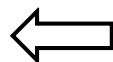
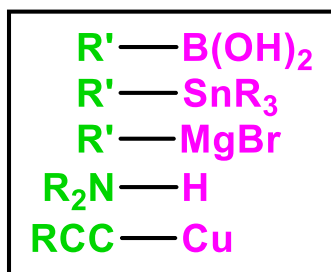
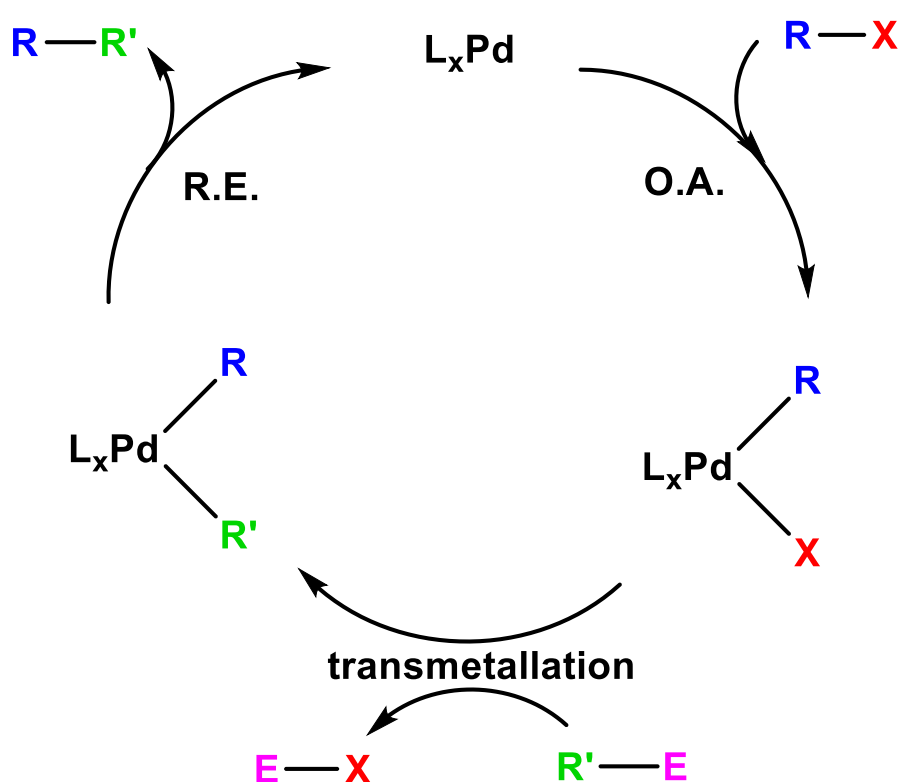


Palladium Catalyzed Coupling Reactions

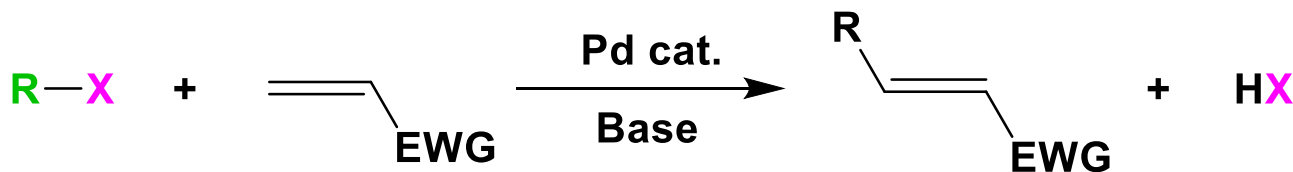
Mechanism:



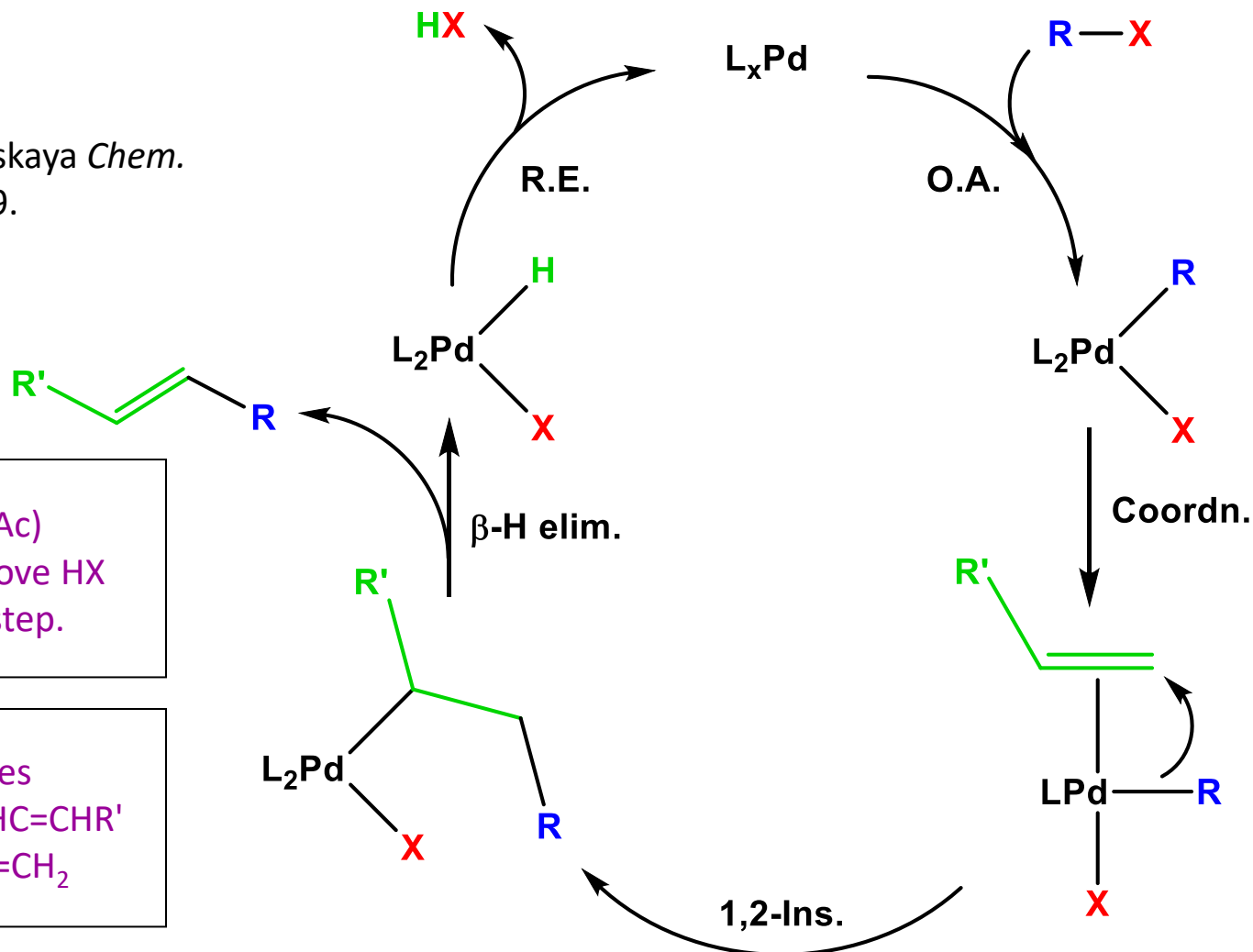
Formed from RC_2H and CuI

- $Pd(PPh_3)_4$ is OK for simple substrates.
- $Pd_2(dba)_3 + 4 PR_3 \rightarrow "Pd(PR_3)_2"$ often much more active and can choose PR_3 . (dba = dibenzylidene acetone)
- $PdCl_2$ or $Pd(OAc)_2$ + several equiv. of PR_3 are often used $\rightarrow Pd^{II}$ is mysteriously reduced to Pd^0 before catalysis can begin.
- CsF or KF often added $\rightarrow F^-$ coordinates to $ArB(OH)_2$ or $ArSnR_3$ to make a better leaving group.
- $KOtBu$ often present: (1) often necessary to remove HX formed in the reaction, (2) can do same thing as F^- , (3) may help with pre-catalysis reduction of Pd^{II} to Pd^0 .

Heck Reaction Mechanism



- Review = Belatskaya *Chem. Rev.* **2000**, 3009.



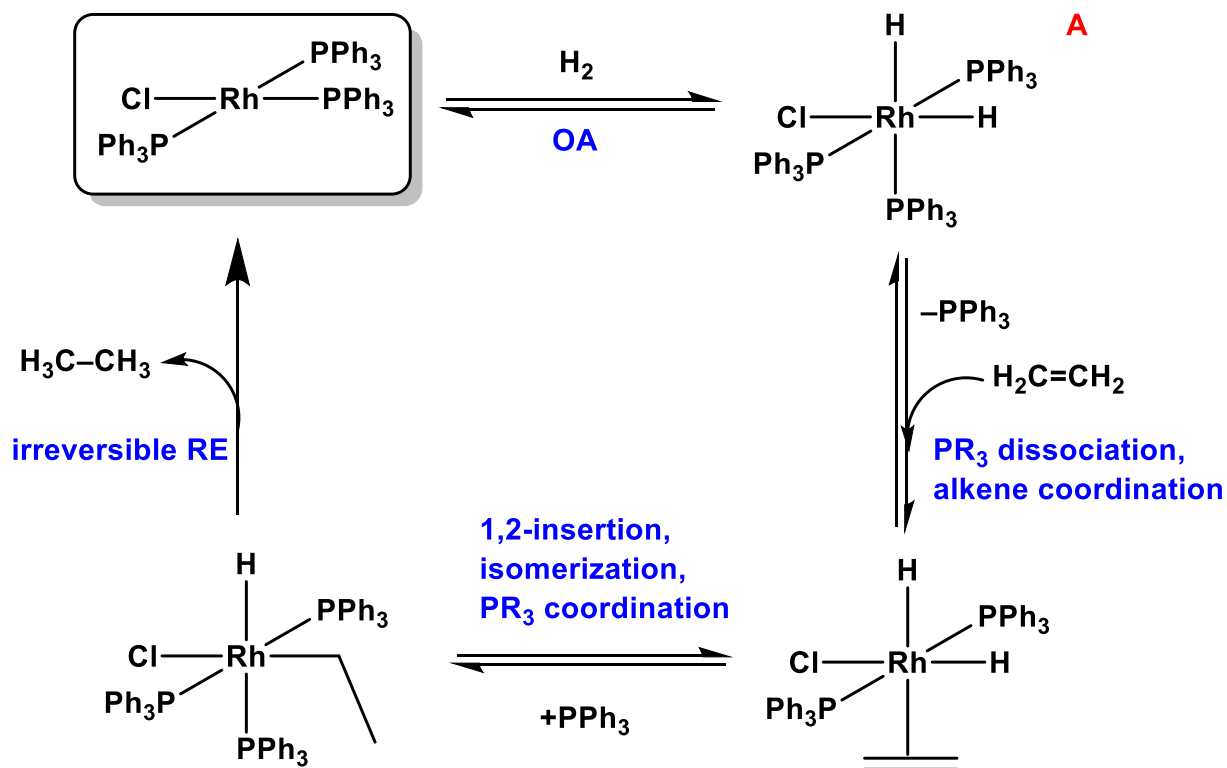
- Base (e.g. NaOAc) needed to remove HX formed in last step.

- $R' = \text{EWG}$ ensures formation of $RHC=CHR'$ instead of $RR'C=CH_2$

Alkene Hydrogenation (Dihydride Intermediate)

Rh or Ir

- $[\text{RhCl}(\text{PPh}_3)_3]$ (Wilkinson's Catalyst)
- $\{[\text{Rh}(\text{NBD})(\text{m-Cl})_2]\}_2 + 4 \text{PR}_3$ or $\{[\text{Ir}(\text{COD})(\text{m-Cl})_2]\}_2 + 4 \text{PR}_3$
- $[\text{Ir}(\text{COD})(\text{PMePh}_2)_2][\text{PF}_6]$ or $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{Py})][\text{PF}_6]$
- $[\text{Rh}(\text{NBD})(\text{bidentate phosphine})][\text{PF}_6]$
- (NBD = norbornadiene)
- (COD = 1,5-cyclooctadiene)



- Note: Hydrogenation involves 1,2-insertion, so *syn*-addition to the alkene is observed.
- Note: Less substituted alkenes are hydrogenated faster.

