Organometallic Chemistry
between organic and inorganic

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Course Roadmap

- A real example: the Monsanto Acetic Acid process
- Introduction: what is organometallic chemistry, and why should you care?
- Electron counting: the basis for understanding structure and reactivity
- An overview of Main-group and Transition metal chemistry
- Main group metal chemistry and "Umpolung"
- Intermezzo: characterization of organometallic compounds
- Transition metal chemistry: overview of common ligands
- Ligand substitution
- Insertion and elimination
- Oxidative insertion and reductive elimination
- More exotic steps
- Your own presentations
- Applications in catalysis
Example: Acetic Acid synthesis

Acetic acid is an important industrial chemical.

The traditional synthesis uses bio-oxidation of ethanol obtained via fermentation:

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6 & \rightarrow 2 \text{C}_2\text{H}_5\text{OH} + 2 \text{CO}_2 \\
\text{C}_2\text{H}_5\text{OH} + \text{O}_2 & \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}
\end{align*}
\]

This is not a clean and efficient process!

Industrial acetic acid synthesis:

\[
\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}
\]

Catalyzed by a rhodium complex.
Acetic Acid synthesis

Moderately complex catalytic cycle:

\[
\begin{align*}
\text{CH}_3\text{COOH} & \rightleftharpoons \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COI} \\
\text{CH}_3\text{COI} & \rightleftharpoons \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{I} \\
\text{CH}_3\text{I} & \rightleftharpoons \text{Rh(CO)}_2\text{I}_2 \\
\text{Rh(CO)}_2\text{I}_2 & \rightleftharpoons \text{MeRh(CO)}_2\text{I}_3 \\
\text{MeRh(CO)}_2\text{I}_3 & \rightleftharpoons \text{MeCORh(CO)}_3 \\
\text{MeCORh(CO)}_3 & \rightleftharpoons \text{CO} \\
\end{align*}
\]
Acetic Acid synthesis

This cycle is known in considerable detail:

To understand it, you need to be familiar with electron counting and common reaction types.
What is organometallic chemistry?

Strictly speaking, the chemistry of compounds containing at least one metal-carbon bond.

Metal hydrides are often included, H being considered as the "smallest organic group" (as in propyl, ethyl, methyl, hydride). Metal-carbon bonds are often formed temporarily or potentially, so in practice many compounds are included that do not actually contain metal-carbon bonds.
Why should you care?

Organometallic chemistry is the basis of **homogeneous catalysis**, which is the method of choice for clean and efficient synthesis of fine chemicals, pharmaceuticals and many larger-scale chemicals.

Many **plastics** (polythene, polypropene, butadiene rubber, ...) and **detergents** are made via organometallic catalysis.

Organometallic chemistry is also the basis for understanding important steps in **heterogeneous catalysis** reactions such as olefin hydrogenation and CO oxidation.

Organometallic compounds are used on a large scale as precursors for **generation of semiconductors** (AlN, GaAs, etc).

**Silicone rubbers** are one of the few classes of organometallic compounds used as "final products".
Course Objectives

By the end of this course, you should be able to:

• Make an educated guess about stability and reactivity of a given compound, based on (a.o.) electron counting rules

• Propose reasonable mechanisms, based on "standard" organometallic reaction steps, for many metal-catalyzed reactions

• Use steric and electronic arguments to predict how changes in reactants, metal or ligands affect the outcome of reactions

• Read a current research literature paper, understand and explain its content and significance
Organometallic chemistry (CHEM 4680) is a 4th-year course because it builds on:

- Organic chemistry: reaction mechanisms, primarily nucleophilic and electrophilic attack
- Inorganic Chemistry: electronegativity; electron counting and stability; properties of (transition) metals
- Physical chemistry: orbitals and MO theory; free energy, enthalpy and entropy

You will (now and then) need this background to understand the material or make assignments etc.