Step 5: Reductive Elimination

```
RhCl(H)(CH₂CH₂R)(PPh₃)₂ → RhCl(PPh₃)₂(S) + CH₃CH₂R
```

Complete Cycle:

```
Catalyst → H₂ addition → Olefin coordination → Insertion → Elimination → Catalyst
```

Selectivity Features

1. **Chemoselectivity:**
    - Reduces alkenes > alkynes > carbonyls
    - Terminal alkenes faster than internal
2. **Stereoselectivity:**
    - Syn addition of H_2
    - Less stereoselective than heterogeneous
3. **Functional Group Tolerance:**
    - Does not reduce: $-NO_2$, -CN, -COOR, -C=O
    - Sensitive to sulfur, phosphorus compounds

Modified Catalysts

1. **Crabtree's Catalyst:** $[Ir(COD)(PCy_3)(py)]PF_6$
    - More active for hindered alkenes
2. **Noyori's Catalyst:** Ru-BINAP complexes
    - Asymmetric hydrogenation (Nobel 2001)

4. Ziegler-natta polymerization of olefins

Historical Background

- **1953:** Karl Ziegler (Germany) - Polymerization of ethylene at low pressure
- **1954:** Giulio Natta (Italy) - Stereospecific polymerization of propylene
- **1963:** Nobel Prize in Chemistry

Catalyst Systems

First Generation (Ziegler-Natta)

$TiCl_4 + Al(C_2H_5)_3$ (Al/Ti ≈ 1-3)

- **Active Species:** Ti(III) with vacant sites
- **Product:** Isotactic polypropylene (50-60%)

Modern Supported Catalysts

- $TiCl_4$ on $MgCl_2$ support
- Lewis base modifiers (esters)
- Higher activity and stereospecificity

- ## Mechanism of Polymerization
- **Cossee-Arlman Mechanism**
- **Step 1: Catalyst Activation**
- $TiCl_4 + AlR_3 \rightarrow TiCl_3R + AlR_2Cl$
- Reduction: Ti(IV) → Ti(III)

Step 2: Olefin Coordination

- π-complex formation at vacant site

Step 3: Migratory Insertion

$Ti\text{-}R + CH_2{=}CHR' \rightarrow Ti\text{-}CH_2CHR'\text{-}R$

- Chain propagation

Step 4: Chain Transfer

1. **β-H elimination:**

$Ti\text{-}CH_2CH_2\text{-}P \rightarrow Ti\text{-}H + CH_2{=}CH\text{-}P$

With AlR_3:

$Ti\text{-}P + AlR_3 \rightarrow Ti\text{-}R + AlR_2\text{-}P$

Stereochemical Control

- **Isotactic:** All chiral centers same configuration
- **Syndiotactic:** Alternating configuration
- **Atactic:** Random configuration

Factors Affecting Stereoselectivity:

1. **Catalyst Structure:** Chiral environment
2. **Monomer Structure:** Steric bulk
3. **Temperature:** Lower temperatures favor isotactic

4. Types of Ziegler-Natta Catalysts

Type	Components	Applications
Heterogeneous	$TiCl_4/MgCl_2 + AlR_3$	Polyethylene, polypropylene
Homogeneous	Cp_2ZrCl_2 + MAO	Polyethylene, elastomers
Metallocene	Bridged metallocenes + MAO	Stereoregular polymers

Industrial Applications

1. **High-Density Polyethylene (HDPE):**
   - Linear chains, high crystallinity
   - Ziegler-Natta catalyst
2. **Polypropylene:**
   - Isotactic (molding), syndiotactic (films)
   - Worldwide production: ~70 million tons/year
3. **Ethylene-Propylene Rubber (EPR):**
   - Copolymerization with dienes

5. Catalytic reactions involving CO

A. HYDROFORMYLATION (OXO REACTION)

Introduction

- **Discovery:** Otto Roelen (1938, Ruhrchemie)
- **Reaction:**
- $R\text{-}CH{=}CH_2 + CO + H_2 \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}CHO$ (linear) + $R\text{-}CH(CH_3)\text{-}CHO$ (branched)
- **Products:** Aldehydes → Alcohols (by hydrogenation)

Catalyst Systems

1. Cobalt Carbonyl Catalysts:

$Co_2(CO)_8 + H_2 \rightarrow HCo(CO)_4$

- **Conditions:** 100-200°C, 200-300 atm
- **n/iso ratio:** 3:1 to 4:1

2. Rhodium Catalysts:

$HRh(CO)(PPh_3)_3$

- **Conditions:** 80-120°C, 10-30 atm
- **Higher n/iso ratio:** 10:1 to 20:1
- **Higher activity:** 10^3 times Co catalyst

Mechanism (Rh-catalyzed)

Step 1: Catalyst Activation

$HRh(CO)(PPh_3)_3 \rightleftharpoons HRh(CO)(PPh_3)_2 + PPh_3$

Step 2: Olefin Coordination

$HRh(CO)(PPh_3)_2 + CH_2{=}CHR \rightarrow HRh(CO)(CH_2{=}CHR)(PPh_3)_2$

Step 3: Migratory Insertion

$HRh(CO)(CH_2{=}CHR)(PPh_3)_2 \rightarrow Rh(CO)(CH_2CH_2R)(PPh_3)_2$

Regioselectivity determined here: Markovnikov vs anti-Markovnikov

Step 4: CO Coordination and Insertion

$Rh(CO)(CH_2CH_2R)(PPh_3)_2 + CO \rightarrow Rh(CO)_2(CH_2CH_2R)(PPh_3)_2$
$\rightarrow Rh(C(O)CH_2CH_2R)(CO)(PPh_3)_2$

Step 5: Oxidative Addition of H_2

$Rh(C(O)CH_2CH_2R)(CO)(PPh_3)_2 + H_2 \rightarrow Rh(H)_2(C(O)CH_2CH_2R)(CO)(PPh_3)_2$

Step 6: Reductive Elimination

$HRh(CO)(PPh_3)_2 + R\text{-}CH_2CH_2CHO$

Factors Affecting Selectivity

1. **Ligand Effects:**
   - **Bulky phosphines:** Higher n/iso ratio
   - **Electronic effects:** Electron-donating ligands favor linear product
2. **Pressure Effects:**
   - Higher CO pressure favors branched product
3. **Temperature Effects:**
   - Lower temperatures favor linear product

Industrial Applications

1. **Butyraldehyde:** From propylene → n-butanol, 2-ethylhexanol
2. **Plasticizers:** Phthalates from C_7-C_{10} alcohols
3. **Detergents:** C_{12}-C_{15} alcohols

- **Global capacity:** ~10 million tons/year

- **B. HYDROCARBONYLATION OF OLEFINS**
- **Related to hydroformylation but with different nucleophiles**
- **Monsanto Acetic Acid Process:**

$$CH_3OH + CO \rightarrow CH_3COOH$$

- **Catalyst:** Rh/Ir with iodide promoter
  Mechanism: Similar to hydroformylation but with methanol

6. OXOPALLADATION REACTIONS

Wacker Process (Ethylene → Acetaldehyde)

Discovery: 1957 by J. Smidt (Wacker-Chemie)

Reaction

$$CH_2{=}CH_2 + \tfrac{1}{2}\,O_2 \rightarrow CH_3CHO$$

Catalyst: $PdCl_2/CuCl_2$ in aqueous HCl

Mechanism

Step 1: Ethylene Coordination

$$PdCl_4^{2-} + CH_2{=}CH_2 \rightarrow [PdCl_3(C_2H_4)]^- + Cl^-$$