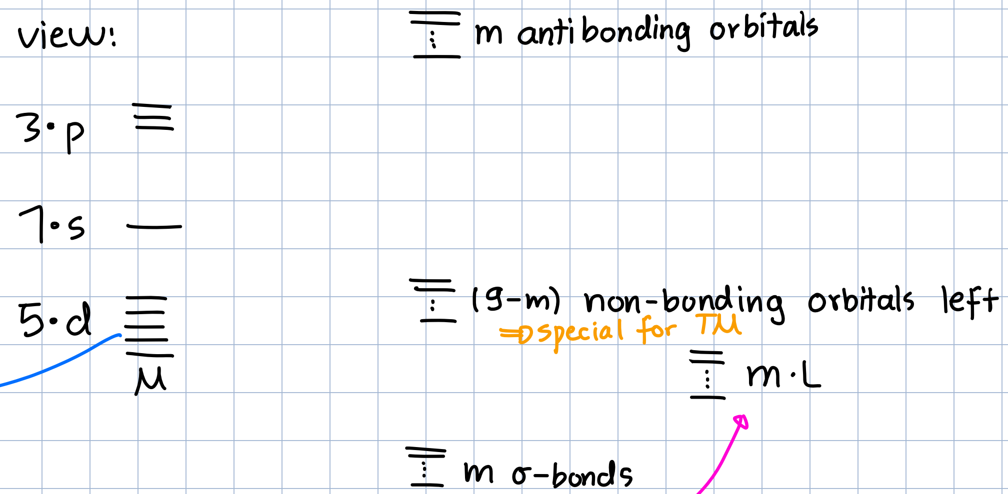
08.11.

Prof. C. Copéret takes over

$18e^-$ rule ⇒ He thinks its useless as catalysis is about active species

↳ Where does it come from?

Orbital view:



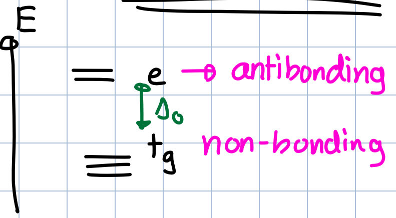
degeneracy won't exist, unless we are in gas phase ⇒ add some ligands (assume to be pure σ-donors)

octahedral complex very happy

⇒ ML_6 has $(9-6) = 3$ non-bonding orbitals ↔ d^6

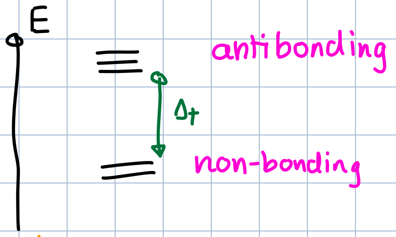
⇒ Adds up to 18 electrons

remember from ACI for ML_6 (O_h)



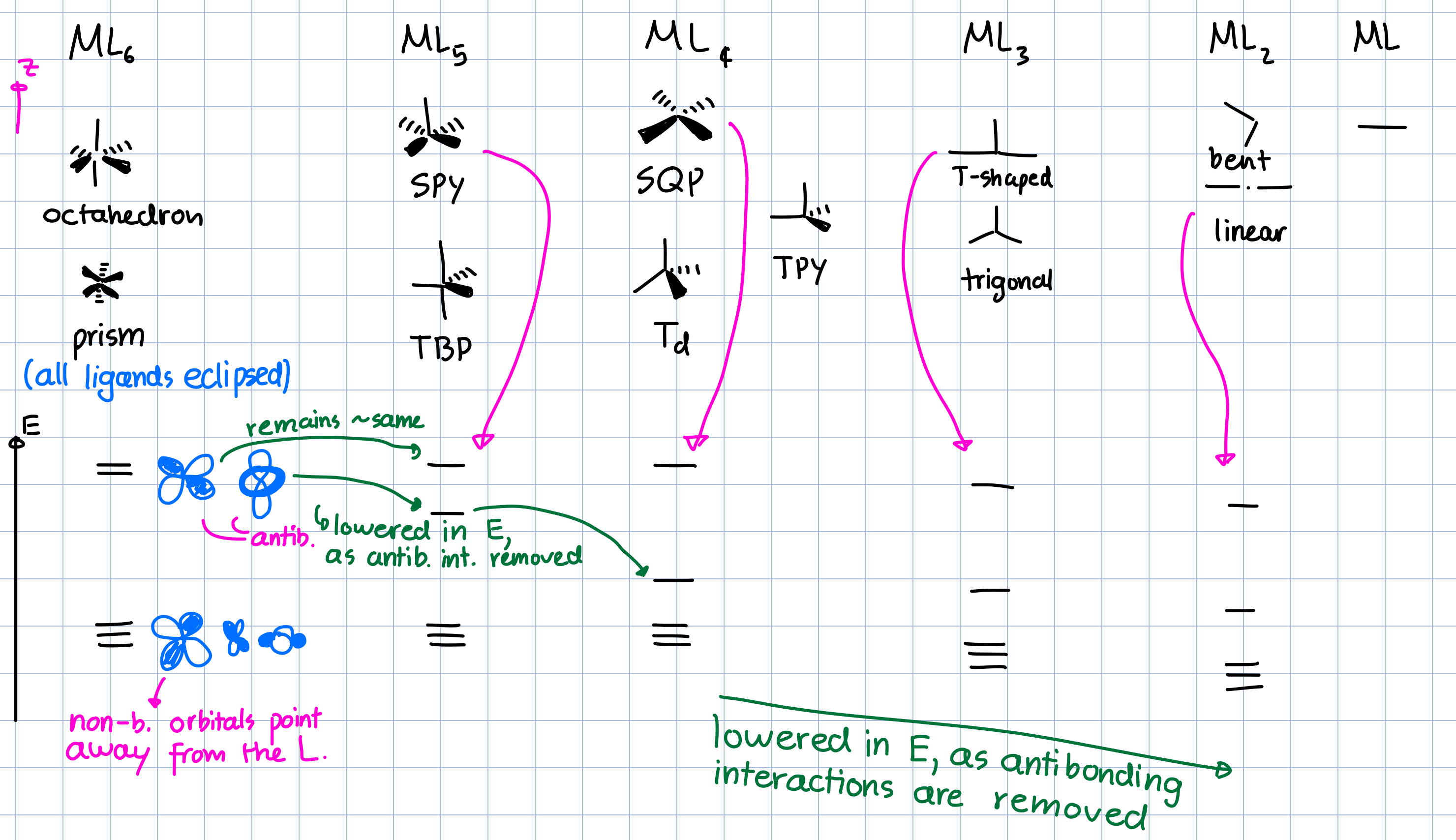
from crystal field theory

or for ML_4 (T_d)

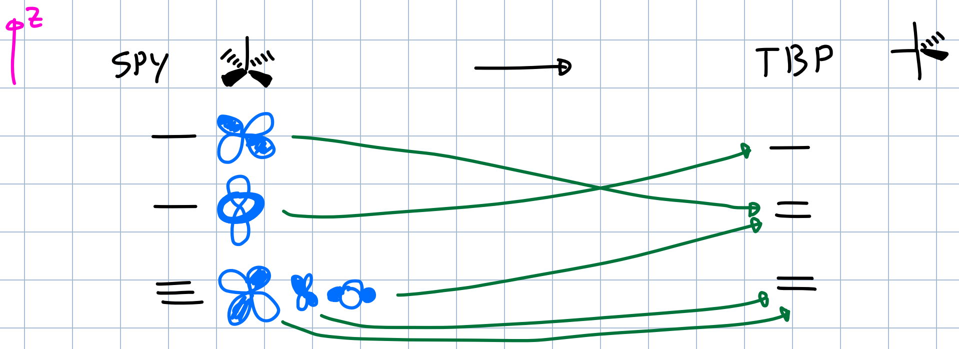


↳ there are more orbitals below & above, but we ignore them (they don't matter) and only consider the Frontier Molecular Orbitals (FMOs)

Geometries & MOs of ML_n



Walsh-diag.: Influence on MO diag. from changing angles in complex



⇒ Can derive MO diag. just from geom. structure

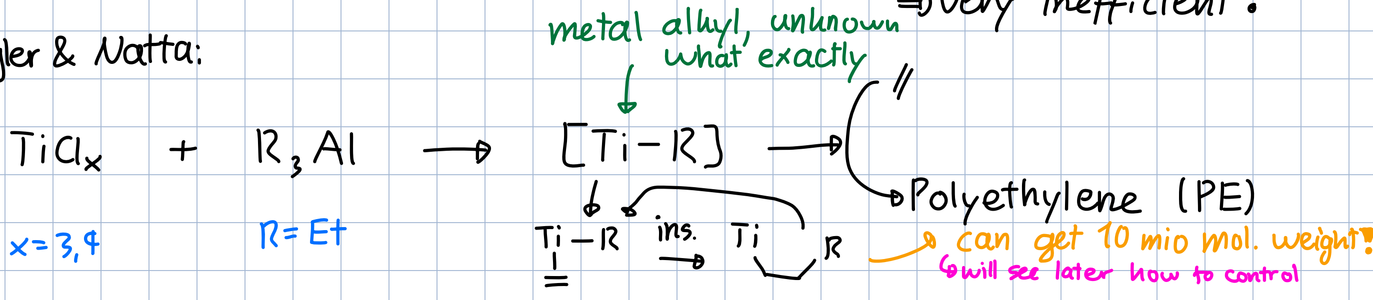
Now we want to find out more about the reactivity

"Organometallic chemistry – Compared to you – is old ⇒ discuss by history"

Metal-Alkyls

Very important e.g. for polymer manufacture. Before radical rxn ⇒ very inefficient!

↳ Ziegler & Natta:



↳ Further work

$WCl_6 \xrightarrow{MeLi} WMe_6$ (70's, Wilkinson)

$Cp_2ZrCl_2 + R_3Al \xrightarrow[\text{"}H_2O\text{"}]{=} PE$ (80's)

trace amount

MOA: don't know what it is exactly

⇒ If you buy that for a lab, you first test it

used on multimillion ton scale!

Synthesis

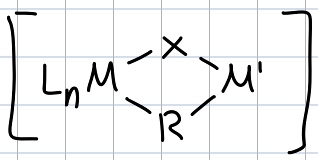
1. Transmetalation

$L_nM{-}X + RM' \longrightarrow L_nM{-}R + M'{-}X\downarrow$

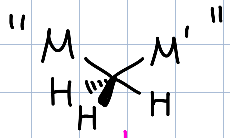
typically make a more polar bond ⇒ precipitates

$M' = Li, MgX, ZnX, AlX_2, SnX_3, \ldots$

TS:

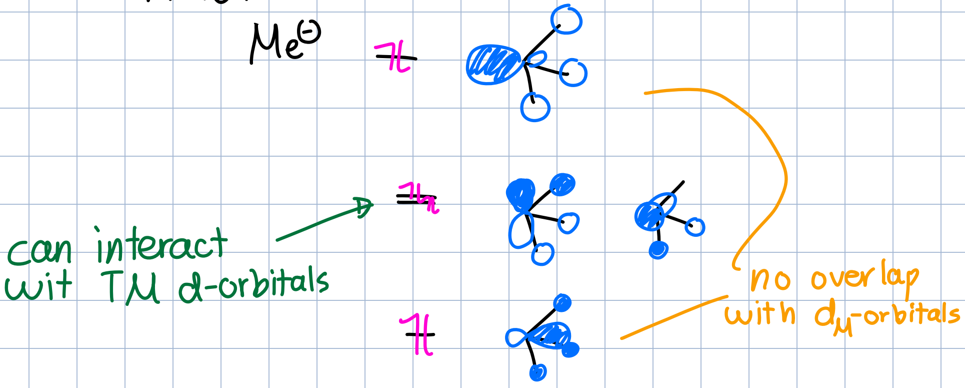


where



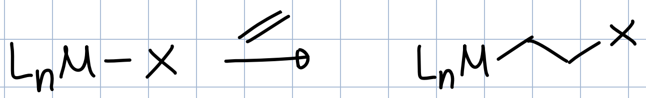
penta-coord. carbon ⇒ How is the octet rule still satisfied?

FMO:

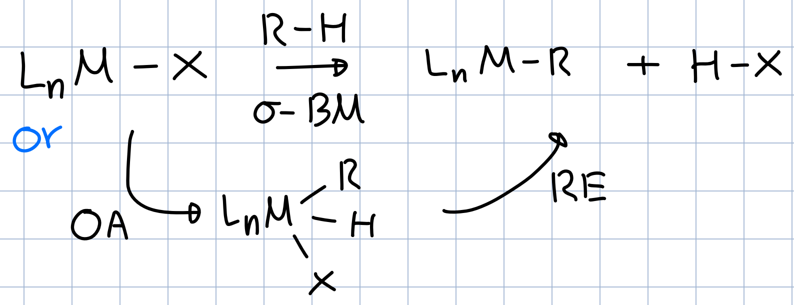


⇒ It's a 3-center, $4e^-$ interaction

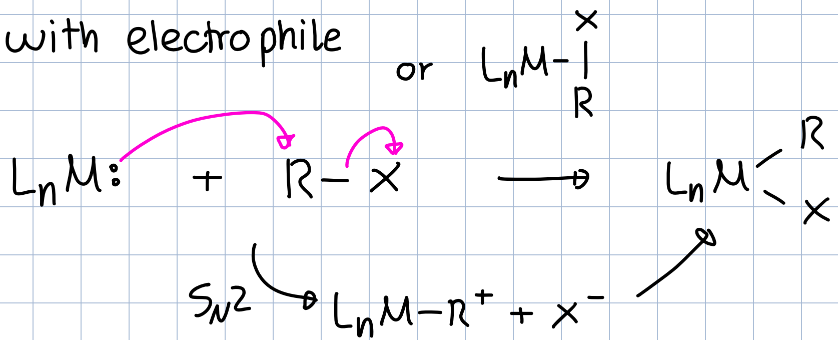
2. Insertion

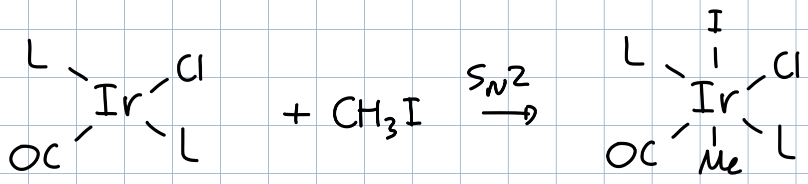


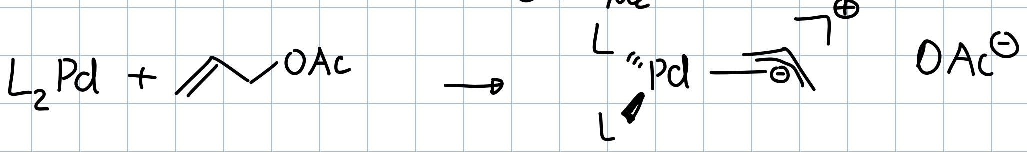
3. C-H Activation



4. Rxn with electrophile

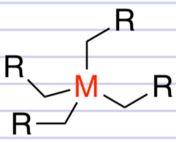




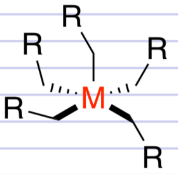


Classes

Late TM → d^6 to d^8 need extra ligands to stabilize

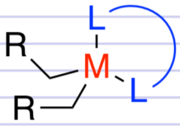


R = H for M = Ti, Zr, Hf
R = tBu for M = Ti, Zr, Hf, Cr
R = Ph for M = Zr, Hf



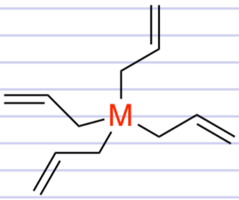
R = H for M = Ta, Mo
R = Ph for M = Ta

all d^0

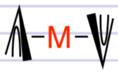


M = Mn - R = tBu
(no ligand, $Mn_2(CH_2R)_4$)

M = Mn, Fe, Ru, Co, Ni, Pd, Pt
with R = H and L2 =
tmeda, dppe, (COD), Pyridine…



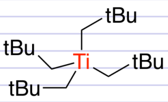
M = Ti, Zr, Hf
Nb, Mo, W

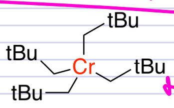


M = Ni, Pd, Pt

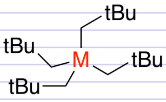
M = Cr, Re, Rh, Ir

α- H abstraction, decomposes ligand ⇒ highly insat MC bond

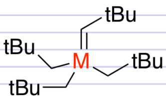




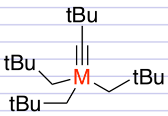
$CrCl_3$ + Organometal gives Cr(IV) (CC still doesn't underst.)



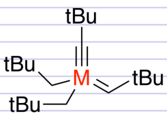
M = Zr, Hf



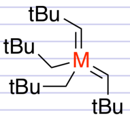
M = Nb, Ta



M = Mo, W



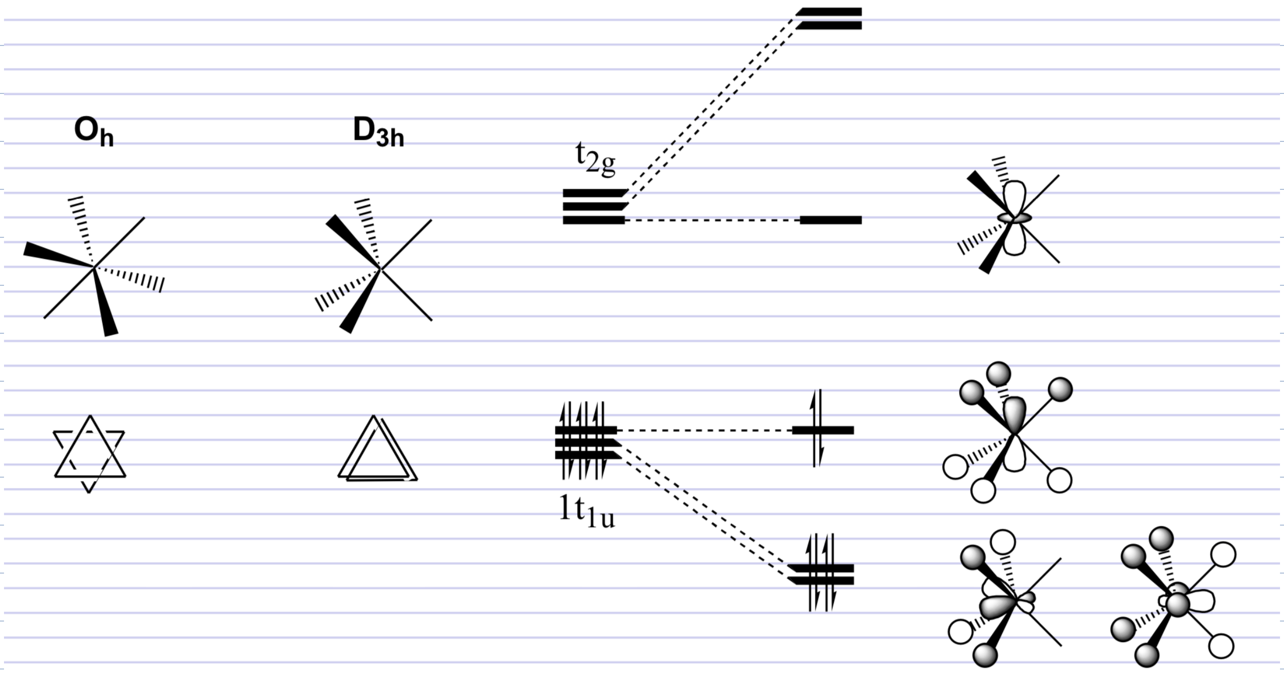
M = Re



M = Os

Ox. state no phys. meaning.
Eg $W^{VI}Me_6$ has ~same Eion as $W^0(CO)_6$

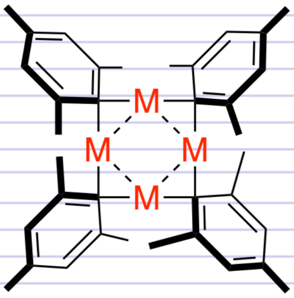
WMe_3 geometry actually prismatic (D_{3h}) because Me is a very strong σ-donor and the respective MOs are lowered in E:

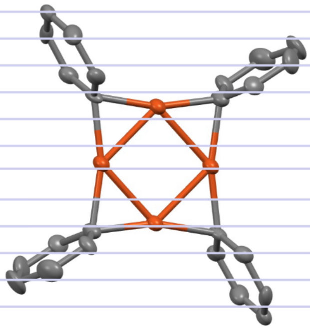


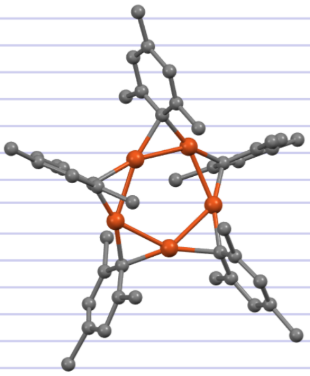
↳ predicted first by theorists, later confirmed by X-Ray

Aryl (Ar) Derivatives, e.g. Ar = mesityl

MAr_4 for M = Ti, Zr, Hf, V, Cr, Mo, W, Ru, Os
MAr_3 for M = Cr, Rh, Ir
MAr_2 for M = Mn, Fe, Ni, Zn
M_nAr_n for M = Cu, Ag, Au with n = 4/5



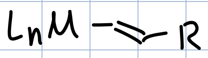




Metal alkyl classes

L_nM-R

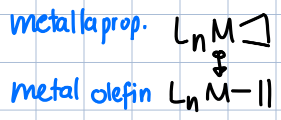
alkyl

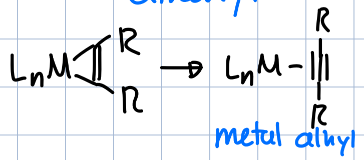


alkenyl

$L_nM-\equiv-R$

alkylyl





Spectroscopy

$M-CH_2R$

IR:

$2800\,cm^{-1} < \tilde{\nu}_{C-H} < 3000\,cm^{-1}$

↓

can go down to $2700\,cm^{-1}$ ⇒ sth. is special about the C on the metal alkyl

^{13}C NMR: $-10 < \delta_{^{13}C} < 170$ ppm ⇒ wide range

$J_{C-H} = 125 - 140$ Hz

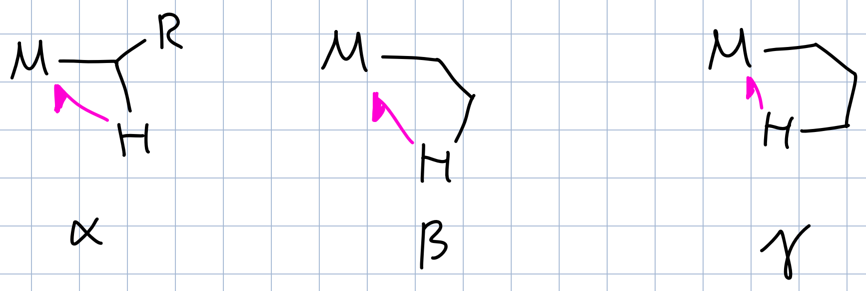
↓

can go to 80 Hz ⇒ bond must be longer

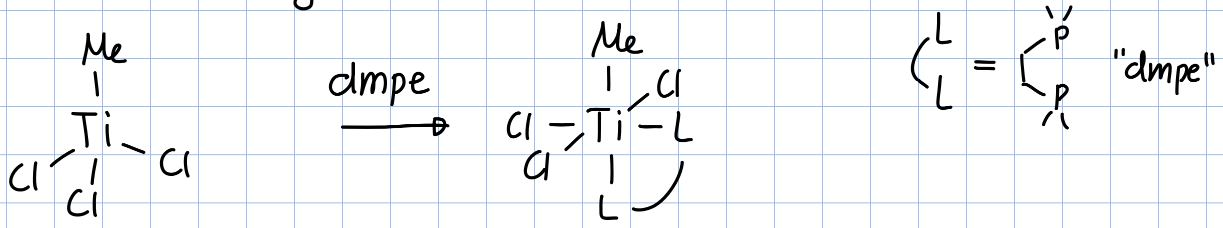
↳ correlates with low $\tilde{\nu}_{C-H}$ in IR

⤳ Good empirical rule: $J_{C-H} = \frac{500}{n+1}$ for sp^n

⇒ Decrease $\tilde{\nu}_{C-H}$, J_{C-H} explained by agostic int.:



↓ How does this agostic int. work?

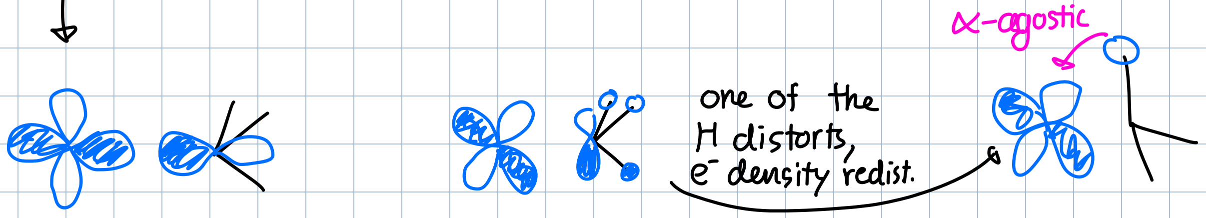


8e⁻ — no α-H agostic int.

12e⁻ — α-H agostic int.

⇒ T_d has no open coord. site, while O_h a bit more finniky.

Have to consider the orbitals



one of the H distorts, e^- density redist.

⇒ Methyl group gives part of its e^- density to the metal, spectroscopy hints at