ISBN: 978-81-970675-0-1

5. Organometallic and Microwave Chemistry

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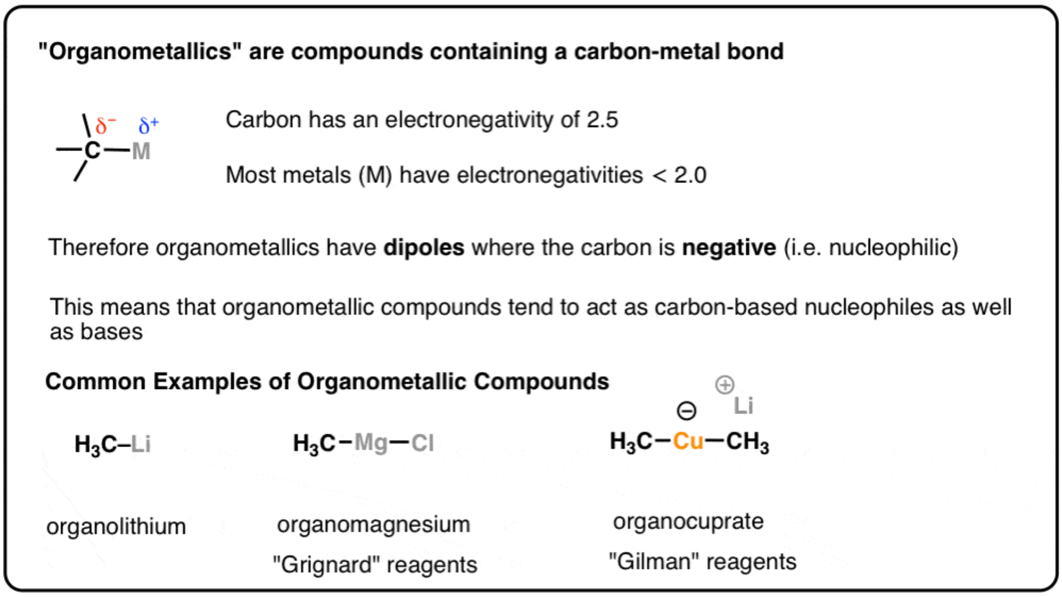
5.1 Organometallic Compounds:

5.1.1 Introduction:

Chemical compounds known as organometallic compounds are those that have at least one bond between a metallic element and an organic molecule's carbon atom; metalloid elements like silicon, tin, and boron are also known to form these compounds, which are utilized in certain industrial chemical reactions. Chemical compounds containing at least one covalent link between a metal atom and a carbon atom from an organic molecule—usually hydrocarbons or their derivatives—are known as organometallic compounds. The interaction between the organic component, referred to as the ligand, and the metal core causes these compounds to frequently display unusual reactivity. The study of these substances' characteristics, structures, and reactions is known as organometallic chemistry. These compounds are important to materials science, medicinal chemistry, catalysis, and other scientific and technological domains.



"Organometallics" are compounds containing a carbon-metal bond

Carbon has an electronegativity of 2.5

Most metals (M) have electronegativities < 2.0

Therefore organometallics have **dipoles** where the carbon is **negative** (i.e. nucleophilic)

This means that organometallic compounds tend to act as carbon-based nucleophiles as well as bases

Common Examples of Organometallic Compounds

Figure 5.1: Organometallic Compounds

5.1.2 Evolution of Metallic Compounds:

Although organometallic compounds have been around since the early 19th century, their actual relevance and investigation took off in the 20th century. Here is a quick summary:

A. Early Discoveries (1800s): Edward Frankland created diethylzinc, the first organometallic compound, in 1849. This finding established the discipline of organometallic chemistry. William Christopher Zeise developed Zeise's salt, a compound with ethylene complexed to a platinum atom, comprising a metal-carbon double bond, in 1848. This discovery established the presence of metal-alkene interactions.

B. Ferrocene (1951): Ferrocene is a sandwich chemical that was inadvertently discovered in 1951 by Thomas Zeisel and Ludwig Mond. It is composed of two cyclopentadienyl anions coordinated with a central iron atom. Inorganic chemistry, ferrocene was a major turning point, and its discovery sparked a wave of curiosity about other sandwich compounds.

C. Development of Transition Metal Complexes (1950s-1960s): Many transition metal organometallic complexes have been synthesised and characterised as a result of the seminal work of Ernst Otto Fischer and Geoffrey Wilkinson in the late 1950s and early 1960s. Metallocenes are organometallic compounds with a metal atom wedged between two cyclopentadienyl ligands. Fischer and Wilkinson's research led to the discovery of these compounds.

D. Nobel Prize in Chemistry (1973): In 1973, Ernst Otto Fischer and Geoffrey Wilkinson shared the Chemistry Nobel Prize in recognition of their revolutionary work in organometallic chemistry. Specifically, they synthesised ferrocene and other sandwich compounds and clarified their structures.

E. Expansion and Applications: In the 20th and 21st centuries, there was a notable expansion in the field of organometallic chemistry research. Numerous domains, including medicinal chemistry, materials science, catalysis, and others, have discovered extensive uses for organometallic compounds. Industrial processes and organic synthesis were revolutionised by the discovery of several catalytic processes, including olefin metathesis and cross-coupling reactions.

5.1.3 Need for the Study:

From basic scientific knowledge to real-world applications in a variety of sectors, the study of organometallic compounds is essential for several reasons. Here are some main reasons for the significance of studying organometallic compounds:

- **Understanding Chemical Bonding:** Unique examples of chemical bonding that involve interactions between organic ligands and metal centers can be found in organometallic compounds. Researching these substances advances our knowledge of chemical structure and dynamics by clarifying basic concepts of bonding and reactivity.

- **Catalysis:** Many organometallic compounds function as catalysts in chemical processes, enabling reactants to be transformed into desired products with increased sustainability, selectivity, and efficiency. To create novel and enhanced catalytic processes for industrial uses including polymerization, environmental remediation, and pharmaceutical synthesis, it is essential to comprehend the mechanisms of organometallic catalysis.
- **Materials Science:** The development of sophisticated materials with specialised features for use in coatings, electronics, optics, and other fields depends heavily on organometallic compounds. By facilitating the creation of innovative polymers, nanoparticles, and coordination complexes, they provide chances to design materials with improved functionality and performance.
- **Medicinal Chemistry:** studies involving metal-based medications, such as organometallic complexes and platinum anticancer medicines, are expanding. Organometallic compounds provide novel approaches to treating illnesses because of their distinct modes of action and potential to overcome the drawbacks of conventional organic medications.
- **Discovery of New Reactions:** The study of organometallic compounds frequently results in the identification of novel chemical reactions and their processes. The synthesis of complicated compounds and the study of unexplored chemical space are made possible by these discoveries, which add to the toolset of synthetic chemists.

5.1.4 Classification of Organometallic Compounds:

A. Based on the nature of metal-carbon bonds organometallic compounds are classified into

a. Ionic Bonded Organometallic Compounds:

Ionic compounds are primarily formed by the organometallic compounds of actinides, lanthanides, alkali, and alkaline earth metals. These tend to be insoluble in organic solvents, colourless, highly reactive, and non-volatile solids. Examples: $Ph_3C^-Na^+$, Cp_2Ca, Cs^+Me^-, Na^+Cp^-.

b. Covalent Bonded Organometallic Compounds:

- **σ- bonded organometallic compounds:** In these compounds, a two-electron, two-cantered (2e-2c) covalent connection forms between the carbon atom of the organic ligand and the metal. Usually composed of the majority of elements having electronegativity values greater than 1. Examples: $Ni(CO)_4$, $Fe(CO)_5$

- **π-bonded organometallic compounds:** These are alkene, alkyne, or any other carbon group with an electron system in π-orbitals that overlap these π- π-orbitals with the metal atom's inactive orbitals, resulting in an arrangement where the metal atom is linked to many carbon atoms rather than just one.
  Examples: $[(-C_5H_5)_2Fe)]$, $K[PtCl_3(-C_2H_2)]$ (Zeise's salt)

c. Multicenter Bonded Organometallic Compounds:

Compounds with loosely connected species are inadequate in electrons that coordinate with metals such as Li, Be, Al, etc. Examples: MeLi or $(CH_3)_4Li_4$, Al_2Me_6

B. Classification of Ligands Based on Hapticity:

Organic ligands are classed based on the "number of carbon atoms within a bonding distance of a metal atom or the number of carbon atoms through which an organic ligand is attached to a central metal atom," also known as the ligand's "hapticity."

- Monohepto ligands: Organic ligands attached to the metal through one carbon. Ex: $-CH_3$, $-C_2H_5$
- Dihepto ligands: Example: $CH_2{=}CH_2$, $K[PtCl_3(-C_2H_2)]$ (Zeise's salt)
- Trihepto ligands: Example: Allylic radical $CH_2{=}CH{-}CH_2{-}$
- Tetrahepto ligands: Example: Butadiene $CH_2{=}CH{-}CH{=}CH_2$
- Pentahepto ligands: Example: Metallocene M $(-C_5H_5)_2$
- Hexahepto ligands: Example: Dibenzene Chromium$(-C_6H_6)_2$

5.1.5 Properties of Organometallic Compounds:

The brief highlights of a few characteristics of organometallic compounds are given below.

- Most organometallic compounds are found in solid forms, particularly those containing aromatic or ring-structured hydrocarbon groups.
- The link between the metal and the carbon atom is frequently extremely covalent in character.
- Compounds containing strongly electropositive metals, such lithium or sodium, are extremely flammable and capable of spontaneous combustion.
- Human toxicity to organometallic compounds has been shown on several occasions (particularly those that are volatile in nature).
- These substances, particularly those made up of highly electropositive metals, have the ability to function as reducing agents.

5.1.6 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:

- Tetracarbonyl nickel [Ni (CO)4] and pentacarbonyl iron [Fe (CO)5] were first identified in 1888.
- Mond's procedure for purifying metallic nickel is based on the reversible synthesis of [Ni (CO)4], making it an essential industrial process. The simplest metal carbonyls are neutral binary Mx (CO)y molecules, which can be mononuclear (x=1) or polynuclear (x>1). The bulk of metal carbonyls have low melting points and may be sublimated in vacuo. A tiny percentage of the chemicals are volatile liquids.

B. Reductive Carbonylation:

- Reductive carbonylation is the process of reducing a transition metal from a high oxidation state to a zero-oxidation state in the presence of CO gas. This process creates mononuclear and polynuclear metal carbonyls.
- In steel explosives, these reactions are frequently carried out at extremely high pressure.
- The explosives are often operated in explosion-proof chambers on the top floor of a chemical building to minimize the chance of an accident.

C. Photolysis and Thermolysis: Photolysis is a technique for synthesizing carbonyl compounds, in addition to direct reaction and reductive carbonylation. During synthesis, photochemical bond cleavage takes place. E.g., Synthesis of iron pentacarbonyl.

$$2\ \mathrm{Fe\ (CO)5} \longrightarrow \mathrm{Fe2(CO)9 + CO}$$

5.1.7 Applications

There are several uses for organometallic compounds in the scientific field. Below are a few of them:

- Organometallic compounds are utilized as homogeneous catalysts in some commercial chemical processes.
- These compounds are utilized in commercial and scientific chemical methods as stoichiometric reagents.

- Specific semiconductors, which call for the usage of substances like trimethylgallium, trimethylaluminum, trimethylindium, and trimethyl antimony, are also made using these compounds.
- They are also utilized in the manufacturing of light-emitting diodes (LEDs)
- The manufacturing of margarine and other bulk hydrogenation procedures use these chemicals.
- These substances function as reagents and catalysts in the production of certain organic molecules.
- Organometallic complexes contribute in the fabricating of several chemical-based molecules.

5.2 Microwave Chemistry:

5.2.1 Introduction:

A microwave is a type of electromagnetic wave that typically has a frequency of 0.3–300GHz and a wavelength of 1–1000 mm.

The international conventions on microwave frequency are strictly regulated for industrial, civil, and scientific research in the frequency of heating and drying are different, in order to avoid microwave interference in various fields. The most commonly used frequency, 2450MHz, is equivalent to 12.2 cm microwave wavelength.

Hertz established the existence of electromagnetic waves towards the end of the 19th century, and American scientists later verified that these waves can be transmitted via hollow metal tubes. As a result, microwave technology developed quickly and is now extensively employed in a variety of industries. Therefore, the microwave technology in chemical and chemical applications, and the chemical and chemicalindustry's sustainable development has great practical significance.

Microwave irradiation offers an alternative to traditional approaches in the context of green chemistry for heating or injecting energy into the system. It makes use of electromagnetic energy's capacity to be converted into heat by mobile electric charges found in liquid or conducting ions in solid. Microwave-aided reactions are quick, inexpensive, tidy, and environmentally benign.

Microwave chemistry involves the use of microwave radiation to conduct chemical reactions, and essentially pertains to chemical analysis and chemical synthesis. Microwave radiation has been successfully applied to numerous industrial applications (drying, heating, sintering, etc.). In the electromagnetic spectrum, between radio waves and infrared waves, exist microwaves. Their operating frequency range is between 0.3 and 30 GHz, and their wavelengths span from 0.01 to 1 meter.

On the other hand, 2.45 GHz is the recommended frequency for their application in lab reactions since it has the appropriate penetration depth. After 30 GHz, there is an overlap between the microwave and radio frequency ranges.

The microwave electromagnetic spectrum is divided into sub-bands comprising the following frequency ranges (Table 5.1):

Table 5.1: Microwave Frequency Bands

BANDS	FREQUENCY
L	1-2 GHz
S	2-4 GHz
C	4-8 GHz
X	8-12 GHz
Ku	12-18 GHz
K	18-26 GHz
Ka	26-40 GHz
Q	30-50 GHz
U	40-60 GHz
V	46-56 GHz
W	56-100 GHz

5.2.2 Evolution of Microwave Chemistry:

Since the Second World War began in September 1939, people have learned a great deal about microwave radiation due to the quick development of radar technology. At the same time, the usage of microwave radiation has grown significantly. Microwave irradiation technology was widely applied at the end of the 1960s in a variety of fields, including waste treatment, protein and peptide bond hydrolysis, sterilisation, and preparation of analytical samples. Its use in the chemical and chemical applications started with the temperature jump experiment, which used microwave heating. Reports on the microwave's application in chemical research were published in the 1970s. In 1986, several researchers discovered that chemical reactions in conventional microwave ovens might be swiftly accelerated, leading to the successful completion of chemical synthesis reactions in a little amount of time. In order to accomplish chemical processes, people also started concentrating on microwave heating; nevertheless, a great deal of study on this technology has led to the development of microwave chemistry. The Netherlands hosted the inaugural World Congress of Microwave Chemistry in 1992. This was the initial emergence of microwave chemistry. Following that, a large number of scientists conducted a wide variety of research in the fields of inorganic, organic, analytical, polymer, and catalytic chemistry, with a focus on the organic synthesis of applications for microwave technology.

5.2.3 Importance and Scope:

Microwave chemistry is limited to the use of microwaves in chemical reactions; hence, this research does not cover application areas that employ microwaves for other types of processes, such as industrial drying and heating. Practically speaking, only applications that heat materials using microwaves for chemical synthesis and analysis have been researched. The report includes an overview of the primary fields of use for microwave chemistry, as well as information on the market's size and composition, significant advancements in the field's research, and significant changes in intellectual property related to this field. This study provides a foundational understanding of microwave chemistry for individuals who wish to learn more. Researchers, managers of product development, industrial chemists, and undergraduate and graduate students studying chemistry could find it helpful.

5.2.4 Microwave Chemistry Apparatus:

The following are the two categories into which microwave chemistry apparatuses are classified:

A. Single-Mode Apparatus:

A single-mode apparatus is distinguished by its capacity to produce a standing wave pattern, which is the result of the interference of fields with identical amplitudes but distinct oscillation orientations. Through this interface, an array of nodes with zero microwave energy intensity and an array of antinodes with the maximum microwave energy magnitude are produced (Figure 5.2).

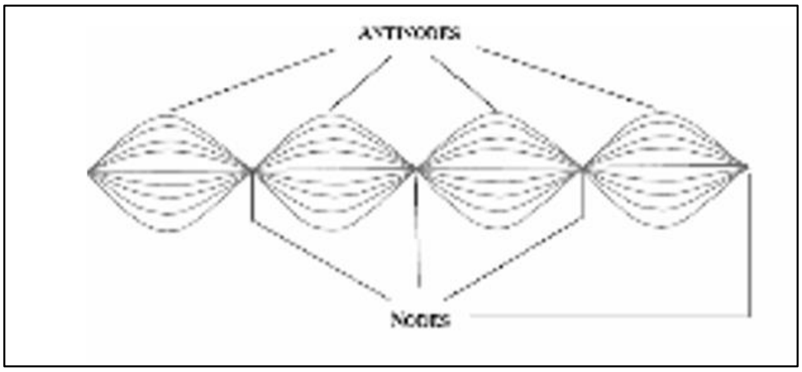


Figure 5.2: Generation of a Standing Wave Pattern1

The sample's distance from the magnetron determines how a single-mode equipment is designed. To guarantee that the sample is positioned at the antinodes of the standing electromagnetic wave pattern, this distance needs to be suitable. (Figure 5.3)

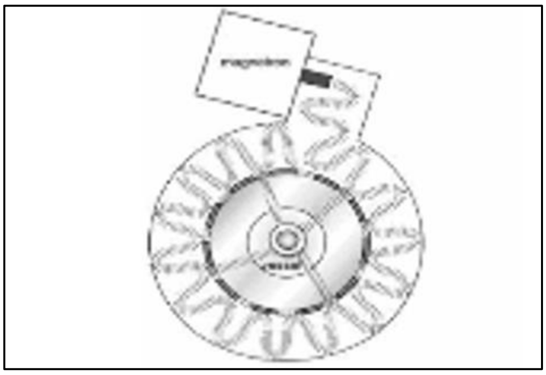


Figure 5.3: Single-Mode Heating Apparatus[10]

B. Multi-Mode Apparatus:

The intentional avoidance of creating a standing wave pattern inside a multi-mode equipment is a crucial component (Figure 5.4). The idea is to cause as much mayhem as you can within the device. The region inside the device that may effectively heat up grows with disorder because chaos causes radiation to disperse more widely. Because of this, a multi-mode microwave heating device can heat many samples at once, in contrast to a single-mode device that can only heat one sample at a time. This feature makes a multi-mode heating device useful for bulk heating and performing chemical analysis procedures like extraction, ashing, and others. In a large multi-mode apparatus, several liters of reaction mixture can be processed in both open and closed-vessel conditions. Recent research has resulted in the development of continuous-flow reactors for single- and multi-mode cavities that enabled the preparation of materials in kilograms. A major limitation of multi-mode apparatus is that heating samples cannot be controlled efficiently because of a lack of temperature uniformity.

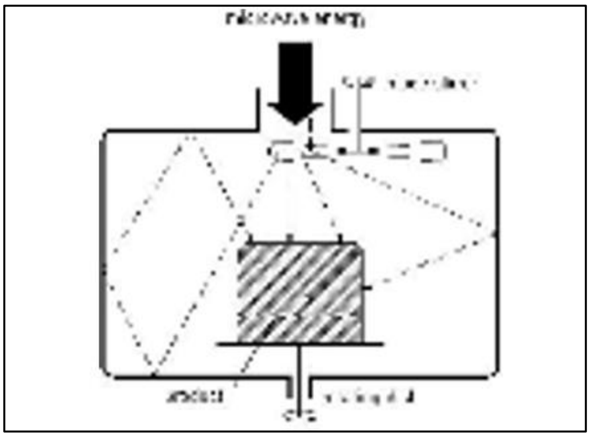


Figure 5.4: Multi-Mode Heating Apparatus [10]

5.2.5 Applications of Microwave Chemistry:

Microwave chemistry is applicable in various industries such as biotechnology, pharmaceuticals, petroleum, plastics, chemicals, etc. and major applications have been developed inthe field of analytical chemistry and chemical synthesis. Dueto the successful development of commercial instrumentation, microwave dielectric heating is now being increasingly applied in chemical reactions. However, most ofthese applications have been limited to small-scale use in laboratories and have not been extended to the production level. The major industrial applications of microwave chemistry can be segmented as:

A. Applications in Analytical Chemistry:

The various applications of microwave radiation in analyticalchemistry are:

- **Ashing:**

Ashing is a technique used in analytical laboratories to determine the ash level of a sample, as well as for process and quality control purposes. Microwave heating is widely utilized for ash removal in the petroleum and fuels, polymers, pharmaceutical, and food sectors. In most of these businesses, ashing is done using microwave-powered muffle furnaces designed expressly for laboratory usage.

- **Digestion:**

Samples are broken down into their most basic components for chemical analysis by the process of digestion. Analytical laboratories employ microwave digestion devices for sample preparation and breakdown. Unlike traditional open-vessel digestion, it entails heating microwave-absorbing reagents inside a pressurised, microwave-transparent container. Pressurisation speeds up the process of digestion and enables faster temperatures to be reached. The process of digestion at 175 °C takes around 100 times less time than it does at 95 °C due to the exponential acceleration of the reaction rate that occurs with rapid heating. Microwave radiation has now become the technology of choice for sample preparation trace and ultra-trace metalsanalysis and is being used in the digestion of even the toughestorganic or inorganic samples in diverse industries.

- **Extraction:**

The Soxhlet extraction process is more traditional than microwave extraction, which has shown to be less successful and efficient. One common method for extracting solvent continuously is the Soxhlet extraction. Routine solvent extractions of soils, sediments, sludge, pulp and paper, plastics and polymers, biological tissues, textiles, and food samples are carried out using extraction systems.

B. Applications in Chemical Synthesis:

Microwave radiation may be used to speed up chemical synthesis, which is one aspect of its application. Organic chemists can work more quickly, produce larger yields, and improve product purity via microwave-enhanced synthesis.

Furthermore, the yields of the tests have now been scaled up from milligrams to kilograms without the need to change reaction conditions, thanks to the availability of high-capacity microwave equipment.

a. Organic Synthesis:

Organic synthesis is the preparation of a desired organic compound from available starting materials. Microwave-assisted organic synthesis has been one of the mostresearched applications of microwaves in chemical reactions.

Chemists have successfully conducted a large range of organic reactions.

- Diels-Alder reaction
- Heck reaction.
- Suzuki reaction
- Mannich reaction
- Hydrogenation of [beta]-lactams
- Hydrolysis
- Dehydration
- Esterification
- Cycloaddition reaction
- Epoxidation
- Reductions
- Condensations
- Protection and deprotection

B. Inorganic Synthesis:

- **Synthesis of Organometallic and Coordination Compounds:**

The production of coordination and organometallic compounds which result from the creation of covalent bonds between organic molecules and metals has been successfully accelerated by microwave radiation.

- **Synthesis of Intercalation Compounds:**

Tests have recently been conducted on microwave chemistry applications for intercalation compounds. Compounds inserted between oxide and sulphide layers are called intercalation compounds, and they might be organic or organometallic. For example, the intercalation of pyridine or its derivatives is a slow and limited process that involves conventional heating techniques.

5.2.6 Application:

- **Organic Synthesis:** Many organic processes, including oxidations, coupling reactions, hydrogenation, and esterification, can be accelerated by microwave radiation. Comparing this acceleration to traditional heating techniques frequently results in quicker reaction times and higher product yields.
- **Peptide Synthesis:** The capacity of microwave-assisted peptide synthesis to quicken the coupling events necessary for the production of peptide bonds has led to its rise in popularity. For the synthesis of peptides with complicated sequences, this approach can be particularly helpful.
- **Materials Synthesis:** Metal-organic frameworks (MOFs) and ceramics, among other materials, may be quickly synthesized under microwave irradiation. Materials with the required morphologies and characteristics may be formed by the controlled heating process facilitated by microwaves.
- **Green Chemistry:** Due to its capacity to lower energy consumption, solvent usage, and reaction durations, microwave chemistry is sometimes seen as a more environmentally friendly alternative to traditional heating methods. This facilitates the creation of synthetic pathways that are less harmful to the environment and more sustainable.
- **Polymer Chemistry:** Polymerization processes may be accelerated by microwave irradiation, resulting in the quick production of polymers with precise molecular weights and topologies. This method is applied in the production of hydrogels and conducting polymers, among other functional polymers.
- **Biomolecule Modification:** It is possible to quickly and effectively modify biomolecules including peptides, proteins, and nucleic acids by using microwave irradiation. This method is applied in a variety of bioconjugation and labelling procedures for medicinal and diagnostic purposes.