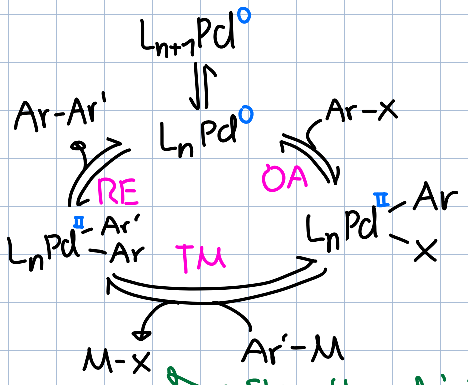
18.10.

Transmetalation (TM)

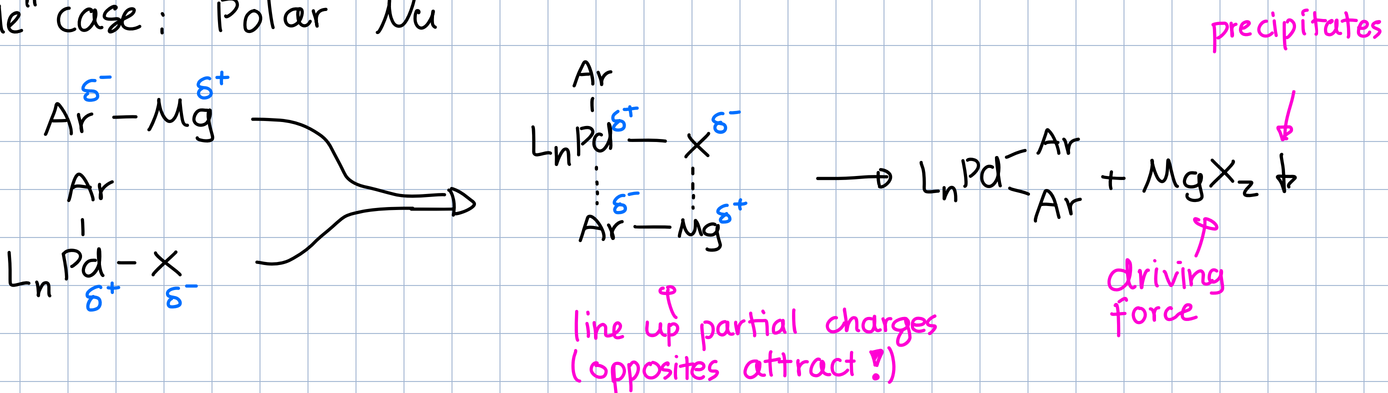
Recall Pd-cat cross-coupling:



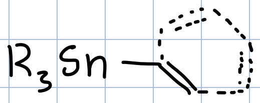
often the driving force of the rxn

TM least understood of the three steps, because it is often not RDS
⇒ kinetic studies are no use

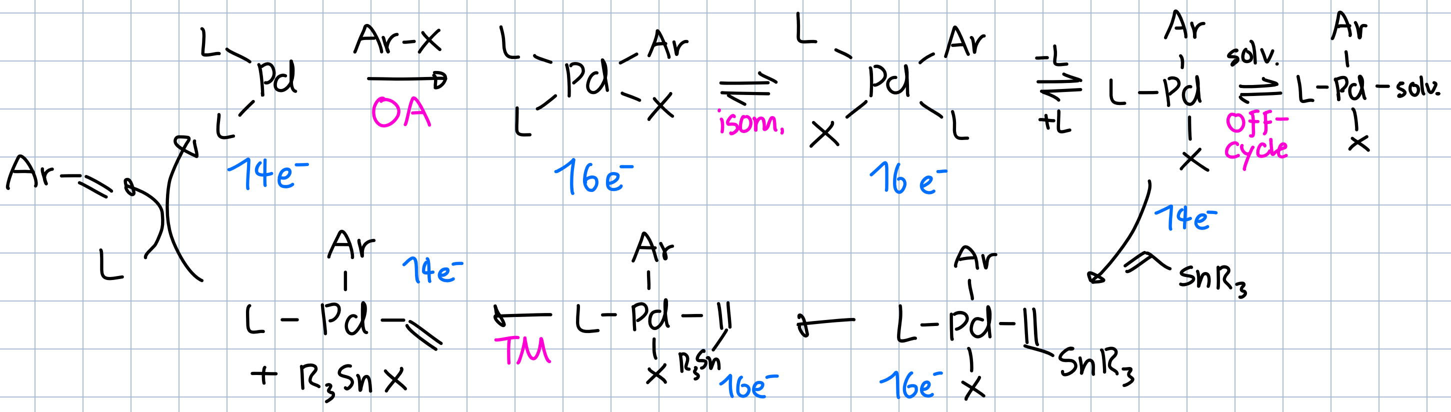
"Simple" case: Polar Nu



TM of Sn

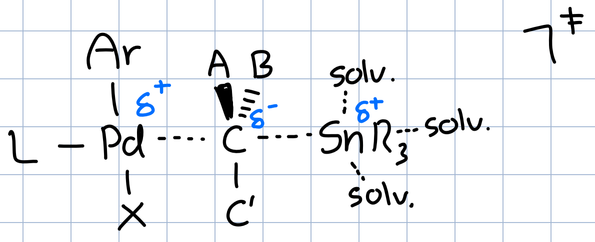


Recall from OA: When we have π-sys., then coord. fav. there



TS? We have two possibilities:

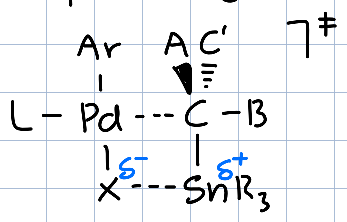
1. very polar solvent (eg MeOH, H_2O):



"Open TS"

⇒ Sn preferentially interacts with the solvent, instead of X.

2. less polar (eg. THF, Toluene):

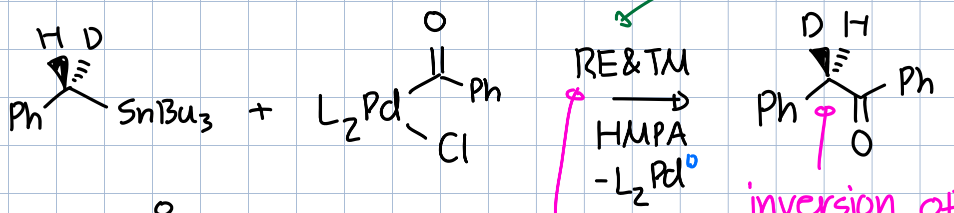


"Closed TS"

⇒ Sn pref. interacts with X, as solv. not so nucleoph.

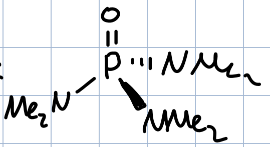
How to differentiate? Stereochemistry!

will immediately follow



inversion of the stereochem

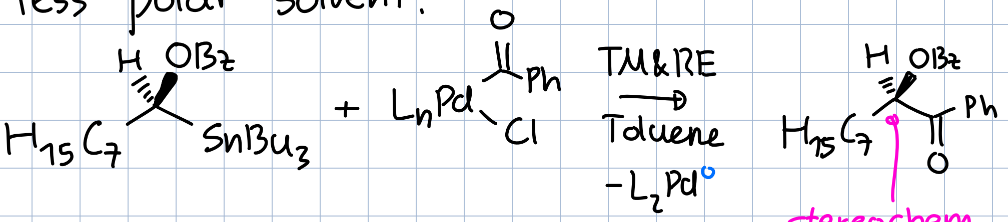
HMPA:



→ very polar solvent

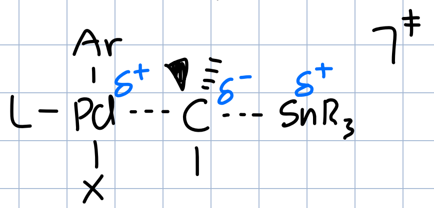
We know that RE should retain stereochem ⇒ inv. in TM

In a less polar solvent:

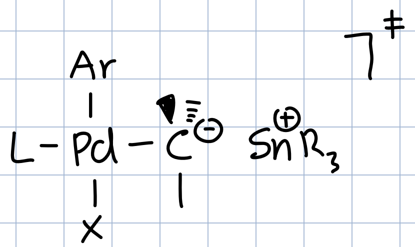


stereochem. retained

Electronic effects:



→ actually better desc. by



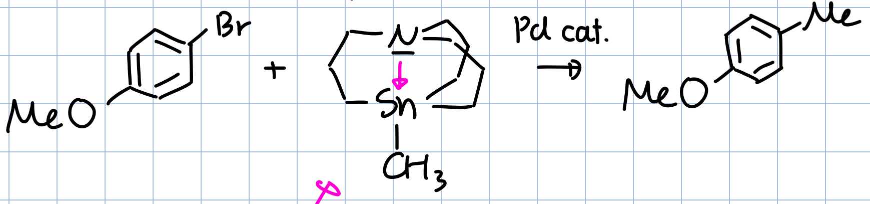
⤳ If that's true: To accelerate either stabilize carbanion or Sn cation by subst.:

$R'SnR_3$ with R': $Ph-C\equiv C > Pr-C\equiv C > Ph-C=C > Ph > CH_3 > Bu$

faster (stabilize $C^{\ominus}$) ← → slower

To stabilize $Sn^{\oplus}$:

1. Add Lewis base (eg F^-)
2. Built-in Lewis base:



if replaced by $SnMe_4$: No rxn

⇒ LB makes possible

What about Suzuki Coupling?

Recall:

$$Ar-X + Ar-B(OR)_2 \xrightarrow[\text{Base}]{\text{Pd cat.}} Ar-Ar'$$

Why the base?

$$\begin{tikzcd}
 & & Ar'-B(OH)_2 + K_2CO_3 \arrow[d, shift left, "H_2O"] & \\
L_nPd \arrow[r, "ArI", "OA"'] & L_nPd\genfrac{}{}{0pt}{}{Ar}{I} \arrow[rr, "Ar'-B(OH)_3K + KHCO_3"] \arrow[d, shift left, "+K_2CO_3+H_2O"] & {} \arrow[u, shift left] & L_nPd\genfrac{}{}{0pt}{}{Ar}{Ar'} \arrow[r, Rightarrow] & {} \\
 & {\left[L_nPd\genfrac{}{}{0pt}{}{Ar}{OH}\right]} \arrow[u, shift left, "-KHCO_3\ -KI"] \arrow[urr, "Ar'-B(OH)_2"] & & &
\end{tikzcd}$$

preform reagent?

pathway that's actually followed