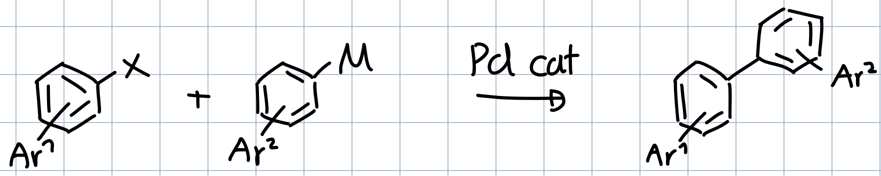
24.10.

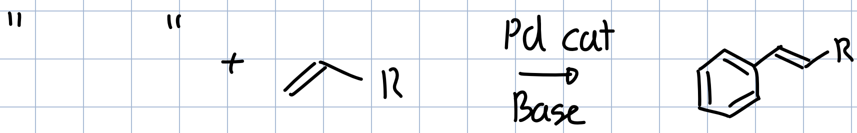
Pd cat. cross-coupling cont'd

Migratory Insertion (MI)

Recall:

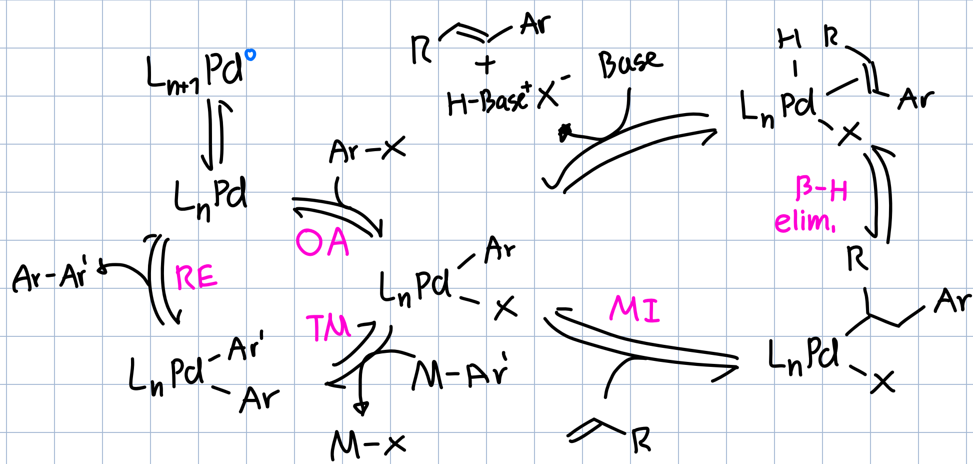


Heck coupling



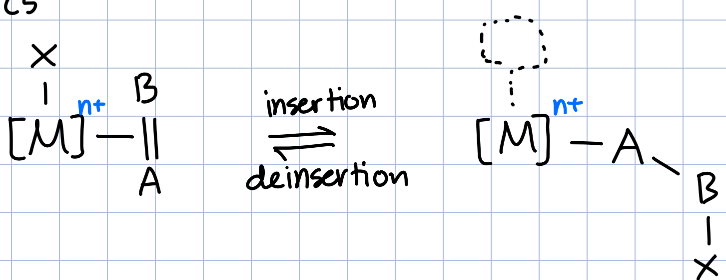
⤳ distinct mech.

Mechanisms are different:



so far — Heck

MI Basics

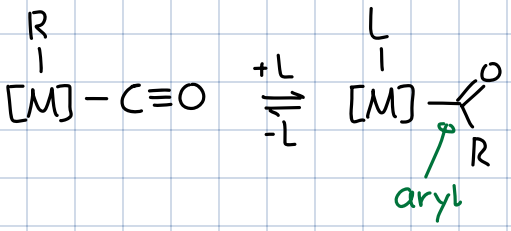


A=B : C=C , C≡O , C≡C

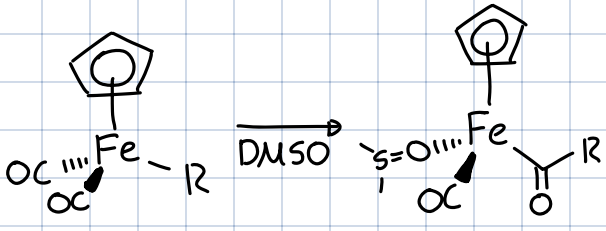
X : H, R, Ar (most common), NR, OR, etc. — not Halogens

Observe:
- Ox. state M preserved
- New coord. site opened up
- VEC decreased by 2
- Net bond breaking ⇒ Eq. gouverned by bond strengths

Ex.:



→ Thermochem:



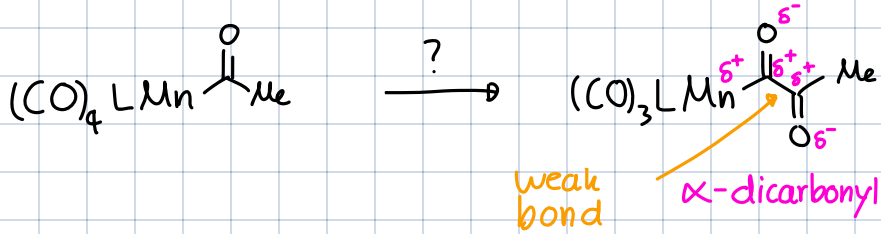
R	k_{rel}
Me	1
^{i}Pr	200
^{t}Bu	500
Np	600

e^--richness
⇒ M-R bond gets weaker ⇒ faster MI
$M^{\delta+}-R^{\delta-}$

With the same argument
→ General trend for metal

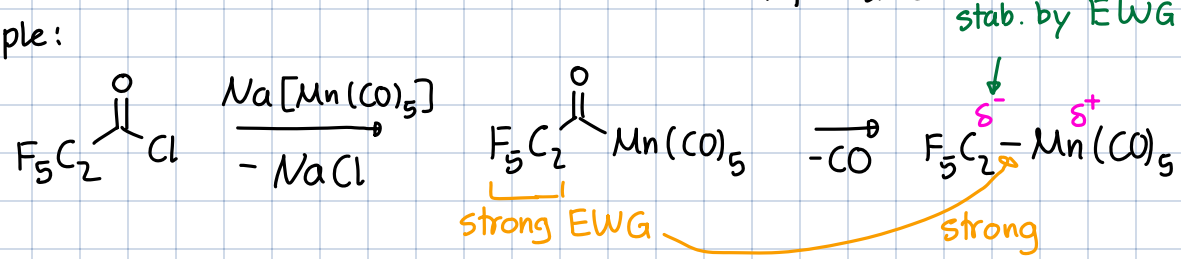
k_{MI}: 1st row > 2nd row > 3rd row
faster, weak M-L — slower, strong M-L

MI of CO "more than once"?

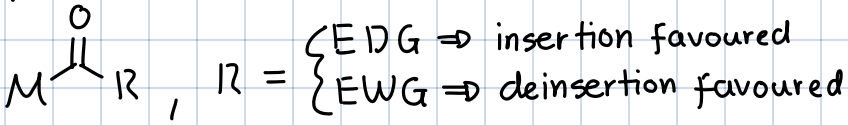


⇒ The product is unstable, as no good way to balance the partial charges
⇒ If even, the eq. would lie strongly on the left side

Example:



→ Summary:



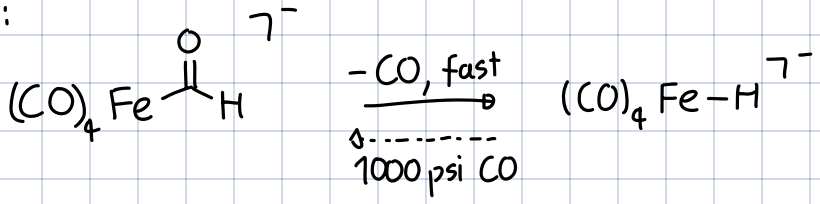
CO MI with M-H

Recall: L_nM-H > $L_nM-C(sp^3)$

L_nM-H: ~60-80 $\frac{kcal}{mol}$; $L_nM-C(sp^3)$: ~30-40 $\frac{kcal}{mol}$

⇒ CO rarely inserts in M-H, as strong bond has to be broken

Ex.:



Rare ex.: