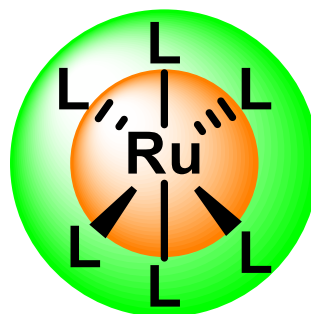
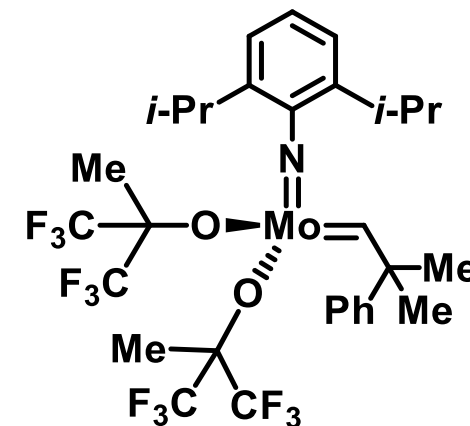
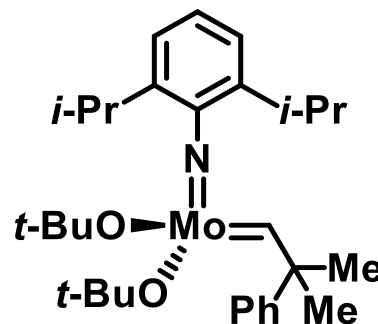
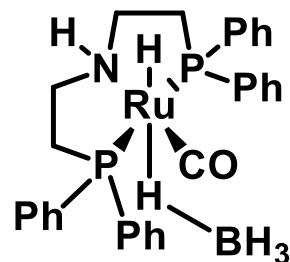
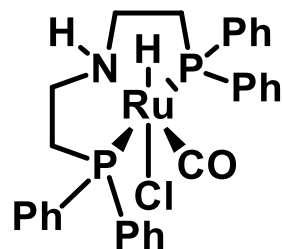


➤ Transition-metal complexes – reactions in outer and inner sphere



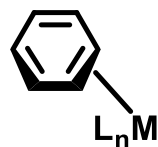
Inner sphere

Outer sphere

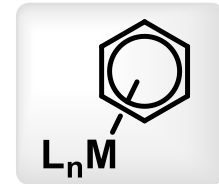
➤ Arene complexes



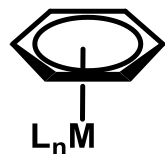
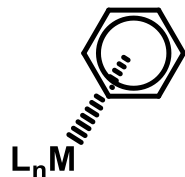
η^6 -arene complexes



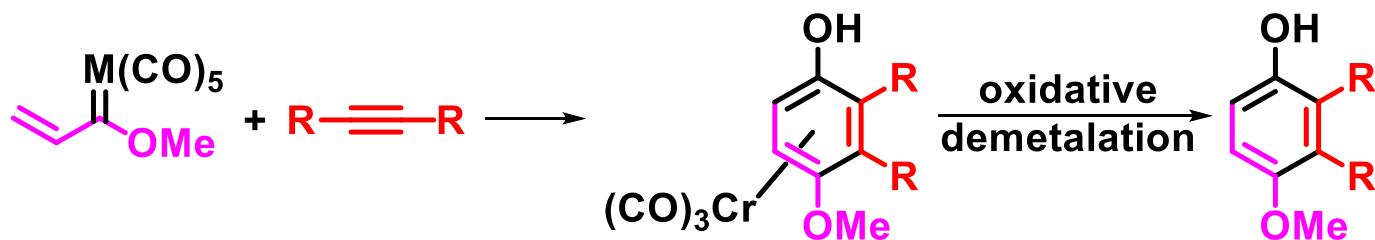
η^2 -arene complexes



- Formalism of arene complexes



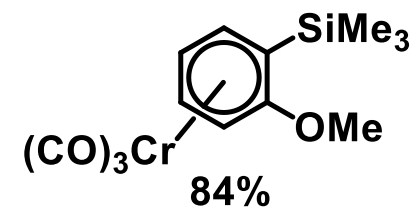
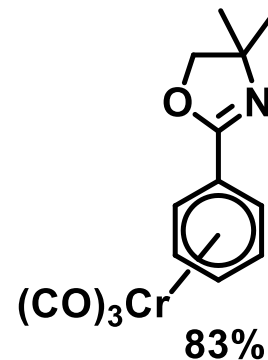
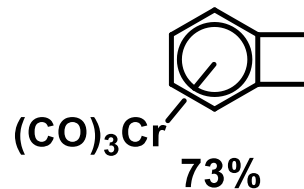
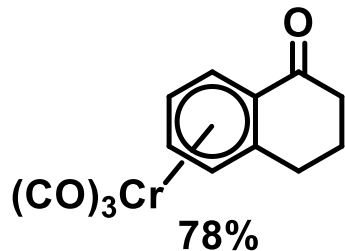
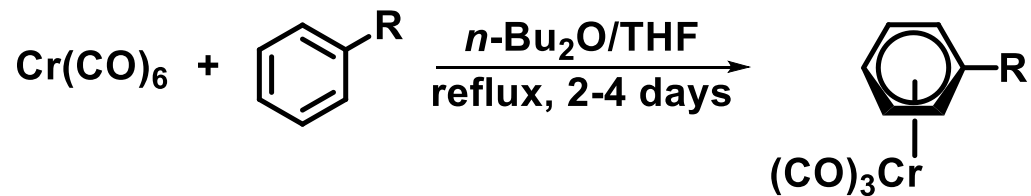
- Already mentioned η^6 -arene complexes – Dötz reaction



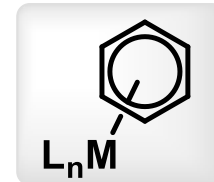
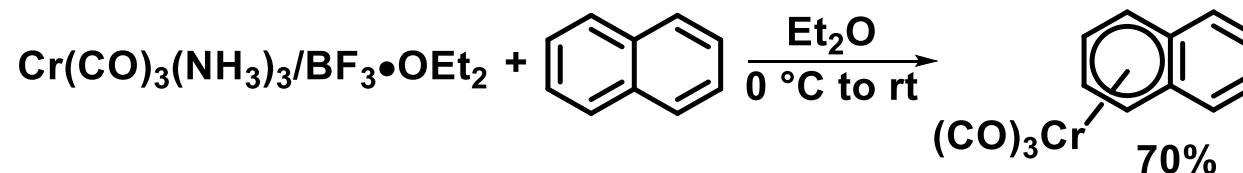
➤ Arene complexes – η^6 -arene complexes

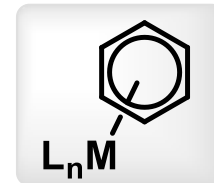
- Synthesis of η^6 -arene complexes (Cr, Mo, Mn)

- Thermolysis of $M(CO)_n$



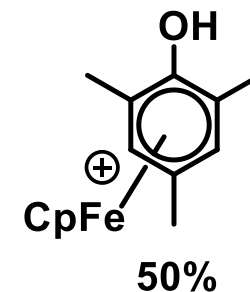
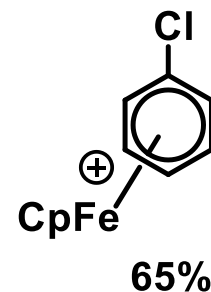
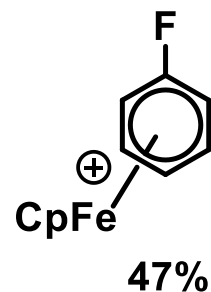
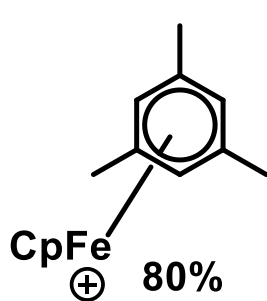
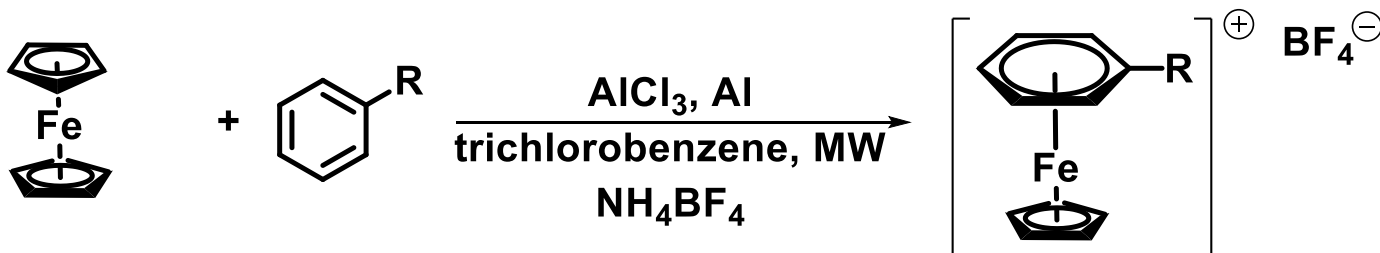
- Ligand substitution





➤ Arene complexes – η^6 -arene complexes

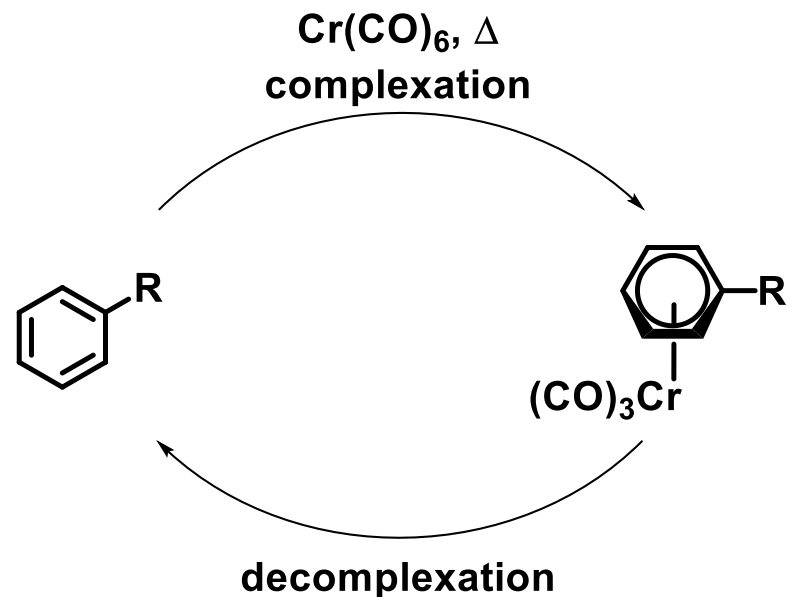
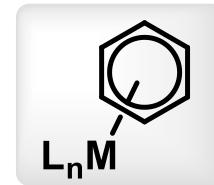
- Synthesis of η^6 -arene complexes (Cr, Mo, Mn)
 - Ligand substitution en route to iron complexes



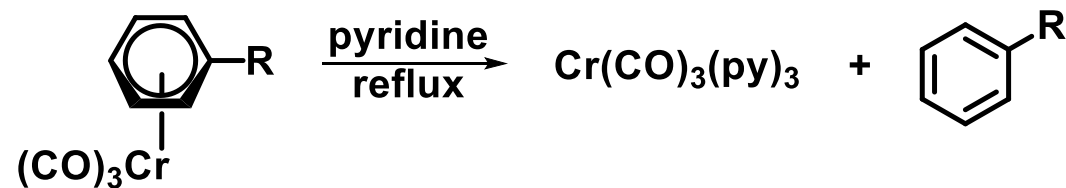
Tetrahedron Lett. 1963, 4, 1725.

➤ Arene complexes – η^6 -arene complexes

- Decomplexation

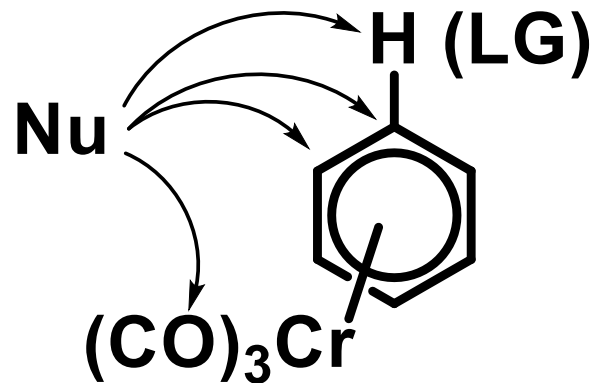
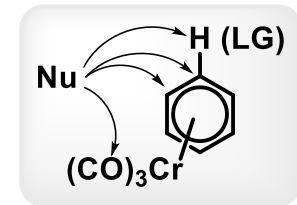


Typical reagents: $Ce^{(IV)}$, $Fe^{(III)}$, I_2 , $h\nu/O_2$



J. Chem. Soc. Chem. Commun. 1978, 989

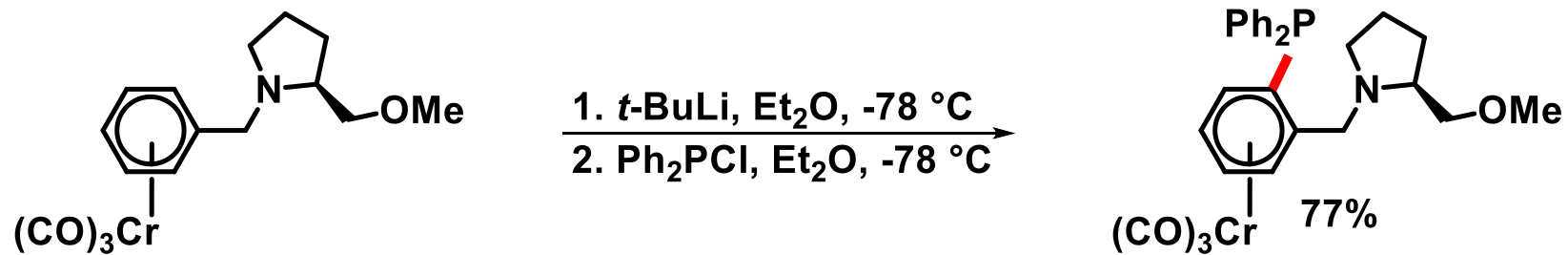
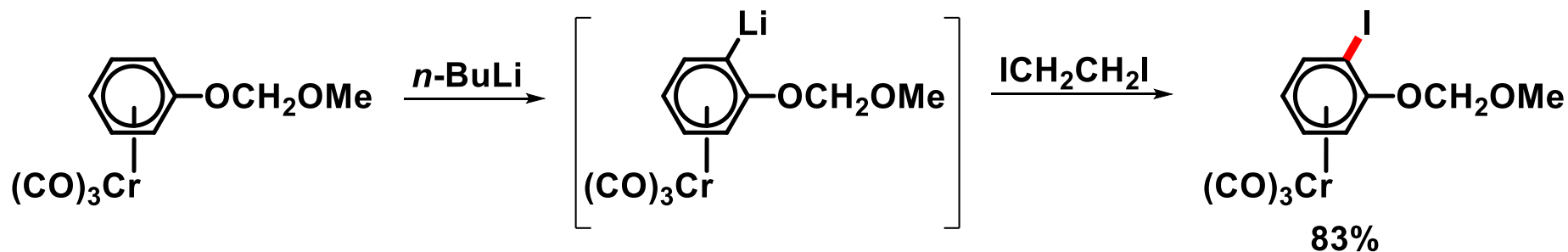
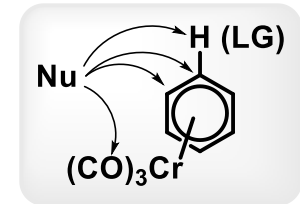
- **Arene complexes – η^6 -arene complexes**
 - **Typical reactivity – reaction with nucleophiles**



➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – Lithiation

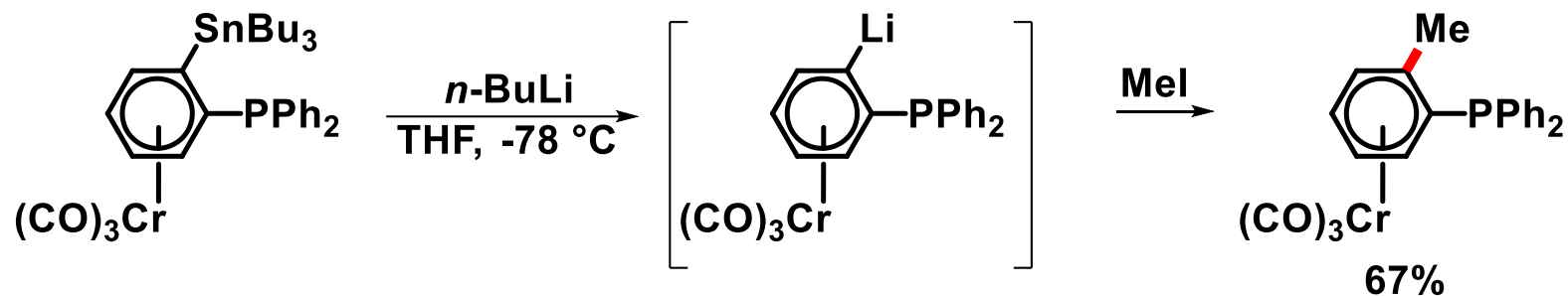
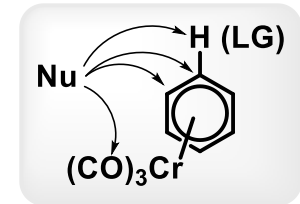
- Ortho lithiation



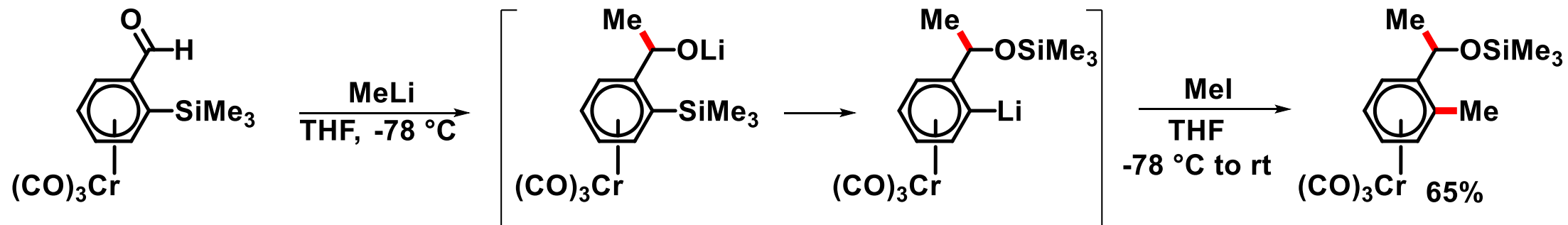
New. J. Chem. 1998, 1371

➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – Lithiation
 - Metal – metal exchange reaction



J. Chem. Soc. Perkin Trans. 1999, 1, 3177

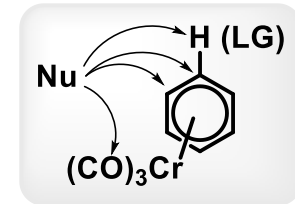
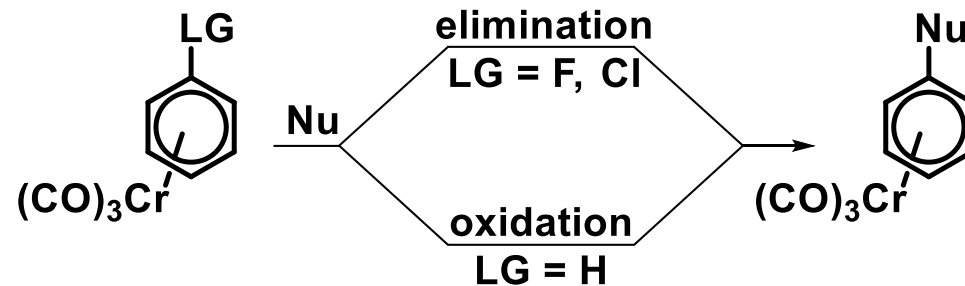


Org. Lett. 2000, 2, 717

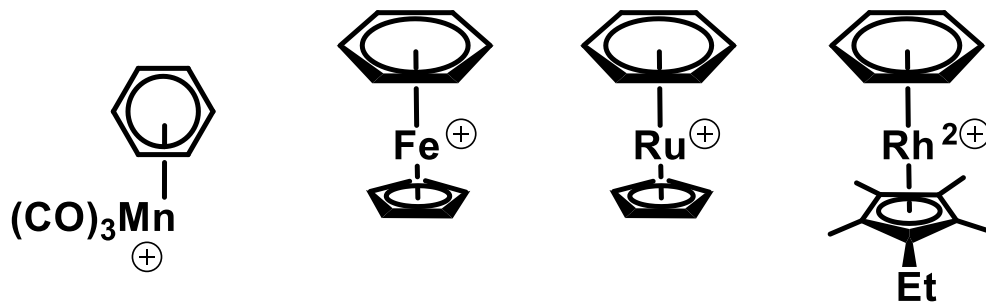
➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution

- Reaction scheme

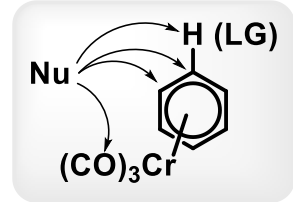


- Other complexes

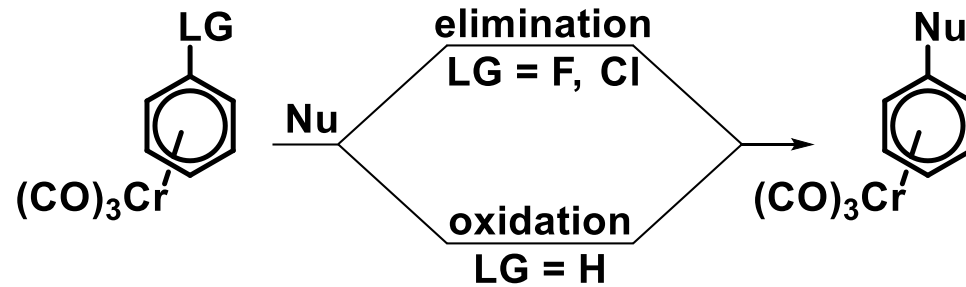


➤ Arene complexes – η^6 -arene complexes

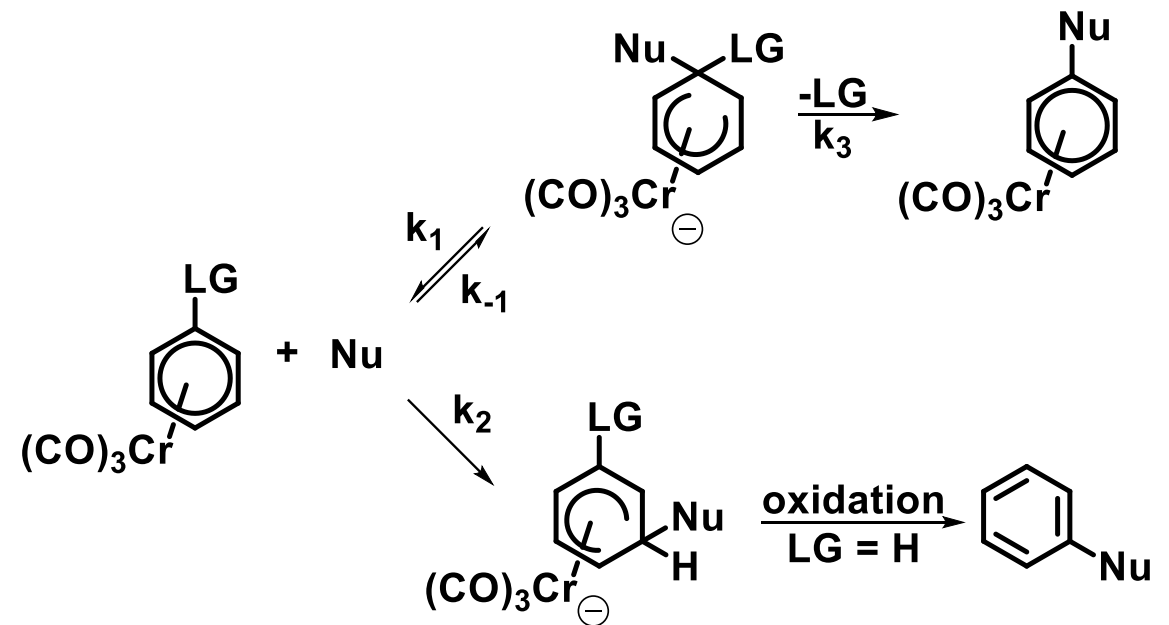
- Reaction with nucleophiles – nucleophilic substitution



- Reaction scheme



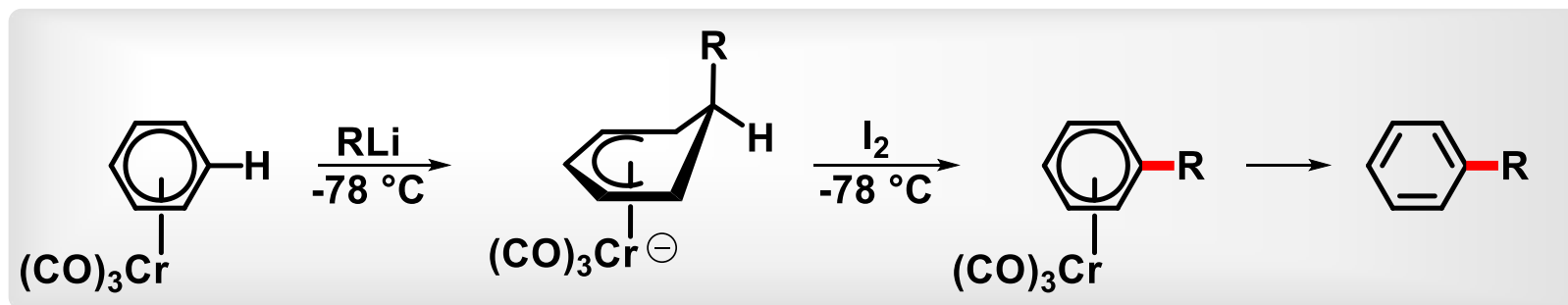
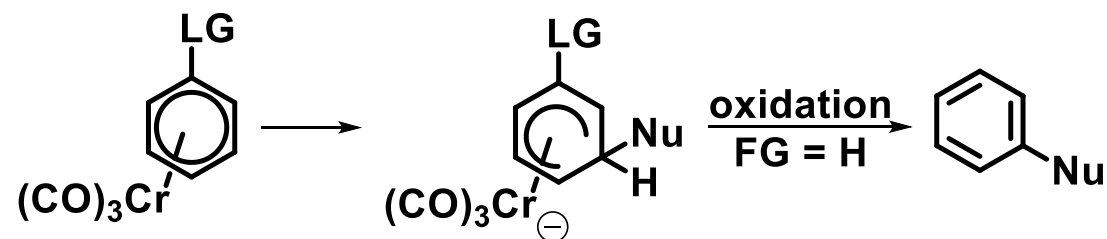
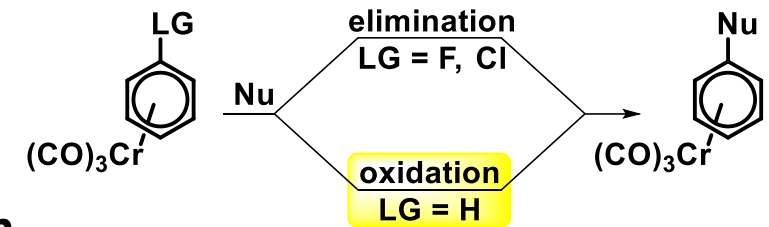
- Two reaction pathways



➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution

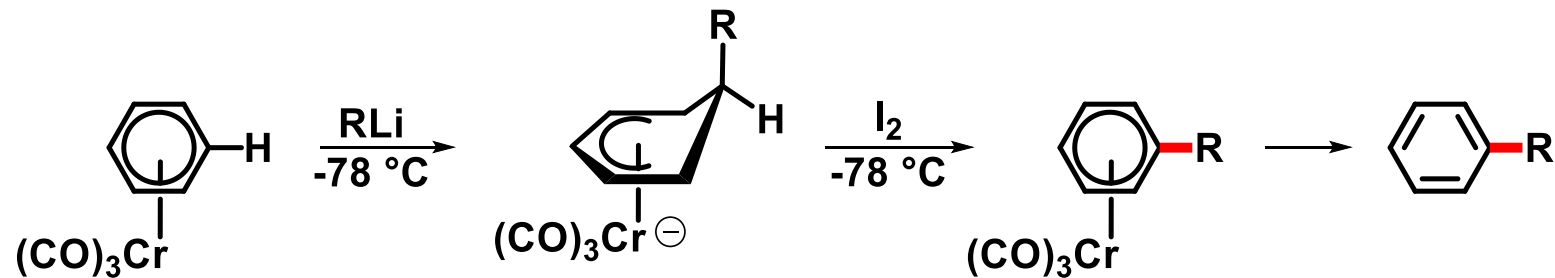
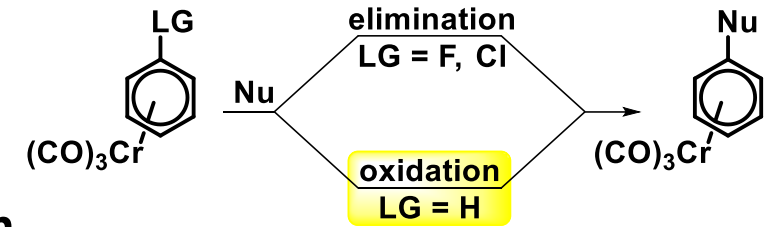
- Leaving-group-free substitution: Addition–Oxidation mechanism



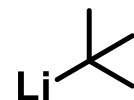
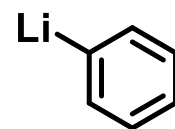
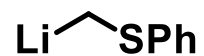
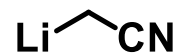
➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution

- Leaving-group-free substitution: Addition–Oxidation mechanism

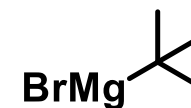
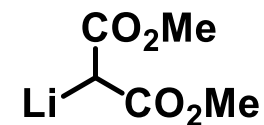


Reactive nucleophiles:



$\text{pK}_a > 22$

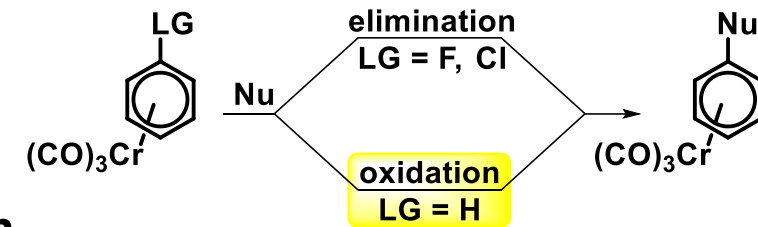
Unreactive nucleophiles:



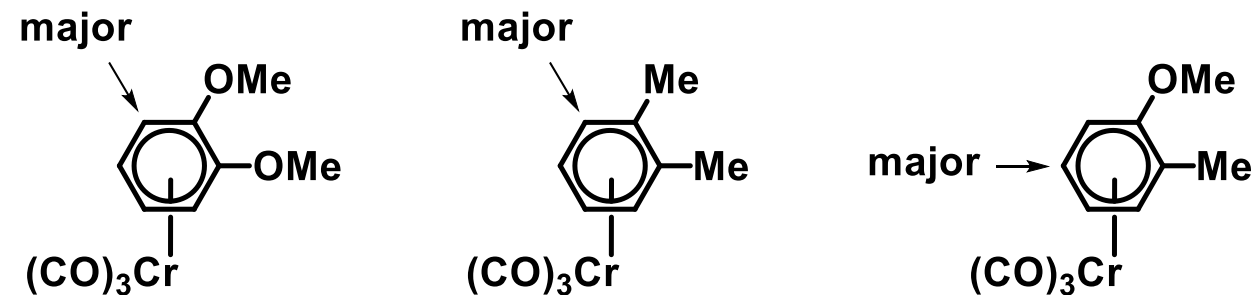
➤ **Arene complexes – η^6 -arene complexes**

- **Reaction with nucleophiles – nucleophilic substitution**

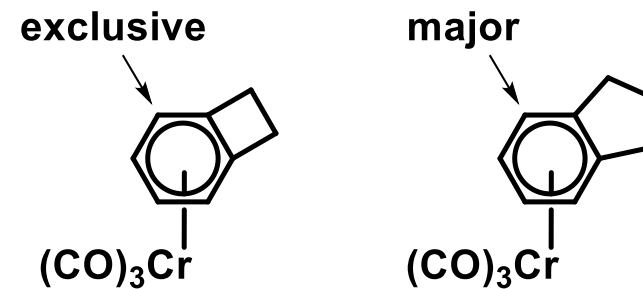
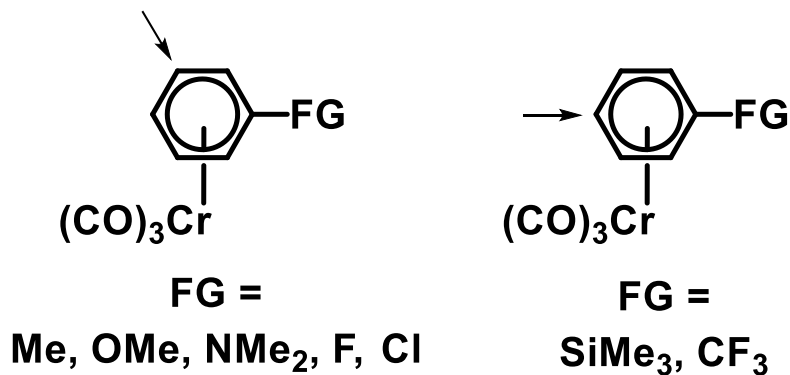
- **Leaving-group-free substitution: Addition–Oxidation mechanism**



✓ **Regioselectivity for disubstituted complexes**



✓ **Regioselectivity for monosubstituted complexes**

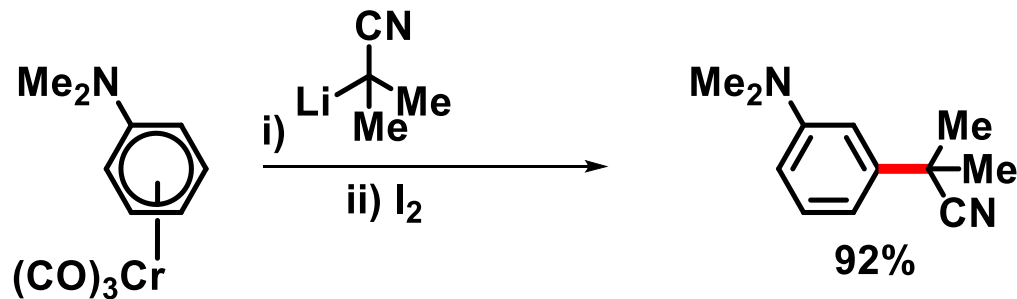
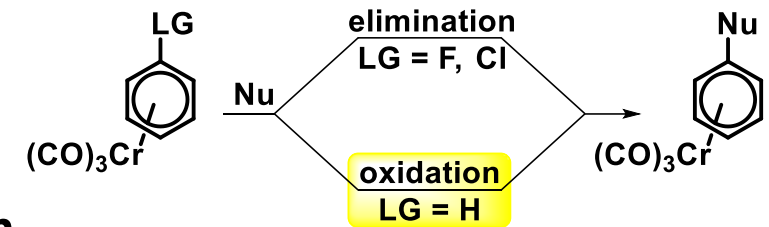


➤ Arene complexes – η^6 -arene complexes

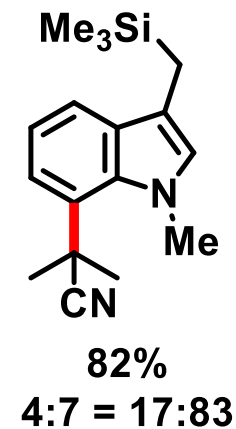
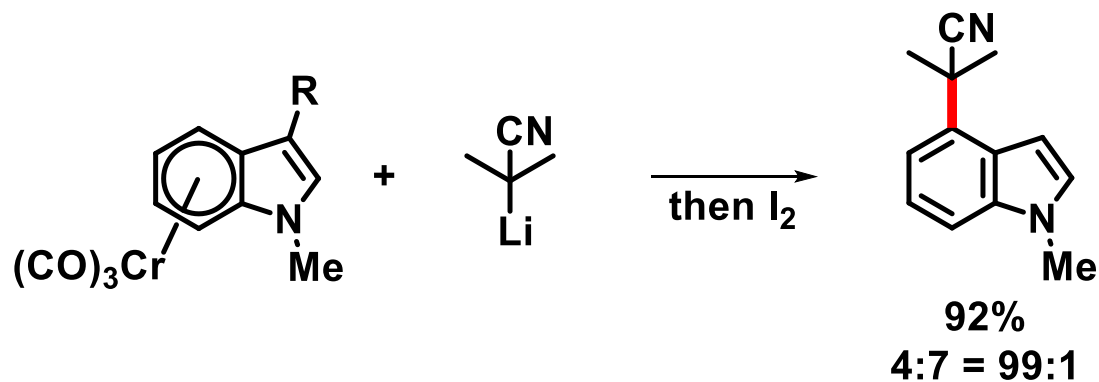
- Reaction with nucleophiles – nucleophilic substitution

- Leaving-group-free substitution: Addition–Oxidation mechanism

✓ Selected examples



J. Am. Chem. Soc. 1979, 101, 217

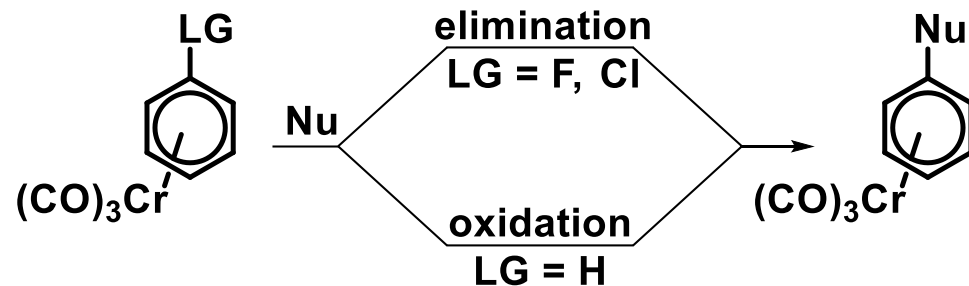


J. Organomet. Chem. 1982, 240, C5

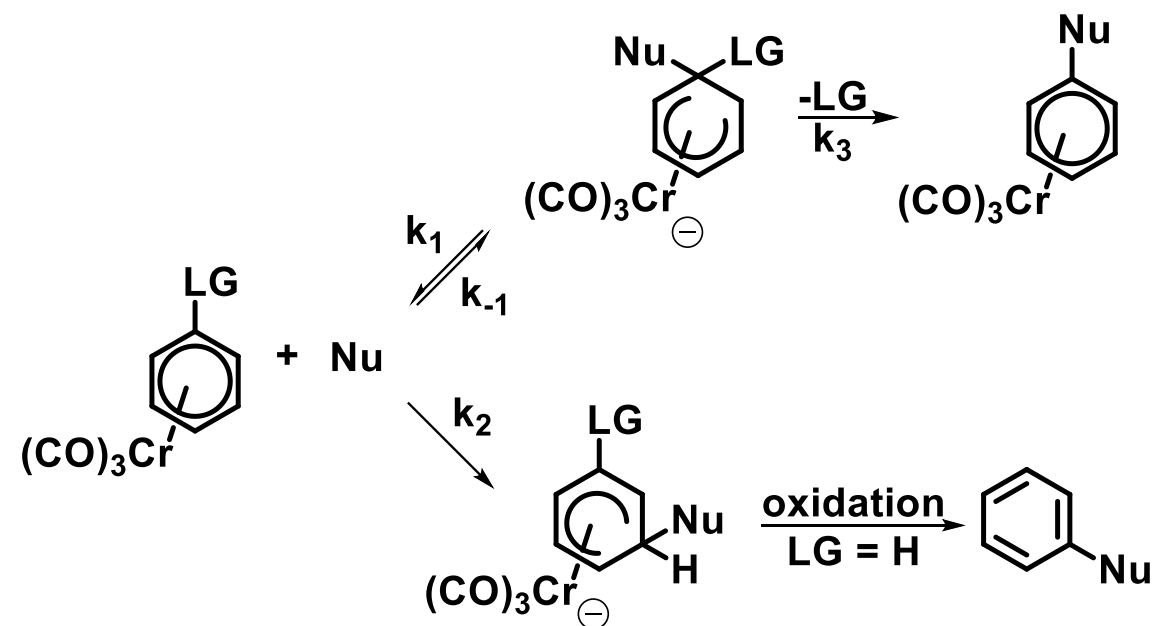
➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution

○ Reaction scheme



○ Two reaction pathways

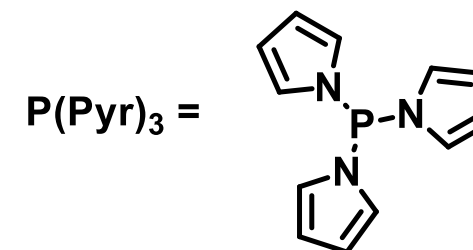
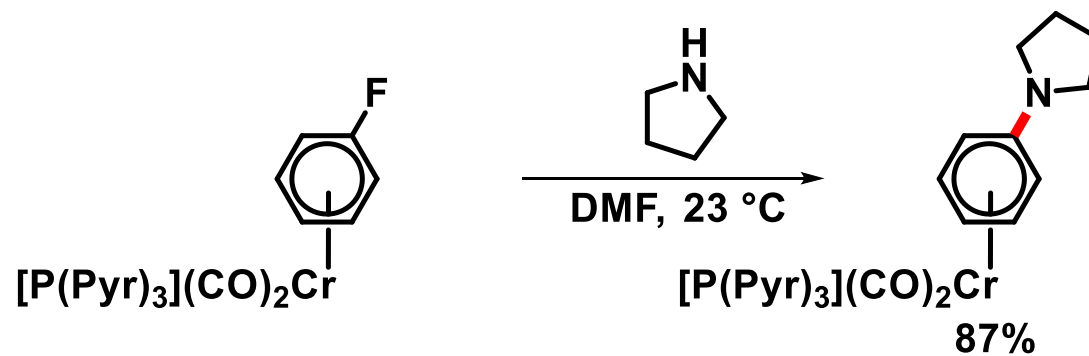
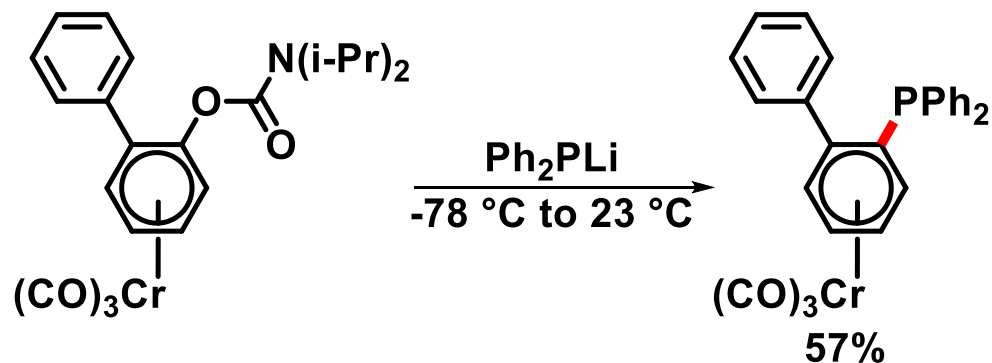
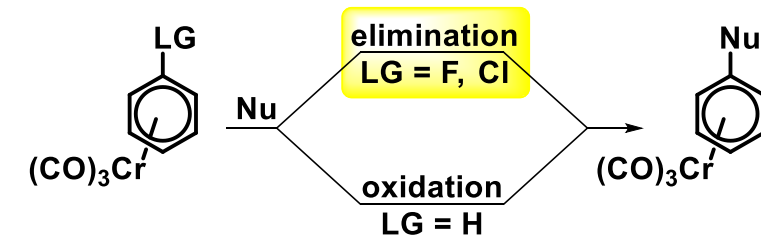


➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution

○ The reaction outcome depends on nucleophile:

- ✓ Hetero-nucleophile



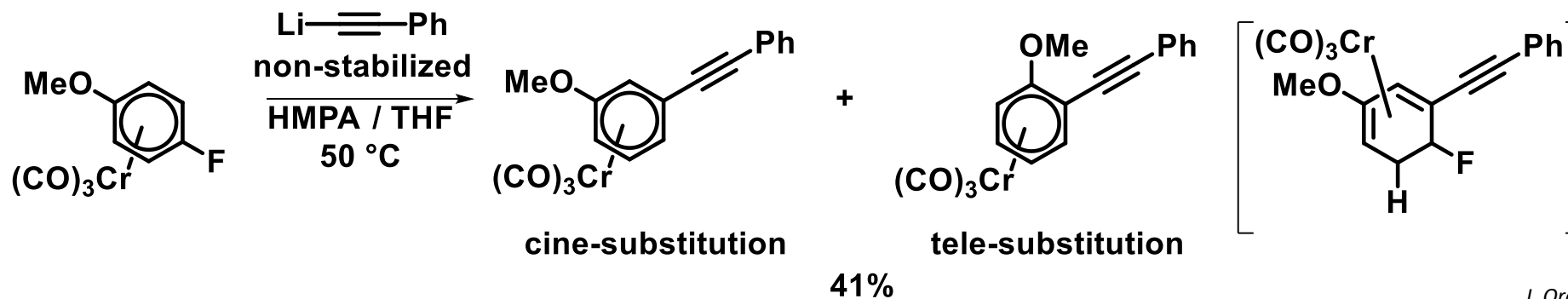
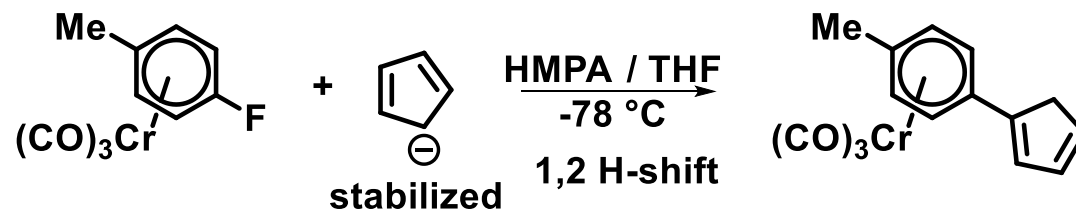
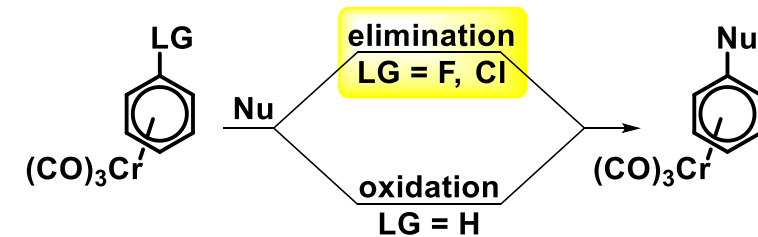
Tetrahedron Lett. 1998, 39, 7683

➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution

○ The reaction outcome depends on nucleophile:

✓ C-nucleophiles – stabilized and non-stabilized ($pK_a = 18$)



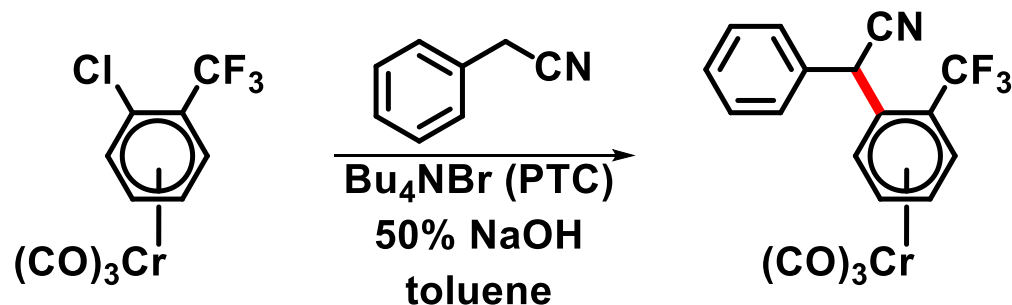
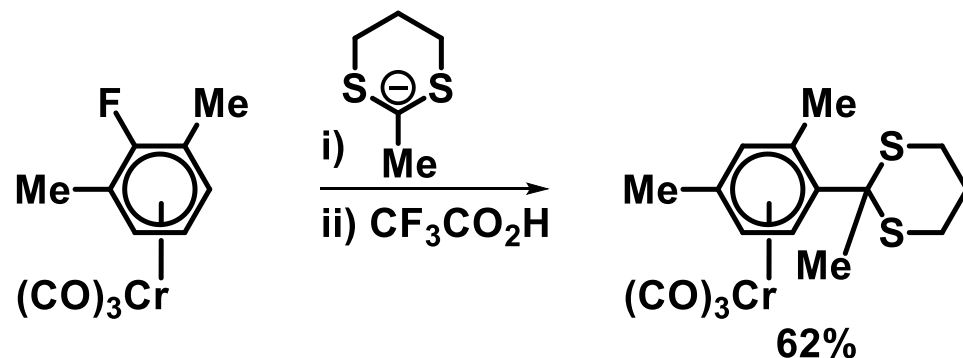
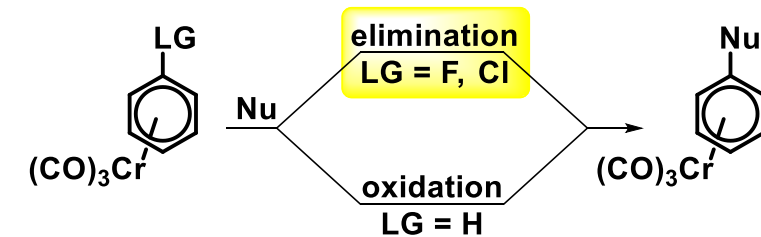
J. Organomet. Chem. 1996, 506, 101.

➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution

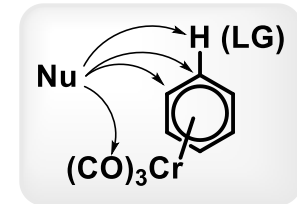
○ The reaction outcome depends on nucleophile

✓ C-nucleophiles – stabilized non-stabilized ($pK_a = 18$)

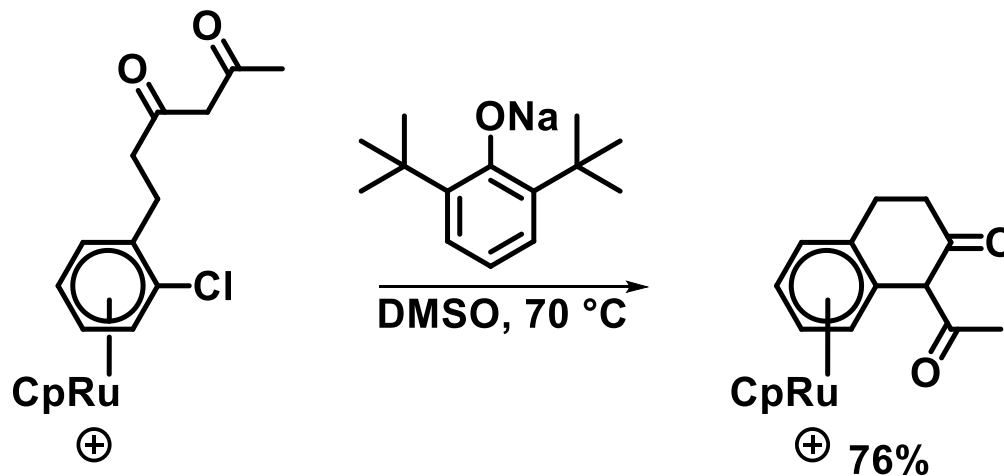


➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – nucleophilic substitution



○ Intramolecular Addition–Elimination substitution

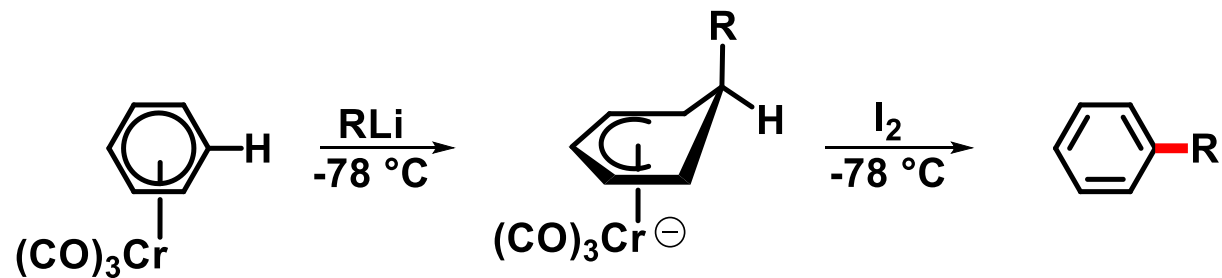


Tetrahedron Lett. 2001, 42, 17

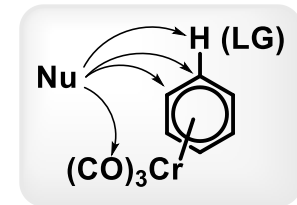
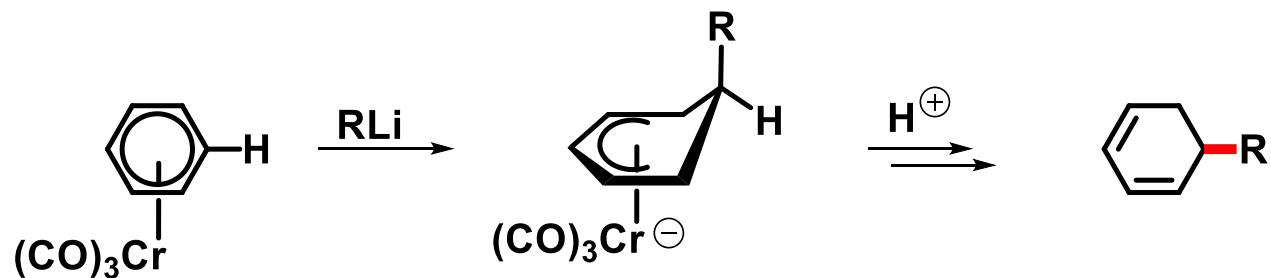
➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – Dearomatization reactions

- General scheme for Addition – Oxidation substitution

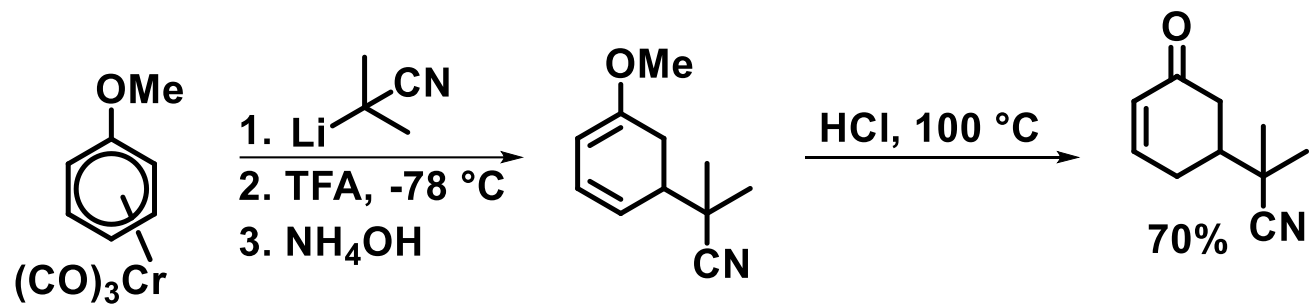
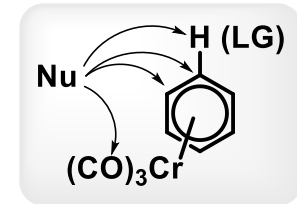


- General scheme for Addition – Dearomatization reactions

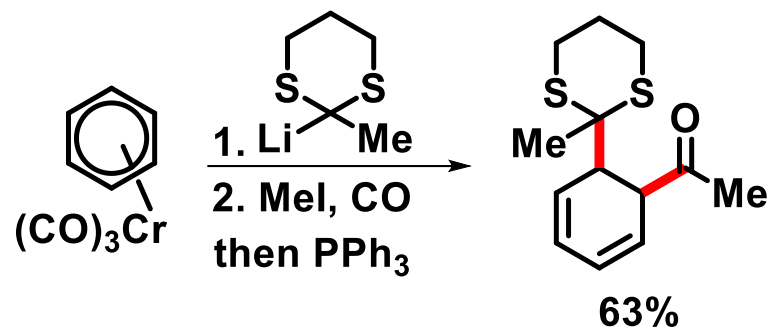


➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – Dearomatization reactions



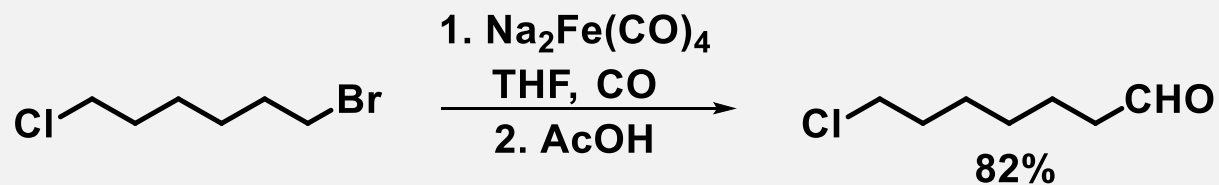
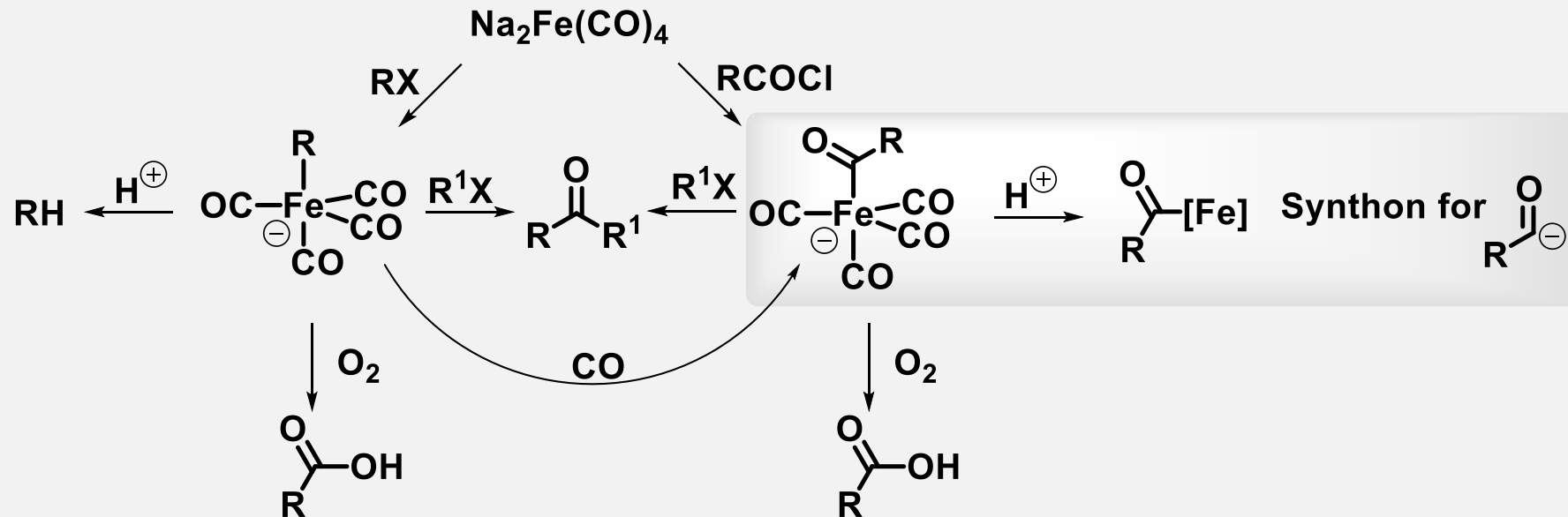
J. Org. Chem. **1979**, *44*, 3275



Hel. Chim. Acta **1990**, *386*

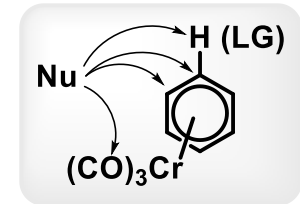
➤ Metal carbonyl complexes

- $\text{Fe}(\text{CO})_5$ – Stoichiometric reactions

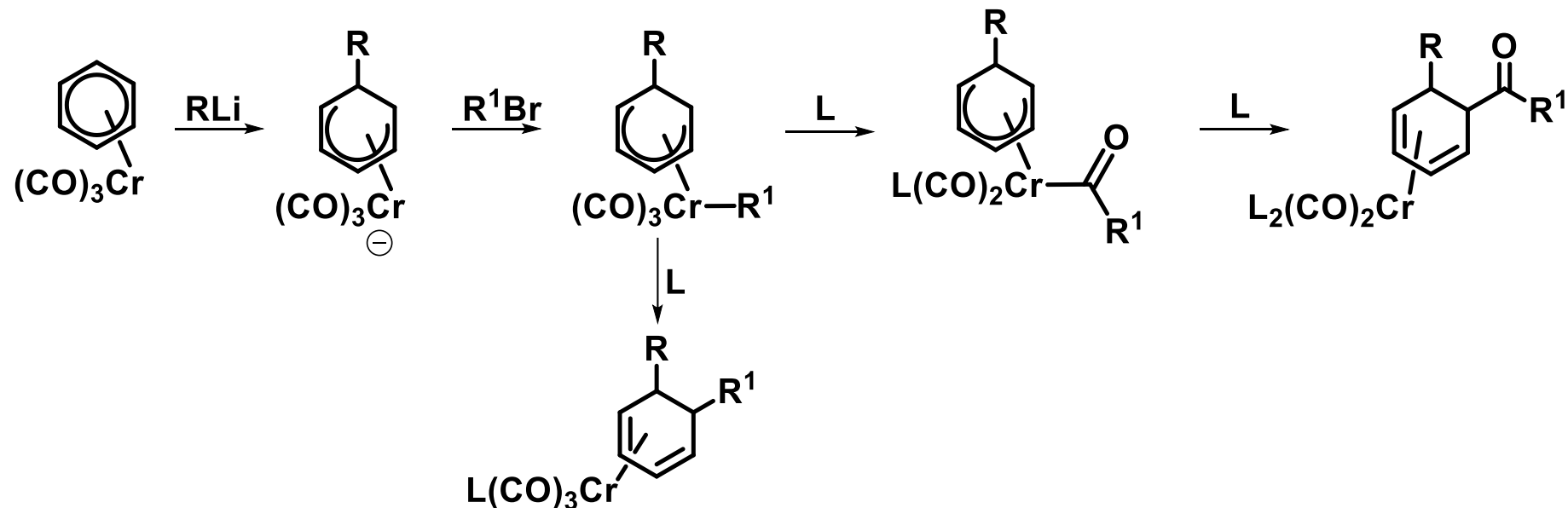
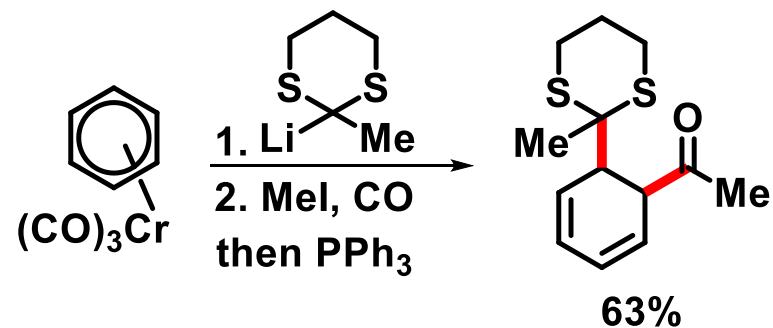


➤ Arene complexes – η^6 -arene complexes

- Reaction with nucleophiles – Dearomatization reactions

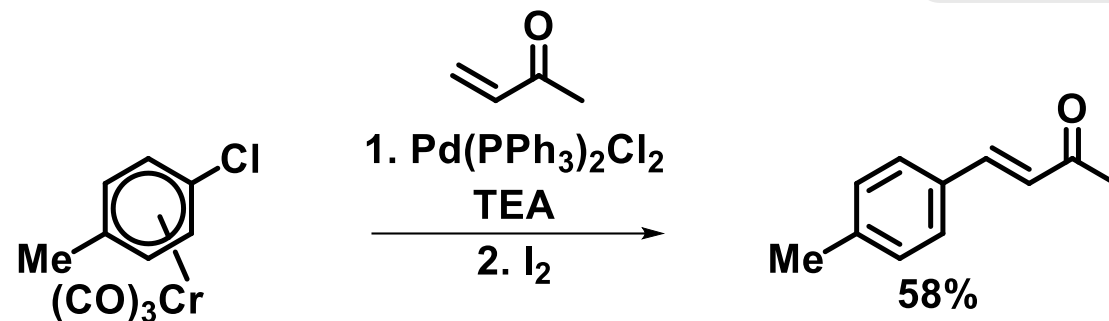
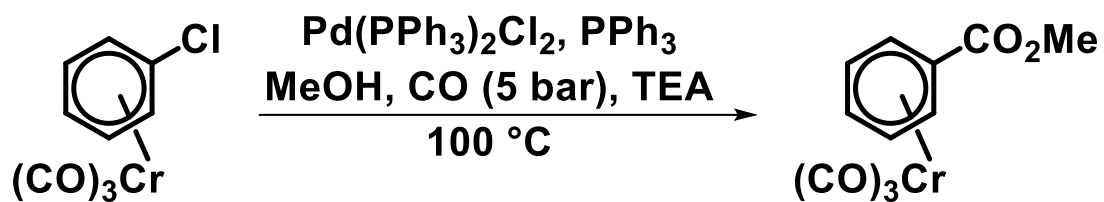
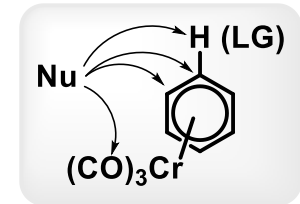


- Proposed mechanism for acylation of η^6 -arene complexes

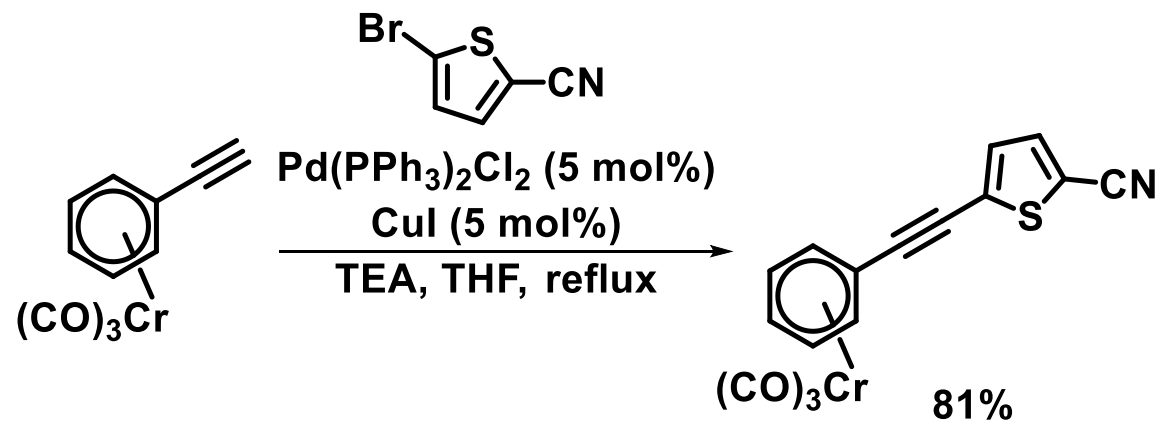


➤ Arene complexes – η^6 -arene complexes

- Cross-coupling reactions

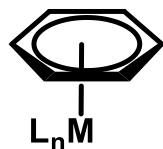
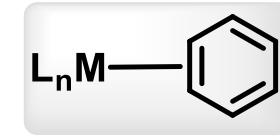


J. Chem. Soc. Chem. Commun. **1987**, 1755

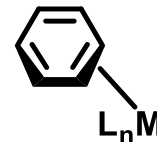


Tetrahedron Lett. **2000**, 41, 3607

➤ Arene complexes – η^2 -arene complexes



η^6 -arene complexes



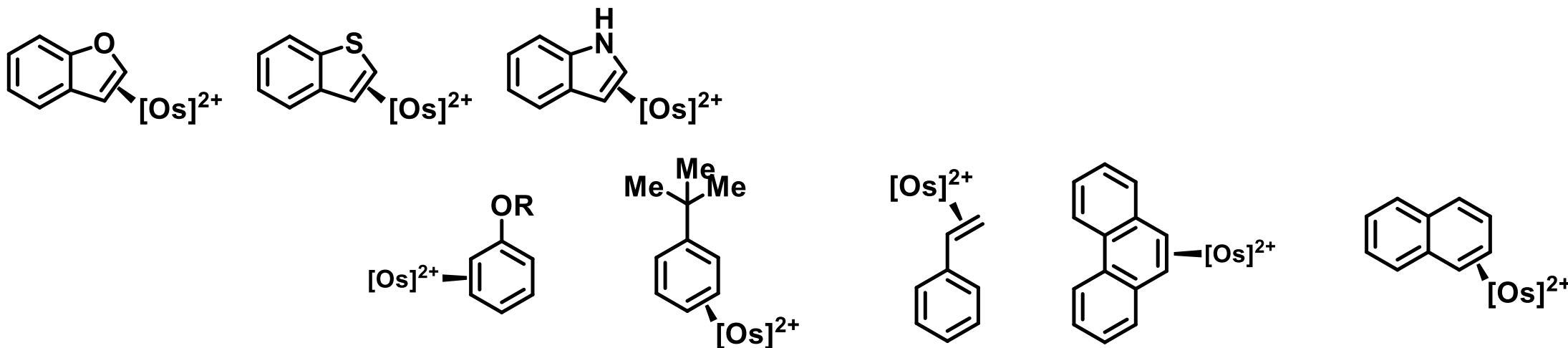
η^2 -arene complexes

- ✓ Less stable than η^6 -arene complexes
- ✓ $[\text{Os}]^{2+}$ complexes have $t_{1/2} = 6 \text{ h}$ in solution (Ligand substitution)

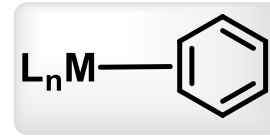
➤ Arene complexes – η^2 -arene complexes



- η^2 -Arene complexes synthesis and binding selectivity



➤ Arene complexes – η^2 -arene complexes



- η^2 -Arene complexes – selected reactions

