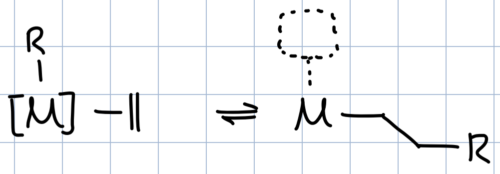
31.10.

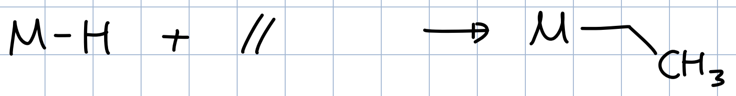
MI continued

Olefin insertion into M−C



R = H vs. C :

Thermodynamics



Bonds broken $\left(\frac{kcal}{mol}\right)$		Bonds Formed $\left(\frac{kcal}{mol}\right)$	
M−H :	60	M−C	40
// (π) :	60	$C(sp^3)-H$	100
	120		140

$\Rightarrow \Delta G° \approx -20 \frac{kcal}{mol}$ for R=H

vs.

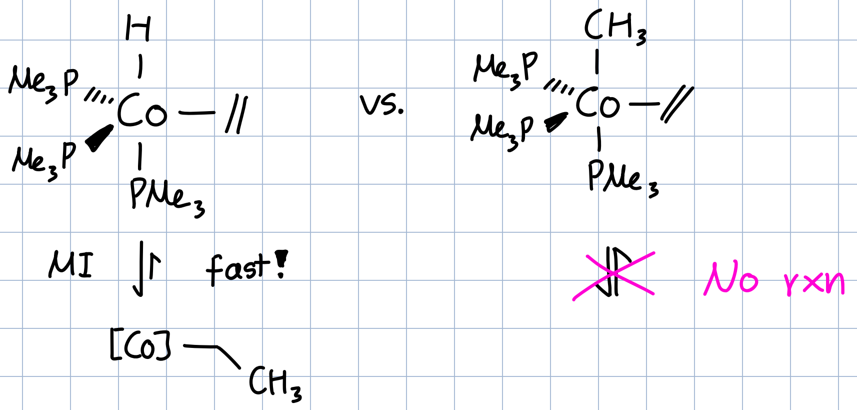
Bonds broken $\left(\frac{kcal}{mol}\right)$		Bonds Formed $\left(\frac{kcal}{mol}\right)$	
M−C :	40	M−C :	40
// (π) :	60	$C(sp^3)-C(sp^3)$:	90
	100		130

$\Rightarrow \Delta G° \approx -30 \frac{kcal}{mol}$

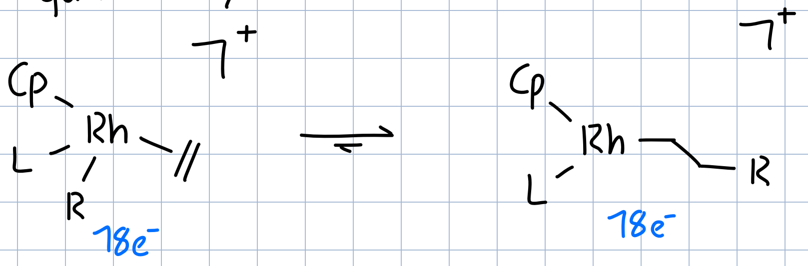
⇒ Thdm. more favourable to insert olefin into M−C than into M−H

Kinetics: Might be tempted to say thdm. more fav. also faster
→ but this is not necessarily the case!

Consider:



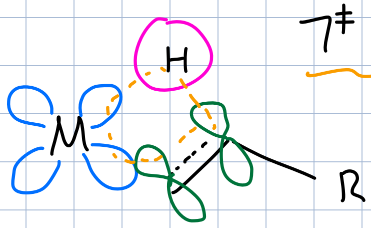
→ More quantatively:



R	L	$\Delta G^{\ddagger}$ ($\frac{kcal}{mol}$)
H	PMe_3	15.0
	$P(OMe)_3$	14.8
CH_3	PMe_3	24.7
	$P(OMe)_3$	25.4

⇒ much higher barrier!

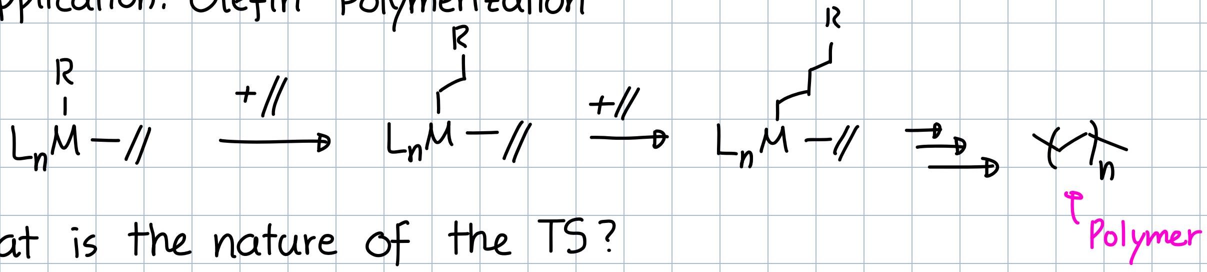
TS:



→ overlap much better for insertion into M-H

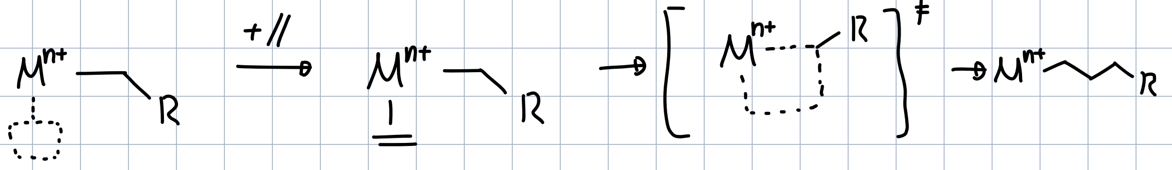
Trend with L by partial charges: $L_nM^{\delta+}-R^{\delta-}$

Key Application: Olefin Polymerization



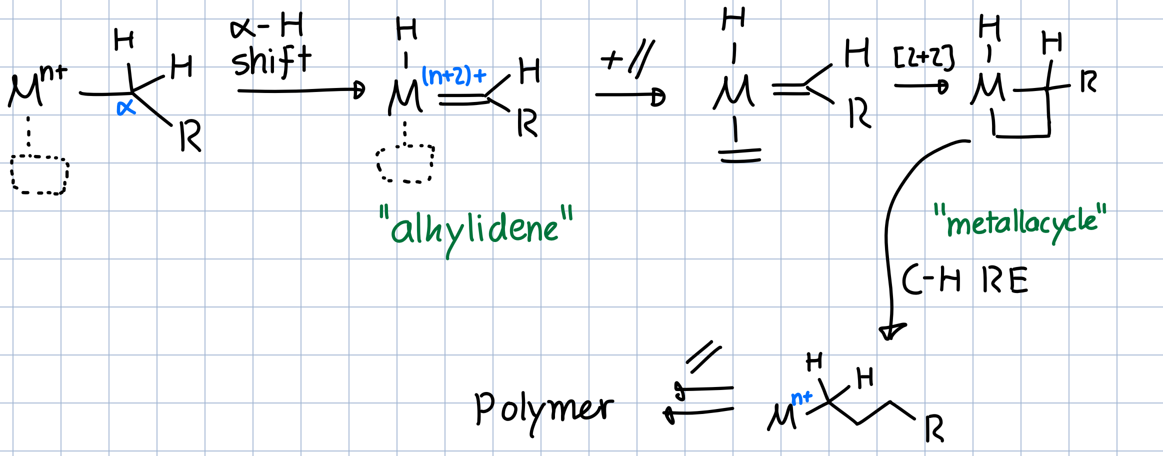
What is the nature of the TS?

① Simplest: Direct insertion ("Cassee-Arlman" ≙ CA)

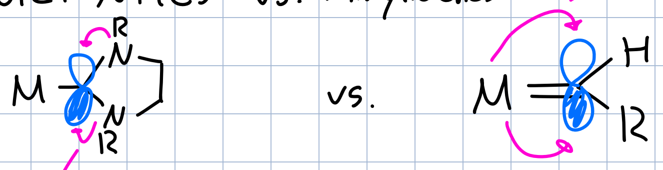


↳ But if this was true, almost all M could do olefin ins.
⇒ But many cant ⇒ Doesn't make sense

② Hydride Shift, [2+2] ("Greene-Rooney", GR)



Side note: NHCs vs. Alkylidenes



metal donate into p-orbitals, forming the double bond

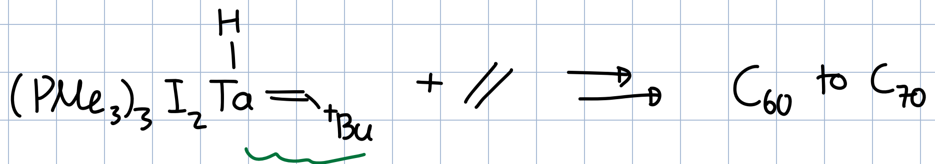
N donate into vacant carbon d-orbitals ⇒ no π-bond
↳ L-type
late M

↳ X_2-type
early M

⇓

Which of the mechanism describes better?

In support of GR:

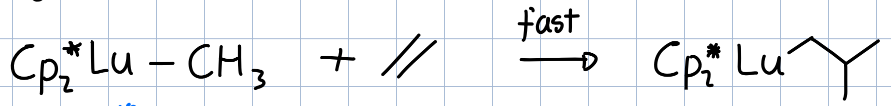


$(PMe_3)_3I_2Ta{=}{}^tBu$ + // ⟶ C_{60} to C_{70}

alkylidene

→ Odd carbon # observed 1:1 with even
⇒ Alkylidene is incorp. into product!

Challenge to GR:



$Cp_2^*Lu-CH_3$ + // $\xrightarrow{fast}$ Cp_2^*Lu

d^0 → but GR needs d-electrons for α-H shift!