

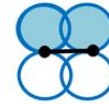
Hydrogen: Alkali metal, halogen, and neither



2s & 2p orbitals
available for bonding



-VS.-



...and overlaps involving nd orbitals sometimes contribute to the bonding (if only to polarize ns & np orbitals)

	11	12												13	14	15	16	17	18
3	Na	Mg		3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	Kr
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	55	56	57		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	87	88	89		104	105	106	107	108	109	110	111	112	113	114	115			
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup				
	Lanthanides			6	58	59	60	61	62	63	64	65	66	67	68	69	70	71	
	Actinides			7	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
					Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

-VS.-

The first row elements have a unique chemistry because their valence shell is only a 1s orbital. In the case of He the 1s orbital is full, compact, and of low energy. Consequently He is extremely inert, to the point where no compounds of He are known.

Hydrogen's 1s orbital is comparatively higher in energy. As a result H is more reactive. It tends to lose or gain its single electron but can also contribute to multicenter bonding.

Because of its chemical versatility the location of H in the periodic table is ambiguous. Even though its electronegativity is much greater than that of lithium, it is usually placed at the head of the alkali metals. This placement is consistent with its possession of a single valence electron and the consequent readiness with which it loses an electron, particularly in aqueous media. However, hydrogen is also just short a single electron and so in other contexts it readily forms hydrides. Thus it might be placed at the head of the halogens. Although it is rare to place H above the halogens in some tables H is placed above the table to emphasize this chemical versatility.

the second row elements are unique in their ability to form strong multiple bonds and resistance to serving as high coordination number centers.

13	14	15	16	17	18
$B_{\infty}(s)$	$C_{60}(s)$ $C_{\infty}(graphite)$ $C_{\infty}(diamond)$	$N_2(g)$	$O_2(g)$	$F_2(g)$	$He(g)$
$Al_{\infty}(s)$	$Si_{\infty}(s)$	$P_4(s)$ $P_{\infty}(s)$	$S_8(s)$ $S_{\infty}(s)$	$Cl_2(g)$	$Ar(g)$
$Ga_{\infty}(s)$	$Ge_{\infty}(s)$	$As_{\infty}(s)$	$Se_8(s)$ $Se_{\infty}(s)$	$Br_2(l)$	$Kr(g)$
$In_{\infty}(s)$	$Sn_{\infty}(s)$	$Sb_{\infty}(s)$	$Te_{\infty}(s)$	$I_2(s)$	$Xe(g)$

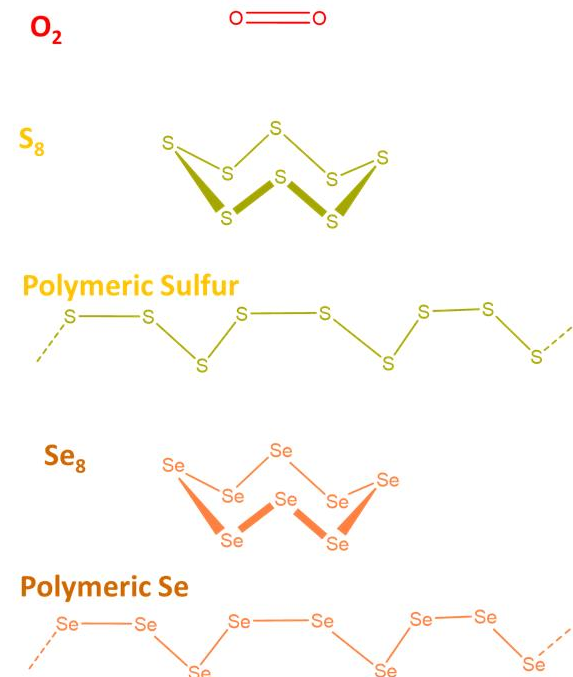
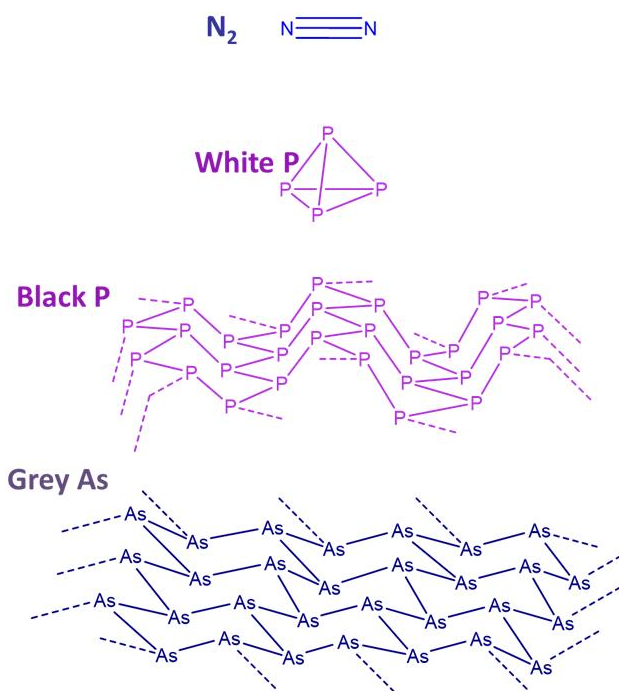
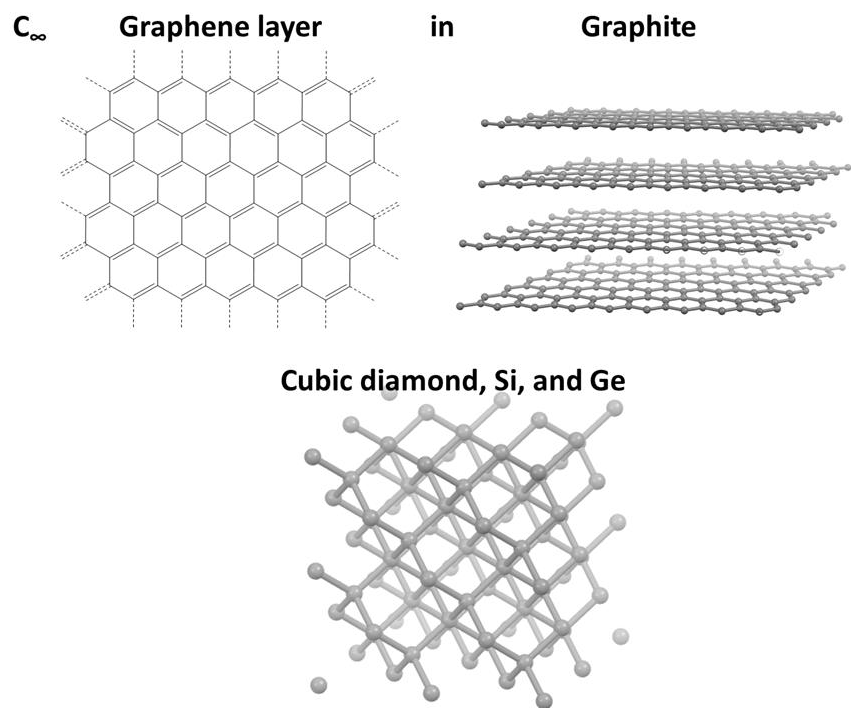
Red = contains multiple bonds
 Blue = single bonds only
 Gray = clear metallic bonding
 Green = cluster bonding
 Orange = monatomic

1. Only the second row elements form strong π -bonds. The second row elements are able to form strong π bonds since the fraction of electron density involved in the π -overlap is significant for the more compact orbitals and shorter bonds of the row 2 elements.
2. In contrast, for row 3 and heavier elements relatively little of the large and diffuse orbitals contribute to the overlap that stabilizes the π -bond. In consequence π -bonds involving these elements are very weak and such bonds are relatively rare. This is because it is almost always more favorable for such elements to form multiple single bonds or engage in cluster bonding.

The tendency of Row 2 nonmetals to form strong π bonds in cases where their heavier congeners form extended structures is apparent from the common allotropes formed by the p-block nonmetals.

Row 3+ elements have a greater tendency to form extended structures held together by single bonds than their Row 2 counterparts.

The Row 2 element carbon forms sheetlike structures involving multiple bonding (graphite, fullerenes, nanotubes) as well as 3D networks held together by single bonds (the diamond structure) while its heavier congeners Si and Ge only form 3D networks. Similarly, nitrogen and oxygen form diatomic gases held together by multiple bonds while their heavier congeners form clusters (P), layers (As, Sb), or chains (S, Se, Te) held together by single covalent bonds.



The valence shell of the second row elements lacks low-lying nd orbitals. As a result only the $2s$ and $2p$ type orbitals of second row elements significantly contribute to the bonding in their compounds. In contrast, the main group elements of row 3 and higher possess low lying unoccupied nd orbitals which enable them to act as a π acid towards a ligand atom by forming $d\pi-p\pi$ and $d\pi-d\pi$ overlaps.

When second row elements serve as a central atom they do not readily exhibit coordination numbers higher than four. In contrast, the larger size of row 3 and heavier elements reduces the steric strain associated with the addition of multiple ligands about an element center. This makes it easier for these elements to form trigonal bipyramidal, octahedral, and other high coordination number structures.

Diagonal Relationship:

	1							18
1	<div>H</div> <div>2.20 166 pm</div>							<div>He</div>
2	<div>Li</div> <div>0.98 320 pm</div>	<div>Be</div> <div>1.57 241 pm</div>	<div>B</div> <div>2.04 170 pm</div>	<div>C</div> <div>2.55 130 pm</div>	<div>N</div> <div>3.04 162 pm</div>	<div>O</div> <div>3.44 137 pm</div>	<div>F</div> <div>3.98 118 pm</div>	<div>Ne</div> <div>140 pm</div>
3	<div>Na</div> <div>0.93 327 pm</div>	<div>Mg</div> <div>1.31 271 pm</div>	<div>Al</div> <div>1.61 203 pm</div>	<div>Si</div> <div>1.90 161 pm</div>	<div>P</div> <div>2.19 214 pm</div>	<div>S</div> <div>2.58 183 pm</div>	<div>Cl</div> <div>3.16 159 pm</div>	<div>Ar</div> <div>174 pm</div>

The increase in electronegativity across a row of the periodic table is sometimes compensated by the decrease in electronegativity down a group so that elements so diagonally related sometimes have similar electronegativities. Some such diagonally related elements have similar physical and chemical properties, although these similarities may not be due to the effect of electronegativity alone. Since atomic size also decreases across a row and increases down a group some similarities reflect size effects as well. In any event, the result is that there are recognized diagonal relationships of chemical and physical similarity among elements diagonal to one another in the periodic table. Some of the more prominent diagonal relationships within the main group are shown

Li & Mg – Lithium acts like Mg in that it is the only alkali metal to form stable nitride (Li₃N), oxide (Li₂O), and THF soluble alkyl carbanion salts as alkaline Earth metals do. This may be seen in the similar compounds formed by Li and Mg show in Table 8.1.2.2 . In contrast, the larger alkali metals form insoluble polymeric carbanion reagents, superoxides or peroxides and not oxides, and extremely unstable nitrides.

Type of compound	Li	Mg
oxide	Li ₂ O	MgO
nitride	Li ₃ N	Mg ₃ N ₂
alkyl carbanion reagent	alkyllithium (RLi)	Gringard Reagent (RMg ⁺)

Be & Al – In contrast to the basic oxides and hydroxides of most alkali metals and the heavier group 13 elements both Be and Al form amphoteric oxides and hydroxides (Table8.1.2.3). Like Be and the remaining alkali metals aluminum also forms a carbide (C4-“salt”) instead of an acetylide (C₂²⁻) or allylide (C₃⁴⁻).

Table 8.1.2.3. Amphoteric behavior of the oxides and hydroxydes of beryllium and aluminum.

Reaction	Be	Al
Oxide hydrolysis to hydroxide	BeO + H ₂ O → Be(OH) ₂ (8.1.2.5)	Al ₂ O ₃ + 3H ₂ O → 2Al(OH) ₃ (8.1.2.6)
Hydroxide as an Arrhenius and Brønsted Base	Be(OH) ₂ → BeO(OH) ⁺ + OH [−] (8.1.2.7)	Al(OH) ₃ → 2AlO(OH) ₂ ⁺ + OH [−] (8.1.2.9)
	or	or
	Be(OH) ₂ + 2H ⁺ → Be ²⁺ + 2H ₂ O (8.1.2.8)	Al(OH) ₃ + 3H ⁺ → Al ³⁺ + 3H ₂ O (8.1.2.10)
Hydroxide as a Lewis Acid	Be(OH) ₂ + 2OH [−] → Be(OH) ₄ ^{2−} (8.1.2.11)	Al(OH) ₃ + OH [−] → 2AlO(OH) ₄ [−] (8.1.2.12)

B & Si –

Both of these elements act as semiconductors, form acidic complex polymeric covalent oxides containing interlinked EO_4 tetrahedra, and their halides (BCl_3 & SiCl_4) act as acid halides.

In contrast, the oxides of carbon (CO and CO_2) are monomeric while the oxides the heavier congeners of these elements (Al_2O_3 , Ga_2O_3 , In_2O_3 , In_2O , Tl_2O and GeO_2 , SnO_2 , PbO_2 , and PbO) are considered ionic oxides.

The halides of the heavier congeners of Si more readily act as ionic oxides while the binary halides of carbon (e.g. compounds like CCl_4) are usually not readily hydrolized.

The alkali metals tend to form +1 cations. Cation formation is favored by the relatively low ionization energies of the free metal (which makes it easier to form the cation) and the high solvation energy of their cations (which indicates that the cation is thermodynamically stabilized in solution). The variations in ionization energy and solvation energies down the alkali metal group help explain why Li is more reducing than the other alkali metals. The ionization energy of the metal decreases by ~20% on going from Li to Cs while the solvation energy of the cation decreases by ~75% over the same range (with ~2/3 of that decrease taking place on going from Li⁺ to Na⁺).

Alkali Metal	Ionization energy (kJ/mol)	Solvation enthalpy of the +1 Cation (kJ/mol)
Lithium, Li	513	-1091
Sodium, Na	496	-515
Potassium, K	419	-405
Rubidium, Rb	403	-321
Cesium, Cs	376	-296
Francium. Fr	400	-263

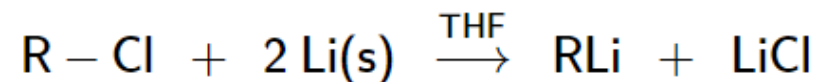
Because of their tendency to form cations, alkali metals are effective reducing agents.

Because of their tendency to form cations, alkali metals are highly reducing. All react vigorously with water to give hydroxides.



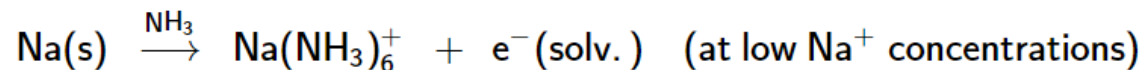
The reactions are all exothermic and often lead to combustion of the evolved H_2 gas. As a result, while Li usually just fizzes as it reacts, Na and K usually result in the formation of a colored flame while the reactions of Rb and Cs result in an explosion.

More synthetically useful is the reduction of alkyl halides by Li metal to give organolithium reagents.

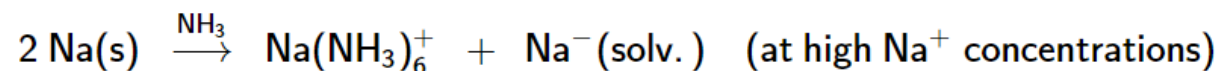


Under conditions where the metal cation is stabilized in the absence of an oxidizing agent it is even possible to form salts of free or solvated electrons.

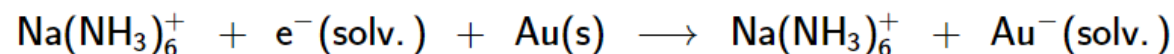
Small amounts of sodium may be dissolved in dry donor solvents (ammonia, tertiary amines, hexamethylphosphoramide) to give paramagnetic blue solutions containing solvated electrons.



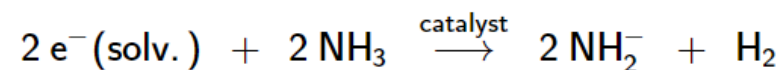
At higher concentrations of sodium bronze solutions containing sodide anions (*e.g.* M⁻) are formed.



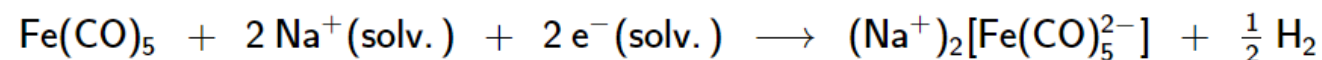
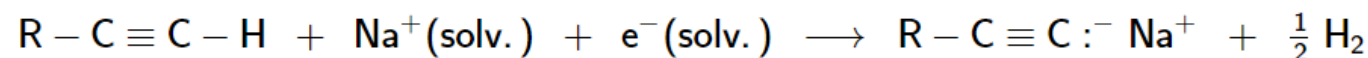
As either electrides or sodides the solutions are excellent reducing agents. In some cases, they can even be used to reduce metals to negative oxidation states.



In the presence of a catalyst the solvated electron decomposes by reducing the ammonia.



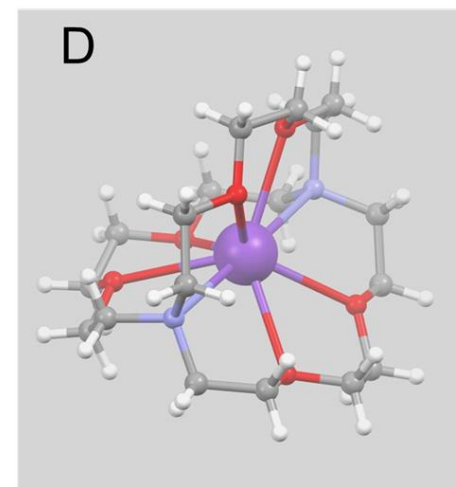
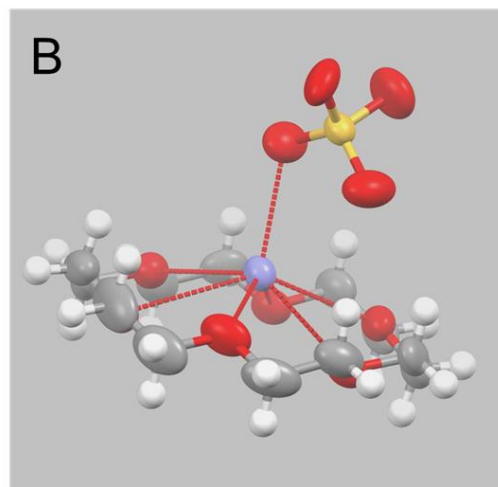
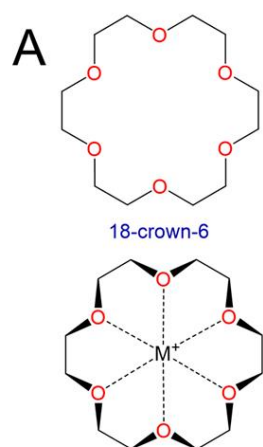
Synthetically, sodium-ammonia solutions are useful for preparing acetylides and reduced organometallic complexes.



Size effects are also believed to be responsible for alkali metal's unusual tendency to form peroxides and superoxides when burned in an excess of oxygen. While most metals form oxides when burnt in an excess of oxygen, Li and Na also form 2:1 salts of the larger peroxide ion (O_2^{2-}) and K, Rb, and Cs 1:1 salts of the similarly large superoxide ion (O_2^-)

Size ↓	Alkali Metal	superoxide O_2^-	Peroxide O_2^{2-}	Oxide O^{2-}	Superoxide preference ↓
	Li	not formed	Li_2O_2 forms but is less stable than Li_2O	Li_2O	
	Na	not formed	Na_2O_2	Na_2O forms but is less stable than Na_2O_2	
	K	KO_2	not formed	not formed	
	Rb	RbO_2	not formed	not formed	
	Cs	CsO_2	not formed	not formed	

The most striking examples of size effects in alkali metal chemistry involve alkali metal complexes with macrocyclic ligands, particularly crown ethers and cryptands like those shown



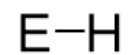
Hydrides:



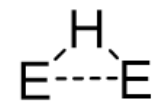
hydrogen
ion



hydride
ion



classical
covalent
element
hydride



bridging
hydride

Ionic hydrides

Network covalent hydrides

Metallic hydrides

Molecular covalent hydrides

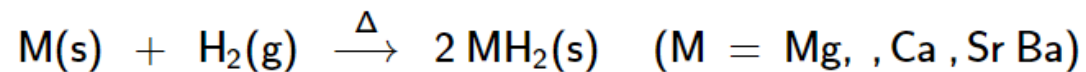
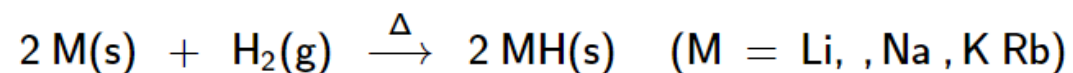
Hydride Gap

Unknown or poorly characterized

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup			
Lanthanides		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
Actinides		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

Ionic hydrides (a.k.a. saline hydrides)

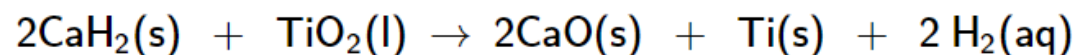
Ionic hydrides are metal salts of the hydride anion, H^- . These are formed by the alkali and all the alkaline earth metals except Be. These are typically prepared by direct reaction of the metal and hydrogen.



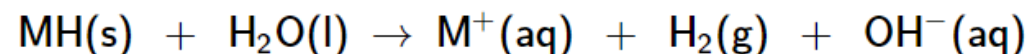
As salts of H^- ionic hydrides form ionic lattices (the NaCl structure is common for MH, the Rutile and PbI_2 for MH_2).

Chemically ionic hydrides act as

- *reducing agents* towards metal oxides. For example

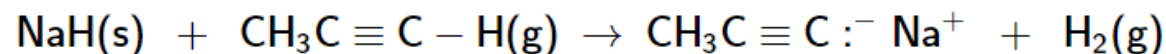


- *strong bases* towards protic E-H bonds. All react exothermically with water to liberate hydrogen gas.



For this reason CaH_2 is widely used as a drying agent for organic solvents.

Reactive metal hydrides may also be used to deprotonate reactive C-H bonds

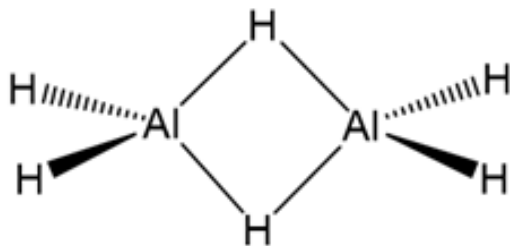


Covalent and intermediate hydrides

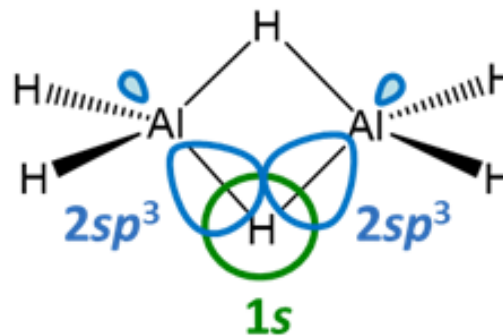
Covalent molecular hydrides are formed by the nonmetals, metalloids, and many post-transition metals. The chemical and physical properties they possess varies across the main group and depends somewhat on the row and whether the element hydride is electron deficient, electron rich, or electron precise. Specifically, electron deficient hydrides are those of Be and the group 13 elements (B, Al, Ga, In, and Tl) for which the neutral monomeric element hydride (BeH_2 , BH_3 , AlH_3 , GaH_3 , InH_3 , and TlH_3) does not possess enough electrons to satisfy the octet rule. Thus these hydrides commonly form dimers (B, Al, Ga, In, Tl) or polymers (Be) held together by bridging E-H-E bonds. These E-H-E bonds are explained as **three-center two-electron bonds** in valence bond theory but may also be described in terms of molecular orbitals.

(A) Bridging E-H-E bonds in Al_2H_6 and (B) their valence bond description in terms of overlap between the H 1s and Al sp^3 orbitals.

(A)



(B)

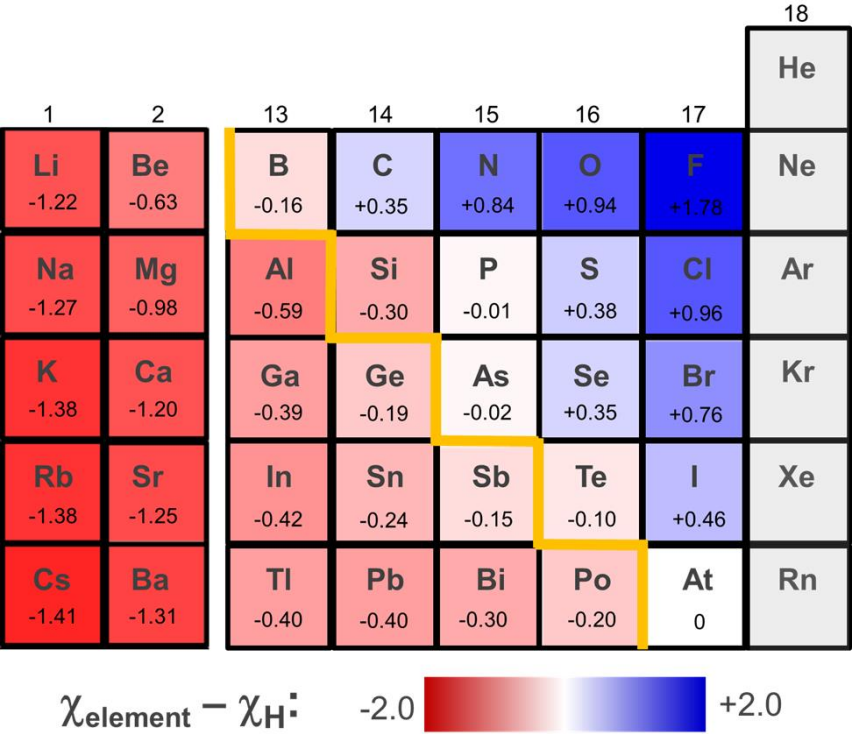


Electron precise and electron rich hydrides are formed by C, N, O, F, and their heavier congeners. These E-H bonds in these may be described as classical two center two electron E-H bonds of Lewis Theory. The electron precise and electron rich hydrides are distinguished in that the electron rich hydrides possess lone pair electrons while electron precise hydrides do not.

In other words, electron precise hydrides are those of the group 14 elements, and include the alkanes, alkenes, and alkynes of carbon along with SiH_4 , GeH_4 , SnH_4 , and PbH_4 , of which the hydride adducts of group 13 EH_3 compounds like BH_4^- and AlH_4^- are analogues.

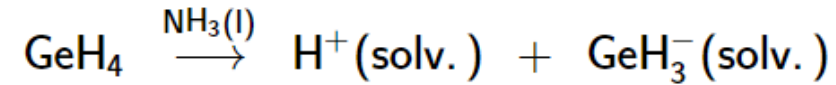
Electron rich hydrides are NH_3 , H_2O , HF and their heavier analogues (PH_3 , H_2S , HCl , etc.).

Regardless of the hydride's classification, the stability of element hydrides decreases down a group. For example, among the group 14 elements it follows the order $\text{CH}_4 > \text{SiH}_4 > \text{GeH}_4 > \text{SnH}_4 > \text{PbH}_4$.

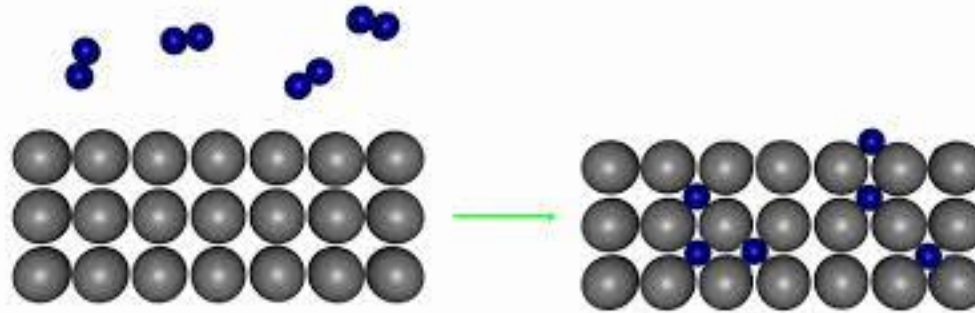


Difference between element and hydrogen Pauling electronegativities. More positive values correspond to positively polarized hydrogen while more negative ones a larger partial negative charge on hydrogen

The ability of a given element hydride to function as an acid or hydride donor may be modified by a number of factors. One of these is the solvation energy of the species formed. Germane (GeH_4) might be expected to function as a hydride donor. However, it can be deprotonated in liquid ammonia, likely because of the large solvation energy of the resulting H^+ ion.



In interstitial or metallic hydrides hydrogen dissolves in a metal to form non-stoichiometric compounds (solid solutions) of formula MH_n . They are called metallic hydrides since they possess the typical metallic properties of luster, hardness, and conductivity and are called interstitial hydrides because the H occupies interstices in a FCC, HCP, or BCC metal lattice



Schematic illustration of the process of formation of an interstitial hydride showing breakup of dihydrogen and its uptake into the metal lattice. The metal lattice expands 10-20% during this process.

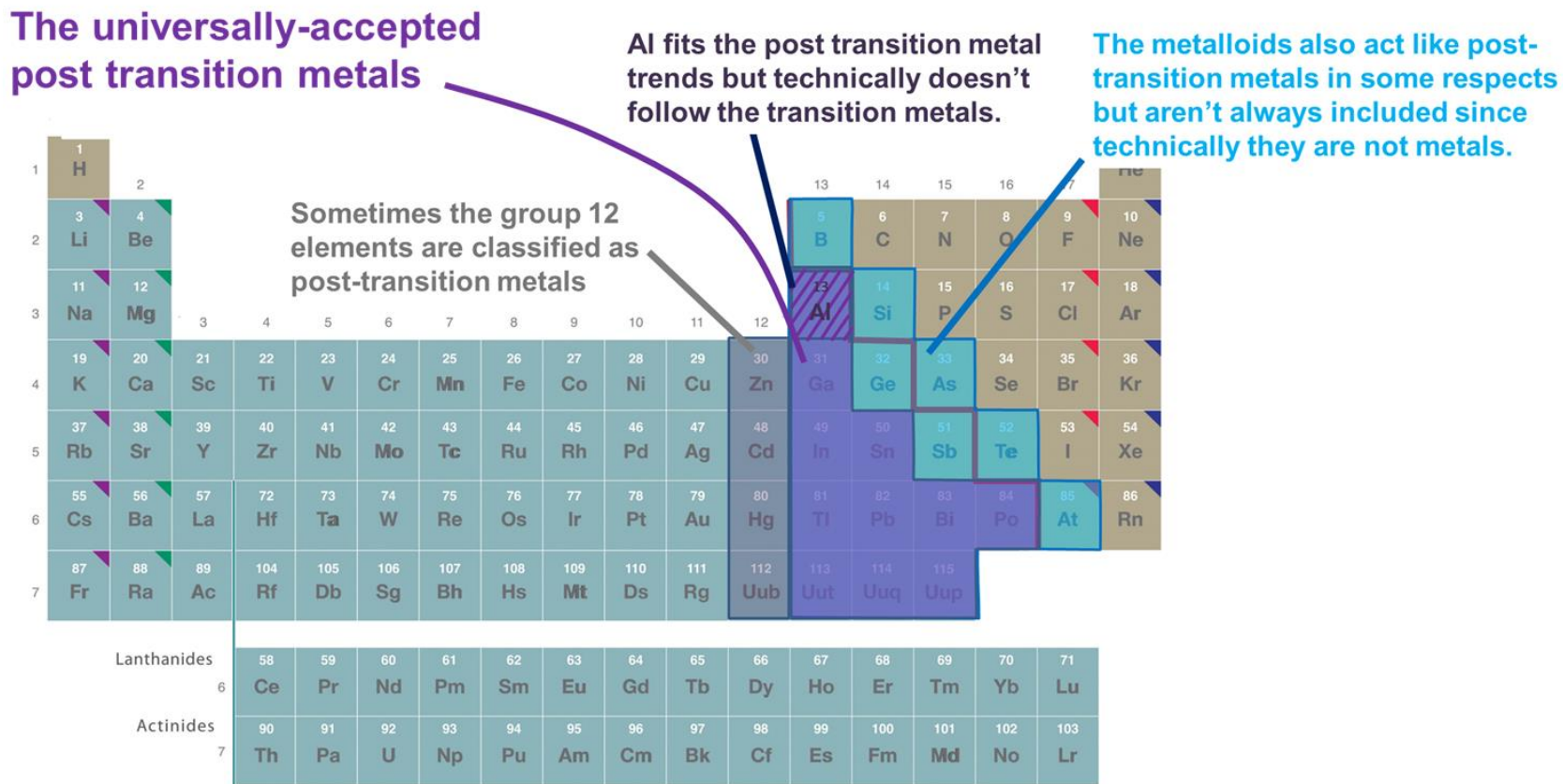
Group 13 elements

The group 13 elements are chemically diverse, comprising elements that are

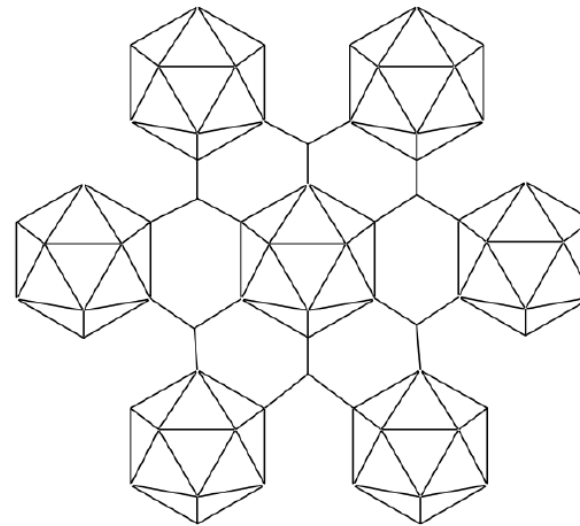
Boron, B, an electron deficient 2nd row element sometimes classified as a nonmetal and occasionally as a metalloid

Aluminum, Al, an electron deficient 3rd row element sometimes classified as a metal and sometimes as a metalloid.

Galium (Ga), Indium (In), Thallium (Tl), and Nihonium (Nh, marked under its old symbol, Uut), post transition metals that exhibit the inert pair effect to varying degrees

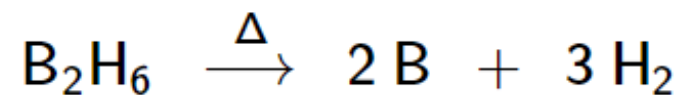


Boron: Network Covalent Solid characterized by the sharing of electrons in boron clusters, primarily linked icosahedra.



The group 13 elements are prepared by reduction of halides or oxides or, in the base of boron, thermal decomposition of the hydride.

Boron can be prepared by reduction of its halides or high temperature thermal decomposition of its hydrides.

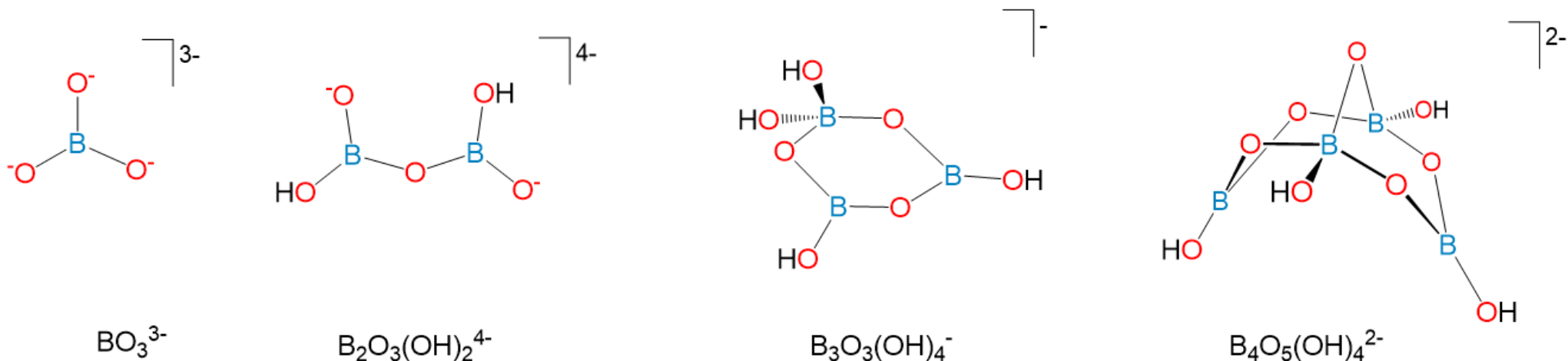


Boron forms covalent bonds and engages in cluster and/or bridge bonding when there are too few electrons to form enough pairwise bonds to satisfy an octet.

Boron possesses only three valence electrons and can be stabilized by sharing five more. It does this in three main ways.

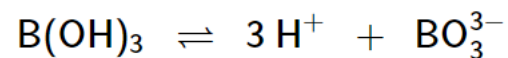
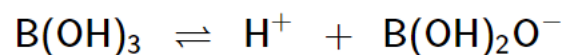
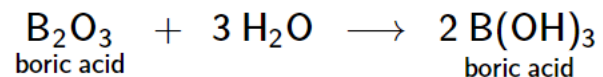
1. Boron forms ordinary covalent bonds and/or gains electrons to give stable molecules or ions. For example, while the boron of B of monomeric BH_3 may not have access to enough valence electrons to achieve a stable octet, it can satisfy its octet by forming an adduct with a Lewis base. A well known example is the borohydride anion, BH_4^- .

The borates and boric acid derivatives which comprise a few ppm of the Earth's crust. These contain borate anions similar to the representative set shown below. Of these, sodium borate or borox is commonly used in household detergents. More precisely, there are a mixture of boraxes, all of which are of formula $[\text{Na}(\text{H}_2\text{O})_x]_2\text{H}_2\text{B}_4\text{O}_7$ (often written as $\text{Na}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$) and differ in the number of waters of hydration. All contain the tetraborate anion, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$.



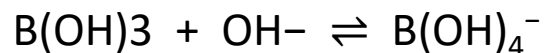
As illustrated by the structures depicted below, the boron in borates is found in BO_4 tetrahedra and trigonal planar BO_3 units linked together in various ways.

The borates illustrate the acid-base properties of these conventional boron compounds. Borate anions may be considered as derived from hydrolysis of boric oxide to boric acid followed by acid dissociation.



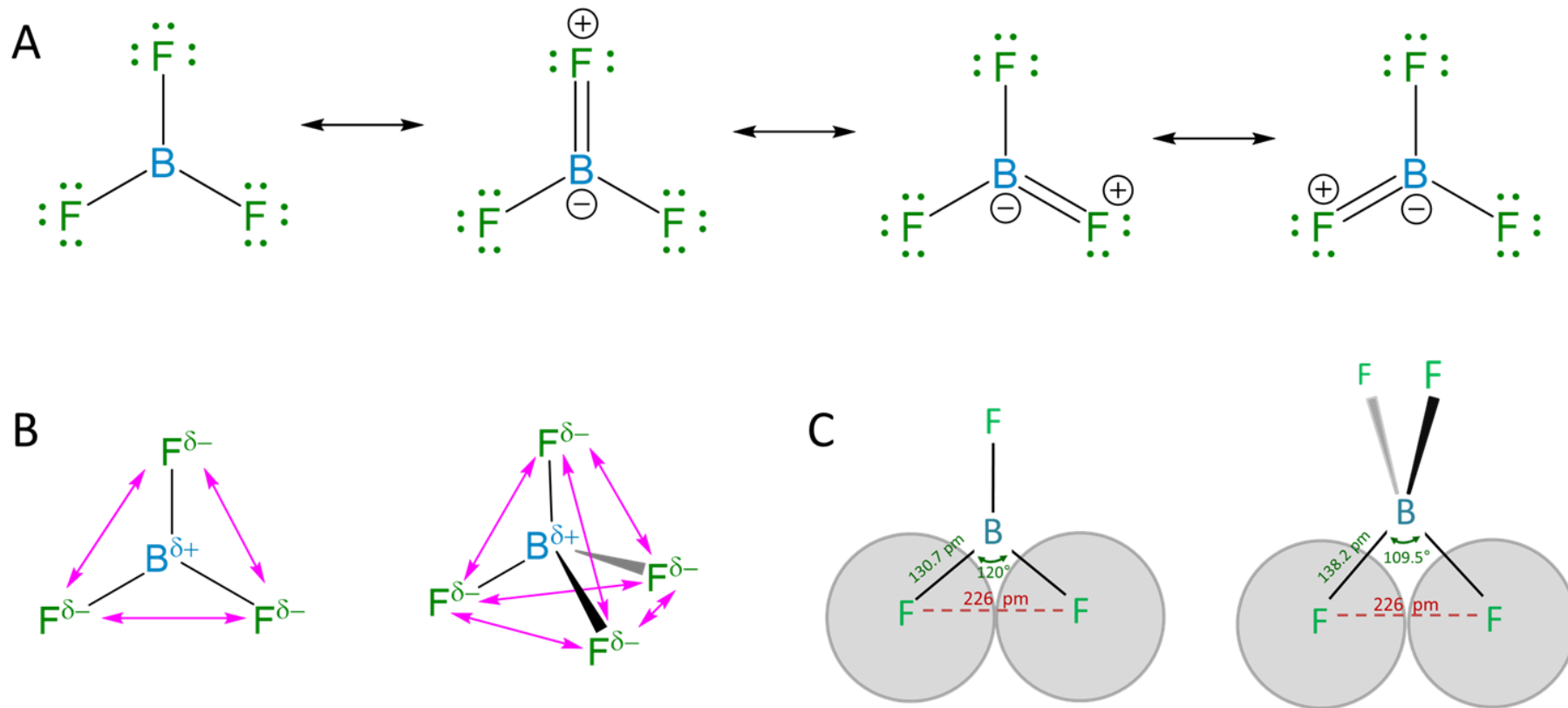
In this respect boron oxides, like all metal oxides, is capable of acting as a Brønsted acid, albeit a very weak one. Consequently the borate anions, as the conjugate bases of weak acids are Brønsted bases.

The trigonal planar boron sites in species like boric acid illustrate the ability of trigonal planar boron to act as a Lewis acid, specifically by forming a Lewis base adduct.



Notice that the three coordinate boron centers are not drawn as possessing an octet, even though it would be possible to draw resonance forms which satisfy boron's octet by drawing resonance structures in which there are $\text{B}=\text{O}$ bonds. This is because it is unclear that such resonance structures contribute significantly to the bonding in trigonal planar boron centers. To see why, it is helpful to consider the boron trihalides.

The boron trihalides. Structurally, boron trihalides like BCl₃ possess a trigonal planar structure like that in the BO₃ units of boric acid and metal borates. What is notable about the structure is that the B-X bonds are shorter than those in analogous tetrahedral structures

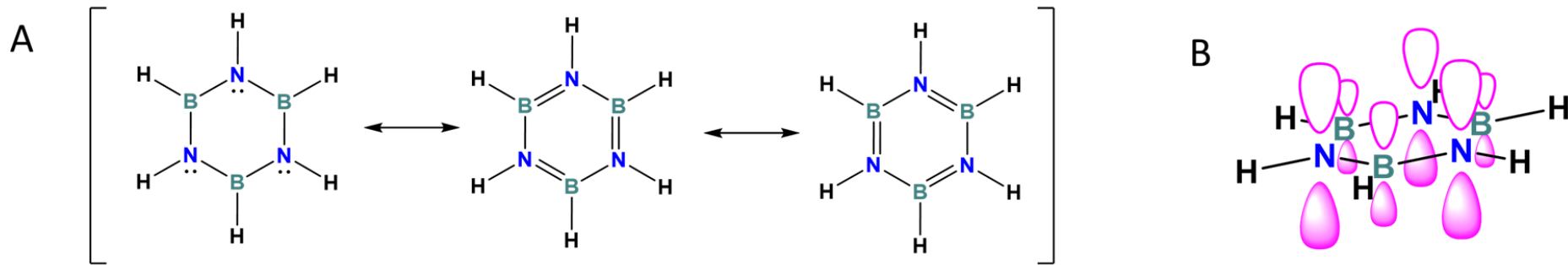


(A) Resonance explanation for short B-F bonds involving contributions from structures in which the partial charges run counter to the expected B ^{δ+} -X ^{δ-} polarity based on electronegativity and calculations, the latter of which support an (B) ionic explanation in terms of a need to reduce the strength of the greater number of repulsions (represented by magenta arrows) between F atoms in tetrahedral geometries compared to trigonal planar ones. (C) The shorter B-X bonds in trigonal planar vs. tetrahedral geometry may also be explained as following from the ligand close packing model.

Borazines:

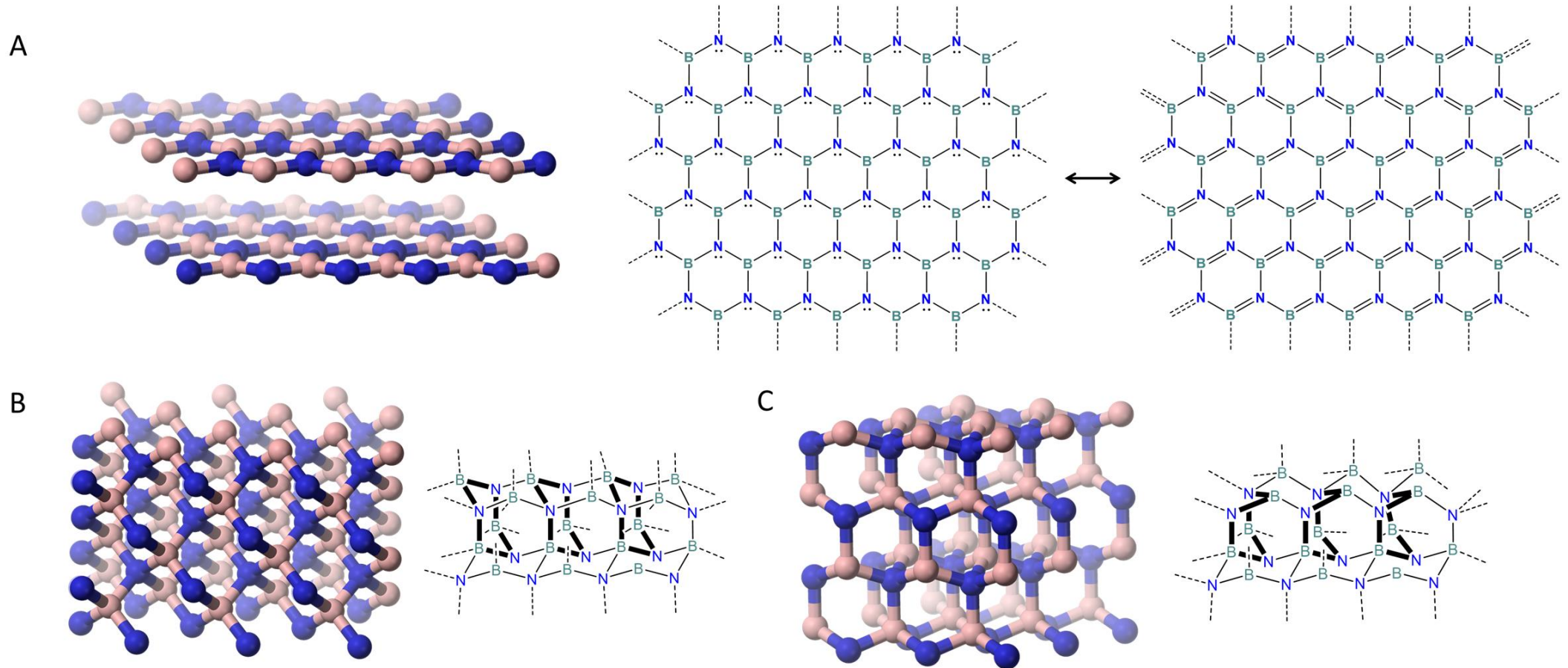
B₃N₃H₆, is isoelectronic and isostructural to benzene, C₆H₆, and have very similar properties. Both have a planar hexagonal molecular structure, are nonpolar, and exist as relatively low boiling liquids at room temperature. The existence of delocalized π bonding in the borazine ring may be inferred in that the B-N bond distances of 1.44 Å in borazine is less than the ~1.6 Å B-N distances typical for B-N single bonds in tetrahedral systems⁸ and close to the 1.42 Å C-C bond distance in benzene. While in benzene the electron delocalization is spread evenly around the carbon ring system, in borazine the greater electronegativity of N ensures that the electron density above and below the borazine more heavily concentrated near the more electronegative N atoms. As a result of the greater electron density on N and the resulting electron deficiency on B, the B and N atoms of borazine retain considerable Lewis acid and base character, respectively.

(A) Resonance representation of the bonding in borazine and (B) representation of the lowest energy π bonding MO in borazine showing the greater electron density on the more electronegative N atoms.



The B and N in each layer are trigonal planar and arranged in planar layers of interlocking hexagonal rings. As with borazine, the π system is delocalized, although again the electron density is somewhat localized on the N atoms and unlike graphite hexagonal BN is not a good conductor. In keeping with the polarity of the B-N bonds and the respective electron densities on B and N the layers are organized so that the B atoms in one layer are arranged directly above and below the N atoms in the next and vice versa, although the intersheet spacing of 3.3 Å suggests that there is no interlayer bonding. Further, as with graphite the ability of the sheets to move about relatively freely makes hexagonal BN a good lubricant.

Although the layered hexagonal structure of boron nitride is the most stable, BN also forms two polymorphs in which the B and N atoms are tetrahedrally coordinated that are analogous to the cubic diamond and Lonsdaleite forms of carbon. They may be thought of as consisting of layers of linked interlocking B₃N₃ chairs. The two forms differ in terms of whether the layers are arranged so as to be linked in the form of chair or boat conformation B₃N₃ rings.



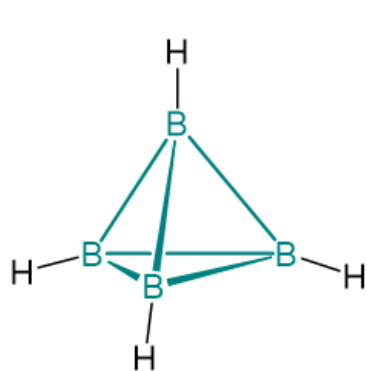
(A) Layered structure of BN along with two resonance structures illustrating the bonding in a boron nitride layer, (B) cubic BN and a schematic depiction emphasizing the linking of layers of chair conformation B₃N₃ rings by chair conformation B₃N₃ rings and (C) Wurtzite-like hexagonal BN and a schematic depiction emphasizing the linking of layers by boat conformation B₃N₃ rings.

Boron can achieve stable bonding configurations by sharing electrons via bridge bonds. These are common in boron hydrides. For instance, another way the B of BH₃ can achieve an octet is to form two center-three electron bridge bonds, as in diborane.

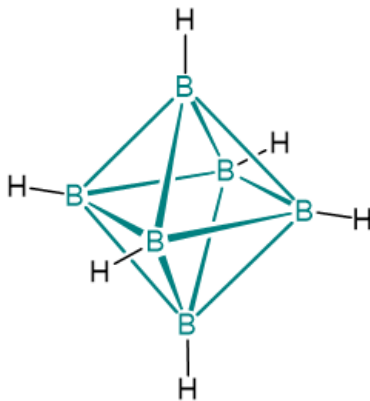


Valence bond and molecular orbital descriptions of these "two-electron-three center" bridge bonds in these molecules

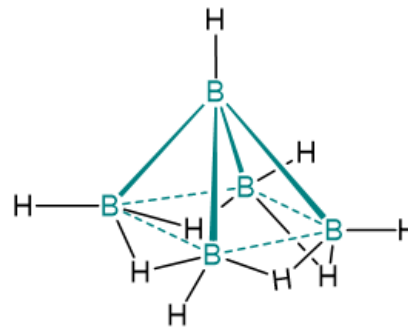
Share electrons among multiple boron and other atoms in a cluster. Such clusters are very common among the boron hydrides (boranes) and their derivatives.



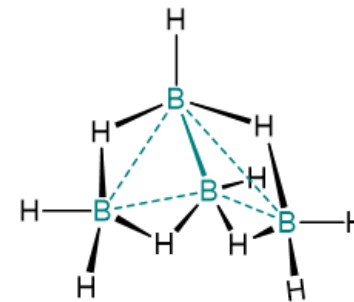
closo-B₄H₄²⁻



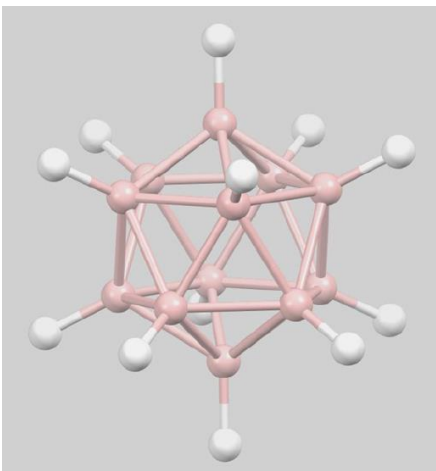
closo-B₆H₆²⁻



nido-B₅H₉

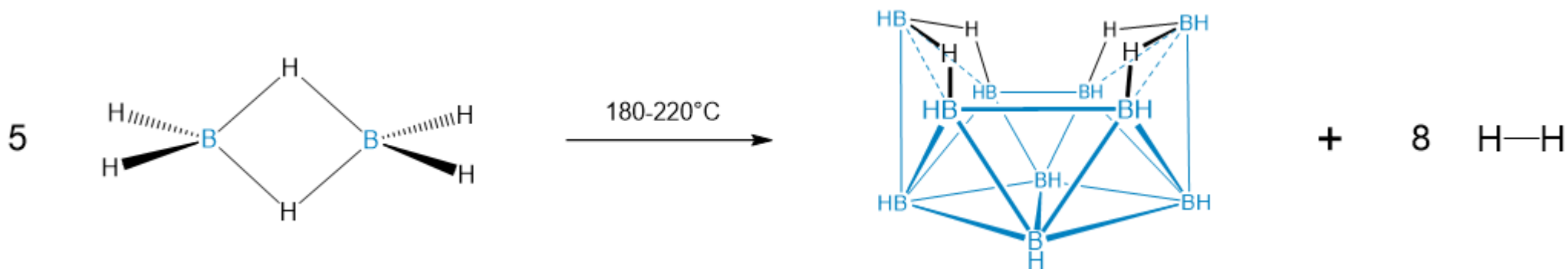


arachno-B₄H₁₀

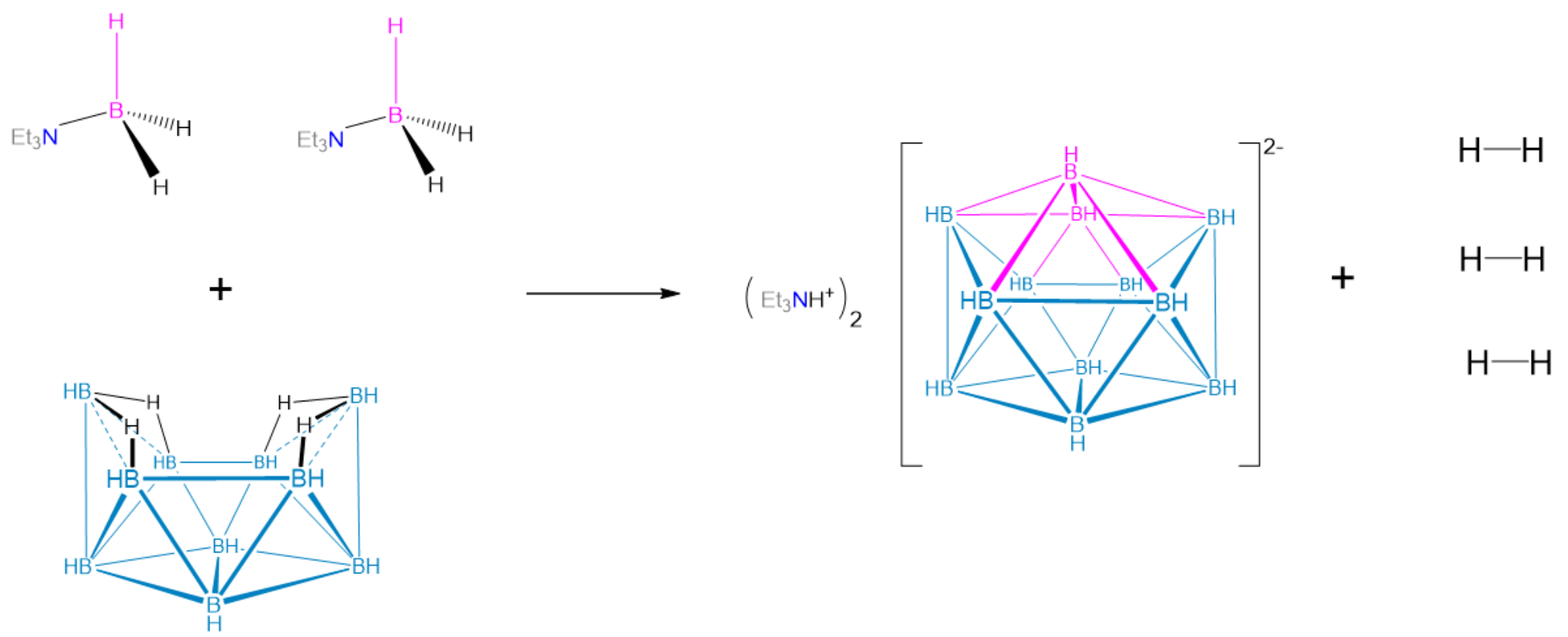


Structure of closo-dodecaborate, $B_{12}H_{12}^{2-}$, showing boron atoms in cream and H atoms in white. The diameter of the cluster is similar to that of a benzene ring.

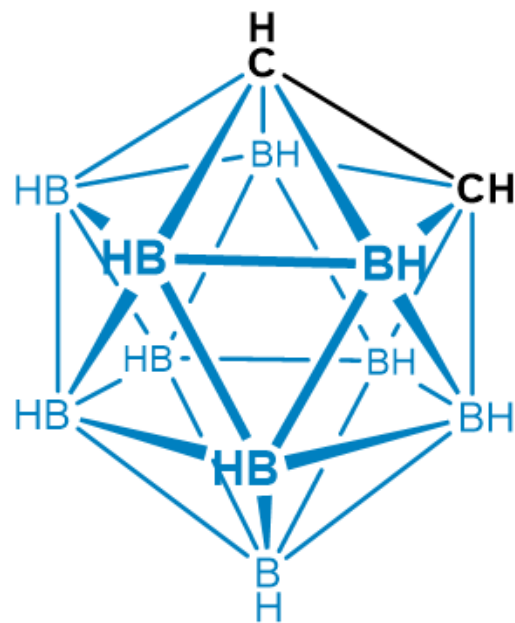
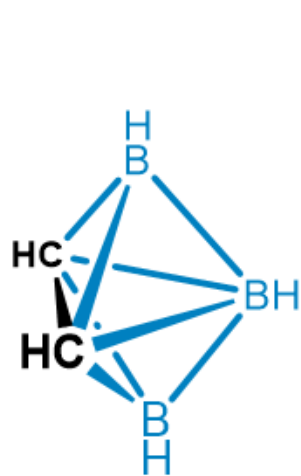
Typically, the higher boranes are formed by pyrolytic removal of H_2 , H^- , and/or H^+ units from BH_3 or BH_4^- . This process may be conceptualized as giving rise to BH , BH^- , and BH_2 units which coalesce into clusters. This process may be seen in part by considering the preparation of closo-dodecaborate. First the diborane is pyrolyzed to give arachno-decaborane(14), $B_{10}H_{14}$, in a process in which the loss of B-H and B-H-B bonds is compensated for by the formation of cluster bonds in which multiple B atoms share the bonding electrons. The resulting arachno-decaborane, $B_{10}H_{14}$, has the icosahedral shape of dodecaborane.



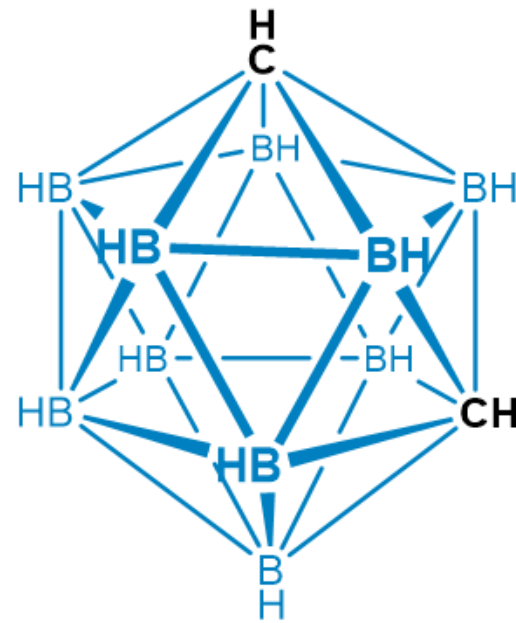
The two missing vertices in the arachno- cluster are added by allowing the cluster to react with additional BH3 units, this time in the form of the Et3N-BH3 adduct.



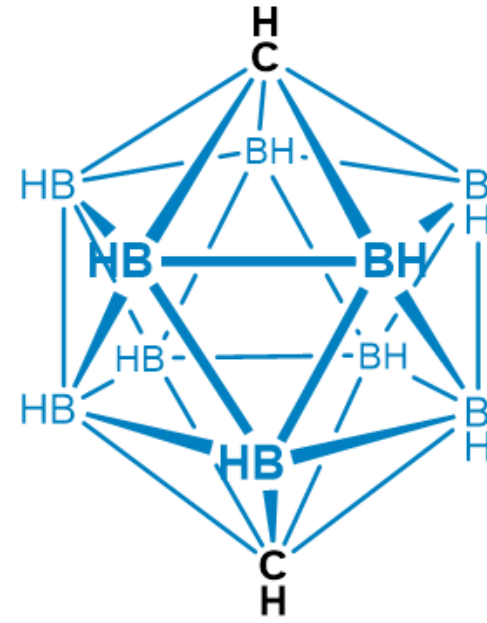
Some carborane clusters, including the ortho-, meta-, and para-"carborane", C₂B₁₀H₁₂.



"ortho-carborane"

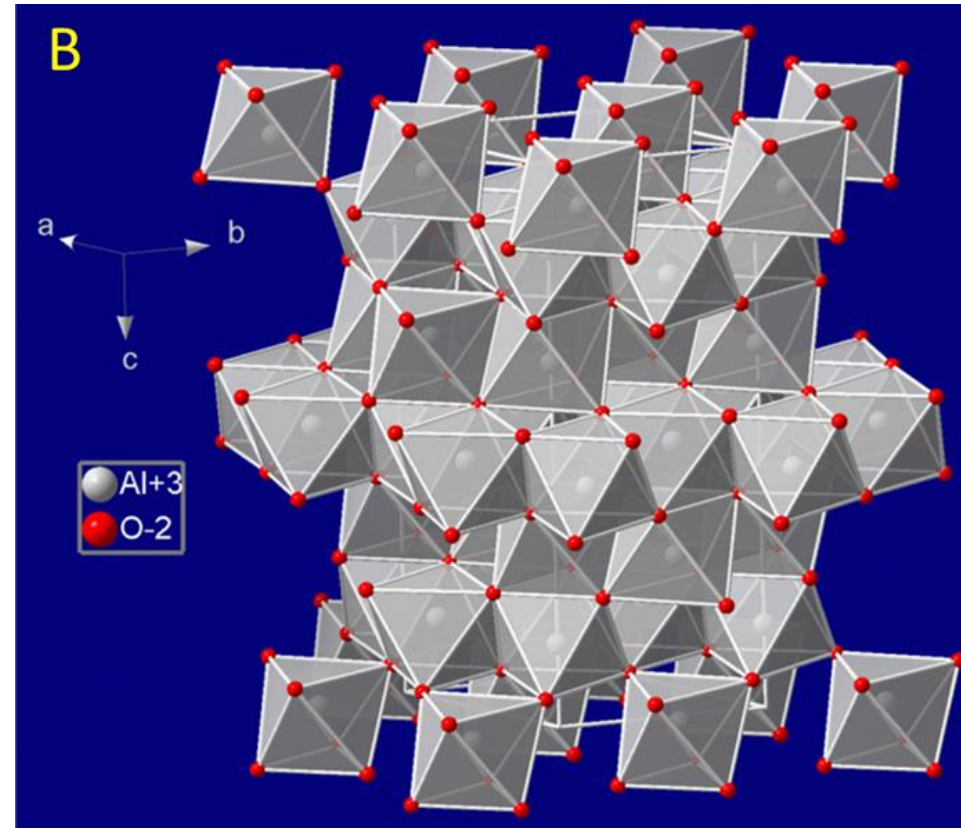


"meta-carborane"



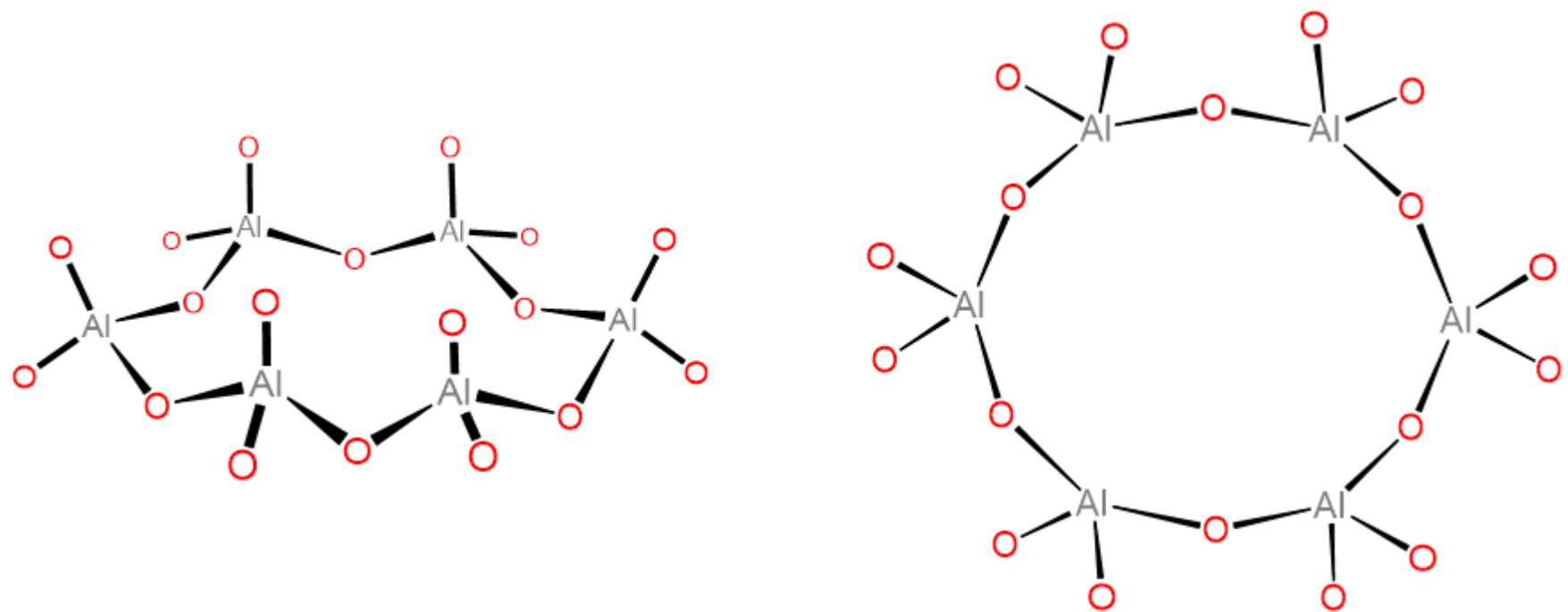
"para-carborane"

The group 13 metals also form conventional compounds as well as M-X-M type bridge bonds and metal-like clusters. The group 13 metals form a wide variety of compounds that may be explained in terms of ionic or pairwise covalent bonding. Their oxides can generally be explained as ionic. Thallium's main oxide, Tl_2O , crystallizes in the CdI_2 lattice, and consists of layers of edge-linked octahedra while the most stable form of Al_2O_3 , Corundum, consists of layers of edge-linked AlO_6 octahedra vertex-linked to adjacent layers.



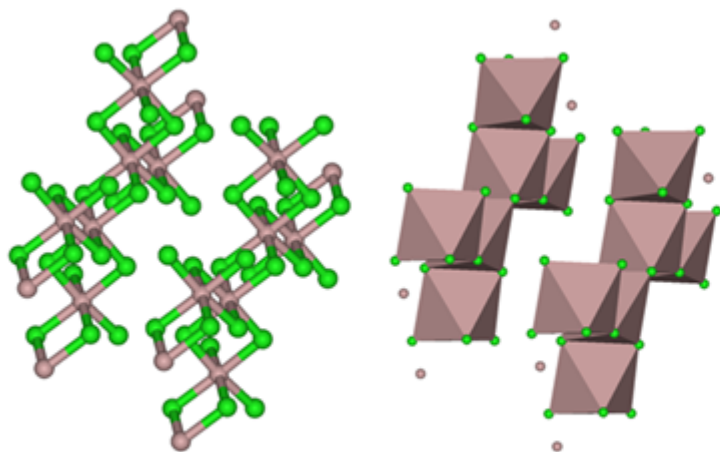
Corundum Al_2O_3 structure consisting of layers of edge-linked AlO_6 octahedra (in the horizontal) vertex-linked adjacent layers (in the vertical direction).

although it is possible to explain the structural chemistry of Al_2O_3 as involving an ionic lattice, Al does form covalently-bonded oxyanions just as Boron does. A particularly well known example is the $\text{Al}_6\text{O}_{18}^{18-}$ anion, which contains AlO_4 tetrahedra covalently vertex-linked into an Al_6O_6 ring. The calcium salt of this anion is found in tricalcium aluminate cements, which as the name suggests are formed by mixing 3 equivalents of CaO with one of Al_2O_3 .



$\text{Ca}_3\text{Al}_2\text{O}_6$ – tricalcium aluminate

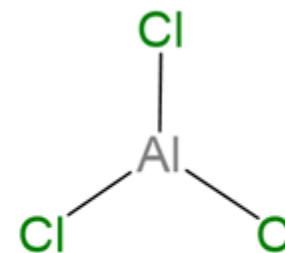
It forms a network structure as a solid, as liquid exists as a E_2X_6 dimer, and in the gas phase is a mixture of dimers and monomers, ultimately giving the monomer only at high temperatures.



solid state crystal structure

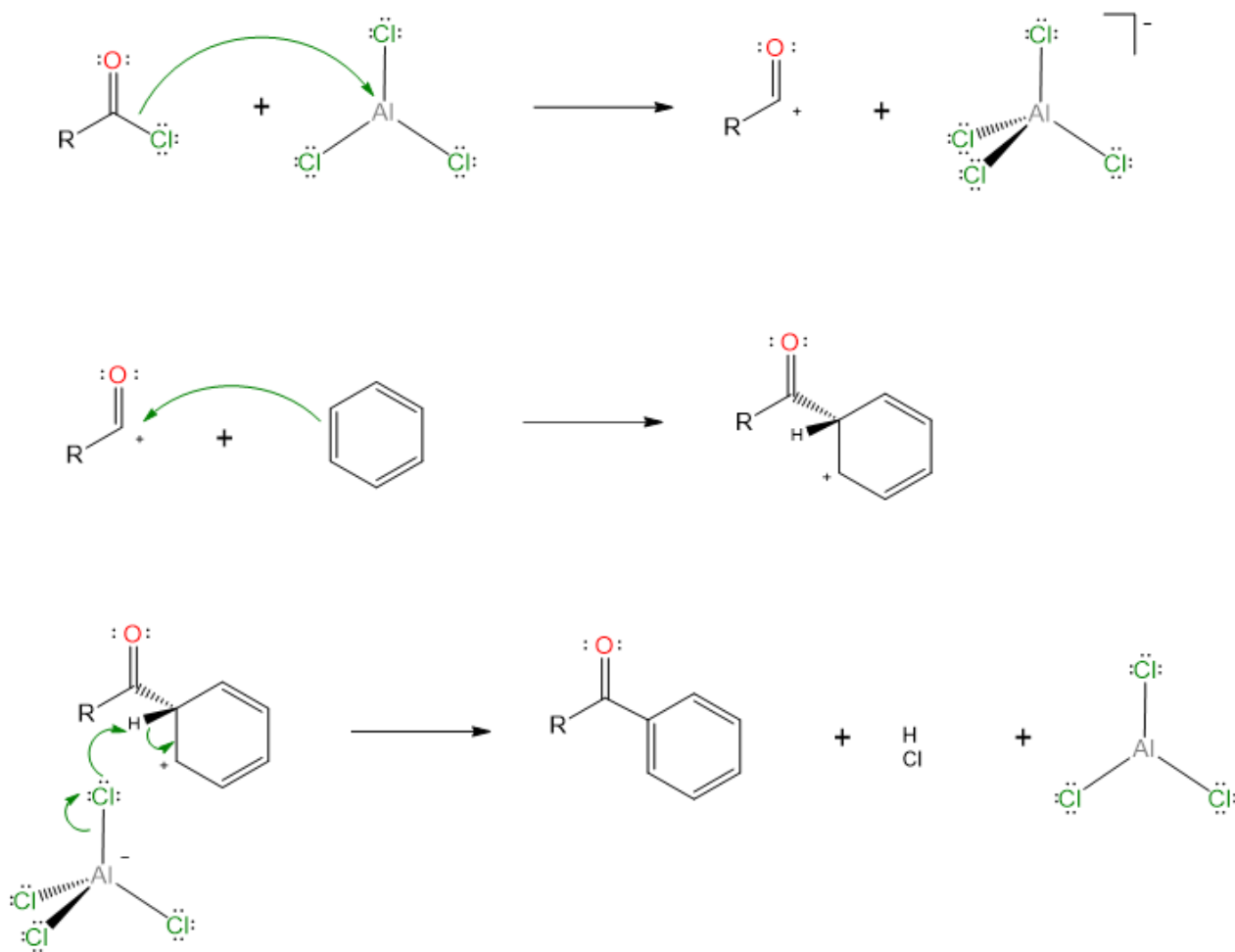


dimer
(liquid and gas phases)

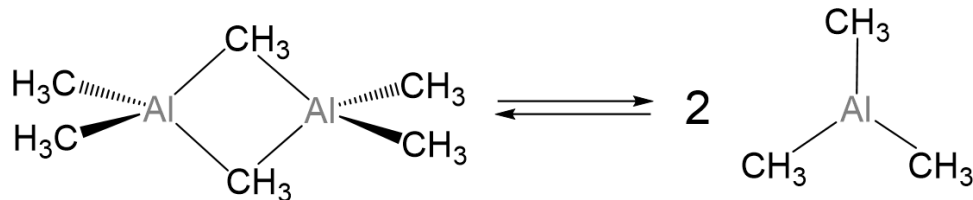


monomer
(high temperature gas phase)

The aluminum trihalides are effective Lewis acids. This property serves as the basis for their use as a catalyst in Friedel-Crafts alkylations and acylations. In these reactions, AlCl_3 acts as a Lewis base to abstract a chloride ion from an alkyl or acyl halide, generating a carbon-based cation that can add to an aromatic ring in an electrophilic aromatic substitution reaction



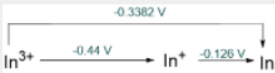
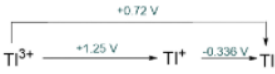


Trialkyl group 13 compounds also exist as monomers and dimers, although the monomer-dimer preference increasingly shifts towards monomer on going from Al to In. In general, GaR₃ and InR₃ species exist as monomers while for Al the monomer and dimer are often in equilibrium for smaller alkyl groups, shifting towards monomer with bulky ones.



As with their boron analogues, trialkyl aluminum and trialkylgallium compounds are effective Lewis acids, reacting with Lewis bases at the group 13 element to give tetrahedral species.

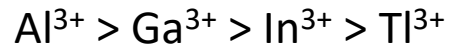
Although the group 13 metals have varying tendencies to form covalent bonds, they tend to act chemically as metals. Some representative features of these elements illustrative of their chemistry are summarized in Table:

Group 13 Metal	Natural Source	Oxides (major product of reaction of the element with O ₂ is given in bold)	Illustrative stable Mononuclear Halides	Redox behavior in acidic solution
Aluminum, Al	Aluminosilicates like <ul style="list-style-type: none">feldspars of formula MAlSi₃O₈ or M'Al₂Si₂O₈ where M = alkali metal and M' = alkaline earth metalclays like kaolinite, Al₂Si₂O₅(OH)₄Bauxites containing Al₂O₃·xH₂O	Al₂O₃	AlX ₃ (X = F, Cl, Br, I)	
Gallium, Ga	As impurities in Aluminum and Fe/Zn ores <ul style="list-style-type: none">Bauxites, Al₂O₃·xH₂OSphalerites, ZnS Small amounts in Gallite, CuGaS ₂	Ga₂O₃ Ga ₂ O	Network covalent GaF ₃ Dimeric Ga ₂ X ₆ (X = Cl, Br, I) Ga ^I Ga ^{III} ₂ Cl ₇ Ga ^I Ga ^{III} X ₄ (X = Cl, Br, I)	
Indium, In	As impurities in Zn and Cu/Fe ores <ul style="list-style-type: none">Sphalerites, ZnSChalcopyrite, CuFeS₂	In₂O₃	InX ₃ (X = F, Cl, Br, I) In ^I ₃ (In ^{III} Cl ₆) (X = Cl, Br) In ^I In ^{III} X ₄ (X = Br, I) InX (X = Cl, Br, I)	
Thallium, Tl	As impurities in sulfide-rich ores <ul style="list-style-type: none">CuFeS₂, CuS, Cu₂SPbSZnS small amounts in minerals like TlCu ₇ Se ₄ , TlPbAs ₅ S ₉ , others	Tl ₂ O ₃ Tl₂O	TlF ₃ TlX (X = F, Cl, Br, I) thallium(I) triiodide, Tl ^I (I ₃)	

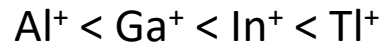
Post-transition exhibit the inert pair effect, in which they act as if their ns^2 valence electrons do not contribute to bonding.

Moreover, there is an increasing preference for the lower oxidation state on going down a group of the periodic table so that

The higher (n^+) oxidation state is favored for lighter elements so that the order of preference is



The lower $(n - 2)^+$ oxidation state is favored for heavier elements



This is why the most stable oxide and chloride of Al are Al_2O_3 and $AlCl_3$ while the most stable oxides and Cl of Tl are Tl_2O and $TlCl$.

The classical explanation for the existence of this behavior is to postulate that the heavier elements' ns^2 valence electrons are chemically inert - i.e. an inert pair. For this reason the observation that many post transition elements have stable n^+ and $(n-2)^+$ oxidation states and that there is an increasing preference for the lower oxidation state on moving down a group has been termed the inert pair effect.

Table 8.5.2.2. Ionization energy costs for formation of M^+ and M^{3+} . Recalculated from the similar table of ionization energies at [en.Wikipedia.org/wiki/Inert_pair_effect](https://en.wikipedia.org/wiki/Inert_pair_effect)

Process	B	Al	Ga	In	Tl
$M \rightarrow M^+$ IE ₁ (kJ/mol)	800	577	578	558	589
$M \rightarrow M^{3+}$ IE ₁ + IE ₂ + IE ₃ (kJ/mol)	6886	5137	5520	5082	5438
Inert pair oxidation: $M^+ \rightarrow M^{3+}$ IE ₂ + IE ₃ (kJ/mol)	6,086	4,560	4,942	4,524	4,849

Table 8.5.2.3. M-Cl homolytic bond energies in kJ/mol.¹⁵

Bond	B-Cl	Al-Cl	Ga-Cl	In-Cl	Tl-Cl
Typical E-Cl Bond Dissociation energy (kJ/mol)	536	494	481	439	372.8

The energy cost for ionization of the "inert pair" is greatest for boron, drops by ~25% on going to Al, and then remains approximately constant for the remaining members of the group. In contrast, the compensating bond dissociation energies drop more slowly on going from B to Tl, with successive ~10% and ~20% decreases on going from Ga to In and In to Tl. Because bond energies drop on going from Al to Tl while ionization energies do not it is thought that the inert pair effect isn't due to the inertness of the ns electrons but rather due to the weakening of bond energies. When the stabilization energy due to M-E bond formation is no longer enough to pay the cost needed to oxidize away the ns electrons the lower oxidation state will be more stable than the higher one, just as it would if the ns electrons really were inert.

The inert pair of electrons exerts structural effects.

Regardless of the origin of the inert pair effect, the inert pair of electrons influences the structure of compounds in the $(n-2)^+$ oxidation state. Electron pairs that do this by altering the observed geometry of compounds are said to be stereochemically active inert pairs. The lone pairs of Sn(II)Cl_2 are the classic example. Gas phase Sn(II)Cl_2 exhibits an AX₂E VSEPR geometry while its in the solid state, hydrates, and salts all exhibit AX₃E geometries, consistent with the influence of a lone pair of electrons.

