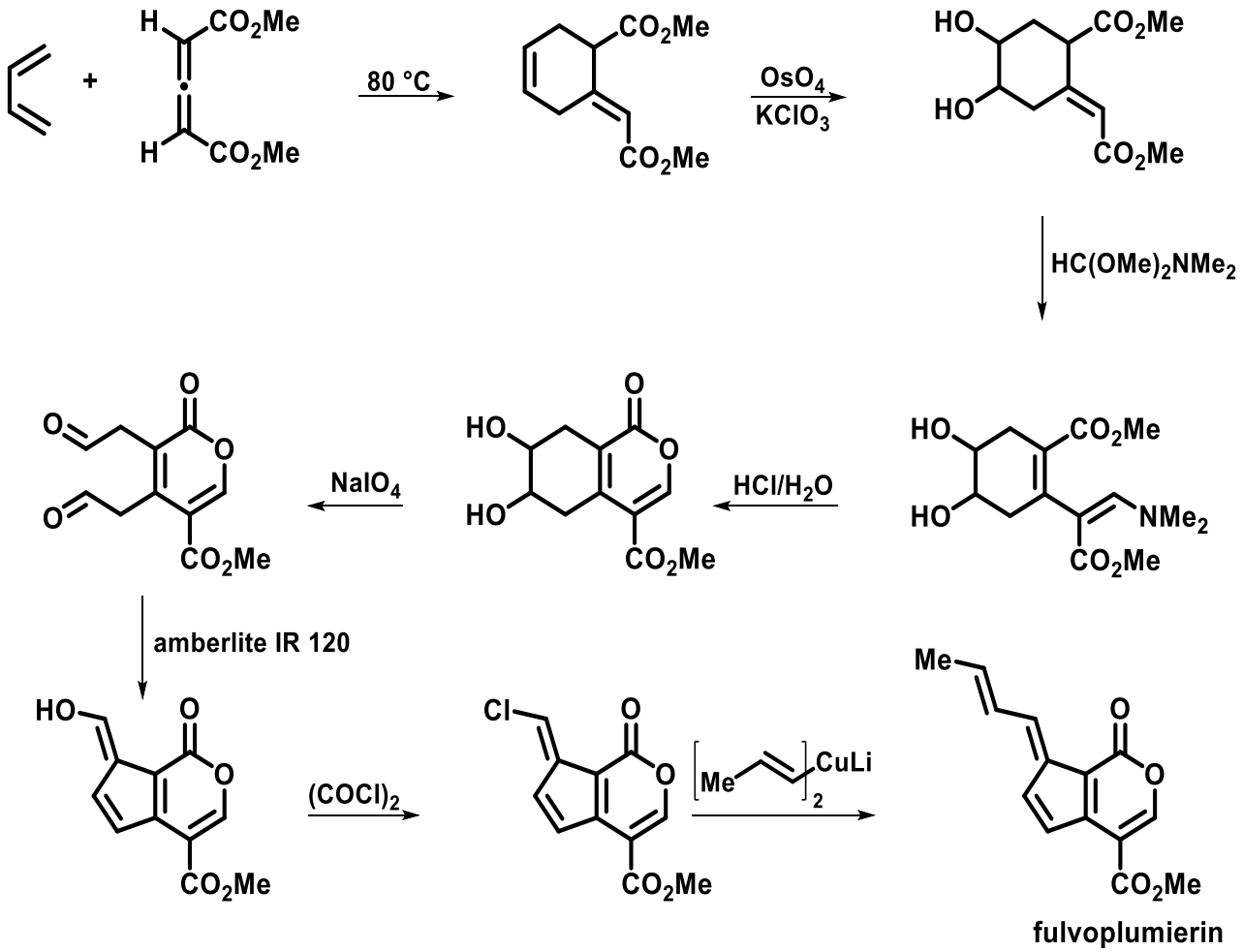
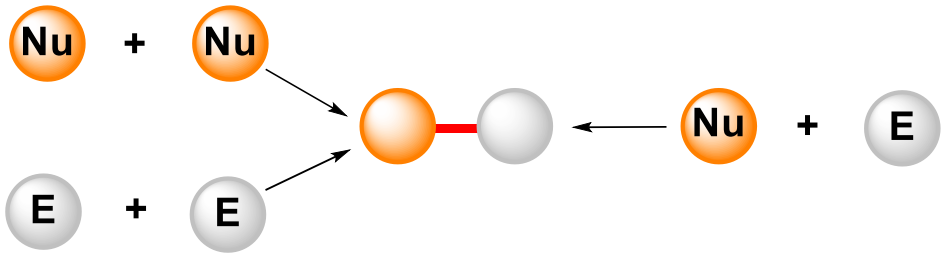
Basic Mechanisms in Organometallic Chemistry

➢ Main objective of organic synthesis – Synthesis of C–C or C–heteroatom bond

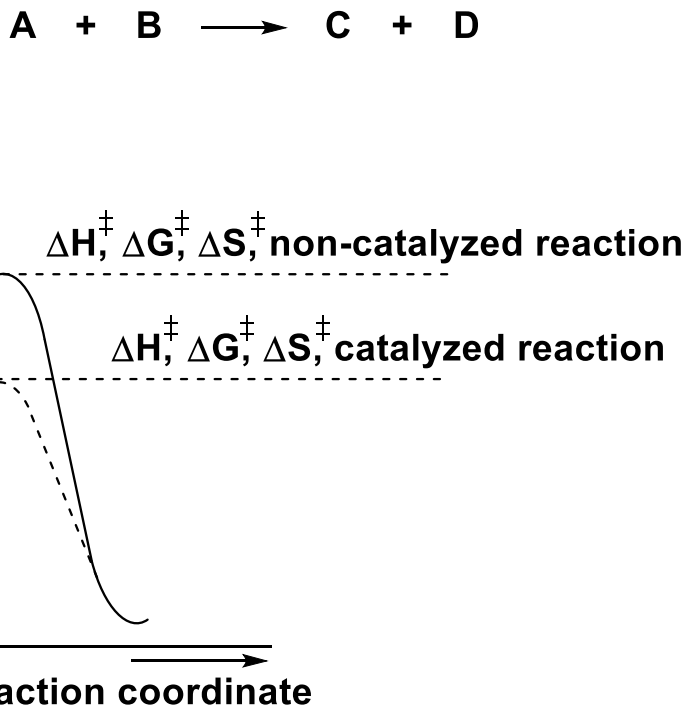


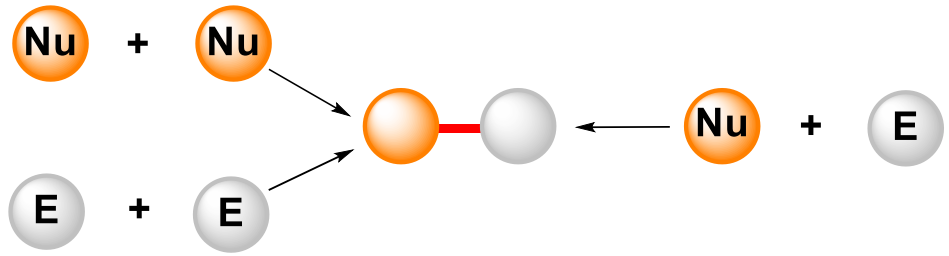


J. Am. Chem. Soc. **1968**, *90*, 5336

Basic Mechanisms in Organometallic Chemistry

- **Catalyzed versus non-catalyzed reaction**



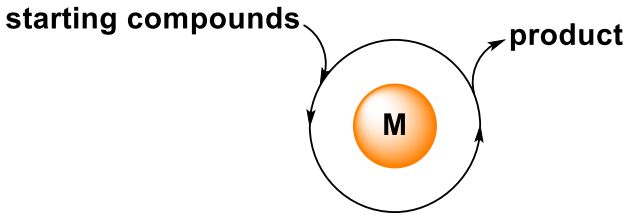


Basic Mechanisms in Organometallic Chemistry

➢ Transition metals en route to bond formation

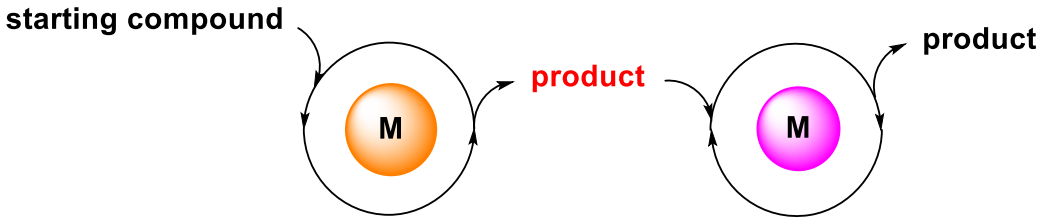
- **Transition-metal-catalyzed reactions**

  ✓ **Monocatalysis**

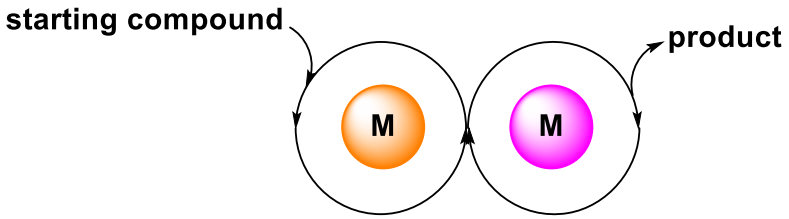


  ✓ **Multicatalysis**

  ○ **Relay catalysis**

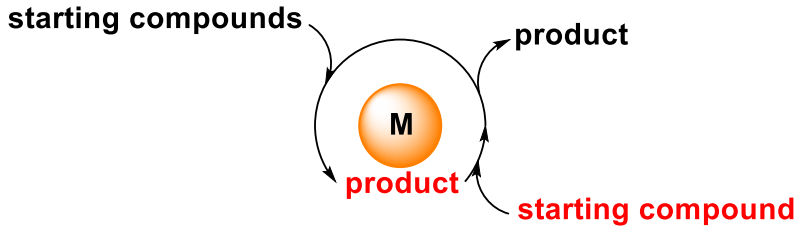


  ○ **Cooperative catalysis**



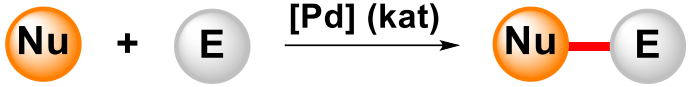
- **Stoichiometric reactions**

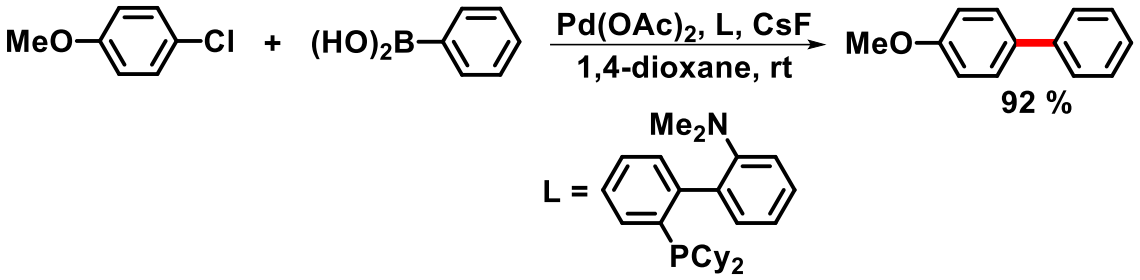
  ○ **Domino catalysis**



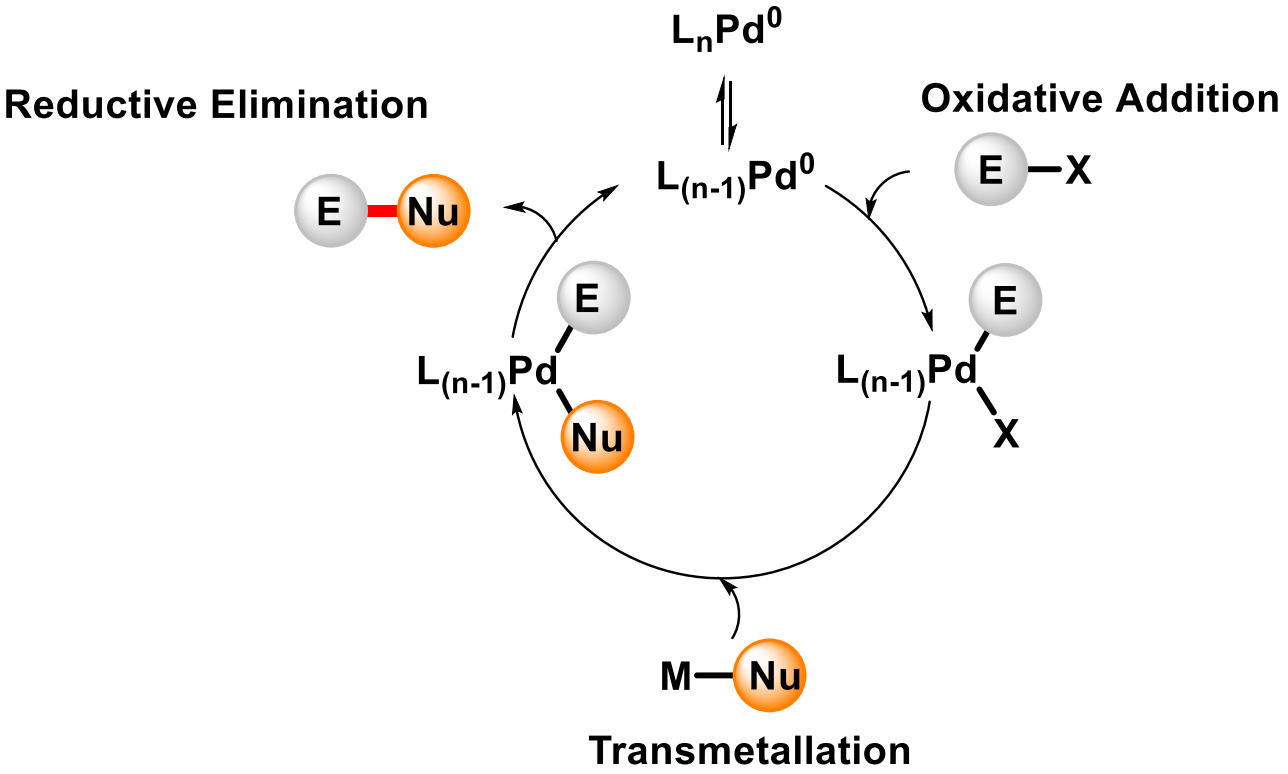
Basic Mechanisms in Organometallic Chemistry

➢ Transition-metal-catalyzed reactions





J. Am. Chem. Soc. **1998**, *120*, 9722

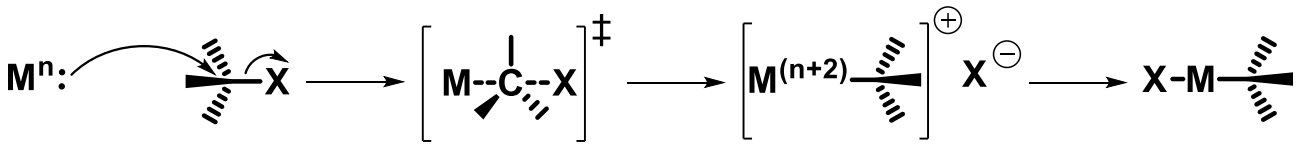


Basic Mechanisms in Organometallic Chemistry

➢ Oxidative addition

$$R{-}X \xrightarrow{M^n} R{-}M^{n+2}{-}X$$

- **Oxidative addition by S_N2 mechanism**

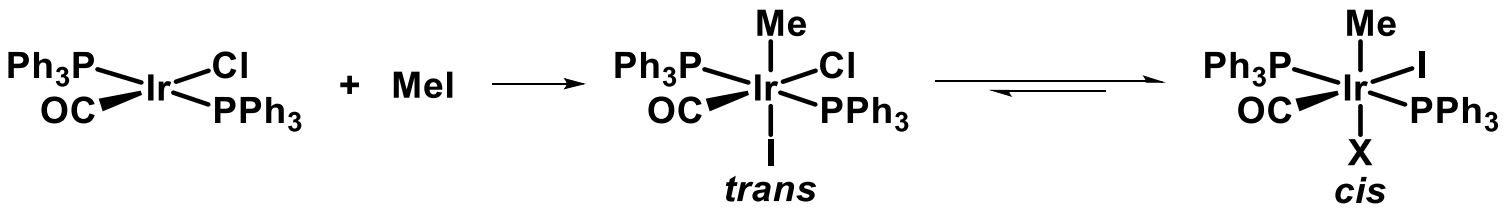


Relative rate

MeI > primary–X > secondary–X > > tertiary–X

I > Br > Cl > > F

- **Typical for Vaska´s complex**

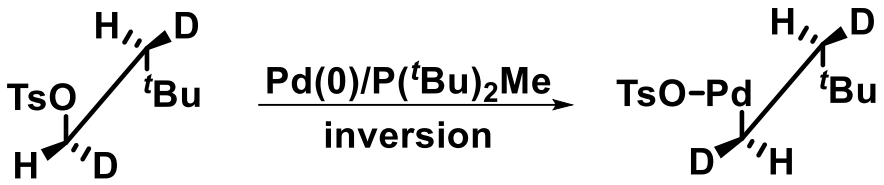


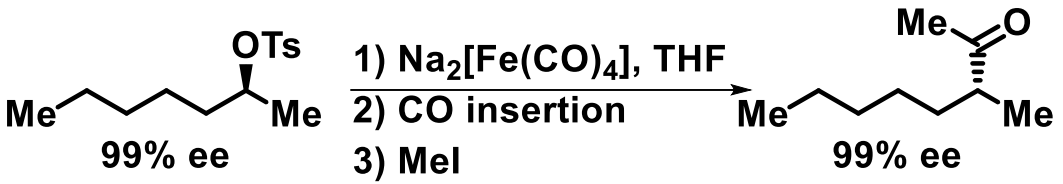
Basic Mechanisms in Organometallic Chemistry

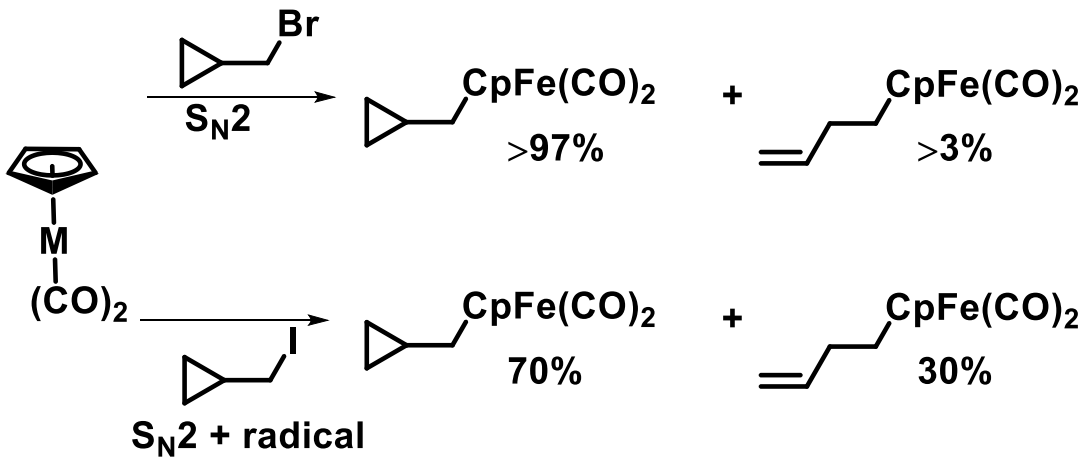
➢ Oxidative addition

$$R{-}X \xrightarrow{M^n} R{-}M^{n+2}{-}X$$

- **Oxidative addition by S_N2 mechanism**



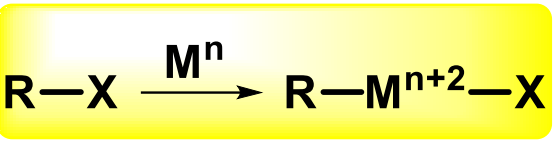




J. Chem. Soc., Dalton Trans. **1984**, 1171

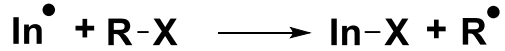
Basic Mechanisms in Organometallic Chemistry

➢ Oxidative addition

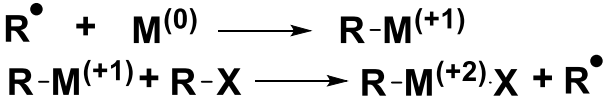


- **Radical chain oxidative addition**

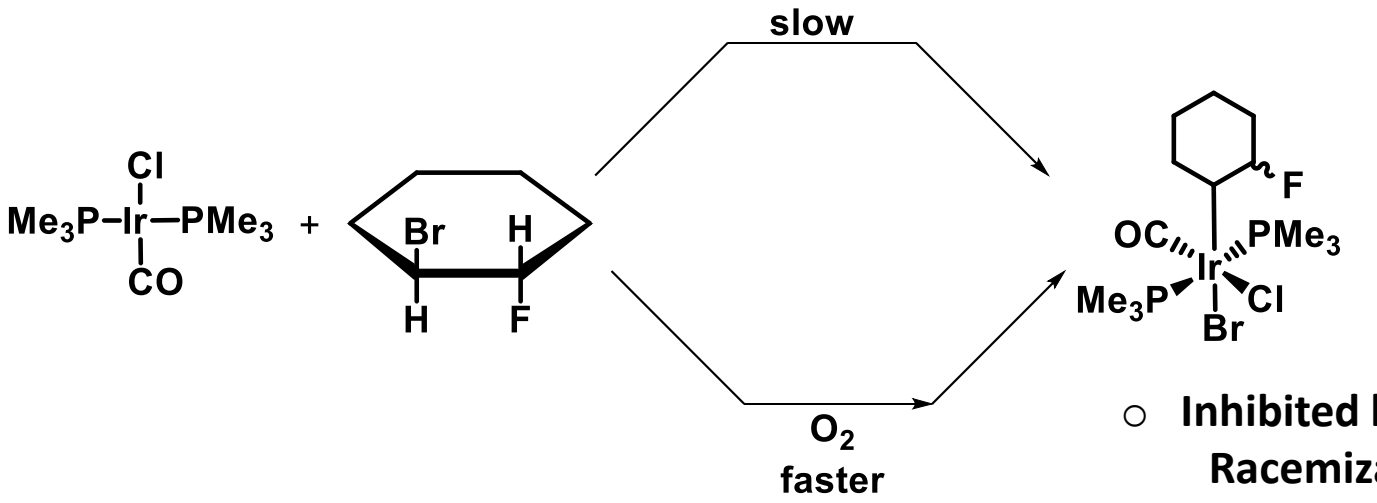
Initiation



Propagation



- Only for coordinatively unsaturated complexes
  requires radical initiator

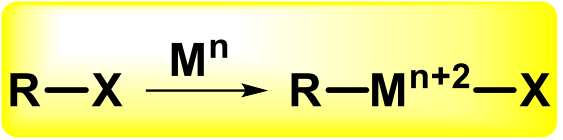


- Inhibited by hydroquinones
  Racemization occured

Inorg. Chem. **1984**, 23, 649; *Acc. Chem. Rec.* **1984**, *17*, 221

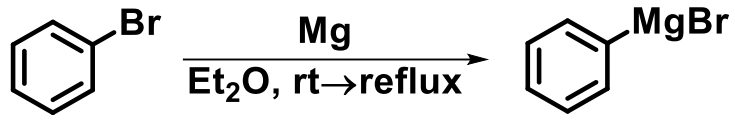
Basic Mechanisms in Organometallic Chemistry

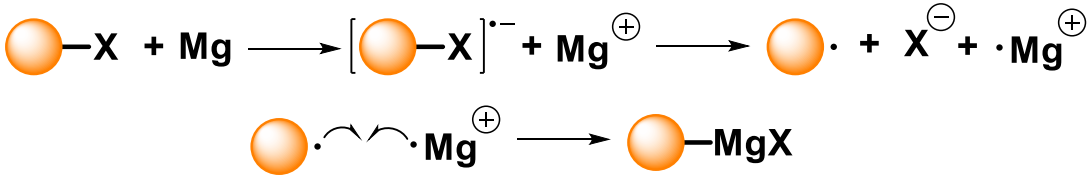
➢ Oxidative addition



- **Concerted oxidative addition (Typical for aryl halides)**

- **Example of oxidative addition from traditional chemistry**



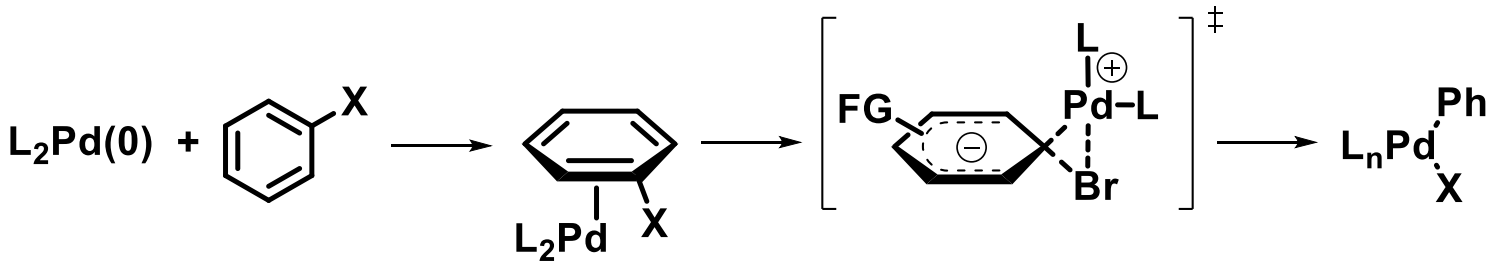


Basic Mechanisms in Organometallic Chemistry

➢ Oxidative addition

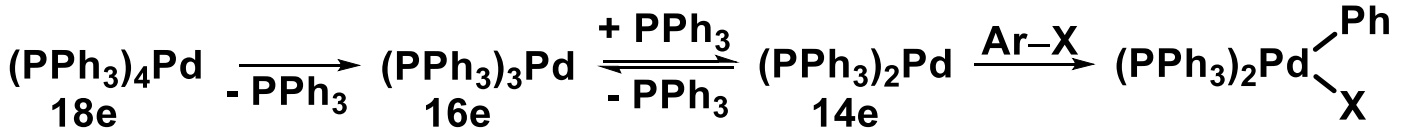
- Concerted oxidative addition (Typical for aryl halides)

○ Proposed mechanism



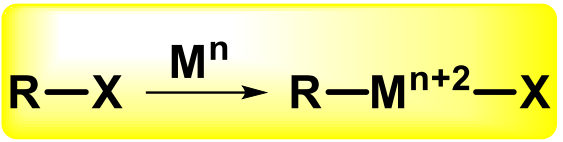
ArI > ArBr > ArCl and EWG-ArX > EDG-ArX

○ 12e or 14e Pd-complexes are the most reactive



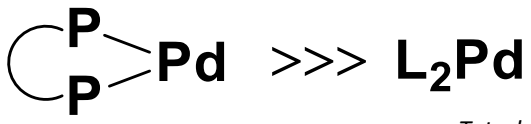
Basic Mechanisms in Organometallic Chemistry

➢ Oxidative addition



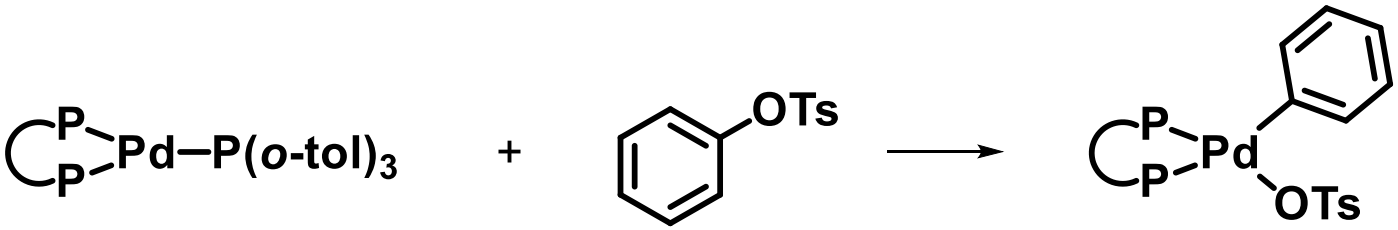
- Concerted oxidative addition (Typical for aryl halides)

○ Complexes with a bidentate ligand are more reactive (The complex is bent to a less stable conformation)



Tetrahedron Lett. **1998**, 39, 6163

○ Extremely hindered P-ligands must dissociate before the oxidative addition



Angew. Chem. Int. Ed. **2003**, 42, 5355

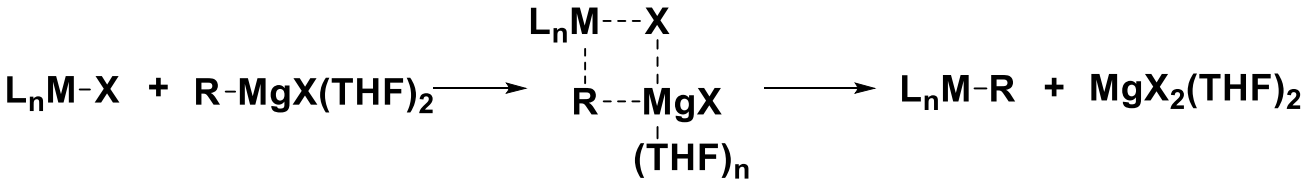
○ Complexes with alkylphosphine ligands react with aryl chlorides faster then complexes with arylphosphines

Angew. Chem. Int. Ed. **2004**, 43, 2968; *Angew. Chem. Int. Ed.* **2004**, 43, 3955

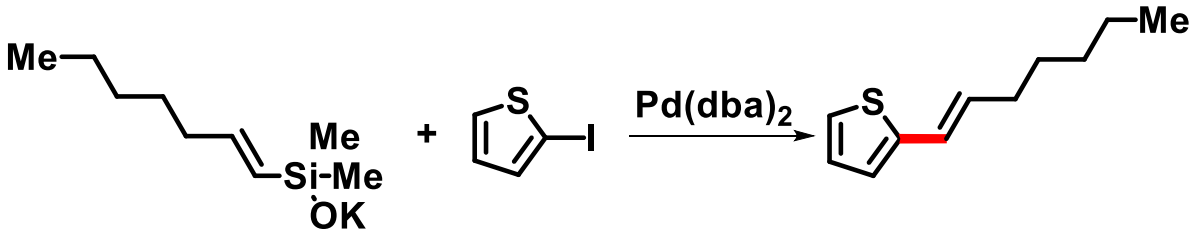
Basic Mechanisms in Organometallic Chemistry

➢ Transmetallation

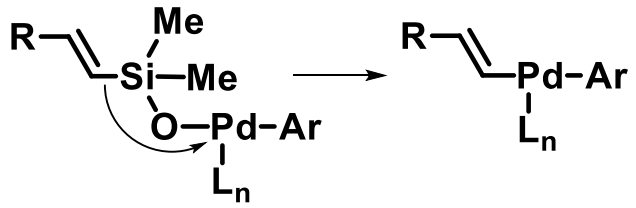
- **Concerted mechanism**



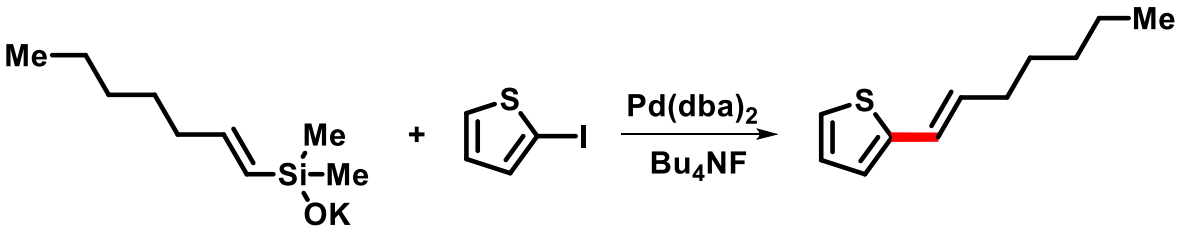
- **Transmetallation mechanism depends on reaction conditions**



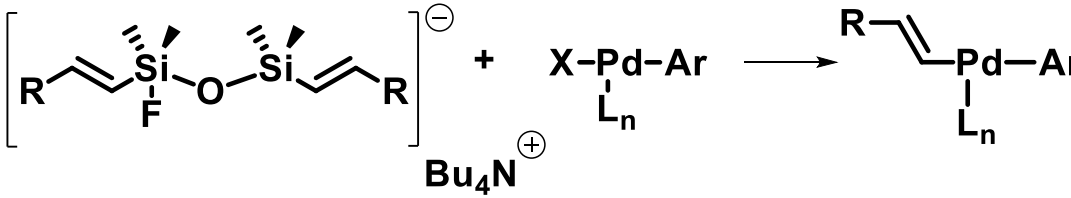
transmetallation step



J. Am. Chem. Soc. **2004**, *126*, 4876



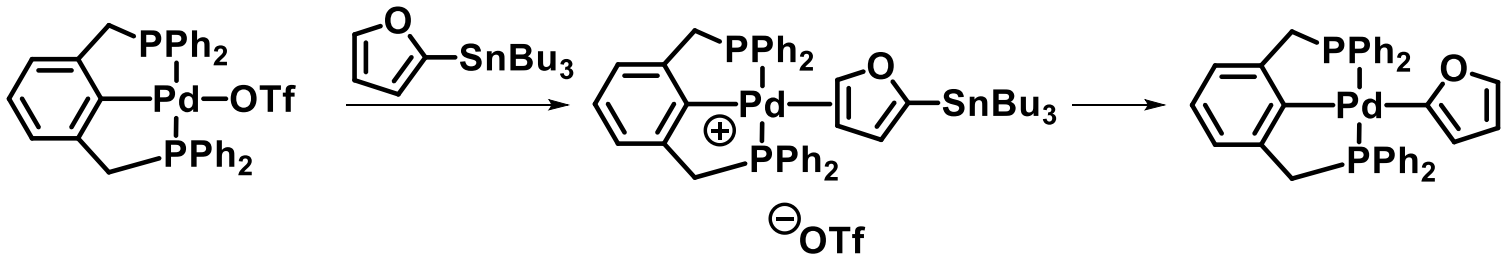
transmetallation step



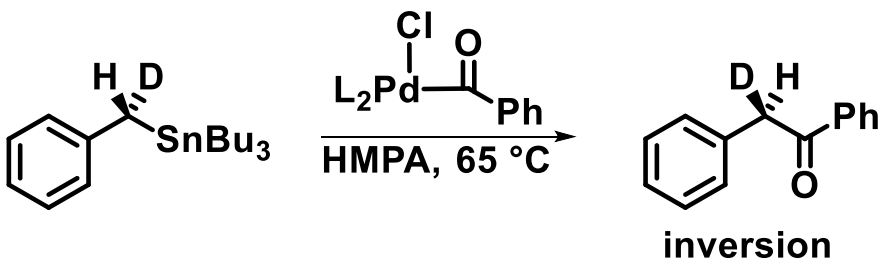
J. Am. Chem. Soc. **2004**, *126*, 4865

➢ Transmetallation

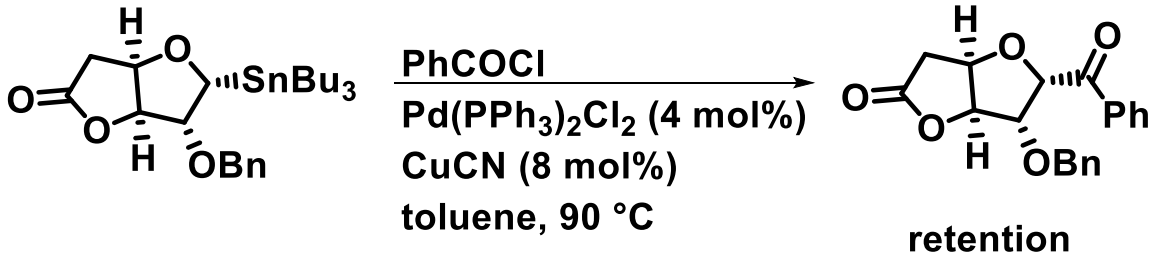
- **Sn→Pd transmetalation starts by coordination**



J. Am. Chem. Soc. **1998**, *120*, 11016



J. Am. Chem. Soc. **1983**, *105*, 6129



Tetrahedron Lett. **1993**, *34*, 8007

Basic Mechanisms in Organometallic Chemistry

➢ Reductive elimination for the formation of C–C bond

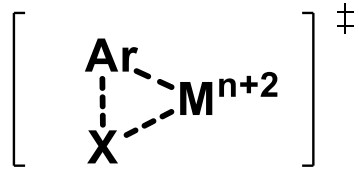
$$R{-}M^{n+2}{-}X \xrightarrow{-M^n} R{-}X$$

- Reverse proces to oxidative addition

oxidative addition

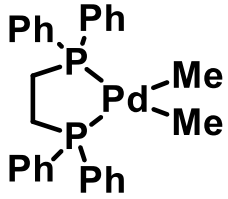
$$Ar{-}X \rightleftharpoons Ar{-}M^{n+2}(X) \quad (\pm M^n)$$

reductive elimination

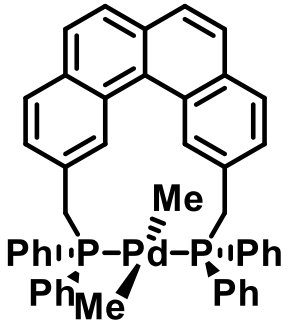


concerted mechanism

- Typical for *cis*-complexes



DMSO, 80 °C → Me–Me



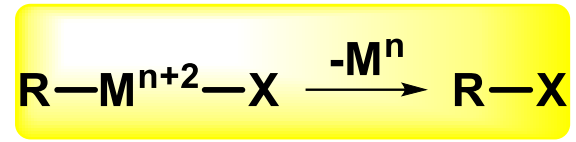
DMSO, 80 °C → no reaction

- First row complexes react faster then second row
- Complexes with sterically more hindered ligands are more reactive
- Electron-poor metal centers eliminate faster

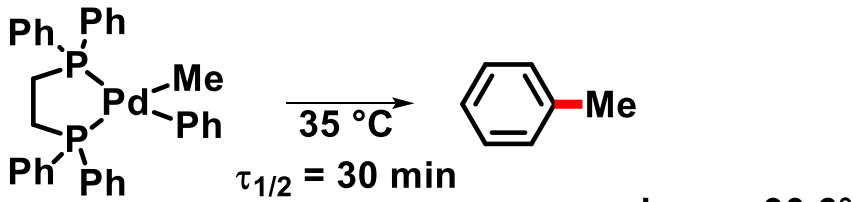
J. Am. Chem. Soc. **1979**, *101*, 4981

Basic Mechanisms in Organometallic Chemistry

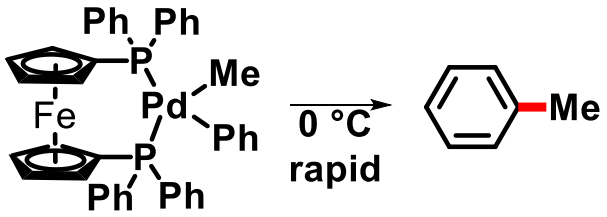
➢ Reductive elimination for the formation of C–C bond



- Higher ligand bite angle = better reductive elimination

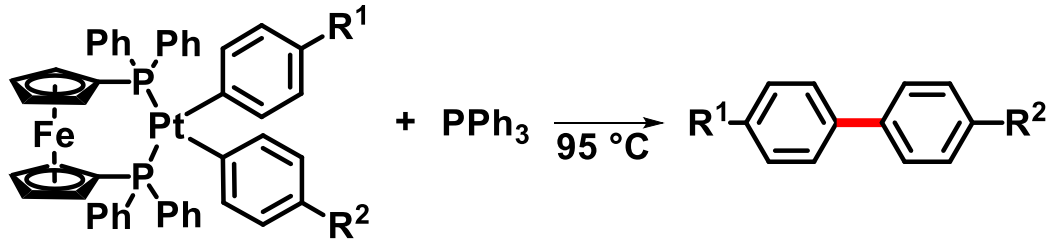


dppe = 90.6°
dppf = 99.1°



Inorg. Chim. Acta. **1994**, *220*, 249

- The rate of reductive elimnation is affected by electronic properties – pairing is the best option



Relative rates:

R^1 = OMe, R^2 = CF_3 > $R^{1,2}$ = OMe > $R^{1,2}$ = CF_3

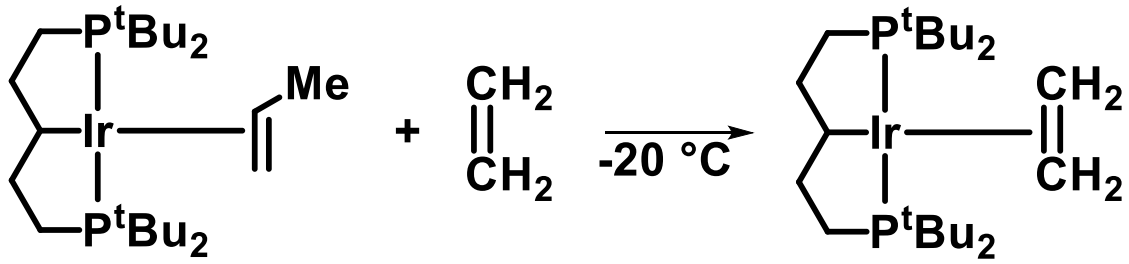
J. Am. Chem. Soc. **2004**, *126*, 13016

Basic Mechanisms in Organometallic Chemistry

➢ Ligand substitution

$L_nM—L \underset{-L}{\overset{+L'}{\rightleftharpoons}} L_nM—L'$

$L_nM—L + L' \rightleftharpoons L_nM—L' + L$



Science **2005**, *307*, 1080.

- **Associative mechanism (S_N2)**

$L_nM \xrightarrow{+L'} L_nM—L' \xrightarrow{-L} L_{n-1}M—L'$

- **Dissociative mechanism (S_N1)**

$L_nM \xrightarrow{-L} L_{n-1}M \xrightarrow{+L'} L_{n-1}M—L'$

Basic Mechanisms in Organometallic Chemistry

➢ Ligand substitution

$$L_nM{-}L \underset{-L}{\overset{+L'}{\rightleftharpoons}} L_nM{-}L'$$

- **Associative mechanism (S_N2)**

$$L_nM \xrightarrow{+L'} L_nM{-}L' \xrightarrow{-L} L_{n-1}M{-}L'$$

- Occurs with 16e and 17e complexes
- Favored for more electrophilic metals
- Favored for more basic attacking ligand
- Departing ligand negligibly affects substitution
- Metal should be sterically accessible
- Typical for square-planar 16-electron complexes (Pd^{II}, Ni^{II}, Au^{III}, Rh^{I}, Ir^{I})

- **Dissociative mechanism (S_N1)**

$$L_nM \xrightarrow{-L} L_{n-1}M \xrightarrow{+L'} L_{n-1}M{-}L'$$

- Typicall for 18e complexes
- Favored for electron-rich and electron-poor metals
- Favored for sterically hindered metals

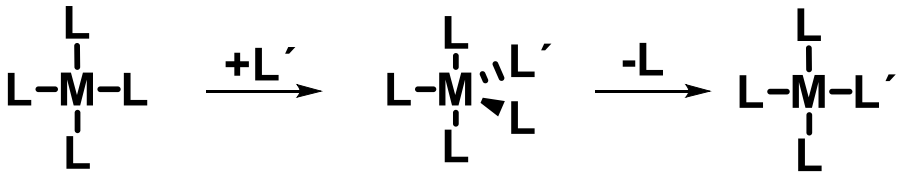
Basic Mechanisms in Organometallic Chemistry

$L_nM—L \underset{-L}{\overset{+L'}{\rightleftharpoons}} L_nM—L'$

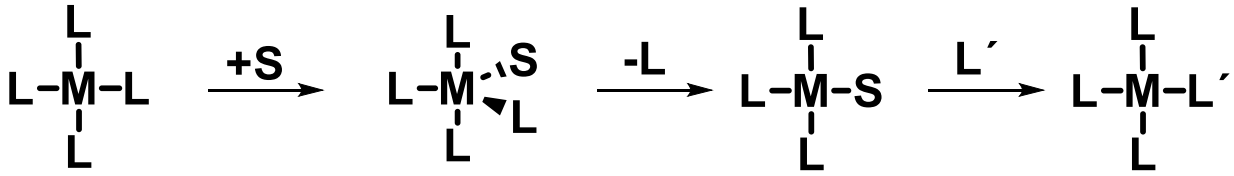
➢ Ligand substitution

- **Associative mechanism (S_N2)**

  - **Without solvent participation**

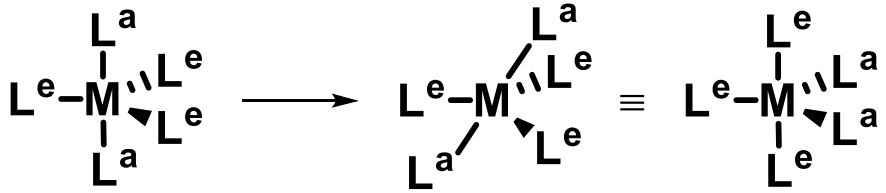


  - **With solvent participation**



Associative mechanism is stereoselective!

  - **Ligand *cis-trans* isomerization – pseudorotation ! (Berry)**



Basic Mechanisms in Organometallic Chemistry

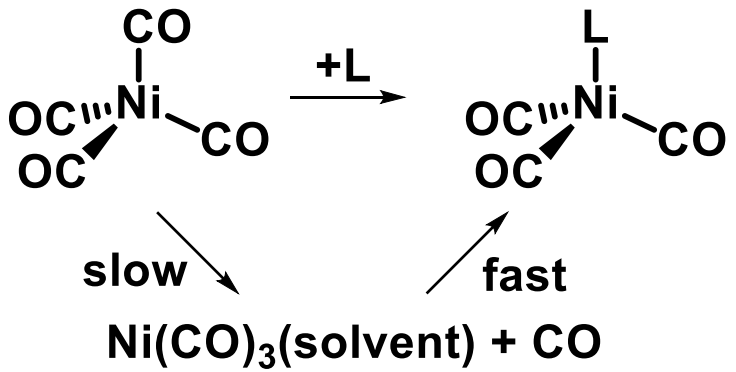
➢ Ligand substitution

$$L_nM{-}L \underset{-L}{\overset{+L'}{\rightleftharpoons}} L_nM{-}L'$$

- **Dissociative mechanism (S_N1)**

$$L_nM \xrightarrow{-L} L_{n-1}M \xrightarrow{+L'} L_{n-1}M{-}L'$$

  - **Ligand elimination is ussually slow**



J. Am. Chem. Soc. **1968**, *90*, 6927; *Inorg. Chim. Acta* **1981**, *50*, 65
Chem. Rev. **1983**, *83*, 557.

  - **Racemization occurs during dissociative mechanism**

Basic Mechanisms in Organometallic Chemistry

➢ Quick summary

$L_nM{-}L \underset{-L}{\overset{+L'}{\rightleftharpoons}} L_nM{-}L'$

Ligand substitution

$$L_nM{-}L + L' \longrightarrow L_nM{-}L' + L$$

Oxidative addition

$$X{-}Y + L_nM^n \longrightarrow L_nM^{n+2}(X)(Y)$$

Transmetallation

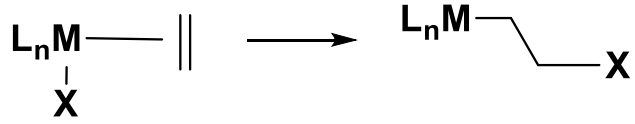
$$R{-}M + M{-}X \longrightarrow X{-}M + M{-}R$$

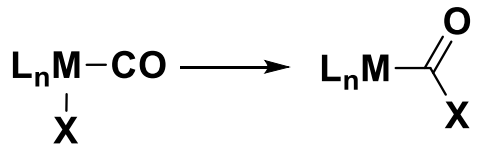
Reductive elimination

$$L_nM^{n+2}(X)(Y) \longrightarrow X{-}Y + L_nM^n$$

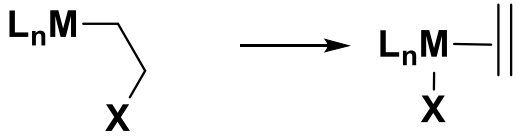
✓ **Finished**

Migratory insertion





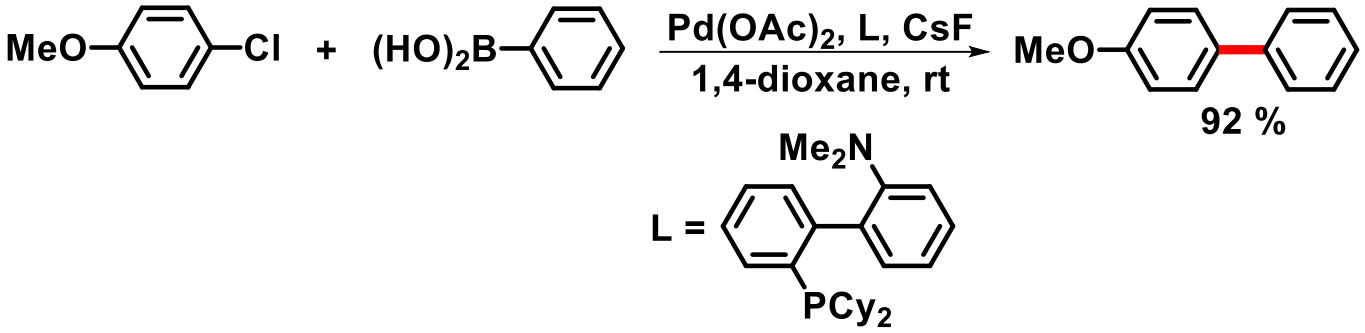
β-Elimination



- **Coming soon…**

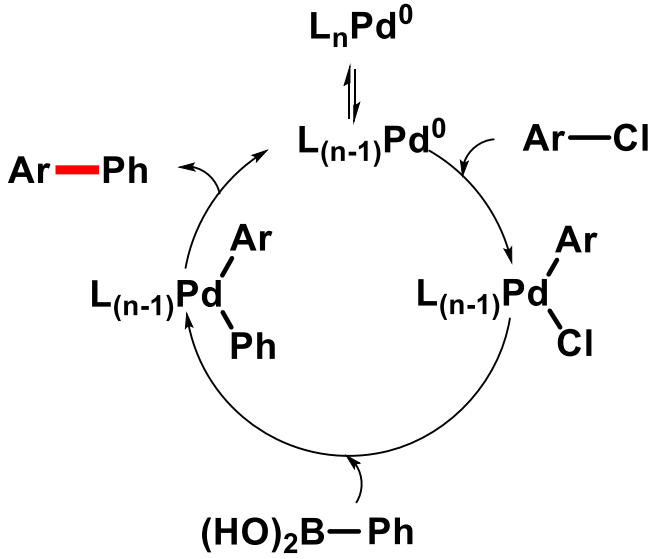
Basic Mechanisms in Organometallic Chemistry

➢ Alkyl, aryl and vinyl ligands en route to C–C bond formation



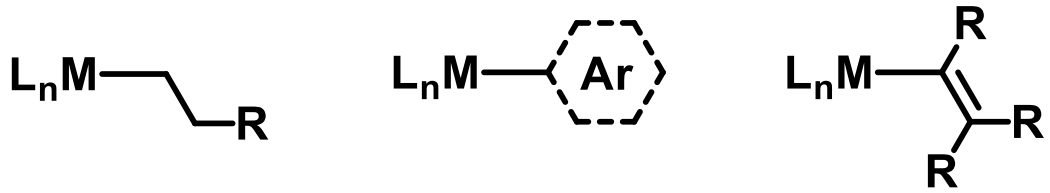
- **Simplified mechanism**

J. Am. Chem. Soc. **1998**, *120*, 9722

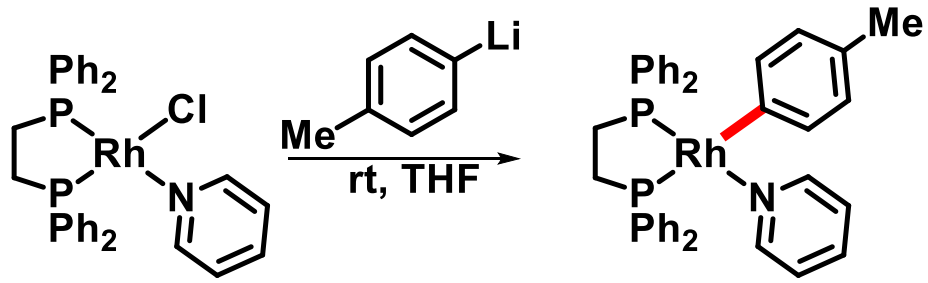


Basic Mechanisms in Organometallic Chemistry

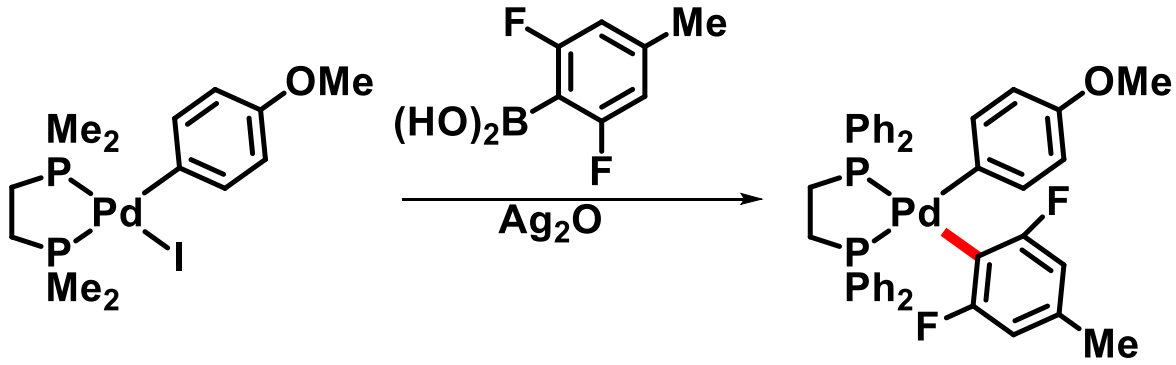
➢ Alkyl, aryl and vinyl ligands en route to C–C bond formation



- **Preparation of M–Alkyl, M–aryl and M–vinyl complexes by transmetallation**



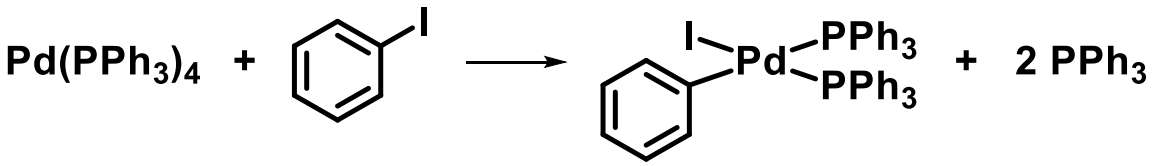
J. Am. Chem. Soc. **2004**, *126*, 2594

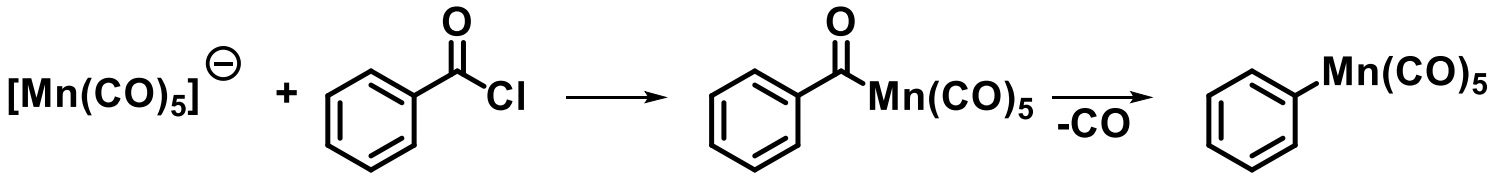


Organometallics **2005**, *24*, 190

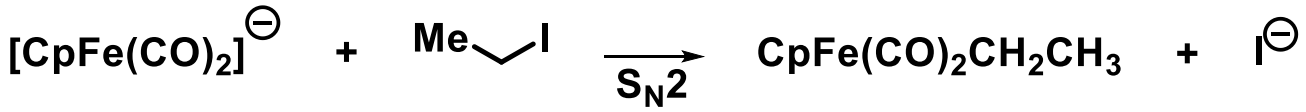
➢ Alkyl, aryl and vinyl ligands en route to C–C bond formation

- **Preparation of M–Alkyl, M–aryl and M–vinyl complexes by oxidative addition**





- **Preparation of M–Alkyl, M–aryl and M–vinyl complexes by alkylation**



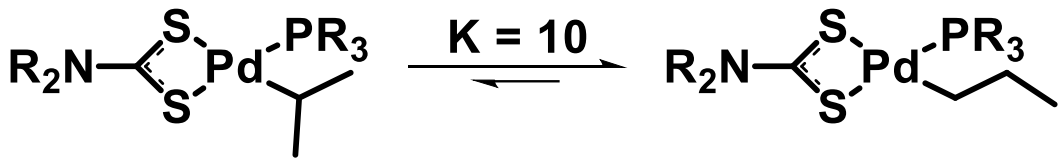
J. Am. Chem. Soc. **1985**, *107*, 3502

Basic Mechanisms in Organometallic Chemistry

➢ Alkyl, aryl and vinyl ligands

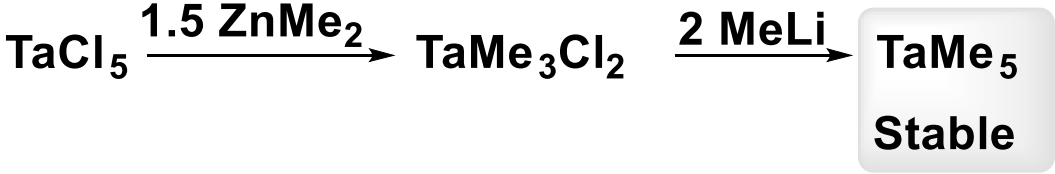
• M-Alkyl complexes – Properties

○ **Isomerization**

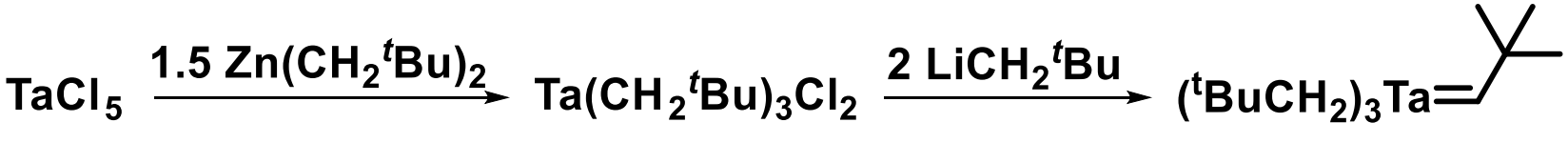


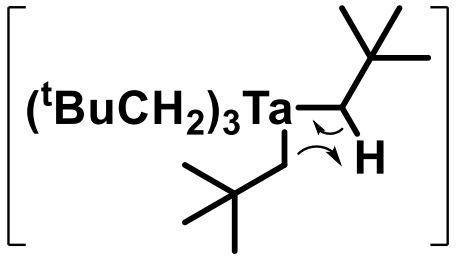
Organometallics **1992**, *11*, 4285; . *Organometallics* **1992**, *10*, 902; *J. Organomet. Chem.* **1981**, *216*, C12

○ **α–Elimination**



J. Organomet. Chem. **1976**, *122*, 209.



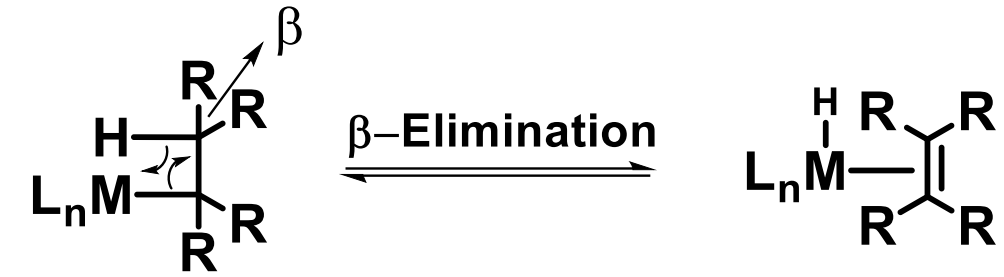


J. Am. Chem. Soc. **1978**, *100*, 3359.

➢ Alkyl, aryl and vinyl ligands

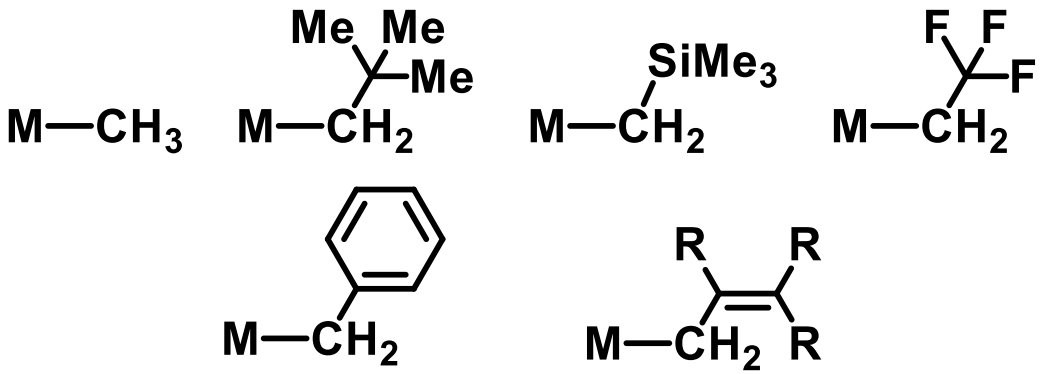
• M-Alkyl complexes – Properties

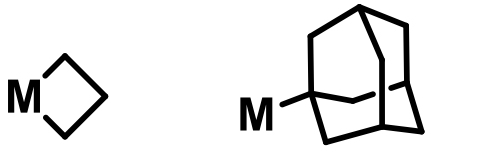
- β–Elimination



cis configuration

- Alkyl groups resistant to β–Elimination:





cis orientation is blocked

➢ Alkyl, aryl and vinyl ligands

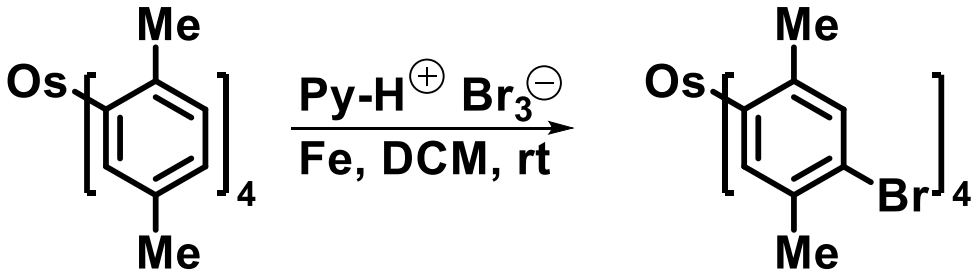
• M-Aryl complexes – Properties

- M–Aryl complexes are more stable then M–Alkyl complexes

$Ph–Mn(CO)_5$ x $Me–Mn(CO)_5$ ΔBDE = 4 kcal/mol

Ph–Ti x Me–Ti ΔBDE = 7.5 kcal/mol

Ph–Ir x Me–Ir ΔBDE = 26 kcal/mol



Chem. Commun. **2001**, 1478