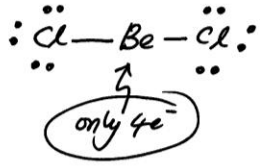
ELECTRON-DEFICIENT MOLECULES

1. Octet rule is used for most molecules with 2nd row (Period 2) central atoms.
2. There are 3 group of molecules which do not obey octet rule:

a) Electron-Deficient Molecules. (fewer than $8e^-$)

eg. Be or B as central atom: $BeCl_2$; BF_3.

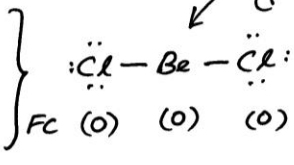
$BeCl_2$: - No. of valence e's $= [1 \times Be(2e^-)] + [2 \times Cl(7e^-)]$
$= (2 + 14)e^- = 16e^-$



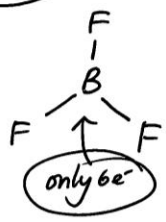
Be 2-2
Cl 2-8-7

- Balance e's $= 16e^- - \underbrace{2(2e^-)}_{\text{bonding e's}}$
$= (16-4)e^- = 12e^-$

(0 dot + 2 lines)
FC of Be $= 2 - 2 = 0$
FC of Cl $= 7 - 7 = 0$
(6 dots + 1 line)



BF_3: No. of valence e's $= [1 \times Be(3e^-)] + [3 \times F(7e^-)]$
$= 3e^- + 21e^- = 24e^-$

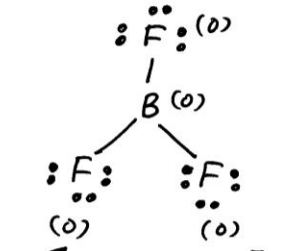


B 2-3
F 2-7

- Balance e's $= 24e^- - \underbrace{3(2e^-)}_{\text{bonding e's}} = (24-6)e^-$
$= 18e^-$

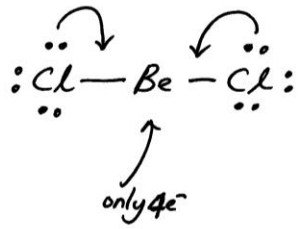
- Remaining $18e^-$ should be assigned to the three terminal F atoms.

(0 dot + 3 lines)
FC of B $= 3 - 3 = 0$
(6 dots + 1 line)
FC of F $= 7 - 7 = 0$



Formal charge, FC

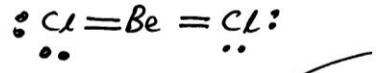
Very stable (FC is very low)



Why!!

Why don't lone pair from the terminal (surrounding) halogen, Cl atom form double bond to the central atom - Be so that Be can has 8e⁻ (octet) ??

If these shifting of lone pairs occurs, then the following structure is obtained:



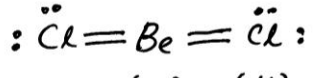
Be
2.2

Cl
2.8.7

FC of Be = 2 − 4 = −2 (0 dot + 4 lines)

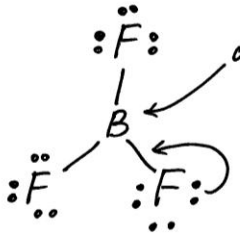
FC of Cl = 7 − 6 = +1 (4 dots + 2 lines)

large FC ∴ not favorable →



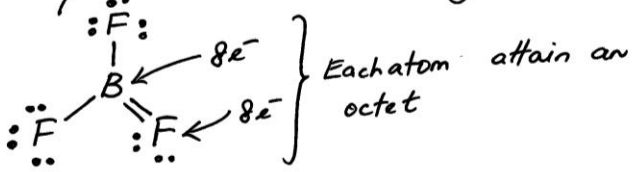
EN (Be) = 1.5
EN (Cl) = 3.0

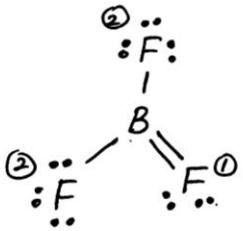
* This structure is unlikely – because the formal charge of Cl is (+1) which is unlikely due to electronegativity of Cl (3.0) is higher than Be (1.5)
(* Negative formal charges should reside on the more electronegative atoms)



Why don't one lone pair from the terminal atom, F form a double bond to the central atom, B so that all the atoms B & F can attain octet ??

If shifting of lone pair occurs, the following structure is obtained:





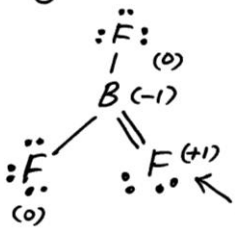
FC of B = 3 − 4 = −1 (0 dot + 4 lines)

FC of $F_{①}$ = 7 − 6 = +1 (4 dots + 2 lines)

FC of $F_{②}$ = 7 − 7 = 0 (6 dots + 1 line)

B (2.3)

F (2.7)



not favorable (should be negative FC 'cos EN of F = 4.0)

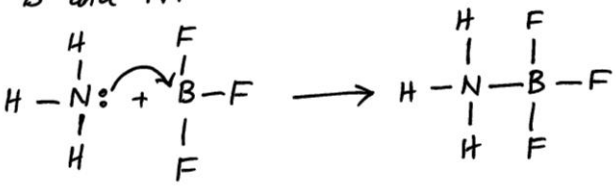
electronegativity

EN (B) = 2.0

EN (F) = 4.0

* Some data for BF_3 show a shorter than expected B–F bond. Shorter bonds indicate double bond character. So the structure with B=F bond may be a minor contributor to a resonance hybrid.

* BF_3 is very reactive. It readily combine with NH_3 to form a compound with the formula BF_3NH_3.
In this case, the nitrogen lone pair provides both of the shared electrons, resulting in an octet of electrons for both B and N.



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