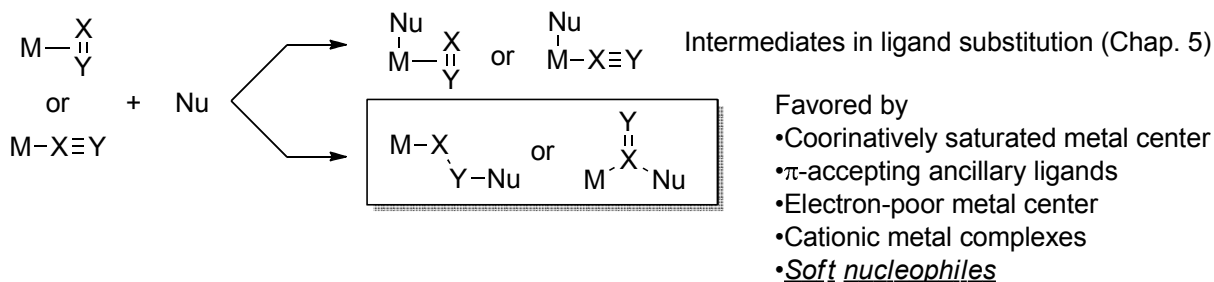


Organometallics Study Meeting

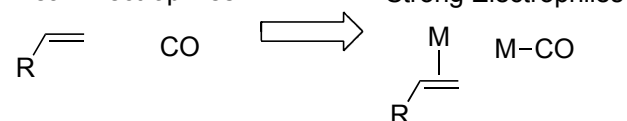
Chapter 11. Nucleophilic Attack on Coordinated Ligands

11.1 Fundamental Principles

General Tendency

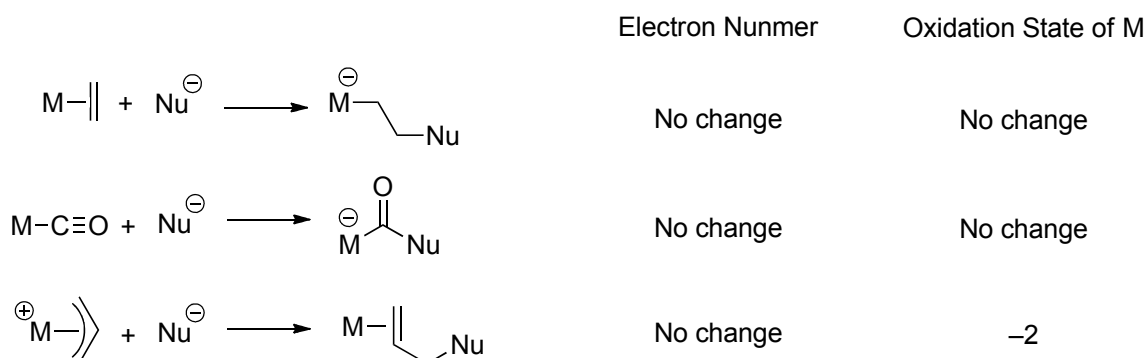


Weak Electrophiles



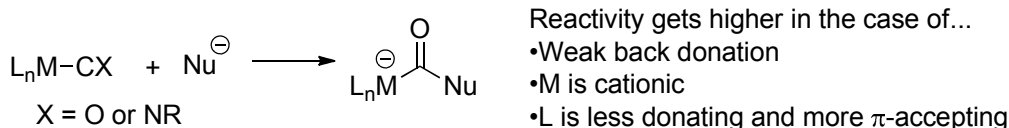
Due to "net flow of electron density to metals"

Electron Number and Oxidation State



11.2 Nucleophilic Attack on Transition Metal Complexes of Carbon Monoxide and Isonitriles

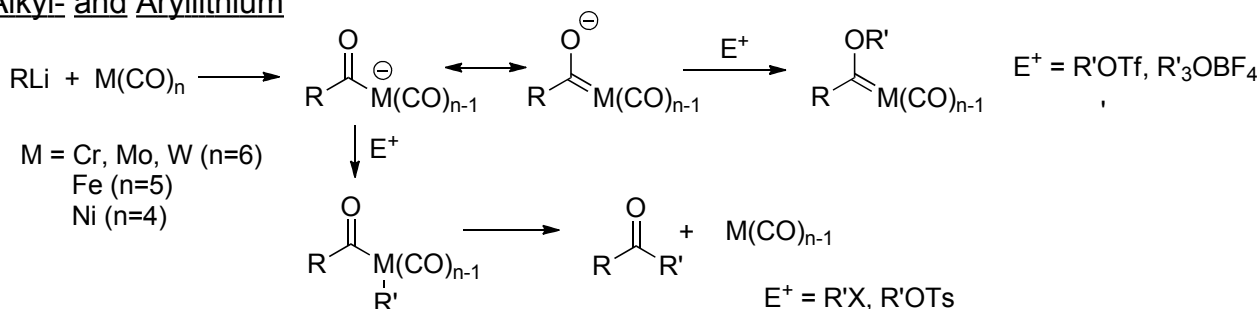
11.2.1 General Trends



As guideline, complexes which has ν_{CO} values below $\sim 2000 \text{ cm}^{-1}$ are relatively inert.

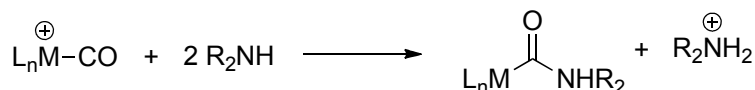
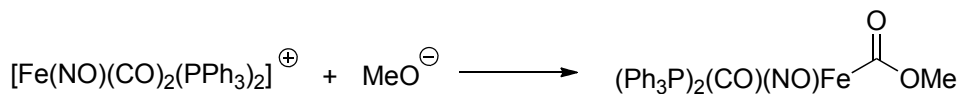
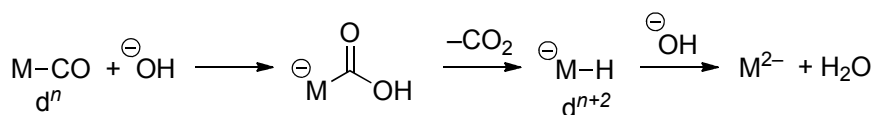
11.2.2 Examples of Nucleophilic Attack on Carbon Monoxide and Isonitriles

Alkyl- and Aryllithium



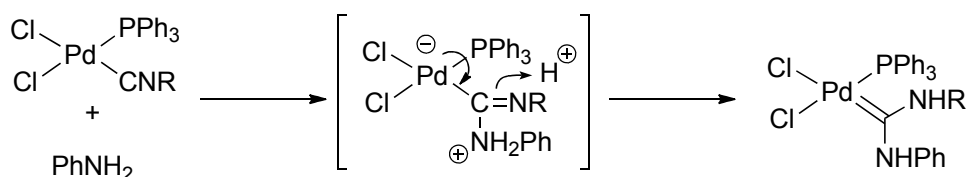
Hydroxide Alkoxides and Amines

Important in some industrial processes and water gas shift.

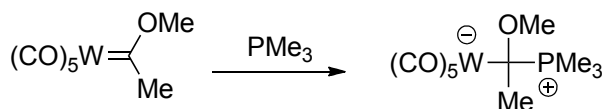
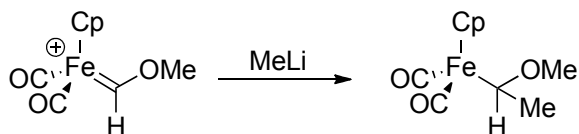


Example of Isonitrile

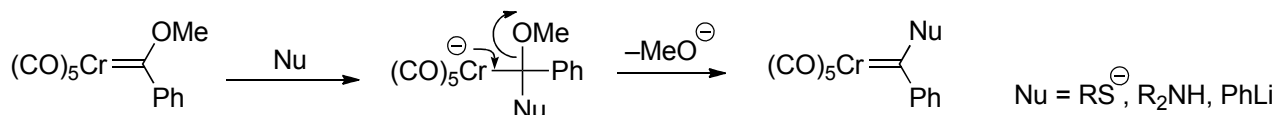
In general, isonitrile is less reactive than CO as an electrophile.



11.3 Nucleophilic Attack on Carbene and Carbyne Complexes



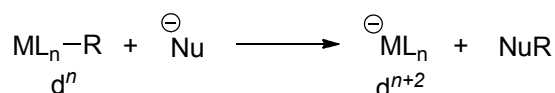
This type reaction is limited to anionic Fischer carbenes or neutral Fischer carbenes with the ligands which stabilize negative charge.



11.4 Nucleophilic Cleavage of Metal-Carbon σ-Bonds

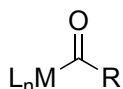
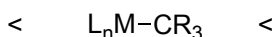
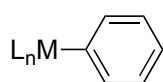
11.4.1 General Principles and Trends

General Scheme

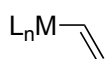


- M is reduced by two.
- Retro reaction of some SN₂ type oxidative addition.
- Uncommon in catalytic process.
- R=alkyl : Slower than addition to CO, carbene, olefins.

Reactivity



Acyl-M is less reactive than corresponding esters, amides or ketones.



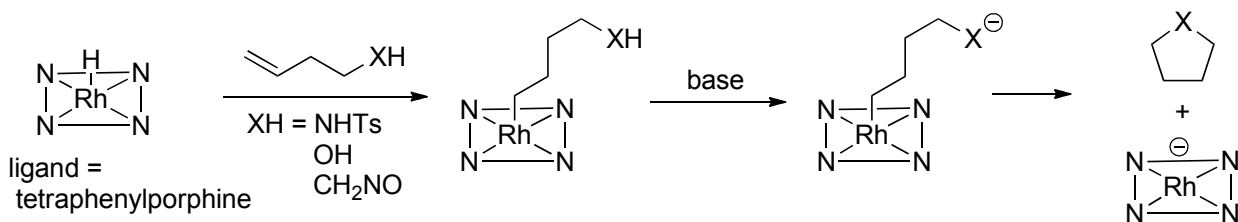
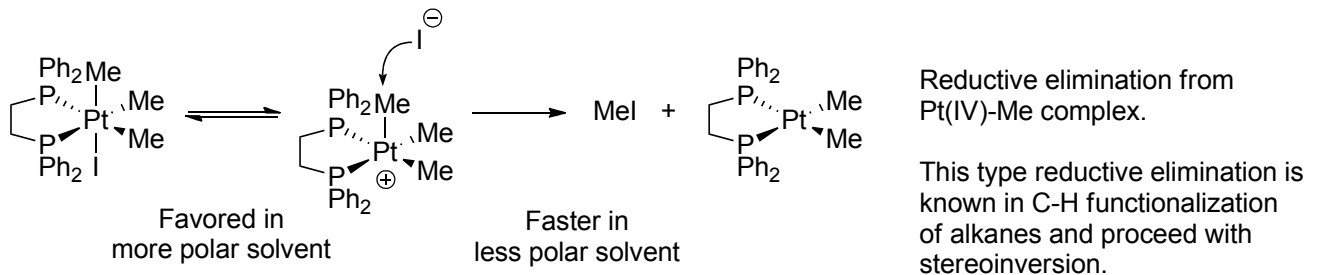
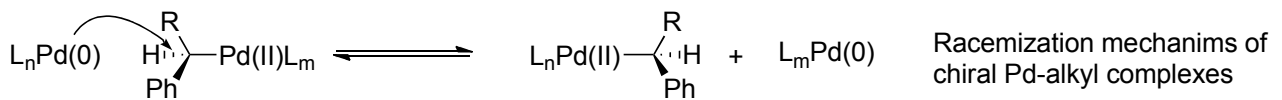
rare or unknown



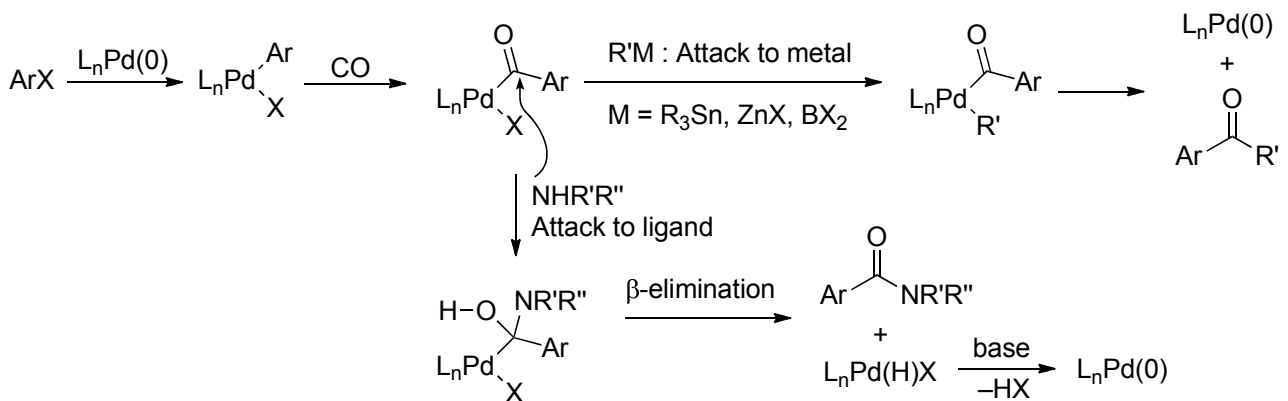
common

11.4.2 Examples of Nucleophilic Attack on σ -Bound Ligands

Attack to Metal-Alkyl Complexes

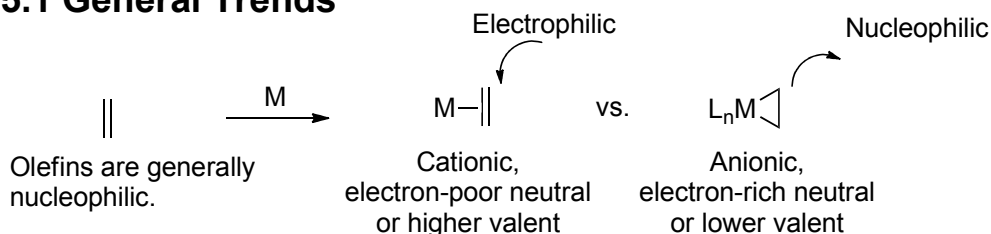


Attack to Metal-Acyl Complexes

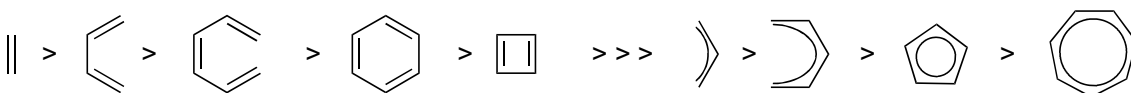


11.5 Nucleophilic Attack on η^2 -Unsaturated Hydrocarbon Ligands

11.5.1 General Trends



Reactivity of Several Unsaturated Systems

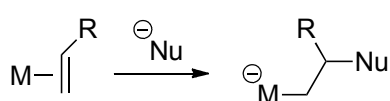


Even System >>> Odd System
Open System > Closed System

Studied about cationic 18 electron complexes and guidelines were developed by Davies, Green and Mingos.

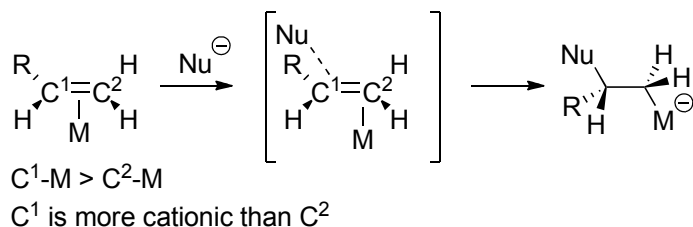
11.5.2 Nucleophilic Attack on η^2 -Olefin Complexes

11.5.2.1 Overview of Nucleophilic Attack on η^2 -Olefin Complexes



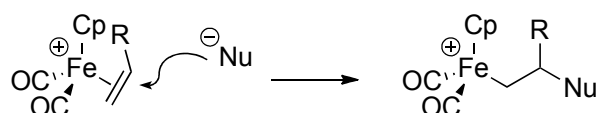
- Well known for Pd(II), Pt(II), Fe(II)
- Forming M-alkyl complexes
- Nucleophilic attack occurs at the opposite face of olefin to metal..
- Nu generally attack more substituted carbon (many exceptions)
- Most examples are limited to mono- and disubstituted olefins.

Mechanism and Regioselectivity



11.5.2.2 Specific Examples of Nucleophilic Attack on η^2 -Olefin Complexes

Reaction with Cationic Iron(II) Complexes

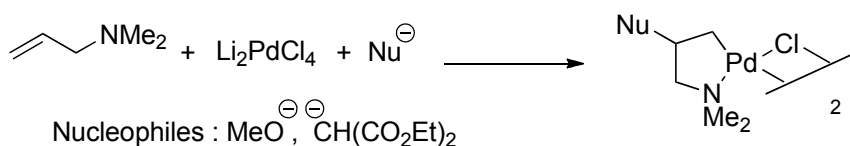


Stereochemistry : trans
 Regiochemistry : depends on nucleophiles

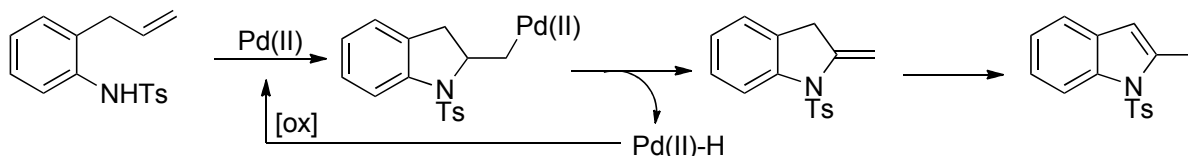
Nucleophiles : MeO^- , $tBuS^-$, Ph_3P^- , $(EtO)_3P^-$, R_2NH^- , $CH_2NO_2^-$, Active methylenes, enamines, $LiCuMe_2$

Reaction with Pd(II) Complexes

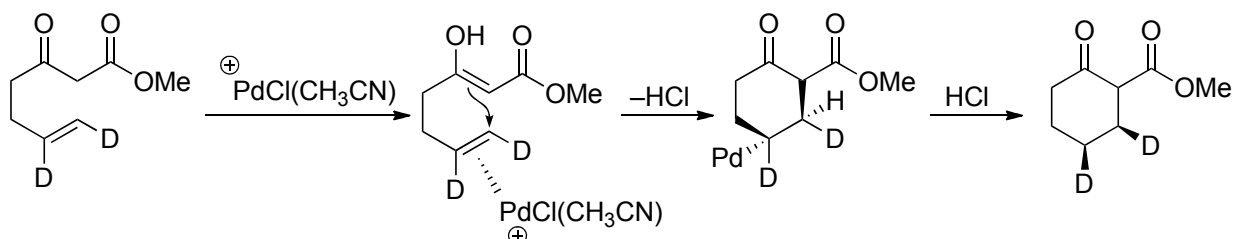
In Pd(II) cases, stabilization by chelation is necessary to avoid β -elimination and isolate σ -alkyl complexes. Nucleophilic Attack occurred at the opposite face to the Pd.



Many catalytic reactions include this type nucleophilic addition.

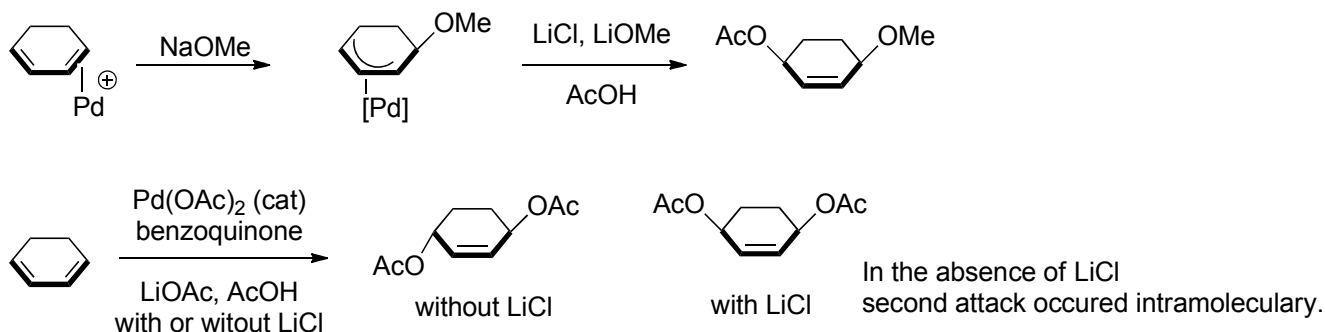


Also catalytic addition of active methylene to olefin has been reported.



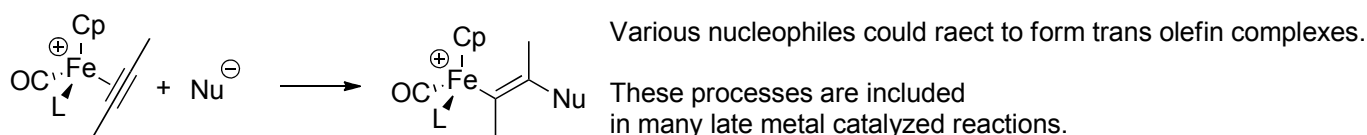
11.5.3 Nucleophilic Attack on Square Planar Pd(II) Diene and Allene Complexes

Dienes can bind to metals in both η^2 and η^4 fashion and this section describe the reaction of the η^2 complexes.

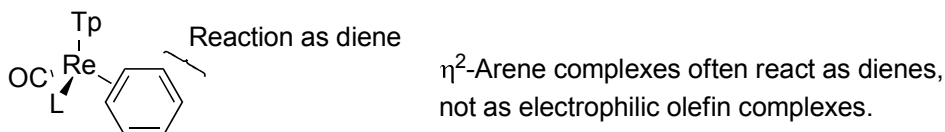


11.5.4 Nucleophilic Attack on η^2 -Alkyne Complexes

η^2 -Alkyne Complexes which are cationic or have high oxidation state are highly reactive.



11.5.5 Reactions of η^2 -Arene Complexes



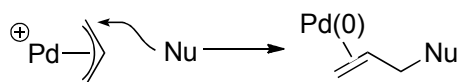
11.6 Nucleophilic Attack on Imine and Aldehyde Complexes

Coordination of imines and aldehydes to Lewis Acid enhances the electrophilicity and most reactions proceeded from η^1 -complexes rather than η^2 -complexes.

11.7 Nucleophilic Attack on Polyhapto (η^3 - η^6) Ligands

11.7.1 Nucleophilic Attack on η^3 -Allyl Complexes

Reactions of Pd(II) Complexes

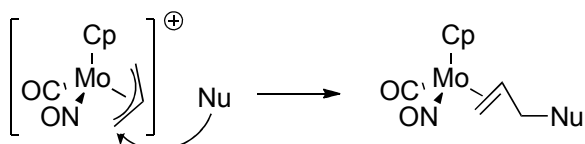


Nu : Stabilized carbanions, amines etc.

Pd(II) complexes tend to react at less substituted carbon.

Important process in allylic substitution reactions and regio- and stereoselective reactions are well studied using Pd, Ir, Mo, W, Ru catalysts. (Chap. 20)

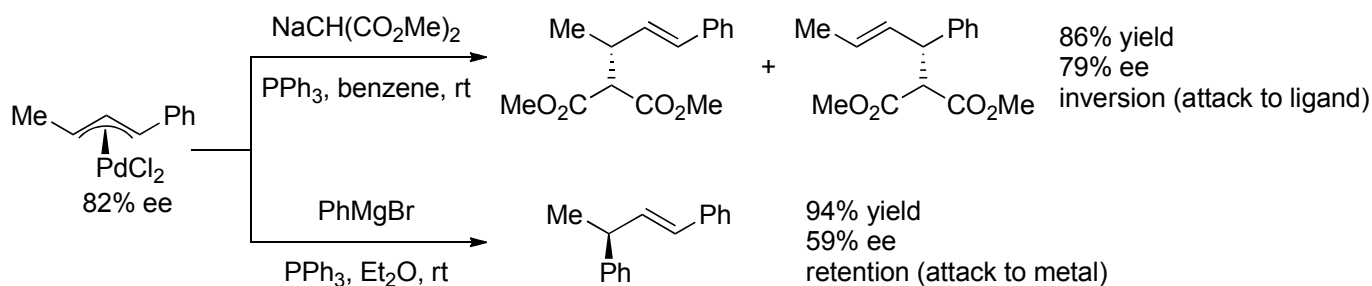
Reactions of Isolated Allyl Complexes



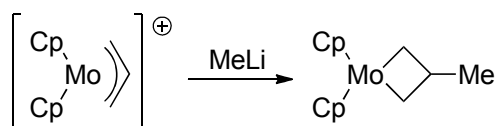
Regiochemistry : Attack to the carbon trans to CO ligand (stronger transinfluence)

Stereochemistry : Attack to the opposite face to metal

In general, ligands with strong donation and transinfluence lengthen M-C(allyl termin) bond located at trans position to result in higher reactivity. Regiochemistry is controllable by electronic factor.



Reactions at Central Carbon of Allyl Group

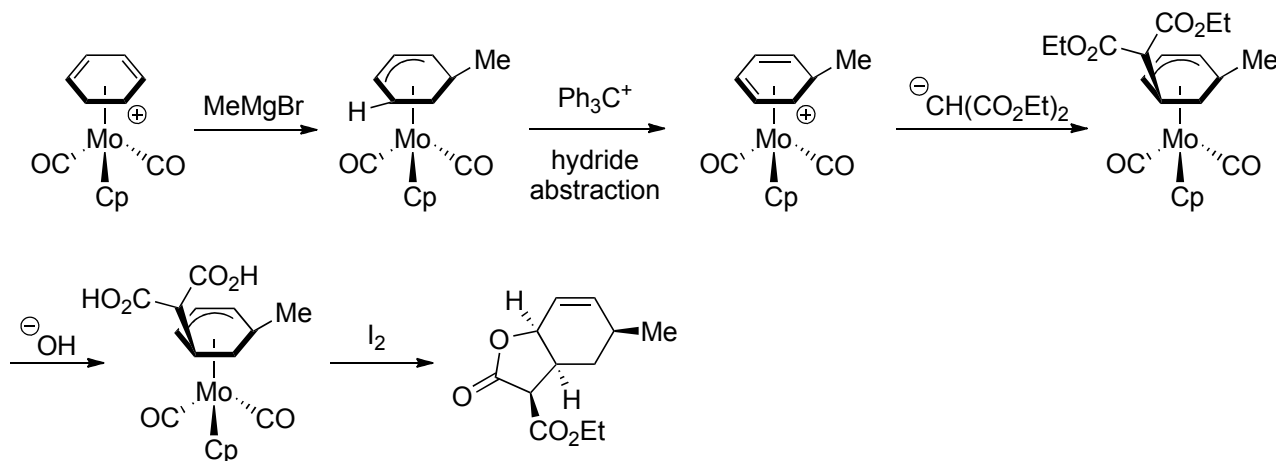


LUMO mainly consists of metal d-orbital and allyl π^* -orbital in less common cases. In those cases, reaction proceeds at central carbon. (Common : d-orbital and allyl non-bonding orbital)

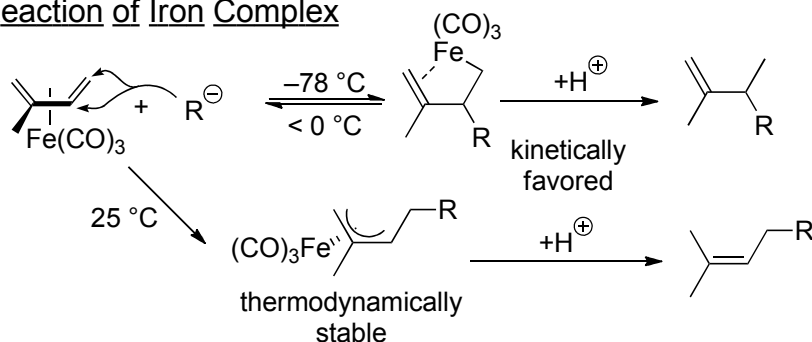
$\text{CpLM}(\eta^3\text{-allyl})^+$ (L=CO, PR_3 ; M=Co, Rh, Ir) also tend to react at central carbon.

11.7.2 Nucleophilic Attack on η^4 -Diene Complexes

Reactions of Cationic Mo- η^4 -Diene Complexes

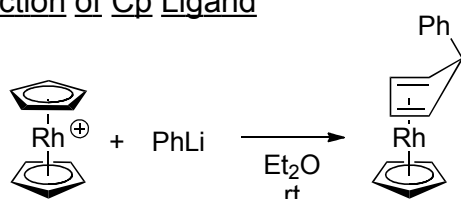


Reaction of Iron Complex



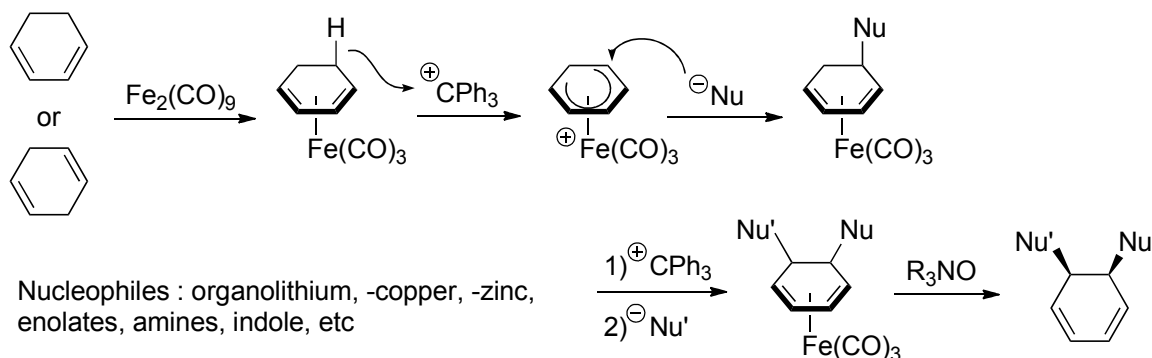
11.7.3 Nucleophilic Attack on η^5 -Dienyl Complexes

Reaction of Cp Ligand



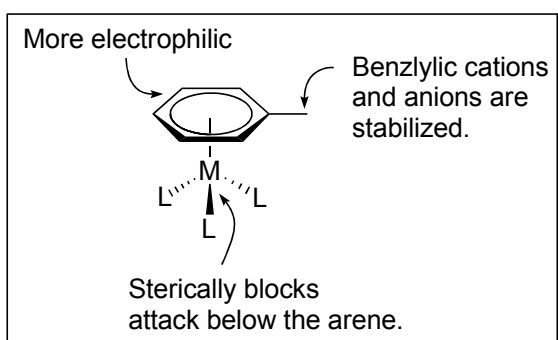
Although Cp is the most common ligand in this class, only strong nucleophile can react.

Reactions of $\text{Fe}(\text{CO})_3$ Dienyl Complexes



11.7.4 Nucleophilic Attack on η^6 -Arene Complexes

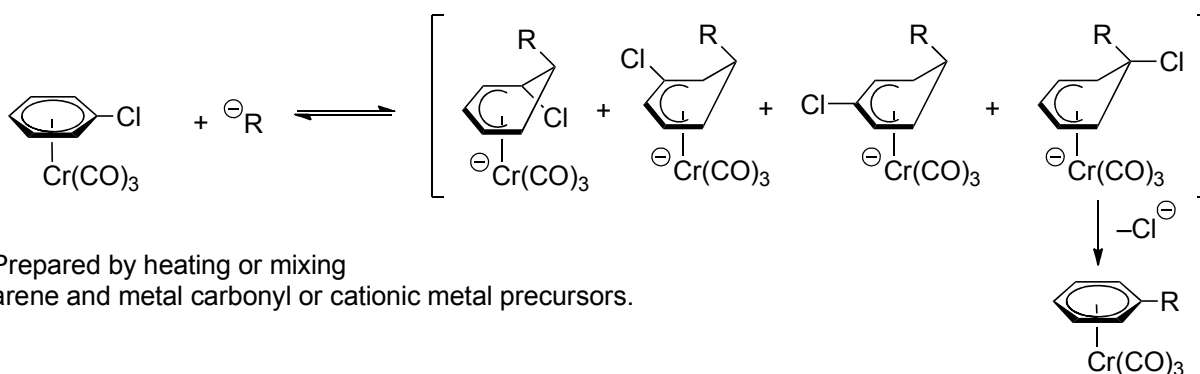
11.7.4.1 Overview of Nucleophilic Attack on η^6 -Arene Complexes



Regioselectivity was complicated and affected by stereo and electronic factors of substituents (usually *ortho* is disfavored.).

In many cases, addition is reversible and product is not kinetically controlled.

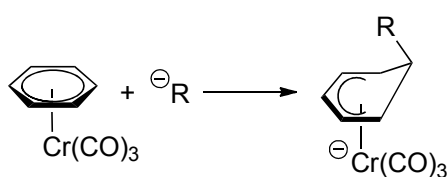
Only strong nucleophiles (organolithium, Grignard reagents) can add irreversibly.



Catalytic process of addition or substitutions have been not reported yet. In general, free arenes are released by oxidation.

11.7.4.2 Examples of Nucleophilic Attack on η^6 -Arene Complexes

Additions to Arene- $\text{Cr}(\text{CO})_3$



Unreactive : $\text{LiCH}(\text{CO}_2\text{R})_2$, LiCH_2COR , MeMgBr , $t\text{BuMgBr}$, Me_2CuLi , vinyl lithium

Reactive : $\text{LiCH}_2\text{CO}_2\text{R}$, LiCH_2CN , $\text{KCH}_2\text{CO}_2t\text{Bu}$, $\text{LiCH}(\text{CN})\text{OR}$, LiCH_2SPh , Li-1,3-dithiane, PhLi , Li acetylide, allyllithium

Reactivity of arene : $\text{PhCl} (o, p) > \text{PhCH}_3 (m)$, $\text{PhOMe} (m)$

Other Examples

Similar reactions are also studied with (arene)CpFe⁺ and (arene)Cp^{*}Ru⁺
There are several examples of application to synthesis of complex molecules.

