

Organometallics Study Meeting

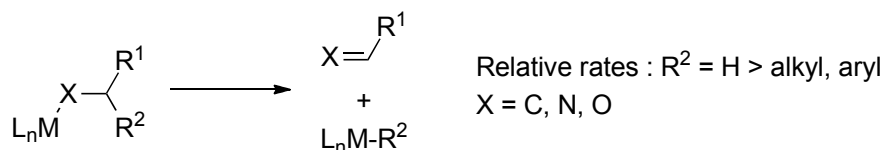
Chapter 10. Elimination Reactions

2011/7/31 Yoshino (D1)

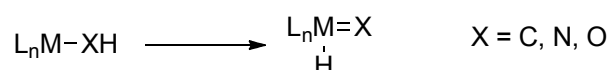
10.1, 10.2. Overview

Elimination reaction is reverse process of "insertion".

β -Elimination The common type of elimination



α -Elimination Slower than β -elimination in most cases

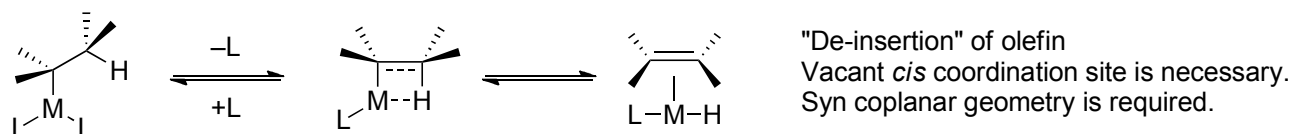


10.3. β -Elimination Processes

10.3.1 β -Hydrogen Eliminations

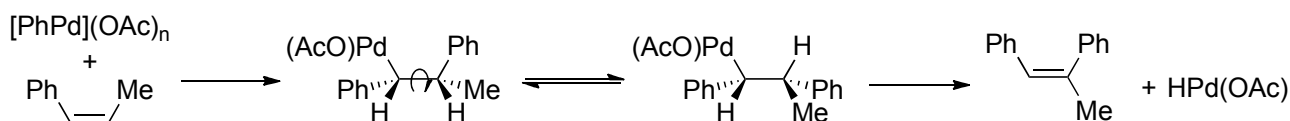
10.3.1.1 β -Hydrogen Eliminations from Metal-Alkyl Complexes

General Scheme

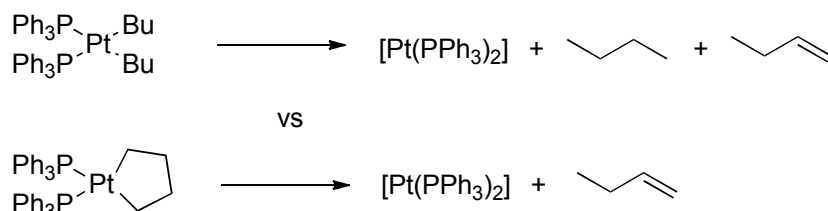


10.3.1 β -Hydrogen Eliminations

Effect of Conformation



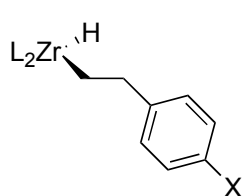
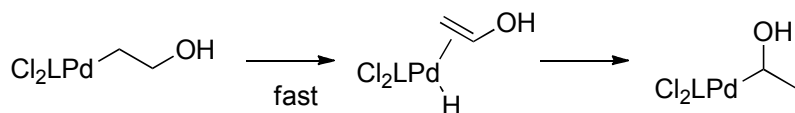
Metalacyclic square planar d^8 complexes are resistant to β -hydrogen elimination.



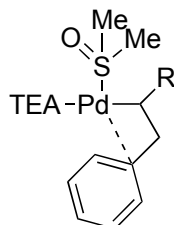
10^4 times slower and decomposition proceeded without β -hydrogen elimination.

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Substituents Effect



β-elimination rates
OMe > Me > H > CF₃



β-elimination rates
Ph > CO₂tBu > CN

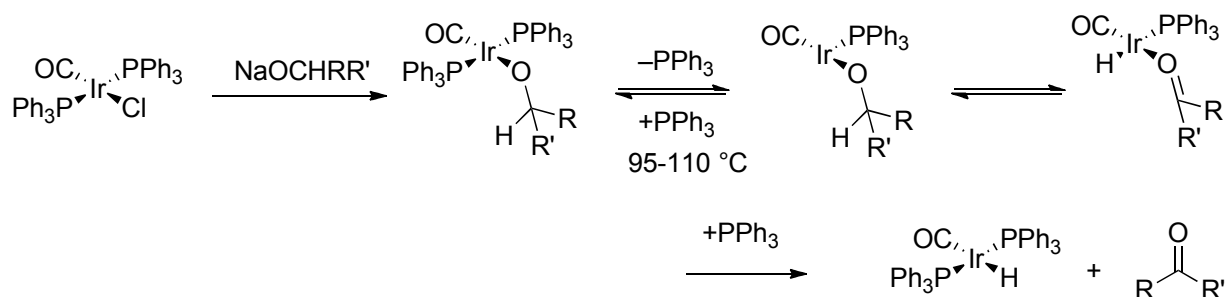
EWG could stabilize M-C bond and inhibit β-elimination.

Effect of Ancillary Ligands

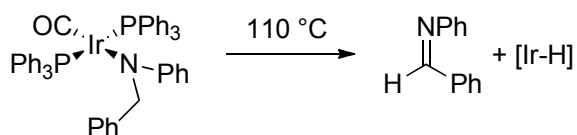
- Sterically hindered ligands decrease the rate of β-elimination because..
 - 1) Syn coplanar conformation is disfavored
 - 2) β-elimination increases the number of ligands and steric hindrance around metal center.
- Electron-donating ligands promote β-elimination. (reason is unclear)

10.3.1.2 β-Hydrogen Eliminations from Metal-Alkoxide and Amides

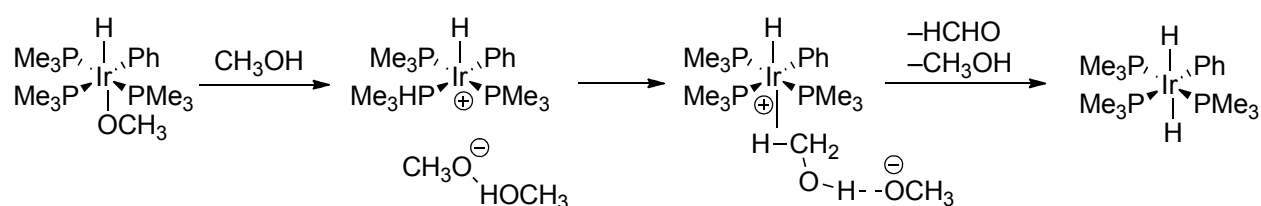
Standard β-elimination Mechanism

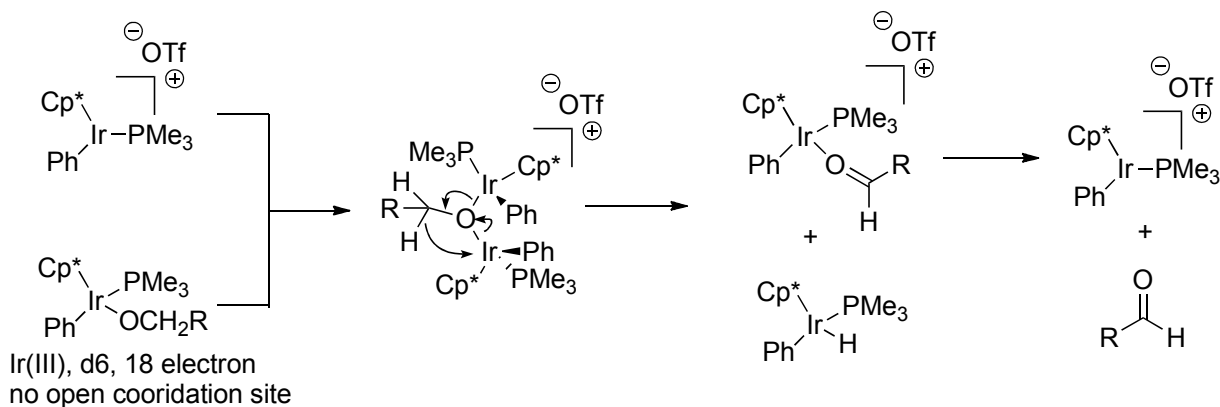


Amido complexes also undergo β-elimination.



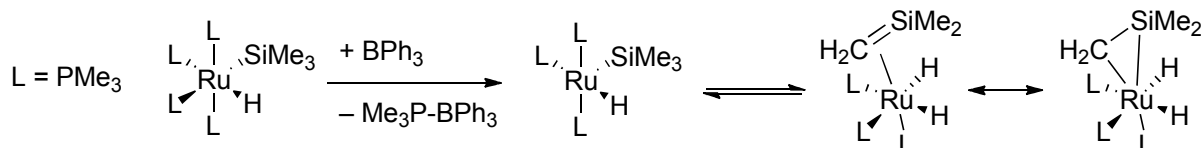
Through Other Pathways





10.3.1.2 β -Hydrogen Eliminations from Metal-Silyl Complexes

This process is uncommon due to instability of Si=C π -bond.

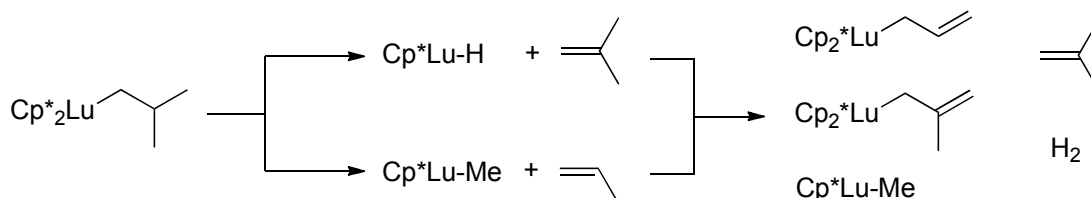


10.3.2. β -Hydrocarbonyl Elimination

10.3.2.1 β -Alkyl Eliminations from Metal-Alkyl Complexes

Early Metal

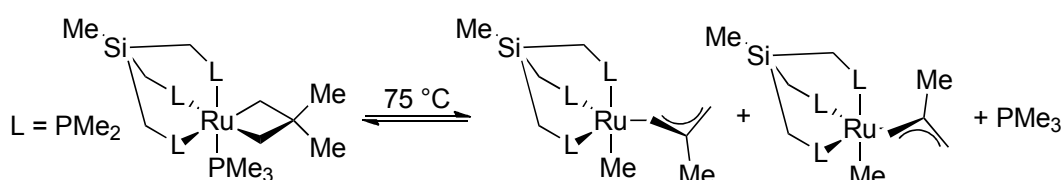
This process is fast in the case of electrophilic d⁰ early metal complexes.



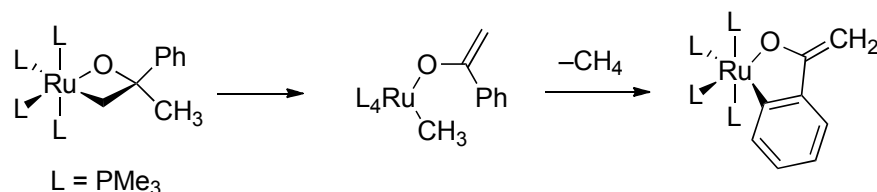
Similar processes are known for zirconocene, hafnocene, scandocene complexes. Mechanism is almost same as β -hydrogen elimination and requires an open coordination site.

Late Metal

β -alkyl elimination is less common in late transition metals.



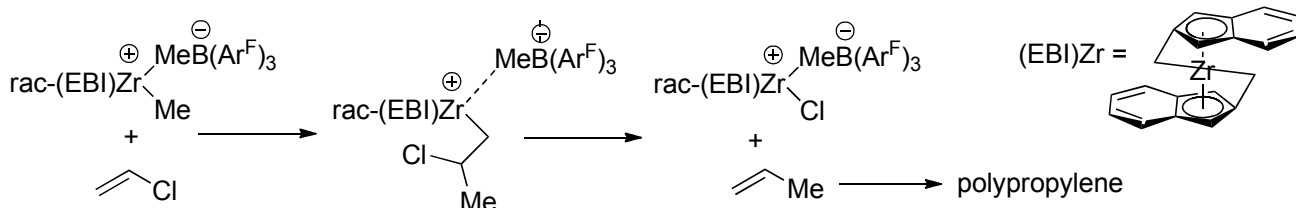
10.3.2.1 β -Alkyl and β -Aryl Eliminations from Metal-Alkoxide and Amido Complexes



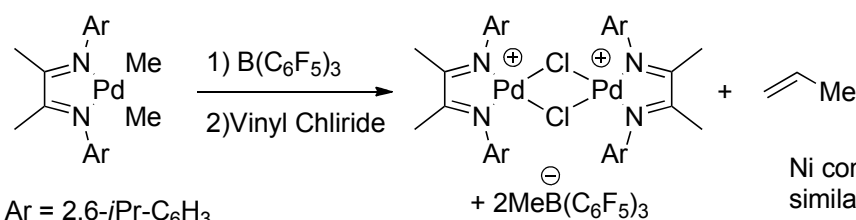
10.3.3. β -Halide and Alkoxide Elimination

β -Chloride Elimination of Early Metal Complexes

β -Chloride elimination has been studied because it is important side reaction in polymerization of vinyl chloride.

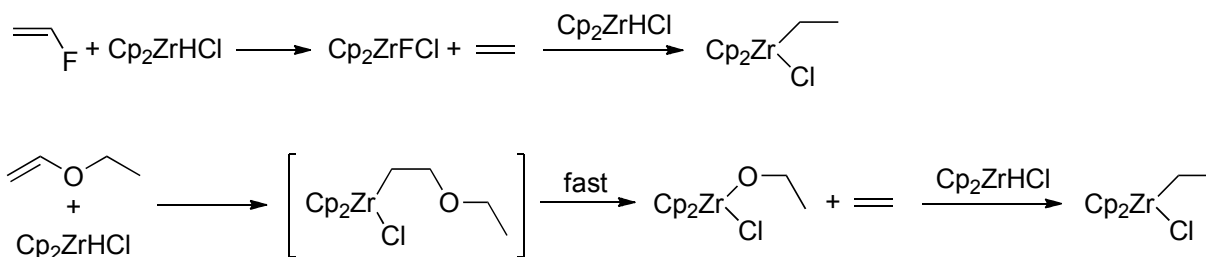


β -Chloride Elimination of Late Metal Complexes



Ni complexes are also known to undergo similar processes.

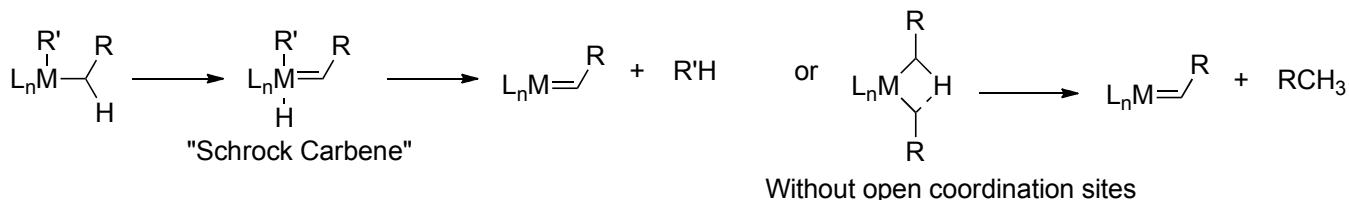
β -Fluoride and Alkoxide Elimination of Early Metal Complexes



10.4. α -Hydrogen Eliminations and Abstractions

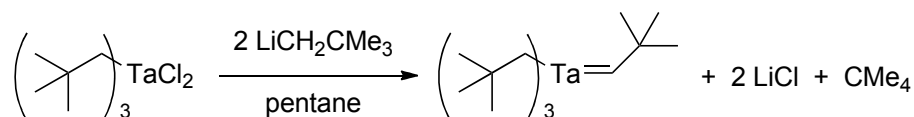
General

α -Hydrogen Eliminations form Schrock-type alkylidene complexes.

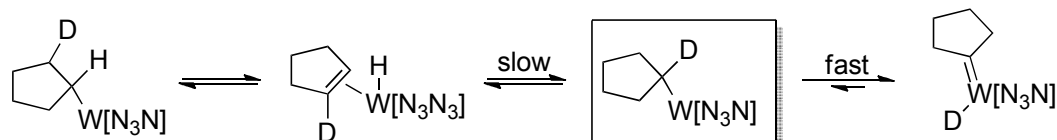
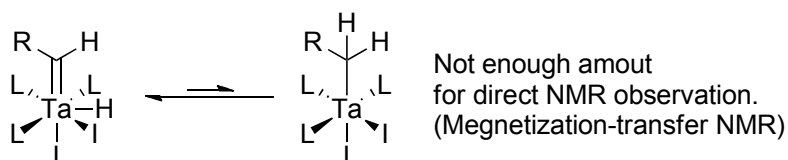


- Slower than β -elimination
- Common for d^0 complexes of group 4 and 6 metals, due to disfavorance of olefin complex from α -elimination.
- Steric hinderance can facilitate α -elimination over β -elimination.

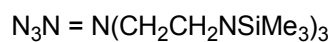
Example from Early Metal Complexes



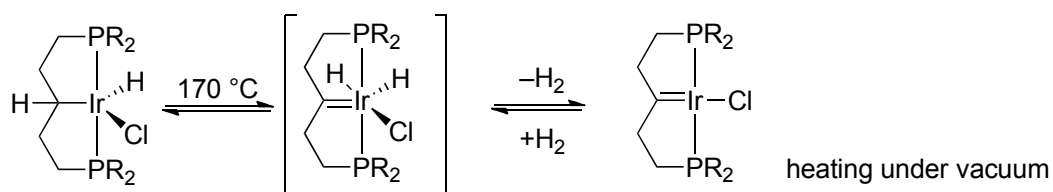
Equilibrium of α -Elimination and Insertion



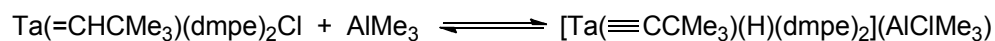
D Scrambling can proceed only at higher temperature.



Example from Late Metal Complexes



Alkylidene Complex to Alkylidene Complex (C-M Triple Bond)



Amide Complex to Imide Complex (M=N Double Bond)

