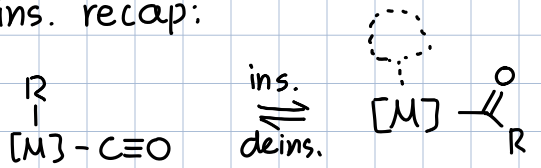
25.10.

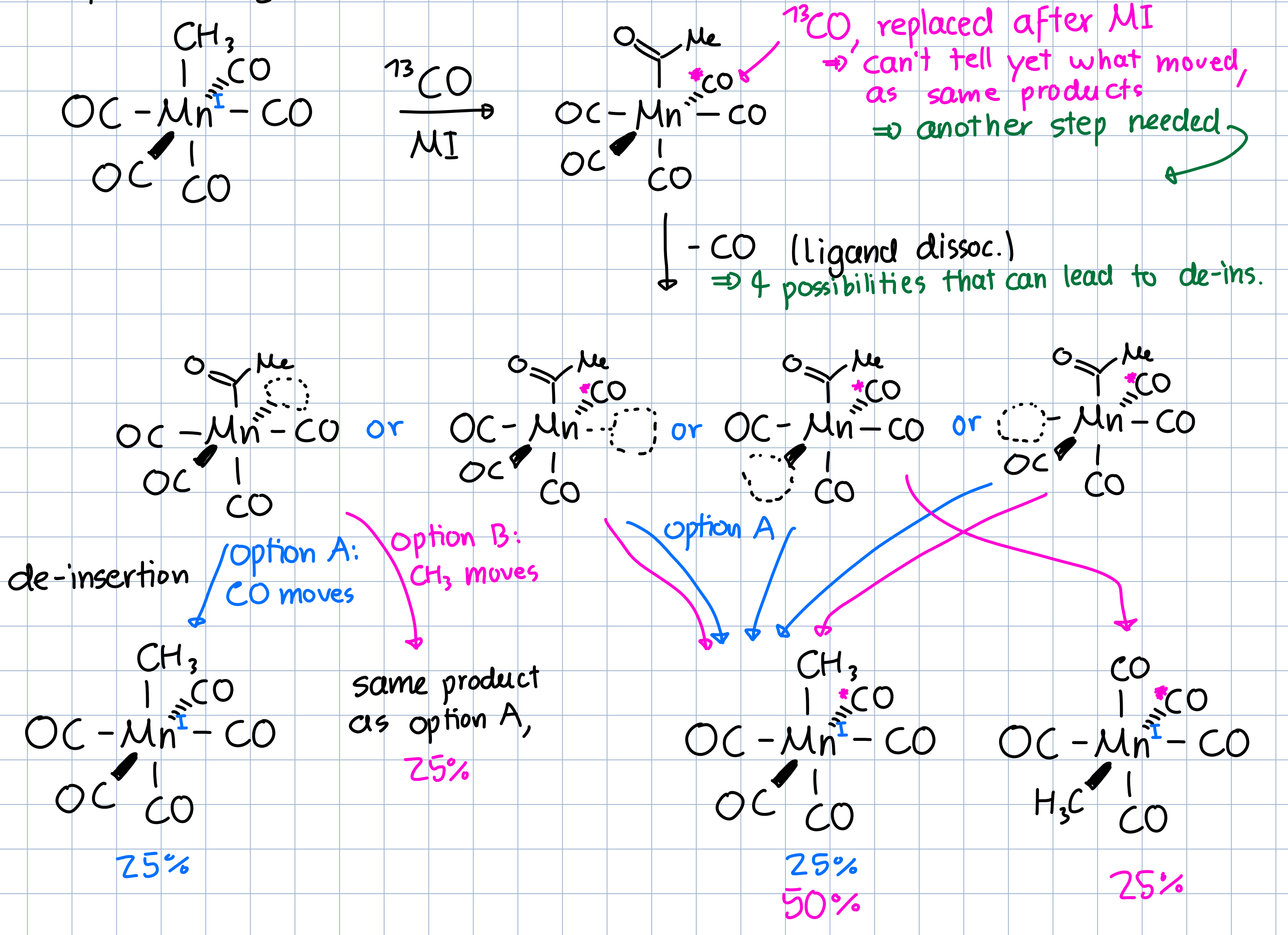
MI continued

CO ins. recap:



What is actually migrating / what moves during MI?

⇒ Isotope labelling with ^{13}C:



^{13}CO replaced after MI

⇒ can't tell yet what moved, as same products

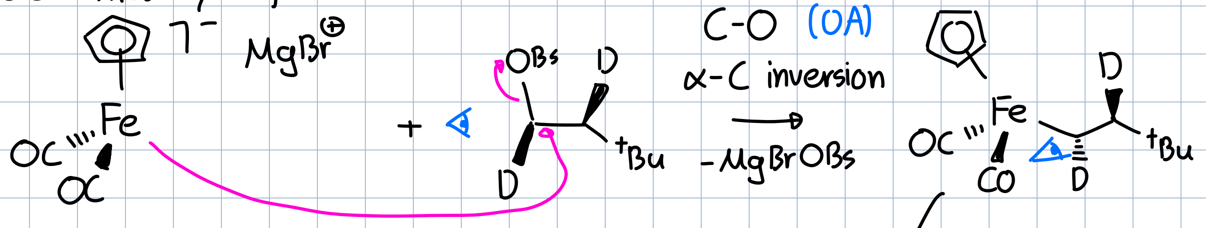
⇒ another step needed

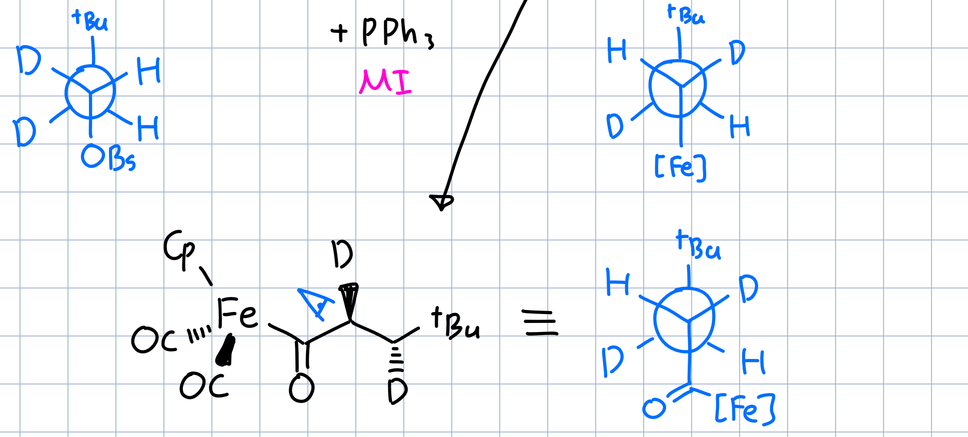
⇒ 4 possibilities that can lead to de-ins.

⇒ Only if CH_3 moves, we get the product where CH_3 is trans to the isotopically labelled carbonyl
⇝ observing is proof that CH_3 moves

⇒ Reported by IR spectroscopy and later confirmed by ^{13}C-NMR

Stereochemistry of MI



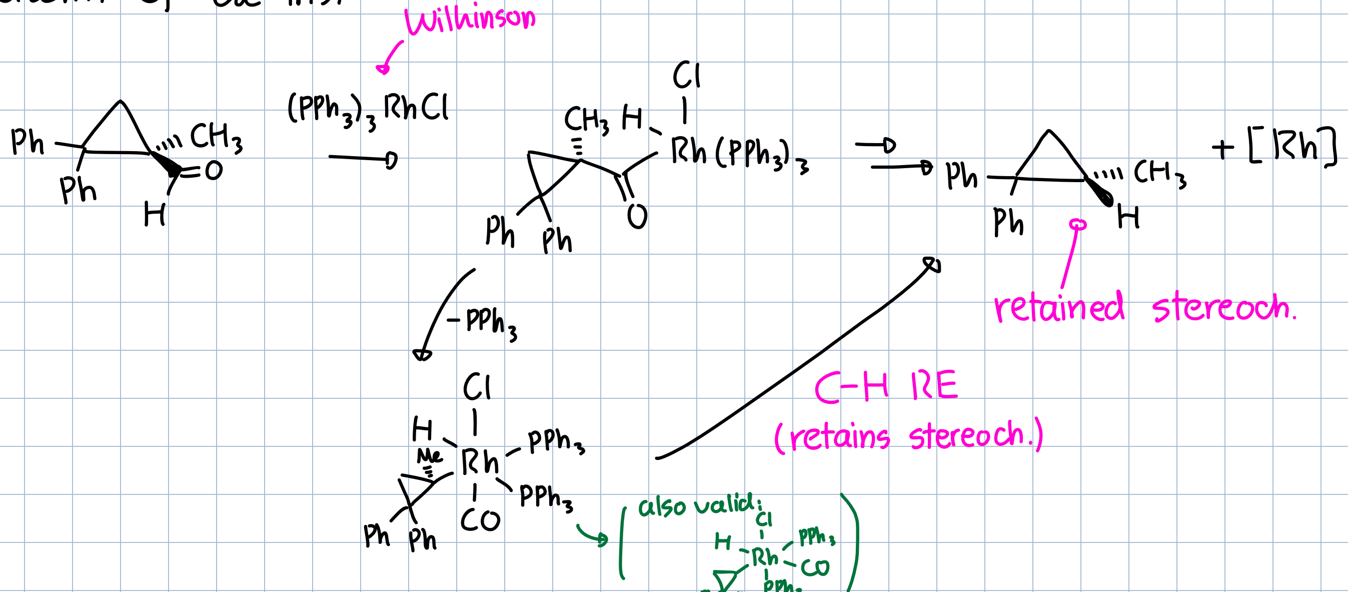


>95% selective

⇒ MI retains the stereochemistry, as inversion happened in polar OA

Is the reverse also true?

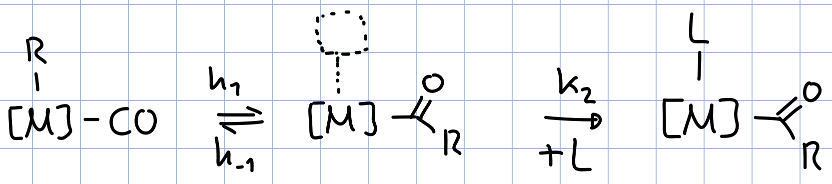
Sterechem. of de-ins.



⇒ Also the de-insertion retains stereoch., principle of microscopic reversibility is supported (same fundamental TS)

MI: Kinetics & Mech.

Recall:



Kinetics:

$$r = \frac{d[M(L)(COR)]}{dt} = k_2[L][M(COR)]$$

⇝ Steady-State approx: $\frac{d[M(COR)]}{dt} = 0 \Leftrightarrow k_1[M(R)(CO)] = k_{-1}[M(COR)] + k_2[L][M(COR)]$

$\Rightarrow [M(COR)] = \frac{k_1}{k_{-1}+k_2[L]}[M(R)(CO)]$

$$\Rightarrow r = \frac{k_1 k_2}{k_{-1}+k_2[L]}[M(R)(CO)][L]$$ ⇒ Overall between first & second order

Possible kinetic regimes (simplifications)

case 1: $k_{-1} \gg k_2[L]$

$$\Rightarrow r = \frac{k_1 k_2}{k_{-1}}[M(R)(CO)]^1[L]^1$$ ⇒ Overall second order

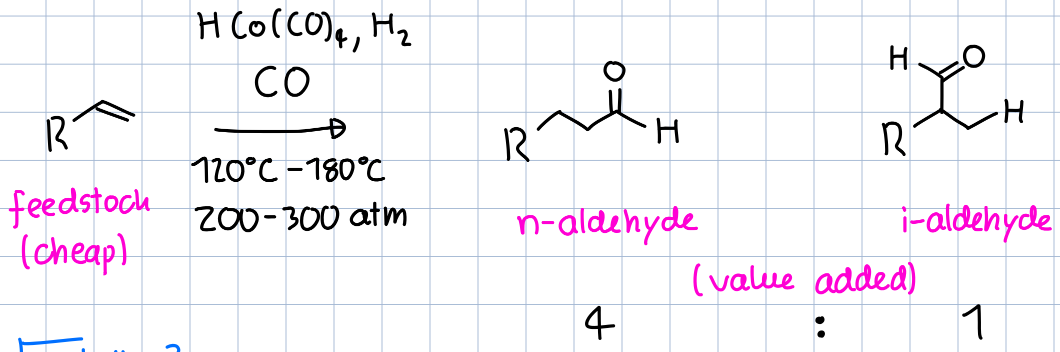
case 2: $k_{-1} \ll k_2[L]$

$$\Rightarrow r = k_1[M(R)(CO)]^1$$ ⇒ Overall first order

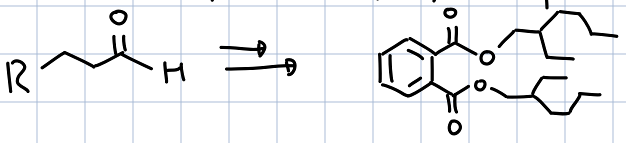
case 3: $k_{-1} \approx k_2[L]$

$$\Rightarrow r = \frac{k_1}{k_{-1}}[M(R)(CO)]^1$$ ⇒ Overall first order

Application of MI: Olefin Hydroformylation



Why?
⤷ Make ~7Mt/a of n-aldehyde, as precursor:

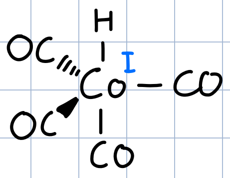


~→ plasticizer for PVC
(otherwise way to hard & brittle)

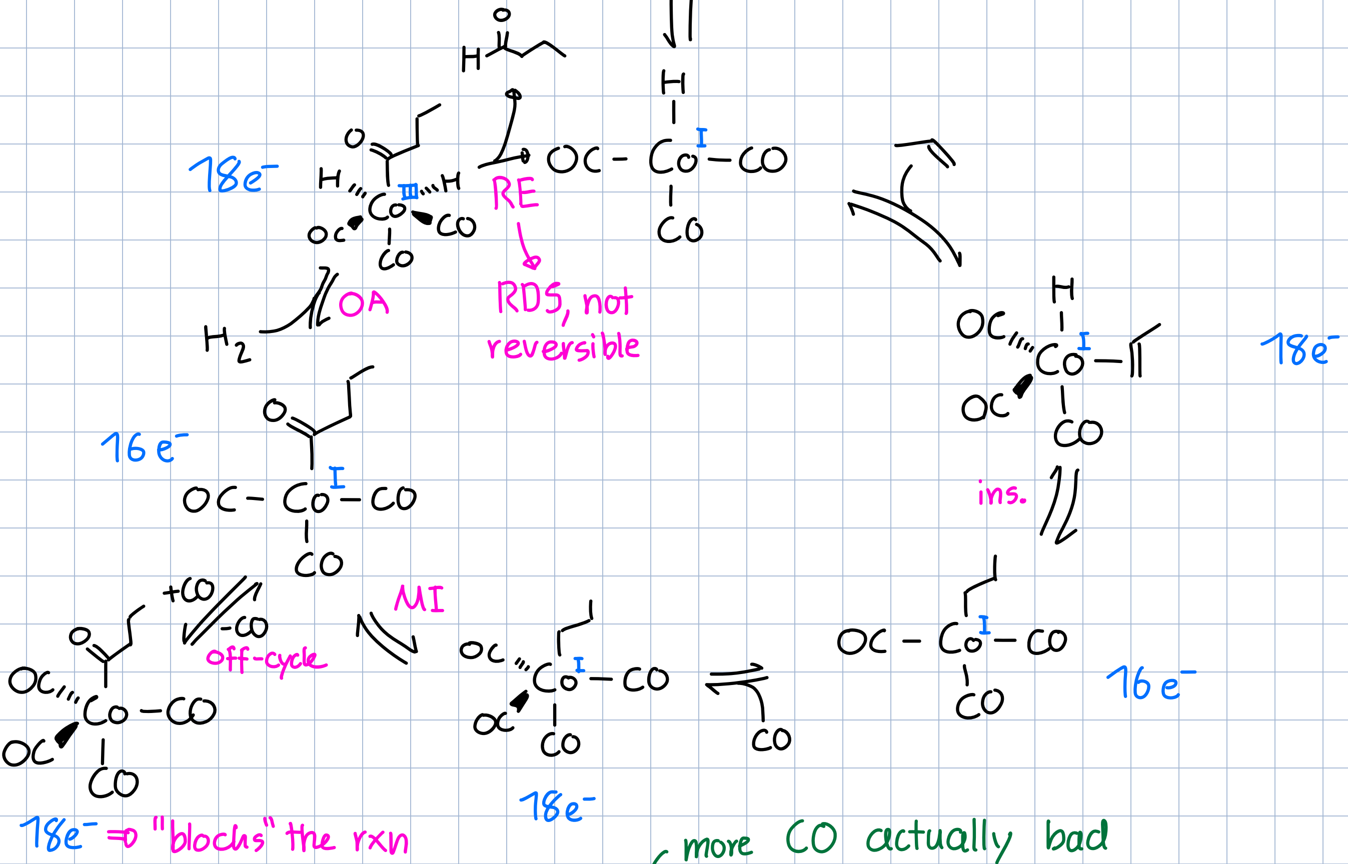
Mechanism:

$\frac{1}{2}Co^{0}_2(CO)_8$

$\downarrow H_2$ OA



$-CO \;\|\; +CO$ cat. activation

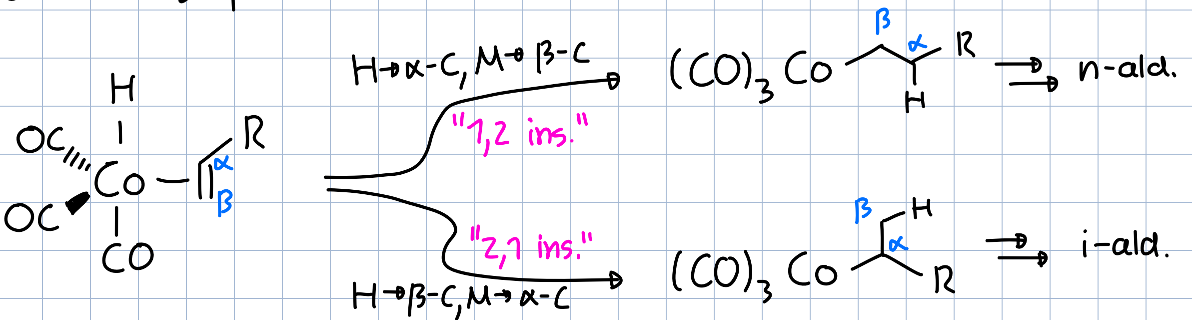


more CO actually bad

$$\Rightarrow \text{rate} \propto [CO]^{-1}, [H_2]^{1}$$

But how do we get i-aldehyde?

Consider the steps:

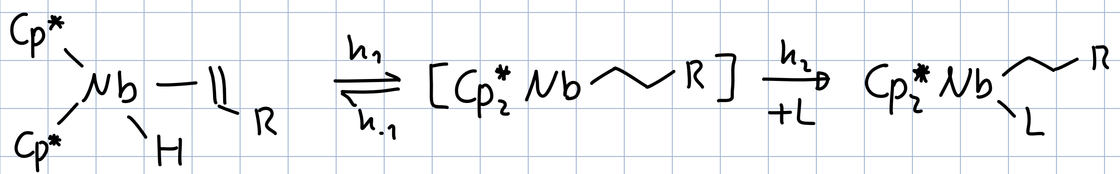


→ Can rationalize why n-aldehyde is pref. due to M-L bond strengths: Terminal bond is stronger than internal

MI of Alkenen

R = H: β-H elimination
R = C: β-C elimination

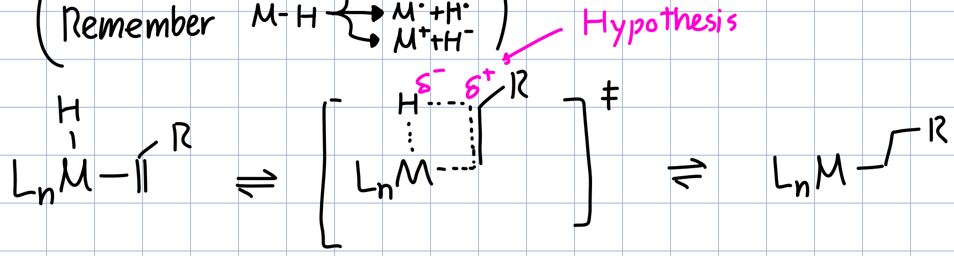
β-H elim. (R = H)



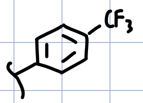
$$\text{rate} = \frac{k_1 k_2 [L]}{k_{-1} + k_2 [L]} [Nb]$$

→ What is the nature of mig. "H"?

(Remember M-H → $M^- + H^+$, $M^\cdot + H^\cdot$, $M^+ + H^-$)



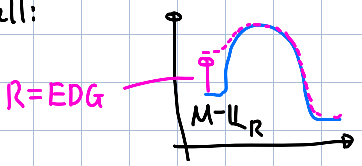
⇝ If H^- : R = EWG should stabilize TS
If H^+ : R = EDG should stabilize TS

R	k_1 / s^{-1}
H	2.6
Me	890
	0.9

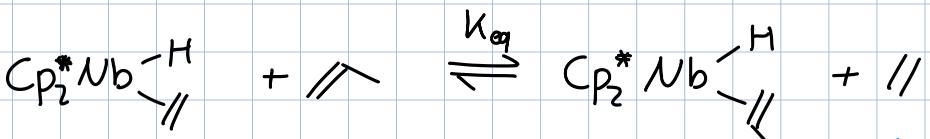
⇒ H migrates as $H^\ominus$ ✓

How to differentiate GS vs. TS effects?

Recall:



⇒ Need to know relative GS energies



Ⓐ ≙ 0 $\frac{kcal}{mol}$ Ⓑ ⇒ +1.1 $\frac{kcal}{mol}$

⇒ Only a marginal difference ⇝ only explains ~10× faster rxn rate, but we have almost 1000×

⇒ Difference in TS req., TS effect dominates!