Organometallic Chemistry

CHM 4317

between organic and inorganic
Overview

• 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
• 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:

\[ C_6H_{12}O_6 \rightarrow 2 \text{C}_2\text{H}_5\text{OH} + 2 \text{CO}_2 \]
\[ \text{C}_2\text{H}_5\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} \]
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:

\[
\begin{align*}
\text{CH}_3\text{COOH} & \quad \text{HI} \quad \text{CH}_3\text{OH} \\
\text{CH}_3\text{COI} & \quad \text{H}_2\text{O} \quad \text{CH}_3\text{I} \\
\text{Rh(CO)}_2\text{I}_2^- & \quad \text{MeCORh(CO)}_2\text{I}_3^- \quad \text{MeRh(CO)}_2\text{I}_3^- \quad \text{CO} \\
\text{MeCORh(CO)}_2\text{I}_3^- & \quad \text{MeCORh(CO)}_2\text{I}_3^- \\
\end{align*}
\]
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.

![Chemical reaction diagram]

\[
\text{H}_2 \quad \text{(Ph}_3\text{P)}_3\text{RhCl} \quad \text{Li} \quad \text{OMe} \quad \text{OMe} \quad \text{Li} \\
\text{C}_{	ext{Li}} \quad \text{C}_{	ext{OMe}} \quad \text{C}_{	ext{OMe}} \quad \text{C}_{	ext{Li}}
\]
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
Useful Background Knowledge

Organometallic chemistry 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.
Between organic and inorganic...

Organic chemistry:
• more or less covalent C-X bonds
• rigid element environments
• fixed oxidation states (better: valencies)

??Organometallic chemistry??

Inorganic chemistry:
• primarily ionic M-X bonds, dative M-L bonds
• variable and often fluxional environments
• variable oxidation states
Organometallic reactivity

Since most organometallics are intermediates, the focus in organometallic chemistry is usually on understanding and tuning reactivity.

This starts with analyzing reaction mechanisms in terms of elementary steps.

The number of possible elementary steps is larger than in "pure organic" chemistry, but the ideas are similar.
**Organometallic structures**

Knowledge of inorganic and coordination chemistry is useful to understand geometries, electron counts and oxidation states of organometallic compounds.

Organometallics are more covalent and often less symmetric than coordination compounds, so orbital symmetry arguments are not as important.
Organometallic chemistry is concerned with *all* metals, in combination with *all* "organic" elements.

there are *many* metals!

Generalization is important

the chemistry of e.g. Fe is not much more complicated than that of C, but after that there are 80 *more* metals...

we divide reactions in broader categories than organic chemists do

We concentrate on the M side of the M-C bond,
and on how to tune its reactivity
## Elements of interest

<table>
<thead>
<tr>
<th>Organic elements</th>
<th>Main group metals</th>
<th>Transition metals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H</strong></td>
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<td>Li</td>
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<td>Lw</td>
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</table>

**Table:**
- **Elements of interest**
- **Main group metals**
- **Transition metals**
Organic vs organometallic reactivity

Organic chemistry:
C-C / C-H : nearly covalent
C\(\delta^+\)-X\(\delta^-\) : polar (partly ionic)
reactivity dominated by nucleophilic attack at C
\(S_{N2}\) and \(S_{N1}\) like reactivity

Organometallic chemistry:
C is the *negative* end of the M-C bond ("umpolung")
reactivity dominated by electrophilic attack at C
or nucleophilic attack at M
associative and dissociative substitution at M
Main-group organometallics

$s$ and $p$ orbitals.

8-e rule, usually.

with a lot of exceptions

More electropositive and larger:

higher coordination numbers, regardless of the number of electrons.

“Early” groups and not very electropositive:

lower coordination numbers.

Me–Zn–Me

4-e
Main-group organometallics

Metal is the "δ+" side of the M-C bond.
Chemistry dominated by nucleophilic attack of Cδ- at electrophiles.
this is also the main application in organic synthesis

MeMgBr + Me₂CO → Me₃COMgBr

note: this is a simplified picture of the Grignard reaction
Main-group organometallics

M-M multiple bonds are fairly weak and rather reactive
they are a curiosity and relatively unimportant,
certainly compared to C-C multiple bonds

Bond strengths in kcal/mol:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Measured Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>85</td>
</tr>
<tr>
<td>C=C</td>
<td>150</td>
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<tr>
<td>N-N</td>
<td>40</td>
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<tr>
<td>N=N</td>
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<tr>
<td>P-P</td>
<td>50</td>
</tr>
<tr>
<td>P=P</td>
<td>75</td>
</tr>
</tbody>
</table>

Multiple-bonded compounds often have unusual geometries
Transition-metal organometallics

$s, p$ and $d$ orbitals
18-e rule, sometimes 16-e
other counts relatively rare
Transition-metal organometallics

Lower electron counts if metals are *sterically saturated*:


c

\[
\text{nor} = \begin{array}{c}
\text{nor} \\
\text{nor} \\
\text{nor}
\end{array}
\]

\[
\begin{array}{c}
\text{Co} \\
\text{nor}
\end{array}
\]

\[
\begin{array}{c}
\text{nor} \\
\text{nor}
\end{array}
\]

\[
\begin{array}{c}
\text{nor} \\
\text{nor}
\end{array}
\]

13-e

12-e

16-e
Transition-metal organometallics

Often ligands capable of donating 2-8 electrons
  Preference for \( \pi \)-system ligands (good overlap with \( d \)-orbitals)

- olefin
- carbene
- allyl
- cyclopentadienyl

Bonding to neutral ligands (olefin/diene/CO/phosphine)
  relatively weak
  Important for catalysis!
Transition-metal organometallics

An olefin complex: $(\text{Acac})\text{Ir(NCMe)(C}_2\text{H}_4)$

[Diagram of molecular structure with labels for donation and back donation]
Transition-metal organometallics

“Forbidden” reactions?

Mo + \rightarrow Mo

No symmetry
Very fast
Reactivity of the M-C bond

Polar $\Rightarrow$ reactive towards e.g.

- **Water**: $\rightarrow$ M-OH + H-C
  
  Me$_3$Al explodes with water; Me$_4$Sn does not react.

- **Oxygen**: $\rightarrow$ M-O-O-C
  
  Me$_2$Zn inflames in air; Me$_4$Ge does not react.

- **Carbonyl groups**: $\rightarrow$ M-O-C-C
  
  MeLi adds at -80° C, Me$_3$Sb not even at +50° C.
Reactivity of the M-C bond

Oxidation and hydrolysis: large driving force

Bond strengths in kcal/mol:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-C</td>
<td>65</td>
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<tr>
<td>As-C</td>
<td>55</td>
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<tr>
<td>Si-C</td>
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<td>Al-O</td>
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<td>As-O</td>
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<tr>
<td>Si-O</td>
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<tr>
<td>Al-Cl</td>
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<tr>
<td>Si-Cl</td>
<td>91</td>
</tr>
</tbody>
</table>
Organometallic reaction steps

Ligand dissociation / coordination

Me$_3$Al + NMe$_3$ $\rightleftharpoons$ Me$_3$Al-NMe$_3$

note: free Me$_3$Al dimerizes to Me$_6$Al$_2$
Organometallic reaction steps

*Insertion* and β-elimination

\[
\text{MeMgBr} + \text{MeC}≡\text{N} \rightarrow \text{Me}_2\text{C}=\text{NMgBr}
\]

\[
\text{N}^-\text{Fe}^+\text{Me} \rightarrow \text{N}^-\text{Fe}^+\text{Me} \rightarrow \text{N}^-\text{Fe}^+\text{N}
\]

\[
\text{N}^-\text{Fe}^+\text{Me} = \text{Ar} \quad \text{Ar} = \text{Ar}
\]
Organometallic reaction steps

Insertion and $\beta$-elimination

$$\text{P-Pd-P} \xrightarrow{\text{H}} \text{P-H-Pd-P} \rightleftharpoons \rightarrow \text{P} = \text{Ph}_2\text{P-CH}_2\text{PPh}_2$$
Organometallic reaction steps

Oxidative addition / Reductive elimination

\[
P\text{Rh}Cl \xrightarrow{H_2} P\text{Rh}H \quad "P" = \text{PPh}_3
\]
Organometallic reaction steps

Oxidative addition / Reductive elimination

\[
\begin{align*}
\text{Oxidative addition:} & \quad \text{MeL} \\
\text{Reductive elimination:} & \quad \text{L = P(OPh)_3} \\
\text{L = PPh}_3
\end{align*}
\]
Organometallic reaction steps

σ-bond metathesis

\[
\text{Lu-CH}_3 \rightarrow \text{Lu-*CH}_4 \rightarrow \text{Lu-*CH}_3
\]
Organometallic reaction steps

Redox reactions

Homolysis

\[ \text{Et–Hg–Et} \rightarrow \text{Et–Hg}^* + \text{.Et} \]
Organometallic reaction steps

Reactivity of coordinated ligands
Factors governing structure and reactivity of organometallic compounds

- M-C, M-X bond strengths
- Electronegativity of M (polarity of M-C etc bonds)
- Number of (d) electrons
- Coordination number
- Steric hindrance
**Trends in the periodic table**

Main group metals:
- left and down: more electropositive
- down: higher oxidation states *less* stable

Transition metals:
- middle: strongest preference for 18-e
- 2\textsuperscript{nd} and 3\textsuperscript{rd} row: strong preference for paired electrons (low-spin states)
- down: higher oxidation states *more* stable
Working with organometallics

Synthesis and reactivity studies (inert atmosphere!):
- Glove box
- Schlenk line, specialized glassware

Characterization:
- X-ray diffraction $\Rightarrow$ structure $\Rightarrow$ bonding
- NMR $\Rightarrow$ structure en dynamic behaviour
- (calculations)

- IR
- MS
- EPR

Not:
- GC
- LC