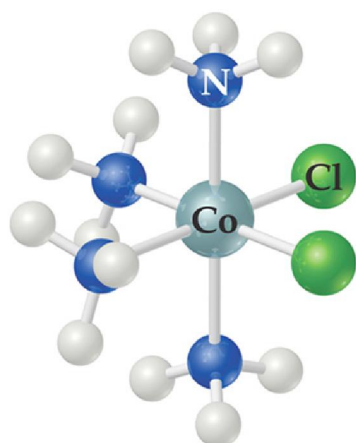


# Homogeneous catalysis



## Ligand Substitution Reactions



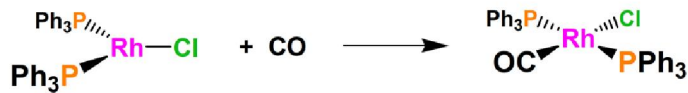
The mechanism of this substitution will almost always depend on whether the parent  $ML_n$  complex is coordinatively **saturated** or not!

**Saturated Complex:** Dissociative Pathway!

**Unsaturated Complex:** Associative Pathway (usually)  
Dissociative pathway (sometimes)

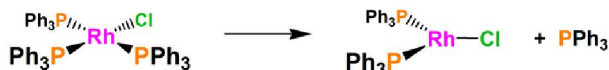
Most of the substitutions we will study will involve 2e- pathways. Odd e- or radical pathways are known, but less common.

**Ligand Addition (association):** this is when an incoming ligand coordinates to a metal center that has one or more empty orbitals available.

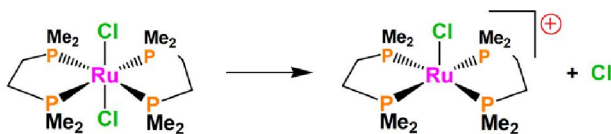


This Rh(+1) complex is  $d^8$  and only 14e<sup>-</sup>. Adding a ligand takes one to the more stable 16e<sup>-</sup> square-planar complex.

**Ligand Dissociation:** this is when a ligand coordinated to a metal dissociates (falls off). The probability of a specific ligand dissociating depends on how strongly or weakly it is coordinated to the metal center and steric effects.

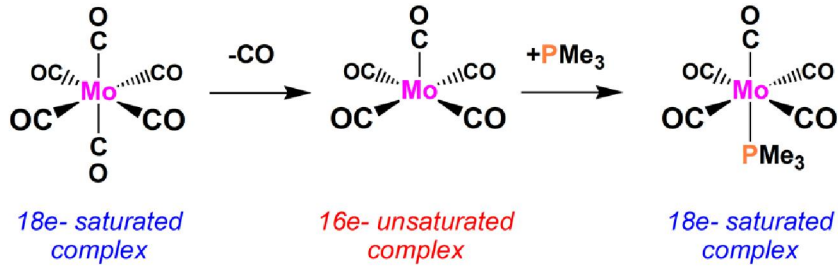


The steric hindrance of the three bulky  $PPh_3$  ligands favors dissociation of one to form the 14e<sup>-</sup>  $RhCl(PPh_3)_2$  complex. The moderate electron-donating ability of the  $PPh_3$  ligand (not a strongly coordinating ligand) makes this fairly facile.

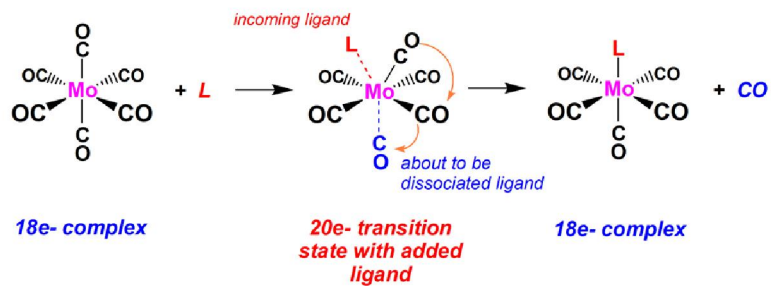


The strongly donating ability of the  $dmpm$  ligands combined with their strong chelate effect makes it difficult to dissociate one of the  $PMe_2$  arms. In this case the  $Cl^-$  anion is the one that dissociates, leaving a cationic complex behind. The two  $dmpm$  ligands donate enough electron-density to the Ru center to make it reasonable to dissociate a  $Cl^-$ .

A **ligand substitution** can occur either by an **associative** or **dissociative** route. The exact mechanism depends in large part on the electron-count of the metal complex undergoing the ligand substitution. The simplest case is when one is dealing with an **18e<sup>-</sup>** metal complex. In this case one almost always has a **dissociative substitution**.



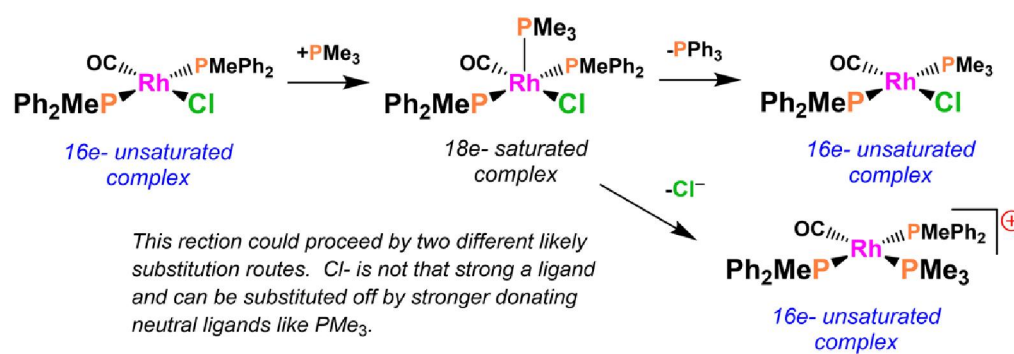
Almost NO evidence for this type of reaction:





### Associative Substitutions

These occur first by a **ligand addition** to the metal complex followed by the **dissociation** of one of the original ligands.

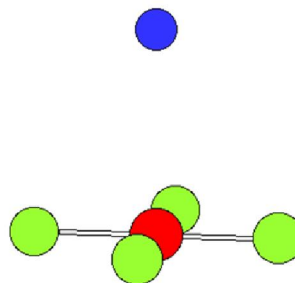


*The filled axial Pt d<sub>z<sup>2</sup></sub> orbital partially blocks coordination of ligands via the empty axial p<sub>z</sub> orbital. This limits, but does not stop ligand association, which is quite common for Rh(I) and Pd(II).*

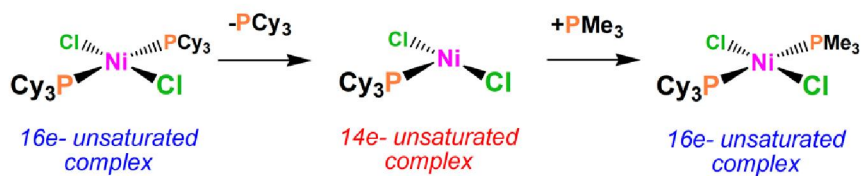
### Associative Substitutions

These occur first by a **ligand addition** to the metal complex followed by the **dissociation** of one of the original ligands.

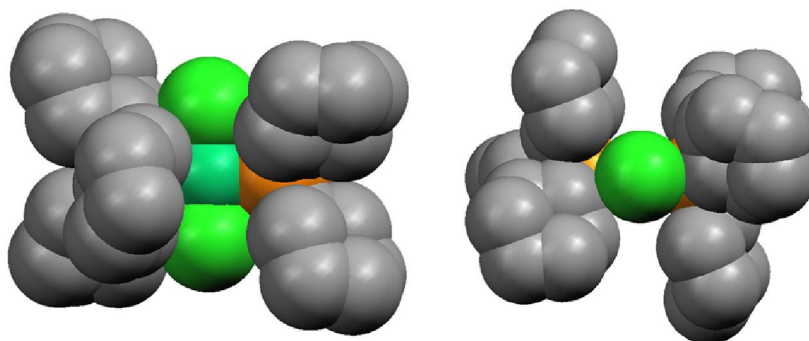
**Berry pseudorotation**  
Formation of a trigonal bipyramid intermediate

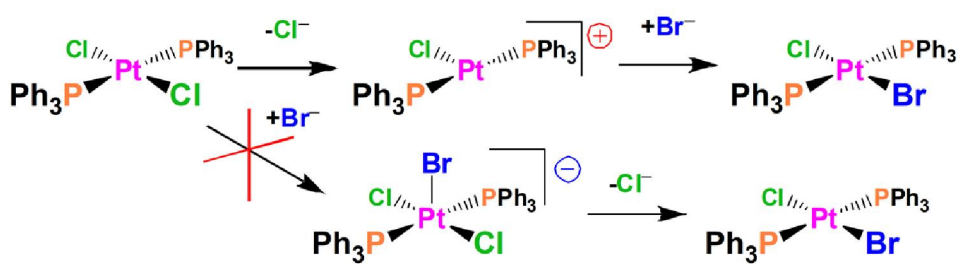


**Dissociative substitution** can also occur in 16e- (or in very unusual cases, lower electron count systems) complexes. These cases either involve **sterically bulky ligands** that block the open coordination site, or third row square planar  $d^8$  complexes like Pt(+2) where there are strong electronic factors that limit the coordination of an additional ligand to the empty axial site.



The large  $\text{PCy}_3$  ligands sterically block access to the empty axial  $p_z$  orbital

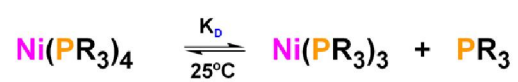




*The spatially extended filled axial Pt  $d_{z^2}$  orbital partially blocks coordination of ligands via the empty axial  $p_z$  orbital. This limits ligand association, although it can occur.*

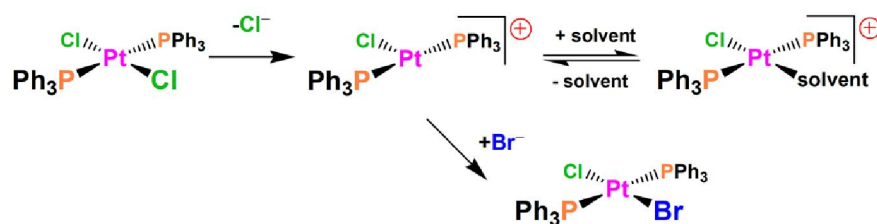
**Problem:** The rate of substitution reactions on square planar  $d^8$  complexes goes in the order:  $\text{Ni} > \text{Pd} \gg \text{Pt}$ . Explain why.

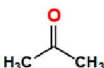

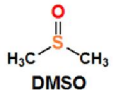
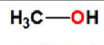

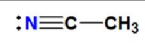

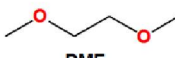

## Steric Factors



Ligand:	P(OEt) <sub>3</sub>	P(O- <i>p</i> -tolyl) <sub>3</sub>	P(O- <i>i</i> -Pr) <sub>3</sub>	P(O- <i>o</i> -tolyl) <sub>3</sub>	PPh <sub>3</sub>
Cone angle:	109°	128°	130°	141°	145°
K <sub>D</sub> :	< 10 <sup>-10</sup>	6 x 10 <sup>-10</sup>	2.7 x 10 <sup>-5</sup>	4 x 10 <sup>-2</sup>	> 1000

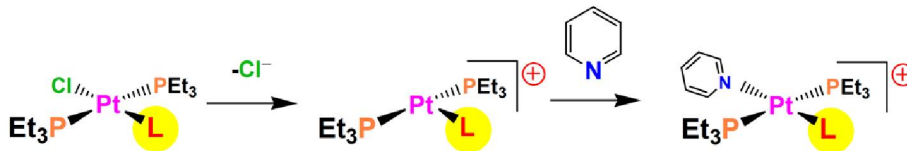
## Solvent Effects



 <p><b>acetone</b></p>	 <p><b>THF</b> (tetrahydrofuran)</p>	 <p><b>DMSO</b> (dimethylsulfoxide) bp = 189°C mp = 18°C</p>
 <p><b>methanol</b></p>	 <p><b>ethanol</b></p>	 <p><b>acetonitrile</b></p>
 <p><b>DMF</b> (dimethylformamide) bp = 153°C mp = -61°C</p>	 <p><b>DME</b> (dimethoxyethane)</p>	 <p><b>water</b> (rarely used)</p>

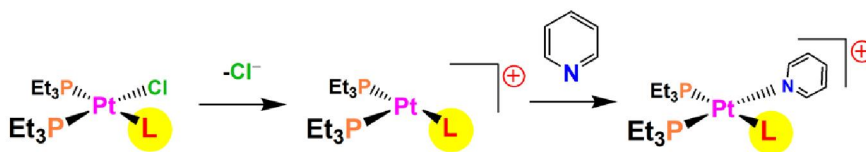
## Trans Effect

The **trans effect** concerns the electronic effect of one ligand on another ligand when they are **trans** (opposite) to one another. The classical *trans* effect involves two  $\sigma$ -donating ligands *trans* to one another.



Relative rate of substitution based on *trans* ligand  $\bullet$  :  
 $\text{Cl}^- = 1$ ,  $\text{Ph}^- = 100$ ,  $\text{CH}_3^- = 10^3$ ,  $\text{H}^- = 10^4$

There is a *cis* effect, but it is much weaker and basically ignored:



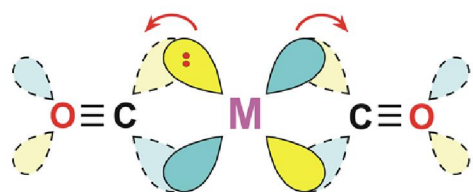
Relative rate of substitution based on *cis* ligand  $\bullet$  :  
 $\text{Cl}^- = 1$ ,  $\text{Ph}^- = 2$ ,  $\text{CH}_3^- = 4$ ,  $\text{H}^- = 4$

Note that when most chemists talk about the *trans* effect they are referring to the  $\sigma$ - $\sigma$  type of *trans* effect, where a strong  $\sigma$ -donor weakens the  $\sigma$ -donating ligand *trans* to it.

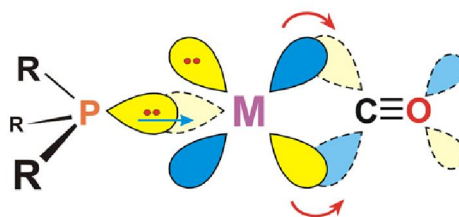
Do NOT overestimate the importance of the *trans*-effect. There are other forms that have different effects.

### $\pi$ -Acceptor *Trans* Effects

*Trans* effects that involve  $\pi$ -backbonding ligands. CO ligands represent the most common type.



$\pi$ -backbonding to a metal is **weakened** when it is *trans* to another good  $\pi$ -backbonding ligand

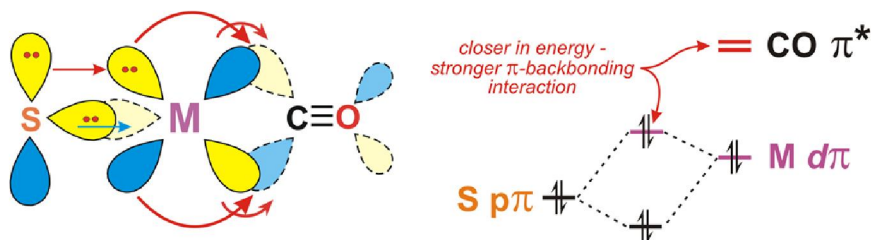


$\pi$ -backbonding to a metal is **strengthened** when it is *trans* to a good  $\sigma$ -donating ligand that can't  $\pi$ -backbond

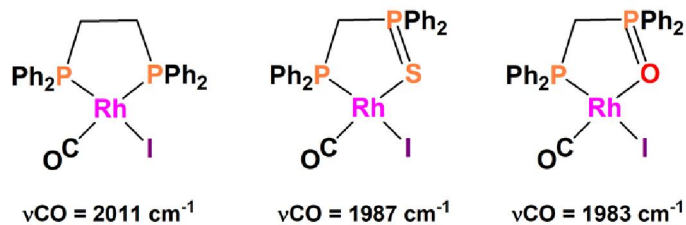


### $\pi$ -Pushing Effect

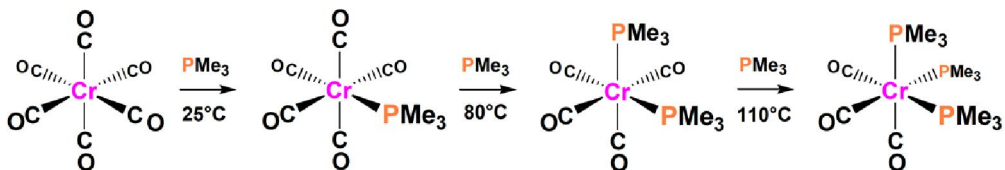
There is a further strengthening of M-CO  $\pi$ -backbonding when the *trans* ligand has  $\pi$ -donation properties that can push up the energy of the filled  $d$  orbitals and, in turn, make them better  $\pi$ -donors to the CO. This can occur even when the ligand is not an especially strong donor.



An example of this can be seen in the following three complexes and their "anomalous"  $\nu_{\text{CO}}$  stretching frequencies:

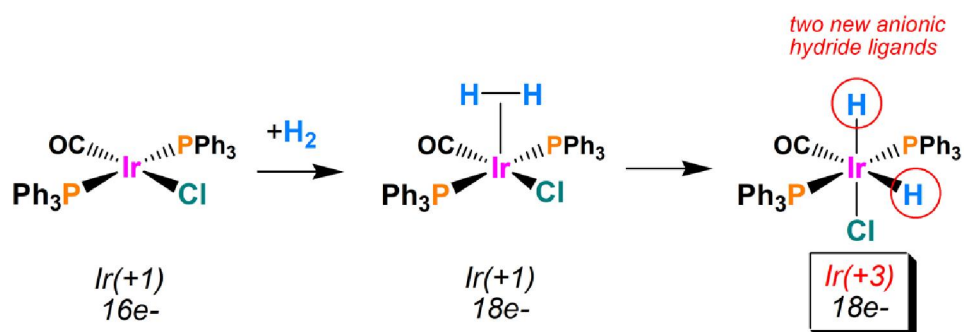


**Problem:** Consider the following series of substitution reactions.



As one replaces each CO ligand with a  $\text{PMe}_3$ , the next CO substitution is progressively more and more difficult requiring higher temperatures and longer times. Once one forms  $\text{Cr(CO)}_3(\text{PMe}_3)_3$ , it is extremely difficult to replace another carbonyl ligand. Why? Give all the major reasons?

## Oxidative Addition



There are three main classes of molecules (substrates) that can perform oxidative additions to metal centers:

- Non-Electrophilic
- Non-Electrophilic "Intact"
- Electrophilic

**Non-electrophillic:** these molecules do NOT contain electronegative atoms and/or are not good oxidizing agents. These molecules usually require the presence of an **empty orbital** on the metal in order for them to pre-coordinate prior to being activated for the oxidative addition rxn.

**H<sub>2</sub>, C-H bonds, Si-H bonds, S-H bonds,  
B-H bonds, N-H bonds, S-S bonds, C-C bonds, etc.**

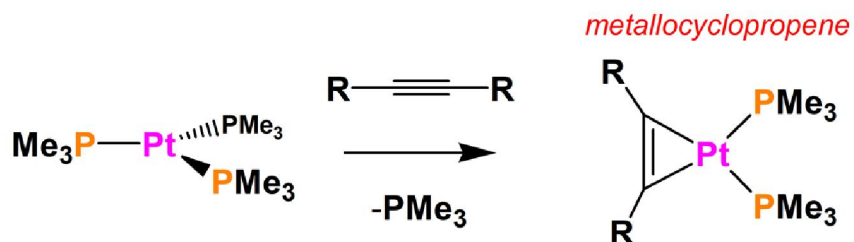
**H<sub>2</sub>** is by far the most important for catalytic applications, followed by Si-H bonds, B-H, N-H, and S-H bonds.

C-H bond activation and functionalization is very important, but still not practical.

**Non-electrophillic "Intact":** these molecules may or may not contain electronegative atoms, but they do need to have a **double** or **triple bond** present. One also needs a metal center with an **empty orbital** (16e- or lower count) in order to pre-coordinate the ligand before the oxidative addition occurs.

Typical "intact" ligands that can perform an oxidation addition without fragmenting apart are ( $O_2$  can also act as an **electrophillic** substrate):

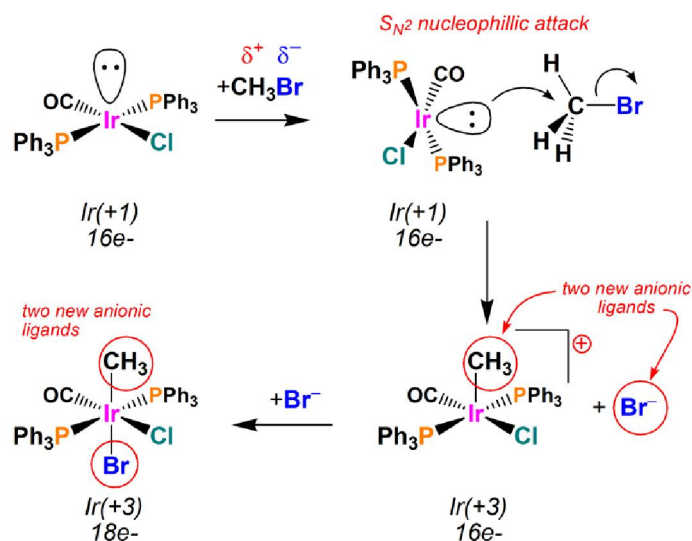
alkenes, alkynes, and  $O_2$



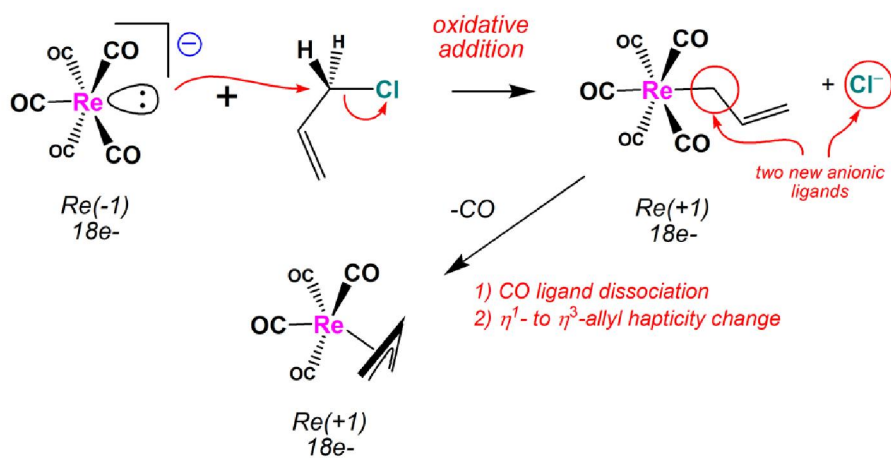
**Electrophillic:** these molecules **do** contain electronegative atoms and are good oxidizing agents. They are often considered to be “**reactive**” substrates.

These molecules do **NOT** require the presence of an **empty orbital** (18e- is OK) on the metal center in order to perform the oxidative addition rxn.

**X<sub>2</sub> (X = Cl, Br, I), R-X, Ar-X, H-X, O<sub>2</sub>, etc.**



In the case of a starting **18e<sup>-</sup>** complex (shown below) only **one** of the two anionic ligands (usually the strongest binding) generated from the oxidative addition will end up coordinated to the metal unless a separate substitution reaction occurs.



**WARNING:**

$d^0$  metals can **NOT** do ***oxidative additions!!***

So always electron count the starting and final metal complexes to check out the overall electron-count, metal oxidation state and *d*-electron count!



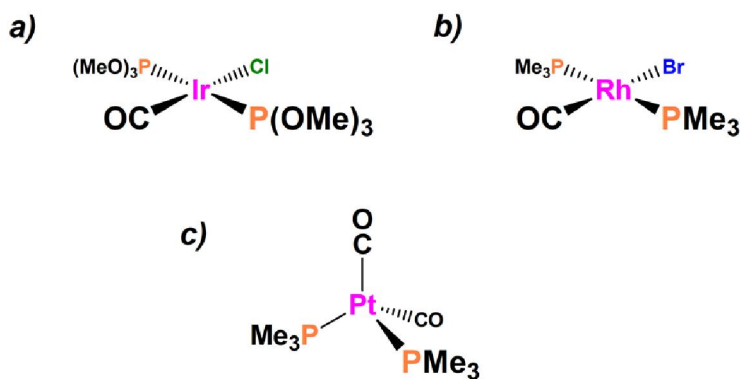
### Kinetic Data for Oxidative Addition Reactions of $\text{MX}(\text{CO})(\text{PR}_3)_2$

M	X	$\text{PR}_3$	Reactant	Rate Const ( $\text{M}^{-1} \text{sec}^{-1}$ )	$\Delta\text{H}^\ddagger$ (kcal/mol)	$\Delta\text{S}^\ddagger$ (J/mol K)
Ir	Cl	$\text{PPh}_3$	$\text{H}_2$	0.67	10.8	-23
	Br			10.5	12.0	-14
	I			> 100		
Ir	Cl	$\text{PPh}_3$	$\text{O}_2$	$3.4 \times 10^{-2}$	13.1	-21
	Br			$7.4 \times 10^{-2}$	11.8	-24
	I			$30 \times 10^{-2}$	10.9	-24
Ir	Cl	$\text{PPh}_3$	$\text{CH}_3\text{I}$	$3.5 \times 10^{-3}$	5.6	-51
	Br			$1.6 \times 10^{-3}$	7.6	-46
	I			$0.9 \times 10^{-3}$	8.8	-43
Ir	Cl	$\text{P}(\rho\text{-C}_6\text{H}_4\text{-OMe})_3$	$\text{CH}_3\text{I}$	$3.5 \times 10^{-2}$	8.8	-35
		$\text{P}(\rho\text{-C}_6\text{H}_4\text{-Cl})_3$		$3.7 \times 10^{-5}$	14.9	-28
Rh	Cl	$\text{PPh}_3$	$\text{CH}_3\text{I}$	$12.7 \times 10^{-4}$	9.1	-44
		$\text{P}(\rho\text{-C}_6\text{H}_4\text{-OMe})_3$		$51.5 \times 10^{-4}$	10.2	-43

Data adapted from "Principles and Applications of Organotransition Metal Chemistry", Coleman, Hegedus, Norton & Finke, University Press, 1987; refs: Chock & Halpern, *JACS*, 1966, 88, 3511; Ugo, Pasini, Fusi, Cenini, *JACS*, 1972, 94, 7364; Douek & Wilkinson, *J. Chem. Soc. (A)*, 1964, 2604. Rxns generally run in benzene at 25°C.

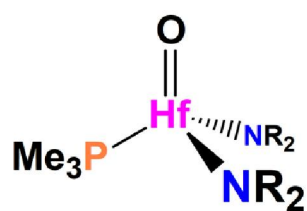
**Oxidative additions** are easy to identify **IF YOU ELECTRON COUNT** the metal complexes. When an oxidative addition rxn occurs the metal will be oxidized, usually by  $2e^-$ . So, if you start with a metal in the 0 oxidation state ( $d^8$ ), after the oxidative addition the metal will be in the +2 oxidation state ( $d^6$ ). Once you get used to looking at organometallic rxns you will be able to identify common oxidative additions quite quickly.  $H_2$ ,  $R-X$ , and  $H-SiR_3$  are three of the most common substrates that perform **oxidative addition** reactions in catalytic cycles.

**Problem:**  $H_2$  will do an **oxidative addition** most readily to which of the following complexes. Why?

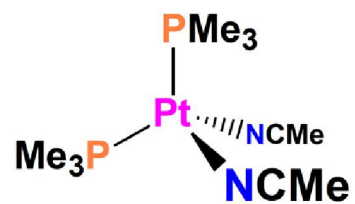


**Problem:**  $\text{CH}_3\text{Br}$  will do an **oxidative addition** most readily to which of the following complexes. Why?

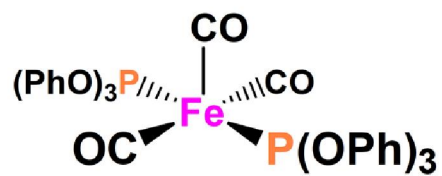
a)



b)

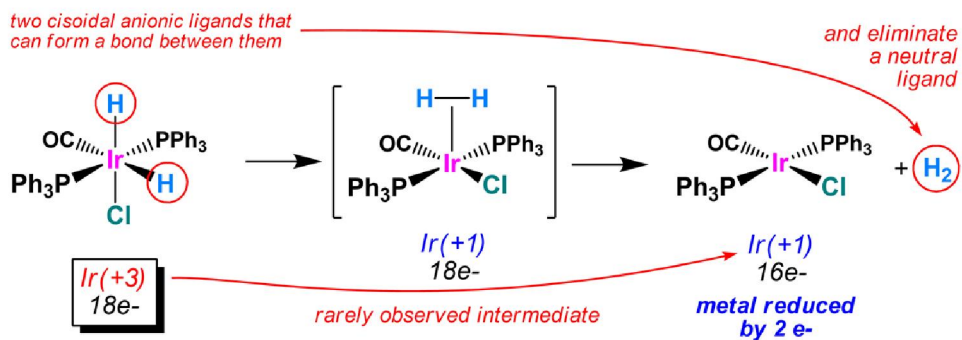


c)

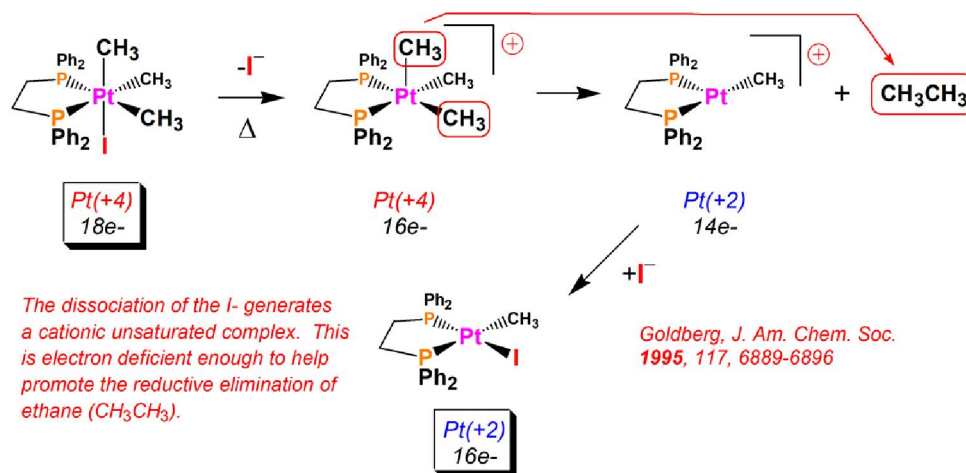


## Reductive Elimination

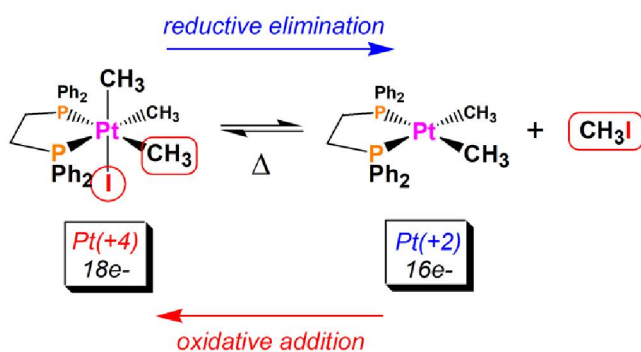
A **reductive elimination** reaction is the reverse of an **oxidative addition**. It is a reaction in which **two cisoidal anionic ligands** on a metal center couple together. Each anionic ligand pushes one electron back onto the metal center (in the case of a monometallic complex) to reduce it by  $2e^-$ . The coupled anionic ligands then usually fall off the metal center as a **neutral** molecule.



While **reductive elimination** can occur from saturated 18e- complexes (so long as the two ligands that you want to reductively eliminate are **cisoidal** to one another), it has been shown that reductive elimination can be promoted by a ligand dissociation generating an unsaturated and more electron-deficient metal center.

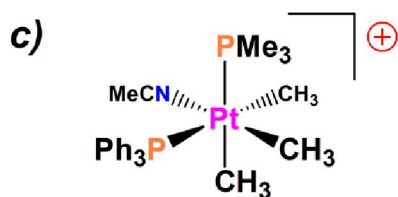
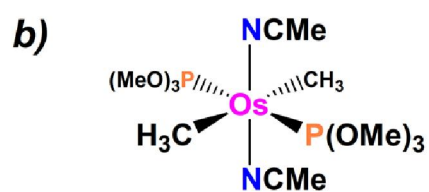
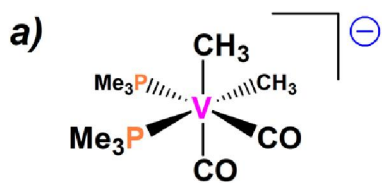


In studying the above system, it was also found that one could have **reductive elimination** of  $\text{CH}_3\text{I}$  from the starting 18e<sup>-</sup> complex. This reaction, however, is very reversible due to the high reactivity of  $\text{CH}_3\text{I}$  for doing an **oxidative addition** back reaction with the electron-rich neutral Pt(+2) complex to make the Pt(+4) octahedral compound.



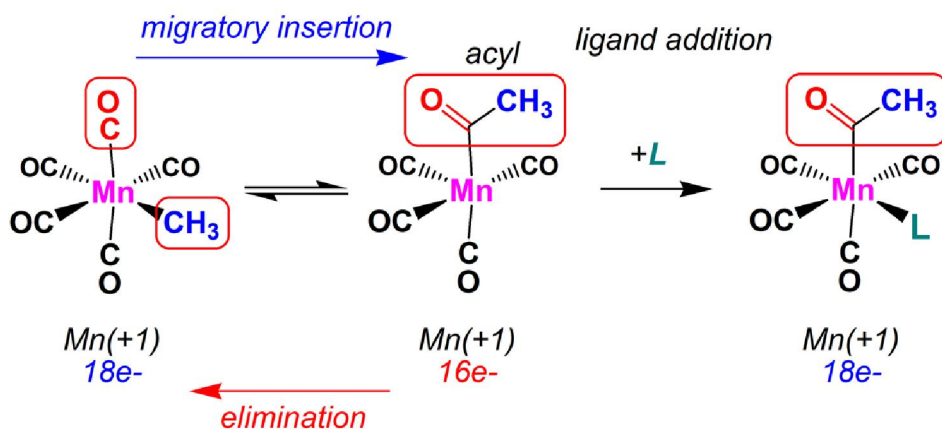
The reductive elimination of the  $\text{CH}_3\text{I}$  is kinetically favored. This is because the orbitals around the iodide anion are spherically symmetric and this makes it much easier to overlap with the alkyl group orbital to perform the reductive elimination. The  $\text{sp}^3$  directed orbitals on the two  $\text{CH}_3$  groups are more difficult to overlap in order to get the reductive elimination to occur. But the reductive elimination of the  $\text{CH}_3\text{CH}_3$  is thermodynamically considerably more favorable and the back oxidative addition much more difficult.

**Problem:** Which of the following compounds will be most likely to do a reductive elimination of ethane ( $\text{CH}_3\text{-CH}_3$ )? Why?



## Migratory Insertion & Elimination Reactions

A *migratory insertion* reaction is when a **cisoidal anionic and neutral** ligand on a metal complex couple together to generate a new coordinated **anionic** ligand. This new anionic ligand is composed of the original neutral and anionic ligands now bonded to one another. **There is NO change in the oxidation state or d electron-count of the metal center.**





### General Features of Migratory Insertions:

- 1) No change in formal oxidation state
- 2) The two groups that react must be **cisoidal** to one another
- 3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g.,  $\beta$ -hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the back elimination reaction.
- 4) Migratory insertions are usually favored on more electron-deficient metal centers.

The following are common **anionic** and **neutral** ligands that can do **migratory insertion** reactions with one another:

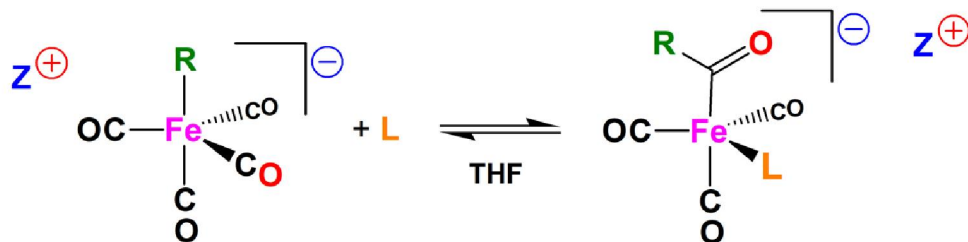
**Anionic:**  $\text{H}^-$ ,  $\text{R}^-$  (alkyl),  $\text{Ar}^-$  (aryl),  $\text{acyl}^-$ ,  $\text{O}^{2-}$  (oxo)

**Neutral:** CO, alkenes, alkynes, carbenes

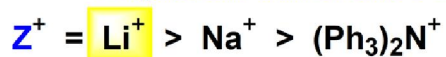
CO and alkyl migratory insertions (as shown on previous slide) are extremely important and are often generically referred to as **carbonylation** reactions.

Hydride and CO migratory insertions to produce formyl groups are not common due to the *thermodynamic instability* of the formyl-metal interaction.

### Some Electronic effects



*best Lewis acid - can coordinate to electron-rich CO ligands and drain off some e- density*



*strongest coordinating ligand - best trapping ligand*

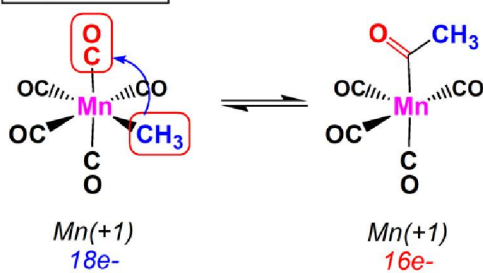


*most electron-rich alkyl group makes the best nucleophile for migrating to the electron-deficient CO*



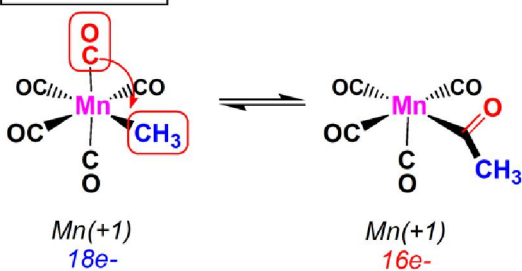
## Migration vs. Insertion

### Migration



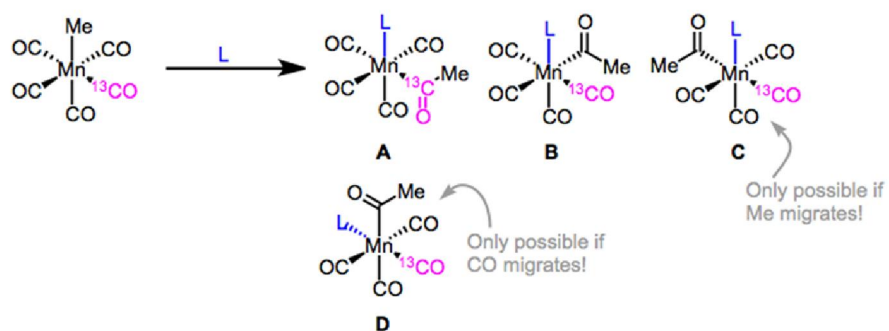
a **MIGRATION** rxn involves the anionic ligand doing a nucleophilic-like attack on the neutral ligand. This involves the anionic ligand moving to the site where the neutral ligand is coordinated. An empty coordination site is left behind.

### Insertion



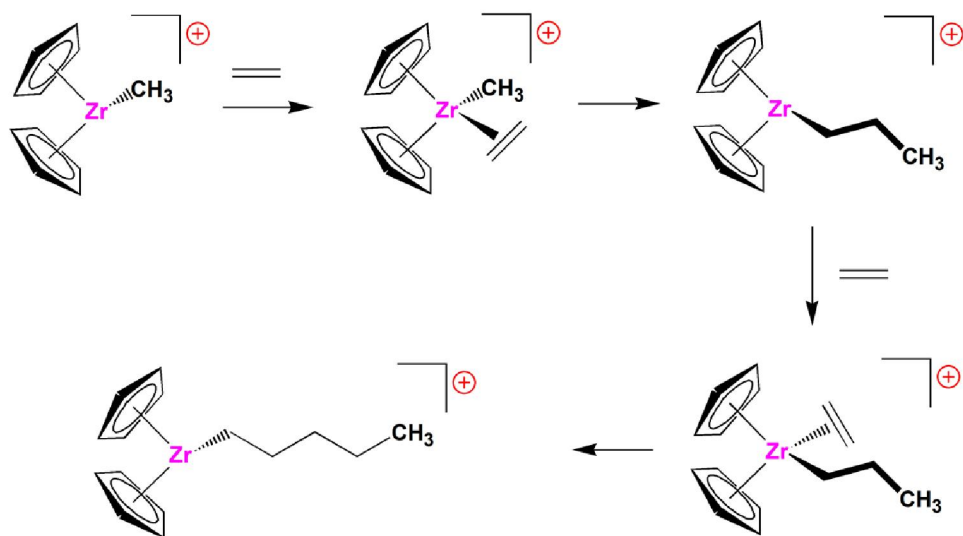
an **INSERTION** rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and "inserting" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.

## Migration vs. Insertion

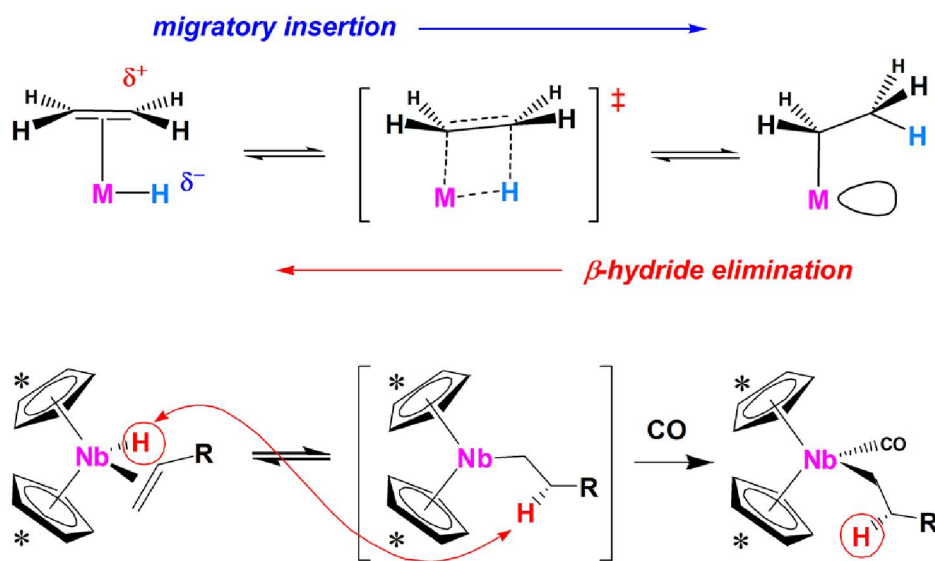


Product D has been **NEVER** observed!!!!

### Alkene Migratory Insertions

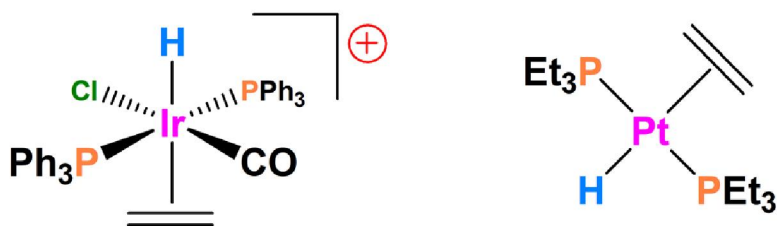


## Alkene Migratory Insertion – $\beta$ -Hydride Elimination

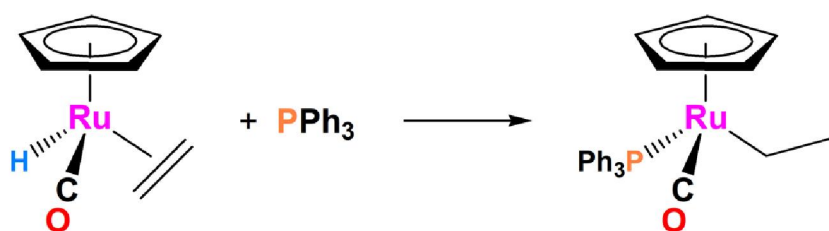


*NMR irradiation of the Nb-hydride resonance affects the NMR resonance for the alkyl hydride, demonstrating that they are connected by the migratory insertion mechanism*

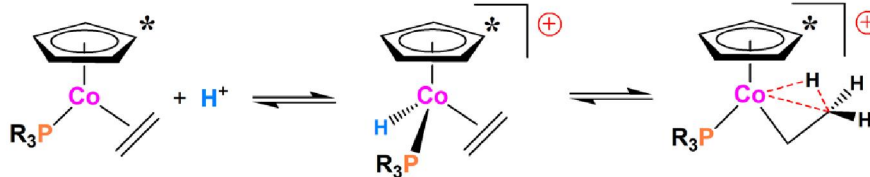
**Problem:** Why don't either of the complexes shown below do alkene-hydride migratory insertions at room temperature?



**Problem:** Sketch out and label the two mechanistic steps (in the correct order) that are occurring for the following reaction.



### Agostic C-H to Metal Interactions – “Frozen Migratory Insertion”



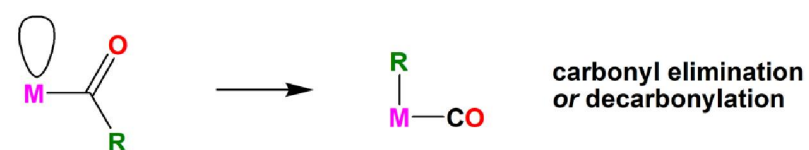
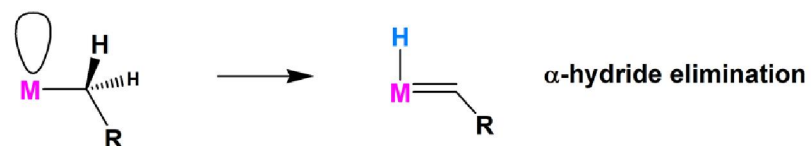
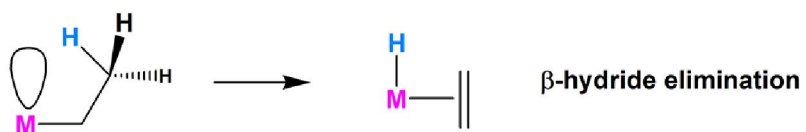
*One of the C-H bonds of the methyl group is within bonding distance to the Co center. This is called an **Agostic** C-H bond interaction.*

Because the C-H bond is sharing some of its  $\sigma$ -bond electron density with the metal, the C-H bond is *weakened*. This produces some relatively clear-cut spectroscopic characteristics:

- 1)  $\nu_{\text{C-H}}$  infrared stretching frequency is lowered to the mid-2500  $\text{cm}^{-1}$  region from a normal value of 2900-3000  $\text{cm}^{-1}$
- 2) the  $J_{\text{C-H}}$  coupling constant in the  $^{13}\text{C}$  NMR is lowered to around 70-90 Hz from a normal value of 150 Hz.
- 3) the  $^1\text{H}$  chemical shift of the agostic proton is in the -10 to -15 ppm region, much like a metal-hydride resonance.

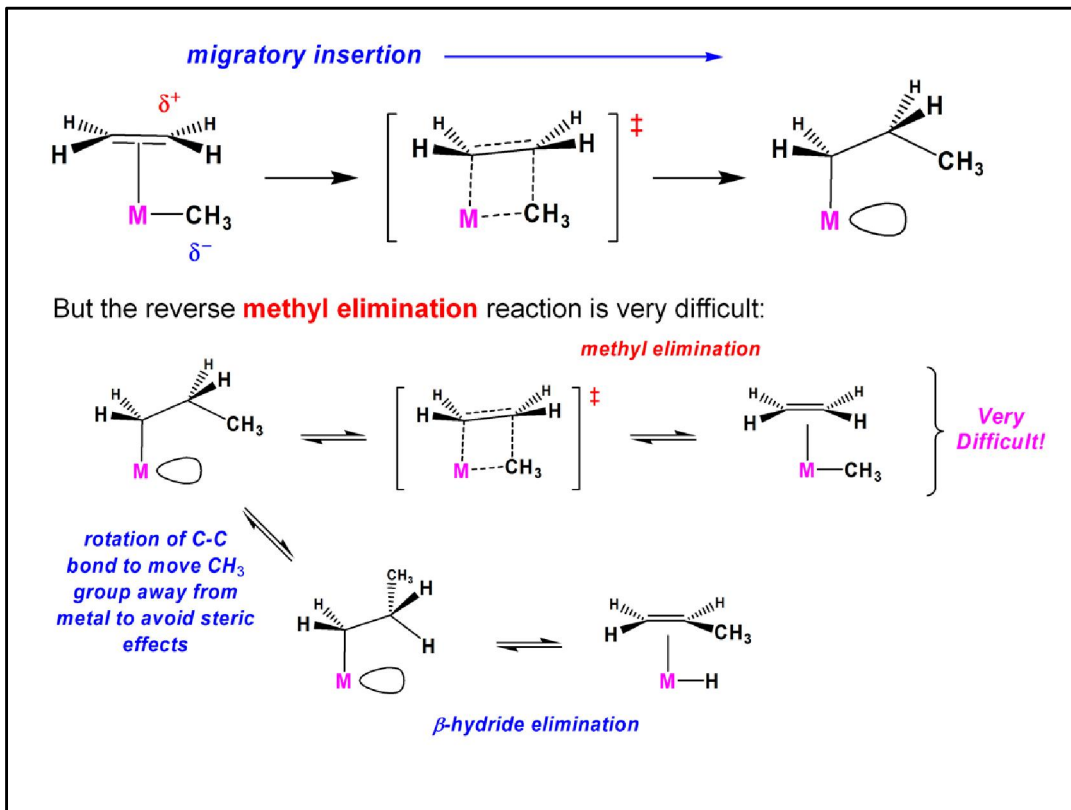


## Eliminations

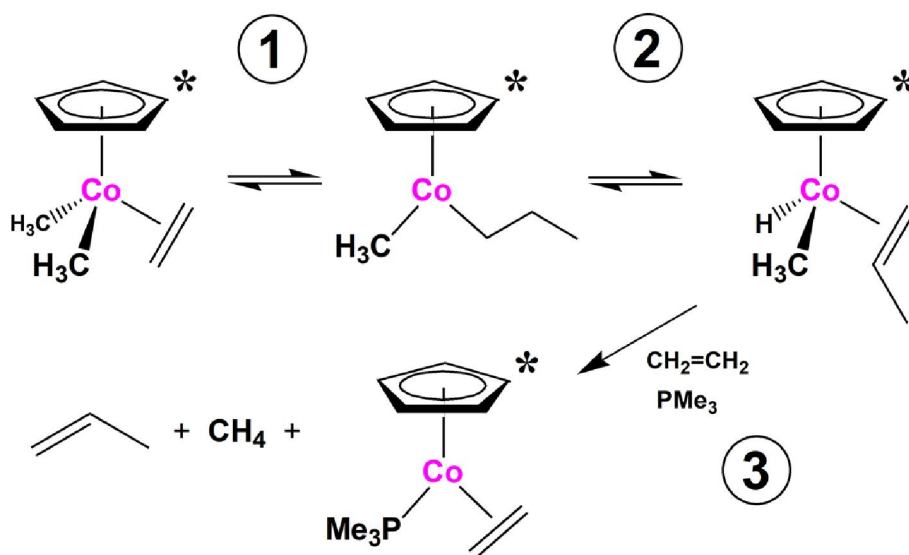


The key points are:

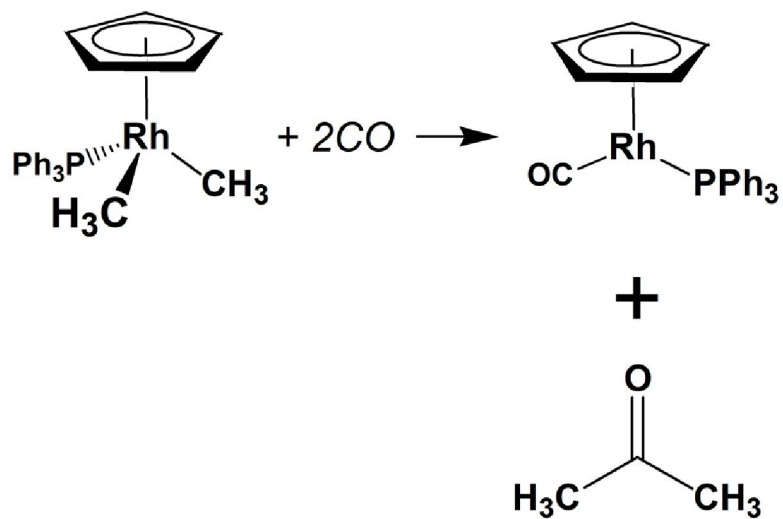
- 1) No change in formal oxidation state
- 2) You must have an empty orbital that is **cisoidal** to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.



**Problem:** Identify each step in the following mechanism. Some steps may have several things occurring.



**Problem:** Sketch out a detailed mechanism and label each step for the following overall reaction.



## Relevant homogeneous processes

***“A mechanism is a theory deduced from the available experimental data. The experimental results are facts; the mechanism is conjecture based on those facts”***

Lowry & Richardson

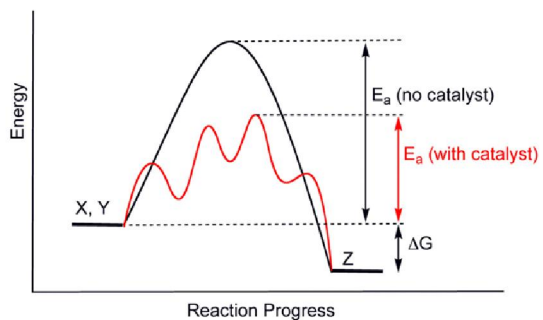
***“You can never prove that your mechanism is right - only wrong.”***

Guy in the audience asking  
about your proposed mechanism

- **Hydrogenation**
- **Hydroformilation**
- **Monsanto process (carbonylation of methanol)**
- **Polymerization**

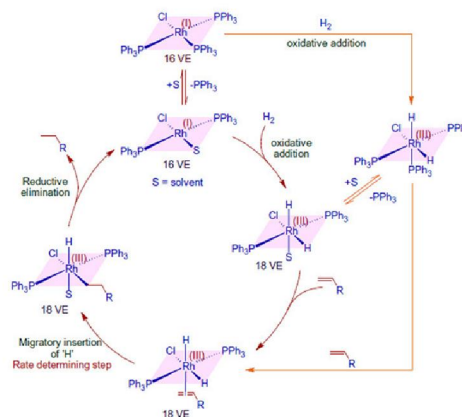
## Reaction mechanisms

Sequence of elementary steps that lead to the overall reaction.



Regeneration of the active species

Rate Determining Step:  
higher  $E_{att}$



## Hydrogenation

- Addition of  $H_2$  across a multiple bond, such as  $C=C$ , alkynes or even  $C=O$ , constitute an important synthetic procedure both lab and industrial scale.
- It finds increasing use in the production of specialty chemicals and pharmaceuticals.
- Activation energy of uncatalyzed reactions can be as high as 60 kJ/mol.
- Hydrogenation catalysts add molecular hydrogen to the  $C=C$  group of an alkene to give an alkane.
- Three general types have been distinguished, according to the way each type activates  $H_2$ .

**1. oxidative addition**

**2. heterolytic activation**

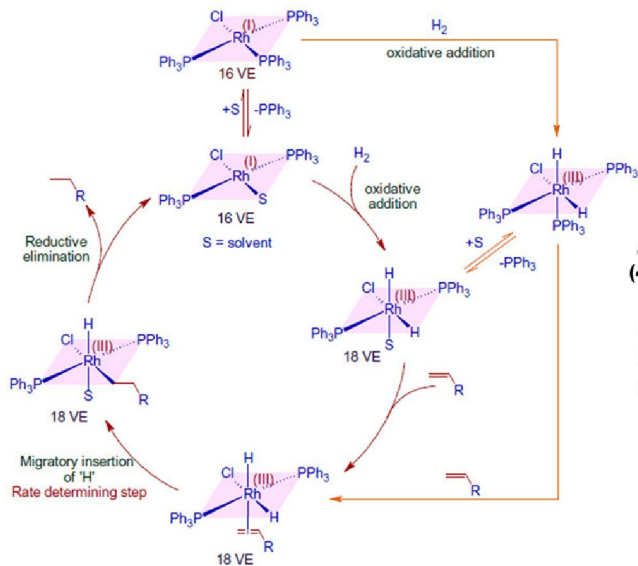
**3. homolytic activation**

## Hydrogenation – Wilkinson catalysts

### Oxidative addition



Sir G. Wilkinson



Ligand:  
Relative rates  
for hydrogenation  
of cyclohexene:

$(4\text{-ClC}_6\text{H}_4)_3\text{P}$	1.7
$\text{PPh}_3$	41
$(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$	86
$(4\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$	100

Simplistically, the relative rates suggest that the rate-determining step is OA of  $\text{H}_2$ .

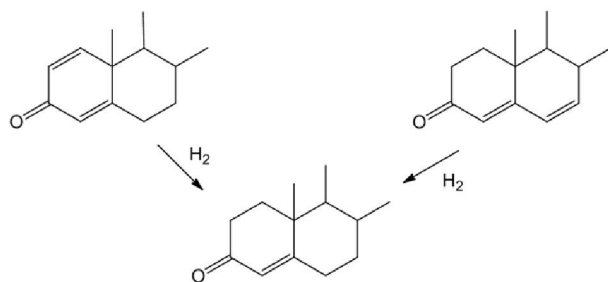
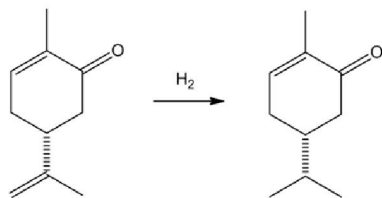


## Hydrogenation – Wilkinson catalysts

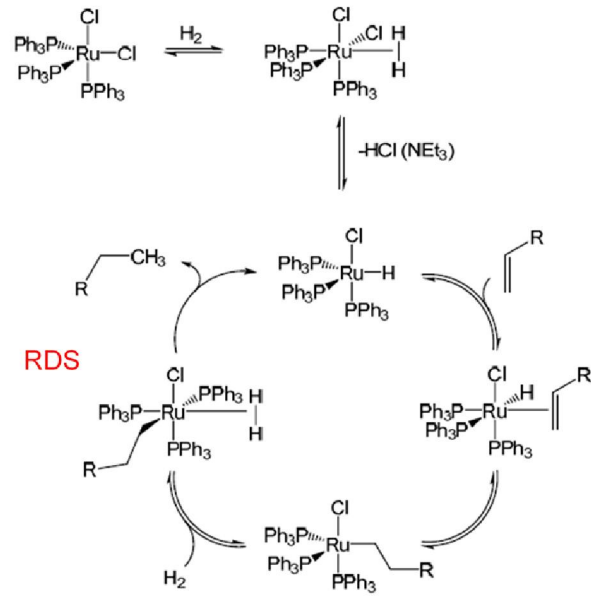
Highly selective catalyst!!!



Sir G. Wilkinson

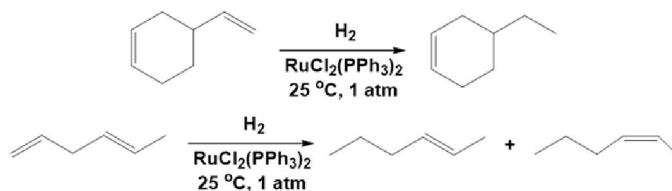


## Hydrogenation – Heterolytic H<sub>2</sub> activation

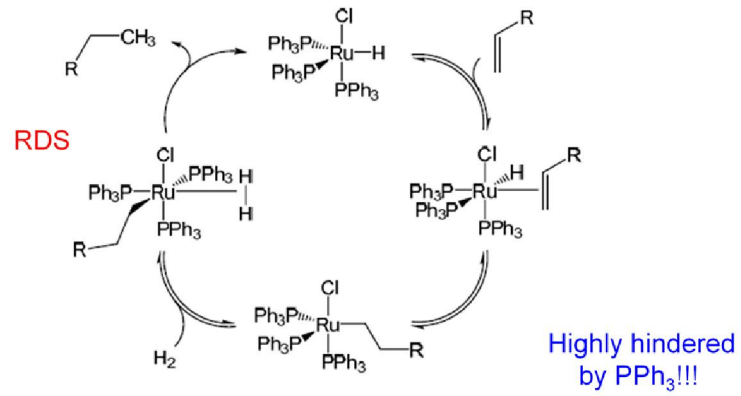
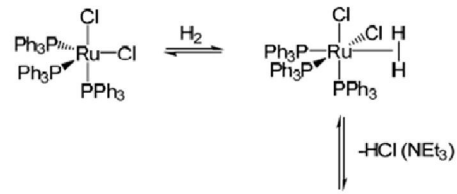


## Hydrogenation – Heterolytic H<sub>2</sub> activation

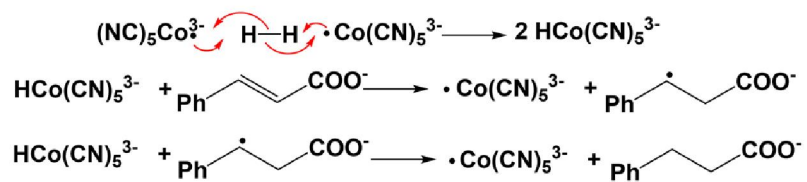
RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> hydrogenates selectively terminal double bonds over internal double bonds:



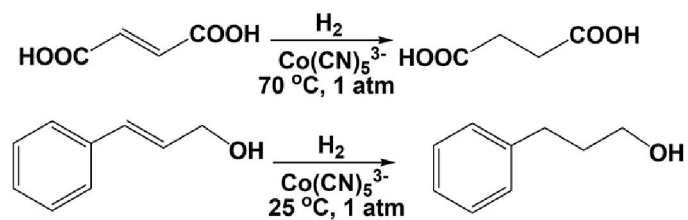
## Hydrogenation – Heterolytic H<sub>2</sub> activation



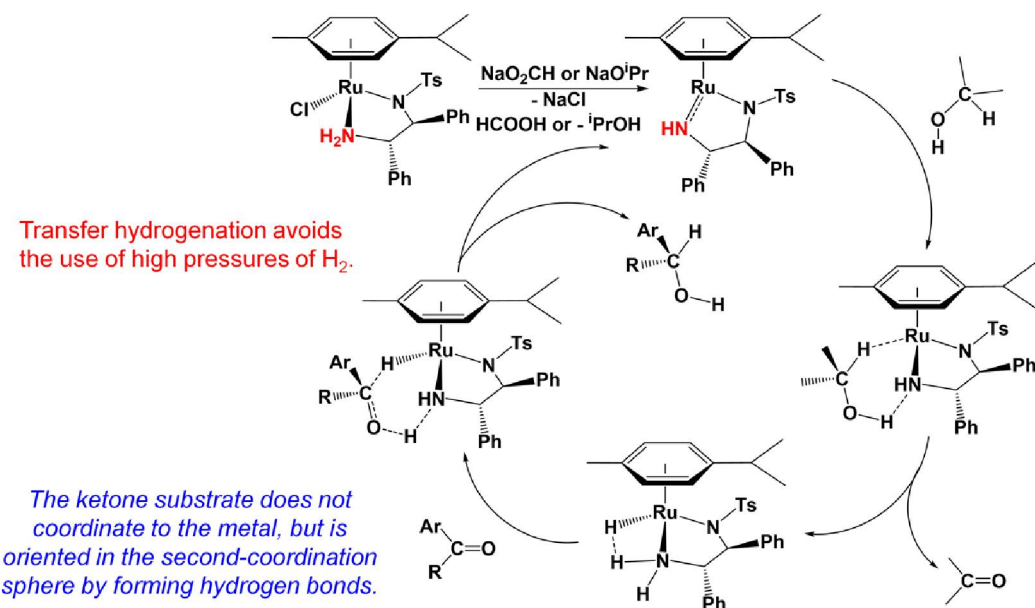
## Hydrogenation – Homolytic H<sub>2</sub> activation



The resulting organic radical needs to be moderately stable: only “activated” alkenes will be hydrogenated (formation of a conjugated radical).



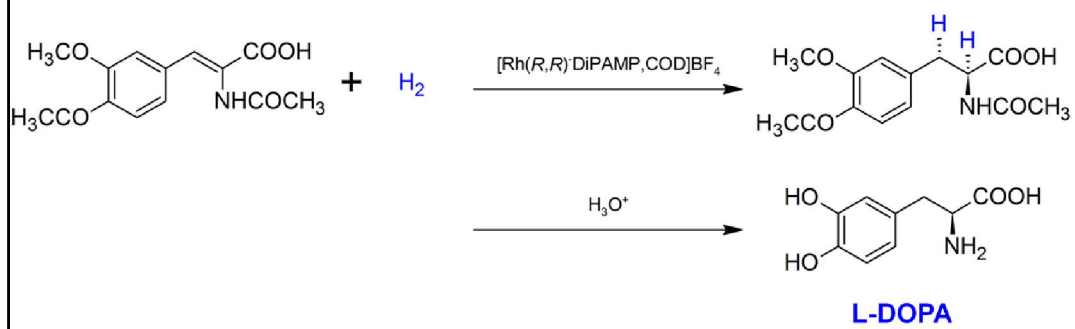
## Hydrogenation – H-transfer reaction



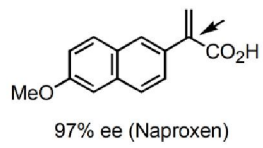
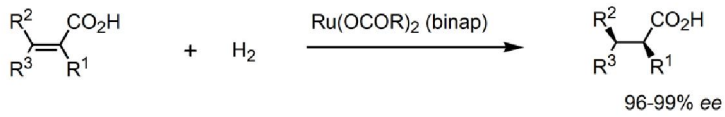
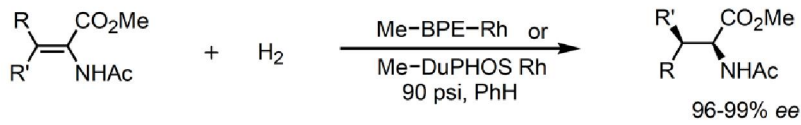
Morris, R. H. et al. *Coord. Chem. Rev.* 2004, 248, 2201

## Hydrogenation – Asymmetric catalysis

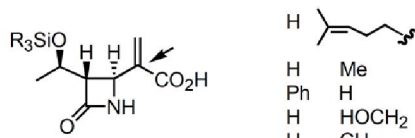
Knowles  
Noyori  
Sharpless  
Noble Prize 2011

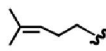


## Hydrogenation – Asymmetric catalysis



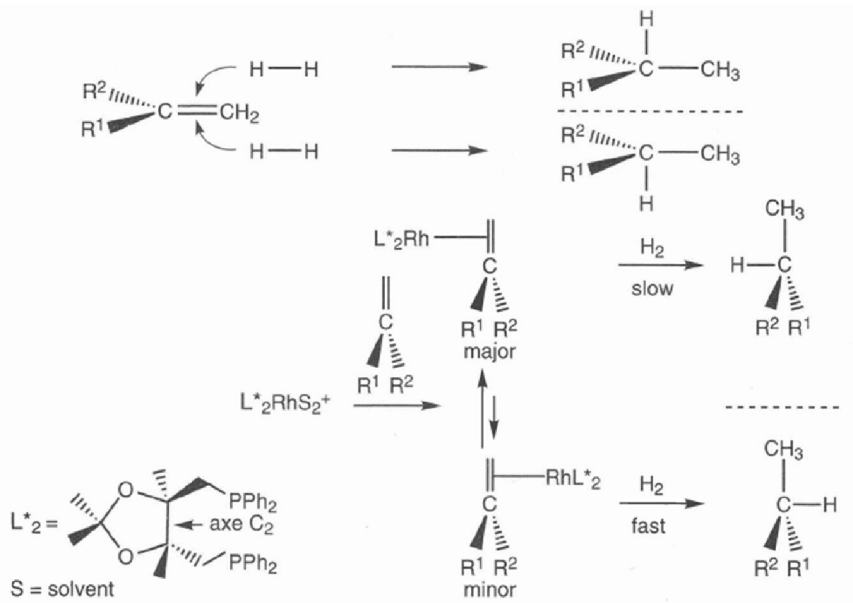
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	ee
Me	Me	H	91



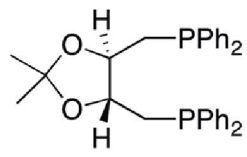
H		Me	87
H	Me	Ph	85
Ph	H	H	92
H	HOCH <sub>2</sub>	Me	93
H	CH <sub>3</sub>	COOCH <sub>2</sub> CMe	95



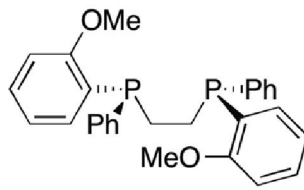
## Hydrogenation – Asymmetric catalysis



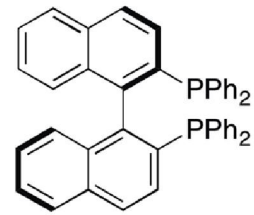
## Hydrogenation – Asymmetric catalysis



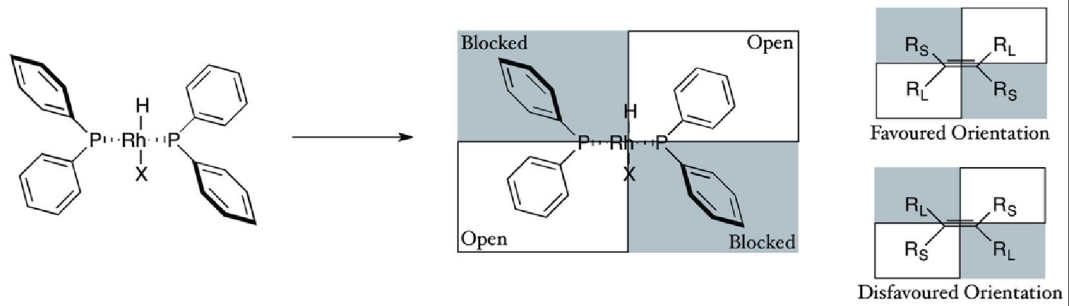
(*R,R*)-DIOP



(*R,R*)-DIPAMP

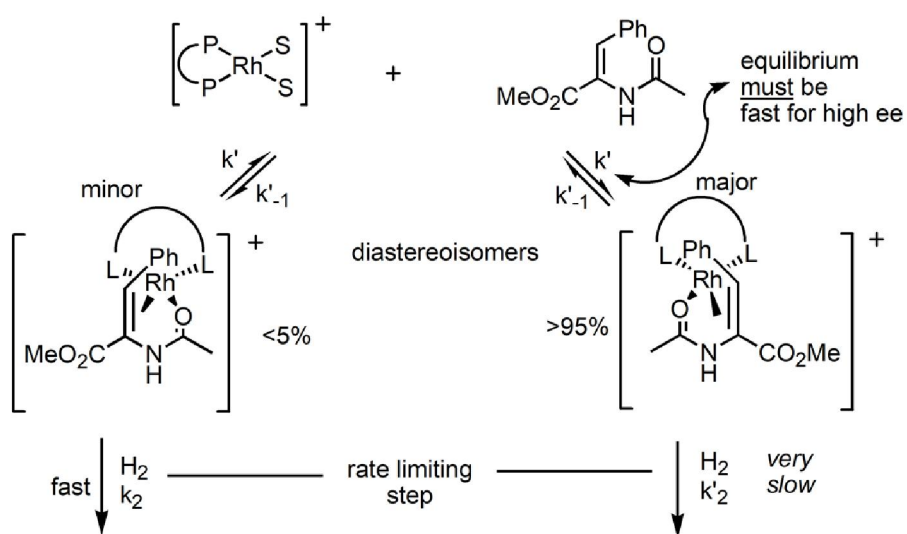


(*R*)-BINAP



## Hydrogenation – Asymmetric catalysis

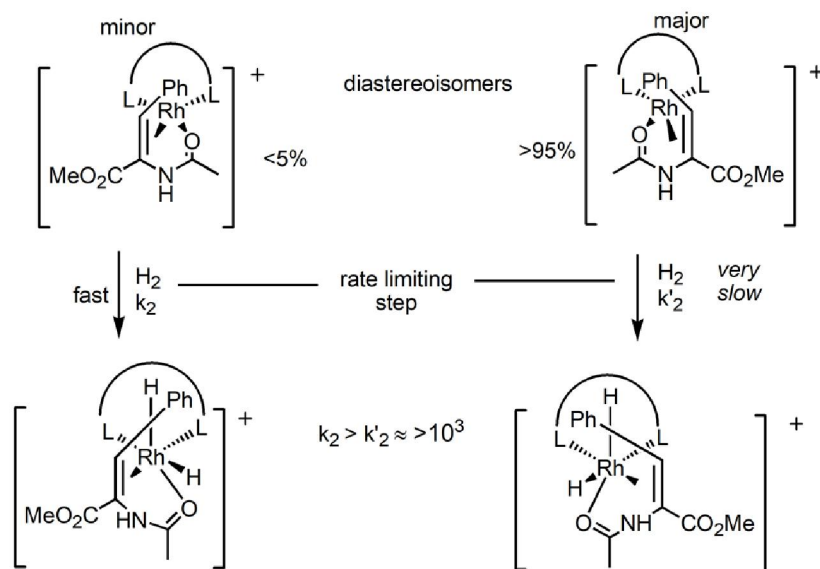
Knowles



Halpern, J. *Science* **1982**, 217, 401-407.

## Hydrogenation – Asymmetric catalysis

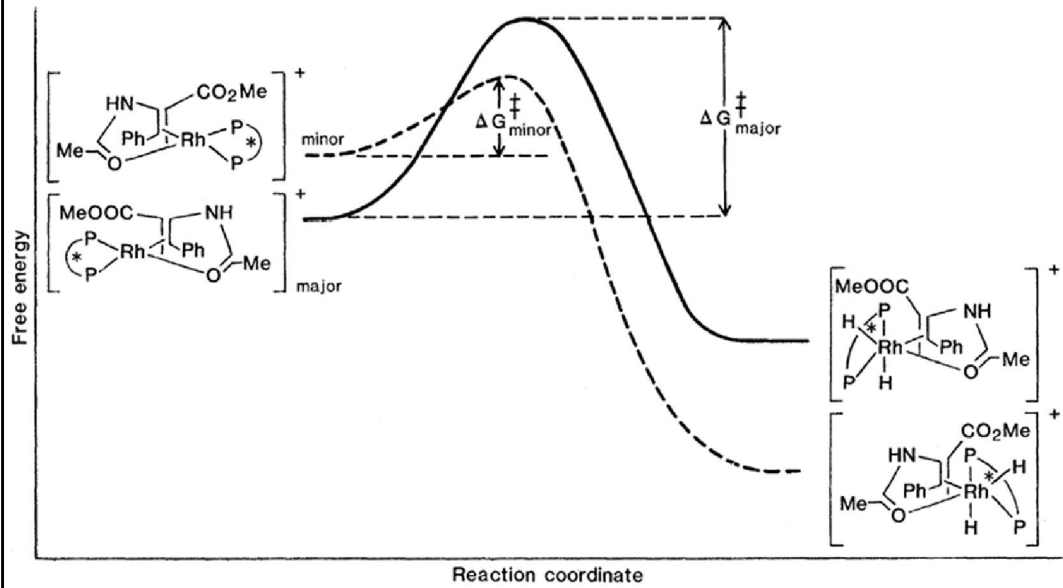
Knowles



Halpern, J. *Science* **1982**, 217, 401-407.

# Hydrogenation – Asymmetric catalysis

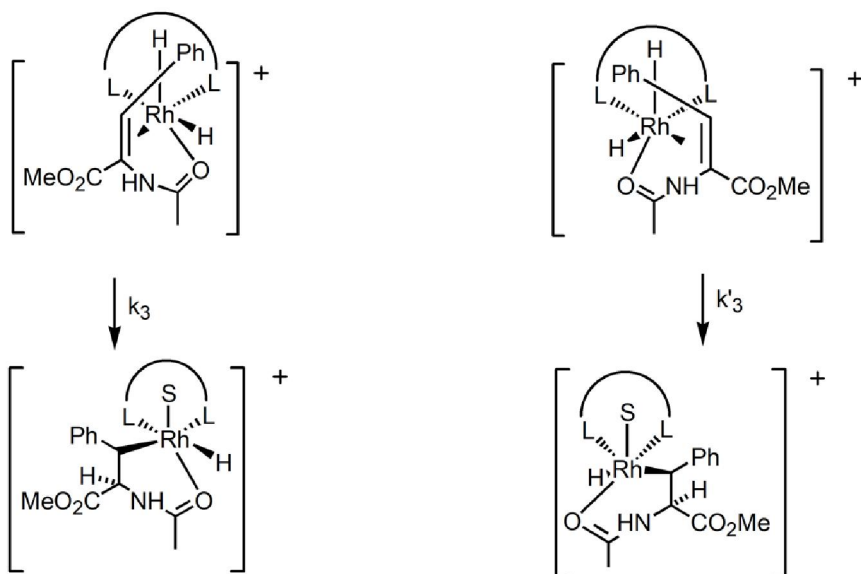
Knowles



Halpern, J. *Science* **1982**, 217, 401-407.

## Hydrogenation – Asymmetric catalysis

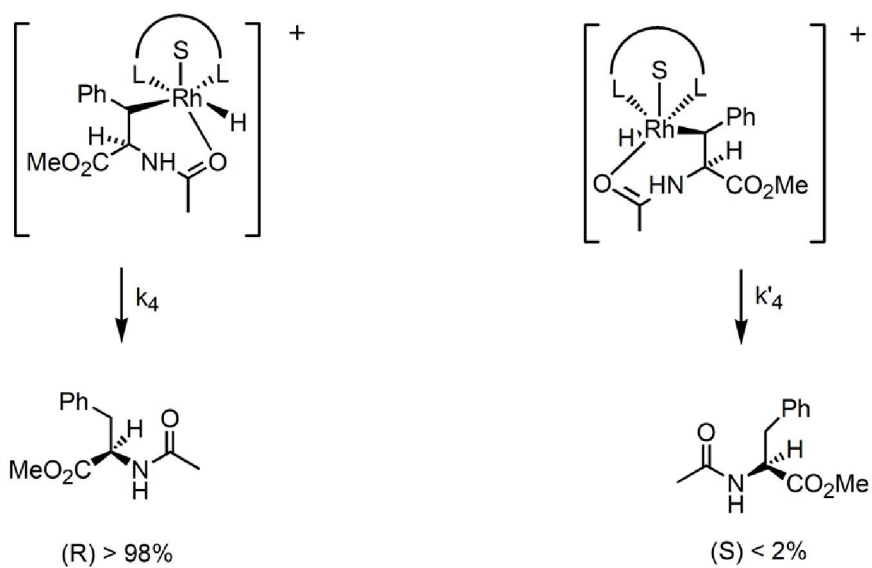
Knowles



Halpern, J. *Science* **1982**, 217, 401-407.

## Hydrogenation – Asymmetric catalysis

Knowles



Halpern, J. *Science* **1982**, 217, 401-407.

## Hydrogenation – Asymmetric catalysis

Knowles

Relazione fra e.e. prodotto e  $\Delta\Delta G^\ddagger$  calcolato  
a 25°C

$k_R/k_S$	$\Delta\Delta G^\ddagger$ (Kcal/mole)	e.e. prodotto
1	0	0 50-50
3	0.648	50 75-25
10	1.358	82 91-9
100	3.717	98 99-1
1000	4.076	99.8 99.9-0.1

Conclusione: bastano piccole differenze nelle  $E_{att}$  per ottenere e.e. elevati

Può sembrare facile discriminare i 2 cammini. Nella pratica non è affatto facile.  
L'obiettivo è ottenere  $\Delta\Delta G^\ddagger$  di 4 Kcal/mol (almeno per i farmaci).

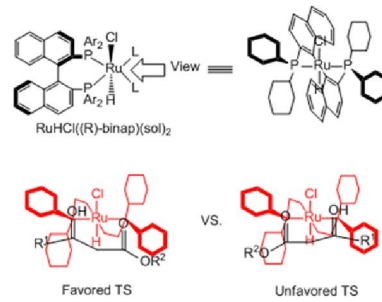
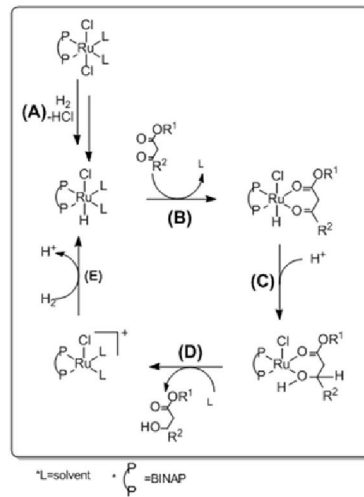
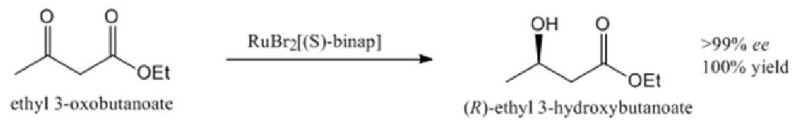
Per riuscire ad ottenere e.e. così elevati si deve procedere per via sperimentale, modificando i leganti non partecipativi.

Halpern, J. Science 1982, 217, 401-407.

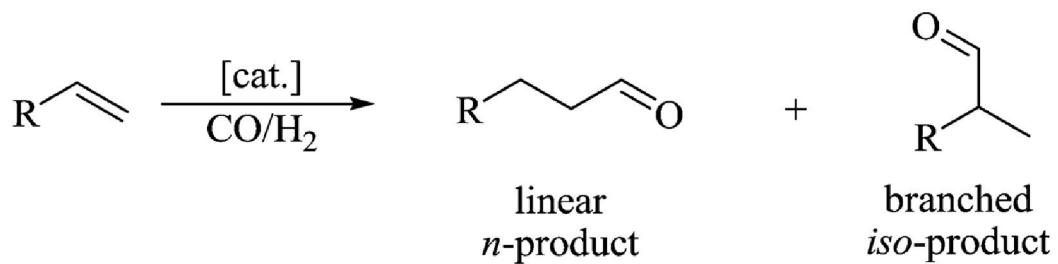


## Hydrogenation – Asymmetric catalysis

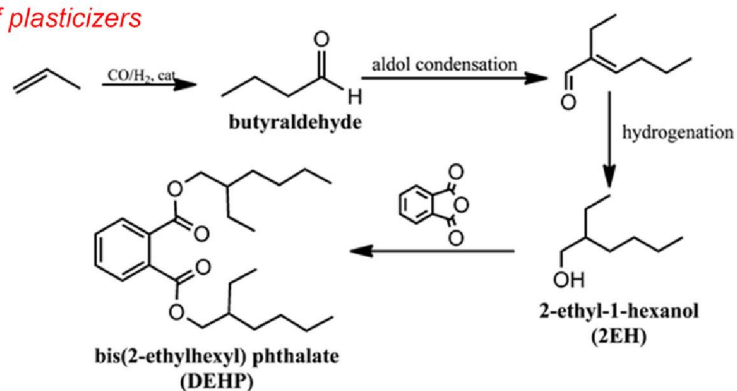
Noyori



## Hydroformylation

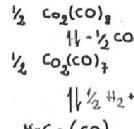


### Synthesis of plasticizers

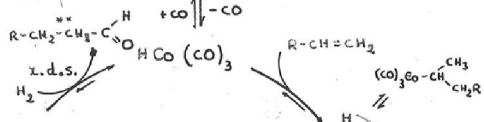


# Hydroformylation - $\text{HCo(CO)}_4$

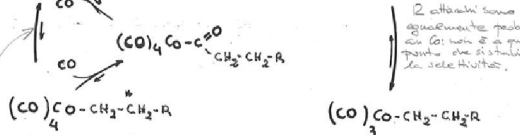
Si passa che la reazione passi per add. di  $\text{H}_2$  ed eliminazione selettiva di alchene



Declusterizzazione nelle condizioni di reazione.



$\text{HCo(CO)}_4$  dissocia un CO per generale la specie attiva



Migrazione del gruppo e ramificazione è circa la stessa; non rende conto della selettività. Dato considerato i vari parametri ( $P_{\text{Co}}, P_{\text{H}_2}, T$ )

$$T = 110-180^\circ\text{C} ; P_{\text{CO-H}_2} = 200-300 \text{ Atm.}$$

$$X = k_{\text{obs}} [\text{Co}] [\text{alchene}] [\text{H}_2] [\text{CO}]^{-1}$$

se di fatto il rateo di decarburazione a Co metallico

$P_{\text{CO}}$  minima 10 Atm. a 100°C  
100 Atm. a 200°C

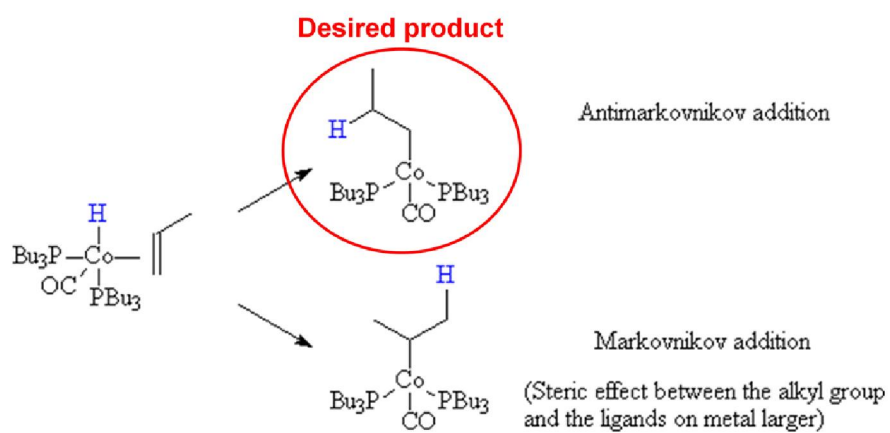
Sottoprodotti: \* alcano ~ 1%; \*\* alcool ~ 10%

2 alchani sono egualmente possibili su Co: non è a questo punto che si stabilisce la selettività.

12 alchani organici totali sono in completo equilibrio tra loro; se niente si consuma, uno più dell'altro non si sposta d'eq.

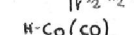
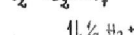
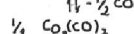
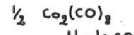
CO agisce positivamente ed selettivamente una negativa su alchene. Si consuma con  $P_{\text{Co}}$ .

## Hydroformylation – $\text{HCo}(\text{CO})_4$

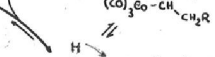
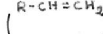
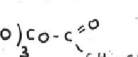
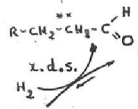


# Hydroformylation - $\text{HCo}(\text{CO})_4$

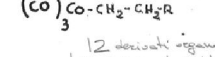
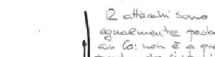
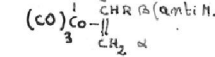
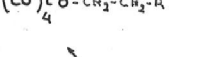
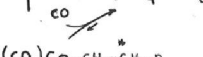
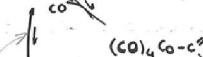
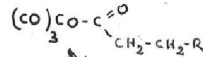
Si passa che la reazione passi per add. di  $\text{H}_2$  ed eliminazione selettiva di alchene



Declusterizzazione nelle condizioni di reazione.



$\text{HCo}(\text{CO})_4$   
dissocia un CO  
per generale la  
specie attiva



Migrazione del gruppo  $\text{CH}_2-\text{CH}_2-\text{R}$  e formazione di  $\text{HCo}(\text{CO})_3-\text{CH}_2-\text{CH}_2-\text{R}$  non avviene con la stessa selettività. Dato considerato i vari parametri ( $P_{\text{CO}}, P_{\text{H}_2}, T$ )

12 alchani organici e taluni sono in completo equilibrio tra loro e in natura si consumano uno più dell'altro nelle varie specie d'eq.

$$T = 110-180^\circ\text{C} ; P_{\text{CO-H}_2} = 200-300 \text{ Atm.}$$

$$X = k_{\text{obs}} [\text{Co}] [\text{alchene}] [\text{H}_2] [\text{CO}]^{-1}$$

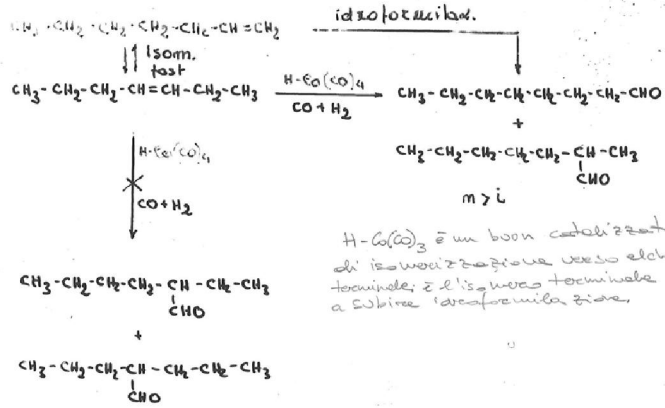
se di fatto il rateo di consumo di  $\text{Co}$  metallico

$P_{\text{CO}}$  minima 10 Atm. a  $100^\circ\text{C}$   
100 Atm. a  $200^\circ\text{C}$

Sottoprodotti: \* alcano ~ 1%; \*\* alcool ~ 10%

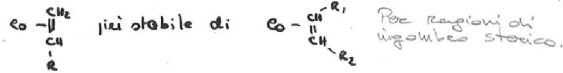
## Hydroformylation – $\text{HCo}(\text{CO})_4$

Idroformilazione 3-epene.



$\text{H-Co}(\text{CO})_3$  è un buon catalizzatore di isomerizzazione verso alcheni terminali e l'isomero terminale a subire idroformilazione.

Isomerizzazione  $\gg$  idroformilazione



Con Co si può usare una miscela di isomeri poiché i prodotti della reazione saranno sempre gli stessi. Non si sapeva che specifico da olefine interne.

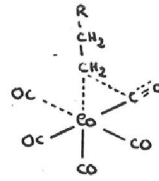
## Hydroformylation – $\text{HCo(CO)}_4$

idrossimetilazione propene:

cat:  $\text{H-Co(CO)}_4$

Andamento del rapporto  $m/i$  con la  $p_{\text{CO}}$ ,  $p_{\text{H}_2}$ , temperatura

	$m/i$	
$\Delta p_{\text{CO}}$ (2,5 → 90 Atm.) (a 100°C)	1,6 → 4,4 (61,5% → 81,5% m)	↳ limite della selettività con $\text{Co}$ : $\Delta(\Delta G^\ddagger) \approx 2 \text{ kcal/mol}$
$\Delta p_{\text{H}_2}$	rat. ind.	
$\Delta t$	"	



Mentre sta avvenendo la migrazione di R su CO coordinato, entra la nuova molecola di CO. L'ingressò di questa crea un ingombro sterico tale da favorire la migrazione dell'alchile lineare rispetto a quello ramificato.

stato di transizione

responsabile dello selettività;

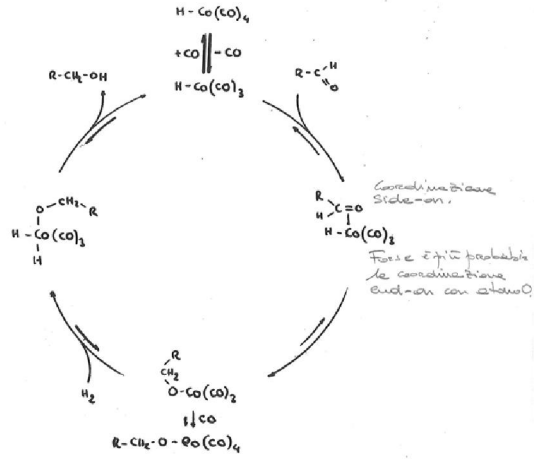
meccanismo concertato:

l'acile lineare è favorito rispetto a quello ramificato.

$\Delta(\Delta G^\ddagger)$  è molto piccolo: l'influenza sulla selettività è scarsa.

# Hydroformylation – $\text{HCo}(\text{CO})_4$

ciclo catalitico per la idrogenazione delle aldeidi ad alcoli ; cat :  $\text{H-Co}(\text{CO})_3$ .



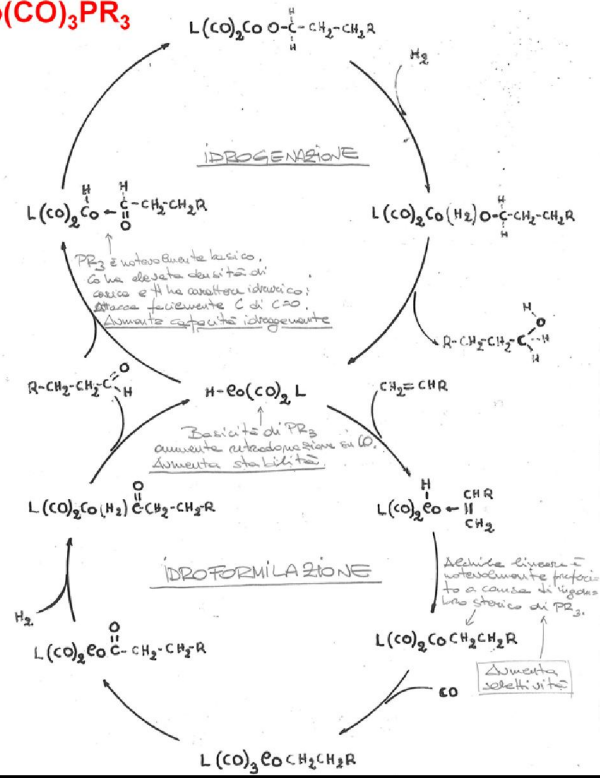
$$r = k_{obs} [\text{aldeide}] [\text{Co}] [\text{H}_2] [\text{CO}]^{-2}$$

↑  
Aumentando  $P_{\text{CO}}$  si inibisce fortemente questa reazione.



# Hydroformylation – $\text{HCo}(\text{CO})_3\text{PR}_3$

$\text{HCo}(\text{CO})_3\text{PR}_3$   
dissocia un CO per  
generare la specie  
attiva



## Hydroformylation – $\text{HCo(CO)}_4$ vs $\text{HCo(CO)}_3\text{PR}_3$

Confronto  $\text{H-Co(CO)}_4$  :  $\text{H-Co(CO)}_3\text{PR}_3$  2-n-butile

cat. prec.	$p_{\text{min}}(\text{Atm})$	$t(^{\circ}\text{C})$	prodotto	m/i	att. cat.	alcami(%)
$\text{H-Co(CO)}_4$	10 - 100	100 - 180	aldeidi	4:1	5 (145 $^{\circ}\text{C}$ )	1
$\text{H-Co(CO)}_3\text{PR}_3$	5 - 10	100 - 200	alcoli	8:1	1 (180 $^{\circ}\text{C}$ )	15

↑  
Aumento della  
stabilità del  
sistema catalitico

↑  
90% di conversione  
Aumento  
selettività.

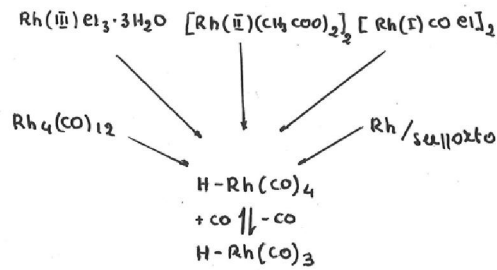
↑  
Meno  
attivo

↑  
Più alcoli.

È un sistema importante se  
il prodotto voluto sono gli  
alcoli; si fanno avanti  
2 reazioni nello stesso impianto.

## Hydroformylation – $\text{HRh}(\text{CO})_4$

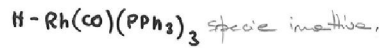
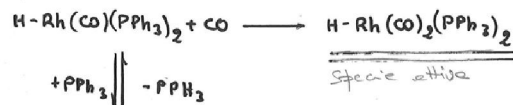
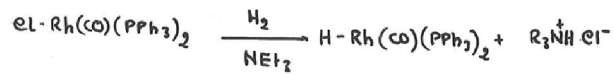
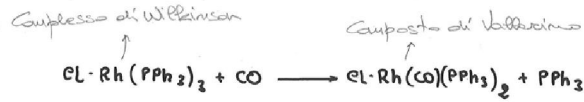
Formazione della specie catalitica  
nel caso del rodio.  
 ( $t = 70-150^\circ\text{C}$ ;  $p_{\text{CO}/\text{H}_2} = 50 \text{ Atm.}$ )



- $\text{Co}:\text{Rh}$
- 1) attività: 1 : (100 - 10.000); costo 1 : 3500
  - 2) elevata attività come cat. isom. olefine
  - 3) inattivo nella idrogenazione delle aldeidi
  - 4) selettività  $m/i = 1$  Non può essere usato per la idrogenazione delle alchene.
  - 5) k.d.s.: idrogenolisi dello specie acilica  $\text{R-CO-Rh(CO)}_3$   
Il grosso svantaggio è la selettività. Viene usato per la produzione di aldeide propionica da etilene.

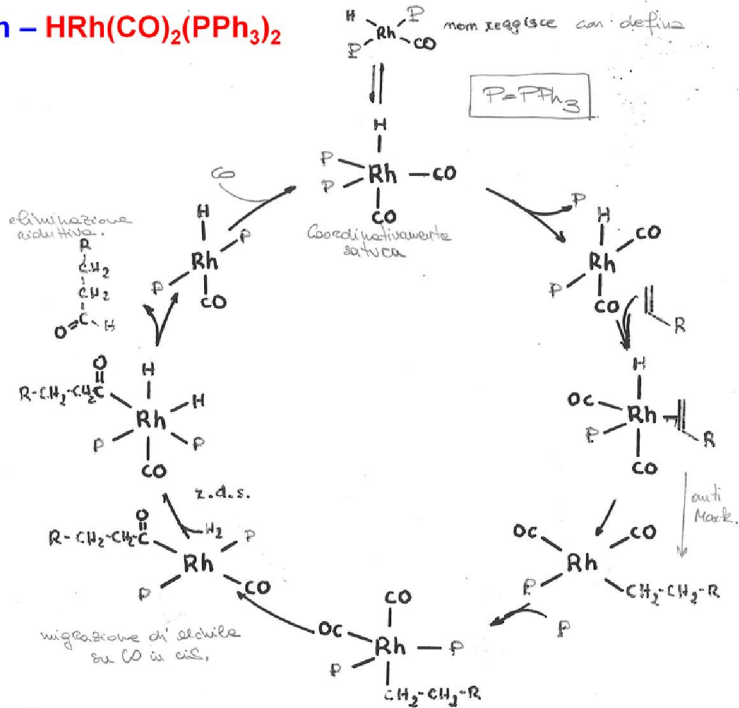
## Hydroformylation – $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$

Sintesi della specie catalitica  
attiva.



1965: Wilkinson dimostra che il suo cat. è in grado di dare idroformilazione di  $\alpha$ -olefine a T<sub>ep</sub> ambiente con buona selettività.

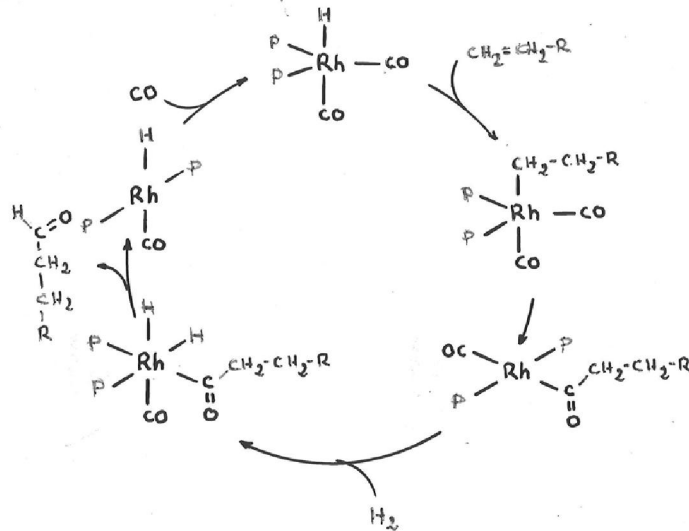
**Hydroformylation –  $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$**



Questo meccanismo non risponde della selettività del sistema

## Hydroformylation – $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$

Questo meccanismo è stato proposto per giustificare la selettività. Si ammette che l'entità catalitica interagisce con olefine per dare l'alchile derivato. Si ipotizza un meccanismo concertato. È necessario avere 2 molecole di  $\text{PPh}_3$  per avere un campo sterico sufficiente da dare alta selettività  $n/1$ .

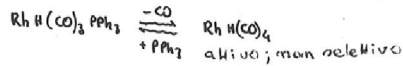
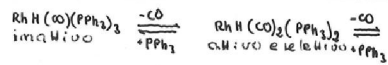


## Hydroformylation – $\text{HRh}(\text{CO})_2(\text{PPh}_3)_2$

Idroformilazione del propene:  
andamenti della selettività e  
attività.

cat.:  $\text{H-RhCO}(\text{PPh}_3)_3$

T (°C)	p (Atm)	P/Rh	m/i	$\bar{x}$ (g./mim.)
100	30	3	1:1 (50% m)	Per ottenere buona selettività, si deve sacrificare l'attività.
100	30	13	2:1 (66.7% m)	
125	12.5	603	15.3:1 (94% m)	
100	35	5	13	
100	35	50	2.5	



Per avere alta selettività, devo abbassare  $P_{\text{CO}}$  e aumentare rapporto P/Rh.

Si lavora in  $\text{PPh}_3$  fuso.

A bassi P/Rh tende a formarsi  $\text{RhH}(\text{CO})_4$ : attivo ma non selettivo.

Aumentando P/Rh, produce la specie selettiva ma anche quella inattiva: perdita in attività.

## Hydroformylation – Co vs Rh

Come il cobalto - Cobalto - Rodio.

Verrà probabilmente sostituito da cat. con elettivi selettività: ci ha guadagnato in selettività (97%) e più facile recupero del catalizzatore.

	$H-Co(CO)_4$	$H-Co(CO)_3PR_3$	$H-Rh(CO)_2(PPh_3)_2$
Temp. (°C)	140-180	160-200	80-120
p (Atm.)	350-360	50-100	15-25
M%/ol.	0.1-1	0.5-1	$10^{-2}-10^{-3}$
n/i	3-4:1 (80% lim.)	6-8:1 (88% lim.)	10-14:1 (93.3% lim.)
aldeidi %	~ 80	-	~ 96
alcoli %	~ 10	~ 80	-
alcani %	~ 1	~ 15	~ 2 <sup>⊗</sup>
altri prod.	~ 9	~ 5	~ 2

⊗ La idrogenazione degli alcani viene inibita sia dal Co che dallo  $PPh_3$ .

Il  $H-Rh(CO)_2(PPh_3)_2$  è un ottimo cat. di idrogenazione degli alcani.

Rh ha vari vantaggi: impianto meno costoso (lavora a condizioni più blande) e vita più alta.  
 L'inconveniente è l'altissimo costo del metallo.

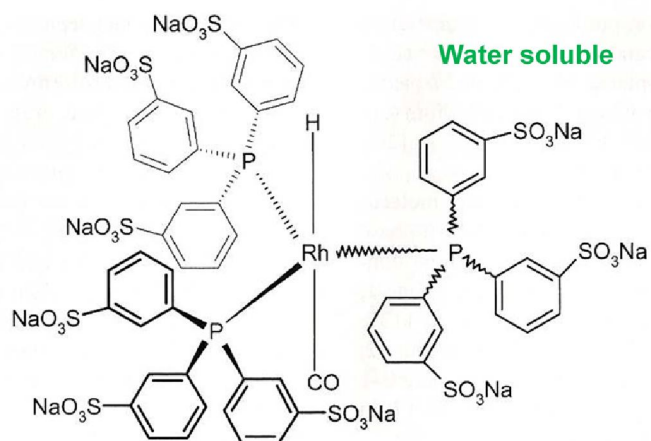


## Hydroformylation – Co vs Rh

Table 3. Comparison of industrial hydroformylation processes of different companies [5, 11]

Process parameters	RuhrChemie	Shell	UCC
Catalyst	$\text{HCo}(\text{CO})_4$	$\text{Co}(\text{CO})_2\text{PR}_3$	$\text{HRh}(\text{CO})(\text{PPh}_3)_3$
Pressure, MPa	20–30	4–8	1.5–2.0
Temperature, °C	140–180	160–200	85–115
Propylene conversion, %			85–89
<i>n</i> -Butanal/ <i>iso</i> -butanal selectivity	80/20	88/12	92/8
Expenses for catalyst separation	High	High	High

## Hydroformylation – Modified Rh catalysts



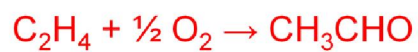
The process is limited to short alkenes that have an appreciable solubility in water.  
Reaction is slower because of low alkenes concentration.

## Hydroformylation – Co vs Rh

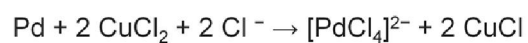
Table 3. Comparison of industrial hydroformylation processes of different companies [5, 11]

Process parameters	RuhrChemie	Shell	UCC	RuhrChemie/Rhone-Poulenc
Catalyst	$\text{HCo}(\text{CO})_4$	$\text{Co}(\text{CO})_2\text{PR}_3$	$\text{HRh}(\text{CO})(\text{PPh}_3)_3$	$\text{HRh}(\text{CO})(\text{TPPTS})_3$
Pressure, MPa	20–30	4–8	1.5–2.0	4–6
Temperature, °C	140–180	160–200	85–115	110–130
Propylene conversion, %			85–89	85–99
<i>n</i> -Butanal/ <i>iso</i> -butanal selectivity	80/20	88/12	92/8	94/6
Expenses for catalyst separation	High	High	High	Low

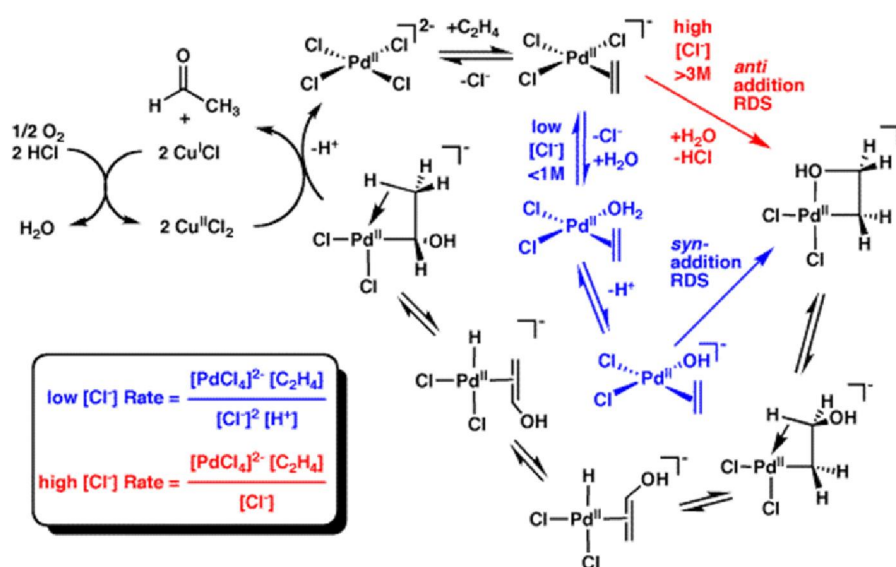
## Wacker process: synthesis of acetaldehyde



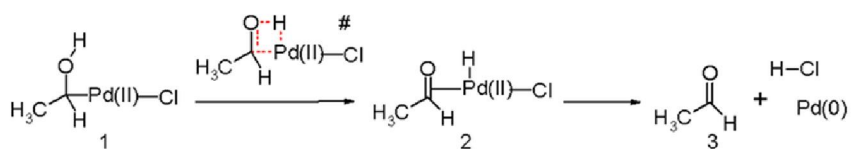
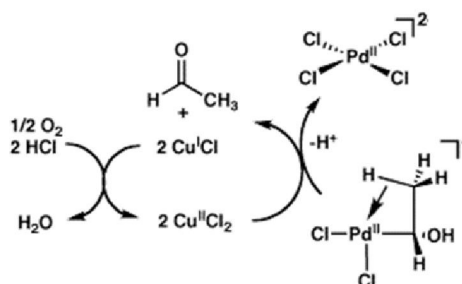
It is a multi-step process:



## Wacker process: synthesis of acetaldehyde

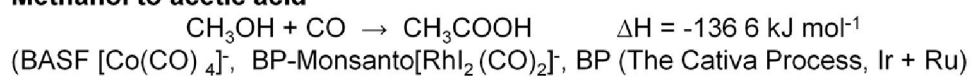


## Wacker process: synthesis of acetaldehyde

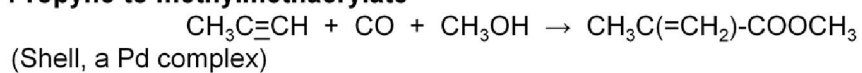


## Carbonylation

### 1. Methanol to acetic acid



### 2. Propyne to methylmethacrylate



### 3. Carbonylation of appropriate secondary alcohol in the synthesis of Ibuprofen (Hoechst, Pd catalyst)

### **Methanol to acetic acid**

1. BASF Process based on  $\text{Co}(\text{CO})_4$  complex
1. Monsanto-BP Process based Rh carbonyl complex
2. BP-Cativa process based on Ir carbonyl complex

**More than 60% of the world acetic acid production  
employs the Methanol Carbonylation route**



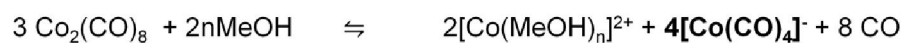
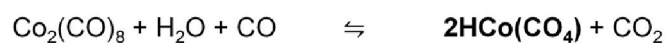
## Acetic acid Processes

Options	Catalyst	Reaction conditions	Yield	By-product
Methanol Carbonylation	Rh complex	180-220°C 30-40 atm	MeOH:99% CO:85%	none
Acetaldehyde Oxidation	Mn acetate or Co acetate	50-60°C atm.press	CH <sub>3</sub> CHO: 95%	none
Direct oxidation Of Ethylene	Pd/heteropoly	150-160°C acid/metal80 atm	ethylene: 87%	CH <sub>3</sub> CHO CO <sub>2</sub>
Hydrocarbon Oxidation (n-butane, Naphtha)	Co acetate or Mn acetate	150-230°C 50-60 atm	nC <sub>4</sub> : 50% naphtha: 40%	Formic acid propionic acid, etc.

### Catalyst Systems For Methanol Carbonylation

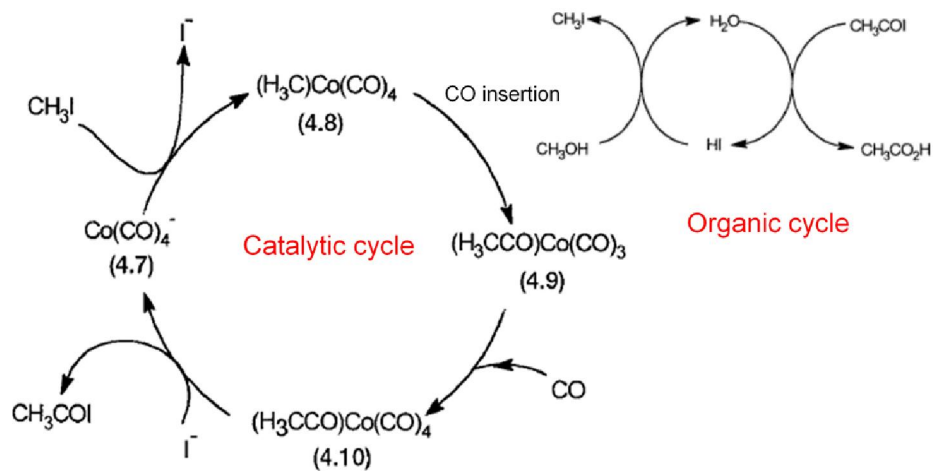
Company/Technology	Central Catalyst Atom	Cocatalyst (Promoter)
Monsanto/BP	Rhodium	CH <sub>3</sub> /HI
Celanese AO Plus	Rhodium	Li/CH <sub>3</sub> I
BP Cativa	Iridium	CH <sub>3</sub> /Re or Ru
Chiyoda Acetica	Rhodium	CH <sub>3</sub> /Immobilized Complex on solid support

## BASF Process - Formation of active Co catalyst

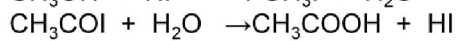
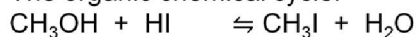


- $\text{HCo}(\text{CO})_4$  produced in these reactions catalyze FT type reactions and lead to the formation of by products
- The rate of Co catalyzed carbonylation is strongly dependent on both CO and MeOH concentrations and pressure.
- The complex  $\text{Co}(\text{CO})_4^-$  is an 18 e<sup>-</sup> nucleophile.
- The attack on  $\text{CH}_3\text{I}$  is a comparatively slow step.
- High temperatures are therefore required with the Co catalyst.
- This in turn necessitates high pressure of CO to stabilize the  $\text{Co}(\text{CO})_4^-$  at high temperatures.

## The BASF Process: The Catalytic & Organic cycles



The organic chemical cycle:

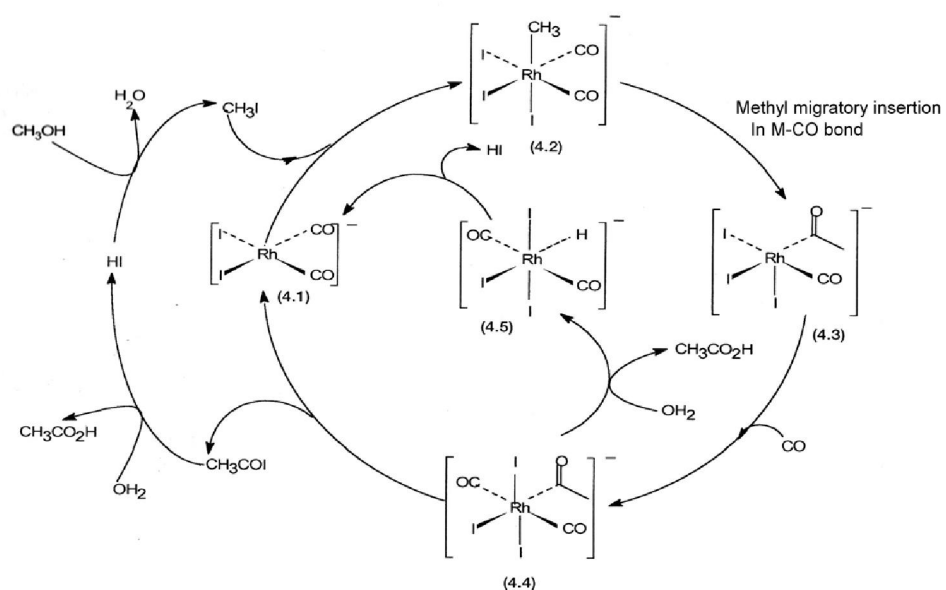


1. Nucleophilic attack by  $\text{Co(CO)}_4^-$  on  $\text{CH}_3\text{I}$
2. Carbonyl insertion into a metal-alkyl bond
3. Another CO group adds to the 16 e<sup>-</sup> species
4. Reaction with I<sup>-</sup> to eliminate acetyl iodide

## Methanol to Acetic acid by Carbonylation- Process

	<b>BASF(1955)</b>	<b>BP-Monsanto (1970)</b>
Metal concentration	10 <sup>-1</sup> mole per liter of <b>Co</b>	10 <sup>-3</sup> mole per liter of <b>Rh</b>
Temperature, °C	230	180 – 190
Pressure, bar	500 – 700	30 – 40
Selectivity (%) based on		
a) methanol	90	> 99
b) CO	70	90
By-Products	CH <sub>4</sub> , glycol acetate other oxygenated HCs	CO <sub>2</sub> , H <sub>2</sub>
Effect of H <sub>2</sub>	Amount of by-products increases	No effect
Promoter, CH <sub>3</sub> I	Essential	Essential

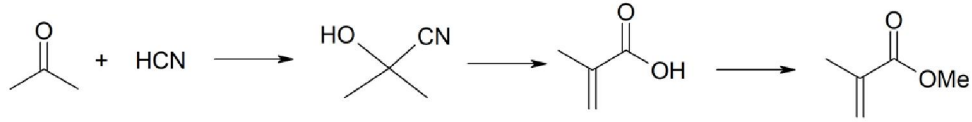
## BP-Monsanto Process with Rh- Methanol to acetic acid



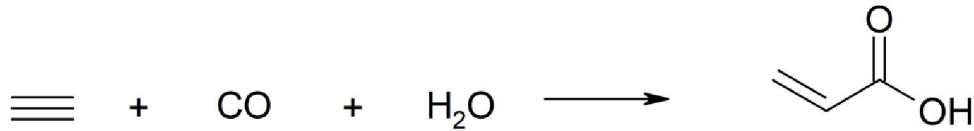
**Figure 4.2** Monsanto process: The organic and organometallic cycles are combined. The inner cycle shows an additional pathway for product formation.

## Carbonylation of alkynes: Methyl methacrylate (MMA)

- The conventional method: A large amount of solid wastes



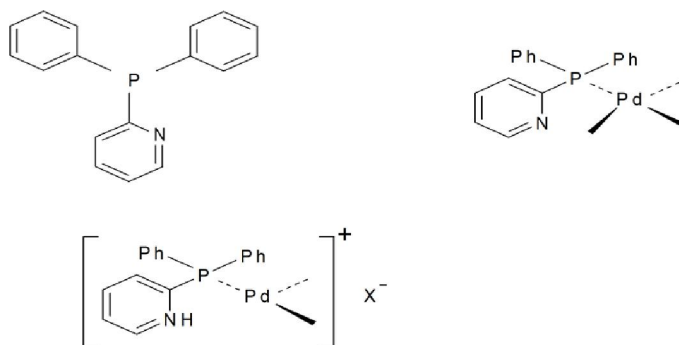
- Pd catalyzed homogeneous reaction by **Shell**
- A Pd complex catalyzes the reaction between propyne, methanol and CO



Regioselectivity as high as 99.95%

## Shell Process for MMA

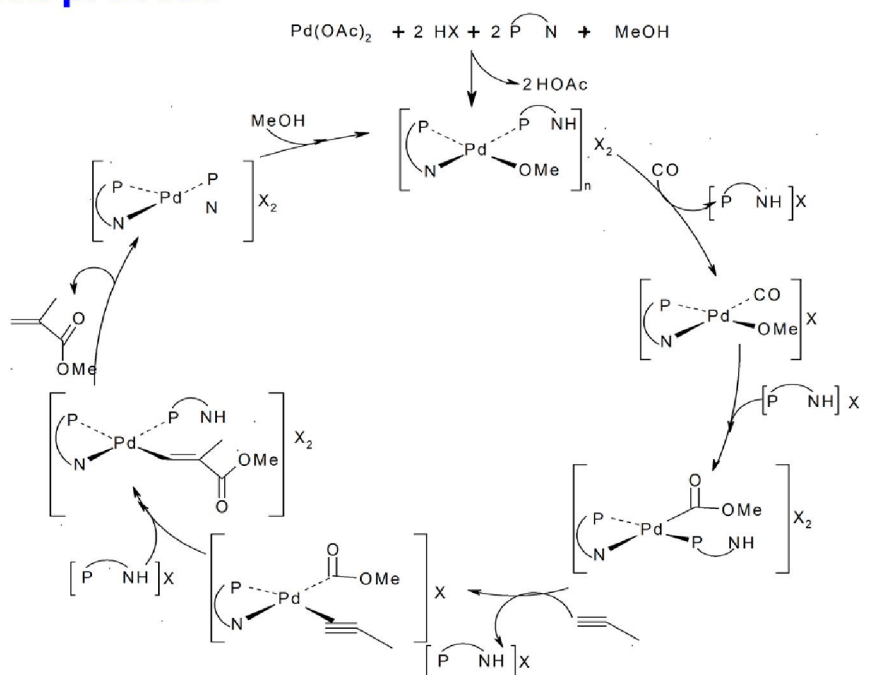
- Milder conditions, 60°C & 10-60 bar pressure.
- Methanol as a solvent as well as a reactant
- The pre catalyst is Pd(OAc)<sub>2</sub> mixed with an excess of phosphine ligand to generate the active catalytic intermediate in situ.
- HX as a co-catalyst.



Pd can chelate with P and N. The fourth coordination may be a solvent molecule. In the protonated form, the ligand acts as a labile, weakly coordinating ligand and easily displaced by reactants, such as CO, methylacetylene, etc.

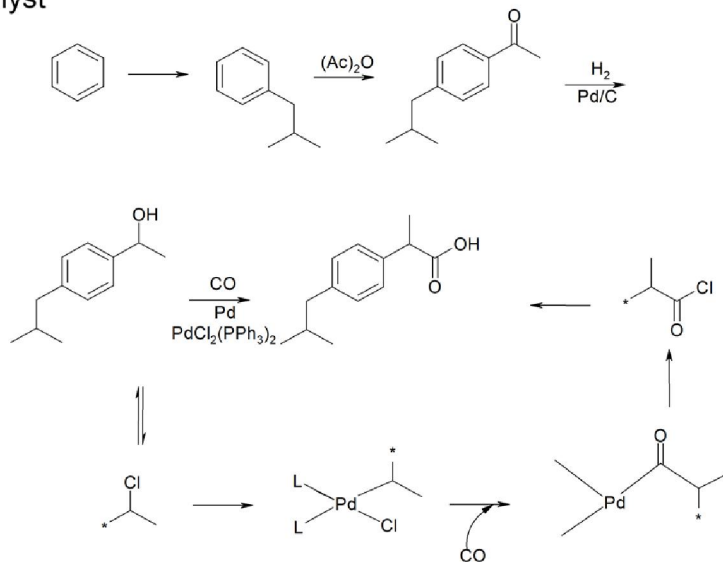


## Carbonylation of propyne in methanol to MMA-Shell process

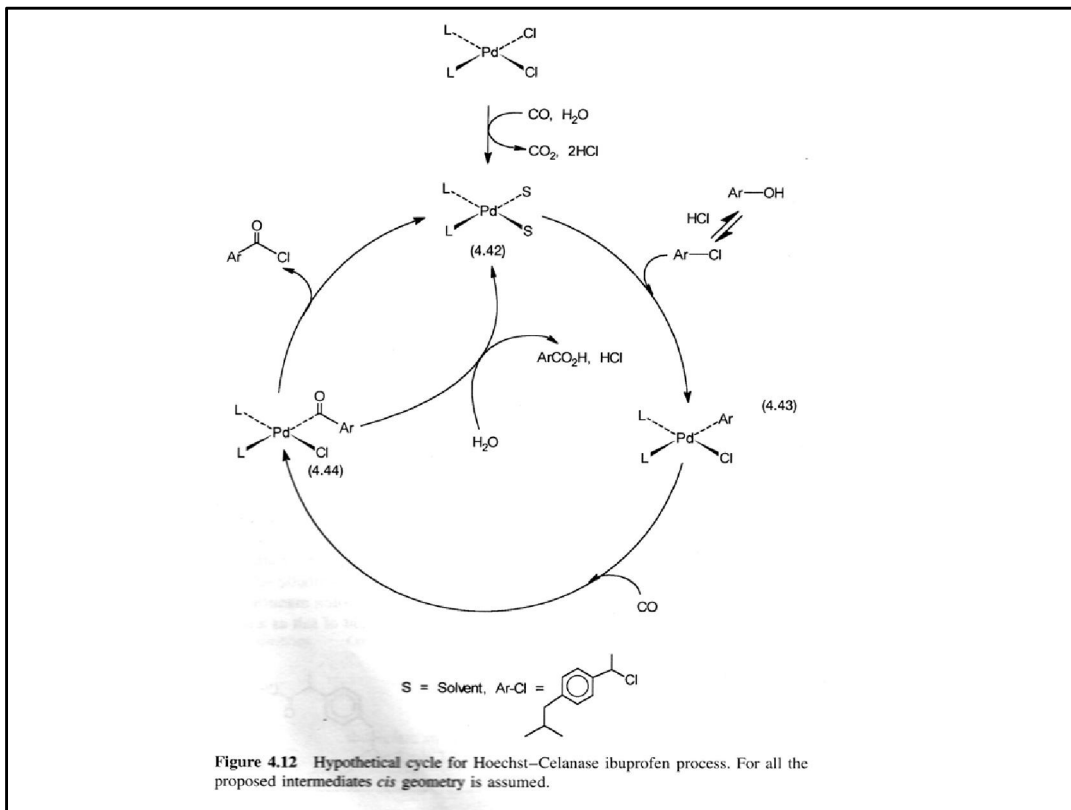


## Ibuprofen synthesis - Hoechst

Carbonylation of appropriate secondary alcohol with a Pd catalyst



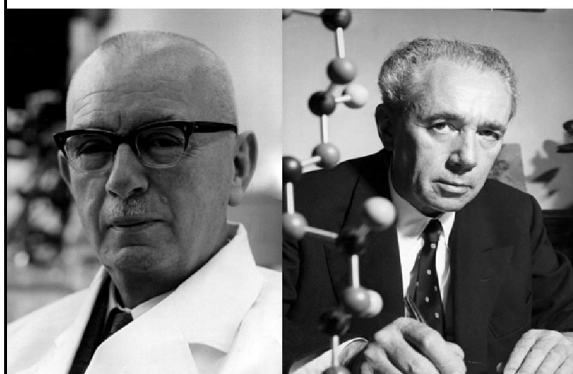
[ organic solvent + HCl : 50 bar : 130 °C ]





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**UNIVERSITY**  
KNOWLEDGE & BEYOND

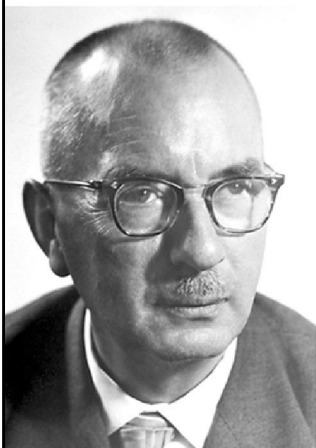
# ZIEGLER-NATTA CATALYST



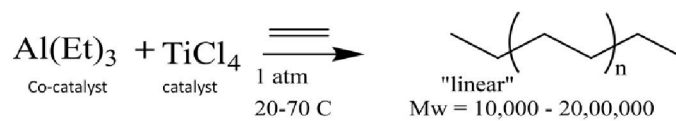
## History

- Karl Ziegler in 1953 polymerized ethylene catalytically to polyethylene.
- Giulio Natta utilized Ziegler's catalyst to produce polypropylene in 1954.
- In 1963, both Karl Ziegler and Giulio Natta were awarded the Nobel Prize for their discoveries.
- In 1973 the 2<sup>nd</sup> generation Ziegler-Natta catalysts were introduced with  $\beta$ -TiCl<sub>3</sub> at lower temperatures.
- In 1980 3<sup>rd</sup> generation catalysts supported on MgCl<sub>2</sub> were commercialized by many companies.
- In 1991 4<sup>th</sup> generation Ziegler-Natta catalysts based on aluminoxane activated metallocene complexes were used.
- Two broad classes:
  - ❖ Heterogeneous Catalyst: Based on Ti compounds
  - ❖ Homogeneous Catalyst: Based on complexes of Ti, Zr and Hf

## Ziegler's Discovery (Germany, 1953)

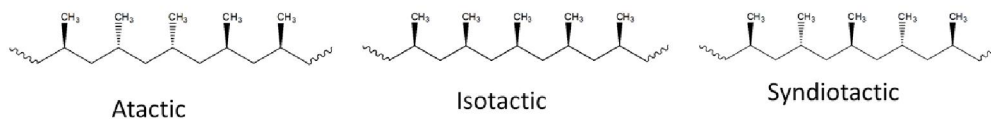


Karl Ziegler-the last Al-Chemist  
"...because he turned aluminium into gold."

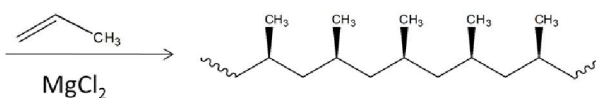


## Using propylene

- Propene can polymerize in three ways:

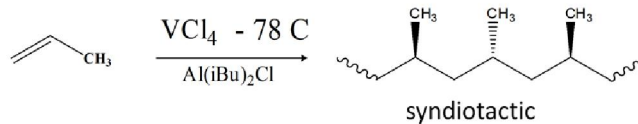
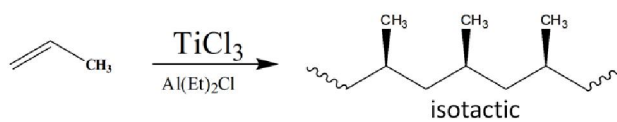


- $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$



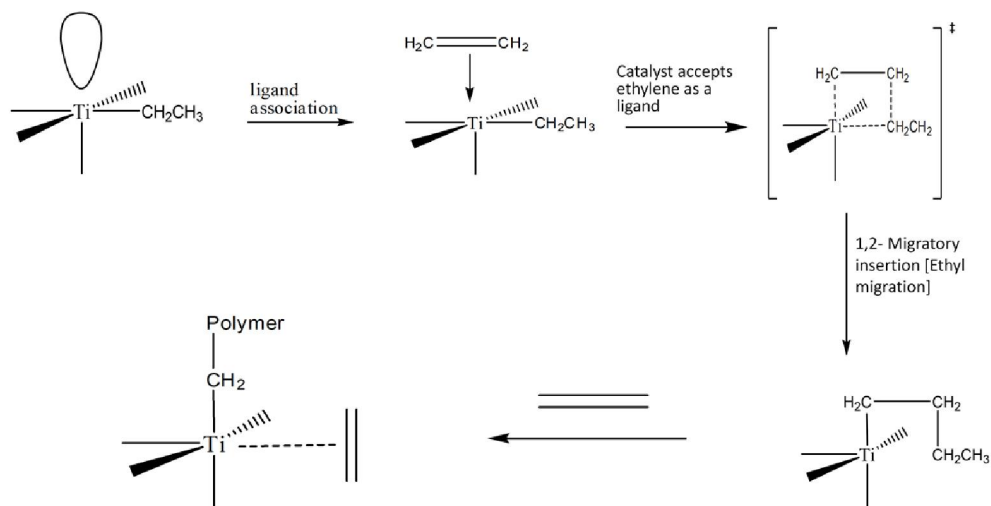
- Highly selective towards isotactic product
- Highly stable product

## Natta's Discovery (Italy, 1954)

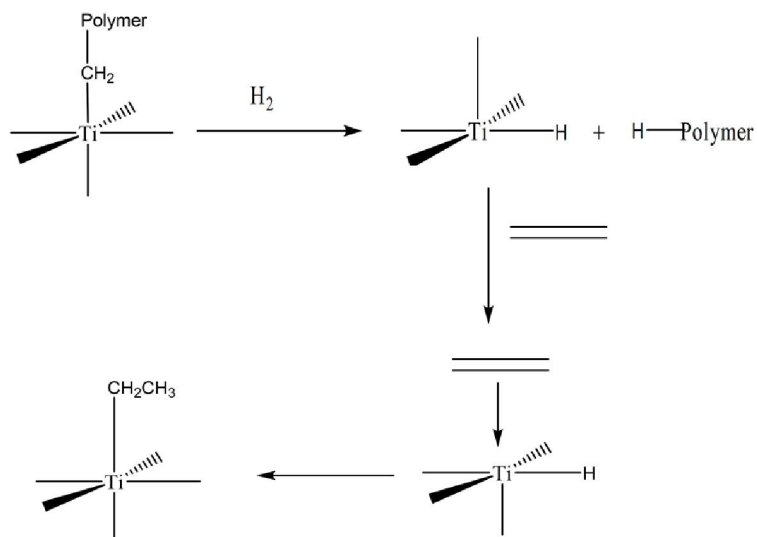




## Mechanism of Ziegler-Natta Polymerization: The Cossee Mechanism

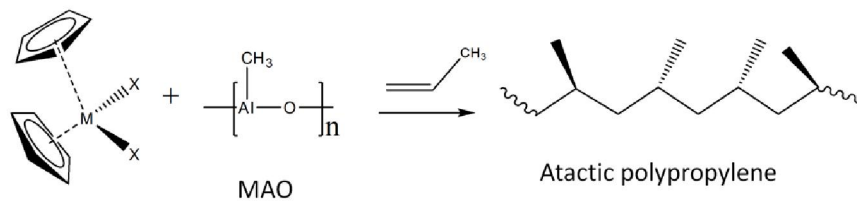
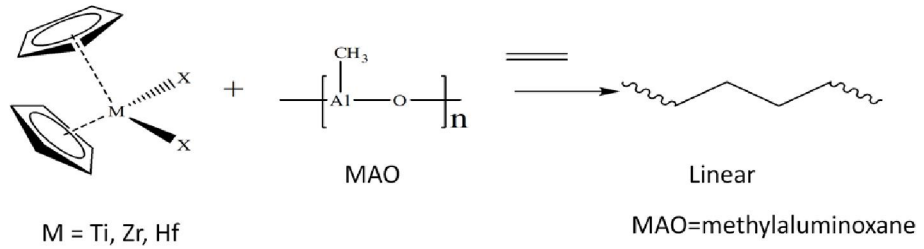


## Termination Step: Chain Transfer

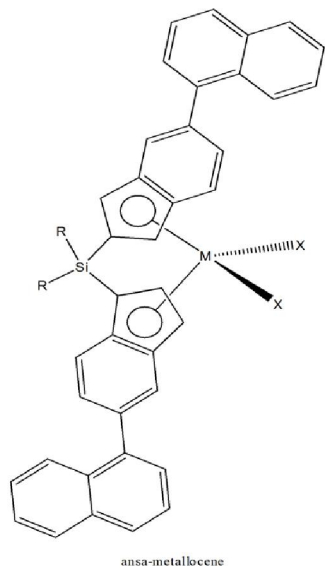


# Kaminsky Catalyst System

Homogeneous Ziegler Natta Catalyst



## Brintzinger System



R= CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>

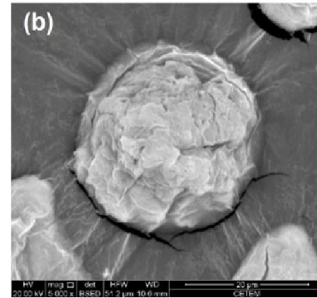
X= Cl, Br, CH<sub>3</sub>

M= Ti, Zr

Brintzinger developed these catalysts which when activated with MAO catalysed the stereoselective polymerizations of propylene with very high activities. Thus for the first time isotactic polyolefins were obtained using homogeneous Ziegler-Natta catalyst

# Importance of Ziegler Natta Catalyst

- High Efficiency
- High Stereoregularity (99% tacticity)
- Longer Lifetime
- High concentration of polymer product
- Lower cost in production
- Easy regeneration of catalyst
- Controls growth and formation of polymer product
- Control of polymer particle morphology in spherical shape
- Higher stability



# Applications of Ziegler-Natta Catalyst

Production of:

- High density polyethylene (HDPE)
- Linear low density polyethylene (LDPE)
- Ultra-high molecular weight polyethylene (UHMWPE)
- Thermoplastic polyolefins (TPO's)
- Polybutylene (PB)
- Shiny lustrous polyacetylene film which have semiconducting properties
- Crystalline polypropylene
- Carbon nanotubes nanocomposites



