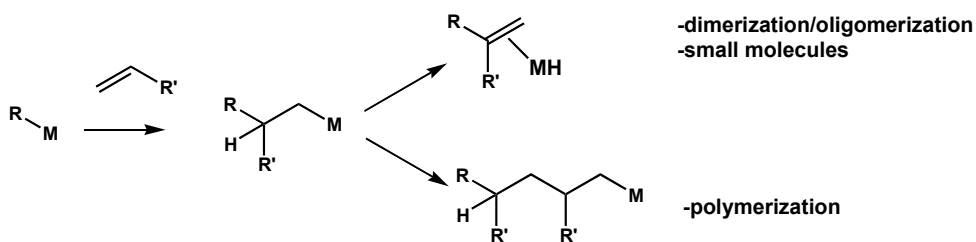
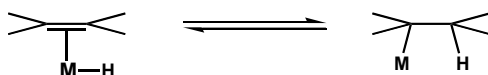


Olefin insertion into Metal alkyl can be followed by hydride elimination or additional olefin insertions:



Recall:

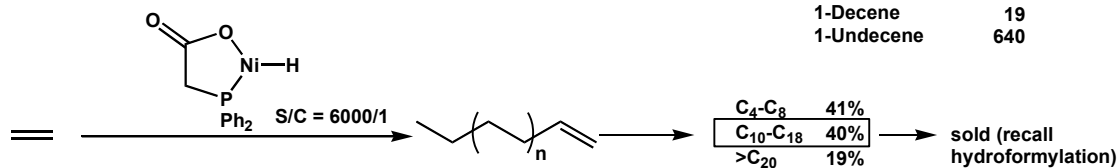


electron rich M (late transition metal) $K_{eq} < 1$ \rightarrow dimerization, etc
 electron poor M (early transition metal) $K_{eq} > 1$ \rightarrow polymerization

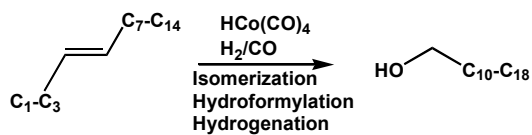
Shell Higher Olefin Process (SHOP)

- SHOP process operates on 1 MILLION TON scale
- One of the largest applications of homogeneous transition metal catalysis
- Explains Adrich prices:

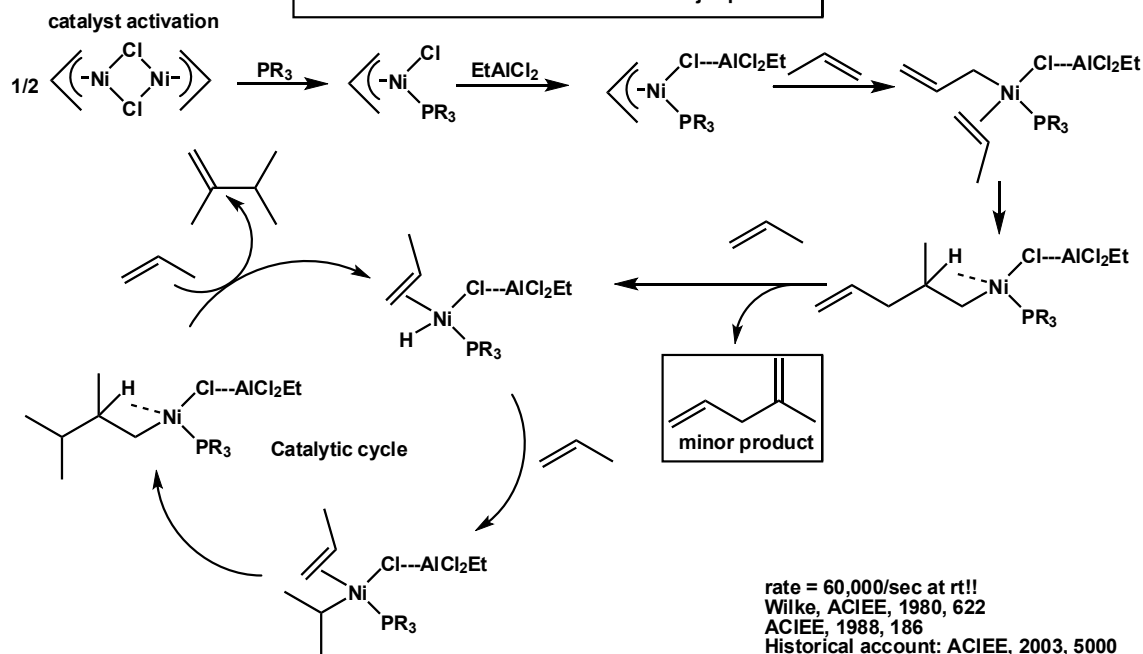
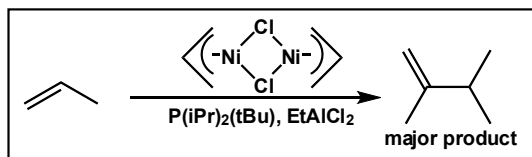
Terminal Olefin	Price (100mL)
1-Hexene	\$13
1-Heptene	191
1-Octene	23
1-Nonene	720
1-Decene	19
1-Undecene	640



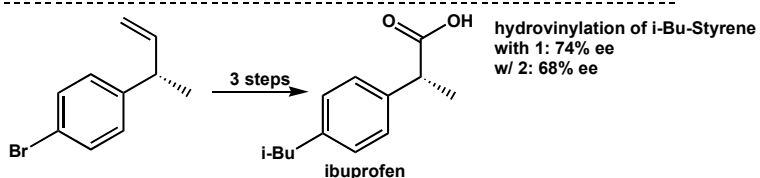
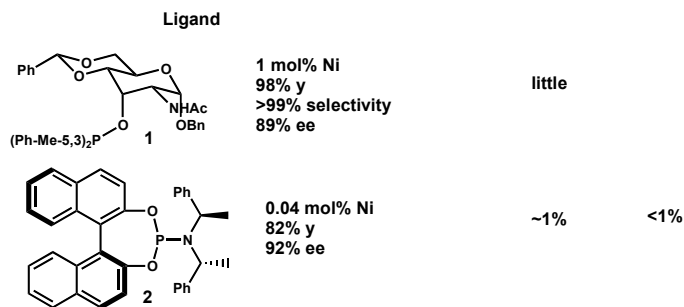
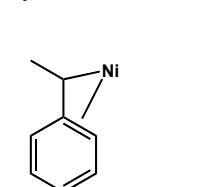
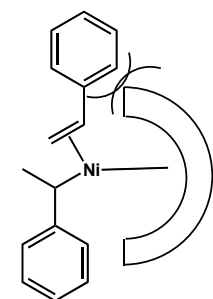
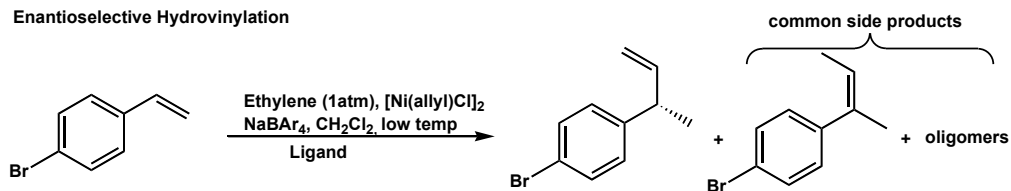
Chauvin, Schrock, Grubbs: 2005 nobel prize in chemistry. For a history, see; <http://nobelprize.org/chemistry/laureates/2005/chemadv05.pdf>



See CHNF, Chapter 11, p593

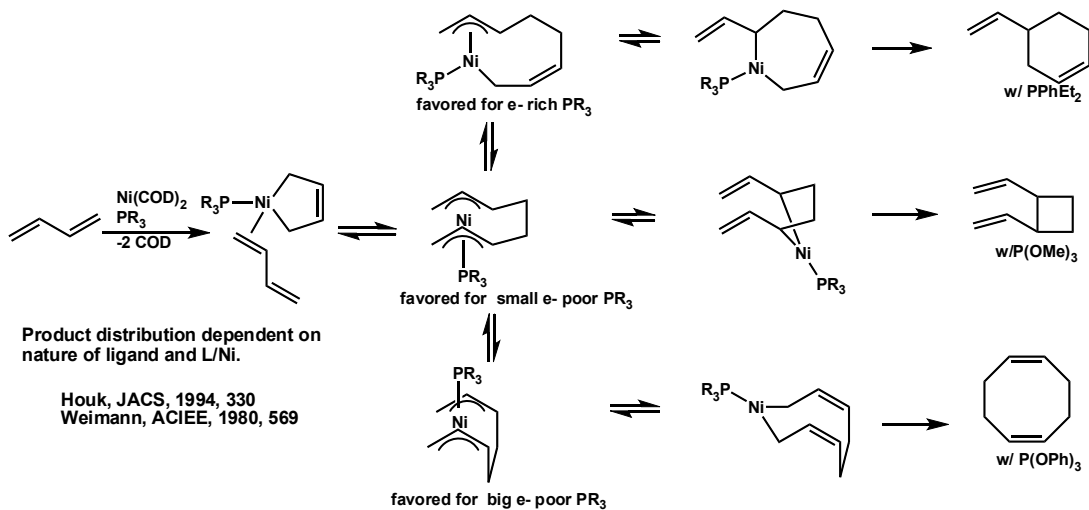
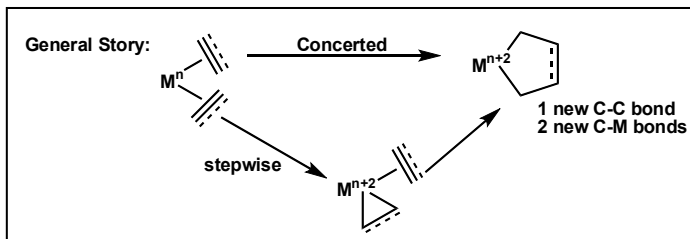
Ni-Catalyzed Dimerization
aka hydrovinylation

Enantioselective Hydrovinylation

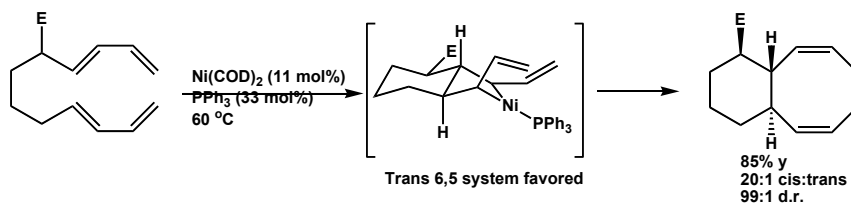
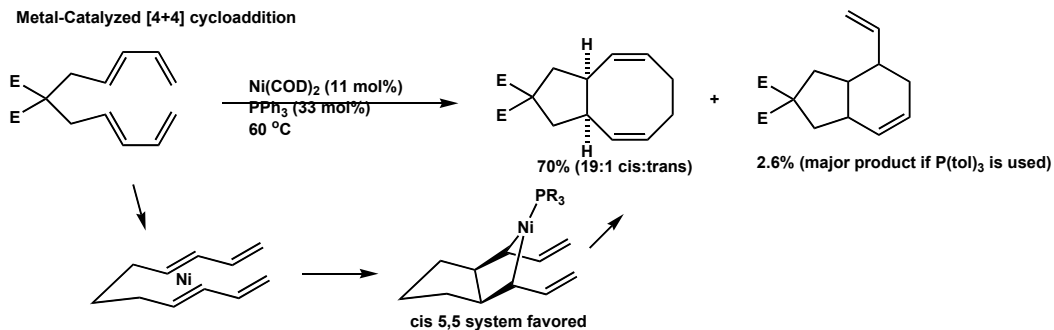


1: Rajanbabu, JACS, 2001, 734
2: Leitner, JACS, 2001, 736

Metal-mediated dimerization:
 -common use
 -mild conditions
 -many applications



Metal-Catalyzed [4+4] cycloaddition

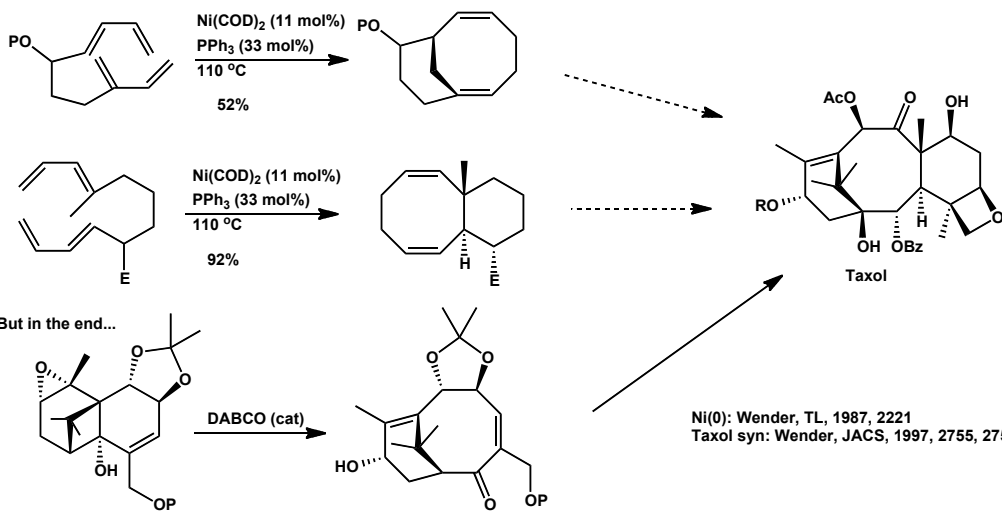
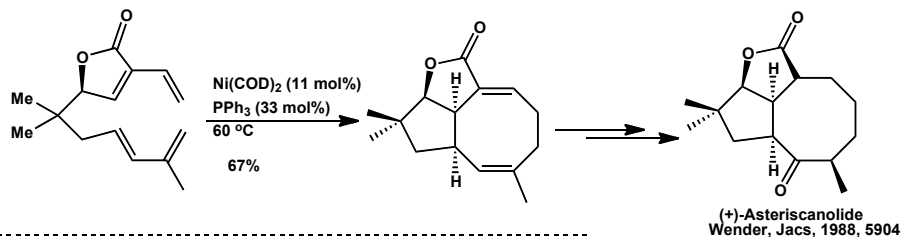


Recall thermal [4+4] forbidden under Woodward-Hoffman rules

Ready; Catalysis

Isomerization/cyclization-10

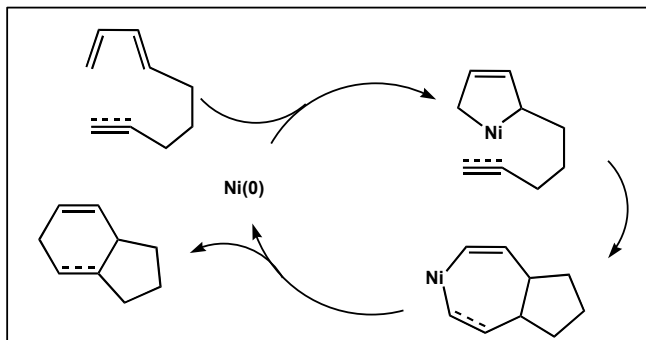
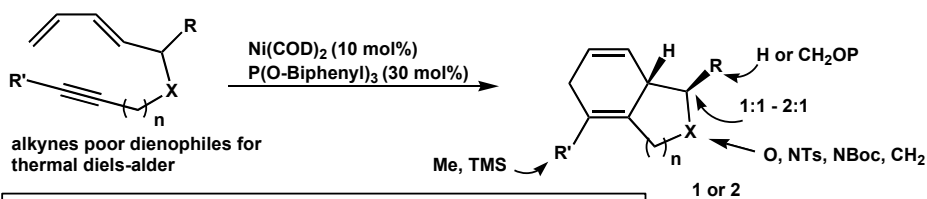
Synthetic Applications of [4+4]



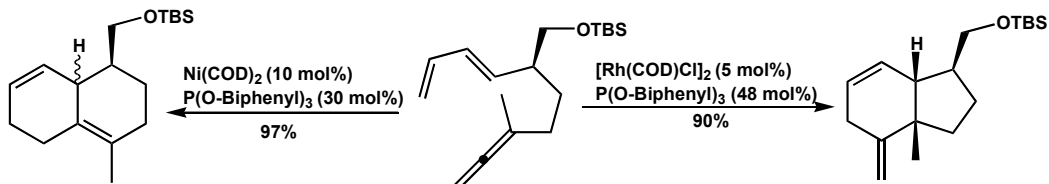
Ready; Catalysis

Isomerization/cyclization-11

Catalytic [4+2] Cycloadditions



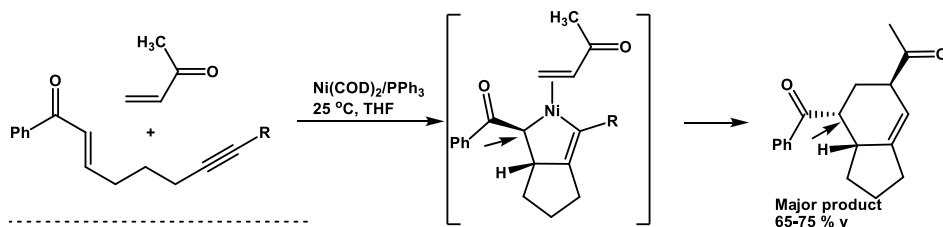
Wender Jacs 1989, 6432
jacs 1995, 1843



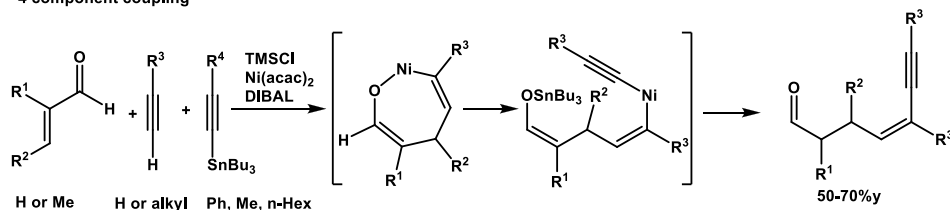
$\text{Ni}(0)$ may prefer the less hindered olefin while $\text{Rh}(I)$ prefers the more e- rich olefin

Ready; Catalysis

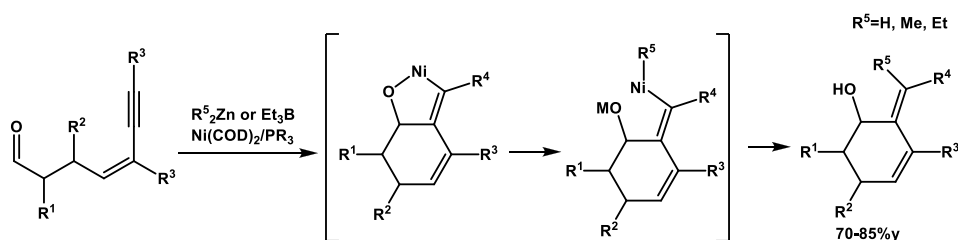
Isomerization/cyclization-12



4 component coupling



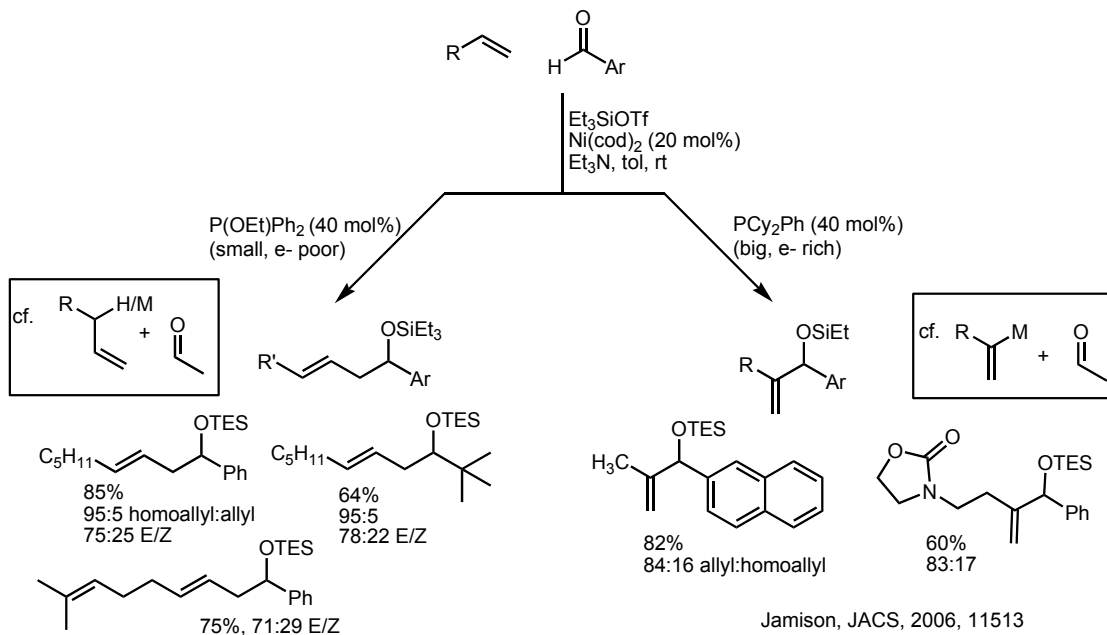
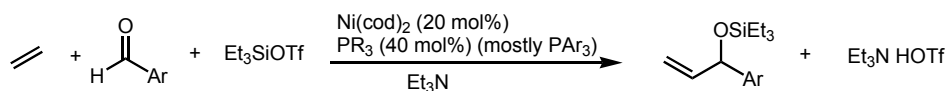
H or Me H or alkyl Ph, Me, n-Hex

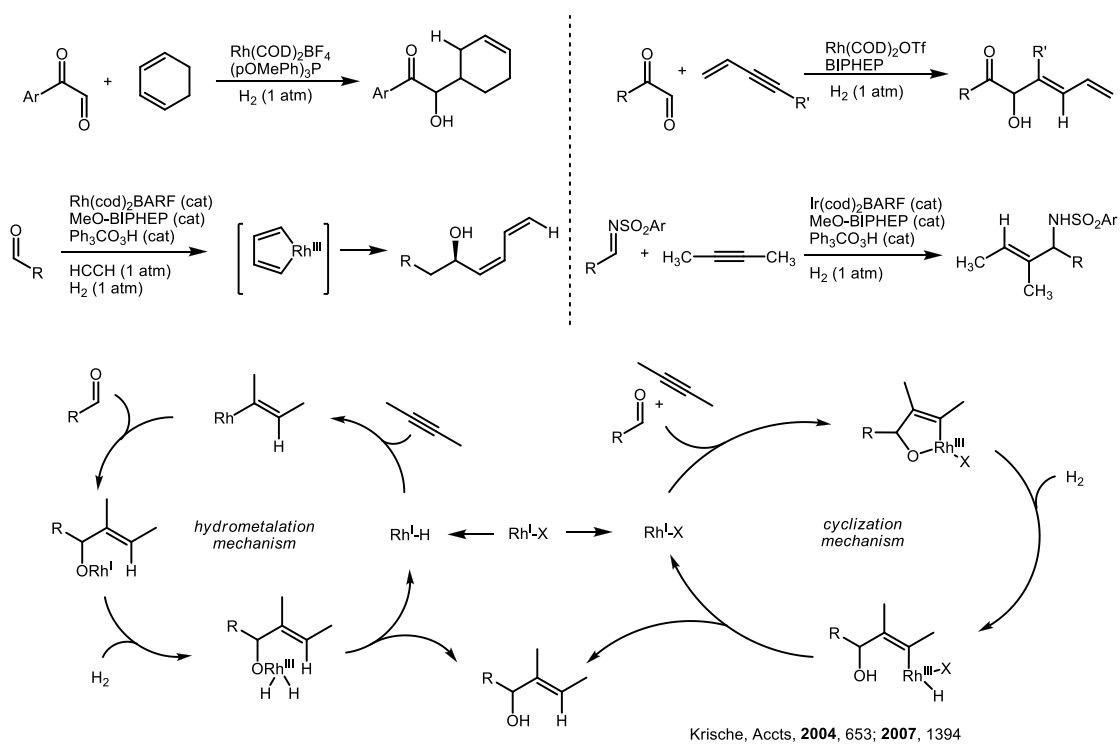
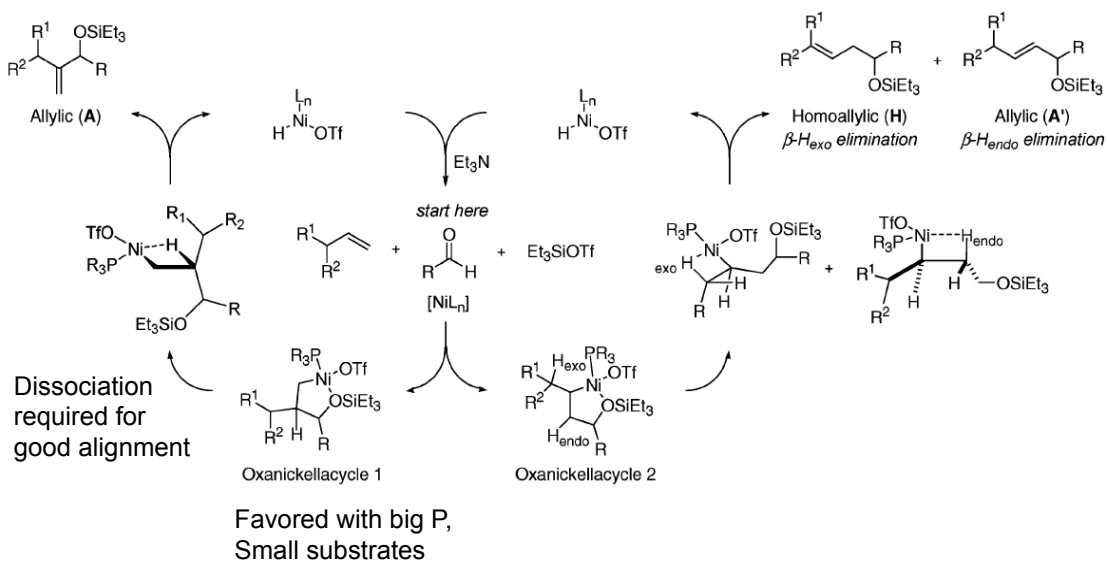


Montgomery Jacs, 1999, 476; 2002, 2106; 2002, 9366

Ready; Catalysis

Isomerization/cyclization

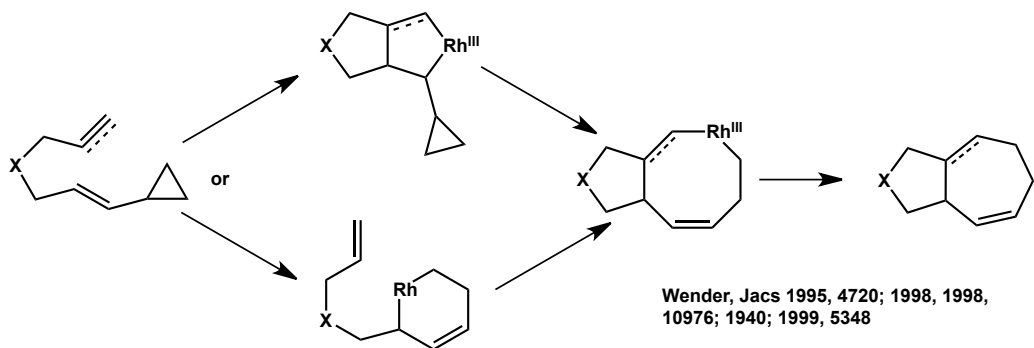
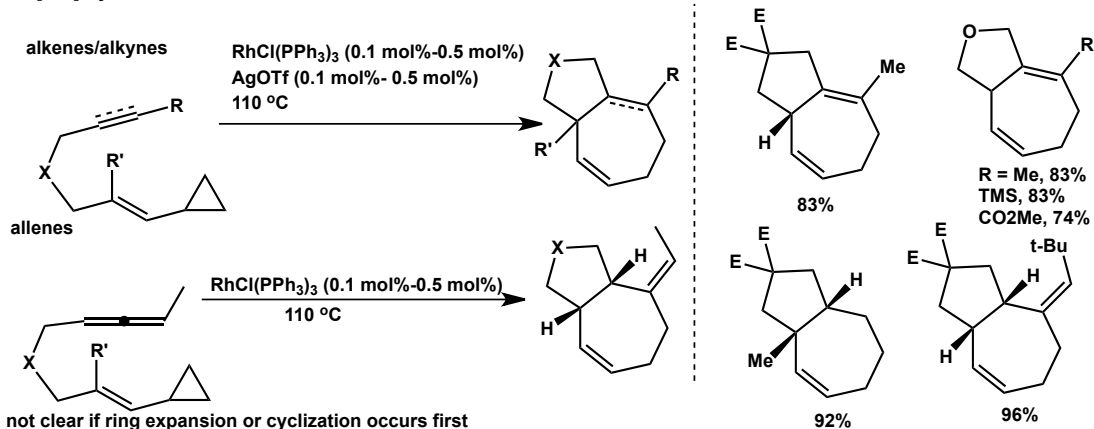




Ready; Catalysis

Isomerization/cyclization-13

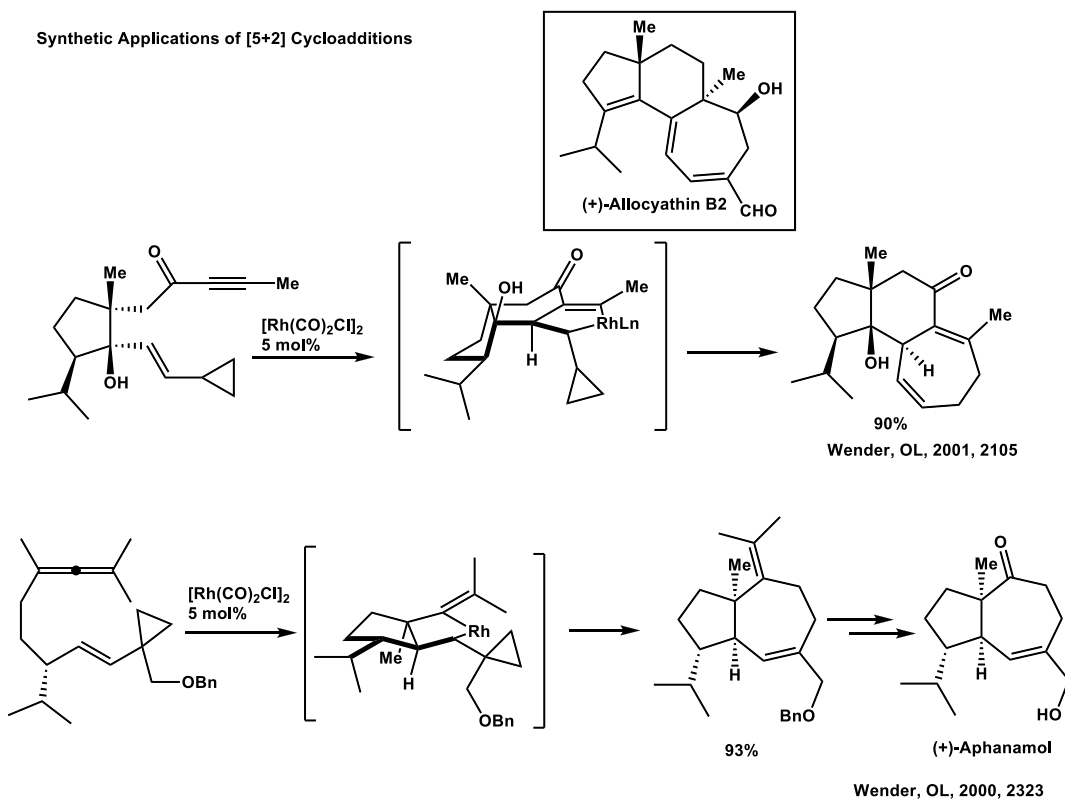
[5+2] Cycloaddition



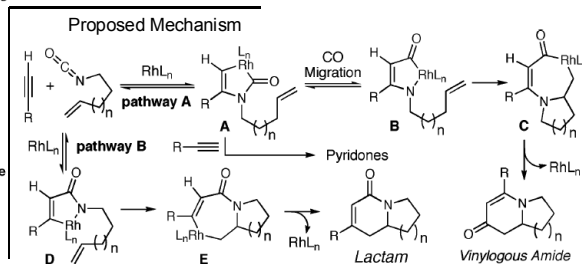
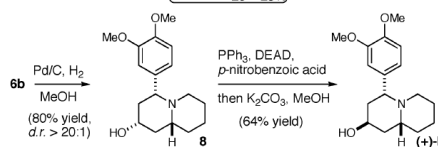
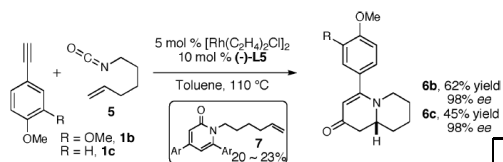
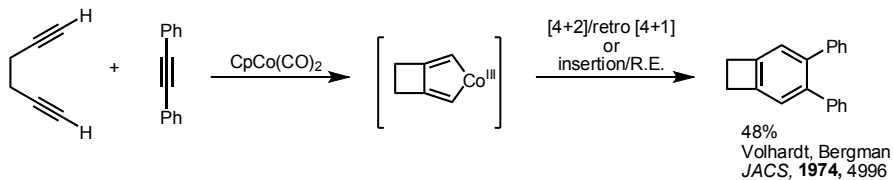
Ready; Catalysis

Isomerization/cyclization-14

Synthetic Applications of [5+2] Cycloadditions



Metal-mediated trimerization:
Key early discoveries: Vollhardt, *ACIEE*, 1984, 539



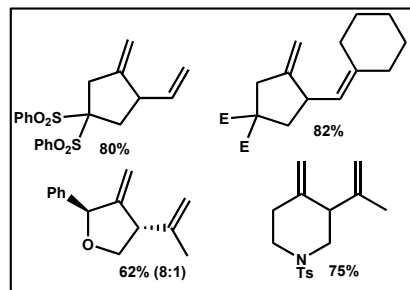
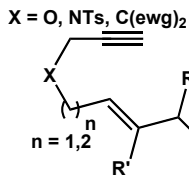
Rovis, *JACS*, 2006, 12370

Ru-Catalyzed enyne isomerization

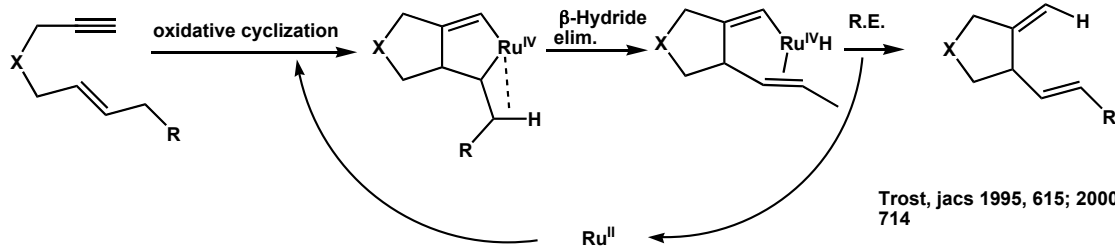


Can tune b:l (better for b-selective)
Trost, *JACS*, 1995, 615; *JACS*, 2001, 12504

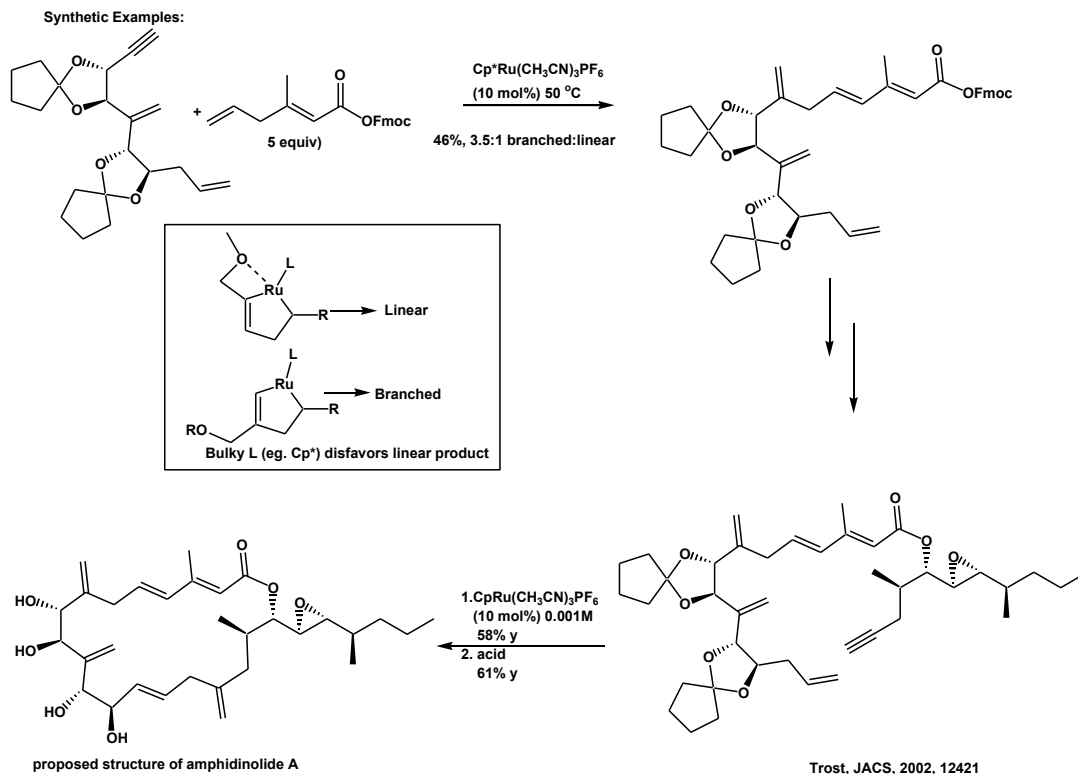
Intramolecular version:



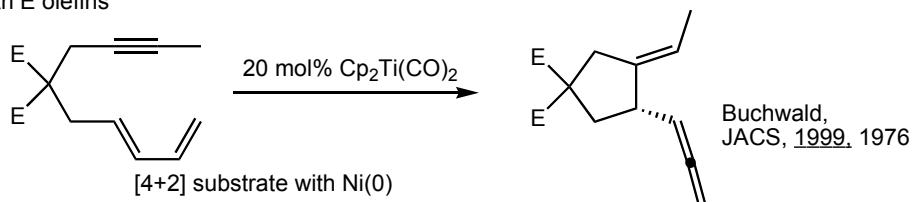
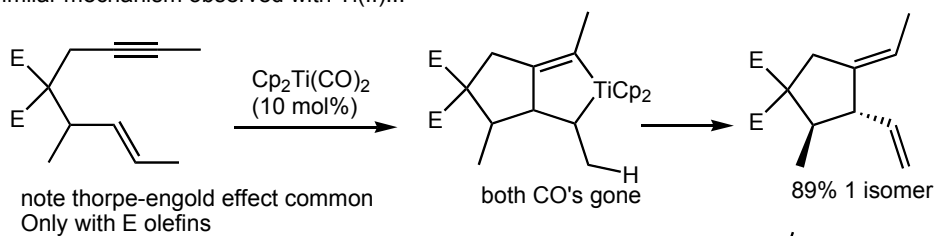
Rxns also referred to as Alder-ene or metallo-ene reactions, but that is misleading given the most likely mechanism:



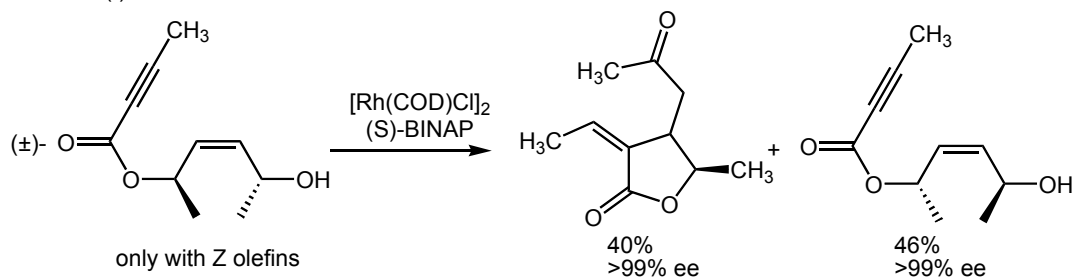
Trost, *JACS* 1995, 615; 2000, 714



Similar mechanism observed with Ti(II)...



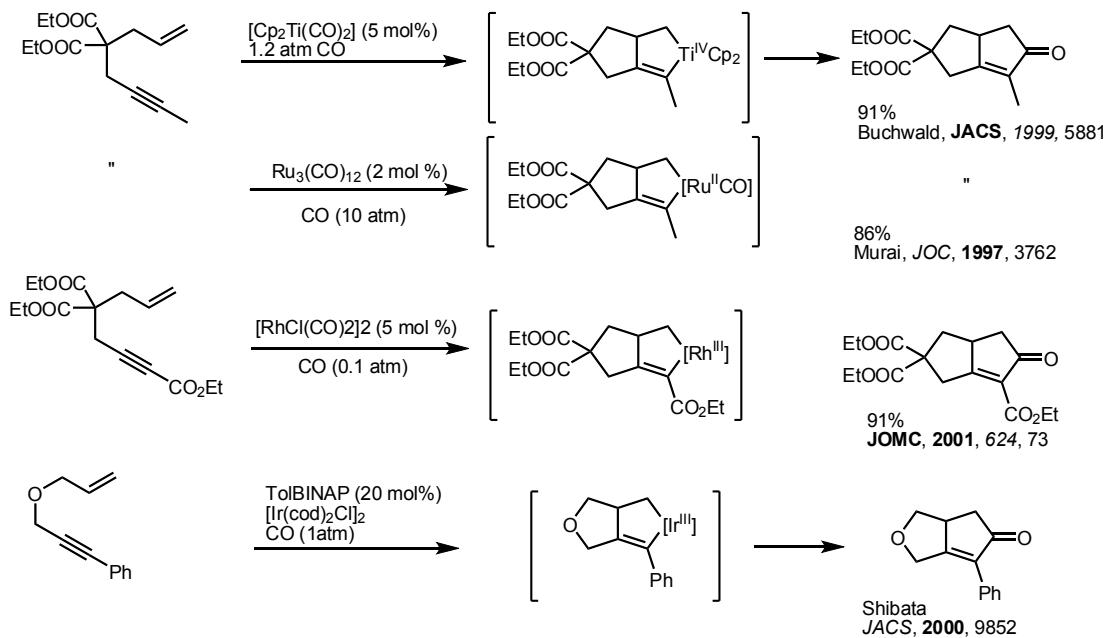
...and Rh(I)



Ready; Catalysis

Isomerization/cyclization

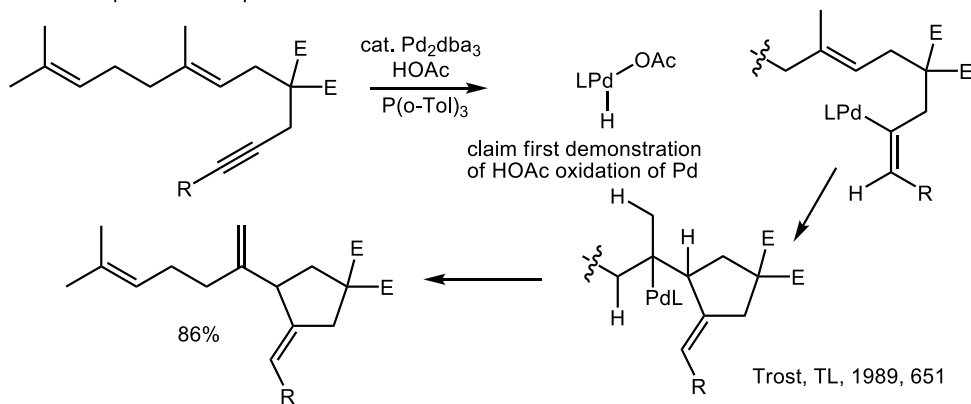
General mechanism with electron rich transition metals:
Catalytic Pauson-Khand type reactions (review: ACIEE, 2003, 1800)



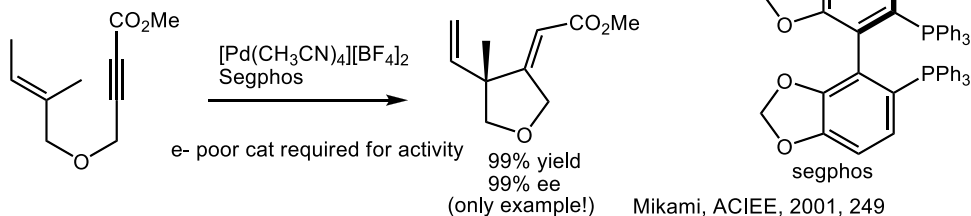
Ready; Catalysis

Isomerization/cyclization

Pd-H mechanism provides ene products:



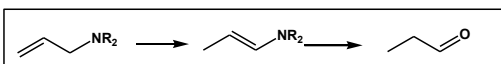
enantioselective version



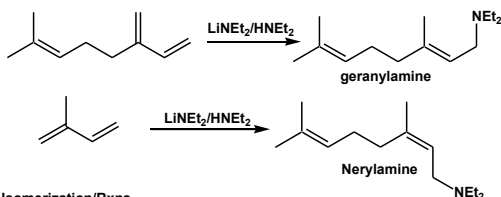
question: Why would a metallocycle mechanism be unlikely with (chelating ligand)Pd ?

Ready; Catalysis

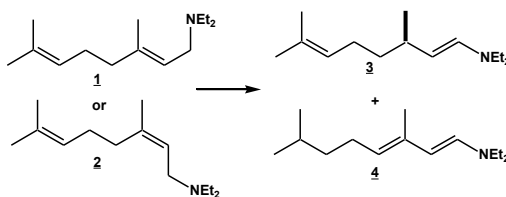
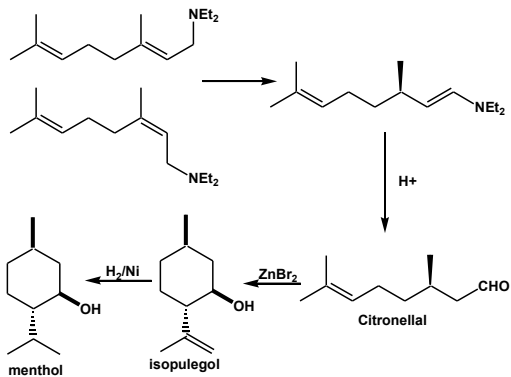
Isomerization/cyclization-17



Starting Materials:



Isomerization/Rxns



Catalyst	Substrate	Products	ee(%)
$\text{Cp}_2\text{TiCl}_2/\text{iPrMgBr}$	1	4 (100%)	
$\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$	1	3 (85%); 4 (15%)	
$[\text{Rh}(\text{PPh}_3)_3(\text{COD})]^+$	1	3 (100%)	
$[\text{Rh}(\text{DIOP})(\text{COD})]^+$	1	3 (100%)	22
$[\text{Rh}(\text{R-BINAP})(\text{COD})]^+$	1	S-3 (100%)	97
$[\text{Rh}(\text{S-BINAP})(\text{COD})]^+$	2	S-3 (100%)	96

Ready; Catalysis

Isomerization/cyclization-18

Process Development

Catalyst	Modification	Turnover number
$\text{Rh}(\text{BINAP})(\text{COD})^+$	none	100
$\text{Rh}(\text{BINAP})(\text{COD})^+$	added Red-AL	1,000
$\text{Rh}(\text{BINAP})(\text{COD})^+$	Substrate purification	8,000
$\text{Rh}(\text{BINAP})_2$	catalyst recycling	400,000

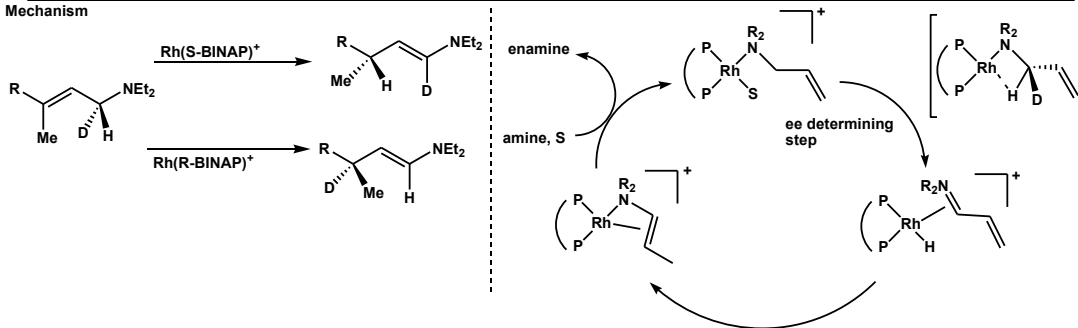
Red-AL = Vitride = $(\text{MeOCH}_2\text{CH}_2\text{O})_2\text{AlH}_2 \text{Na}$

compound	ee (%)	Production (tons/yr)	use
	97	1,500	synthetic intermediate those stinky candles
	98	10	insect growth regulator
	100	1,000	pharmaceuticals tobacco household products

Ready; Catalysis

Isomerization/cyclization

Mechanism



Axial chirality results in gearing of Ph.
It is the location of the Ph's that gives a good "chiral environment" near the metal

