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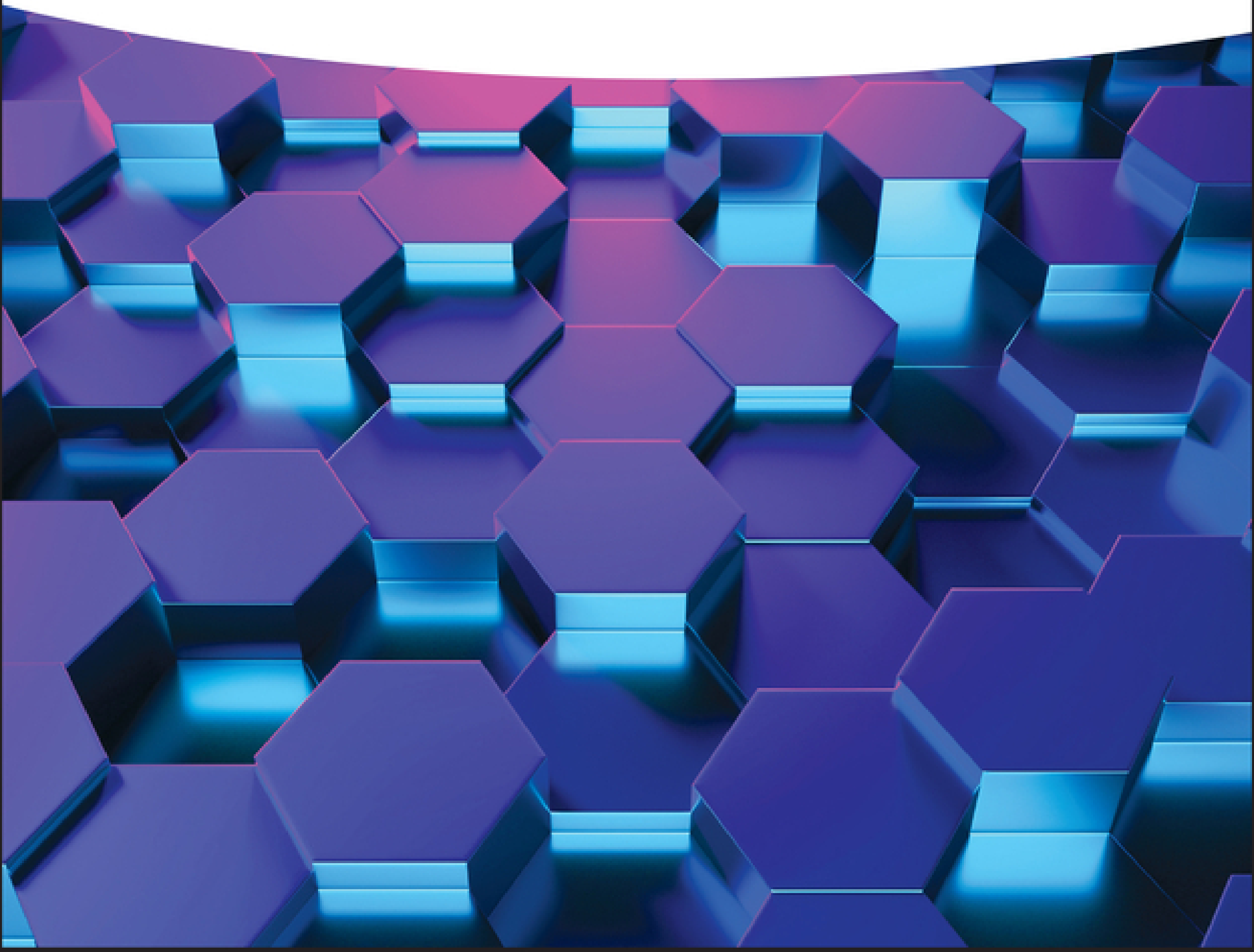
Jeenat Aslam

Organometallic Compounds

Synthesis, Reactions, and Applications



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Preface

The present edited book titled *Organometallic Compounds: Synthesis, Reactions, and Applications* discusses the basics, current trends, challenges, and future prospects, showing the value and scope of organometallic compounds toward current applications. This edited book will be carefully written to present a modern account of traditional methods and the latest details of recent advances in organometallic chemistry. The edited book will contain a traditional and logical approach in detail about introduction, nomenclature, synthesis methods, current applications, metallocenes, natural organometallic compounds, emerging role of organometallic compounds, F-block-based organometallic compounds, toxicity and applications of computational modeling for organometallic compounds. The book will be of significant interest to students of chemistry, pharmacy, biochemistry, and chemical engineering at the advanced undergraduate, graduate, and postgraduate levels, as well as academic and industry researchers who wish to familiarize themselves with the concepts and applications of organometallic chemistry. A book to wrap the developments in detailed synthetic reaction mechanisms and industrial applications is long overdue, and the present one will be a milestone in the field.

This will be the only book that provides chronological advancements of organometallic compounds (both synthetic and natural), their synthesis mechanisms, and recent industrial applications in the fields of material science, engineering, and science. The book will also serve as a valuable source for new learners about fundamentals, basics, reactions, catalytic mechanisms, and modern applications such as carbon dioxide fixation, reduction, gas adsorption and gas purification, drug delivery, renewable energy, and waste water treatment. It serves as a valuable reference for scientists, organochemists, biochemists, pharmacists, and engineers who are searching information on organometallic compounds, their current applications, toxicity, and computational modeling.

To confine the comprehensive description of organometallic compounds and to propose a rational and expressive design of the topic and a concentrated up-to-date reference, the book is divided into many chapters. Topics covered in Chapters 1–4 are fundamental aspects, nomenclature, classification properties, and synthesis methods of organometallic compounds. Chapter 5 explains the metal carbonyls' synthesis, properties, and structure. Chapter 6 covers metal-carbon multiple-bonded compounds. Chapter 7 describes the metallocenes' synthesis, properties, and structure. Chapter 8 explains σ-complexes, p-complexes, and

η_n-C_nR_n carbocyclic polyenes-based organometallic compounds. Chapter 9 covers the organometallic complexes of the lanthanoids and actinoids. Chapter 10 describes bio-organometallic chemistry. Chapter 11 explains the important reactions of organometallic compounds. Chapter 12 shows the characterization techniques of organometallic compounds. Chapter 13 discusses the organometallic compounds based on important reagents. Chapter 14 covers homogeneous and heterogeneous catalysis by organometallic complexes. Chapter 15 explains the cluster compounds boranes, heteroboranes, and metallaboranes. Chapter 16 covers the applications of organometallic compounds for carbon dioxide fixation, reduction, gas adsorption, and gas purification. Chapter 17 shows the emerging role of organometallic compounds for drug delivery, renewable energy, and waste water treatment. Chapter 18 explains the toxicity of organometallic compounds. Chapter 19 describes the computational approaches for some important organometallic catalysis reactions.

This book aims to deliver the recent evidences from fundamentals and synthesis to applications on organometallic compounds. The book will be intended for a very broad audience working in the fields of organic synthesis, environmental science and engineering, nanotechnology, energy, chemistry, etc. This book will be a valuable reference source for libraries in universities and industrial institutions, government and independent institutes, individual research groups, and scientists working in the field. Overall, this will be a valuable reference for government and non-government agencies, research scholars of the field, teachers and research supervisors, policy makers, organometallic-compounds-related industries, chemists and chemical engineers working in both R&D and academia who want to learn more on fundamental aspects of organometallic chemistry. The book will be a valuable source and guidebook for science (B. Sc. and M. Sc.), environmental science, pharmaceuticals, biomedical engineering, and engineering (B. Tech. and M. Tech.) students to learn the basics of recent evidences on the proposed title.

The editors and contributors of all chapters are well-known researchers, scientists, and experts from academia and industry.

On behalf of John Wiley & Sons, Inc., we thank all contributors for their exceptional and whole-hearted contribution. Invaluable thanks to Dr. Sakeena Quraishi (Associate Commissioning Editor), Miss Katherine Wong (Senior Managing Editor), and the Editorial Team at John Wiley & Sons, Inc. for their wholehearted support and help during this project. In the end, all appreciation to John Wiley & Sons, Inc. for publishing the book.

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1

Organometallic Compounds: The Fundamental Aspects

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1.1 Introduction

1.1.1 Organometallic Chemistry

The branch of chemistry deals with the study of molecules having a metal–carbon bond, in which a compound is said to be an organometallic compound when the metal–carbon bond in a molecule should be completely or partially covalent. Depending upon the elements in the periodic table, organometallic chemistry is mainly classified into main groups metal, transition metal, lanthanide, and actinide-based organometallics.

1.1.2 Organometallic Compounds

The organic compounds contain at least one metal–carbon bond in which metal is directly attached to the carbon atom in which there should be a bonding interaction (covalent, ionic, localized/delocalized) between the metal and the carbon atom are defined as organometallic compounds. The metals may be alkaline metals, alkaline earth metals, and metalloids (boron, silicon, arsenic, germanium, tellurium, and selenium). The bond present between the metal atom and the carbon is likely covalent in nature.

Examples: Organocadmium compounds, organoboron compounds, organozinc compounds, organomagnesium compounds, organolithium compounds, organolead compounds, and organotin compounds.

1.1.3 Structure of Organometallic Compound

The nature of the metal–carbon bond varies from ionic to covalent. The organometallic compounds have some effect on the nature of metal–carbon and these compounds have both organic and metal portions in which the metallic

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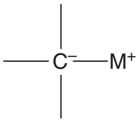


Figure 1.1 General representation of organometallic compound.

portion has greater importance. The electropositive nature of metal will be the ionic nature of the metal–carbon bond.

In organometallic compounds, the carbon is bonded to an electropositive atom, which has a negative charge, whereas the metal has a slightly positive charge; hence, the organometallic compounds having the organic part behave as nucleophilic or basic as shown in Figure 1.1.

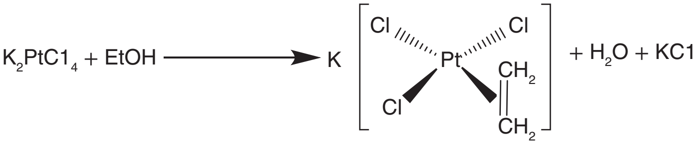
1.2 Milestones in Organometallic Compounds

In 1760, the first organometallic compound of the main group (Eq. (1.1)), cadet fuming liquid was discovered. In the Paris military pharmacy, a cadet discovered a fuming liquid while working on ink while preparing cobalt salt from cobalt minerals consisting of arsenic, which is called cacodyl(malodorous)oxide [1, 2].

$$As_2O_3 + 4CH_3COOK \longrightarrow [(CH_3)_2As]_2O \tag{1.1}$$

1.2.1 Equation (1.1): Synthesis of First Organometallic Compound

In 1827, W. C. Zeise, a Danish pharmacist, discovered the first organometallic compound with a transition metal called Zeise's, $K[PtCl_3C_2H_4]H_2O$. When K_2PtCl_4 was refluxed in ethanol, it resulted in the formation of Zeise's salt (Eq. (1.2)). It was characterized as the first organometallic olefin complex. Herein, they have used platinum because the Nobel metal complexes are stable toward air and moisture [3, 4].



(1.2)

1.2.2 Equation (1.2): Preparation of Zeise's Salt

In 1849, Edward Frankland prepared diethylzinc (a pyrophoric liquid), while trying to prepare an ethyl radical, he ended up with ethylzinc iodide (solid) and diethylzinc (liquid) [5, 6]. Whereas in 1852, he used sodium amalgam and methyl halide to prepare dimethyl mercury. Furthermore, many people have used R_2Hg and R_2Zn following an alkyl transfer reaction to prepare main group elements of organometallic compounds.

In the same year 1852, Schweizer and Lowig used an alloy of Na/Pb to prepare tetraethyllead (Eqs. (1.3) and (1.4)). In 1863, organochlorosilane was prepared by Friedel and Craft using alkylzinc as a reagent (Eq. (1.5)).

$$3C_2H_5I + 3Zn \longrightarrow (C_2H_5)_2Zn + C_2H_5ZnI + ZnI_2 \tag{1.3}$$

$$2CH_3X + 2Na/Hg \longrightarrow (CH_3)_2Hg + 2NaH \tag{1.4}$$

$$SiCl_4 + m/2\, ZnR_2 \longrightarrow RmSiCl_{4-m} + m/2\, ZnCl_2 \tag{1.5}$$

1.2.3 Equations (1.3)–(1.5): Preparation of Organochlorosilane Compound

In 1868, $[PtCl_2(CO)]_2$ the first metal carbonyl compound (Eq. (1.6)) was prepared by Schutzenberger [7].

$$PtCl_2 + CO \longrightarrow [PtCl_2(CO)]_2 + \text{cis } PtCl_2(CO)_2 \tag{1.6}$$

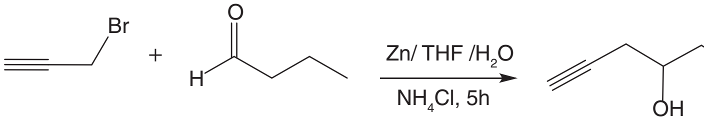
1.2.4 Equation (1.6): Synthesis of First Metal Carbonyl Compound

In 1890, Ludwig Mond prepared the first binary metal carbonyl $Ni(CO)_4$ (Eq. (1.7)), which is used for the refining of nickel [8–10].

$$Ni + 4CO \xrightarrow{1\text{ bar},25^\circ C} Ni(CO)_4 \tag{1.7}$$

1.2.5 Equation (1.7): Synthesis of First Binary Metal Carbonyl Complex

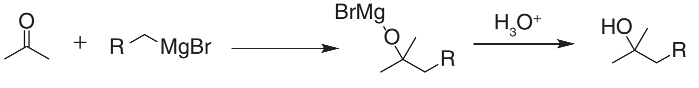
In 1899, the Philippe Barbier, Grignard's teacher introduced Barbier reaction (Eq. (1.8)). It was a one pot reaction carried out in the presence of water. Compared to Grignard reaction this is less versatile.



(1.8)

1.2.6 Equation (1.8): Barbier Reaction

Whereas in 1900, in RMgX, Zn was replaced by Mg in Barbier by Grignard and called as Grignard reagent (Eq. (1.9)). This reagent is more versatile than the Barbier reaction and has more applications compared to organozinc reagents [11].



(1.9)

1.2.7 Equation (1.9): Synthesis of Organic Compound Using a Grignard Reagent

In 1912, P. Sabatier and V. Grignard were awarded the Nobel Prize for Grignard reagent, and they followed Sabatier's method for the hydrogenation by using metal powders.

In 1917, the first alkyllithium derivatives (Eqs. (1.10) and (1.11)) were prepared by Wilhelm Schlenk, and he followed the transalkylation of organomercury compounds. Whereas the synthetic strategies of lithium derivatives replace the Grignard reagent as the primary anionic intermediate (1.10).

$$2\mathrm{Li} + \mathrm{R_2Hg} \longrightarrow 2\mathrm{RLi} + \mathrm{Hg} \tag{1.10}$$

$$2\mathrm{EtLi} + \mathrm{Me_2Hg} \longrightarrow 2\mathrm{MeLi} + \mathrm{Et_2Hg} \tag{1.11}$$

1.2.8 Equations (1.10) and (1.11): Synthesis of Alkyllithium Compound

In 1921, Thomas Midgley introduced tetraethyllead as an additive in gasoline while working on GE motors [12].

In 1930, K. Ziegler prepared organolithium compounds (Eqs. (1.12) and (1.13)) by a simple synthetic procedure and, furthermore, fine-tuned by Gilman. Later on, this compound was widely used.

$$2\mathrm{Li} + \mathrm{PhCH_2OMe} \longrightarrow \mathrm{PhCH_2Li} + \mathrm{MeOLi} \tag{1.12}$$

$$\mathrm{RX} + 2\mathrm{Li} \longrightarrow \mathrm{RLi} + \mathrm{LiX} \tag{1.13}$$

1.2.9 Equations (1.12) and (1.13): Synthesis of Organolithium Compound

In 1938, hydroformylation (Eq. (1.14)) was discovered by Otto Roelen, for the first time in homogeneous catalysis an organometallic compound has been used [13, 14].

(1.14)

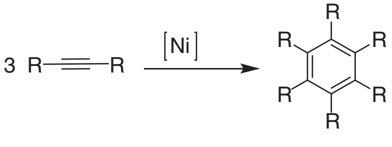
1.2.10 Equation (1.14): Hydroformylation Reaction

In 1943, direct synthesis of organochlorosilane (Eq. (1.15)) was discovered by E G Rochow, further it initiated for large scale production of silicones [15].

$$2\mathrm{CH_3Cl} + \mathrm{Si(Cu)} \longrightarrow \mathrm{(CH_3)_2SiCl_2} \tag{1.15}$$

1.2.11 Equation (1.15): Synthesis of Organochlorosilane Compound

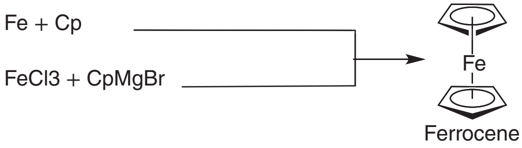
In 1948, acetylene trimerization (Eq. (1.16)), which was catalyzed by nickel was discovered by W. Reppe [16].



(1.16)

1.2.12 Equation (1.16): Trimerization of Acetylene

In 1951, the sigma bonded structure of ferrocene (Eq. (1.17)) was suggested and independently prepared by two groups. Fischer, Woodward, and Wilkinson proposed the sandwich structure of ferrocene [17].



(1.17)

1.2.13 Equation (1.17): Synthesis of Ferrocene

In 1955, W. Hafner and E. O. Fischer followed rational synthesis to prepare bis (benzene)chromium (Figure 1.2), even though in 1919 same reaction was carried by F. Hein with $CrCl_3$ and PhMgBr [18, 19].

In 1955, G Natta and K Ziegler used a mixed metal catalyst to develop olefin polymerization at lower pressure.

In 1959, the stabilization of cyclobutadiene was done by complexation in $[(C_4Me_4)NiCl_2]_2$.

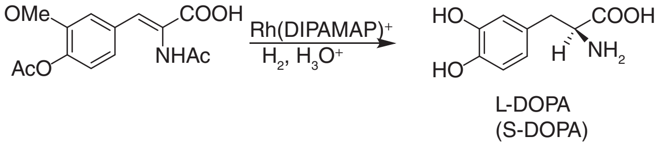
In 1961, Vaska's complex was discovered, which binds reversibly to O_2 trance $IrCl(CO)(PPh_3)_2$ [20].

In 1963, Ziegler and Natta both were awarded Nobel prize for Ziegler Natta catalyst.

In 1964, the first carbene complex with metal W (tungsten) (Figure 1.3) by E. O. Fischer [21].

In 1965, Coffey and Wilkinson, for hydrogenation of alkenes, they have used $(PPh_3)_3RhCl$ as a homogeneous catalyst [22].

In 1968, asymmetric catalysis (Eq. (1.18)) was discovered by William S. Knowles, the achiral substrates can be converted into chiral products with the help of complexes consisting of ligands that are chiral with high enantiomers [23].



(1.18)

1.2.14 Equation (1.18): Asymmetric Catalysis Reaction

In 1972, T Mizorki and R. F. Heck discovered the substitution reaction of aryl halides with vinylic hydrogen atom a palladium based catalysis reaction [24].

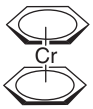


Figure 1.2 Bis(benzene)chromium compound.

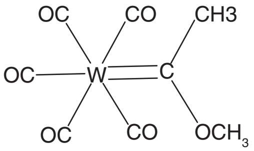


Figure 1.3 First carbene complex with tungsten.

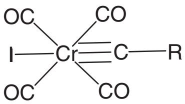


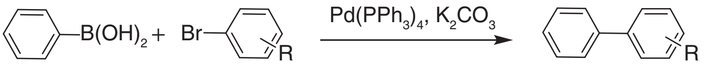
Figure 1.4 First chromium carbene complex.

In 1973, the first Chromium carbene complex (Figure 1.4) was prepared by E. O. Fischer. In the same year G. Wilkinson and E. O. Fischer were awarded Nobel Prize for working on metal sandwich compound [25].

In 1976, M. F. Lappert prepared first double bonded compound tin–tin using dimetallenes first main group element [26].

$$[(Me_3Si)_2CH]_2Sn = Sn[CH(SiMe_3)_2]_2$$

In 1979, the first paper on palladium catalyzed Suzuki coupling reaction (Eq. (1.19)) of aryl boronic acids was published by Suzuki and Miyaura [27].



(1.19)

1.2.15 Equation (1.19): Palladium Catalyzed Suzuki Coupling Reaction

In 1980, the zirconocene-based catalyst (Figure 1.5a,b) was prepared by Walter Kaminsky only for syndiotactic and isotactic polypropylene.

In 1981, the compound having Si=Si (silicon–silicon double bond) was prepared by Robert West [28].

$$(1{,}3{,}5 - Me_3C_6H_2)_4Si_2$$

In 1990, for olefin metathesis, a molybdenum-based catalyst (Figure 1.6) was discovered by Richard Schrock [29].

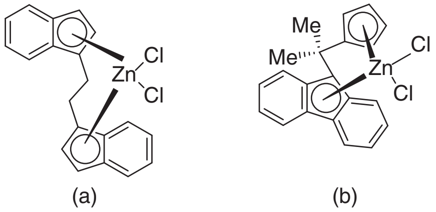


Figure 1.5 Zirconocene-based catalyst.