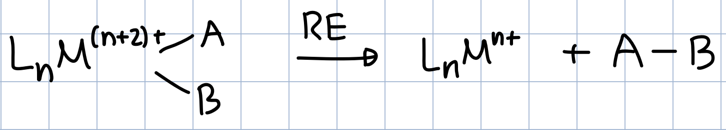
11.10.

Reductive Elimination (RE)

"Microscopic inverse of OA" : They share the same TS



$$L_nM^{(n+2)+}(A)(B) \xrightarrow{RE} L_nM^{n+} + A-B$$

⇒ Metal oxidation state and d-electron count are reduced

Survey of effects : M

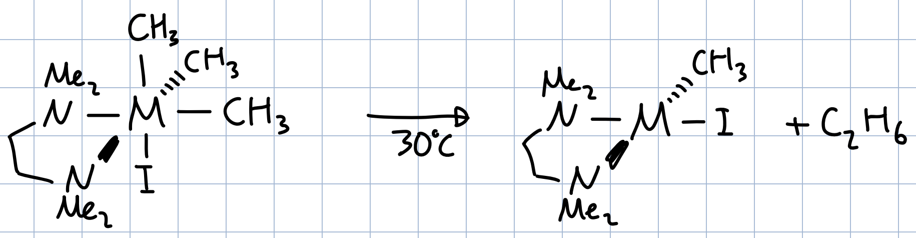
⤳ Opposite trends to OA:

- Electron poor metal ⇒ faster RE than e^--rich metal

  ⇒ $k_{1^{st}row} > k_{2^{nd}row} > k_{3^{rd}row}$

Also related to M-L BDEs : As they get stronger with the row #, RE slower (as M-L bonds break)

Example:



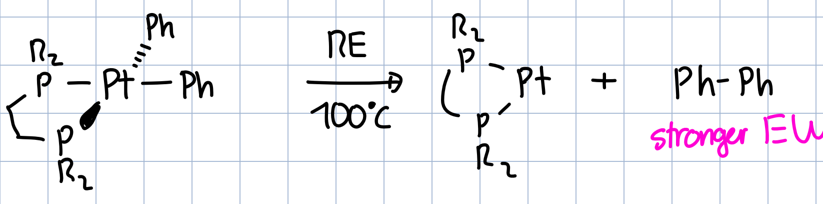
M	k_{obs}
Pd	$10^{-2}\,s^{-1}$
Pt	no rxn up to 270°C

⇒ Moving down a row stops RE from happening because M-L bonds are too strong!

Survey of effects: "Ancilliary Ligands" L

a) Electronics: e^- rich L ⇒ slower than e^- poor L

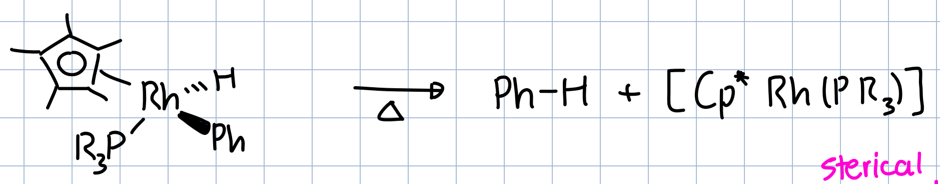
⤳ also makes M e^- rich / poor



stronger EWG ↓

R	k_{rel}
Ph	1
C_6F_5	1240

b) Sterics: "Squeeze effect" ⇒ The more sterically demanding L, the closer the elim. ligands A,B will be in the GS ⇒ closer to the TS ⇒ faster



PR_3	k_{rel}
PMe_3	1
$PPhMe_2$	3.2
PPh_2Me	33

sterical demand

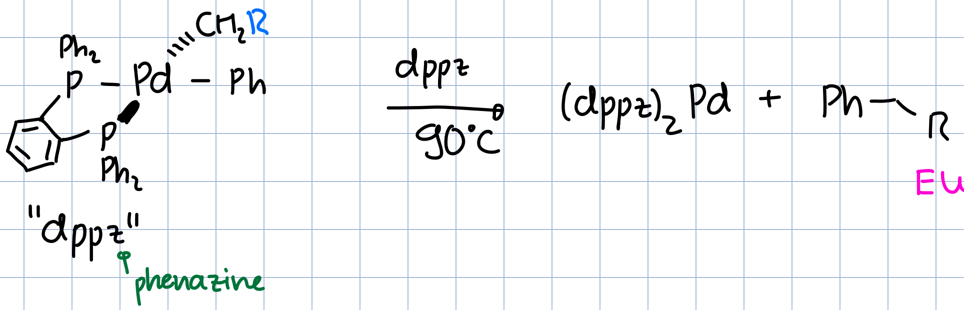
But we did not only change sterics but also electronics!
→ How do we disconnect? ⇝ Use descriptors we have ☺

PR_3	k_{rel}	$\%V_{bur}$	TEP/cm^{-1}
PMe_3	1	26	2064
$PPhMe_2$	3.2	29	2065
PPh_2Me	33	33	2067

TEP doesn't change so much
⇒ effect mainly due to sterics

Survey of effects: "Leaving Ligands" A,B

a) Electronics: Larger M–A,B BDE ⇒ slower RE



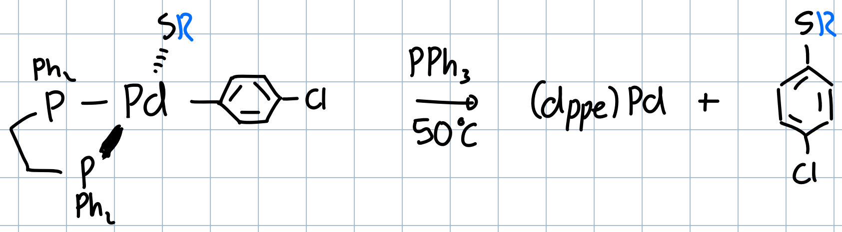
R	k_{rel}
H	>600
Ph	>250
CF_3	1
CN	no rxn

EWG

Trend other way around than for ancilliary ligands!
↳ Recall: $M^{\delta+}$—$R^{\delta-}$ → EWG

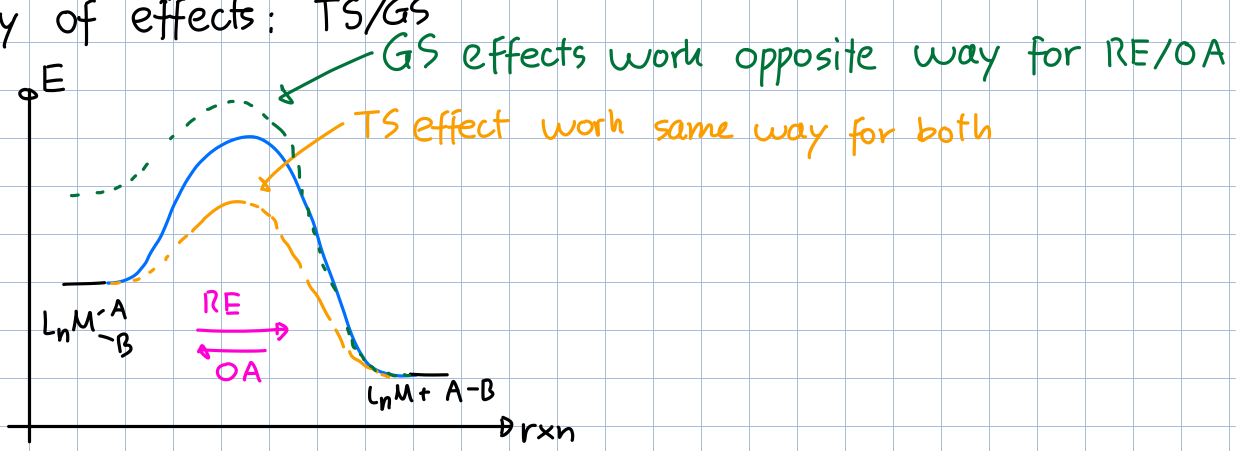
⇒ EWG stabilizes δ^- ⇒ Strengthens M–R bond
⇒ Slower rxn

b) Sterics: Same as for L_n



R	k_{rel}
Me	0.1
${}^tBu$	1

Study of effects: TS/GS

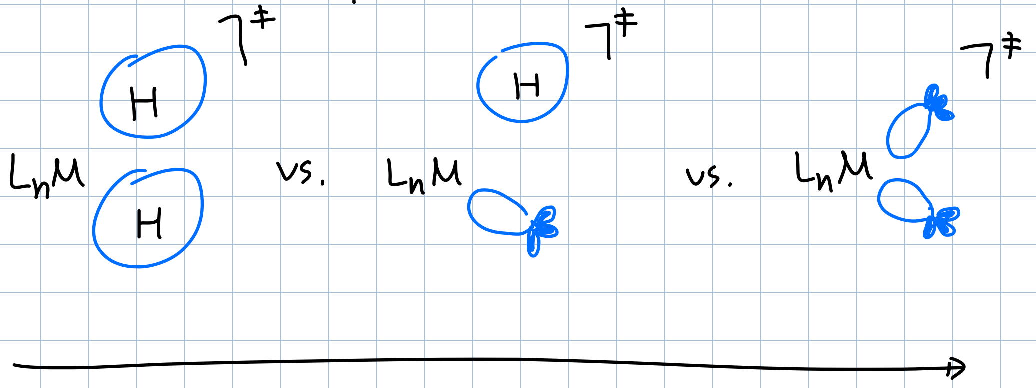


Example:

H–H vs. H–C vs. C–C

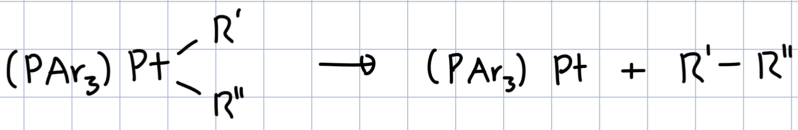
OA/RE fast ← slow

→ Reason: Orbital overlap



creating overlap gets increasingly harder due to the orbital symmetries

How to differentiate TS & GS effects?



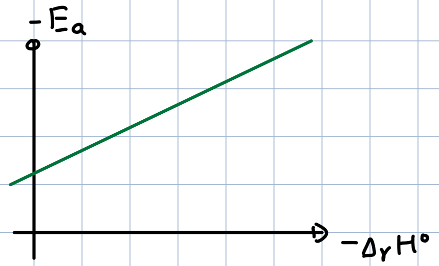
$$(PAr_3)Pt\langle^{R'}_{R''} \longrightarrow (PAr_3)Pt + R'-R''$$

R'	R''	ΔH° $\frac{kcal}{mol}$	ΔH‡ $\frac{kcal}{mol}$
H	H	12.5	14
H	CH_3	−6	16
CH_3	CH_3	−11.2	41

→ But why do ΔH° and ΔH‡ have opposite trends?

ΔBDE (M–H vs. M–C) > ΔBDE (C–H vs. C–C) explains ΔH°

Usually: Bell-Evans-Polyani Relation :

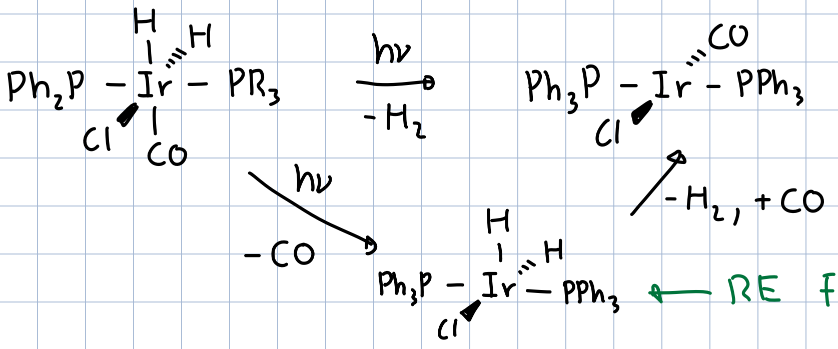


⇒ E_a is directly related to driving force with slope $\alpha \approx 0.5$

↓

However here we have the orbital considerations from above ⤳ TS effect
⤳ Same for OA/RE

Study of effects: Light (hν)

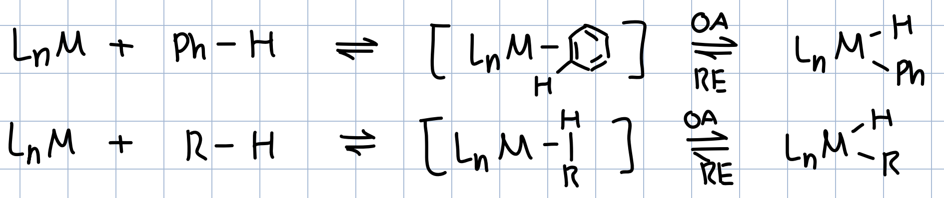


← RE faster for 5 coord. comp.

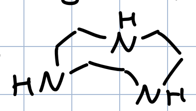
hν promotes d_M electrons into low-lying π^*_{CO} ⇒ promotes L dissoc.

C–H RE

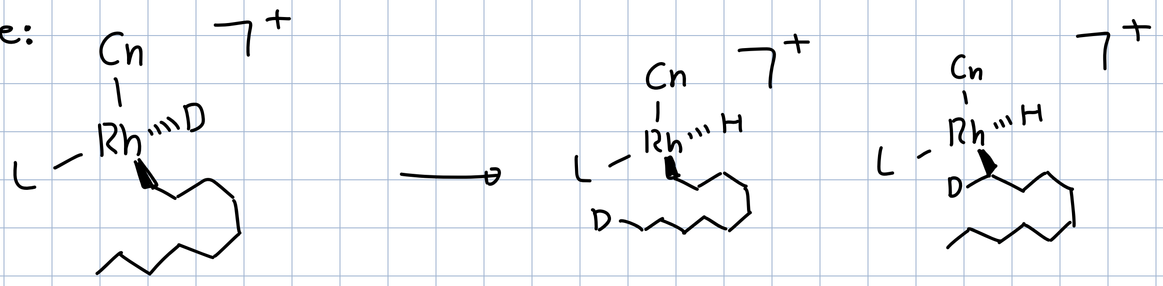
⤳ Opposite to OA, principle of microscopic inversion



Get insights from kinetics: Isotope Labeling

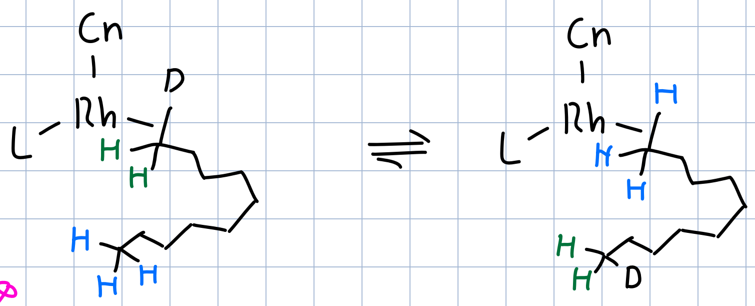
Cn:  ⤳ "L_3" , L = P(OMe$_3$)

Observe:



⇒ Must have gone through RE and subsequent OA

↳ Went through intermediates (σ-alkanes):



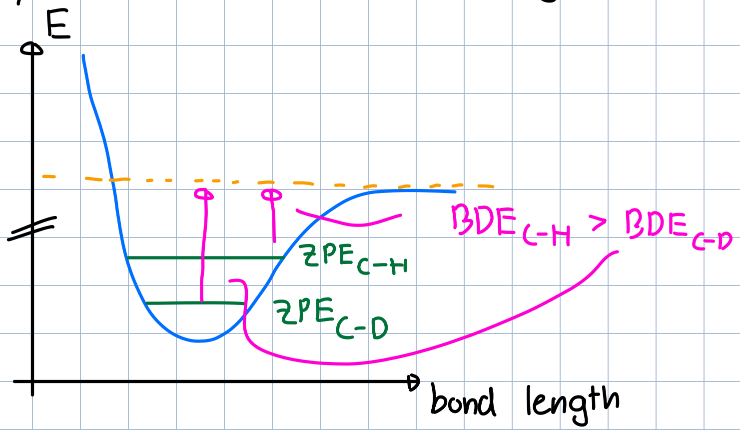
Only terminal possible, as already quite high in E (1° alkane σ-complex ☹)

⇝ More Direct Evidence: Kinetic Isotope Effects (KIEs):

Introduce C–D (H)

⇒ If the rxn-rate changes ($\frac{k_H}{k_D} \neq 1$), there is a C–H bond breaching in the mechanism.

Why are C–D bonds stronger than C–D bonds?



In the H.O. we have the vib. levels

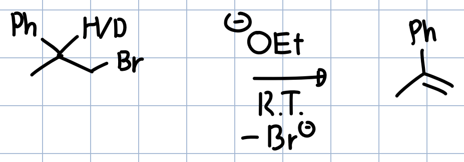
$$E_n = (n+\tfrac{1}{2})h\nu \Rightarrow E_0 = ZPE = \frac{h\nu}{2}$$

with $\nu = \frac{1}{2\pi}\sqrt{\frac{k_f}{\mu}}$, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ reduced mass

As $k_f \approx$ constant for isotopes and $\mu_{C-D} > \mu_{C-H}$ we get $\nu_{C-D} < \nu_{C-H} \Rightarrow ZPE_{C-D} < ZPE_{C-H}$

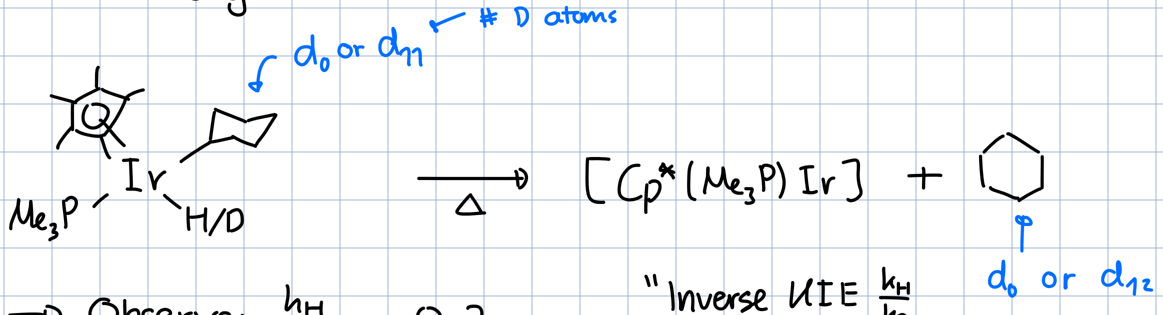
$\Rightarrow BDE_{C-D} > BDE_{C-H}$

Example from OC:

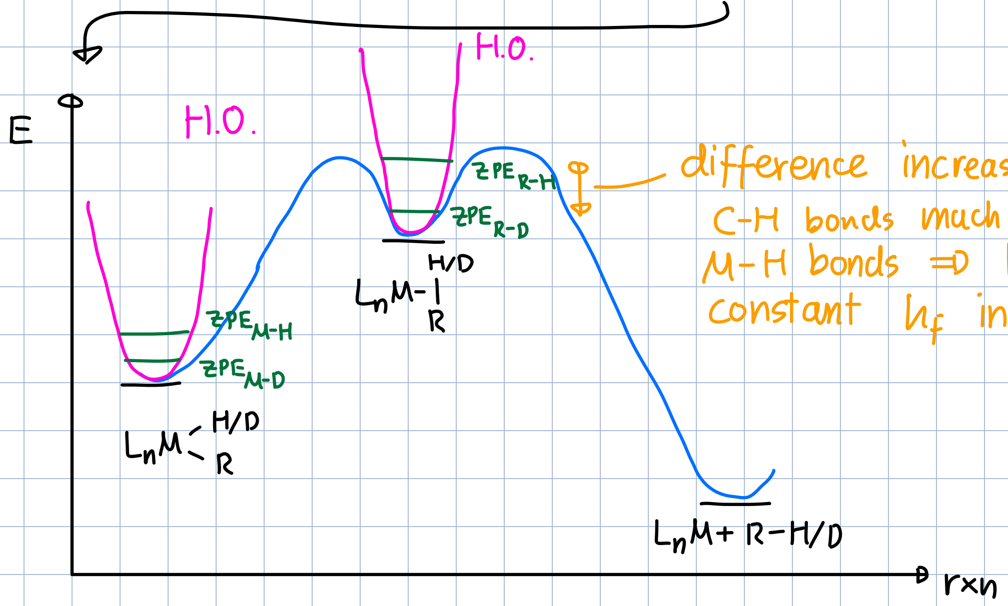


$\Rightarrow \frac{k_H}{k_D} = 7.8 \rightsquigarrow$ primary/normal KIE with $\frac{k_H}{k_D} > 1$

However in organometallic chem.:

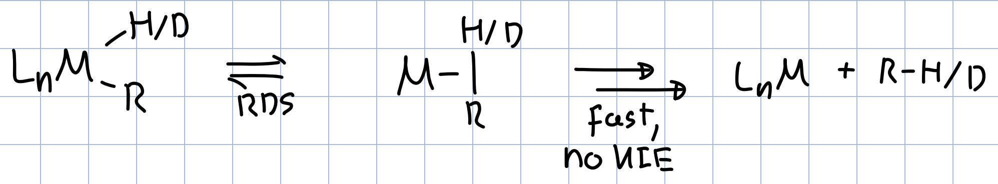


⇒ Observe: $\frac{k_H}{k_D} = 0.7$ ⇒ "Inverse KIE $\frac{k_H}{k_D}$" Inverse of what was expected?



difference increased because C–H bonds much stronger than M–H bonds ⇒ larger force constant k_f in $\nu = \frac{1}{2\pi}\sqrt{\frac{k_f}{\mu}}$

↳ Overall:

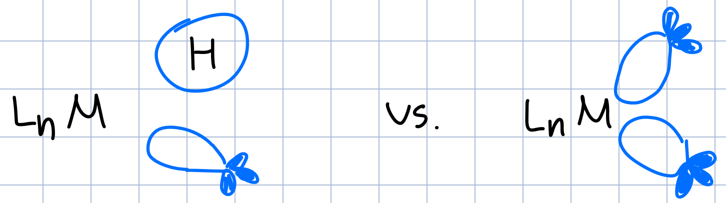


⇒ Have found kinetic evidence that mechanism proceeds over a σ-alkane complex as postulated

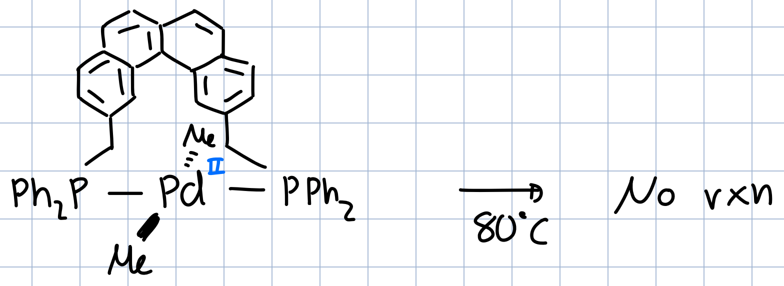
Same argument can also be made for Ar–H/D.

C–C RE:

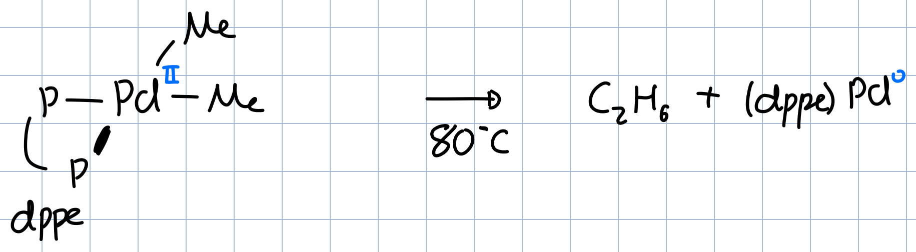
Harder than C–H:



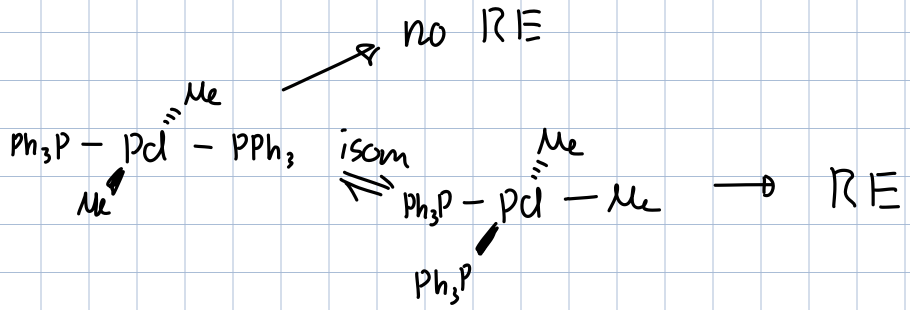
→ Need cis geometry:



but



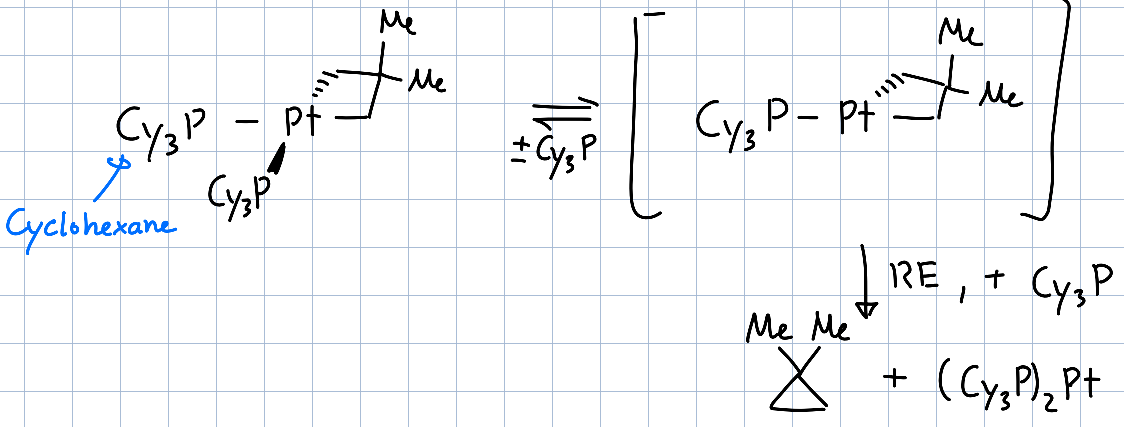
and for mono dentate



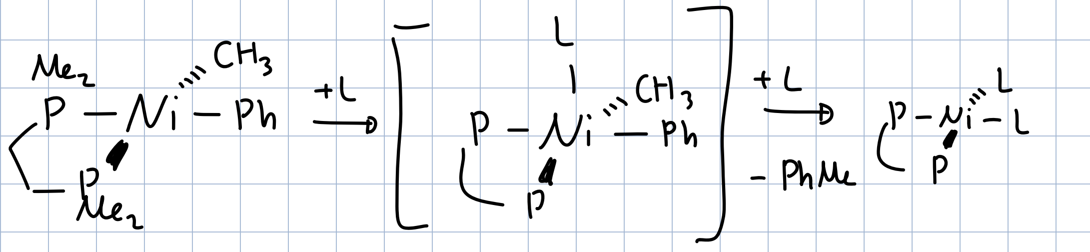
Ligand association / dissoc.

a) dissoc. induced RE:

triccord. complexes elim. faster than tetrac.



b) assoc. induced RE



L	$k_{obs} / 10^{4} s^{-1}$
–	0.2
PEt_3	20
$P(OEt)_3$	> 50