Chapter 11

Organometallic compounds

Organometallics

Reactions using organometallics

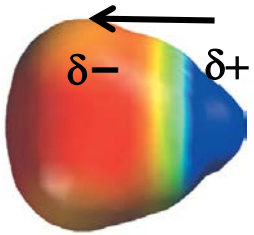
Organometallic compounds

= comp's containing a carbon-metal bond

$CH_3CH_2CH_2CH_2Li$
butyllithium

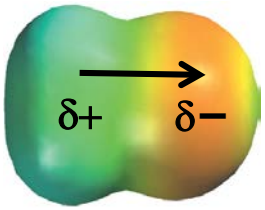
CH_3CH_2MgBr
ethylmagnesium bromide

$(CH_3CH_2CH_2)_2Cd$
dipropylcadmium



CH_3Li

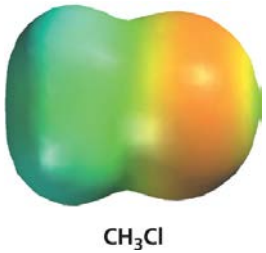
- C in organometallic comp'ds are nucleophilic.
  - C in organic comp'd (like ROH, RNH_2, and RX) are electrophilic.
  - due to ΔEN

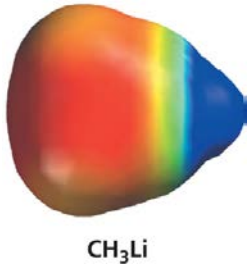


CH_3Cl

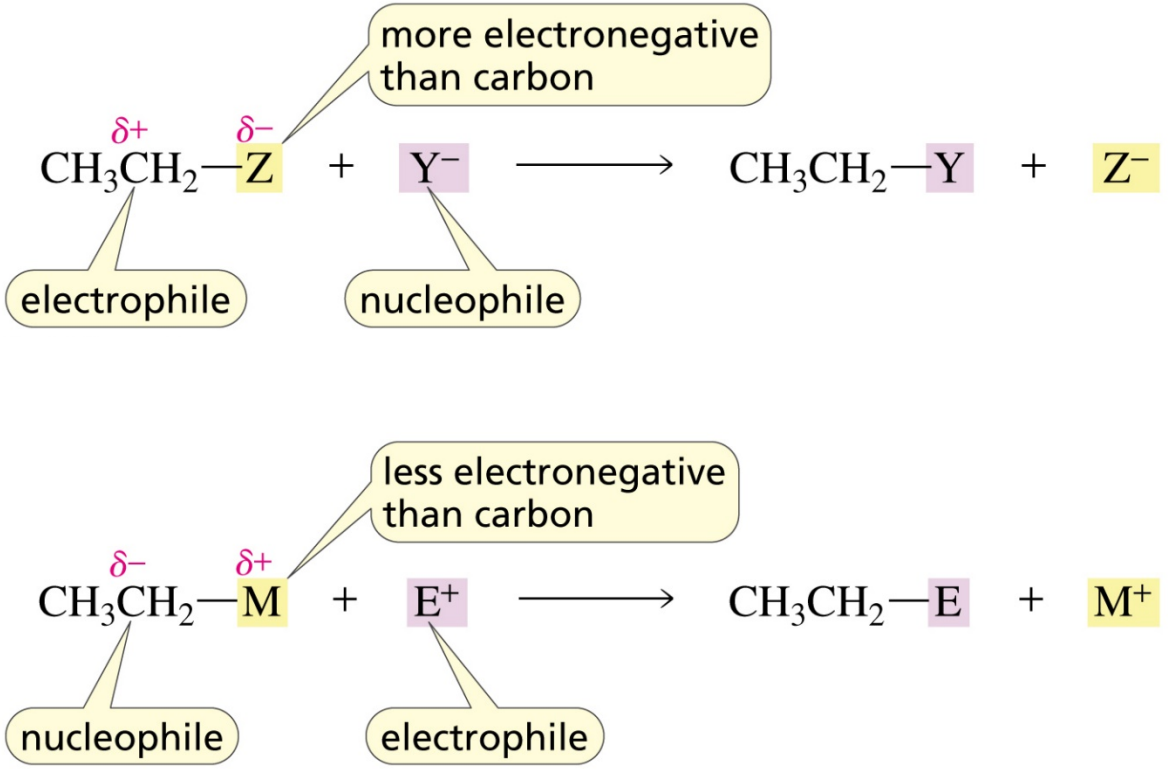
H 2.1										
Li 1.0	Be 1.5					B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2					Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Co 1.7	Ni 1.7	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0			Br 2.8
		Rh 2.4	Pd 2.4	Ag 1.8	Cd 1.5		Sn 1.7			I 2.5
					Hg 1.5		Pb 1.6			

- in substitution reactions





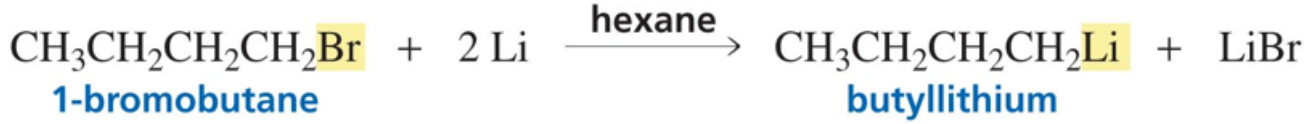
a carbon Nu:



R-Li and R-MgX

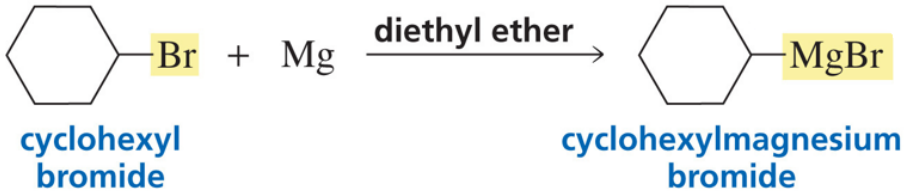
- (used to be) the two most common organometallics
- organolithium comp'ds

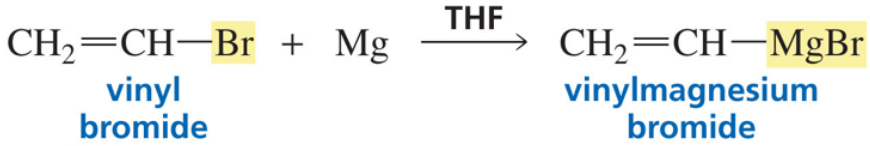
BuLi = an alkyl lithium

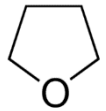


1912
Nobel Prize

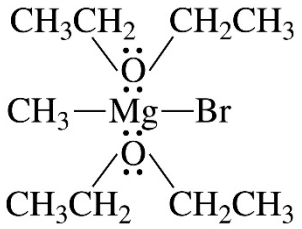
- organomagnesium comp'ds = Grignard reagents





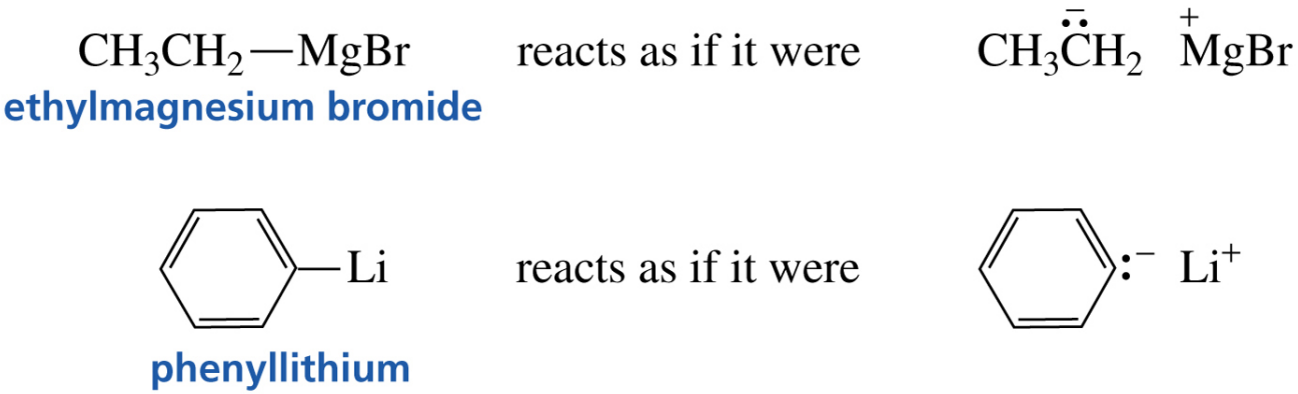


  - R, Ar, vinyl all possible; Br (as X) popular
- Ether (solvent) coordinates Mg, stabilizing it.



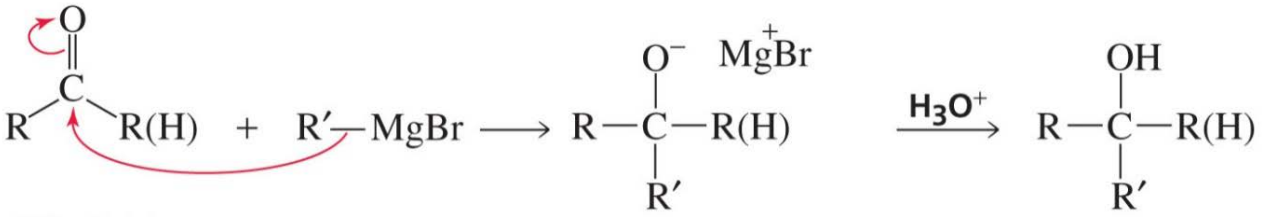
Reactions of R-Li and R-MgX

- reacts like a carbanion C:⁻ ~ a C Nu:



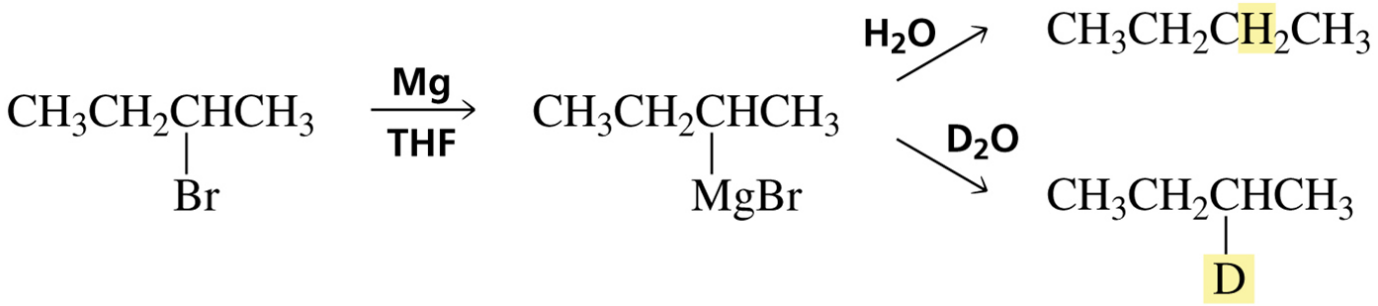
  - reactions as C Nu: (like $S_N(2)$)
  - nucleophilic addition to carbonyls ~ more often

Chapt 16



- R-Li and R-MgX are very strong B:
  - react even with very weak acid

how strong? pK_a?
stronger than ^-OH? $^-NH_2$?



useful for preparing deuterated HC

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

Transmetal(l)ation

- R-Li is more reactive than R-MgX is.
  - C–Li more polar than C–Mg
  - C of R-Li more nu-philic [better Nu:]
- transmetalation [metal exchange]
  - to less reactive [more stable] organometallic

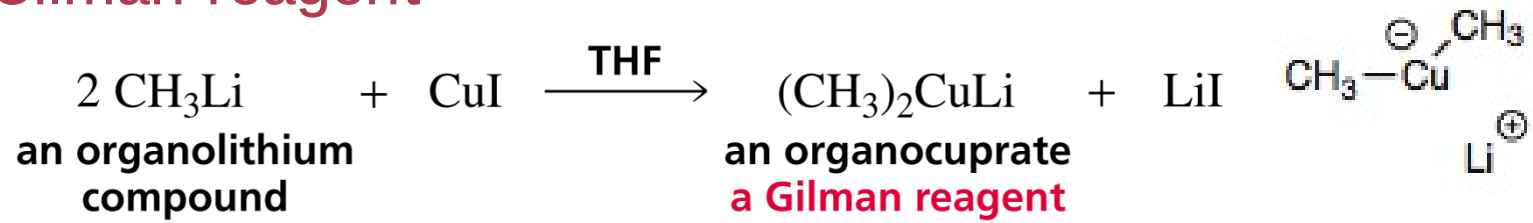
$$2\ CH_3CH_2MgCl + CdCl_2 \longrightarrow (CH_3CH_2)_2Cd + 2\ MgCl_2$$

ethylmagnesium chloride — diethylcadmium

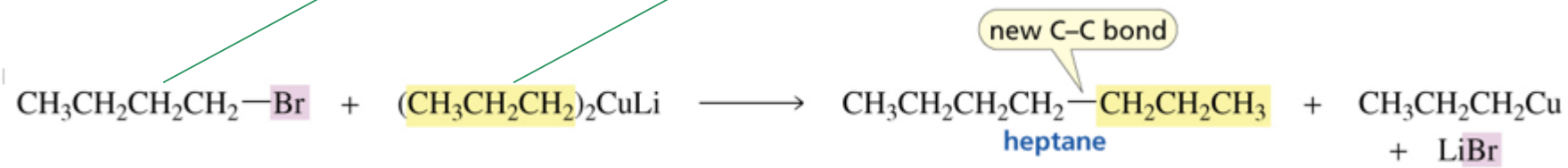
H 2.1										
Li 1.0	Be 1.5					B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2					Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Co 1.7	Ni 1.7	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0			Br 2.8
		Rh 2.4	Pd 2.4	Ag 1.8	Cd 1.5		Sn 1.7			I 2.5
					Hg 1.5		Pb 1.6			

Coupling using Gilman reagent

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

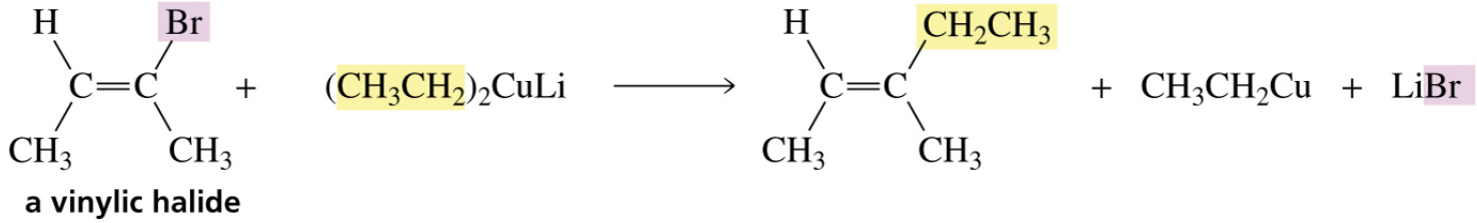


- coupling of R of R-X and R' of Gilman reagent



  - RX + R'$_2$CuLi → R–R'
  - mechanism? substitution of X with R'? not clear

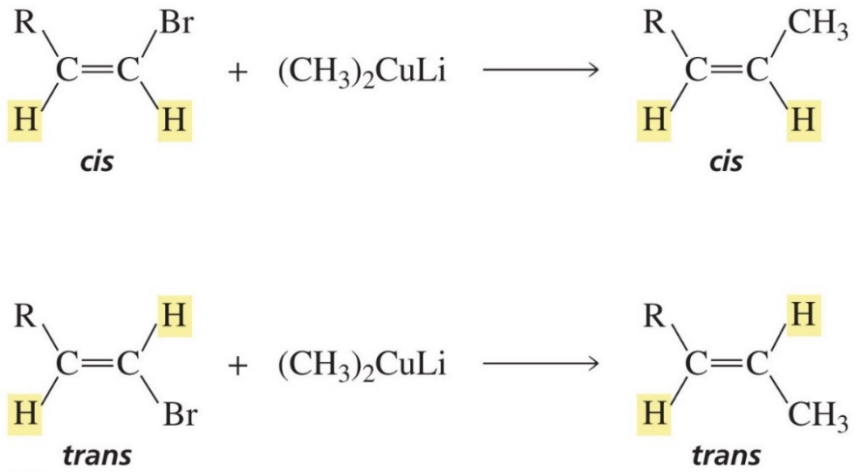
- R can be alkyl, aryl, or alkenyl [vinyl]



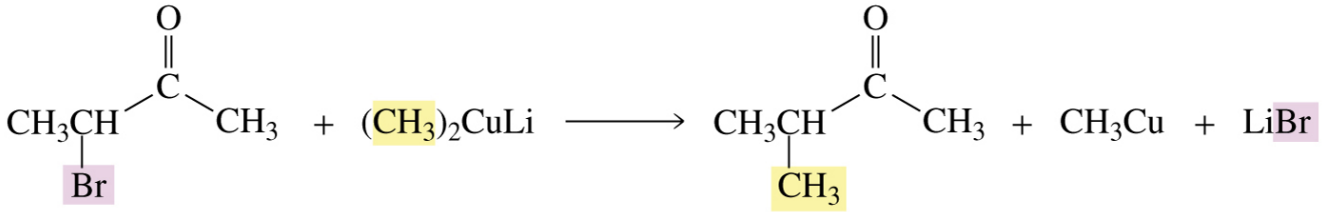
  - which is <u>not</u> possible by R-Li or R-MgX
    - why? they are $S_N(2)$.
  - not for (2°or) 3° alkyl
    - why? E intervenes; then mechanism S_N2?

Is R of Gilman reagent a Nu:? maybe yes and maybe no

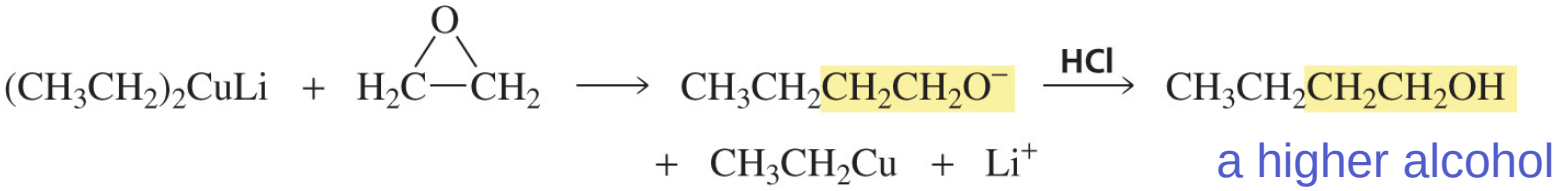
- stereospecific



- not sensitive to other functional groups

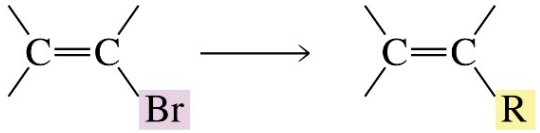


- also undergo S_N reaction (as a Nu:) with EO

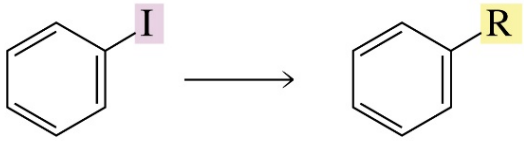


Pd-catalyzed couplings

- Suzuki rxn and Heck rxn representative
- couples (new) R with R of
  - vinyl or aryl halide (w/ sp^2 C) (only*)



a vinylic halide



an aryl halide

The Nobel Prize in Chemistry 2010

Photo: U. Montan
Richard F. Heck

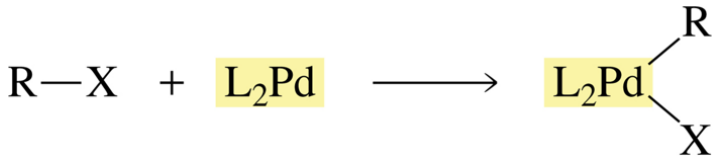
Photo: U. Montan
Ei-ichi Negishi

Photo: U. Montan
Akira Suzuki

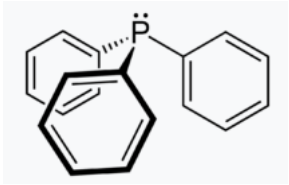
  - not* for sp^3 C – X

*others becoming possible

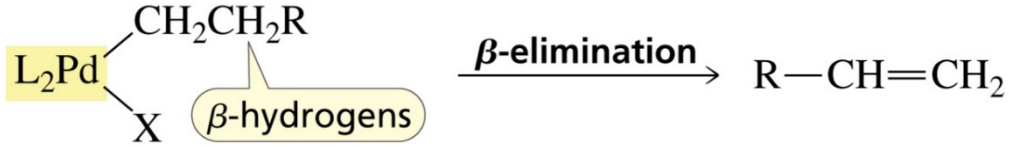
- why not for sp^3 C–X?
  - Rxn start with formation of



    - L = ligand (with :) like PPh_3
    - X = Br or I



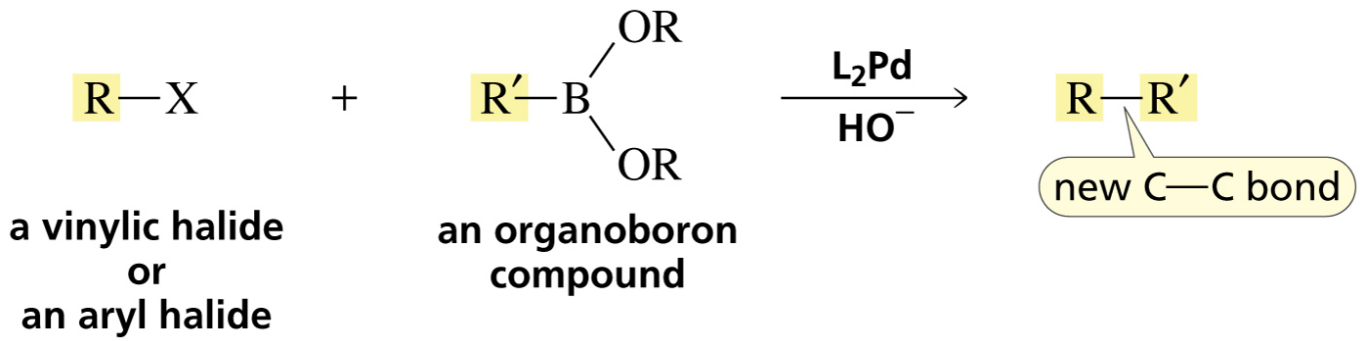
  - β-elimination (may) occur on sp^3 C–X



  - becoming possible by varying catalyst [L]
- insensitive to other groups, stereospecific
  - why Pd? (instead of Cu, despite --) ~ high yield

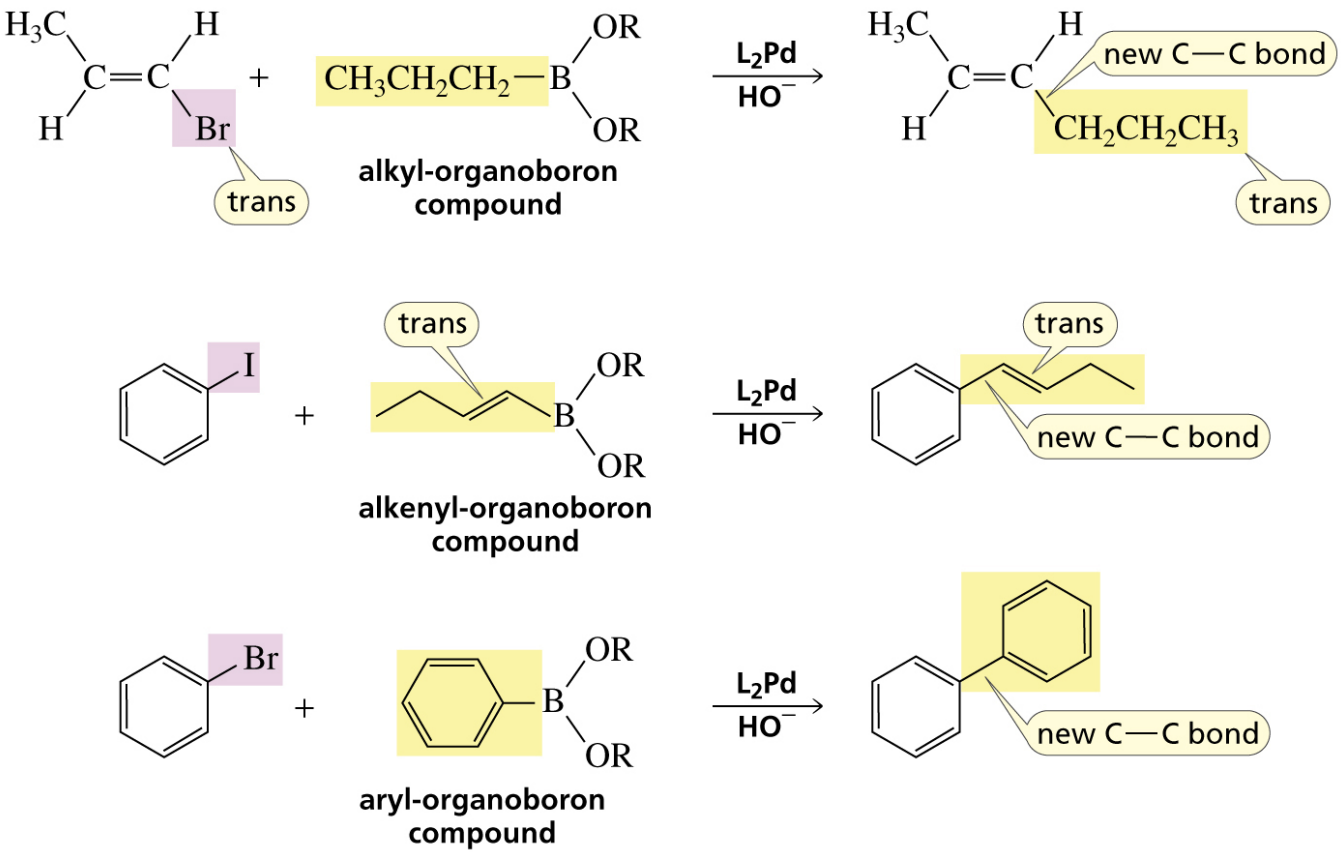
Suzuki reaction [coupling]

- couples R of R-X and R' of organoborane [R'-BY_2]

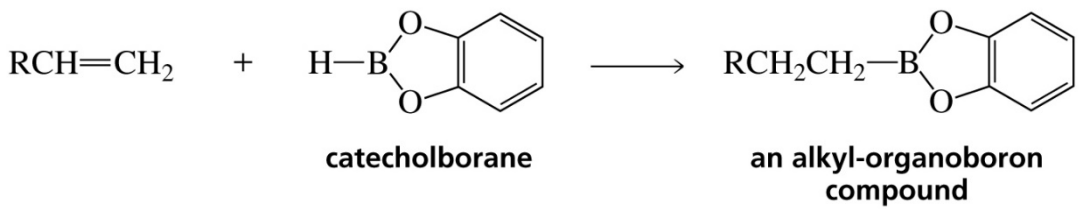


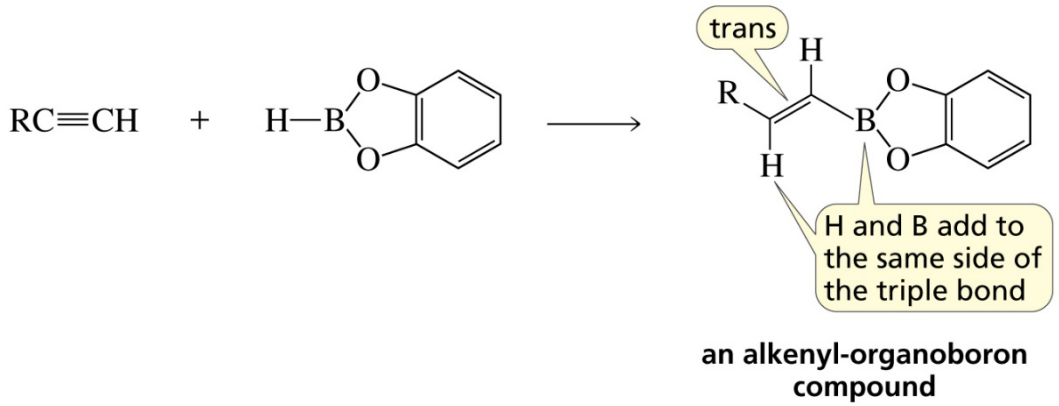
  - R = (usually) aryl or vinyl (not alkyl)
  - R' can be alkyl, alkenyl, or aryl
  - Y ~ H, OH, OR, --
  - L ~ ligand ~ PPh_3, Cl, ---
  - in basic condition ~ NaOH, K_2CO_3, --

- examples


H3C
H
C=C
H
Br
trans
+
CH3CH2CH2—B
OR
OR
alkyl-organoboron compound
L2Pd
HO−
H3C
H
C=C
H
new C—C bond
CH2CH2CH3
trans
stereospecific
I
+
trans
B
OR
OR
alkenyl-organoboron compound
L2Pd
HO−
trans
new C—C bond
always trans
why?
Br
+
B
OR
OR
aryl-organoboron compound
L2Pd
HO−
new C—C bond

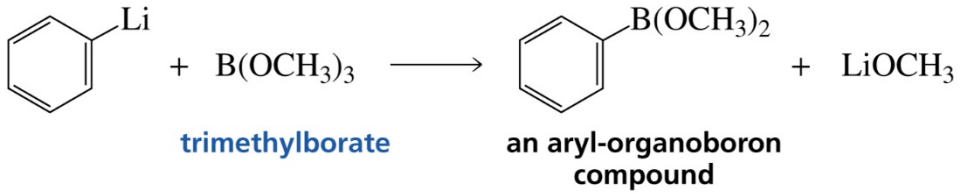
- preparation of organoboron comp'd



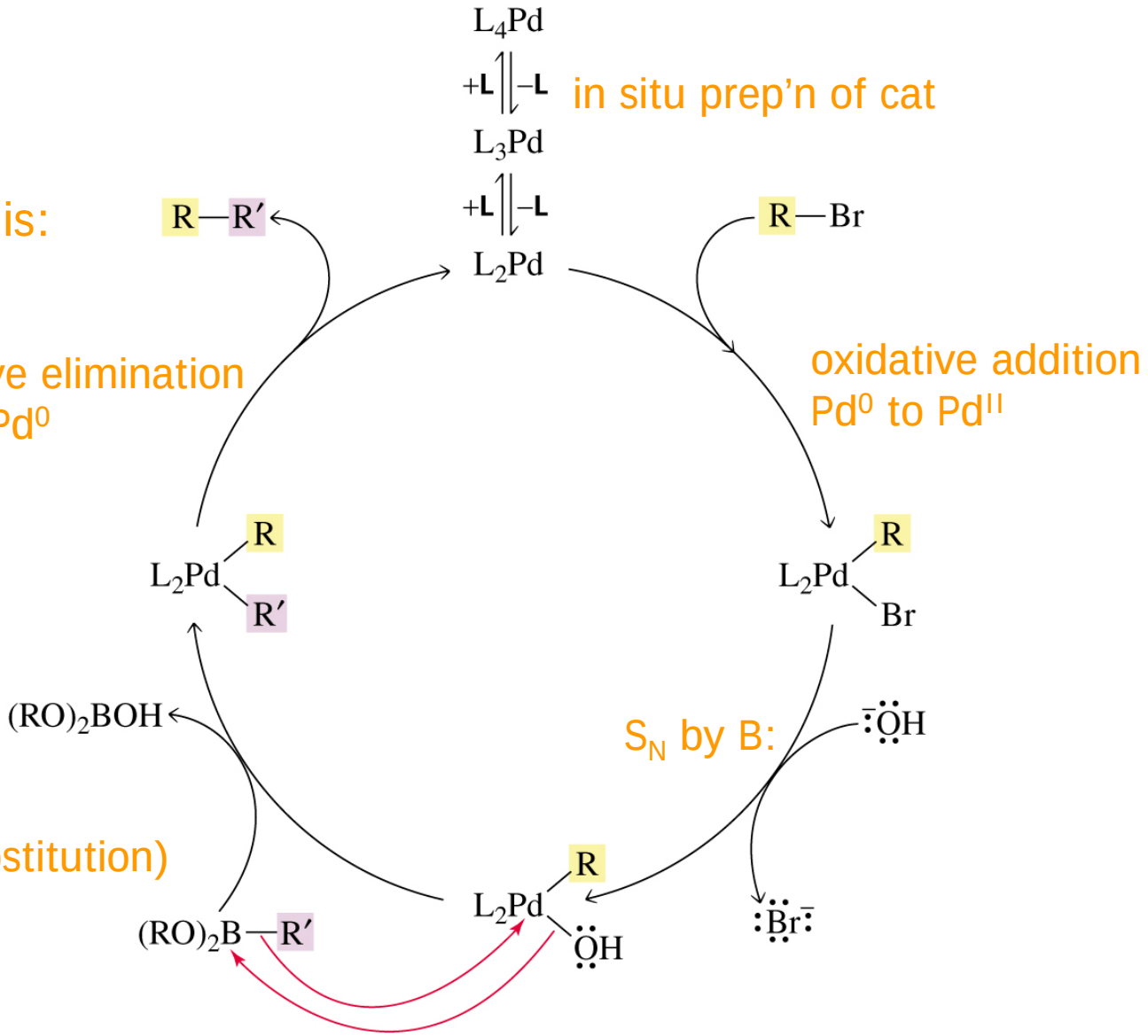


syn addition
→ *trans*

See §6.8

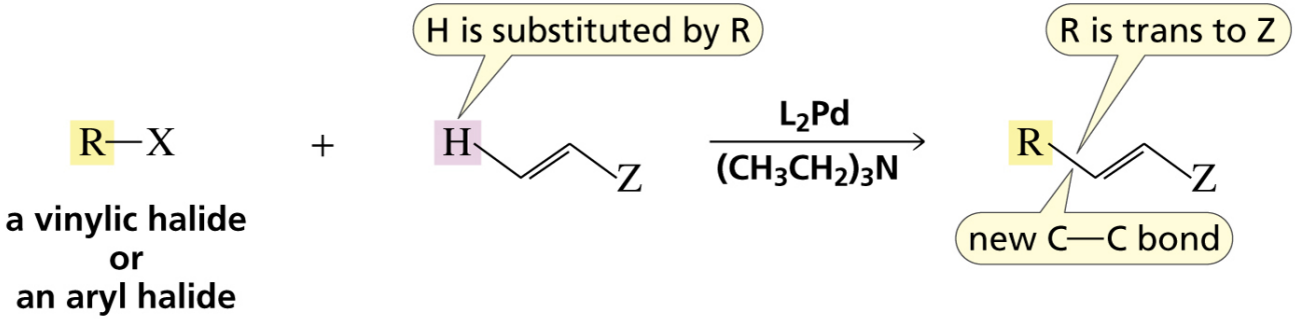


- mechanism
  - not clear yet; the (current) most plausible is:



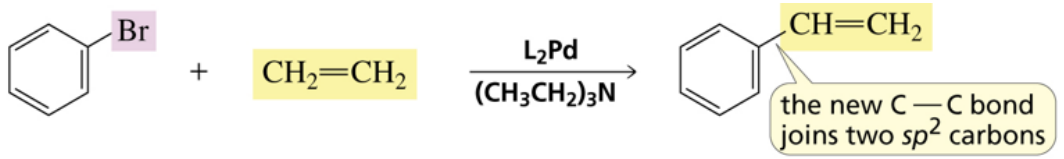
Heck reaction

- couples R of R-X and alkene

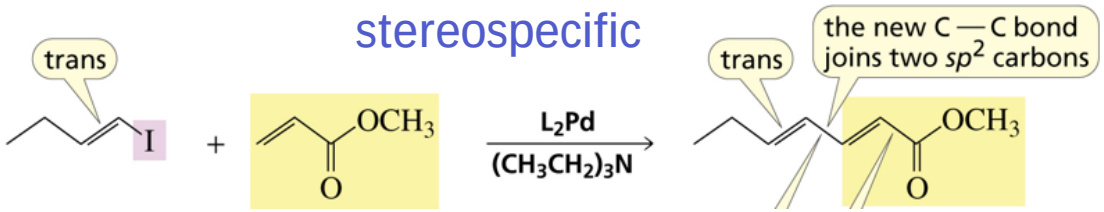


  - R = aryl or vinyl (not alkyl)
  - L ~ ligand ~ Cl, OAc, ---
  - in basic condition ~ Et_3N, KOAc --

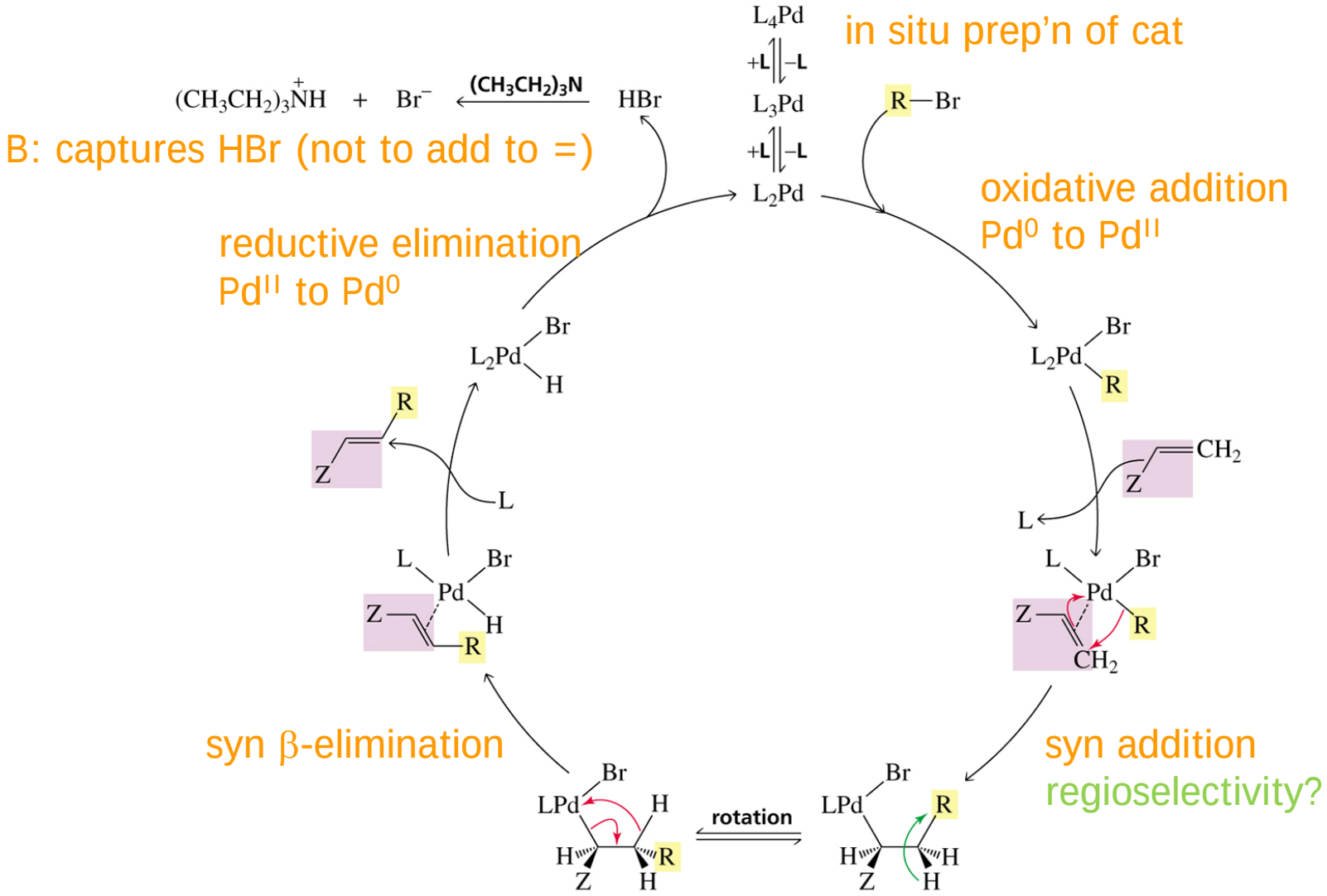
- examples

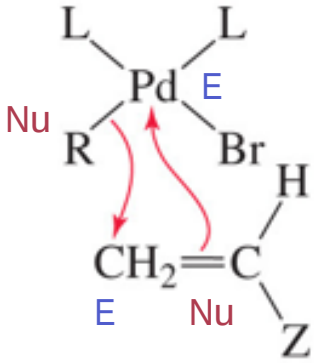


stereospecific

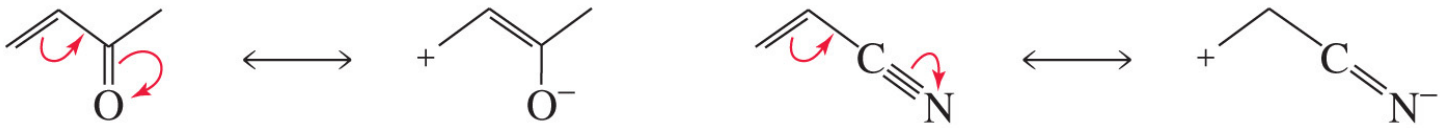


- mechanism ~ also <u>not</u> clear yet



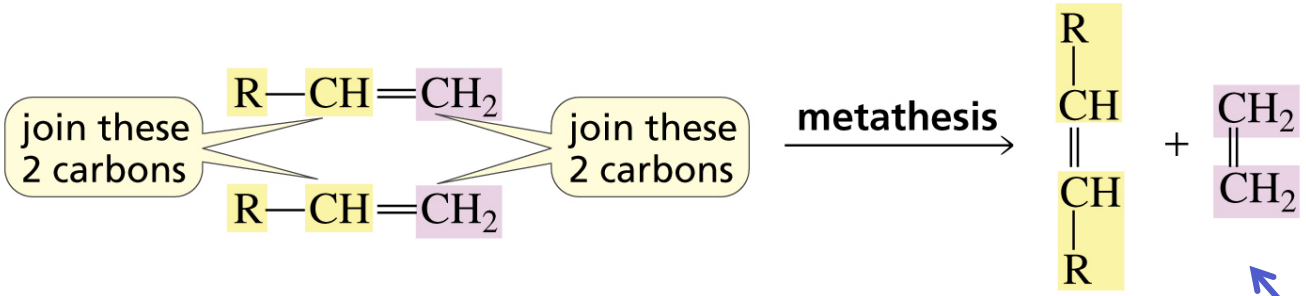


- syn addition not regioselective → high yield when
  - symmetrical alkene
  - one C sterically hindered (like in terminal alkene)
  - Z (strongly) e-withdrawing

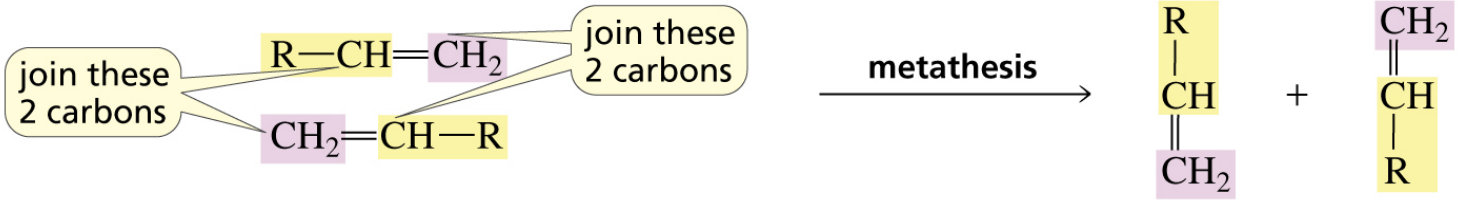


Alkene metathesis

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

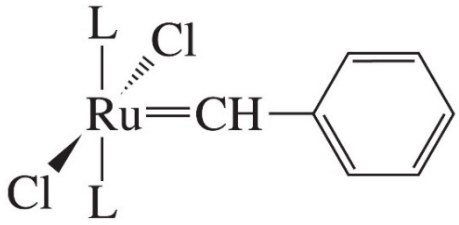


- if



- Terminal alkene gives high yield. ← ethene (g)

- OM made possible by Grubbs' catalyst
  - transition metal carbene [R_2C:] complex



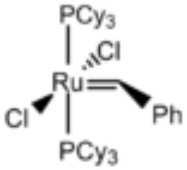
Grubbs catalyst

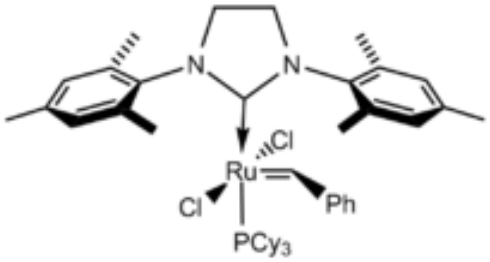
The Nobel Prize in Chemistry 2005

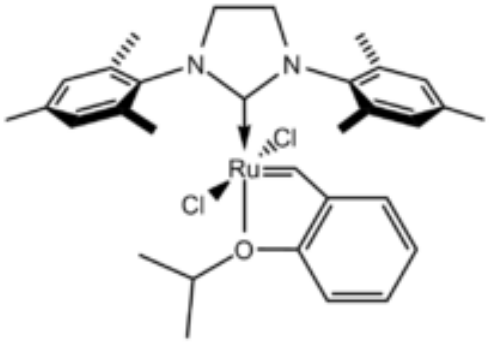
Photo: U. Montan
Yves Chauvin

Photo: R. Paz
Robert H. Grubbs

Photo: L.B. Hetherington
Richard R. Schrock

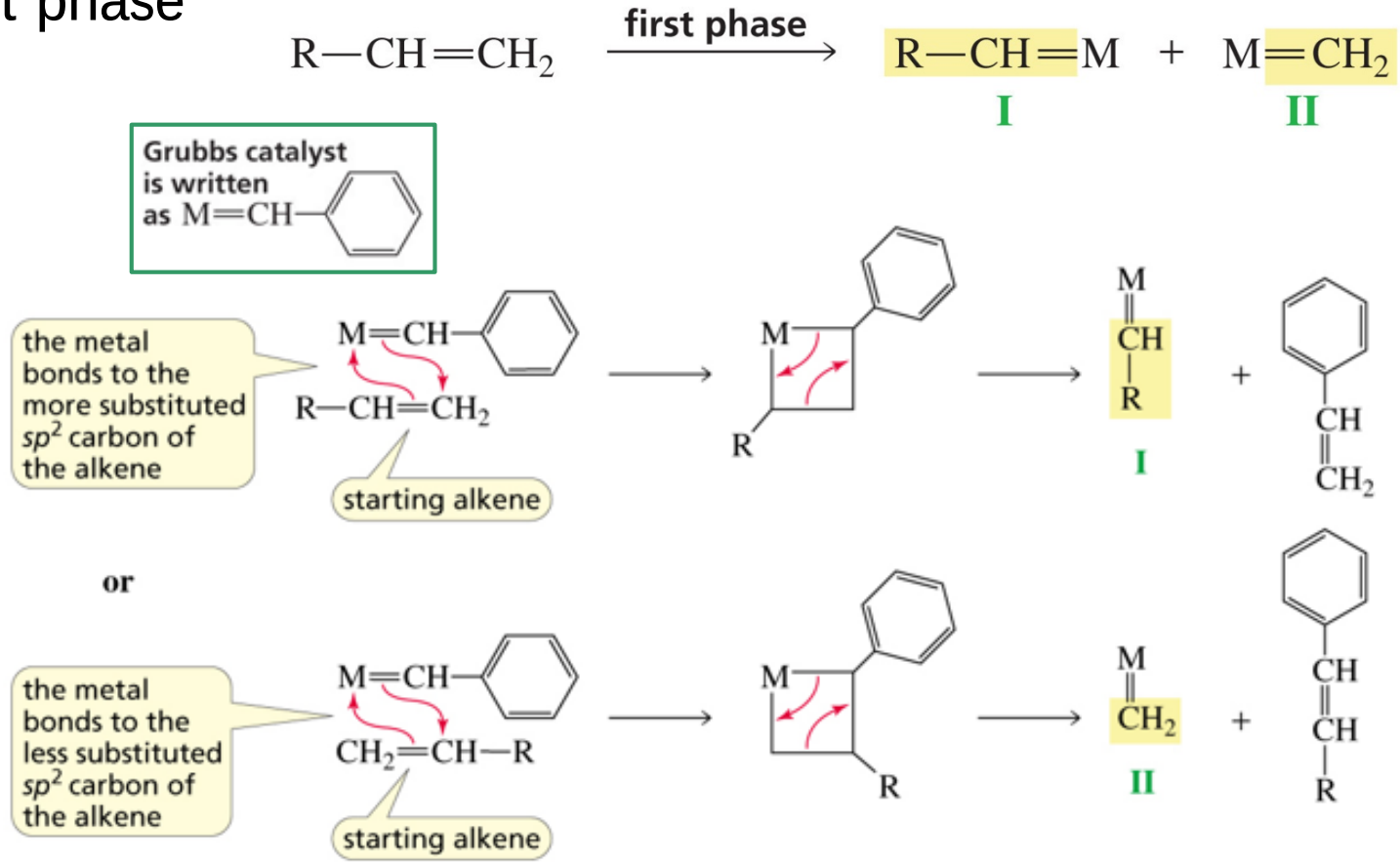






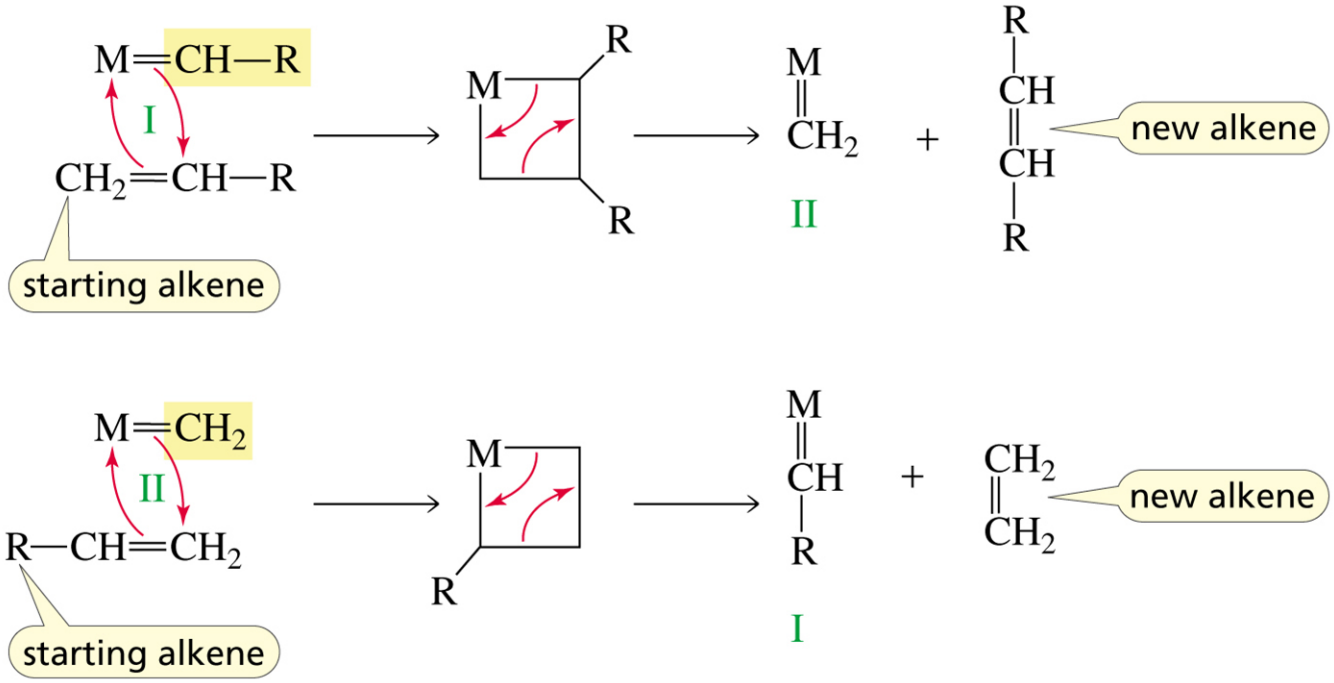
Cy = cyclohexyl

- mechanism ~ 2 phases
  - 1st phase



[2+2] cycloaddition
followed by ring-opening

- mechanism (cont'd)
  - 2nd phase



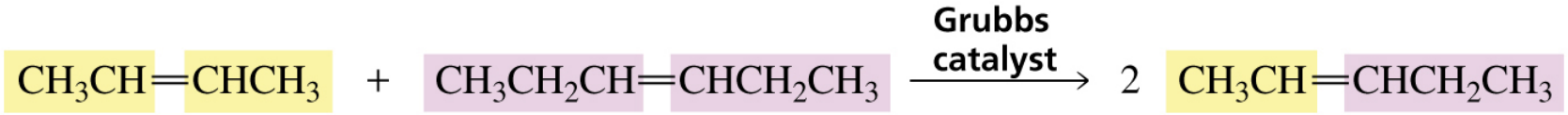
[2+2] cycloaddition
followed by ring-opening

OM reactions

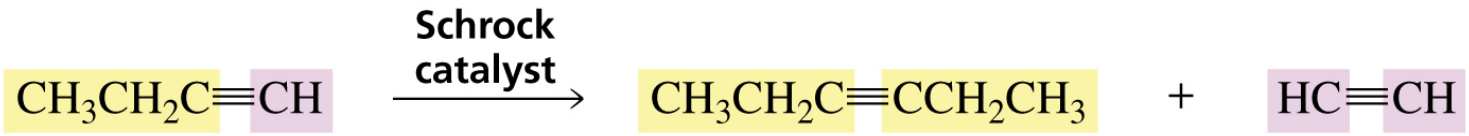
- cross-metathesis

  - not stereospecific

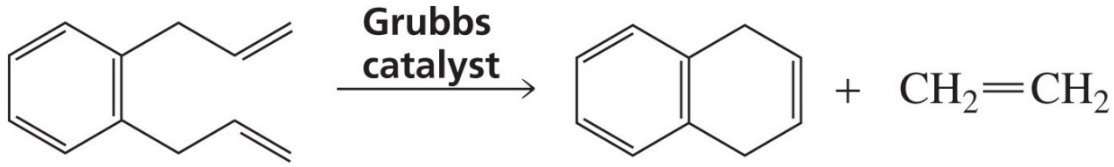
- cross-metathesis btw 2 different alkenes



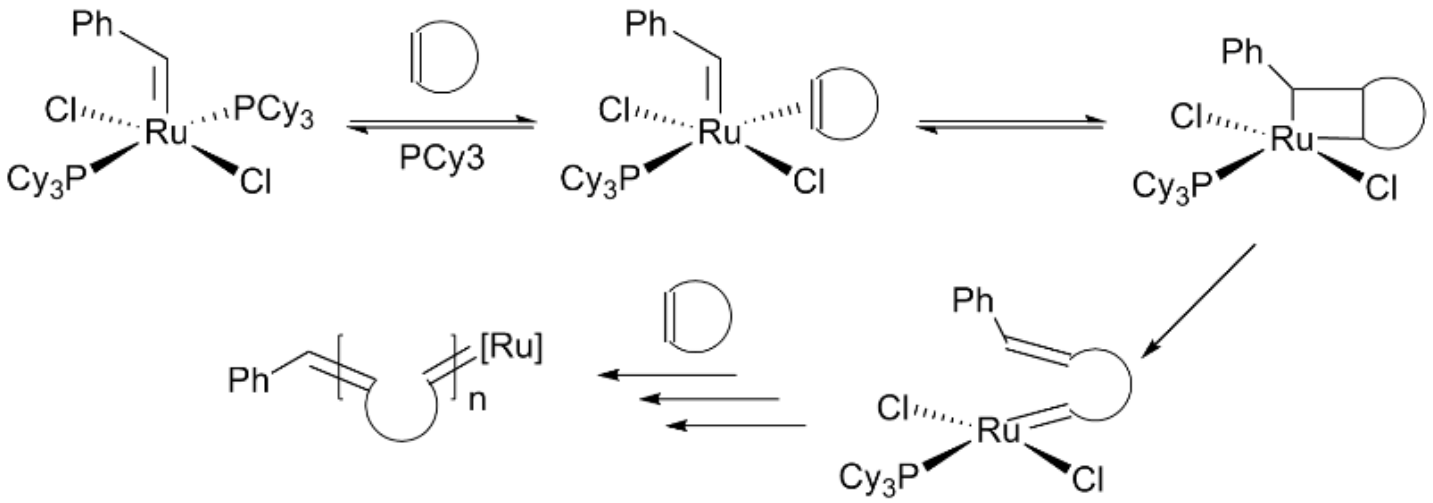
- cross-metathesis of alkynes



- ring-closing metathesis



- ring-opening metathesis (polymerization) [ROMP]



Summary

- RLi and RMgX
  - C Nu: (for addition to C=O)
- Gilman reagent
  - RX + R'_2CuLi → R–R'
- Suzuki coupling
  - RX + $R'B(OR)_2$ → (Pd cat) → R–R'
- Heck reaction
  - RX + HC=CR' → (Pd cat) → R–C=CR'
- olefin metathesis
  - $RCH=CH_2$ → (Grubbs cat) → $RCH=CHR + CH_2=CH_2$