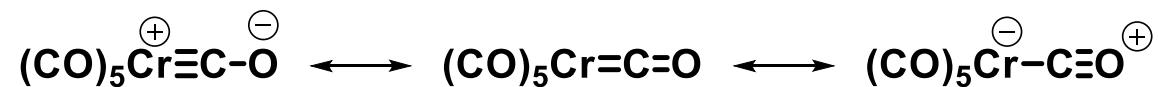
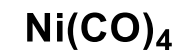
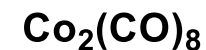
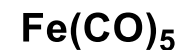
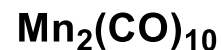
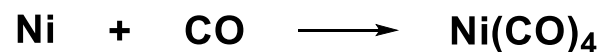


## ➤ Metal carbonyl complexes

- Selected examples



- Preparation by direct synthesis



- Preparation by photolysis of thermolysis

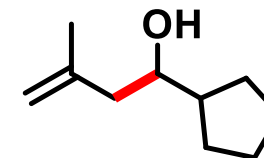
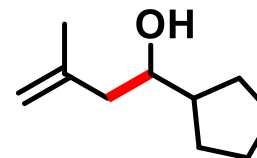
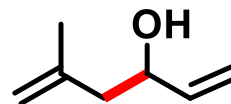
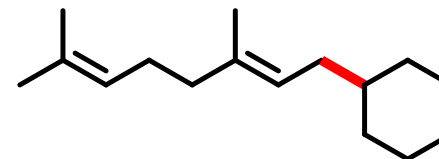
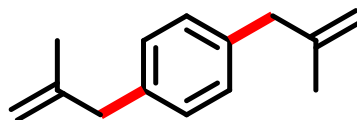
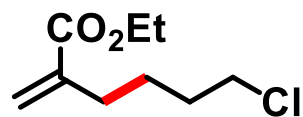
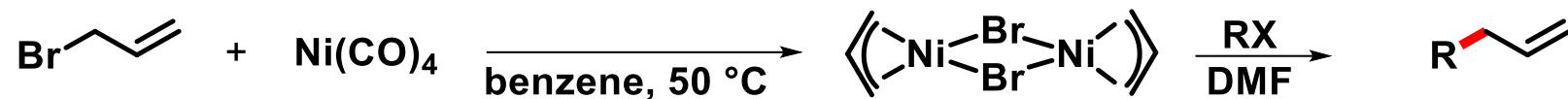


- Preparation by reductive carbonylation



## ➤ Metal carbonyl complexes

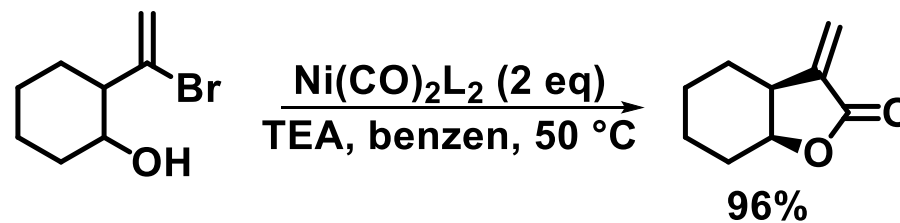
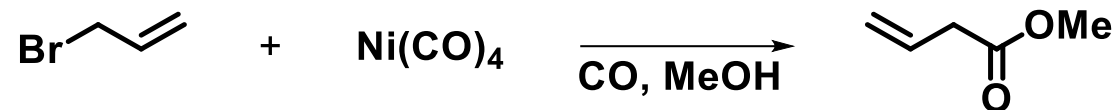
- $\text{Ni}(\text{CO})_4$  – Stoichiometric alkylations



*J. Am. Chem. Soc.* **1967**, *89*, 2755

## ➤ Metal carbonyl complexes

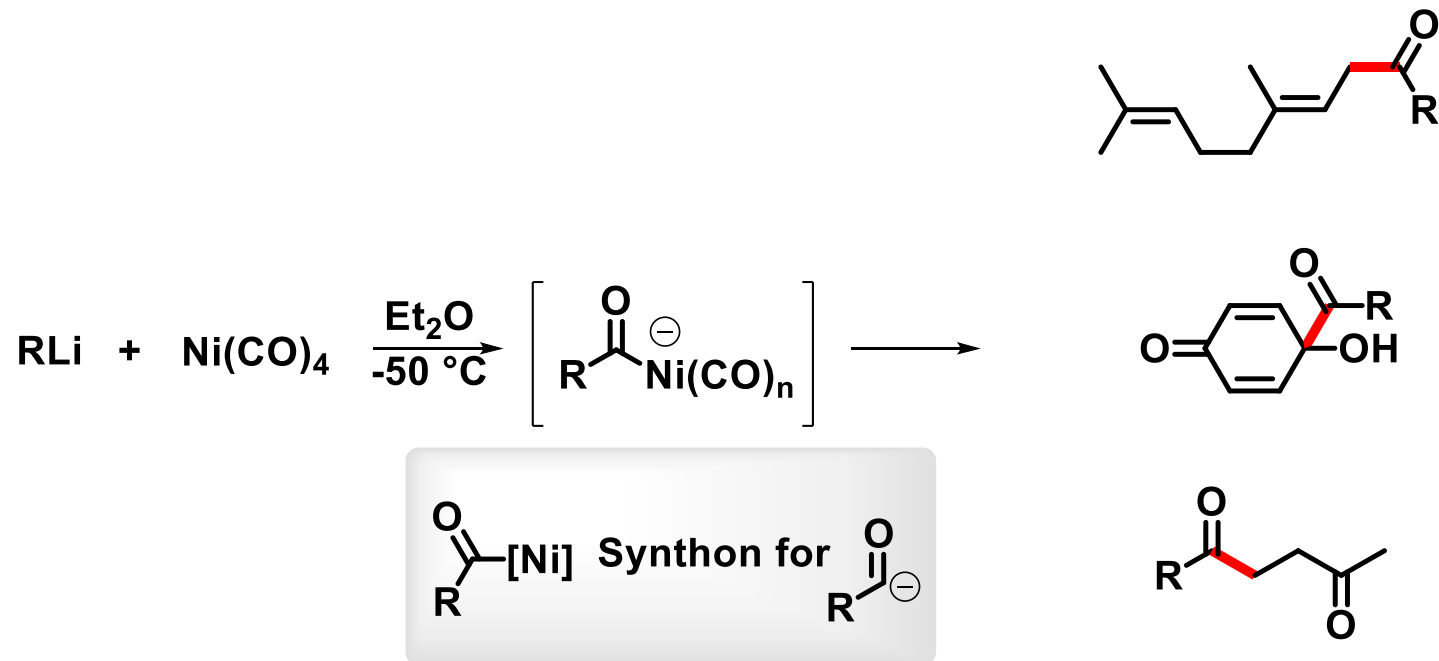
- $\text{Ni}(\text{CO})_4$  – Stoichiometric carbonylations



*J. Org. Chem.* **1981**, *46*, 1723

## ➤ Metal carbonyl complexes

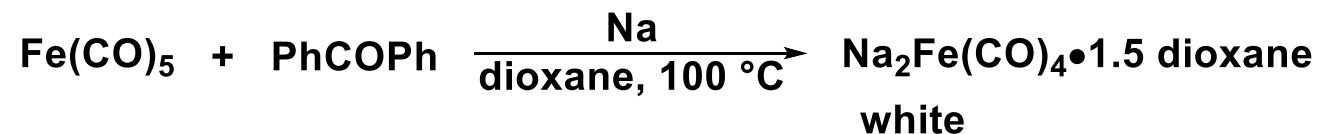
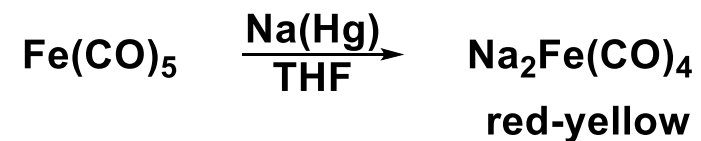
- $\text{Ni}(\text{CO})_4$  – Stoichiometric carbonylations



*J. Am. Chem. Soc.* **1969**, *41*, 4926

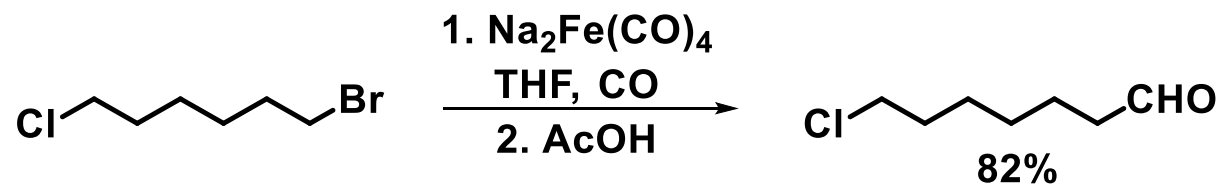
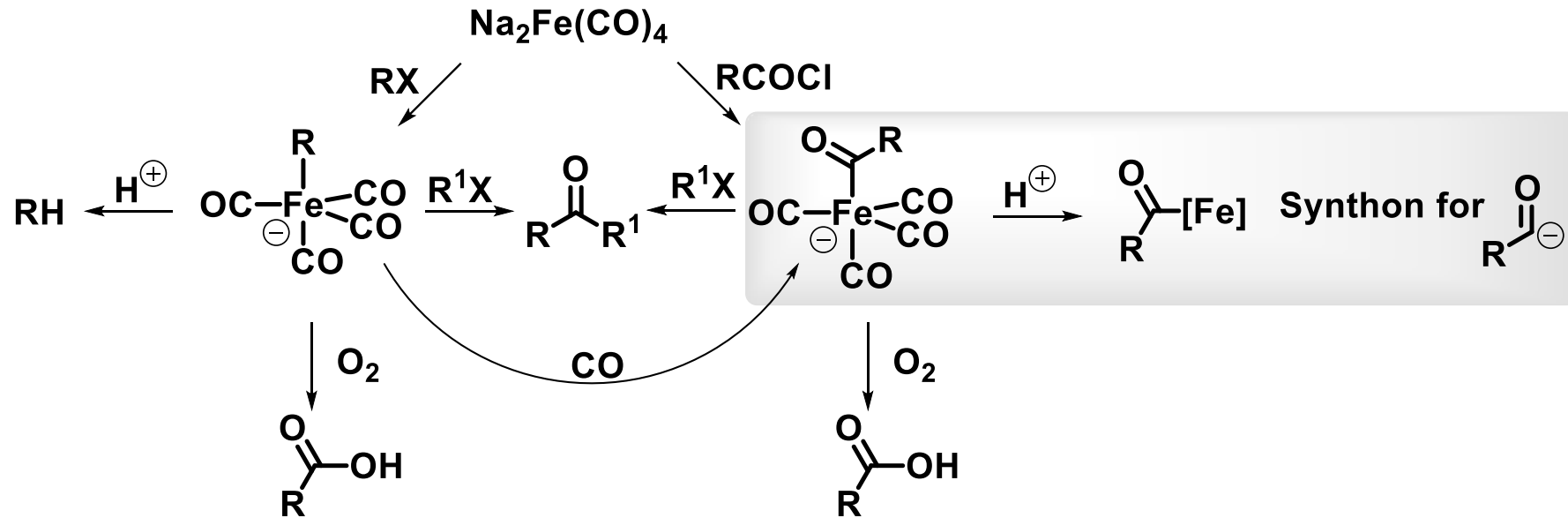
## ➤ Metal carbonyl complexes

- $\text{Fe}(\text{CO})_5$  – Stoichiometric reactions (Collman's reagent)

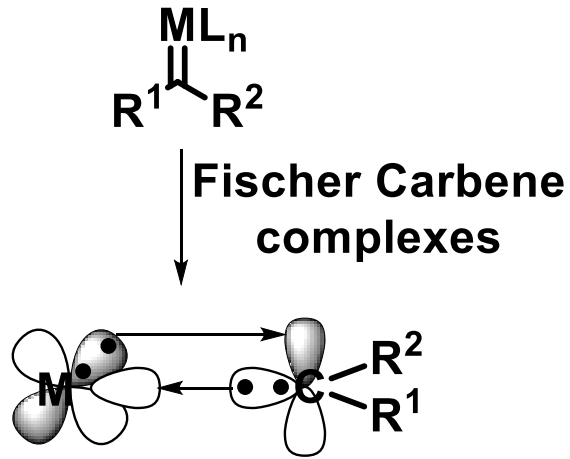


## ➤ Metal carbonyl complexes

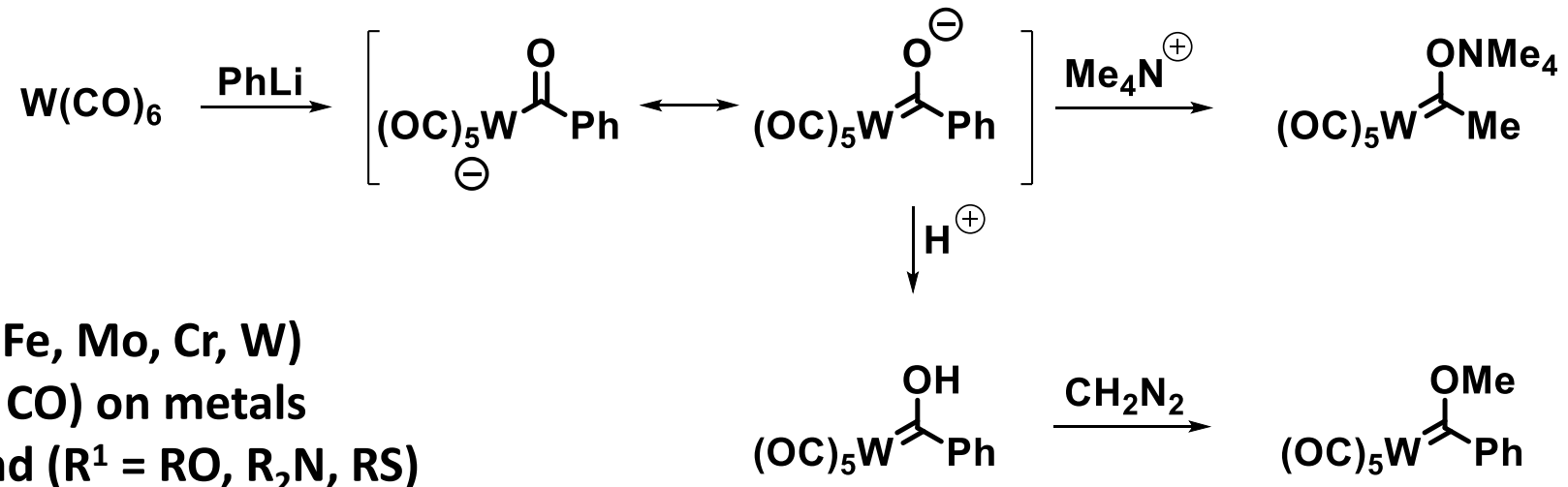
- $\text{Fe}(\text{CO})_5$  – Stoichiometric reactions (Collman's reagent)



## ➤ Fischer Carbene complexes



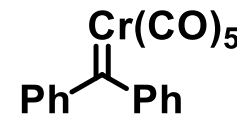
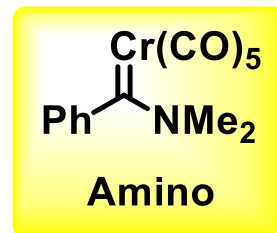
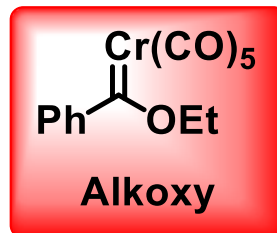
- First complex was isolated in 1964



*Angew. Chem. Int. Ed.*, 1964, 3, 580

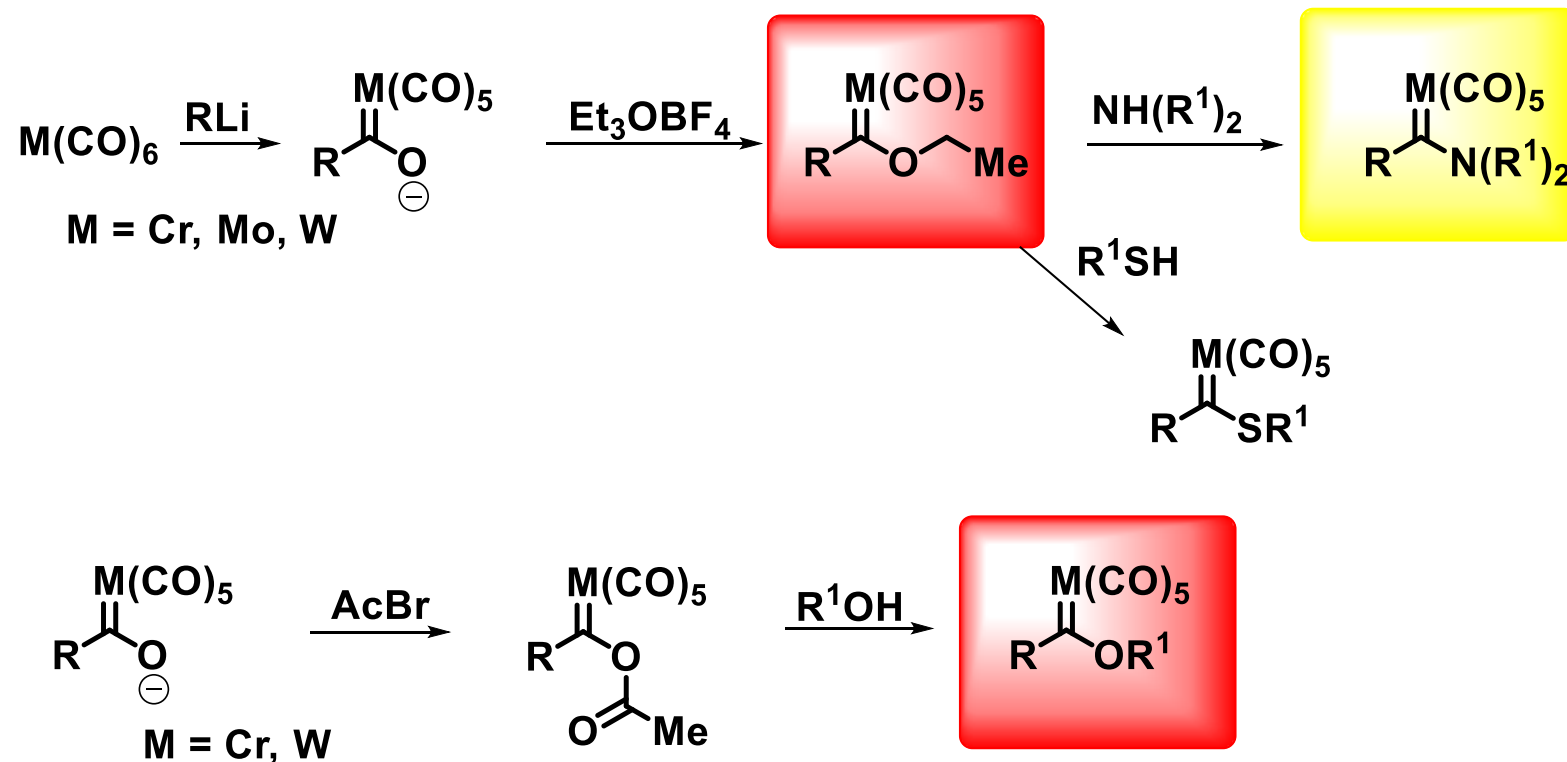
- Low oxidation state metals (M = Fe, Mo, Cr, W)
- $\pi$ -electron acceptors ligands (L = CO) on metals
- $\pi$ -donor ligands on carbene ligand (R<sup>1</sup> = RO, R<sub>2</sub>N, RS)

### • Selected examples



## ➤ Fischer carbene complexes

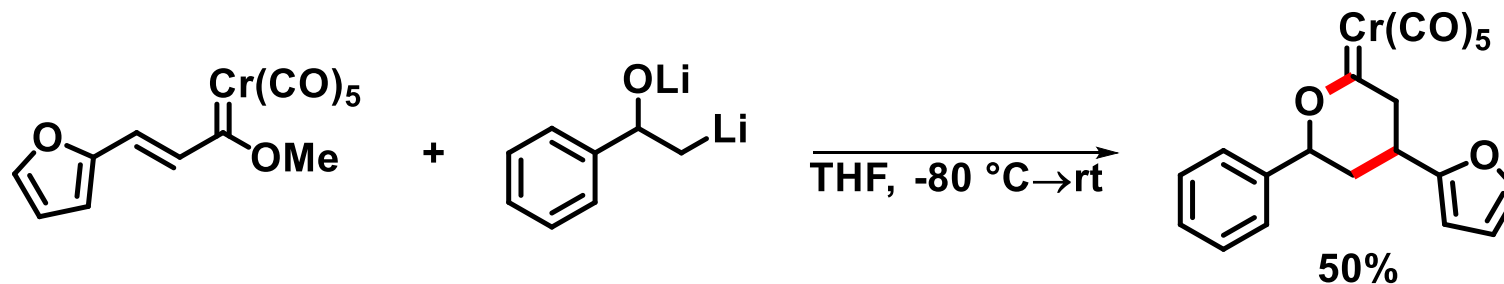
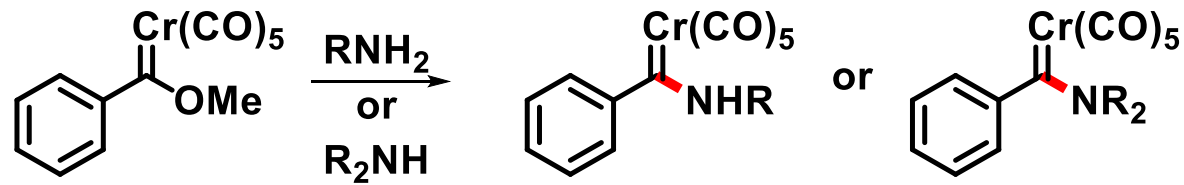
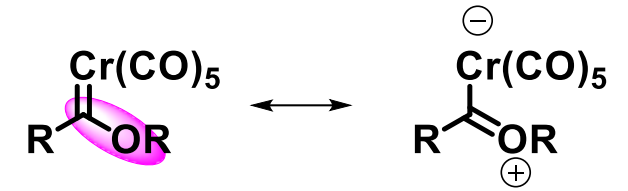
- Synthesis of Fischer carbene complexes





## ➤ Fischer carbene complexes

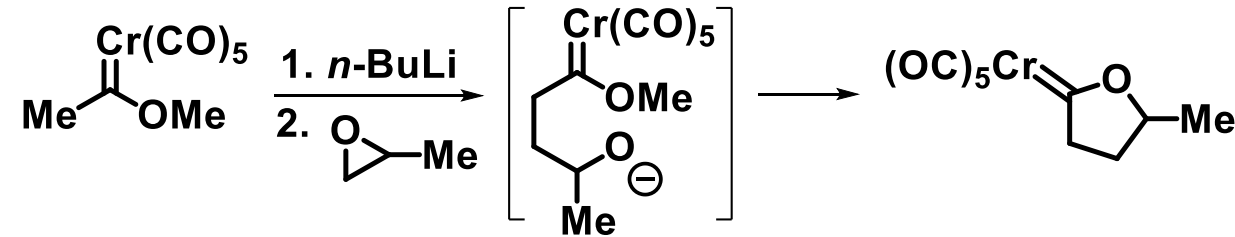
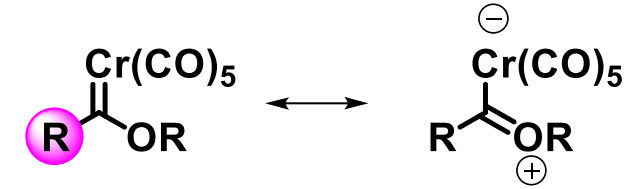
- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )



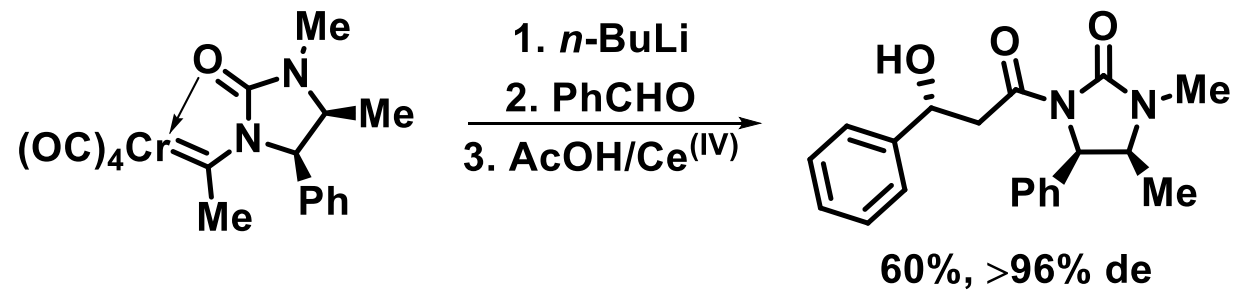
*J. Chem. Soc., Chem. Commun.* **1993**, 1068

## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )



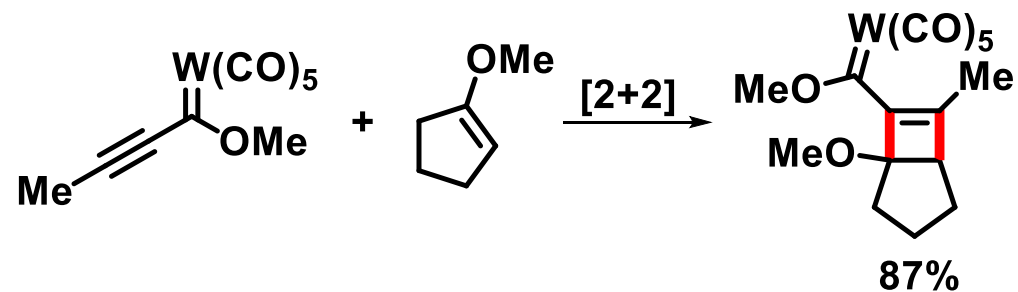
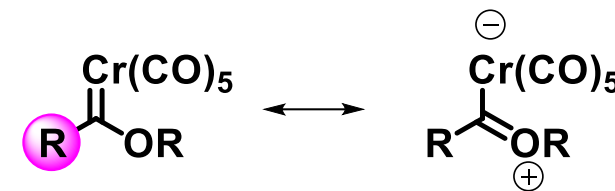
*J. Am. Chem. Soc.*, **1993**, *115*, 4602



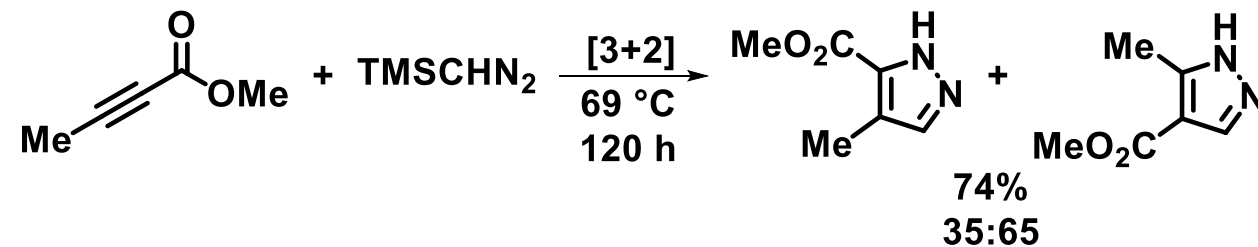
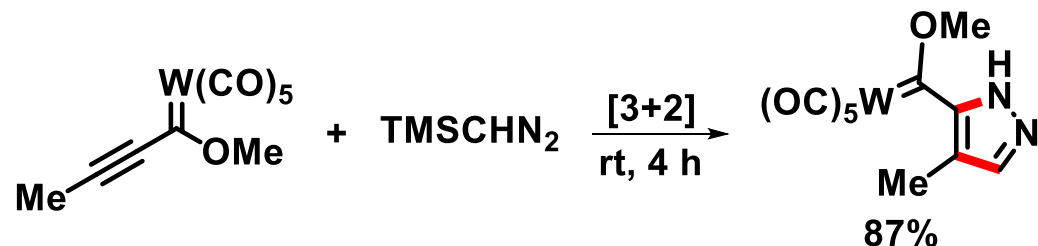
*J. Org. Chem.*, **1994**, 6882

## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )
- [2+2] and [3+2] cycloadditions



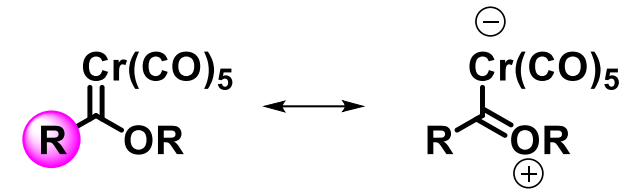
*J. Am. Chem. Soc.* **1988**, *110*, 8727



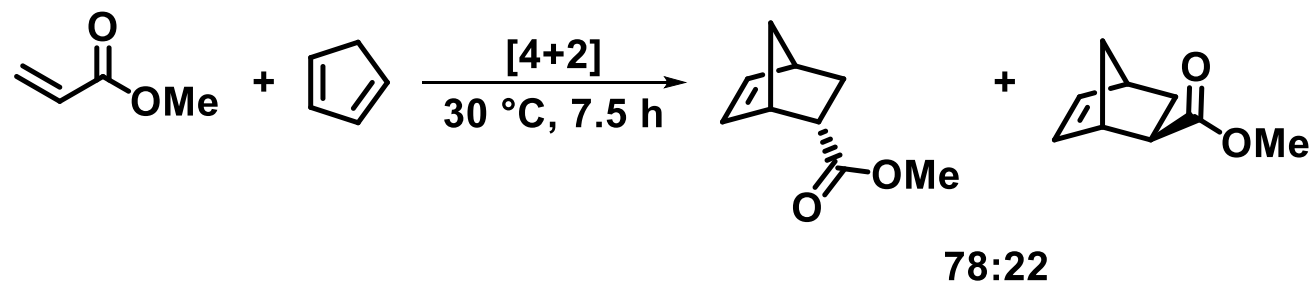
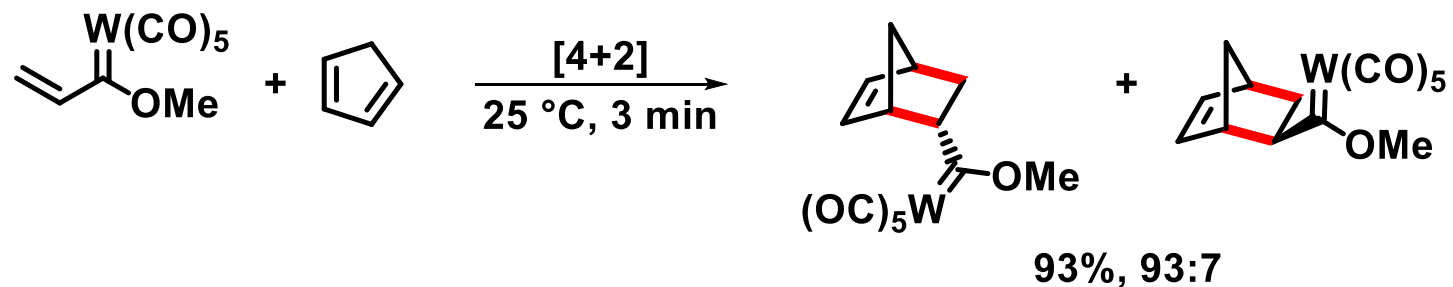
*J. Am. Chem. Soc.* **1986**, *108*, 5229

## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )



- [4+2] cycloadditions

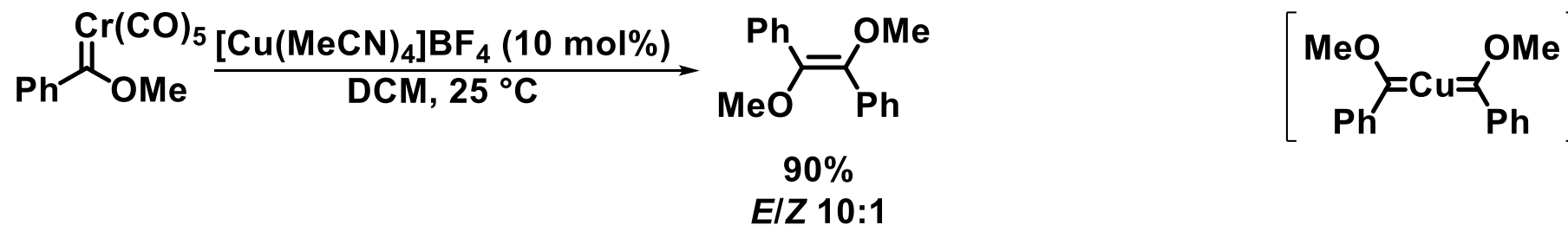
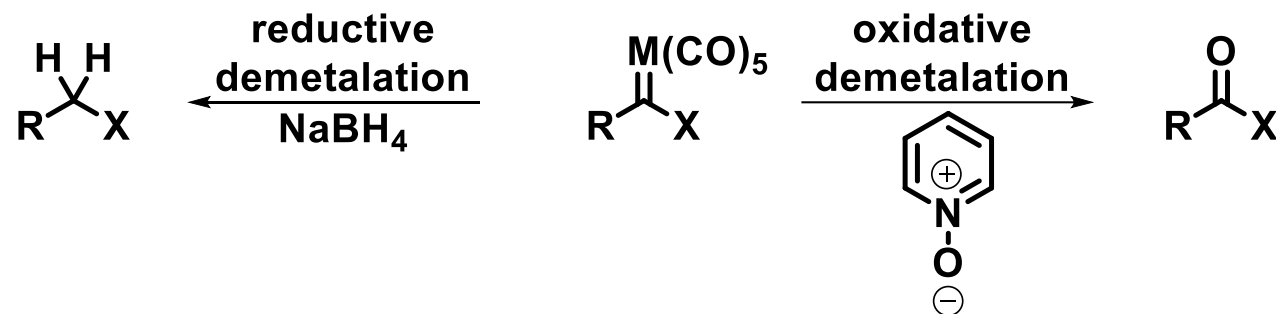


*J. Am. Chem. Soc.* **1986**, *108*, 5229

## ➤ Fischer carbene complexes

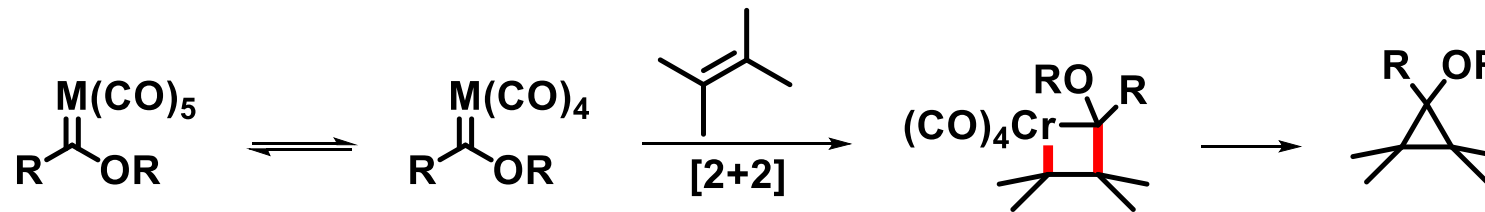
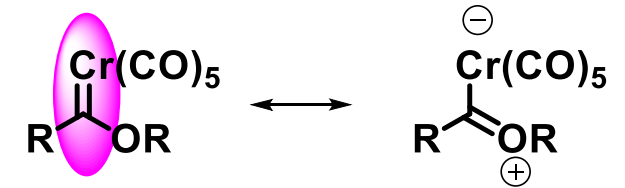
- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )

### ○ Demetalation



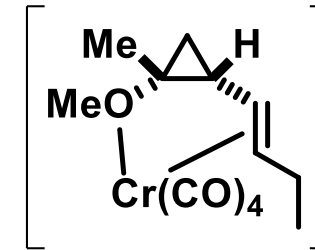
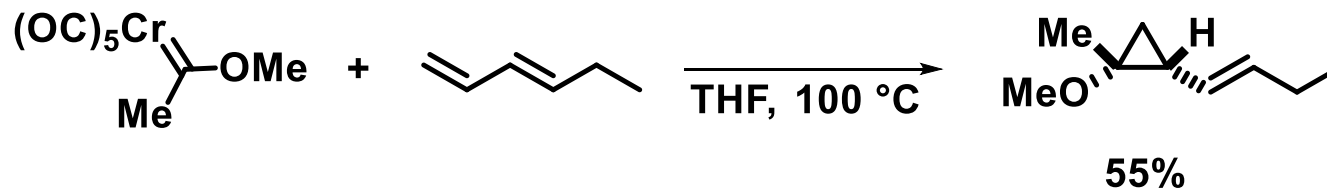
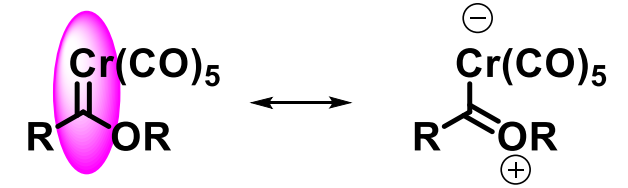
## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )
- Reaction with alkenes – Cyclopropanations



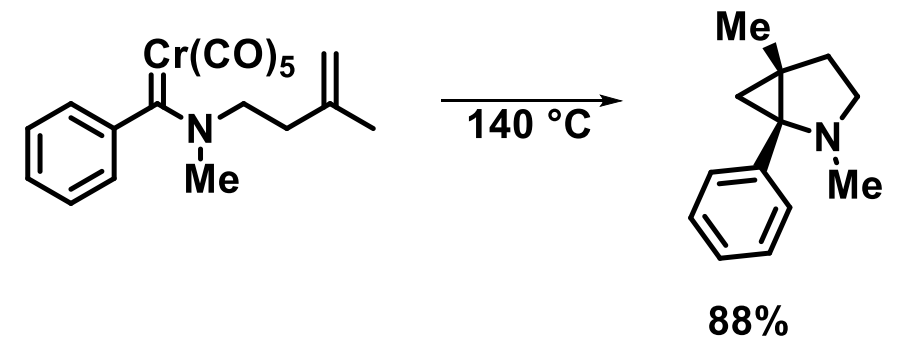
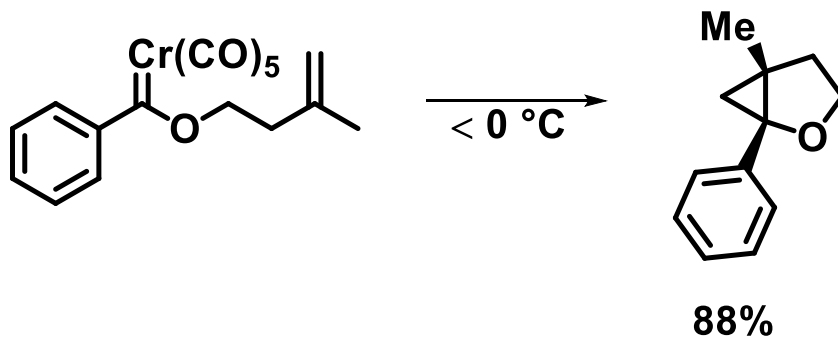
## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )
- Reaction with alkenes – Cyclopropanations



*J. Am. Chem. Soc.*, 113, 23, 1991, 8916

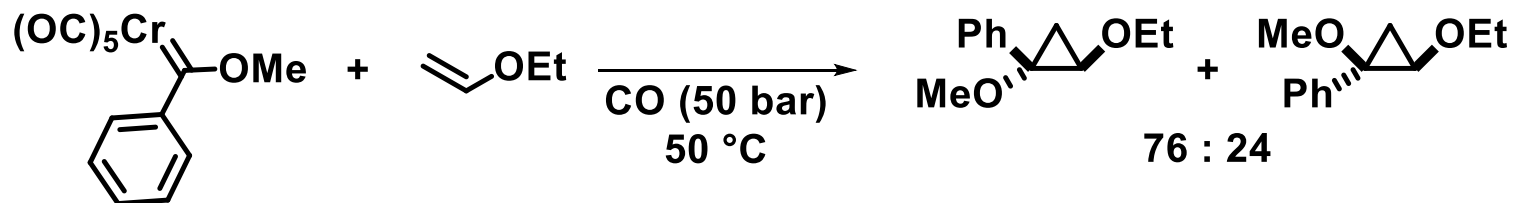
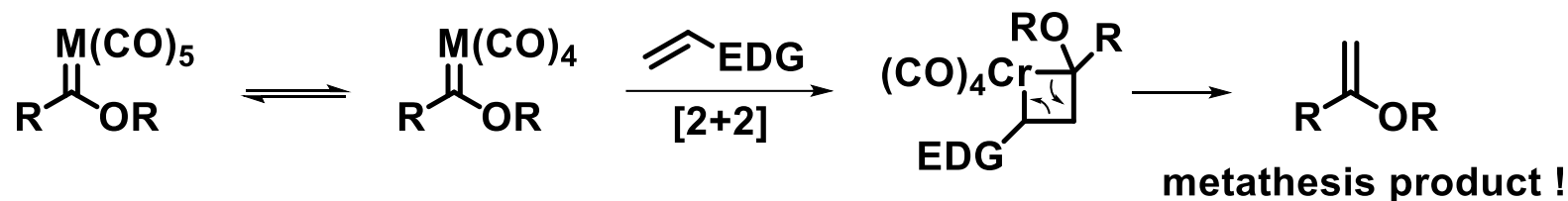
## ✓ Intramolecular version



*Organometallics* 1990, 9, 3113

## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )
- Reaction with alkenes – Cyclopropanations
  - ✓ Reaction with electron-rich alkenes

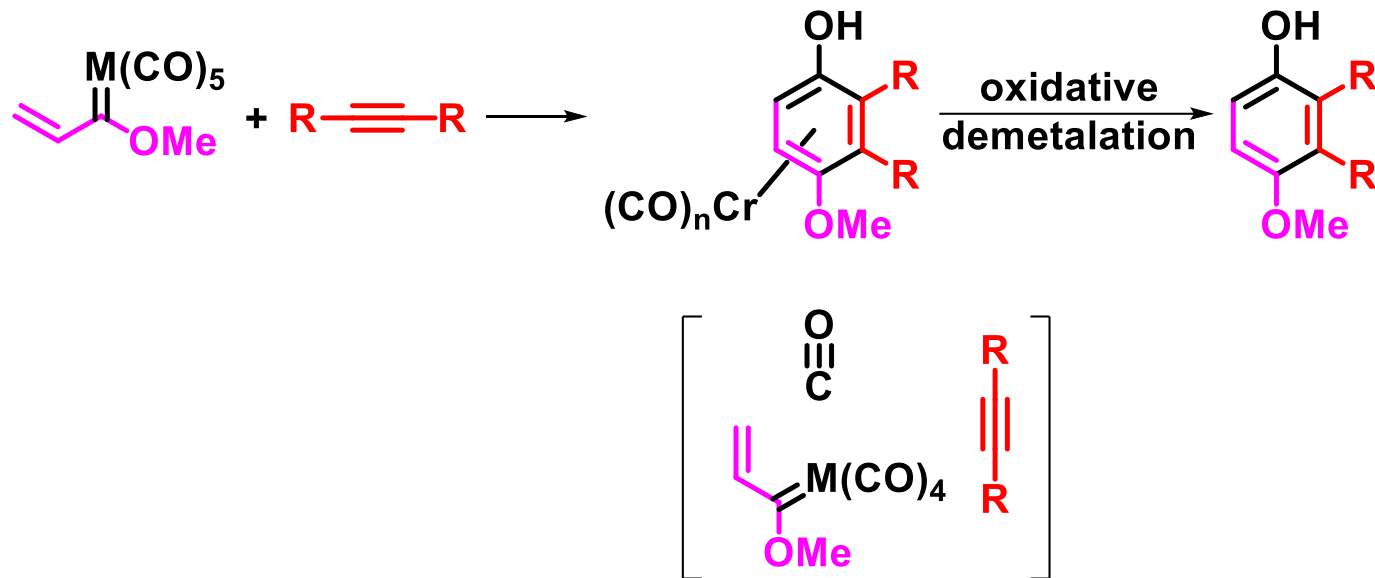
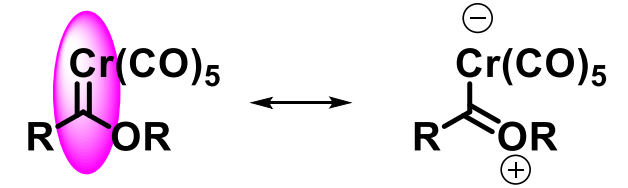


*Chem. Rev.* 1987, 87, 411



## ➤ Fischer carbene complexes

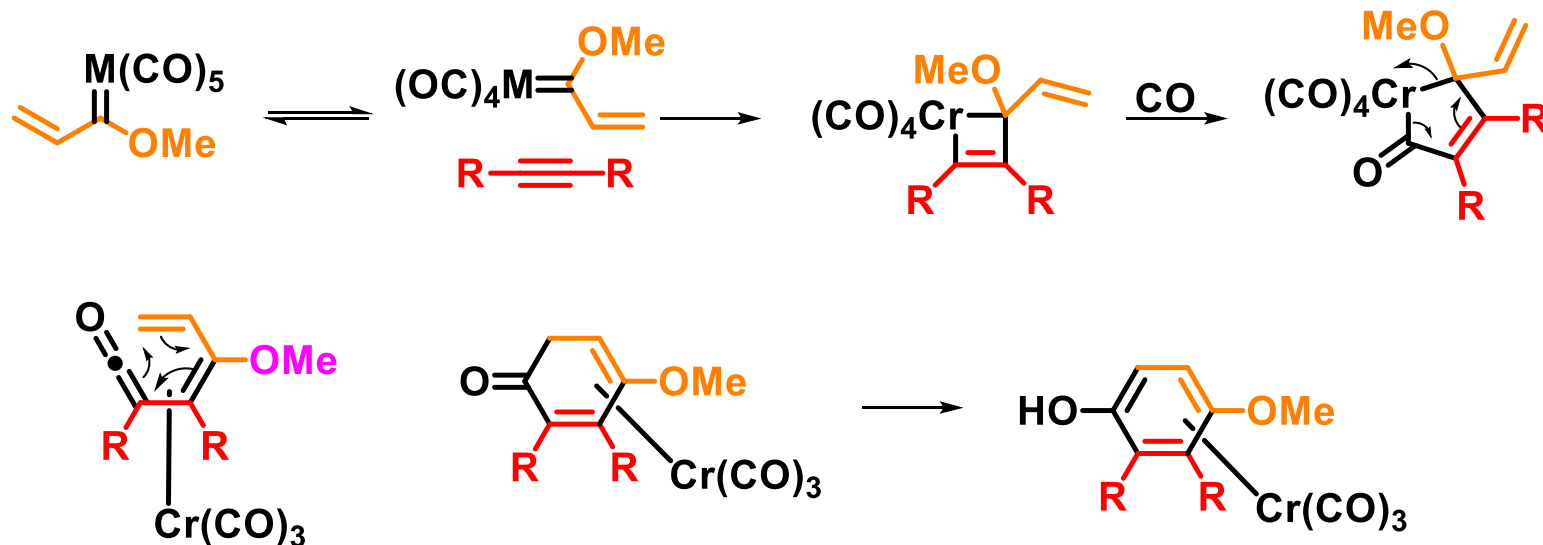
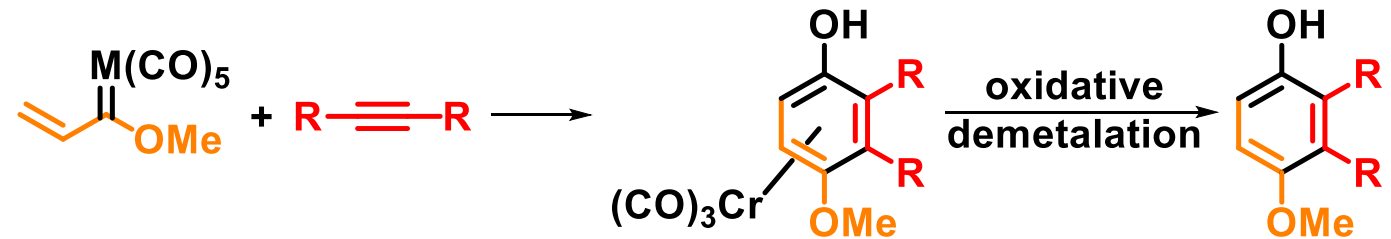
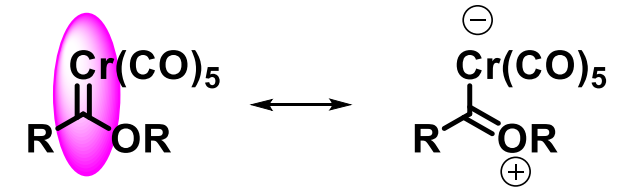
- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )
- Reaction with alkynes – Dötz reaction



## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $C=Cr(CO)_5 \cong C=O$ )
- Reaction with alkynes – Dötz reaction

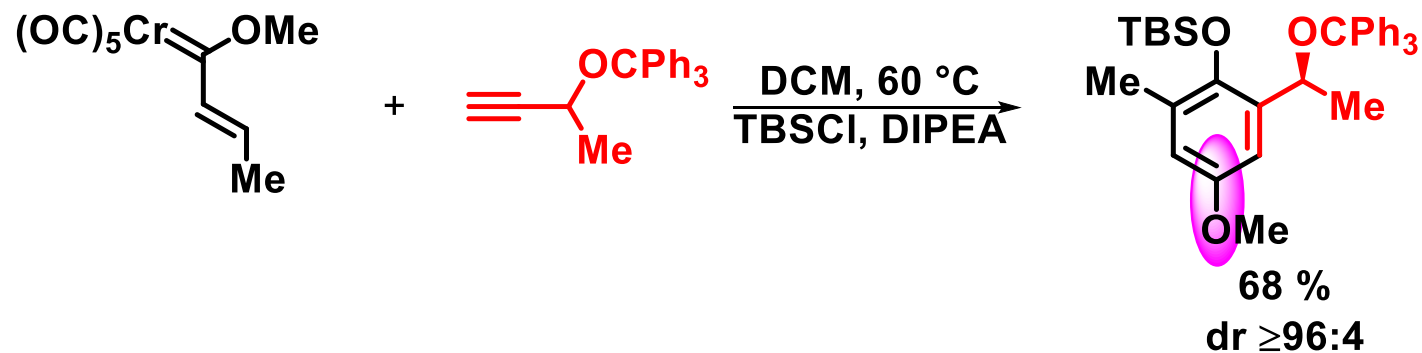
✓ Proposed mechanism



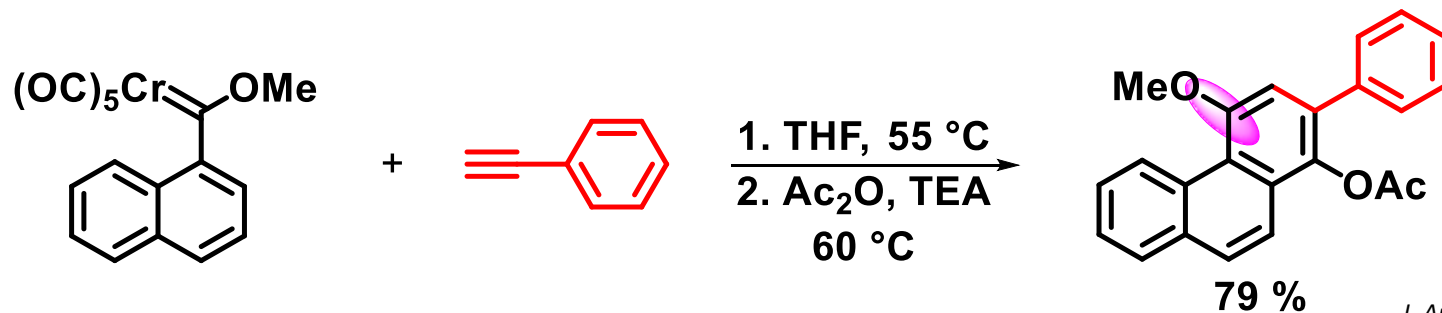
## ➤ Fischer carbene complexes

- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )
- Reaction with alkynes – Dötz reaction

### ✓ Selected examples



*J. Am. Chem. Soc.*, 1994, 116, 6449

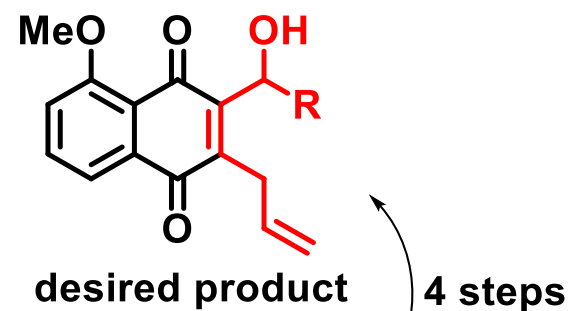
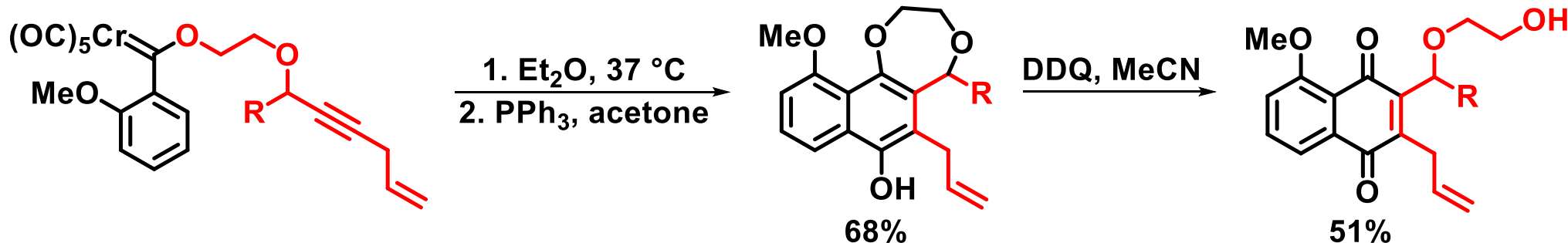
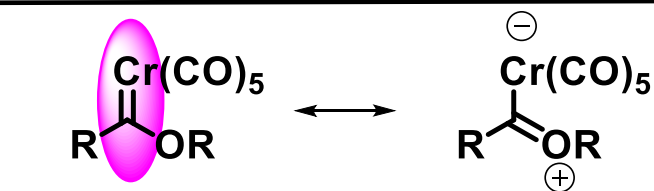
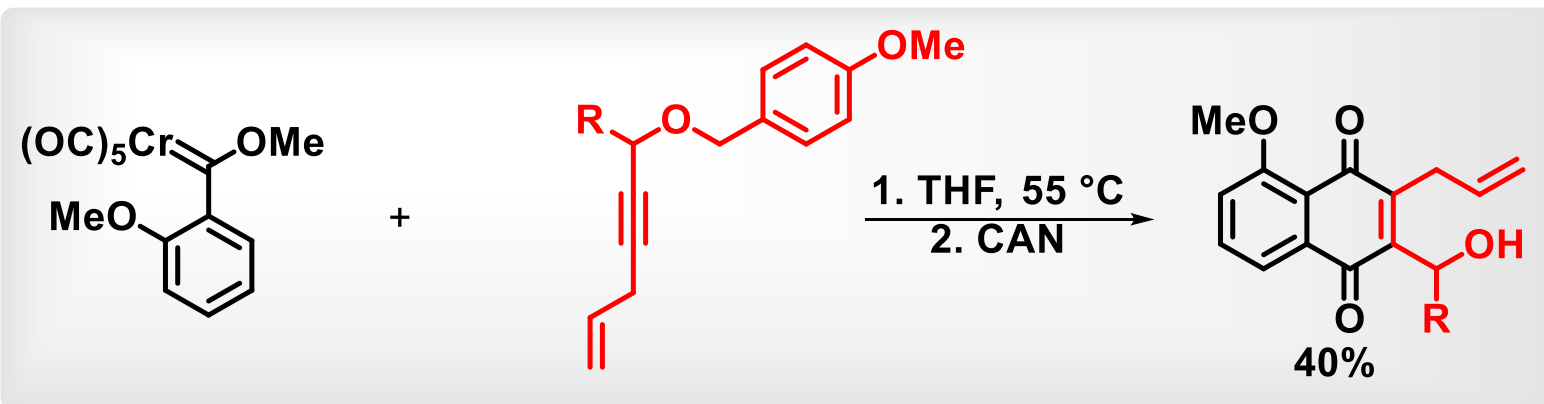


*J. Am. Chem. Soc.* 1996, 118, 3392

## ➤ Fischer carbene complexes

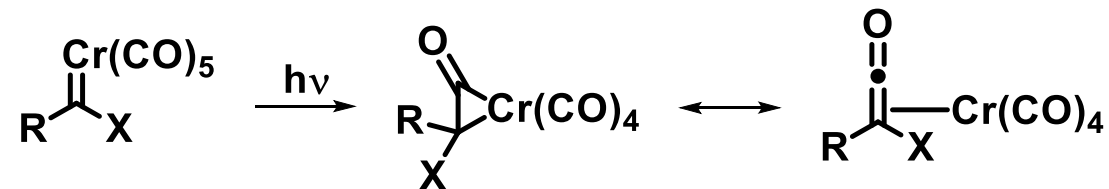
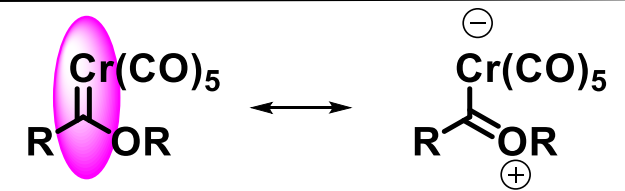
- Reactivity of Fischer carbene complexes ( $C=Cr(CO)_5 \cong C=O$ )
- Reaction with alkynes – Dötz reaction

### ✓ Selected examples

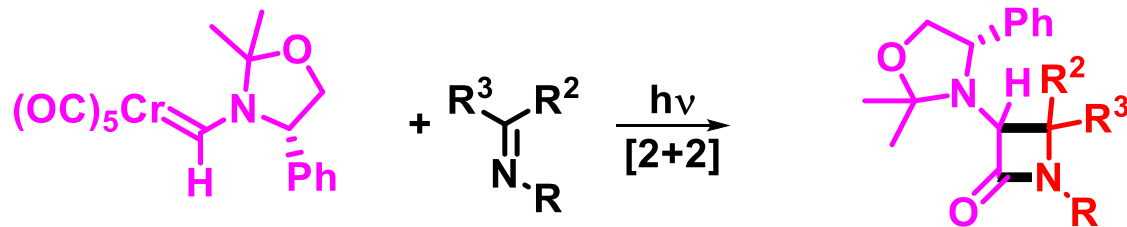


## ➤ Fischer carbene complexes

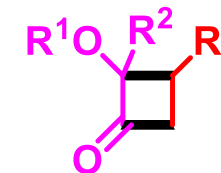
- Reactivity of Fischer carbene complexes ( $\text{C}=\text{Cr}(\text{CO})_5 \cong \text{C}=\text{O}$ )
- Photochemistry of Fischer carbene complexes – ketene elimination



- Lactams and cyclobutanones synthesis



*J. Am. Chem. Soc.* **1990**, 112, 1109



*J. Am. Chem. Soc.* **1990**, 112, 4364