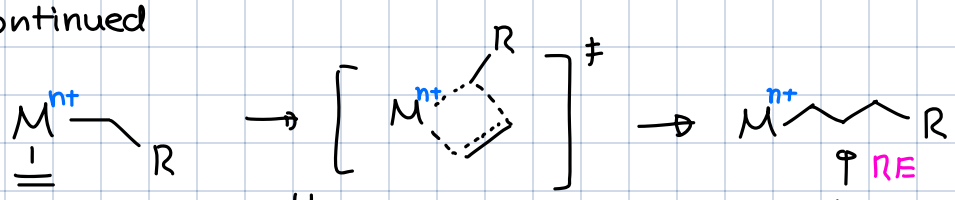
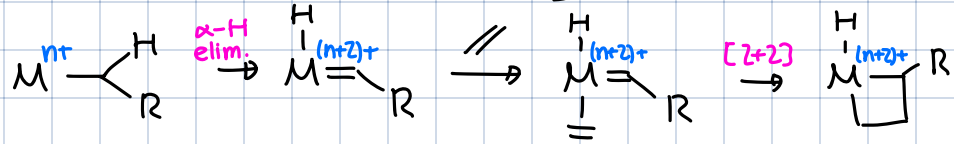
01.11.

Olefin MI continued

1) CA: 

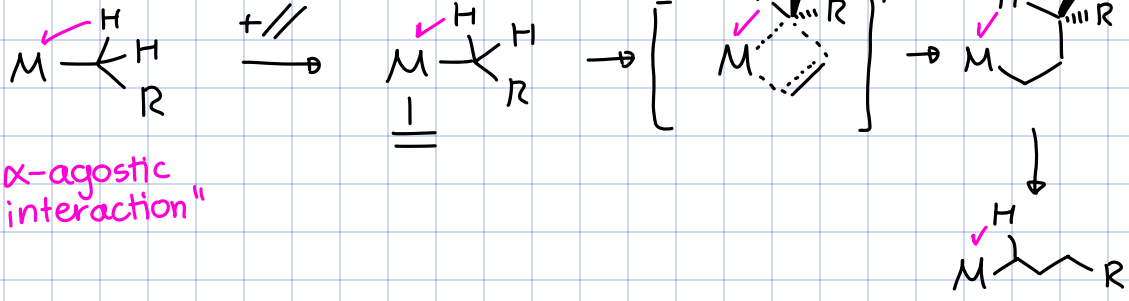
2) GR: 

→ Neither explains mechanism (both contradict experiment)

↳ Two extrema: · In 1) CH bond stays fully intact
· In 2) CH bond is fully broken

⇒ Could it be sth. in between?

3) Modified GR

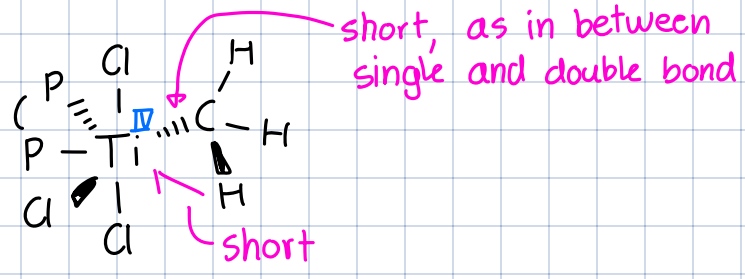


"α-agostic interaction"

⇒ Makes it possible for d° metals, but also limits the number of metals, as a special el. structure is req.

Structural evidence for α-agostic interaction

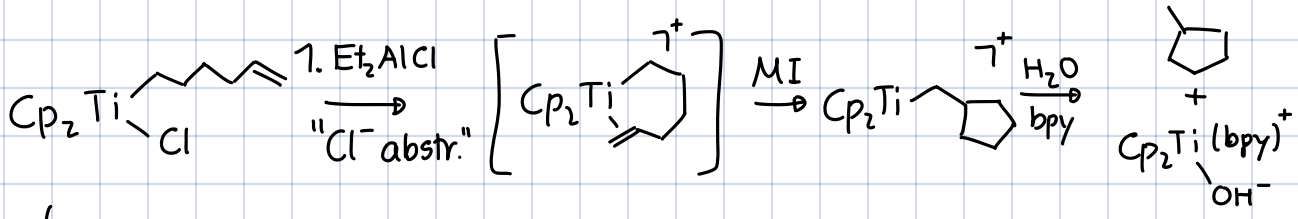
(dmpe) $TiCl_3CH_3$ Polym. cat.



Probing α-agostic assisistance

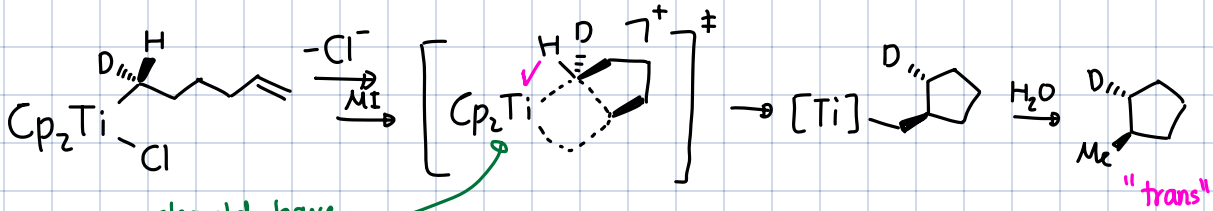
- Stereochemical Isotope Effect

Design:

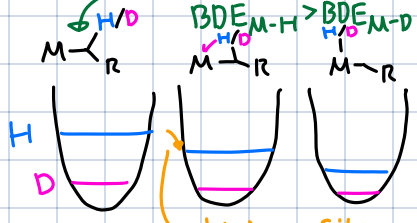


↓

Introduce deuterium label:

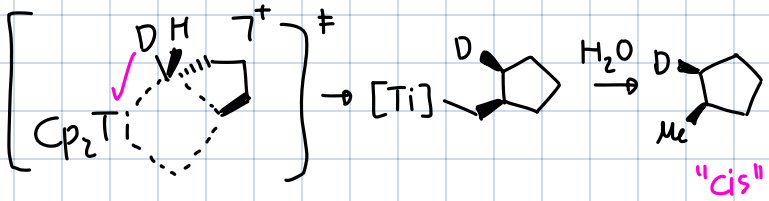


should have lower E_a as $BDE_{M-H} > BDE_{M-D}$



H benefits more than D !

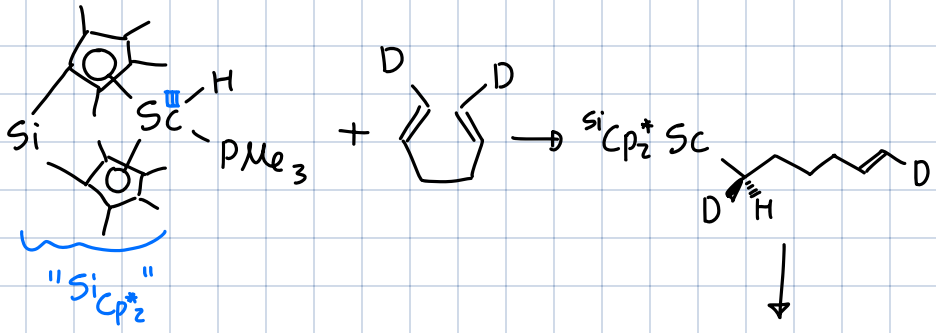
Or

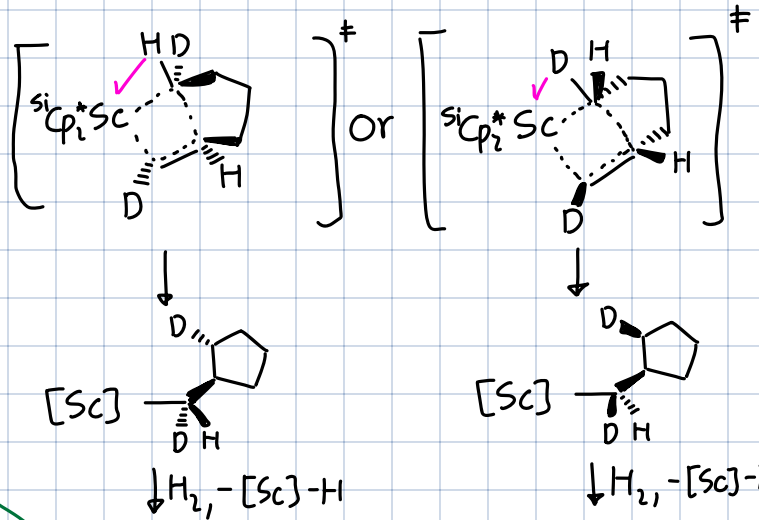


⇒ Would expect excess of trans-product

However, we observe $\frac{[cis]}{[trans]} = 1.00 \pm 0.05$ ∴

Different Complex:

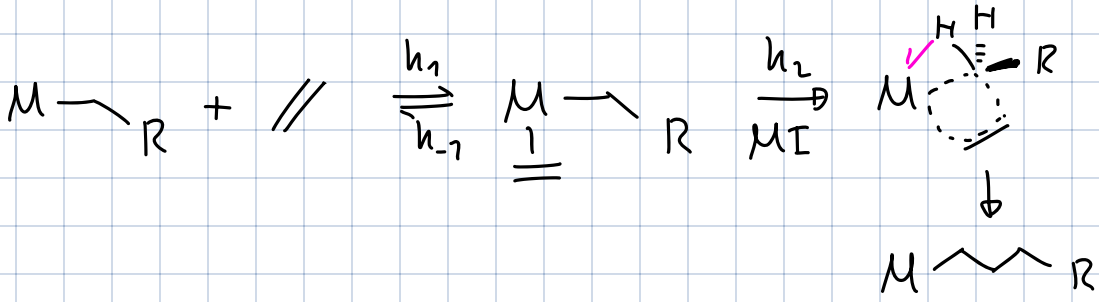




measured $\frac{[trans]}{[cis]} = 1.79 \pm 0.04$ ☺

But why did it not work with the Ti complex?

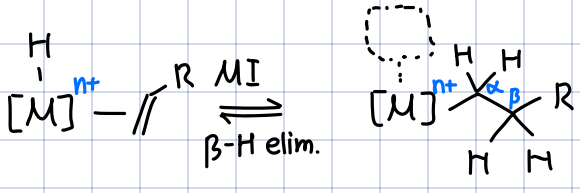
↝ Unifying Theory:



RDS det. if KIE observed:

1. $k_2 < k_{-1}$ ⇒ MI is RDS ⇒ KIE ([Sc])
2. $k_2 >> k_{-1}$ ⇒ Coord. is RDS ⇒ no KIE ([Ti])

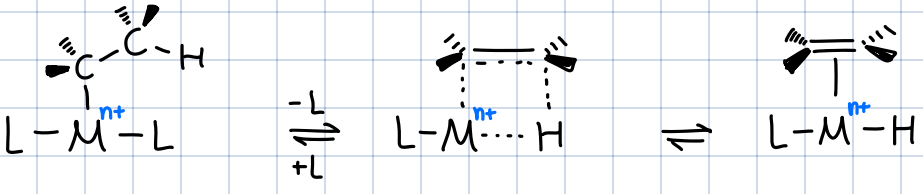
β-H Elimination



↝ Microscopic reverse of MI

⇒ Requires an open coordination

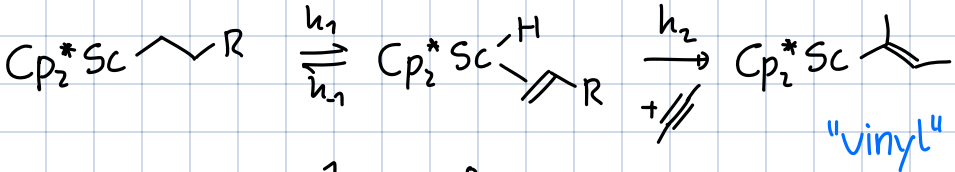
TS:



"syn-coplanar"

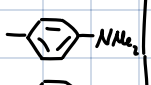
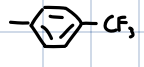
Electronic effects: Effect of R in

↝ β-H elim. is an uphill process (in E) ⇒ Have to couple to other rxns to study it



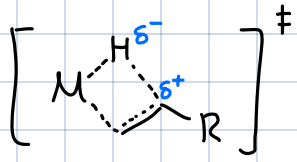
"vinyl"

$r = k_{obs}[Sc]^1[C_4H_6]^0$ ⇒ $k_2 >> k_{-1}$, β-H elim is RDS!

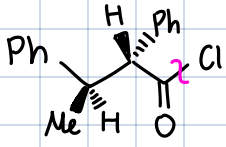
-R	k_1 (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
-H	$0.9 \cdot 10^{-4}$	21.2
$-CH_3$	$6 \cdot 10^{-4}$	20.5
	$4.2 \cdot 10^{-3}$	19.4
	$0.1 \cdot 10^{-4}$	22.7

⇒ If R = EDG, the reaction becomes faster

↝ supports that H eliminates as H^- (reverse of MI where H migrates as H^-)



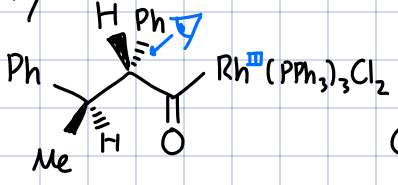
Stereochem: "Syn coplanarity"

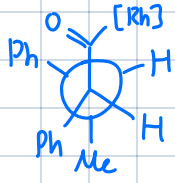


$(PPh_3)_3RhCl$

$-PPh_3$

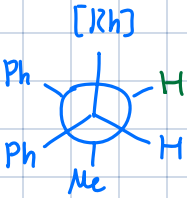
C-Cl OA

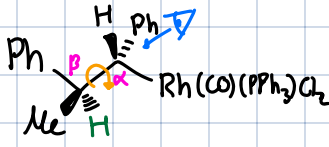




CO - deins.

$-PPh_3$



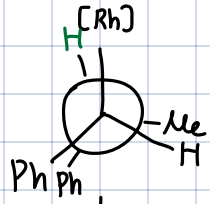


twist to achieve syn-coplanarity

If were to start with terminal stereocenter inv., E-olefin would have been obtained

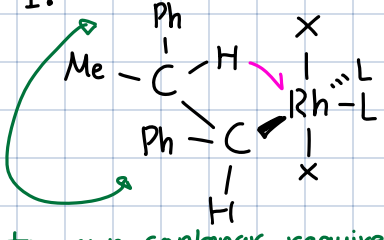
Z-olefin

β-H elim.



What is the nature of intermediate I?

I:

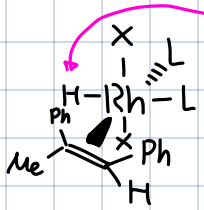


due to syn-coplanar requirement, the Z-olefin is obtained

β-H elim.

↝ β-agostic complex, CH bond is weakened

H completes coord. sphere of [Rh]



Other examples of β-H elim.: M-OR, M-NR$_2$