Chapter 11

Organometallic compounds

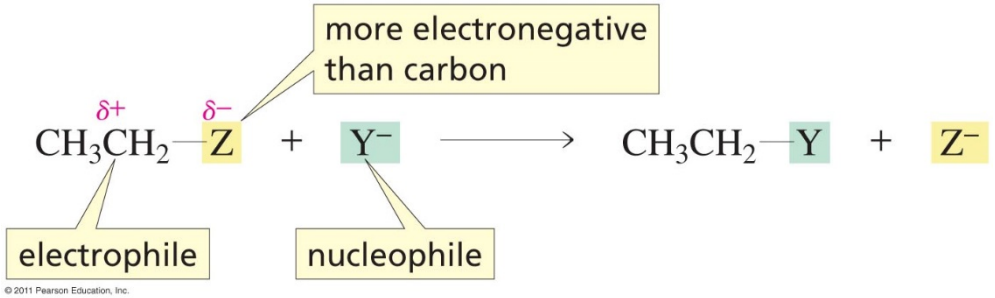
Organometallics

Reactions of organometallics

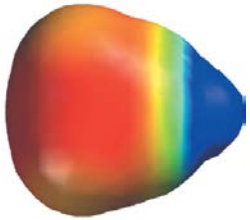
Organometallic compounds

- C in ROH and RX is e-philic.

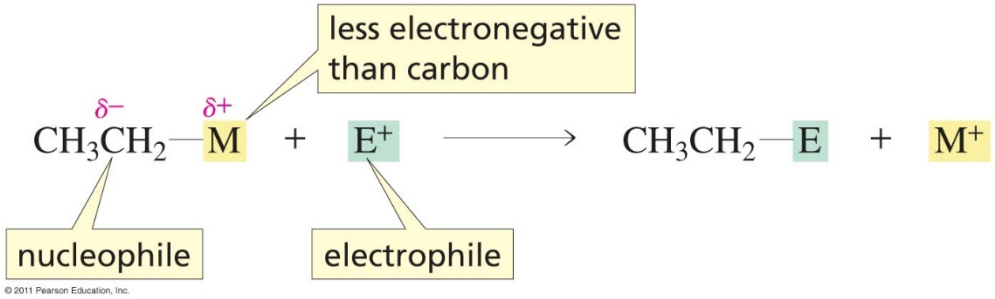
CH_3Cl



- C in organometallic comp'd is nucleophilic.
  - a carbon Nu:



CH_3Li



Li 1.0	Be 1.5					B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2					Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Co 1.7	Ni 1.7	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0			Br 2.8

CH_3CH_2MgBr
ethylmagnesium bromide

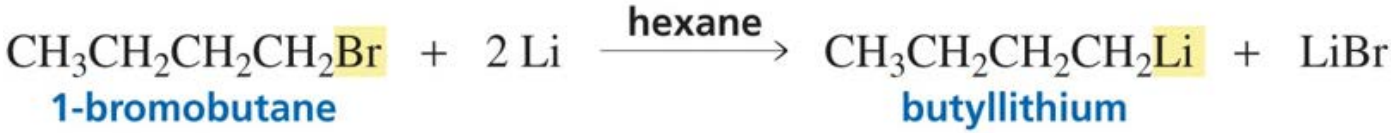
$CH_3CH_2CH_2CH_2Li$
butyllithium

$(CH_3CH_2CH_2)_2Cd$
dipropylcadmium

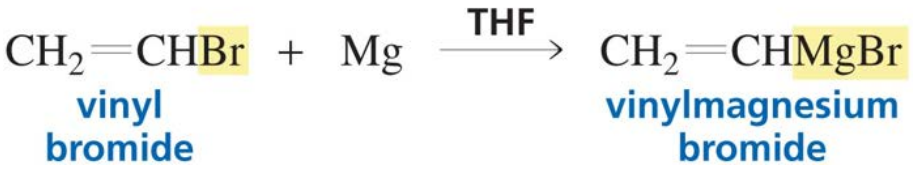
$(CH_3CH_2)_4Pb$
tetraethyllead

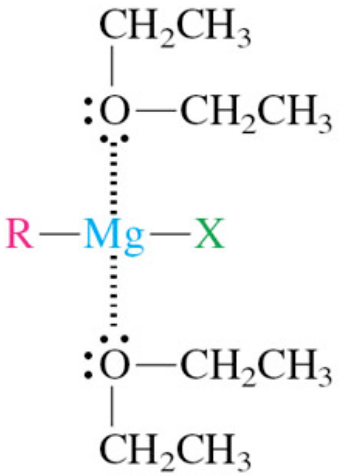
R-Li and R-MgX

- the two most common organometallics
- organolithium comp'ds



- organomagnesium comp'ds = Grignard reagents

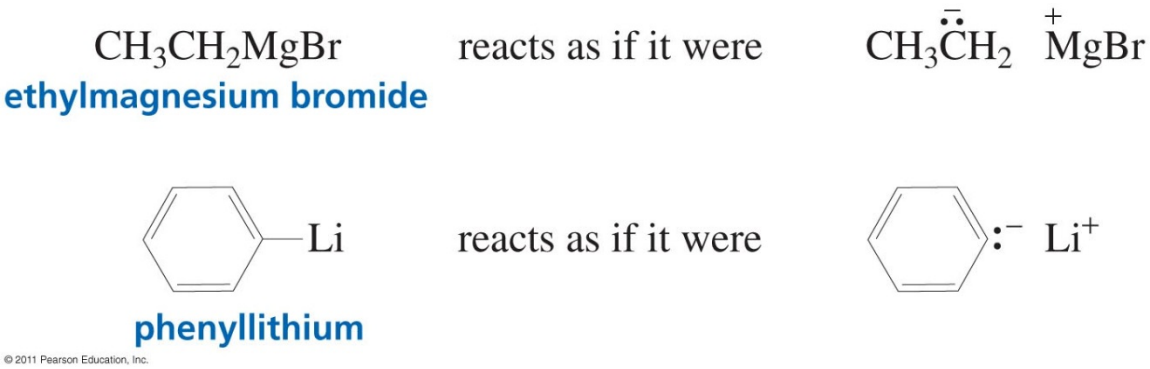




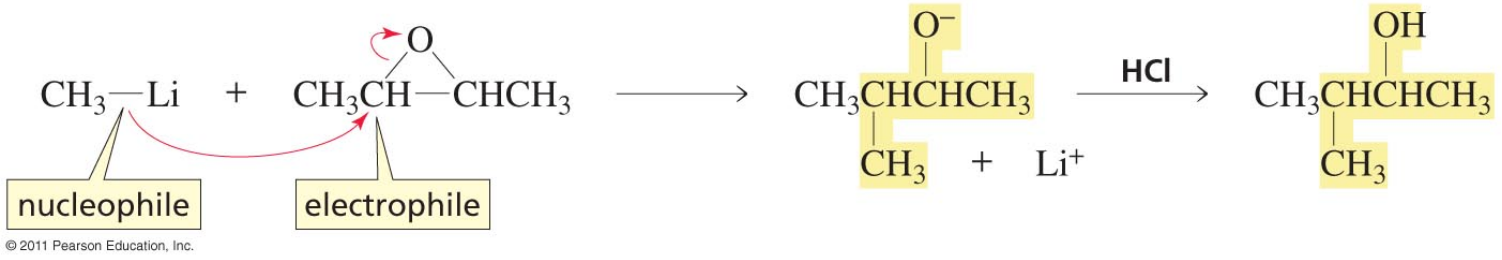
  - Ether coordinates Mg, stabilizing it.

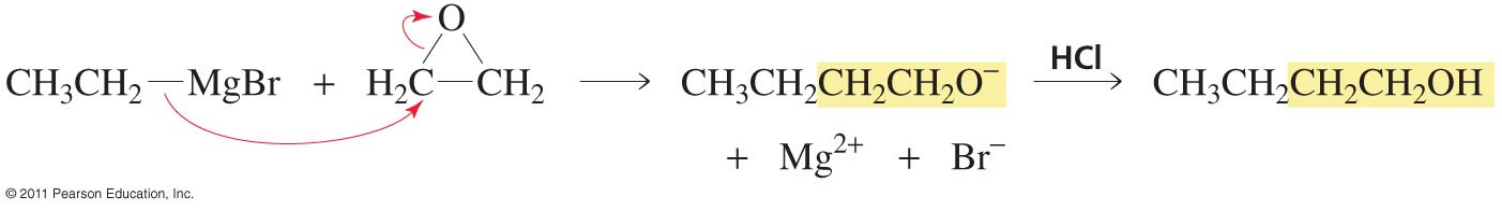
Reactions of R-Li and R-MgX

- reacts like a carbanion

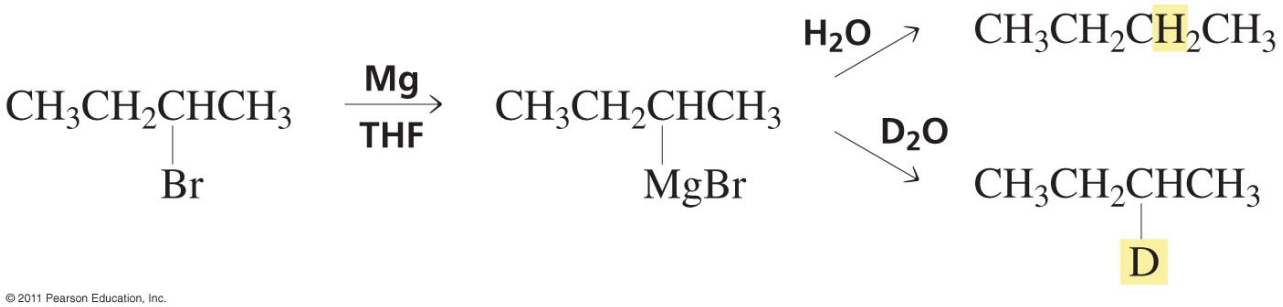


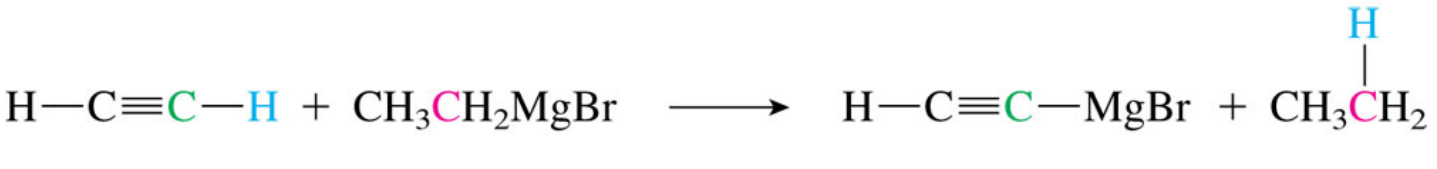
- S_N2 reaction forming C–C bond





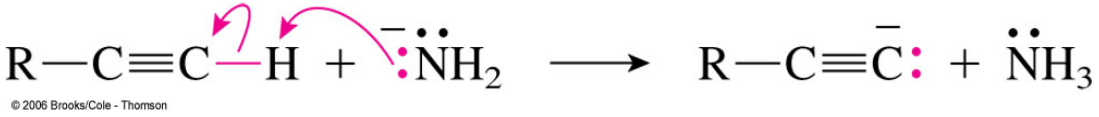
- R-Li and R-MgX are very strong B: ~ a C:⁻
  - react even with very weak acid





  - Storage and reaction must be acid- and moisture-free.

- Acetylide is an another carbon Nu:.



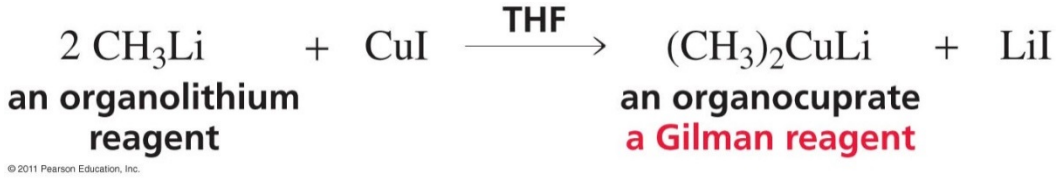
Transmetal(l)ation

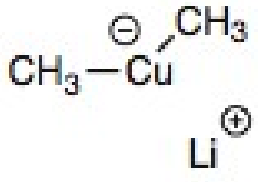
- R-Li is more reactive than R-MgX is.
  - Li (1.0) – C (2.5) vs Mg (1.2) – C (2.5)
- transmetalation
  - metal (or ligand) exchange
  - to less reactive organometallic

EN of Cd = 1.5

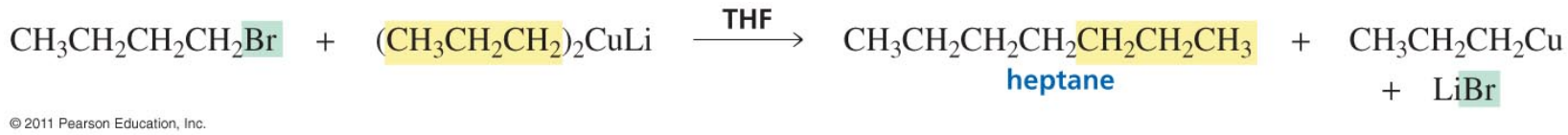
Coupling using Gilman reagent

- coupling reaction (in organic chemistry)
  - two hydrocarbon fragments are coupled [forming C–C]
  - with the aid of a (transition) metal catalyst
- Gilman reagent



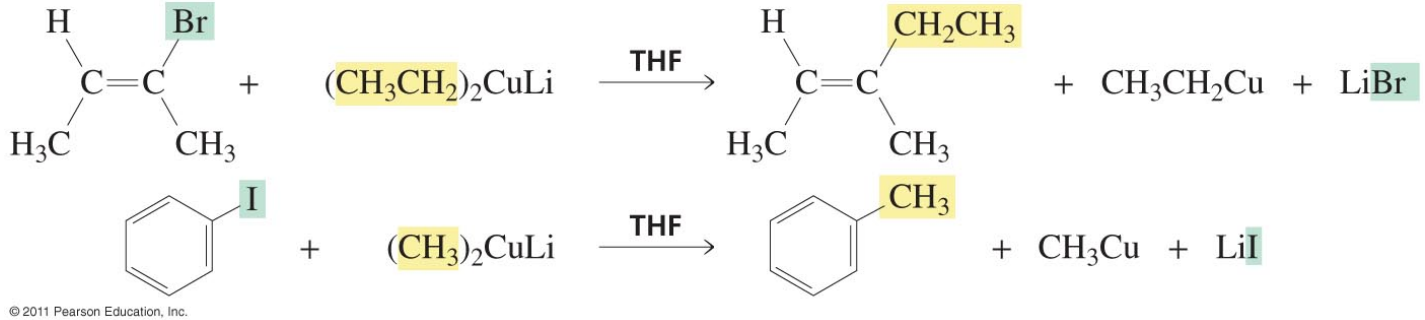


- coupling



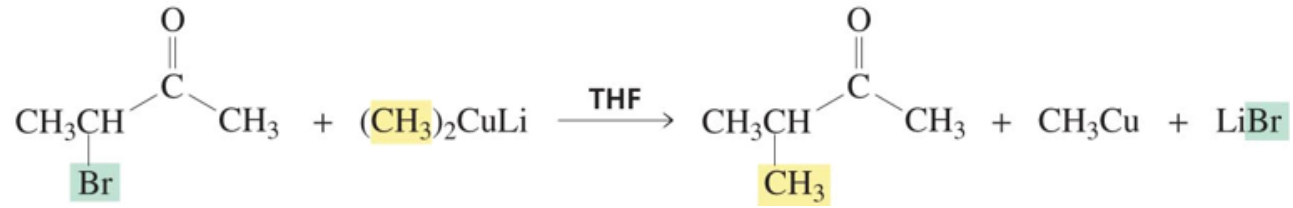
  - R of R_2CuLi replaces X forming R–R’
  - mechanism not clear

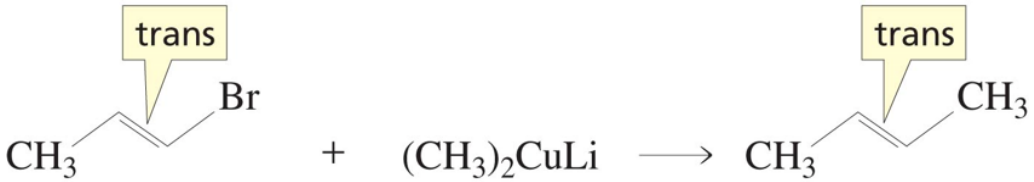
- R can be alkyl, aryl, or alkenyl [vinyl]



  - which is not possible by R-Li, R-MgX or RC≡C:⁻
    - why? an S_N2

- not sensitive to other functional groups





stereospecific

Pd-catalyzed couplings

- coupling using Pd
  - Suzuki rxn and Heck rxn representative
  - start with insertion of Pd betw R–X

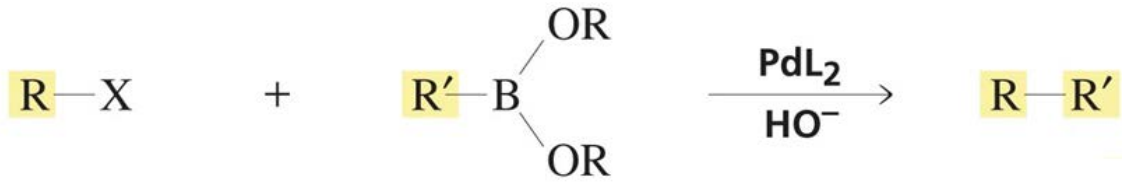
  - for vinyl or aryl halide (with sp^2 C)

  - not for sp^3 C – X ~ β-elimination (sometimes)

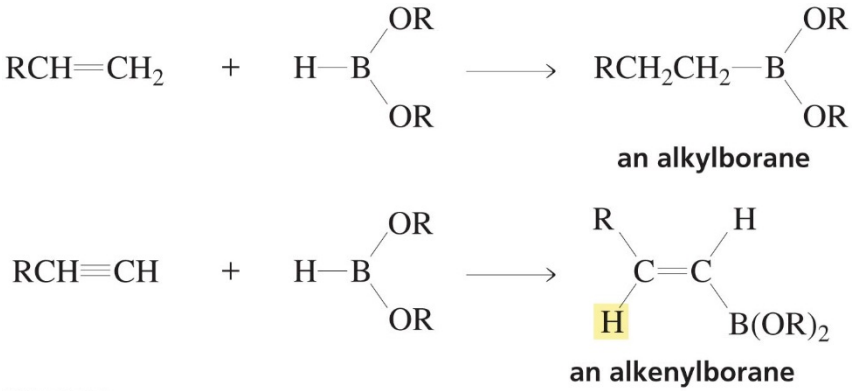
  - X can be Br, I, or OTf.
  - high yield, insensitive to other groups, stereospecific

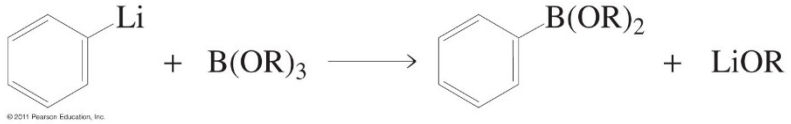
Suzuki reaction

- (cross-)coupling of R-X and organoborane [R'-BY_2]

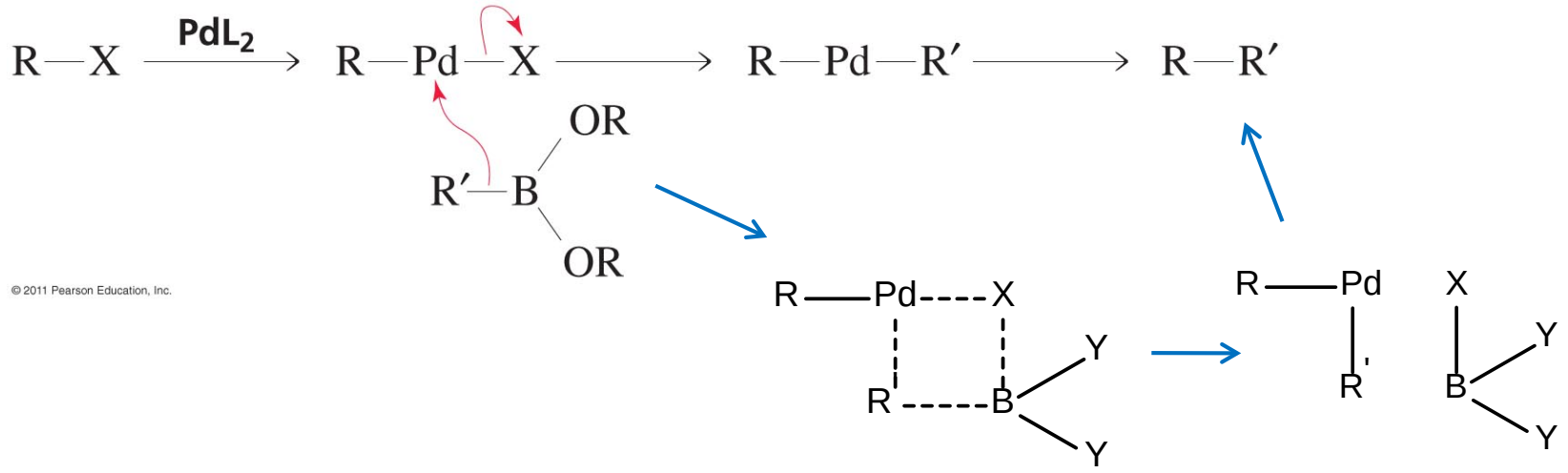


  - R must be aryl or vinyl
  - R' can be alkyl, alkenyl, or aryl
  - Y ~ H, OH, OR, --
  - L ~ ligand ~ PPh_3, Cl, ---
  - in basic condition ~ NaOH, K_2CO_3, -- ~ role not clear





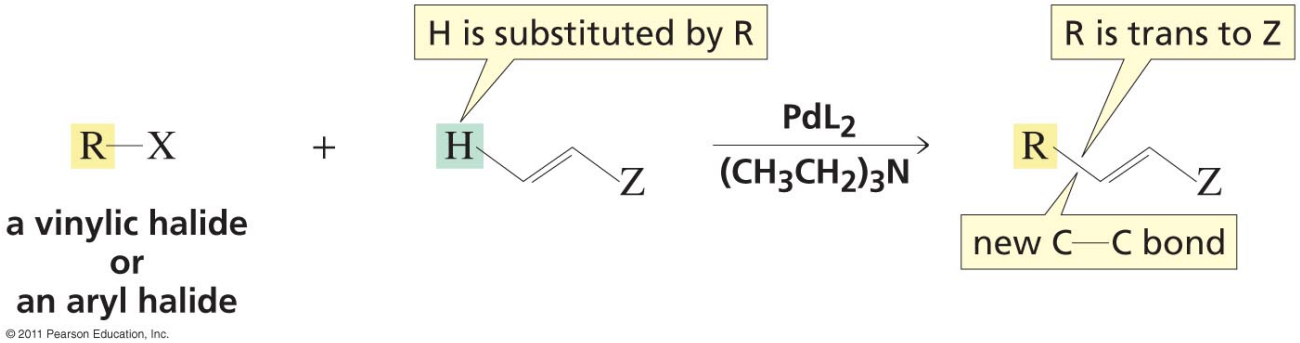
- (3-step) mechanism



1. oxidative addition ~ Pd^0 to Pd^{II}
2. transmetalation ~ from B (2.0) to Pd (2.4)
   - S_N2 of R' on Pd ~ X leaving
3. reductive elimination ~ Pd^{II} to Pd^0

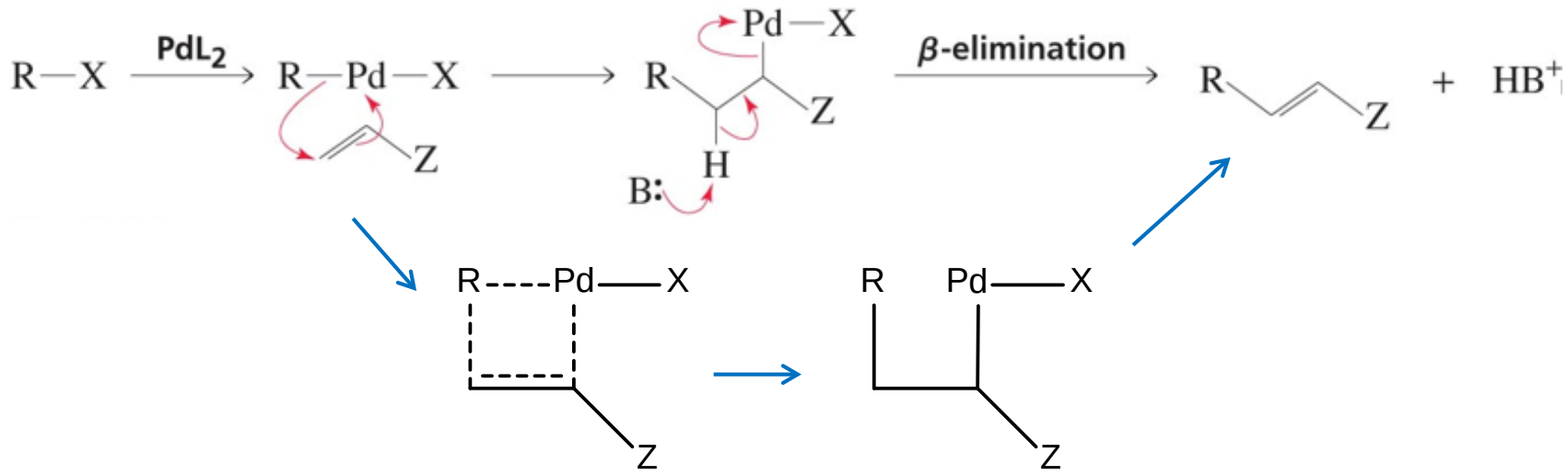
Heck reaction

- coupling of R-X and alkene

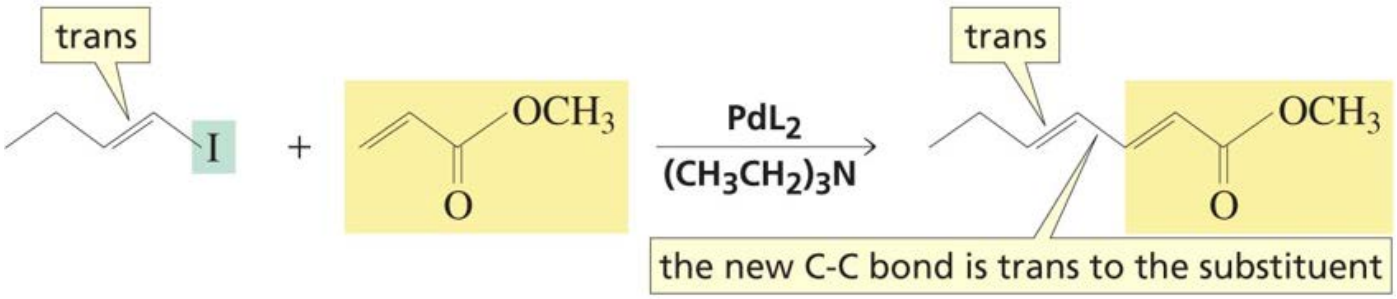


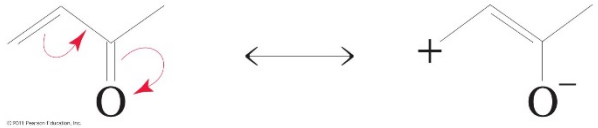
  - R must be aryl or vinyl
  - alkene is ethene or monosubstituted alkene
  - L ~ ligand ~ Cl, OAc, ---
  - in basic condition ~ Et_3N, KOAc -- ~ role not clear

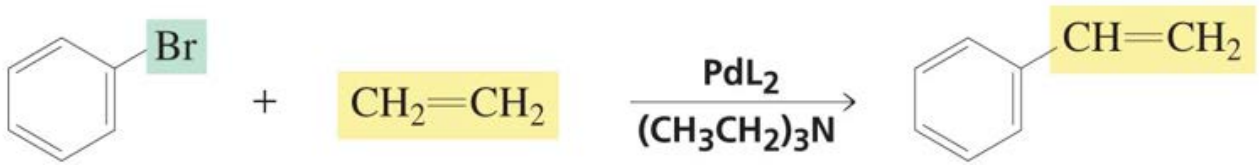
- (3-step) mechanism

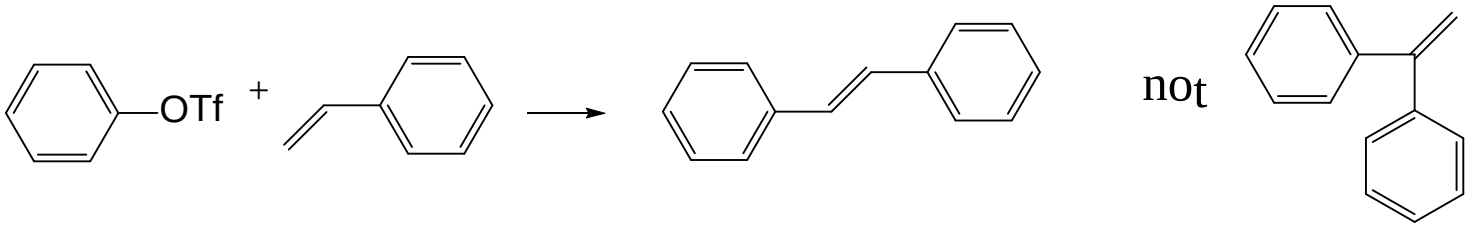


1. oxidative addition ~ Pd^0 to Pd^{II}
2. addition of R–Pd on =
3. β-elimination ~ Pd-X leaving


trans
I
+
OCH3
O
PdL2
(CH3CH2)3N
trans
OCH3
O
the new C-C bond is trans to the substituent

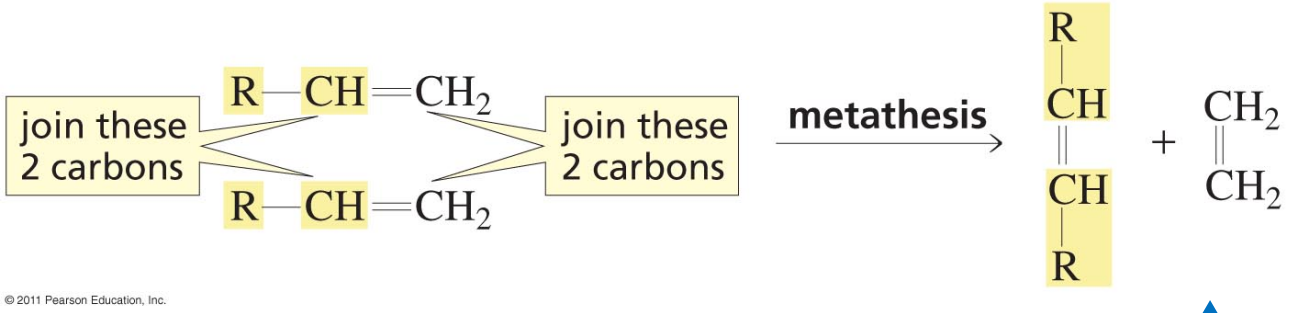

O
+
O−


Br
+
CH2=CH2
PdL2
(CH3CH2)3N
CH=CH2

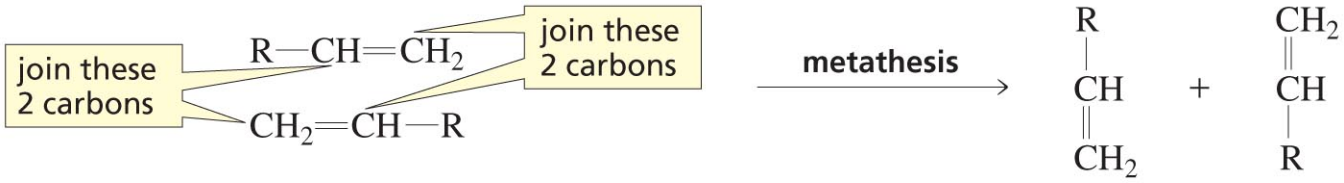

OTf
+
not

Olefin metathesis

- metathesis ~ exchange of bonds between reactants
- olefin [alkene] metathesis ~ breaking and rejoining =‘s
- cross-metathesis

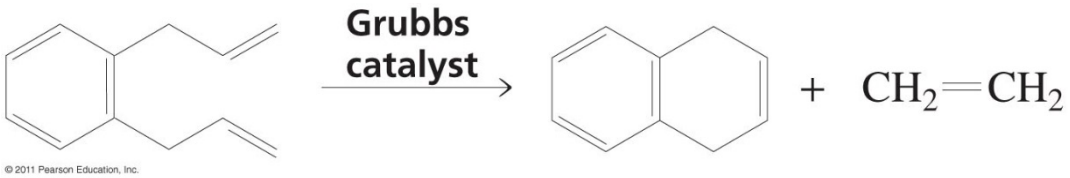


- if

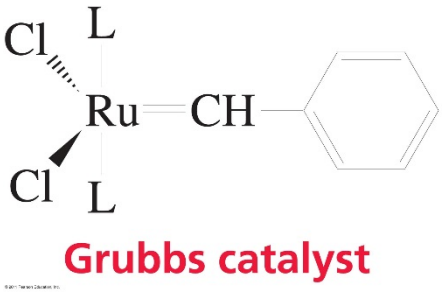


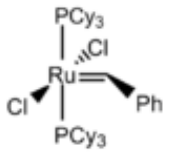
- Terminal alkene gives high yield. ← ethene ↑

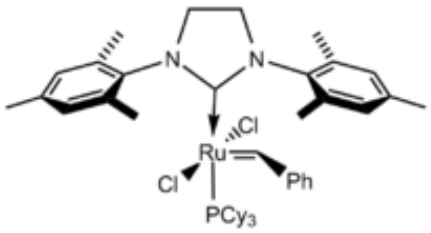
- ring-closing metathesis

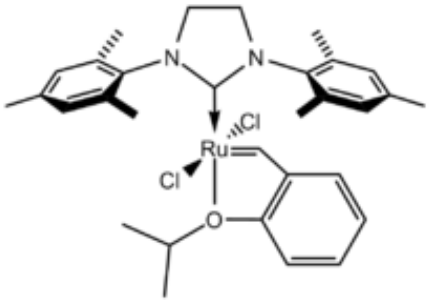


- OM made possible by Grubbs' catalyst
  - Ru-containing carbene [R_2C:]

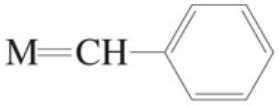


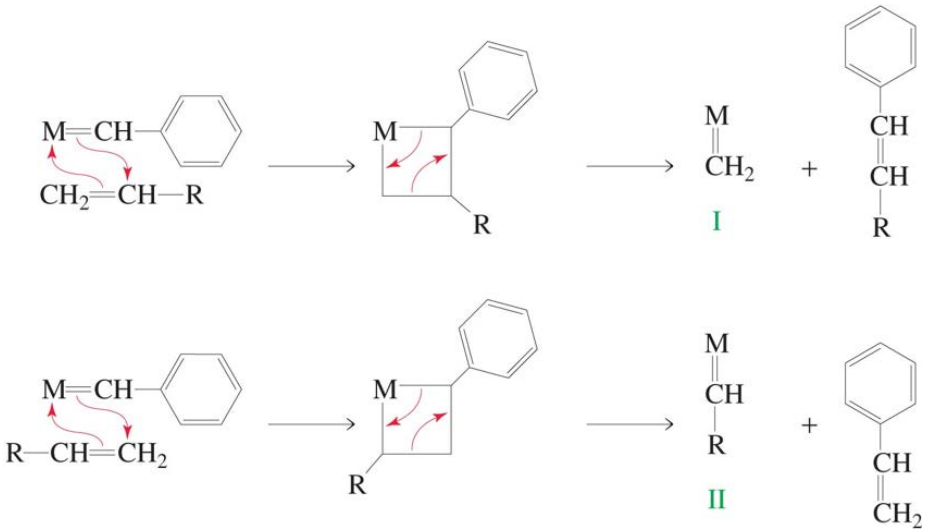




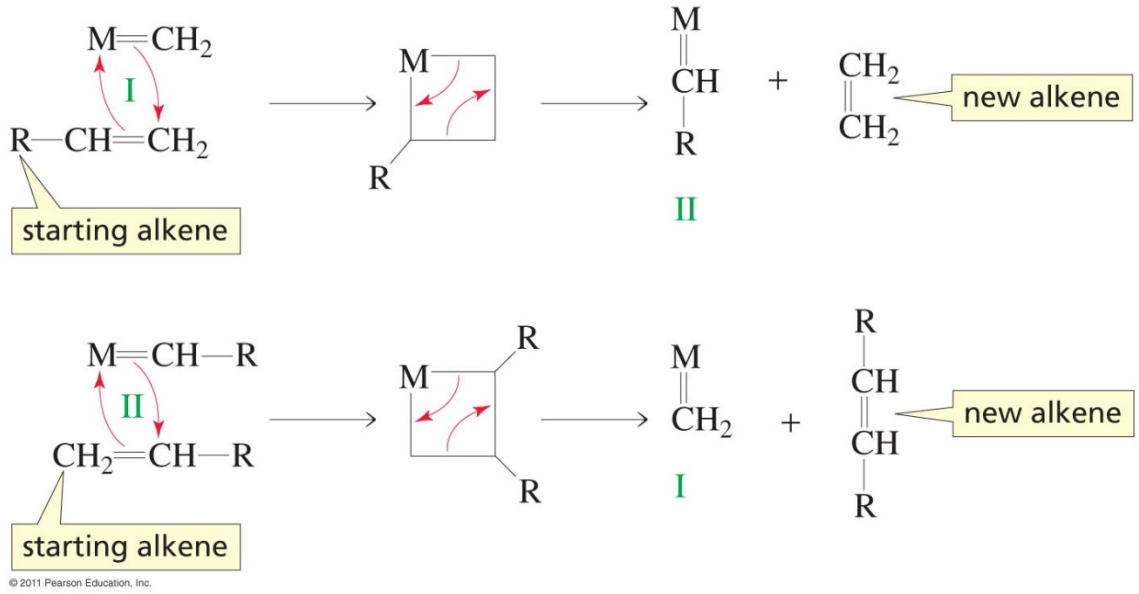


- mechanism

Grubbs catalyst is written as 

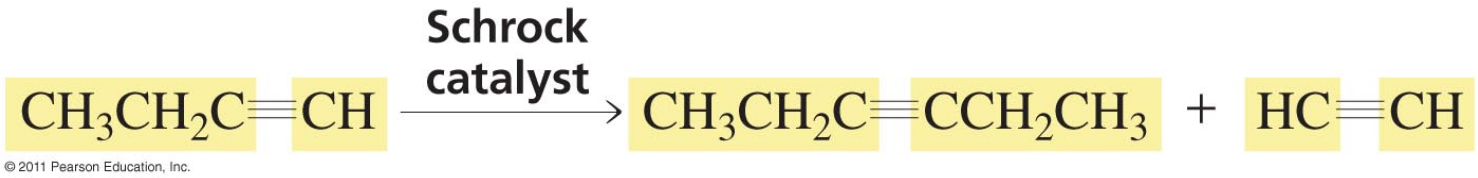


- RC=C → RC=CR + =



[2+2] cycloaddition followed by ring-opening

- cross-metathesis of alkynes



- ring-opening metathesis (polymerization) [ROMP]