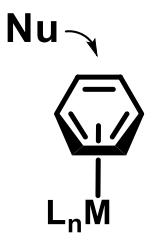
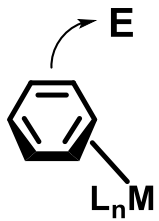
Reaction of Coordinated Ligands

➢ Reaction of coordinated ligands

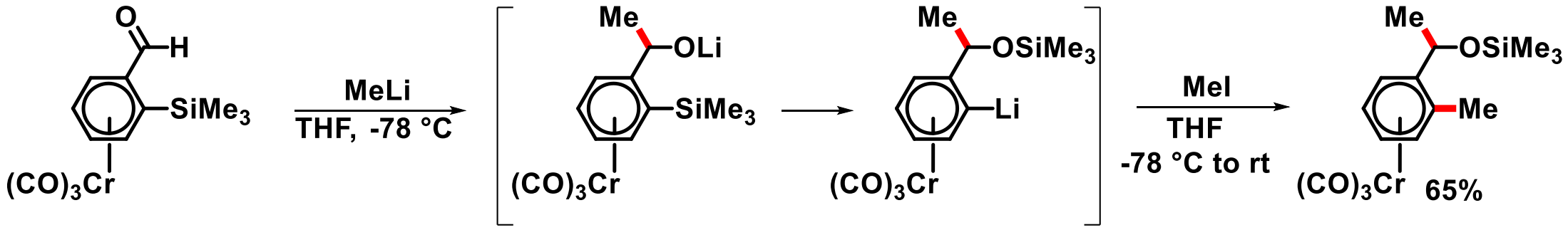
- Already mentioned reaction of coordinated ligands
  - Arene complexes



η^6-arene complexes



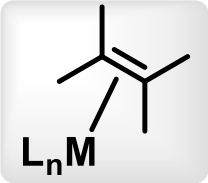
η^2-arene complexes



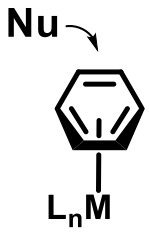
Org. Lett. **2000**, *2*, 717

Reaction of Coordinated Ligands

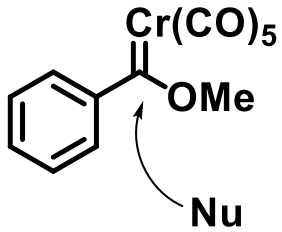
➢ Alkene complexes



✓ Stoichiometric reactions

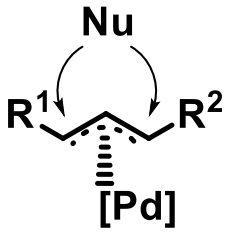


η^6-arene complexes



carbene complexes

✓ Catalytic reactions



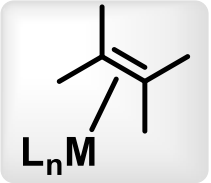
Tsuji-Trost reaction

○ Transformation of coordinated alkenes

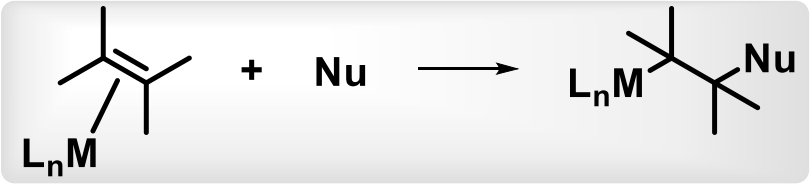
✓ Stoichiometric and catalytic reactions

Reaction of Coordinated Ligands

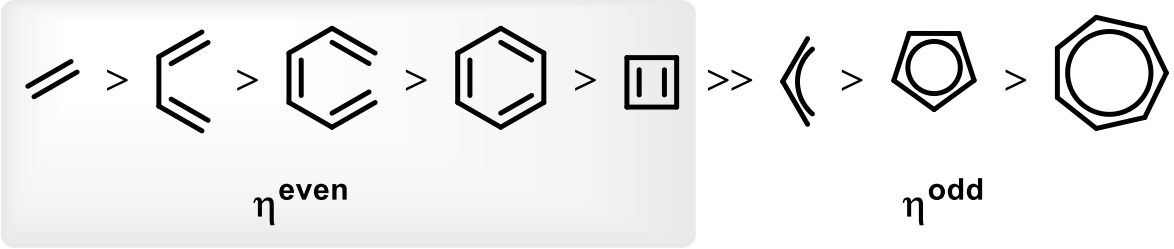
➢ Alkene complexes



- General rules for nucleophilic attack on coordinated alkenes



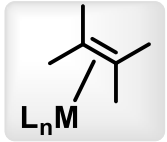
○ Order of reactivity of π-ligands according to the Davies–Green–Mingor rules



Tetrahedron **1978**, *34*, 3047

✓ Divided according to hapticity

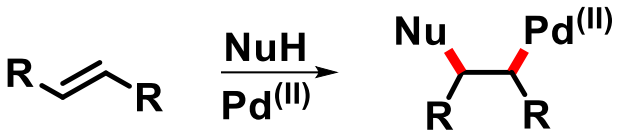
Reaction of Coordinated Ligands

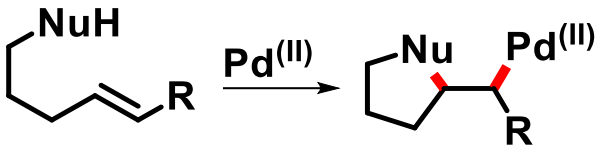


➢ Alkene complexes

- **Catalytic reactions: Nucleopalladation**

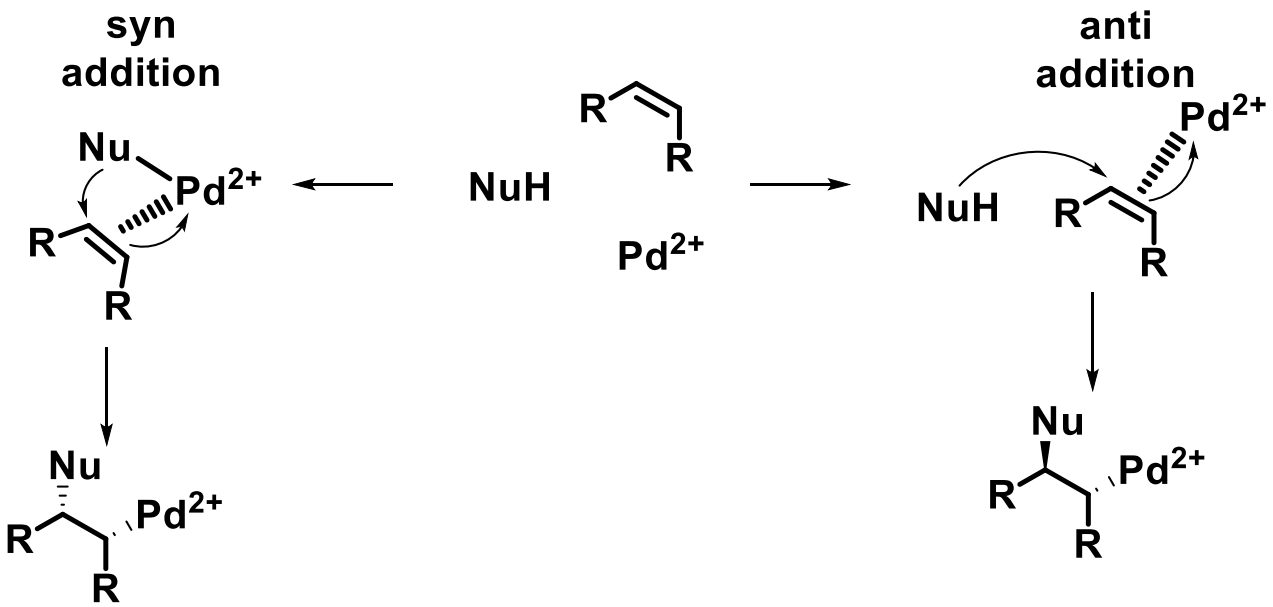
○ **Overall reaction scheme**

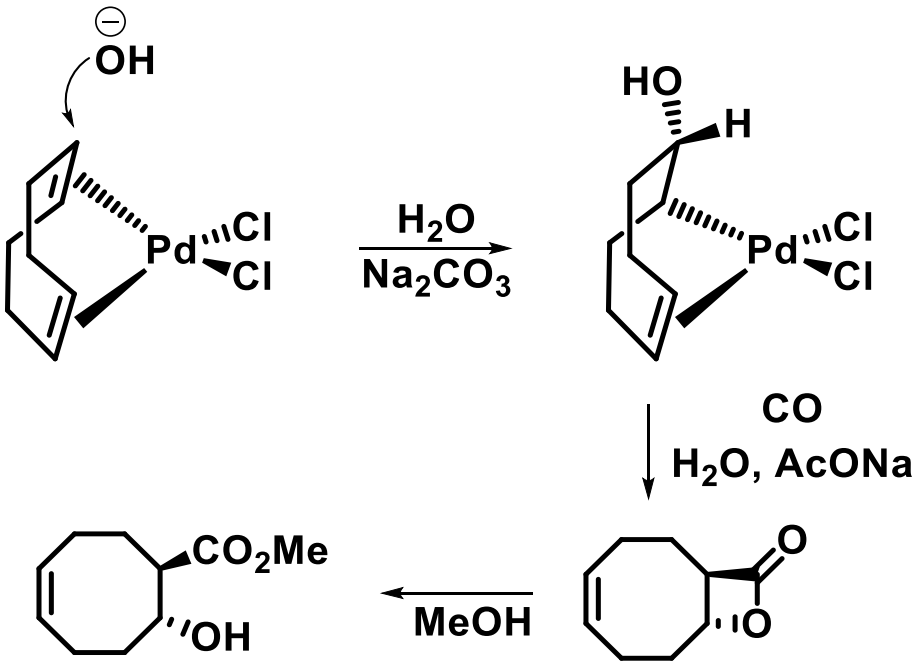




○ **In some cases *anti*-addition prevails**

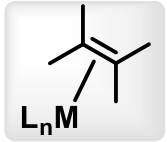
○ **Stereochemistry**





J. Am. Chem. Soc. **1975**, *97*, 674; *J. Organomet. Chem.* **1976**, *108*, 401

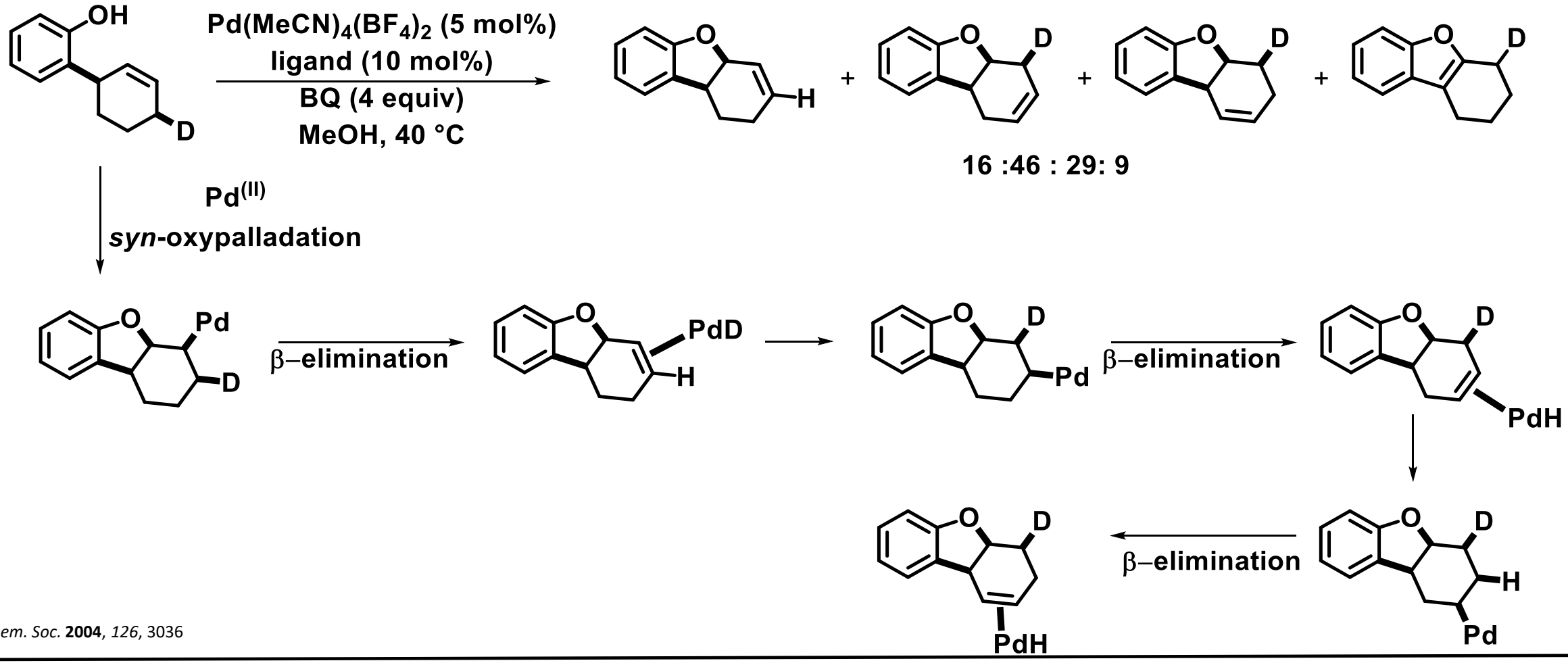
Reaction of Coordinated Ligands



➢ Alkene complexes

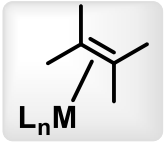
- **Catalytic reactions: Oxypalladation**

○ **The mechanism of oxypalladation depends on reaction conditions**



J. Am. Chem. Soc. **2004**, *126*, 3036

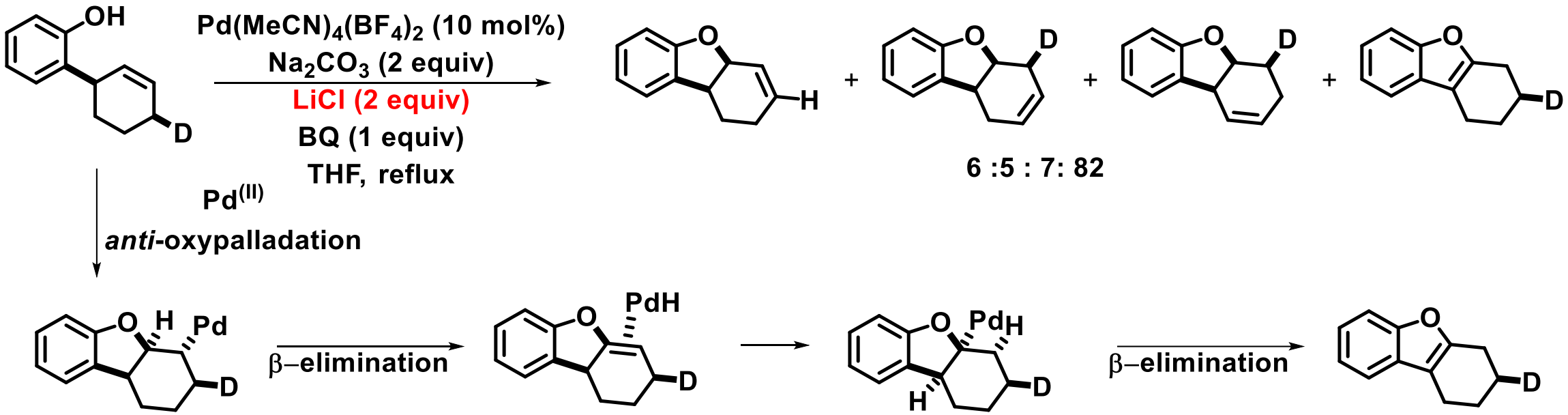
Reaction of Coordinated Ligands



➢ Alkene complexes

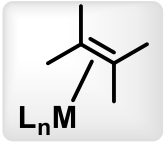
- Catalytic reactions: Oxypalladation

○ The mechanism of oxypalladation depends on reaction conditions



J. Am. Chem. Soc. **2004**, *126*, 3036

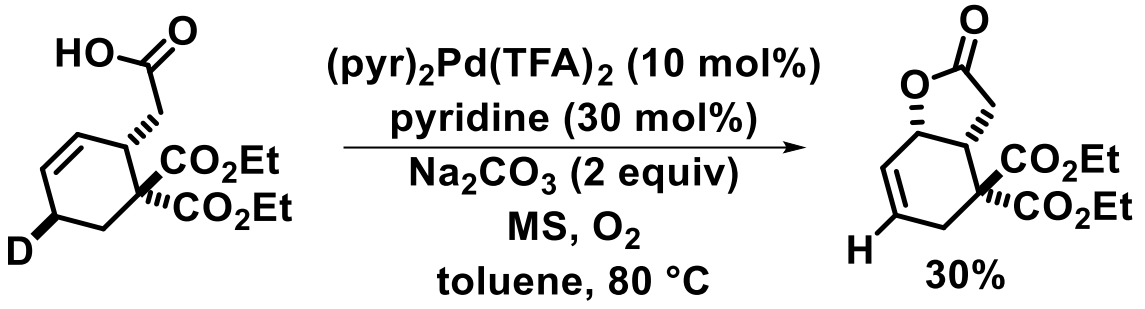
Reaction of Coordinated Ligands



➢ Alkene complexes

- **Catalytic reactions: Oxypalladation**

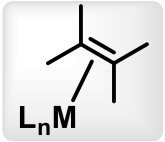
○ **The mechanism of oxypalladation depends on reaction conditions**



exclusive *anti*-oxypalladation

J. Am. Chem. Soc. **2005**, *127*, 17778

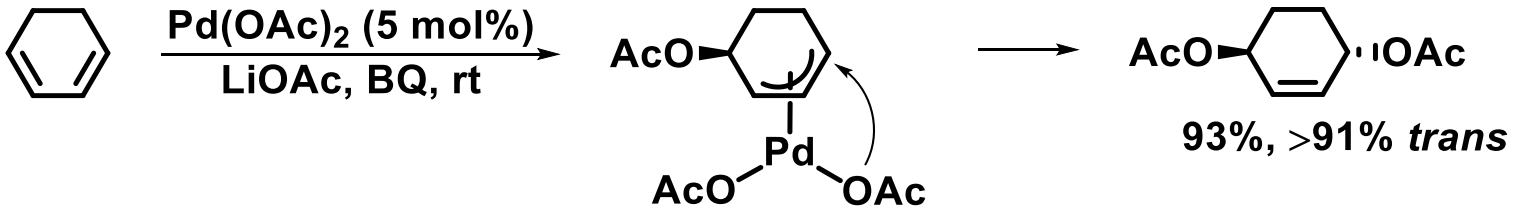
Reaction of Coordinated Ligands

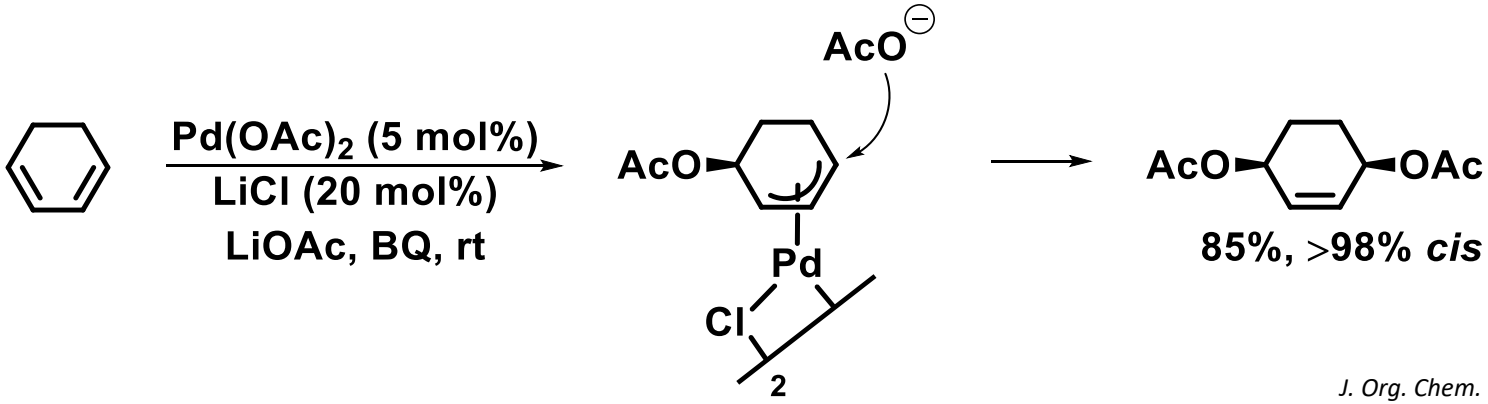


➢ Alkene complexes

- **Catalytic reactions: Oxypalladation**

○ **The mechanism of oxypalladation depends on reaction conditions – Diacetoxylation of 1,3-dienes**



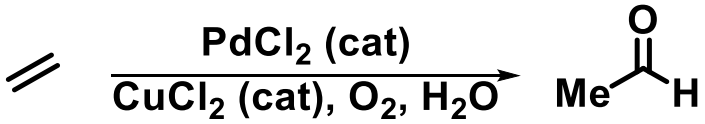


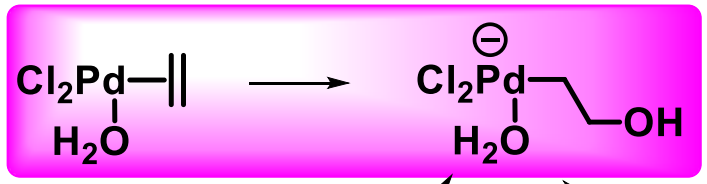
J. Org. Chem. **1984**, *49*, 4619

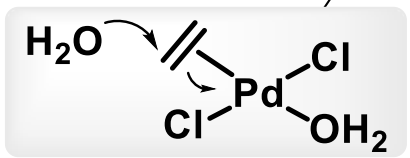
Reaction of Coordinated Ligands

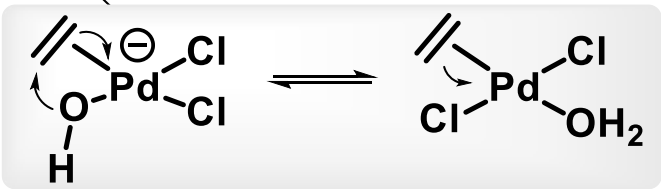
➢ Alkene complexes

- Catalytic reactions: Tsuji–Wacker reaction
  - Generally accepted mechanism



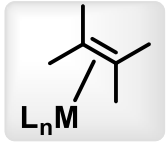






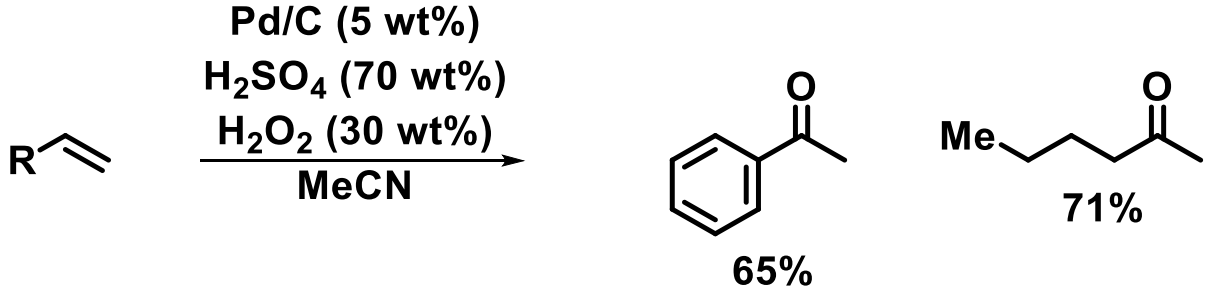
Angew. Chem. Int. Ed. **2009**, *48*, 9038

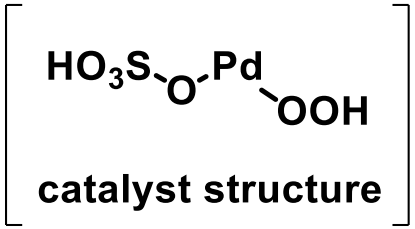
Reaction of Coordinated Ligands



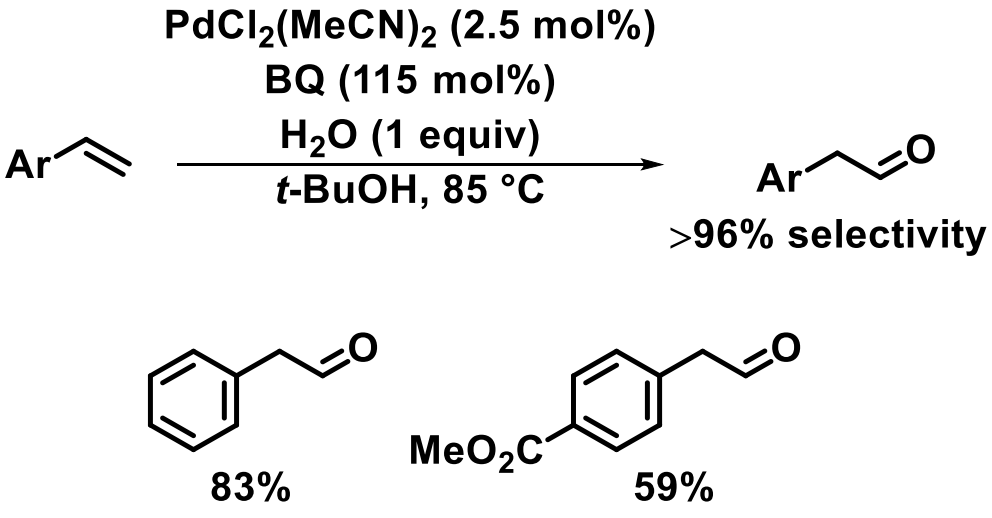
➢ Alkene complexes

- **Catalytic reactions: Tsuji–Wacker reaction**
  - **Applications**

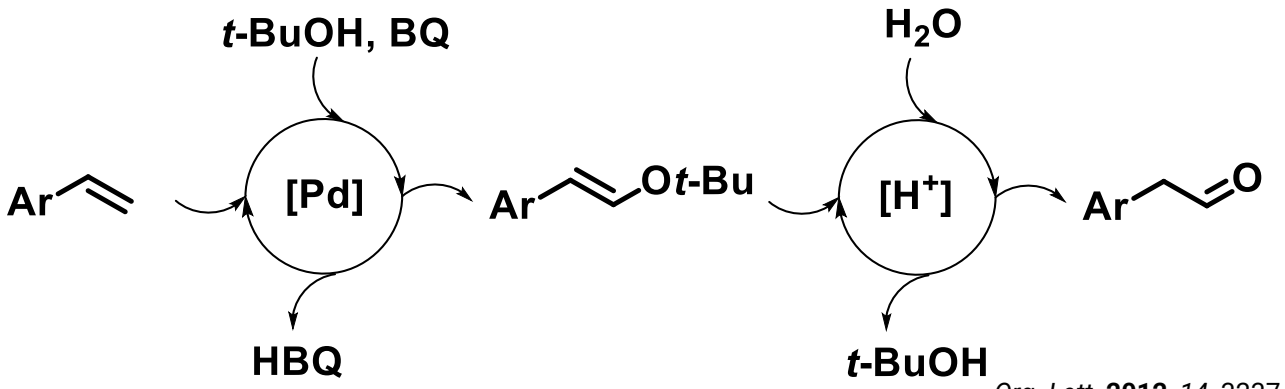




Synlett **2017**, *28*, 607

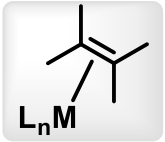


- **Proposed mechanism**



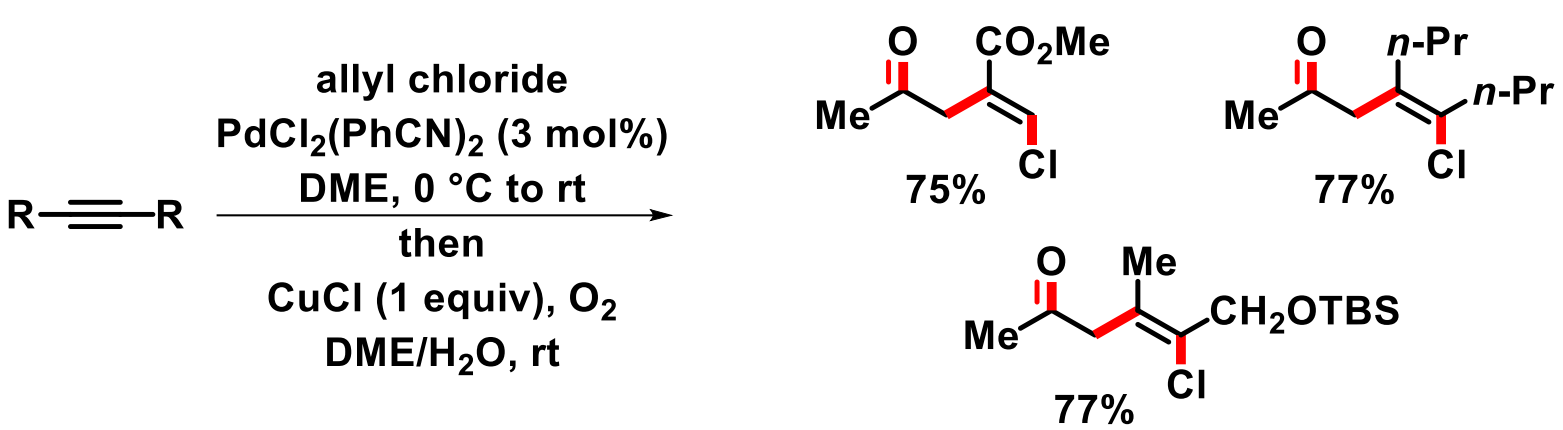
Org. Lett. **2012**, *14*, 3237

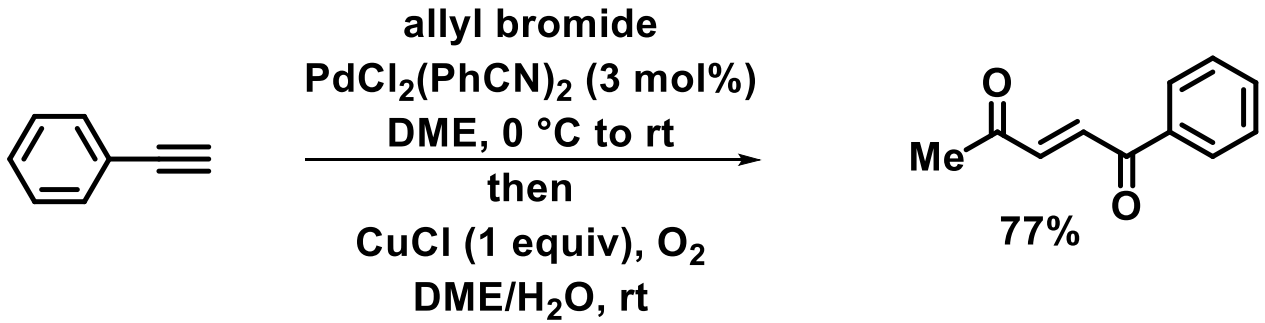
Reaction of Coordinated Ligands

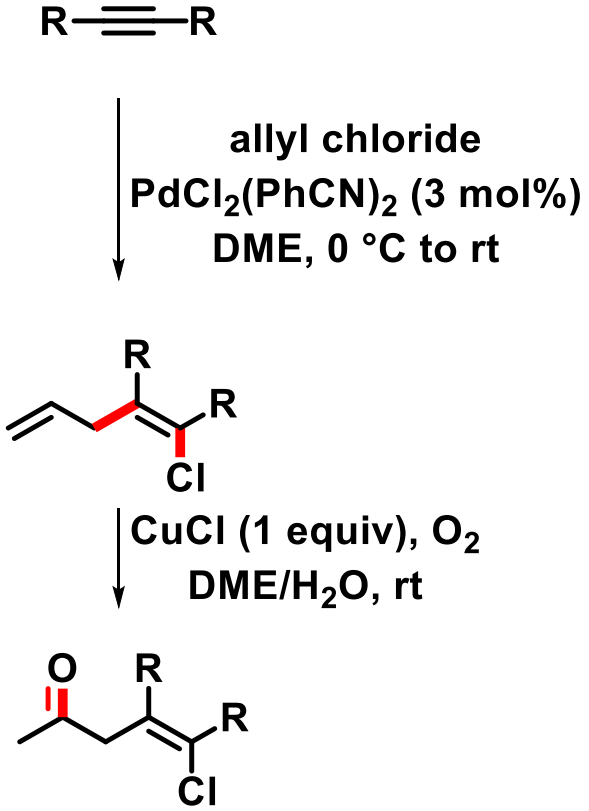


➢ Alkene complexes

- Catalytic reactions: Tsuji–Wacker reaction
  - Applications

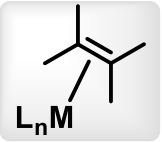






Org. Lett. **2002**, *4*, 4321

Reaction of Coordinated Ligands

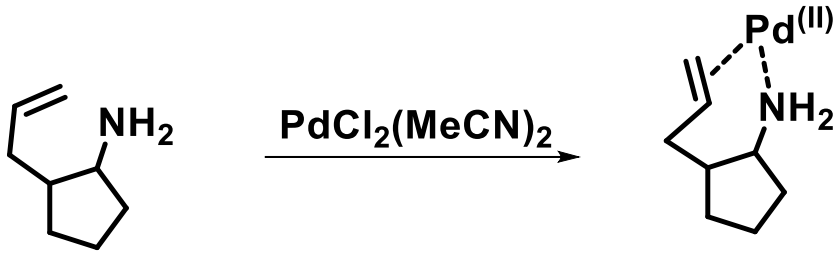


➢ Alkene complexes

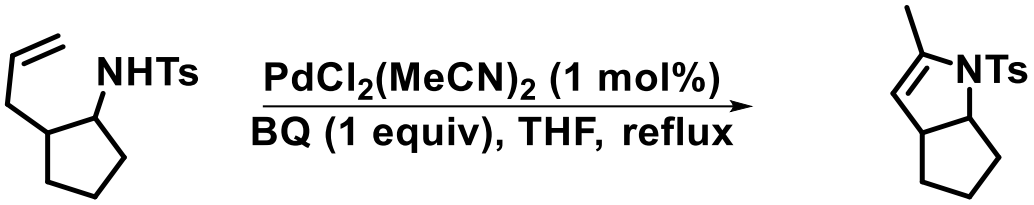
- Catalytic reactions: Nucleopalladation

○ Aminopalladation – similar to oxypalladation

✓ Aliphatic amines



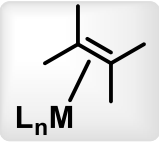
stable complex = unreactive!



85%

J. Am. Chem. Soc. **1982**, *104*, 2444

Reaction of Coordinated Ligands

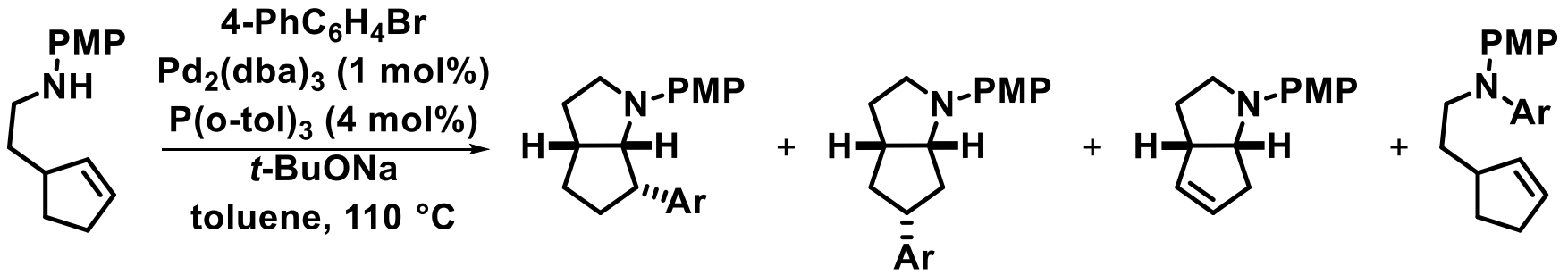


➢ Alkene complexes

- **Catalytic reactions: Nucleopalladation**

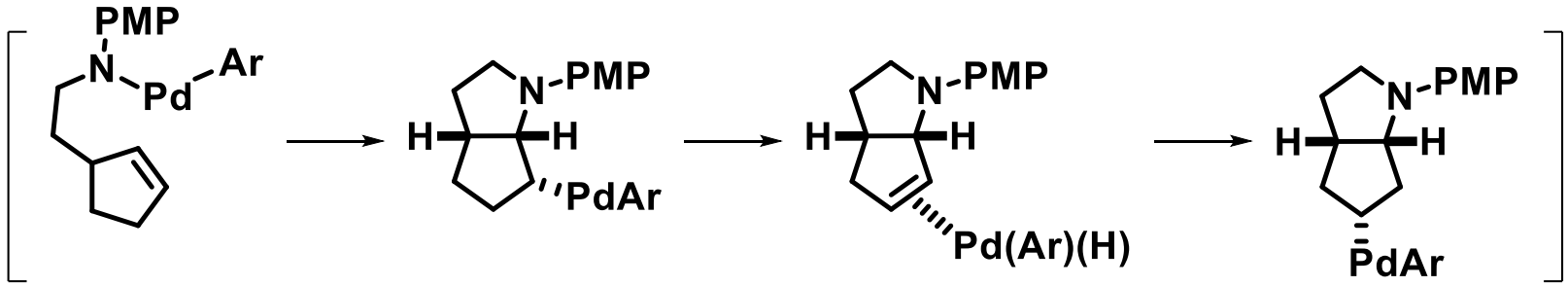
○ **Aminopalladation – similar to oxypalladation**

✓ **Aromatic amines**



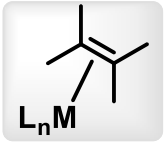
30% : 12% : 5% : 19%

exclusive
***syn*-aminopalladation**



Angew. Chem., Int. Ed. **2004**, *43*, 3605

Reaction of Coordinated Ligands

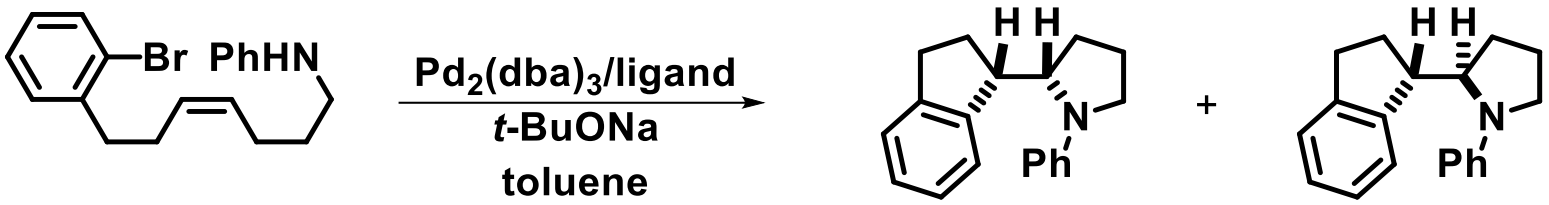


➢ Alkene complexes

- Catalytic reactions: Nucleopalladation

○ Aminopalladation – similar to oxypalladation

✓ Aromatic amines

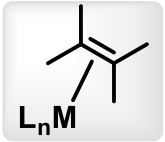


***syn*-aminopalladation** ***anti*-aminopalladation**

$PCy_3 \bullet HBF_4$	>20 : 1
(±)-BINAP	1 : 1

J. Am. Chem. Soc. **2006**, *128*, 2893

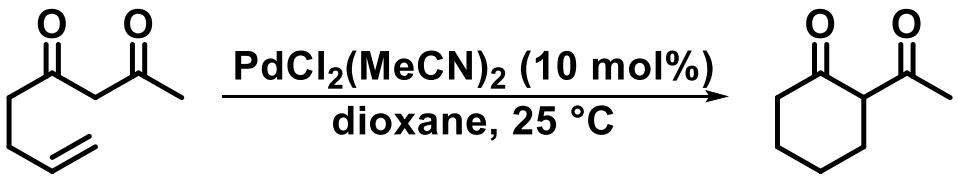
Reaction of Coordinated Ligands



➢ Alkene complexes

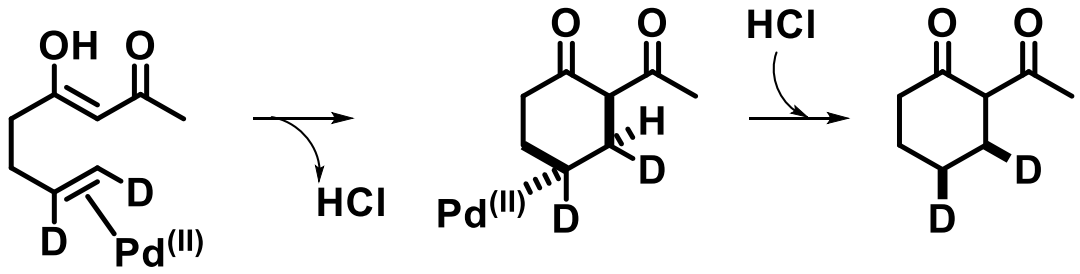
- Catalytic reactions: Nucleopalladation
  - Carbopalladation

✓ Hydroalkylation



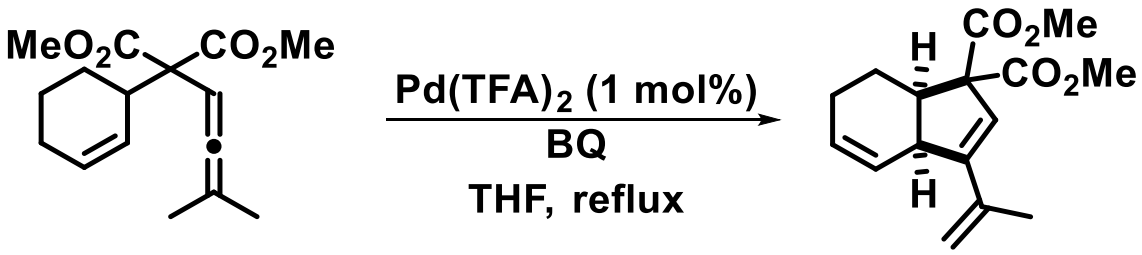
anti-carbopalladation 81%

✓ Selected steps from proposed mechanism

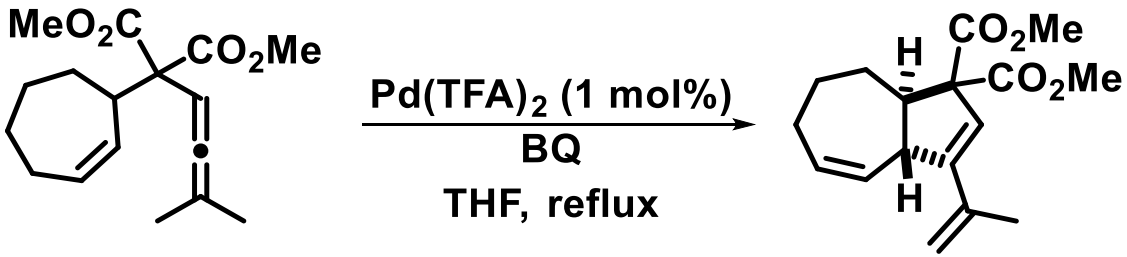


J. Am. Chem. Soc. **2001**, *123*, 11290; *Chem. Commun.* **2002**, 650

✓ Allene nucleophiles



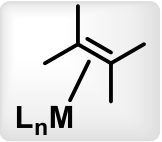
syn-carbopalladation 94%



anti-carbopalladation 82%

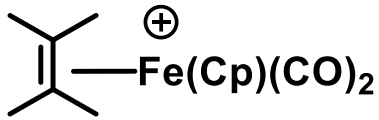
J. Am. Chem. Soc. **2003**, *125*, 6056

Reaction of Coordinated Ligands



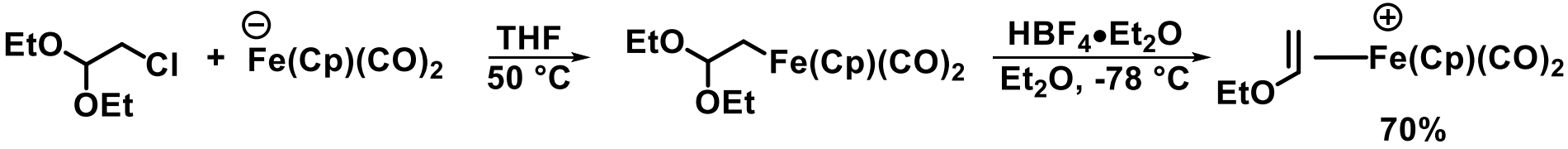
➢ Alkene complexes

- Stoichiometric reactions: η^2-alkene–Fe(Cp)(CO)$_2$ complexes
  - Synthesis of η^2-alkene–Fe(Cp)(CO)$_2$ complexes

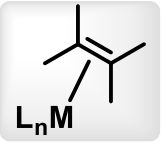


✓ Synthesis by ligand substitution

✓ Synthesis by alkylation



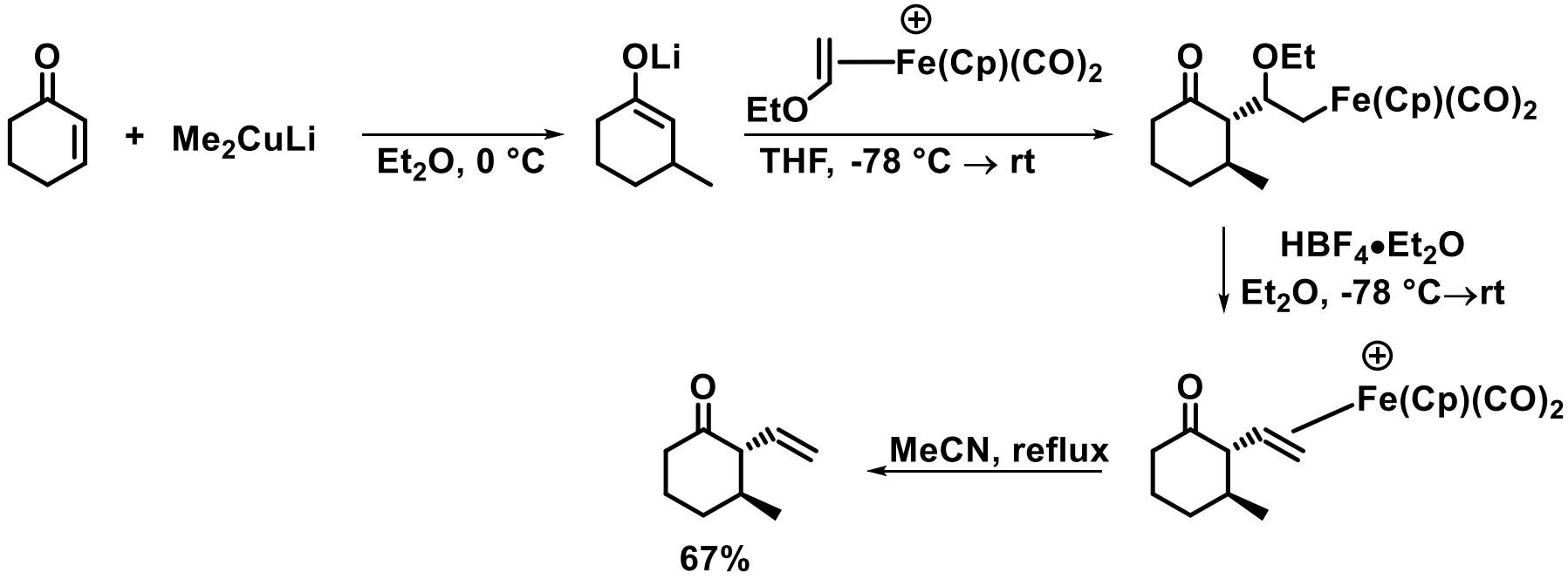
Reaction of Coordinated Ligands



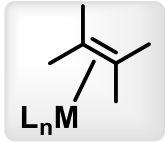
➢ Alkene complexes

- Stoichiometric reactions: η^2-alkene–$Fe(Cp)(CO)_2$ complexes
  - Reaction of η^2-alkene–$Fe(Cp)(CO)_2$ complexes with nucleophiles

✓ Reaction with enolates

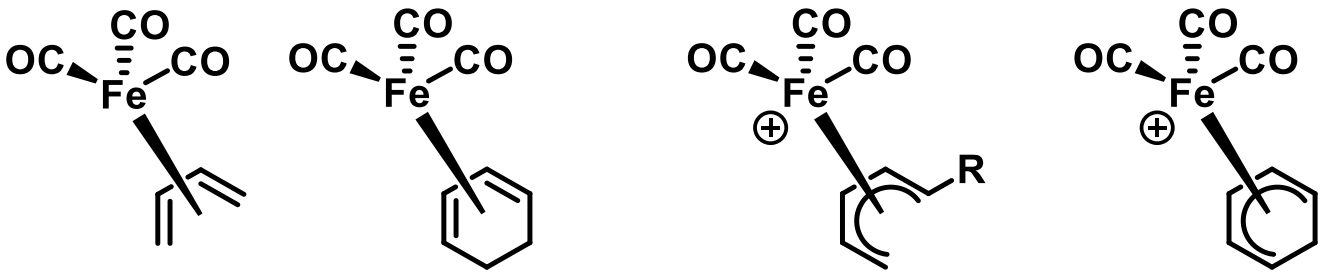


Reaction of Coordinated Ligands



➢ Alkene complexes

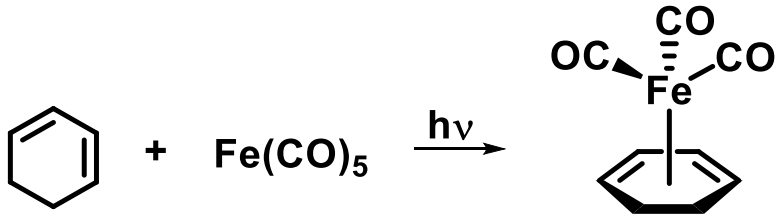
- **Stoichiometric reactions: η^4-diene–$Fe(CO)_3$ and η^5-dienyl–$Fe(CO)_3^+$ complexes**



η^4-diene complexes η^5-dienyl complexes

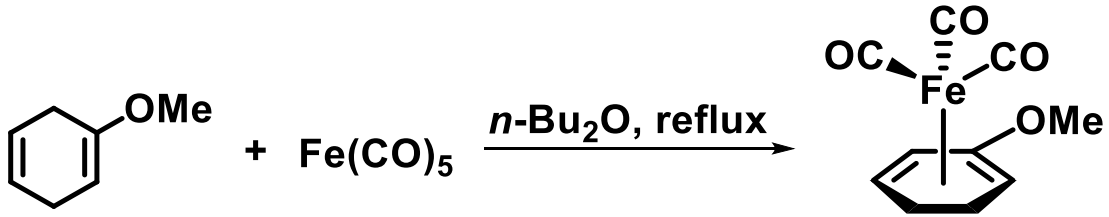
○ **Synthesis of η^4-diene–$Fe(CO)_3$ complexes**

✓ **Light mediated ligand substitution**



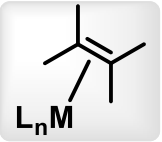
58%

✓ **Thermal mediated ligand substitution**



62%

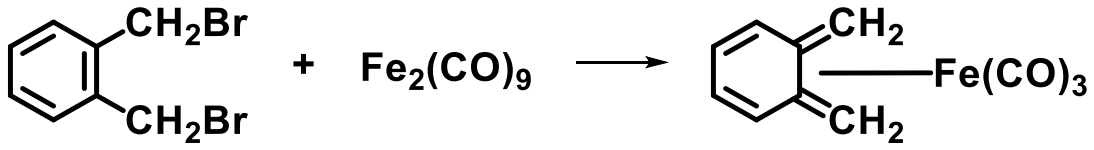
Reaction of Coordinated Ligands



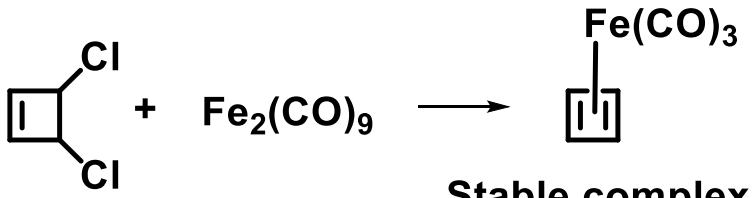
➢ Alkene complexes

- **Stoichiometric reactions: η^4-diene–$Fe(CO)_3$ and η^5-dienyl–$Fe(CO)_3^+$ complexes**

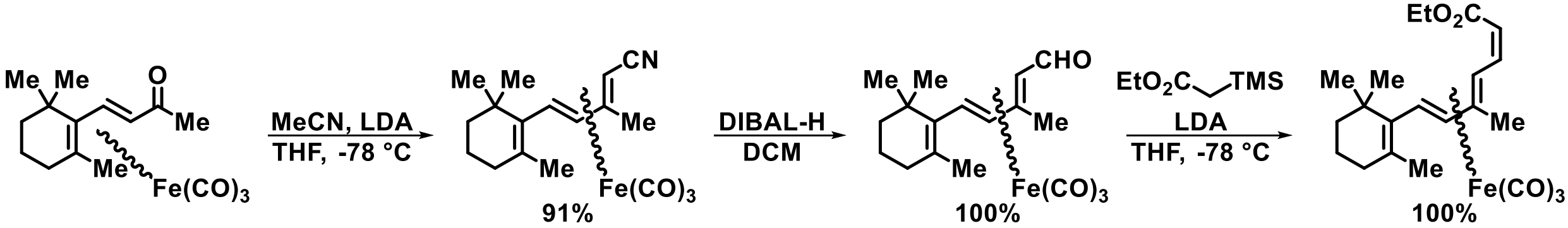
○ **η^4-diene–$Fe(CO)_3$ complexes as protecting group**



Stable complex



Stable complex

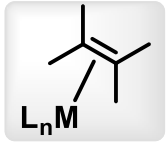


92% (77% *Z*)

○ **$Fe(CO)_3$ undergoes 1,3-migration and prefers *Z*-olefination**

J. Org. Chem. **2000**, *65*, 2438; *J. Org. Chem.* **1997**, *62*, 4343

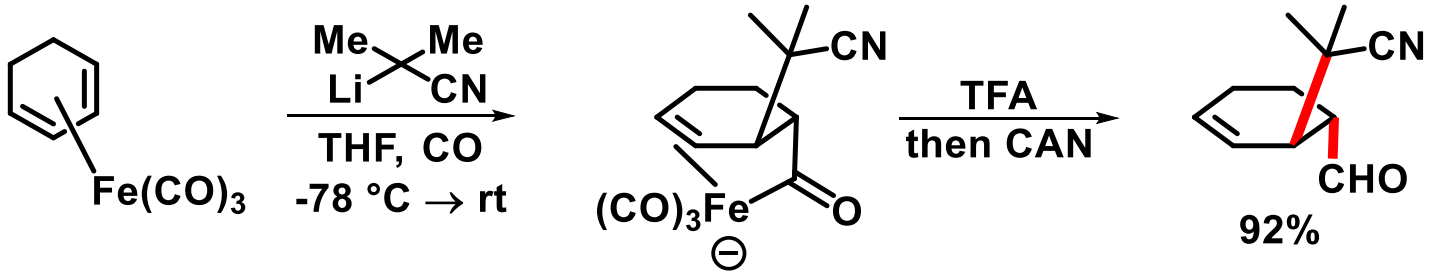
Reaction of Coordinated Ligands



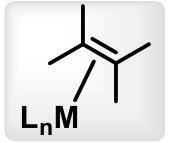
➢ Alkene complexes

- **Stoichiometric reactions: η^4-diene–$Fe(CO)_3$ and η^5-dienyl–$Fe(CO)_3^+$ complexes**

○ **η^4-diene–$Fe(CO)_3$ complexes and nucleophiles**

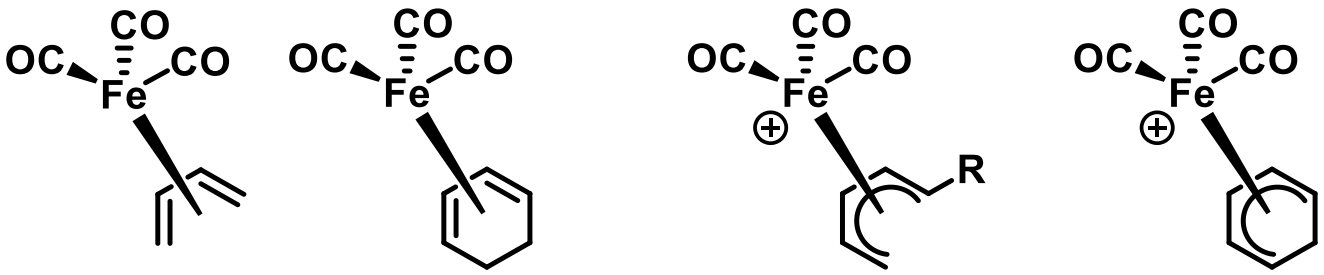


Reaction of Coordinated Ligands



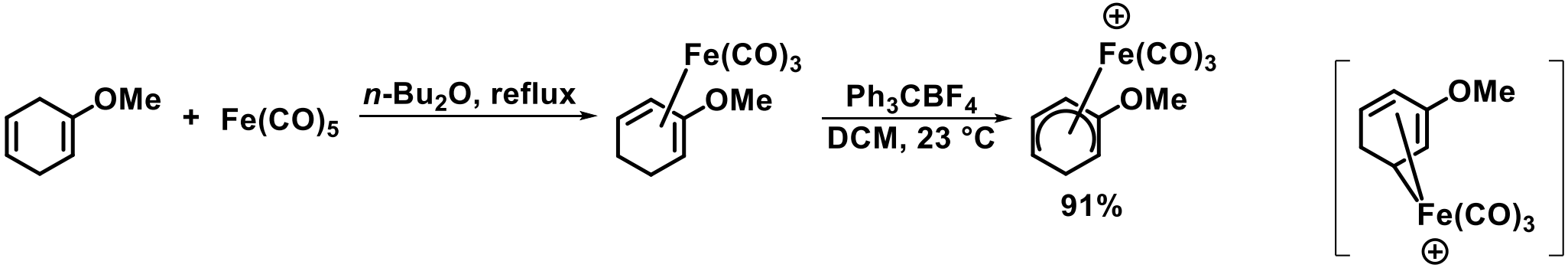
➢ Alkene complexes

- **Stoichiometric reactions: η^4-diene–$Fe(CO)_3$ and η^5-dienyl–$Fe(CO)_3^+$ complexes**

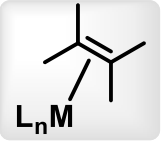


η^4-diene complexes $\qquad$ η^5-dienyl complexes

- ○ **Synthesis of η^5-dienyl–$Fe(CO)_3^+$ complexes (hydride abstraction)**



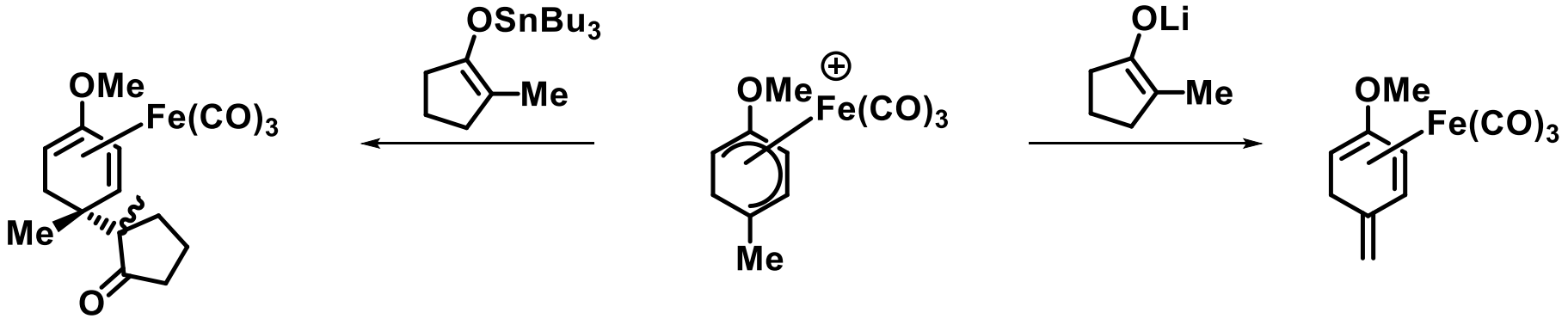
Reaction of Coordinated Ligands



➢ Alkene complexes

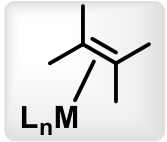
- Stoichiometric reactions: η^4-diene–$Fe(CO)_3$ and η^5-dienyl–$Fe(CO)_3^+$ complexes
  - η^5-Dienyl–$Fe(CO)_3^+$ complexes and nucleophiles

✓ Reaction outcome is influenced by nature of nucleophile



87%

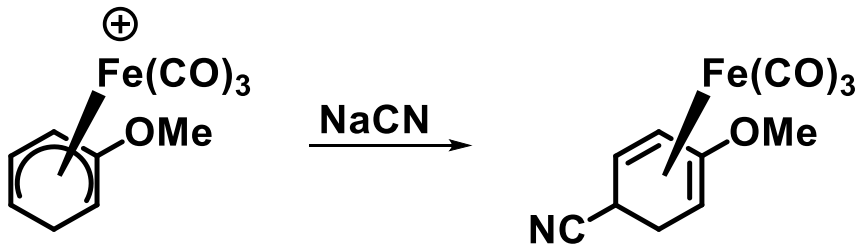
Reaction of Coordinated Ligands

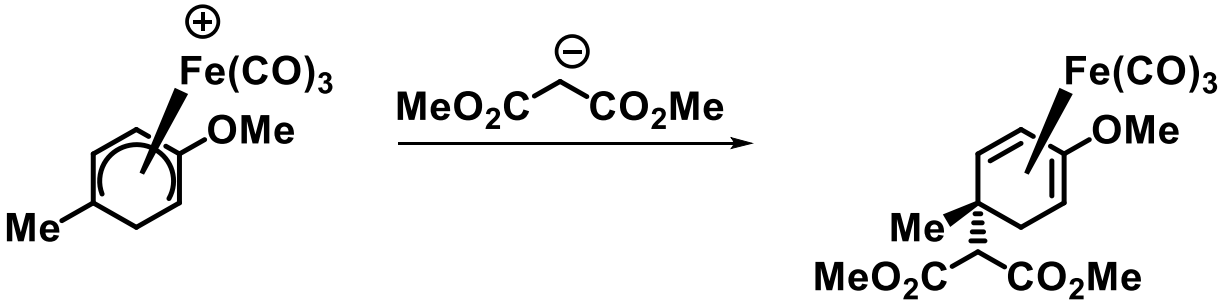


➢ Alkene complexes

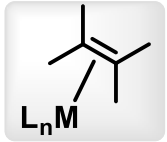
- **Stoichiometric reactions: η^4-diene–$Fe(CO)_3$ and η^5-dienyl–$Fe(CO)_3^+$ complexes**
  - **η^5-Dienyl–$Fe(CO)_3^+$ complexes and nucleophiles**

✓ **Reaction outcome is influenced by nature of nucleophile – always *anti*-addition and into para position to MeO group**





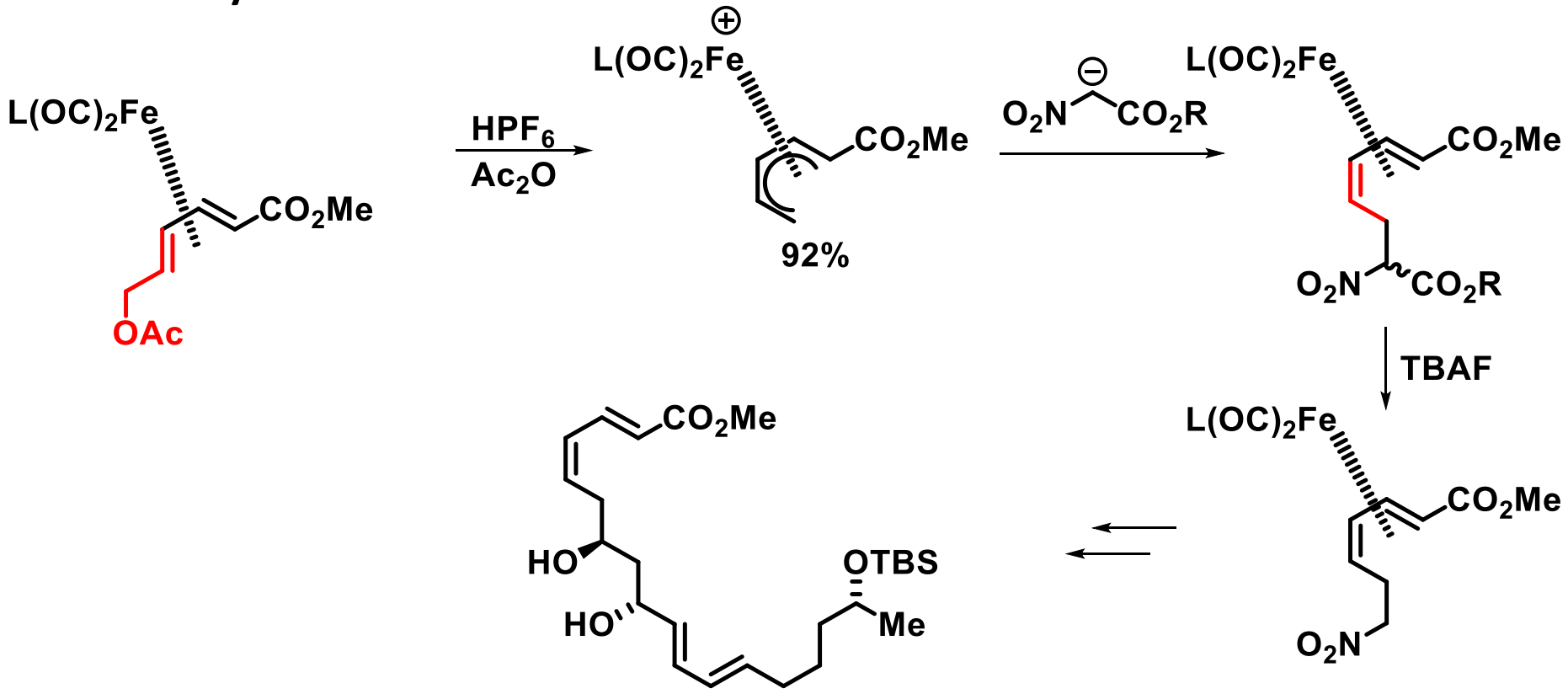
Reaction of Coordinated Ligands



➢ Alkene complexes

- **Stoichiometric reactions: η^4-diene–$Fe(CO)_3$ and η^5-dienyl–$Fe(CO)_3^+$ complexes**
  - **η^5-Dienyl–$Fe(CO)_3^+$ complexes and nucleophiles**

✓ **Application in total synthesis:**



Synthesis **2003**, 2064