

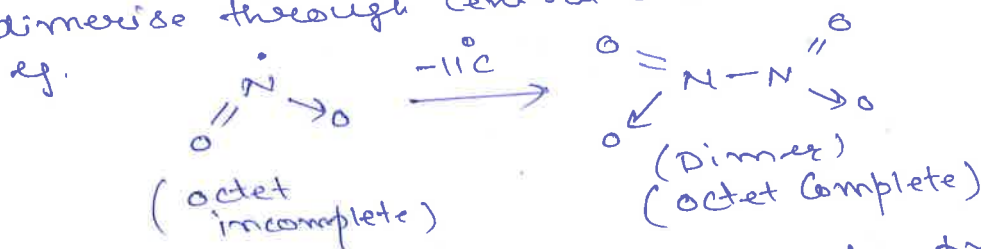
Bridge Bonding!

①

- Electron deficient cpd try to minimise their deficiency.
 - For that purpose either they form back bond or they form multicentred bond. (Bridge bond)
- condition for multicentred bond | Bridge bond

① Tendency to form back bond must be very low or absent in molecule. (∴ in bridge bonding cyclic strain occurs ∴ the molecule that are unable to form back bonding forms bridge bond). Preference for a molecule $B \cdot B > \text{Bridge bonding}$
 eg. BF_3 .

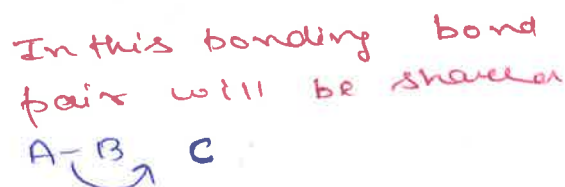
② central atom must not have unpaired electron, otherwise they dimerise through central atom.



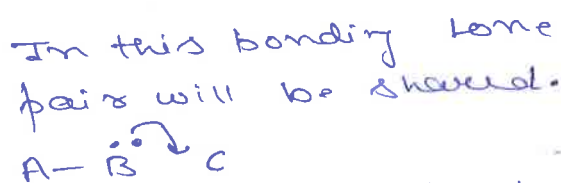
So above types of molecule don't prefer bridge bonding.

Type of multicentred bond

1) 3C-2e⁻ bridge bonding
 center (bridging atom don't have l.p)



2) 3C-4e⁻ bridge bonding
 (bridging atom contains l.p)



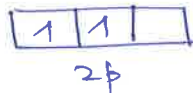
↳ out of l.p & b.p, bridging atom prefer to donate its l.p than b.p. This minimises the repulsion between l.p & b.p.

1. 3C-2e⁻ bridge bonding

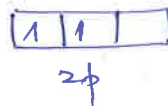
B_2H_6 (Diborane)

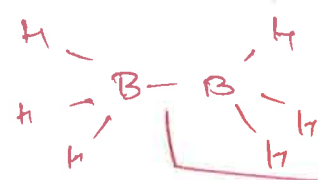
↳ under ordinary condition BH_3 can't exist.

B

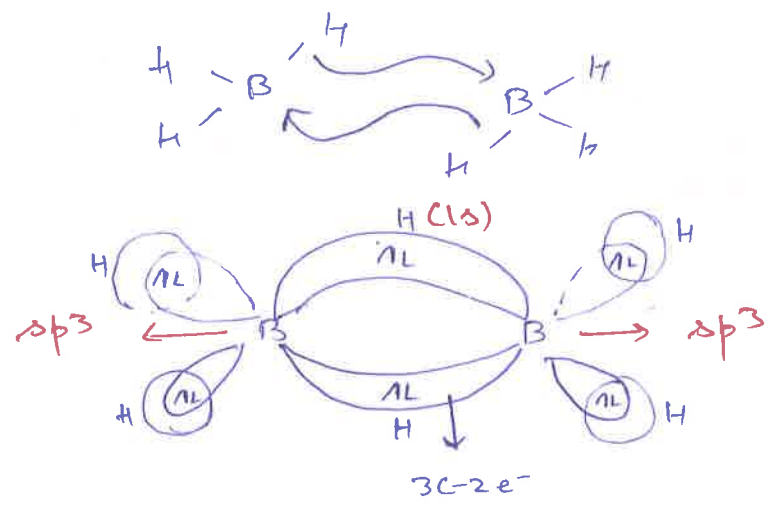
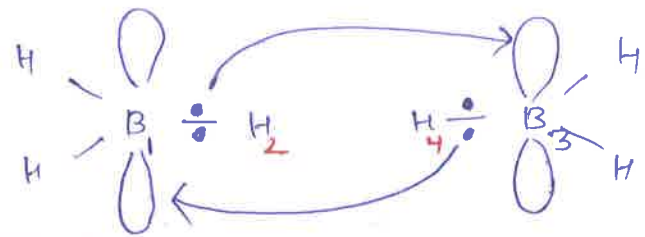
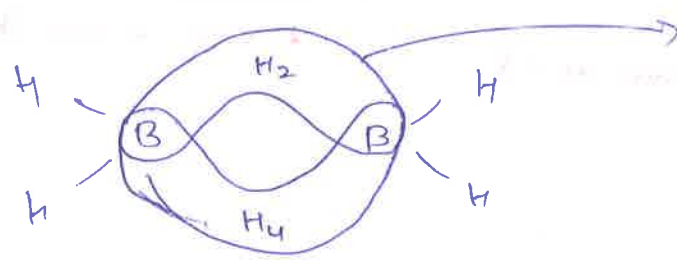


B





Not possible
 ∵ B don't contain any unpaired electron



Bridge bond
 banana bond
 3C-2e bond.

In diborane molecule.

Hyb (B) = sp^3

Non planar; Non polar (Sym str); Lewis acidic
 strength or behavior

3C-2e bond

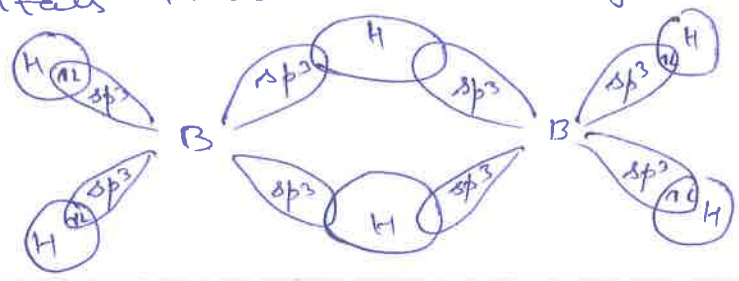
No of (3C-2e) bonds = 2 ;

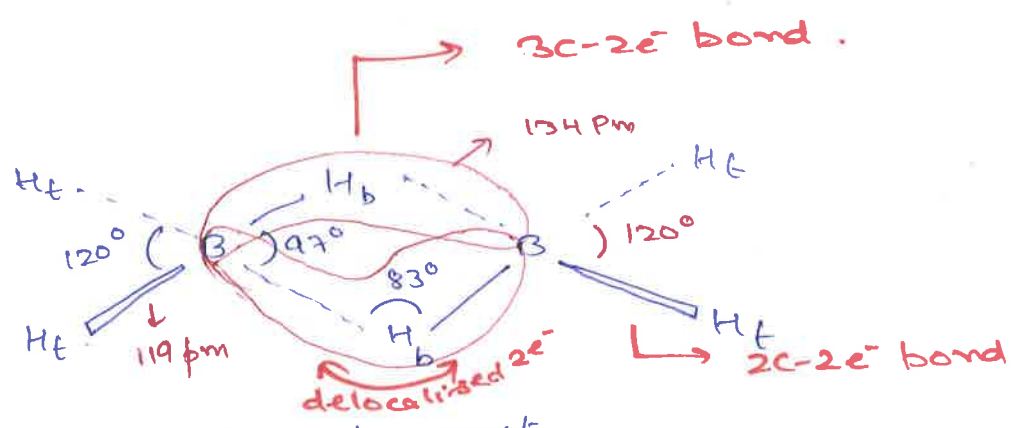
No of (3C-4e) bonds = 0

No of (2C-2e) bonds = 4

max no of atoms lying in one plane = 6

orbitals involved in bridge bonding = sp^3-s-sp^3





In $BH_3 = 6e^-$ are present

Driving force $\rightarrow$ to form temporary completed octet

%age affecting bond length

- ① Bond order $\times$ B.O same.
- ② Atomic size $\times$ B-H same
- ③ s character

H_t b.l is low due to greater s character

H_b B.L is high due to low s character

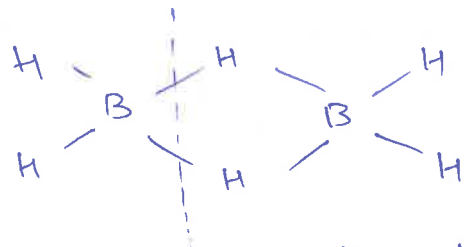
Generally

$\rightarrow$ Greater the B.L weaker is the bond, but here the case is different. H_b is bonded with B on either side. H_t is bonded with B on one side only. $\therefore H_t$ breakage is easily than H_b .

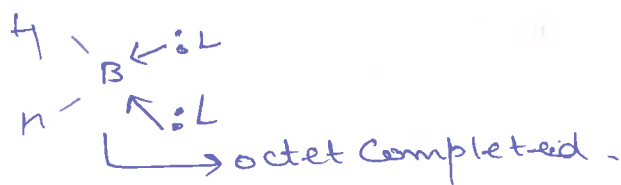
Justification $\rightarrow$ Bridge bond is more stronger than terminal



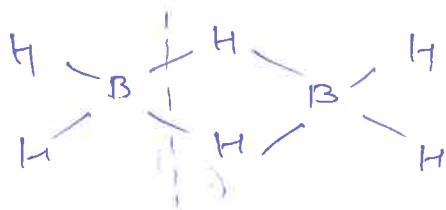
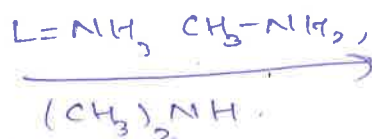
Lewis acidic behavior of B_2H_6



During rxn with Lewis base, bridge bond will get break. Because if there is a breakage of terminal bonds there is not effect on octet completion. [because terminal bonds are always (2c-2e bond)] After Lewis base interaction the bond form will also be 2c-2e. If there is a breakage of bridge bond chances of octet completion will get increase

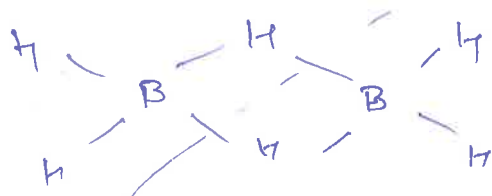


Heterolytic bond cleavage

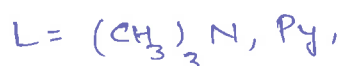


(Always we require 2 mols of Lewis base)

Here 3^o amine can't be present because in product there will be more steric crowding.



Homolytic bond cleavage



Q1: $\text{B}_2\text{H}_6 + 2\text{THF} \rightarrow \text{Product}$

hyb of which element get changed in the given rxn.

- A) B (B) C (C) O (D) None of these

Q2 In the given rxn



the amine X is here

1) NH_3 (ye ammonia)

✓ 2) CH_3NH_2

✓ 3) $(\text{CH}_3)_2\text{NH}$

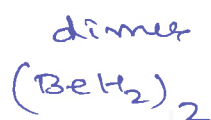
4) $(\text{CH}_3)_3\text{N}$

Q3 In $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ which type of bonds are present

- ✓ (1) Covalent bond
 ✓ (2) Coordinate bond
 ✓ (3) Ionic Bond.
 (4) None of these

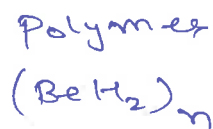


Vapour

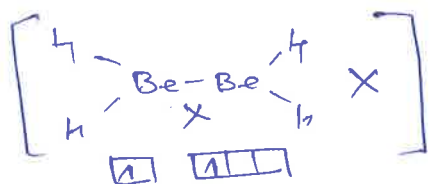


(5)
[In vapour phase min no of molecules interact]

Solid



[In solid state max molecules interact.]



→ No Back Bonding takes place.

→ No dimerization (∵ no unpaired e^- left).

→ ∴ bridge bonding is the way to increase its octet.

①

Dimer →



→ sp^2

→ planar

→ Non-planar polar.

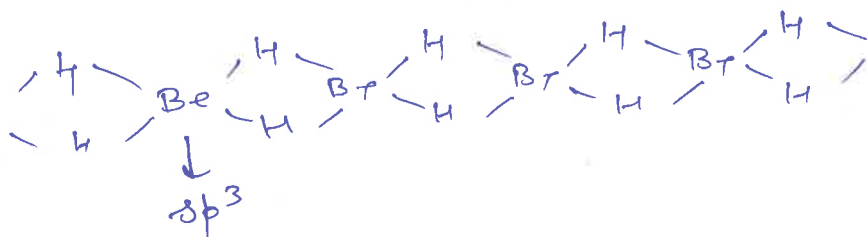
→ No octet completion

Driving force (temporary $6e^-$ system)

→ All atoms are lying on same plane.

②

Polymeric → $(\text{BeH}_2)_n$

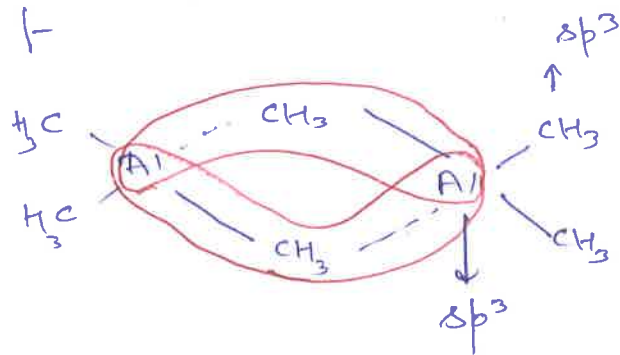


→ Non planar

→ non polar

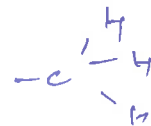
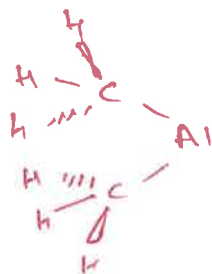
→ No octet completion (temporary at an instant octet completion can takes place).

Driving force → temporary completion of octet.



Satons on same plan

Satons on same plane

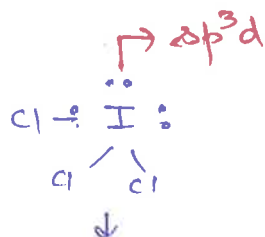


- $\rightarrow$ max atoms in a plane 10
- $\rightarrow$ 22 bonds ($2c-2e^-$) bond
- $\rightarrow$ 2 bonds ($2e-3c$) bond.

2] $3c-4e^-$ multicenter bonding :-

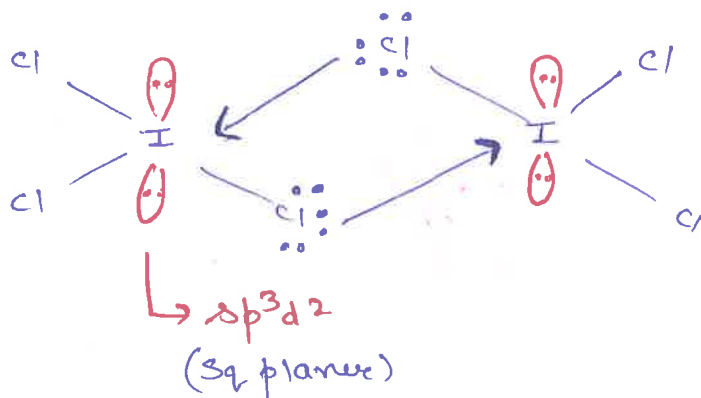
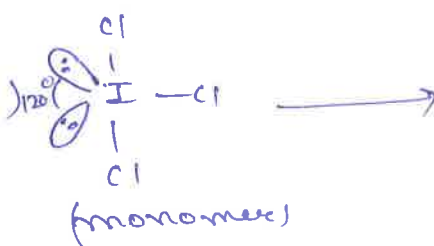
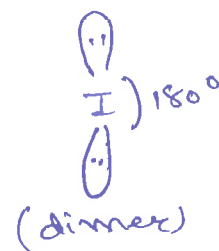


(e^- should be present)



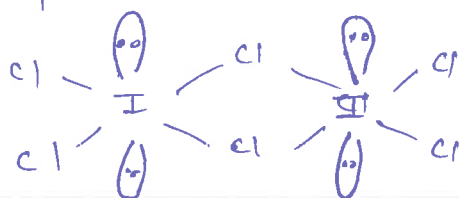
octet completion is not the driving force for octet completion.

driving force f
(to minimise
 $e^-p - e^-p$ repulsion)



Q] Find no of e^-p -bond pair repulsions at 90° in I_2Cl_6 .

Ans $\rightarrow 16$



In liquid state I_2Cl_6 exists as ICl_2^+ & ICl_4^-

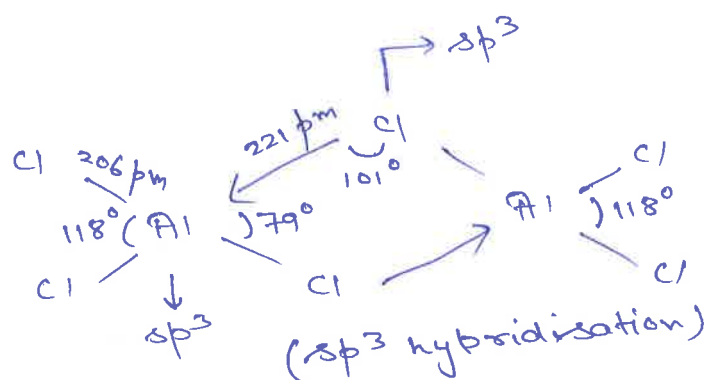
(7)

Now Al_2Cl_6 $\rightarrow$ $AlF_3 \rightarrow$ ionic

$AlCl_3 \xrightarrow{aq} \text{Ionic form} \rightarrow Al^{+3} + 3Cl^-$
[Due to High hydration energy]

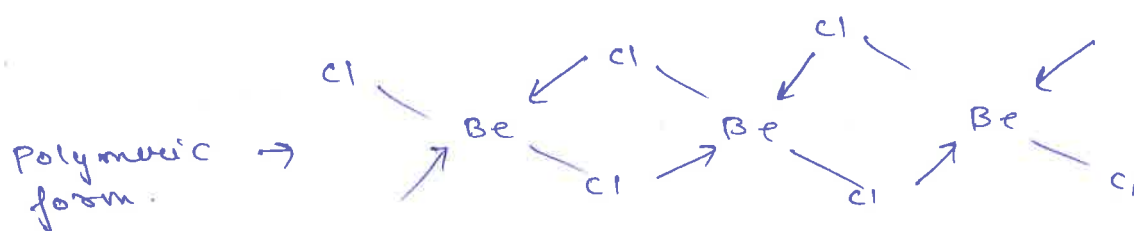
anhydrous $\rightarrow$ Covalent form. (liquid or solid)

$AlCl_3 \xrightarrow{\text{vapour form}} \text{dimer}$
 $\xrightarrow{\text{solid form}} \text{polymer}$



- $\rightarrow$ Non planar
- $\rightarrow$ Non polar
- $\rightarrow$ octet Completed ($8e^-$)
- $\rightarrow$ Can act as Lewis acid (not due to $8e^-$, but due to presence of vacant d orbital)
- $\rightarrow$ Another reason of Lewis acid character is due to angle strain. (79°). It tends to change its angle from $79^\circ \rightarrow 109^\circ 28'$.

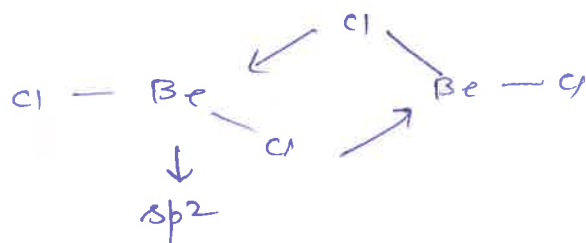
Polymer of $BeCl_2$ $\rightarrow$ Vapour phase $\rightarrow$ dimer
Solid state $\rightarrow$ polymer



- $\rightarrow$ Non planar
- $\rightarrow$ octet Completed.

Dimer of BeCl_2 vapour state

(8)



→ planar

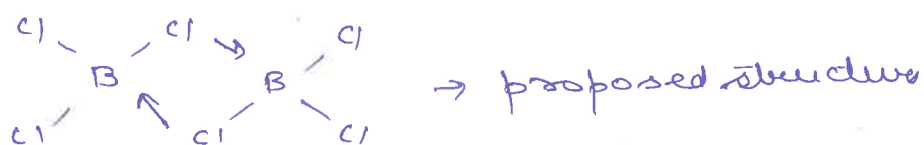
→ $6e^-$ (hypovalent nature)

→ Sym molecule (N. polar)

Q Hyb of $\text{BeCl}_2(\text{S}) = sp^3$ (polymeric form)

Q BeCl_2 doesn't form dimer but AlCl_3 can form. Explain?

Ans →



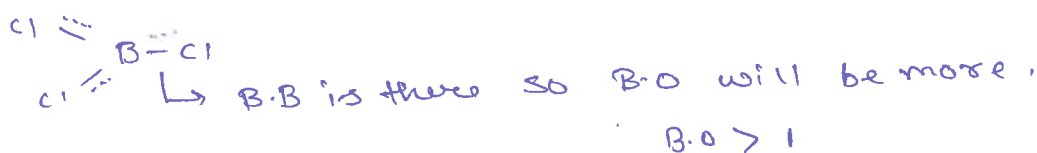
Reason 1/- B can't accommodate 4 large Cl atoms. So can't form dimer.

Reason 2/- B can form back bonding with Cl. But AlCl_3 Al can't form back bonding, $\therefore$ in BeCl_2 don't need of Bridge bonding.

Q B-Cl bond length in BeCl_2 is smaller as compared to Al-Cl in AlCl_3 . Explain?

Ans ① B.O

② Atomic Size $\text{Al} > \text{B}$ (size)



In AlCl_3 $\text{B.O} = 1$

Q In which of the following molecule, at least 1 valence shell orbital of central atom remains unhybridised?

(A) B_2H_6

✓ (B) BCl_3

(C) BH_4^-

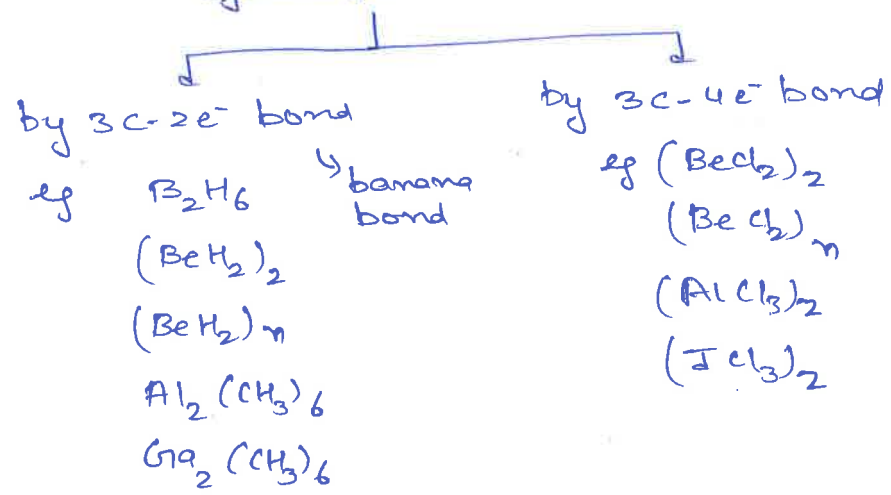
✓ (D) AlCl_3

- Q) 2c-2e⁻ bonds is/are present in
- ✓(A) B₂H₆ ✓(B) Me₄B₂H₂
- ✓(C) BH₄⁻ ✓(D) Al₂Cl₆

Ans:-

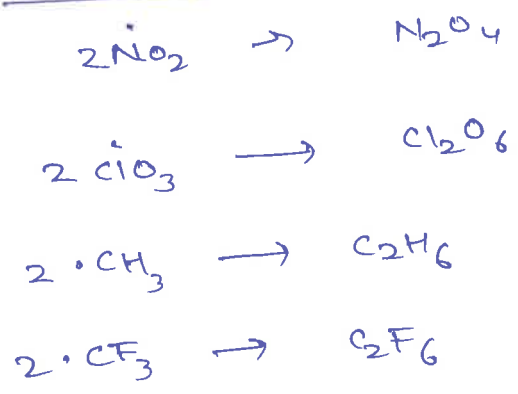
Dimmerisation | Polymerisation

Types of Dimmerisation



- Note | ① BCl₃, BB₃, BI₃ don't form dimer due to smaller size of Boron & larger size of halogen. (due to more steric repulsion).
- ② BF₃ Can't form dimer due to presence of back-bonding.
- ③ AlF₃ Can't form dimer due to ionic nature. (Cation, anion octet is completed)

2c-2e- bond



(No need of vacant orbitals in dimer formation)

