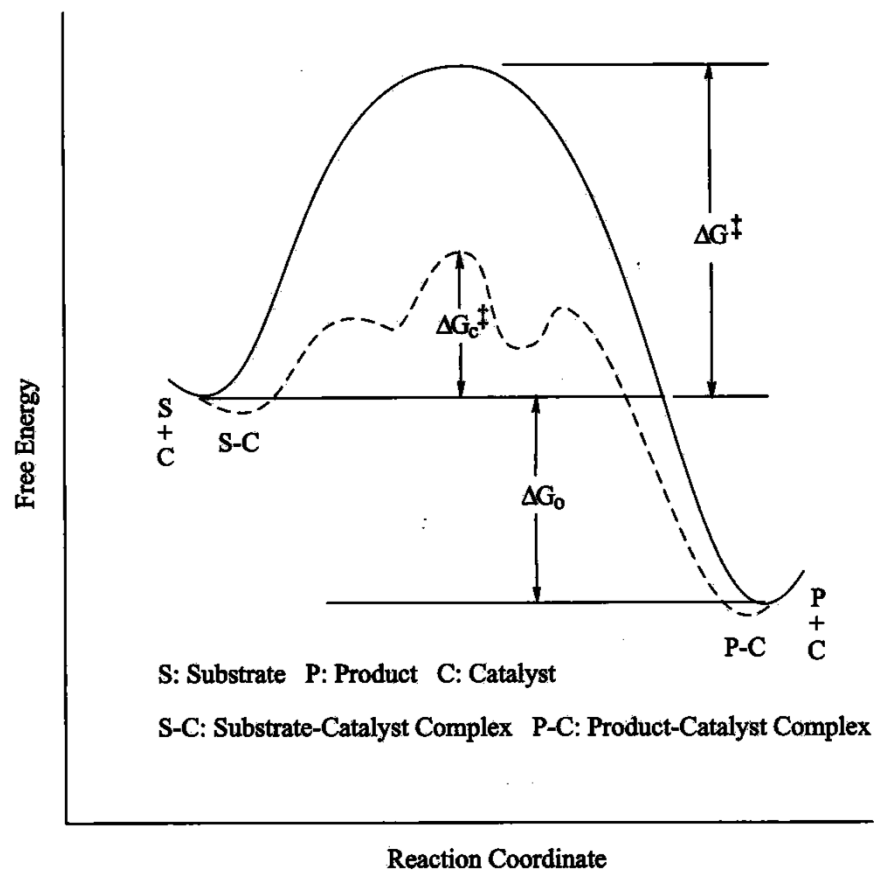


## H Organometallic Catalysis in Industry

**Figure 9-1**  
Reaction Coordinates  
for a Catalyzed and  
Uncatalyzed Chemical  
Reaction



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**Table 9-1 Major Differences between Homogeneous and Heterogeneous Catalysts**

---

<b>Characteristic</b>	<b>Homogeneous</b>	<b>Heterogeneous</b>
1. Catalyst composition and nature of active site	Discrete molecules with well-defined active site	Nondiscrete molecular entities; active site not well-defined
2. Determination of reaction mechanism	Relatively straightforward using standard techniques	Very difficult
3. Catalyst properties	Easily modified, often highly selective, poor thermal stability, mild reaction conditions	Difficult to modify, relatively unselective, thermally robust, vigorous reaction conditions
4. Ease of separation from product	Often difficult	Relatively easy

---

## Some terminology:

**Catalytic cycles:** a circular path meant to show **productive reactions**, in order, that lead from the catalytically active species and its reaction with a substrate through to product elimination and regeneration of the catalyst.

**Turnover number:** number of times a cycle is completed before the catalyst dies. Typically this is  $> 1000$ ; a stoichiometric reaction has a TON of 1.

**Turnover rate or frequency:** the **rate** at which a cycle is completed. This can be reported in many ways but it is usually in mol product per mol catalyst per time. Eg. a good ethylene polymerization catalyst might have a turnover rate of 5000 kg polyethylene per mol of catalyst per hour.

**Resting State:** this is the stable, and usually inactive, form of the catalyst when no substrate is provided or when it has been used up. Eg. with a coordinated solvent molecule occupying the active coordination site.

**Pre-catalyst:** the stable compound put into the reactor; it must be transformed **in situ** into the active species. Eg.  $\text{Cp}_2\text{ZrCl}_2$  in Z-N polymerizations where MAO is the **activator**.

## So why transition metals?

- ***wide range of bonding modes***
  - $\sigma$  and  $\pi$  bonds
  - many valence electrons
- ***wide choice of ligands***
  - ionic or neutral
- ***tunable properties***
  - choice of metal
  - electronic and steric effects of ancillary ligands
- ***variable coordination numbers***
  - 4 and 5 or 5 and 6 coordinate geometries accessible for same metal
- ***variable oxidation states***
  - ox. states separated by 2 units facilitate oxidative addition and reductive elimination reactions

**Tolman's rules:** (really only apply to middle and late T.M.)

- Diamagnetic organometallic complexes may exist in **significant concentration** only if the metal's valence shell contains 16 or 18 electrons. A significant concentration is one that can be detected spectroscopically or kinetically.
- Organometallic reactions, including catalytic ones, **proceed by elementary steps** involving only intermediates with 16 or 18 valence electrons.

As a corollary, there is an old saying in catalysis that says:

***'If you can isolate it, then it isn't the active catalyst'***

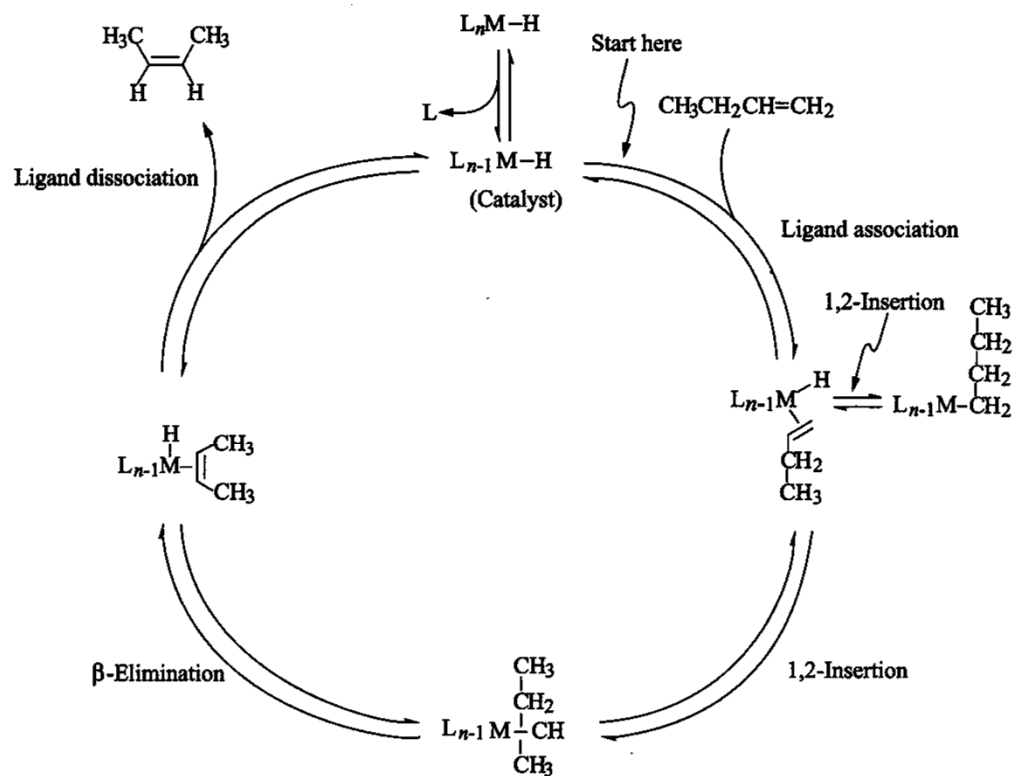
**This statement has been shown to be untrue in many catalytic systems in more recent work**

## Industrial Importance of Homogeneous Catalysis

<b>Reaction and Products</b>	<b>Ann. Production World (2015) 10<sup>3</sup> metric tons</b>
<b>Olefin additions</b>	
Adiponitrile (for nylon)	1,200
<b>Olefin polymerizations (all types)</b>	100,000+
<b>Carbonylations</b>	
Oxo alcohols (hydroformylation)	2,000
Acetic acid/anhydride (from MeOH)	2,500
<b>Olefin oxidation</b>	
Acetaldehyde	1,250+
Propylene oxide	7,500
<b>Alkane and arene oxidations</b>	
Terephthalic acid and esters	5,000+
Adipic acid (for nylon)	1,200+

## 1. Isomerization of Alkenes

- often unwanted side reaction but can be useful in some cases
- most metal hydride species will do this to some extent



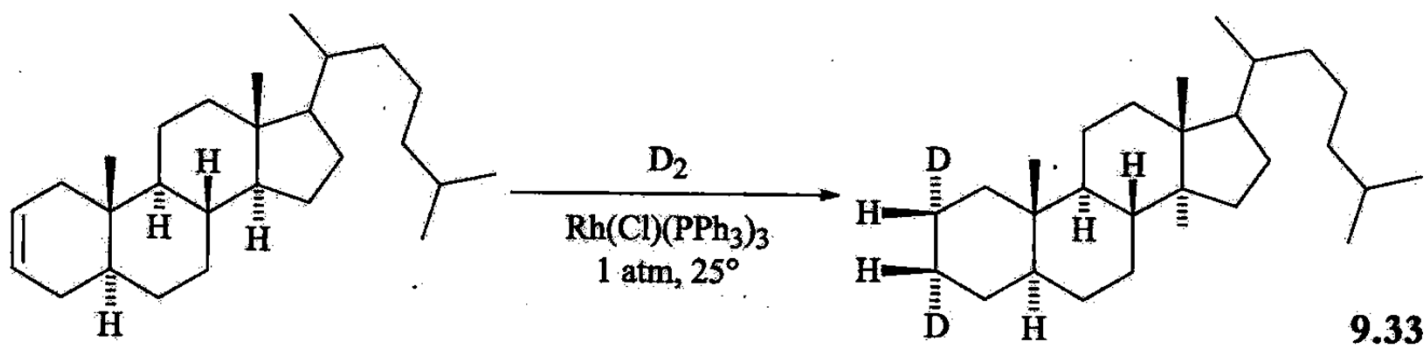
**Scheme 9-1**  
A Schematic Picture of a Catalytic Cycle  
Showing Double Bond Isomerization

## 2. Hydrogenation

**Most important for alkenes:** *usually* oxidative addition / reductive elimination sequences

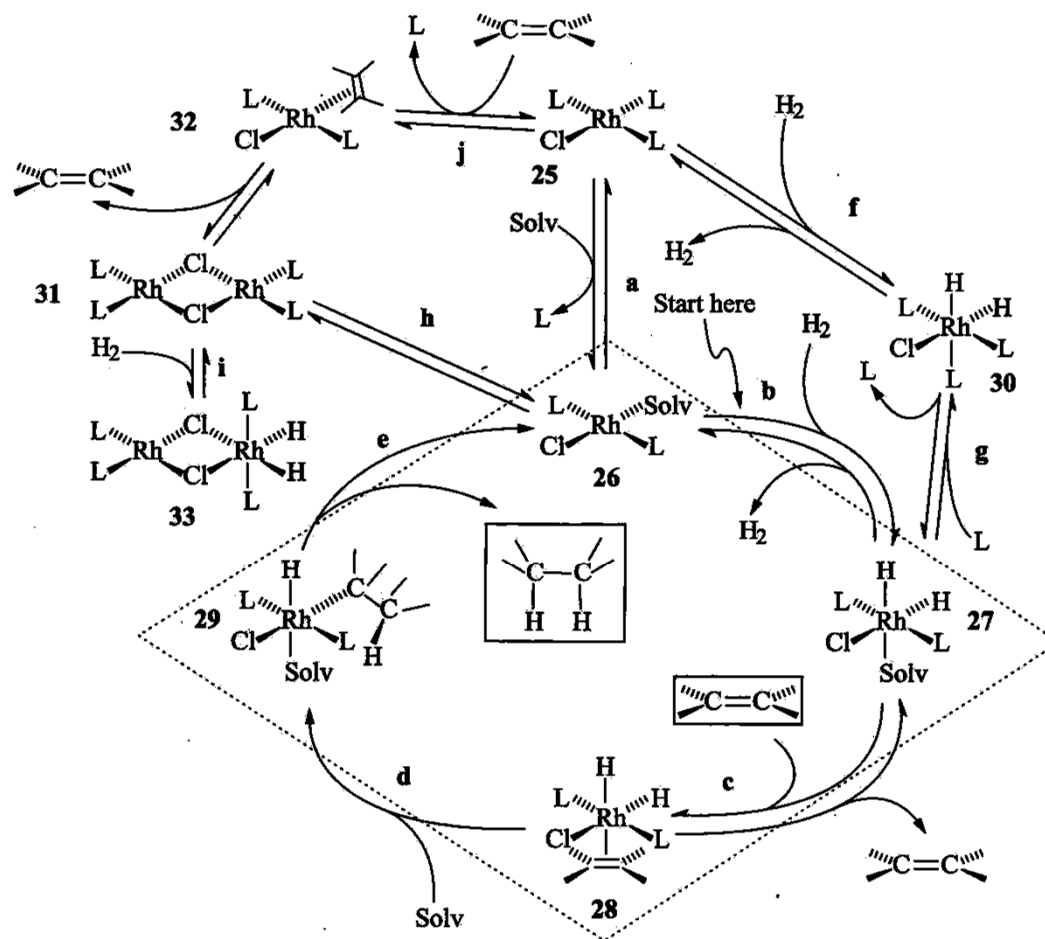
**Wilkinson's catalyst** is the original system and most famous but many are now known

- **selective for C=C** over C=O and CN
- does not scramble H and D
- **exclusively syn H<sub>2</sub> addition** (see e.g. below)
- commercially available





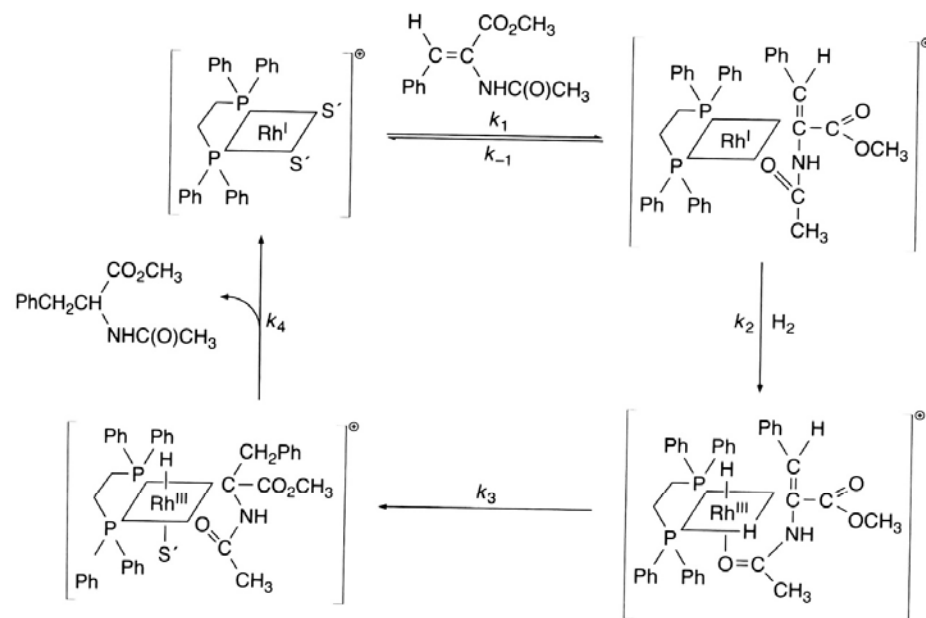
**Wilkinson's catalyst:**  
**Insertion is turnover limiting**



Key Steps: a, b, c, d, e  
 L = PPH<sub>3</sub>; Solv: EtOH, THF

**Scheme 9.7**  
 Mechanism of Hydrogenation  
 with Wilkinson's Catalyst

Many cationic hydride complexes are also used: one example is  $[\text{Rh}(\text{dppe})(\text{L})_2]^+$



Oxidative-addition is turnover limiting



Unsaturated substrate	$K_{\text{eq}}(\text{M}^{-1})$
Benzene	18
Toluene	97
<i>o</i> -, <i>m</i> -, or <i>p</i> -Xylene	500
1-Hexene	2
Styrene	20
Methyl acrylate	3

## Asymmetric hydrogenation:

Chiral chelating ligands result in preferential delivery of H<sub>2</sub> to one **enantiotopic** face of the alkene

Chiral chelating phosphines are among the most popular

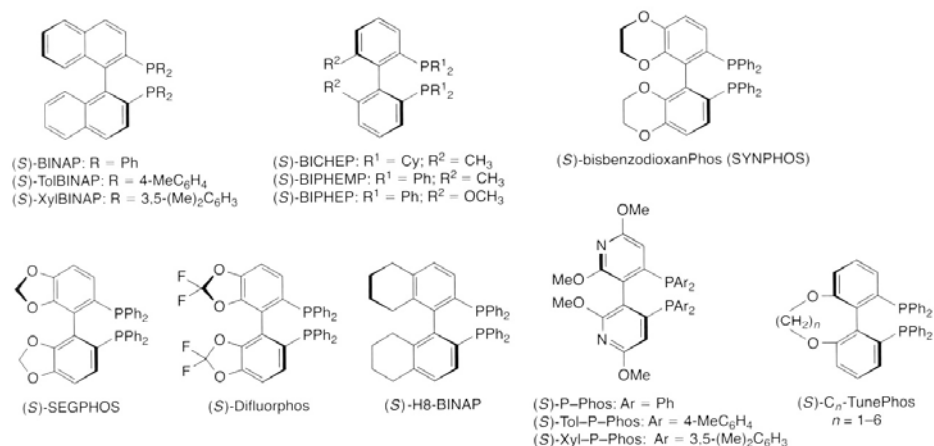
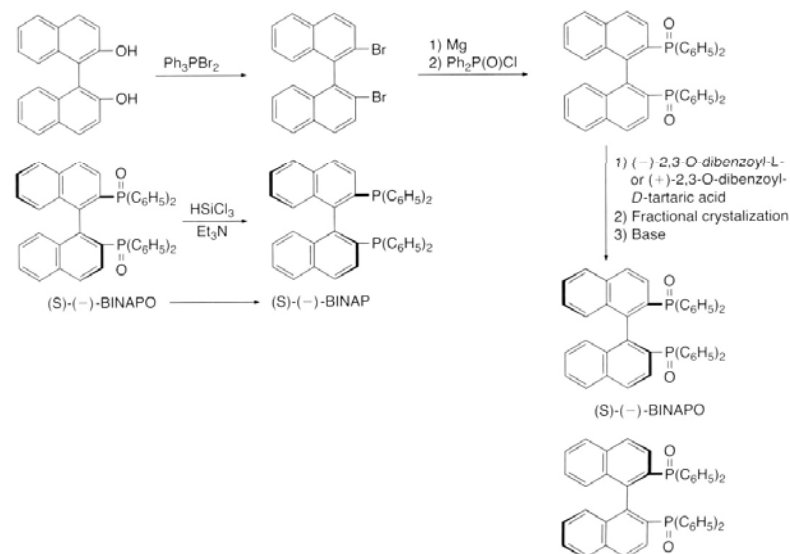
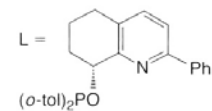
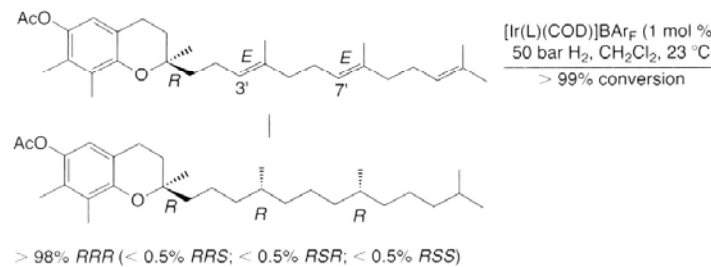
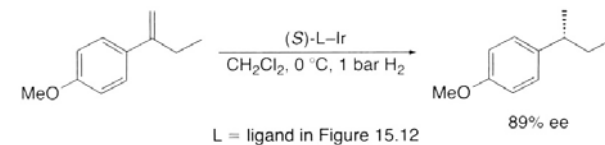
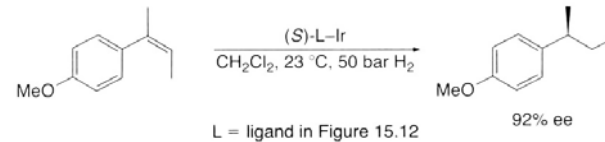
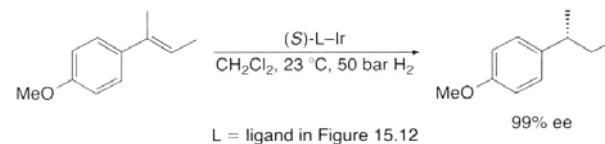
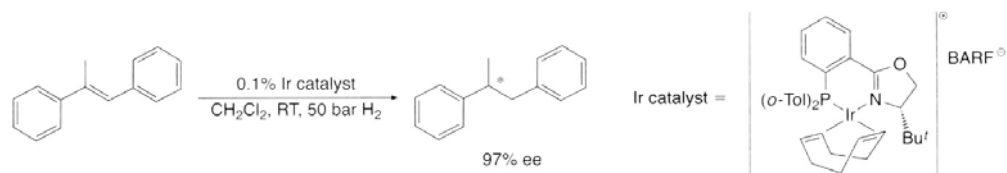
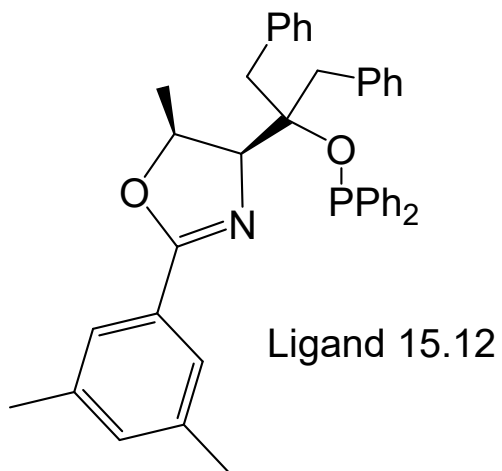


Figure 15.2.  
A selection of axial chiral bisphosphine ligands. The original BINAP ligand is shown at the top left of the figure.

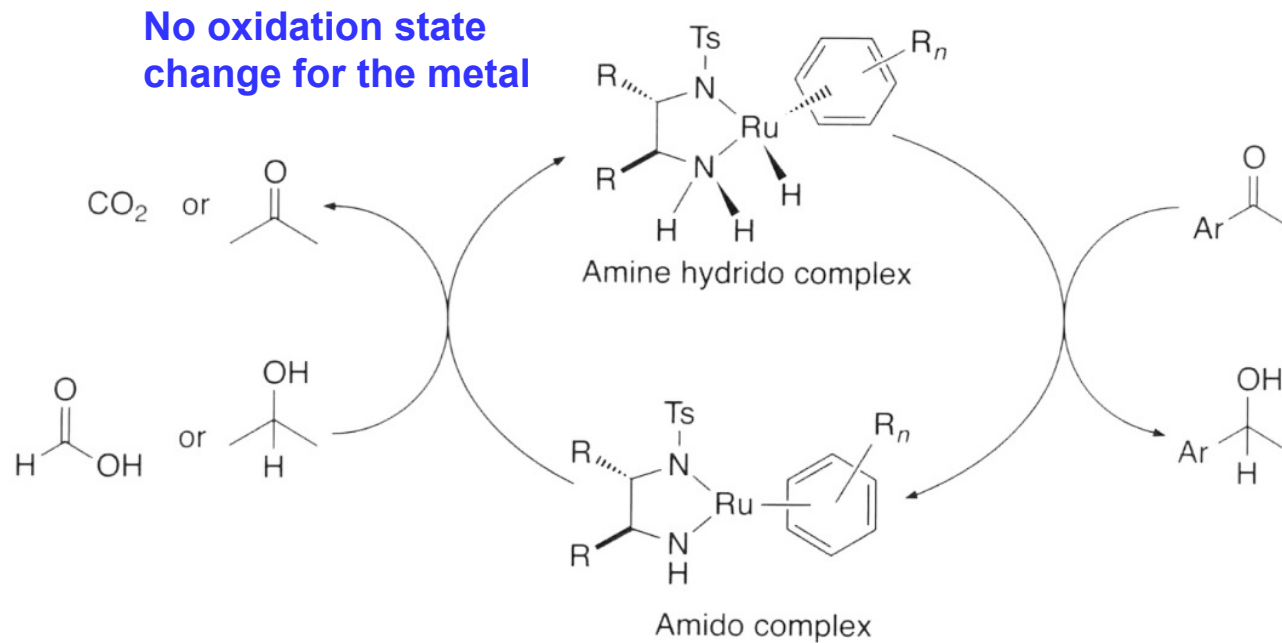


Some examples of asymmetric hydrogenation of alkenes using a related Ir catalyst:

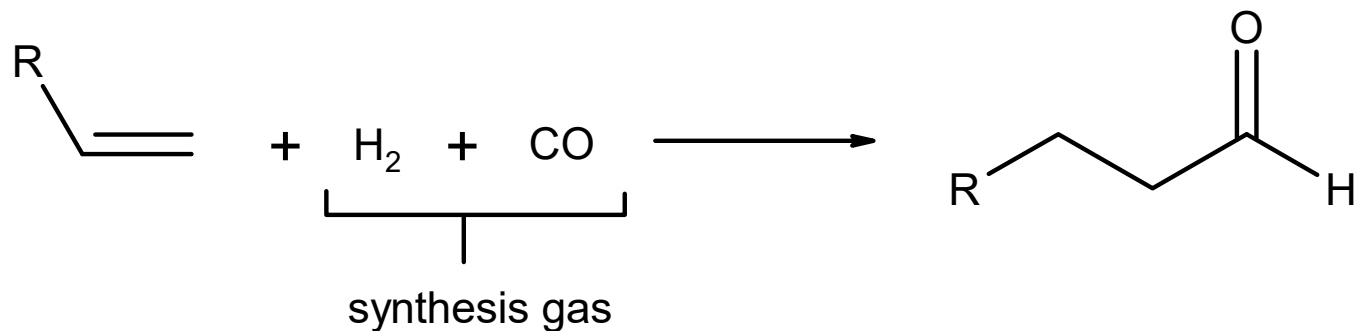


## Asymmetric transfer hydrogenation of ketones: asymmetric Meerwein-Ponndorf-Verley reduction

Reaction occurs with Lewis acids too: alumina, lanthanide and group 4 metal complexes

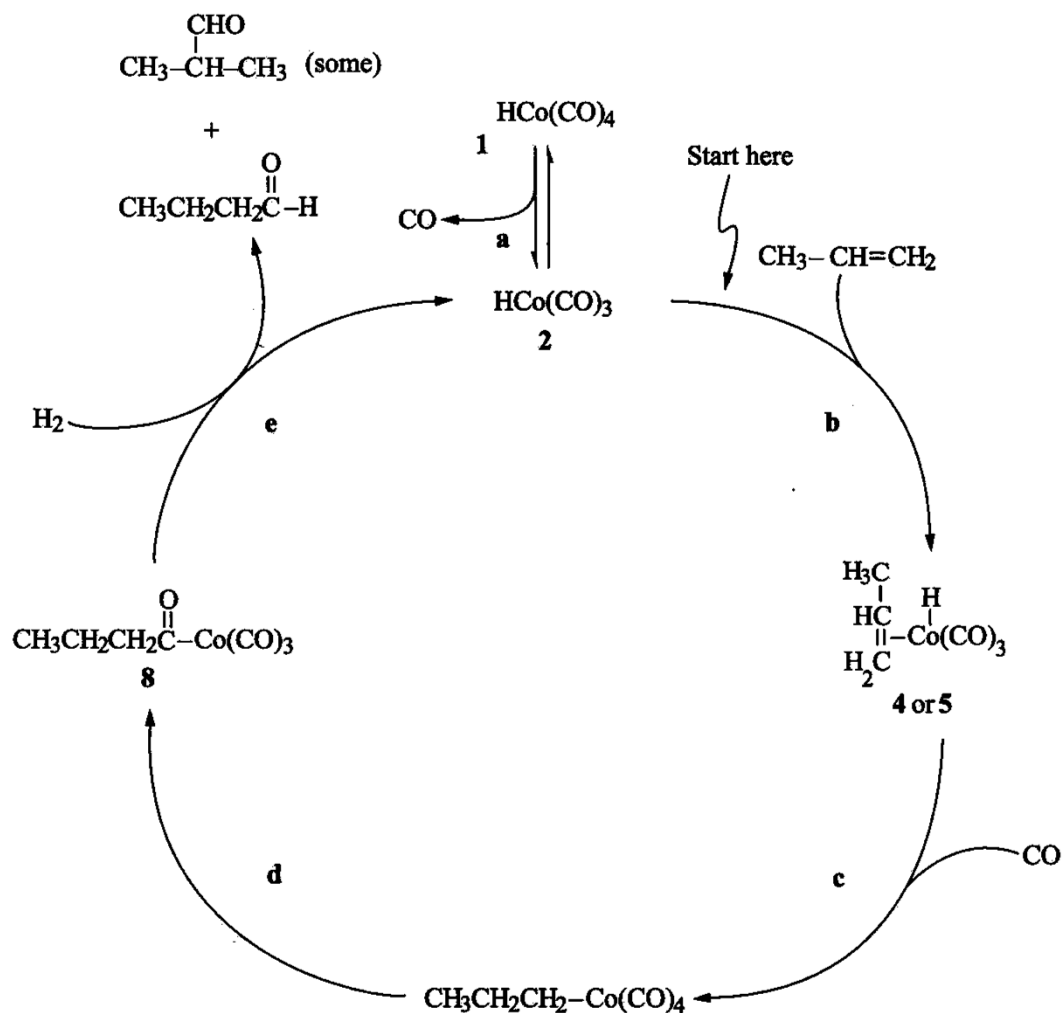


### 3. Hydroformylation (Oxo process)



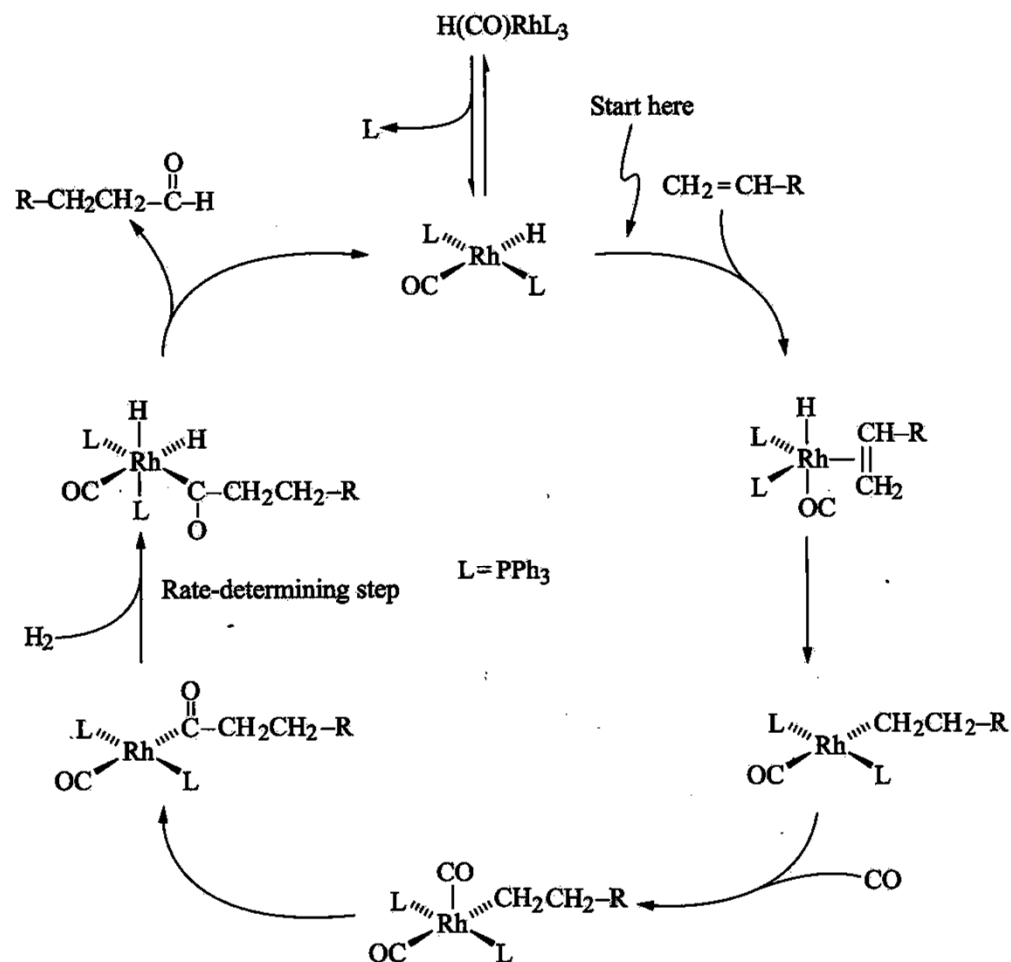
- Formally addition of formaldehyde across a double bond
- Discovered by BASF by Otto Roelen using Co catalysts
- **Worldwide scale: about 7 BILLION kgs per year**

- $\text{HCo}(\text{CO})_4$  catalyst:  
conditions 110-180 °C / 200-300 atm
- **linear/branched** ratio is about **3:1**
- internal alkenes isomerize to terminal so only  $\alpha$  or  $\beta$  aldehydes formed
- **problem:** catalyst loss due to volatility of  $\text{HCo}(\text{CO})_4$  and  $\text{Co}_2(\text{CO})_8$



**Scheme 9.3**  
Heck-Breslow Mechanism  
for Hydroformylation

- $\text{HRh}(\text{CO})(\text{PPh}_3)_2$  allows lower T (100 °C) and P (6 atm)
- **linear to branched** ratio: > 10:1
- **hydrogenation is much slower** under the conditions used and does not compete as a side reaction.

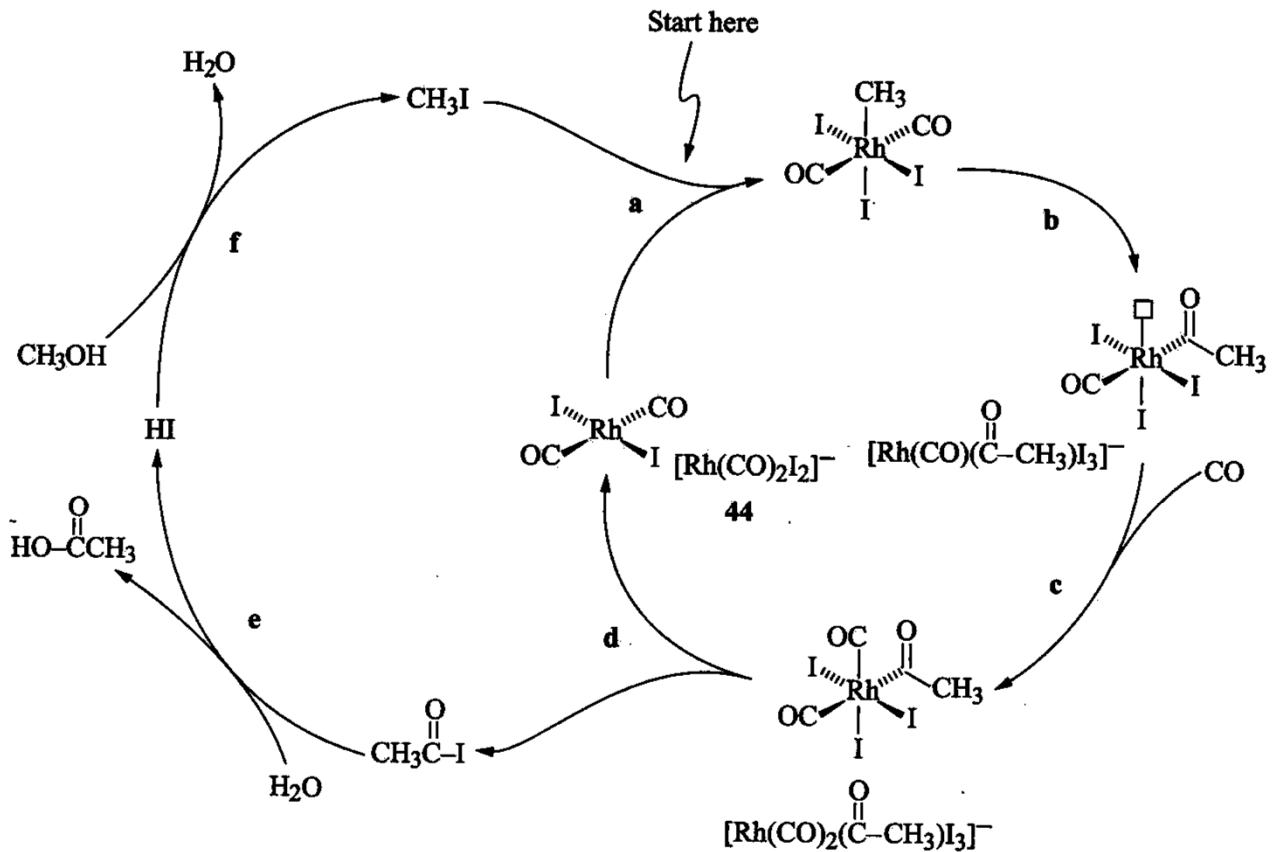


**Scheme 9.4**  
Phosphine-Rhodium-Catalyzed Hydroformylation



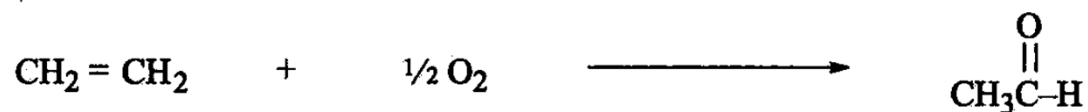
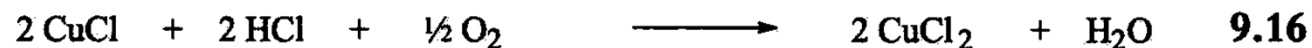
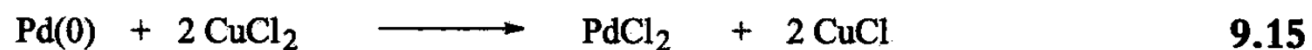
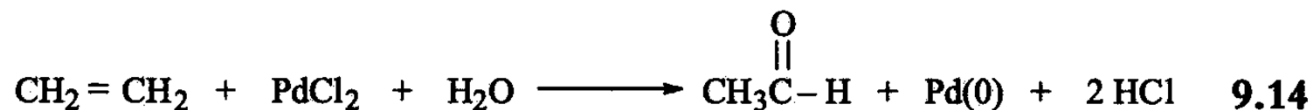
#### 4. Monsanto Acetic Acid Process (carbonylation of MeOH)

- acetic acid for industrial uses: vinyl acetate, cellulose acetate, pharmaceuticals, dyes and pesticides.
- Monsanto process dominates the market but older methods such as the **oxidation of ethylene via acetaldehyde** are still practiced.
- conditions:** 180 °C / 30-40 atm /  $10^{-3}$  M catalyst

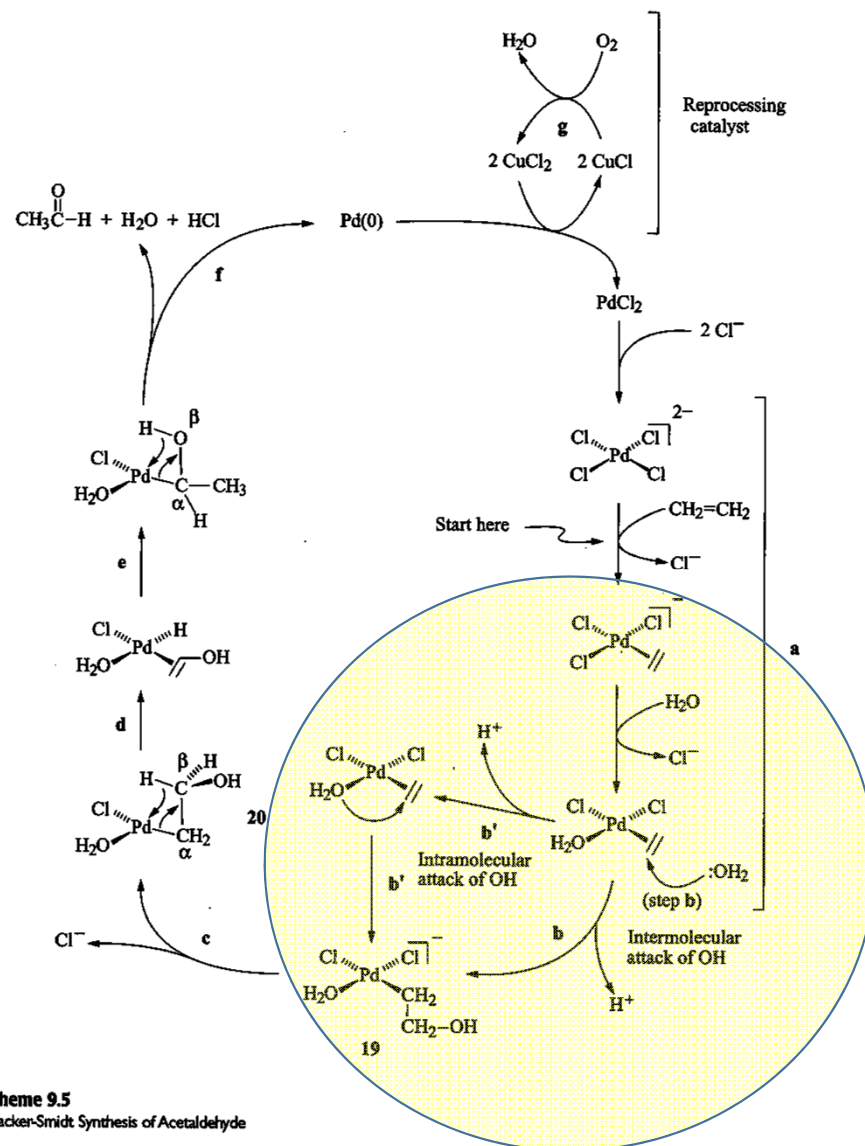


**Scheme 9.8**  
Mechanism of Rh-Catalyzed  
Carbonylation of Methanol

## 5. Alkene Oxidations: the **Wacker** process



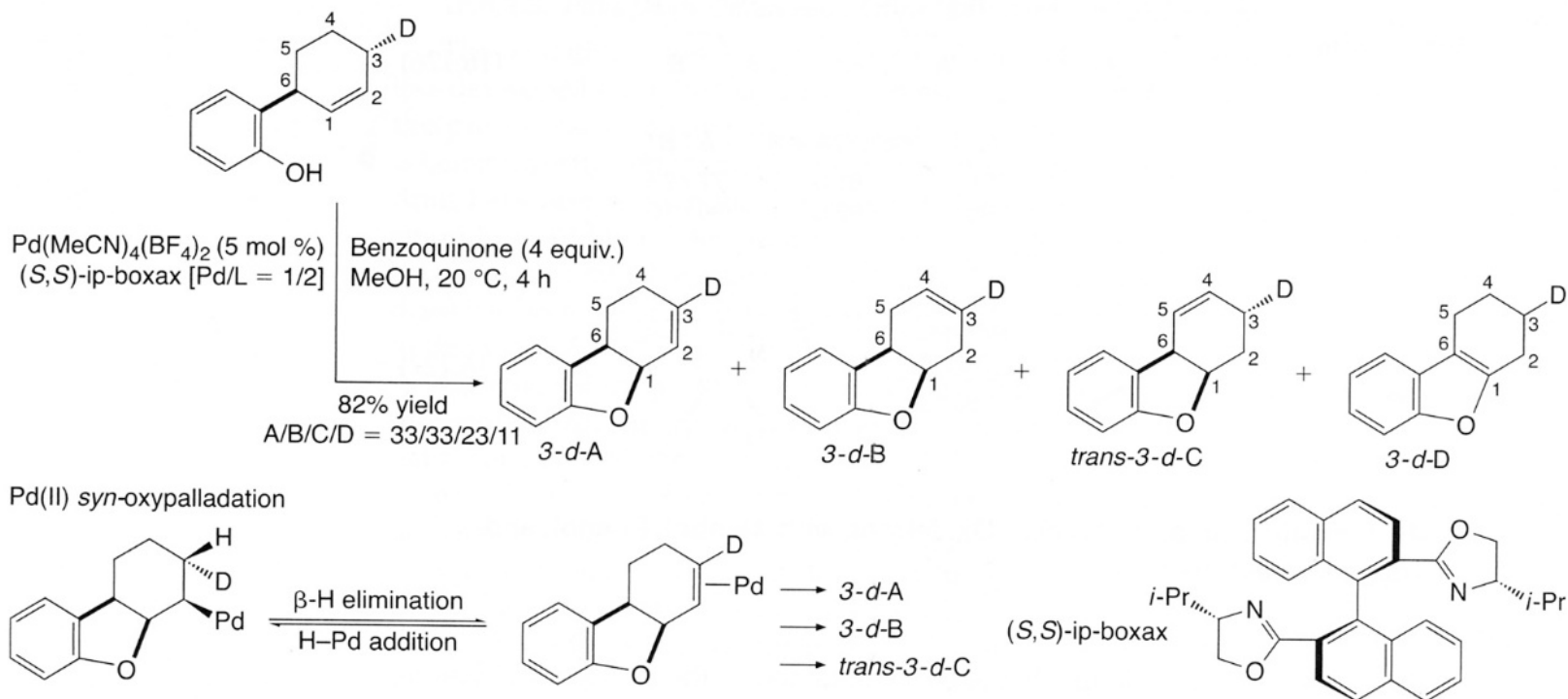
- used to prepare acetaldehyde for conversion to acetic acid
- replaced dangerous hydration of acetylene in 1950's
- now largely superceded by Monsanto process
- ultimate oxygen source is air although the reaction chemistry occurs solely at Pd



Some debate over whether inter- or intramolecular attack occurs

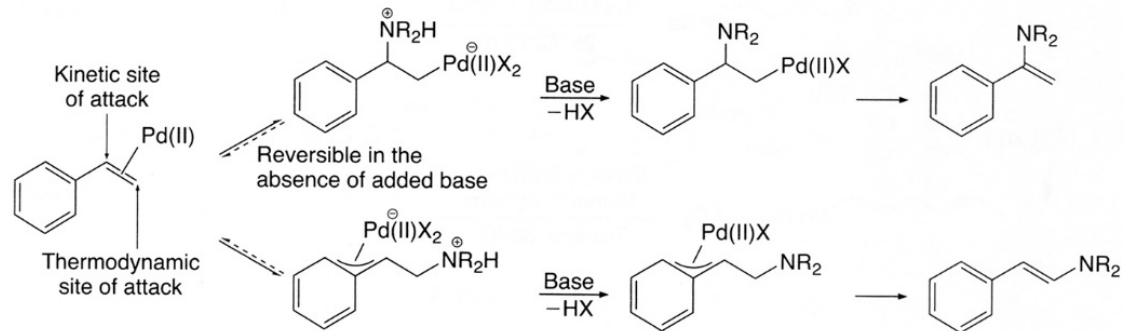
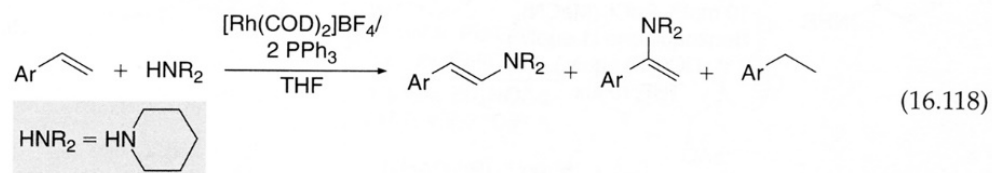
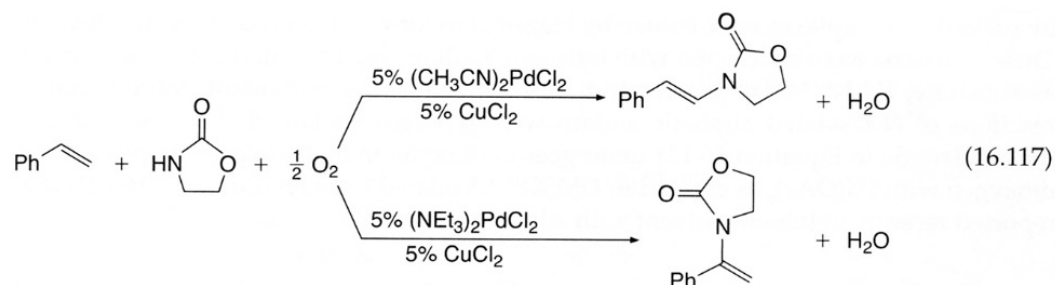
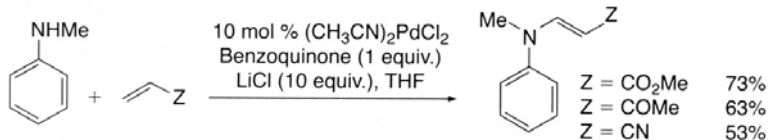
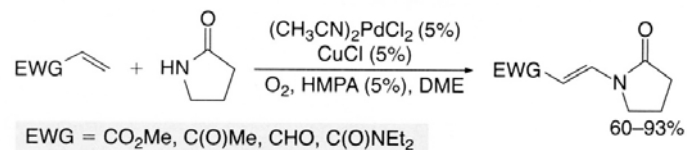
**Scheme 9.5**  
Wacker-Smidt: Synthesis of Acetaldehyde

## Evidence for intramolecular attack from labelling studies:



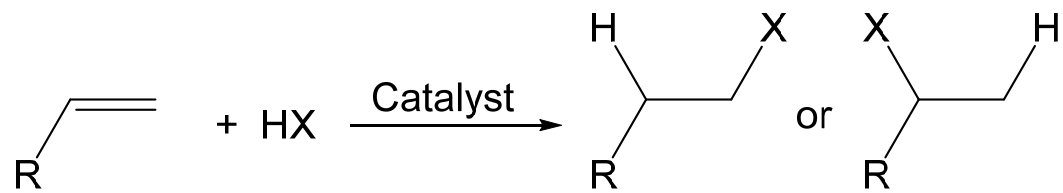
Scheme 16.32

## Oxidative Amination: closely related to Wacker Chemistry



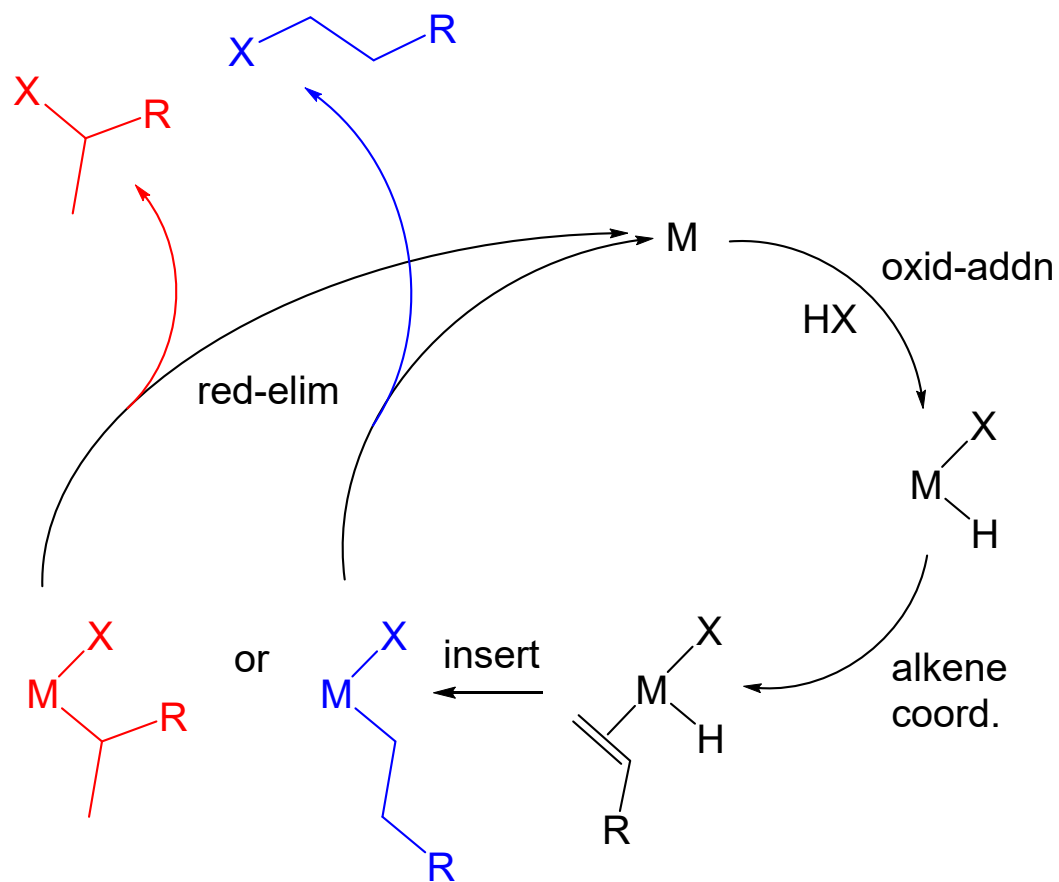
Scheme 16.31

## 6. Hydrofunctionalization of Alkenes



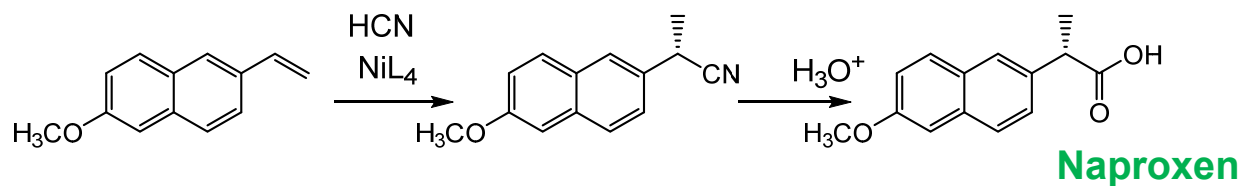
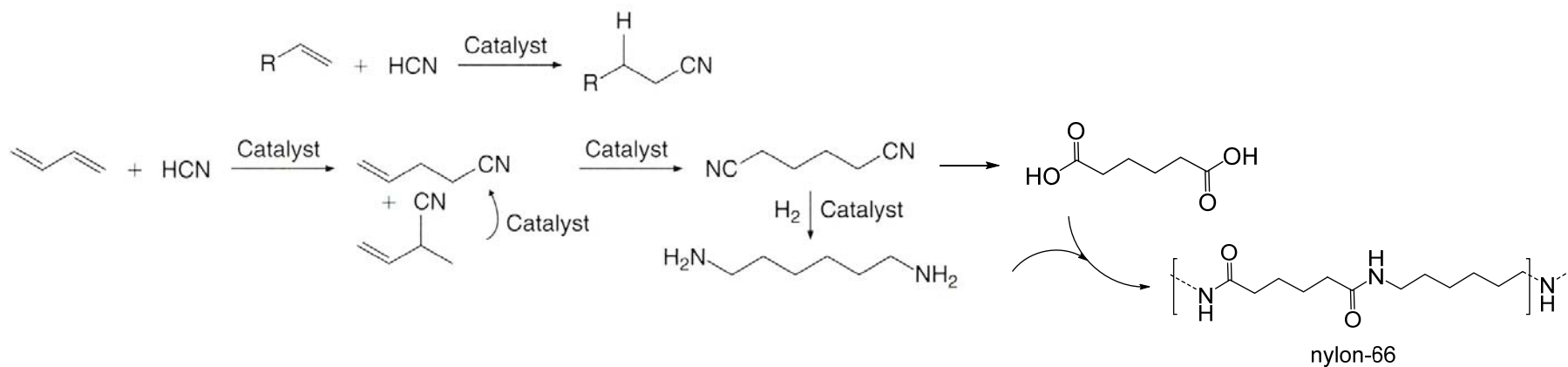
- **Hydroamination** H-NR<sub>2</sub> (covered earlier)
- **Hydrozirconation** H-ZrX<sub>3</sub> (covered earlier)
- **Hydrocyanation** H-CN
- **Hydrosilylation** H-SiX<sub>3</sub>
- **Hydroboration** H-B(OR)<sub>2</sub>

General mechanism is pretty much the same for all later transition metals:



## Hydrocyanation

- By far the most common catalysts are  $\text{Ni}^0$  complexes like  $\text{NiL}_4$  or chiral variants,  $\text{Ni}(\text{L}_2^*)_2$
- Used industrially to produce **adiponitrile for nylon synthesis** and one route to **Naproxen** (tradename: Alleve)



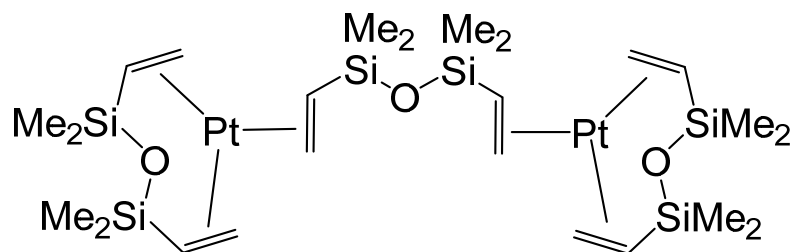


## Hydrosilylation

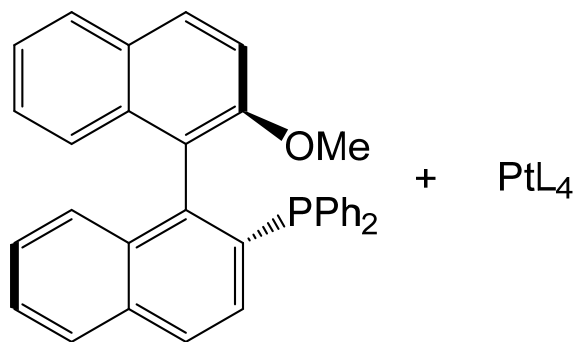
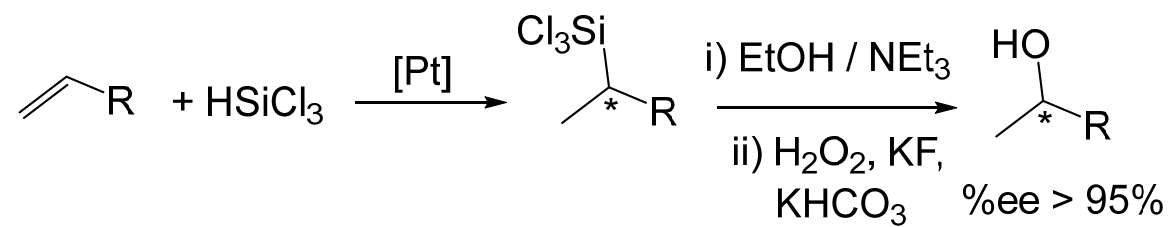
- Usual catalysts are  $\text{Pt}^0$  complexes like **Speier's** and **Karstedt's** catalysts (below)
- Catalyst loadings are incredibly low (highly active catalysts):  $10^{-5}$  mol% common
- Still controversy over whether it is actually **colloidal Pt** that is the catalyst (induction period?)
- **Industrial uses:** **polysiloxanes** for caulking, gaskets, coatings, etc.

**Speier's catalyst:**  $\text{H}_2\text{PtCl}_6$

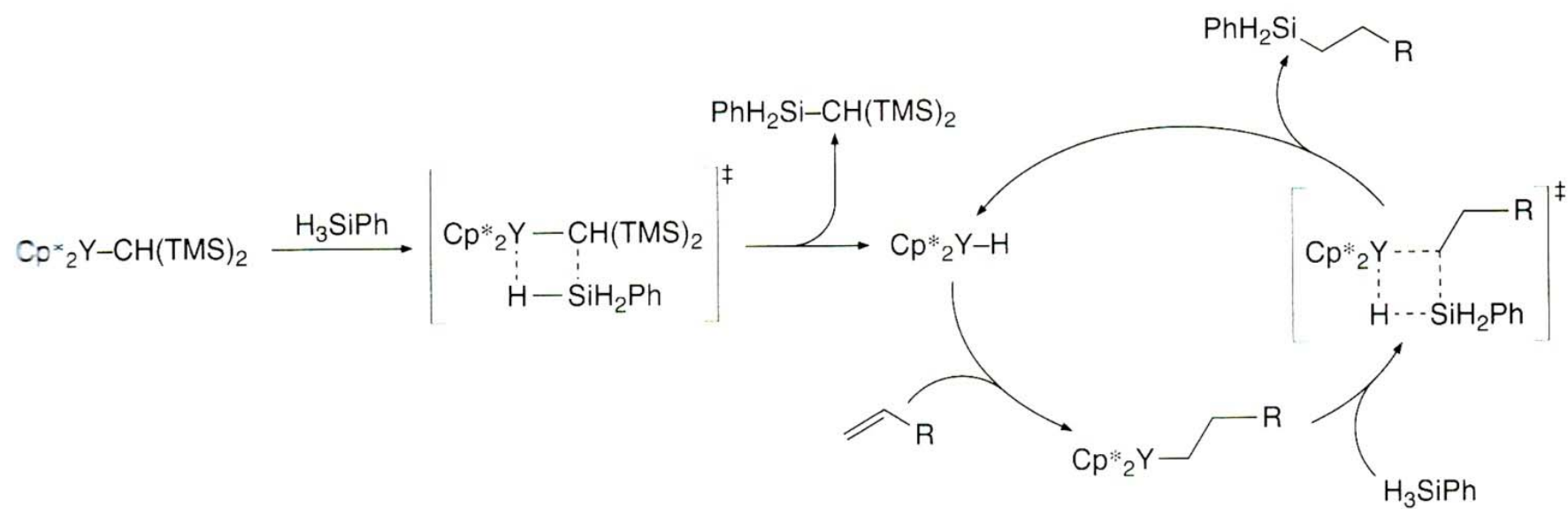
**Karstedt's catalyst:** widely used  $\text{Pt}^0$  but still induction period



## Asymmetric variants used in organic synthesis



$\sigma$ -bond metathesis alternative: no oxidative-addn / red. elim



## Hydroboration

- Late transition metal catalysts (Rh, Ir, Pd, Pt, Ni) by **oxid. add. / red. elim.** **AND** early transition metals and lanthanides by  **$\sigma$ -bond metathesis**
- Mostly used in organic synthesis for regio- and stereoselective alcohol formation

