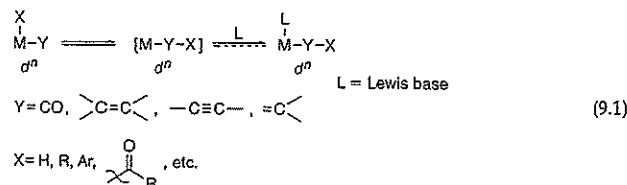


## Chapter 9. Migratory Insertion Reaction

1. Overview & basic principles
2. Insertions of single-atom-bound ligands
  - 2-1. Carbon monoxide
  - 2-2. Carbene
  - 2-3. Others
3. Insertions of poly-hapto ligand
  - 3-1. Into M-H bonds
  - 3-2. Into M-C bonds
  - 3-3. Into M-X bonds

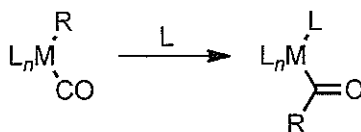
### 1. Overview & basic principles



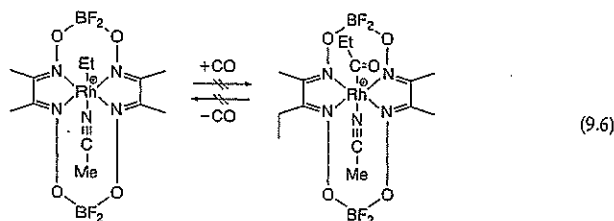
- Migratory insertion doesn't change the oxidation state of the metal.
- X and Y must be coordinated cis to each other.
- Occurs by a concerted process (= retention of stereochemistry)
- 1e oxidation, coordination of Lewis acids, and attack by Lewis bases can accelerate the insertion.

### 2. Insertions of single-atom-bound ligands

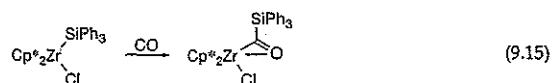
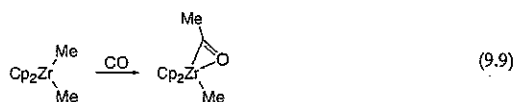
#### 2-1. Insertions of carbon monoxide



- CO insertions into metal-alkyl bonds are common.
- Need to be cis to each other for CO and alkyl group



- CO insertions into metal-heteroatom bonds are less common.
- For electrophilic metal centers, reactions are driven by strong M-O interactions.



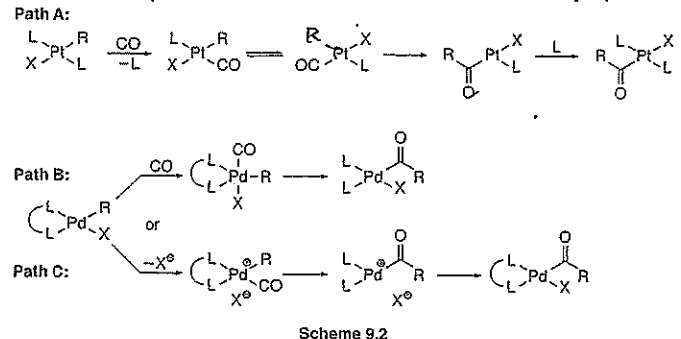
- Kinetics and mechanisms

into 18-electron complex

one step, two steps, or mixed

into 16-electron complex

4-Coordinated  $d^8$  complexes have been studied extensively. (M = Pt, Pd, and Ni)

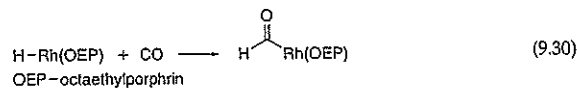
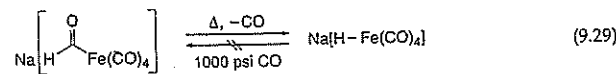


- Solvents sometimes affect the rate of migration.

CO insertions in polar solvents are usually faster than those in non-polar solvents.  
(maybe because of chelating to the intermediate  $M[C(O)R]$ )  
But sometimes prevents insertion by affecting ion pairing.

- Migratory aptitudes depend on thermodynamics and kinetics.

If thermodynamically unfavorable, the aptitudes result from **thermodynamic** effects.

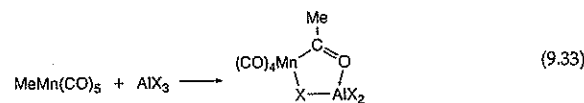


If thermodynamically favorable, the aptitudes result from **kinetic** effects.

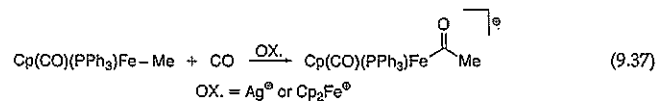
- having electron donating substituents > having electron withdrawing substituents
- more sterically hindered > less sterically hindered
- alkyl groups > aryl groups
- first row metal > second row metal > third row metal
- alkoxide > alkyl > aryloxide > arylamide

- Catalysis of CO insertion

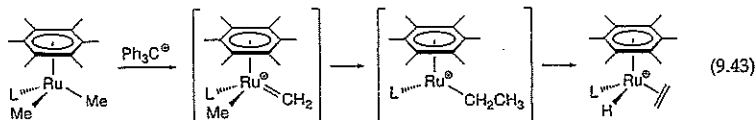
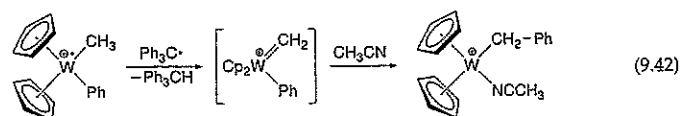
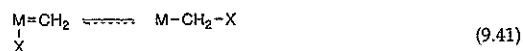
Lewis acid



redox acceleration

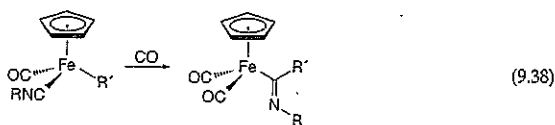


## 2-2. Insertions of carbene



## 2-3. Insertions of others

Isonitrile, thiocarbonyl, nitrosyl ligands are known.

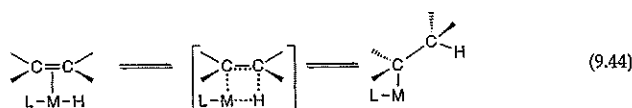


## 3. Insertions of poly-hapto ligands

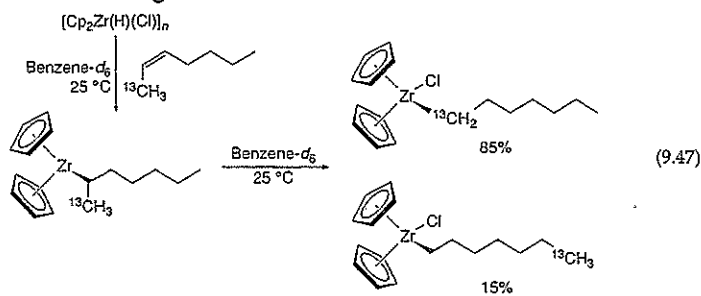
### 3-1. Insertions into metal-hydride bonds

#### 3-1-1. Insertions of olefins

- The intramolecular migration of a hydride to olefin is very fast.
- The reverse reaction is  $\beta$ -H elimination.

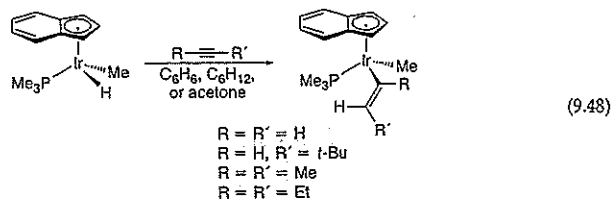


- Example: Schwartz's reagent

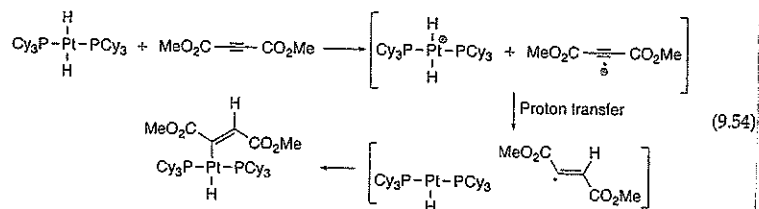
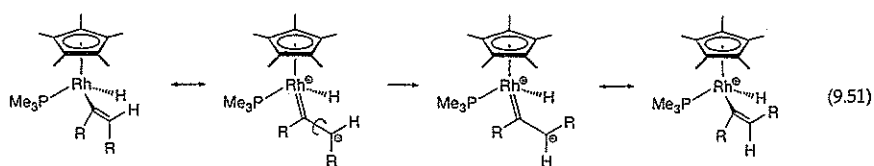


#### 3-1-2. Insertions of alkynes

- A migratory insertion process gives *cis* addition products.



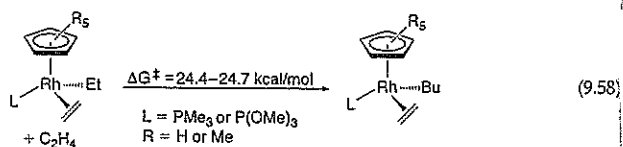
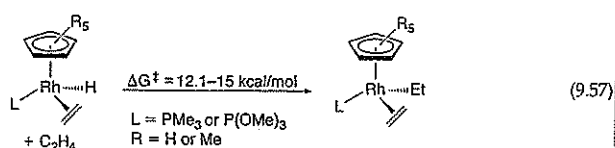
- But sometimes **trans** addition products are obtained.  
(because of isomerization after addition or electron-transfer addition mechanism)



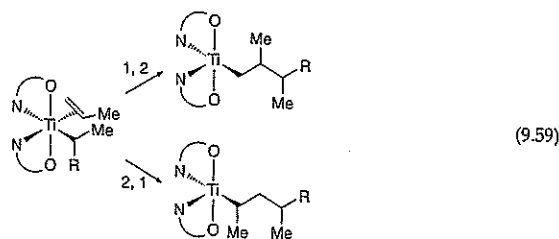
### 3-2. Insertions into metal-carbon bonds

#### 3-2-1. Insertions of olefins into metal-hydrocarbyl $\sigma$ -bonds

- Slower than insertion into M-H bonds

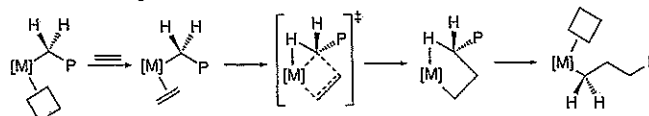


- Occurs by a concerted migratory insertion pathway

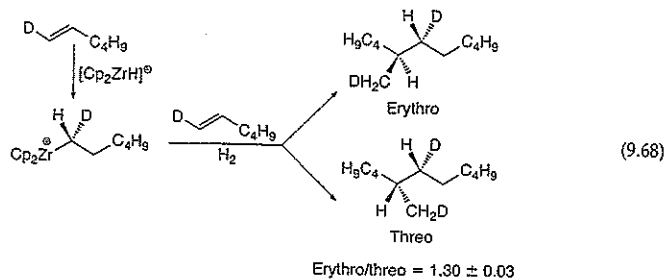


- $\alpha$ -agostic interaction controls the rate and the selectivity.

Transition state  $\alpha$ -agostic mechanism



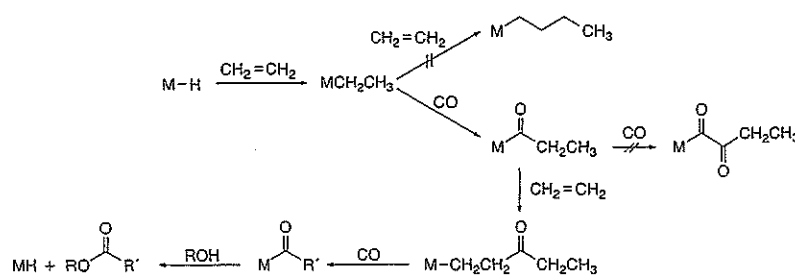
Scheme 9.9



Erythro/threo = 1.30  $\pm$  0.03

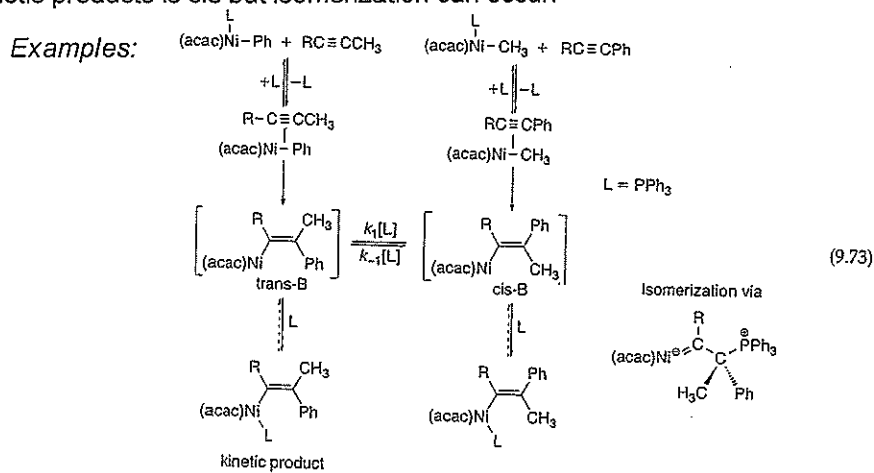
### 3-2-2. Insertions of olefins into metal-acyl bonds

- The relative rates for insertion of alkene into alkyl or acyl groups are important for selective copolymerization of alkenes and CO.



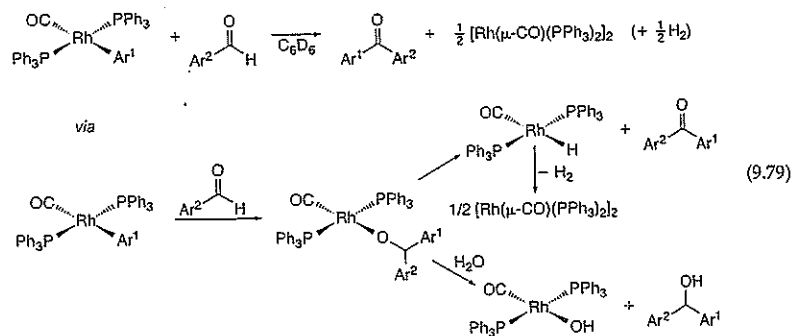
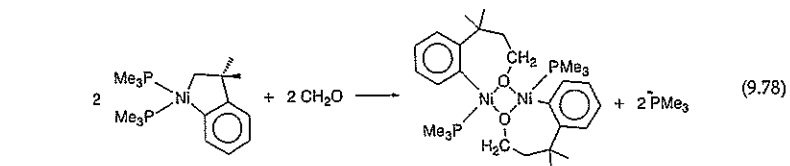
### 3-2-3. Insertions of alkynes

- Less common but thermodynamically more favoured than those of olefins
- Kinetic products is cis but isomerization can occur.



### 3-2-4. Insertions of aldehydes and imines

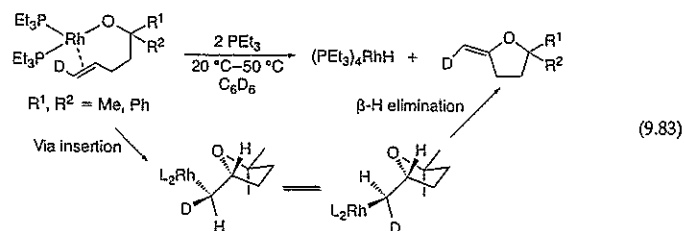
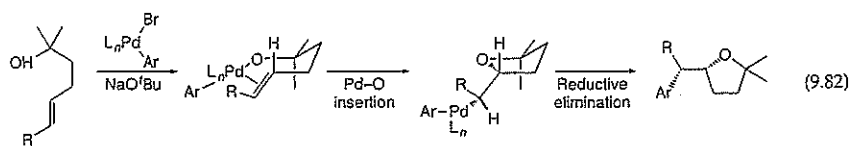
Examples:



### 3-3. Insertions into metal-heteroatom bonds

#### 3-3-1. Into metal-oxygen bonds

- Insertions occur by a concerted pathway.



#### 3-3-2. Into metal-nitrogen bonds

- Insertions also occur by a concerted pathway.

