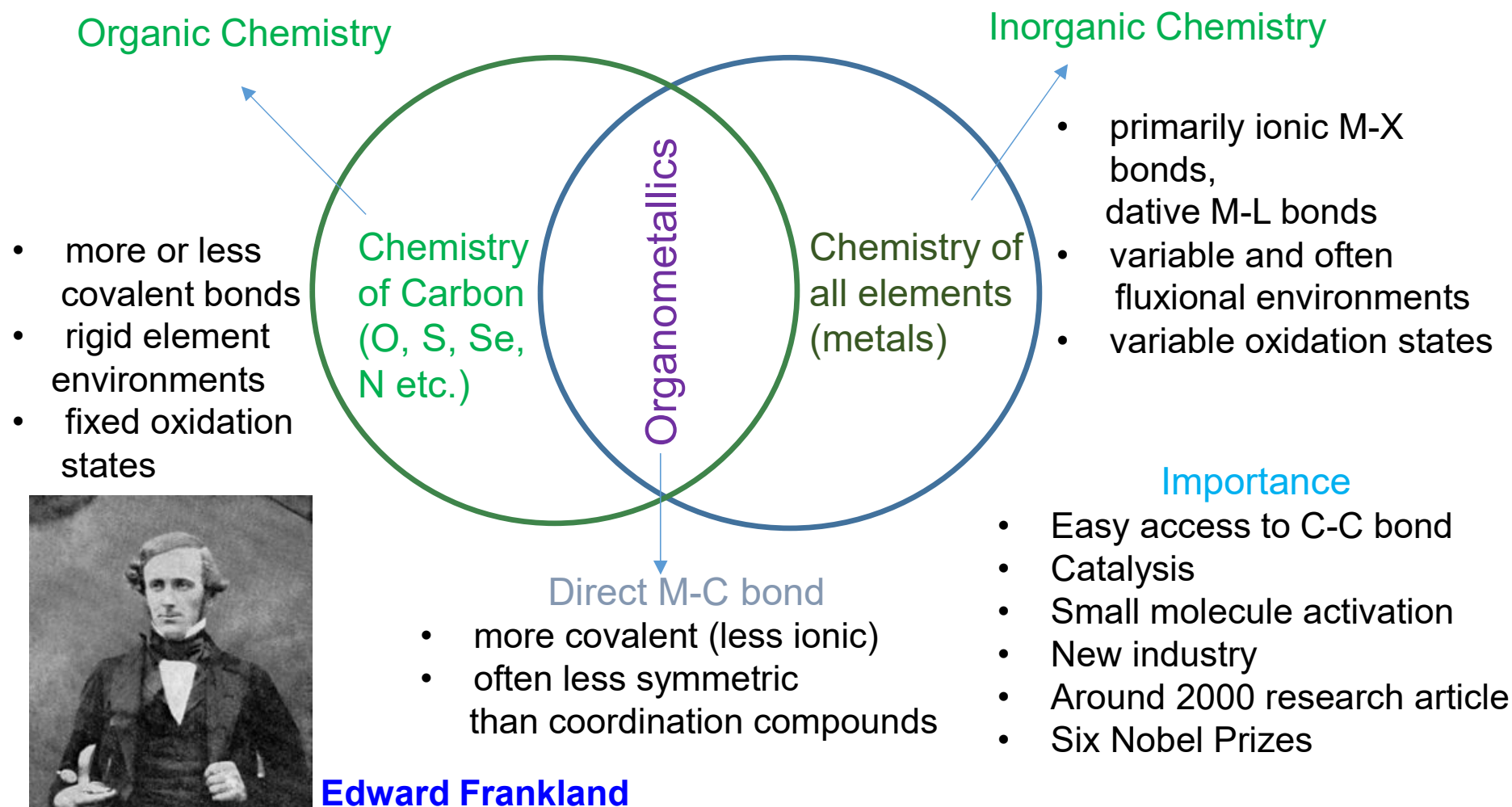


Organometallic Chemistry

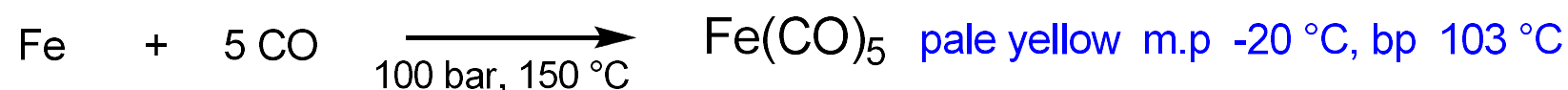


Innocent Ligands: In a metal complex, if the ligands whose oxidation state is clearly known, **Eg:** O^{2-} , Cl^-

Non-innocent ligands: In a metal complex, if the ligands whose oxidation state is not known, **Eg:** NO

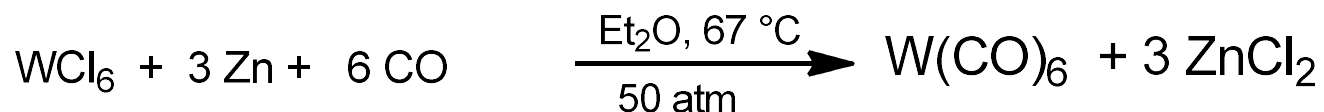
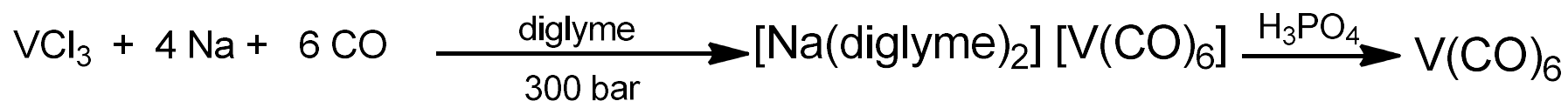
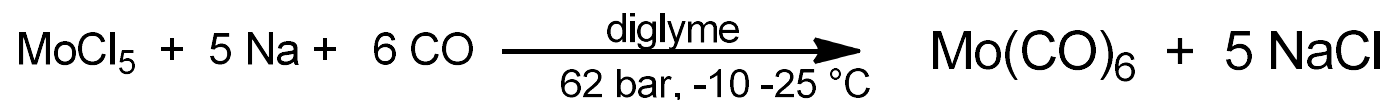
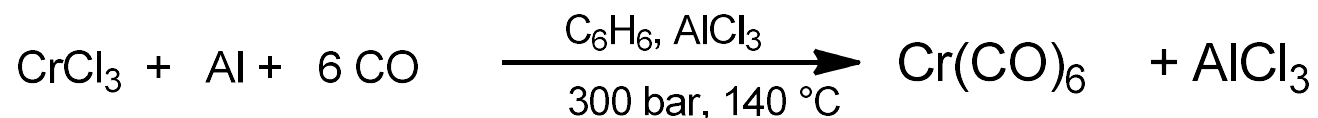
Synthesis of Metal Carbonyls

Direct carbonylation



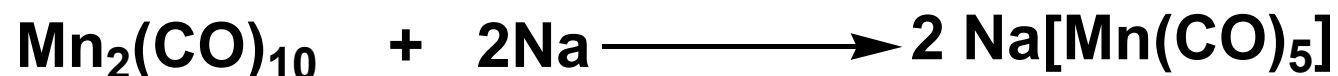
Reductive carbonylation

From Metal Halides

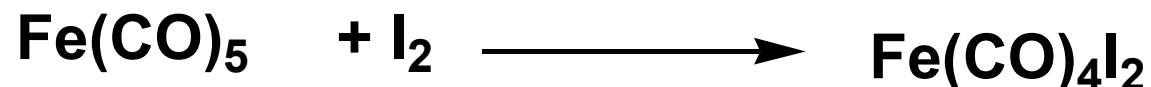


Reactions of Metal Carbonyls

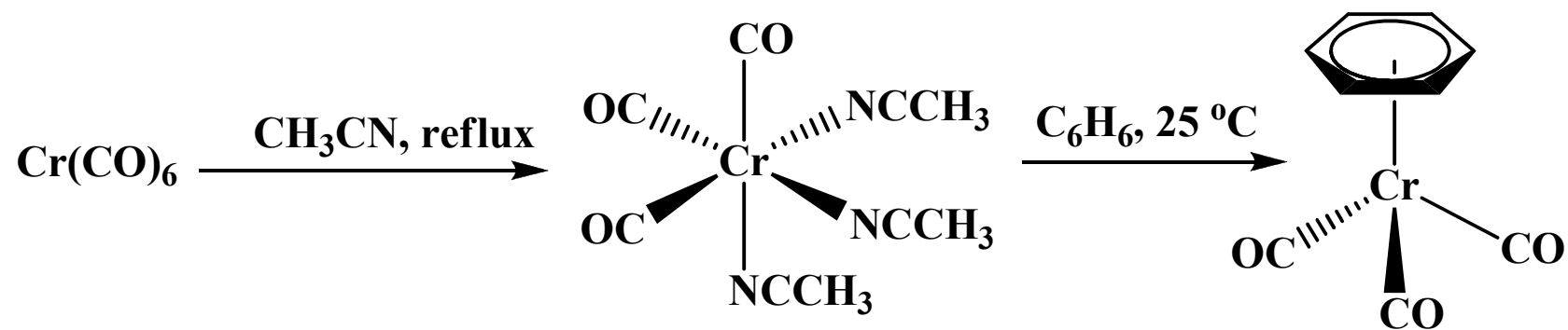
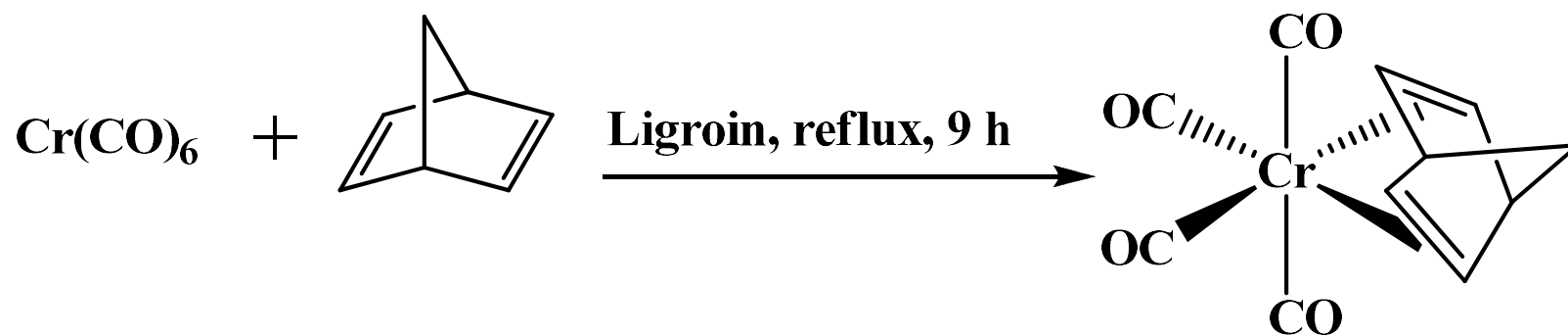
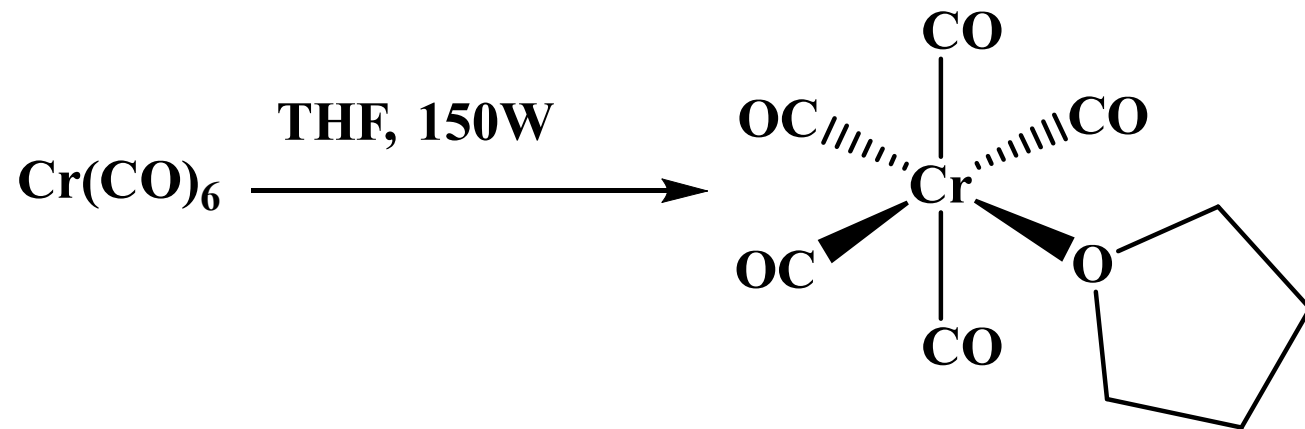
Reduction : Carbonyl anions



Oxidation : Iodocarbonyls



Activation of metal carbonyls

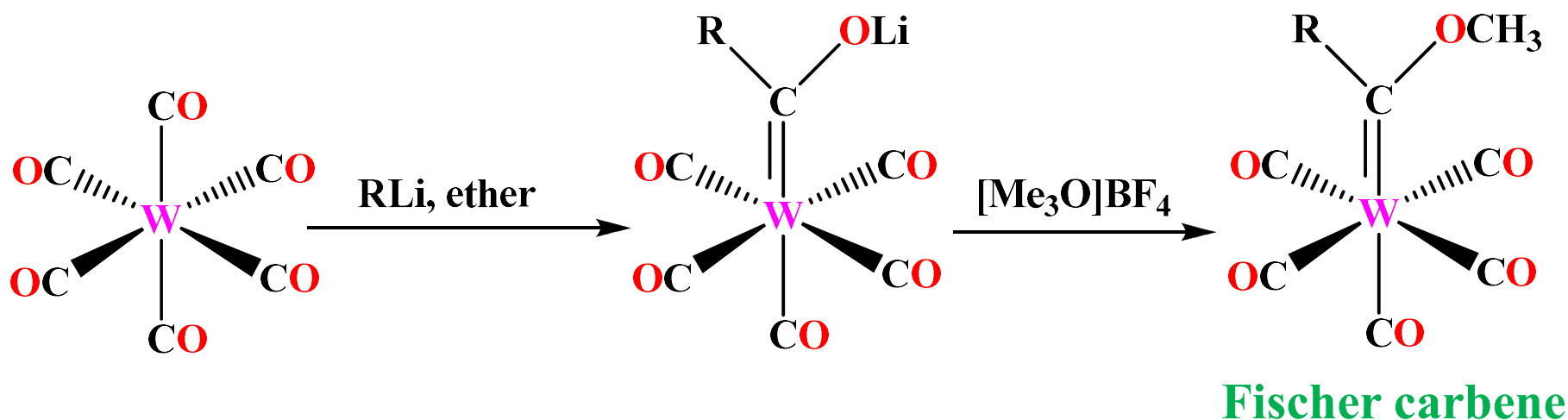


Disproportionation

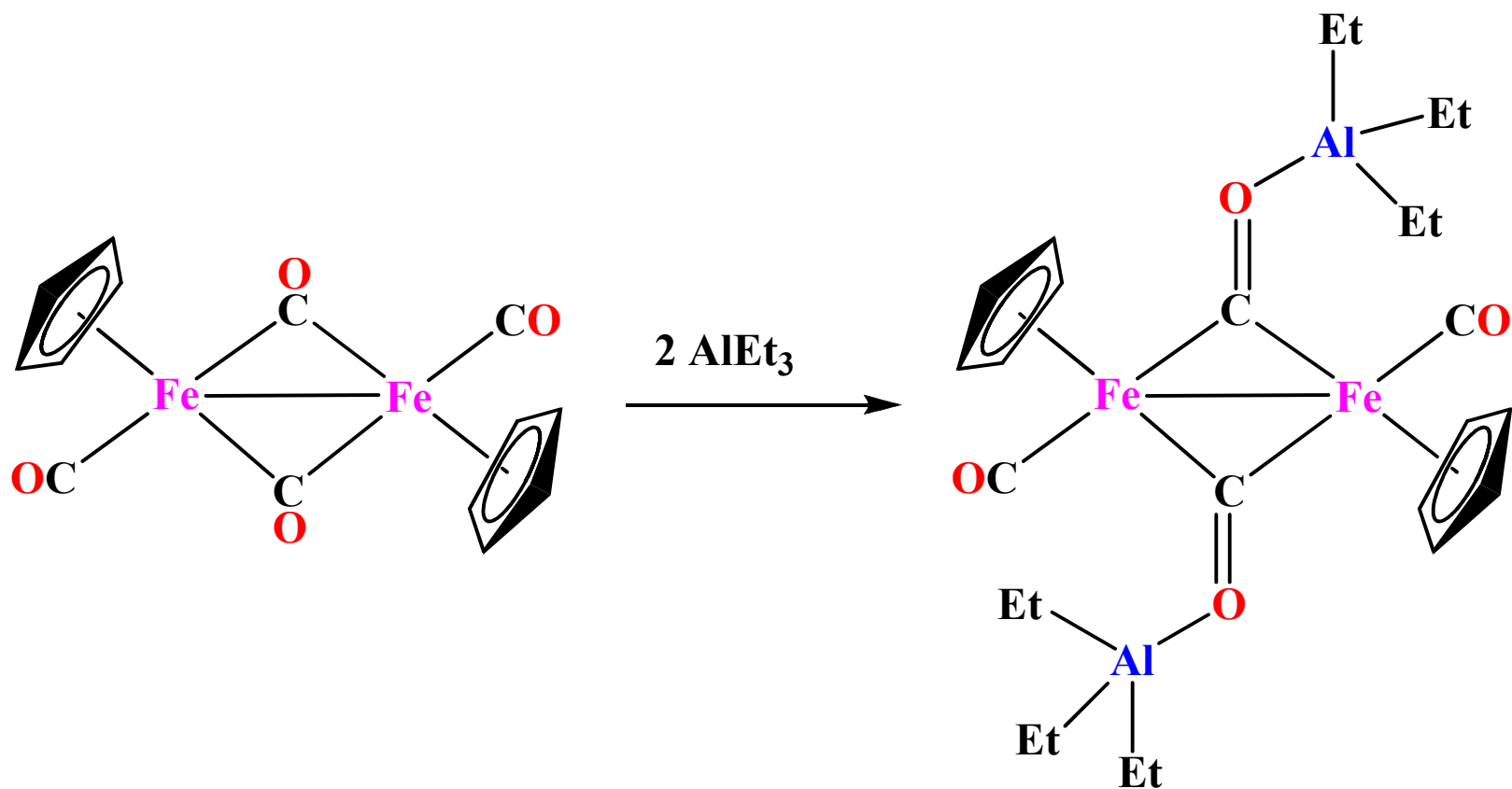
Some multi-metal carbonyls can undergo **disproportionation** in the presence of suitable ligands



Nucleophilic addition to CO

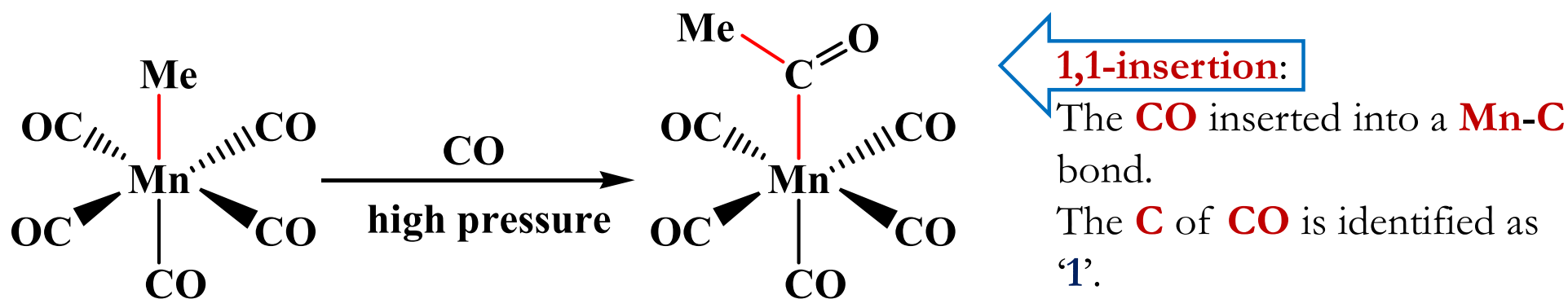


Electrophilic addition to the carbonyl oxygen

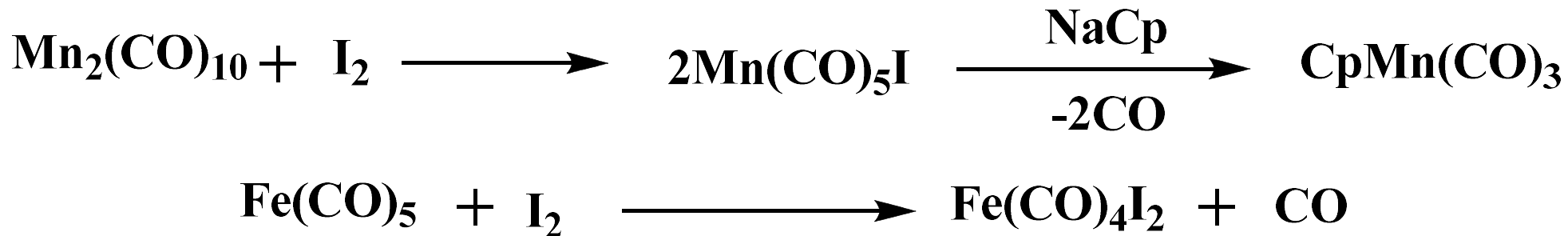


Migratory Insertion of carbonyls

- The ability of metal carbonyls, especially metal carbonyl anions, to undergo **migratory insertion** has been utilized in organic synthesis for the preparation of **acyl substituted metal carbonyls**.
- These are good precursors for a host of carbonyl containing organic molecules.

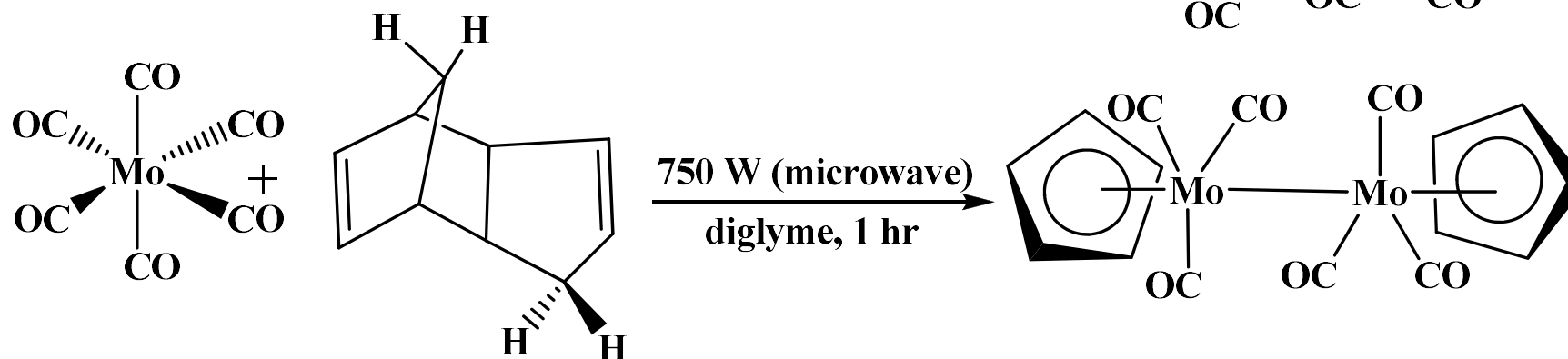
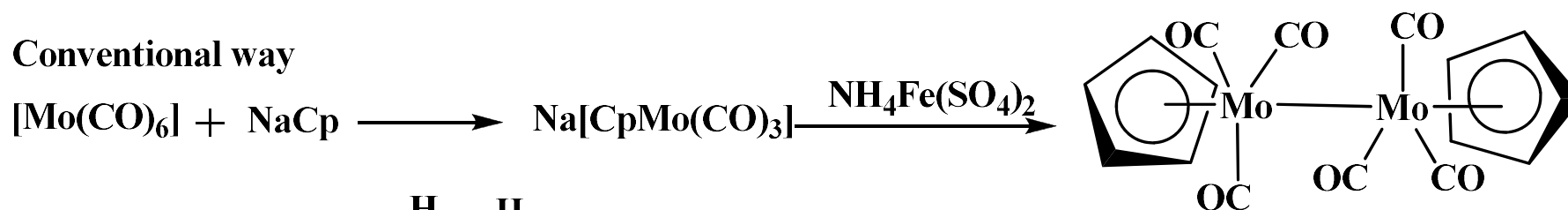


Oxidative decarbonylation



Microwave assisted carbonyl substitution

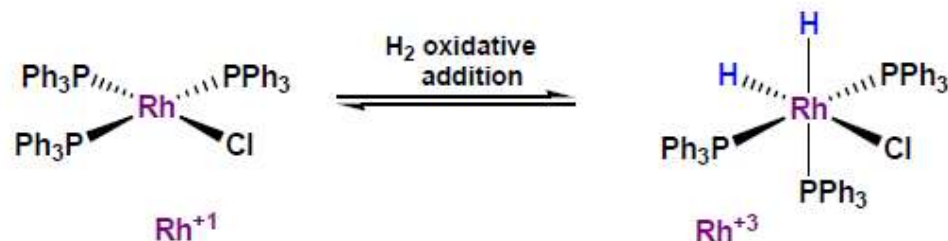
Conventional way



Carbonyl substitution reactions under **thermal condition** can often be improved by **accelerated** and **simplified** by using **microwave radiation**.

Oxidative addition & Reductive elimination

- When **addition** of ligands are accompanied by **oxidation** of the **metal**, it is called an **oxidative addition** reaction

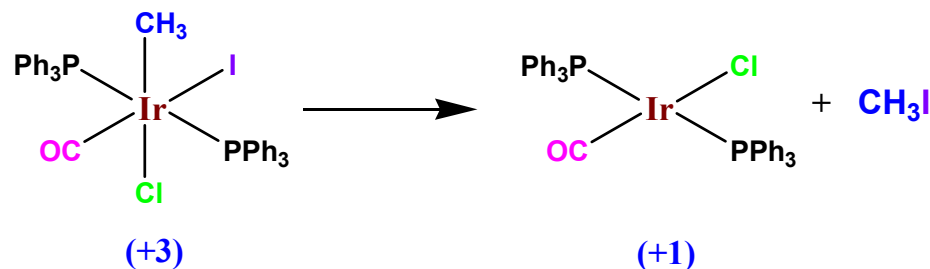


- **Oxidation state** of the **metal** increase by **2**
- **Coordination number** of the **metal** increase by **2**
- **2 anions** get coordinated to the **metal**

Conditions to be satisfied by **metal**

1. Availability of **non-bonded electron density**
2. Availability of **2 vacant coordination sites**
3. **Stable oxidation** states separated by **2**

- **Elimination** of ligands are accompanied by **reduction** of the **metal**, it is called an **reductive elimination** reaction



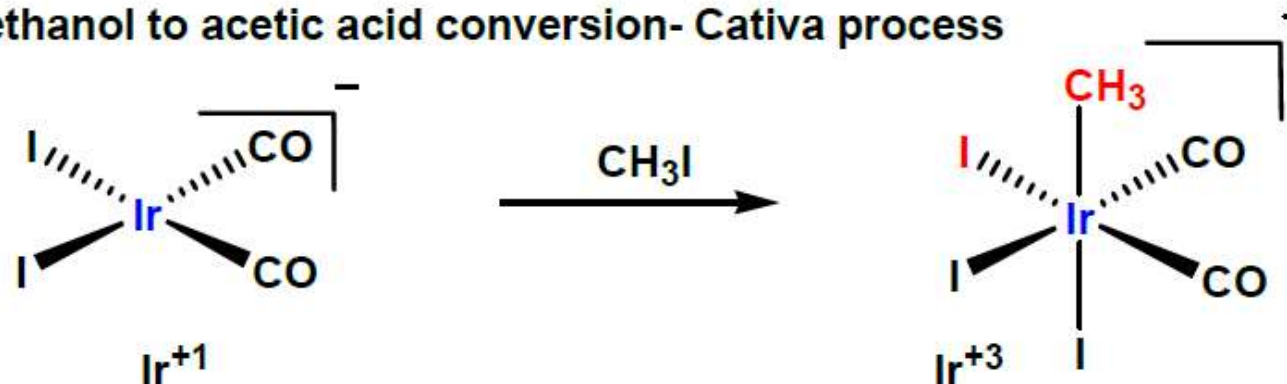
- **Oxidation state** of the **metal** decrease by **2**
- **Coordination number** of the **metal** decrease by **2**
- **2 cis** oriented **anionic ligands** form a **σ bond** and leave the metal

Requirements

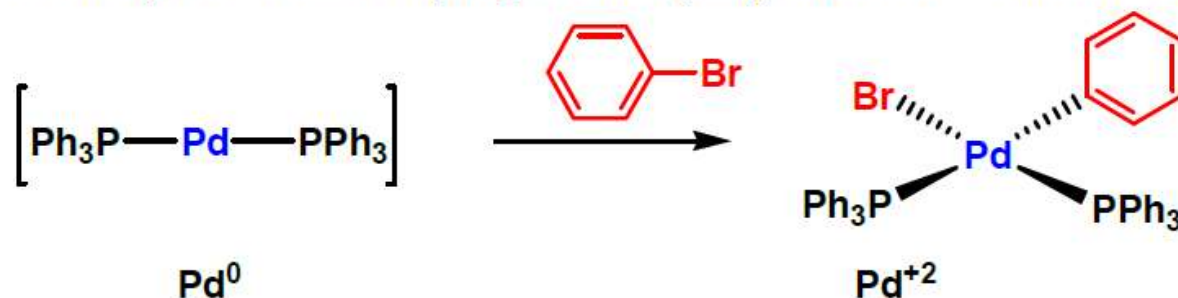
1. **High formal positive charge** on the metal
2. Presence of **bulky groups** on the metal
3. **Electronically stable** product

Oxidative addition: examples

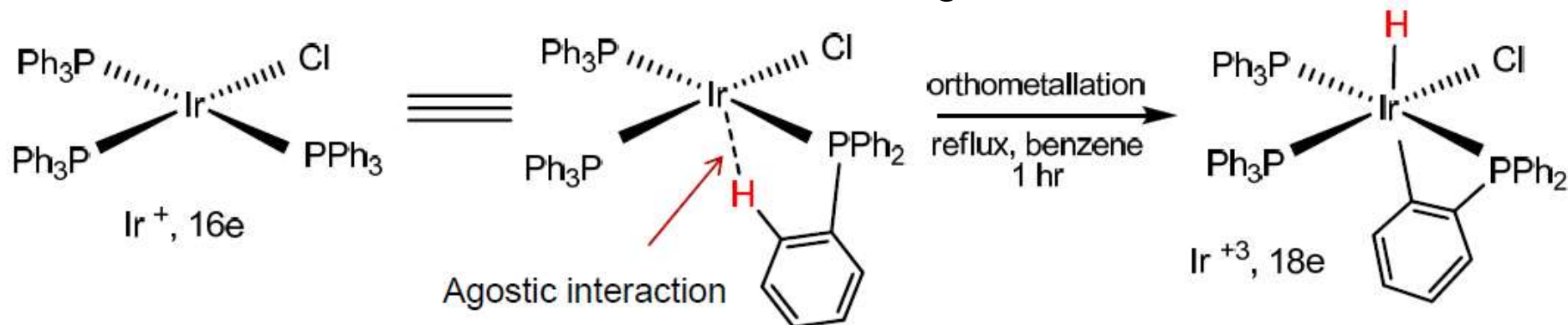
Methanol to acetic acid conversion- Cativa process



Pd catalyzed Cross coupling of Ar-B(OH)_2 and Ar-X – Suzuki Coupling

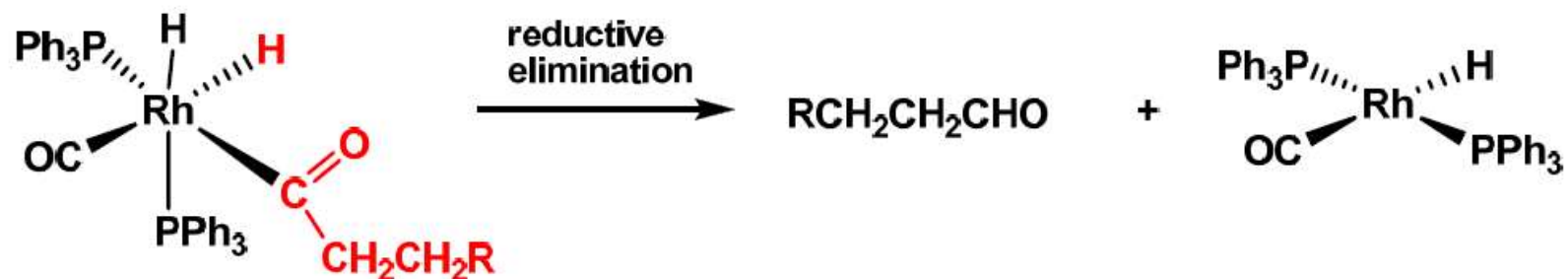


Oxidative addition involving **C-H** bonds

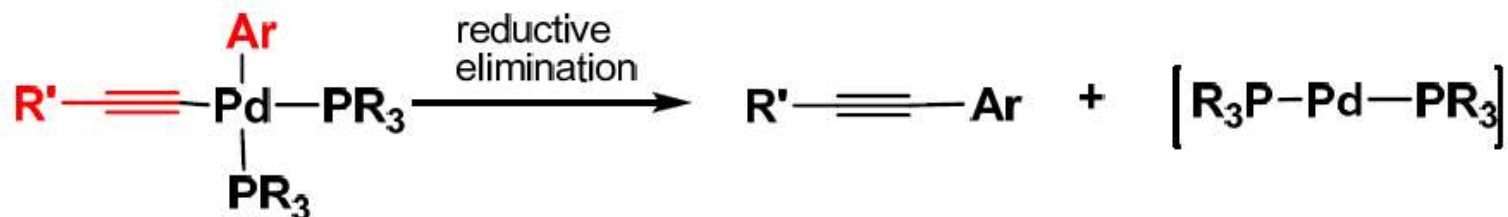


Reductive elimination: examples

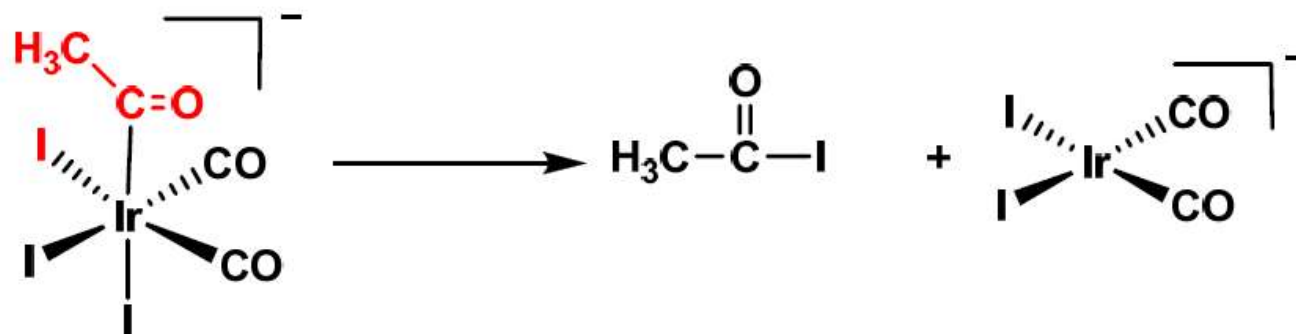
Hydroformylation (conversion of an alkene to an aldehyde)



Sonogashira Coupling (coupling of a terminal alkyne to an aryl group)



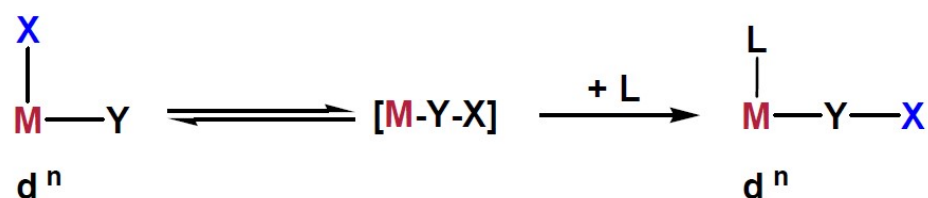
Cativa Process (Methanol to Acetic acid)



Migratory insertion & β -hydride elimination

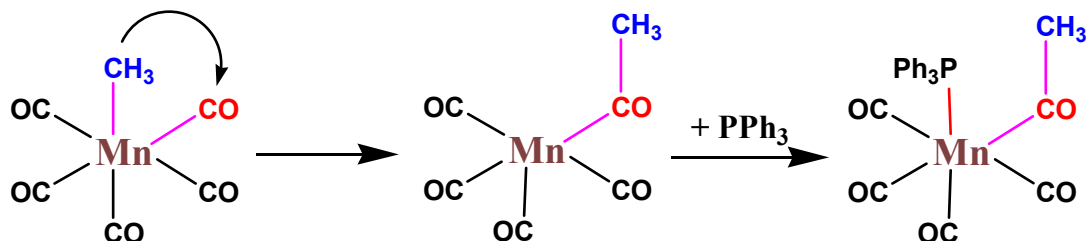
Migratory insertion

A reaction in which a **ligand** or a **group of atoms** **cis** to one another **migrate** to the other, and **forms a bond with an atom of the other group**



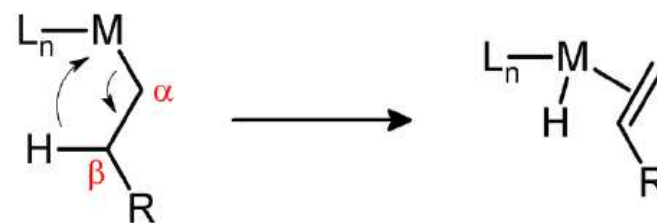
Features

- No change in **oxidation state** of the **metal**
- A **vacant coordination** sites is created
- The **vacant site** is occupied by a **ligand**
- The **ligand/groups** involved, must be **cis** to each other



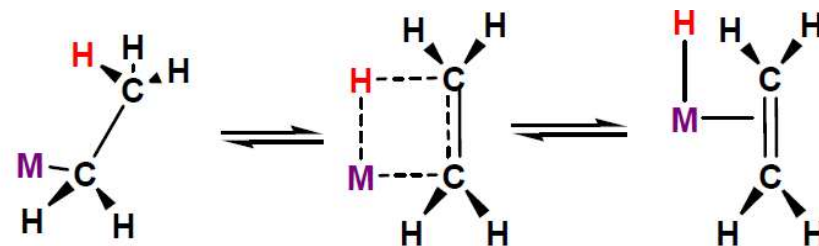
β -hydride elimination

A reaction in which an **alkyl group** having a **β -hydrogen**, **σ -bonded** to the **metal** is converted to **metal bonded hydride** and **π -bonded alkene**.



Condition

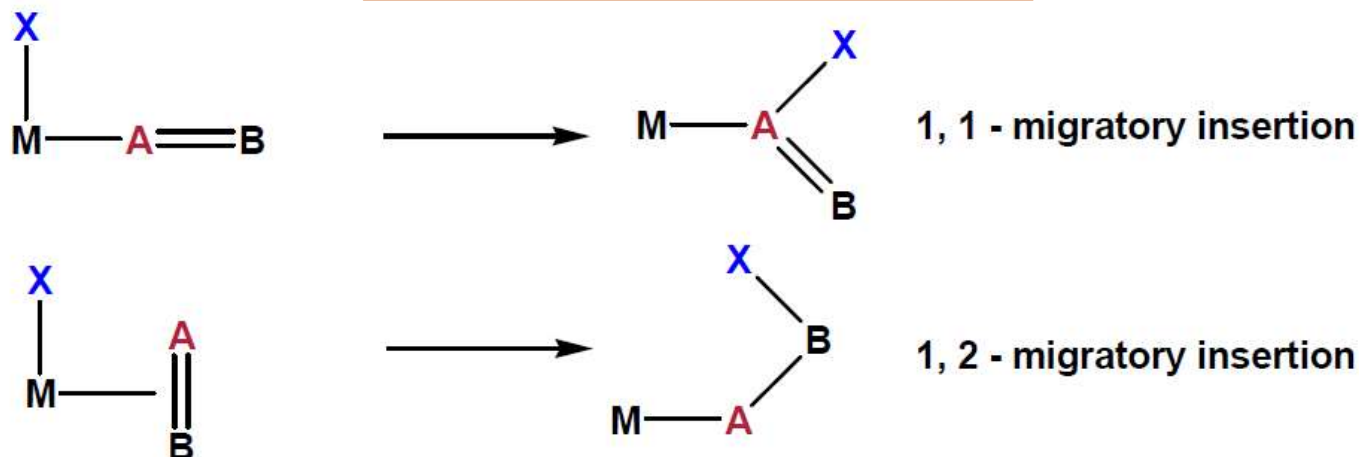
- The **alkyl group** should have a **β -hydrogen**
- A **vacant site** **cis** to the **σ -bonded alkyl group**
- If the **alkyl** is **CH₃**, it **wont**. But **ethyl**, **propyl**, **butyl** having **β -hydrogen** do.



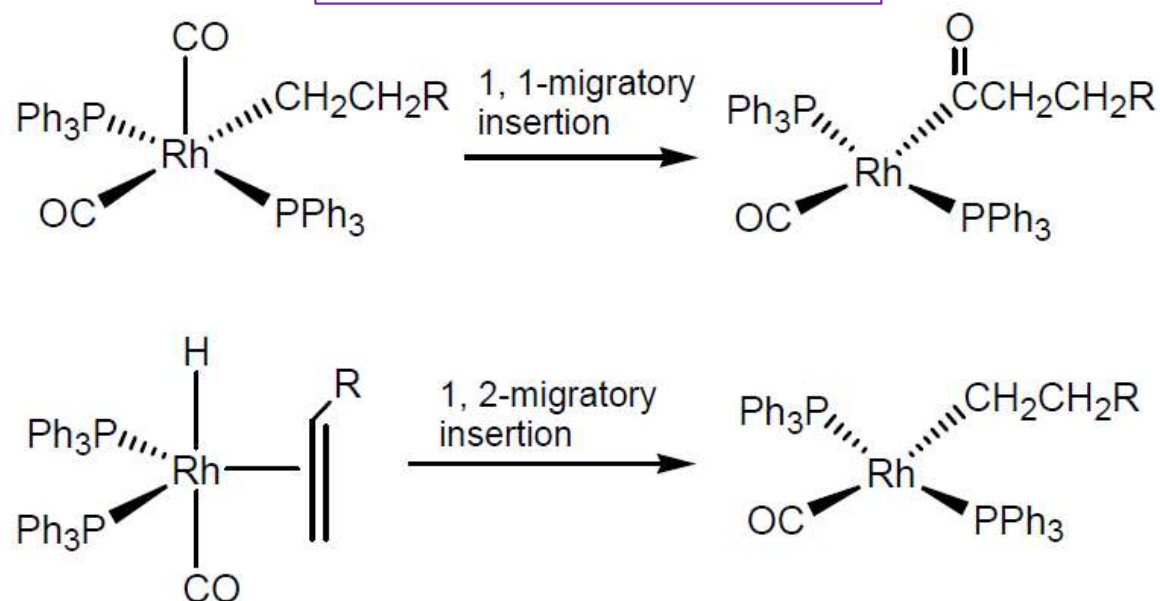
Mechanism

Migratory insertion: examples

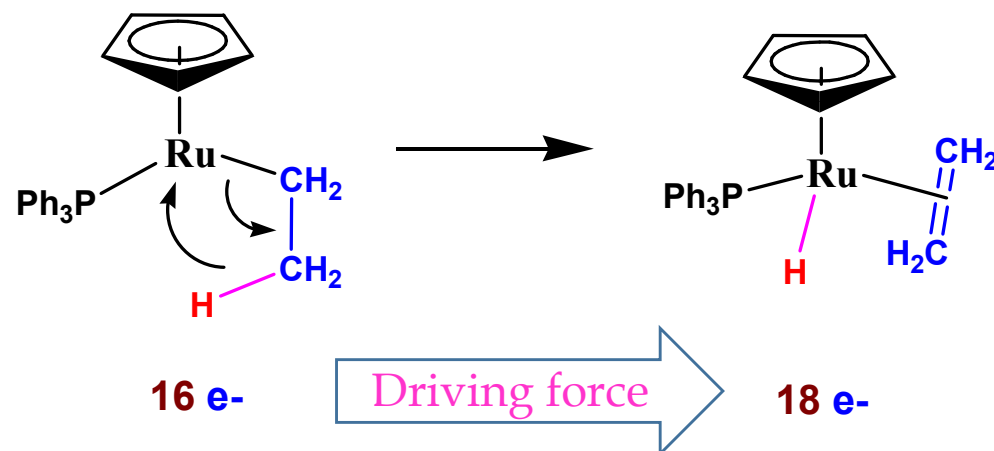
Types of Migratory Insertion



Examples of either type



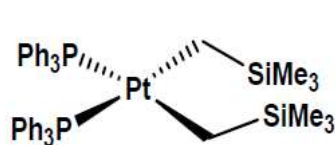
β -hydride elimination: examples



β -hydrogen elimination does not occur if,

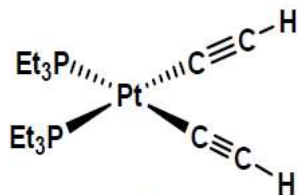
- The alkyl group does not have a β -hydrogen.
Eg.: $-\text{CH}_2\text{Ph}$, $-\text{CH}_2-\text{C}(\text{CH}_3)_3$, $-\text{CH}_2\text{Si}(\text{CH}_3)_3$
- β -hydrogen on the alkyl is unable to approach the metal.
Eg.: $-\text{C}\equiv\text{CH}$
- The $\text{M}-\text{C}-\text{C}-\text{H}$ unit is not in the same plane

Select the most unstable from the following. Justify your choice.



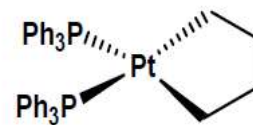
A

No β -H



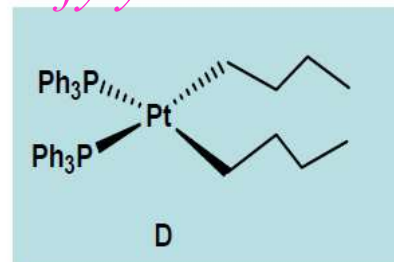
B

β -H unable to approach M



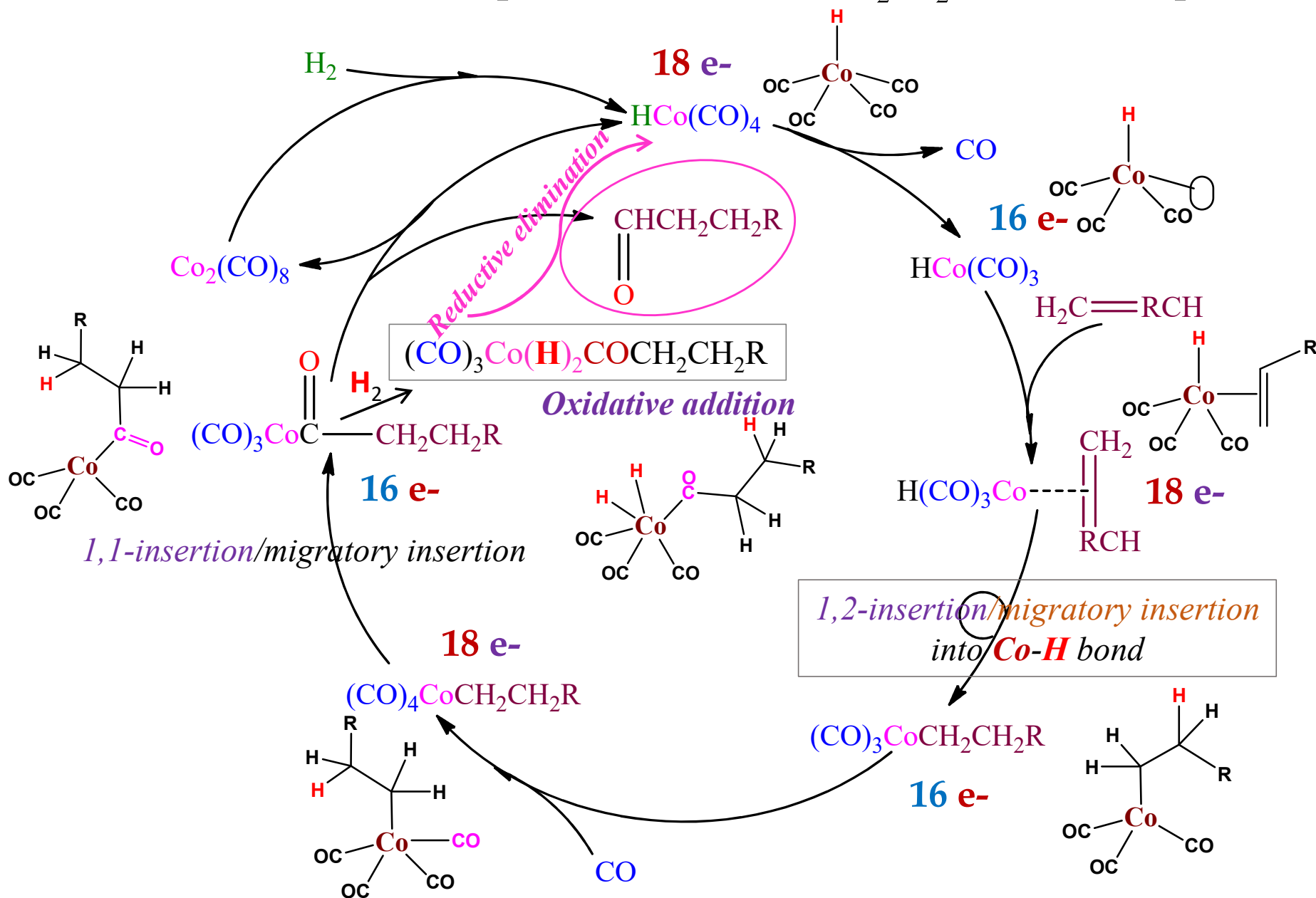
C

MCCH unit will not be coplanar



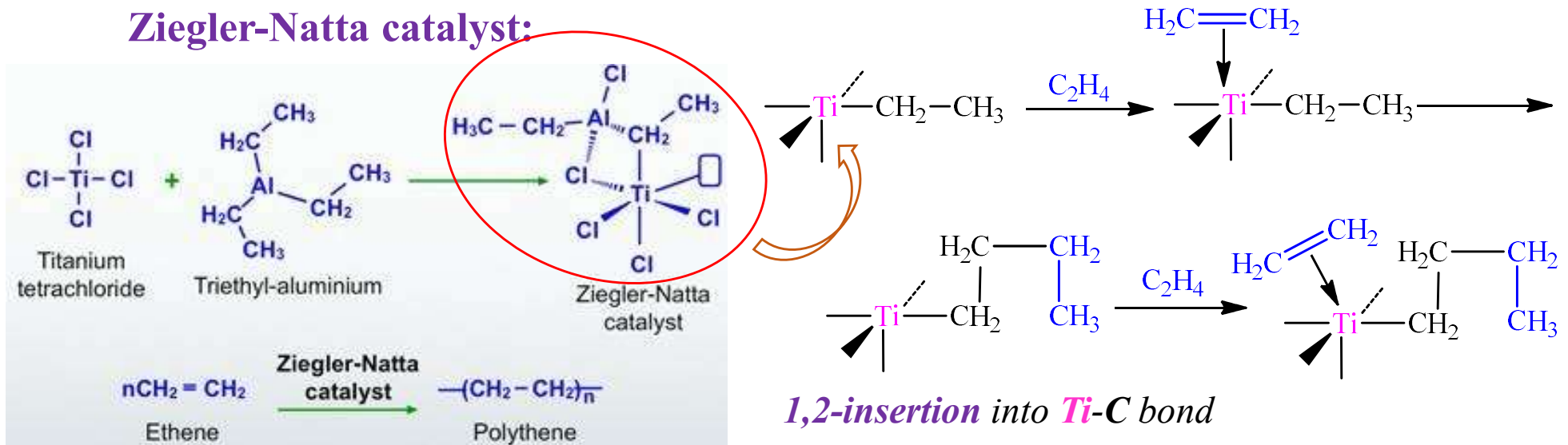
D

Hydroformylation



Ziegler-Natta catalysis

Ziegler-Natta catalyst:



- **Isotactic polymer** is formed by **stereo-regular polymerization**
- Polymerized product is released by **β -hydride** elimination a) from polymer, b) by Hydride transfer to monomer c) by hydrogenation

