Organometallic Chemistry

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Unit 5: Organometallic Chemistry

- Definition of Organometallic compounds and Organometallic chemistry
- CO as a $\pi$-acid donor ligand
- Binary metal carbonyls
- Methods of synthesis –
  (a) Direct reaction
  (b) Reductive carbonylation
  (c) Photolysis and thermolysis
- Molecular and electronic structures (18 electron rule) of metal carbonyls
Organometallic chemistry

- Organometallic (OM) chemistry is the study of compounds containing, and reactions involving, metal-carbon bonds.
- Main group elements, transition metals as well as lanthanides and actinides form bonds to carbon.
- They are used widely as reagent or catalysts in organic synthesis.
- They are getting emphasis due to potential applications in homogeneous catalysts, as reagents in organic synthesis and as makers in molecular biology.

https://www.slideshare.net/satyabratasendh/metal-carbonyls-92974314
Organometallic compounds

• Organometallic compounds are chemical compounds which contain at least one bond between a metallic element and a carbon atom belonging to an organic molecule.

• Even metalloid elements such as silicon, tin, and boron are known to form organometallic compounds which are used in some industrial chemical reactions.
Properties of Organometallic Compounds

- The bond between the metal and the carbon atom is often highly covalent in nature.
- Most of the organometallic compounds exist in solid states, especially the compounds in which the hydrocarbon groups are aromatic or have a ring structure.
- The compounds consisting of highly electropositive metals such as sodium or lithium are very volatile and can undergo spontaneous combustion.
- In many cases, organometallic compounds are found to be toxic to humans (especially the compounds that are volatile in nature).
- These compounds can act as reducing agents, especially the compounds formed by highly electropositive metals.
- The properties of organometallic compounds differ amongst each other based on the properties of the metals that constitute them.
Applications of Organometallic Compounds

- In some of the commercial chemical reactions, organometallic compounds are used as homogeneous catalysts.
- These compounds are used as stoichiometric reagents in both industrial and research-oriented chemical reactions.
- These compounds are also used in the manufacture of some of the semiconductors, which require the use of compounds such as trimethylgallium, trimethylaluminum, trimethylindium, and trimethyl antimony.
- They are also used in the production of light emitting diodes (or LEDs).
- These compounds are employed in bulk hydrogenation processes such as the production of margarine.
- These compounds are used as catalysts and reagents during the synthesis of some organic compounds.
- The complexes formed from organometallic compounds are useful in the facilitation of the synthesis of many organic compounds.
Carbonyl complexes

• An analysis of Metal-CO bonding shows two types of bonding –
  a) A sigma - σ bond formed by donation of an electron pair from the carbon atom of CO into a vacant orbital on the metal centre
  b) Two pi-bonds are formed by back donation of electrons form filled metal d_1 orbitals into π2 orbitals of CO. this back bonding leads to an increase in bond order of M-C bond and a decrease in C-O bond order.
**CO as a π-acid donor ligand**

- π acid ligands are one which are capable of accepting an appreciable amount of electron density from the metal atom into empty or orbital of their own are called as acid or acceptor ligands.

- This type of interaction increases the value of crystal field splitting energy and thus are classified as strong filed ligands.

- Example of pi acid ligands are CO, NO$^+$ and CN$^-$
\[ \text{σ-type orbital interaction} \]
\[ d_{x^2-y^2} \]

\[ \text{π-type orbital interaction} \]
\[ d_{xy} \]

Electron donor!  Electron acceptor!
• The electron pair located on carbon is more loosely bound and it is available for donation to metal.

• CO has a pair of empty mutually perpendicular \( \pi^* \) orbitals that overlap with filled metal orbitals of \( \pi \) symmetry and help to drain excess negative charge from the metal to the ligands.

• Because the ligands containing empty \( \pi^* \) orbitals accept electrons, they are Lewis acids and are called \( \pi \) acids.

• Metal to ligand electron donation is referred as back bonding.
carbon and the oxygen are both sp²
• https://youtu.be/y9FZQBvgWPo
• Energetically σ bond is formed between metal and ligand, a σ bond is formed by donation of an electron pair from the carbon atom of CO into vacant orbital on the metal (L→ M)

• Back bonding assumes greater relative importance when metal has many electrons to dissipate, thus low oxidation states are stabilized by π acid ligands.

• σ and π bonding reinforce each other, this mutual reinforcement is called as synergism.
Binary metal carbonyls

• Binary carbonyls are the simplest class of \( \pi \) acid complexes.
• Most of them are available commercially.
• Table 5.1
**Methods of synthesis**

- Simple transition metal carbonyls are made by various methods, the important ones are –
  
  (a) Direct reaction

  (b) Reductive carbonylation

  (c) Photolysis and thermolysis
(a) Direct reaction

- First of all tetracarbonyl nickel \([\text{Ni(CO)}_4]\) and pentacarbonyl iron \([\text{Fe(CO)}_5]\) were discovered in 1888.
- The synthesis of \([\text{Ni(CO)}_4]\) is industrially important because the reaction is reversible and this is the basis of the Mond’s process for purification of metallic nickel.

\[
\text{Ni} + 4\text{CO} \xrightarrow{25^\circ\text{C, 1 atm}} \text{Ni(CO)}_4 \xrightarrow{\Delta, \text{Distill}} \text{Ni} + 4\text{CO}
\]

Impure \hspace{1cm} \text{Pure}
The simplest metal carbonyls are the neutral binary Mx(CO)y compounds, these may be mononuclear (x=1) or polynuclear (x>1). The majority of metal carbonyls are ow melting point solids that can be sublimated in vacuo. A small number of the compounds are volatile liquids.

The other mononuclear metal carbonyls are prepared by direct reaction of metal with gaseous CO at appropriate temperatures and pressures.

Example –

Fe + 5 Co $\xrightarrow{200^\circ C\atop 100\ atm}$ Fe (CO)$_5$, Mo + 6 CO $\xrightarrow{200^\circ C\atop 250\ atm}$ Mo(CO)
(b) **Reductive carbonylation**

- Mononuclear and polynuclear metal carbonyls are synthesized by a process known as reductive carbonylation in which a transition metal in a high oxidation state is reduced to zero oxidation state in presence of CO gas.

- Often these reactions are performed at very high pressures in steel bombs.

- To reduce the possibility of an accident the bombs are usually operated in explosion proof rooms, located on the top floor of a chemistry building.
Some typical metal carbonyls synthesis employing reductive carbonylation are shown as —

- \[ \text{CrCl}_3 + \text{Al} + 6\text{CO} \xrightarrow{\text{AlCl}_3} \text{Cr(CO)}_9 + \text{AlCl}_3 \]

- When halide is not present, CO can serve as the reducing agent

- \[ \text{Re}_2\text{O}_7 + 17\text{CO} \xrightarrow{} \text{Re}_2\text{(CO)}_{10} + 7\text{CO}_2 \]

- \[ 2\text{CoCO}_3 + 2\text{H}_2 + 8\text{CO} \xrightarrow{150^\circ\text{C}} 250\text{ atm} \text{Co}_2\text{(CO)}_8 + 2\text{CO}_2 + 2\text{H}_2\text{O} \]
(c) Photolysis and thermolysis

- In addition to direct reaction and reductive carbonylation methods, carbonyl compounds can also be synthesized by a route called occurs photolysis. Photochemical bond cleavage occurs during synthesis.

- Eg. Synthesis of iron ennearcarbonyl.

\[
\text{hv} \\
2 \text{Fe(CO)}_5 \rightarrow \text{Fe}_2(\text{CO})_9 + \text{CO}
\]

\[
\text{hv} \\
2\text{Na}[\text{V(CO)}_6] + 2 \text{HCl} \rightarrow 2 \text{V(CO)}_6 + 2 \text{NaCl} + \text{H}_2
\]
Molecular and electronic structures

• 5.5. book
18 electron rule of metal carbonyls

• The 18-electron rule is used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds.

• The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs.

• This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding.

• When a metal complex has 18 valence electrons, it has achieved the same electron configuration as the noble gas in the period.

• The rule and its exceptions are similar to the application of the octet rule to main group elements.
18 electron rule of metal carbonyls

• This rule applies primarily to organometallic compounds, and the 18 electrons come from the 9 available orbitals in d orbital elements (1 s orbital, 3 p orbitals, and 5 d orbitals).

• The rule is not helpful for complexes of metals that are not transition metals, and interesting or useful transition metal complexes will violate the rule because of the consequences deviating from the rule bears on reactivity.

• If the molecular transition metal complex has an 18 electron count, it is called saturated.

• This means that additional ligands cannot bind to the transition metal because there are no empty low-energy orbitals for incoming ligands to coordinate.

• If the molecule has less than 18 electrons, then it is called unsaturated and can bind additional ligands.
18 electron rule of metal carbonyls

The transition metal complexes may be classified into the following three types -

(i) The ones that do not obey the 18 valence electron rule are of class I type
(ii) The ones that do not exceed the 18 valence electron rule are of class II and
(iii) The ones that strictly follow the 18 valence electron rule.
18 electron rule of metal carbonyls

Depending upon the interaction of the metal orbitals with the ligand orbitals and also upon the nature of the ligand position in spectrochemical series, the transition metal organometallic compounds can form into any of the three categories.
18 electron rule of metal carbonyls

To count electrons in a transition metal compound:

1. Determine the oxidation state of the transition metal and the resulting d-electron count.
   a) Identify if there are any overall charges on the molecular complex.
   b) Identify the charge of each ligand.
2. Determine the number of electrons from each ligand that are donated to the metal center.
3. Add up the electron counts for the metal and for each ligand.

Typically for most compounds, the electron count should add up to 18 electrons. However, there are many exceptions to the 18 electron rule, just like there are exceptions to the octet rule.
• Examples

• https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/24%3A_Organometallic_chemistry%3A_d-block_elements/24.03%3A_The_18-electron_Rule
Homogenous catalysis

• Hydroformylation (Oxo Process) and
• Wacker Process.
Hydroformylation (Oxo Process)

- Hydroformylation, popularly known as the "oxo" process, is a Co or Rh catalyzed reaction of olefins with CO and H₂ to produce the value-added aldehydes.

- The reaction, discovered by Otto Roelen in 1938, soon assumed an enormous proportion both in terms of the scope and scale of its application in the global production of aldehydes.

- The metal hydride complexes namely, the rhodium based HRh(CO)(PPh₃)₃ and the cobalt based HCo(CO)₄ complexes, catalyzed the hydroformylation reaction as shown below.
This chemical reaction entails the addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond. This process has undergone continuous growth since its invention in 1938: Production capacity reached $6.6 \times 10^6$ tons in 1995.

It is important because the resulting aldehydes are easily converted into many secondary products.
For example, the resulting aldehydes are hydrogenated to alcohols that are converted to plasticizers or detergents.

Hydroformylation is also used in specialty chemicals, relevant to the organic synthesis of fragrances and natural products.

The development of hydroformylation, which originated within the German coal-based industry, is considered one of the premier achievements of 20th-century industrial chemistry.
Wacker Process

- The Wacker oxidation was originally developed as the process of producing acetaldehyde from ethylene using the PdCl$_2$-CuCl$_2$ cocatalytic system. Molecular oxygen can be used as the terminal oxidant.

- The reaction can be used to oxidize various terminal alkenes to give the corresponding methyl ketones. DMF is used often as the solvent.

- Internal alkenes are usually unreactive, thus terminal alkenes can be oxidized selectively when both are present in the same molecule.
• The cooperative catalytic cycle involves the oxidation of the alkene by Pd(II), the oxidation of Pd(0) by Cu(II), and the oxidation of Cu(I) by molecular oxygen.

• Similar cycle is used to manufacture acetone from propylene if OH\(^-\) is replaced by acetate, vinyl acetate can be made.