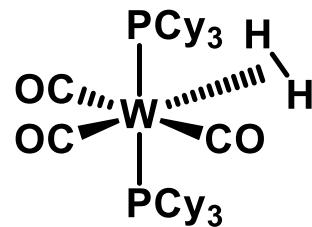


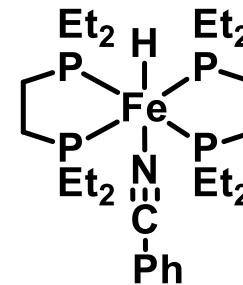
Hydride Complexes in Organic Synthesis

➤ Dihydrogen and hydride complexes

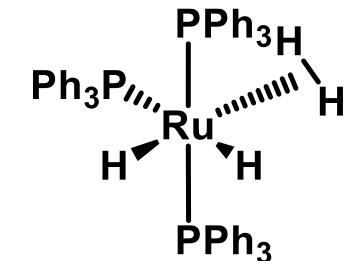
- Dihydrogen complex



- hydride complex

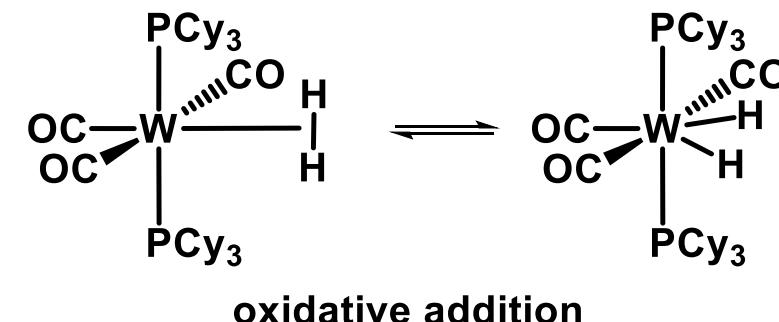
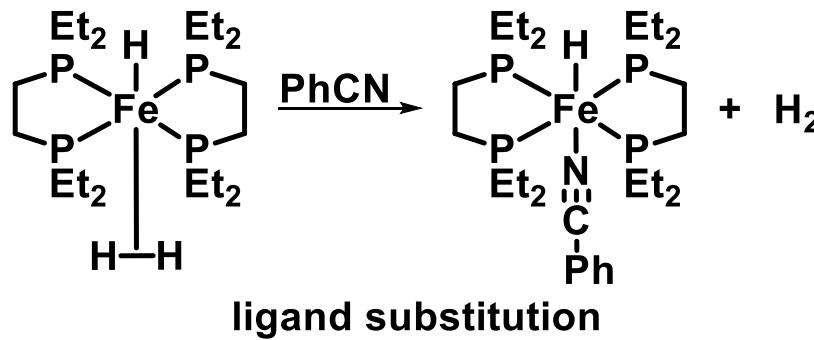


- Mixed complex



- Dihydrogen complexes

- Typical for metals in low oxidation state, strong backbonding from the metal



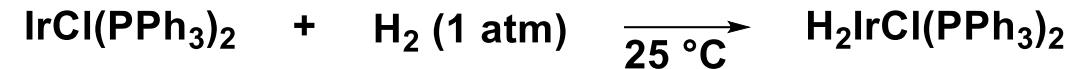
Hydride Complexes in Organic Synthesis

➤ Dihydrogen and hydride complexes

- Hydride complexes

 - Preparation

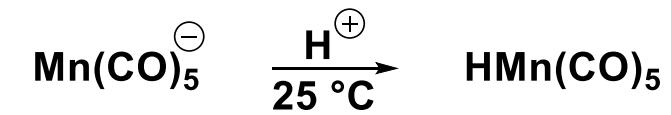
✓ From hydrogen



✓ From main group hydrides



✓ By protonation



Hydride Complexes in Organic Synthesis

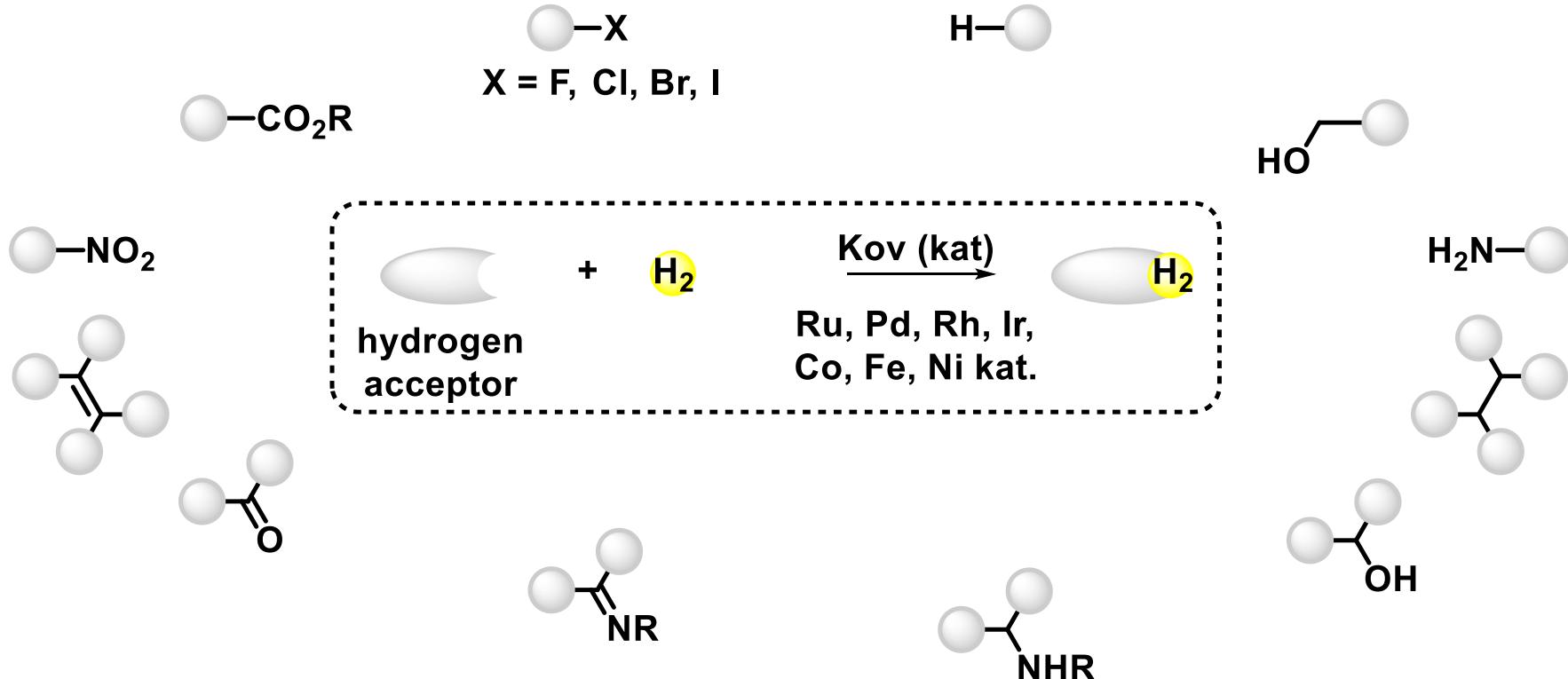
➤ Dihydrogen and hydride complexes

- Hydride complexes
 - Acidity

| Metal hydride | pK _a in MeCN |
|--|-------------------------|
| Cp* ₂ OsH | 9.9 |
| CpCr(CO) ₃ H | 13.3 |
| HPd(EtXanthPhos) ₂ ⁺ | 18.5 |
| CpW(CO) ₂ (PMe ₃)H | 26.6 |
| HPt(EtXanthPhos) ₂ ⁺ | 27.3 |

Hydride Complexes in Organic Synthesis

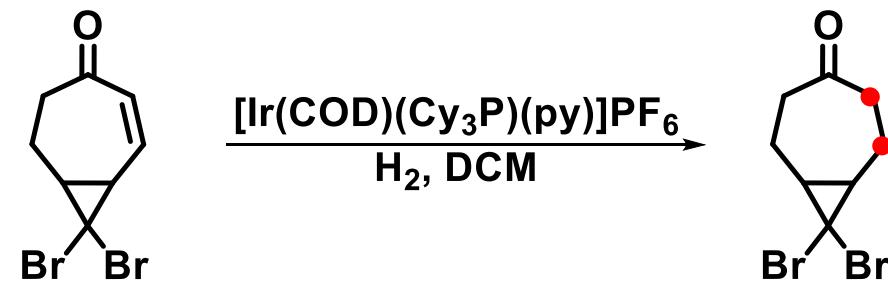
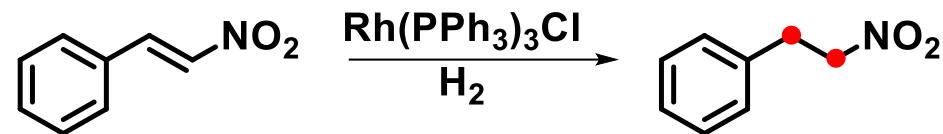
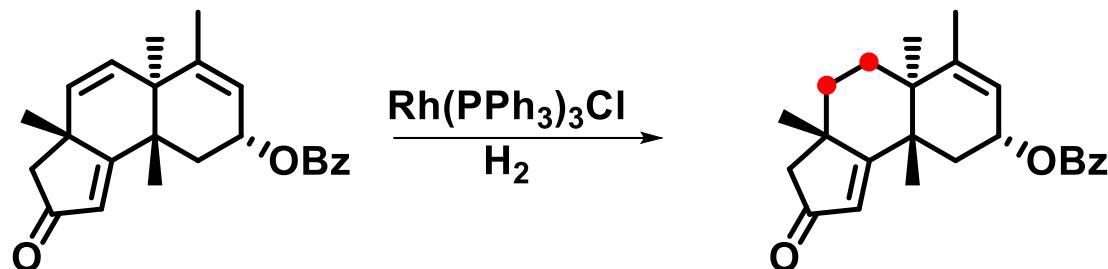
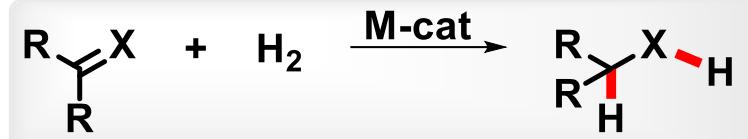
➤ Homogeneous Hydrogenation

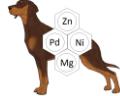


Hydride Complexes in Organic Synthesis

➤ Homogeneous Hydrogenation

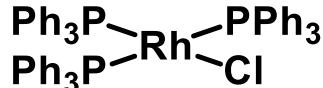
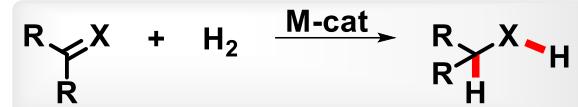
- Selected examples



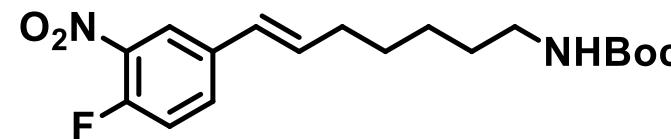


➤ Homogeneous Hydrogenation

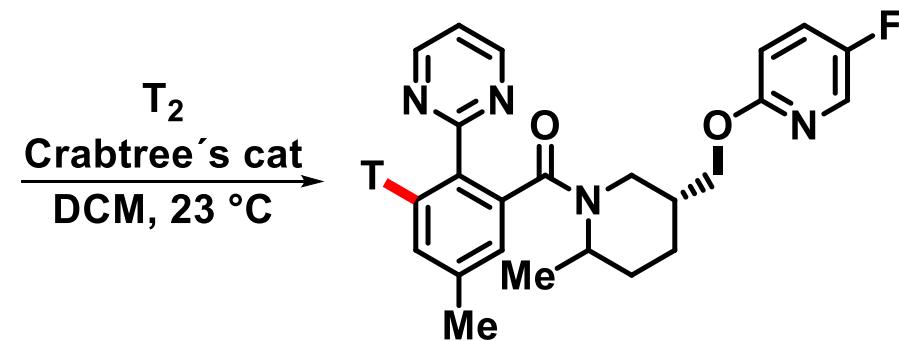
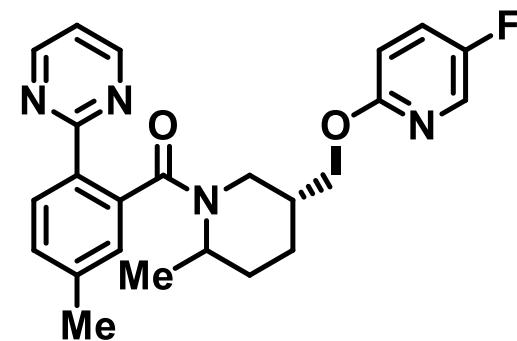
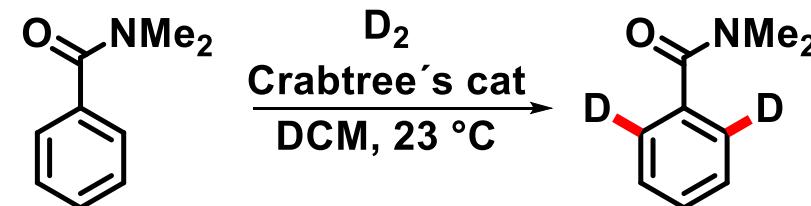
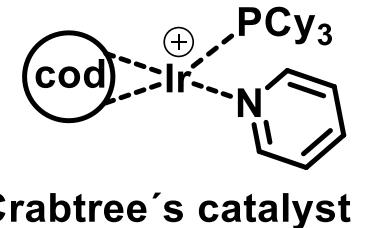
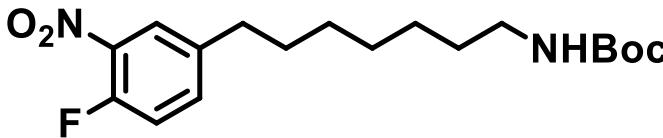
- Hydrogenation catalysts



Wilkinson's catalyst

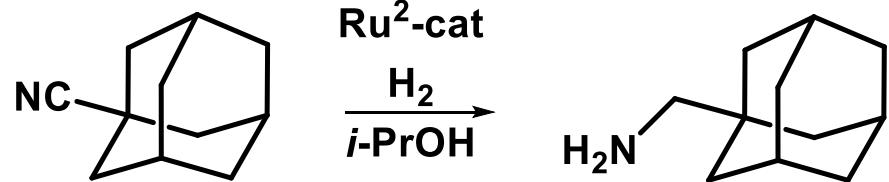
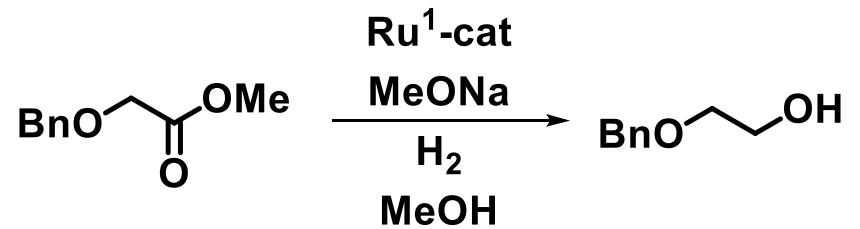
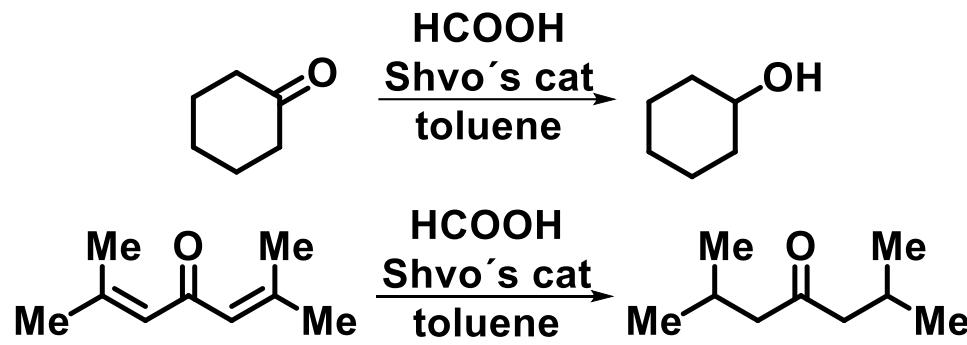
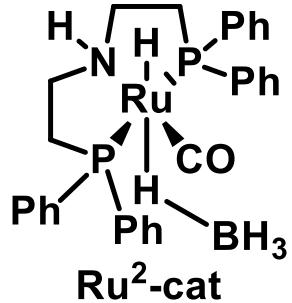
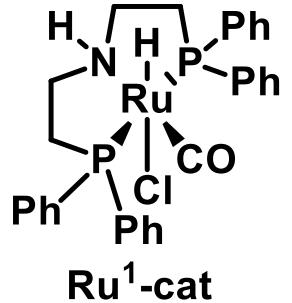
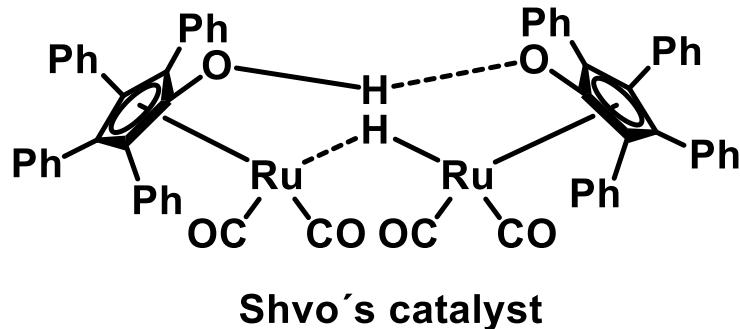


\downarrow
 H_2
 Wilkinson's cat
 $t\text{-BuOH-THF}$



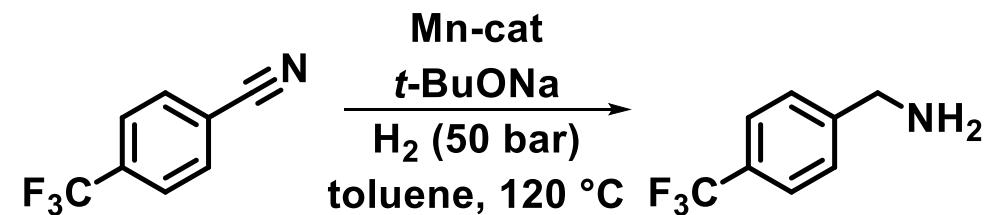
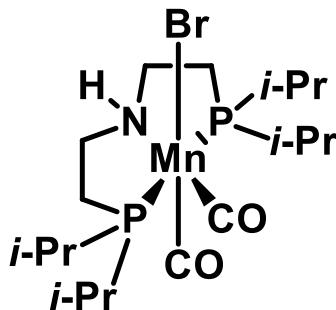
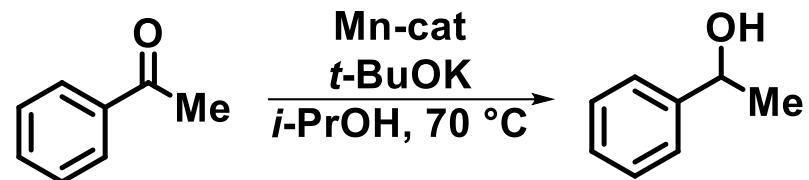
Hydride Complexes in Organic Synthesis

► Hydrogenation catalysts



Hydride Complexes in Organic Synthesis

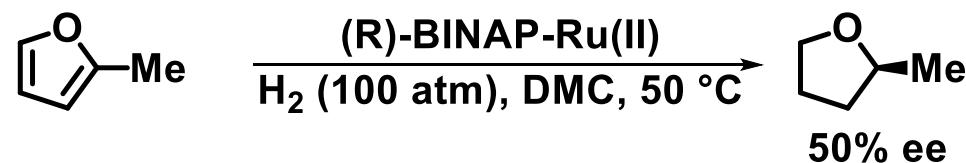
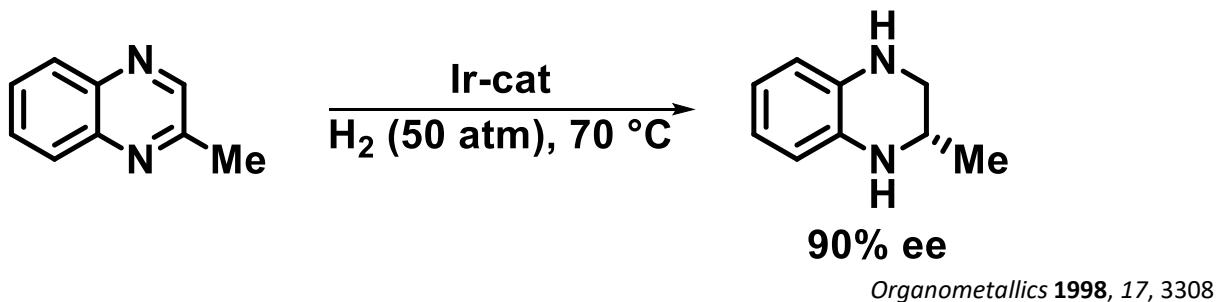
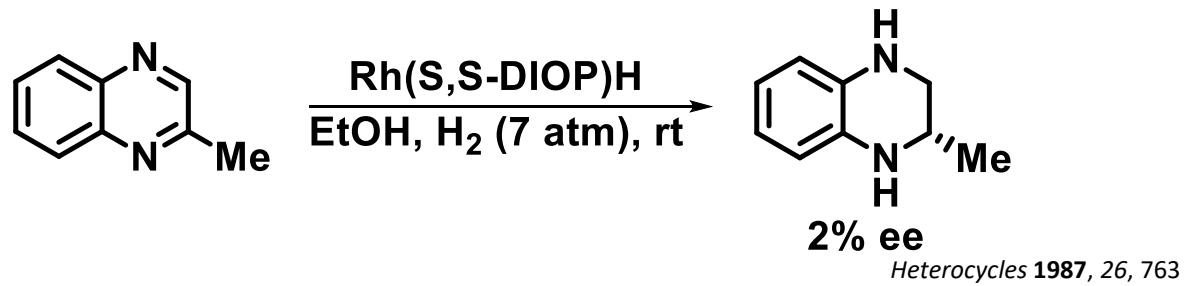
► Hydrogenation catalysts



Hydride Complexes in Organic Synthesis

➤ Homogeneous Hydrogenation

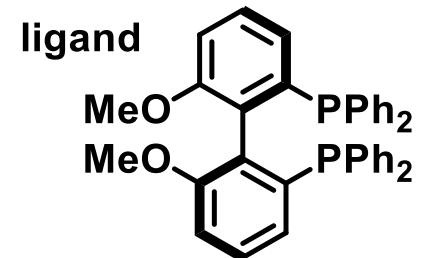
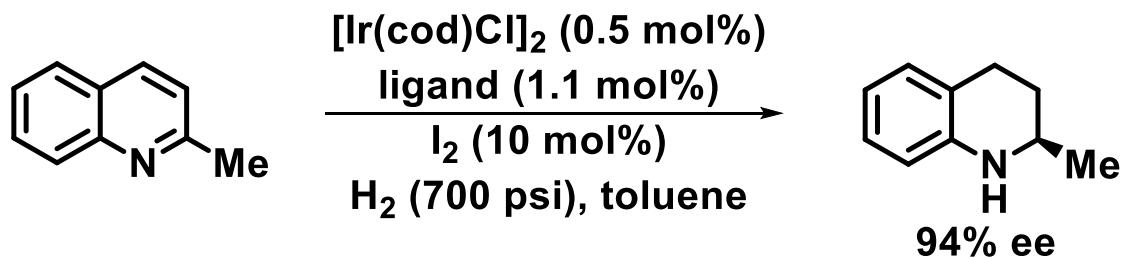
- Asymmetric Hydrogenation of heterocycles – early examples



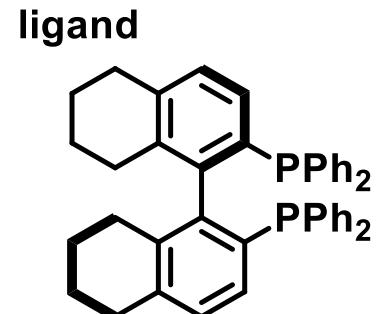
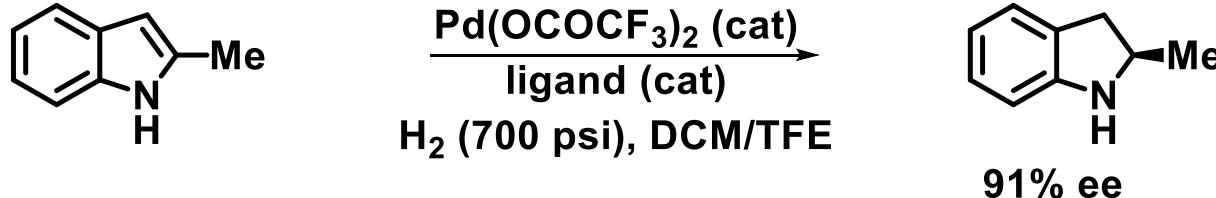
Hydride Complexes in Organic Synthesis

➤ Homogeneous Hydrogenation

- Asymmetric Hydrogenation of heterocycles – recent examples



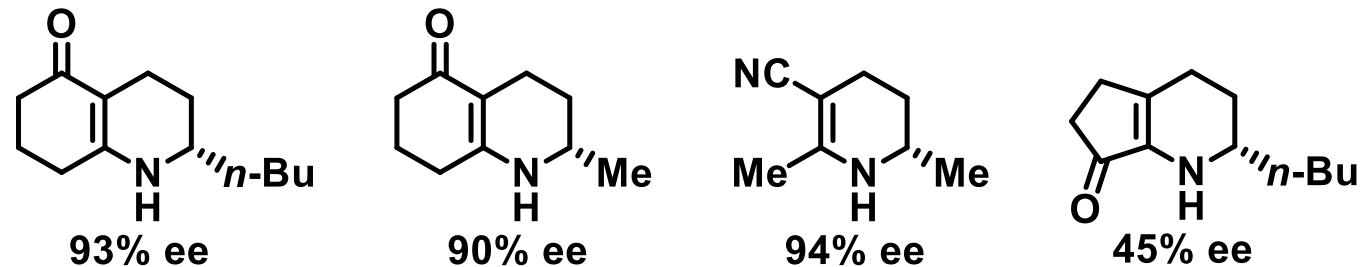
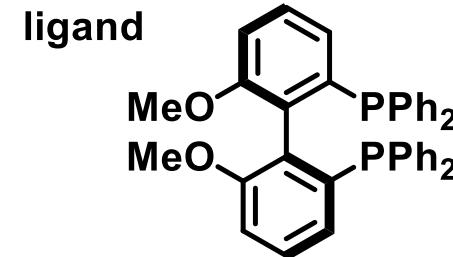
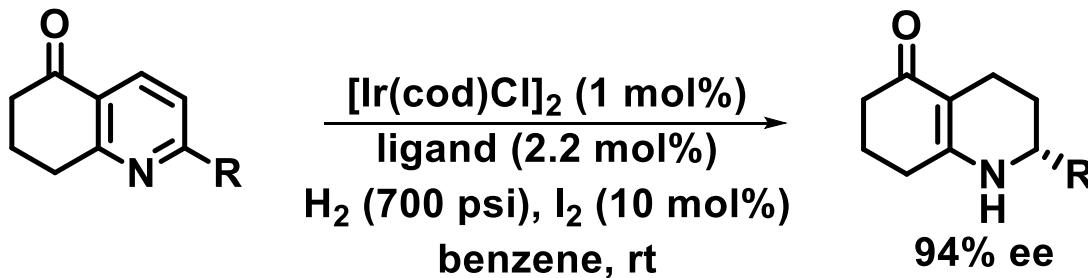
J. Am. Chem. Soc. **2003**, 125, 10536



Hydride Complexes in Organic Synthesis

➤ Asymmetric Hydrogenation ligands

- Asymmetric Hydrogenation of heterocycles – recent examples



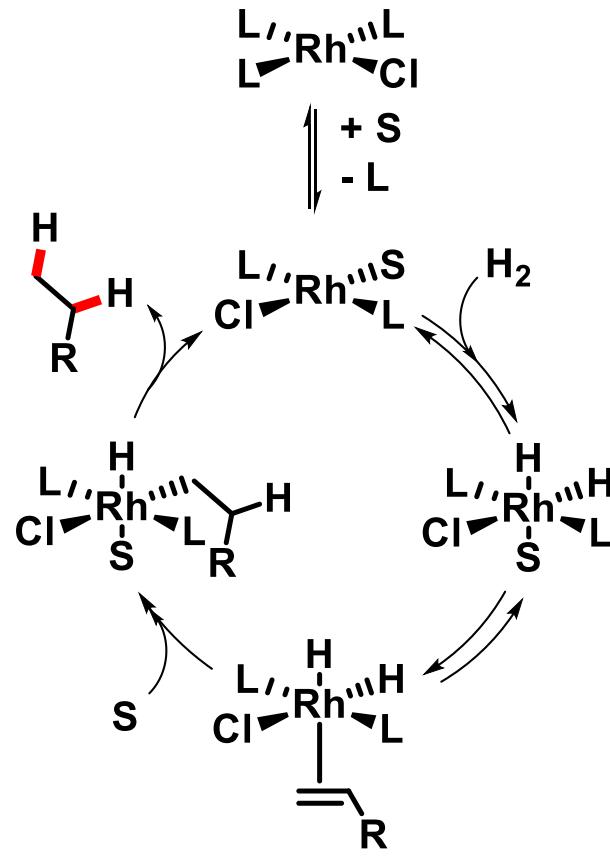
Tetrahedron Lett. 2008, 49, 4922

Hydride Complexes in Organic Synthesis

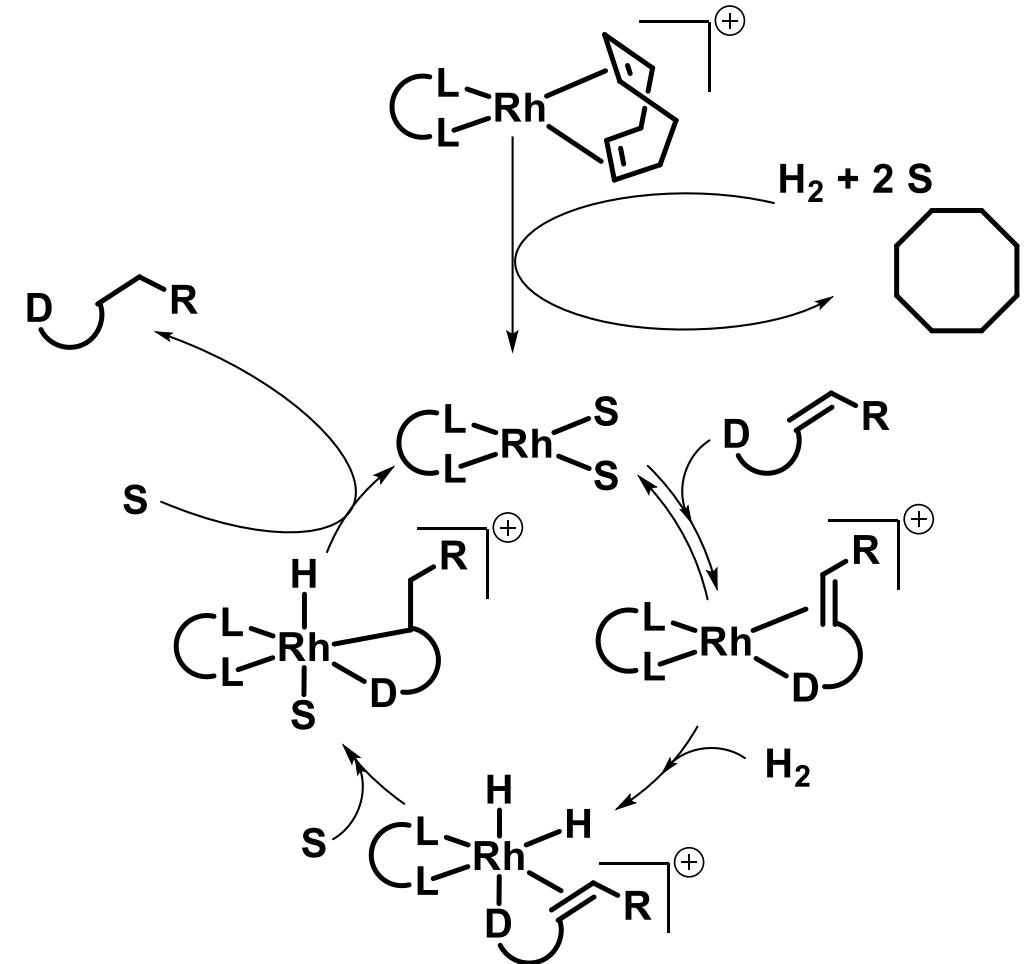
➤ Selected hydrogenation mechanisms



- Hydrogen-first mechanism



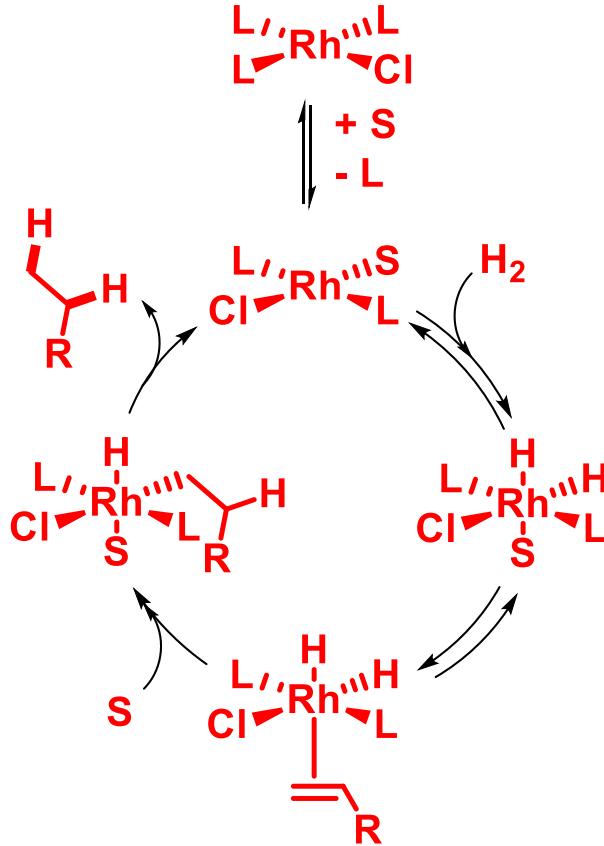
- Alkene-first mechanism for alkenes with a donor group (D)



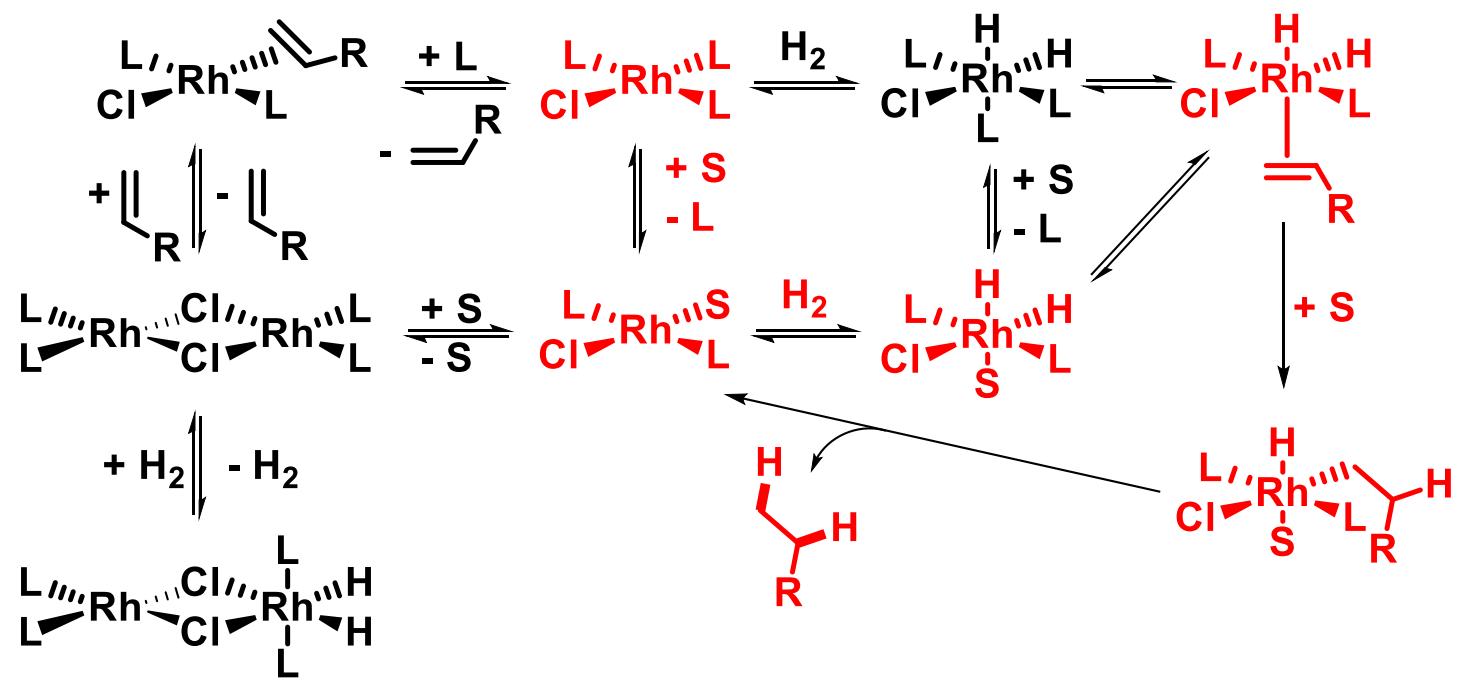
Hydride Complexes in Organic Synthesis

➤ Selected hydrogenation mechanisms

- Simplified hydrogen firt mechanism



- Complete mechanism for hydrogen firt mechanism

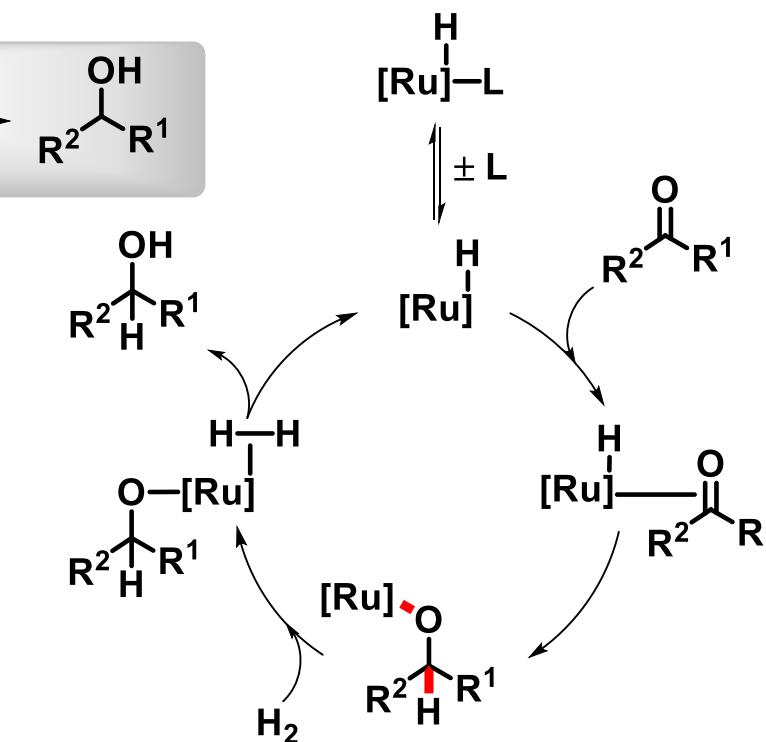
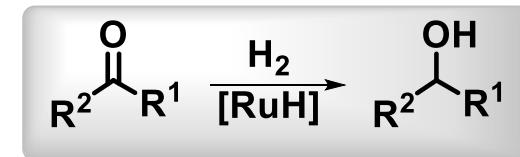
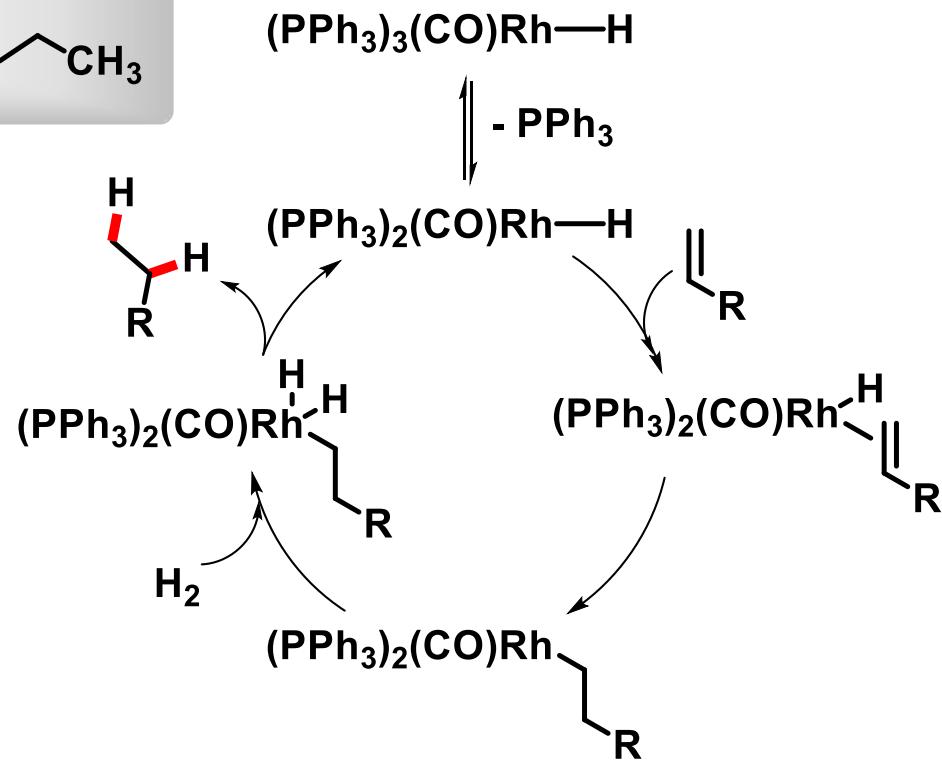
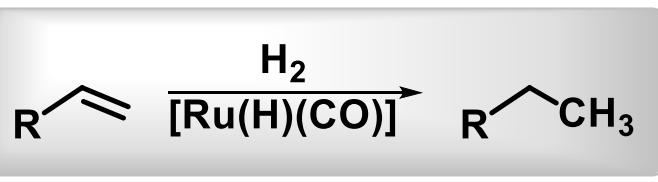


Hydride Complexes in Organic Synthesis

➤ Selected hydrogenation mechanisms



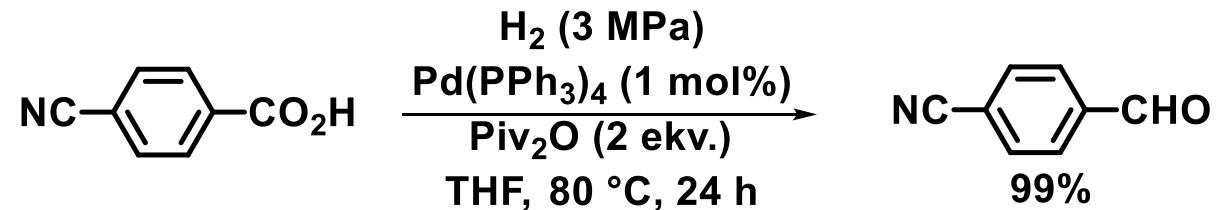
- Mechanism of alkenes hydrogenation by $[\text{Rh}(\text{H})\text{CO}]$
- Mechanism of ketones hydrogenation by $[\text{Ru}(\text{H})]$



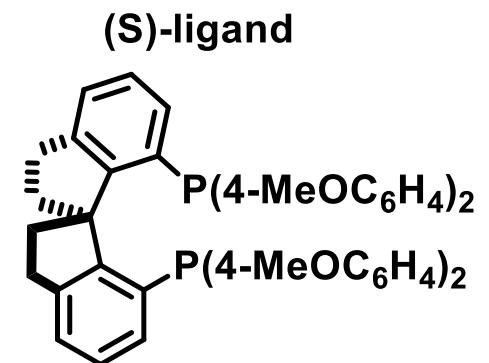
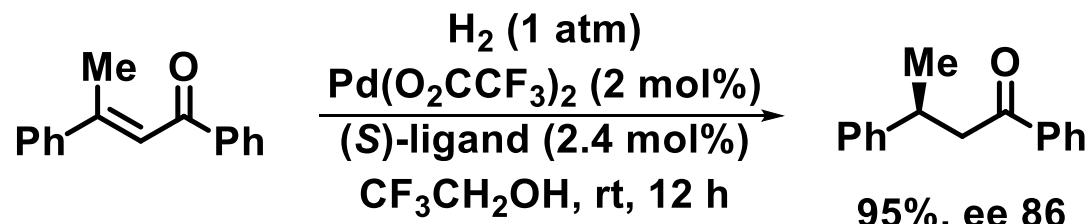
Hydride Complexes in Organic Synthesis

➤ Selected hydrogenation mechanisms

- Palladium-catalyzed hydrogenation



Chem. Lett. 1998, 27, 1143

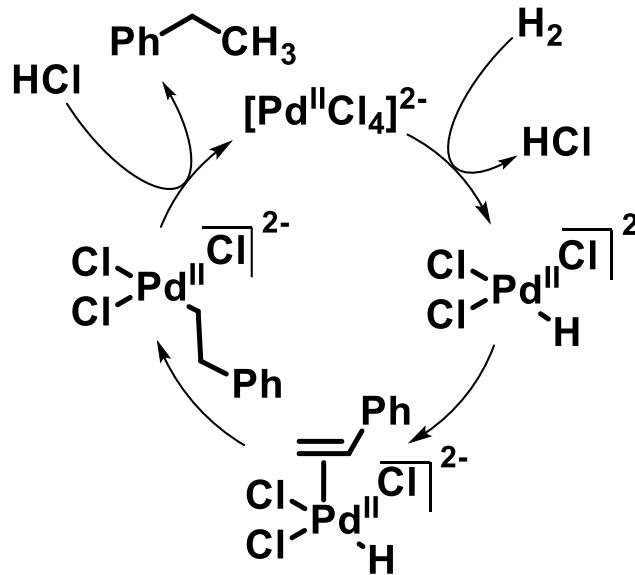
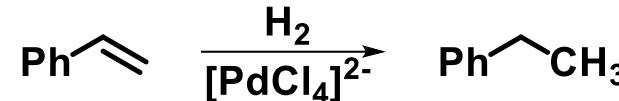


Synlett 2011, 947

Hydride Complexes in Organic Synthesis

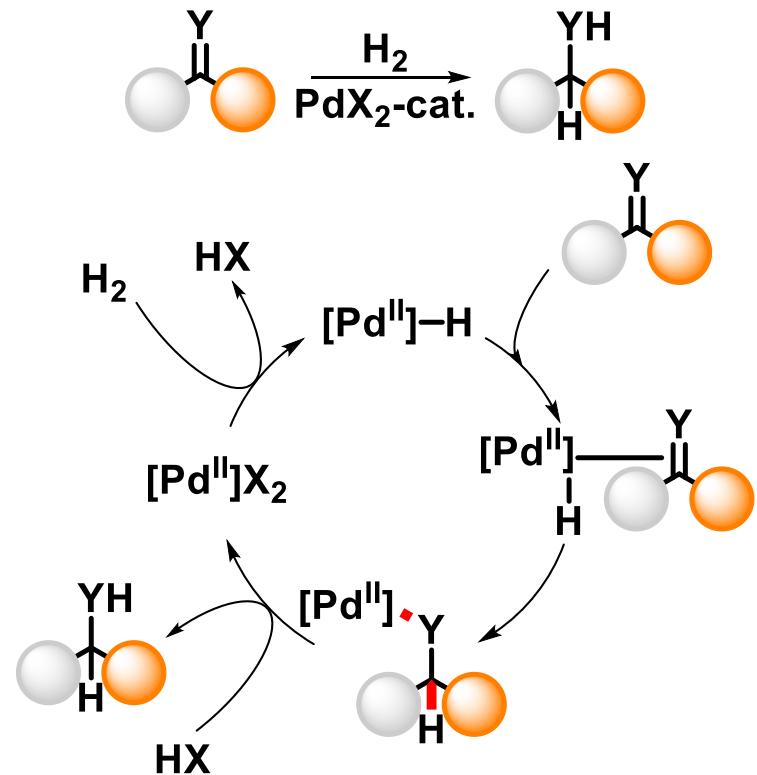
➤ Selected hydrogenation mechanisms

- Mechanism for palladium-catalyzed hydrogenation



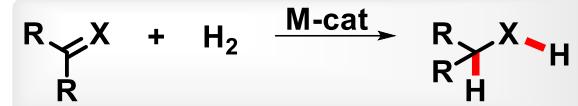
J. Catal. 1977, 48, 8

- General mechanism

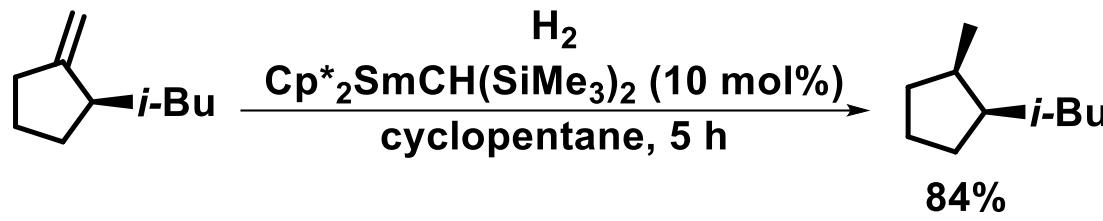


Hydride Complexes in Organic Synthesis

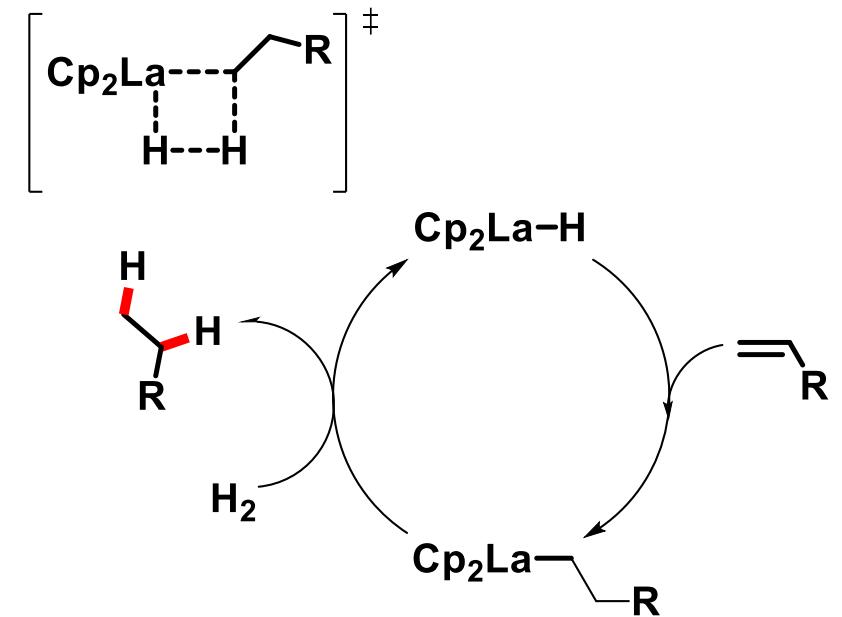
➤ Selected hydrogenation mechanisms



- Lanthanide hydrogenation through σ -bond metathesis step

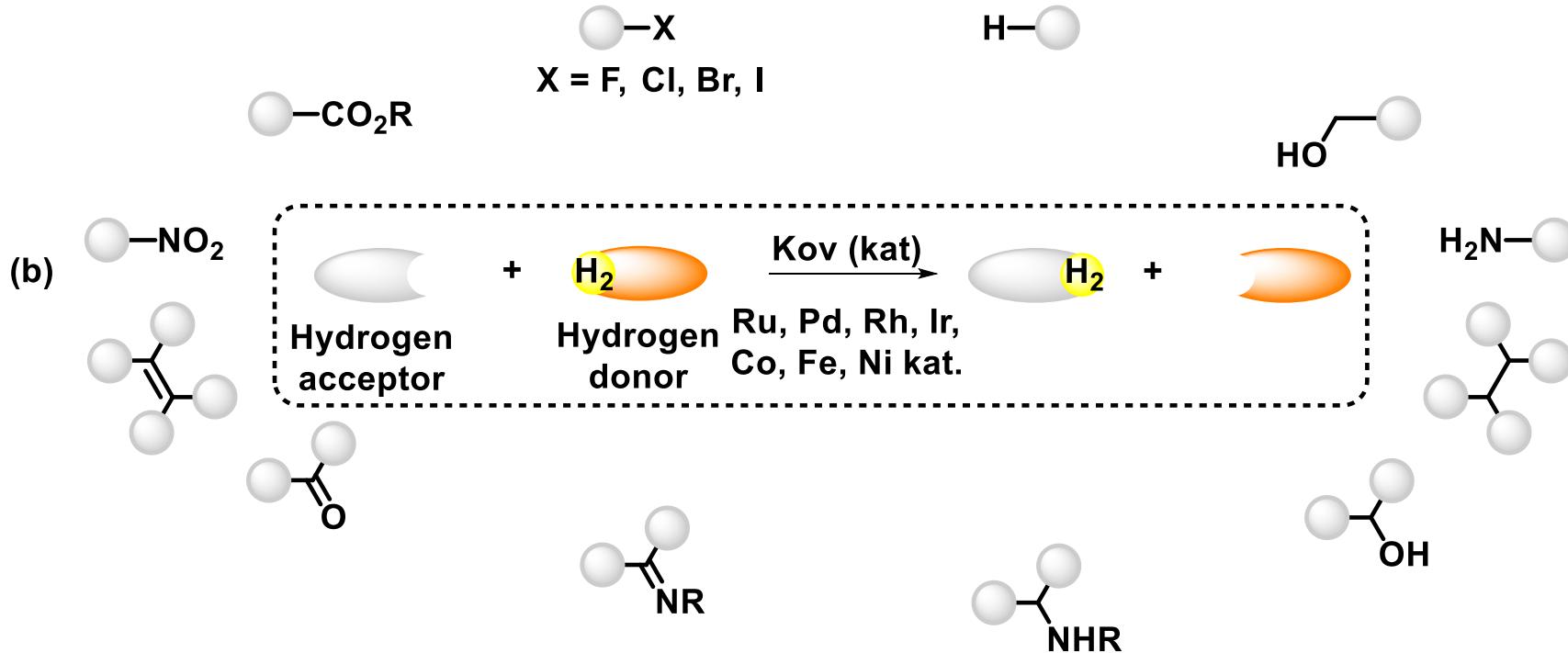


J. Organometal. Chem. **1996**, *524*, 275

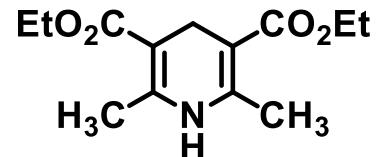
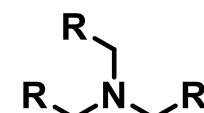
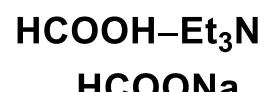
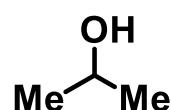


Hydride Complexes in Organic Synthesis

Transfer hydrogenation



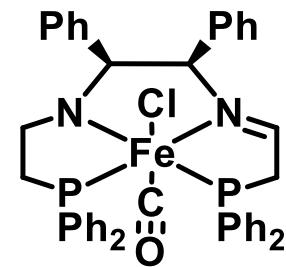
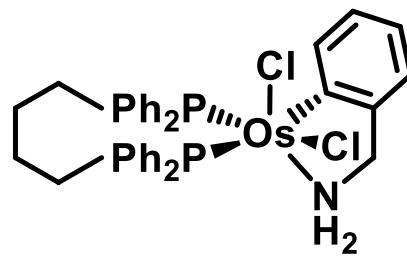
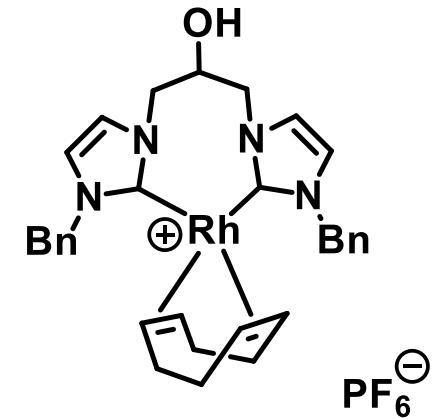
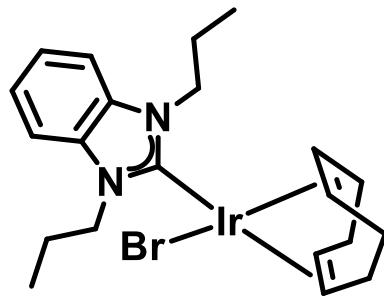
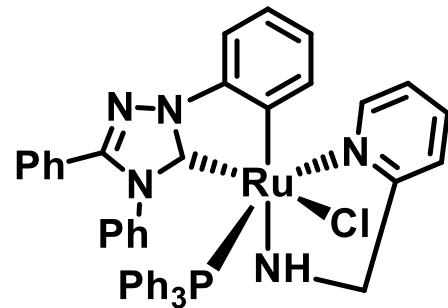
Typical hydrogen donors:



Hydride Complexes in Organic Synthesis

➤ Transfer hydrogenation

- Modern catalysts for transfer hydrogenation

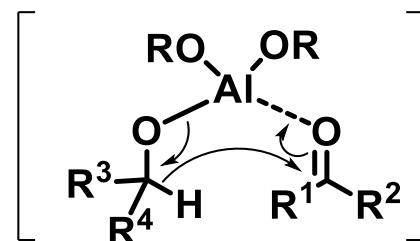
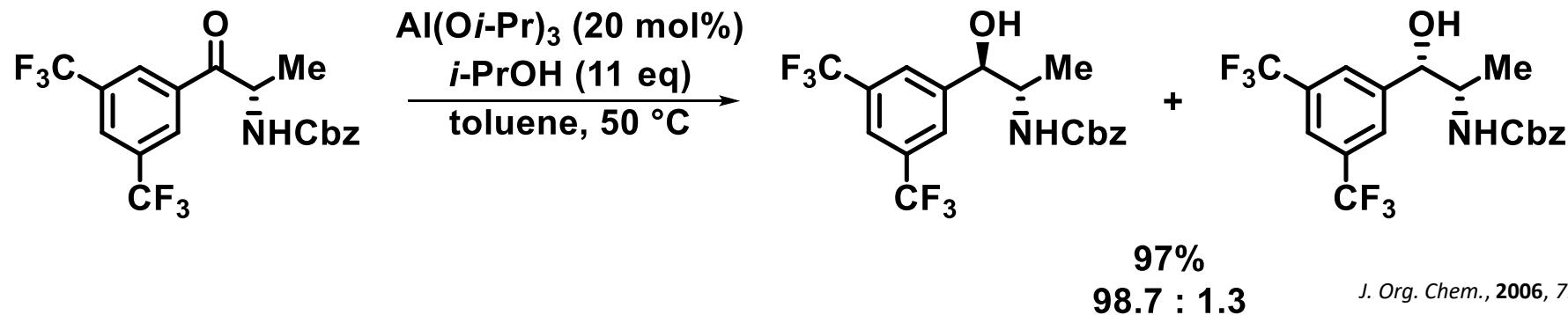


Hydride Complexes in Organic Synthesis

Transfer hydrogenation



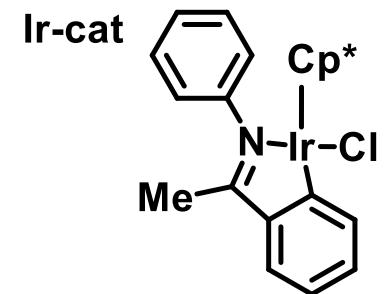
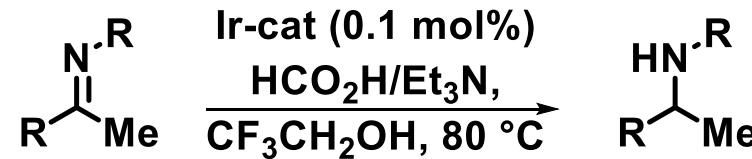
- Meerwin-Ponndorf-Verley reduction



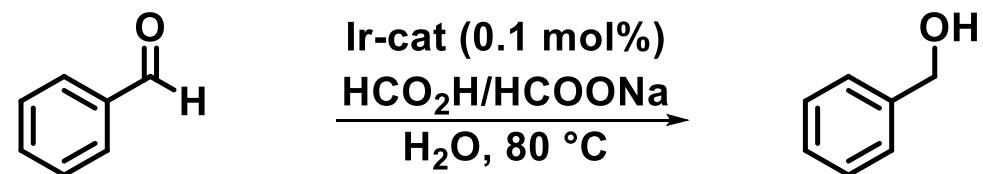
Hydride Complexes in Organic Synthesis

➤ Transfer hydrogenation

- Selected examples



Angew. Chem. Int. Ed. **2010**, *49*, 7548

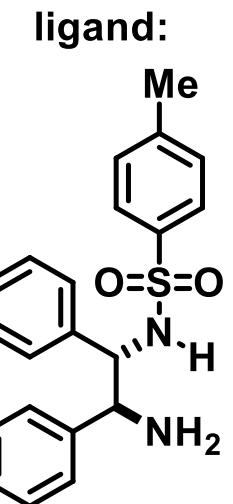
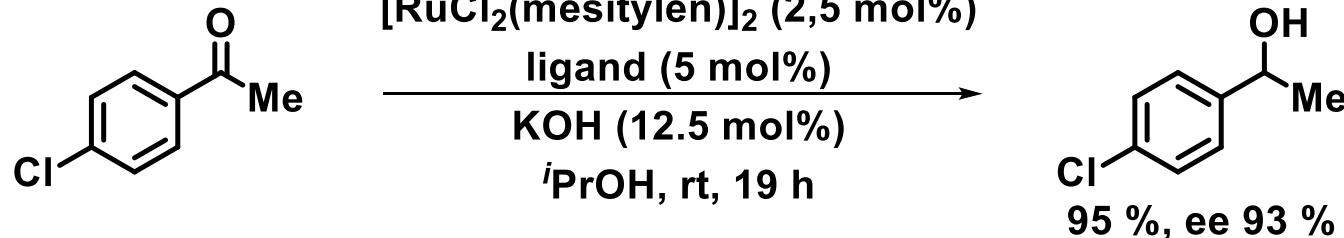
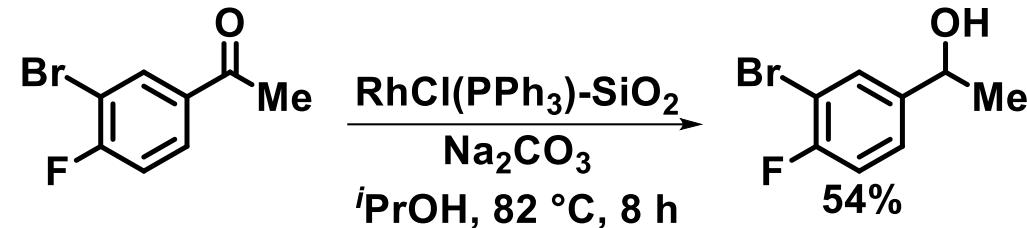
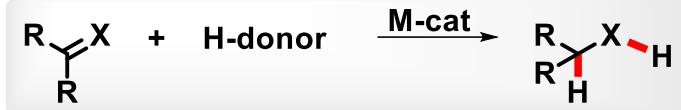


Green Chem. **2013**, *15*, 629; *Chem. Eur. J.* **2014**, *20*, 12835

Hydride Complexes in Organic Synthesis

➤ Transfer hydrogenation

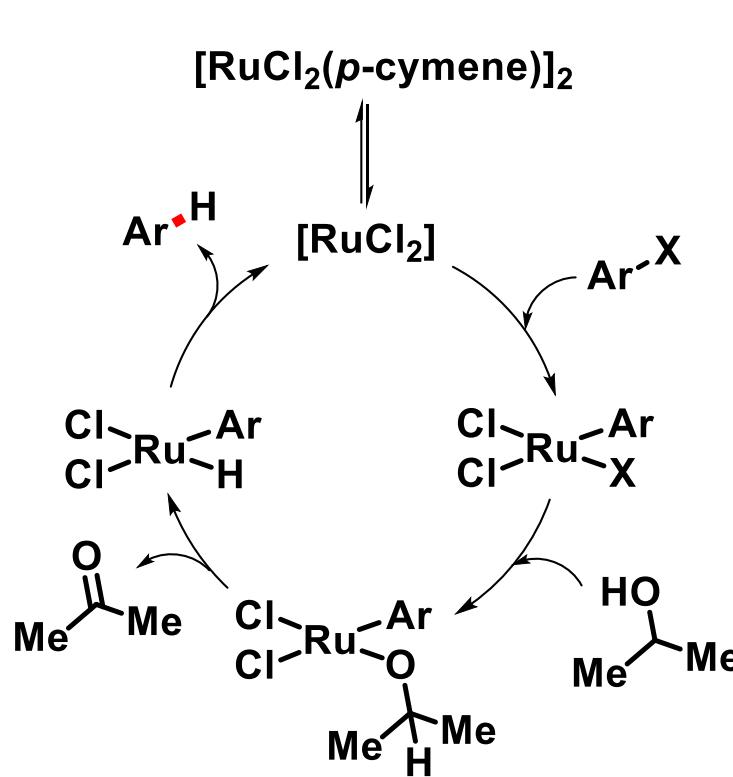
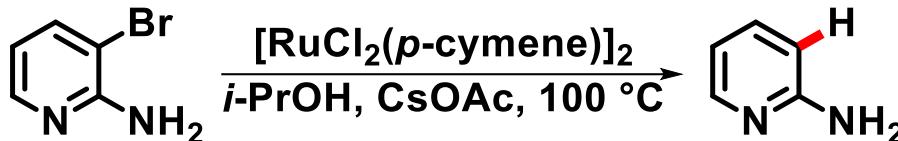
- Selected examples



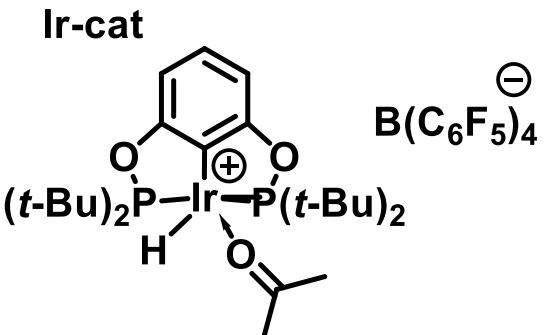
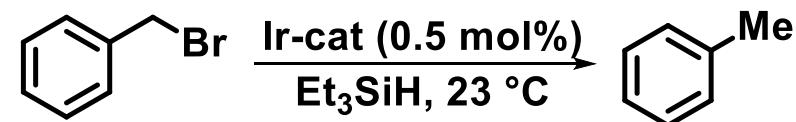
Hydride Complexes in Organic Synthesis

Transfer hydrogenation

- Transfer hydro-dehalogenation



J. Org. Chem. 2017, 82, 1340

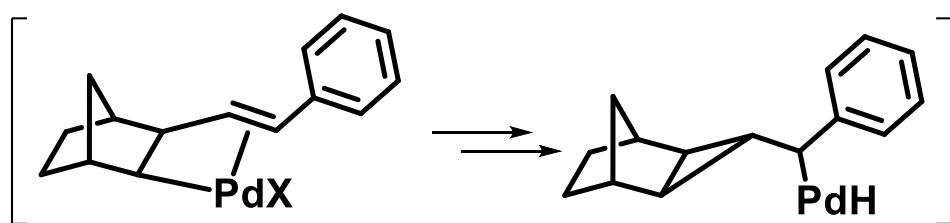
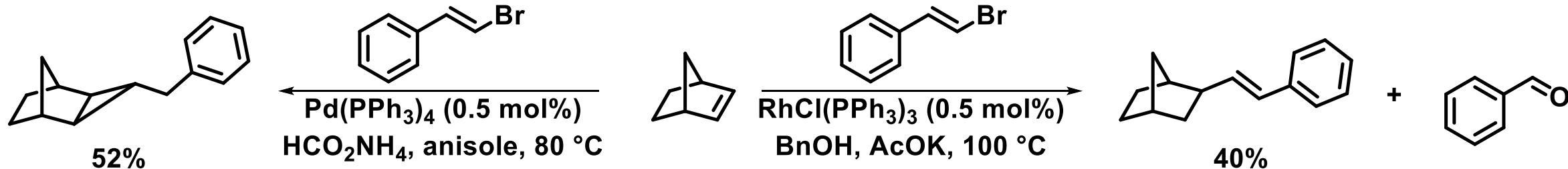
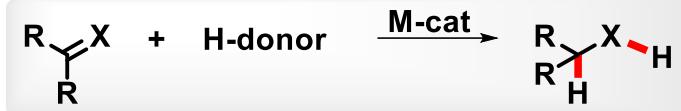


J. Am. Chem. Soc. 2007, 129, 42, 12656

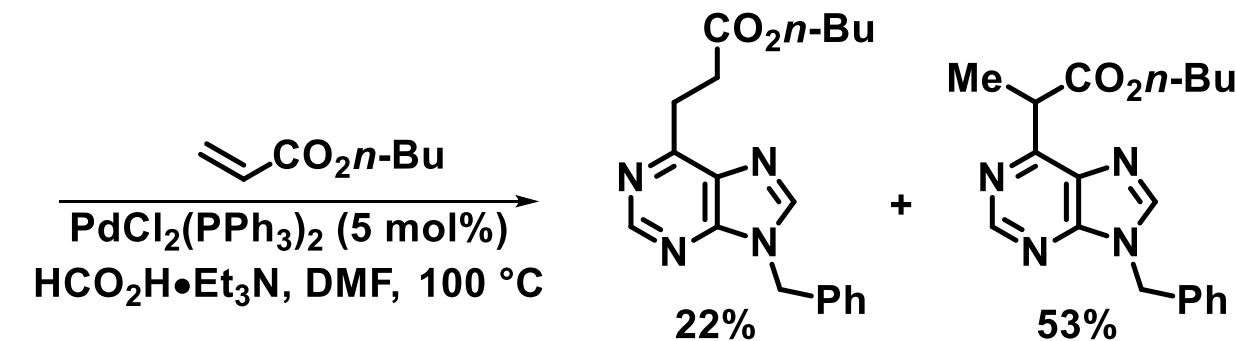
Hydride Complexes in Organic Synthesis

➤ Transfer hydrogenation

- Reductive Heck reaction



J. Organomet. Chem. 1980, 199, C21

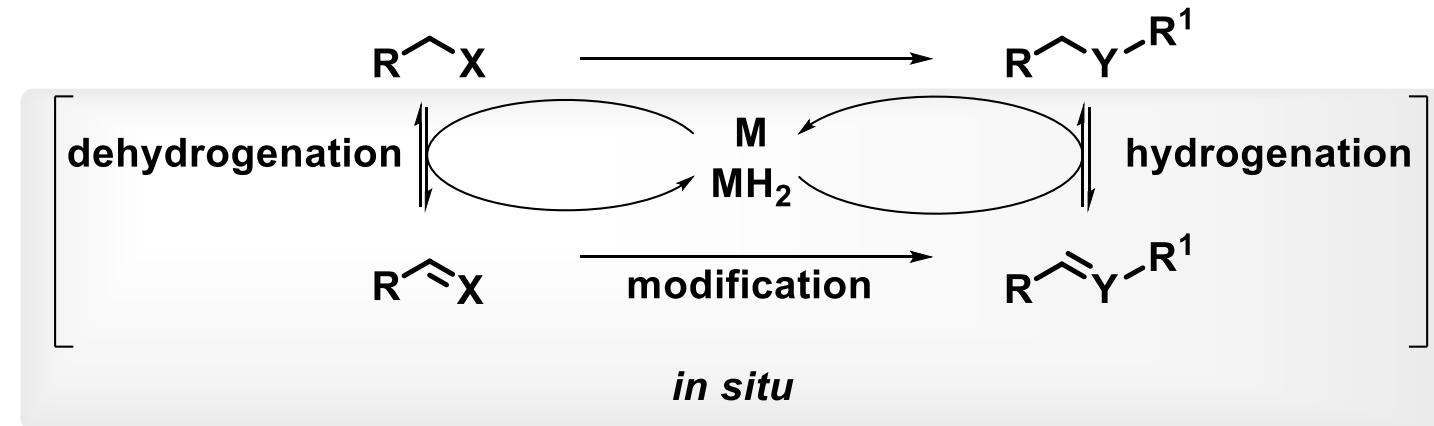
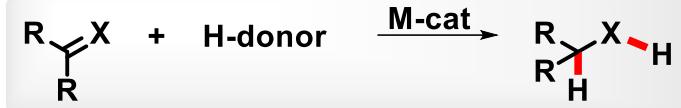


Tetrahedron Lett. 2004, 45, 273

Hydride Complexes in Organic Synthesis

- Borrowing hydrogen catalysis (hydrogen auto-transfer)

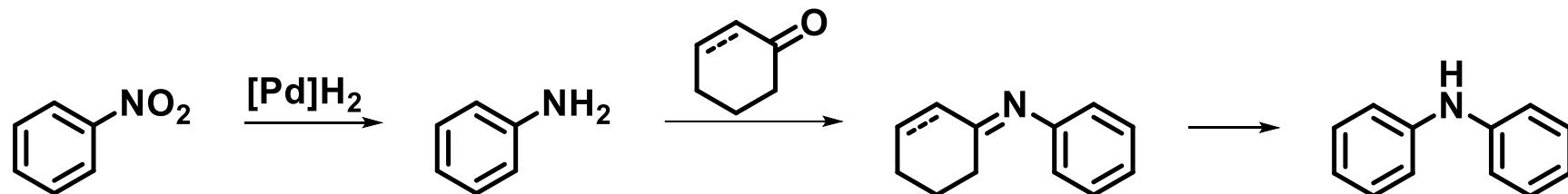
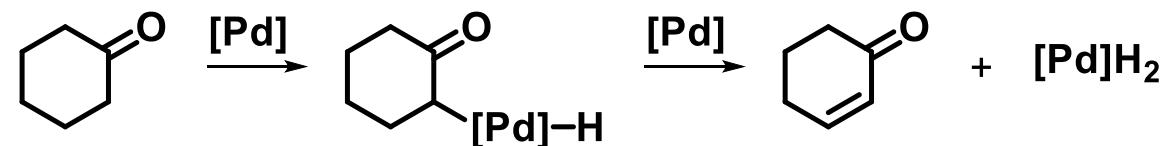
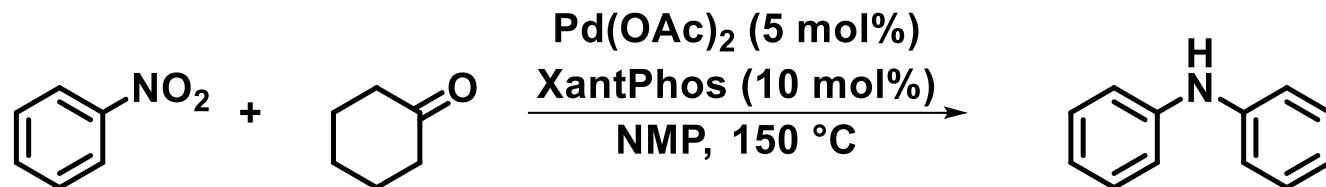
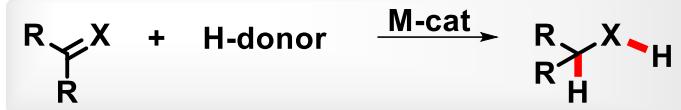
- Concept



Hydride Complexes in Organic Synthesis

- Borrowing hydrogen catalysis (hydrogen auto-transfer)

- Selected examples

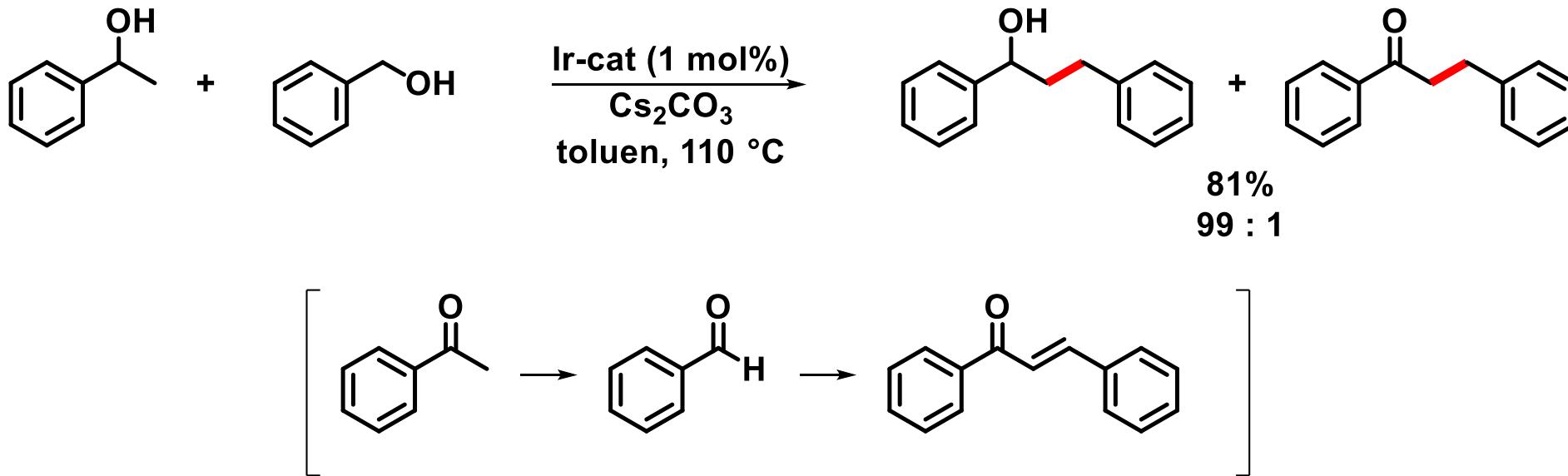


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Hydride Complexes in Organic Synthesis

- Borrowing hydrogen catalysis (hydrogen auto-transfer)

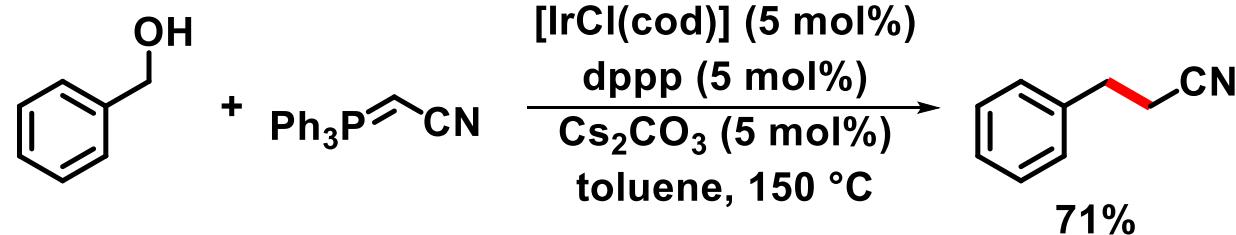
- Selected examples



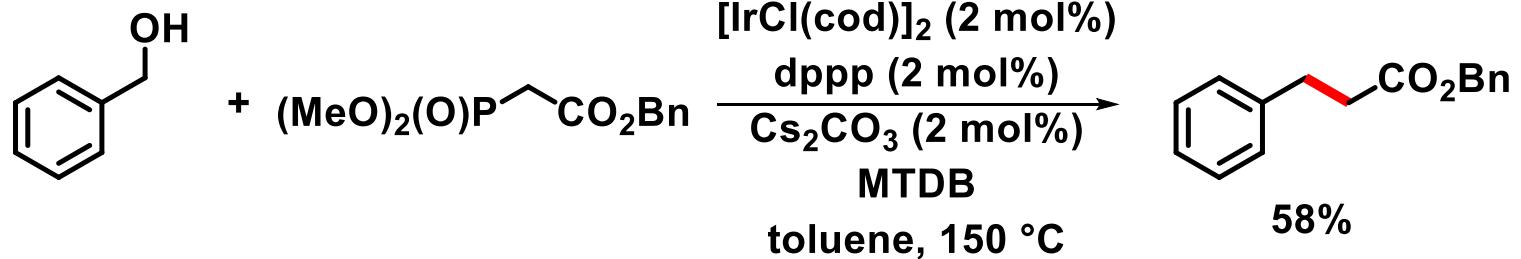
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Hydride Complexes in Organic Synthesis

- Borrowing hydrogen catalysis (hydrogen auto-transfer)
 - Selected examples



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