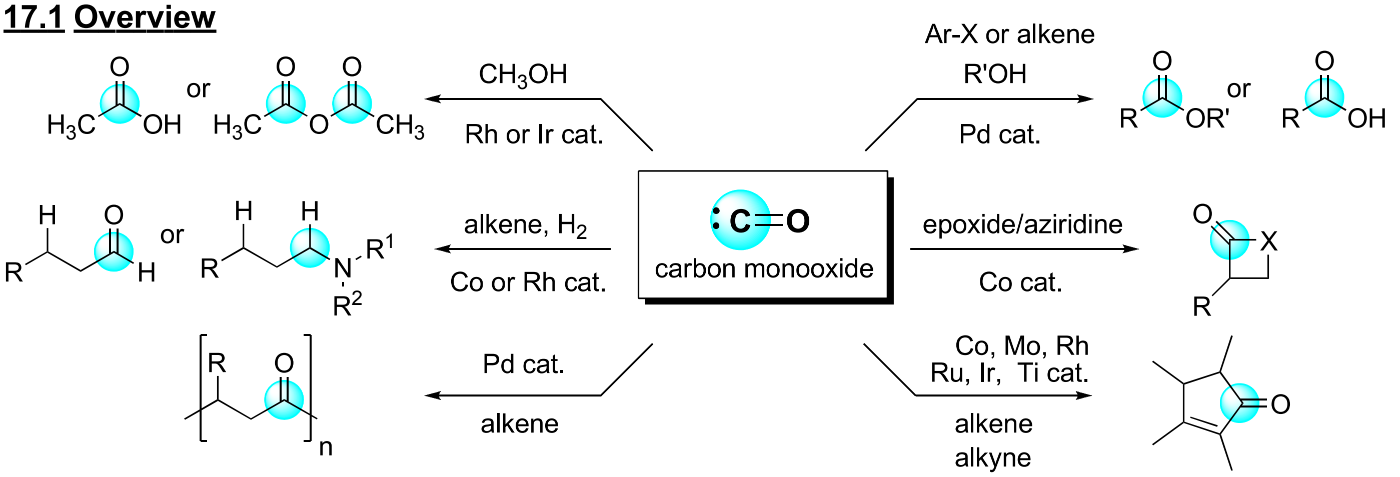
Organometallic Study Meeting

2011/10/6 K.Oisaki

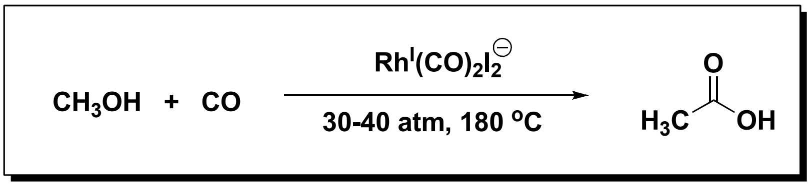
Chapter 17. Catalytic Carbonylation

17.1 Overview



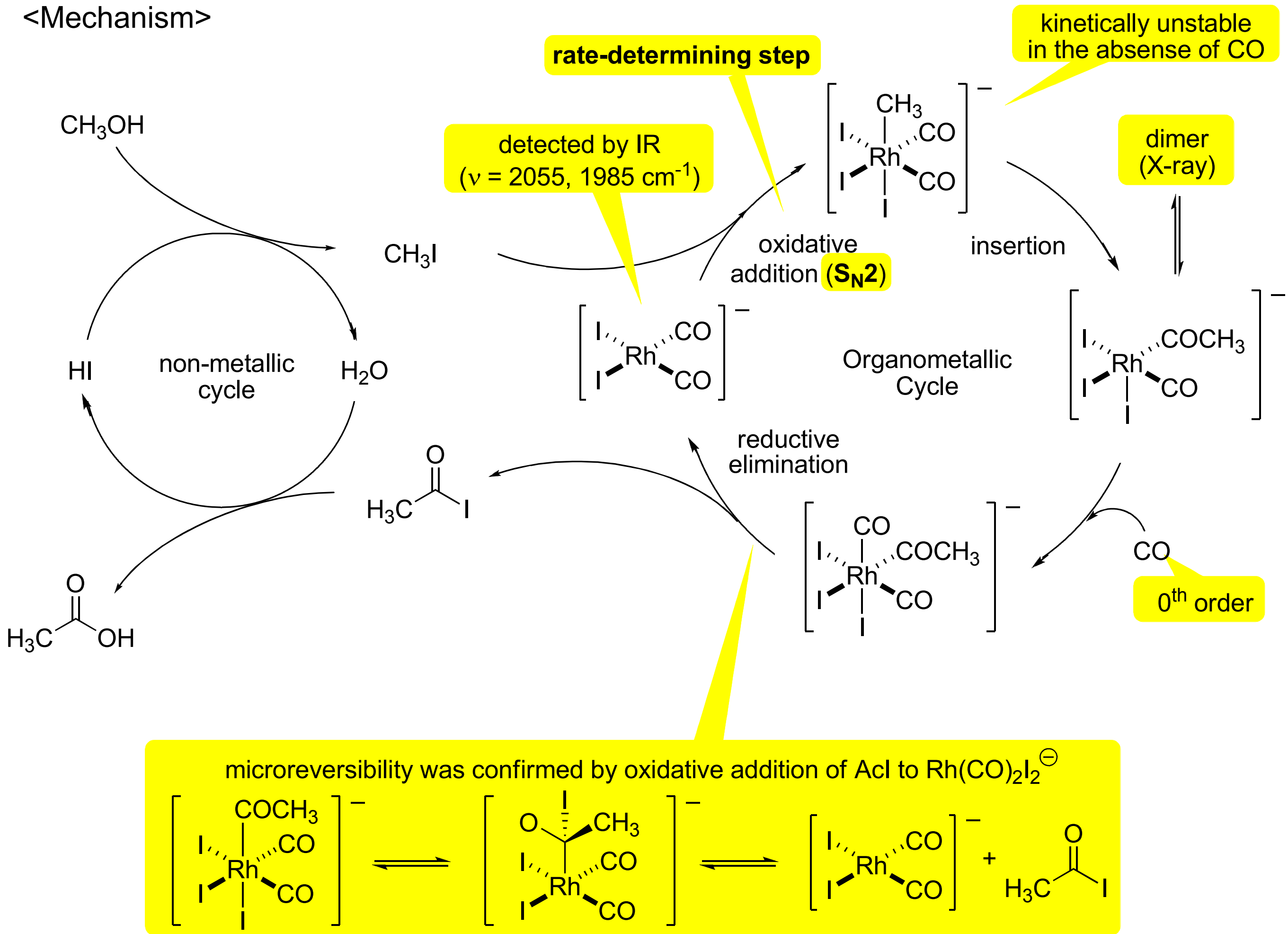
17.2. Carbonylation to Produce Acetic Acid

17.2.1. Rh-catalyzed carbonylation of MeOH to produce AcOH (Monsanto Process)

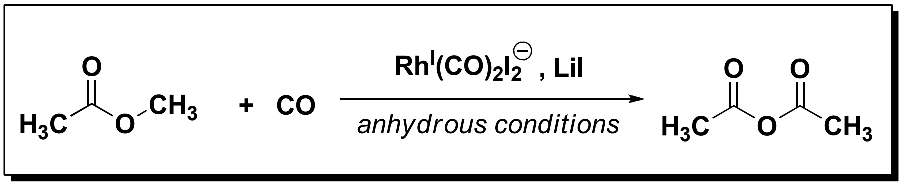


commercialized in 1970

<Mechanism>

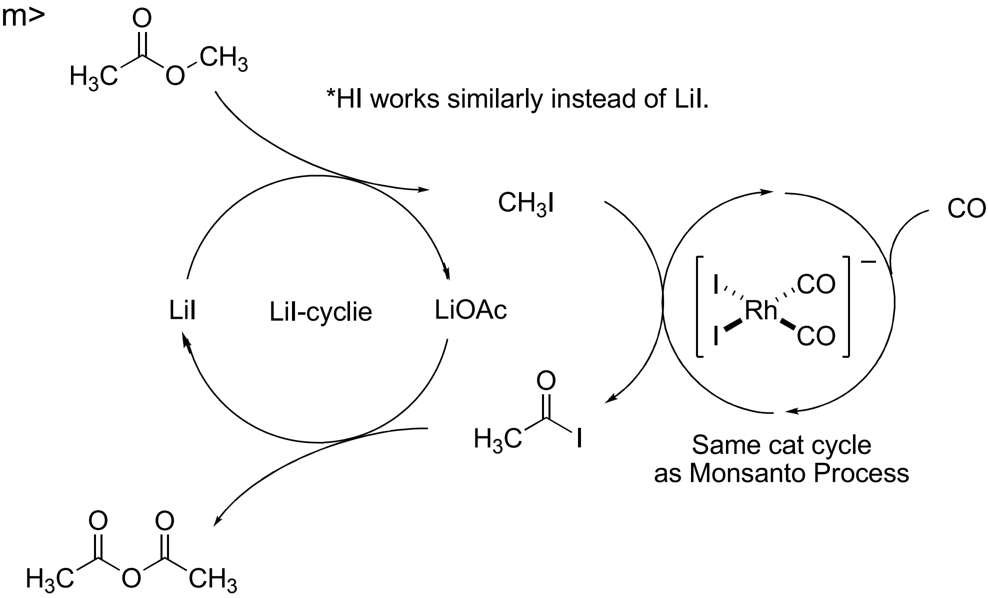


17.2.2. Rh-catalyzed carbonylation of MeOAc to produce Ac_2O (Eastman Process)

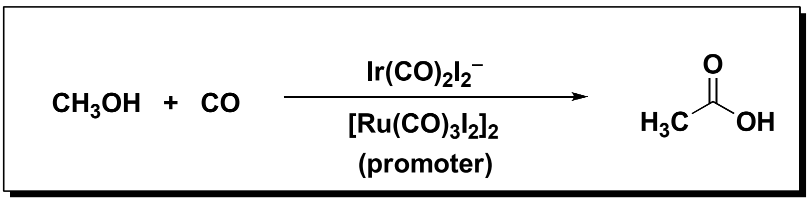


commercialized in 1983

<Mechanism>



17.2.3. Ir-catalyzed carbonylation of MeOH to produce AcOH (Cativa Process)



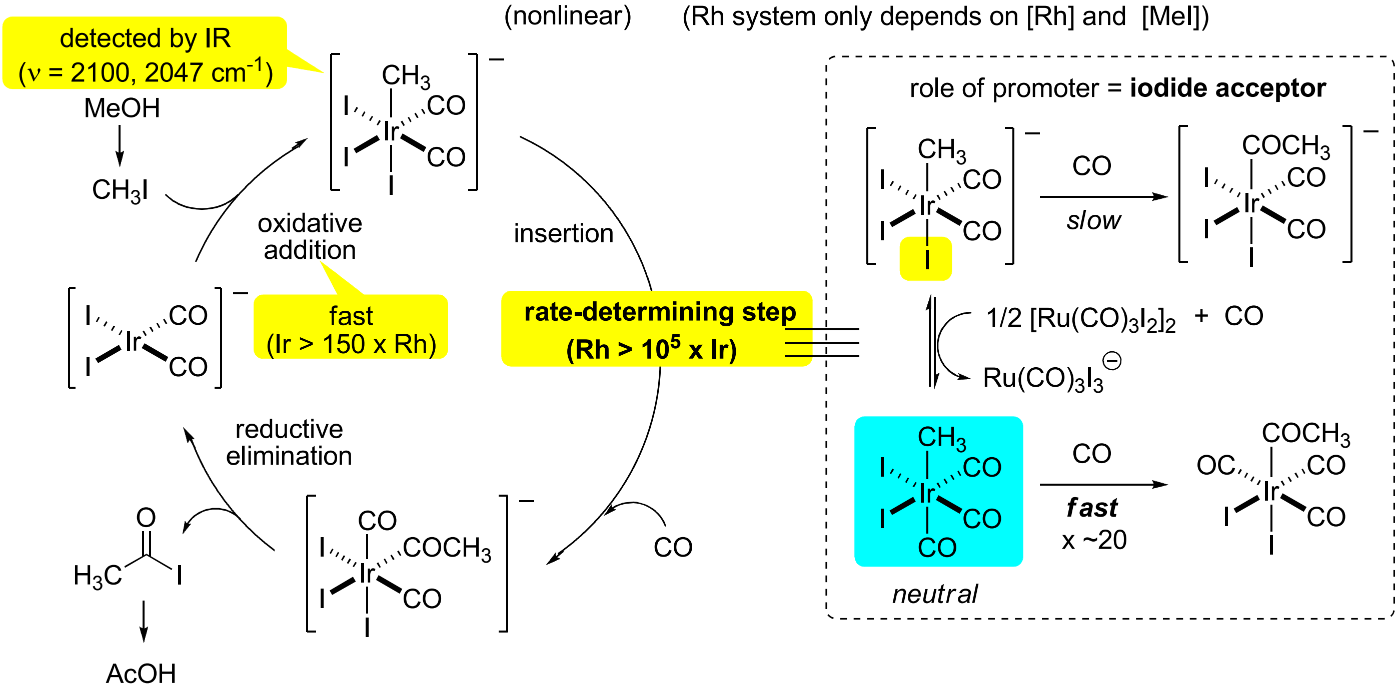
established in 1990s

- # 5 times more active
- # more H_2O tolerant
- # more soluble catalyst
- # less expensive metal

than Rh

<Mechanism>

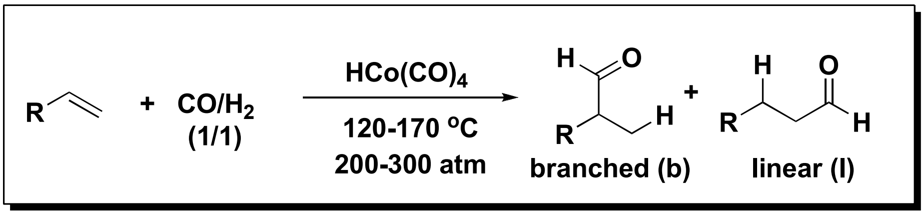
the rate depends on [CO], [H_2O], [MeOAc], [MeI], [Ru promoter], [Ir] (nonlinear) (Rh system only depends on [Rh] and [MeI])



17.3. Hydroformylation

17.3.1. Overview

17.3.2. $HCo(CO)_4$ catalysis (Oxo process)



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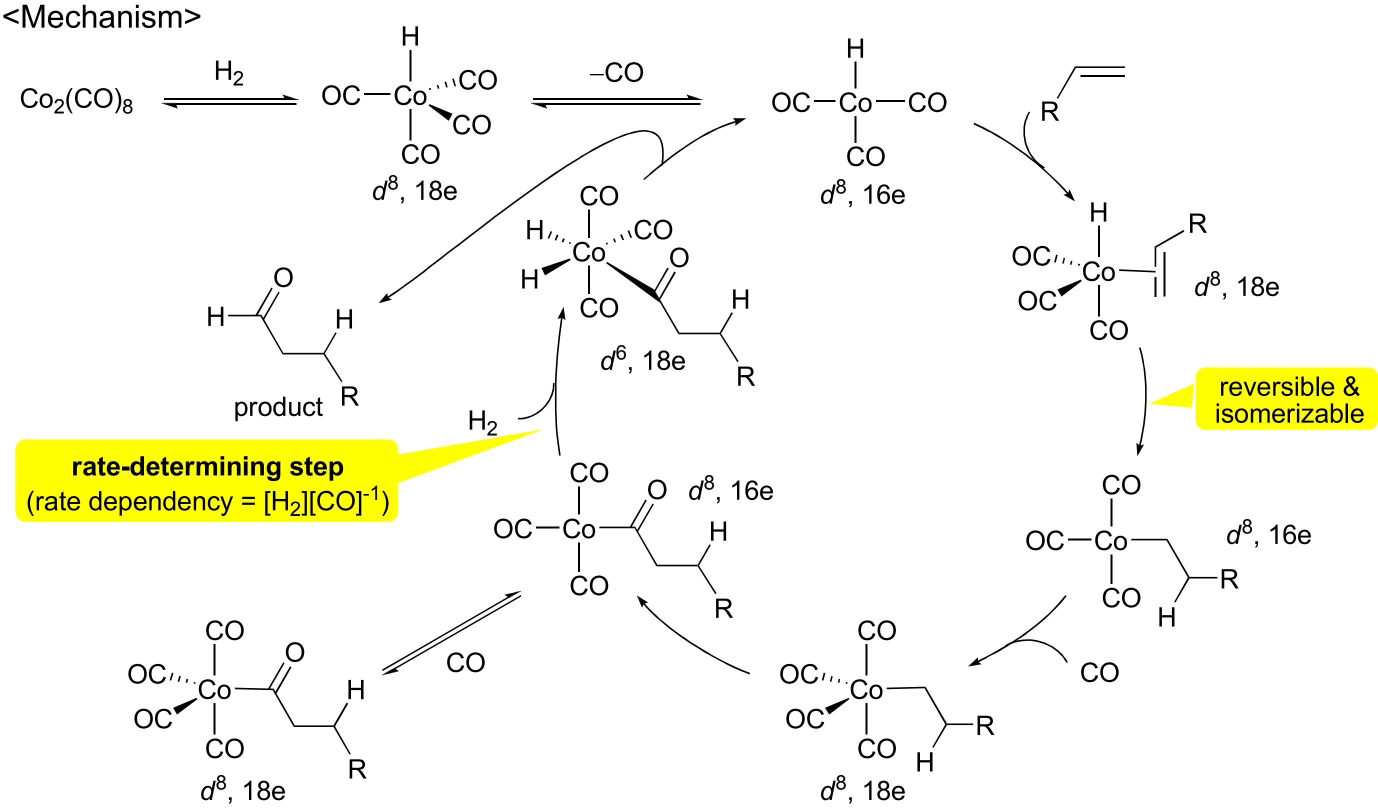
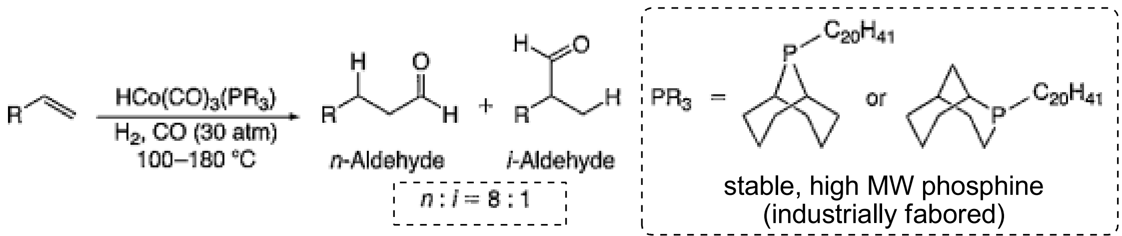
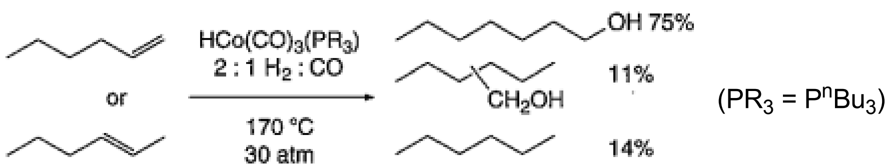


high pressure of CO is required to suppress cat decomp (formation of Co cluster or metallic Co)
all reactions have the potential to be reversible
l/b ratio = 3~4 : 1 at best

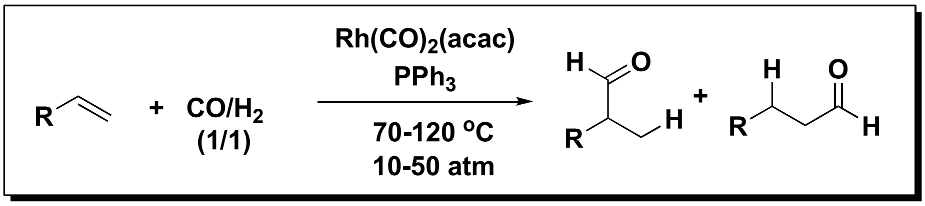
17.3.3. $HCo(CO)_3(PR_3)$ catalysis





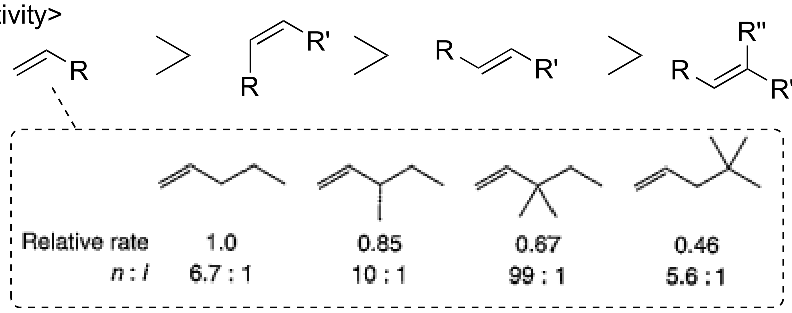
C=C isomerization is very fast.

17.3.4. Rh catalysis



commercialized in 1970s
- lower pressure
- improved l/b
- less byproduct
- lab-scale application

<reactivity>



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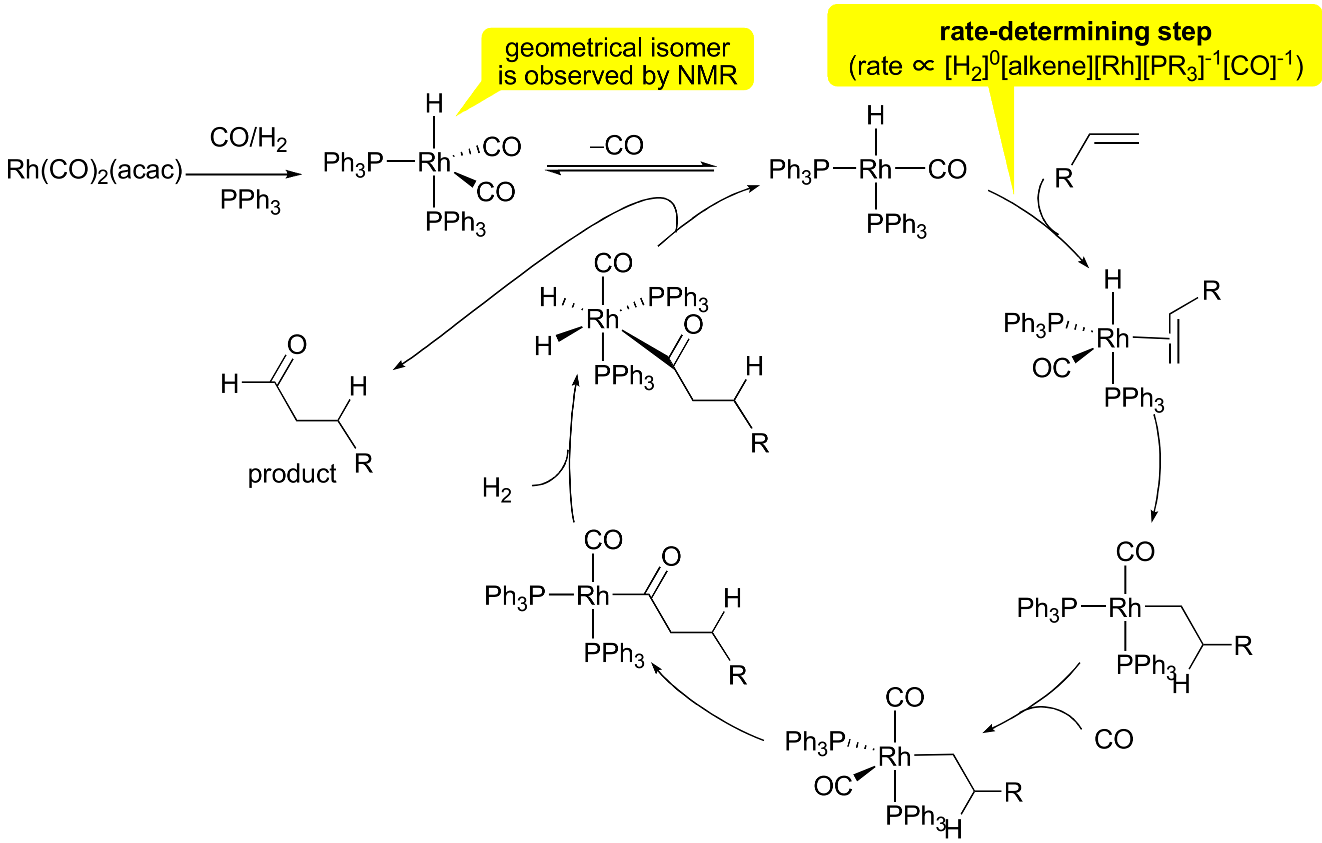
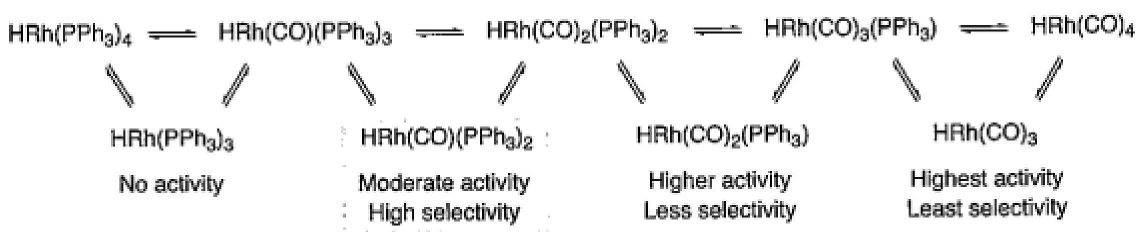
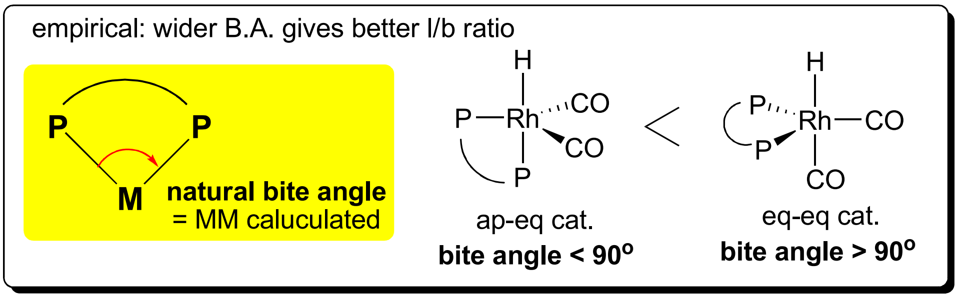
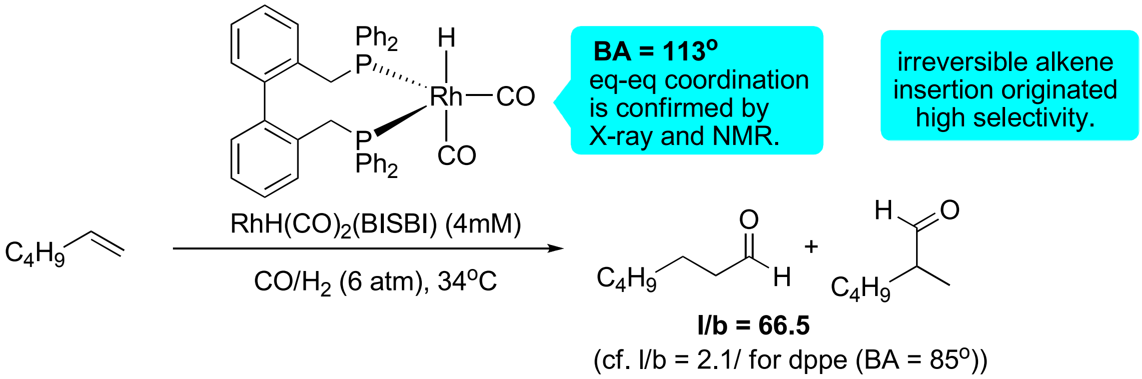
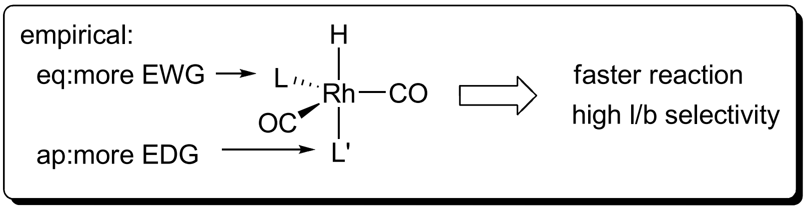




<Phosphine Effect>







Piet W. N. M. van Leeuwen et al. *JACS* **1998**, *120*, 11616.

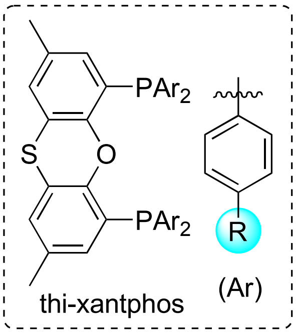


Table 1. Selected Data for Ligands 1−7

ligand	R	β_n,[a] deg	flexibility range,[a] deg	χ_i,[b] cm^{-1}	σ_p[c]	% ee[b]
1	N(CH$_3$)$_2$	109.1	92−124	1.8	−0.83	44−50
2	OCH$_3$	106.9	91−123	3.4	−0.27	56−62
3	CH$_3$	106.7	91−125	3.5	−0.17	63−69
4	H	106.4	91−127	4.3	0.00	69−75
5	F	106.6	92−128	5.0	0.06	76−83
6	Cl	107.8	91−126	5.6	0.23	81−88
7	CF$_3$	109.3	92−128	6.6	0.54	89−96

similar B.A.

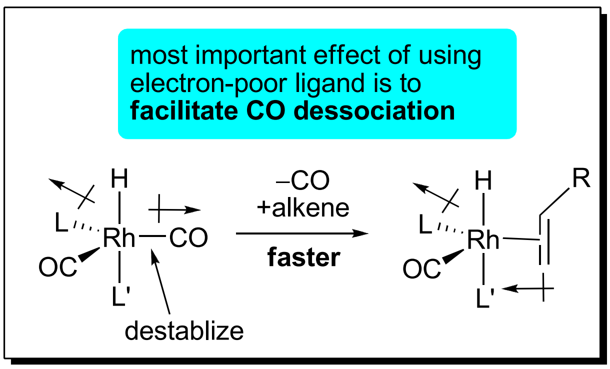
% ee = [eq-eq]-[ap-eq] / [eq-eq]+[ap-eq] of RhH(CO)$_2$(L)

bite angle does not always correlate.

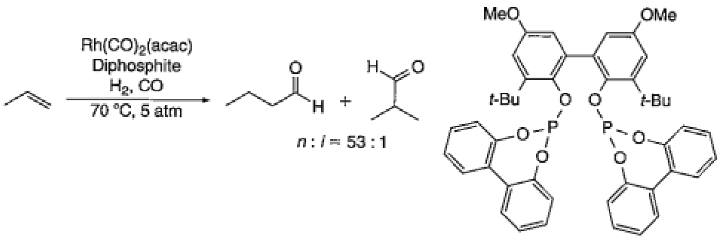
Table 7. Results of the Hydroformylation of 1-Octene at 80 °C[a]

ligand	R	σ_p	l:b ratio[b]	% select[b]	% isomer[b]	tof[b,c]
1	N(CH$_3$)$_2$	−0.83	44.6	93.1	4.8	28
2	OCH$_3$	−0.27	36.9	92.1	5.3	45
3	CH$_3$	−0.17	44.4	93.2	4.7	78
4	H	0.00	50.0	93.2	4.9	110
5	F	0.06	51.5	92.5	5.7	75
6	Cl	0.23	67.5	91.7	6.9	66
7	CF$_3$	0.54	86.5	92.1	6.8	158

conditions:
CO/H$_2$ = 1, P(CO/H$_2$) = 20 bar, ligand/Rh = 5
substrate/Rh = 637, [Rh] = 1.00 mM

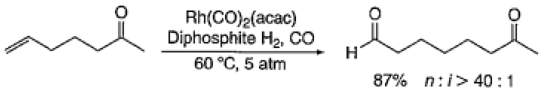


<Phosphile Ligand>



high l/b ratio
faster reaction
suppressed side reaction (hydrogenation)

than PAr_3



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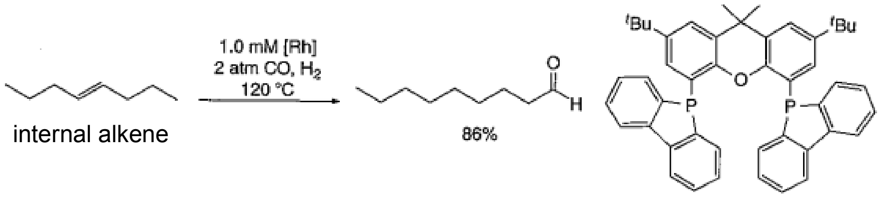
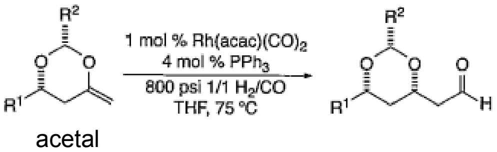
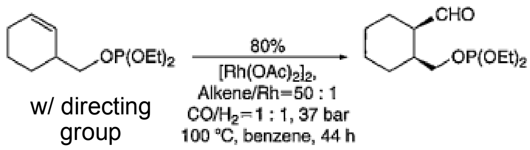
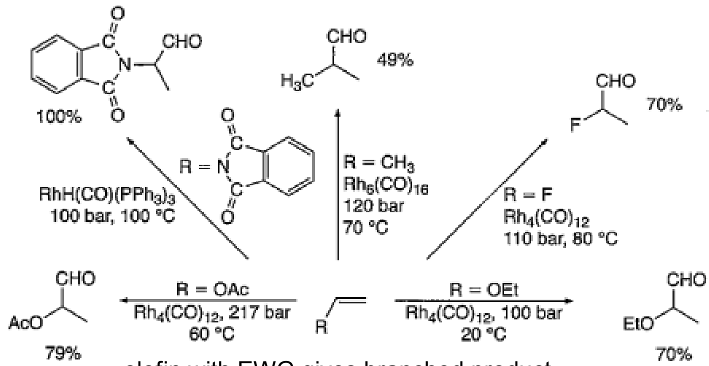








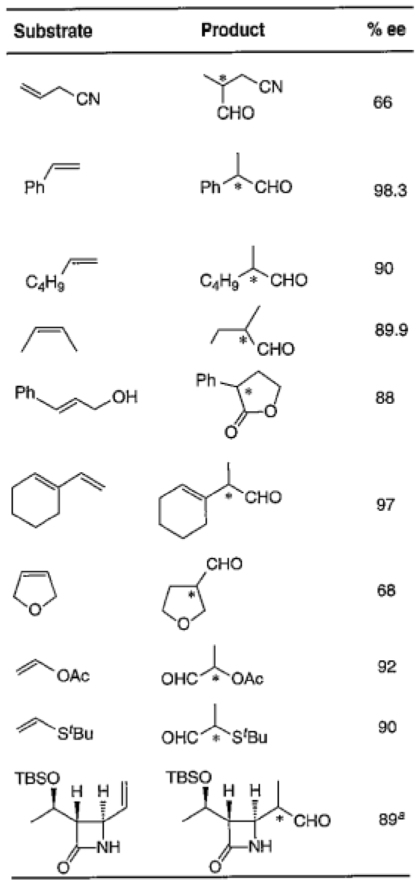
olefin with EWG gives branched product.

<Enantioselective reaction>

challenges

- branched product should be selectively formed.
- simple alkene's directing nature is small.
- racemization must be suppressed.
- chiral phosphine is far from reaction space.

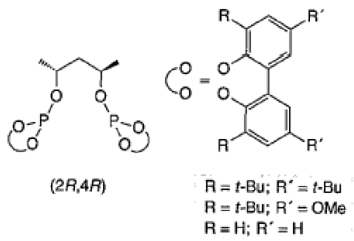
scope with Rh-BINAPHOS



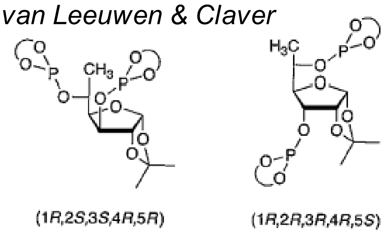
^{a} Diastereomeric excess.

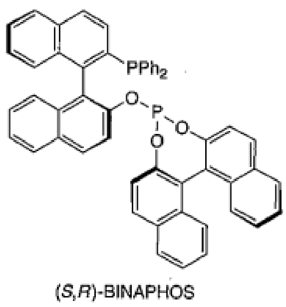
successful ligand families

Babin & Whiteker

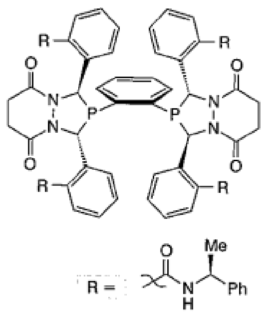


van Leeuwen & Claver



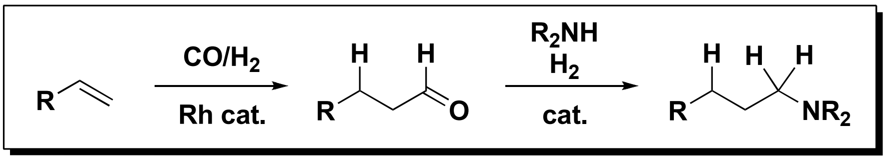


Nozaki & Takaya



Landis

17.4. Hydroaminomethylation



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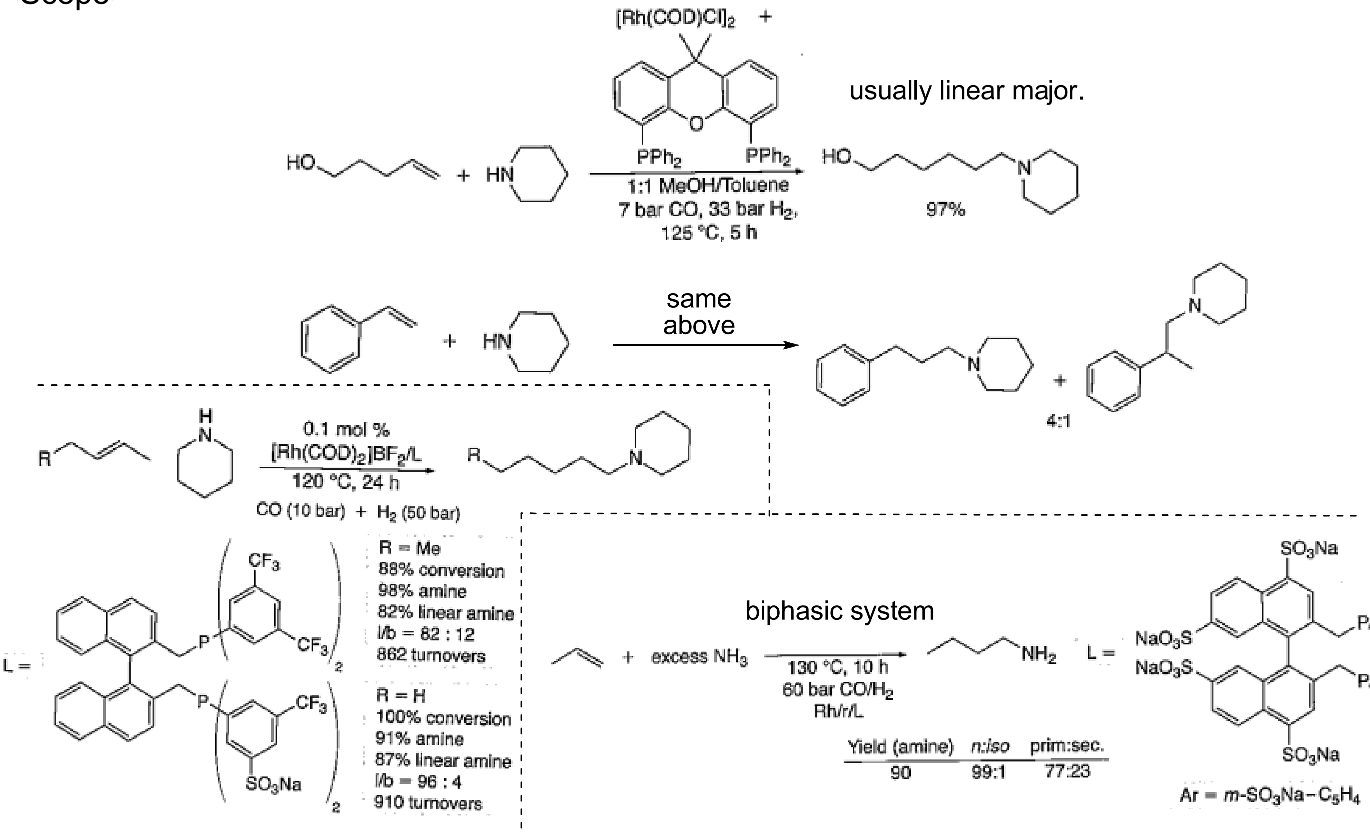
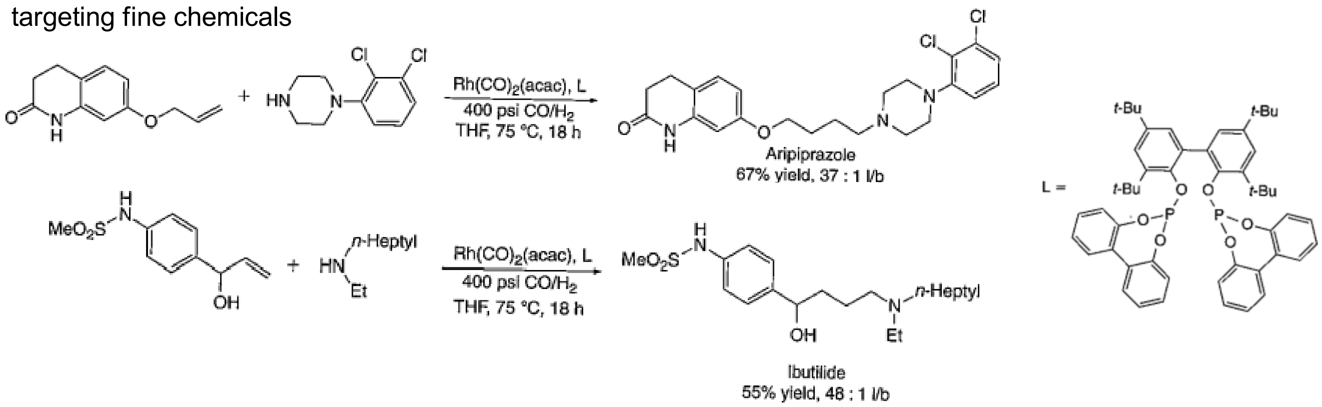
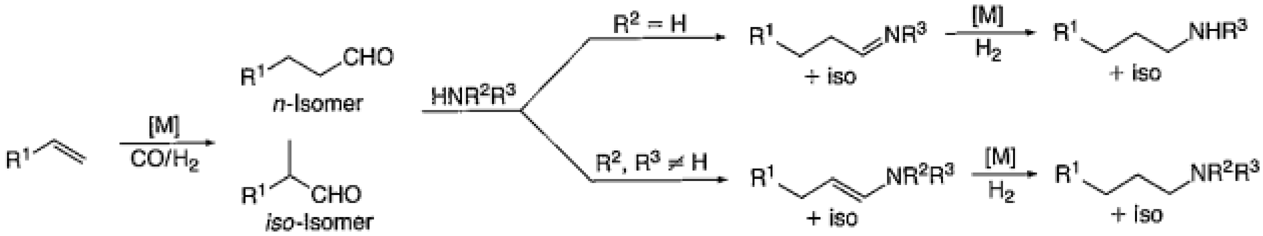


targeting fine chemicals



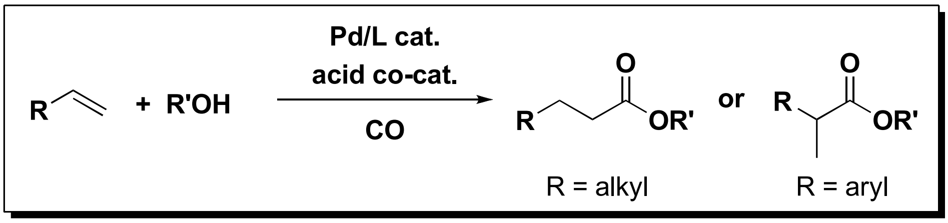
<Mechanism>

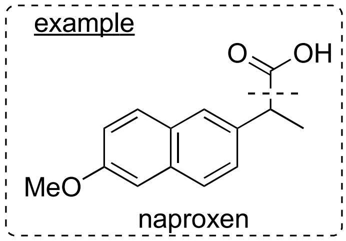


challenges

prevent catalyst deactivation with excess amines
e-rich cat enough to reduce e-rich enamine not to prevent hydroformylation

17.5. Hydrocarboxylation / Hydroesterification





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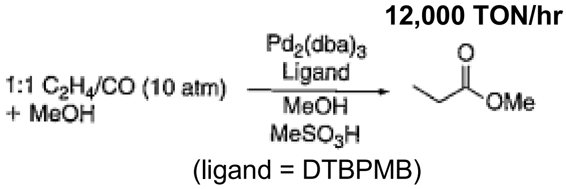
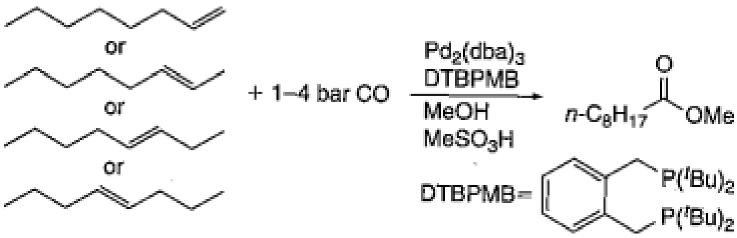
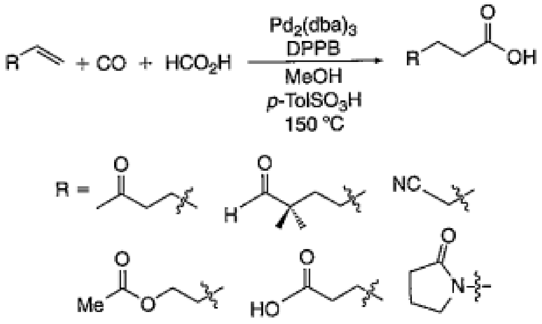
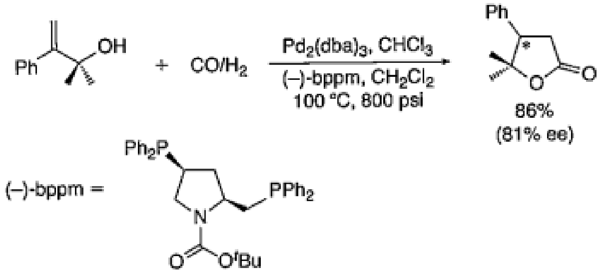


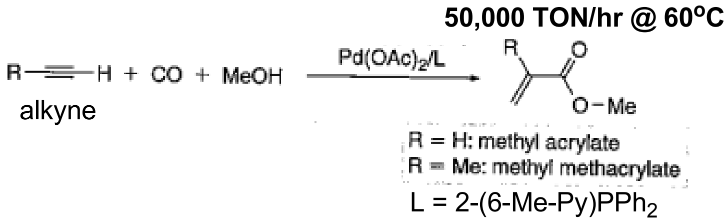




high FG tolerance

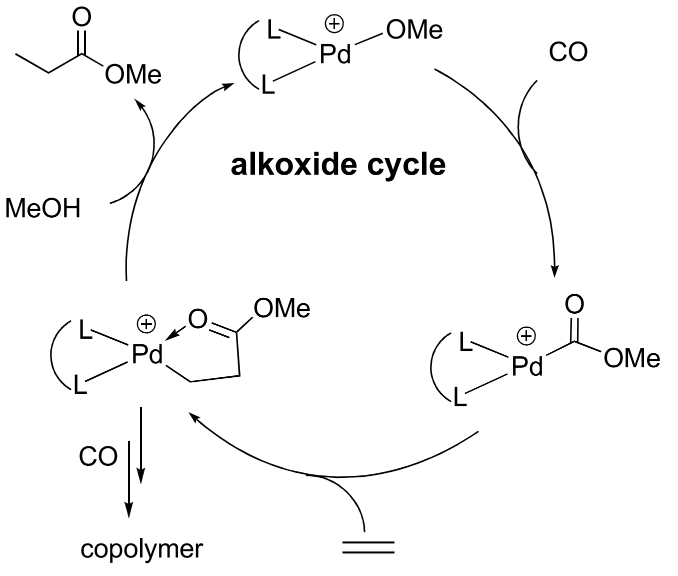
intramolecular rxn

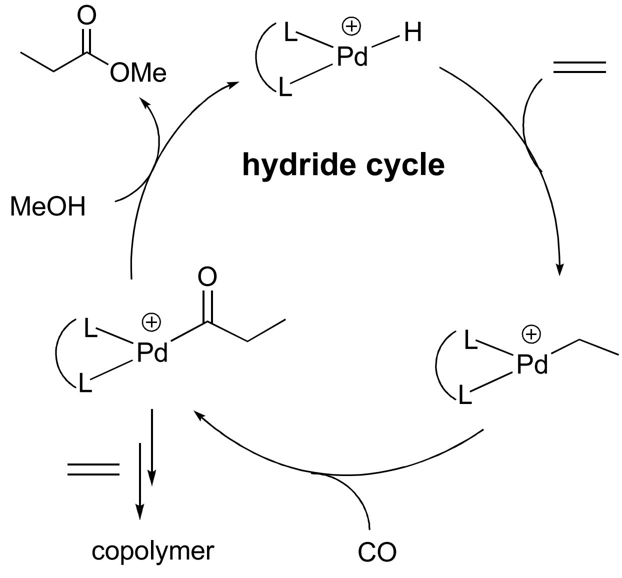




<Mechanism>

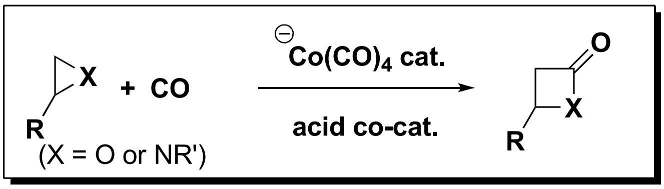
depends on the ligand nature.





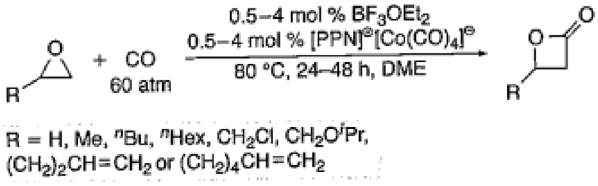
(more probable in Pd/DTBPMB)

17.6. Carbonylation of Epoxides / Aziridines



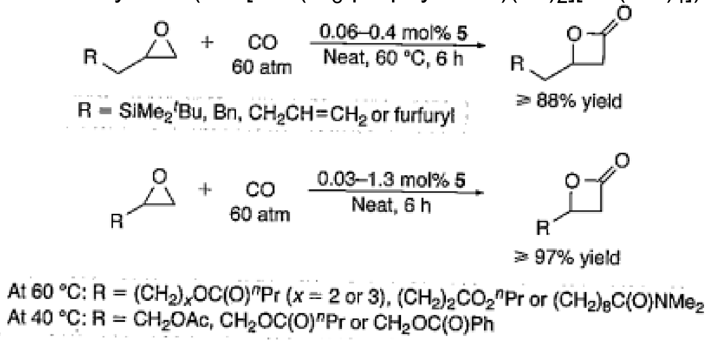
<Scope>

Alper's system

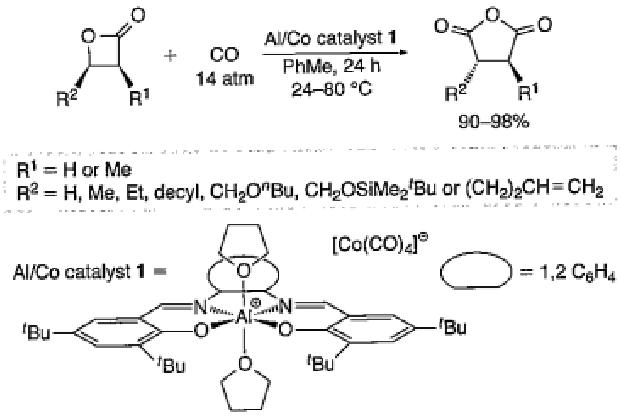


(PPN = bis(triphenylphosphine)iminium)

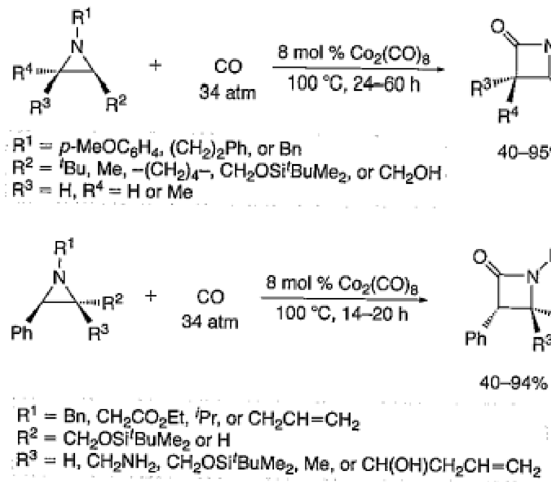
Coates' system (**5** = [Cr^{III}(Et_8-porphyrinato)$(thf)_2$][$Co(CO)_4$])



double carbonylation

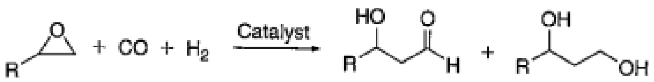


aziridines



addition of Lewis acid acclerate the rxn.

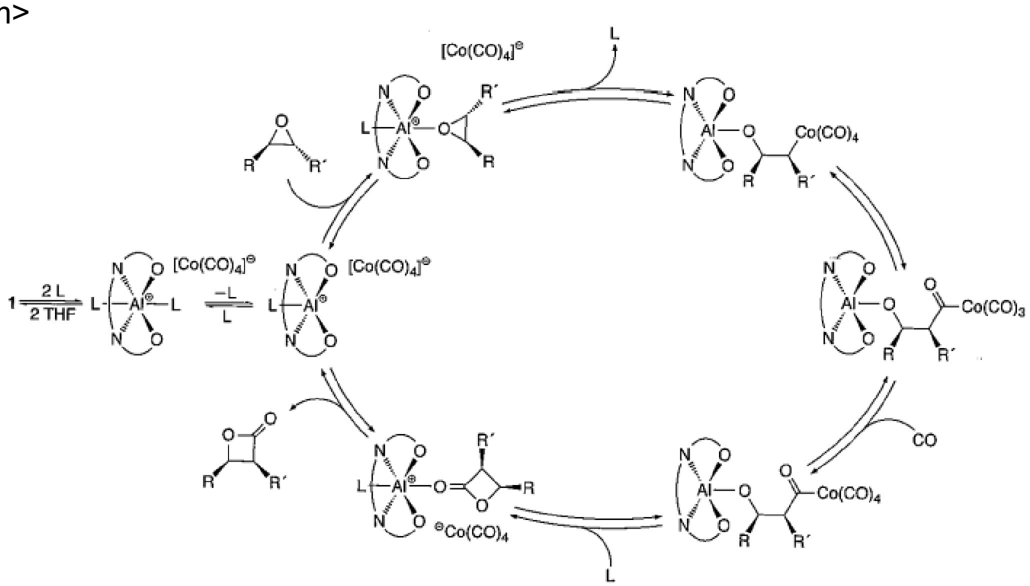
ring-opening carbonylation



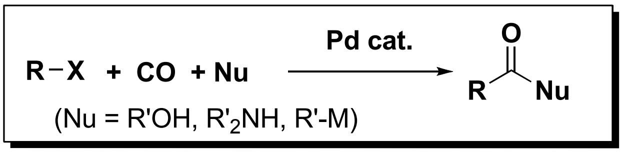
$Co_2(CO)_8$ + $Ru_3(CO)_{12}$ system

$Co_2(CO)_8$ + 1,10-Phen + BnBr system
w/o H_2

<Mechanism>



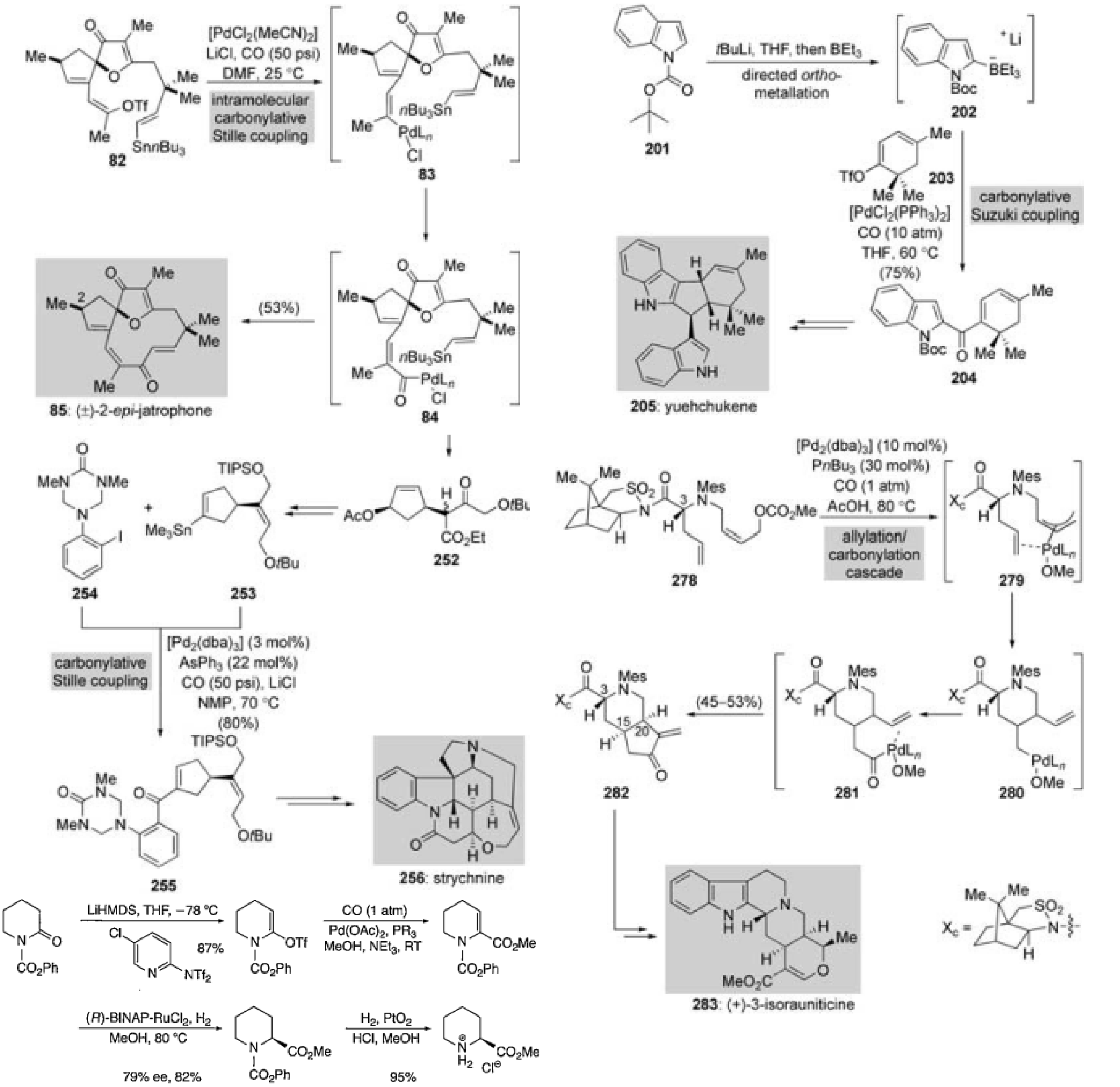
17.7. Carbonylation of Organic Halides (Carbonylative Cross Coupling)



scope is similar to that of cross coupling.
R = alkyl is remains to be developed.

<Scope>

review: Nicolaou, K. C. et al. *ACIE* **2005**, *44*, 4442.



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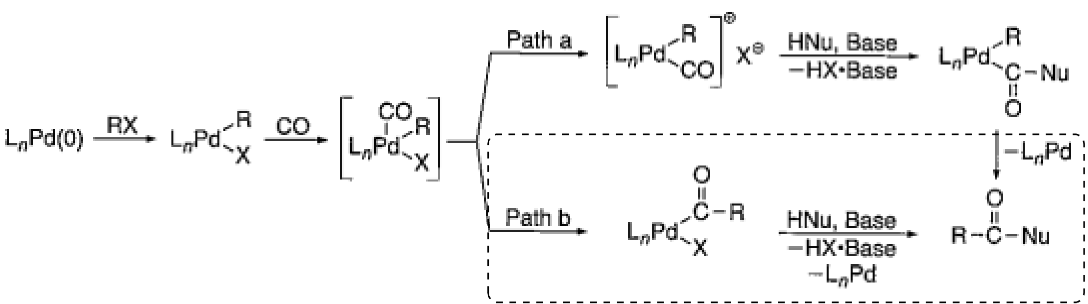
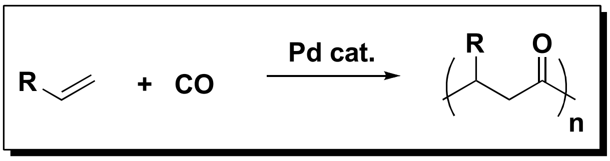


details depend on R-X and HNu.

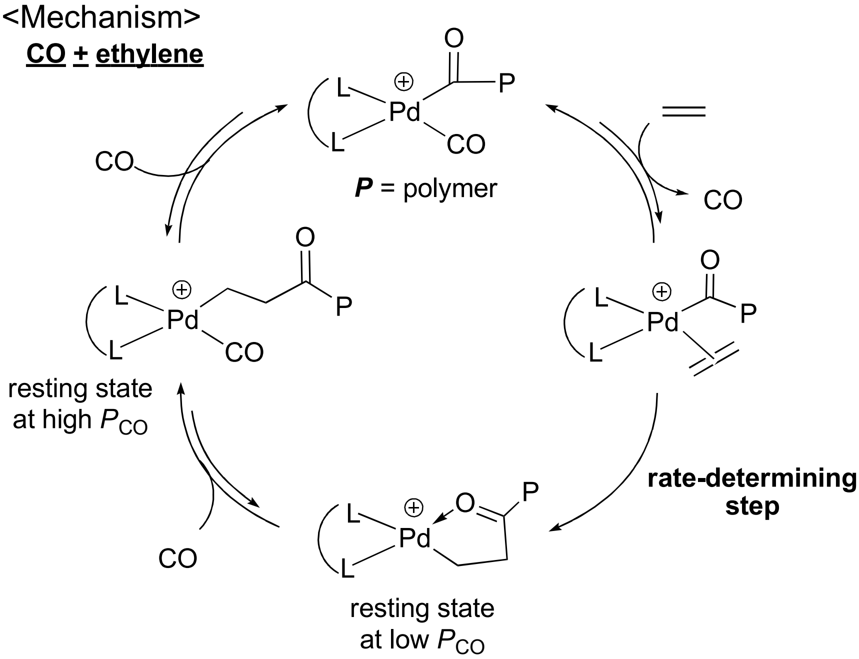
17.8. Copolymerization of CO and Olefins



similar conditioins of hyroesterification
in the absence of acid co-catalyst
weakly nucleophilic alcohol or aprotic solvent is preferred.

<Mechanism>

CO + ethylene



bidentate ligand(dppp) is favored.

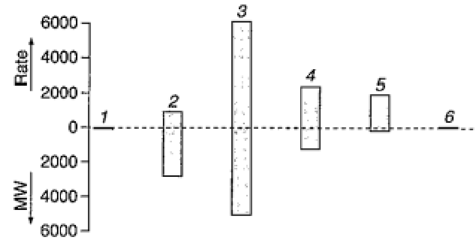
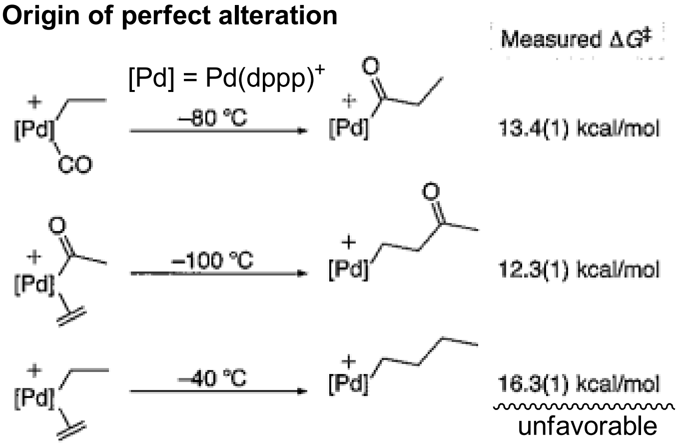


Figure 17.9.
Influence of chain length of ligand $Ph_2P(CH_2)_nPPh_2$ on the rate and molecular weight of polyketone from the copolymerization of CO and ethylene. Figure adapted from reference 304.

Origin of perfect alteration



CO insertion into M-acyl bond is thermodynamically unfavorable.

Catalyst decomposition

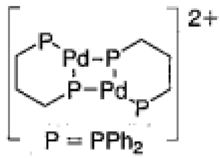
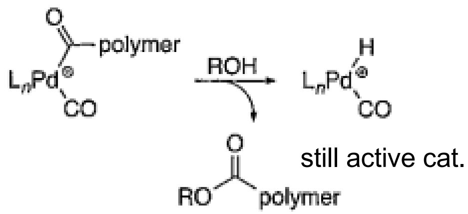


Figure 17.12.
One catalyst decomposition product identified in the copolymerization of CO and olefins.

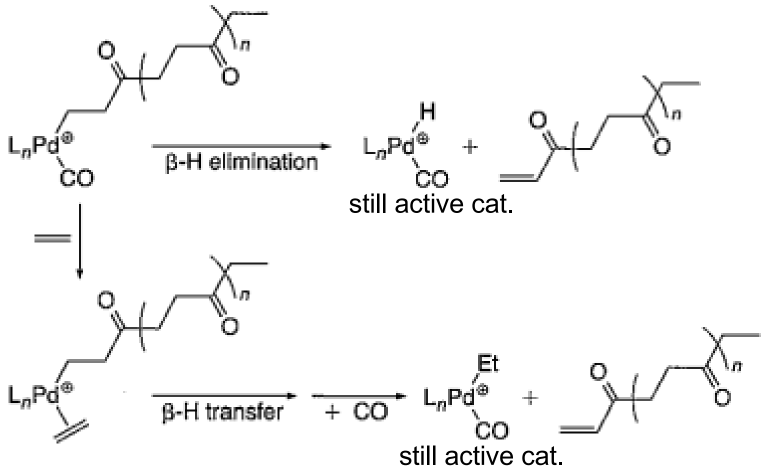
or generation of
Pd(0) metal
from Pd hydride

Chain Termination

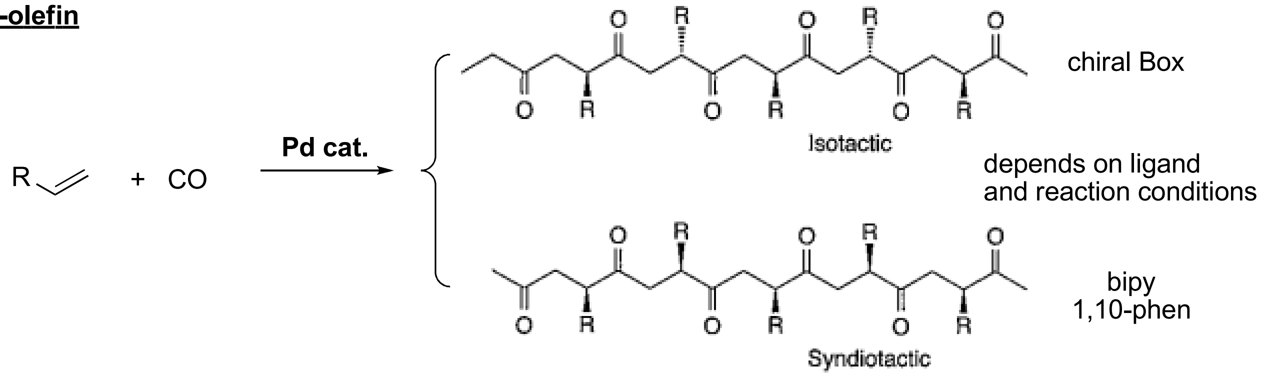
presence of ROH



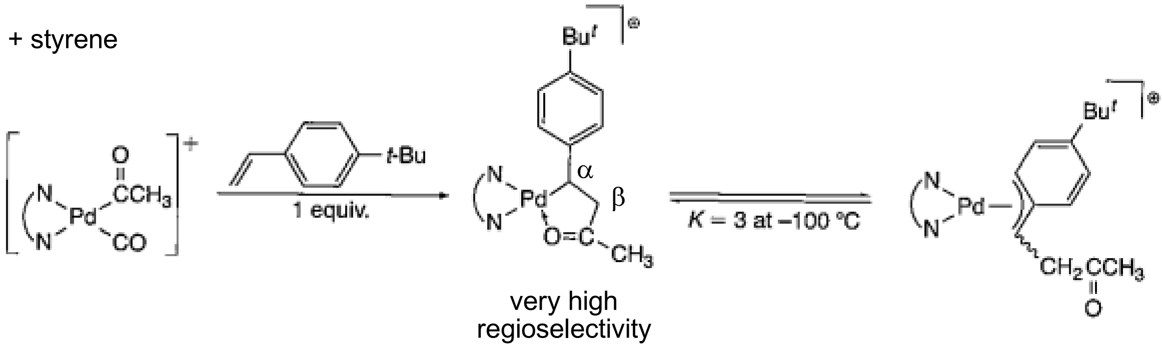
absence of ROH



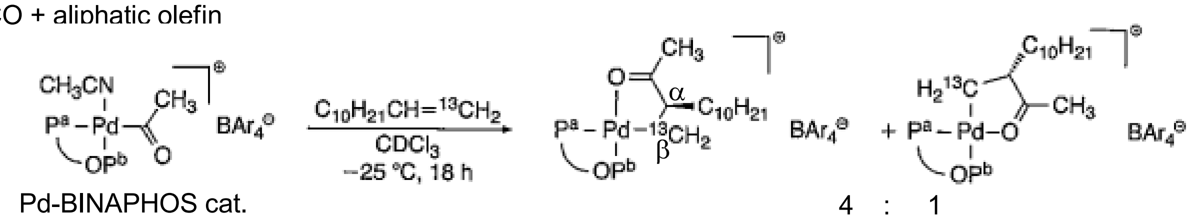
CO ± α-olefin

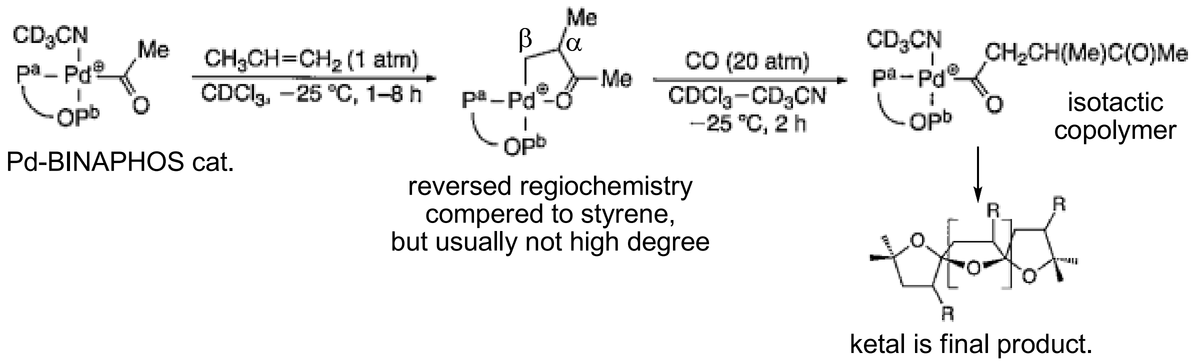


CO + styrene

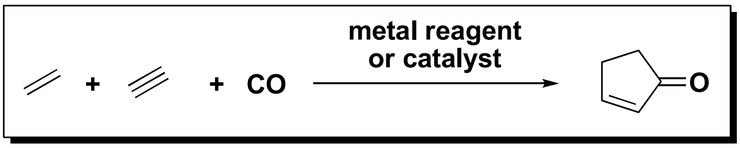


CO + aliphatic olefin





17.9. Pauson-Khand Reactions (PKR)

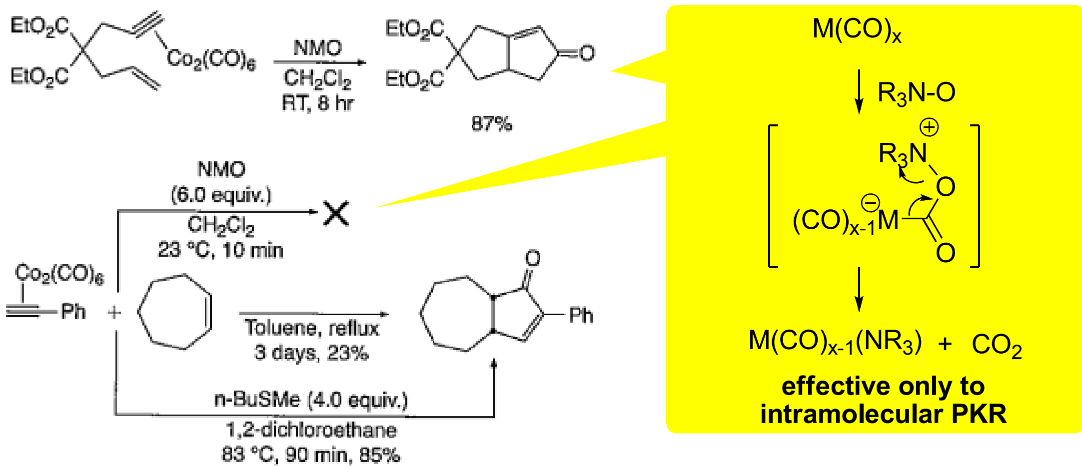


discovered in eary 1970s

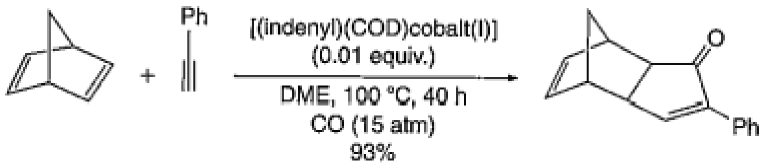
typical conditions:
stoichiometric $Co_2(CO)_8$

additive effect

(also see Oisaki's handout, chapter 5)



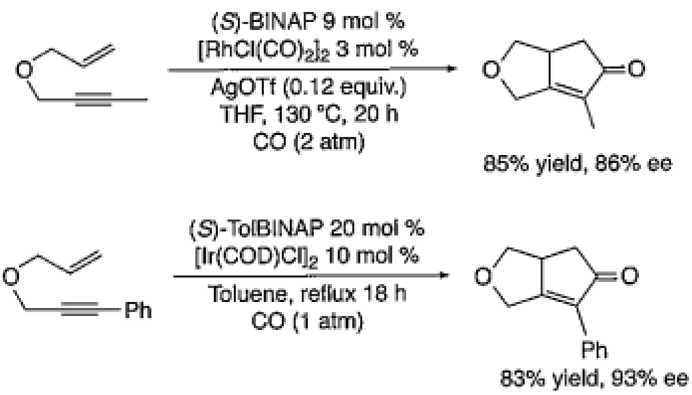
catalytic conditions

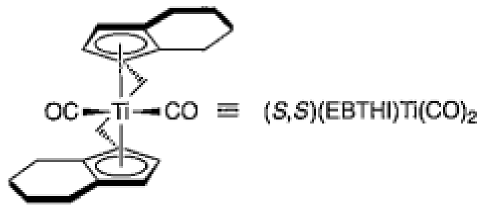


$Cp_2Ti(CO)_2$, $Ru_x(CO)_y$, $[Rh(CO)_2Cl]_2$, Fe, Pd, $Ir(cod)Cl(PPh_3)$, $Mo(dmf)_3(CO)_3$, $W(CO)_5(thf)$ also showed catalytic activity.

* $Co_2(CO)_8$ is thermally unstable

Catalytic asymmetric PKR



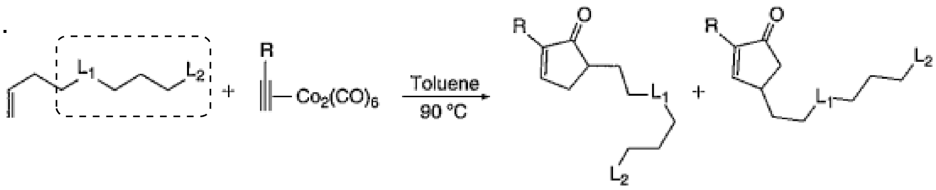


is also active.

Intermolecular PKR

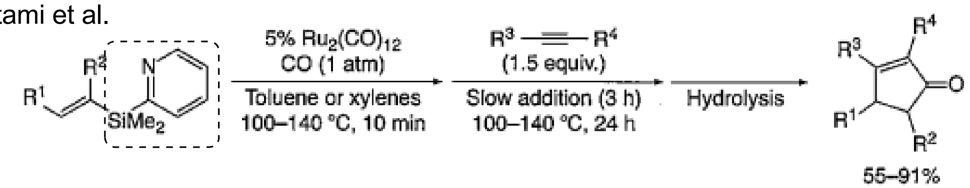
: difficult to control the regioselectivity → chelating auxiliary is the choice.

Kraft et al.



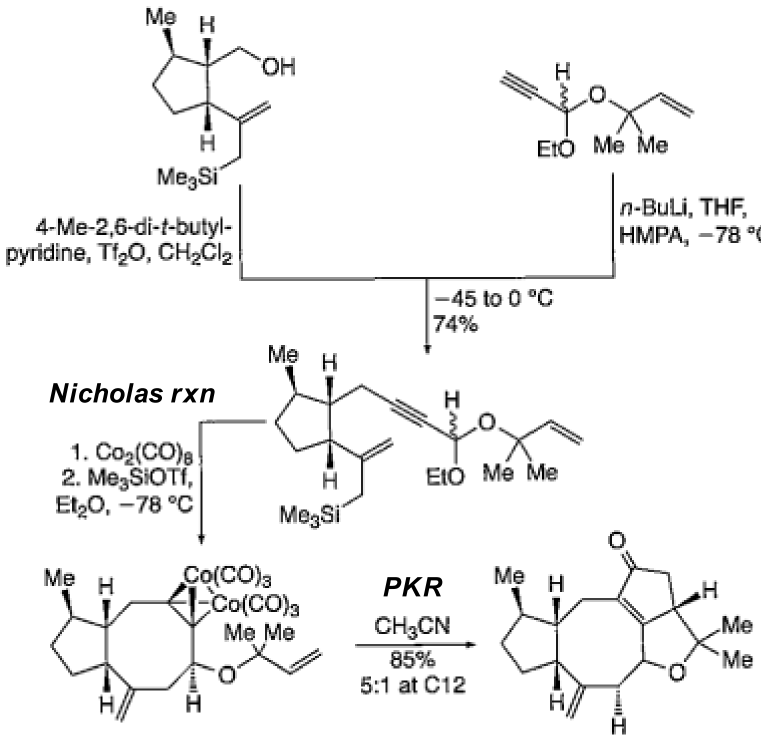
L_1 = S, L_2 = NMe_2, R = Ph, 85%	15	:	1
L_1 = S, L_2 = SEt, R = Bu, 85%	> 40	:	1

Yoshida & Itami et al.

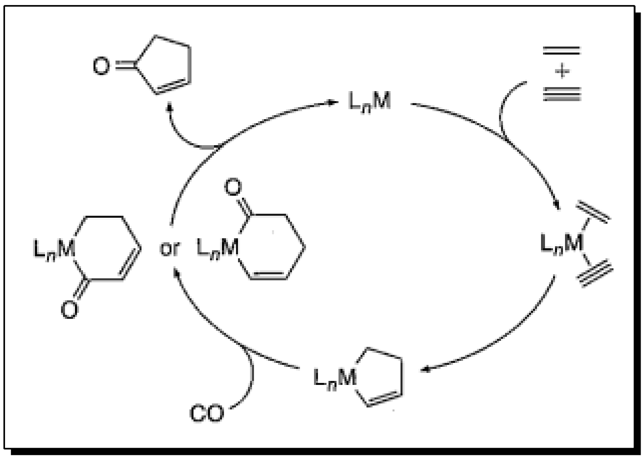


Application in Total Synthesis

Jamison & Schreiber et al.: synthesis of (+)-epoxydictymene



<Mechanism> Magnus, P. et al. *TL* **1985**, *26*, 4851.



totally irreversibe in the presence of CO