

Revise

Knades Rule

$B_n h_n$

SEP

$Bh = 2e^0$
 $B-h$
 $h \rightarrow 1e^0$

$n+1 = \text{Close}$
 $\text{Nodo} = n+2$
 $\text{Arach} = n+3$
 $\text{Hypo} = n+4$
 $\text{Knado} = n+5$

Structure Determination

STYX Code

S	T	Y	X
$B-h-B$	$B \begin{cases} B \\ B \end{cases}$	$B-B$	Bh_2

B₆H₁₀: ① Total Bonds = $\frac{3B+H}{2} = \frac{3 \times 6 + 10}{2} = \frac{28}{2} = \textcircled{14}$

② $3C-2e^- = \text{No. of } B = 6$

③ $2C-2e^- = \frac{B+H}{2} = \frac{6+10}{2} = \frac{16}{2} = \textcircled{8}$

④ SEP = $n+2 = 6+2 = 8 e^- \text{ pair.}$

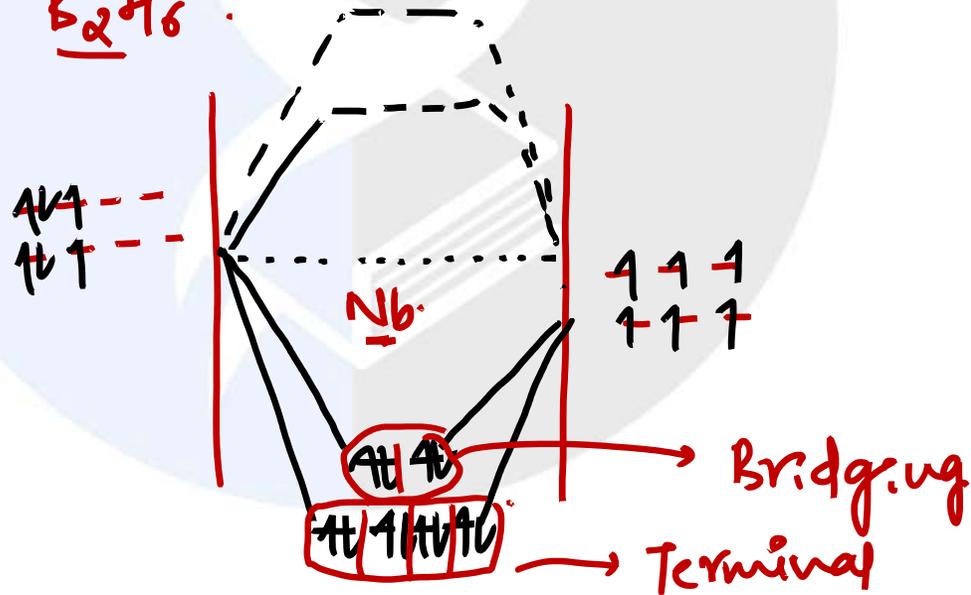
✓ Reactivity of Boranes:

- ① Acidity of "
- ② Thermal stability
- ③ Rxn with d.B.
- ④ Electrophilic Substn Rxn.
- ⑤ Cage Degradatn Rxn.
- ⑥ Deprotonatn rxn.
- ⑦ Base addition Rxn.
- ⑧ Carborane Synthesis.

① Acidity of Boranes :

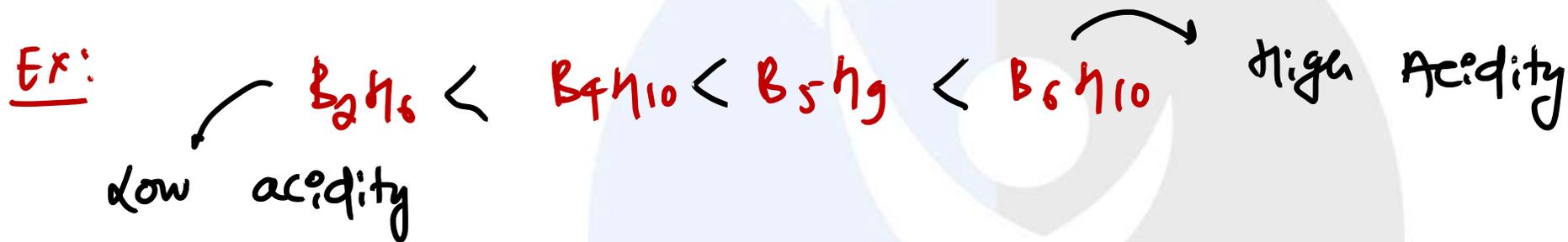
- ① M.O diagram of Borane
- ② size of borane
- ③ deapared change

① M.O diagram of B_2H_6 :



As No. of B atom \uparrow , NB MO \uparrow

\rightarrow If no. of empty non bonding orbital \uparrow Acidity \uparrow



② size of Boranes : — depends on delocalizatⁿ

$B_nH_m \xrightarrow{\text{deprotonat}^n} (B_nH_{m-1})^-$

If no. of B. atom \uparrow^s , delocalization \uparrow^s , Acidic strength \uparrow

③ Decaped change : — Applicable for same no. of B atom.

More open str \rightarrow More proton transfer
 \therefore (Arachno > Nido > Closo)

Ex: B_2H_6 Nido B_5H_9 Arachno B_5H_{11} B_6H_{10} $B_{10}H_{14}$

$B_{10}H_{14} > B_6H_{10} > B_5H_{11} > B_5H_9 > B_2H_6$

\rightarrow T.S: $B_2H_6 > B_5H_9 > B_5H_{11} > B_6H_{10} > \underline{B_{10}H_{14}}$

priority

① B \uparrow A.S \uparrow

② Arachno >

Nido > Closo.

② Thermal stability

$$T.S. \propto \frac{1}{\text{Rxtivity}} \propto \frac{1}{\text{Acidity}}$$

③ Rxn with Lewis Base :-

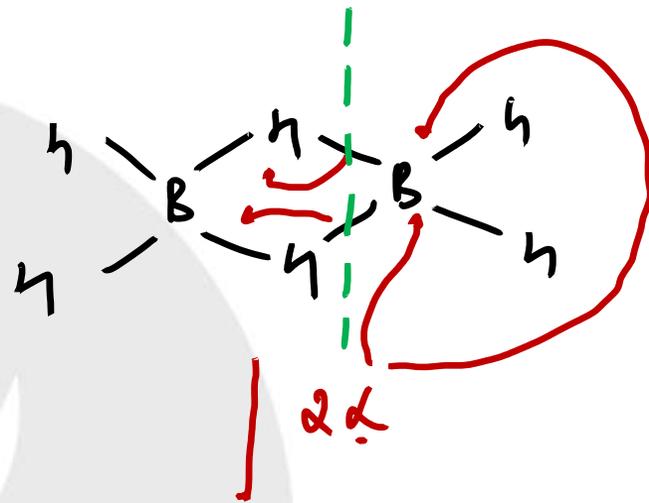
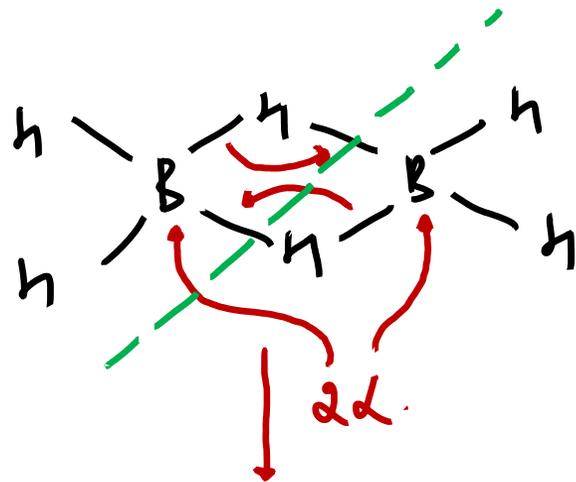
Types of rxn with L.B

① Cleavage Rxn.

② Deprotonation

③ Addition of Base

① Cleavage Rxn : — 2 types



Symm cleavage



Neutral product

In presence of soft/Bulkier ligand (Base)

Ex: $\text{NMe}_3, \text{NEt}_3, \text{PMe}_3, \text{PPh}_3, \text{SEt}_2$
 OR_2, CO

Unsymm Cleavage



Ionic product

In presence of hard/less bulkier ligand/Base

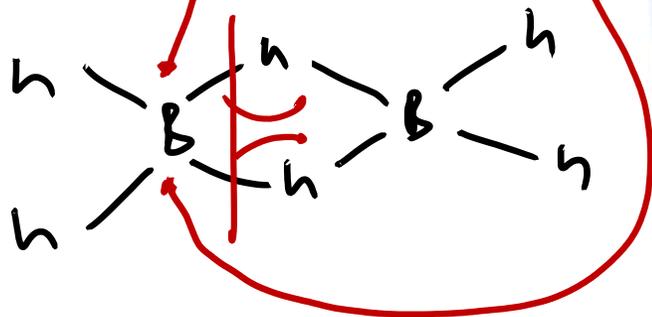
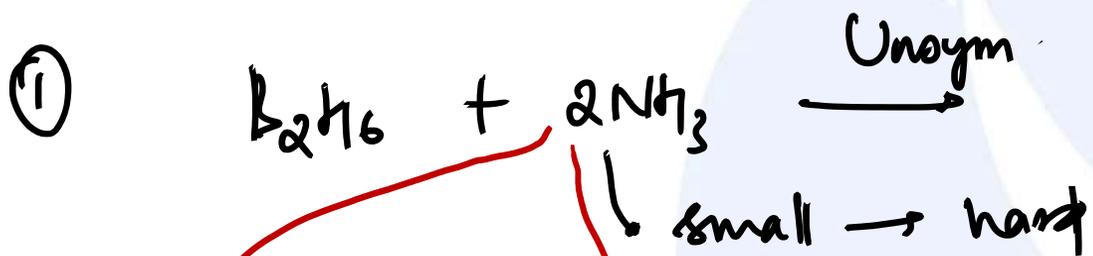
Ex: $\text{NH}_3, \text{OH}^-, \text{Na/Hg}, \text{K/Hg}$



$$2nI+1$$

$$= 2 \times 1 \times \frac{1}{2} + 1$$

$$= \textcircled{2}$$



$${}^1B = (n+1)$$

$$= 2+1 = \textcircled{3}$$

$${}^1H = 2nI+1$$

$$= 2 \times 1 \times \frac{3}{2} + 1 = \textcircled{4}$$



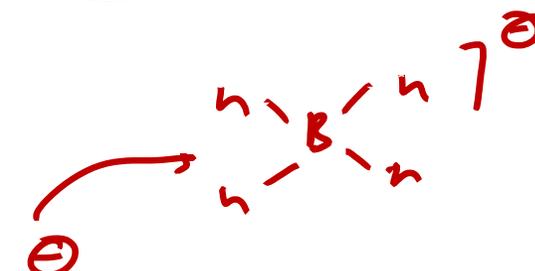
$${}^9B \text{ NMR} = 2nI+1$$

$$= n+1$$

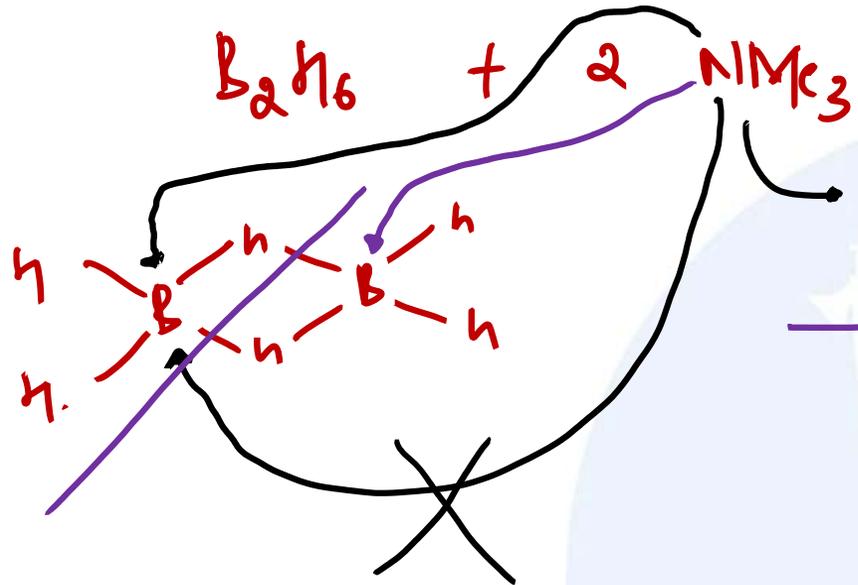
$$= 4+1 = \textcircled{5}$$

$${}^1H = 2nI+1$$

$$= 2 \times 1 \times \frac{3}{2} + 1 = \textcircled{4}$$



②



Sym. Cleavage

$B_2H_6 \rightarrow 2 BH_3$

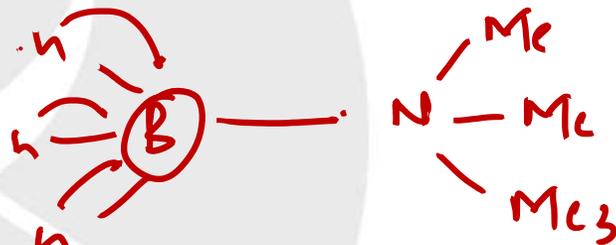
$2 BH_3 \cdot NMe_3$

$H \rightarrow I = \frac{1}{2}$
 $B \rightarrow I = \frac{3}{2}$

$n = 3$

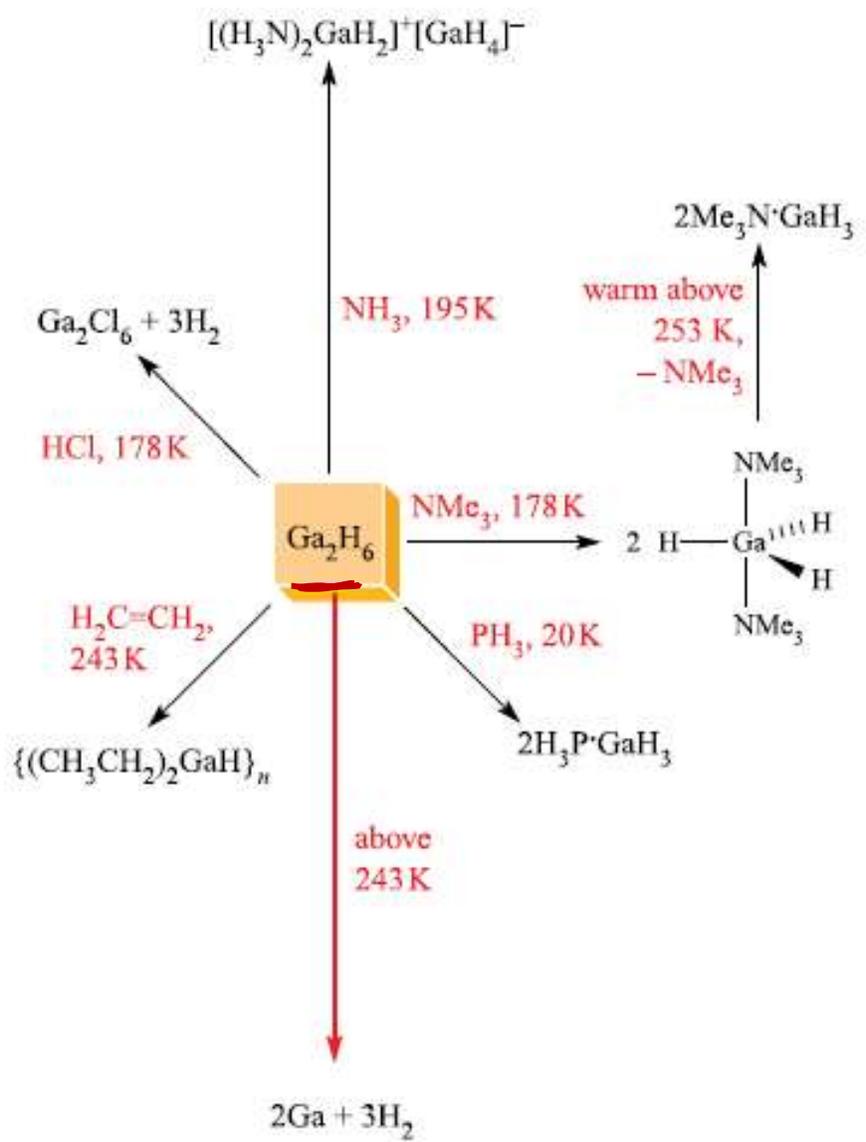
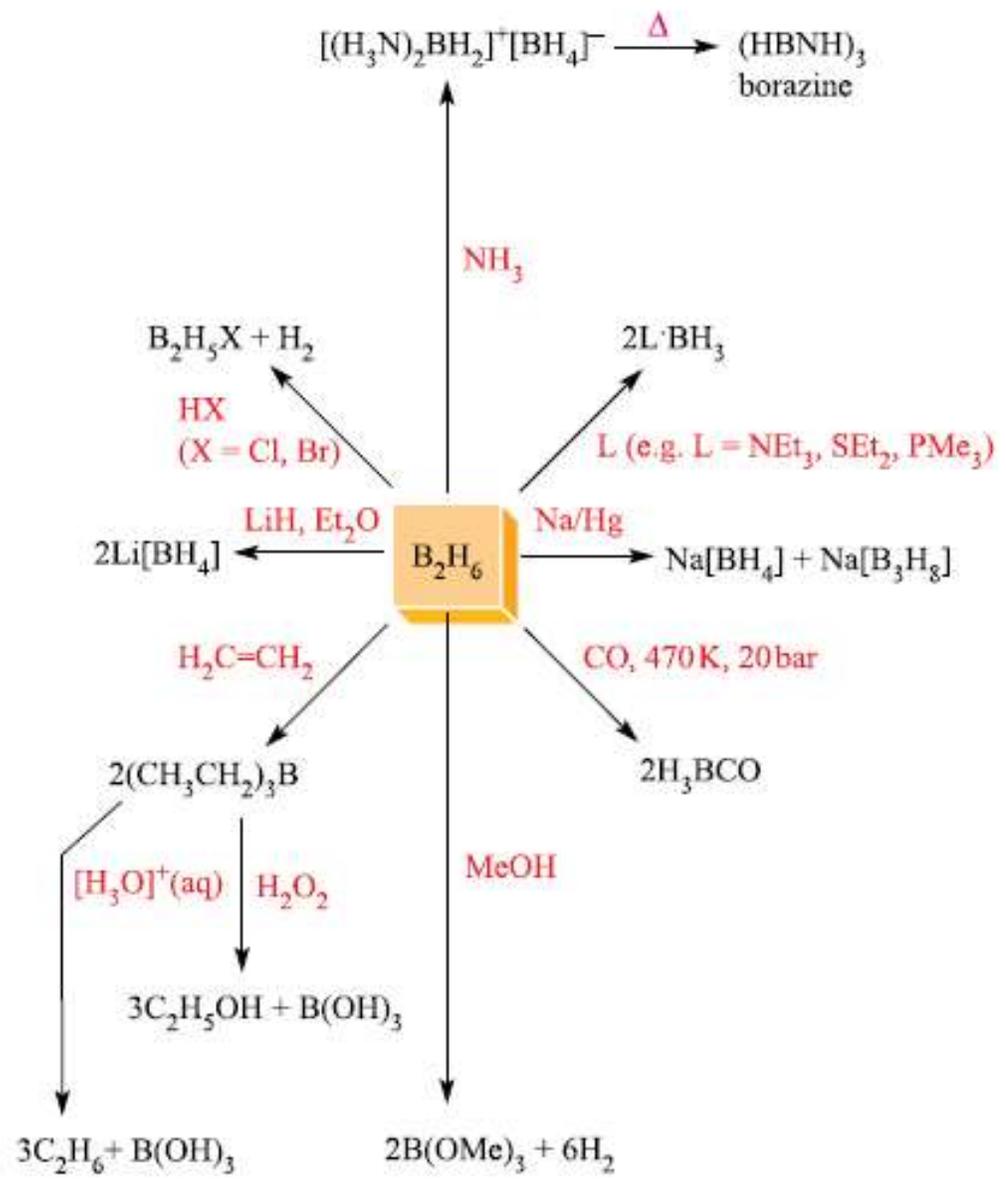
$B = 2nI + 1$
 $= 2 \times 3 \times \frac{1}{2} + 1$

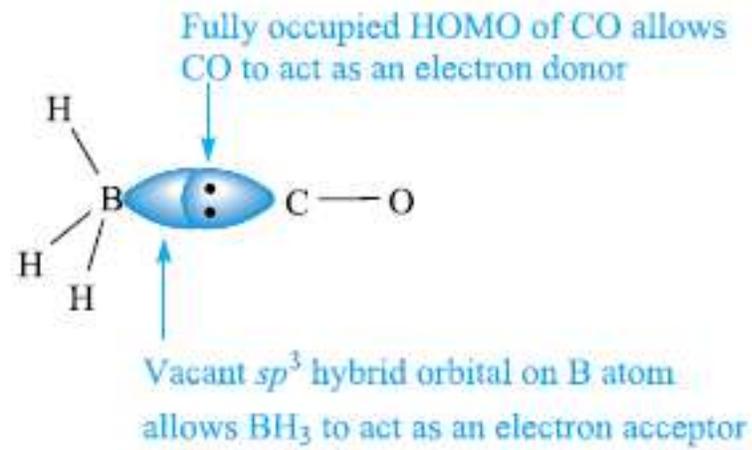
$= 4$



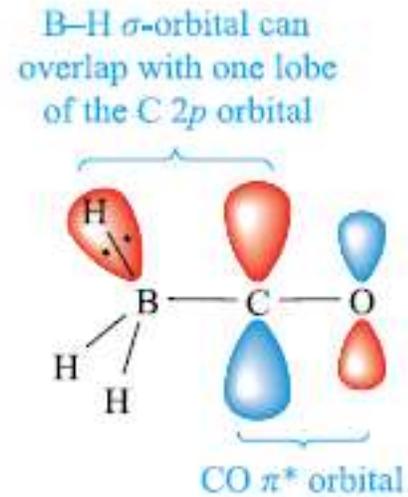
$n = 2nI + 1$
 $= 2 \times 1 \times \frac{3}{2} + 1$
 $= 4$

Ga₂H₆: ① Rapidly decomposes.

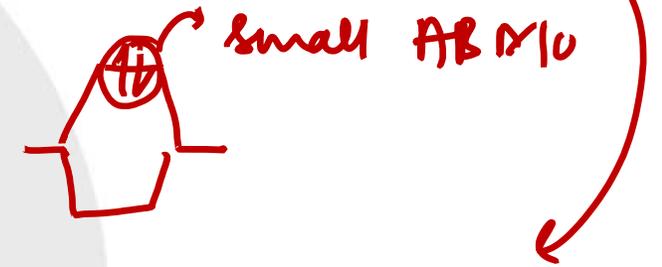
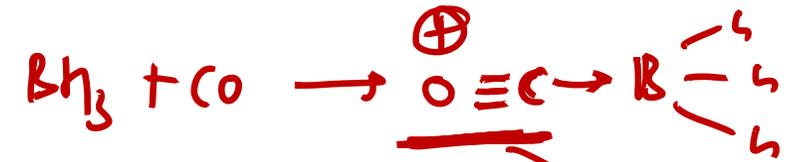




The LUMO of CO is a π^* orbital (Fig. 2.15). This orbital can act as an electron acceptor. Electrons can be donated from a B-H σ -bond (hyperconjugation):



The dominant effect is the σ -donation from CO to BH_3 .

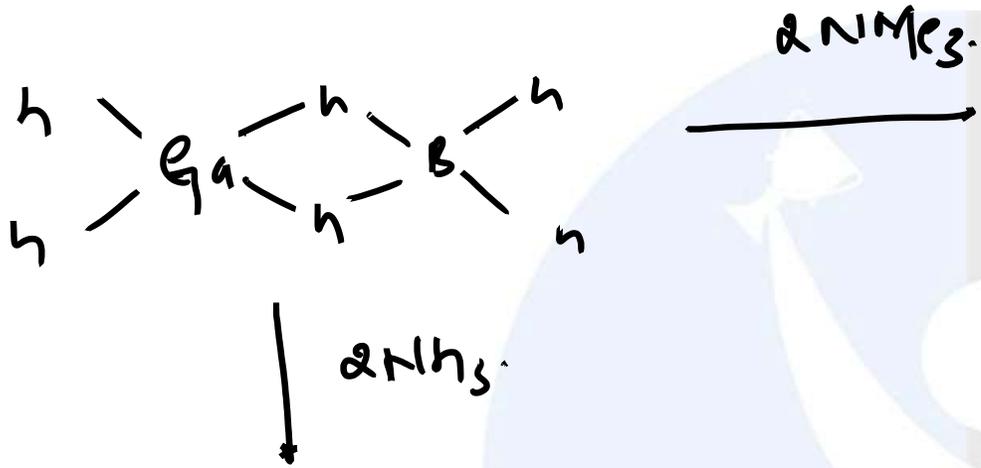


IR cm^{-1} greater than free CO
 $\rightarrow 2143 \text{ cm}^{-1}$

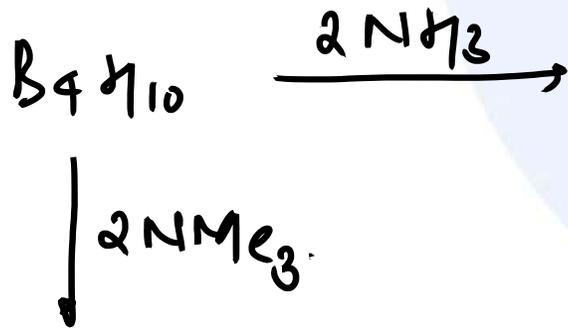
- ① $\text{Ga}_2\text{H}_6 \rightarrow$ rapidly decomposes while B_2H_6 does not.
- ② Ga_2H_6 & B_2H_6 both react with HCl but in case of borane substituents of a terminal H by Cl is observed. where as both terminal & bridging H atoms can be replaced in Ga_2H_6
- ③ Ga_2H_6 is like B_2H_6 in that it reacts with L.B.

HW

①



②



Thank you

