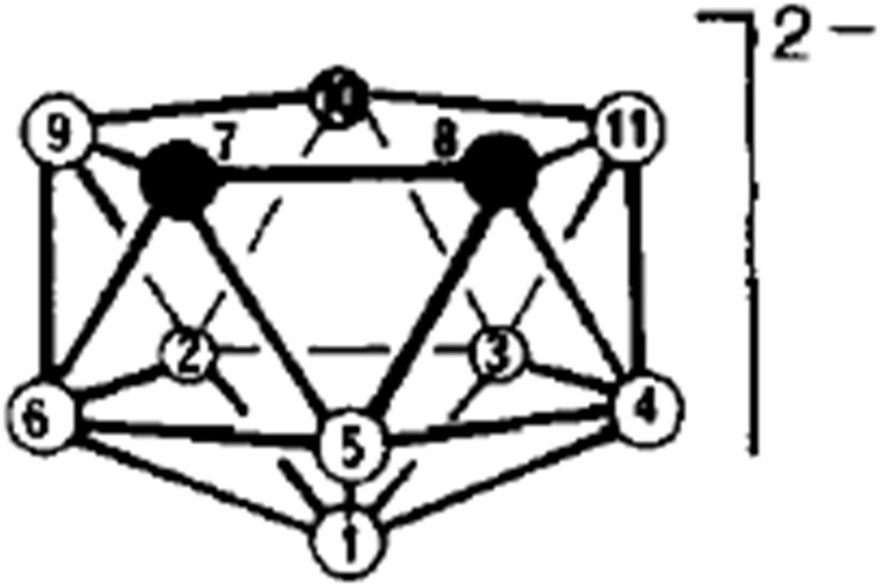


Synthesis Nido-$C_2B_9H_{11}^{2-}$

Because of this similarity, it is possible to use this ligand in place of Cp:

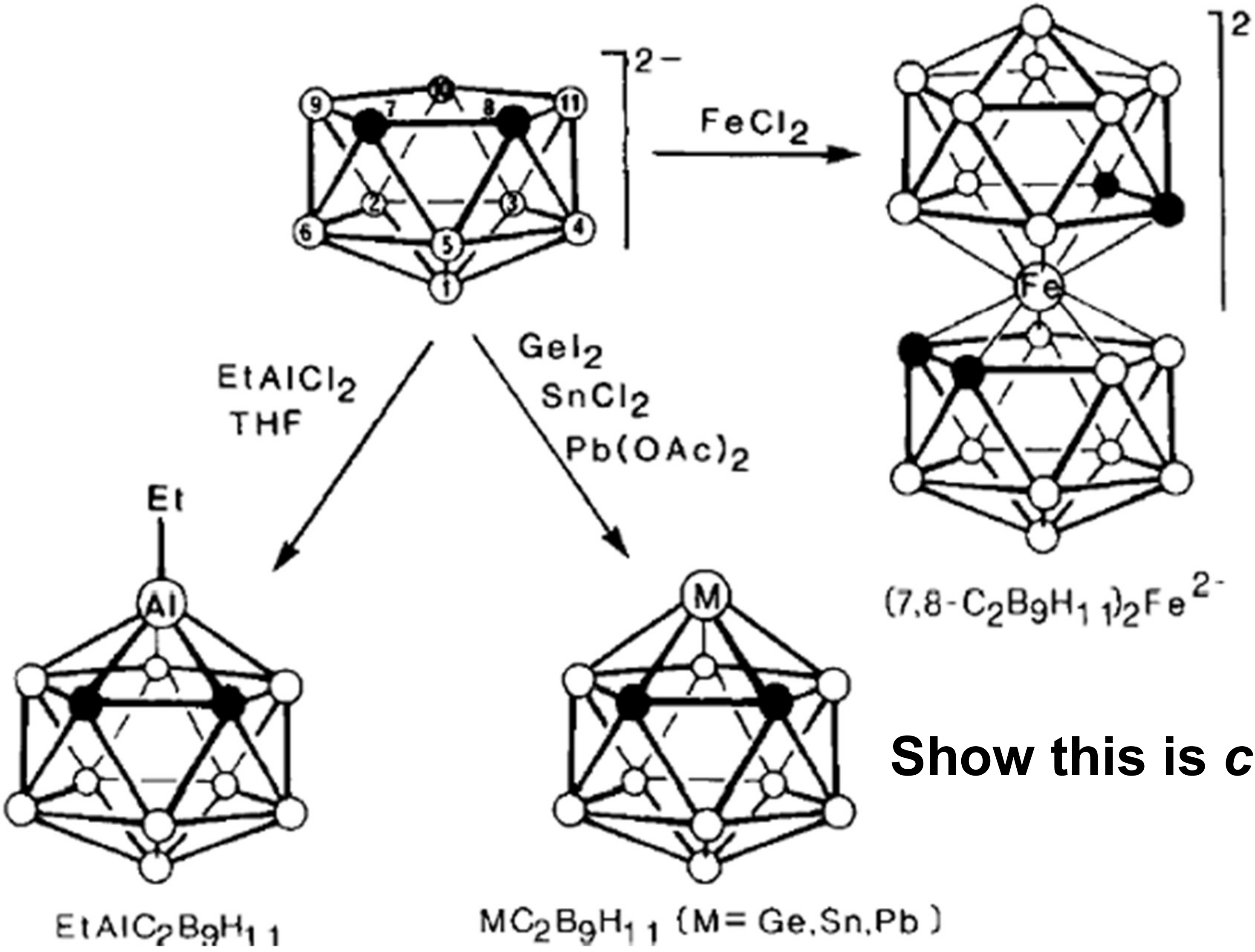


$$\text{closo-1,2-}C_2B_{10}H_{12} \xrightarrow[\substack{-B(OEt)_3 \\ -H_2}]{EtO^-,\ EtOH} [\text{nido-7,8-}C_2B_9H_{12}]^- \xrightarrow[-H_2]{NaH} [\text{nido-7,8-}C_2B_9H_{11}]^{2-}$$



Using Nido-$C_2B_9H_{11}^{2-}$

Because of this similarity, it is possible to use this ligand in place of Cp:



$(7,8\text{-}C_2B_9H_{11})_2Fe^{2-}$

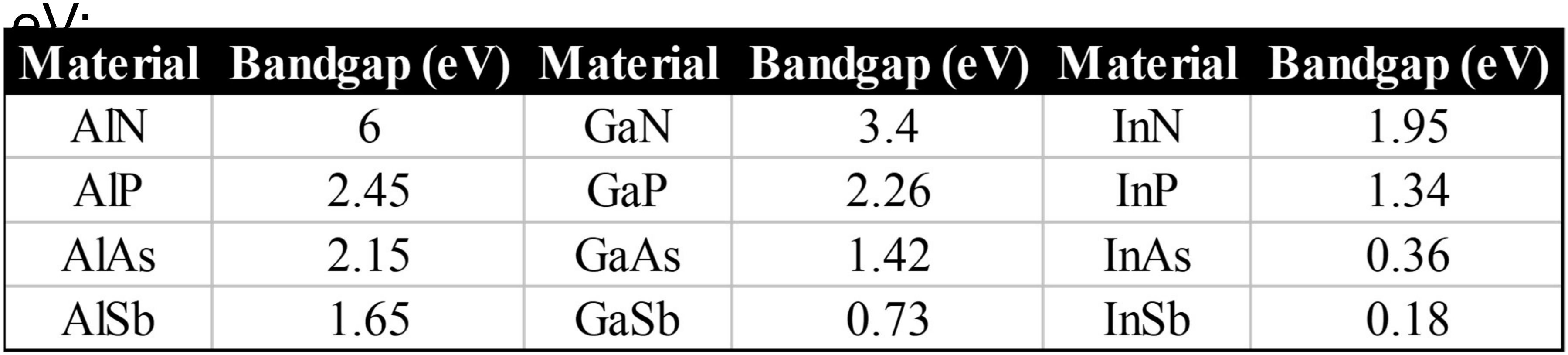
$EtAlC_2B_9H_{11}$

$MC_2B_9H_{11}$ (M= Ge,Sn,Pb)

Show this is *closo*

Chemical Vapour Deposition

The binary minerals of the group 13 and 15 (e.g. gallium nitride – GaN) are semiconductors with bandgaps ranging between 0.18 – 6 eV:

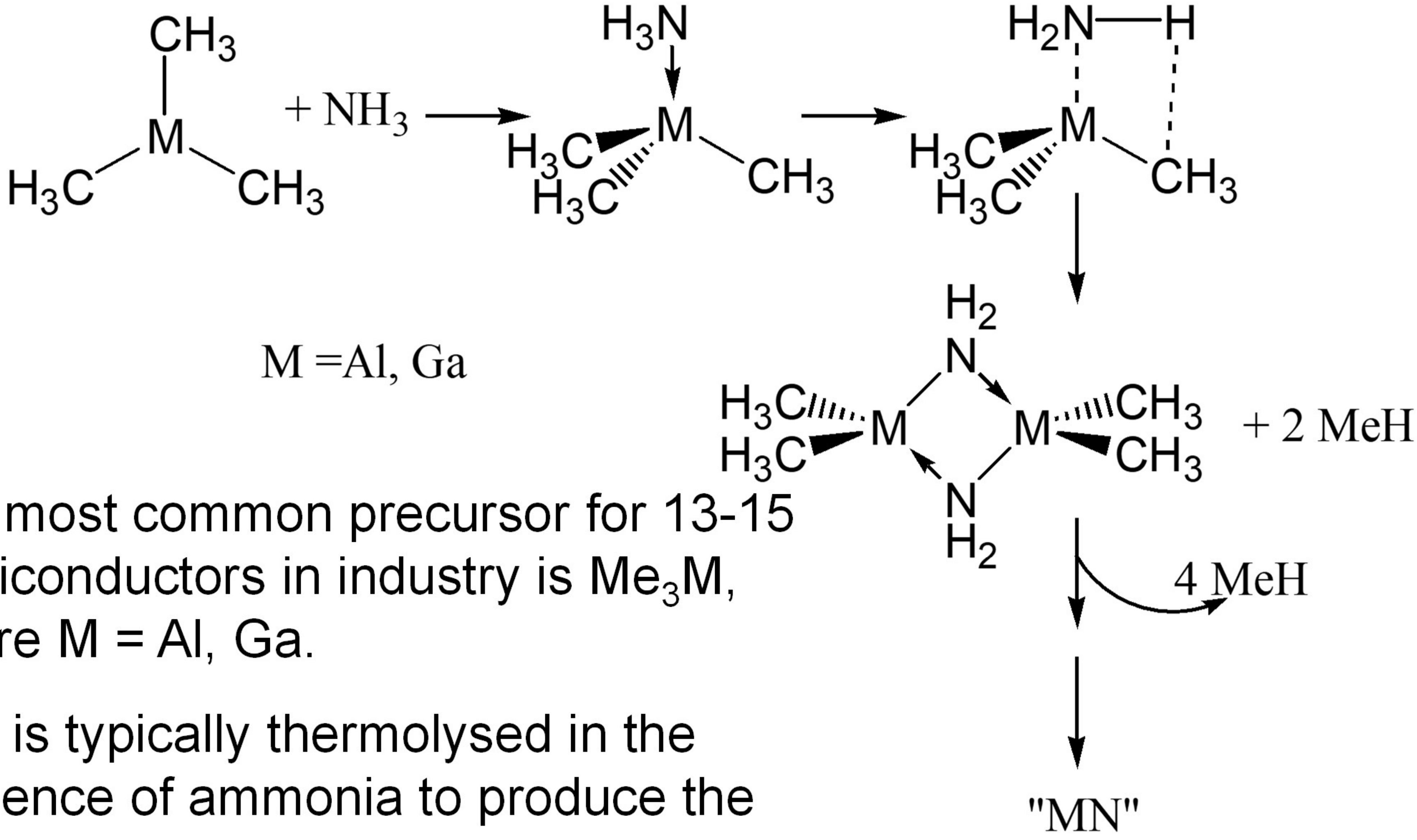


Material	Bandgap (eV)	Material	Bandgap (eV)	Material	Bandgap (eV)
AlN	6	GaN	3.4	InN	1.95
AlP	2.45	GaP	2.26	InP	1.34
AlAs	2.15	GaAs	1.42	InAs	0.36
AlSb	1.65	GaSb	0.73	InSb	0.18

Group 15 orbitals are more stabilized than group 13 (higher Z_{eff} across the family).

Down the group, the orbitals become less stabilized (farther from the nucleus). For any given metal, the bandgap becomes lower down the group.

Group 13 as Precursor Materials

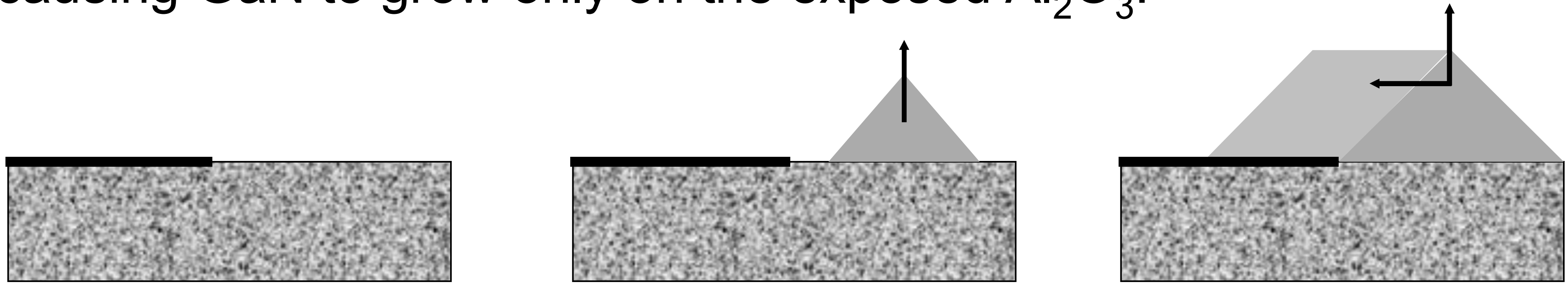


The most common precursor for 13-15 semiconductors in industry is Me_3M, where M = Al, Ga.

This is typically thermolysed in the presence of ammonia to produce the metal nitride.

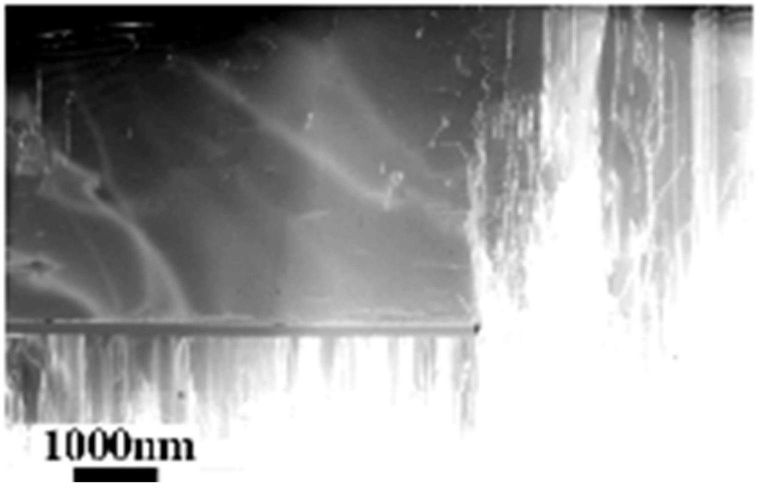
Lateral Epitaxial Overhang - LEO

This technique masks a portion of a sapphire substrate with SiO_2, causing GaN to grow only on the exposed Al_2O_3:



The growing GaN eventually starts to overgrow the mask.

Since the growth is horizontal, and the defects propagate mainly vertically, a very defect-free layer of GaN is grown.



TEM of GaN grown by LEO

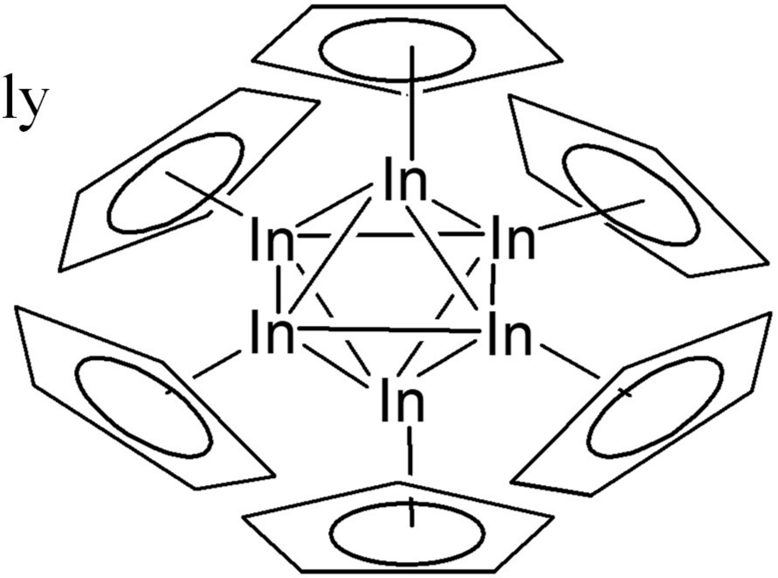
Low Valent Group 13 Compounds

Thermodynamically, thallium and indium monovalent compounds have been known for a long time:

Monovalent thallium halides will precipitate from aqueous solution when reacted with a halide acid

Both CpTl and CpIn have been known since the 1950s:

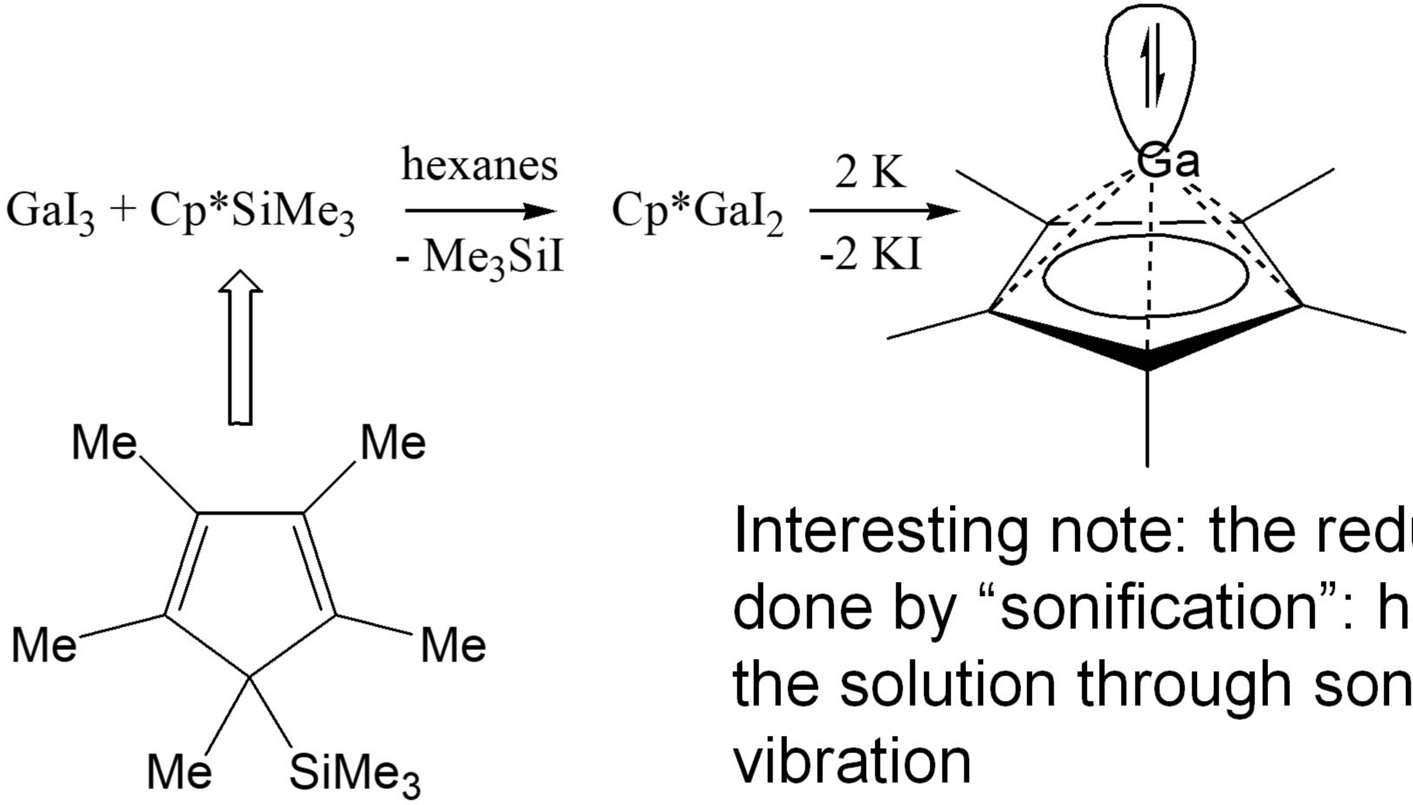
- CpTl is a zigzag polymer, like CpK
- CpIn is a capped octahedron that readily dissociates into monomers in hydrocarbon solvents



Low Valent Group 13

Recently, the oxidation state +1 has become a hot topic for main group organometallic chemistry.

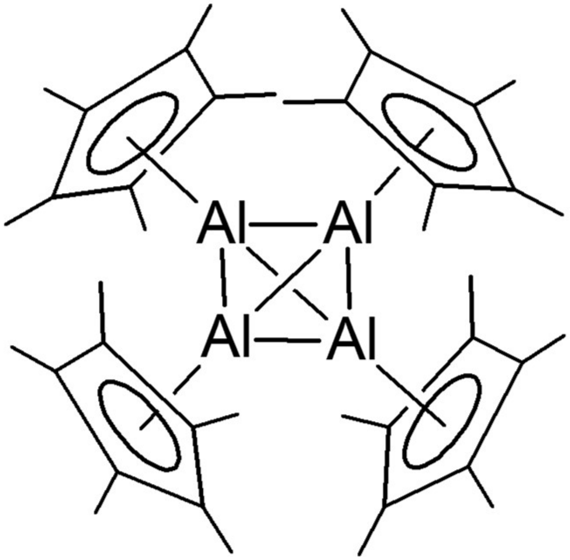
This oxidation state is stabilized by bulky, basic ligands:



Interesting note: the reduction is done by “sonification”: heating the solution through sonic vibration

Low Valent Group 13

MCl + $MgCp^*_2$ (-78°C, ether) → $MgCl_2$ + 2 MCp^*

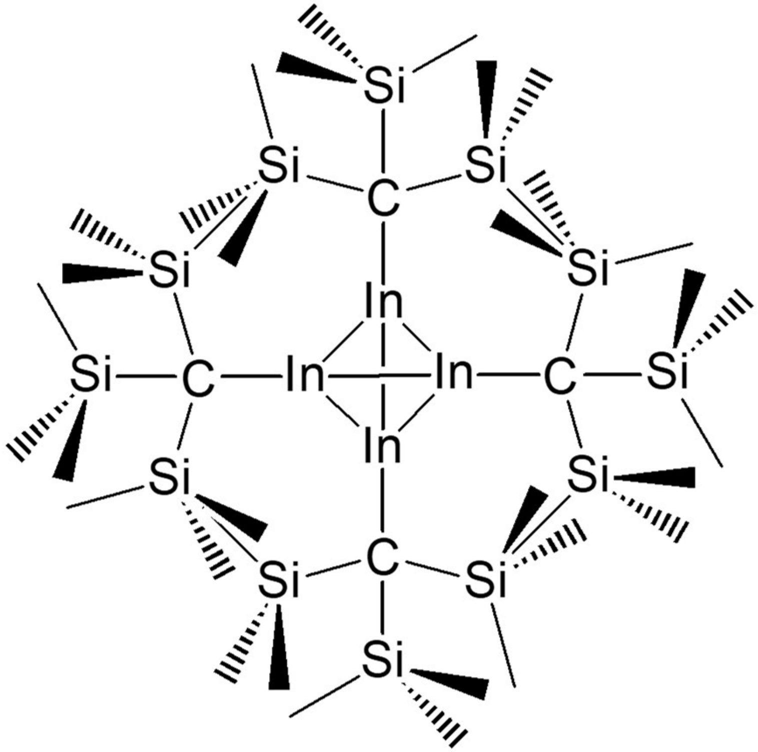


The bonding in the tetrahedron are M-M sigma bonds, and the Cp donates to an empty sp^3 orbital in a sigma fashion, as a Lewis base with its spherically symmetric aromatic orbital.

Unlike the lithium tetrahedron we saw, this is not face capped.

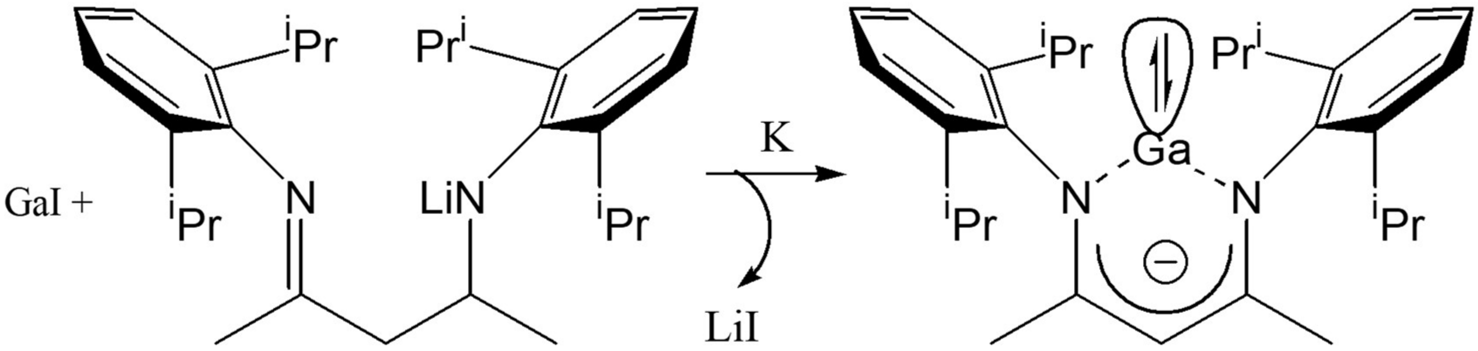
Low Valent Group 13 Organometallics

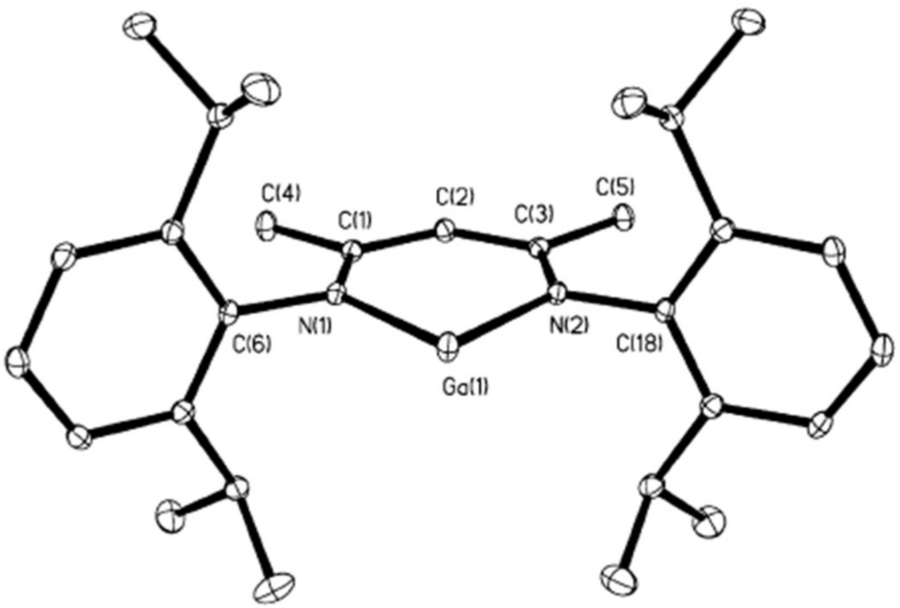
This same connectivity is seen in the case of R_3CIn (where $R=Me_3Si$), made through a similar reaction:



The nature of the bonding makes it unclear if there is a lone pair on the metal

An Example of an Inorganic Ga(I)



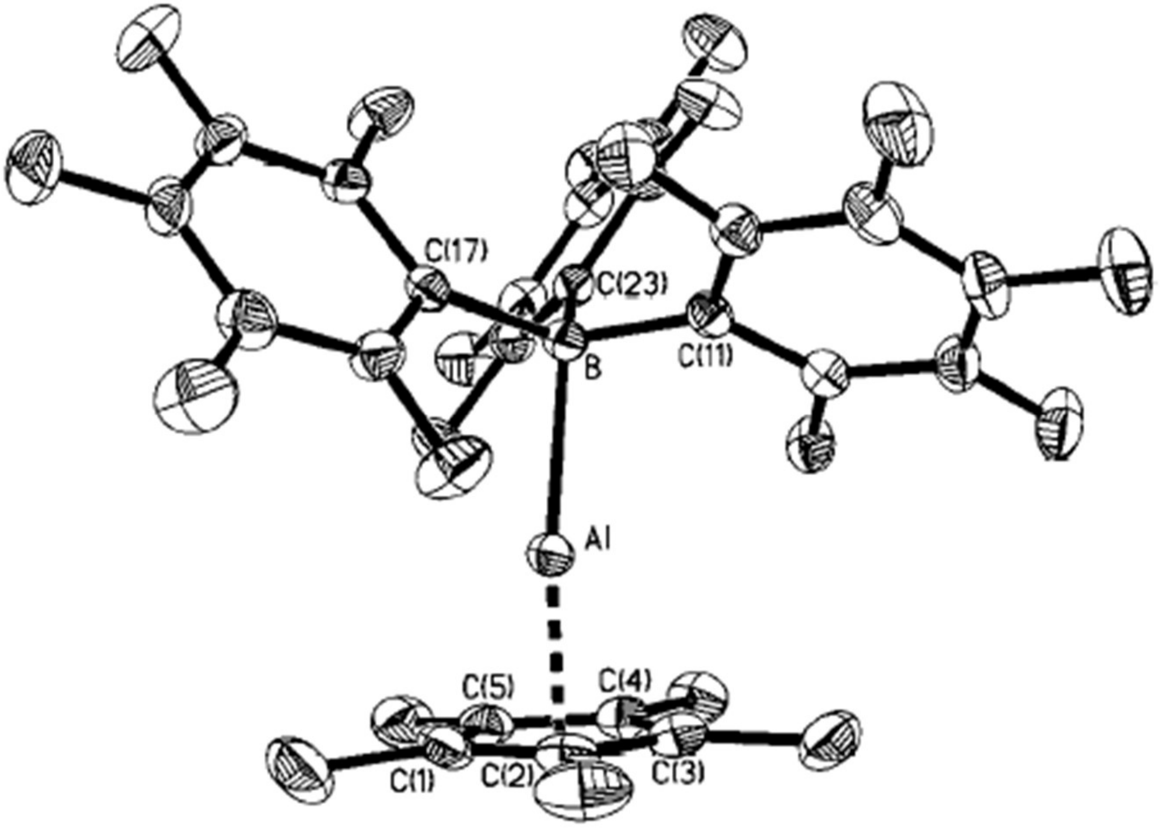


The steric demand on this compound is so great as to preclude oligomerization in the crystalline phase

Lewis Basicity in Low Valent Group 13

Recent work by Cowley and group at the University of Texas shows that these compounds can be considered to have a lone pair (i.e. singlet state).

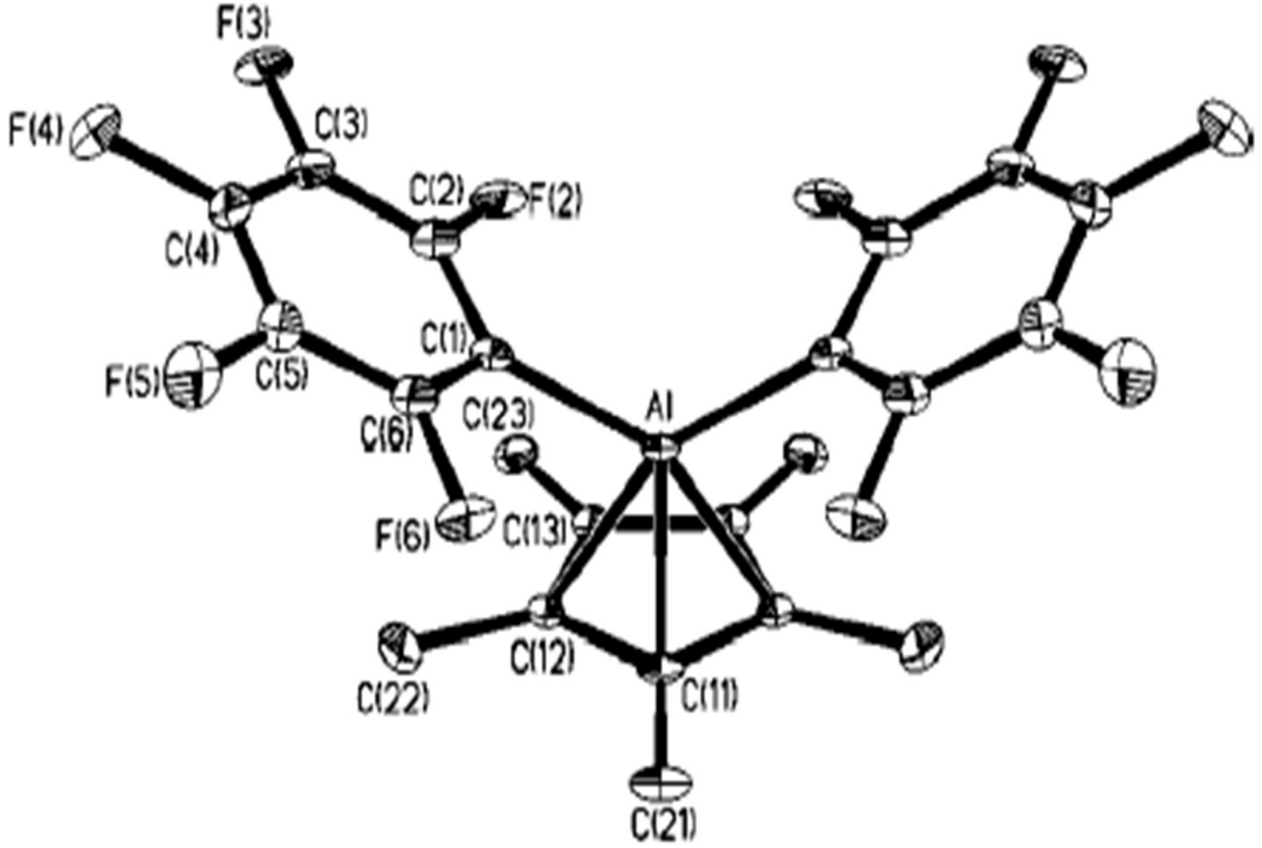
$(Cp^*Al)_4 + B(C_6F_5)_3 \rightarrow Cp^*Al\text{-}B(C_6F_5)$



Oxidation of Low Valent Group 13

Interestingly, the same reaction with $In(C_6F_5)_3$ resulted in the +3 oxidation state of aluminium.

Now the aluminium is η^3 bonded to the Cp and has σ bonds to two pentafluorophenyl rings:

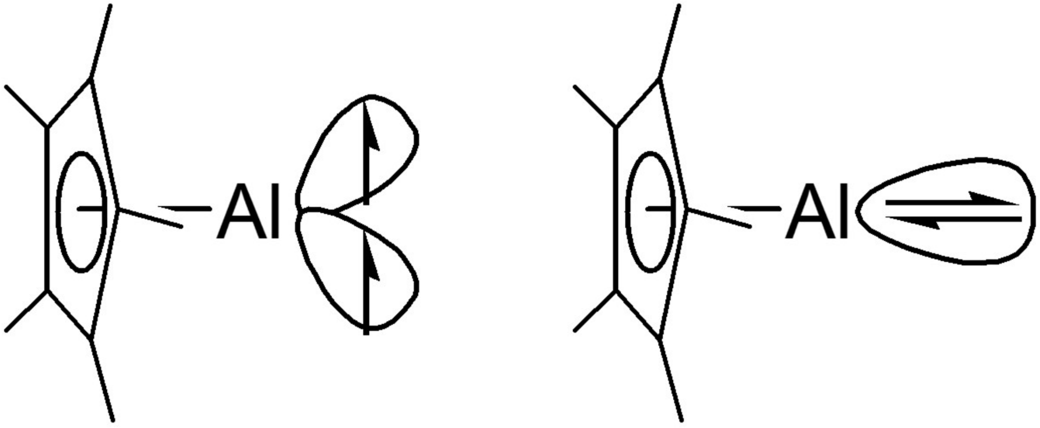


Singlet vs. Triplet

It was suggested that this compound forms with the Lewis base adduct as an intermediate:

$(Cp^*Al)_4 + In(C_6F_5)_3 \rightarrow Cp^*Al\text{-}In(C_6F_5) \rightarrow Cp^*Al(C_6F_5)_2 + In(C_6F_5)$

This shows that the hybridization at Al can react as either singlet) or triplet:



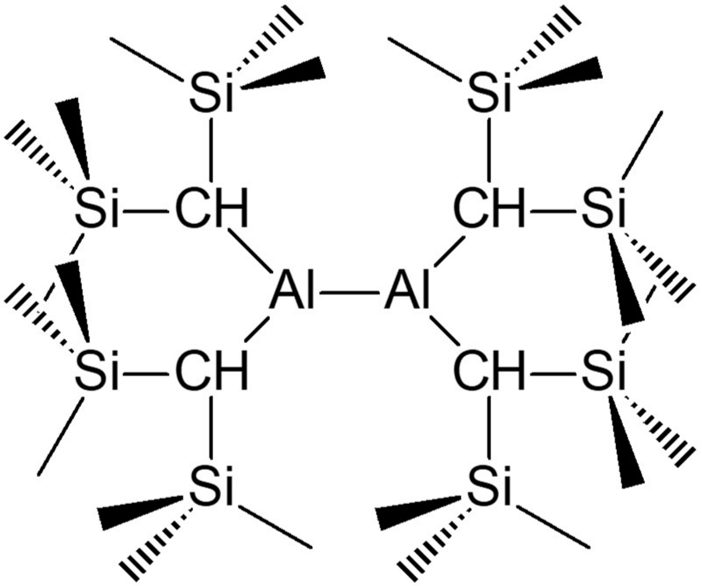
triplet **singlet**

J. Am. Chem. Soc. **2000**, *122*(5), 951.

Mid-valent Group 13 Compounds

With intermediate steric bulk, it is possible to isolate M^{2+} compounds of group 13:

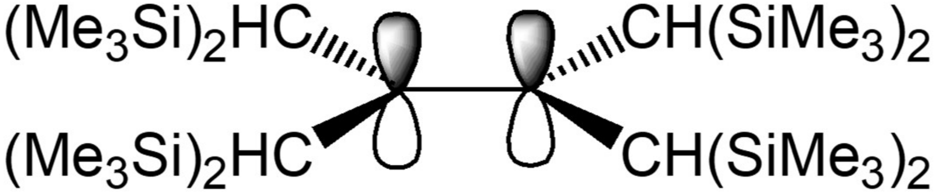
$$2\ (Me_3Si)_2CHLi + AlCl_3 \rightarrow ((Me_3Si)_2CH)_2AlCl$$
$$2\ K + ((Me_3Si)_2CH)_2AlCl \rightarrow [((Me_3Si)_2CH)_2Al]_2 + 2\ KCl$$



Mid-valent Group 13 Compounds

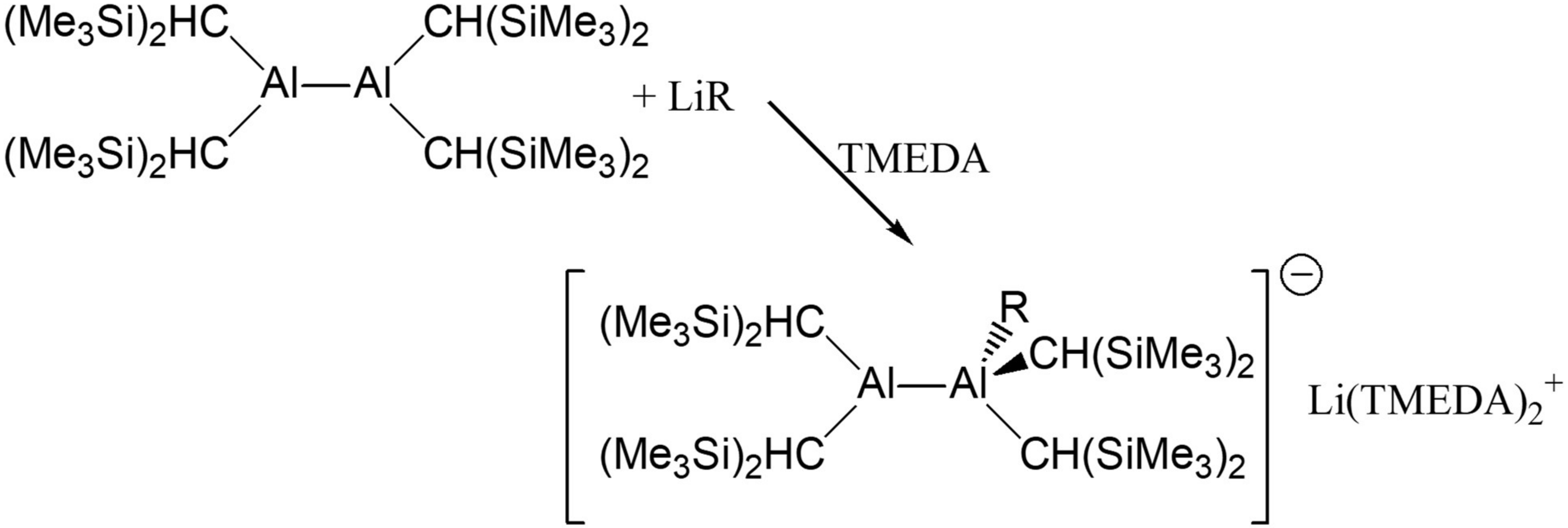
This compound is known for Al, Ga, and In, but the gallium and indium analogues were made by metathesis with $M_2Br_4.2\ L$ and the lithium salt of the ligand.

The hybridization at the metal centre is sp^2, and there is an empty p orbital perpendicular to the plane of the molecule:



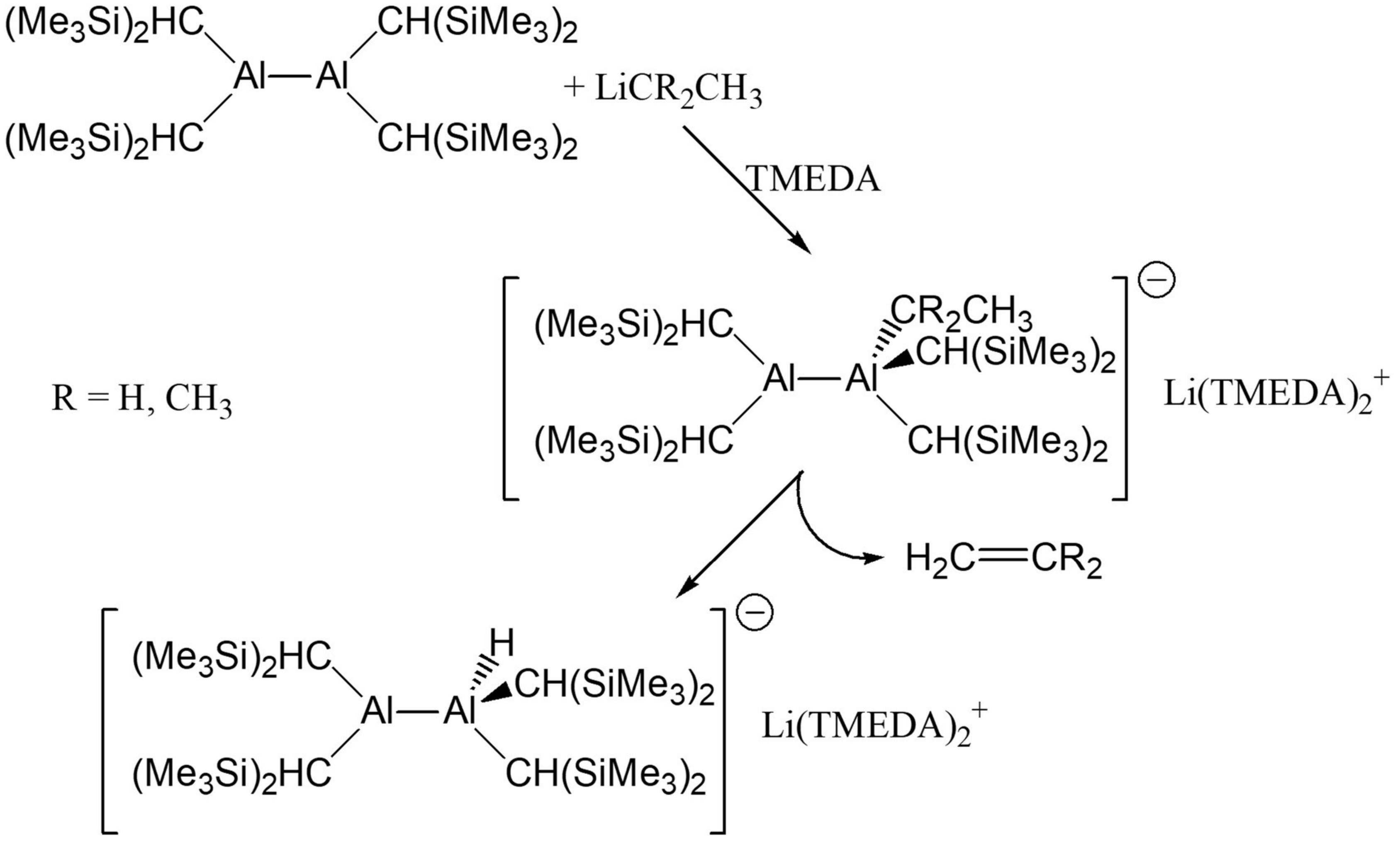
Reaction with A Lewis Base

These compounds will react with methyllithium to stabilize the methyl carbanion, and with LiBr to stabilize the the bromide anion:



Hydride Abstraction

Interestingly, if the same reaction is attempted with EtLi or ^{t}BuLi, a hydride is abstracted and an alkene is formed (reverse of hydroalumination):



Reduction

Having an unfilled π system allows for the accommodation of extra electrons. These species can be reduced by alkali metals to produce radical anion species:

$$[((Me_3Si)_2CH)_2M]_2 + M' + n\,L \rightarrow [((Me_3Si)_2CH)_2M]_2^{-\cdot}\ M'(L)_n^{+}$$