

# ORGANOMETALLIC CATALYSIS

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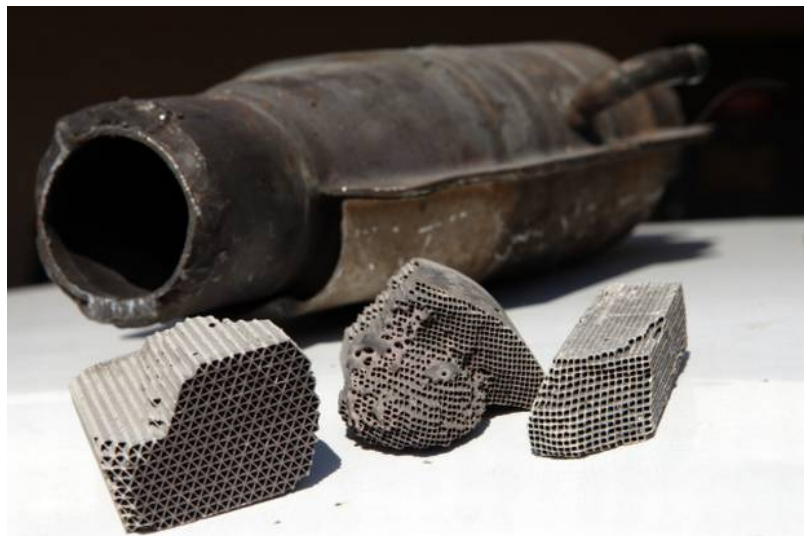
MFT Ch 14

CH 431



# Importance of Catalysis

- Overstating commercial importance of catalysis is virtually impossible



Vehicle Catalytic Converter

- Transform vast reservoirs of cheap and readily available chemical feedstocks into products such as nylon and polyethylene polymers
- Provide efficient routes toward fine chemicals used for pharmaceuticals, perfumes, and food
- Protect the environment by controlling vehicle and industrial emissions



# Importance of Catalysis

- In economic terms, catalysts add an estimated annual \$2.4 trillion of value worldwide to raw chemical ingredients
- Worldwide market for catalysts (heterogeneous and homogeneous) rose above \$11 billion in 2000



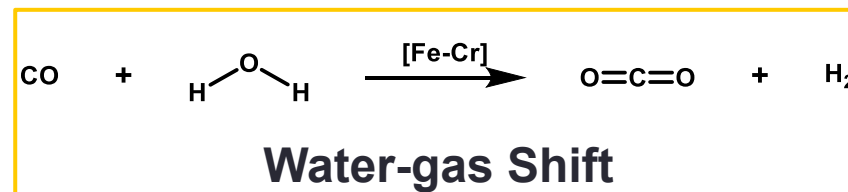
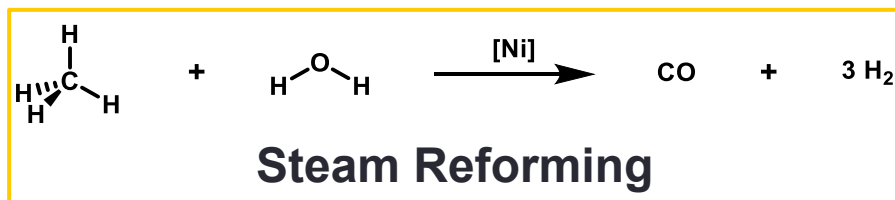
Polypropylene Plant

Hyosung Builds Additional PP Plant with 200,000 Tons Annual Production Capacity. <http://www.businesskorea.co.kr/english/news/industry/12154-polypropylene-hyosung-builds-additional-pp-plant-200000-tons-annual-production> (accessed April 15, 2016)



# Heterogeneous Catalysis

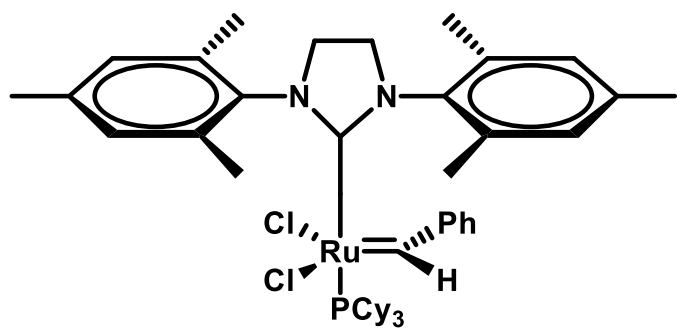
- The term “catalysis” was widely understood to refer to a heterogeneously catalyzed process up until about 1938
- Heterogeneous catalyst – catalysts which is in a different phase than that of the reactants
  - Typically where a solid catalyst is in contact with a reactive liquid or gaseous phase
- Example: Steam reforming and water-gas shift



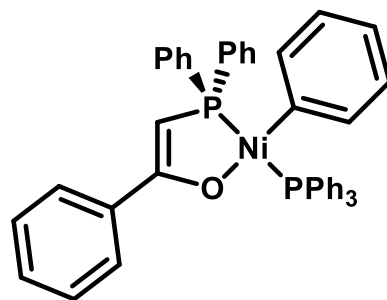


# Homogeneous Catalysis

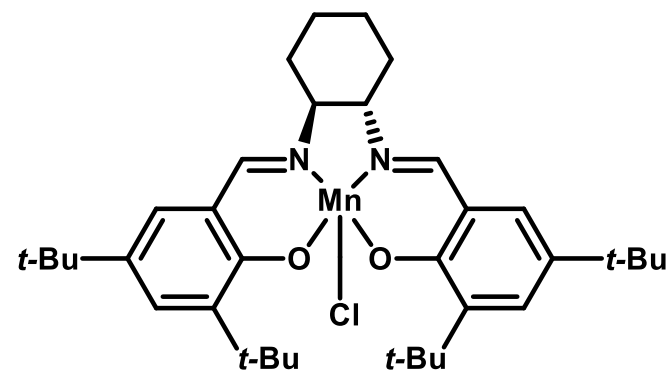
- Homogeneous catalyst – catalyst which is in the same phase as the reactants
  - Typically done in solution rather than gas or solid phase



Grubb's Catalyst  
(2<sup>nd</sup> generation)



Shell Higher  
Olefin Process  
(SHOP) Catalyst



Jacobsen's Catalyst

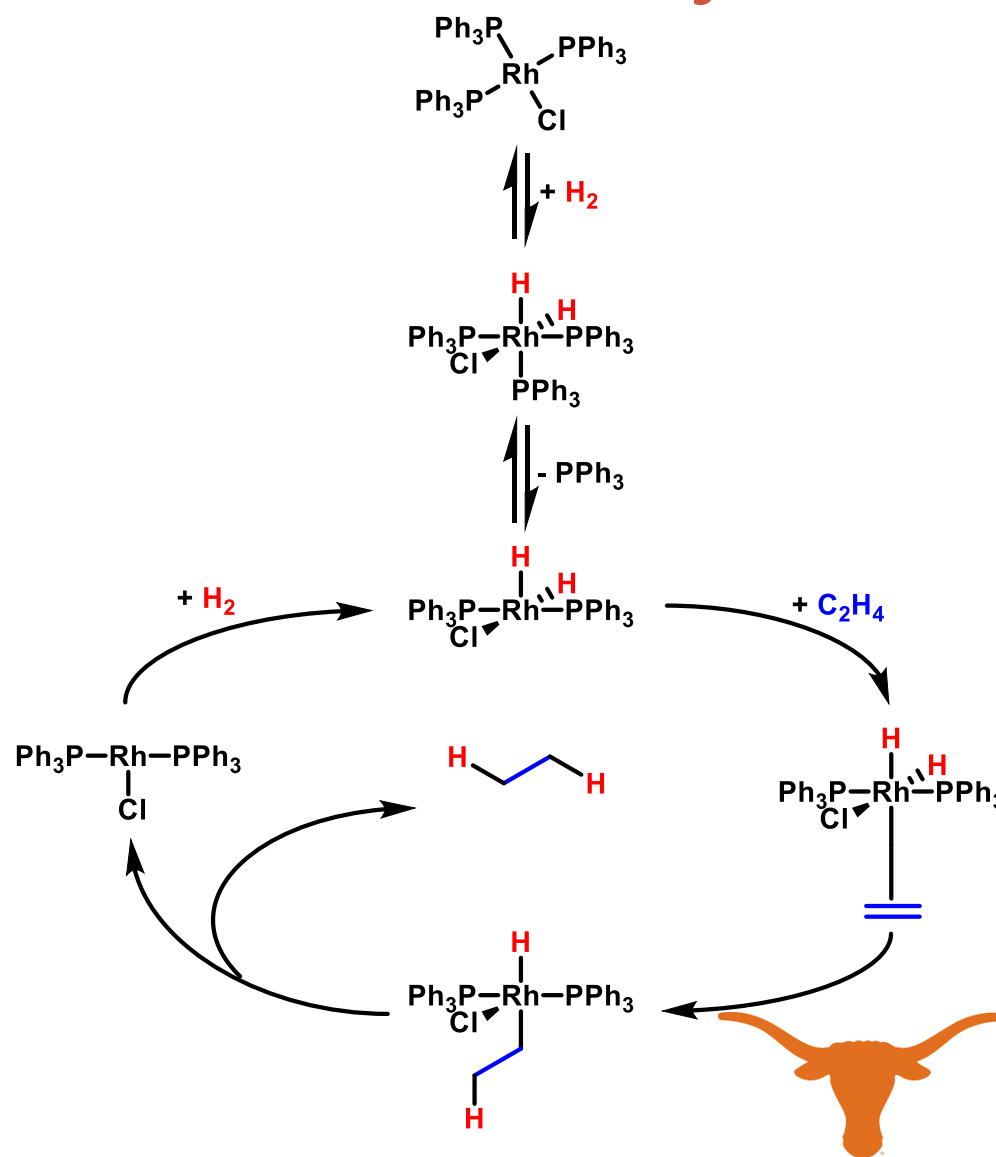


# Heterogeneous vs. Homogeneous

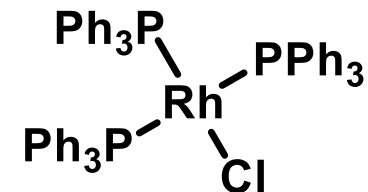
	Heterogeneous	Homogeneous
Activity	Very fast	Variable
Selectivity	Often poor	Good/excellent
Reaction conditions	Gas/solid or liquid/solid	Solution phase
Life of catalyst	Endless	Variable
Diffusion problems	Variable	None
Catalyst recycling	No need	Difficult
Variability of steric & electronic properties	Low	High
Mechanistic understanding	Poor/non-existent	High
Sensitivity towards poisons	Low poisoning	Variable

# Hydrogenation: Wilkinson's Catalyst

- First known homogeneous hydrogenation catalyst (1966)
- The choice of ligand plays an important role in selectivity of the catalyst
- The bulky  $\text{PPh}_3$  ligands (cone angle) make the catalyst selective for unhindered positions on alkenes



# Wilkinson's Catalyst



**Table 14.5 Relative Rates of Hydrogenation Using Wilkinson's Catalyst at 25 °C**

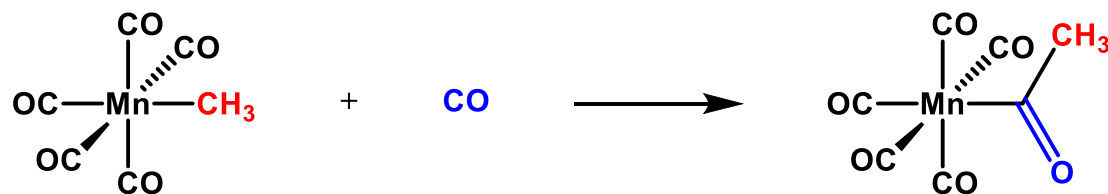
Compound Hydrogenated	Rate Constant x 100 (L mol <sup>-1</sup> s <sup>-1</sup> )
	31.6
	9.9
	1.8
	0.6
	< 0.1



# Migratory Insertion vs Insertion

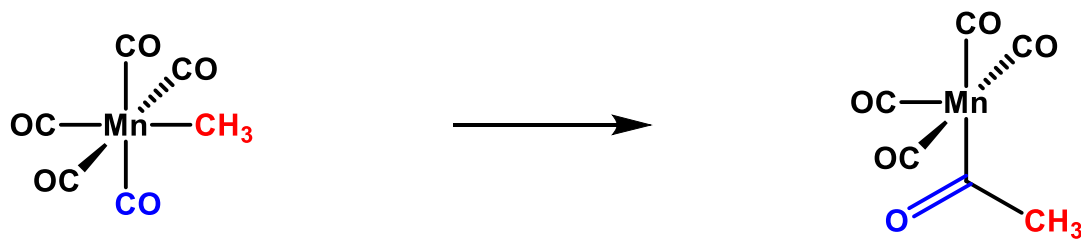
## 1,1 insertion

- 1,1 insertion when incoming ligand binds to the atom which is also bound to the metal center



## 1,1 migratory insertion

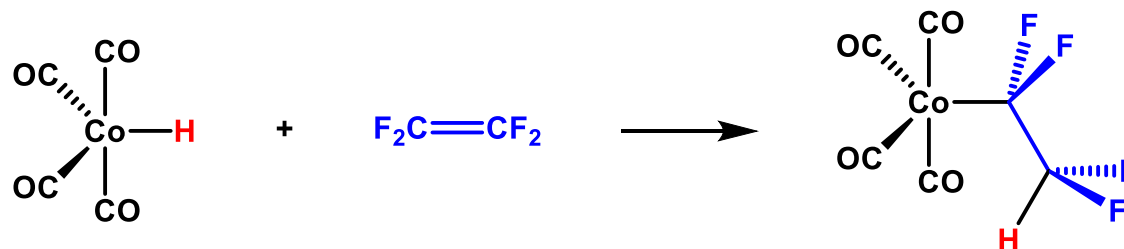
- 1,1 migratory insertion is when incoming ligand is already bound to the metal center



# Migratory Insertion vs Insertion

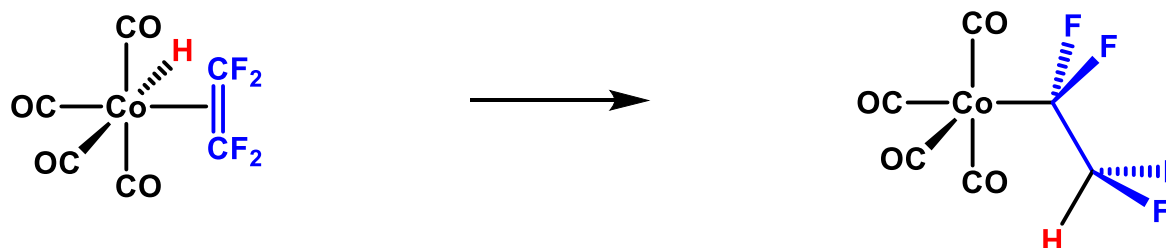
## 1,2 insertion

- 1,2 insertion when the bonds are made to adjacent (1,2) atoms



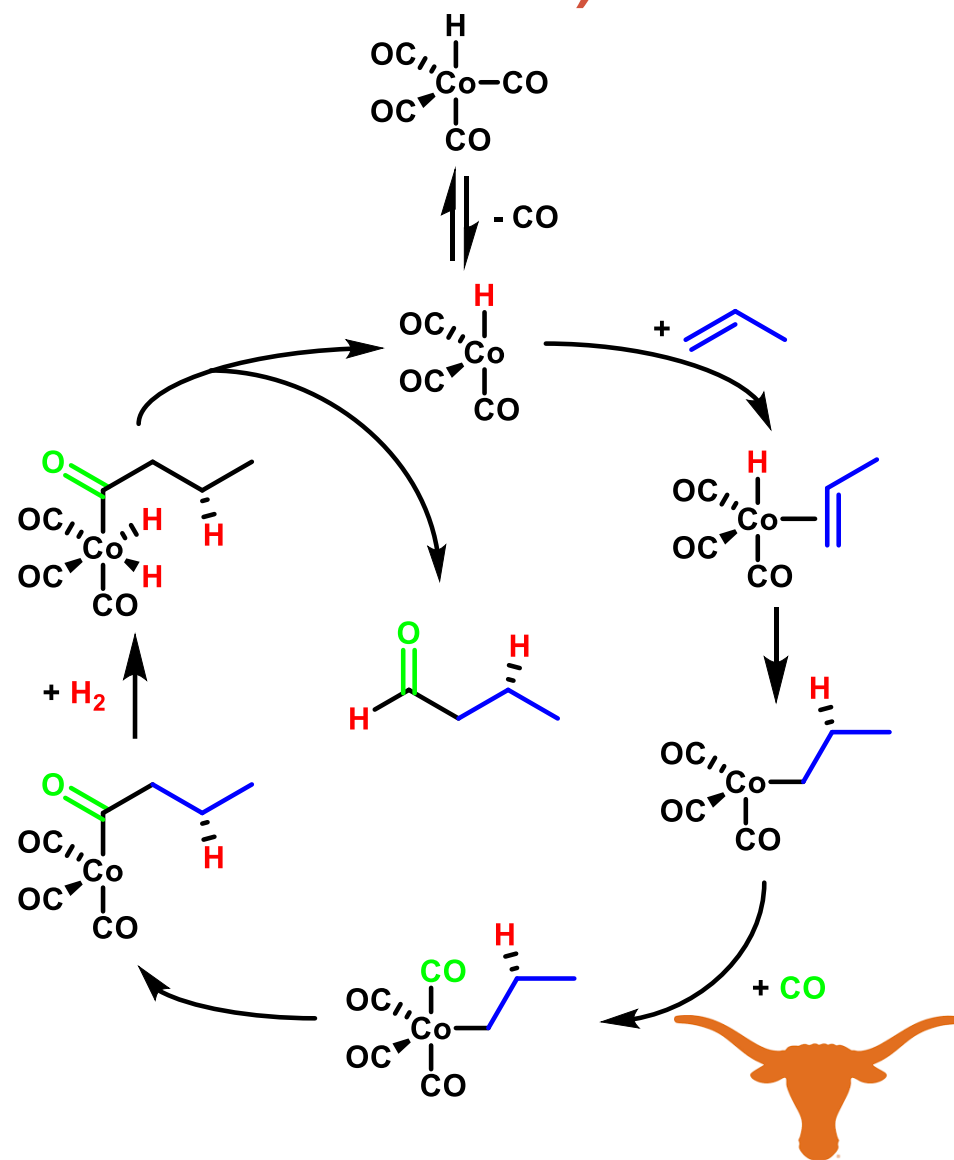
## 1,2 migratory insertion

- 1,2 migratory insertion is when incoming ligand is already bound to the metal center and it attacks the 2 position of the other ligand



# Hydroformylation (Oxo Process)

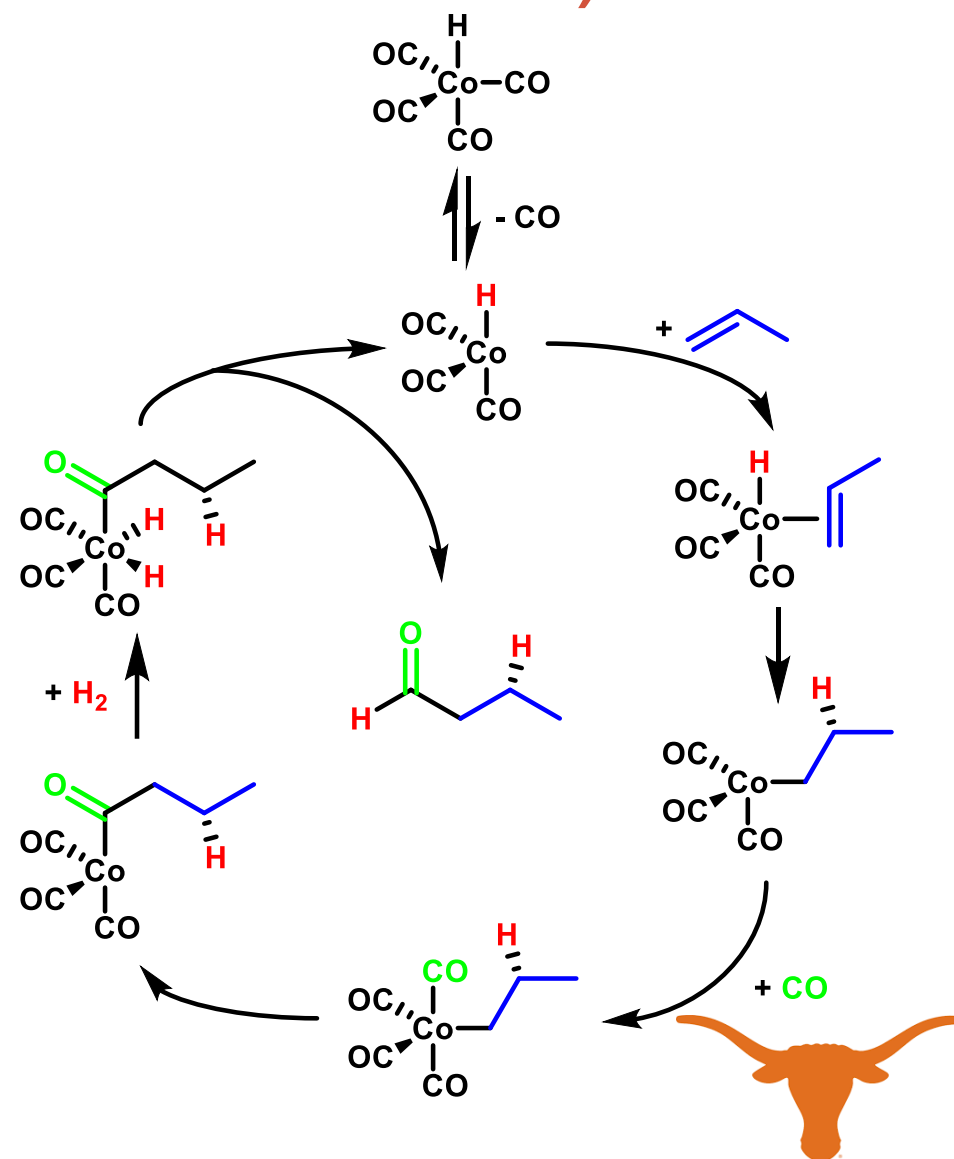
- Introduced in 1938 and is oldest homogeneous catalytic process in commercial use
  - Main industrial application is the production of butanal from propene
- Approximately 10 million tons of hydroformylation products produced annually





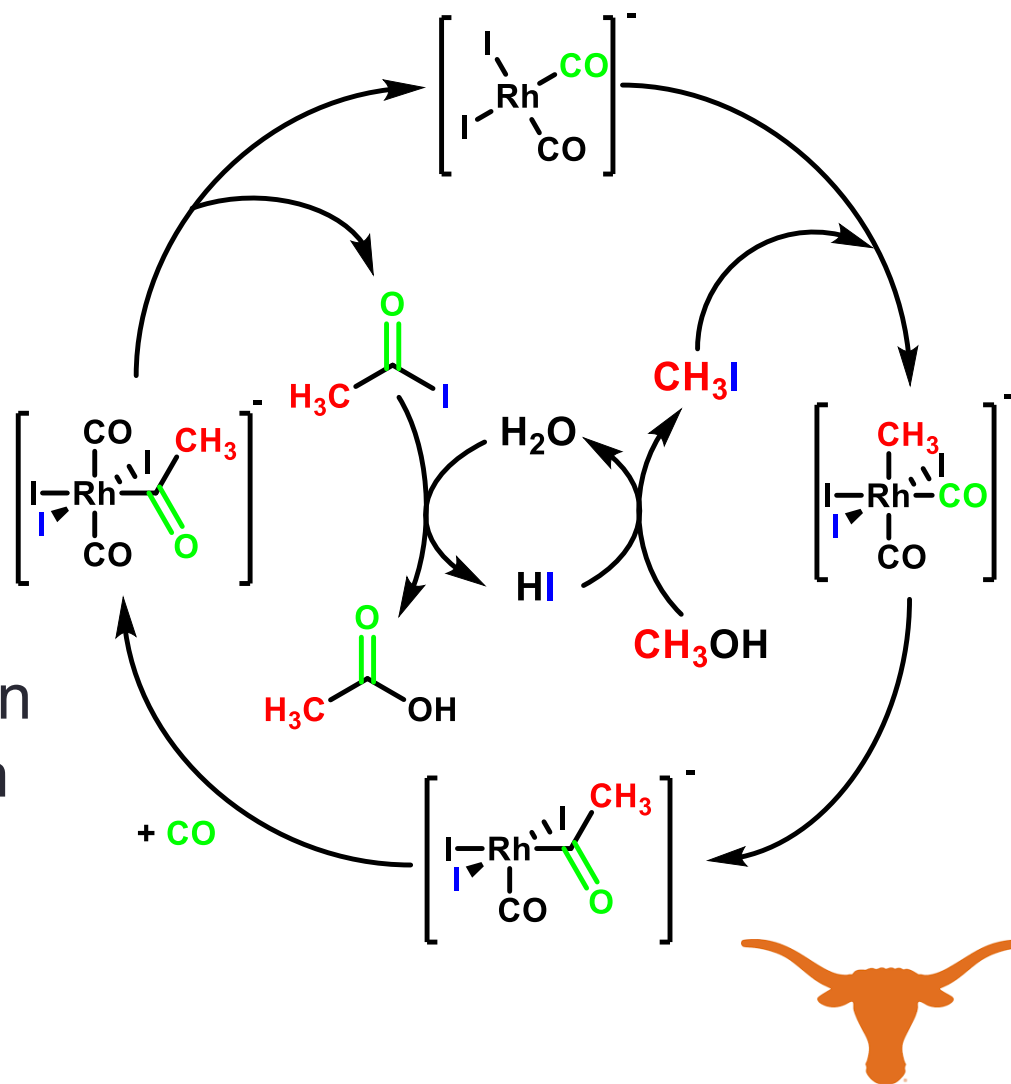
# Hydroformylation (Oxo Process)

- Classical example of a catalytic cycle which displays alternating between 16 e<sup>-</sup> and 18 e<sup>-</sup>
- Rate determining step is the addition of the alkene
- Catalyst typically has a Co or Rh metal center



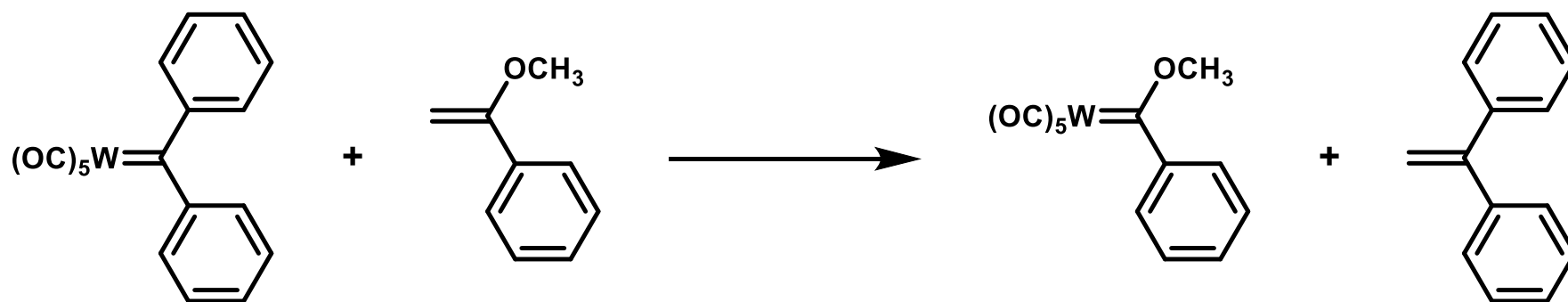
# Monsanto Process

- Synthesis of acetic acid from methanol and CO using a Rh catalyst
- Rate determining step is the oxidative addition of  $\text{CH}_3\text{I}$
- Can also be done using an Ir catalyst, which is known as the Cativa Process



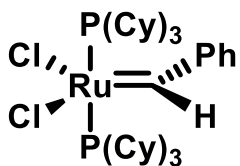
# Olefin (Alkene) Metathesis

- Olefin metathesis, which was first discovered in the 1950's, is the formal exchange of  $\text{:CR}_2$  fragments between alkenes
  - Y. Chauvin, R. Grubbs, and R. Schrock won the Nobel Prize in Chemistry in 2005 for their development of olefin metathesis

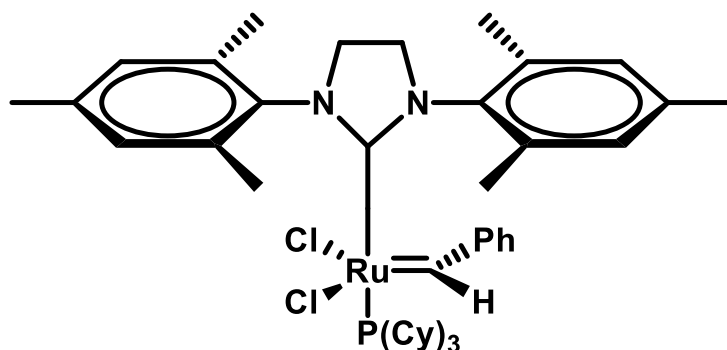


# Grubb's Catalyst

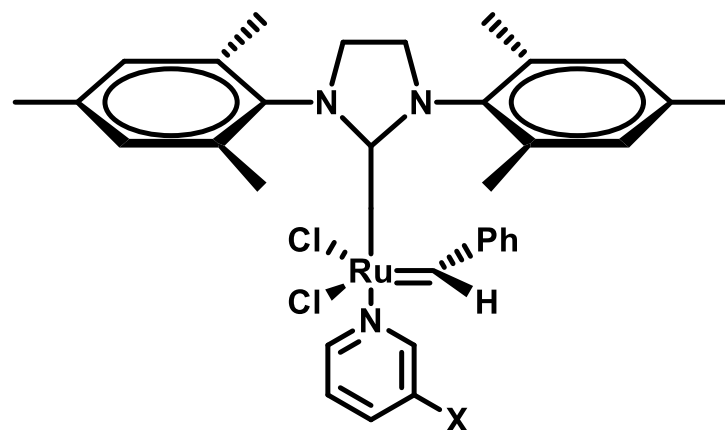
- Probably the most famous organometallic carbene is Grubb's catalyst
  - Capable of performing ring-opening metathesis (ROM), ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP)



Grubb's 1<sup>st</sup>  
Generation



Grubb's 2<sup>nd</sup> Generation



X = H or Br

Grubb's 3<sup>rd</sup> Generation

