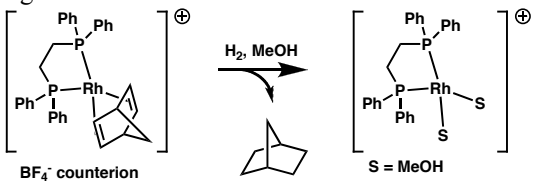
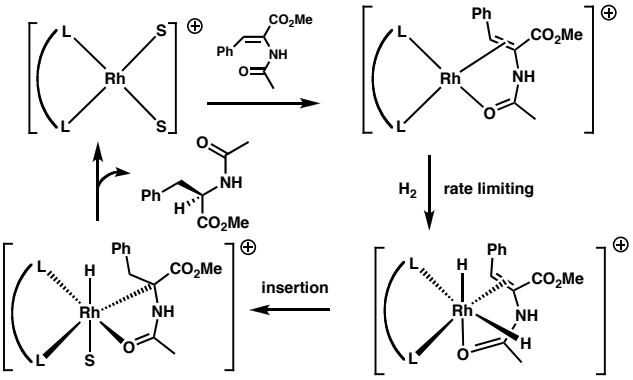
# *CHEM 6352*

## *Enantioselective Hydrogenations*

### *Mechanism [(Diphos)Rh(NBD)]⁺ Catalysts*

Hydrogenation of the Diene Generates the Active Catalyst

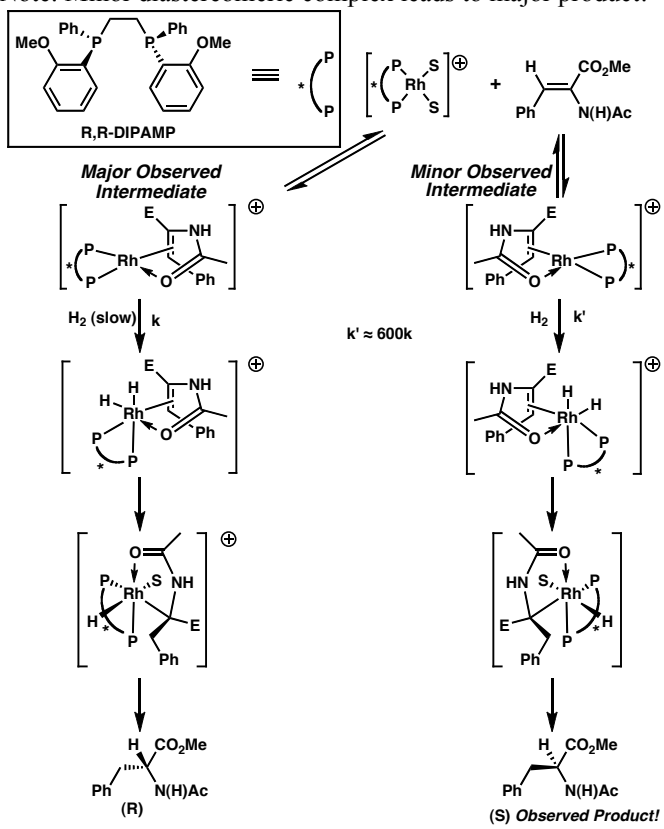



See Halpern *Science* **1982**, *217*, 401.

### *Asymmetric Hydrogenation*

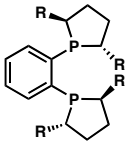
Note: Minor diastereomeric complex leads to major product!




Halpern *Science* **1982**, *217*, 401 and *Asymmetric Synthesis*, Vol. 5, Ch. 2, p 41 (especially p. 53)

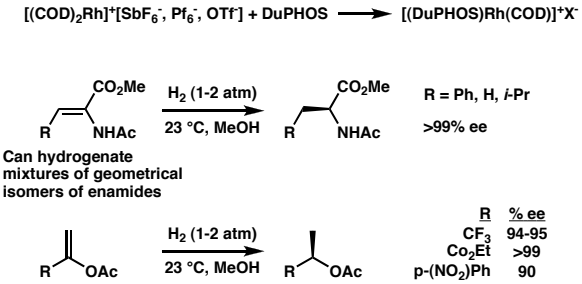
Halpern's law: If you can observe a structure, it is probably not catalytically relevant.

### DuPHOS



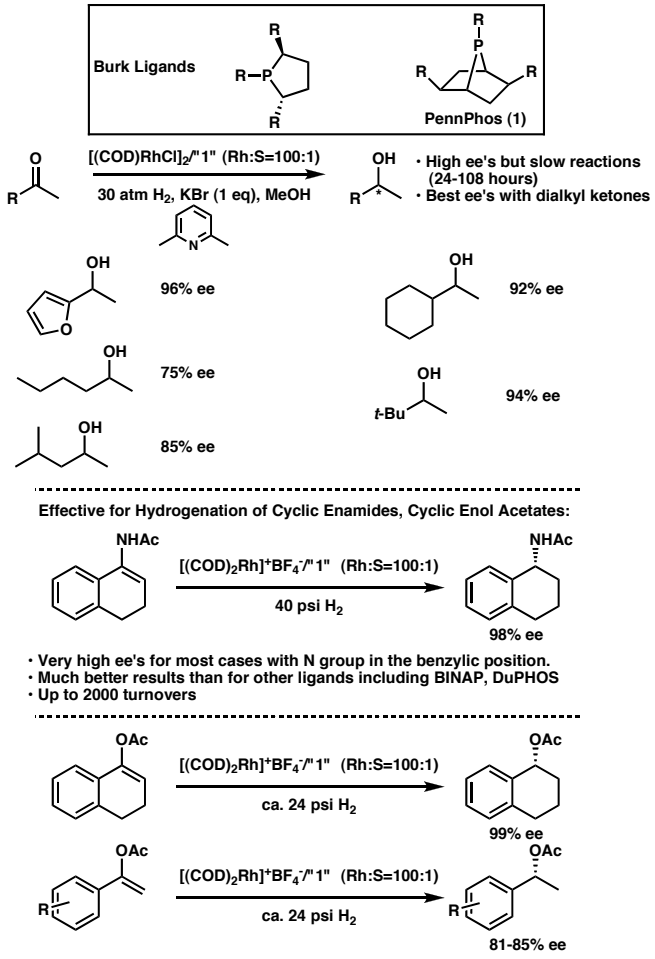
- Electron rich – 2 alkyl on each P atom
- Asymmetry rigidly held close to metal
- Can vary R groups
- Chelation in mechanism necessary
- Commercially available; expensive

**Preparation of Catalyst:**



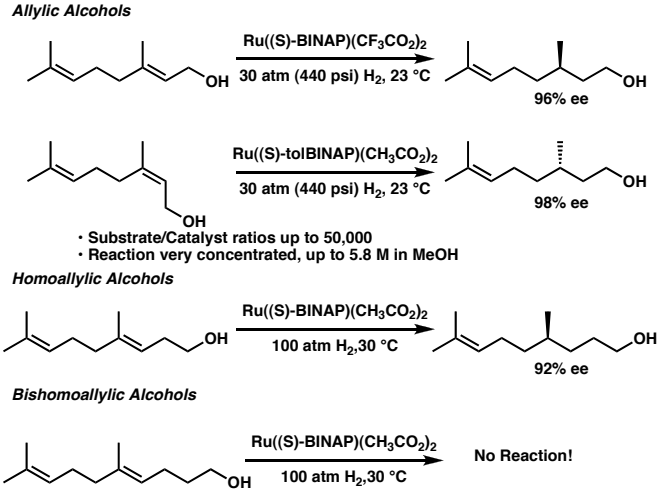

Burk *JACS* **1992**, *114*, 8518 and *JACS* **1993**, *115*, 10125

### Penn-Phos



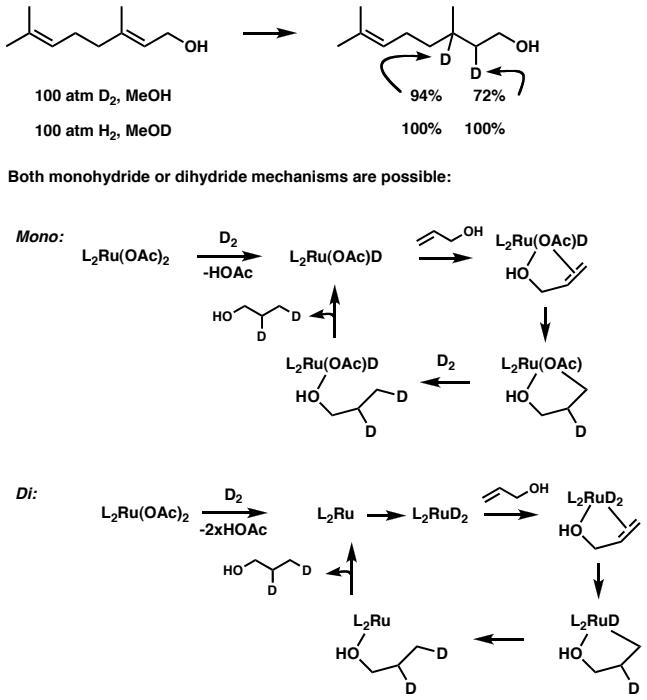

Zhang *ACIEE* **1998**, *37*, 1100; *ACIEE* **1999**, *38*, 516; *JOC* **1999**, *64*, 1774

## Ruthenium BINAP/Allylic Alcohols



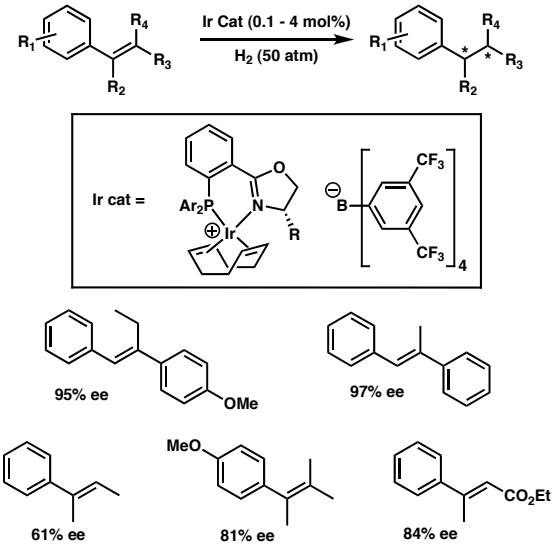

Noyori *JACS* **1987**, *109*, 1596

## Ru-BINAP Mechanism




Noyori *Asymmetric Catalysis in Organic Synthesis* Ch. 2

## Asymmetric Reduction of Highly Substituted Olefins




Pfaltz *ACIEE* **1998**, *37*, 2897

## Other References:

Burgess *JACS* **2001**, *123*, 8878

Burk *Modular Phospholane Ligands in Asymmetric Catalysis*, p. 363-372

*Acc. of Chem. Res.* **2000**, *33*, issue 6