Note: Organometallic Compounds and Complexes Contain a M-C Bond.
1760 Louis Claude Cadet de Gassicourt investigates inks based on cobalt salts and isolates Cacodyl from cobalt mineral containing arsenic.

1827 William Christopher Zeise produces Zeise's salt; the first platinum / olefin complex.

1848 Edward Frankland discovers diethylzinc.

1863 Charles Friedel and James Crafts prepare organochlorosilanes.

1890 Ludwig Mond discovers nickel carbonyl.

1899 Introduction of Grignard reaction.

1899 John Ulric Nef discovers alkylation using sodium acetylide.

1900 Paul Sabatier works on hydrogenation of organic compounds with metal catalysts. Hydrogenation of fats kicks off advances in food industry; see margarine!

1909 Paul Ehrlich introduces Salvarsan for the treatment of syphilis, an early arsenic based organometallic compound.

1912 Nobel Prize Victor Grignard and Paul Sabatier.

1930 Henry Gilman works on lithium cuprates, see Gilman reagent.

1951 Walter Hieber was awarded the Alfred Stock prize for his work with metal carbonyl chemistry—\textit{(but not the Nobel Prize)}. 

Organometallic chemistry timeline
1951 Ferrocene is discovered
    1963 Nobel prize for Karl Ziegler and Giulio Natta on Ziegler-Natta catalyst: Polymerization of olefins
    1965 Discovery of cyclobutadieneiron tricarbonyl
    1968 Heck reaction
    1973 Nobel prize Geoffrey Wilkinson and Ernst Otto Fischer on sandwich compounds
    2001 Nobel prize W. S. Knowles, R. Noyori and Karl Barry Sharpless for asymmetric hydrogenation
    2005 Nobel prize Yves Chauvin, Robert Grubbs, and Richard Schrock on metal-catalyzed alkene metathesis
    2010 Nobel prize Richard F. Heck, Ei-ichi Negishi, Akira Suzuki for palladium catalyzed cross coupling reactions
The following slides are meant merely as examples of the catalytic processes we will explore later this semester. Please don’t get disturbed that there is too much new information at this point. Believe me, you will see them again.
Catalysis (ca. 25% of US GNP)
Catalyst Development

Heterogeneous

Determine overall rate law and selectivity as a function of concentration

General

Postulate mechanism

Determine rate laws of individual steps

Homogeneous

Infer best mechanism
Catalyst Development

**Heterogeneous**
- Determine adsorption isotherms
- Identify surface species; note analogies with organometallic compounds

**General**
- Determine overall rate law and selectivity as a function of concentration
- Postulate mechanism
- Determine rate laws of individual steps

**Homogeneous**
- Determine formation of metal complex
- Identify reaction intermediates; note analogies with known reactions

**Additional Notes**
- Note support effects
- Note differential poisoning
- Note isotope effects
- Note stereochemistry
- Note solvent and ligand effects
- Infer best mechanism
Schematic representation of physisorption and chemisorption of Hydrogen on a nickel metal surface

Schematic representation of diverse sites exposed on a metal surface—a) different exposed planes, edges; b) steps and kinks from irregularities.
Hydrogenation of alkenes on supported metal
Involves H₂ dissociation and migration of H-atoms
to an adsorbed ethene molecule. (Paul Sabatier, 1890)

**Mechanism:** All isotopomers are seen, therefore highly
Reversible processes precede loss of the ethane.

Volcano diagrams relate stability of products on
Surface: Temp. for a set rate of release vs. the
Enthalpy. *Intermediate values of ΔHᵣ, with the rate
being a combination of the rate of adsorption and
the rate of desorption gives best catalyst.*

![Volcano Diagram](image)

**The Goldilocks’ Effect**

© 2009 W.H. Freeman
Hydrogenation of Alkenes: Wilkinson’s catalyst and (one of several versions of) the mechanism
Catalytic homogeneous hydrogenation.

Mechanism:
$H_2$ activation prior to olefin addition

Typical catalysts (achiral):

Wilkinson's catalyst

Mechanism:
Olefins add first to cationic catalyst
With the Rh(I) cationic precursor: Olefin adds prior to \( H_2 \) oxidative addition.

*This mechanistic route followed by asymmetric Hydrogenation process*
Wilkinson’s Catalyst: Mechanism for Olefin Hydrogenation

[Diagram showing the mechanism of olefin hydrogenation catalyzed by Wilkinson’s catalyst, with arrows indicating the reaction steps and intermediates.]
Some homogeneous catalytic processes  

Hydroformylation of alkenes (Oxo process)

\[
RCH == CH_2 + CO + H_2 \xrightarrow{\text{Co(I), Rh(II), or Pt(II)}} RCH_2CH_2C == CH + RCH-C=O
\]

Oxidation of alkenes (Wacker process)

\[
H_2C == CH_2 + O_2 \xrightarrow{\text{Pd(II) or Cu(II)}} H_3CC == CH
\]

Carbonylation of methanol to acetic acid (Monsanto process)

\[
CH_3OH + CO \xrightarrow{\text{[RhL_2(CO)_2]^+}} H_3CC == CH
\]

Hydrocyanation of butadiene to adiponitrile

\[
H_2C == CHCH == CH_2 + 2HCN \xrightarrow{\text{Ni(OR)_3}} NCCH_2CH_2CH_2CH_2CN
\]

Asymmetric hydrogenation of prochiral alkenes

\[
\begin{align*}
\text{H} & \quad \text{COOR} \\
\text{C} == \text{C} & \quad \text{R} \quad \text{NHCOR} \\
\quad \text{H} & \quad \text{COOR} \quad \text{RCH_2C^*} \\
\quad \text{NHCOR} & \\
\end{align*}
\xrightarrow{\text{[Rh(DiPAMP)_2]^+}} \]

Cyclotrimerization of acetylene

\[
3CH == CH \xrightarrow{\text{Ni(acac)_2}} \text{C}_3H_6
\]

90 per cent L
Hydroformylation:

\[ \text{Propen (Aiken)} \xrightarrow{\text{CO} / \text{H}_2 \text{ Kat.}} \text{CH}_3 \text{H} \left( \text{n-Butanal (linearer Aldehyd)} \right) + \text{CH}_3 \text{H} \left( \text{iso-Butanal (verzweigter Aldehyd)} \right) \]
Hydroformylation:

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CO} + \text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COH} + \text{HCo(CO)}_4 \]

C = 6-coordinate intermediate

\[ \text{C} \]

A

B

CO

CH\(_3\)CH\(_2\)CH\(_2\)CO\(\text{Co(CO)}_4\)
Hydroformylation: Union Carbide process
Olefin Isomerization
Monsanto Acetic Acid Synthesis

\[ \text{MeOH} + \text{CO} \rightarrow \text{MeC(=O)OH} \]

- The reaction is independent of CO pressure.
- First order in both rhodium and Mel.
- Rate determining step is the oxidative addition of Mel to the \([\text{Rh(CO)}_2\text{I}_2]^-\) catalyst.
Olefin hydroformylation

Monsanto Acetic Acid Process

hydroformylation

cross-coupling
Cossee mechanism for olefin polymerization

Acetyl co-A synthase

ring-opening metathesis polymerization

water-gas shift
CO₂ reduction catalyst

Chauvin mechanism for olefin metathesis

Active catalyst