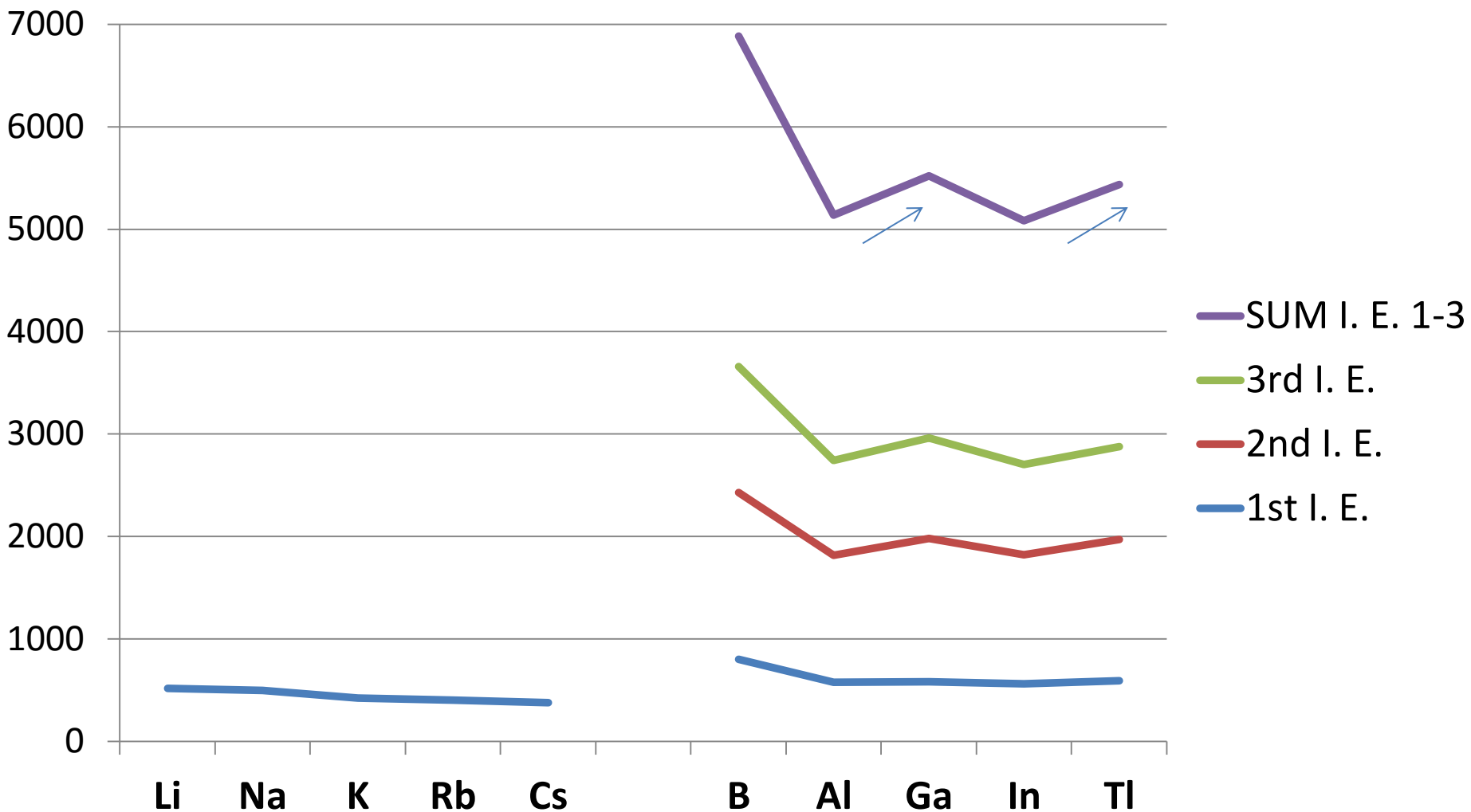


# Group 13: B, Al, Ga, In, Tl

- Much higher electronegativity than groups 1, 2, since one more proton in nucleus.
- Top member is unique: Boron, non-metal
- heavier members metals (valence e-s further from nucleus, shielding)
- Group “oxidation state”, 3+, dominates at the top of the group: elements are  $ns^2p^1$ , all valence electrons used in bonds,  $ns^0$ . e.g.  $BF_3$ ,  $AlCl_3$ ,  $B_2O_3$ , etc. however,  $B^{3+}$  so polarizing it gets them back, so oxidation state just a formalism.
- Towards bottom of group, 1+ oxidation state ( $ns^2$ ) becomes increasingly stable.(e.g.  $TlCl$  more stable than  $TlCl_3$ )

# Ionization Energies (kJ mol<sup>-1</sup>)



# Ionization Energies: trends

- Li-Cs: smooth slight decrease
  - As expected: further from nucleus, charge shielded by inner shells.
- B-Tl 1st I.E. higher than for alkalis (increased  $Z_{\text{eff}}$ )
- 2<sup>nd</sup> and 3<sup>rd</sup> Higher than 1<sup>st</sup>
  - As expected.
- Sum of I.E. 1-3 for Boron is prohibitive:
  - No  $B^{3+}$ : covalent bonding. Non-metal.
  - For later elements, not so extreme (metals).
- B-Tl: overall decrease, yes, but irregular.....

# Ionization Energies: Exceptions

- IE decrease B to Al, but INCREASE Al-Ga!
  - ‘post transition anomaly’
  - Filling 3d, 10 more protons, and they shield poorly, so significant contraction, Significant increase in  $Z_{\text{eff}}$ , overcomes fact that  $n$  is greater for Ga than Al.
  - Ga metallic bonding is weak. V. unusual metal structure, m. p. 30 °C.
- IE decrease Ga to In, but INCREASE In-Tl!
  - Relativistic contraction of 6s: Very heavy elements: INERT PAIR effect.

# Inert Pair Effect: in words

- **Classical component:** Nuclear charge is very large, since filled f-orbitals (3 angular nodes) and d-orbitals (2 angular nodes) so 6s electrons (which penetrate through to nucleus) are more tightly held
  - This alone will not explain the data
- **Relativistic component:** as pull from nuclear charge increases, electrons are attracted more into nucleus. In order to stay 'in orbit', they have to move faster, so fast that they attain a significant fraction of the speed of light. This results in a relativistic increase in their mass, which results in a contraction of the orbit radius, in order to conserve angular momentum.
- **RESULT: 6s electrons are more tightly held** than otherwise expected.
  - We can now explain the data.

# Final part of the jigsaw: weaker bonds

- 6s e- are more tightly held than expected, but they are still much less tightly held than 2s and 2p electrons
- Yet B(III) compounds are more stable than Tl(III) compounds.
- The bonds formed between boron and the other element in the compound have much better overlap, much greater strength, overcomes the energy required to promote them from atomic orbitals into shared molecular orbitals.
- Not true of Tl, Bonds are diffuse and weak.

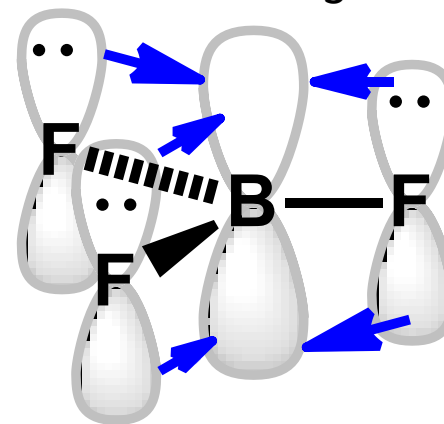
# The results: Group 13 halides: B, Al

- All  $\text{MX}_3$  are **LEWIS ACIDS**. Trivalent, but 4 valence orbitals: one spare.
- $\text{BF}_3$   $\text{BCl}_3$   $\text{BBr}_3$   $\text{BI}_3$  : all molecular; gases ( $\text{BF}_3$  and  $\text{BCl}_3$ ), liquids ( $\text{BBr}_3$ ) and solids (but still molecular,  $\text{BI}_3$ ) Polar covalent. All planar Monomers.

They don't dimerize, instead they have  $p\pi$ - $p\pi$  bonding from lone pairs on ligands to central boron's empty  $p$ -orbital. Overlap is best for  $\text{BF}_3$ .

VSEPR prediction works!

- $\text{AlF}_3$  : "ionic" 3D lattice.  $\text{AlCl}_3$  2D layered structure in solid, dimer in melt ( $180^\circ\text{C}$ ), dimer in non-coordinating solvent.  $\text{AlBr}_3$ ,  $\text{AlI}_3$ , dimer in solid, melt and non-coordinating solution



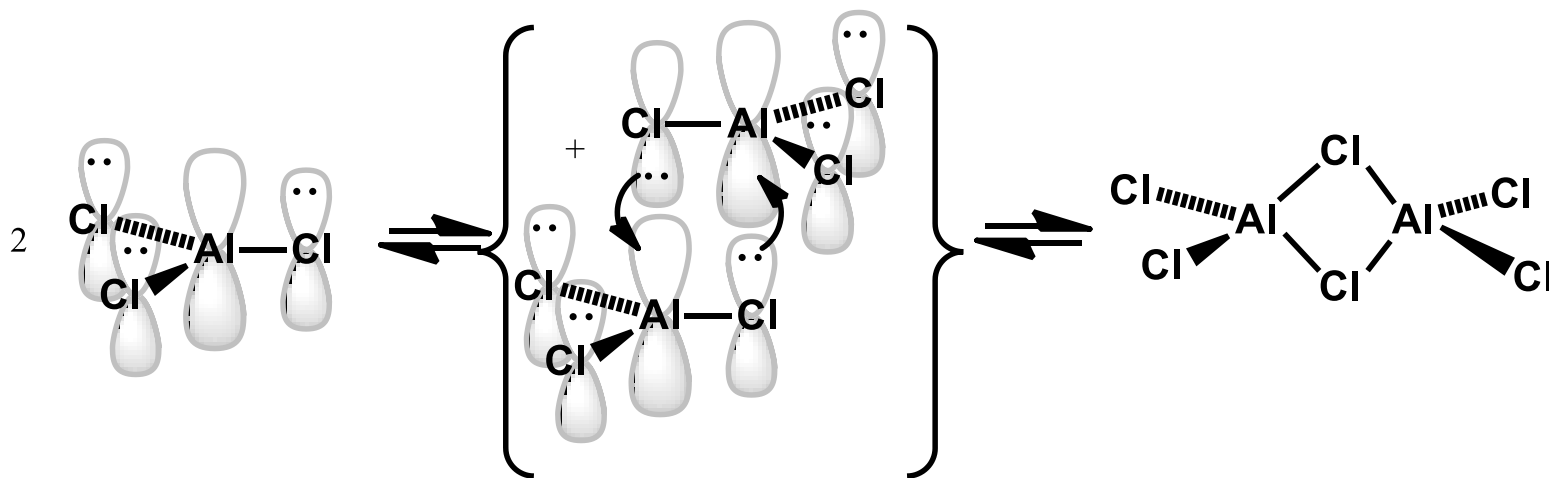
# The results: Group 13 halides: Ga-Tl

- For Ga and In, all halides **MX<sub>3</sub>** are known, similar to B, Al (Lewis acids, dimers, etc.)
- But also, MX become increasingly stable, especially for In. While thf solutions of GaCl can be prepared, can isolate **solid InCl**, distorted NaCl lattice, as well as **InCl<sub>3</sub>**.
- For Tl, MX is the **more** stable. TlCl, TlBr, TlI all adopt CsCl ionic lattice. Tl<sup>+</sup> is very like K<sup>+</sup>, but softer. Totally different to top of group.
- TlI<sub>3</sub> is also known, seems like an exception, but it proves the rule: it is in fact Tl<sup>+</sup> (I<sub>3</sub>)<sup>-</sup>
  - Inert pair effect holds true.



# Why dimers?

- Heavier group members have less-efficient  $p\pi$ - $p\pi$  overlap, but are still Lewis acids. Halides have more than one lone pair, so can bridge. Also, larger metal ions find it easier to accommodate 4, rather than 3, ligands.
- Al, Ga and In with Cl, Br and I all do this....

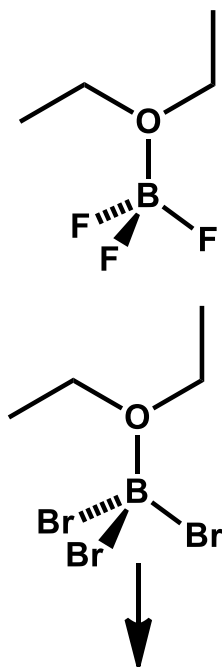


- In solution and gas-phase, often in equilibrium with monomer.

# $MX_3$ in Co-ordinating solvents

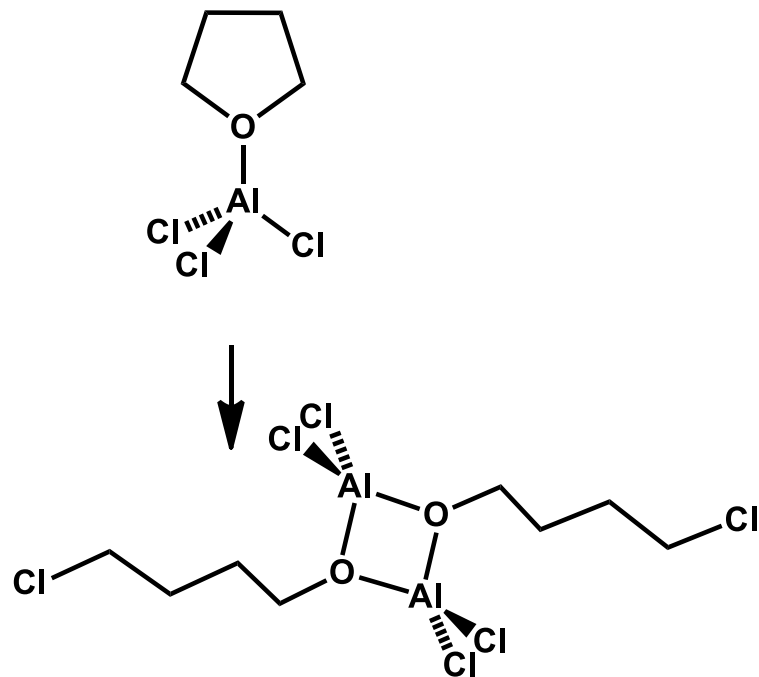
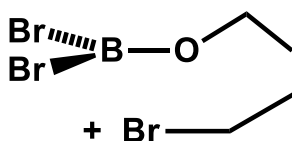
- $MX_3$  are Lewis acids. In solvents with lone pairs (diethyl ether, thf)...

All will do this..... $BF_3 \cdot OEt_2$  is very stable, can be distilled like this.



But the strongest Lewis acids will be so polarizing that they then do this....

Hence, use low temperatures, and slow additions, for clean reactions.



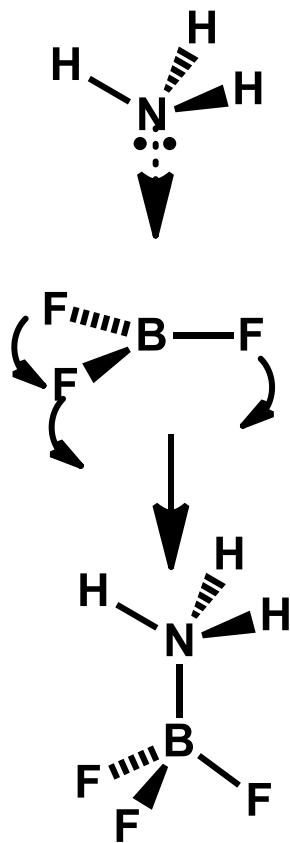
# Order of Lewis Acid strength in $BX_3$

- **Expect:** F is v electronegative, so will strip electrons from B most efficiently, so strongest Lewis acid, I least electronegative, so weakest.
- **But in fact:**  $BF_3 < BCl_3 < BBr_3 < BI_3$  !!!

Why is  $BF_3$  the weakest acid? Because it has best  $p\pi$ - $p\pi$  overlap.

Also, it costs more energy to force the BF bonds from planar to pyramidal, than the larger more diffuse bonds of the heavier halides. F are already tightly packed in  $BF_3$ , can't displace them downward without lengthening the bond substantially. Also, moving the F out of the plane of B loses the  $\pi$ -overlap

# Lewis Acid strength: Evidence: $\text{NH}_3$ complexes $\text{X}_3\text{B-NH}_3$ .



| $\text{H}_3\text{NBX}_3$              | $\text{BF}_3$ | $\text{BCl}_3$ | $\text{BBr}_3$ | $\text{BI}_3$ |
|---------------------------------------|---------------|----------------|----------------|---------------|
| $r(\text{B-N}) / \text{pm}$           | 170           | 163            | 162            | 161           |
| $\Delta H / \text{kJ mol}^{-1}$       | -84.73        | -96.78         | -100.83        | -106.78       |
| $E_{\text{pyr}} / \text{kJ mol}^{-1}$ | 98.87         | 97.91          | 88.74          | 78.53         |

- Less energy needed to pyramidalize the Boron for  $\text{BI}_3$ ,  $E_{\text{pyr}}$  accounts for difference in  $\Delta H$ .
- Weaker bond is longer, stronger bond shorter.

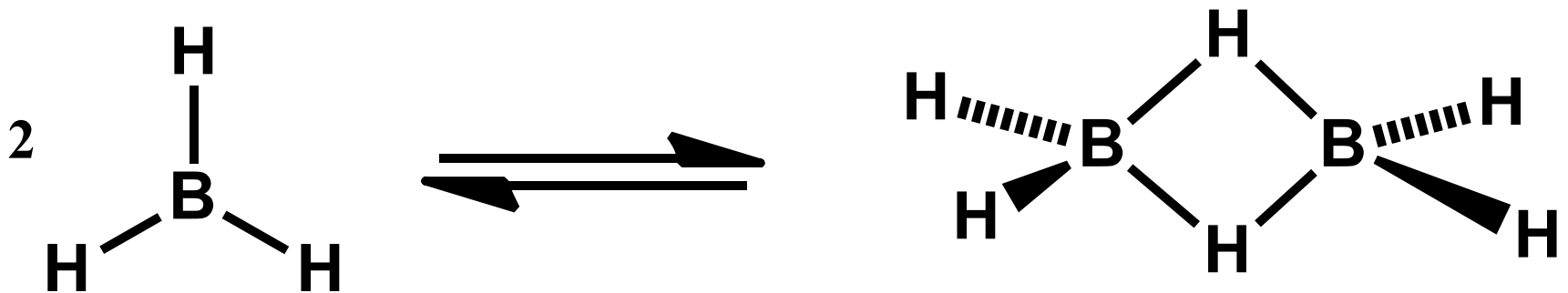
# The relative strength of bonds in $BX_3$

| monomers              | $BF_3$ | $BCl_3$ | $BBr_3$ | $BI_3$ |
|-----------------------|--------|---------|---------|--------|
| $r(B-X)/pm$           | 130    | 175     | 187     | 210    |
| $E(B-X)/kJ\ mol^{-1}$ | 646    | 444     | 368     | 267    |

- BF is the strongest 'Single' bond known!
  - Efficient overlap for  $\sigma$  and  $\pi$ , but also significant polar component re-enforcing covalent bond.
- But what if there are no p-electrons for  $p\pi-p\pi$ ?
- STILL get dimers! Even when  $X = H$ !

# Electron-deficient/Orbitally rich bonding: Diborane

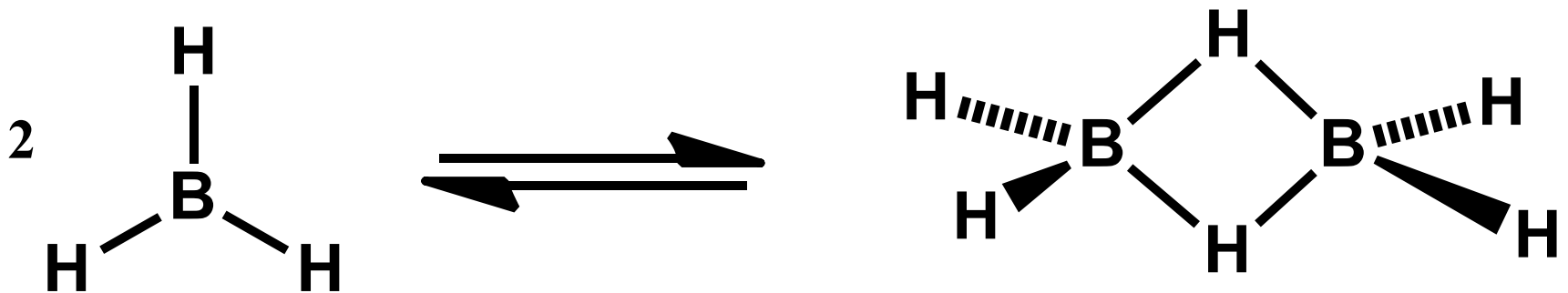
- For Borane,  $\text{BH}_3$ , VSEPR predicts planar monomer. But reality is more intriguing....



- How can this be?  $2 \times \text{B}: 2 \times 3 e^- = 6 e^-$ ;  $6 \text{ H} = 6 e^-$ . Total 12 electrons, 6 pairs, but 8 'bonds'

# Electron-deficient/Orbitally rich bonding: Diborane

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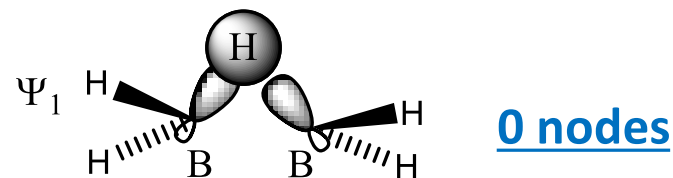
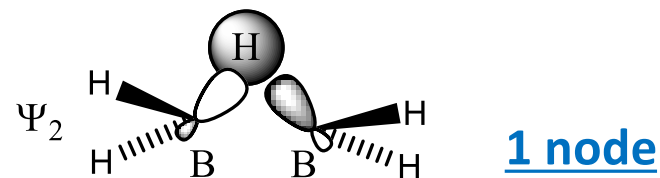
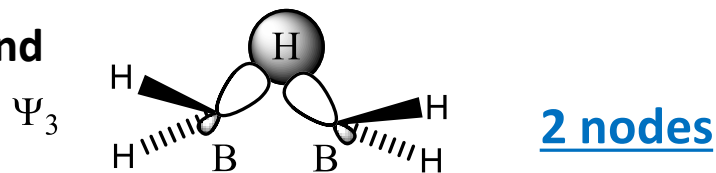
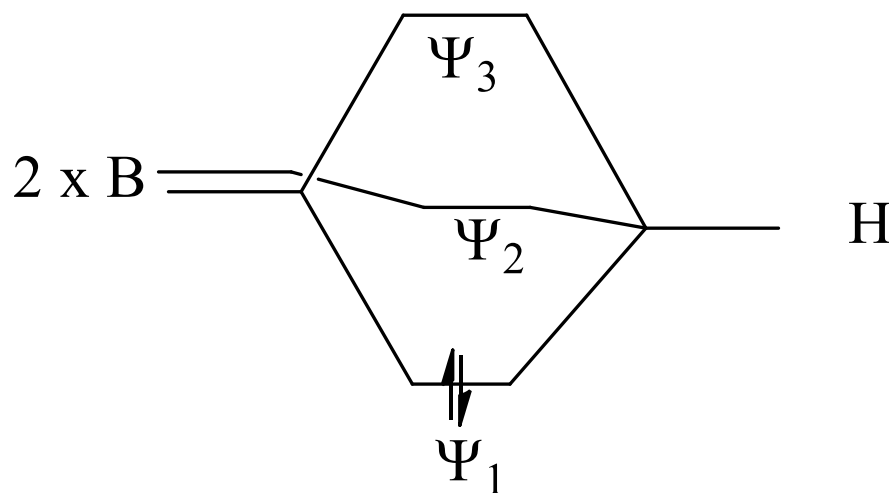


- How can this be?  $2 \times \text{B}: 2 \times 3 e^- = 6 e^-$ ;  $6 \text{ H} = 6 e^-$ . Total 12 electrons, 6 pairs, but 8 'bonds'

# 3-centre, 2-electron bonds

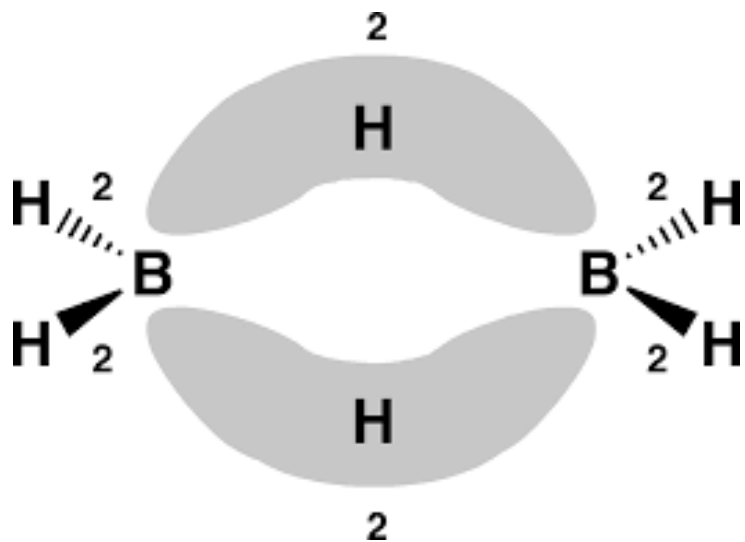
- Most bonds you have met so far have been 2 centre, 2 electron (**2c 2e-**).
- But boron has more valence orbitals than valence electrons, so it shares around the electrons it does have in **multi-centre** bonds.
- **Diborane:** four standard 2c-2e<sup>-</sup> BH bonds, and two **3c-2e<sup>-</sup>** bonds, accounts for the 6 bonding pairs of electrons available.

Simplified MO diagram for one 3c-2e- BHB bridge bond

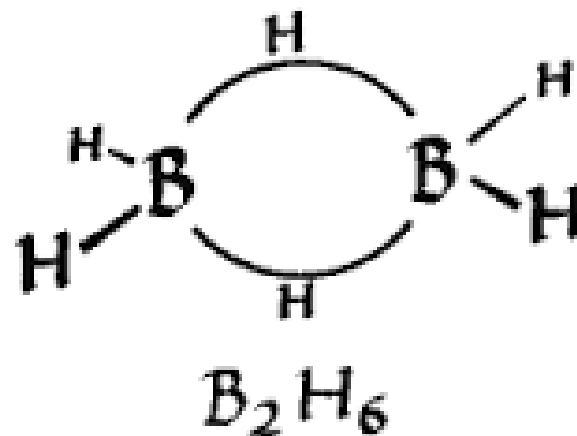




# Other representations of 3c2e bonds



'Banana' bonds



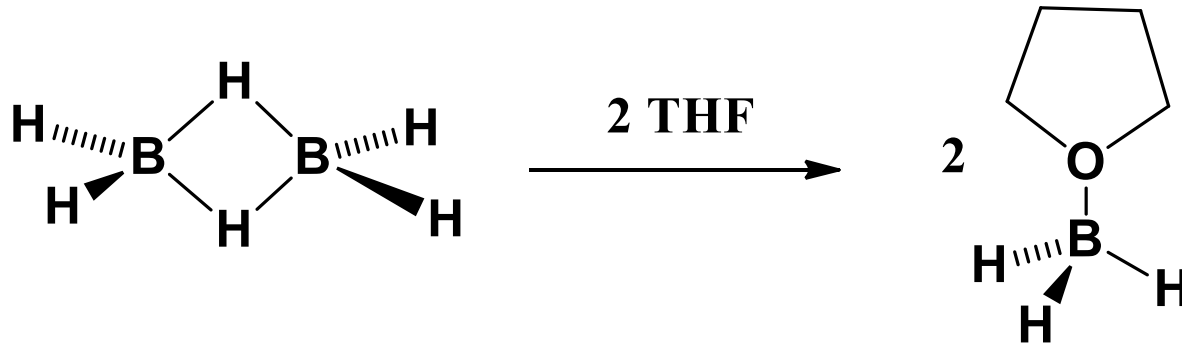
Each black line still represents an electron Pair. 2c2e are straight, 3c2e are bent.

This makes it easier to 'account' for electrons.

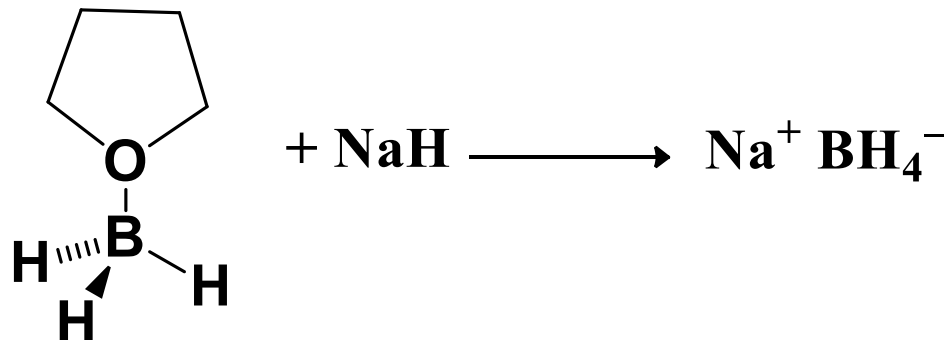
Note on MO: **all** bonding orbitals are full. Non-bonding and antibonding orbitals are empty. Just enough electrons to fill all bonding orbitals. Electron-deficient? Not really.

# Still Lewis Acid

- If further electron pairs provided by solvent, doesn't have to share anymore.

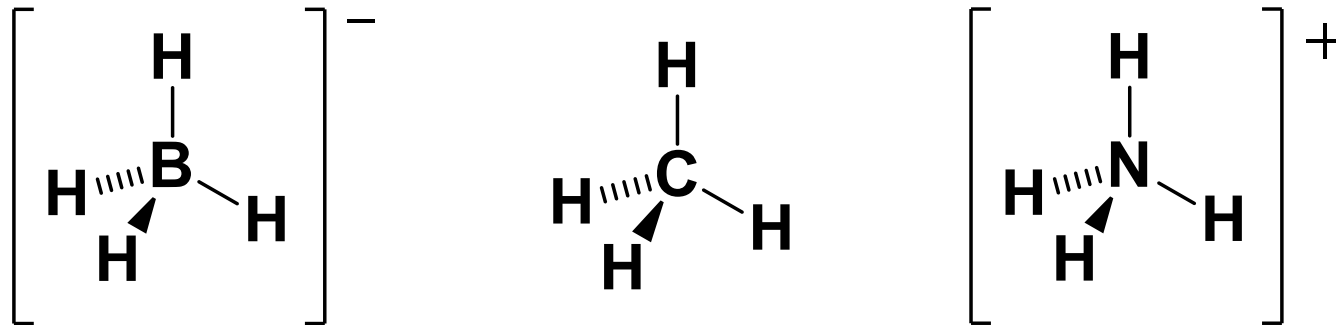


- Reactions: will react with any base:



# ISOELECTRONIC PRINCIPLE

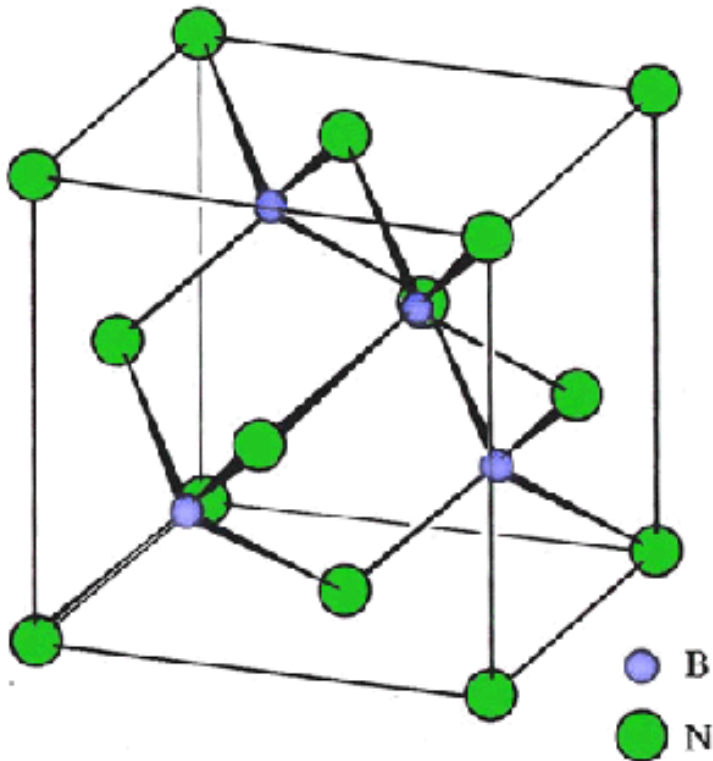
- Same number of valence electrons, same structure.
- e.g.



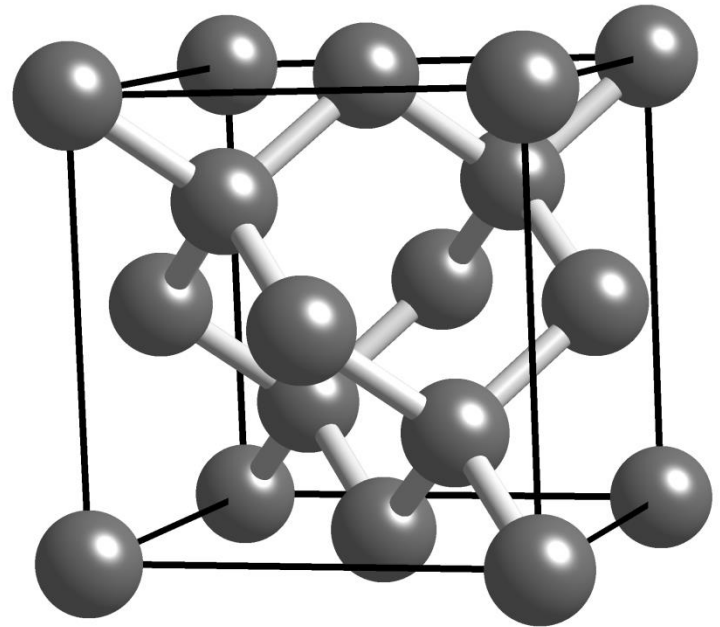
- Also, CC bond isoelectronic with BN bond.

# Isoelectronic pair

- Cubic boron nitride
- Zincblende lattice

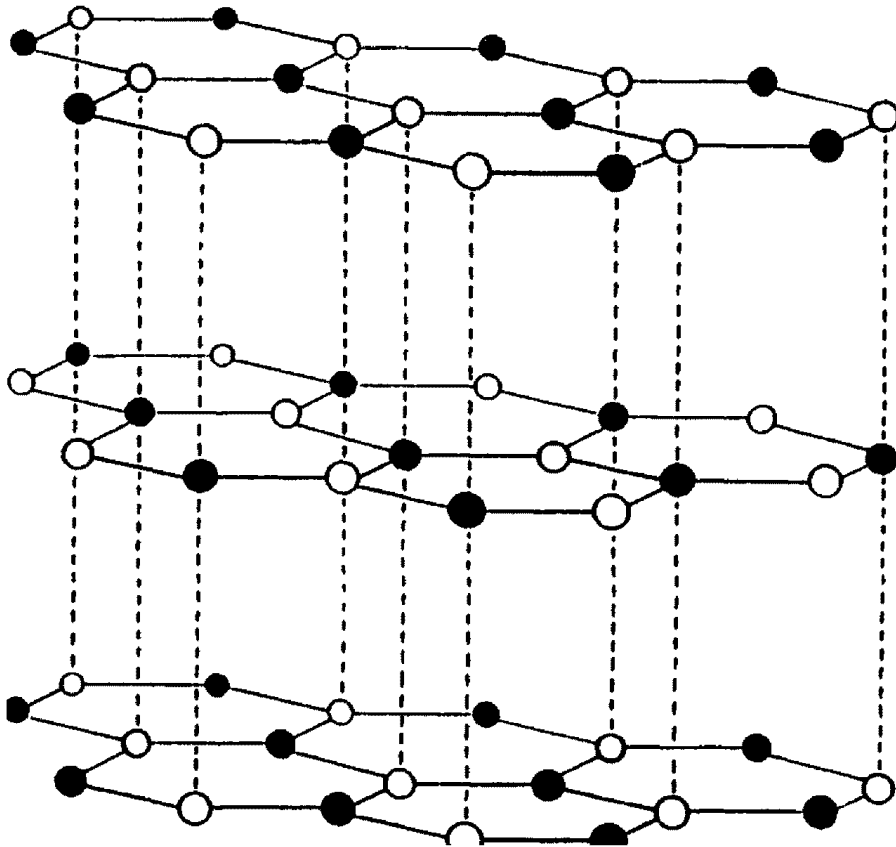


- Cubic carbon
- Diamond lattice

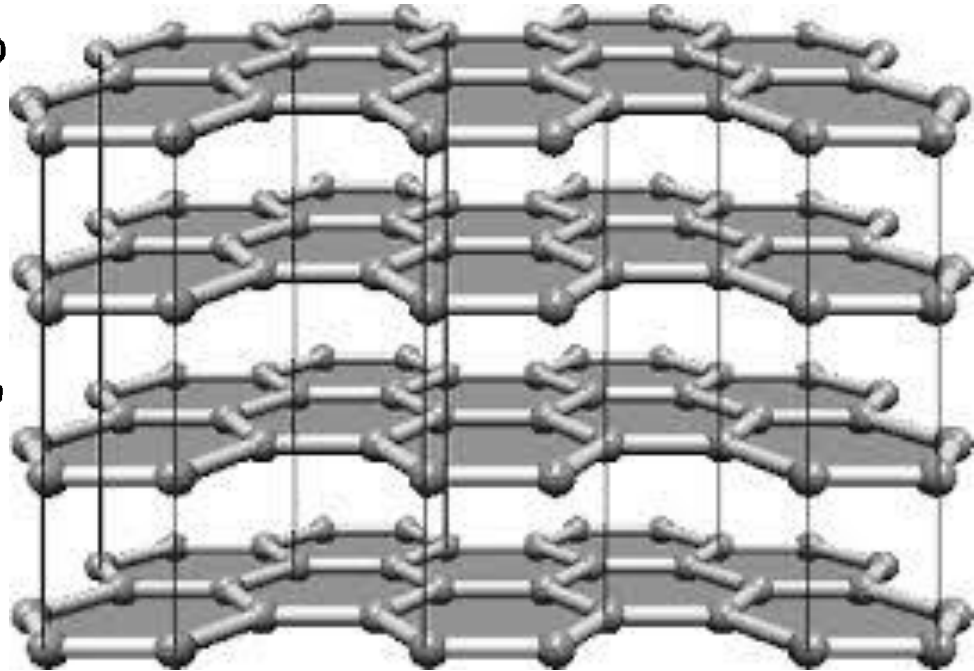


# Another Isoelectronic pair

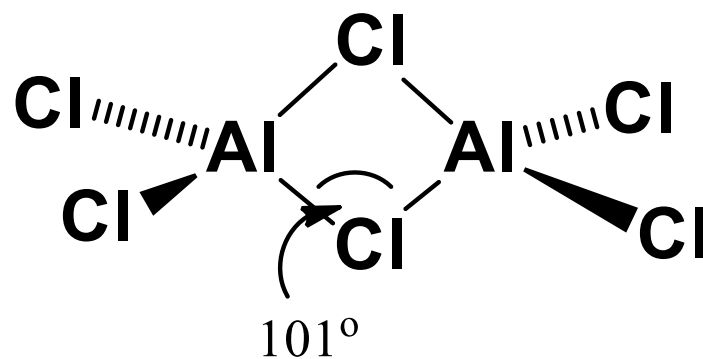
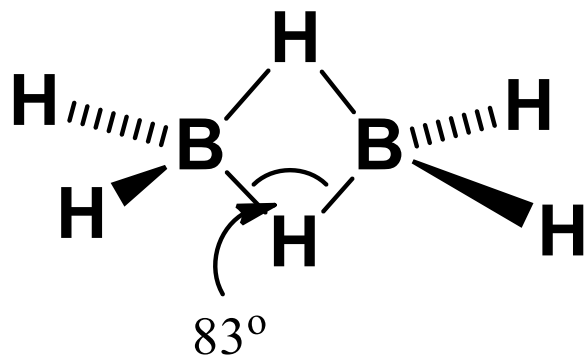
- Hexagonal Boron Nitride



- Graphite



# Similar, not identical structures:



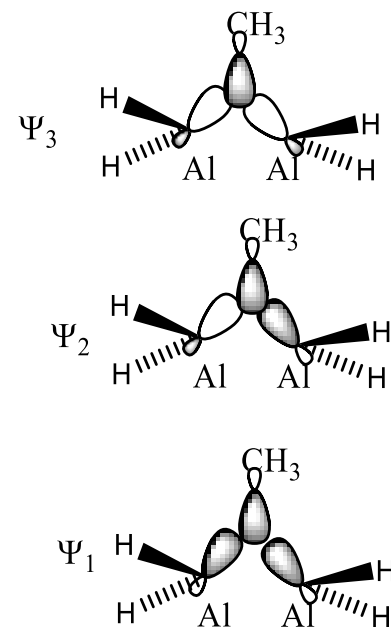
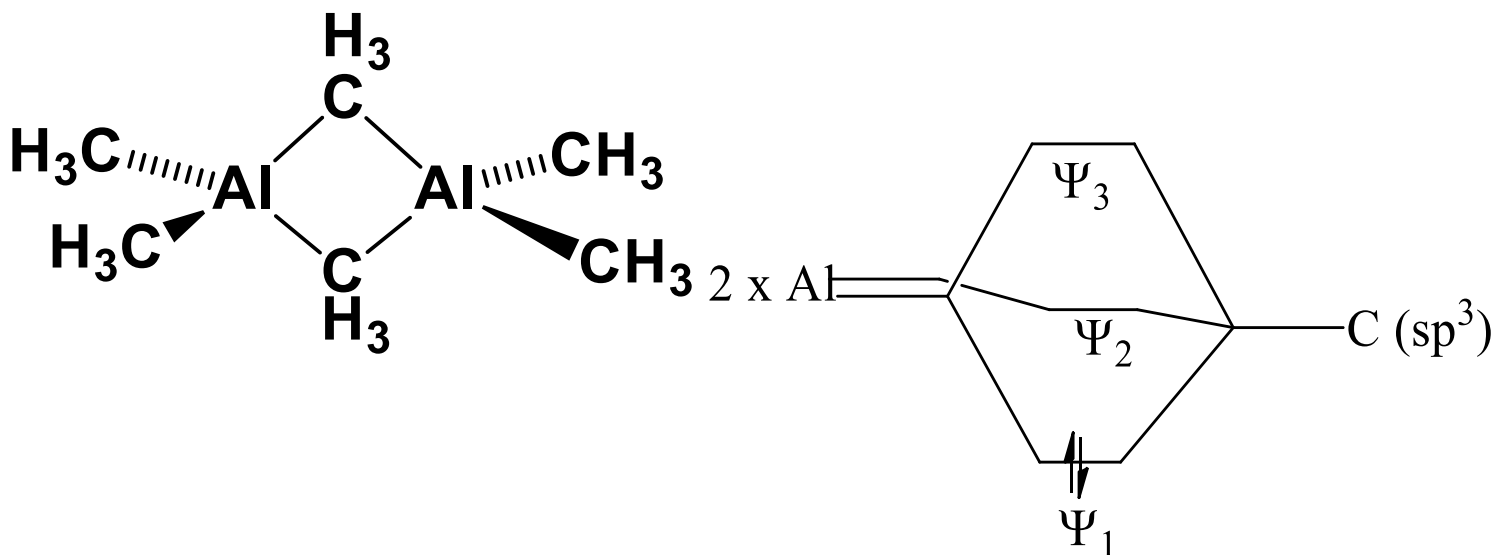
‘electron deficient’

‘electron precise’

- Though structures superficially similar, two borons fighting over the same pair of electrons give sharper angle than electron-precise structure, where Chloride has a lone pair directed at each Aluminium. NOT isoelectronic.

# Group 13 reactions

- Any Element halide + RLi or RMgX does similar:
- e.g.  $6 \text{ "H}_3\text{CMgCl" + Al}_2\text{Cl}_6 = \text{Al}_2(\text{CH}_3)_6 + \underline{6 \text{ MgCl}_2}$



- Not just BHB bonds are electron-deficient
- 5-co-ordinate carbon!