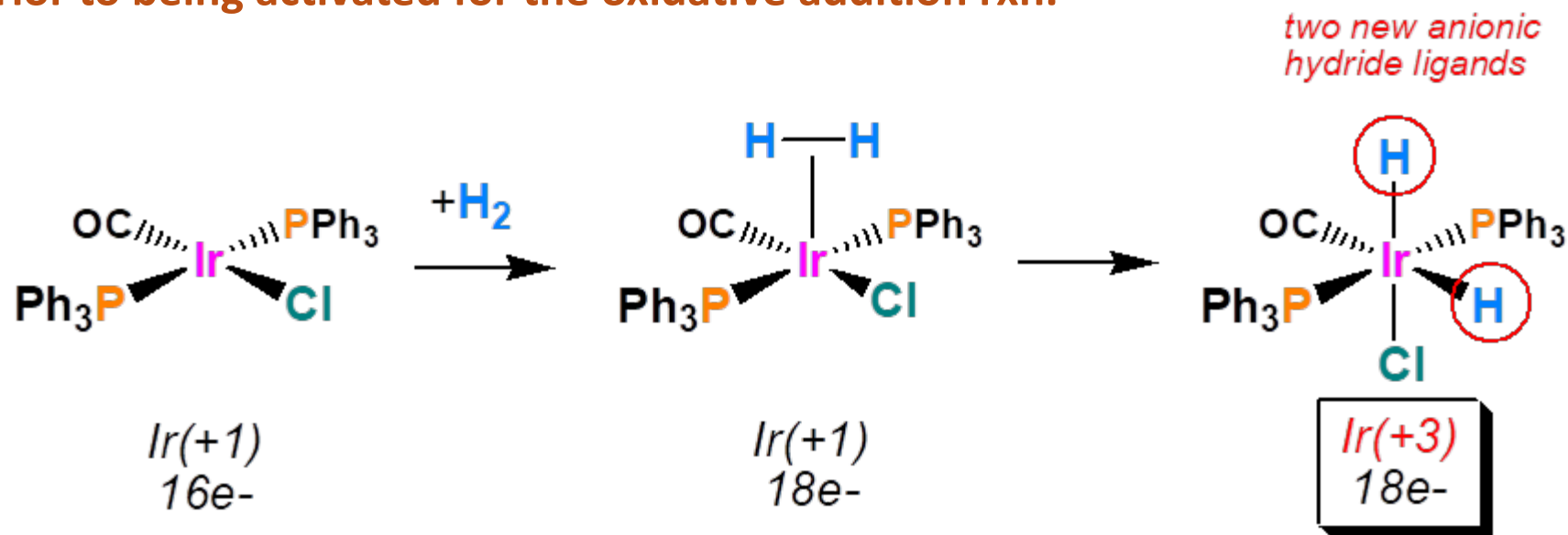


# Types of Substrates (X-Y)

- Depending on the nature of the substrate (X-Y), the mechanism of the oxidative addition may differ .
- There are three main classes of molecules (substrates) that can perform oxidative additions to metal centers:
  - **Non-Electrophillic**; **Non-Electrophillic “Intact”**; **Electrophillic**

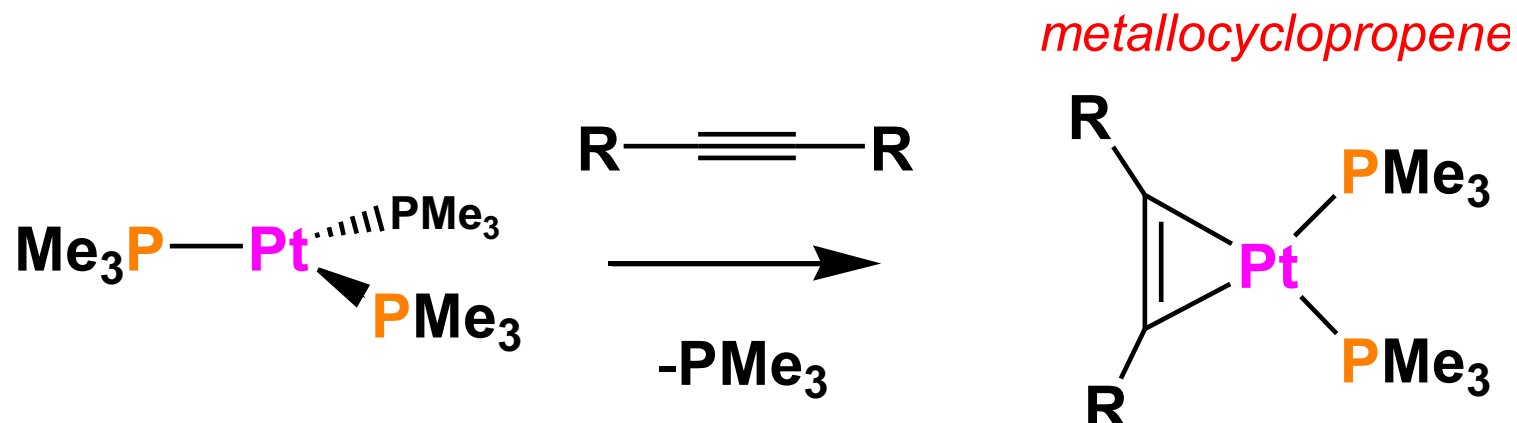
**Non-electrophillic:** These molecules do NOT contain electronegative atoms and/or are not good oxidizing agents. These molecules usually require the presence of an empty orbital on the metal in order for them to pre-coordinate prior to being activated for the oxidative addition rxn.



# Non Electrophilic Substrates that Do Not Fragment

**Non-electrophilic “Intact”:** These molecules have a double or triple bond present. One also needs a metal center with an empty orbital (16e<sup>-</sup> or lower count) in order to pre-coordinate the ligand before the oxidative addition occurs.

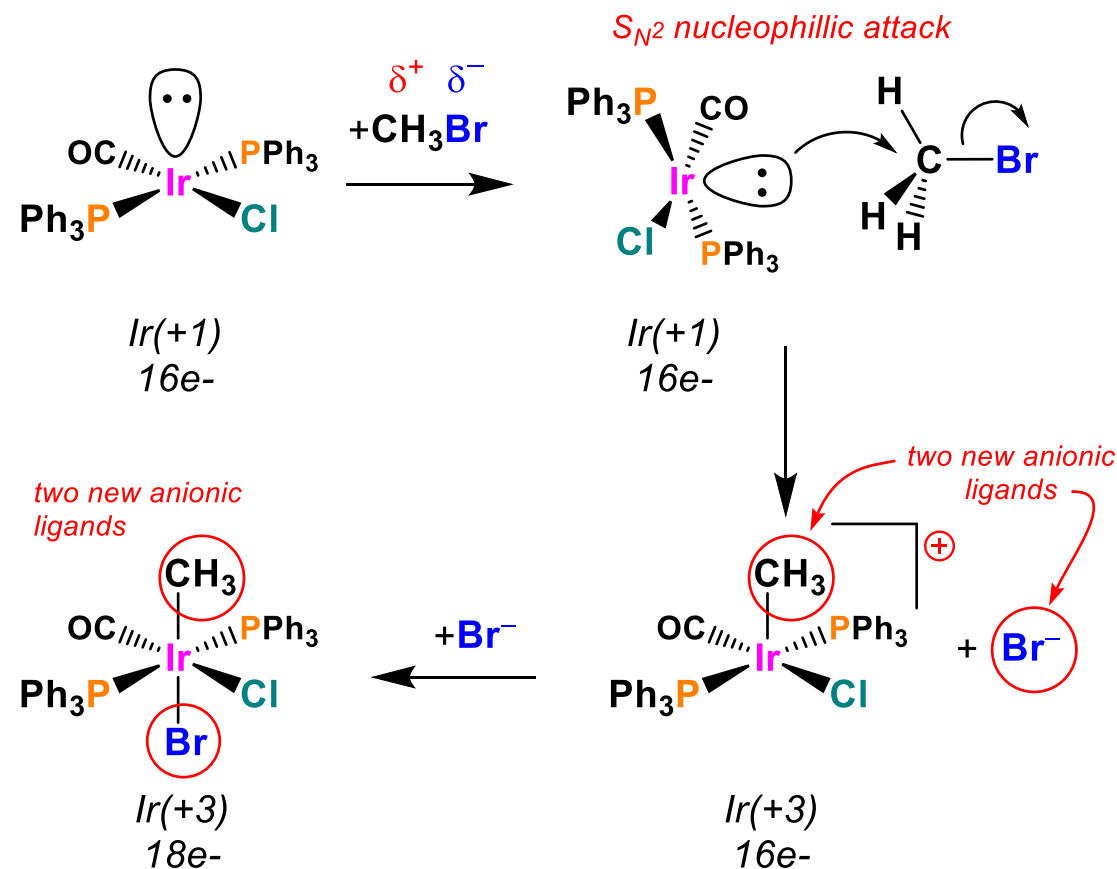
- Alkenes and alkynes are typical “intact” ligands that can perform an oxidative addition without fragmenting apart.



# Electrophilic Substrates

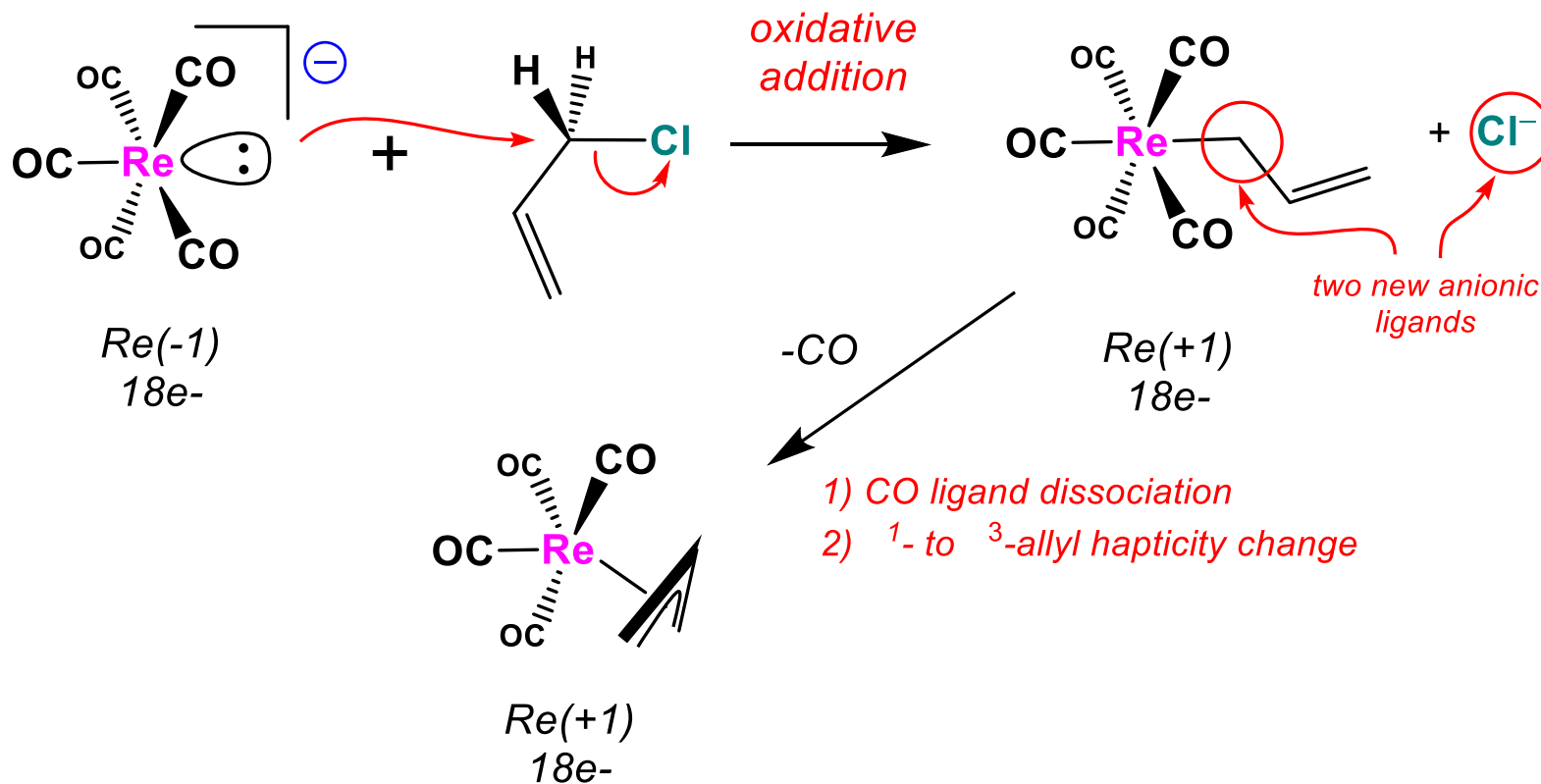
**Electrophilic:** These molecules do contain electronegative atoms and are good oxidizing agents. They are often considered to be “**reactive**” substrates.

Examples:  $X_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{R-X}$ ,  $\text{Ar-X}$ ,  $\text{H-X}$ ,  $\text{O}_2$ , etc.



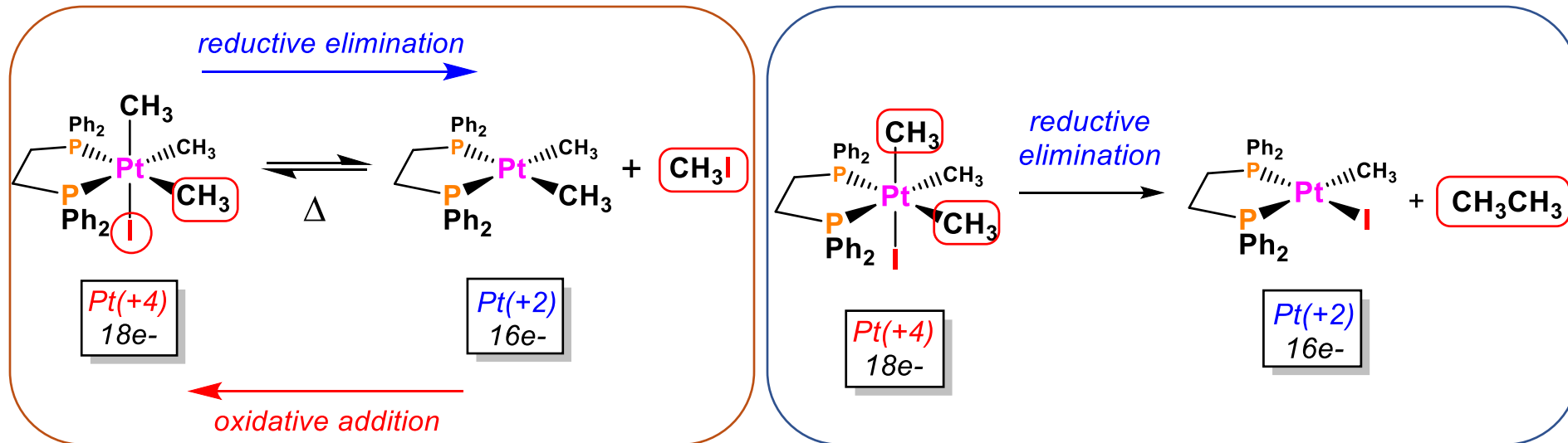
# Oxidative Addition: Electrophilic Substrates

- 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.



# Reductive Elimination: Effect of Ligand Dissociation

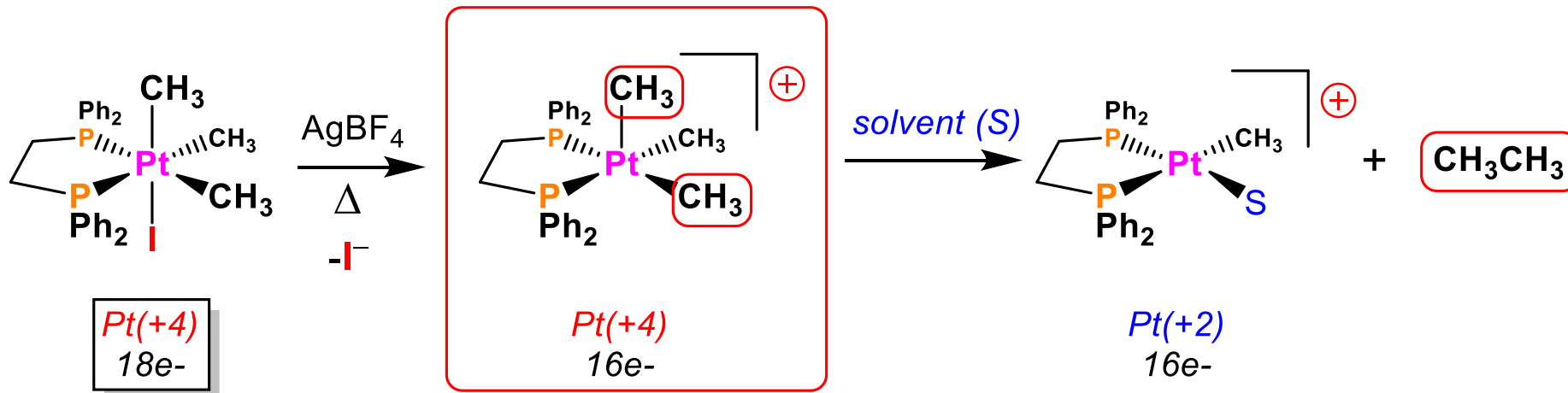
- Sometimes, more than one **reductive elimination** possibilities arise from saturated 18e<sup>-</sup> complexes (so long as the two ligands that you want to reductively eliminate are **cisoidal** to one another).
- An understanding of the electronic requirements can facilitate reaction engineering to favour one option over the other.



*Both pathways occurred; reaction was slow (~ many hours)*

# Reductive Elimination: Effect of Ligand Dissociation

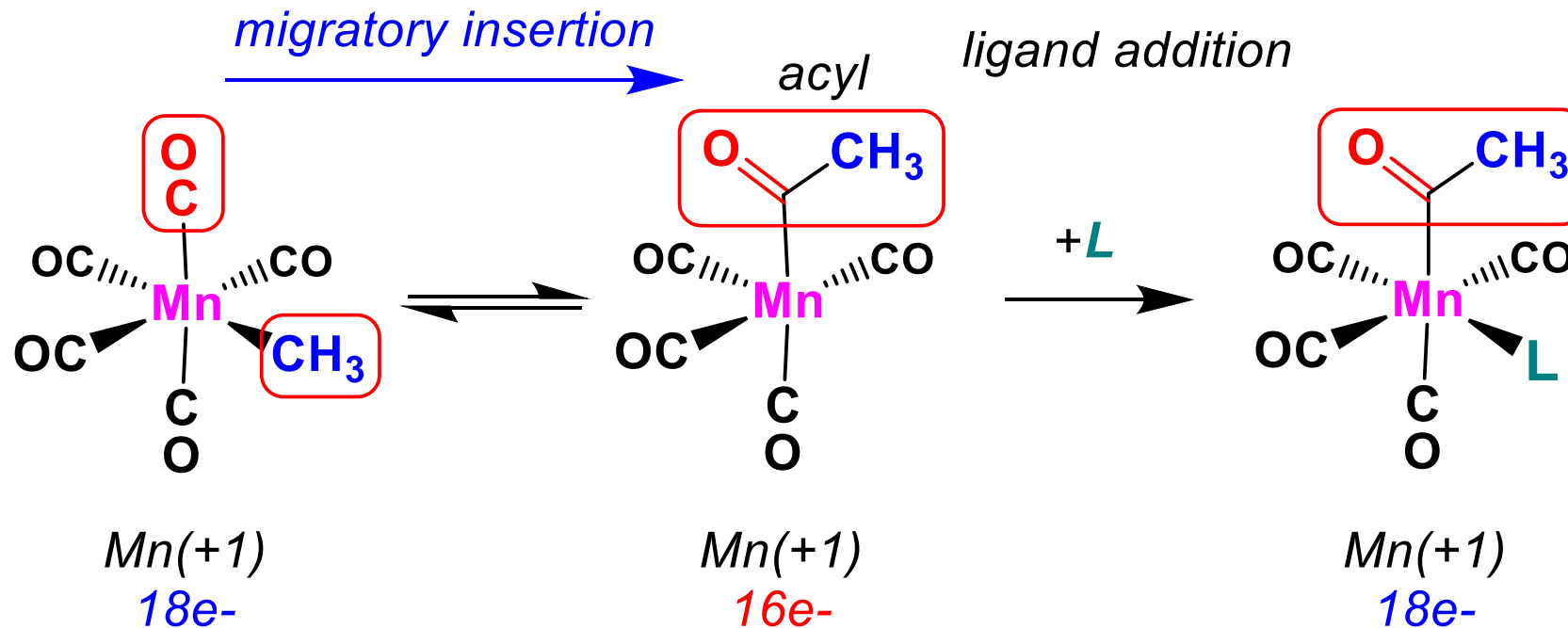
- It has been shown that reductive elimination can be promoted by a ligand dissociation generating an unsaturated and more electron-deficient metal center.



*The dissociation of the I<sup>-</sup> generates a cationic unsaturated complex. This is electron deficient enough to help promote the reductive elimination of ethane ( $CH_3CH_3$ ).*

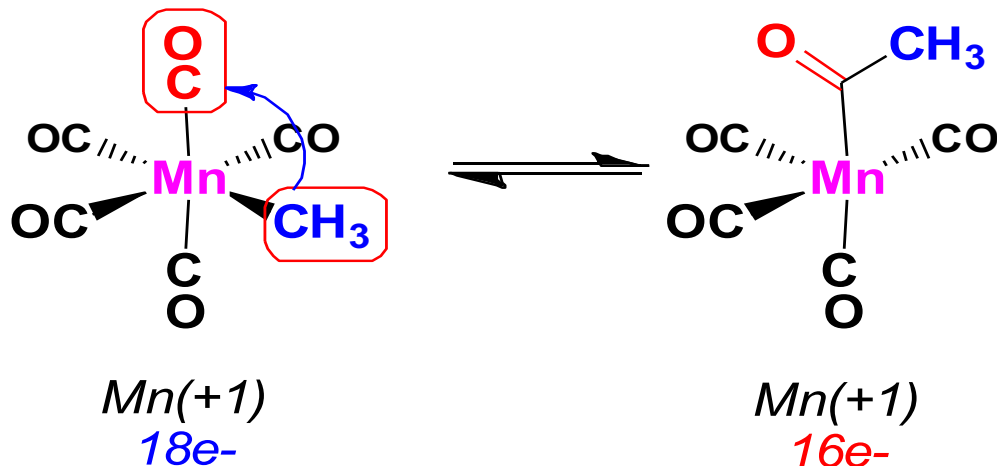
# Migratory Insertion

- 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.



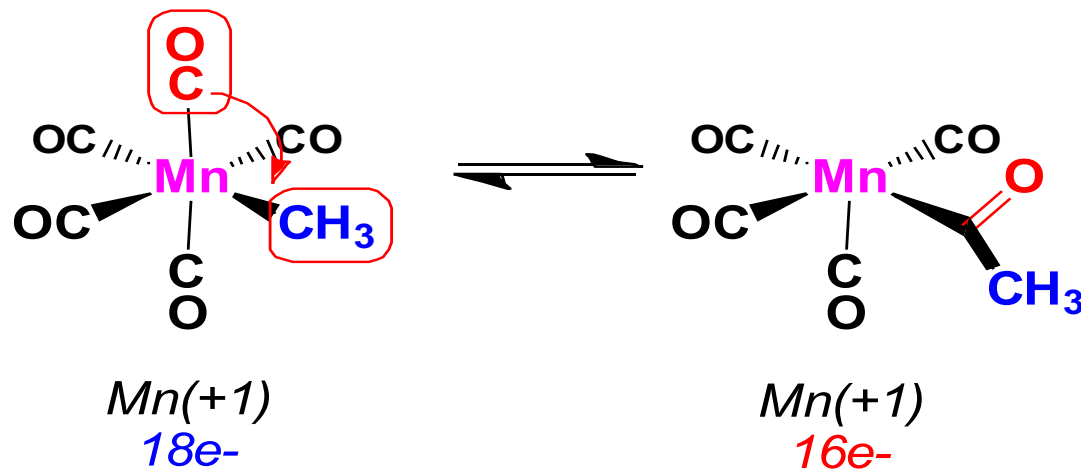
# Migratory Insertion: Who Migrates to Whom?

## 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

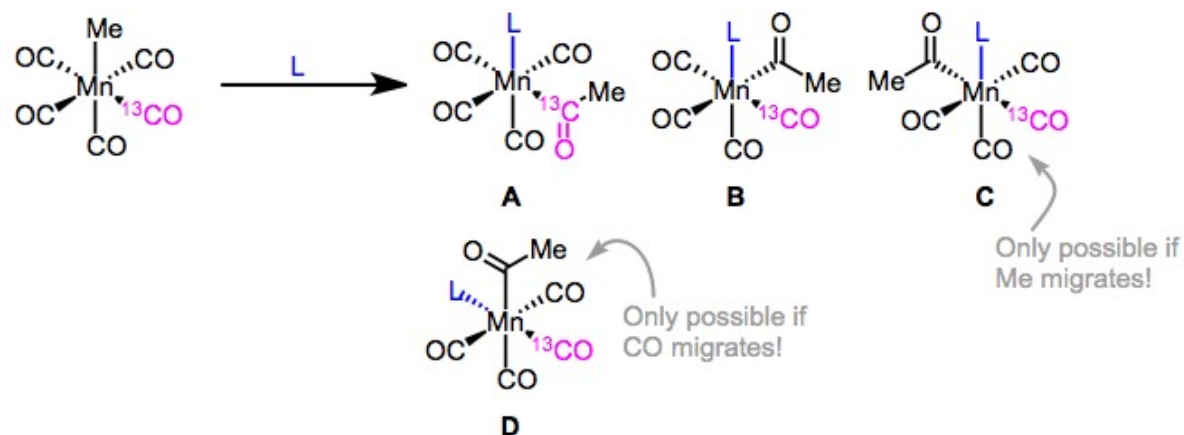


an INSERTION rxn involves the neutral ligand moving over to where the anionic ligand is coordinated and "inserting" into the anionic ligand-metal bond to generate the new anionic ligand. An empty coordination site is left behind from where the neutral ligand originally was located.



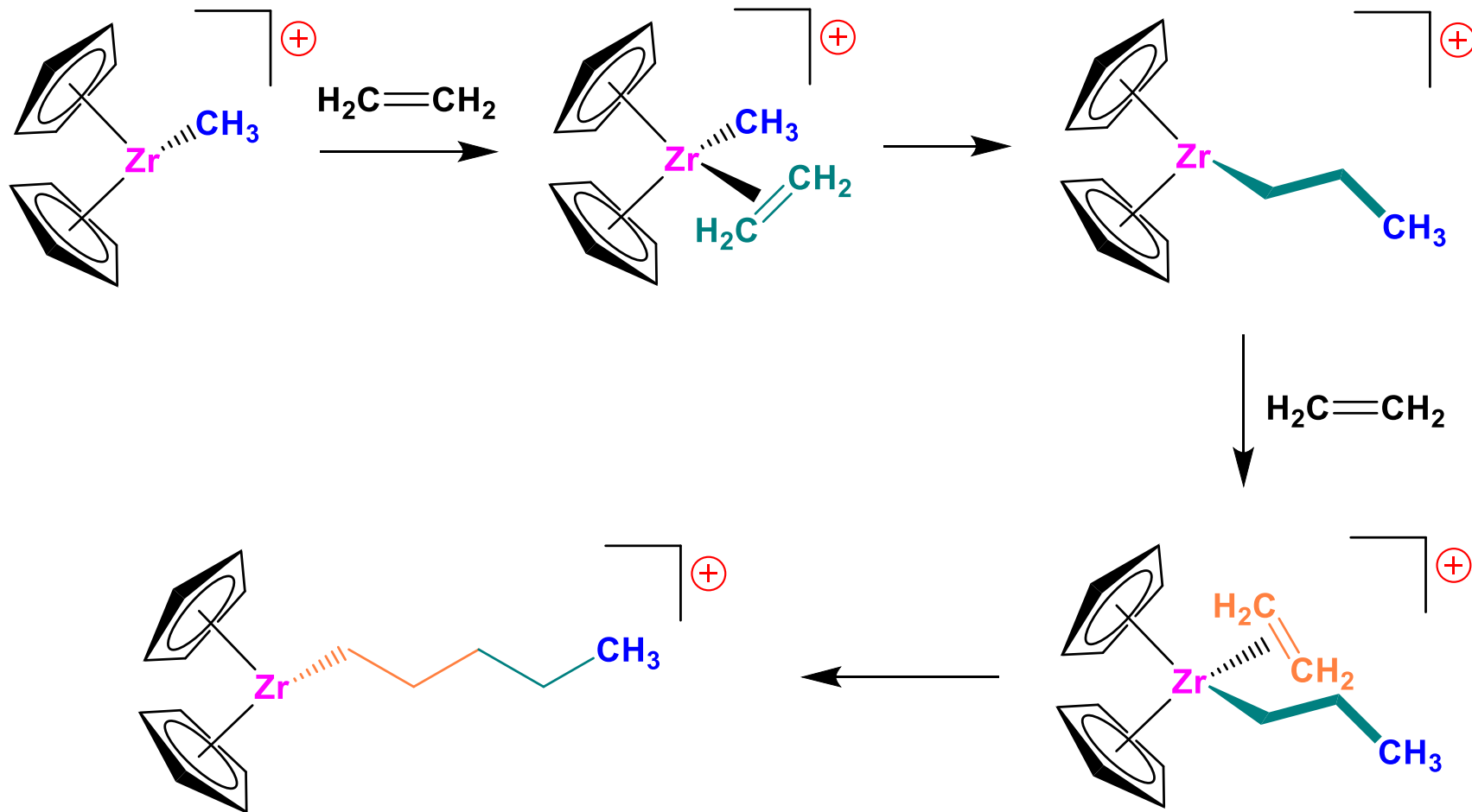
# Who Migrates to Whom? Experiment Design

- Four products of insertion are possible, corresponding to reaction of the four CO ligands cis to the methyl ligand. Consider both CO migration and Me migration as possible at this point.



- Product D is impossible if we only allow the Me group to migrate—the spot *trans* to the labelled CO is another CO ligand, so that spot can only pick up L if CO migrates (not if Me migrates).
- On the other hand, product C must have come from the migration of Me, since the Me group has moved from a *cis* to a *trans* position relative to the labeled CO in product C.
- Products A, B, and C were observed, but not D, supporting a mechanism involving Me migration. Other experiments since support the idea that most of the time, the alkyl group migrates onto CO.

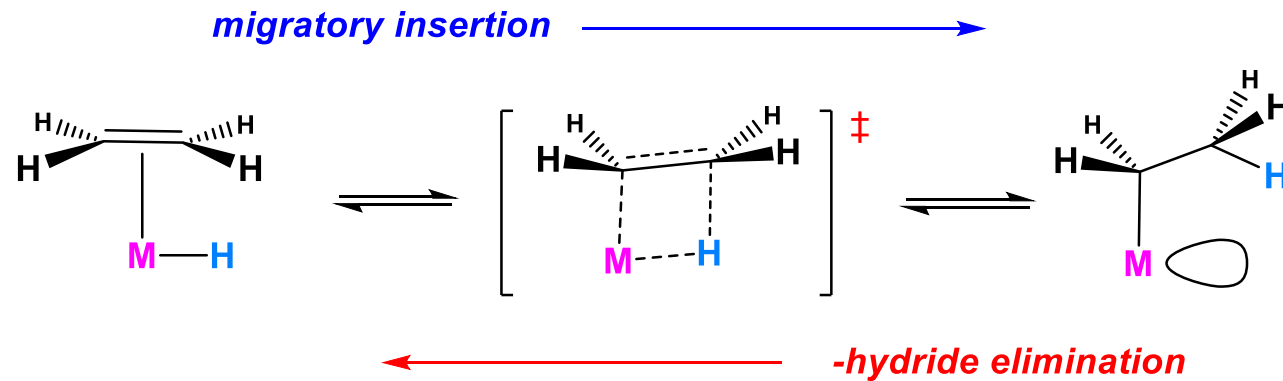
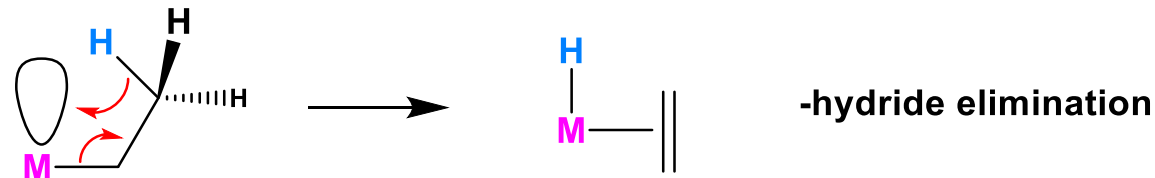
# Migratory Insertion of Alkenes



□ Successive migratory insertions can lead to chain elongation

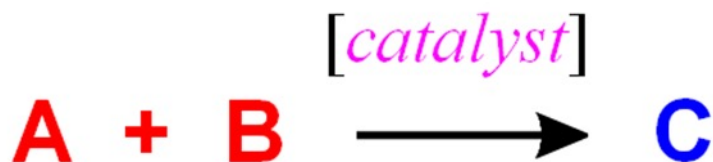
# Eliminations

- The most common elimination is  $\beta$ -hydride elimination. It can be thought of as the opposite of migratory insertion.

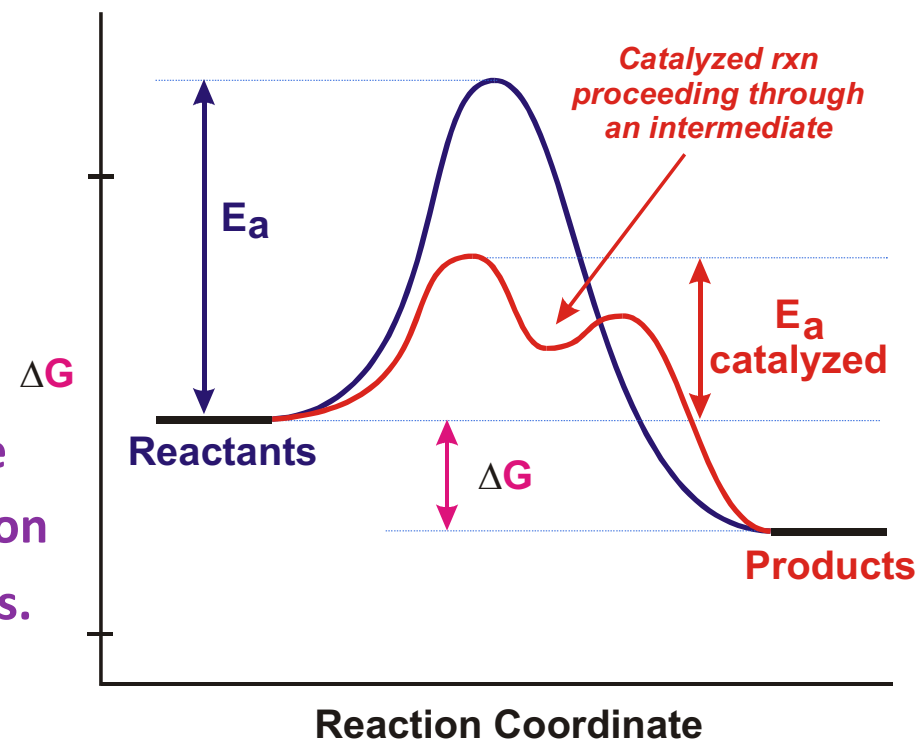


- No change in formal oxidation state
- You must have an empty orbital that is **cisoidal** to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.

# Catalytic Applications of Organometallic Complexes



- ❑ 1850 Berzelius
- ❑ 1895 Ostwald: a catalyst is a substance that changes the rate of a chemical reaction without itself appearing into the products.

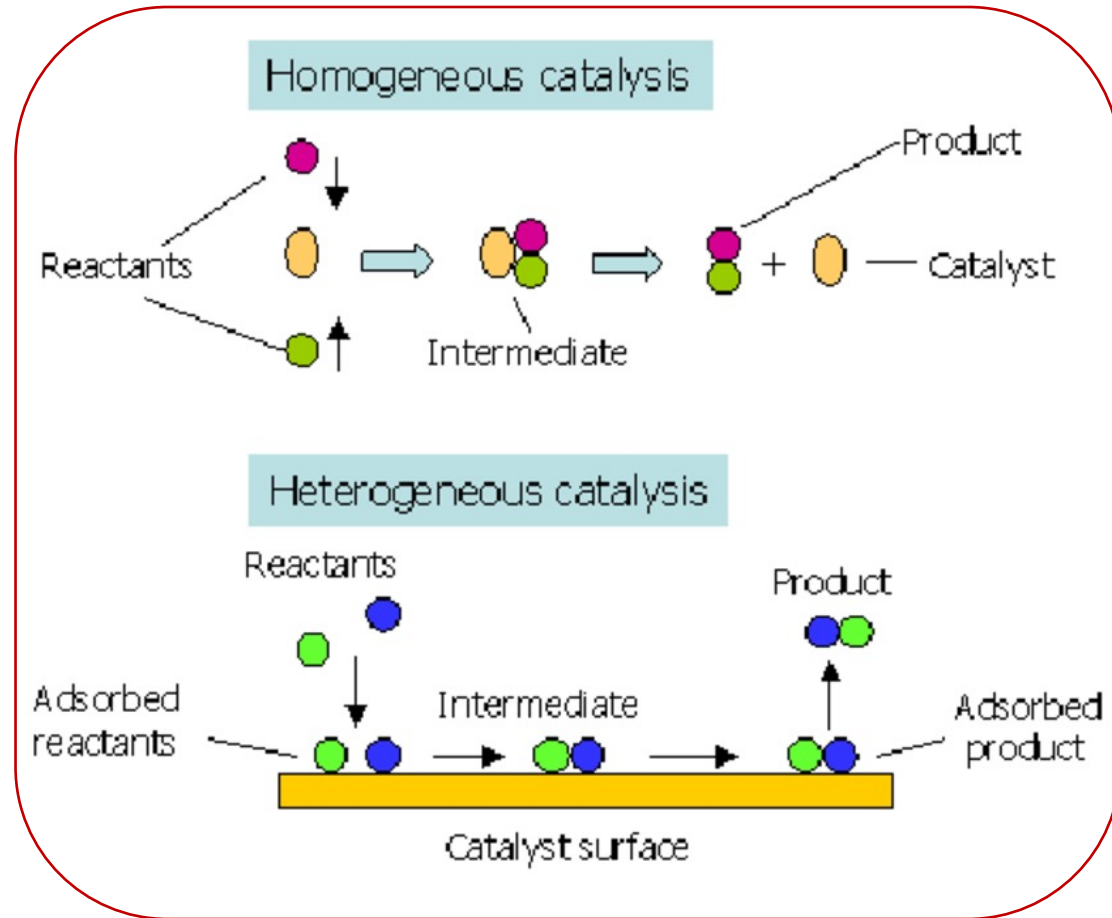
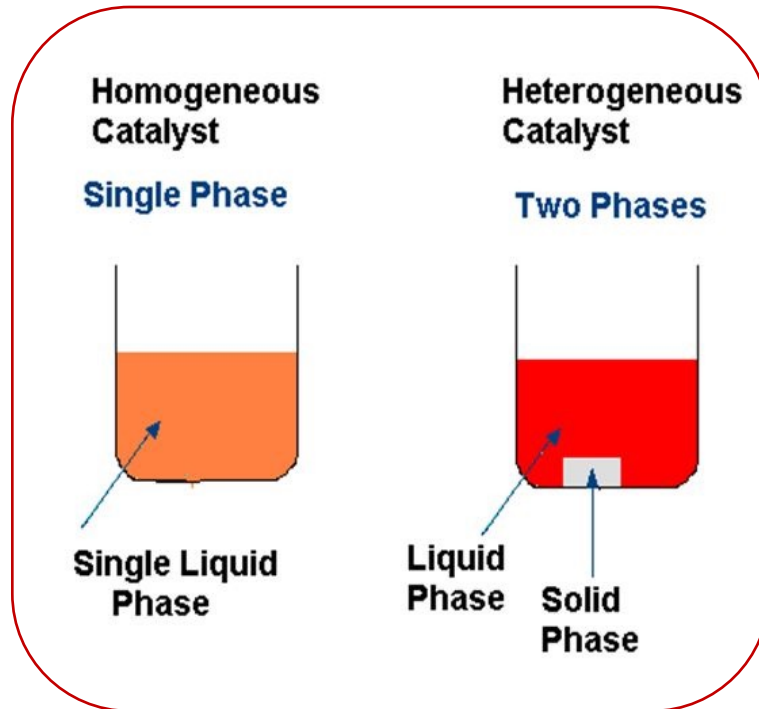


## A *catalyst*

- ~~❑ Speeds up a reaction~~ Alters the rate of the reaction
- ❑ Enables a reaction to proceed that otherwise does not without it
- ❑ Typically added in non-stoichiometric amounts
- ❑ Remains unchanged at the end of the reaction

**Catalysis is a *kinetic* phenomenon.**

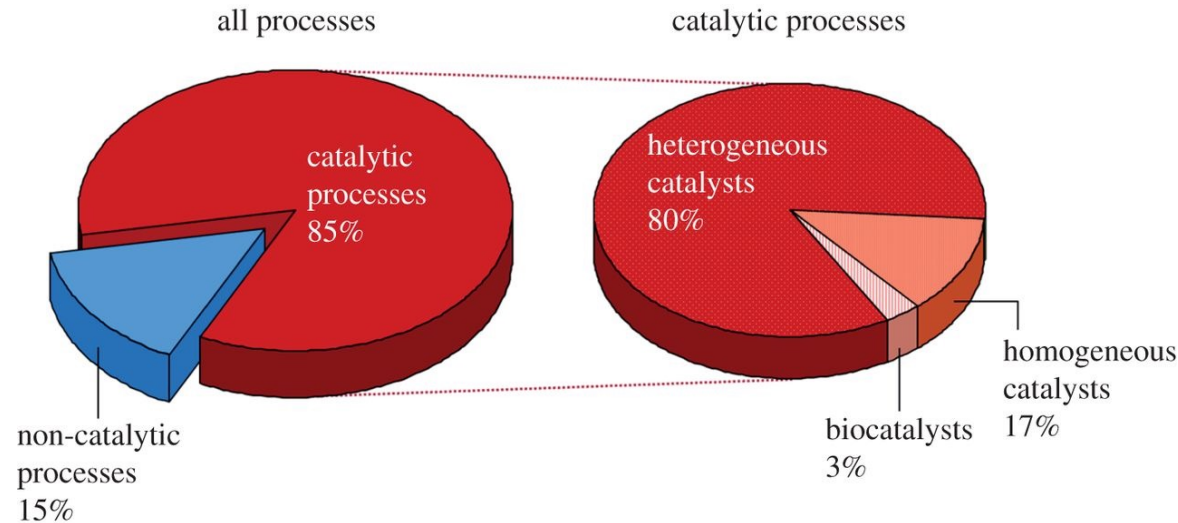
# Homogeneous And Heterogeneous Catalysis



- ❑ Homogeneous catalysis: Catalyst and reactants are in the same phase.
- ❑ Heterogeneous catalysis: Catalyst and reactants are in the different phase (the catalyst is usually insoluble; reaction occurs on its surface).

# Homogeneous And Heterogeneous Catalysis

- ❑ Most catalytic reactions in industry use heterogeneous catalysis



## Homogeneous catalysts:

### **Advantages**

- generally far more selective for a single product
- far more active
- far more easily studied from chemical & mechanistic aspects
- far more easily modified for optimizing selectivity

### **Disadvantages**

- far more sensitive to permanent deactivation
- far more difficult for achieving product/catalyst separations

# Terminologies in Catalysis

**Turnover (TO)** -- One loop through the catalyst cycle. Typically one equivalent of reactant is converted to one equivalent of product (per equivalent of catalyst).

**Turnover Frequency (TOF) or Turnover Rate** -- The number of passes through the catalytic cycle per unit time (typically sec, min or hrs). This number is usually determined by taking the # of moles of product produced, dividing that by the # of moles of catalyst used in the reaction, then dividing that by the time to produce the given amount of product.

Example: If 1 mole of catalyst converts 1000 moles of  $\text{CO} \rightarrow \text{CO}_2$  in 10 seconds then  $\text{TOF} = (1000 / (1 \cdot 10 \text{ s})) = 100 \text{ s}^{-1}$

**Turnover Number (TON)** -- The absolute number of passes through the catalytic cycle before the catalyst becomes deactivated. A large TON (e.g.,  $10^6 - 10^{10}$ ) indicates a stable, very long-lived catalyst. TON is defined as the amount of reactant (moles) divided by the amount of catalyst (moles) times the % yield of product.

Example: If 1 mole of catalyst converts 1000 moles of  $\text{CO} \rightarrow \text{CO}_2$  (100% yield) then  $\text{TON} = 1000$

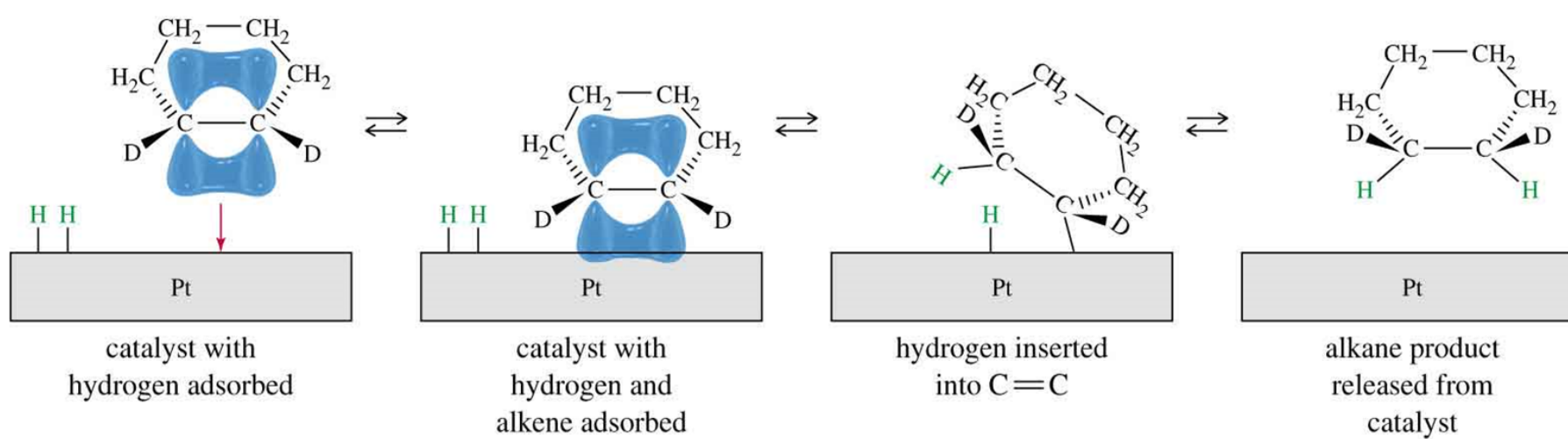
# Important Catalytic Reactions: Alkene Hydrogenation

- $\text{Alkene} + \text{H}_2 \rightarrow \text{Alkane}$
- Catalyst required, usually Pt, Pd, or Ni.
- Finely divided metal, heterogeneous

Table 7.2 Heats of Hydrogenation of Some Alkenes

Substitution	Alkene	$\Delta H^\circ_{\text{hydrog}}$	
		(kJ/mol)	(kcal/mol)
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	-137	-32.8
Monosubstituted	$\text{CH}_3\text{CH}=\text{CH}_2$	-126	-30.1
Disubstituted	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (cis)	-120	-28.6
	$\text{CH}_3\text{CH}=\text{CHCH}_3$ (trans)	-116	-27.6
	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	-119	-28.4
Trisubstituted	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	-113	-26.9
Tetrasubstituted	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	-111	-26.6

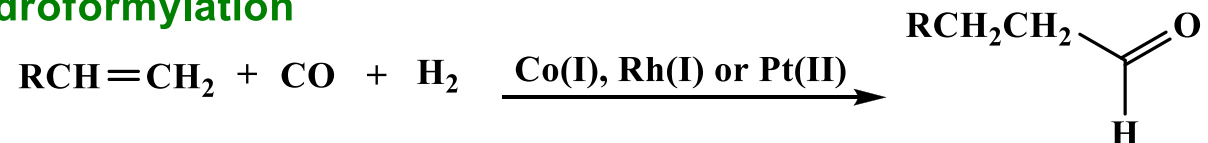
- Syn addition



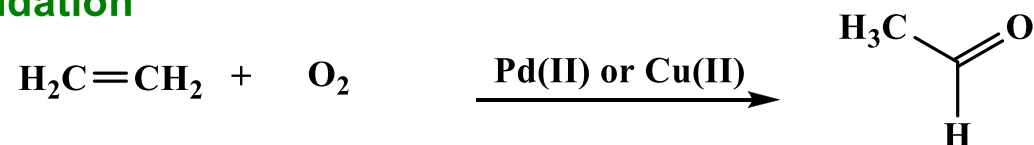


# Homogeneous Catalytic Processes

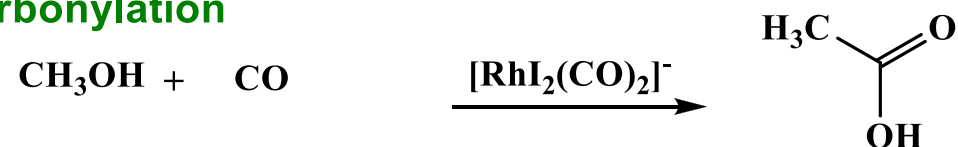
## Hydroformylation



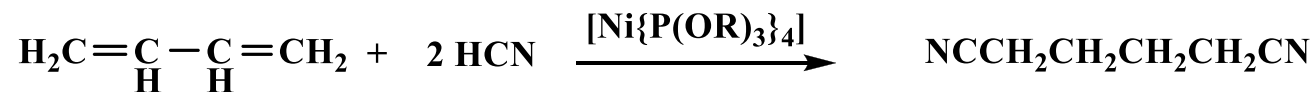
## Oxidation



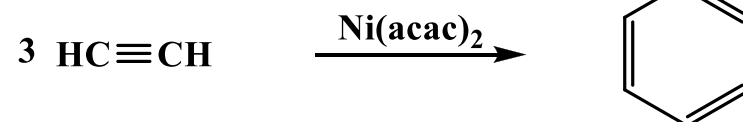
## Carbonylation



## Hydrocyanation



## Cyclotrimerization



## Hydrogenation of Alkenes



The most commonly used catalyst is the Wilkinson's Catalyst



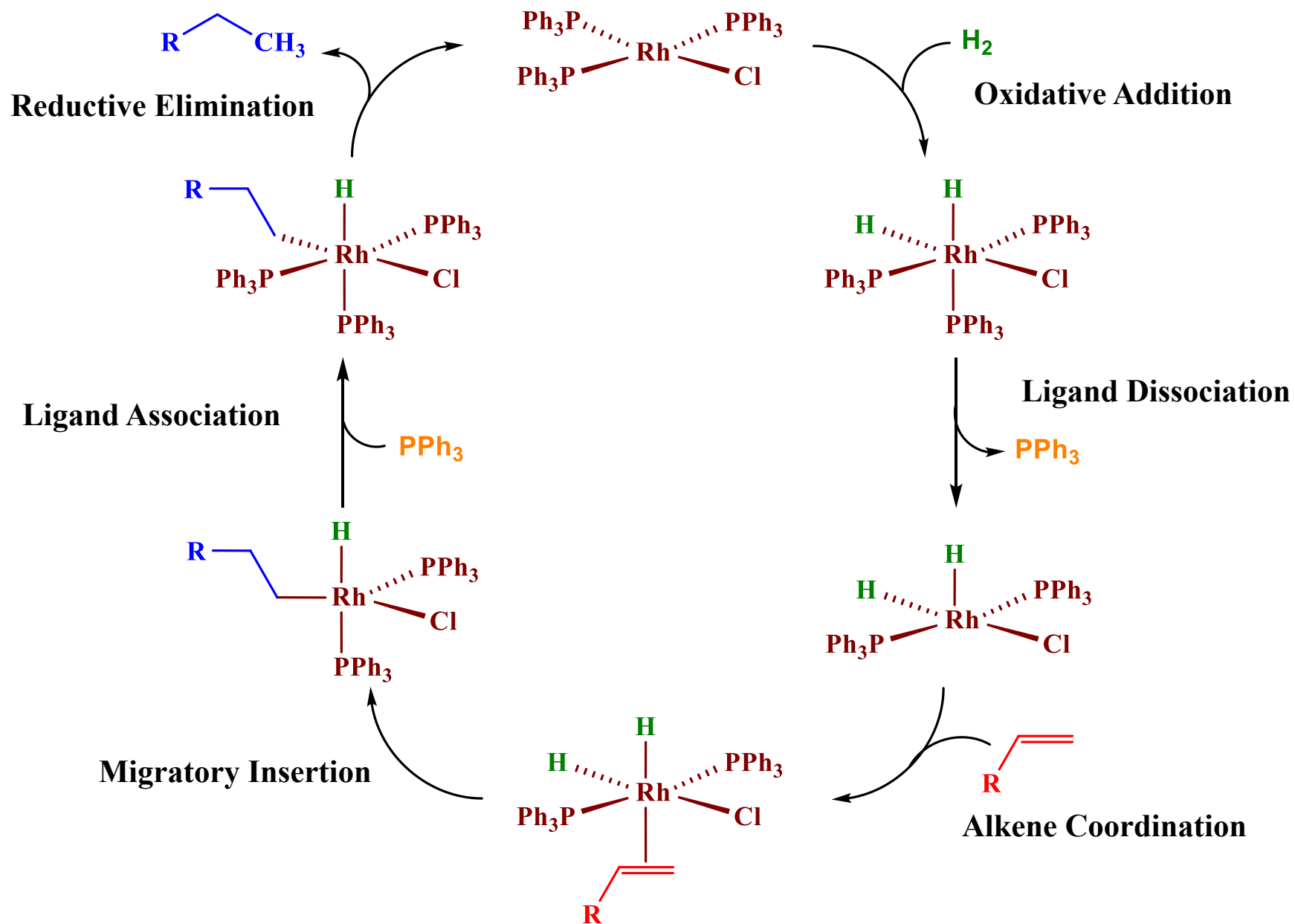
Many alkenes are hydrogenated with hydrogen at 1 atm pressure or less.

Wilkinson's catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate.

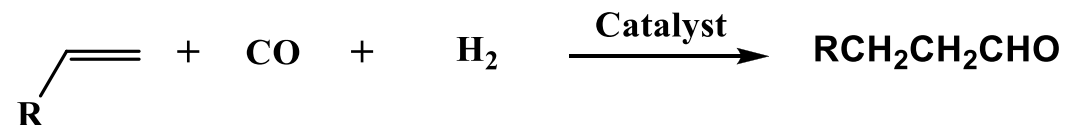
Analogous catalysts with alkyl phosphine ligands are inactive

Highly hindered alkenes and ethylene are not hydrogenated by the catalyst

# Wilkinson's Catalyst



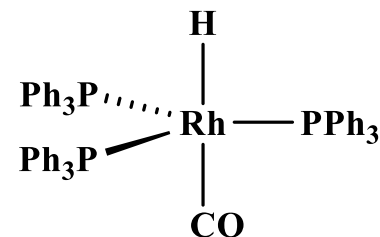
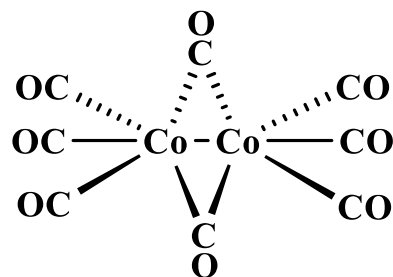
# Hydroformylation



A less common, but more appropriate name is hydrocarbonylation

Both cobalt and rhodium complexes are used as catalysts.

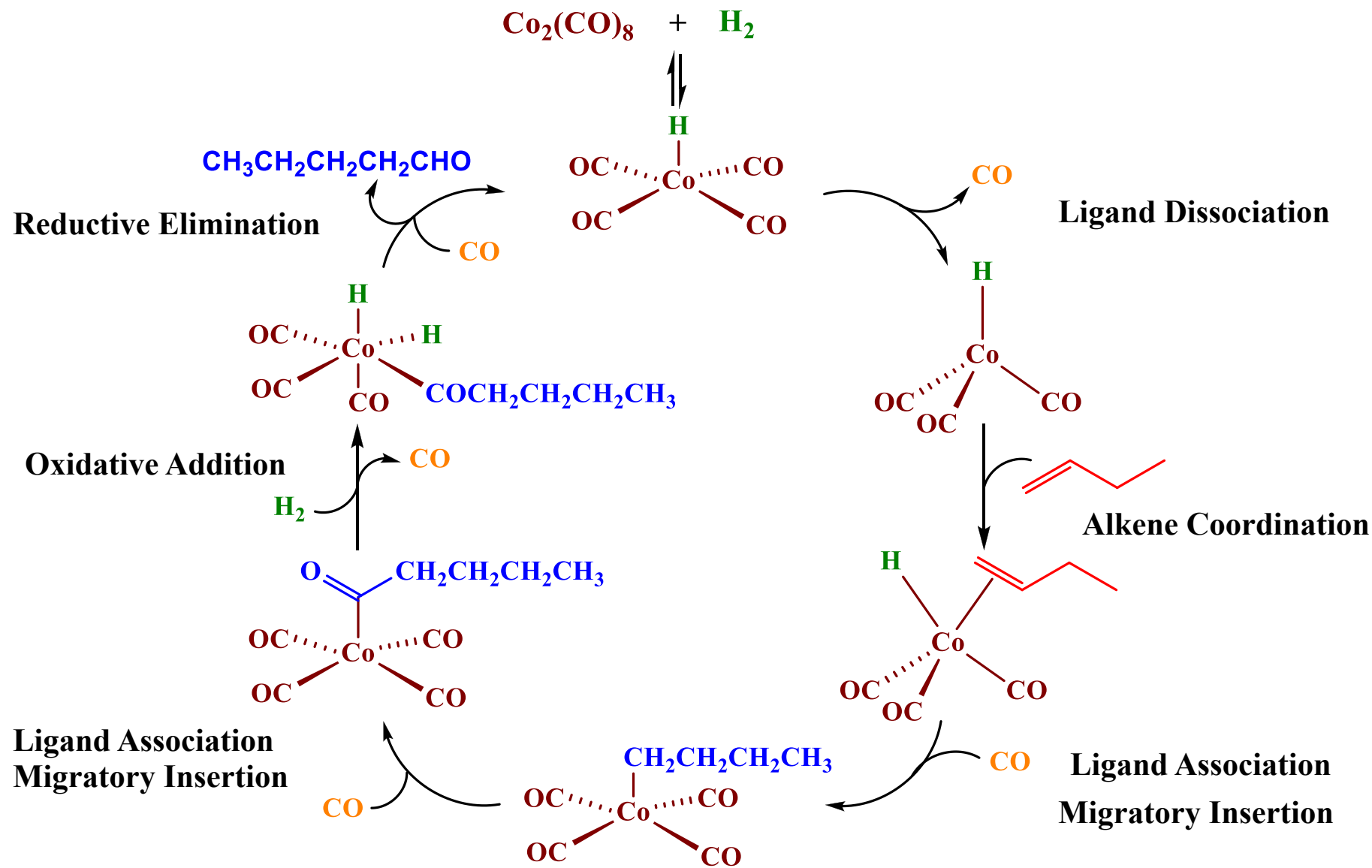
Alkene isomerization, alkene hydrogenation and formation of branched aldehydes are the possible side reactions.



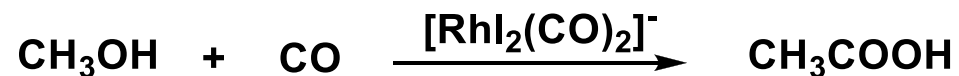
Cobalt catalysts operate at 150 °C and 250 atm, whereas Rhodium catalysts operate at moderate temperatures and 1 atm.

Rhodium catalysts promotes the formation of linear aldehydes. Cobalt catalysts do so if modified with alkylphosphine ligands.

# Hydroformylation



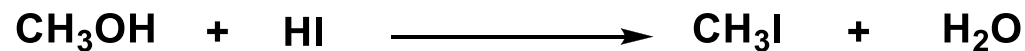
## Monsanto Acetic Acid Synthesis



All three members of the group 9 (Co, Rh and Ir) can catalyze this reaction.

A cobalt complex was initially used, which was replaced with the rhodium complex later on.

Methanol initially reacts with hydroiodic acid to give methyl iodide and  $\text{H}_2\text{O}$ . Methyl iodide reacts with the  $16e^-$  catalyst, which forms the rate-determining step.



The final product formed after the catalytic cycle is acetyl iodide, which is hydrolyzed by water to acetic acid and HI.



# Monsanto Acetic Acid Synthesis

