1

Organometallic Compounds: The Fundamental Aspects

Geetha B. Markandeya and Srinivasa Budagumpi

Jain University, Centre for Nano and Material Sciences, Jain Global Campus, 45 km, NH – 209,
Jakkasandra Post, Kanakapura Taluk, Ramanagaram 562112, Bangalore, Karnataka, India

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

Organometallic Compounds: Synthesis, Reactions, and Applications, First Edition.
Edited by Dakeshwar Kumar Verma and Jeenat Aslam.

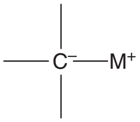


Figure 1.1 General representation of organometallic compound.

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.

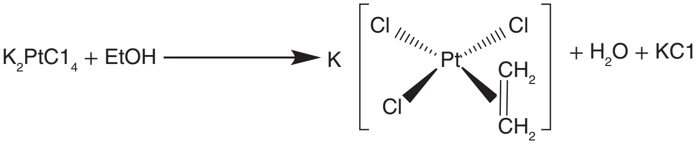
1.2 Milestones in Organometallic Compounds

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].

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

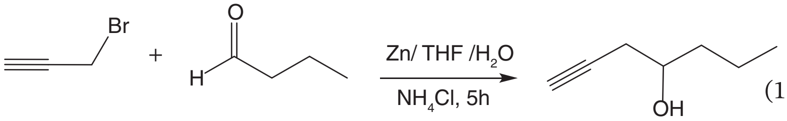
1.2.4 Equation (1.6): Synthesis of First Metal Carbonyl Compound

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

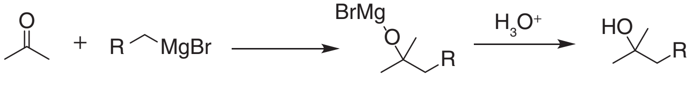
In 1899, the Philippe Barbier, Grignard's teacher introduced Barbier reaction (Eq. (1.8)). It was a one pot reaction carried out in the presence of water. Compared to Grignard reaction this is less versatile.



(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].

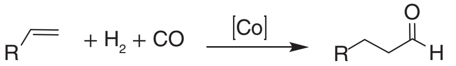
In 1930, K. Ziegler prepared organolithium compounds (Eqs. (1.12) and (1.13)) by a simple synthetic procedure and, furthermore, fine-tuned by Gilman. Later on, this compound was widely used.

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

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

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)

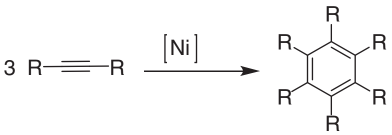
1.2.10 Equation (1.14): Hydroformylation Reaction

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

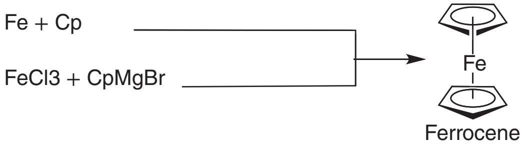
In 1948, acetylene trimerization (Eq. (1.16)), which was catalyzed by nickel was discovered by W. Reppe [16].



(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 $[(C_4Me_4)NiCl_2]_2$.

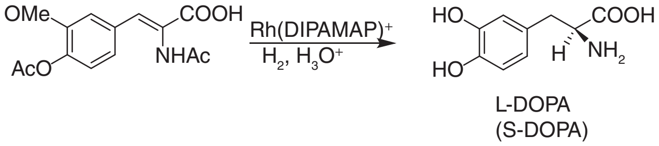
In 1961, Vaska's complex was discovered, which binds reversibly to O_2 trance $IrCl(CO)(PPh_3)_2$ [20].

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].

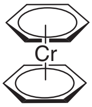


Figure 1.2 Bis(benzene)chromium compound.

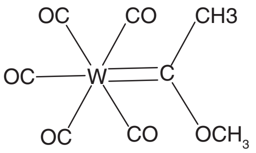


Figure 1.3 First carbene complex with tungsten.

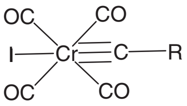


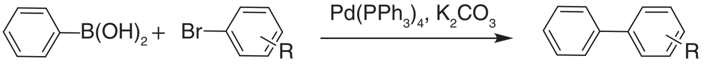
Figure 1.4 First chromium carbene complex.

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].

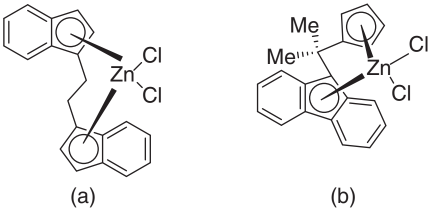


Figure 1.5 Zirconocene-based catalyst.

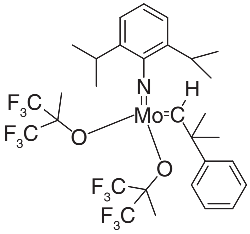


Figure 1.6 Molybdenum-based catalyst.

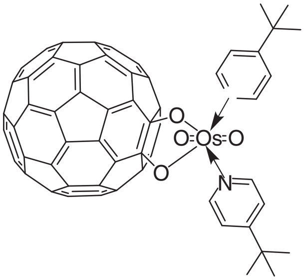


Figure 1.7 Fullerene-based organometallic compound.

In 1991, the fullerene-based organometallic compound (Figure 1.7) was made by J. M. Hawkins, which is also the derivative of structurally characterized fullerene $C_{60}(OsO_4)(4\text{-}t\text{-BuPy})_2$. Furthermore, the organometallic compounds with η^2-bonding directly with metal–carbon bonds were discovered [30].

In 1995, the olefin metathesis catalyst, also called first-generation Grubbs catalyst (Figure 1.8), was prepared by Robert Grubbs [31].

In 1997, the organometallic compound having C atom as a ligand was showed by C C Cummins $[(R_2N)_3MoC]^-$. In the same year G. M. Robinson prepared the salt of sodium $Na_2[ArGaGaAr]$ and postulated [32, 33].

$$\mathrm{Ga} \equiv \mathrm{Ga}$$

In 2001, for asymmetric hydrogenation, W. S. Knowles, K. B. Sharpless, and R. Noyori received Nobel Prize.

In 2002, the molecular hybrids of fullerene and ferrocene together called bucky ferrocene (Eq. (1.20)) was prepared by E. Nakamura by treating $[FeCp(CO)_2]_2$ with $C_{70}HMe_3$ or $C_{60}HMe_5$ [34].

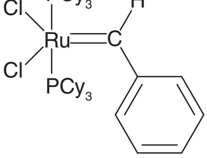
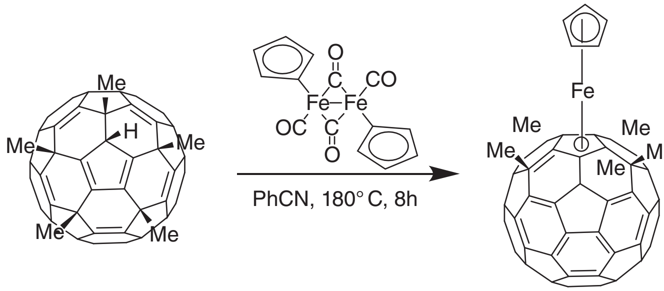


Figure 1.8 First generation Grubbs catalyst.



(1.20)

1.2.16 Equation (1.20): Synthesis of Bucky Ferrocene

In 2004, the preparation and structural characterization of first Si–Si (Figure 1.9, Si—Si triple bonded) molecule was done by A. Sekiguchi [35].

In the same year 2004, the first zinc organometallic compound $Zn_2(Cp)_2$ was prepared by E Carmona [36].

In 2005, for olefin metathesis R. R. Schrock, Y. Chauvin, and R. H. Grubbs, received Nobel Prize. In the same year, the first stable organometallic compound with quintuple bond was prepared by P. Power [37].

In 2006, hexaferrocenylbenzene (Figure 1.10) was prepared by P. C. Vollhardt [38].

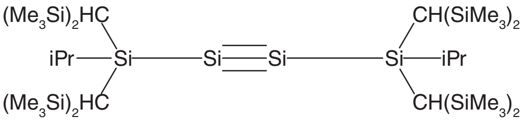


Figure 1.9 First Si compound.

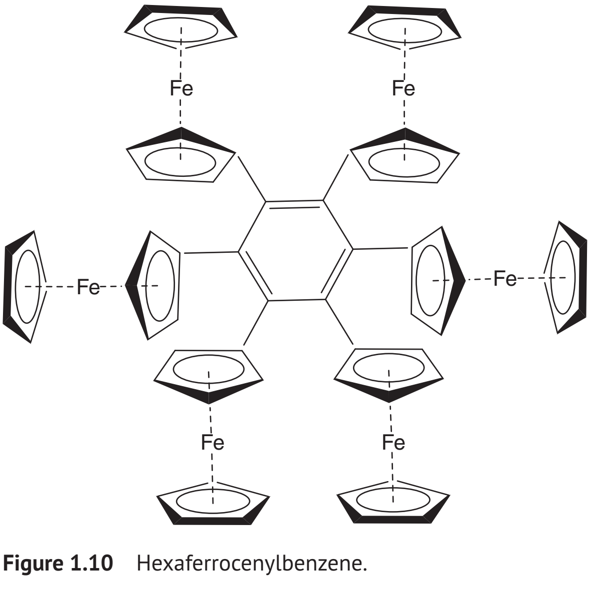


Figure 1.10 Hexaferrocenylbenzene.

1.3 Stability of Organometallic Compounds

The oxidation of the organometallic compounds will plays a vital role in the stability of the compounds, whereas the organometallic compounds are thermally unstable due to the negative free energy of carbon dioxide, metal oxide, and water production. In addition to that, at lower room temperatures, the organometallic compounds are unstable to oxidation due to the presence of empty orbitals of metal or due to non-bonding electrons [39].

The hydrolysis of organometallic compounds will also affect the stability of compounds

1. Hydrolysis involves the reaction of nucleophilic attack of water.
2. The rate of hydrolysis is determined by the polarity of the metal–carbon bond, the higher the polarity of the metal–carbon bond, the faster will be the rate of hydrolysis.

1.4 Properties of Organometallic Compounds

1. Most organometallic compounds with aromatic and hydrocarbon groups are solid.
2. The metal–carbon bond is covalent.
3. Organometallic compounds with metals such as lithium and sodium are volatile and burn spontaneously.
4. Organometallic compounds having electropositive metals behave as reducing agents.
5. Organometallic compounds are toxic to human beings in most cases.
6. Organometallic compounds have low melting point.
7. Organometallic compounds are soluble in ether, whereas insoluble in water.
8. Organometallic compounds are very reactive compounds.
9. The electronegativity of carbon in organometallic compound is 2.5 and for metals the electronegativity is below 2.0.
10. Many organometallic compounds occur in solid state, particularly the compounds having hydrocarbons and aromatic groups. Few of organometallic compounds are liquids and gases.

1.5 Basic Concepts in Organometallic Compounds

(1) 18-electron rule
(2) Π – back bonding or back donation
(3) Hapticity

1.5.1 18-Electron Rule

The structure and bonding present in the organometallic compound are studied based on the 18-electron rule and this is the combination of the ability of the ligand for pi acceptor or sigma donor and the back bonding and bonding nature of the ligand. In addition to that, the stability of the metal complexes is predicted and characterized by the 18-electron rule. A total of 18 electrons are present in the valence shell of MT, whereas a total of 10 electrons in the d orbital (2 each from five d orbitals), 6 electrons from the p orbital (2 each from three p orbitals) and 2 electrons from 1 s orbital. The combination of these atomic orbitals (5d+3p+1s) results in 9 molecular orbitals. These 9 molecular orbitals are metal–ligand non–bonding or bonding orbitals, and there might be a few higher energy antibonding molecular orbitals. These 9 molecular orbitals are filled by electrons originating from ligand or metal [39].

1.5.1.1 Statement of 18 Electron Rule

Thermodynamically stable transition metal organometallic compounds are formed when the sum of the metal d electrons and the electrons conventionally considered as being supplied by the surrounding ligands equals 18. In this way, the metal attains the electronic configuration of the next higher Nobel gas in general ns2 (n−1)d10 np6. It is also called the EAN (effective atomic number) rule or inert gas rule [39].

The presence or absence of a metal–metal bond and the stability of the complex can be determined by counting the number of electrons surrounded in the outer shell of the metal atom in the complex.

Two methods were used for counting the electrons

1. Neutral atom counting method–it is difficult for organometallic compounds because it doesn't require oxidation state assignment
2. Oxidation state/ionic counting method in this method a change in the oxidation state of the metal is required.

In 1921, Irwing Langmuir formulated the 18-electron rule and derived the equation.

$$V_c = s - e$$

where

V_c = number of shared electrons in a metal complex or compound.
s = number of electrons for the completion of the valence shell.
e = number of valence electrons in an isolated atom.

In organic chemistry, the compounds have to obey the octet rule, the value of s is 8.

$$V_c = 8 - e$$

For Example, NH_3, $3 = 8-5$

In organometallic complexes, such as transition metal carbonyls, the value of s is 18.

$$V_c = 18 - \mathrm{e}$$

Example, $Ni(CO)_4$, $8 = 18-10$, $Cr(CO)_6$, $12 = 18-6$

1.5.1.2 Examples

(1) $TiCl_4$

Electronic configuration: $3s^2 3p^6 3d^2 4s^2$

By neutral counting method: for Ti 4 electron, for Cl 1 electron:

$$TiCl_4 : 4 + 4(1) = 8 \text{ valence electrons.}$$

By oxidation/ionic counting method: for Ti^{4+} 0 electron, for Cl 2 electron

$$TiCl_4 : 0 + 4(2) = 8 \text{ valence electrons.}$$

$TiCl_4$ is having only 8 electrons, but it should be 18 electrons to satisfy 18- electron rule. $TiCl_4$ will act as good Lewis acid and it reacts with alcohol, water and amines.

(2) $Fe(CO)_5$

Electronic configuration: $3s^2 3p^6 3d^6 4s^2$

By neutral counting method: for Fe 8 electron, for CO 2 electron:

$$Fe(CO)_5 : 8 + 2(5) = 8 + 10 = 18 \text{ valence electrons.}$$

By oxidation/ionic counting method: in this case all the fragments are neutral in nature.

This is a stable compound with 18-electron complex.

(3) $Fe(C_5H_5)_2$ or $FeCp_2$

Electronic configuration: $3s^2 3p^6 3d^6 4s^2$

By neutral counting method: for Fe 8 electron, for C_5H_5 2 electron:

$$Fe(C_5H_5)_2 : 8 + 2(5) = 8 + 10 = 18 \text{ valence electrons.}$$

By oxidation/ionic counting method: for Fe^{2+} 6 electron, for C_5H_5 2(6) = 12 electron

$$Fe(C_5H_5)_2 : 6 + 12 = 18 \text{ electrons}$$

This is a stable compound with 18-electron complexes.

(4) $[CpFe(CO)_2]_2$

Neutral counting method

$$\text{Cp } 5 + \text{Fe } 8 + 2\text{CO } 4 + \text{Fe—Fe } 1 = 18$$

Electrons were counted for only one iron center since the other iron will contribute one electron.

(5) $CpFe(CH_3)(CO)_2$

Neutral counting method

$$\text{Cp } 5 + \text{Fe } 8 + CH_3 1 + 2\text{ CO } 4 = 18$$

(6) $Fe_2(CO)_9$

Neutral counting method

$$3\text{CO } 6 + 3 - \text{CO } 3 + \text{Fe } 8 + \text{Fe—Fe } 1 = 18$$

1.5.2 Π –Back Bonding or Back Donation

When electrons move from one atomic orbital to another anti–bonding orbital π* of a ligand or atom in the process relieves the metal that has an excess negative charge.

Example: Zeise's salt, $Ni(CO)_4$.

1.5.3 Hapticity η^x

The term hapticity is defined as total number of donor atoms of a ligand that are coordinated (attached) to the central metal atom (it is also defined as how a contiguous group of atoms of a ligand, which are coordinated to the central metal atom).

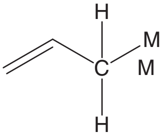
Hapticity is denoted by a Greek word η^x.
Where, x – number of donor atoms attached to the metal.

1.6 Hapticity of Ligands

Ligands are an atom or group of atoms, ions, or molecules that are capable of donating a pair of electrons to the metal atom and are called ligands.

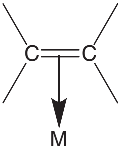
The hapticity of ligands ranges from 1 to 8 that is monohapto ligands to octohapto ligands.

(1) Monohapto ligands η^1: these are the ligands joined with one atom and it has the capacity to donate one electron (1 electron donor ligands).
Examples: Alkyl groups($-CH_3$) ($M-CH_3$), Aryl($-C_6H_5$), Alkenyl($M-CR=CR_2$) (where R_2-alkyl)



$\eta^x = \eta^1$ number of donor atoms.

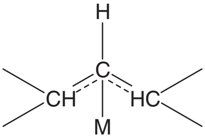
(2) Dihapto ligands η^2: Two ligands atoms are directly bonded to metal (2 electron donor ligands).
Examples: Alkenes ($=CH_2=CH_2=$), Zeise's salt($K[PtCl_3C_2H_4]H_2O$)



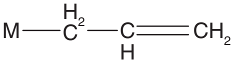
(3) Trihapto ligands η^3: three atoms of the ligands are directly bonded to metal atom (three-electron donor). There are two types of complexes, π-allyl complexes and σ-allyl complexes.

$\eta^x = \eta^3$ number of donor atoms.

π-allyl complexes: when π-bond will be delocalized around all the three carbon atoms time to time. The π-allyl complexes are 3 electron donor complexes.



σ-allyl complexes: when metal is directly attached to one carbon atom of the ligand.

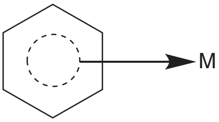


$M{-}\overset{H_2}{C}{-}\underset{H}{C}{=}CH_2$

(4) Tetrahapto ligands η^4: these are the ligands joined with four atoms and it has the capacity to donate 4 electrons.
Example: Cyclobutadiene it has delocalized electron around all the four–carbon atom.

(5) Pentahapto ligands η^5: these are the ligands joined with five atoms and it has the capacity to donate 5 electrons.
Example: Ferrocene bis[η^5-cyclopentadienyl]iron

(6) Hexahapto ligands η^6: these are the ligands joined with six atoms and it has the capacity to donate 6 electrons.
Example: benzene



(7) Heptahapto ligands η^7: these are the ligands joined with seven atoms and it has the capacity to donate 7 electrons.

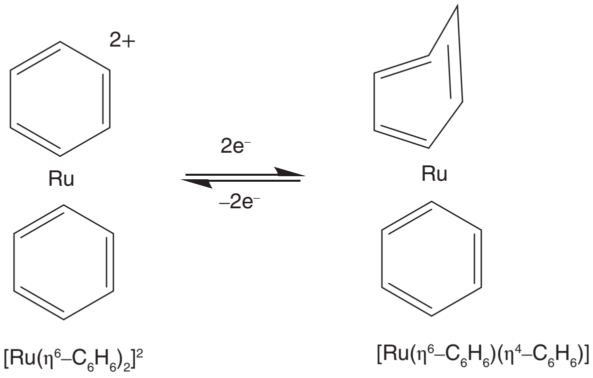
(8) Octahapto ligands η^8: these are the ligands joined with eight atoms and it has the capacity to donate 8 electrons.
Example: Uranocene-bis(η^8-1,3,5,7-cyclooctatetraene)uranium.

1.7 Change in Hapticity

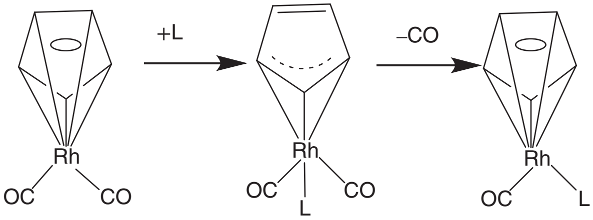
During the course of the reaction the hapticity of the ligand changes (Schemes 1.1 and 1.2).

The η^5-Cp changes to η^3-Cp, by making room on the metal where one molecule of CO is removed and ligand L is donating extra two more electrons.

- The hapticity will changes the electron count.
- Hapticity will change for dienes, indenyl and it will change for cyclopentadienyl for some time.



Scheme 1.1 Change in hapticity in Ru compound.



Scheme 1.2 Change in hapticity in Rh compound.

- Hapticity does not change the oxidation state.
- It makes a path for a system "giving room" for other reactions or it will avoid electron counts above 18 electron.

1.8 Hapticity Verses Denticity

Table 1.1 Differences between hapticity verses denticity[40].

Hapticity	**Denticity**
• Hapticity refers to how a contiguous group of atoms of a ligand is coordinated to the central metal atom • It is denoted by η. • The contiguous atoms are involved in the coordination process. • Ferrocene where the iron(Fe) is sandwiched between two hydrocarbon rings.	• Denticity refers to the number of donor atoms in the same ligand that binds to the central metal atom in the coordination complex. • It is denoted by k. • The donor atoms will attach to the central metal atom. • EDTA coordinated to central metal atom through six atoms two nitrogen and the other four oxygen.

1.9 Counting of Electrons and Finding out Metal–Metal Bonds

Metal carbonyl clusters are the compounds that contain metal in the lower oxidation state, these compounds also consist of metal–metal bonds. The larger and structurally complex clusters come under this category. The total number of metal–metal bonds and the number of bonds present in one metal to the other metal in a complex cluster can be determined by following the procedure and this holds good for the complexes with nuclearity ≤ 4. The electronic structure of the complex can be understood by the bond between the metal atoms, whereas each metal atom has to attain 18 electronic configurations [39].

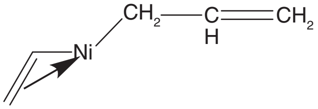
1.9.1 Calculating the Number of Metal–Metal Bonds

1. First, find out the total number of valence electrons in the molecule and consider it as X.
2. Let us consider an equation, Y = (nX8)-X, where "n" is the number of metals present in the complex.
   - i) Y/2 is the number of metal–metal bonds present in the complex.
   - ii) X/2 is the number of electrons per metal. If the number of electrons is equal to 18, that shows there is no metal–metal is present. If the number of electrons is equal to 17, it shows one metal–metal bond is present. If the number of electrons is equal to 16, two metal–metal bonds are present.

1.9.2 Writing the Probable Structure of Compound

1. The first step is to write the metal core(center)
2. The ligands and metal carbonyls can be arranged to the metal core in which the metal core has to satisfy the 18-electron rule, additionally the carbonyl group has to occupy either a bridged or terminal position.

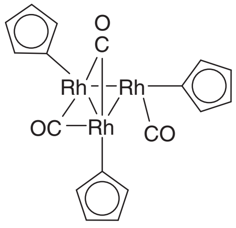
1.9.3 How to Draw the Probable Structure of Ni(η^1-C_3H_5) (η^3-C_3H_5)



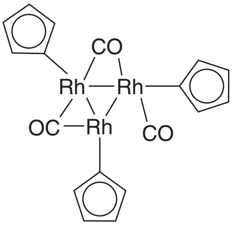
1.9.4 How to Draw the Probable Structure of (μ-CO)-[η^5-CpRh]$_3$(CO)

Total valence electron = 4 + [(6 + 8)X3] + 2 = 48
The number of metal–metal bond = (3X8)–48 = 6/2 = 3
Number of bonds per metal center = 2 (48/3 = 16)

1 and 2 are the plausible structure of (μ-CO)-[η^5-CpRh]$_3$(CO). Among 1 and 2 structures, 1 is proper, whereas, in structure 2, the electron count on metal 3Rh is found to be 17, 18, and 19e$^-$, but it should be 16.



1



2

The 18e$^-$ rule is not applicable for all the f–block elements, there are exceptions to transition metal organometallics. The 18e$^-$ rule for organo–transition metal compounds can be explained by various physical and chemical properties.

From 18e$^-$ rule, one can predict the total number of ligands coordinated to a particular metal and also the reactivity/stability of the complex. This method holds good for the metals having low valency and also with the small ligands that are strong sigma donors and π–acceptors. The ligands are small enough that allow metal that coordinates saturated and that give more ligand field splitting value. 18e$^-$ are required to fill the dπ orbitals similar to the octet rule. There are some exceptions to 18e$^-$ rule also few of them are mentioned below.

1. Metals having d^8 electrons: the metals having d^8 electrons have the tendency to form a square planar complex with 16e$^-$ this tendency is strong for the groups 9, 10, and 11 except for higher energy orbitals $d_{x2\text{-}y2}$. The d^8 metals have a square planar complex with 16e$^-$ have a completely filled orbital.
2. Metals having d^0 electrons: the d^0 complexes formed by high valency have a less electron count than 18. Also, the complexes having sterically demanding bulky ligands as substitution force the complexes to have less than 18 electrons.
3. When the size is considered the organometallic clusters with moderate to big size fails to obey 18e$^-$ rule while bonding. Therefore, the stability and bonding of organometallic clusters are considered on the electron counting rule, not on the 18e$^-$ rule.
4. This rule is not applicable for organometallic compounds of lanthanides, actinides, and main group metals.

1.10 Metals of Organometallic Compounds

As we discussed above organometallic compounds are the substances having at least one metal–carbon bond, where the carbon is directly attached to carbon atom, in which the carbon atom is found to be a part of organic group. Organometallic compounds play an important role as catalysts and also act as intermediates. One such example is ferrocene, where the iron(Fe) is sandwiched between two hydrocarbon rings.

The metals of organometallic compounds are discussed as transition metals or main group compounds. It includes s-block elements (group 1 and 2), p-block elements (group 13–15) transition metals of d and f block elements (group 3–12) [39].

1.10.1 Organometallic Compounds of Transition Metals

- (n-1)d, ns and np orbitals are the valence orbitals for transition metals.
- When (n-1)d, ns and np orbitals occupy partially, it gives the electron-donating and electron-accepting property for transition metals.
- It forms different multiple bonds between metal–metal with or without an bridging ligand.
- It has the capacity to vary the coordination number.

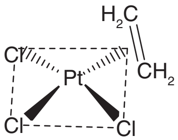
1.10.2 The Bonding and Structure in Different Metal complexes [37]

(1) Alkene complexes
(2) Allyl complexes
(3) Carbonyl complexes
(4) Metallocene
(5) Dihydrogen complexes
(6) Transition metal carbene complexes

1.10.2.1 Alkene Complexes

- In alkene complexes, the bond between the alkene and transition metal will activate the ligand, either to nucleophilic or electrophilic attack, and that will be decided by the nature and charge of metal center.
- If σ-donation is greater to metal center, π-back donation is also greater.
- If the electron density of alkene complex is greater due to back donation of π* orbital, the reduction in C=C bond order will be greater.
- The stability of alkene complexes that are substituted is less when compared to ethylene complexes.

  Example: Zeise's salt.



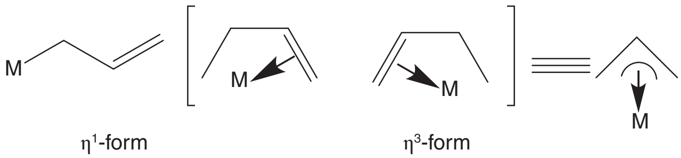
1.10.2.2 Allyl Complexes

The ligands in allyl complexes are ambidentate, which can bind to both trihapto and monohapto form (Scheme 1.3).

1.10.2.3 Carbonyl Complexes

These complexes have (carbon monoxide) CO as coordinating ligand. These complexes have synergistic bonding. Greater the sigma donation given by carbonyl complexes, stronger will be the π-back donation.

Examples: $Ni(CO)_4$, $Co(CO)_4$



Scheme 1.3 Hapticity in allyl complexes.

1.10.2.4 Metallocenes

The compounds have two cyclopentadienyls (Cp) anions that bind to a metal with an oxidation state of two (II). They are also known as "sandwich compounds". Metallocene derivatives with two Cp ring like Cp_2TiCl_2 are known as "bent metallocene". The complex with one Cp ring is known as a "half sandwich," which has the geometry of three-legged piano stool (Figure 1.11).

1.10.2.5 Dihydrogen Complexes

The transition metal complexes having molecular hydrogen that donates two electrons to central metal atom (Figure 1.12).

1.10.2.6 Transition Metal Carbene Complex

The organometallic compounds with transition metals bear a divalent carbene carbon as a ligand. Carbenes are specific species that contain a neutral carbon atom with valence electrons in which two electrons are nonbonding in nature and they are highly reactive neutral species with a divalent carbon atom. The two nonbonding electrons of the carbene carbon can exist in two states singlet and triplet. In the singlet state, the two unshared electrons are paired in the same σ and π-orbitals, whereas in the triplet state two unshared electrons in two different orbitals (Figure 1.13).

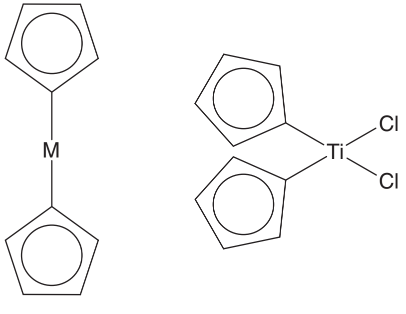


Figure 1.11 Metallocene compounds.

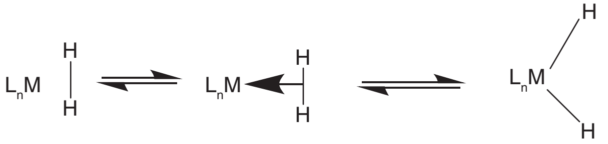


Figure 1.12 Dihydrogen complexes.

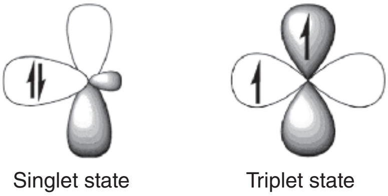


Figure 1.13 Singlet and triplet state carbene complex.

1.11 Importance of Organometallic Compounds

Most organometallic compounds are used for synthesis purposes because bond polarity made them highly reactive.

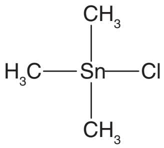
(1) The Grignard reagent (R-Mg-X) organomagnesium halides are used in organic synthesis for organoboron and organolithium compounds.
(2) Alkylaluminium compounds are used for organic synthetic purposes.
(3) When an organometallic compound is used with titanium salts can act as a catalyst for the polymerization of ethylene and propylene that is unsaturated hydrocarbons.
(4) The organometallic compounds of tin, mercury, and lead are used for commercial purposes.
For example, organotin compounds are used as pesticides, pharmaceuticals, and stabilizers for polyvinylchloride (PVC) and also, they are used as fire retardants.
(5) Metal carbonyls are used as catalysts in most reactions such as in the petrochemical industry.

1.11.1 Types of Organometallic Compounds

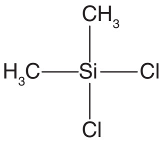
Depending upon the nature of the metal–carbon bond, these organometallic compounds are classified into four types.

1. Ionic bonded compounds
2. σ–σ bonded compounds
3. π–π bonded compounds
4. Multicenter bonded compounds
5. Ionic bonded compounds: The elements of lanthanides, actinides, alkaline metals, and alkaline earth metals will form ionic bonded organometallic compounds. These are colorless solid salts that are insoluble in nonpolar solvents and upon hydrolysis liberate hydrocarbons which also act as electrolytes.
6. σ–σ bonded compounds: The metal atom and carbon atom will form σ/covalent. Generally, the metals/nonmetals with less/weak electropositive atoms will form this type of compound. The pair of electrons are shared by a metal atom and carbon atom to form a σ–σ bond.

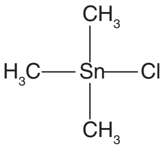
Examples:



$H_3C-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$



$H_3C-\overset{CH_3}{\underset{Cl}{Si}}-Cl$



$H_3C-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$

7. π–π bonded compounds: The compounds containing metals with an alkene, alkyne, benzene, and aromatic ring compound will together form π–π bonded organometallic compounds. These compounds have metal and ligands that form a π–π bond.
   Examples: dibenzene and ferrocene chromium, Zeise's salt, aromatic, acetylene, and ethylene compounds.
8. Multicenter bonded compounds: These are the compounds where the electron-deficient species are coordinated to metals like Be, Li, and Al.
   Examples: MeLiMeLi and $Al_2Me_6Al_2Me$

1.11.2 Uses of Organometallic Compounds

Generally, organometallic compounds are used as reagents and catalysts, such as homogeneous and heterogeneous catalysts, for most synthetic reactions.

1. Organometallic compounds as homogeneous and heterogeneous catalysts: The organometallic compounds with a transition metal such as Rh i.e. $[RhCl(PPh_3)_3]$ act as catalysts for the hydrogenation of alkenes. Similarly, organometallic compounds such as trialkyl aluminum with titanium tetrachloride or trichloride are used as heterogeneous catalysts for the polymerization of alkanes.
2. Organometallic compounds for metal purification: During the process of metal purification initially, the impure metals are converted into carbonyls, further they should be decomposed to form pure metals.
3. Organometallic compounds for the synthesis of organic compounds: Organometallic compounds, such as organolithium and organomagnesium compounds, were used to prepare for organic synthesis.
4. Organometallic compounds can be used as reagents.
5. Organometallic compounds can be used as additives.

Agriculture and medicine: Organometallic compounds were also used in the field of agriculture and medicine. When seeds were treated with ethyl mercury chloride to prevent infection in plants. The organoarsenic compounds were used in the treatment of syphilis, in modern surgery, silicone rubbers were used.

1.12 Conclusions

The compounds containing metal–carbon bonds are meant to be organometallic compounds in the current chapter the fundamental aspects of organometallic compounds were discussed and they are used for different applications such as the synthesis of medicinal products, organic compounds, and agricultural products, they were used as a catalyst both heterogeneous and homogeneous, used for the purification of metals. In addition to that they are used as additives and reagents.

References

1 Seyferth, D. (2001). Cadet's fuming arsenical liquid and the cacodyl compounds of Bunsen. *Organometallics* 20 (8): 1488–1498.

2 Thayer, J.S. (1966). Cadet's fuming liquid: an historical survey. *J. Chem. Educ.* 43 (11): 594–595.

3 Hunt, L.B. (1984). The first organometallic compounds. *Platinum Met. Rev.* 28 (2): 76–83.

4 Thayer, J.S. (1969). Historical origins of organometallic chemistry – part 1 Zeise's salt. *J. Chem. Educ.* 46 (7): 442–443.

5 Thayer, J.S. (1969). Historical origins of organometallic chemistry. Part II, Edward Frankland and diethylzinc. *J. Chem. Educ.* 46 (11): 764.

6 Seyferth, D. (2001). Zinc alkyls, Edward Frankland, and the beginnings of main-group organometallic chemistry. *Organometallics* 20 (14): 2940–2955.

7 Davis, T.L. (1929). Paul Schutzenberger. *J. Chem. Educ.* 6 (9): 1403.

8 Morris, P. (1989). The legacy of Ludwig Mond. *Endeavour* 13 (1): 34–40.

9 Abel, E. (1990). Ludwig Mond – father of metal carbonyls – and so much more (7 March 1839–11 December 1909). *J. Organomet. Chem.* 383 (1–3): 11–20.

10 Herrmann, W.A. (1990). 100 years of metal carbonyls: a serendipitous chemical discovery of major scientific and industrial impact. *J. Organomet. Chem.* 383 (1–3): 21–44.

11 Rheinholdt, H. (1950). Fifty years of the Grignard reaction. *J. Chem. Educ.* 27 (9): 476.

12 Seyferth, D. (2003). The rise and fall of tetraethyllead. 2. *Organometallics* 22 (25): 5154–5178.

13 Cornils, B., Herrmann, W.A., and Rasch, M. (1994). Otto Roelen, pioneer in industrial homogeneous catalysis. *Angew. Chem., Int. Ed. Engl.* 33 (21): 2144–2163.

14 Herrmann, W.A. and Cornils, B. (1997). Organometallic homogeneous catalysis – Quo vadis? *Angew. Chem., Int. Ed. Engl.* 36 (10): 1048–1067.

15 Seyferth, D. (2001). Dimethyldichlorosilane and the direct synthesis of methylchlorosilanes. The key to the silicones industry. *Organometallics* 20 (24): 4978–4992.

16 Reppe, W., v. Kutepow, N., and Magin, A. (1969). Cyclization of acetylenic compounds. *Angew. Chem., Int. Ed. Engl.* 8 (10): 727–733.

17 Wilkinson, G., Rosenblum, M., Whiting, M.C., and Woodward, R.B. (1952). The structure of iron bis-cyclopentadienyl. *J. Am. Chem. Soc.* 74 (8): 2125–2126.

18 Seyferth, D. (2002). Bis(benzene)chromium. 2. Its discovery by E. O. Fischer and W. Hafner and subsequent work by the research groups of E. O. Fischer, H. H. Zeiss, F. Hein, C. Elschenbroich, and others. *Organometallics* 21 (14): 2800–2820.

19 Seyferth, D. (2002). Bis(benzene)chromium. 1. Franz Hein at the University of Leipzig and Harold Zeiss and Minoru Tsutsui at Yale. *Organometallics* 21 (8): 1520–1530.

20 Vaska, L. and DiLuzio, J.W. (1961). Carbonyl and hydrido-carbonyl complexes of iridium by reaction with alcohols. Hydrido complexes by reaction with acid. *J. Am. Chem. Soc.* 83 (12): 2784–2785.

21 Fischer, E.O. and Maasböl, A. (1964). Zur frage eines wolfram-carbonyl-carben-komplexes. *Angew. Chem.* 76 (14): 645–645.

22 Osborn, J.A., Jardine, F.H., Young, J.F., and Wilkinson, G. (1966). The preparation and properties of tris(triphenylphosphine)halogenorhodium(I) and some reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives. *J. Chem. Soc. A* 1: 1711.

23 Knowles, W.S. and Sabacky, M.J. (1968). Catalytic asymmetric hydrogenation employing a soluble, optically active, rhodium complex. *Chem. Commun.* 22: 1445–1446.

24 Dieck, H.A. and Heck, R.F. (1975). A palladium-catalyzed conjugated diene synthesis from vinylic halides and olefinic compounds. *J. Org. Chem.* 40 (8): 1083–1090.

25 Fischer, E.O., Kreis, G., Kreiter, C.G. et al. (1973). *trans*-Halogeno[alkyl(aryl) carbyne]tetracarbonyl complexes of chromium, molybdenum, and tungsten – A new class of compounds having a transition metal-carbon triple Bond. *Angew. Chem., Int. Ed. Engl.* 12 (7): 564–565.

26 Goldberg, D.E., Harris, D.H., Lappert, M.F., and Thomas, K.M. (1976). A new synthesis of divalent group 4B alkyls M[CH(SiMe3)2]2 (M = Ge or Sn), and the crystal and molecular and molecular strcuture of the tin compound. *J. Chem. Soc., Chem. Commun.* 227 (7): 261–262.

27 Miyaura, N., Yamada, K., and Suzuki, A. (1979). A new stereospecific cross-coupling by the palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides. *Tetrahedron Lett.* 20 (36): 3437–3440.

28 West, R., Fink, M.J., and Michl, J. (1981). Tetramesityldisilene, a stable compound containing a silicon-silicon double Bond. *Science (80-.).* 214 (4527): 1343–1344.

29 Schrock, R.R., Murdzek, J.S., Bazan, G.C. et al. (1990). Synthesis of molybdenum imido alkylidene complexes and some reactions involving acyclic olefins. *J. Am. Chem. Soc.* 112 (10): 3875–3886.

30 Hawkins, J.M., Meyer, A., Lewis, T.A. et al. (1991). Crystal Structure of Osmylated C60: Confirmation of the Soccer Ball Framework. *Science (80-.).* 252 (5003): 312–313.

31 Schwab, P., France, M.B., Ziller, J.W., and Grubbs, R.H. (1995). A series of well-defined metathesis catalysts–synthesis of $[RuCl_2(CHR')(PR_3)_2]$ and its reactions. *Angew. Chem. Int. Ed. Engl.* 34 (18): 2039–2041.

32 Peters, J.C., Odom, A.L., and Cummins, C.C. (1997). A terminal molybdenum carbide prepared by methylidyne deprotonation. *Chem. Commun.* 20: 1995–1996.

33 Grunenberg, J. and Goldberg, N. (2000). How strong is the gallium≡gallium triple bond? Theoretical compliance matrices as a probe for intrinsic bond strengths. *J. Am. Chem. Soc.* 122 (25): 6045–6047.

34 Sawamura, M., Kuninobu, Y., Toganoh, M. et al. (2002). Hybrid of ferrocene and fullerene. *J. Am. Chem. Soc.* 124 (32): 9354–9355.

35 Sekiguchi, A., Kinjo, R., and Ichinohe, M. (2004, 5691). A Stable Compound Containing a Silicon-Silicon Triple Bond. *Science (80-.).* 305: 1755–1757.

36 Resa, I., Carmona, E., Gutierrez-Puebla, E., and Monge, A. (2004). Decamethyldizincocene, a Stable Compound of Zn(I) with a Zn-Zn Bond. *Science (80-.).* 305 (5687): 1136–1138.

37 Nguyen, T., Sutton, A.D., Brynda, M. et al. (2005). Synthesis of a Stable Compound with Fivefold Bonding Between Two Chromium(I) Centers. *Science (80-.).* 310 (5749): 844–847.

38 Yu, Y., Bond, A.D., Leonard, P.W. et al. (2006). Hexaferrocenylbenzene. *Chem. Commun.* 24: 2572–2574.

39 Elias, A.J. and Gupta, B.D. (2010). *Basic Organometallic Chemistry*. University Press (India) Pvt, Ltd.

40 Difference between hapticity and denticity. Chemistry LibreTexts, Libretexts, 23 Feb. 2019.