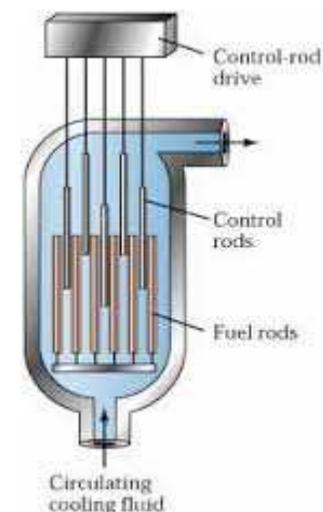


Chemistry of boron

Unique properties of boron

- Boron and its compounds on burning produces a green colored flame.
- Boron-10 isotope has a high propensity to absorb thermal neutrons.
- Borosilicate glasses (SiO_2 80% + B_2O_3 13%) have very low coefficient of linear thermal expansion ($\sim 3.3 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$). They withstand thermal shock better than other glasses (e.g. soda glass (SiO_2 73% + Na_2O 14% $\sim 8.9 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$)).
- Boron forms trivalent electron deficient compounds which are excellent Lewis acids
- Boron halides, unlike other halides of the same group do not dimerize due to smaller size and higher electro-negativity of boron.
- Boron compounds do not show observable toxicity and are therefore sought after intermediates in pharmaceutical and cosmetic industry.



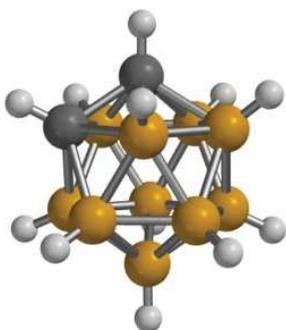
- Sodium perborate, $\text{Na}_2\text{H}_4\text{B}_2\text{O}_8$ otherwise $[\text{B}_2\text{O}_4(\text{OH})_4]^{2-}$ at around 60 °C releases oxygen. Hydrolysis of this salt gives H_2O_2 . This property makes it an oxidizer and chlorine free bleach which is also less aggressive.

- Aryl boronic acids are excellent reagents for palladium catalyzed cross-coupling reactions (Suzuki Coupling).

- Carboranes have higher air stability to form useful and stable organo derivatives with high boron content and steric bulkiness to make them weak anionic counterions.

- Boron carbide and boron nitride have hardness close to diamond and high melting points making them useful materials in nuclear (control rods) and defence (e.g. bullet proof vests) industry

- Boron is a minor nutrient for plants



Boric acid in antiseptic and skin irritation removal creames



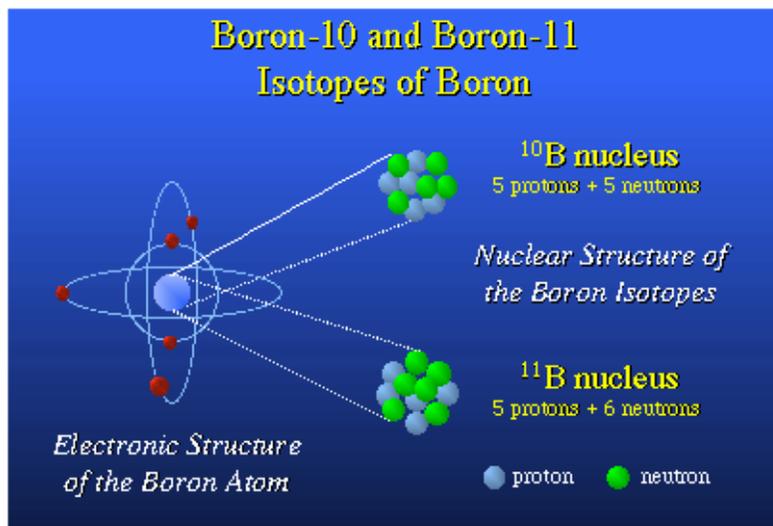
Containing Tankan Amla (Boric Acid) - 1%w/w,
Jasad Bhasma (Zinc Oxide) - 3.1%w/w
Bhaishajya Ratnavali & Rastarangini
Mineral Oil, Paraffin Wax, Lanolin & Perfume -q.s.



TANKAN AMLA (Boric Acid): Anti diaphoretic (anti sweating) agent reduces oiliness of the skin. Gives nourishment and luster to the skin. It is a germicidal (Local anti-infective) and non-irritant agent. It has also got an antibacterial effect. Keeps the skin soft, smooth and healthy.

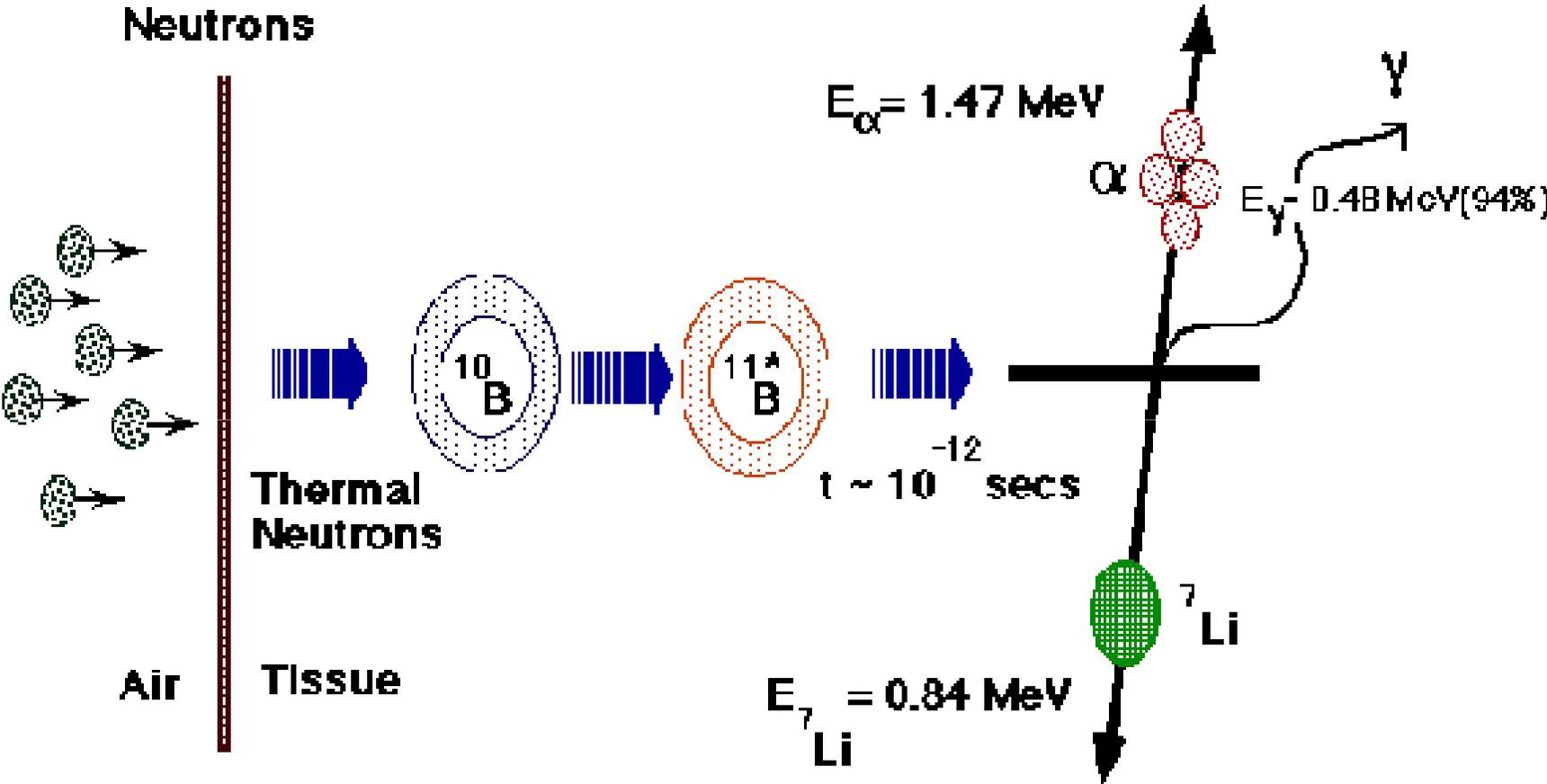
Boron was not isolated until 1808 by Sir Humphry Davy, Gay-Lussac and Thenard (1777-1857). This was accomplished by the reaction of boric acid (H_3BO_3) with potassium metal. Elemental boron is a dopant in semiconductor industry.

Crystalline boron, a black solid not found in the elemental form on earth is inert chemically and is resistant to attack by boiling HF or HCl. It has two isotopes B-11 (80%) and B-10 (20%). When finely divided it is attacked slowly by hot concentrated nitric acid.

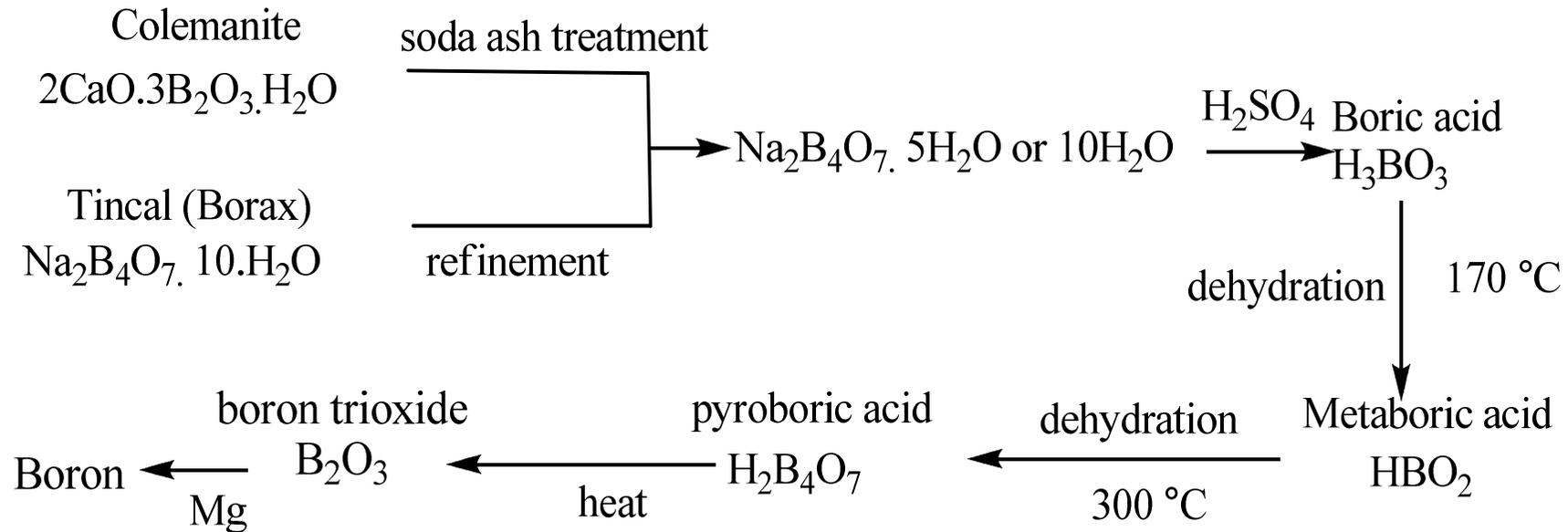


Boron neutron capture

Incident Epithermal
Neutrons



Preparing Boron from Borax



High purity boron is also available through the thermal decomposition of boron halides such as BBr_3 in the presence of hydrogen gas using a heated tantalum wire. Better results are obtained at temperatures over 1000°C .

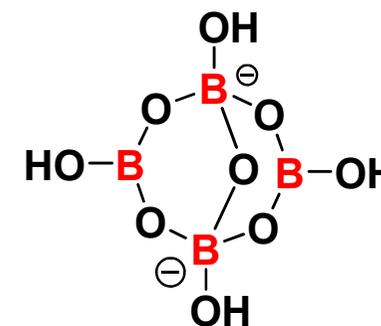
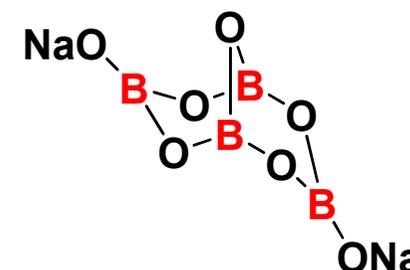
Industrially Important boron compounds

Borax (decahydrated sodium borate)

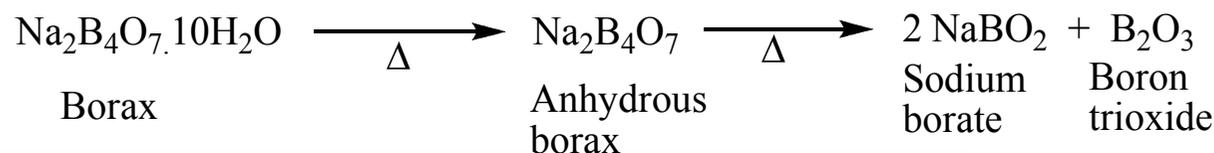
The compound is also called tincal which originates from Sanskrit as borax was discovered early in the dry lakebeds of Tibet.

- It is the precursor for all other well known boron-oxygen containing compounds
- It has fire retardant properties and is mildly alkaline.
- It is added in fertilizers as boron is a micronutrient for plants. An adequate amount of boron in the soil is 12 mg/kg. If the boron content of the soil drops below 0.14 mg/kg then boron deficiency is observed.
- It is used as a flux and glass former in metallurgy.
- It is also used for 'timborising', a process by which wood is inserted into hot borax solution to make a protective impregnation against wood boring insects.
- In a traditional method of gold mining, borax has been used as a substitute for toxic mercury in the gold extraction process.

While two structural forms are commonly used to depict borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. The actual form seems to be $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ having two anionic tetra coordinate boron atoms.

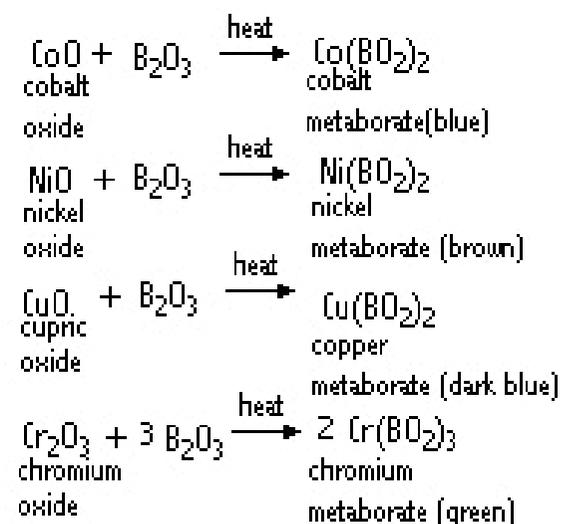


The borax bead test introduced by Berzelius in 1812, is a convenient flame test for many transition metal ions. In a borax bead test a small amount of borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ is taken on a red hot nichrome or platinum loop and is further heated to remove water of hydration and to convert to a glass like bead (mostly sodium borate). By dipping this bead in a metal salt, the sodium ions are exchanged for the metal ions being analyzed generating the corresponding metal borate and a flame test of this bead will now show a characteristic flame color for that metal.



Borax Bead Tests

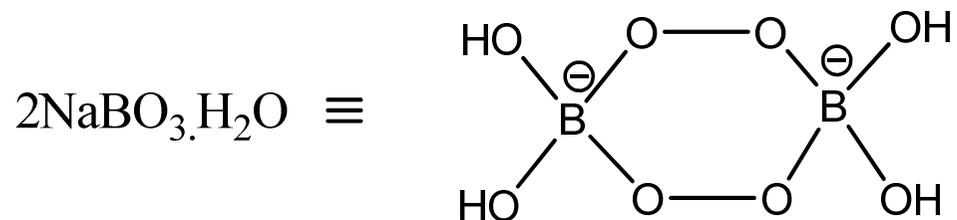
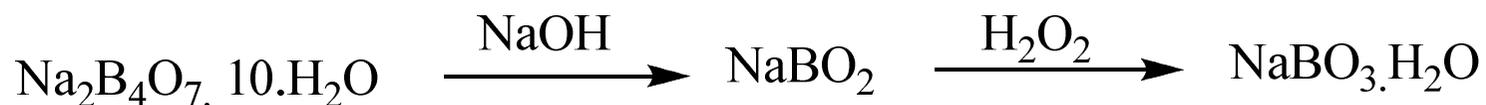
Color of Cooled Bead		
Heated in Oxidizing Flame	Element	Heated in Reducing Flame
Green	Chromium	Green
Blue	Cobalt	Blue
Blue	Copper	Brown
Yellow	Iron	Green
Violet	Manganese	Colorless
Brown	Nickel	Colorless
Colorless	Titanium	Yellow



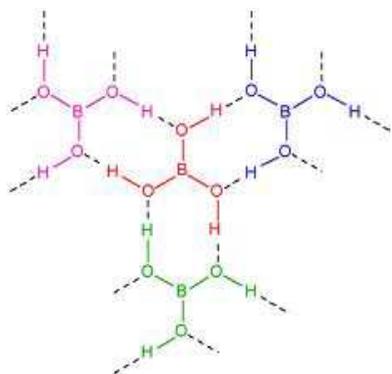
Sodium perborate



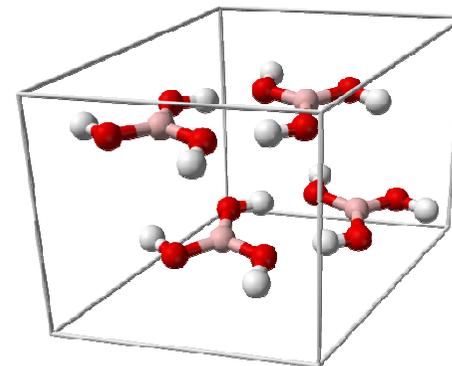
Sodium perborate, $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ is prepared from borax by treatment with NaOH (to convert it to sodium borate, NaBO_2) and further reaction with hydrogen peroxide. The elementary structural unit is a dimeric dianion $\text{B}_2\text{O}_4(\text{OH})_4^{2-}$. It is a source of active oxygen used in teeth whiteners and bleaches and is also a disinfectant. It releases oxygen rapidly above 60°C .



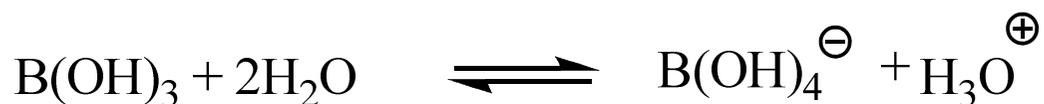
The teeth brightening gel is both legal and safe. It contains the active ingredient Sodium Perborate which forms a very low concentration of Hydrogen Peroxide on your teeth (0.035% Hydrogen Peroxide where the legal limit is 0.1%). This gives great results without any irritation of the gums or teeth sensitivity.



Orthoboric acid, H_3BO_3



Boric acid in the crystalline form consists of layers of $B(OH)_3$ molecules held together by hydrogen bonding. The distance between two such adjacent layers is 3.18 Å. It is readily prepared by reacting borax with a mineral acid such as HCl or H_2SO_4 . **As an acid, boric acid does not dissociate releasing H^+ but effectively donates a proton to another molecule of water itself acting as a Lewis acid as shown in the equation.** So although it is not a protonic acid it **is a weak monobasic acid with pKa 9.14**, comparable in acid strength to ammonium ion. Registered in 1983 for control of cockroaches, ants, grain weevils and several beetles, it has also been used as an herbicide as a fungicide for citrus. As an insecticide, boric acid acts as a stomach poison for ants, cockroaches, silverfish and termites. As a herbicide, boric acid causes desiccation or interrupts photosynthesis in plants. Also used as an eye wash especially for conjunctivitis (red eye) disease.



<p>First Aid <i>eye wash</i></p> <p>Buffered • Isotonic • Saline</p> <p>SINGLE USE</p> <p>(STERILE)</p> <p>4 FL OZ (118 mL) Order #4105</p> <p>GREEN GUARD</p> <p>Distributed by Green Guard®, St. Louis, MO 63045</p>	<p>Drug Facts</p> <p>Active ingredient Purified water 98.3%</p> <p>Purpose Eyewash</p> <p>Use For cleansing the eye to help relieve irritation or burning by removing loose foreign material</p> <p>Warnings For external use only</p> <p>Do not use ■ if you experience any open wounds in or near the eyes and obtain immediate medical treatment ■ if solution changes color or becomes cloudy</p> <p>When using this product ■ to avoid contamination, do not touch tip of container to any surface ■ do not reuse ■ once opened, discard</p> <p>Stop use and ask a doctor if you experience ■ changes in vision ■ eye pain ■ condition worsens or persists ■ continued redness or irritation of the eye</p> <p>Keep out of reach of children. If swallowed, get medical help or contact a Poison Control Center right away.</p> <p>Directions Flush the affected eye as needed, controlling the rate of flow of solution by pressure on the bottle.</p> <p>Other information ■ lot number is printed on the bottle ■ store at 20° to 25° C (68° to 77° F) ■ for your protection, this bottle has an imprinted white seal with black printing "TAMPER EVIDENT SEAL" ■ do not use if this seal is missing or broken ■ use before expiration date marked on bottle</p> <p>Inactive ingredients boric acid, sodium borate, sodium chloride</p> <p>Questions ? ☎ Call 800-869-6970</p>
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Treats eye infections
Heals minor wounds
Controls pests
Preserves timber

Metaoboric acid, HBO₂

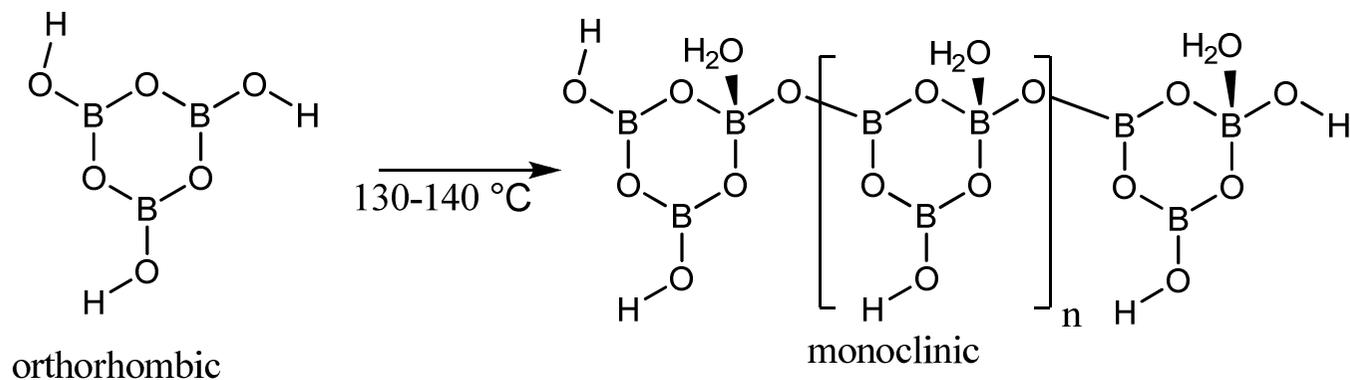


Heating of boric acid at 80-100 °C releases one equivalent of water to give orthorhombic metaboric acid:



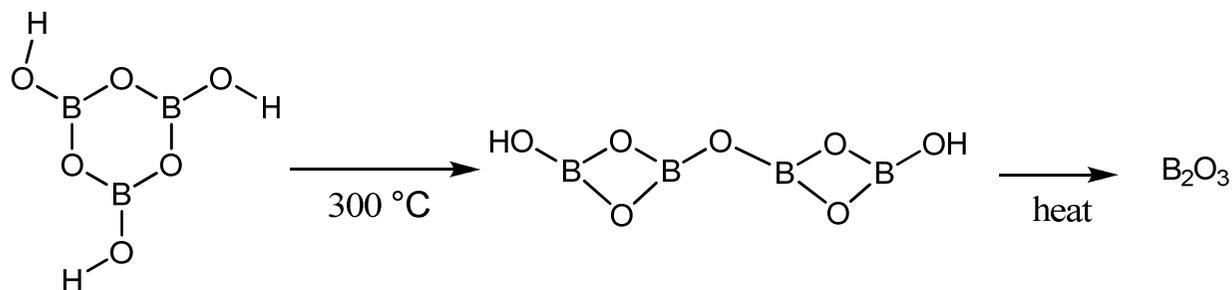
This form is molecular, consisting of discrete trimers. This molecule has C_{3h} symmetry and forms a sheet-like structure, similar to that of boric acid itself.

Upon heating at 130-140 °C in a sealed ampoule (to prevent dehydration), orthorhombic metaboric acid converts to the monoclinic form which has one B in tetrahedral geometry



Boron trioxide, B₂O₃

Boron trioxide is prepared by reacting borax with sulfuric acid in a fusion furnace. At temperatures above 750 °C, the molten boron trioxide layer separates out from the sodium sulfate layer which can be separated by decanting. By heating boric acid above 300 °C also one can get boron trioxide. This goes through metaboric acid and pyroboric acid to the network of tricoordinate boron surrounded by three oxygens.



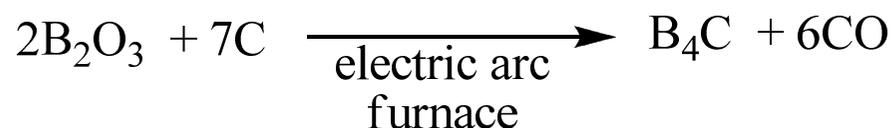
One of the most important use of B₂O₃ is in glass industry. Borosilicate glasses, well known for their unbreakability with sudden temperature variations are basically vitreous solutions of SiO₂ (80%) B₂O₃ (13%), Al₂O₃ (4%) and Na₂O (4%). In contrast, the soda lime glass, which has a higher coefficient of linear thermal expansion and is used for making window panes has as major components SiO₂ (73%), Na₂O (14%), CaO (9%) and MgO (4%). Boron trioxide is also an essential ingredient in high quality vitreous enamels. Modern day TV, laptops and mobile phones require specialty glasses which do not contain sodium ions. Boric oxide is a key constituent of alkali-free LCD glass. It acts as a connecting network in the glass structure, improving optical properties, and reducing the melting temperature.



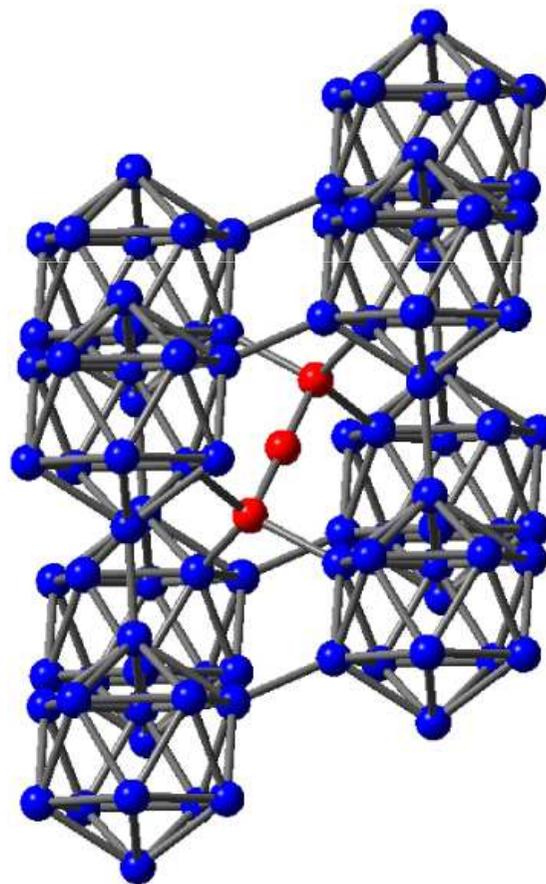


Boron carbide, B₄C

Henri Moissan, the father of fluorine chemistry was also the person who prepared boron carbide for the first time by the reduction of boron trioxide with magnesium in the presence of carbon in an electric arc furnace. It can also be prepared by the reaction of carbon on B₂O₃ at high temperature with the release of CO as side product.



With the more accurate chemical formula of B₁₂C₃, boron carbide consists of B₁₂ icosahedra surrounding a CCC chain at the center. (At the carbon-rich limit, the crystal lattice is predominantly composed of B₁₁C icosahedra and C–B–C chains, with some intrinsic disorder and defects) it is **one of the hardest known materials with a hardness of 9.5** mohs which is slightly less than cubic boron nitride and diamond. This ceramic material is used for making bullet proof vests, tank armor etc. It has also immense use in nuclear reactors as control rods and shutdown pellets due to the ability of boron-10 to absorb thermal neutrons and the **very high melting point of 2763 °C** and boiling point of 3500 °C.



Properties of boron carbide

The unique physical structure of BC gives rise to correspondingly unique properties, several of which have proven anomalous or puzzling due to both inconsistencies in the reported experimental data and/or an incomplete representation of the atomic structure. Boron carbide:

is ultra hard

has an extremely high melting point (~2600 °C)

is chemically inert

is light weight

has a high ^{10}B neutron capture cross section

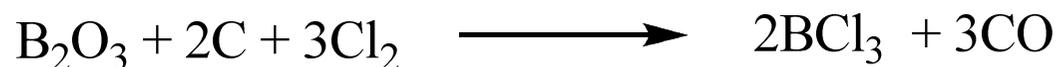
is radiation hard (i.e., can 'self-heal' radiation damage)

exhibits thermally activated conductivity (i.e., behaves as a p-type semiconductor)

exhibits low thermal conductivity

Boron Halides

Based on the relative exothermicities of Lewis base adduct forming reactions, their **relative Lewis acidity** has been determined and follows the order

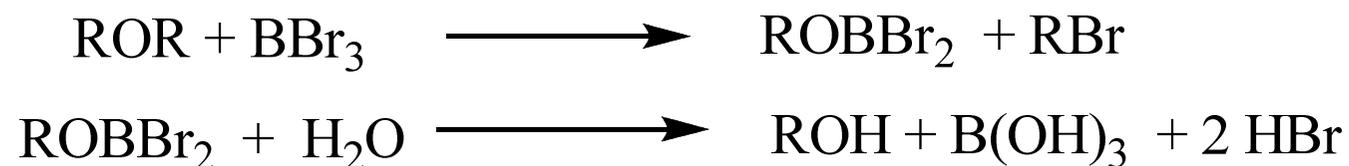


BF_3 and BCl_3 are **gases at room temperature** with boiling points of $-100.3\text{ }^\circ\text{C}$ and $12.6\text{ }^\circ\text{C}$ and both are **corrosive**. A convenient way of handling them for chemical reactions are as adducts, $\text{BF}_3 \cdot \text{OEt}_2$ (B.P. $126\text{ }^\circ\text{C}$), and $\text{BCl}_3 \cdot \text{SMe}_2$ (M.P. $88\text{-}90\text{ }^\circ\text{C}$). While hydrolysis of BF_3 results in HBF_4 and boric acid, hydrolysis of BCl_3 gives HCl and boric acid.

Because of its Lewis acidity and its relatively higher resistance to hydrolysis, in comparison to other boron halides, BF_3 is used as a catalyst in many organic synthesis reactions such as

- polymerization of olefins, vinyl ethers, indene, terpenes, styrene, unsaturated acids etc.
- alkylation of aromatic, phenols with olefins and alcohols
- isomerization and disproportionation of paraffins and unsaturated hydrocarbons
- synthesis of acetals, steroids, hydroxyl fatty acids
- For promoting reactions of acetylenes with acids and addition of organic acids to olefins.

Unlike BF_3 and BCl_3 , BBr_3 is a liquid with a boiling point of $91\text{ }^\circ\text{C}$ and is therefore more convenient to handle although it reacts vigorously with moisture. The most important use of BBr_3 is the cleavage of C-O bonds of alkyl ethers. The mechanism of this reaction goes through a complex formation at the boron centre with the ether oxygen followed by alkyl bromide elimination to yield a dibromo organoborane. This on further hydrolysis will result in alcohol.

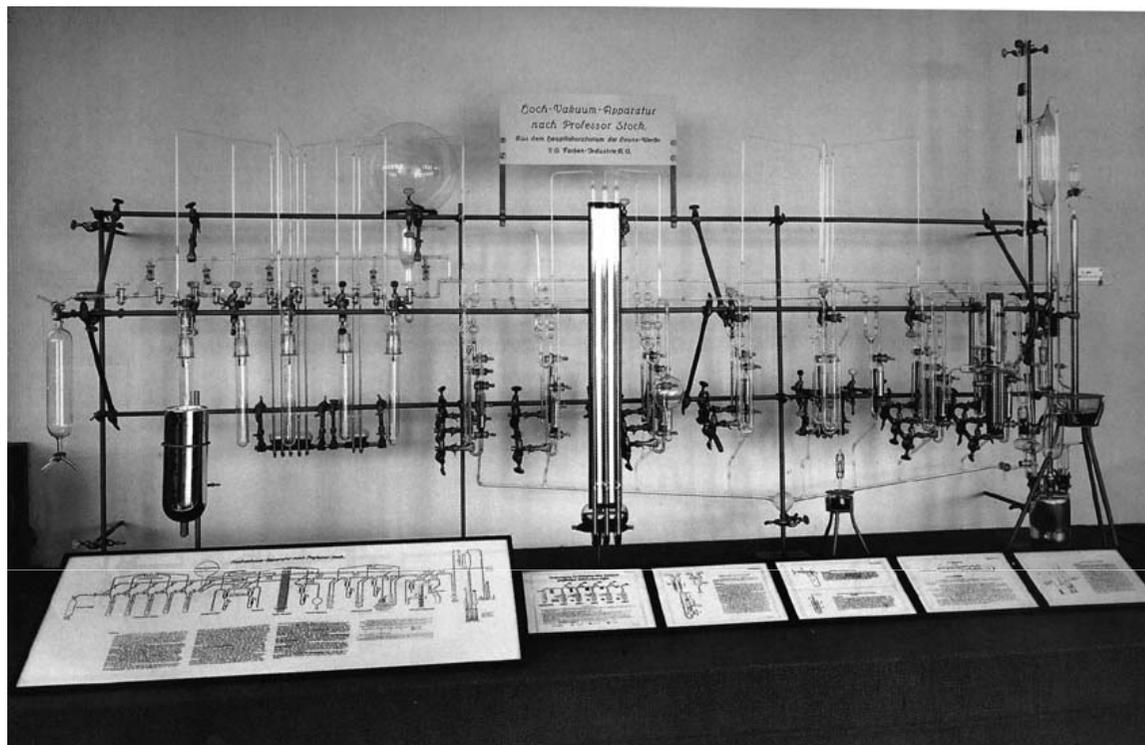


BBr_3 also finds application in olefin polymerization, and dealkylation of aryl alkylethers.

BCl_3 also can cleave C-O bonds of ethers however BBr_3 is more preferred for this reaction for higher reactivity and ease of handling as a liquid reagent.



Alfred Stock- the father of boron hydride chemistry



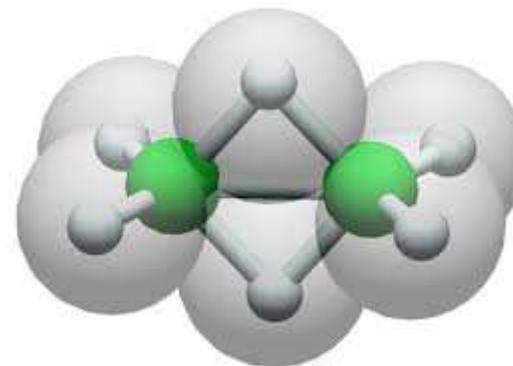
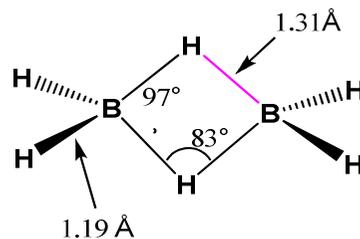
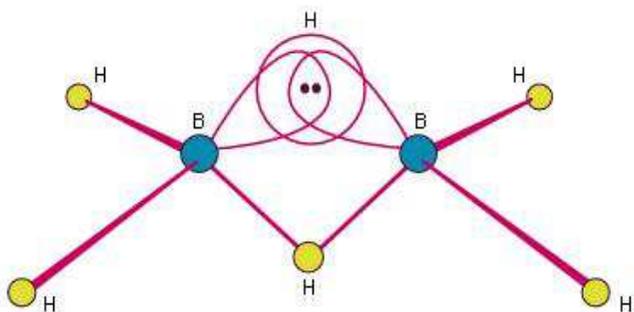
Student of Emil Fischer
 Worked with Henry Moissan
 Hydrides of B and Si
 50 papers on mercury poison
 Coined the term ligand
 Alfred Stock Prize for outstanding
 Inorg. Synth. work
 Died at 70

Alfred Stock prepares a series of boron hydrides including B_2H_6 and separates them using the first sophisticated vacuum manifold. Due to their very high air and moisture sensitivity and flammability, till then they were not separable. He published his work in 1933.

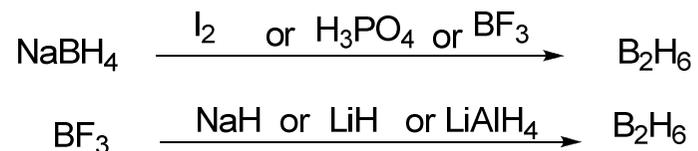
1912



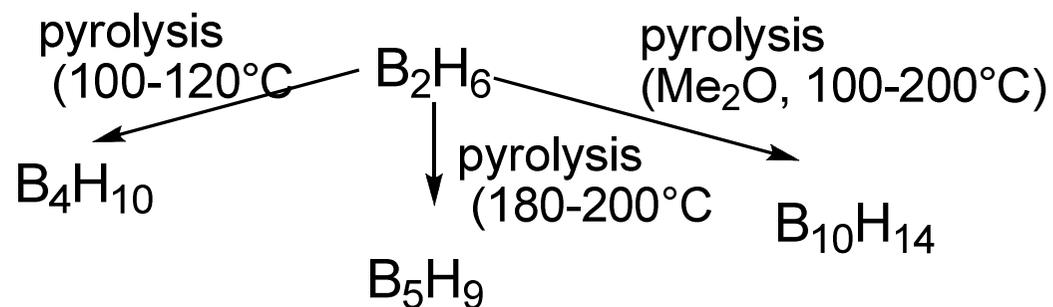
	B. P
B_2H_6	-92.5 °C
B_4H_{10}	16 °C
B_5H_9	58 °C
B_5H_{11}	65 °C
B_6H_{10}	108 °C
$B_{10}H_{14}$	213 °C
	m.p. 99.7 °C



Diborane, B_2H_6 can now be prepared from $NaBH_4$ or BF_3 by many reagents as shown.

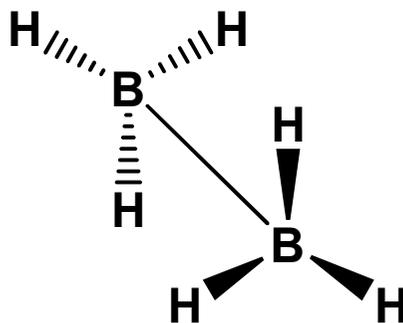


Most of the higher boranes could be prepared from diborane by controlled pyrolysis reactions.



A short history of B₂H₆

- 1912: Boranes first studied by Alfred Stock
- 1925: diborane, ethane-like structure?
- 1934: diborane is diamagnetic
- 1937: Simon Bauer (electron diffraction), ethane-like
- only 12 valence electrons. What is the structure?



On the structure of B_2H_6 : How Pauling was proved wrong by a young chemist



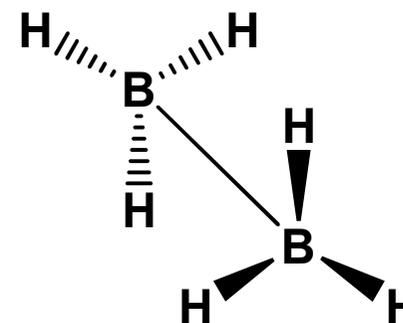
Alfred Stock (karlsruhe)



Linus Pauling (Caltech)



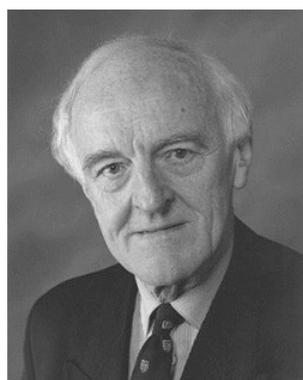
Simon H. Bauer (Cornell)



“I do not feel very friendly towards the structure which you mention in your letter for the diborane molecule. So long as the suggested structure remains vague and indefinite, it is not easy to say that it is eliminated by electron diffraction data or other data. Also the force constant for the B-B vibration is, I think much stronger than that would be expected for the proposed structure in which there is no direct B-B bond” *Linus Pauling*



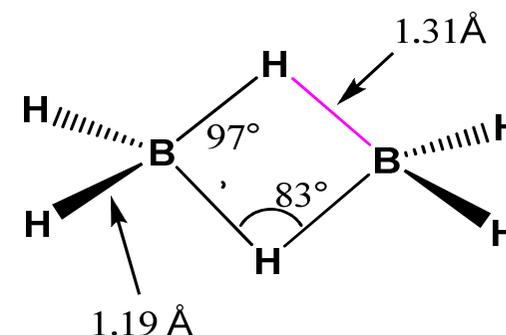
H.I. Schlesinger
U of Chicago
(Guide HC Brown)



Longuet-Higgins (Oxford)



Mulliken (MIT)

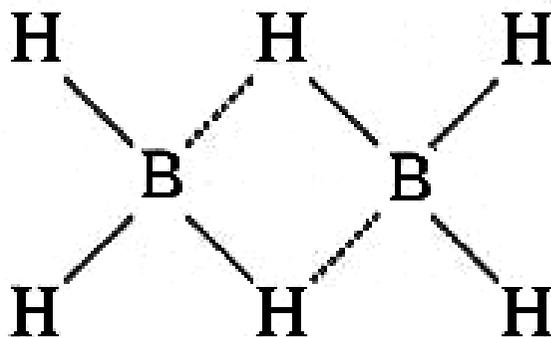


Longuet-Higgins, H. C.; Bell, R. P. (1943). " The Structure of the Boron Hydrides". *Journal of the Chemical Society* **1943**: 250–255. (age 20)



- 1941: Schlesinger in a letter to Pauling

*As a result of our work on the metallo borohydrides I definitely feel that a structure for diborane quite different from those generally proposed, would aid in correlating many of the observations we have made [...] **The structure I have in mind is a bridge structure, in which the two boron atoms are joined to each other through an unusual type of hydrogen bond, perhaps best represented by the following formula***



W. N Lipscomb, the 1976 Nobel Prize winner for chemistry was the first to classify boranes using the now redundant *styx* numbering. The currently accepted and widely used nomenclature based on the shape of boranes began in 1963 when a closed borane polyhedron was first classified as *clovo* which is Latin meant closed. In 1968 the American Chemical Society modified this to *closo* and also named open polyhedra as *nido*. The words *arachno* and *hypho* were introduced later mostly by Williams in 1970 and 1974. The meaning of these names and examples of common lower boranes with electron count and structures are given below.



closo boranes- closed polyhedra- e.g. $B_{12}H_{12}^{2-}$

nido boranes – nest like – B atoms occupy n corners of an n+1 cornered polyhedron e.g. B_2H_6 ,

$B_{10}H_{14}$

arachno- spider web like- more open than nido having B atoms occupying n contiguous corners of an n+2 cornered polyhedron e.g.

B_5H_{11} , B_6H_{12}

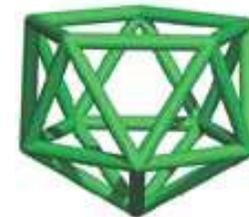
hypho- net like open polyhedra with B atoms occupying n corners of an n+3 polyhedra e.g.

conjuncto- meaning linked; formed by linking two or more of the earlier type of clusters together.

e.g. $B_{10}H_{16}$ i.e. $(B_5H_8)_2$



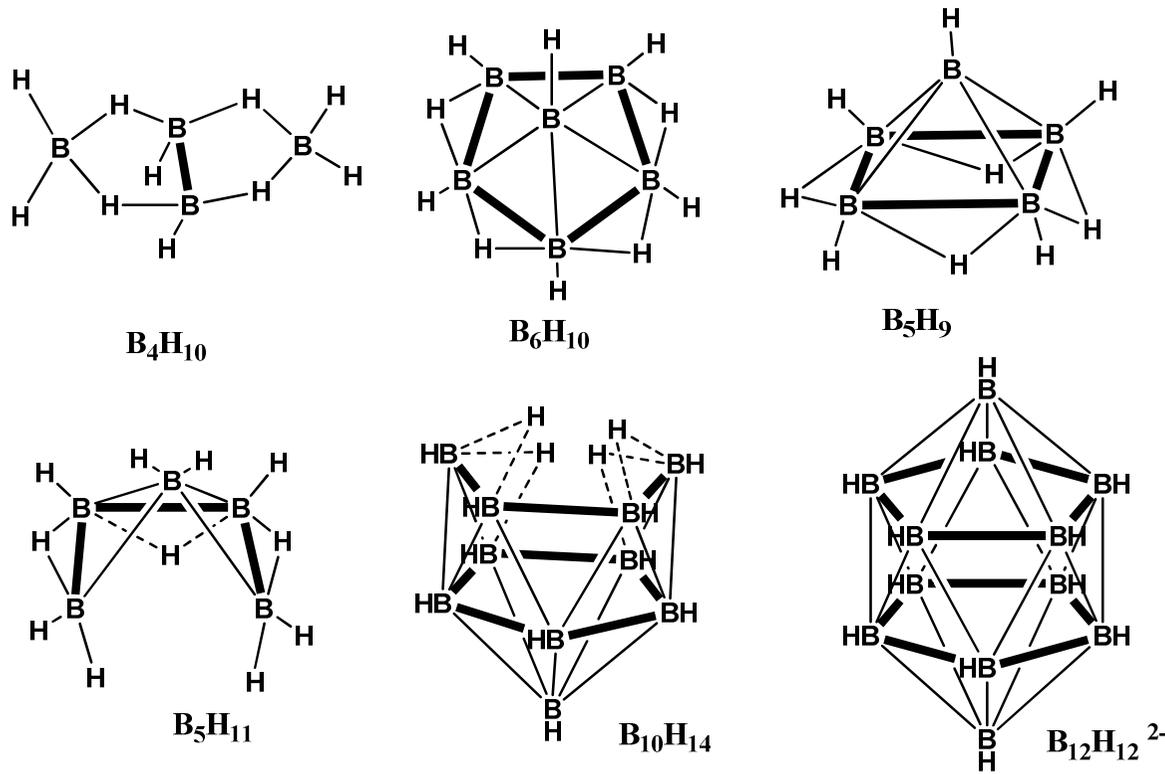
Closo



Nido



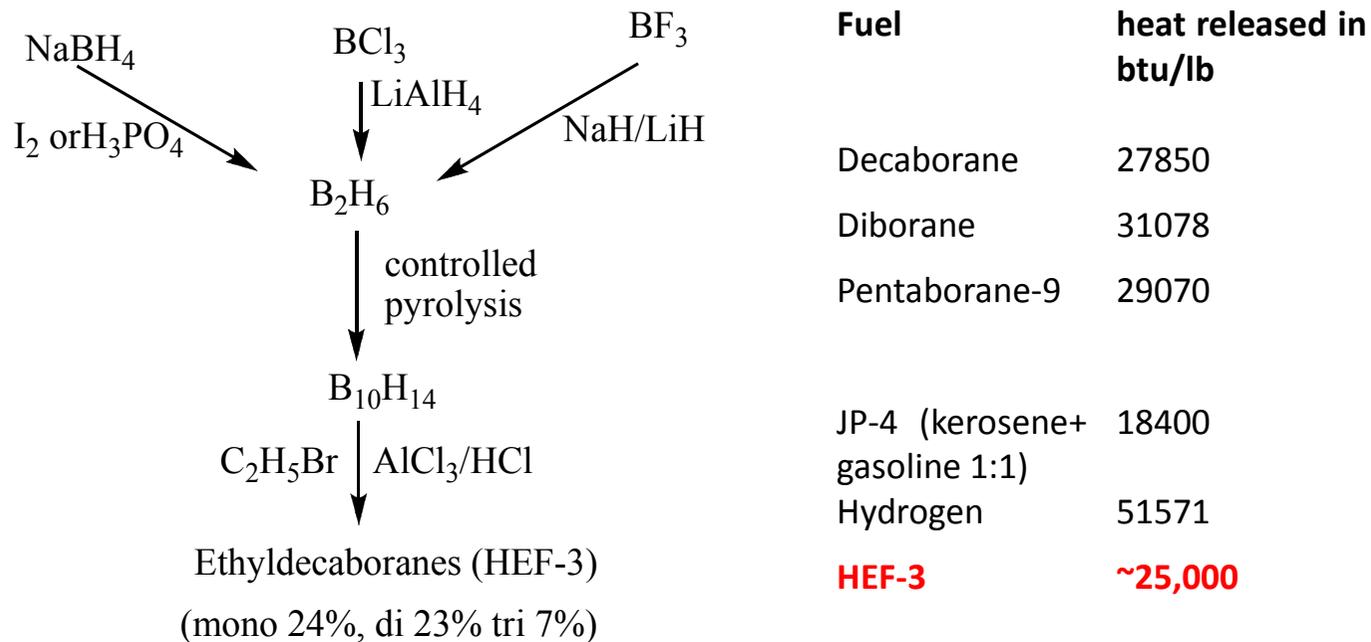
Arachno



Formula	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	B_6H_{10}	$B_{10}H_{14}$	$B_{12}H_{12}^{2-}$
name	diborane	tetraborane	Pentaborane-9	Pentaborane - 11	Hexaborane	decaborane	Dodecaborate anion
B.P °C	-92.5	16	58.4	65	108	213 m.p.99.7	m.p. 650 (Cs salt)
Electron count	B_nH_{n+4}	B_nH_{n+6}	B_nH_{n+4}	B_nH_{n+6}	B_nH_{n+4}	B_nH_{n+4}	B_nH_{n+2}
shape	nido	arachno	nido	arachno	nido	nido	closo

The potential of boron hydrides as rocket/aircraft propellants

In the 1930s, boron's potential began to emerge when it was found that boron-based materials produced more heat than the corresponding carbon-based compounds. It was estimated that boron hydrides could produce up to 30,000 BTUs/lb of energy upon combustion, compared to ~18,000 BTUs/lb for comparable hydrocarbon fuel.



use of boron-enriched "zip fuels", which improved the energy density of the fuel by about 40 percent, and could be used in versions of existing jet engine designs. Zip fuels appeared to offer sufficient performance improvement to produce a strategic bomber with supersonic speed.

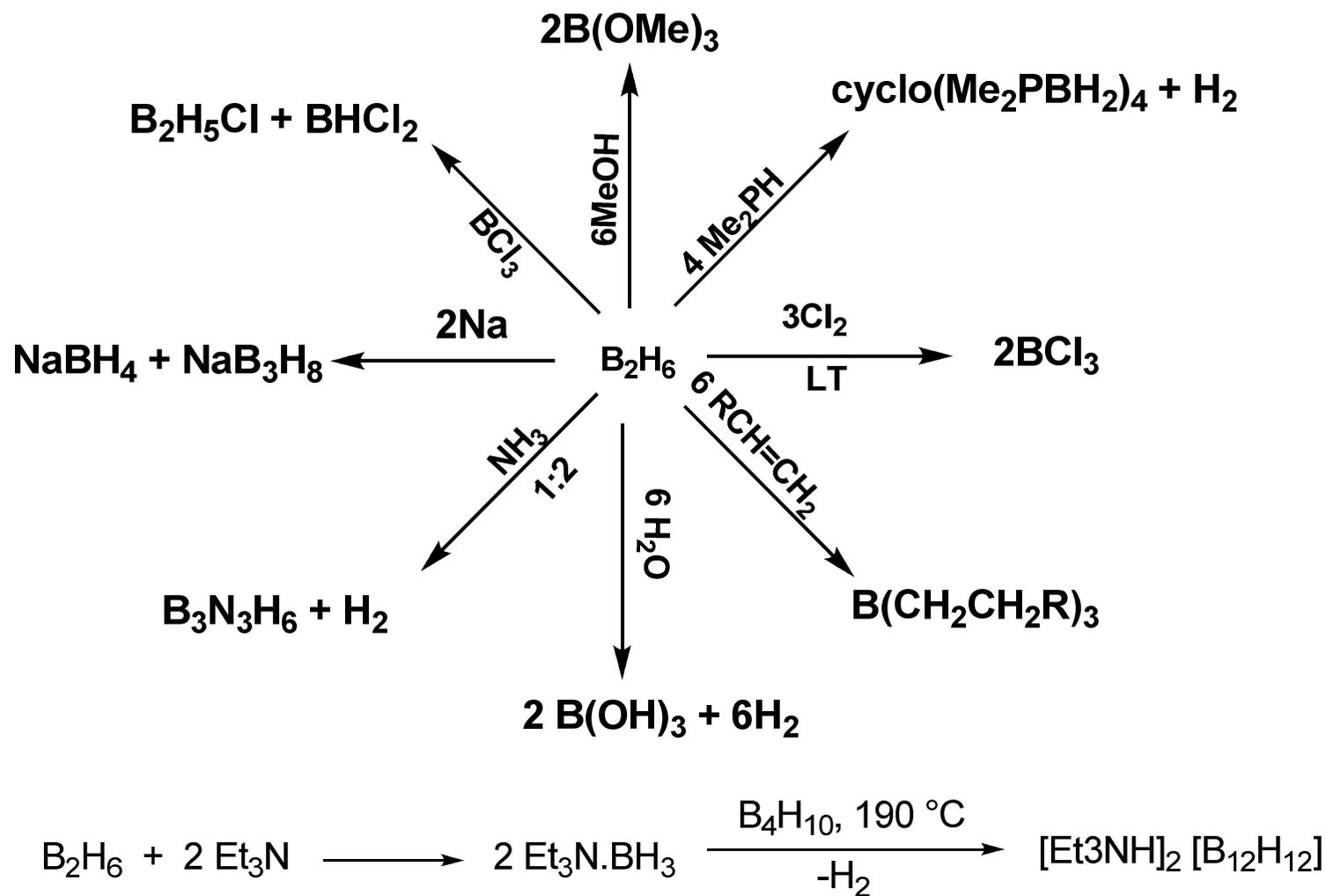
The borane fuel Saga: how a great idea failed when put to practice

The XB-70 Valkyrie was originally designed as a strategic bomber capable of traveling to its target at Mach 3, and delivering nuclear or conventional weapons. After a succession of policy changes, it was decided in 1963 to build only two of them for research. The XB-70 was the world's largest experimental aircraft. Capable of flight at 2,000 miles per hour and altitudes of 70,000 feet.

The ethyl derivatives of decaborane, made by Friedel-Crafts reaction of decaborane with ethyl bromide was found to be more easy to store and handle and was code named HEF-3 (High Energy Fuel-3). This was considered for use as fuel in XB-70 Valkyrie, the prototype version of the B-70 nuclear armed deep penetration strategic bomber which could fly at mach-3 speed similar to ICBM's and reach distant continents. But the program was cancelled after spending millions of dollars. One reason was the borane based fuels are highly corrosive, and could spontaneous ignite. Also when burned, they produced solid combustion byproducts especially hard boron carbide and boron oxides that got attached to the engine parts leading to mechanical faults and corrosion. In addition, the sooty exhaust was highly toxic poisoning populated area and has high visibility in the sky making it unfit for defence use. Adding to this were the exorbitant cost of making such fuels and hence the program of making borane based fuels was shelved.



Reactions of diborane



FROM LITTLE ACORNS TO TALL OAKS- FROM BORANES THROUGH ORGANOBORANES

Nobel Lecture, 8 December, 1979

by
HERBERT C. BROWN

Department of Chemistry, Purdue University, IN



IV. HYDROBORATION

In the course of these studies of selective reductions, a minor anomaly resulted in the discovery of hydroboration. My coworker, Dr. B. C. Subba Rao, was examining the reducing characteristics of sodium borohydride in diglyme catalyzed by aluminum chloride[17]. He observed that the reduction of ethyl oleate under our standard conditions, 4 moles of hydride per mole of compound, one hour at 25°, took up 2.37 equivalents of hydride per mole of ester. This contrasted with a value of 2.00 for ethyl stearate. Investigation soon established

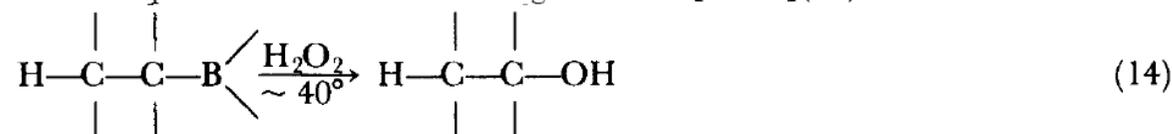
that the reagent was adding an H-B, bond to the carbon-carbon double bond to form the corresponding organoborane[26].

Exploration of this reaction soon established improved procedures for carrying it out. Of special value was the discovery that the addition of diborane to alkenes was markedly catalyzed by ethers[27]. In the presence of such ethers, the reaction is practically instantaneous and quantitative (13).



(My parents were far-seeing in giving me the initials H. C. B.)

Dr. Subba Rao established that oxidation of such organoboranes, in situ, with alkaline hydrogen peroxide, proceeds quantitatively, producing alcohols with the precise structure of the organoborane [26,27](14).



At this stage in the development, Dr. B. C. Subba Rao returned to India,

Hydroboration

Hydroboration, a well known reaction in organic chemistry refers to the addition of a hydrogen-boron bond to C-C, C-N, and C-O double bonds, as well as C-C triple bonds. This chemical reaction is useful in the synthesis of organic compounds. The development of this technology and the underlying concepts were recognized by the Nobel Prize in Chemistry to H. C. Brown of Purdue University USA.



Herbert C. Brown

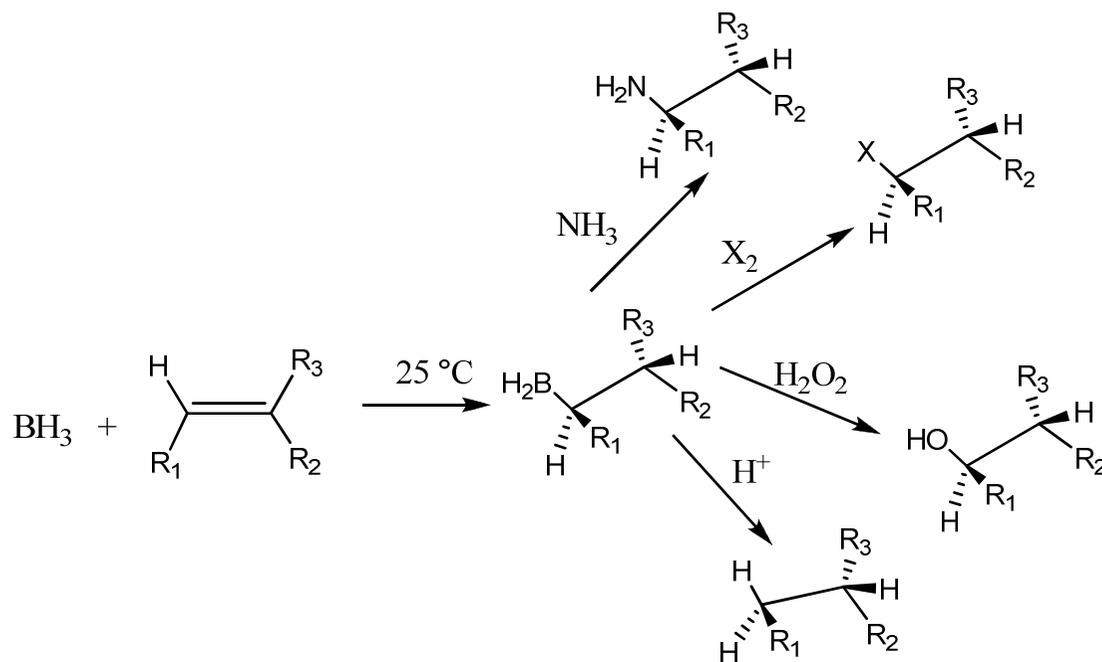
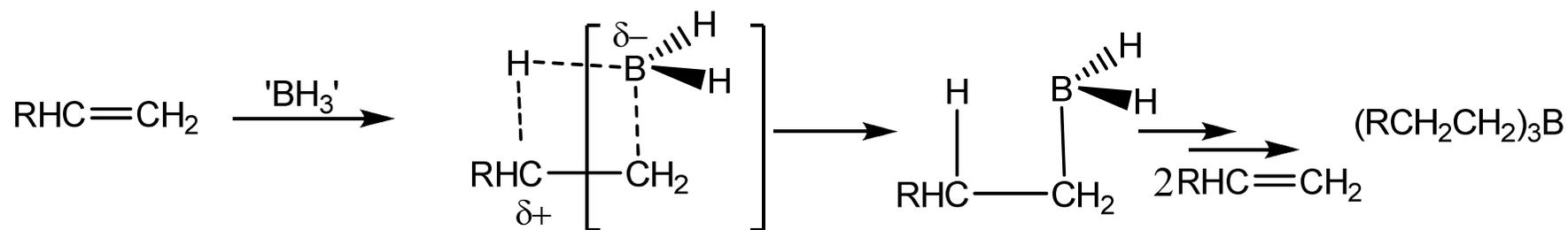
May 22, 1912 –
December 19, 2004



P V Ramachandran

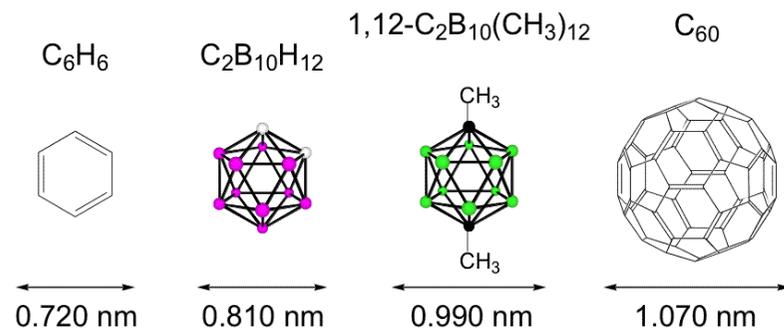
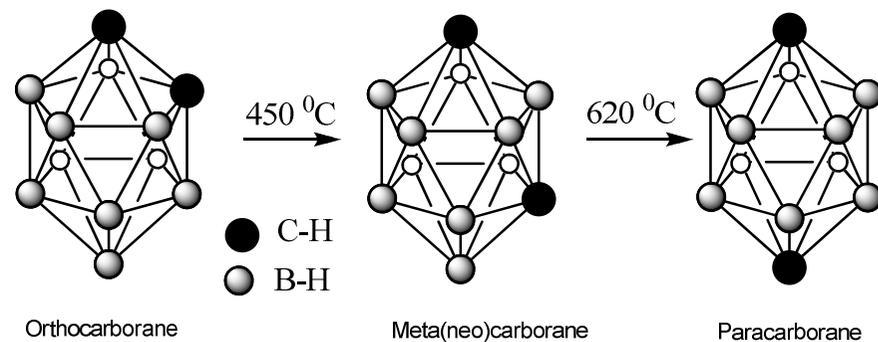
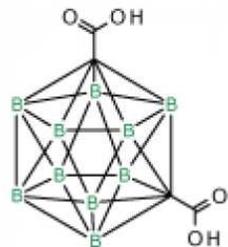
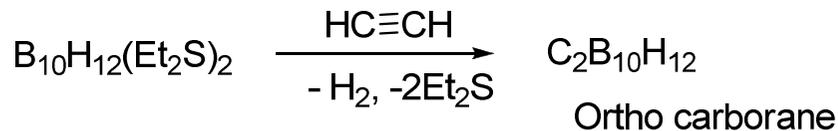
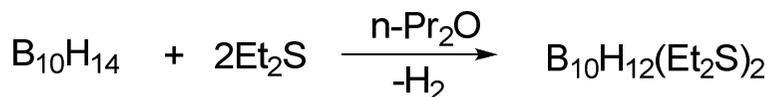
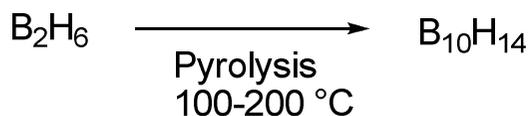
Ph.D from IITK

Hydroboration is typically anti-Markovnikov, i.e. the hydrogen adds to the more substituted carbon of the double bond. The regiochemistry is reverse of a typical HX addition reflects the polarity of the $B^{\delta+}-H^{\delta-}$ bonds. Hydroboration proceeds via a four-membered transition state: the hydrogen and the boron atoms added on the same face of the double bond.

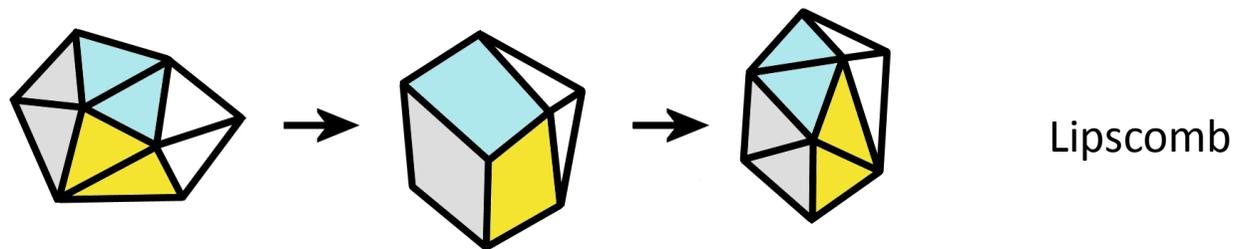
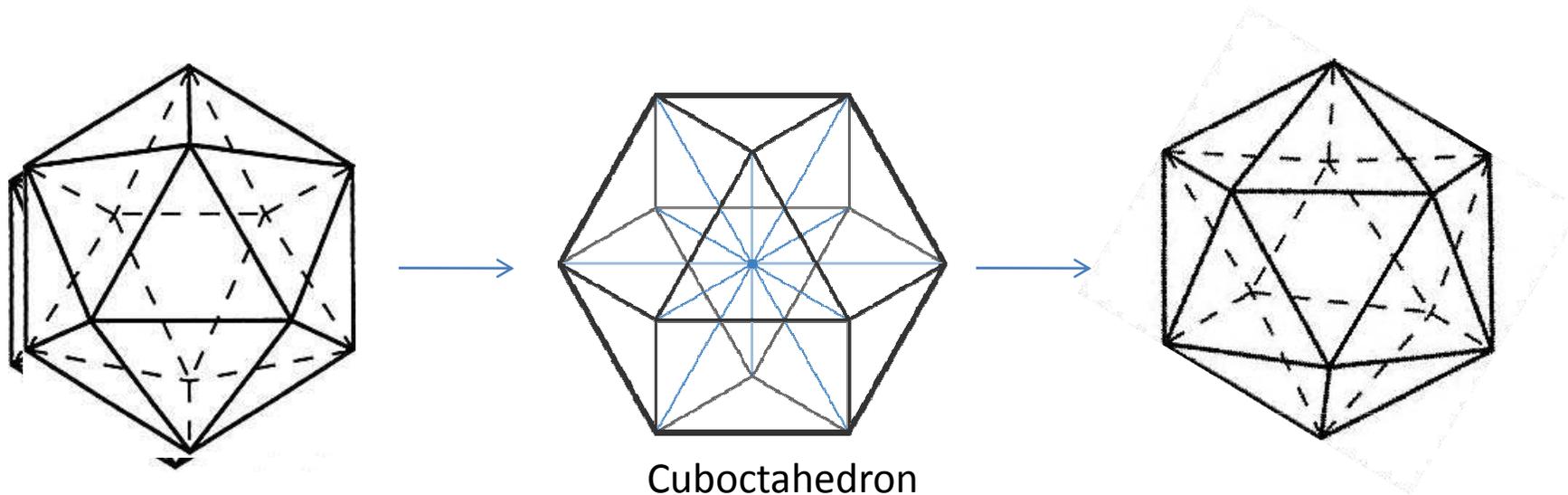


Carboranes

Carboranes are borane clusters having carbon atoms replacing the framework boron atoms. They also has been classified based on the structure like closo, nido, arachno and hypho. The 1,2-closo-dicarbododecaboranes, $C_2B_{10}H_{12}$ (usually simply called carboranes), were reported simultaneously by groups at Olin Corporation and the Reaction Motors Division of Thiokol Chemical Corporation working under the U.S. Air Force and published in 1963. Before its discovery decaborane derivatives were thought to be thermally unstable and reactive with air and water. These groups demonstrated the **unprecedented stability** of the 1,2-closo-dodecaborane group, presented a general synthesis, described the transformation of substituents without destroying the carborane cluster, and demonstrated the ortho to meta isomerization.



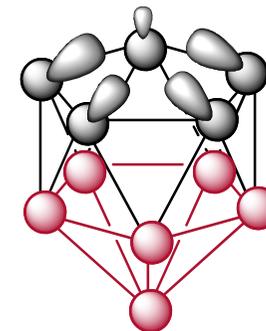
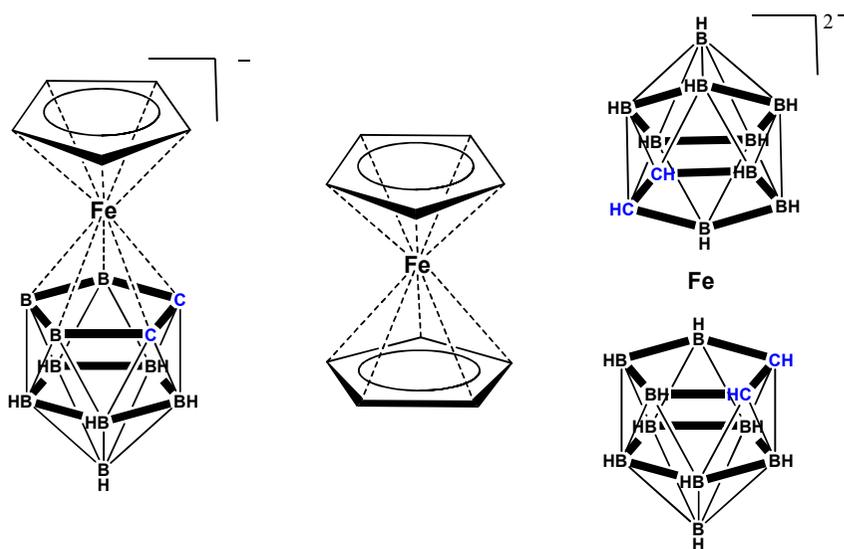
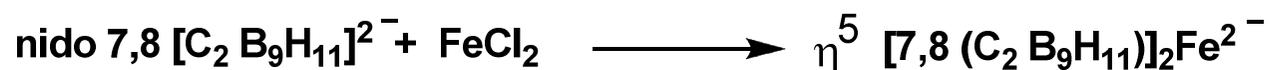
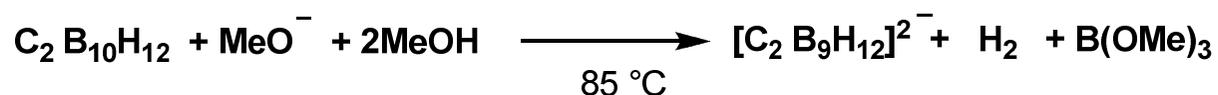
How does the isomerization of 1,2 to 1,7 to 1,12 carborane takes place?



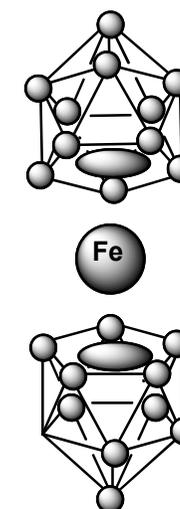
Diamond Square Diamond (DSD) mechanism

Carborane ligands

Numerous studies have been made on derivatives of the so-called **dicarbollide anion, $[B_9C_2H_{11}]^{2-}$** . The first metal dicarbollide complex was discovered by M. Frederick Hawthorne and co-workers in 1965. This anion forms sandwich compounds, referred to as bis(dicarbollides), with many metal ions and some exist in otherwise unusual oxidation states. The dianion is a nido cluster prepared by degradation of the parent dicarborane:

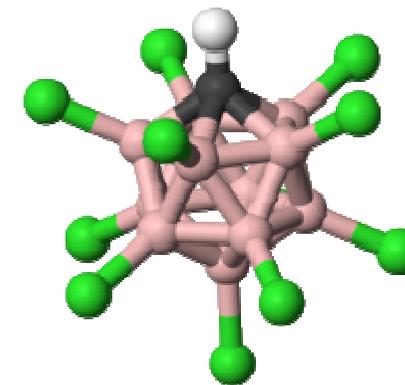


M. Frederick Hawthorne



Carborane Superacids

The carborane superacid $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ is **one million times stronger** than sulfuric acid. The reason for this high acidity is that the acid anion $\text{CHB}_{11}\text{Cl}_{11}^-$ is very stable and substituted with electronegative substituents. $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ and related carborane acids are known to protonate C_{60} fullerene without decomposing it. Additionally, it is the only known anion capable of forming a stable, isolable salt with protonated benzene, C_6H_7^+ .



$\text{CHB}_{11}\text{Cl}_{11}^-$

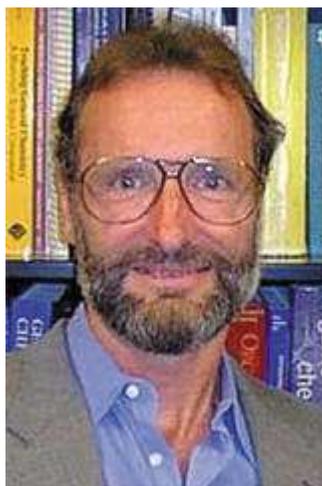


Table 1: Acid-strength ranking from protonation of mesityl oxide in liquid SO_2 .

Acid	$\Delta\delta$ (^{13}C) [ppm]	H_0
$\text{H}(\text{CHB}_{11}\text{Cl}_{11})$	84.0 ± 0.1	[a]
$\text{H}(\text{CHB}_{11}\text{H}_5\text{Cl}_6)$	83.8 ± 0.1	[a]
$\text{H}(\text{CHB}_{11}\text{H}_5\text{Br}_6)$	83.8 ± 0.1	[a]
$\text{H}(\text{CHB}_{11}\text{H}_5\text{I}_6)$	83.3 ± 0.1	[a]
FSO_3H	73.8 ± 0.5	-15.1
$\text{CF}_3\text{SO}_3\text{H}$	72.9 ± 0.4	-14.1
$\text{HN}(\text{SO}_2\text{CF}_3)_2$	72.0 ± 0.4	[a]
H_2SO_4	64.3 ± 3.1 ^[b]	-12.1
Unprotonated mesityl oxide	32.4 ± 0.1	

[a] H_0 values unavailable because acids are solids, not liquids. [b] Incomplete miscibility of H_2SO_4 in liquid SO_2 leads to higher error limits and possible underestimate of $\Delta\delta$.

The Strongest Isolable Acid

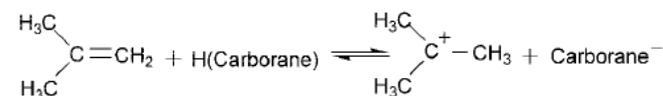
Christopher A. Reed et al, Angew. Chem.Int Ed, 2004 ,43, 5352



Olah Magic Acid ($\text{FSO}_3\text{H}-\text{SbF}_5$)



The compound, called a carborane acid, is the first 'superacid' that can be stored in a bottle, say its creators. The previous record-holder, fluoroantimonic acid, is so corrosive that it would eat straight through the glass.



A benzenium ion can be isolated as a stable compound when benzene is protonated by the carborane superacid $\text{H}(\text{CB}_{11}\text{H}(\text{CH}_3)_5\text{Br}_6)$. The benzenium salt is crystalline with thermal stability up to 150 °C. Bond lengths deduced from X-ray crystallography are consistent with a cyclohexadienyl cation structure.

The World's Strongest Acids: Like Fire and Ice

Posted by **Ross Pomeroy** August 24, 2013

If you paid attention in chemistry class, you'd know not to mess around with sulfuric acid. Even at a fairly dilute concentration, it's about ten times more acidic than the contents of your stomach. You don't want to spill it on your skin.

But you probably never learned not to muck around with **fluoroantimonic acid** H_2FSbF_6 . For the record, you shouldn't. Based on the silvery-white metal antimony, with a pH of -31.3, it's **100,000 billion billion billion** times more potent than stomach acid, and makes its rambunctious cousin sulfuric acid look as gentle as a vanilla milkshake with whipped cream and a cherry on top.

"You couldn't pick up a bottle of it because after it ate through the bottle, it would dissolve your hand," Sam Kean noted in his book *The Disappearing Spoon*. This begs a simple question: how is fluoroantimonic acid stored?

Though the boron-based carborane has a peppy pH of -18, it's also exceedingly gentle, meaning noncorrosive. Like its fellow acids, carborane is incredibly willing to donate a proton (hydrogen atom without an electron) to other substances -- that's what defines the strength of an acid. But what's left afterwards, unlike with sulfuric acid or fluoroantimonic acid, is a very content and stable little set of atoms.

Once losing its proton, fluoroantimonic acid and most other strong acids ravage other substances, often by ripping electrons from their atoms. If the substance in question is your skin, the acid will often cleave the amide bonds of proteins and the ester groups in fats through a process called hydrolysis. Either way, **these corrosive acids wreak havoc on anything they touch, like the Hulk going on a destruction spree after being spurned by his long-time girlfriend.** The aforementioned carborane, on the other hand, doesn't throw a temper tantrum after losing its hydrogen.

"...The boron cage forms one of the most stable molecules ever invented," Kean explains. "Its boron atoms share electrons so generously that it practically becomes helium."

Sadly, carborane is rather rare, and likely won't be making a wide appearance in chemistry classes anytime soon.

*Technically carborane $\text{H}(\text{CHB}_{11}\text{Cl}_{11})$ is the world's strongest solo acid because fluoroantimonic acid is a mixture of antimony pentafluoride and hydrofluoric acid.

Wades rules

Kenneth Wade (1932-2014) was a faculty at Durham University UK. In the early 1970's he formulated the Wades rules which provided a major breakthrough in the qualitative understanding of the electron deficient multicentre bonding of boron hydrides and their shape based classification.

According to Wade his rule correlates skeletal structures of boranes, carboranes, heteroboranes and their anions (closo, nido, arachno, hypho) with the number of skeletal electron pairs they contain.

The rule states **that clusters having n skeletal atoms (vertices) will adopt closo structures if it is held together by n+1 skeletal bonding electron pairs; nido if held together by n+2 skeletal electron pairs, arachno if held together by n+3 skeletal electron pairs, hypho if held together by n+4 skeletal electron pairs and klado if held together by n+ 5 skeletal electron pairs.**

For applying this rule one need to determine the number of skeletal electron pairs in a cluster. **Each BH unit furnishes 2 skeletal bonding electrons, each B as such gives three skeletal electrons, each C-H unit of a carborane furnishes 3 skeletal bonding electrons and each additional H⁻ furnishes 1 skeletal bonding electron.** Ionic charges must be included in the electron count. Extending this to borane clusters with other hetero-elements, one may replace C, Si, Ge and Sn of a cluster with a BH unit; N, P and As with a BH₂ unit and S and Se with a BH₃ unit **for counting purpose.**

Tribute To A Numerical Inorganic Icon: Kenneth Wade

Posted By **Steve Ritter** on Apr 11, 2014 (C&E NEWS American Chemical Society)

University of Durham chemistry professor Kenneth Wade, famously known for the borane electron-counting rule that bears his name, [passed away on March 16](#) at age 81. Chemists at the University of Nottingham, led by big-haired chemistry professor Martyn Poliakoff, have prepared [a lovely video tribute](#) to Professor Wade as part of their [Periodic Table of Video series](#).



Chemists use electron-counting rules to determine bonding patterns in different classes of compounds, such as the familiar octet rule for first- and second-row elements, the 18-electron rule for transition metals, and the Hückel $4n + 2$ rule for aromatic compounds. However, these rules don't readily apply to electron-deficient molecules such as boranes that utilize multicentered bonding—a pair of electrons shared between more than two atoms—so other rules have been devised.

In 1971, building on the collective observations of other chemists, Wade formulated his $n + 1$ rule.

Wade's rule states that a cage molecule with a geometry based on a closed polyhedron constructed of triangles with n vertices will possess $n + 1$ skeletal bonding electron pairs.

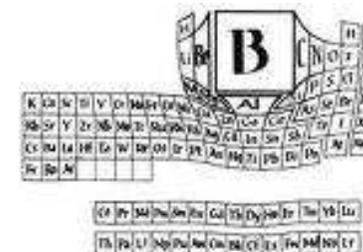
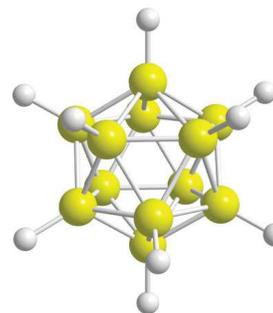
[Wade's rule and its corollaries](#) have been refined and extended by a number of researchers. When coupled with spectroscopic studies and theoretical calculations, these rules have been successful in showing the structural interconnections between boranes, carboranes, other heteroboranes, carbocations, organometallic complexes, and transition-metal cluster compounds.

Hats off to Professor Wade.

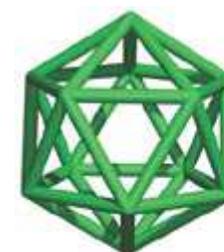


Ken Wade, Durham
1913-2014

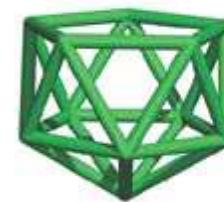
Wade's Rules



For borane and carborane clusters, the structures are based on **deltahedra**, which are polyhedra in which **every face is triangular**. The clusters are classified as *closo-*, *nido-*, *arachno-* or *hypho-*, based on whether they **represent a complete (closo-) deltahedron, or a deltahedron that is missing one (nido-), two (arachno-) or three (hypho) vertices**.



Closo



Nido



Arachno

Boron hydride	Name	No. of skeletal electron pairs	Examples
$[\text{B}_n\text{H}_n]^{2-}$ or B_nH_{n+2}	Closo	n+1	$\text{B}_6\text{H}_6^{2-}$, $\text{B}_{12}\text{H}_{12}^{2-}$
B_nH_{n+4}	Nido	n+2	B_2H_6 , B_5H_9 , $\text{B}_{10}\text{H}_{14}$
B_nH_{n+6}	Arachno	n+3	B_4H_{10}
B_nH_{n+8}	Hypho	n+4	$\text{B}_5\text{H}_{12}^-$

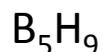
Each BH unit furnishes 2 skeletal bonding electrons, CH unit 3 skeletal bonding electrons

Each additional H· furnishes 1 skeletal bonding electron

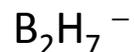
Ionic charges must be included in the electron count

Replace C, Si, Ge, Sn with BH; N, P, As with BH₂ and S, Se with BH₃ during counting

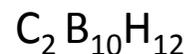
Wades rules: worked out examples



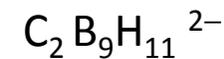
$$\begin{aligned} 5\text{BH} &= 10\text{e} \\ 4\text{H} &= 4\text{e} \\ 14\text{e} &= 7 \text{ pairs} \\ n &= 5 \\ n+2 &= \text{nido} \end{aligned}$$



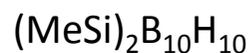
$$\begin{aligned} 2\text{BH} &= 4\text{e} \\ 5\text{H} &= 5\text{e} \\ 1(-) &= 1\text{e} \\ 10\text{e} &= 5 \text{ pairs} \\ n &= 2 \\ n+3 &= \text{arachno} \end{aligned}$$



$$\begin{aligned} 2\text{CH} &= 6\text{e} \\ 10\text{BH} &= 20\text{e} \\ 26\text{e} &= 13 \text{ pairs} \\ n &= 12 \\ n+1 &= \text{closo} \end{aligned}$$

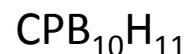


$$\begin{aligned} 2\text{CH} &= 6\text{e} \\ 9\text{BH} &= 18\text{e} \\ 2(-) &= 2\text{e} \\ 26\text{e} &= 13 \text{ pairs} \\ n &= 11 \\ n+2 &= \text{nido} \end{aligned}$$

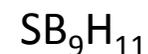


$$\begin{aligned} 2\text{MeSi} &= 6\text{e} \\ 10\text{BH} &= 20\text{e} \\ 26\text{e} &= 13 \text{ pairs} \\ n &= 12 \\ n+1 &= \text{closo} \end{aligned}$$

Considering $\text{Si}\equiv\text{BH}$
 $\text{Me}_2\text{B}_{12}\text{H}_{12}$
 $2\text{Me} = 2\text{e}$
 $12\text{BH} = 24\text{e}$
 $26\text{e} = 13 \text{ pairs}$
 $n = 12$
 $n+1 = \text{closo}$



$$\begin{aligned} \text{Considering } \text{C}\equiv\text{BH} \\ \text{PB}_{11}\text{H}_{12} \\ \text{Considering } \text{P}\equiv\text{BH}_2 \\ \text{B}_{12}\text{H}_{14} \\ 12\text{BH} &= 24\text{e} \\ 2\text{H} &= 2\text{e} \\ 26\text{e} &= 13 \text{ pairs} \\ n &= 12 \\ n+1 &= \text{closo} \end{aligned}$$



$$\begin{aligned} \text{Considering } \text{S}\equiv\text{BH}_3 \\ \text{B}_{10}\text{H}_{14} \\ 4\text{H} &= 4\text{e} \\ 10\text{BH} &= 20\text{e} \\ 24\text{e} &= 12 \text{ pairs} \\ n &= 10 \\ n+2 &= \text{nido} \end{aligned}$$

Considering S has 6 valence electrons
 2 used for vertice
 Remaining 4 electrons for skeletal

$$\begin{aligned} \text{B}_9\text{H}_9 &= 18 \\ 2\text{H} &= 2\text{e} \\ \text{S} &= 4\text{e} \\ 24\text{e} &= 12 \text{ pairs} \\ n &= 10 \\ n+2 &= \text{nido} \end{aligned}$$



TECHNISCHE
UNIVERSITÄT
DARMSTADT

**Eduard-Zintl-Institut für
Anorganische und
Physikalische Chemie**



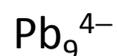
Zintl phase



Eduard Zintl

Before moving to Darmstadt, Zintl was professor of inorganic chemistry at the University of Freiburg. During this period he studied the structure of complex anions formed by metals in a solution of sodium in liquid ammonia. $[\text{Na}(\text{NH}_3)_x]^+_4[\text{Pb}_9]^{4-}$ is one of the examples he discovered. Many such naked anionic clusters were made and stabilized by using crown ethers and cryptands for increasing the size of the cationic part.

Wade's rules are also applicable to most of the Zintl phases (Naked anionic clusters)



$$9 \times 4 = 36 + 4 = 40 \equiv$$

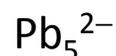
20 pairs

Each Pb atom will have one pair of electrons projecting away from the cluster like B-H of BH units = 9 pairs

$20 - 9 = 11$ pairs available

$n = 9$

$n + 2$: Nido



$$5 \times 4 = 20 + 2 = 22 \equiv$$

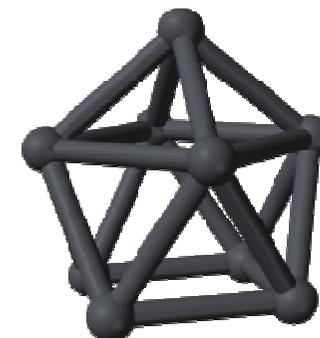
11 pairs

Each Pb atom will have one pair of electrons projecting away from the cluster like B-H of BH units = 5 pairs

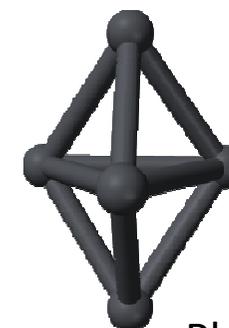
$11 - 5 = 6$ pairs available

$n = 5$

$n + 1$: Closo



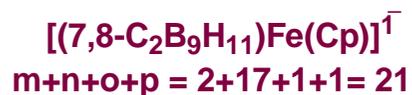
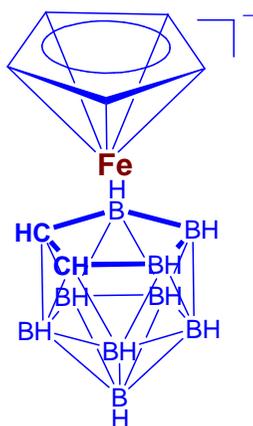
Pb_9^{4-}



Pb_5^{2-}



E.D. Jemmis,
I.I.Sc, Bangalore



skeletal e count
9 BH = 9 pairs
7 CH = 10.5 pairs
Fe ²⁺ = 1 pair
1- = 0.5 pair
total = 21 pairs
stable

Jemmis' rules

Jemmis' mno rule states that $m + n + o$ skeletal electron pairs are necessary for a closed macropolyhedral system to be stable

[or $(m + n + o + p)$ for systems having open polyhedra as well].

Here m = number of condensed polyhedra
 n = number of vertices
 o = number of single atom bridges between two polyhedra
 p = number of vertices missing for open polyhedra if present.

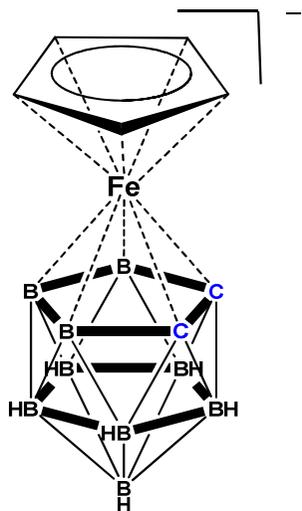
For example, for nido clusters $p = 1$ and for arachno clusters $p = 2$. For a benzene ring or cyclopentadienyl ring as such $p = 2$ and if it is already in an η^6 or η^5 mode, $p = 1$. For transition metals, the oxidation state of the metal should be known and the number of electrons for the electron count should be taken as the same as the number of electrons lost by the neutral metal atom to reach that oxidation state; for example, Fe³⁺ gives 3 electrons.

Jemmis draws together a number of corollaries to Wade's rules into a single, easily employed general rule,"

Thomas P. Fehlner

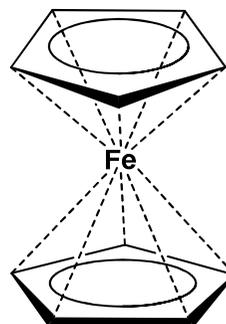
The uniqueness of Jemmis' mno rules is that they are not only applicable to macropolyhedral clusters but also applied to polyhedra, metallocenes, and even unsaturated cyclic organic compounds. Interestingly, Jemmis' rules get reduced to Wade's rules when $m = 1$ and $o = 0$ (one polyhedron).

Jemmis' rules: Examples



$m = \text{no. of condensed polyhedra} = 2$
 $n = \text{no. of vertices} = 17$
 $o = \text{single atom bridges} = 1$
 $p = \text{vertices missing for open polyhedra} = 1$
 $m+n+o+p = 21$

skeletal electron count
 $9BH = 9 \text{ pairs of } e$
 $7CH = 10.5 \text{ pairs of } e$
 $Fe^{2+} = 1 \text{ pair of } e$
 neg charge = 0.5 pair
 total = 21 therefore
 STABLE



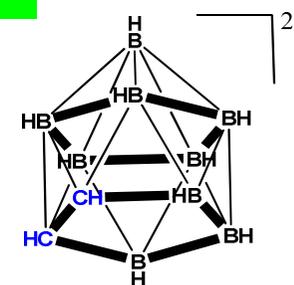
Ferrocene

Ferrocene

$m = 2$
 $n = 11$
 $o = 1$
 $p = 2$
 $m+n+o+p = 16$

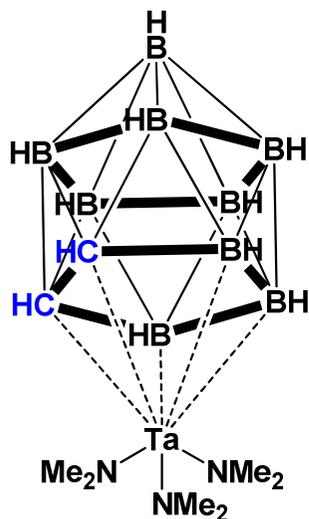
skeletal electron count
 $10CH = 15 \text{ pairs of } e$
 $Fe^{2+} = 1 \text{ pair of } e$

total = 16 therefore
 STABLE



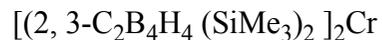
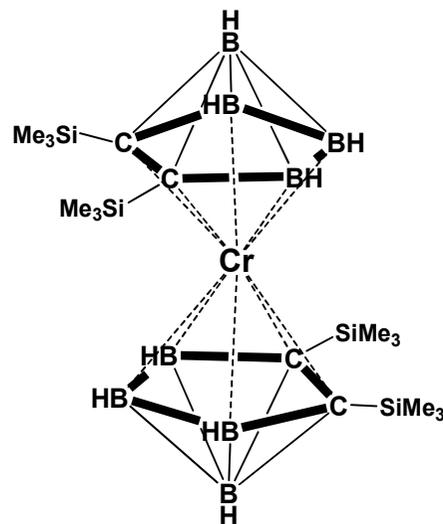
$m = 2$
 $n = 23$
 $o = 1$
 $p = 0$
 $m+n+o+p = 26$

skeletal electron count
 $18BH = 18 \text{ pairs of } e$
 $4CH = 6 \text{ pairs of } e$
 $Fe^{2+} = 1 \text{ pair of } e$
 neg charge = 1 pair
 total = 26 therefore
 STABLE



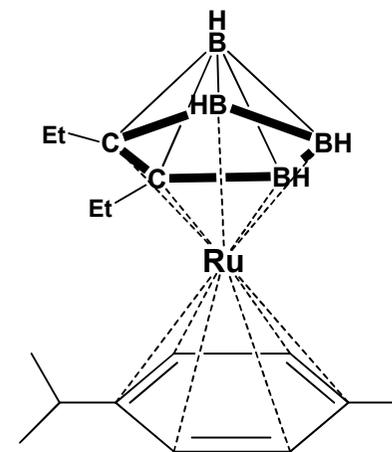
$m = \text{no. of condensed polyhedra} = 1$
 $n = \text{no. of vertices} = 12$
 $o = \text{single atom bridges} = 0$
 $p = \text{vertices missing for open polyhedra} = 0$
 $m+n+o+p = 13$

skeletal electron count
 $9BH = 9 \text{ pairs of } e$
 $2CH = 3 \text{ pairs of } e$
 $Ta^{2+} = 1 \text{ pair of } e$
 total = 13 therefore
 STABLE



$m = \text{no. of condensed polyhedra} = 2$
 $n = \text{no. of vertices} = 13$
 $o = \text{single atom bridges} = 1$
 $p = \text{vertices missing} = 0$
 $m+n+o+p = 16$

skeletal electron count
 $8BH = 8 \text{ pairs of } e$
 $4CR = 6 \text{ pairs of } e$
 $Cr^{4+} = 2 \text{ pair of } e$
 total = 16 therefore
 STABLE

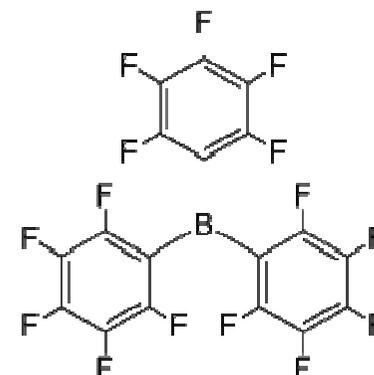


$m = \text{no. of condensed polyhedra} = 2$
 $n = \text{no. of vertices} = 13$
 $o = \text{single atom bridges} = 1$
 $p = \text{vertices missing} = 1$
 $m+n+o+p = 17$

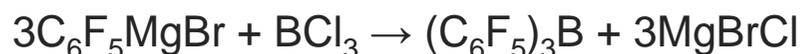
skeletal electron count
 $4BH = 4 \text{ pairs of } e$
 $8CR = 12 \text{ pairs of } e$
 $Ru^{2+} = 1 \text{ pair of } e$
 total = 17 therefore STABLE

Trispentafluorophenylborane: $B(C_6F_5)_3$

$B(C_6F_5)_3$ is a strong Lewis acid which is relatively inert and is hydrolytically more stable than BF_3 . The strong Lewis acidity, which has been determined to be between BF_3 and BCl_3 and substantive steric bulkiness makes its chemistry useful in diverse applications, most well known being the hydride and alkyl group abstraction from titanium group sandwich compounds.

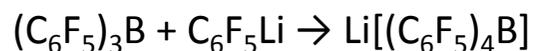


Tris(pentafluorophenyl)borane is prepared using a Grignard reagent derived from bromopentafluorobenzene.



Originally the synthesis employed C_6F_5Li , but this reagent can detonate with elimination of LiF .

Upon reaction with pentafluorophenyllithium, the salt of the noncoordinating anion, tetrakis(pentafluorophenyl)borate is formed.



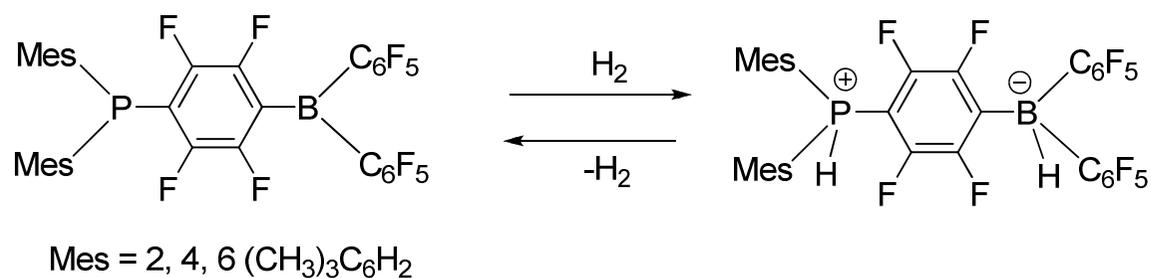
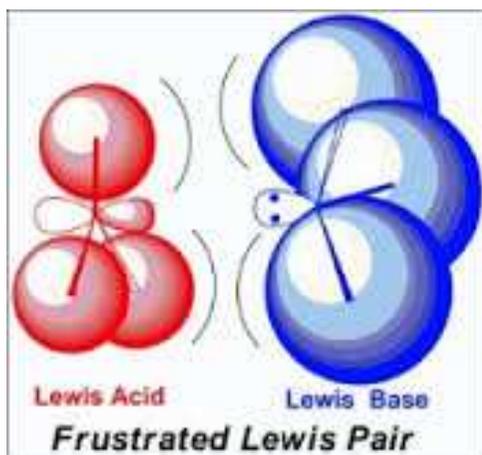
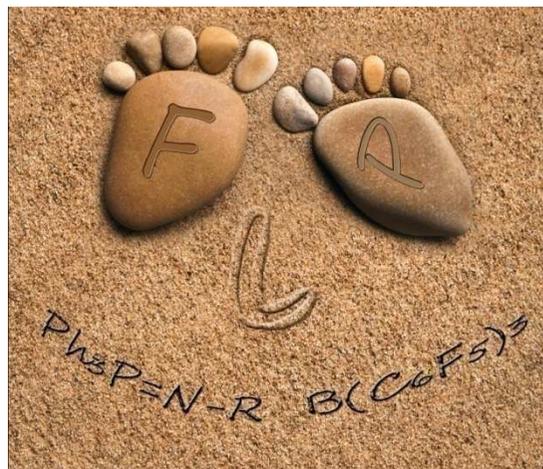
It has been described as the “ideal Lewis acid” because of its versatility and the relative inertness of the B-C bonds. Related fluoro-substituted boron compounds, such as those containing $B-CF_3$ groups, decompose with formation of B-F bonds. It is well known as

- (A) an activator in Zeigler Natta and metallocene based olefin polymerization reactions.
- (B) For preparing frustrated Lewis acid base pairs for activation of H_2 , alkynes, CO_2 etc
- (C) For preparing Xe-C bonded compounds



Douglas Stephan
U of Toronto

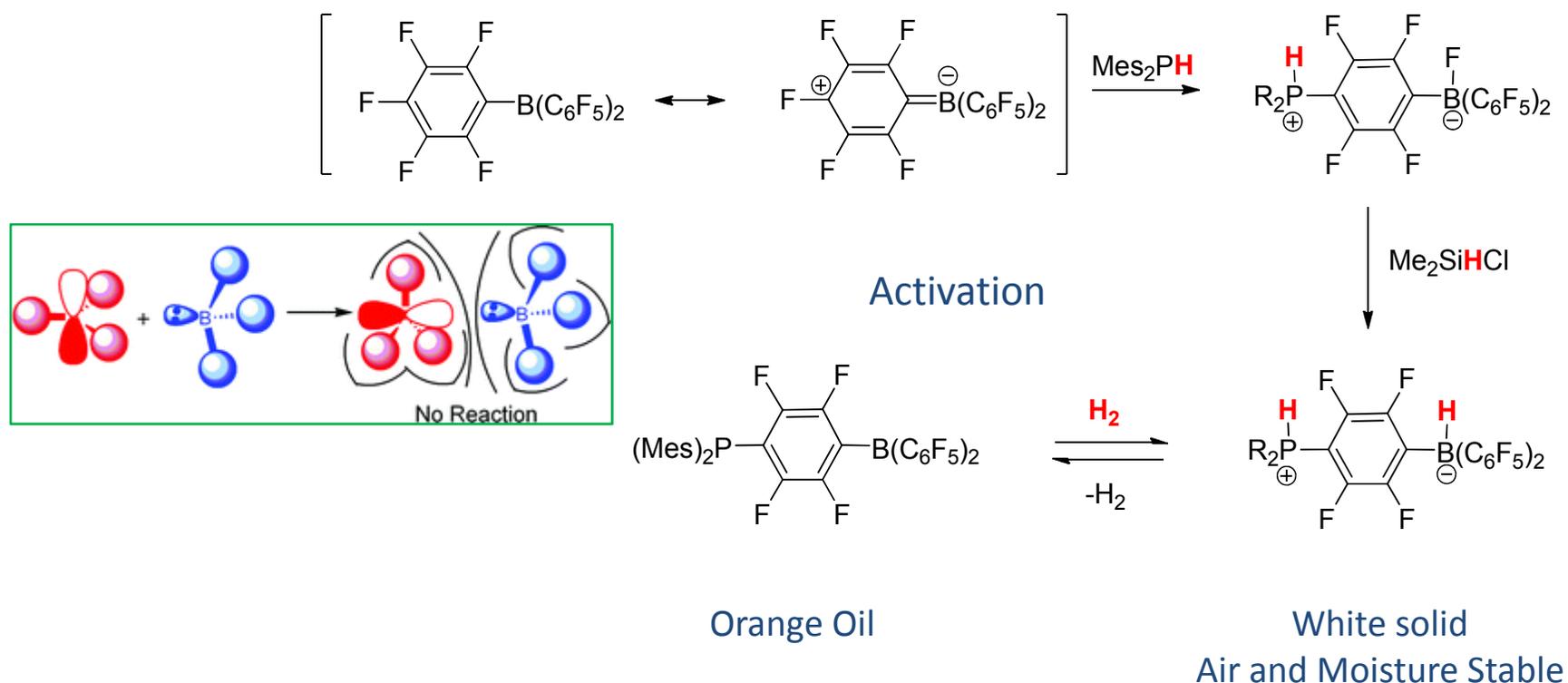
2006

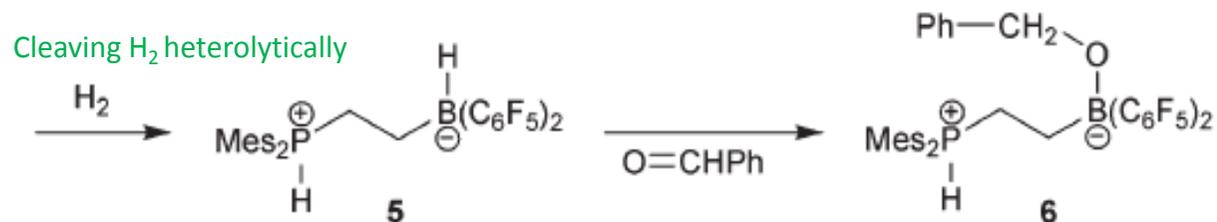
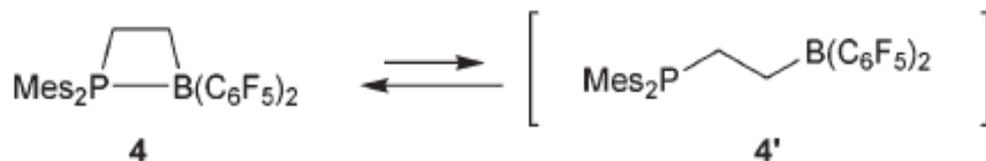
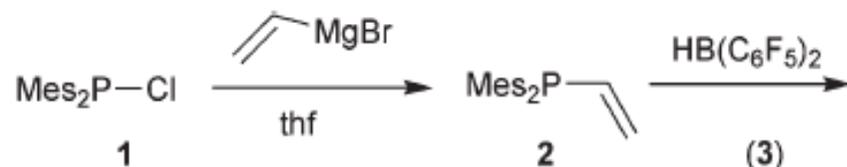
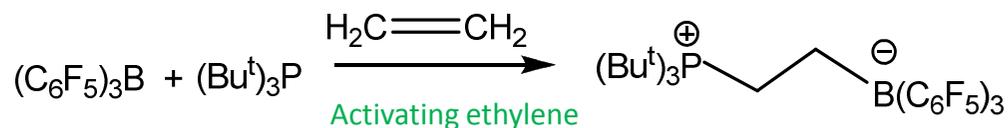
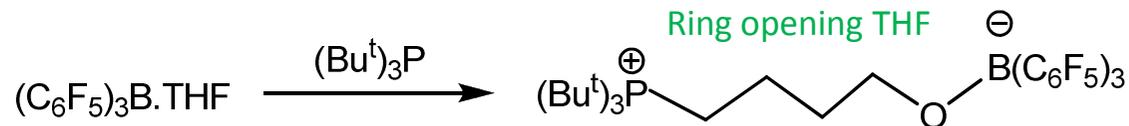
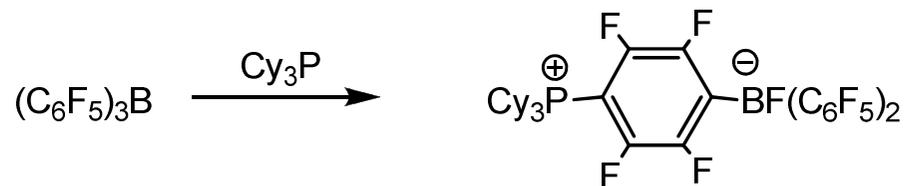


Douglas W. Stephan discovers the first example of a **frustrated Lewis acid base pair** based on boron and phosphorus. Due to their unquenched reactivity such molecules are able to heterolytically cleave dihydrogen molecule making them potential metal free hydrogenation catalysts.

Frustrated Lewis Pairs (FLP's)

Frustrated Lewis pair is a compound or mixture containing a Lewis acid and a Lewis base that, due to steric hindrance, cannot combine to form an adduct. Due of their "unquenched" reactivity, such systems are very reactive. For example some of them are able to split the hydrogen molecule heterolytically, which makes them potentially useful as metal-free catalysts for hydrogenation reactions. The first example of such a system was prepared from $B(C_6F_5)_3$. Also most of the examples use $B(C_6F_5)_3$ as the Lewis acid or a compound having $B(C_6F_5)_2$ group.



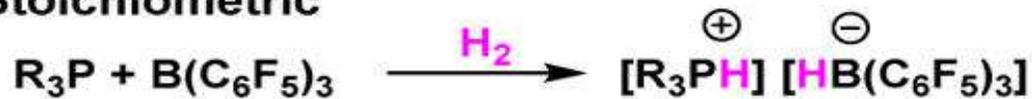


Combinations of Lewis acids and bases which are sterically prevented from forming the classical Lewis acid-base adducts have Lewis acidity and basicity available for interaction/activation of a third molecule.

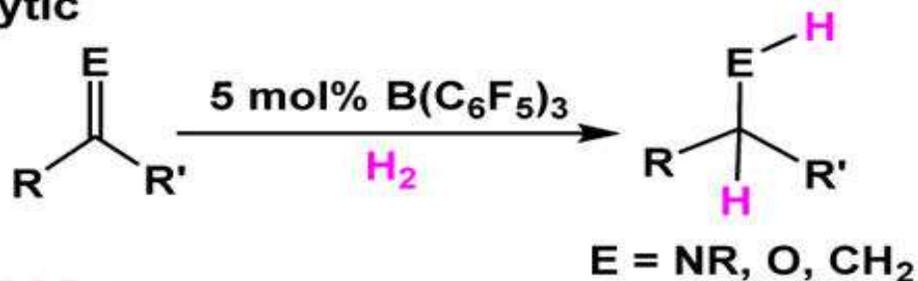
Utilizing the frustration energy!!

Dihydrogen

Stoichiometric



Catalytic

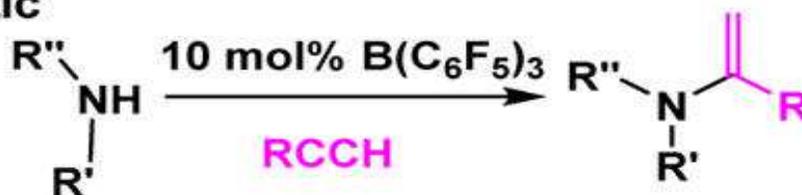


Alkynes

Stoichiometric

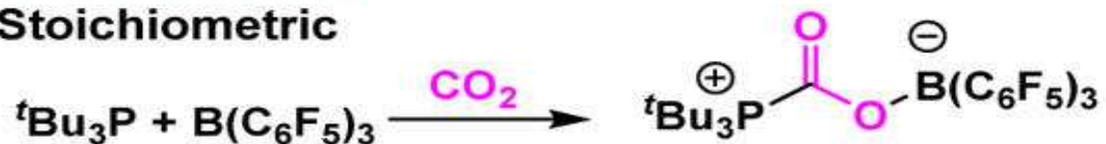


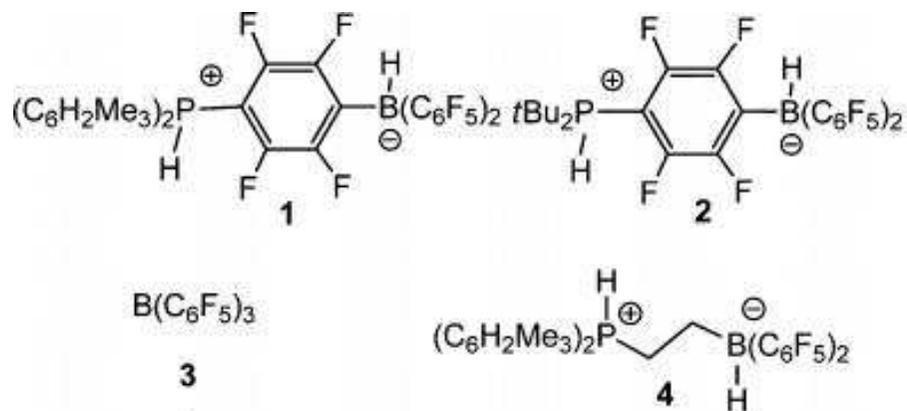
Catalytic



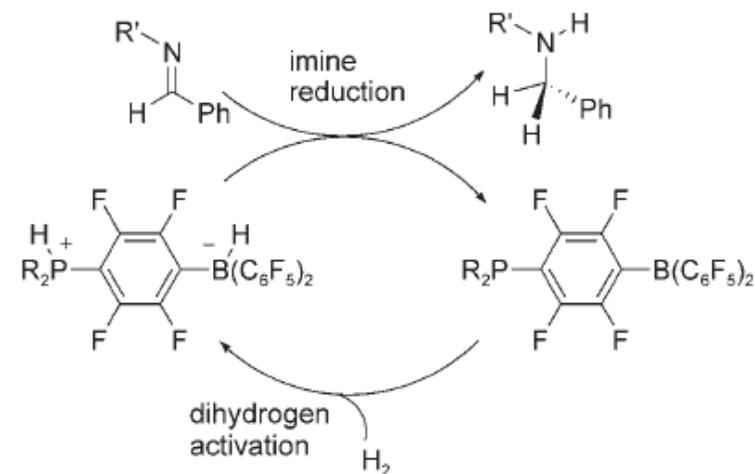
Carbon Dioxide

Stoichiometric



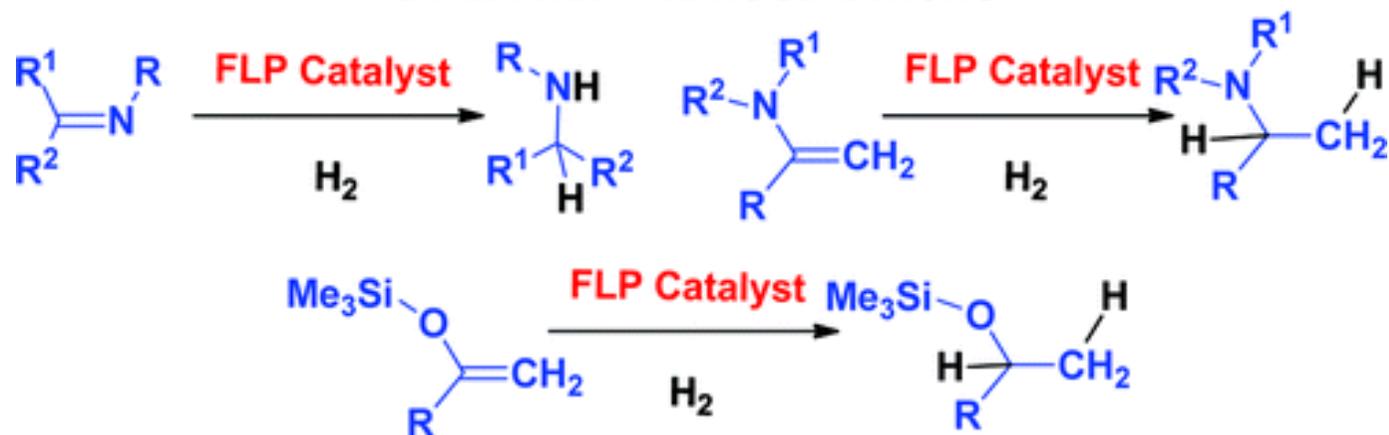


FLP catalysts



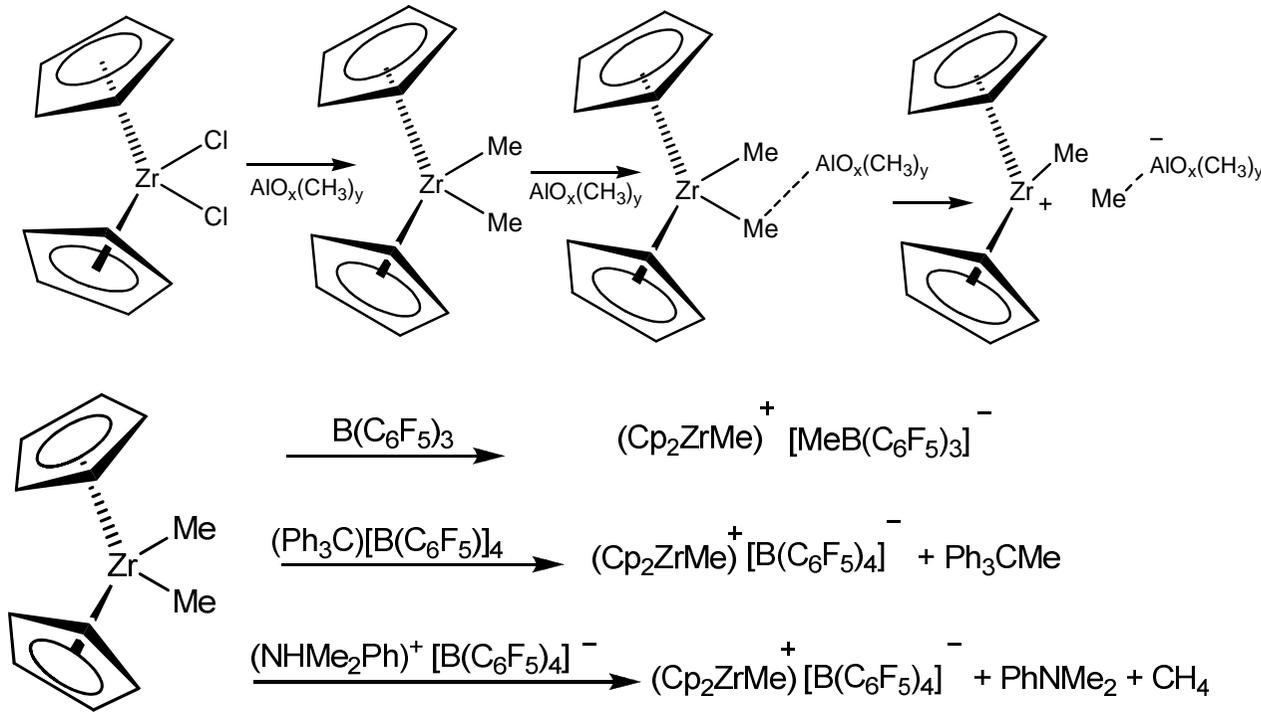
2. Catalytic cycle for reduction of imines.

METAL-FREE HYDROGENATIONS



Douglas Stephan: *Inorg. Chem.*, **2011**, 50 (24), pp 12338–12348

In metallocene based olefin polymerization catalysts- replacing MAO



While the MAO: metallocene ratio required for an active catalyst system is around 5000:1, the ratio of borate:metallocene required is only 1:1.

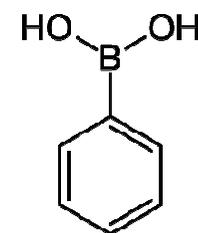
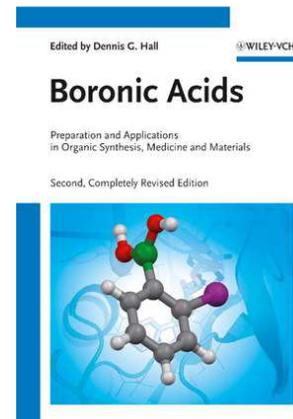
Synthesis of organoxenon compounds



Organoxenon compounds mostly have pentafluorophenyl groups

Boronic Acids and Boronate esters

A boronic acid is an alkyl or aryl substituted boric acid having the general formula $\text{RB}(\text{OH})_2$ belonging to the larger class of organoboranes. Like the rest of the boron compounds boronic acids act as Lewis acids. These compounds came to prominence after the landmark discovery of Suzuki coupling reaction by Akio Suzuki in 1976 which is one of the most sought after aryl halide cross coupling reactions having excellent functional group tolerance using palladium catalyst. The pK_a of a boronic acid is ~ 9 .



Boronic acids are used extensively in organic chemistry as chemical building blocks and intermediates predominantly in the Suzuki coupling. The key step of this reaction is transmetalation of its organic residue to palladium or nickel. The non toxicity, ease of synthesis and cost factor of boronic acids provides an edge for Suzuki coupling in pharmaceutical industry over similar cross coupling reactions.

Phenylboronic acid is produced from phenylmagnesium bromide and trimethyl borate followed by hydrolysis.





Akira Suzuki

Hokkaido Univ

Nobel 2010

The Suzuki- Miyaura Coupling

1979



$BY_2 = B(OH)_2, B(OR'')_2, 9\text{-BBN}, BF_3^-K^+, B(CHCH_3CH(CH_3)_2)_2$

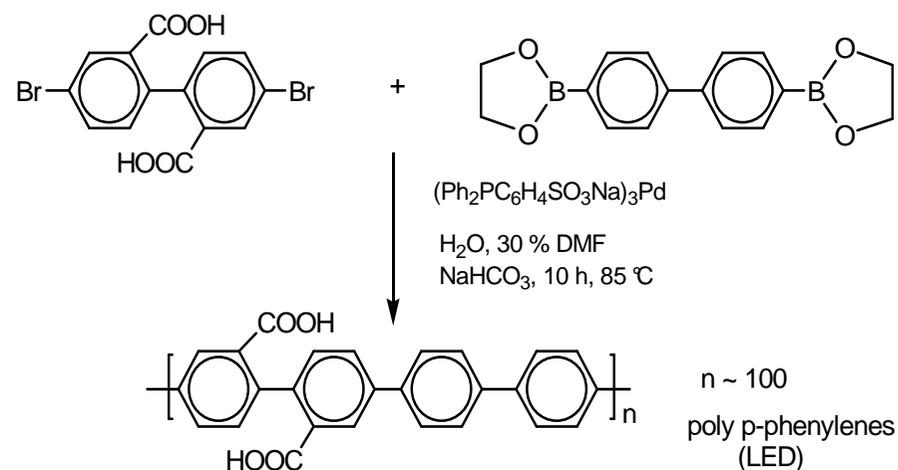
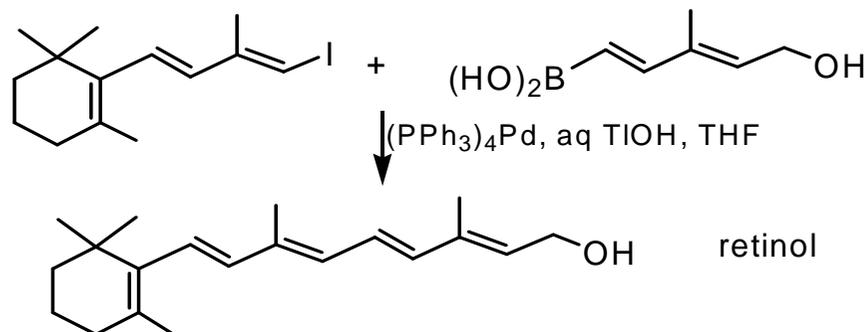
$X = I, Br, OSO_2(C_nF_{2n+1})$ and also Cl (with bulky electron rich phosphines)

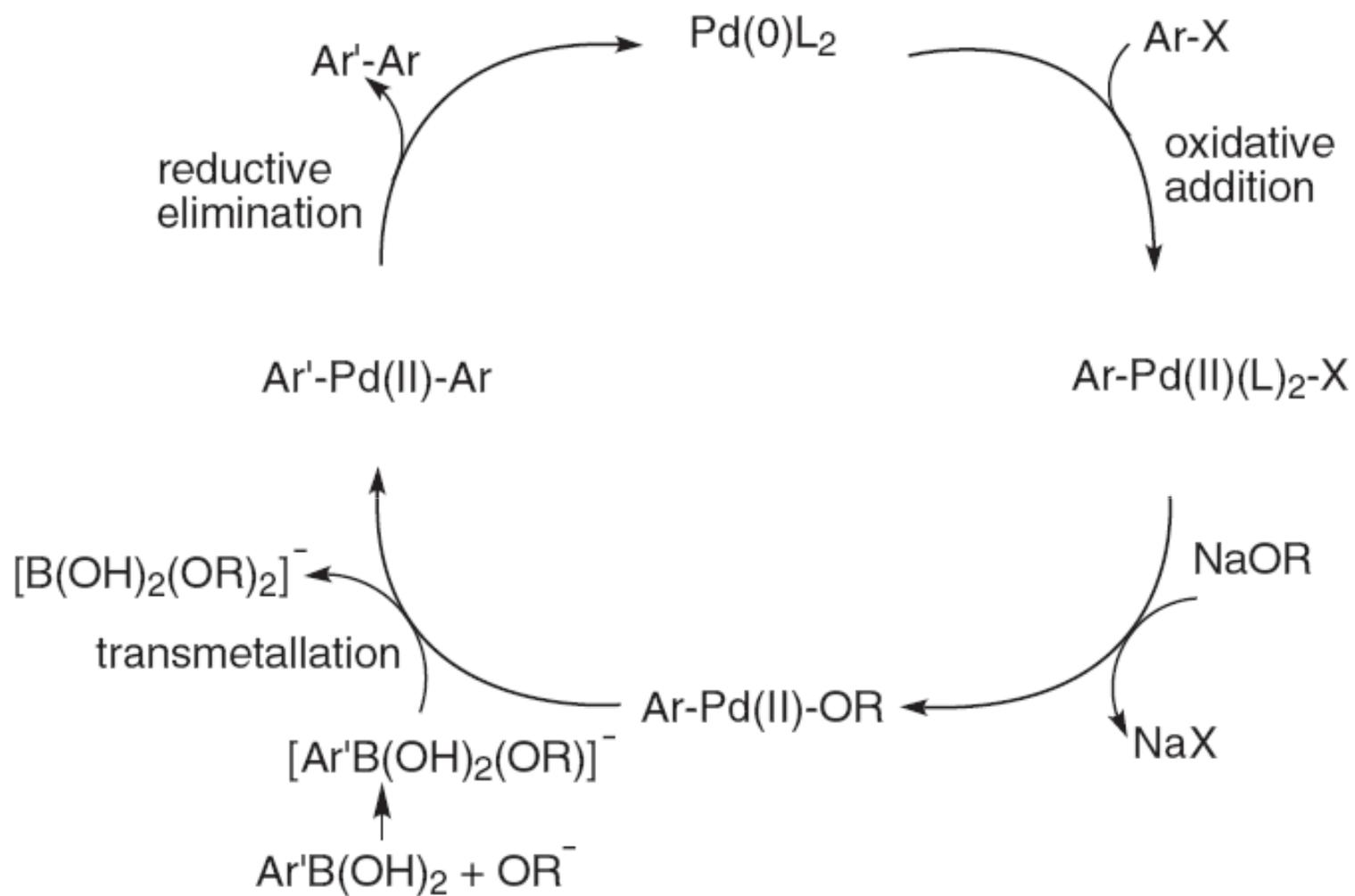
$R = \text{Aryl, Alkenyl and also Alkyl (under special conditions)}$

$R' = \text{Aryl, Alkenyl, Alkynyl, Benzyl, Allyl}$

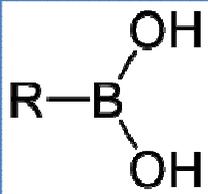
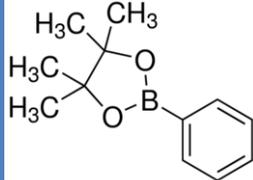
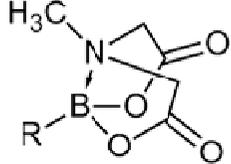
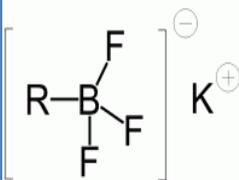
$[Pd] = Pd(PPh_3)_4, PdCl_2(R_3P)_2, Pd(OAc)_2, Pd_2(dba)_2, PdCl_2(dppf)$

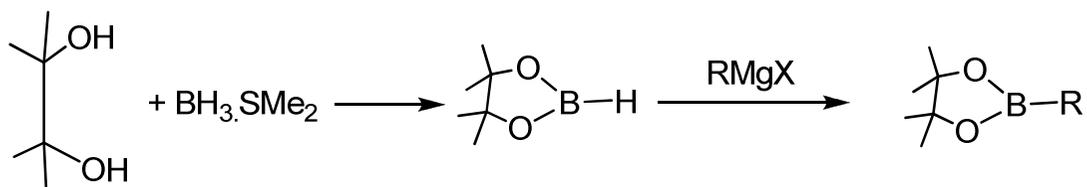
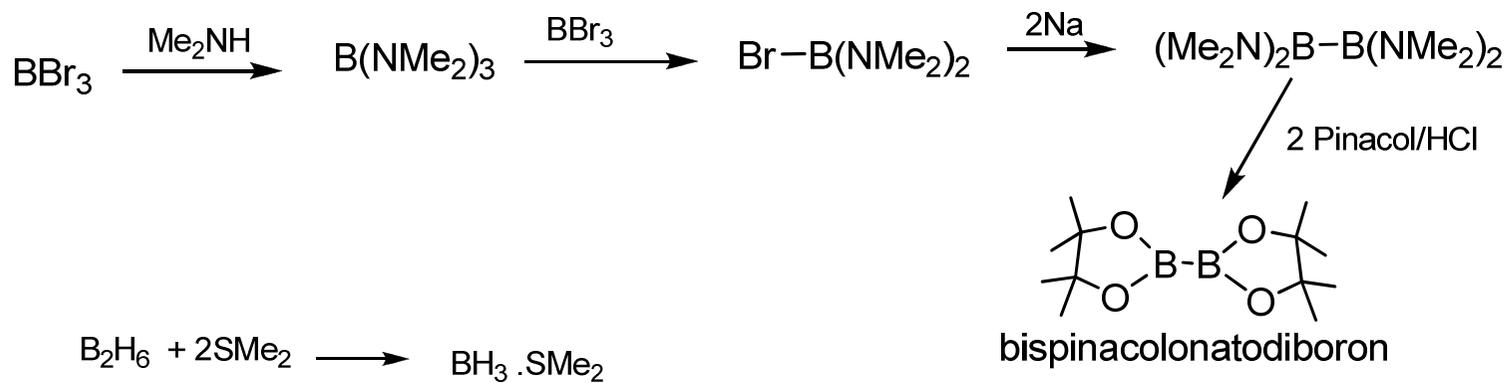
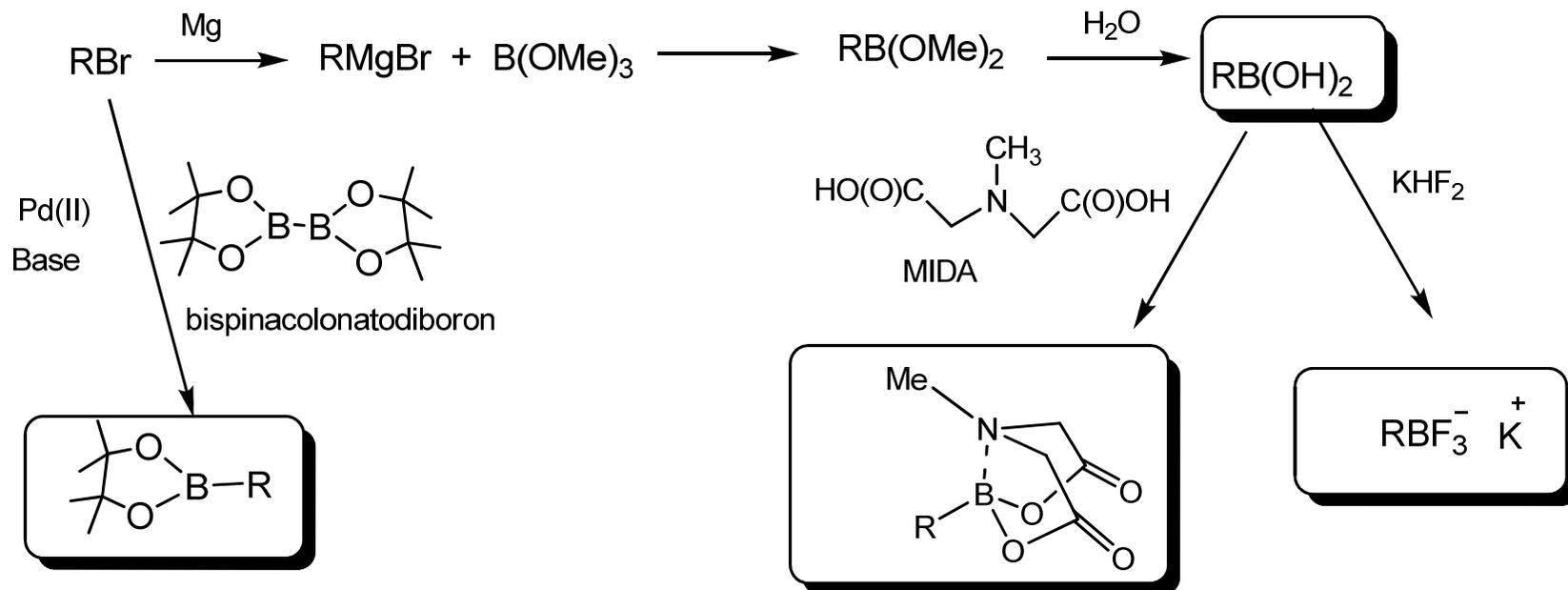
$\text{base} = Na_2CO_3, NaOEt, NEt_3, TIOH, K_3PO_4, CsF \text{ etc.}$





Scheme 16.3 Catalytic cycle for Suzuki–Miyaura coupling

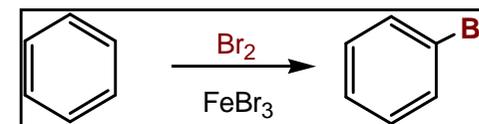
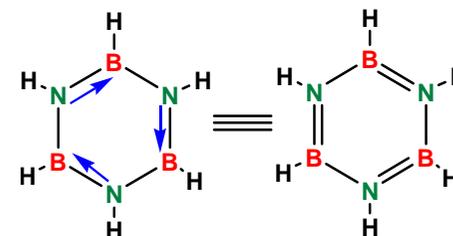
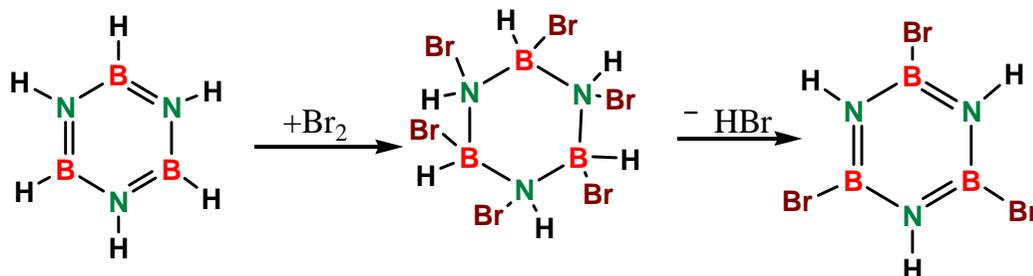
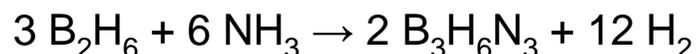
Boron based reagents for Suzuki-Miyaura Coupling	Boronic Acid sp^2 	Boronate Ester sp^2 	MIDA Boronates sp^3 	Organo trifluoroborate sp^3 
Advantages	<ul style="list-style-type: none"> ▪ Inexpensive ▪ Wide range ▪ Pharma-friendly as non toxic and eco friendly ▪ Aryl boronic acids -very stable and easy to handle 	<p>Higher stability of aliphatics. No solvent issue. No stoichiometry issue</p>	<ul style="list-style-type: none"> • Higher reactivity due to sp^3 B • Extended periods of bench-top storage • Good solubility • in situ slow release of boronic acids under aq. basic conditions 	<ul style="list-style-type: none"> • Easy to make with KHF_2 • less expensive • Not hygroscopic • Extended storage and high stability for alkyl-alkenyl and alkynyl • More reactive than boronic acids
Disadvantages	<ul style="list-style-type: none"> • Instability of alkyl, alkenyl and alkynyl boronic acids –difficulty in purification and extended storage. • Also 2-pyridyl BA is unstable- undergoes protodeborylation • Uncertain stoichiometry –due to presence of anhydrides of boronic acid(boroximes). • Polar solvents required • relatively harsh reaction conditions 	<p>Lesser reactivity Diols (bispinacolato diboron) and catechols are expensive</p> <p>Cumbersome as many additional steps in synthesis compared to BA</p>	<p>expensive</p> <p>MIDA= N-methyliminodiacetic acid An effective protecting group for boronic acids, allowing various reactions such as oxidation, cross-coupling reactions, and aldol reaction to be achieved</p>	<ul style="list-style-type: none"> • Polar solvents required • Insoluble in hydrocarbons, ether, CH_2Cl_2 • Electron donating group



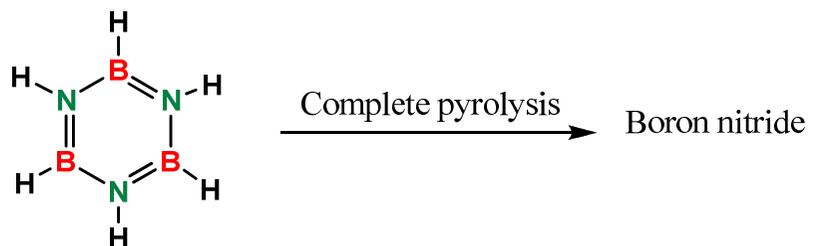
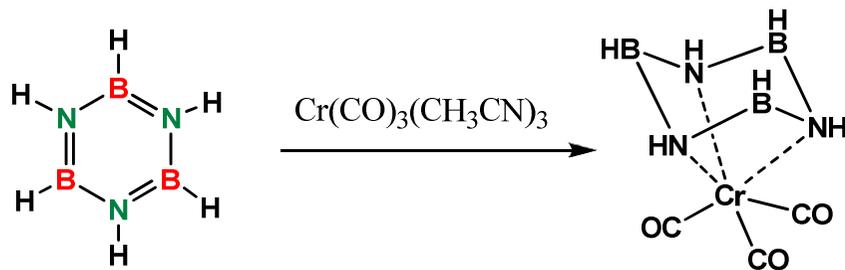
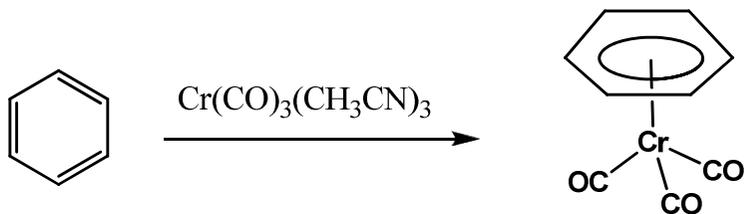
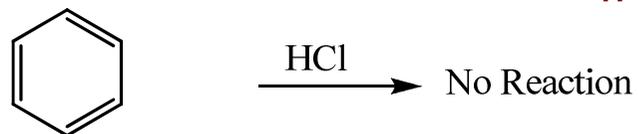
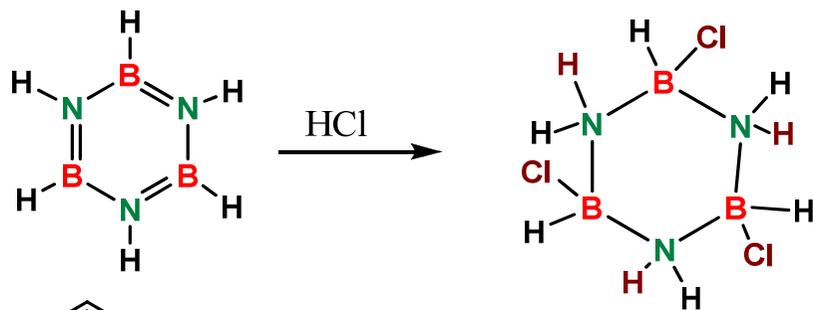
Boron Nitrogen Heterocycles: Borazines

Borazine is a six membered inorganic heterocyclic compound which shows many physical properties similar to benzene and has therefore been called as inorganic benzene. Borazine is isostructural with benzene.

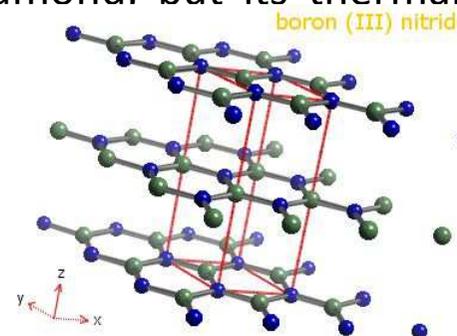
Borazine was first reported in 1926 by Alfred Stock and Erich Pohland by a reaction of diborane with ammonia at 250–300 °C with a conversion of 50%.



Properties	Borazine	Benzene
Mol wt	80.5	78.1
b.p	55°C	80°C
density	0.81	0.81
Trouton const	89.5	88.2
Critc. temp	252°C	288°C
planarity	planar	planar
B-N/C-C Distance Å	1.46	1.42



Boron nitride is a solid with chemical formula BN, isoelectronic to a similarly structured carbon lattice but having both boron and nitrogen in equal numbers. Quite interestingly BN similar to allotropes of carbon exists in three different crystalline forms namely hexagonal boron nitride, cubic boron nitride and wurtzite boron nitride. The hexagonal form has considerable similarities to graphite, is the most stable and softest among BN polymorphs while the cubic variety has structure and properties analogous to diamond. Its hardness is inferior only to diamond. but its thermal and chemical stability is superior.



Property	Hexagonal boron nitride	Graphite
Stability to heat	1000 °C(air), 2800 °C (inert atm)	700 °C (Air)
hardness	1-2	1-2
color	White (also called white graphite)	black
density	~2.1	2.09-2.23
bandgap	5.2	0
B-N/C-C distance	1.45 Å	1.42 Å
Interlayer distance	3.30-3.33 Å	3.33-3.35 Å
Interlayer interaction	more	less
Electron delocalization	less	more
intercalation	Difficult (K, NH ₃)	easy
Lubricant properties	Both high and low temp upto 900 °C in oxidizing atm. Can be used in vacuum also (space applications-	Water vapor necessary. Not effective in vacuum. Useful till 450 °C in oxidizing atm.

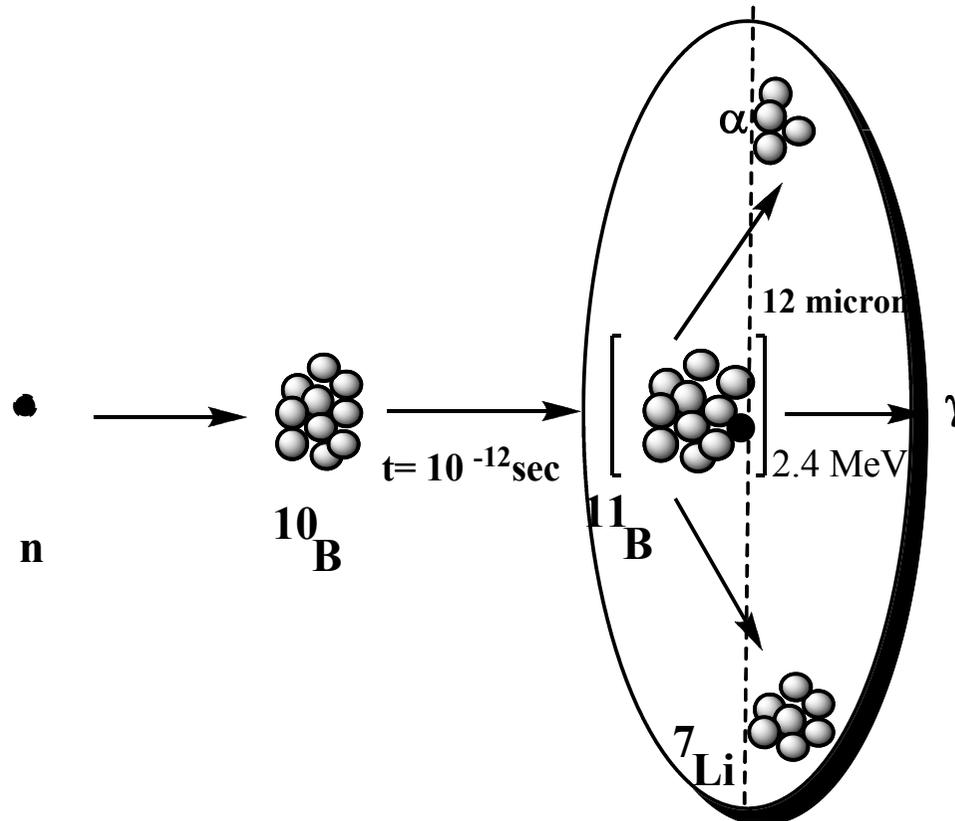
Synthesis of c-BN uses same methods as that of diamond: **Cubic boron nitride** is produced by treating hexagonal boron nitride at high pressure and temperature, much as synthetic diamond is produced from graphite. Direct conversion of hexagonal boron nitride to the cubic form has been observed at pressures between 5 and 18 GPa and temperatures between 1730 and 3230 °C, that is similar parameters as for direct graphite-diamond conversion. The addition of a small amount of boron oxide can lower the required pressure to 4–7 GPa and temperature to 1500 °C

Property	Cubic boron nitride	Diamond
Stability to heat	1300 °C (air), 1525 °C (inert atm, conversion to h-BN) 2973 °C sublimes	720-800 °C ignition point in oxygen, 1700 °C in argon. Above 1700 °C convert to graphite in vacuum
Hardness (mohr scale)	9.5-10	10
Thermal conductivity	13 Watt/(cm·K) (predicted)	High: 4 times that of copper 22 Watt/(cm·K)
Thermal expansion		Very low
color	White (also called as white graphite)	White High optical dispersion.
density	~2.1	3.52
bandgap	6.4	0
B-N/C-C distance	1.45 Å	1.42 Å

Boron based materials for nuclear applications

Boron-10 isotope finds use in two nuclear related applications. These are

- (a) as control/shutoff rod material in nuclear industry, sensors for neutron counting and materials for making neutron shields and
- (b) in boron neutron capture therapy a cancer treatment therapy in which boron-10 based compounds after concentrating in cancer affected cells are irradiated with thermal slow neutrons from outside resulting in high linear energy transfer α - particles and recoiling lithium-7 nuclei whose combined path length is only around 9- 12 μm , approximately the diameter of a cell.



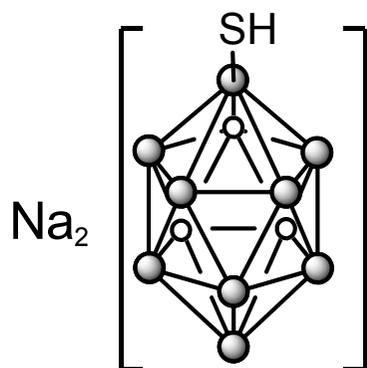
The thermal nuclear cross-section for ^{10}B and ^{11}B are 3835 barn and 0.005 barn respectively. The reaction products helium and lithium are formed as stable, non radioactive isotopes. Boric acid is used as poison in moderator/coolant of research reactors, Boric acid and boron carbide powder are used in concrete while constructing nuclear reactor buildings, ^{10}B enriched boron is used in neutron detectors Boron carbide powder and pellets made of enriched boron carbide powder is used as control rod materials

BNCT

This cancer treatment method has been primarily used for the treatment of *Glioblastoma* multiforme (GBM), which is the most common and most aggressive malignant primary brain tumor found in humans which affects the glial supportive tissues of the central nervous system. The method relies on targeting the tumor cells by an appropriate boron 10 containing chemical compound which preferentially concentrates in the cancer cells. There are many nucleids such as gadolinium -157 (2,59,000 barns) cadmium-113 (20,600 barns), boron 10 (3835 barns) and indium-115 (200 barns) that have a high propensity for absorbing low energy neutrons (named as thermal neutron cross section). However ^{10}B is the most attractive as

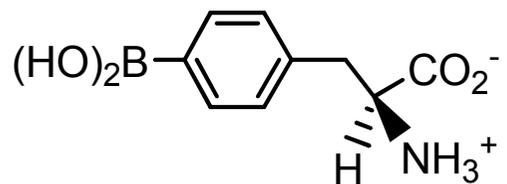
- (a) it comprises 20% of naturally occurring boron
- (b) the particles emitted after it is hit by thermal neutrons are harmless and non radioactive (He and Li^7 has high linear energy transfer
- (c) the combined path length of the daughter nuclei is only 12 microns which is approximately the diameter of a single living animal cell
- (d) boron has no toxicity and its chemistry is well understood to make suitable water soluble derivatives with high boron content.

For BNCT to be successful some of the required criteria are (a) selective uptake of boron containing compound by the tumor cells than the normal cells (b) the concentration of boron should be of the required level for releasing a therapeutic dose (10^9 atoms of ^{10}B per cell) (c) retention of ^{10}B in the tumor cell alone and not in normal tissue and blood (d) easy and cost effective synthesis of the boron compound. Three such compounds have been approved by federal drug approving agencies which are shown below



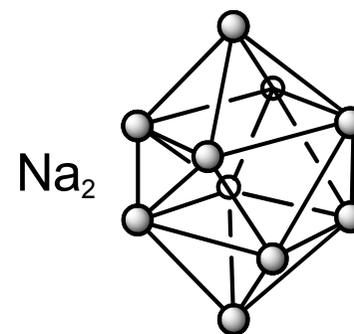
BSH

Mercaptoundecahydro-closo-dodecaborate



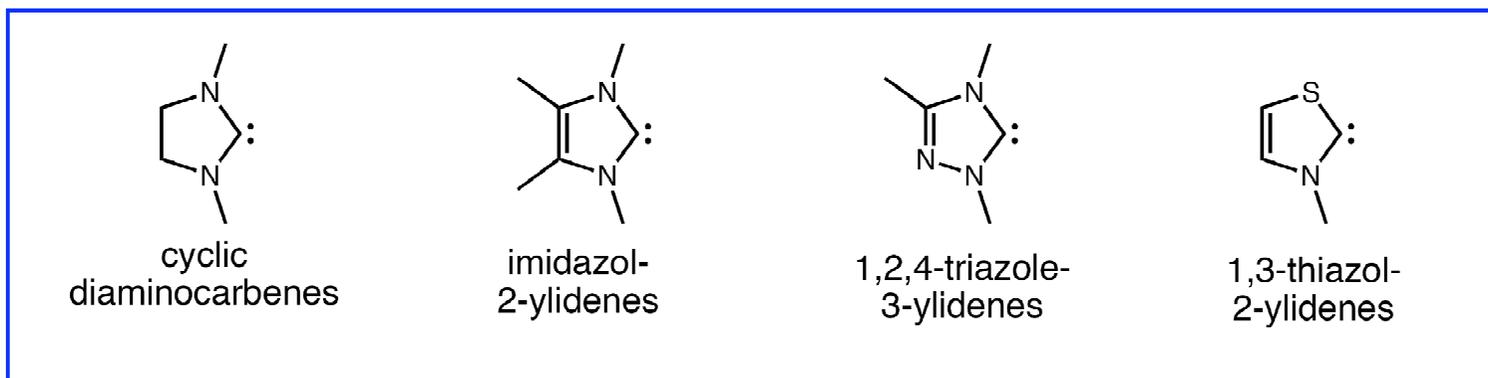
BPA

L-4-hydroxy-boryl phenylalanine



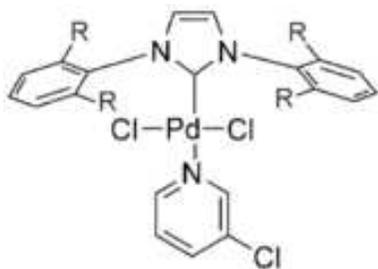
disodium-decahydro-closo-decaborate

N-Heterocyclic Carbenes (NHC)



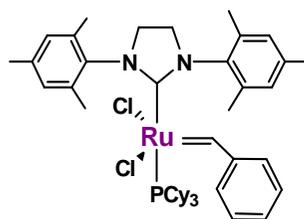
- NHCs are stronger σ -donors than the most electron rich phosphine
- less likely to dissociate from the metal during the reaction
- NHCs have come to replace phosphines in many organometallic and organic reactions
- NHCs can be useful spectator ligands, tunable electronically and sterically
- NHCs are most frequently prepared via deprotonation of the corresponding azolium salts

N- Heterocyclic Carbenes: Better σ donors than phosphines

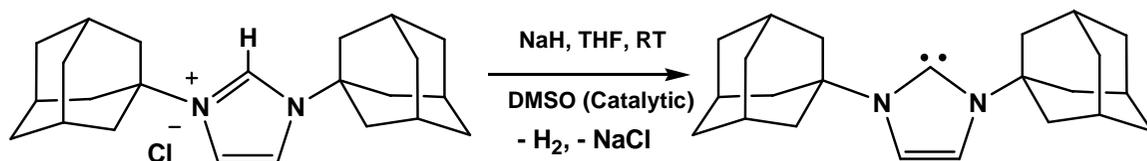


PEPSI catalyst

Pyridine enhanced precatalyst prep. stabil. init

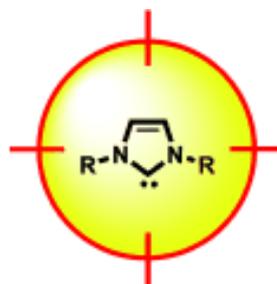


Grubbs' second-generation catalyst

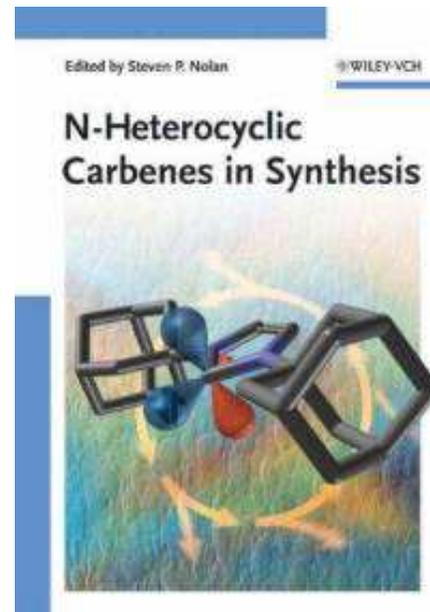


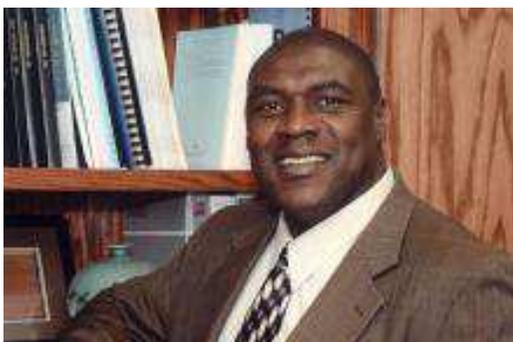
1st NHC :Anthony J Arduengo

Heck and Suzuki Couplings
Aryl Amination
Amide α -Arylation
Hydroxylation
Olefin Metathesis
Metathesis Cross-Coupling
Sonogashira Coupling
Ethylene/Carbon Monoxide Copolymerization



Kumada Coupling
Stille Coupling
C-H Activation
Hydrogenation, Hydroformylation
Furan Synthesis and Alkyne Coupling
Olefin Cyclopropanation
Arylation and Alkenylation of Aldehydes
Reduction of Aryl Halides
Atom-Transfer Radical Polymerization
Asymmetric Catalysis

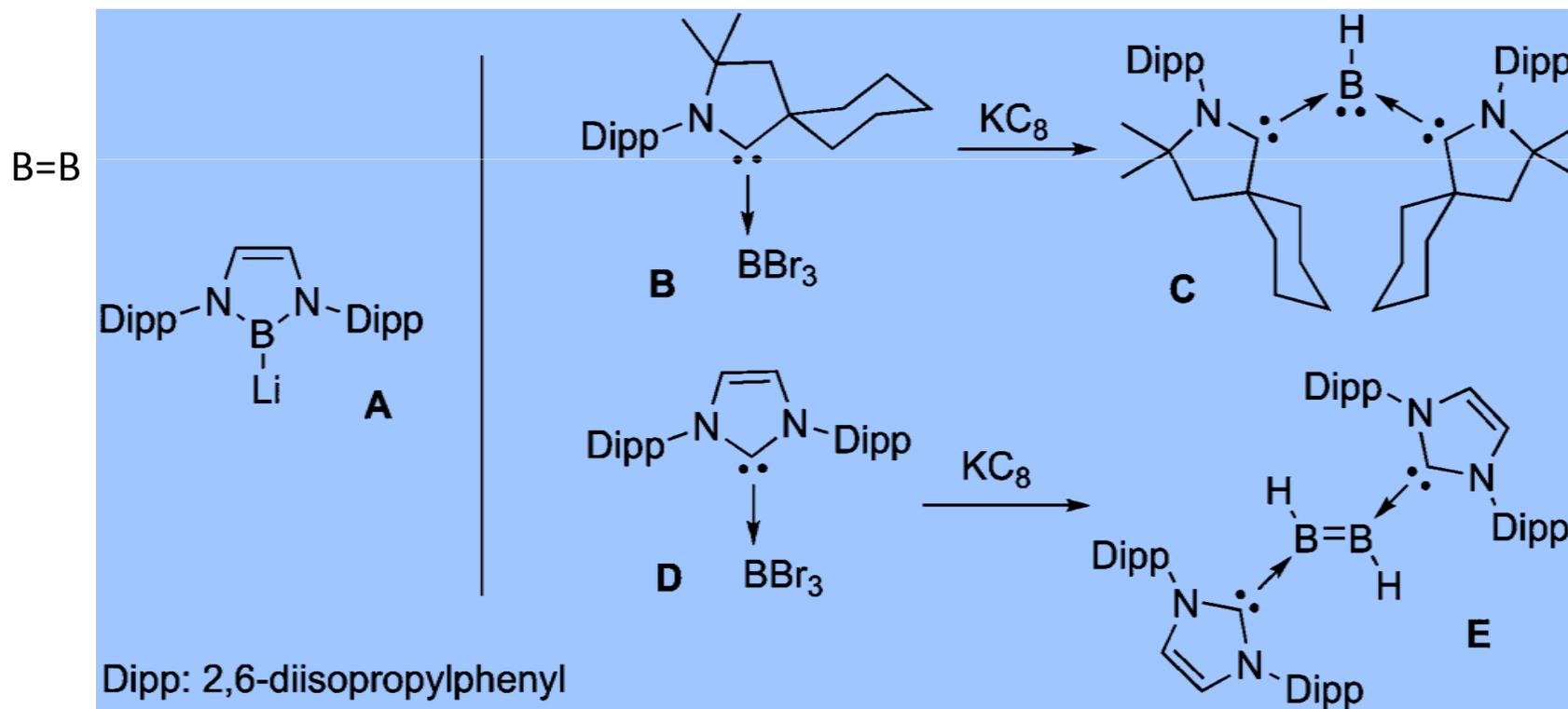




GREG ROBINSON

2007-2008

G.M Robinson proposed the first gallium–gallium triple bonded compound in 1997 which evoked the famous comment from F.A Cotton that, "**That's no more a triple bond than I'm the Dalai Lama!**"



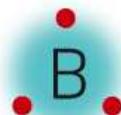


Holger Braunschweig

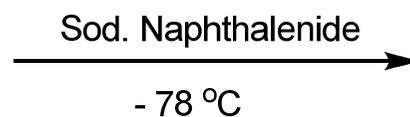
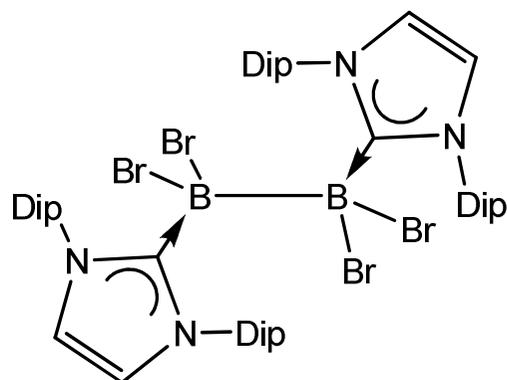
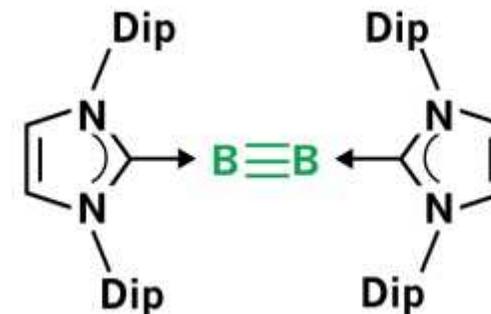
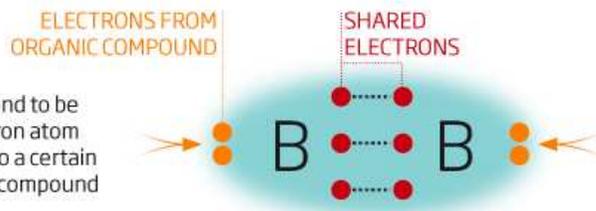
2012

How to make a boron triple bond ©NewScientist

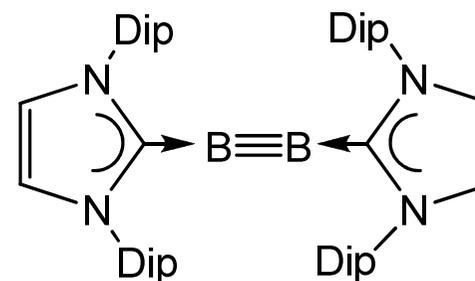
Boron has three free outer electrons, giving it the potential to form a triple bond



For the triple bond to be stable, each boron atom needs to bond to a certain type of organic compound



Dip = 2,6 diisopropylphenyl



First example of a stable diboryne having a B≡B and stabilized by N-heterocyclic carbenes prepared by Holger Braunschweig