

Module 10 : Reaction mechanism

Lecture 3 : Nucleophilic and Electrophilic Addition and Abstraction

Objectives

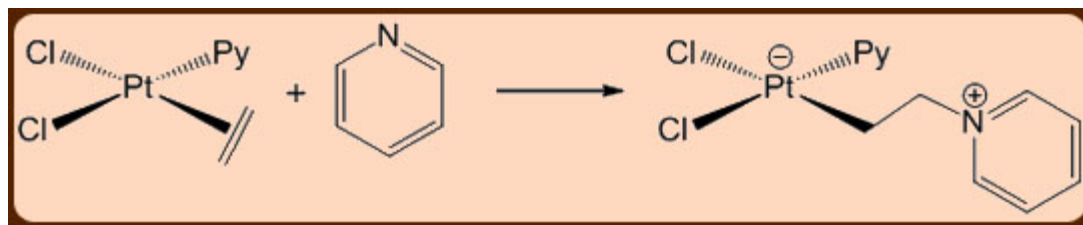
In this lecture you will learn the following

- Ligand activation by metal that leads to a direct external attack at the ligand.
- Nucleophilic addition and nucleophilic abstraction reactions.
- Electrophilic addition and electrophilic abstraction reactions.

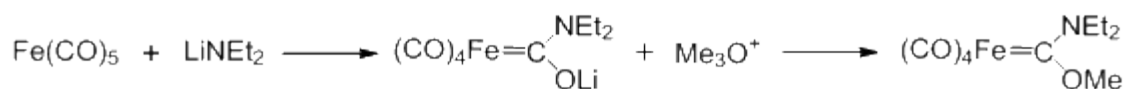
The nucleophilic and electrophilic substitution and abstraction reactions can be viewed as ways of activation of substrates to allow an external reagent to directly attack the metal activated ligand without requiring prior binding of the external reagent to the metal. The attacking reagent may be a nucleophile or an electrophile. The nucleophilic attack of the external reagent is favored if the L_nM fragment is a poor π -base and a good σ -acid *i.e.*, when the complex is cationic and/or when the other metal bound ligands are electron withdrawing such that the ligand getting activated gets depleted of electron density and can undergo an external attack by a nucleophile Nu^- , like $LiMe$ or OH^- . The attack of the nucleophiles may result in the formation of a bond between the nucleophiles and the activated unsaturated substrate, in which case it is called nucleophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the nucleophilic abstraction. The nucleophilic addition and the abstraction reactions are discussed below.

Nucleophilic addition

An example of a nucleophilic addition reaction is shown below.

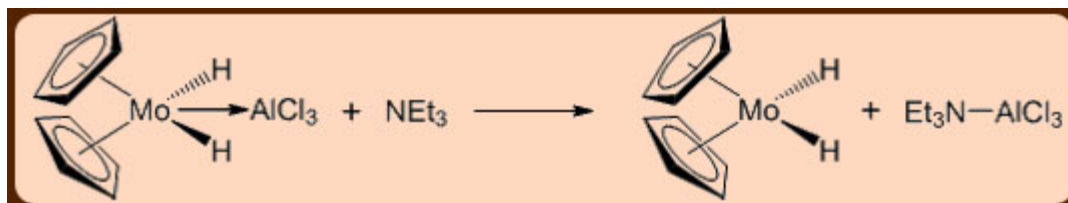


Carbon monoxide (CO) as a ligand can undergo nucleophilic attack when bound to a metal center of poor π -basicity, as the carbon center of the CO ligand is electron deficient owing to the ligand to metal σ -donation not being fully compensated by the metal to ligand π -back donation. Thus, activated CO ligand undergoes nucleophilic attack by the lithium reagent to give an anionic acyl ligand, which upon alkylation generates the famous Fischer carbene complex.



Nucleophilic abstraction

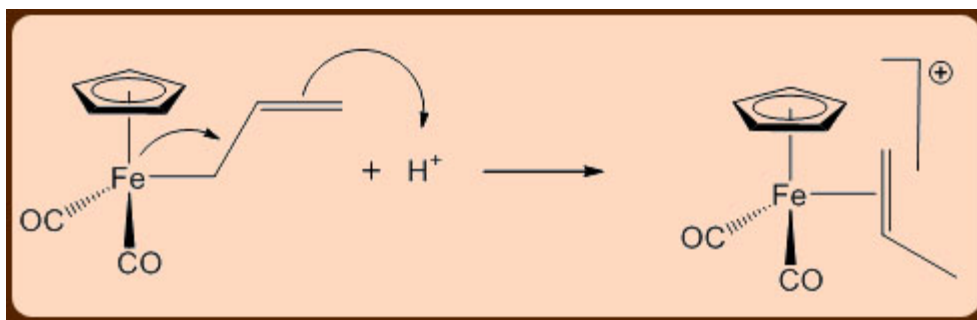
An example of a nucleophilic abstraction reaction is shown below.



Electrophilic addition

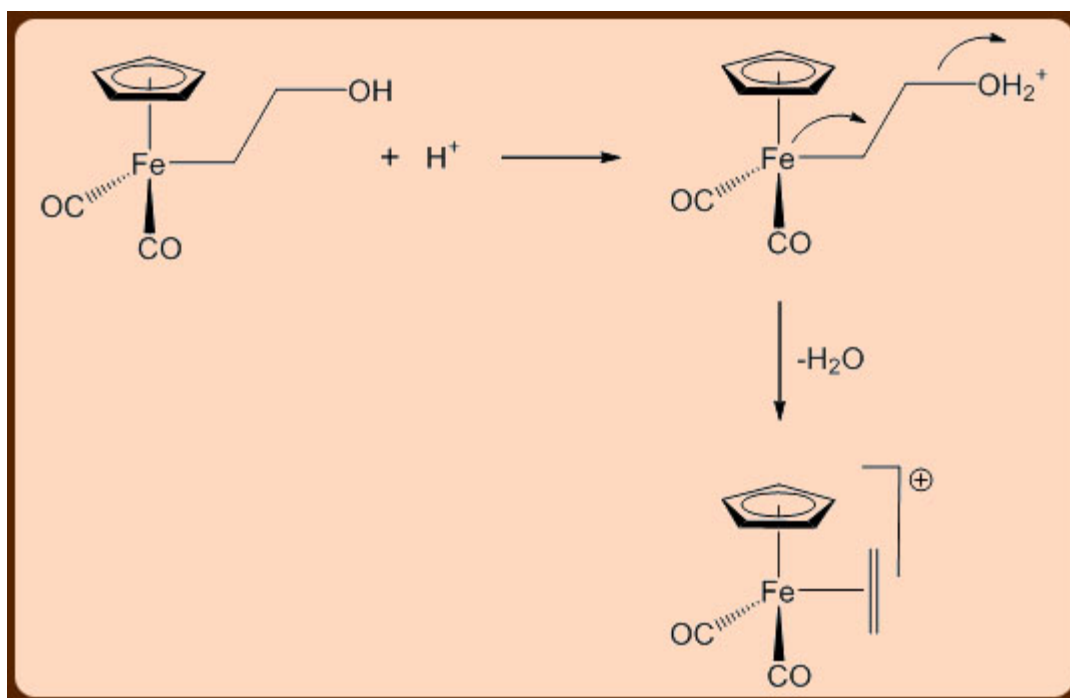
Similar to the nucleophilic addition and abstraction reactions, the electrophilic counterparts of these reactions also exist. An electrophilic attack is favored if the L_nM fragment is a good π -base and a poor σ -acid *i.e.*, when the complex is anionic with the metal center at low-oxidation state and/or when the other metal bound ligands are electron donating such that the ligand getting activated becomes electron rich from the π -back donation of the metal center and thus can undergo an external attack by an electrophile E^+ like H^+ and CH_3I . The attack of the electrophiles may result in the formation of a bond

between the electrophile and the activated unsaturated substrate, in which case it is called electrophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the electrophilic abstraction.

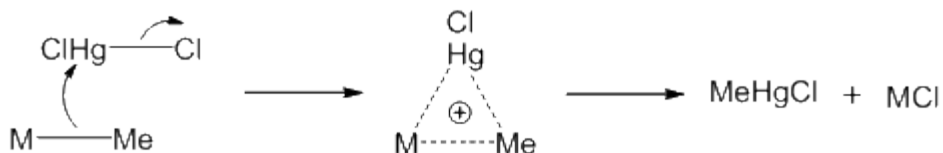


Electrophilic abstraction

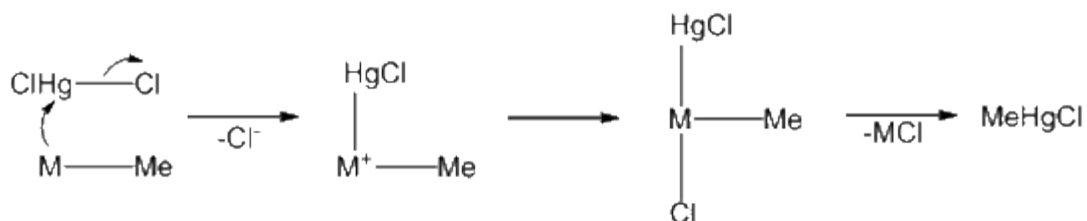
An example of an electrophilic abstraction reaction is shown below.



Alkyl abstractions are often achieved by Hg^{2+} that can proceed in two ways, (i) by an attack at the α -carbon of a metal alkyl bond leading to an inversion of configuration at the alkyl carbon and (ii) by an attack at the metal center leading to retention of configuration at the alkyl carbon. The inversion of configuration proceeds by the following pathway.



The retention of configuration proceeds by the following pathway.



Problems

1. How many types of direct additions of a nucleophile and an electrophile is possible on a metal activated unsaturated ligand substrate?

Ans: Nucleophilic addition and electrophilic addition.

2. How many types of direct abstraction of a nucleophile and an electrophile is possible on a metal activated unsaturated ligand substrate?

Ans: Nucleophilic abstraction and electrophilic abstraction.

Self Assessment test

1. What type of metal center favor nucleophilic addition and abstraction processes?

Ans: Electron deficient metal centers with poor π -basicity and a good σ -acidity.

2. What type of metal center favor electrophilic addition and abstraction processes?

Ans: Electron rich metal centers with good π -basicity and a poor σ -acidity.

Summary

A ligand, when activated by coordination to a metal, may get directly attacked by a nucleophile or an electrophile. Each of these attacks may lead to an addition or an abstraction reaction. In the case of a nucleophilic or an electrophilic addition pathway, there is a direct bond formation between the nucleophile or the electrophile with the activated ligand, while in the case of a nucleophilic or an electrophilic abstraction pathway, a part or the whole of the activated ligand gets abstracted from the starting metal complex. The abstraction reaction may also proceed by several different mechanistic pathways.