(26) **Today**

Chap 6 Acid-Base and Donor-Acceptor Chemistry

Next Class (27)

Chap 6 Acid-Base and Donor-Acceptor Chemistry

Chap 9.1 Introduction to Coordination Chemistry

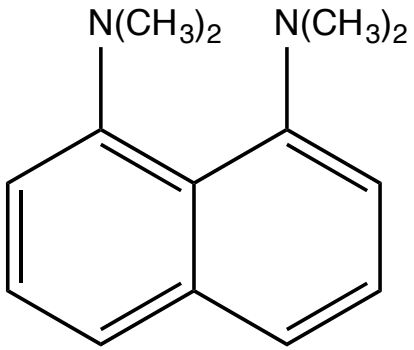
(28) **Second Class from Today**

Chap 9.1 Introduction to Coordination Chemistry

Third Class from Today (29)

Test 3 ?

1 $CH_3CH_2CH_2CH_2Li$



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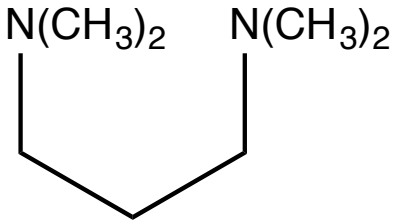

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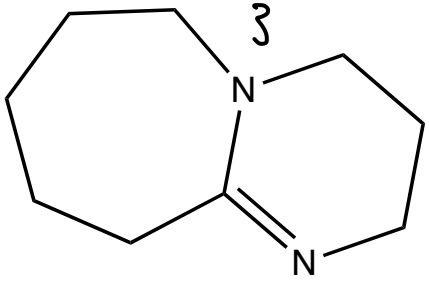

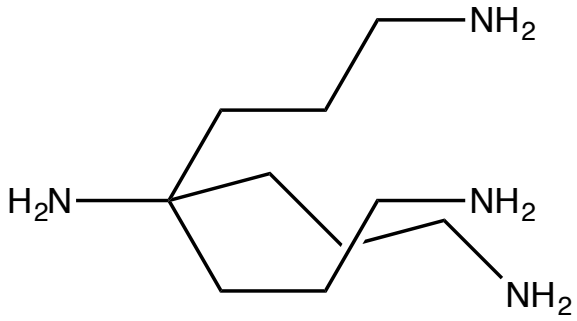

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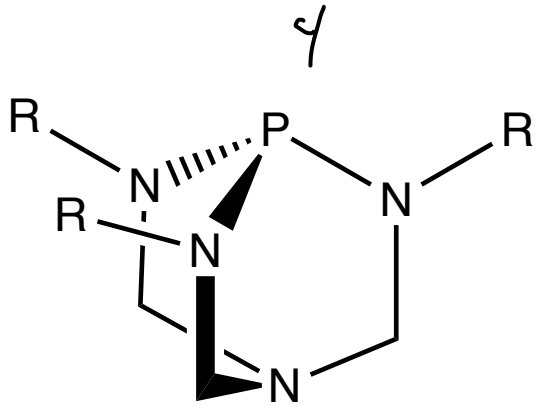


$CH_3CH_2CH_2CH_2Li$

not formed from direct abstraction of an H^+ from butane

$$CH_3CH_2CH_2CH_2Cl + 2\,Li \rightarrow CH_3CH_2CH_2CH_2Li + LiCl$$

methyl lithium can be prepared similarly

$$CH_3Cl + 2\,Li \rightarrow CH_3Li + LiCl$$

dangerous... will react with water and moisture in air to form flamable gases + heat which can lead to fires and explosions if precautions are not taken

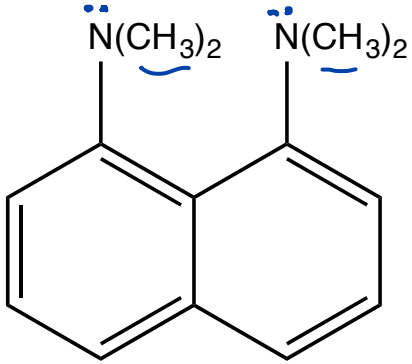
react like $:CH_3^{\ominus}$ + $:CH_2CH_2CH_2CH_3^{\ominus}$

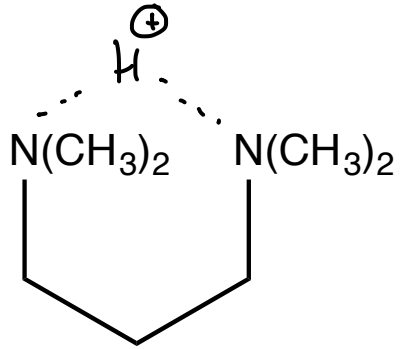
another downside to these super bases is that they are relatively small and can perform nucleophilic attacks on electrophiles in addition to acting like a base

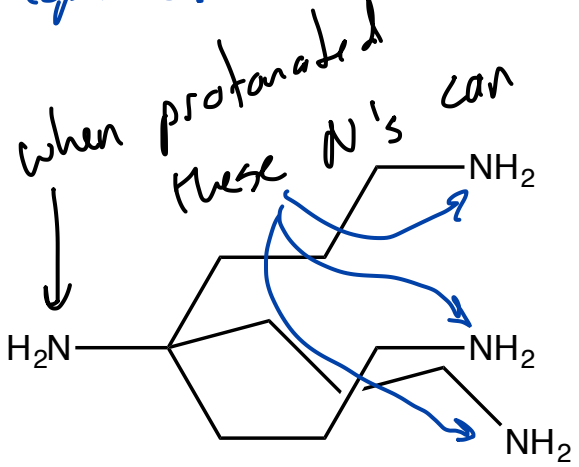
irreversible, product is a gas + leaves the reaction solution

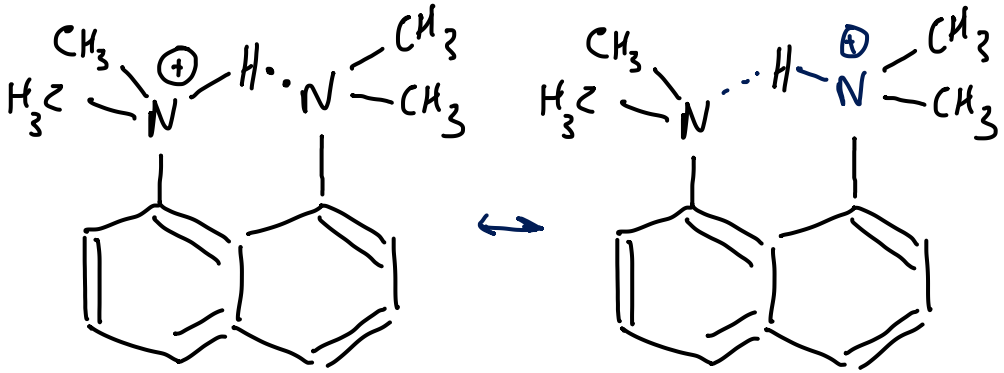
$$CH_3Li + H:base \rightarrow CH_4 + Li^{\oplus}\,{}^{\ominus}:base$$

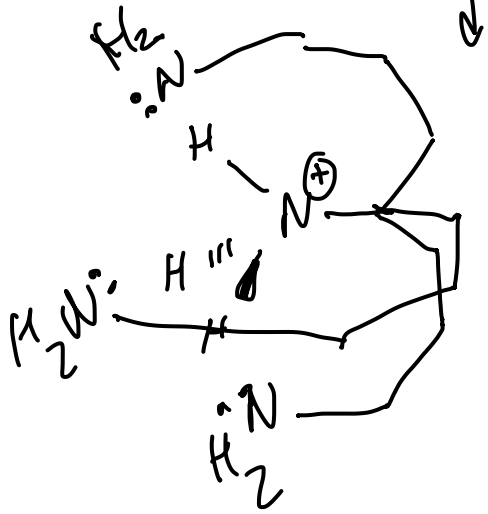
Super bases a lot bigger... more organic material around the N, so they are not good at being nucleophiles. Section 6.3.11





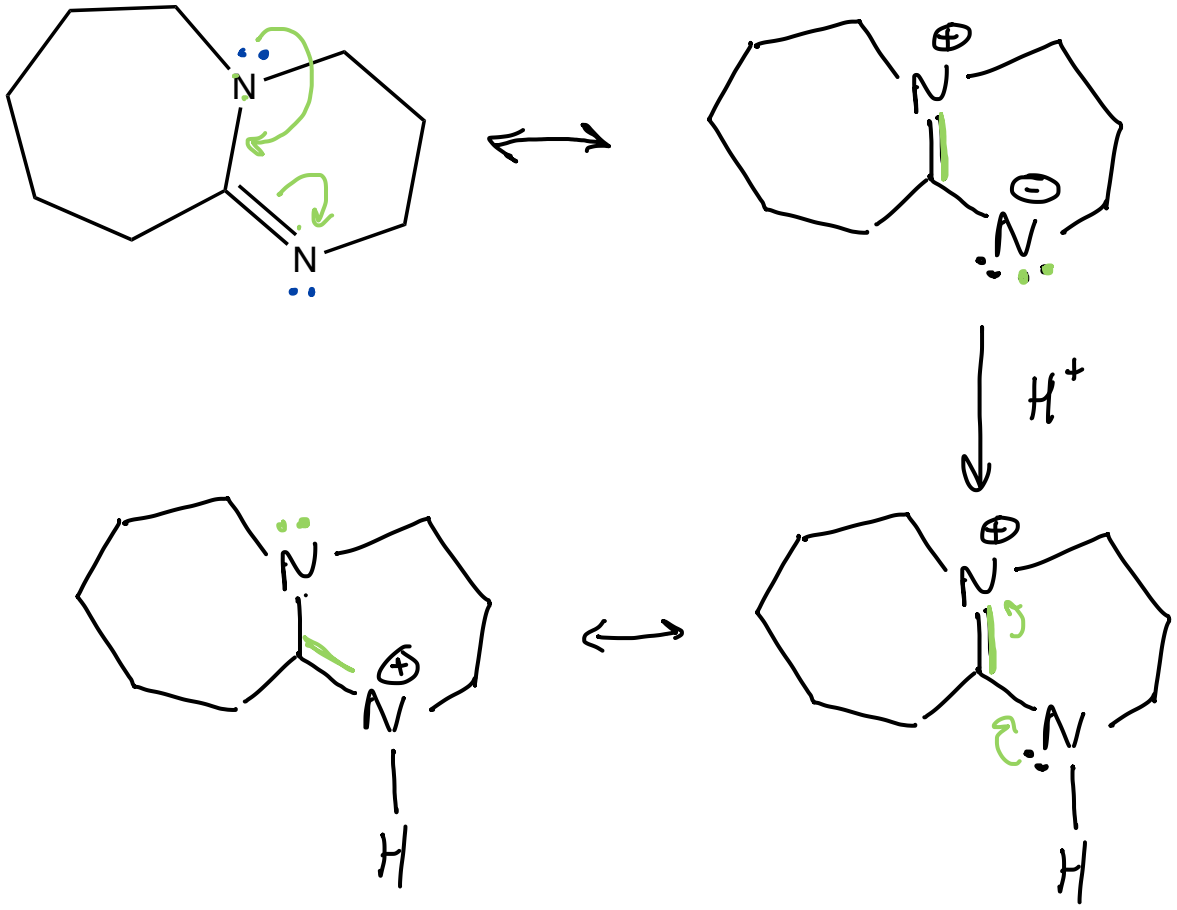




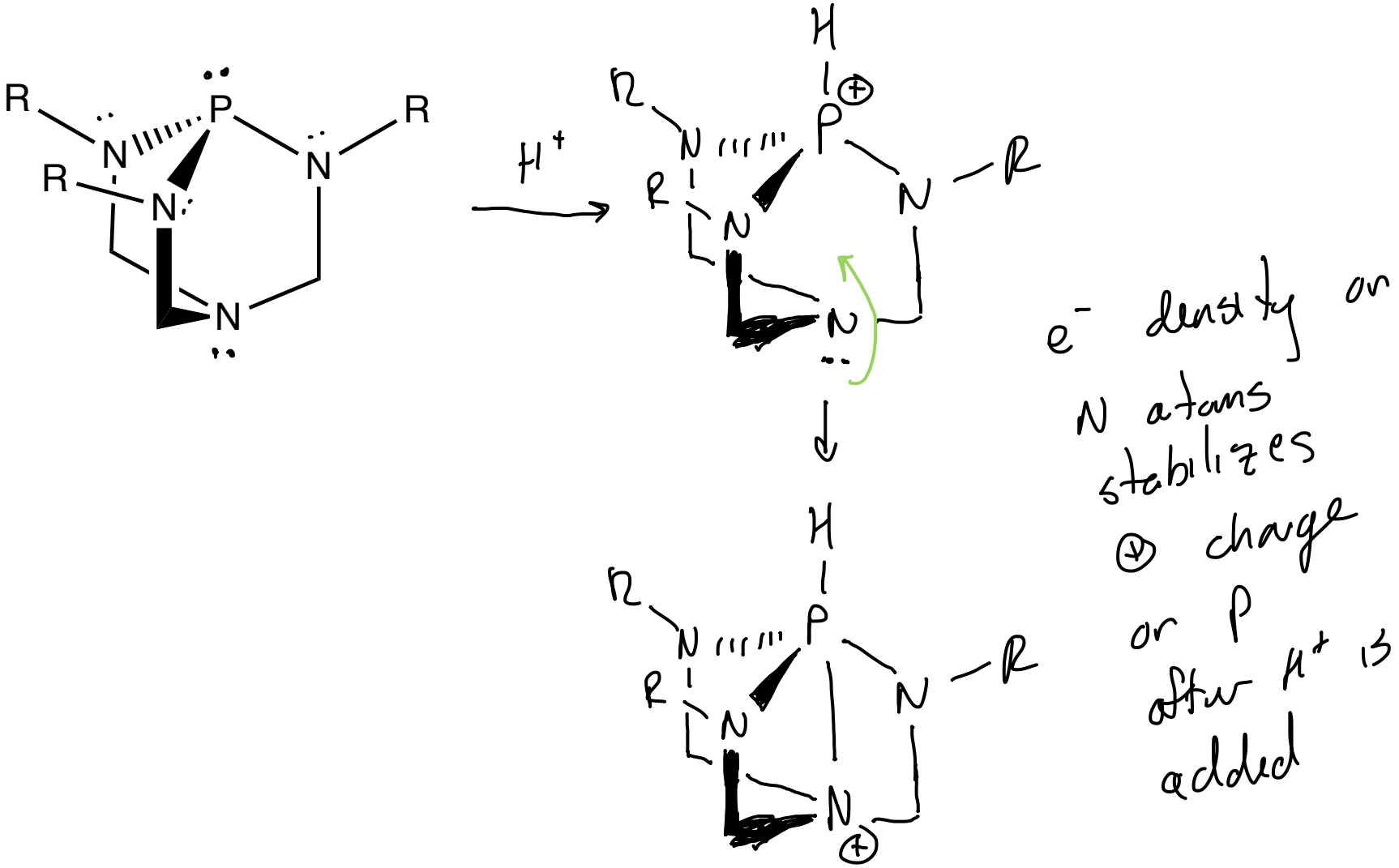


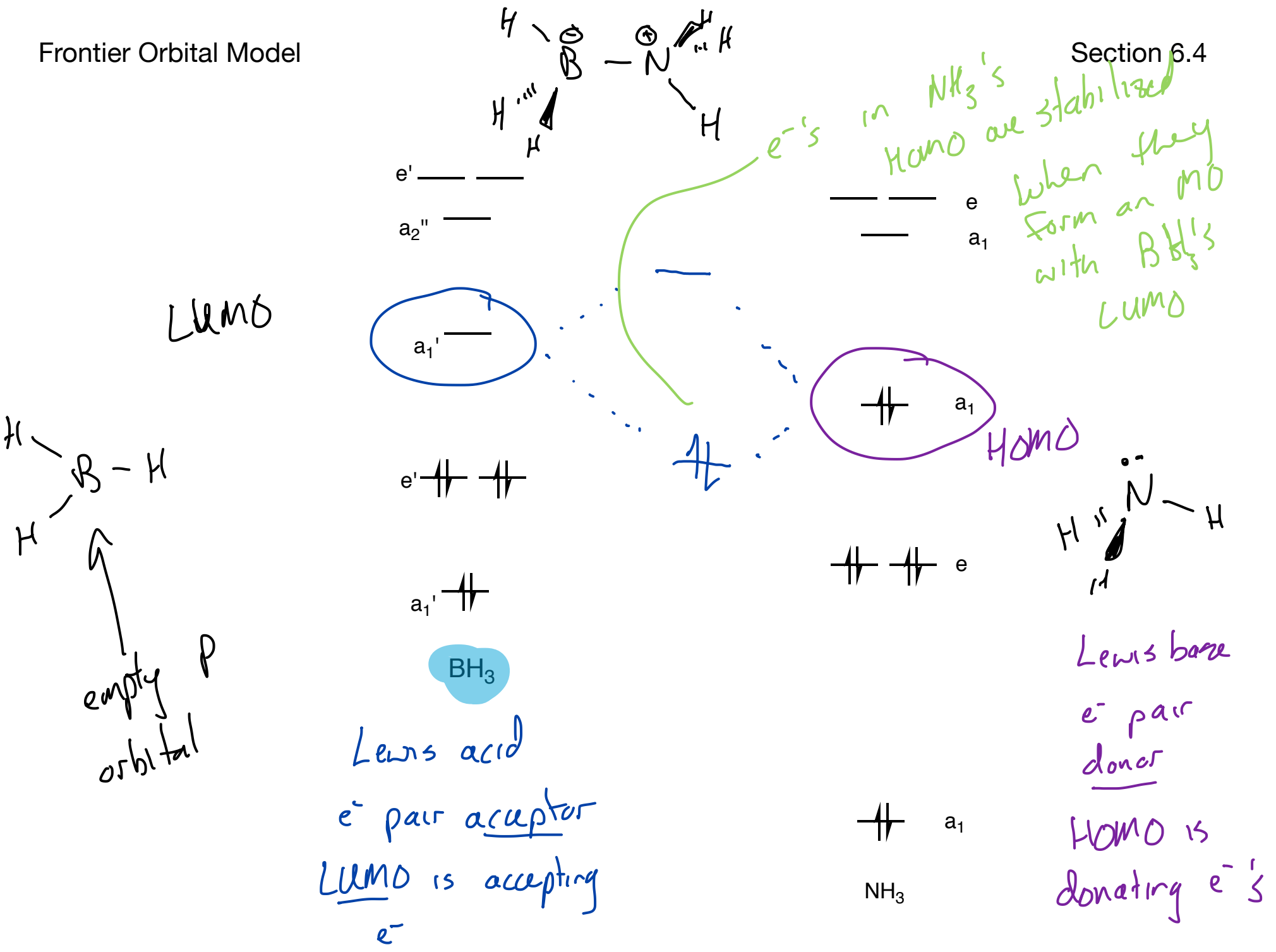
wrap around and stabilize the H⊕

green arrows are a way to visualize the formation of a resonance contributor

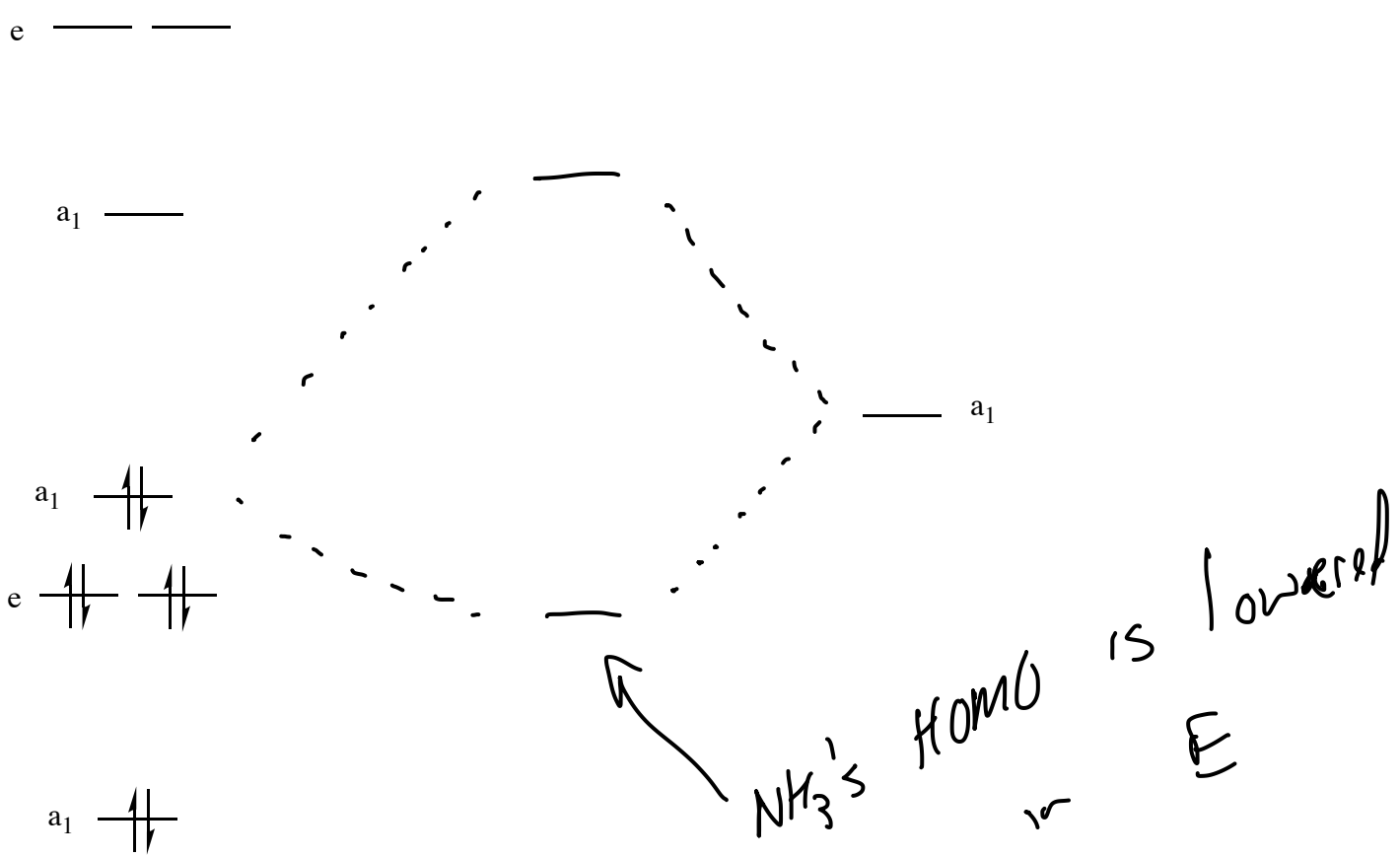


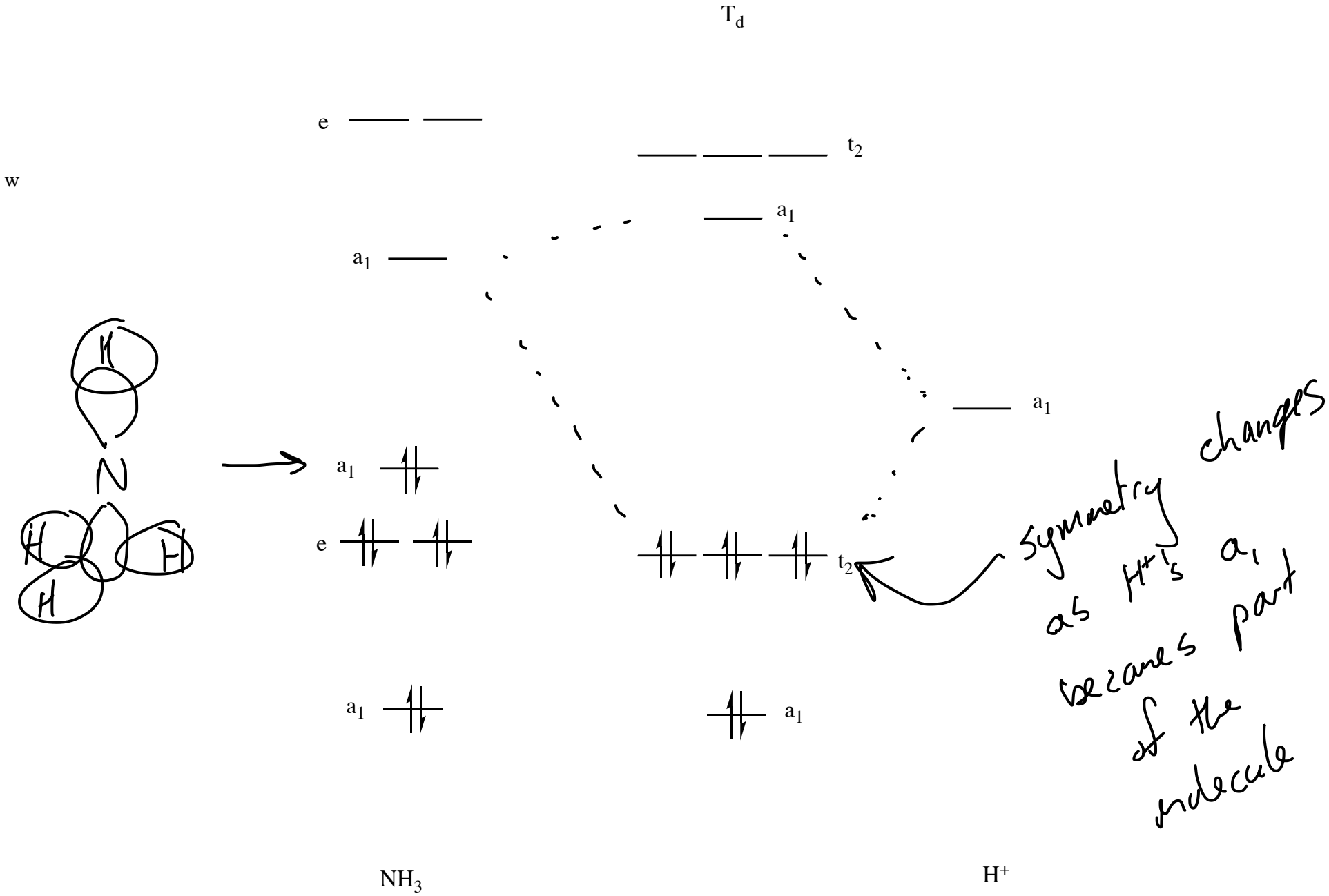
because of e⁻ delocalization, the ⊕ charge is spread out over 2 N atoms so the ⊕ charge is more stable


R
P
R
N
R
N
N
N
H+
H
R
N
P
R
N
N
R
N
e⁻ density on N atoms stabilizes ⊕ charge on P after H+ is added

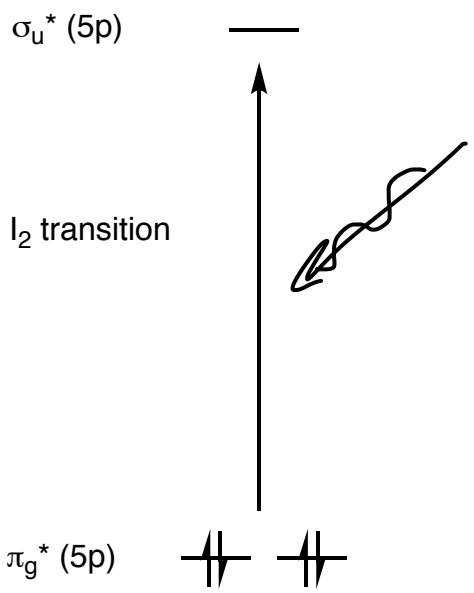

e'
a2"
LUMO
a1'
e'
a1'
BH3
empty p orbital
Lewis acid
e⁻ pair acceptor
LUMO is accepting e⁻
e⁻'s in NH3's HOMO are stabilized when they form an MO with BH3's LUMO
e
a1
a1
HOMO
e
a1
NH3
Lewis base
e⁻ pair donor
HOMO is donating e⁻'s

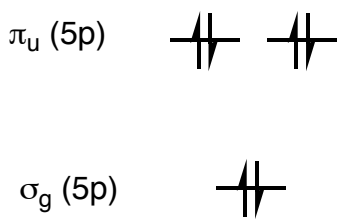
T_d




T_d
e
t_2
w
a_1
a_1
a_1
a_1
e
t_2
a_1
a_1
symmetry changes as H^+'s a_1 becomes part of the molecule
NH_3
H^+

I_2

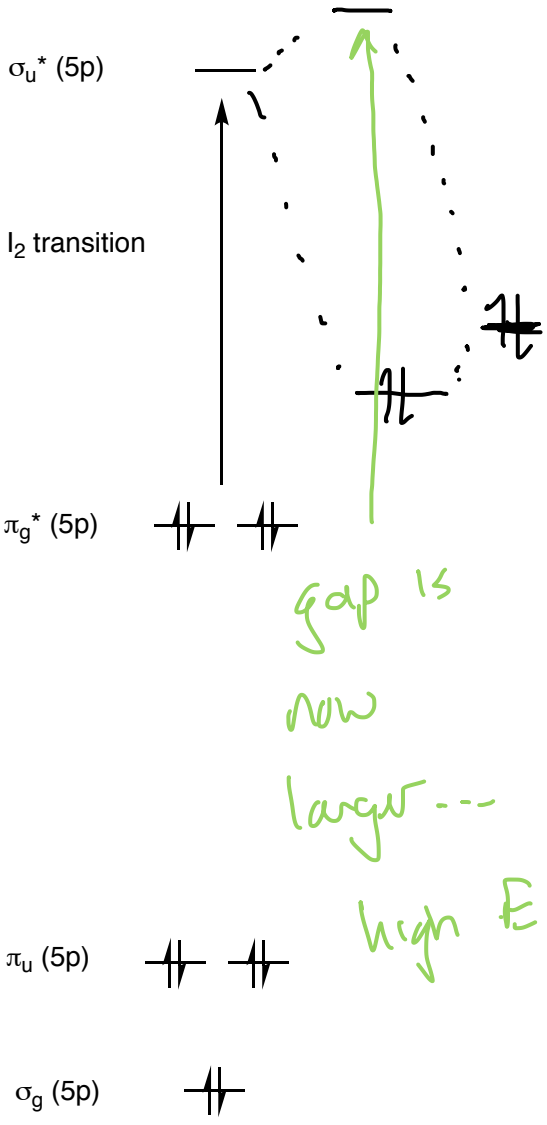




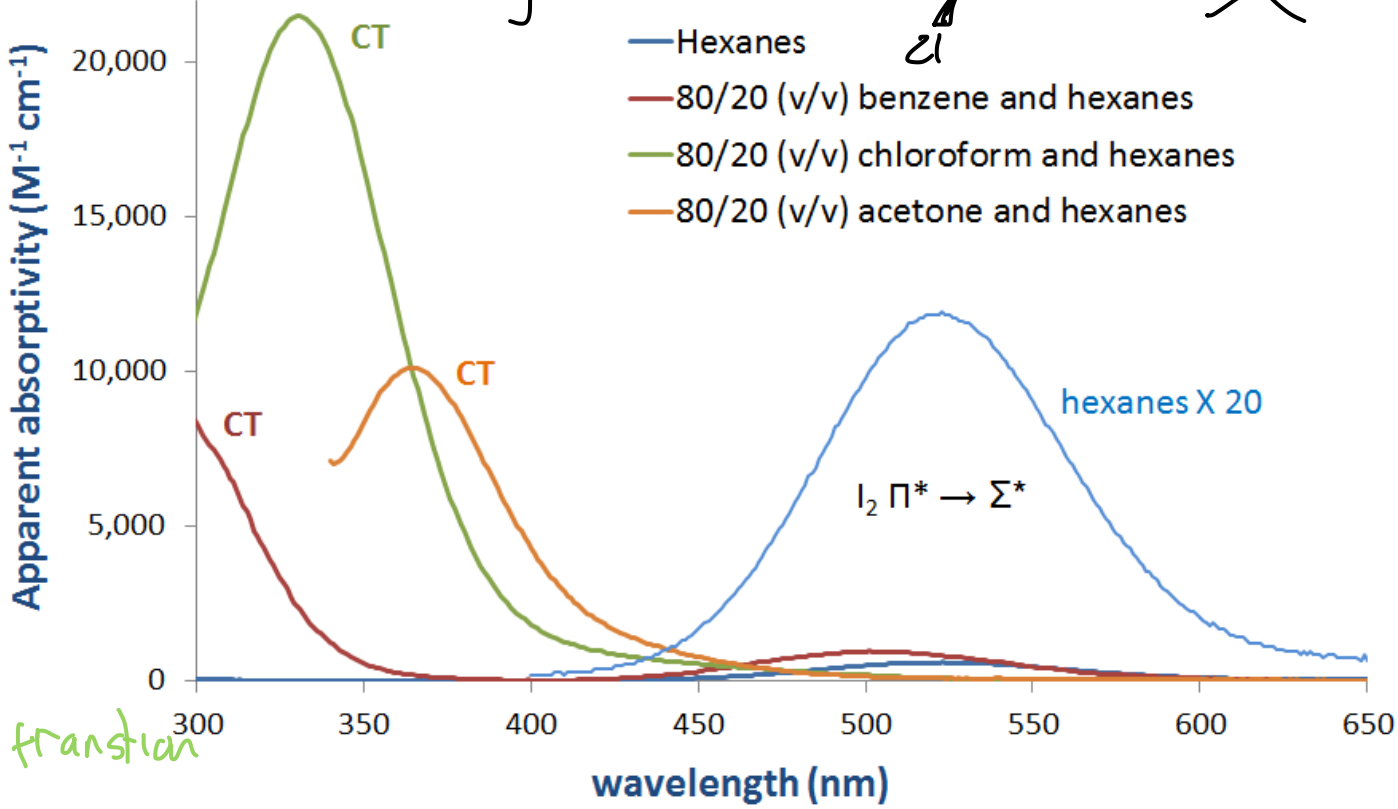
Frontier Orbital Model: Iodine

donor e⁻'s are stabilized by the formation of a bonding orbital

σ_u^* is destabilized as it is now antibonding



gap is now larger --- high E transition



https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Miessler_Fischer_Tarr)/06%3A_Acid-Base_and_Donor-Acceptor_Chemistry/6.04%3A_Lewis_Concept_and_Frontier_Orbitals/6.4.03%3A_The_electronic_spectra_of_charge_transfer_complexes_illustrate_the_impact_of_frontier_orbital_interactions_on_the_electronic_structure_of_Lewis-Acid_base_adducts.

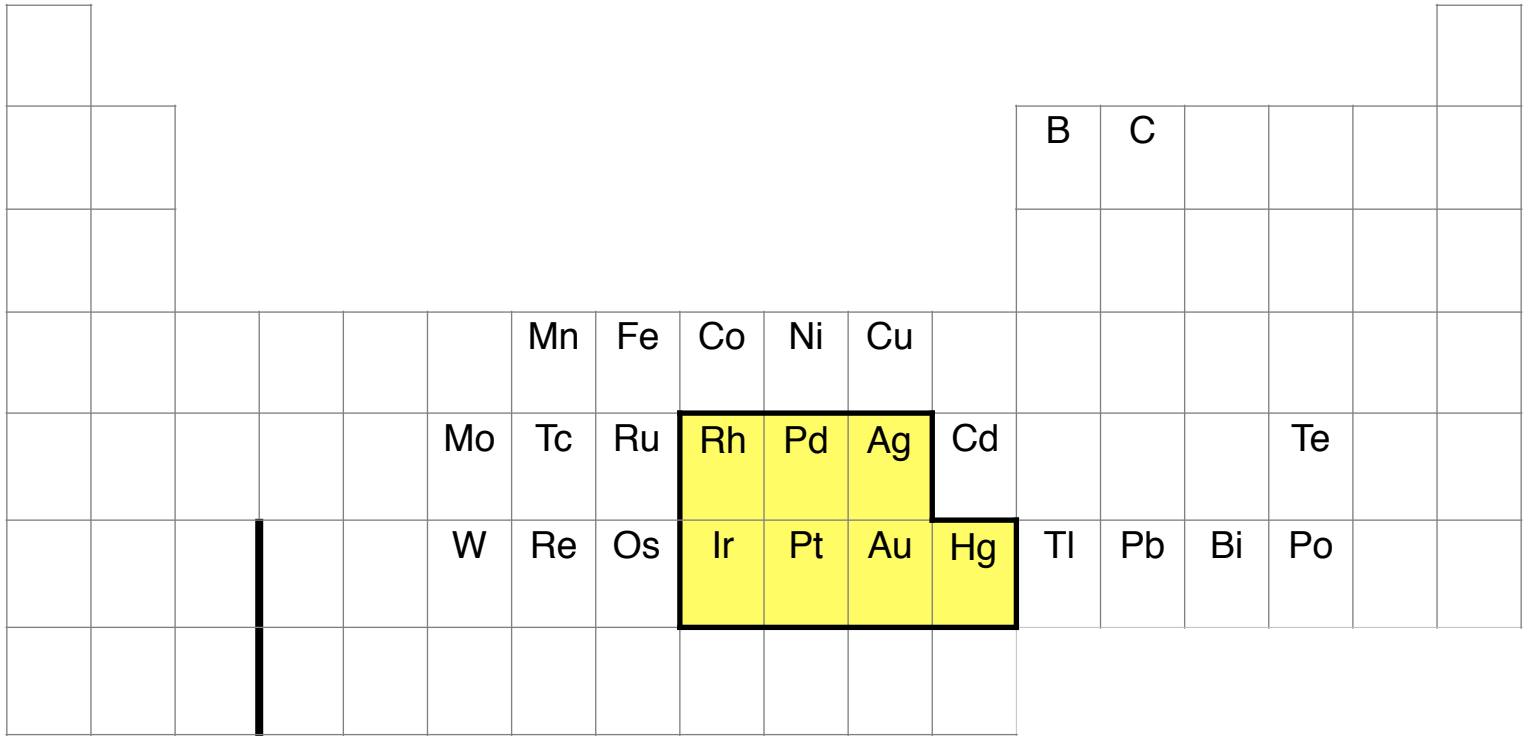
AgF	$K_{sp} = 205$
AgCl	$K_{sp} = 1.8 \times 10^{-10}$
AgBr	$K_{sp} = 5.2 \times 10^{-13}$
AgI	$K_{sp} = 8.3 \times 10^{-17}$

$[Hg(SCN)_4]^{2-}$ vs $[Zn(NCS)_4]^{2-}$

$[CH_3Hg(H_2O)]^+ + HCl \rightarrow CH_3HgCl + H_3O^+ \quad K = 1.8 \times 10^{12}$

$[CH_3Hg(H_2O)]^+ + HF \rightarrow CH_3HgF + H_3O^+ \quad K = 4.5 \times 10^{-2}$

$[Hg(SCN)_4]^{2-}$ vs $[Zn(NCS)_4]^{2-}$


B
C
Mn
Fe
Co
Ni
Cu
Mo
Tc
Ru
Rh
Pd
Ag
Cd
Te
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po

Hard Bases	Borderline Bases	Soft Bases
		H^-
F^-, Cl^-	Br^-	I^-
H_2O, OH^-, O^{2-}		H_2S, SH^-, S^{2-}
ROH, RO^-, R_2O, CH_3COO^-		RSH, RS^-, R_2S
NO_3^-, ClO_4^-	NO_2^-, N_3^-	SCN^-, CN^-, RNC, CO
CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	SO_3^{2-}	$S_2O_3^{2-}$
NH_3, RNH_2, N_2H_4	$C_6H_5NH_2$, C_5H_5N, N_2	PR_3, $P(OR)_3$, AsR_3, C_2H_4, C_6H_6

AgF	$K_{sp} = 205$
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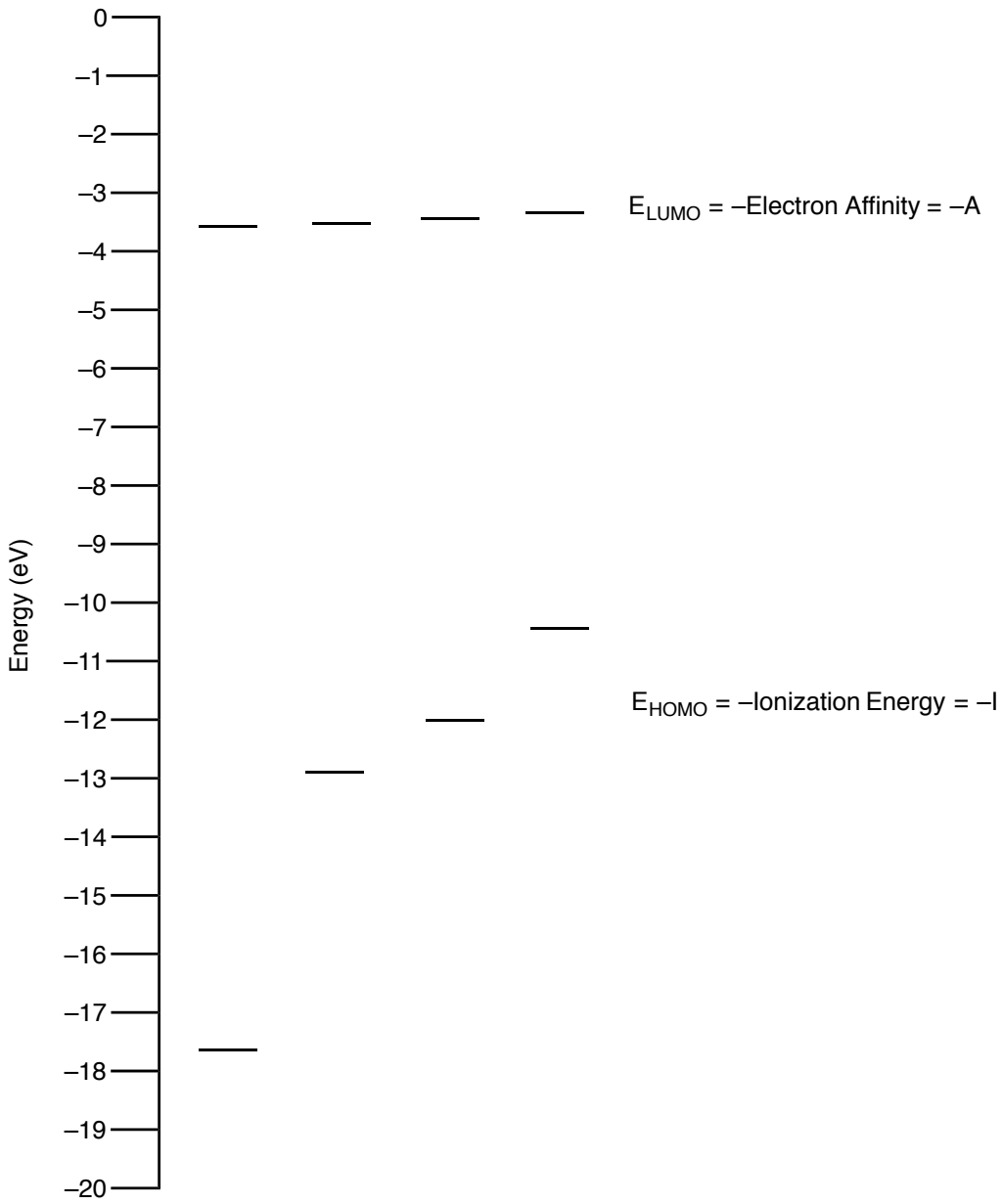
$[CH_3Hg(H_2O)]^+ + HCl \qquad CH_3HgCl + H_3O^+ \;\; K = 1.8 \times 10^{12}$

$[CH_3Hg(H_2O)]^+ + HF \qquad CH_3HgF + H_3O^+ \;\; K = 4.5 \times 10^{-2}$

$$\eta = \frac{I - A}{2}$$


0
–1
–2
–3
–4
–5
–6
–7
–8
–9
–10
–11
–12
–13
–14
–15
–16
–17
–18
–19
–20
Energy (eV)
E_{LUMO} = –Electron Affinity = –A
E_{HOMO} = –Ionization Energy = –I