Step 2: Nucleophilic Attack by Water

$$[PdCl_3(C_2H_4)]^- + H_2O \rightarrow [PdCl_2(CH_2CH_2OH)]^- + H^+ + Cl^-$$

Step 3: β-H Elimination

$$[PdCl_2(CH_2CH_2OH)]^- \rightarrow Pd(0) + CH_3CHO + 2Cl^- + H^+$$

Step 4: Catalyst Reoxidation

$$Pd(0) + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$
$$4CuCl + O_2 + 4HCl \rightarrow 4CuCl_2 + 2H_2O$$

Overall:

$$C_2H_4 + \tfrac{1}{2} O_2 \rightarrow CH_3CHO$$

Selectivity Features

- **Chemoselective:** Terminal alkenes only
- **No overoxidation** to acetic acid under conditions
- **Byproducts:** Chlorinated compounds (suppressed by $CuCl_2$)

Other Oxopalladation Reactions

1. Allylic Oxidation:

$$R\text{-}CH_2\text{-}CH{=}CH_2 + O_2 \rightarrow R\text{-}CH{=}CH\text{-}CHO$$

Catalyst: Pd(II) with benzoquinone

2. Intramolecular Oxopalladation:

- For heterocycle synthesis
- Example: Indole synthesis

7. Activation of C-H bonds

Introduction

- **Challenge:** C-H bonds are strong (400 kJ/mol) and relatively unreactive
- **Importance:** Direct functionalization without pre-activation

Mechanisms of C-H Activation

A. Oxidative Addition

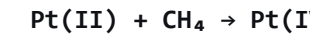
$$L_nM + R\text{-}H \rightarrow L_nM(H)(R)$$

Requirements:

1. Electron-rich metal center
2. Vacant coordination site
3. Appropriate orbital overlap

Examples:

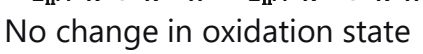
1. **Methane activation by Pt complexes:**



$$Pt(II) + CH_4 \rightarrow Pt(IV)(H)(CH_3)$$

B. σ-Bond Metathesis

For early transition metals and lanthanides

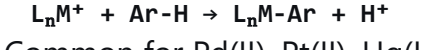


$$L_nM\text{-}R + R'\text{-}H \rightarrow L_nM\text{-}R' + R\text{-}H$$

- No change in oxidation state
- 4-center transition state

C. Electrophilic Activation

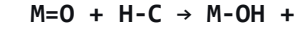
For electron-rich arenes and alkenes



$$L_nM^+ + Ar\text{-}H \rightarrow L_nM\text{-}Ar + H^+$$

- Common for Pd(II), Pt(II), Hg(II)

D. 1,2-Addition (to M=X bonds)



$$M{=}O + H\text{-}C \rightarrow M\text{-}OH + M\text{-}C$$

Examples of Catalytic C-H Functionalization

1. Shilov System (Platinum Catalysis)

$$CH_4 + PtCl_6^{2-} + H_2O \rightarrow CH_3OH + PtCl_4^{2-} + 2HCl$$

Mechanism:

1. **Electrophilic substitution:**

$$Pt(II) + CH_4 \rightarrow Pt(II)(CH_3) + H^+$$

2. **Oxidation to methanol**

2. Fujiwara-Moritani Reaction

Oxidative coupling of arenes with alkenes

$$Ar\text{-}H + CH_2{=}CHR + Oxidant \rightarrow Ar\text{-}CH{=}CHR$$

Catalyst: $Pd(OAc)_2$

Mechanism:

1. **Electrophilic palladation:**

$$Pd(OAc)_2 + Ar\text{-}H \rightarrow Pd(OAc)(Ar) + HOAc$$

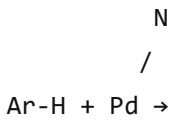
2. **Olefin insertion**
3. **β-H elimination**

3. Directed C-H Activation

Using coordinating groups to direct metallation

Examples:

1. **Ortho-palladation:**



   - Directing groups: -NHR, $-PPh_2$, -COOH
2. **Cyclometalation reactions**

Factors Affecting C-H Activation

1. Bond Strength:

- Primary < Secondary < Tertiary C-H (for radical)
- Opposite trend for electrophilic activation

2. Steric Effects:

- Less hindered positions favored

3. Electronic Effects:

- Electron-rich sites for electrophilic metals
- Electron-deficient sites for nucleophilic metals

4. Solvent Effects:

- Polar solvents for ionic mechanisms
- Non-polar for radical pathways

Applications

1. Pharmaceutical Synthesis:

- Direct functionalization of complex molecules
- Late-stage diversification

2. Natural Product Synthesis:

- Construction of complex frameworks

3. Material Science:

- Functionalization of polymers
- Surface modification

4. Energy:

- Methane to methanol conversion
- Upgrading of natural gas

8. Comparative analysis of catalytic systems