Unique reactions in organometallic chemistry

- Oxidative Addition
- Reductive Elimination
- Migratory Insertion
- $\beta$ - Hydrogen Elimination
When addition of ligands is accompanied by oxidation of the metal, it is called an oxidative addition reaction

\[ L_n M + XY \rightarrow L_n (X)(Y) M \]

- OX state of metal increases by 2 units
- Coordination number increases by 2 units
- 2 new anionic ligands are added to the metal

Requirements for oxidative addition

- availability of nonbonded electron density on the metal,
- two vacant coordination sites on the reacting complex (\(L_n M\)), that is, the complex must be coordinatively unsaturated,
- a metal with stable oxidation states separated by two units; the higher oxidation state must be energetically accessible and stable.
Examples of Oxidative addition: Cis or trans?

Homonuclear systems (H₂, Cl₂, O₂, C₂H₂) Cis

Heteronuclear systems (MeI) Cis or trans
An important step in many homogeneous catalytic cycles

**Hydrogenation of alkenes - Wilkinson catalyst**

$$\text{Rh}^+\text{Cl} \xrightarrow{\text{H}_2 \text{ oxidative addition}} \text{Rh}^3\text{Cl}$$

**Methanol to acetic acid conversion - Cativa process**

$$\text{Ir}^+\text{CO} \xrightarrow{\text{CH}_3\text{I}} \text{Ir}^3\text{CO}$$

**Pd catalyzed Cross coupling of Ar-B(OH)$_2$ and Ar-X - Suzuki Coupling**

$$[\text{Ph}_3\text{P}-\text{Pd}-\text{PPh}_3] \xrightarrow{\text{phenyl-Br}} \text{Ph}_3\text{P}-\text{Pd}^2-\text{PPh}_3$$

The more electron rich the metal, more easy is the oxidative addition.
Oxidative addition involving C-H bonds and cyclo/ortho metallation

This type of reactions help to activate unreactive hydrocarbons such as methane – known as C-H activation
Almost the exact reverse of Oxidative Addition

Oxidation state of metal decreases by 2 units

Coordination number decreases by 2 units

2 cis oriented anionic ligands form a stable $\sigma$ bond and leave the metal

Factors which facilitate reductive elimination

• a high formal positive charge on the metal,
• the presence of bulky groups on the metal, and
• an electronically stable organic product.

Cis orientation of the groups taking part in reductive elimination is a MUST
Final step in many catalytic cycles

Hydroformylation (conversion of an alkene to an aldehyde)

\[
\text{Ph}_3\text{P} \quad \text{H} \quad \text{H} \\
\text{OC} \quad \text{Rh} \quad \text{C} \quad \text{CO} \\
\text{CH}_2\text{CH}_2\text{R} \quad \text{Ph}_3\text{P} \\
\text{OC} \quad \text{Rh} \quad \text{PPh}_3
\]

Reductive elimination

\[
\text{RCH}_2\text{CH}_2\text{CHO} + \quad \text{Ph}_3\text{P} \quad \text{H} \\
\text{OC} \quad \text{Rh} \quad \text{PPh}_3
\]

Sonogashira Coupling (coupling of a terminal alkyne to an aryl group)

\[
\text{R'} \quad \equiv \quad \text{Pd} \quad \text{PR}_3 \\
\text{PR}_3
\]

Reductive elimination

\[
\text{R'} \quad \equiv \quad \text{Ar} + [\text{R}_3\text{P} \quad \text{Pd} \quad \text{PR}_3]
\]

Cativa Process (Methanol to Acetic acid)

\[
\text{H}_3\text{C} \quad \equiv \quad \text{CO} \\
\text{I} \quad \text{C} \quad \equiv \quad \text{O} \\
\text{I} \quad \text{Ir} \quad \text{CO}
\]

\[
\text{H}_3\text{C} \quad \equiv \quad \text{I} + \quad \text{Ir} \quad \text{CO}
\]
Migratory Insertion

No change in the formal oxidation state of the metal

A vacant coordination site is generated during a migratory insertion (which gets occupied by the incoming ligand)

The groups undergoing migratory insertion must be cis to one another

These reactions are enthalpy driven and although the reaction is entropy prohibited, the large enthalpy term dominates
Types of Migratory Insertion

1, 1 - migratory insertion

1, 2 - migratory insertion

1, 1-migratory insertion

1, 2-migratory insertion
Stability of \( \sigma \) Bonded alkyl groups as ligands

Joseph Chatt 1962 - 68

Why does some \( \sigma \) bonded alkyl complexes decompose readily?
Beta-hydride elimination is a reaction in which an alkyl group having a $\beta$ hydrogen, $\sigma$ bonded to a metal centre is converted into the corresponding metal-bonded hydride and a $\pi$ bonded alkene. The alkyl must have hydrogens on the beta carbon. For instance butyl groups can undergo this reaction but methyl groups cannot. The metal complex must have an empty (or vacant) site cis to the alkyl group for this reaction to occur.

No change in the formal oxidation state of the metal

Can either be a vital step in a reaction or an unwanted side reaction
**β-hydrogen elimination does not happen when**

- the alkyl has no β-hydrogen (as in PhCH₂, Me₃CCH₂, Me₃SiCH₂)
- (ii) the β-hydrogen on the alkyl is unable to approach the metal (as in C≡CH)
- the M–C–C–H unit cannot become coplanar

Select the most **unstable** platinum σ complex from the given list. Justify your answer

- **A**
  - No β-H
- **B**
  - β-H unable to approach M
- **C**
  - MCCH unit will not be coplanar
Problem solving

Classify the following reactions as oxidative addition, reductive elimination, (1,1 / 1,2)migratory insertion, β- H elimination, ligand coordination change or simple addition

(a) \([\text{RhI}_3(\text{CO})_2\text{CH}_3]^− \rightarrow \{\text{RhI}_3(\text{CO})(\text{solvent})[\text{C(O)CH}_3]\}^−\]

(b) \(\text{Ir}(\text{PPh}_2\text{Me})_2(\text{CO})\text{Cl} + \text{CF}_3\text{I} \rightarrow \text{Ir}(\text{I})(\text{CF}_3)(\text{PPh}_2\text{Me})_2(\text{CO})\text{Cl}\)

(c) \(\text{TiCl}_4 + 2 \text{Et}_3\text{N} \rightarrow \text{TiCl}_4(\text{NEt}_3)_2\)

(d) \(\text{HCo}(\text{CO})_3(\text{CH}_2=\text{CHCH}_3) + \text{CO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Co}(\text{CO})_4\)

Step 1. determine the oxidation state of the metal in reactant and product
Step 2. count the electrons for reactant and product
Step 3. see if any ligand in the reactant has undergone change
Homogeneous catalysis using organometallic Catalysts

A catalyst typically increases the reaction rates by lowering the activation energy by opening up pathways with lower Gibbs free energies of activation (G).
### Homogeneous versus Heterogeneous Catalysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Heterogeneous</th>
<th>Homogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Gas/solid</td>
<td>Usually liquid/ or solid soluble in the reactants</td>
</tr>
<tr>
<td>Required temperature</td>
<td>High</td>
<td>Low (less than 250°C)</td>
</tr>
<tr>
<td>Catalyst Activity</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Product selectivity</td>
<td>Less (often mixtures)</td>
<td>More</td>
</tr>
<tr>
<td>Catalyst recycling</td>
<td>Simple and cost effective</td>
<td>Expensive and complex</td>
</tr>
<tr>
<td>Reaction mechanism</td>
<td>Poorly understood</td>
<td>Reasonably well understood</td>
</tr>
<tr>
<td>Product separation from catalyst</td>
<td>Easy</td>
<td>Elaborate and sometimes problematic</td>
</tr>
<tr>
<td>Fine tuning of catalyst</td>
<td>Difficult</td>
<td>Easy</td>
</tr>
</tbody>
</table>
Heterogeneous Catalyst- Catalytic Converter of a Car

Chemistry at the molecular level – Poorly understood

Home assignment: See Youtube video ‘Catalysis’
Comparing different catalysts; Catalyst life and Catalyst efficiency

Turnover Number (TON)

*TON is defined as the amount of reactant (in moles) divided by the amount of catalyst (in moles) times the percentage yield of product. A large TON indicates a stable catalyst with a long life.*

Turnover Frequency (TOF)

It is the number of passes through the catalytic cycle per unit time (often per hour). Effectively this is dividing the TON by the time taken for the reaction. The units are just time$^{-1}$. *A higher TOF indicates better efficiency for the catalyst.*
Wilkinson’s Catalyst for alkene hydrogenation

\[
\begin{align*}
\text{RhCl}_3 \ (\text{H}_2\text{O})_3 & \quad + \\
\text{CH}_3\text{CH}_2\text{OH} & \quad + \\
3 \text{PPh}_3 & \quad \longrightarrow \\
\text{RhCl(PPh}_3\text{)}_3 & \quad + \\
\text{CH}_3\text{CHO} & \quad + \\
2\text{HCl} & \quad + \\
3\text{H}_2\text{O} & \quad 
\end{align*}
\]

Wilkinson’s catalyst: The first example of an effective and rapid homogeneous catalyst for hydrogenation of alkenes, active at room temperature and atmospheric pressure.

Square planar 16 electron \(d^8\) complex \((\text{Ph}_3\text{P})_3\text{RhCl}\)

Discovered by G Wilkinson as well as by R Coffey almost at the same time (1964–65)
Conventional Catalytic cycle for hydrogenation with Wilkinson’s catalyst

The first step of this catalytic cycle is the cleavage of a PPh$_3$ to generate the active form of the catalyst followed by oxidative addition of dihydrogen.