ADVANCES IN ORGANOMETALLIC CHEMISTRY

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Organometallic chemistry deals with the study of organic compounds having metal-carbon bonds and in recent decades it has undergone remarkable transformation and significant progress. This field has evolved from early discovery of organometallic compounds to modern science with various advances in material science, medicine and medicinal chemistry, polymeric chemistry, bio-organometallic chemistry, catalysis and optoelectronics. New and recent advancement is in the realm of catalysis in which older simpler and expensive compounds are converted into more economical, commercially beneficial, less toxic and less expensive, complex organometallic compounds with variety of applications. The gap between inorganic chemistry and organic chemistry is bridged due to the exploration of biocatalysts, bio-organometallic enzymes, bio- organometallic co-factors, bio-organometallic co enzymes and metalloenzymes that offers novel pathways for catalytic transformations. This field has broad applications in material science where polymeric organometallic compounds are used for the synthesis of coatings, films, and semiconductor and also finds its applications in the manufacturing of LEDs, diodes, organometallic framework (OMFs) and metalloorganic framework (MOFs) shows unique optical, electronic and mechanical properties. Organometallic compounds such as organolithium compounds, organoplatinum complexes, organorhenium etc. also find its applications in sensing technologies, preparation of biosensors and also used in drug delivery. These organic polymeric organometallic compounds are used in cancer treatment, shows antimicrobial activities and peptide synthesis.

1. Introduction

Organometallic chemistry is the branch of chemistry that deals with the study of organometallic compounds and organometallic compounds are those compounds that contains organic part, metallic part that is actually inorganic part. Organometallic compounds are those chemical compounds which consist of at least one bond that is present between inorganic portion of compound which is metallic element and organic portion of compound which is carbon atom. In some industrial chemical reactions, some metalloids like tin, selenium, boron and silicon are also used in organometallic compounds where these compounds can behave as catalysts to speed up the industrial chemical reactions having polymers as their target molecules. These organometallic compounds can also use in pharmaceutical related chemical reactions in which these compounds can behave as agents which can increase the rate of reaction.

The bond between the carbon atom of organic portion and metallic element of inorganic portion is basically of covalent nature. In some organometallic compounds, the carbon atom has the tendency to show negative character and present in carbanion form if the metal is highly electropositive like lithium, aluminum and sodium and bond becomes polarized covalent bond in which electron pair is shared but not equally shared. The organic portion in organometallic compounds is also called 'ligand' (Crabtree, 2009).

Examples of such organometallic compounds are tetracarbonyl nickel, dimethyl magnesium, Grignard reagents containing magnesium atom as metal, Gilman reagents that contain specifically copper and lithium, polyphophazene and ferrocene that is a highly stable compound containing two hydrocarbon rings in which iron atom is sandwiched etc. An example of organometallic compound is shown below in which carbon atom of benzene ring bond with chromium (Mehrotra, 2007).



1.1 Classification of organometallic compounds

The broad classification of organometallic compounds is based on the type of metal and also on the basis of type or nature of bond present between metal and carbon atom. Following are the main types of organometallic compound on the basis of type of metal:

- **Compound containing normal metal:** Such organometallic compounds mainly consist of metal of s-block (group 1 and 2) which are normal metal or representative elements belongs to A-subgroup of periodic table and present on the left corner of the periodic table. For example, methyl lithium, methyl potassium etc.
- **Compounds containing transition metals:** Such organic compounds mainly consist of metals of d and f- blocks which are transition metals as outer transition metals and inner transition metals (lanthanides and actinides), respectively, belongs to B-subgroup of periodic table and present in the center of the periodic table. For example, dimethyl mercury, tetramethyl lead etc.
- **Compounds containing metalloids:** Such organic compounds mainly consist of metalloids like silicon, tin, boron and selenium etc. belongs to A-subgroup of periodic table as these are also present in p-block of periodic table. For example, tetramethyl silicon etc. (Tyagi et al., 2023).

The following classification is on the basis of type of bond:

- sigma bonded compounds
- pi- bonded compounds
- combination of sigma and pi bonded compounds

1.2 Properties of organometallic compounds:

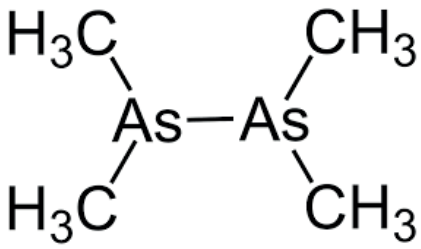
As organometallic compounds belong to diverse class of compounds in which metal is connected to mono-ligand and also poly-ligands to form polymeric compounds showing variety of properties but some are listed below:

- The structure and formation of organometallic compound is based on 18-electron rule.
- The stability and reactivity of organometallic compounds is based on nature and strength of bond between organic part and metallic part of compounds.
- The main cause of reactivity of organometallic compounds is the 'polarity of bond' that also is the main reason of the application of these compounds in organic synthesis.

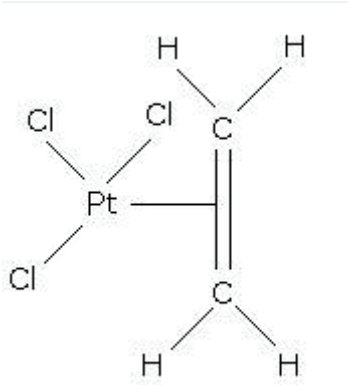
- Organometallic compounds can also act as reducing agents due to the presence of metal.
- These compounds can also be very toxic in nature for human if highly electropositive metal like sodium and lithium etc. is present in them which is volatile and also help in spontaneous combustion.
- Organometallic compounds, consist of aromatic ligand or ring structure in their organic part, mainly exist in the form of solids.
- Some organometallic compounds have ordinary covalent bond in which electrons are shared. Some compounds have bonding that involve two atoms show multicenter covalent bond. Very few compounds can also have bond that is ionic in nature as if lead is present as metal in any compound. The extent of polarization of bond depends on strength with which the metal atom binds electron.
- Their heat and oxidation ability vary from compound to compound (Allardyce & Dyson, 2006).

1.3 Historical development

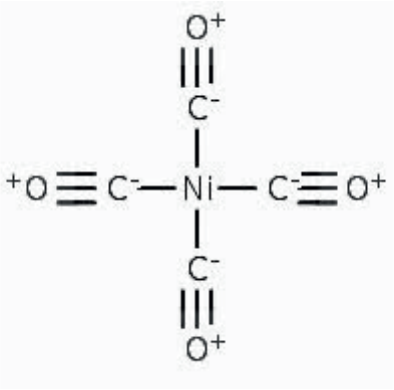
First organometallic compound that is 'tetramethyl diarsine' commonly named as cacodyl abbreviated as TMA or TMAs, (CH3)4As2, was isolated accidently by a French chemist named Louis Claude Cadet de Gassicourt in 1757. He was doing an experiment with invisible inks by the combination of potassium acetate and cobalt ore having arsenic. This was considered an organometallic compound although arsenic is not a true metal but a metalloid. Structure of cacodyl is:



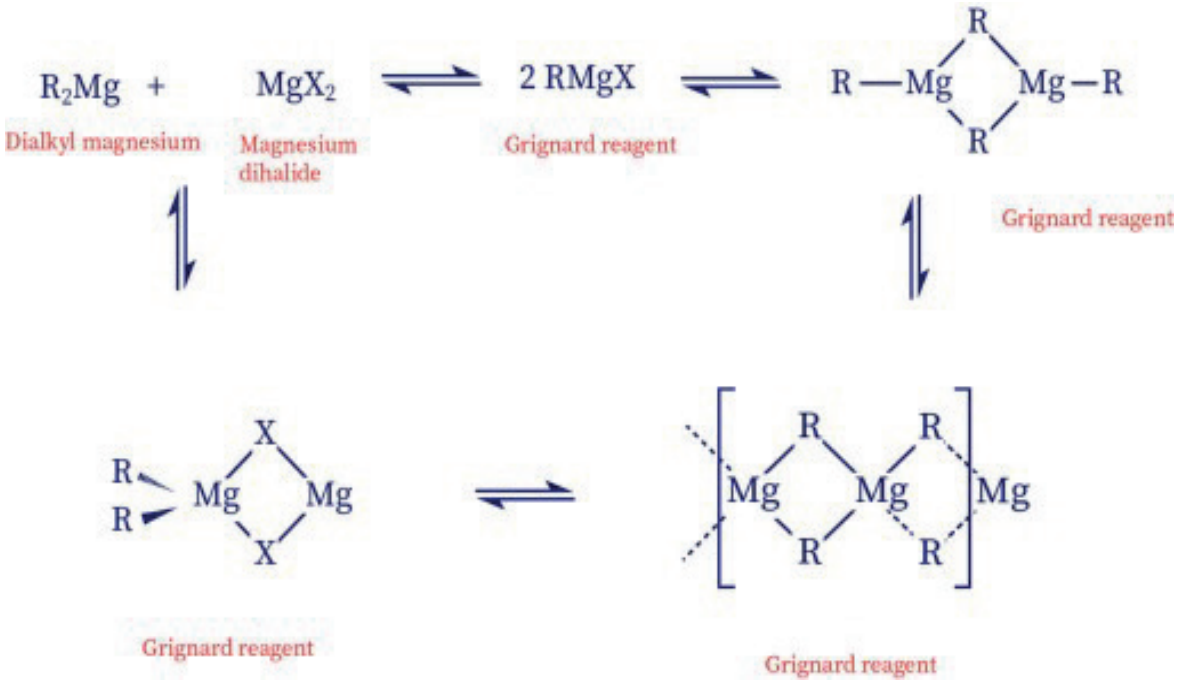
67 years later, a Danish organic chemist William Christopher Zeise discovered first organometallic compound containing a transition metal by placing platinum tetrachloride in boiling ethanol. Trichloro-ethene-platinate (II) anion is formed as a resulting anion, then Zeise salt can be formed when this anion is combined with a potassium counter ion. Structure of Zeise salt is given:



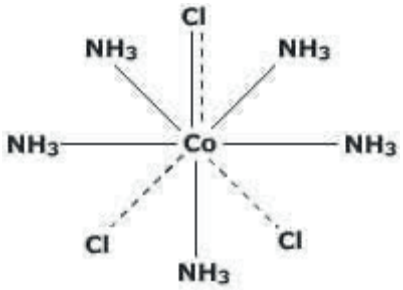
In later 19th century, a British chemist Ludwig Mond synthesized compounds such as diethyl zinc and very toxic nickel tetracarbonyl that initiated an entirely new class of compounds called metal carbonyls. Following is the structure of nickel tetracarbonyl:



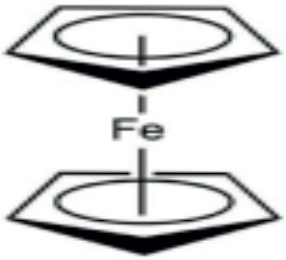
In 20th century, a new method of coupling carbon to the carbon of carbonyl group of aldehyde or ketone that is carbonyl compound by coupling of magnesium metal with alkyl or aryl halide with the help of nucleophilic addition reaction was discovered by French Chemist Victor Grignard and because of his tremendous discovery, he was awarded with Nobel prize of Chemistry in addition with Paul Sabatier. Even 100 years later this Grignard reagent is used in variety of carbonyl derivative as coupling reagent (Bandini, 2009).



In 1913, a Swiss inorganic Chemist named Alfred Werner was awarded with Nobel Prize as his work involved the coordination chemistry of ligands to metals, specifically the structure of hexamine cobalt (III) chloride. His work was important key step in understanding of chemical reactions of compounds, organometallic coordination and greatly contributed in the opening of independent organometallic discipline. Following is the structure of hexamine cobalt (III) chloride (Coates, 2012):



In 1951, American Chemist Peter Pauson and Tom Kealy created orange powdered ferrocene by the reaction of ferric chloride and cyclopentadiene magnesium bromide. They didn't deduce the real structure of organometallic salts and proposed that between the first carbons of two cyclopentadiene molecules, the iron acted as bridge and also presented sandwich model to explain the structure of ferrocene. Later, an English Chemist Sir Geoffrey Wilkerson in collaboration with American Chemist Robert Woodward explained the detail structure of ferrocene in which iron metal was sandwiched between two cyclopentadiene molecules that behave as ligand. Fischer also expanded the study of metallocene by using other metals. In 1973, Fischer and Wilkerson shared Nobel Prize because of their contribution in the expand study of metallocene compounds. Following is the structure of ferrocene:



In 1963, two chemists were awarded with Nobel Prize, Chemist named Karl Ziegler and Giulio Natta created a catalytic organometallic compound named dicyclopentadiene zircon (IV) dichloride by the polymerization of terminal olefins and they led to two entire classes of catalysts which are organometallic named as Ziegler-Natta catalysts.

In late 20th century, chemists introduced new methods to couple carbons together and these include sharpless epoxidation which earned Nobel Prize in 2001, famed Heck reaction that earned Nobel Prize in 2010 and Grubbs olefin metathesis which earned Nobel Prize in 2005 (Adamson, 1993).

2. Catalytic applications of organometallic complexes

The organometallic compounds have their applications as catalyst in different industrial organic reactions. As the process in which catalyst is used called catalysis and it is of two types that is homogenous catalysis and heterogeneous catalysis but the organometallic compounds found its application in homogenous catalysis that is discussed as following.

2.1 Homogenous catalysis

Homogenous catalysis is a process in which the phase of catalyst and reactants is same as both can be in solid, liquid or gas phase. As the organometallic compounds used in homogenous catalysis and its example is 'alkene metathesis' (Herrmann & Cornils, 1997).

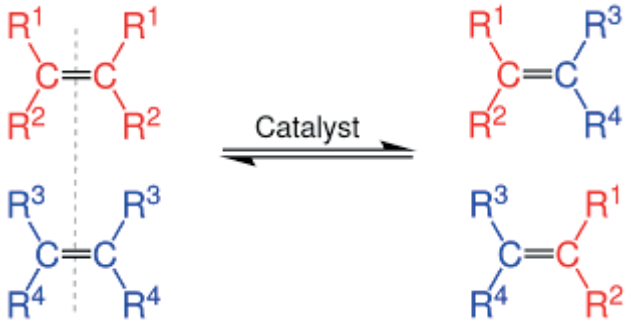
2.1.1 Application and mechanism:

One of the best applications of homogenous catalysis in which organometallic compounds are used is alkene metathesis whose mechanism is also given below.

Alkene metathesis:

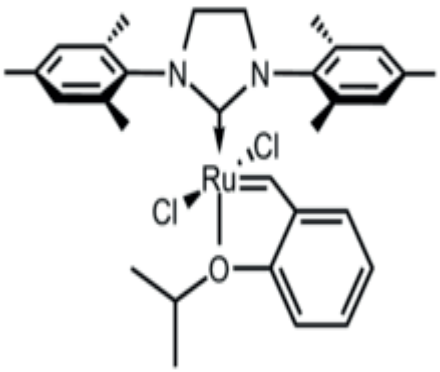
Alkene metathesis reaction is a reaction that is used to synthesize unsaturated polymeric counterparts and olefinic compounds which are unsaturated in nature. The metathesis reaction is famous for a family of reactions in which

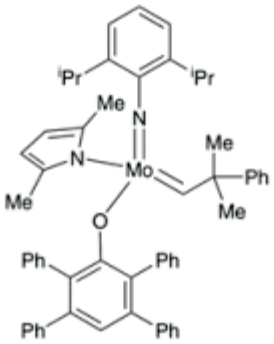
"Cutting and stitching" of olefinic bond involves in order to synthesize different unsaturated compounds. Olefinic compounds and other olefinic polymers are formed by the reaction of olefins with a metal carbene intermediate by varying the reaction conditions of metathesis reaction. Metathesis is an unusual process in which new olefins that are unsaturated in nature can be generated by this catalysis in which C=C is broken and then formed also.



During this metathesis process, metal carbene catalysts are used but many are developed but all of them don't work because all catalysts are not functional group tolerant. Utility of metathesis reaction can be broadened by developing functional group tolerant catalysts.

Schrock's Mo catalyst is effective for metathesis reaction because of display of high activity and Grubb's Ru catalyst is also used because it's easy to handle. Grubb's Ru catalyst is given on the left corner and Schrock's Mo is given below on the right corner.





Further extension of metathesis process is ring closing metathesis (RCM) for conjugated dienes in systems where the final product has no high ring strain. Ring opening metathesis (ROM) is the reverse of ring closing metathesis which occur in the presence of ethene (olefin).

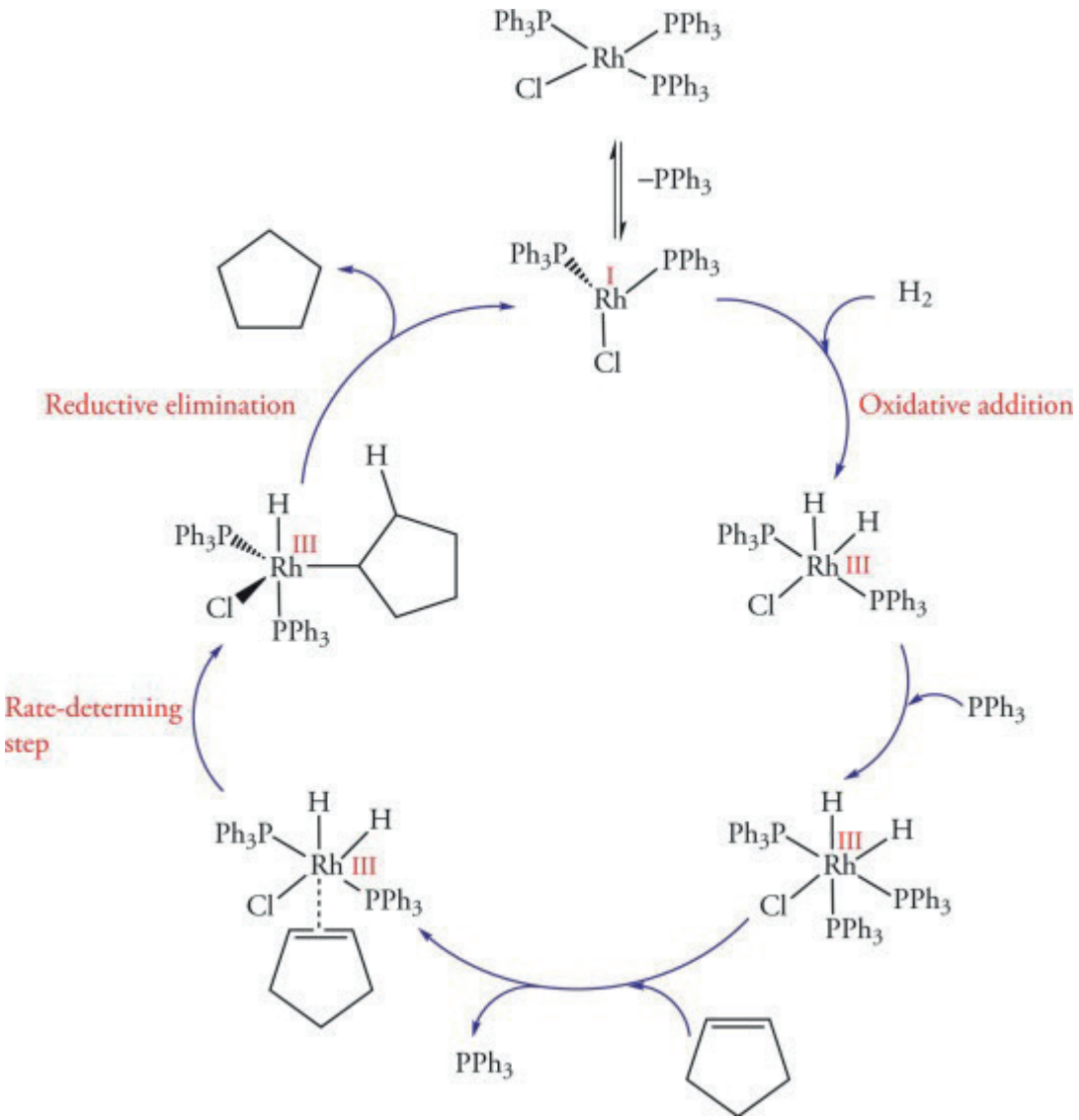
Polymerization reaction can be forwarded by relieving the ring stain of cycloalkenes by using the variants of metathesis like the acyclic diene metathesis (ADMET) and the ring opening metathesis polymerization (ROMP) for producing polymers. These reactions also have their applications in the production of block copolymers (Marciniec & Pietraszuk, 2003).

2.1.2 Industrial organic applications of organometallic catalytic process

1. Hydrogenation catalysis:

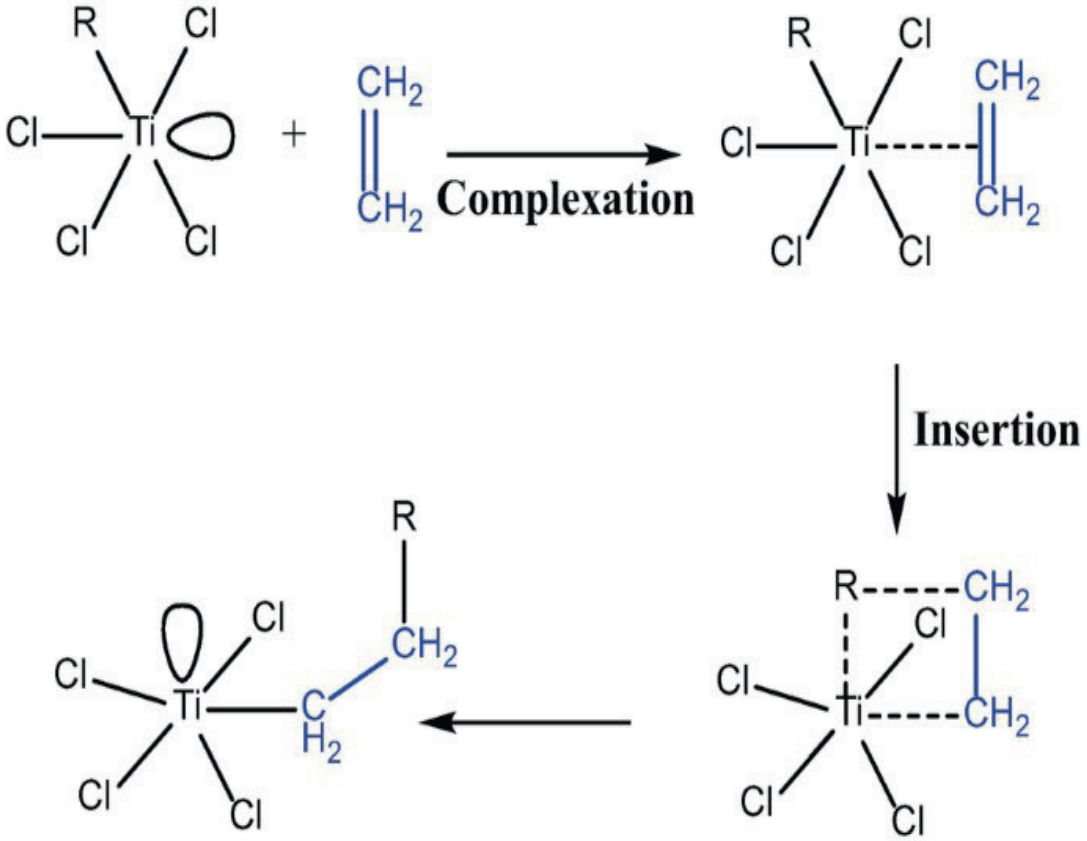
Wilkinson catalyst that is a Rh-catalyst is used for the hydrogenation of olefins. Wilkinson catalyst is a complex that is chlorotris (triphenylphosphine) rhodium (I) complex having a square planar geometry. Chlorobis (triphenylphosphine)rhodium (I) is formed by the loss of triphenylphosphine ligand from Rh-complex and it becomes a real catalyst otherwise firstly it's a pre-catalyst. The catalyst is in equilibrium with the pre-catalyst as the loss of triphenylphosphine ligand is a reversible process. After undergoing a series of events during this equilibrium, a specie named trigonal bipyramidal is formed that has the ability to add an olefin that binds side-on to Rh-complex. Olefin insertion can be done because olefin is in cis-position to hydride ligand.

A branched alkyl complex is formed by the formation of Rh-C bond when the second carbon in the carbon chain of olefin. Linear complex can also be formed by the formation of Rh-C bond with the first carbon in the carbon chain of olefin. The branched alkyl complex has more steric hindrance than the linear alkyl complex so it can regenerate olefin and trigonal bipyramidal Rh-complex by beta-hydride elimination as a side-reaction. The catalytic cycle can be completed when linear alkane and RhCl (PPh3)2 catalyst is formed by reductive elimination of linear alkyl Rh complex and after this a new cycle get starts. Following is the mechanism of hydrogenation catalysis in which an organometallic compound that is Wilkinson catalyst is being used (Jones et al., 2003).



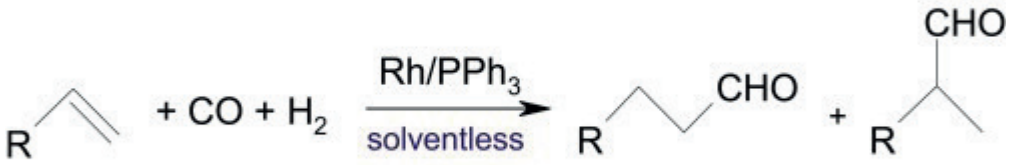
2. Ziegler-Natta polymerization

This reaction has very good reputation and quite important industrially for the synthesis of unsaturated polymeric alkenes like polyethylene. These catalysts are both homogenous and heterogeneous too. ZN catalyst is particularly useful for the polymerization of alpha olefins with high linearity and stereoselectivity. A ZN catalyst consists of two components that is a co-catalyst which is organoaluminium compound and other one is transition metal compound. Homogenous catalyst is metallocene catalysts and their mechanism is well understood than the mechanism of heterogeneous catalyst. Examples of Ziegler-Natta catalyst is TiCl3+ AlEt2Cl, TiCl4 +Et3Cl. A catalyst like mixture of triethyl/methyl aluminum and titanium chloride are added into monomers during Ziegler-Natta polymerization. Performance of catalyst is improved and modification of catalyst is done by the addition of compounds like magnesium chloride then this mixture has the capacity to produce an insoluble solid that is actually a heterogeneous catalyst. Mechanism for Ziegler-Natta polymerization is given below (Eisch, 2012):



3. Hydroformylation:

An aldehyde with and extra carbon atom than the original alkene can be produced by the addition of hydrogen and carbon monoxide to alkene. This catalysis finds its application in petrochemical sector in which radium catalyst and Co2 (CO)8 are used. In this catalytic cycle, catalytic intermediates are used in succession. Hydroformylation results in the production of aldehyde which are further converted into alcohols that have applications as plasticizer, detergents, and solvents and in other products production and these products are produced massively as millions of tons per anum (Pruett, 1979).



4. Cross-coupling reactions:

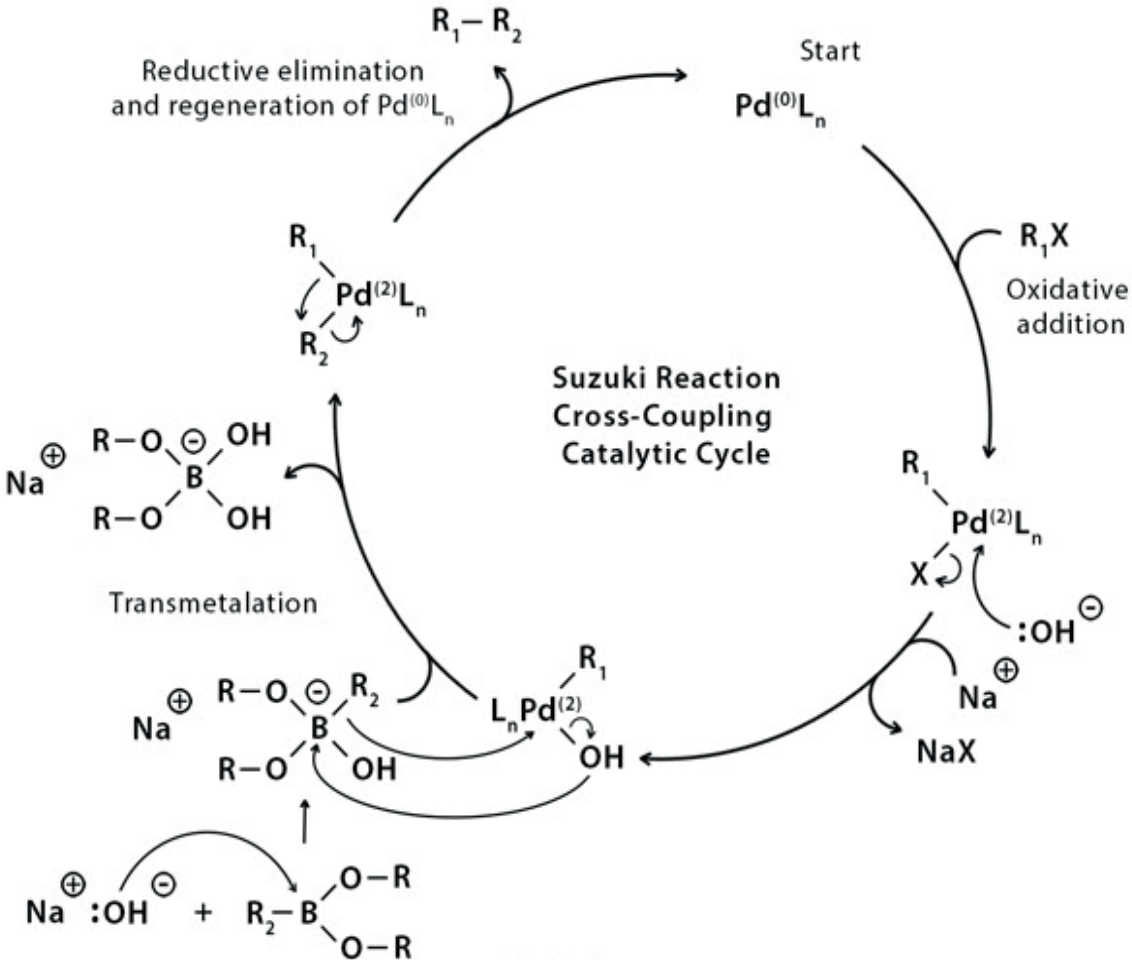
Cross coupling reactions are the reactions in which C-C, C-N, C-H, C-S, C-O, C-M, C-P bond formation take place when an organic electrophile combines with organometallic reagent having metals from A-subgroup of periodic table in the presence of metal catalysts having metals from group VIII to X. Cross coupling reactions are actually a type of synthetic transformations. Many organometallic reagents like organotin, organosilicon, organoboron and organozinc for cross-coupling reactions were prepared in early 1970s by Kumada, Corriu, Murahashi and Kochi. Multiple synthetic methods for molecular assemblies were discovered when metal complexes and different type of electrophiles were employed in these reactions (Campeau & Hazari, 2018).

Preparation of Liquid crystals, polymers, natural products, pharmaceuticals and many other organic synthetic applications are associated with cross-coupling reactions. Some of the examples of cross-coupling reactions are:

- Suzuki reaction
- Heck reaction
- Sonogashira reaction

Suzuki reaction

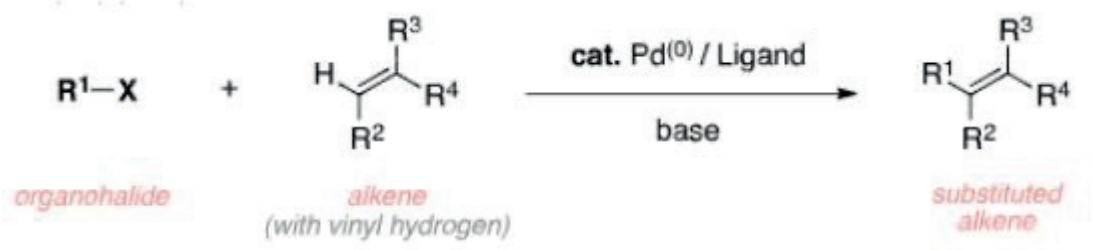
An organohalide and boronic acid are the coupling partners in this organic coupling reaction named Suzuki coupling reaction. In this coupling reaction, palladium (o) complex is used as a catalyst. This reaction is also called ‘Suzuki coupling’ or ‘Suzuki-Miyaura reaction’. A base leads the C-C bond formation by the coupling of halide with organoboron specimen over palladium (o) catalyst. The reaction is illustrated as below:



In Suzuki-Miyaura reaction, organohalide reacts with organoborane in the presence of palladium catalyst, ligands and base to produce coupled product, organoborane and sodium halide (Miyaura & Suzuki, 1995).

Heck coupling reaction

This reaction is also called 'Mizoroki-Heck reaction' after the name of the scientist, Richard Heck, who discovered this and later awarded with a Nobel Prize too in 2010. Palladium (o)/palladium (II) followed by a carbon-carbon bond formation was first time produced by this Heck- reaction. One of the examples of such reaction is given below:



In this reaction, unsaturated halide was added to the palladium by oxidative addition and then palladium has provided a site for the migratory insertion of alkene. Then the starting catalyst is regenerated to end the cycle by the removal of hydride from beta position of alkene and then adding the base to the palladium catalyst.

The mechanism of Heck reaction is described in few steps as in 1st step, a palladium pi complex is formed with unsaturated hydrocarbon that is alkene when palladium is added or inserted

into the aryl-bromide bond by oxidative addition. In 2nd step, sync addition takes place as in this alkene is incorporated in the palladium-carbon bond on the very same side of double/triple bond. In the 3rd step, another alkene-palladium pi complex is formed by the elimination of hydride from the beta position of alkene. In the 4th step, potassium carbonate is added when the palladium-alkene pi complex is disintegrated that results in the regeneration of palladium (0) complex through the reductive elimination of palladium (II).

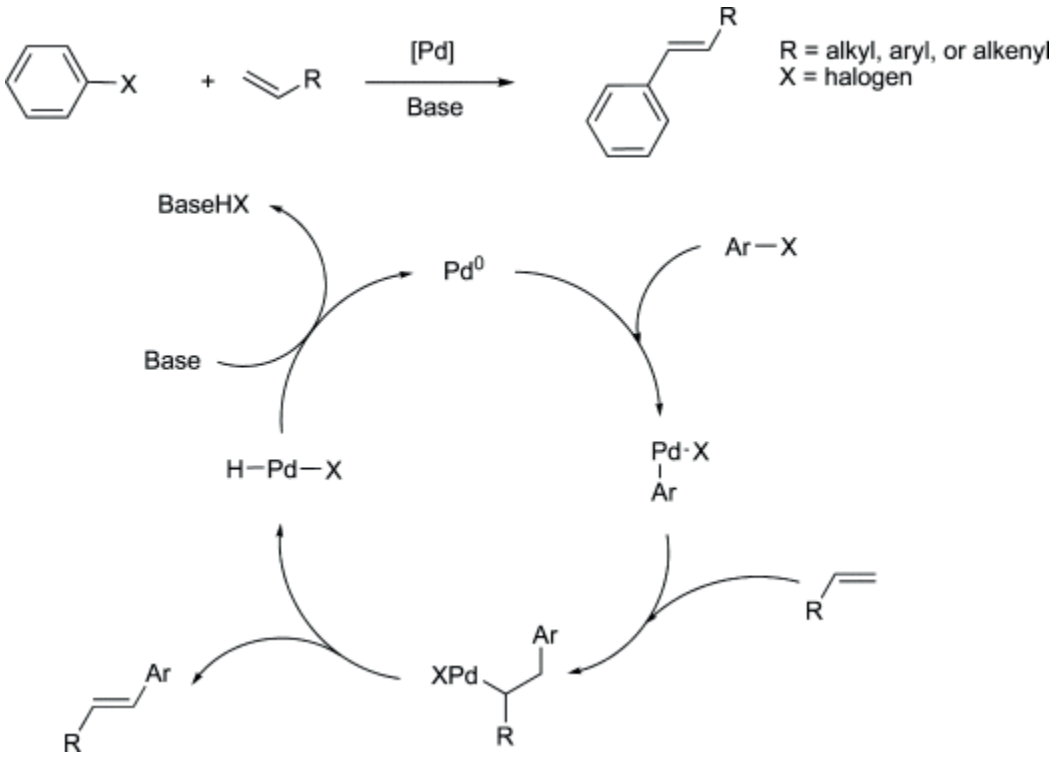
Heck reaction can be modified into the following:

• Heck oxyarylation

• Ionic liquid Heck reaction

• Amino-Heck reaction

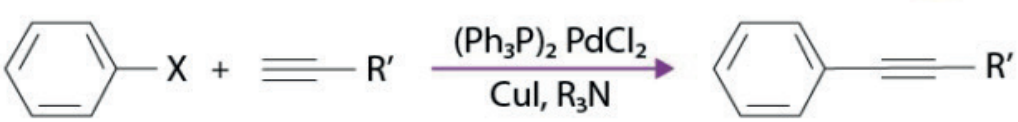
The mechanism of Heck reaction is given below (McGuinness et al., 1999):



Sonogashira coupling reaction

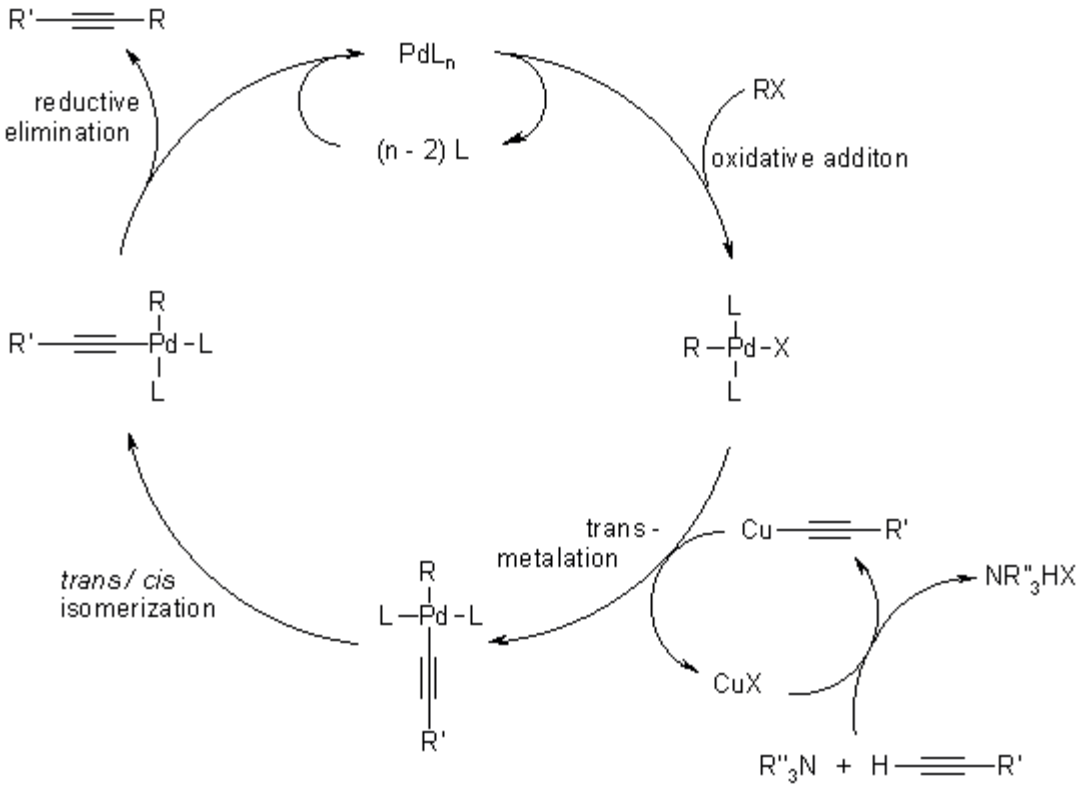
Kenkichi sonogashira, Yasuo tohda and Nobue Hagihara proposed this reaction which is the extension of Heck reaction and Dieck in which palladium was used as a catalyst. But in this sonogashira reaction, palladium as well as copper is used as catalysts. This reaction is very helpful in organic synthesis as it is used to produce C-C bonds. This reaction has found its applications in pharmaceuticals, nanomaterials, natural product chemistry, material science pharmaceuticals. Complex molecules can also be produced by the Sonogashira coupling reaction at room temperature by applying mild conditions.

Altinicline also known as acne and psoriasis can be treated by the synthesis of tazarotene that can be synthesized by the Sonogashira coupling reaction. As given below:



The mechanism of Sonogashira coupling reaction is very hard to understand as organometallic compounds are involved in this reaction which are difficult to isolate and then analyze. Palladium cycle and copper cycle are predicted to be near to be the right mechanism in which organometallic compounds are present as the reaction intermediates.

The presence of base is necessary for the production of complex E and pi-alkyne complex. As the presence of base has the ability to make the proton more acidic which is present in alkyne. The copper halide can be generated by the reaction of palladium with compound F. The mechanism is given below (Chinchilla & Nájera, 2007):



3. Recent advances in transition metal complexes

Very stable range of alkyls containing complexes like alkylcyclopentadienyliron dicarbonyl series RFe (C_5H_5) $(CO)_2$, alkylmanganese pentacarbonyl, RMn $(CO_5$ are prepared by using earlier transition metals like Ti, Mn, Cr, V. These reactions are highly important because these can be used in vivo and vitro catalytic systems. In catalytic processes, these transition metal alkyls behave as main intermediates. As, alkylcobalt carbonyls are involved in the hydroformylation and related carbonylation processes as this cobalt is also present in vitamin B12 as it is a natural organometallic system in which this metal is connected with adenosyl group by carbon. **Titanium alkyls** are also used in Ziegler-Natta olefin polymerization as the chain carriers in which transient intermediates are palladium alkyls.

All these cobalt alkyls and other transition metal alkyls act as 'ligands' which has the capacity to provide stabilizing effects to the whole compound and reaction medium.

3.1 Novel ligand design and its impact on reactivity

In most of the cases, the metal center that electropositive center which is Lewis acidic in nature and is surrounded by ligands which are Lewis's base and electronegative in nature has the capacity to donate electrons to the central metal atom to form coordinate covalent bond according to covalent bond theory. There are all different types of ligands like H, cyclopentadienide, alkyl where the central metal atom and ligands have comparable electro negativities. Metal- ligand bond

is considered to be covalent in nature when the late highly electropositive transition metals are used. According to covalent bond classification (CBC) method also known as LXZ notation, the interactions between these ligands and central metal atoms and their nature can be used as a basis to classify the ligands as:

- L- ligand
- X- ligand
- Z- ligand

These ligands and their interactions are described briefly so their mechanism and impact on reactivity can easily be understood.

• L- ligand

These ligands have the ability to donate two electron means one electron pair to the central metal atom and act as Lewis bases. These electrons which are donated can be sigma donors, pi donors and lone pairs. Coordinate covalent bonds also known as dative bonds are formed between central metal atom and L- type ligands. Examples of these ligands are PR3, H2O, NH3, alkenes, carbenes and CO.

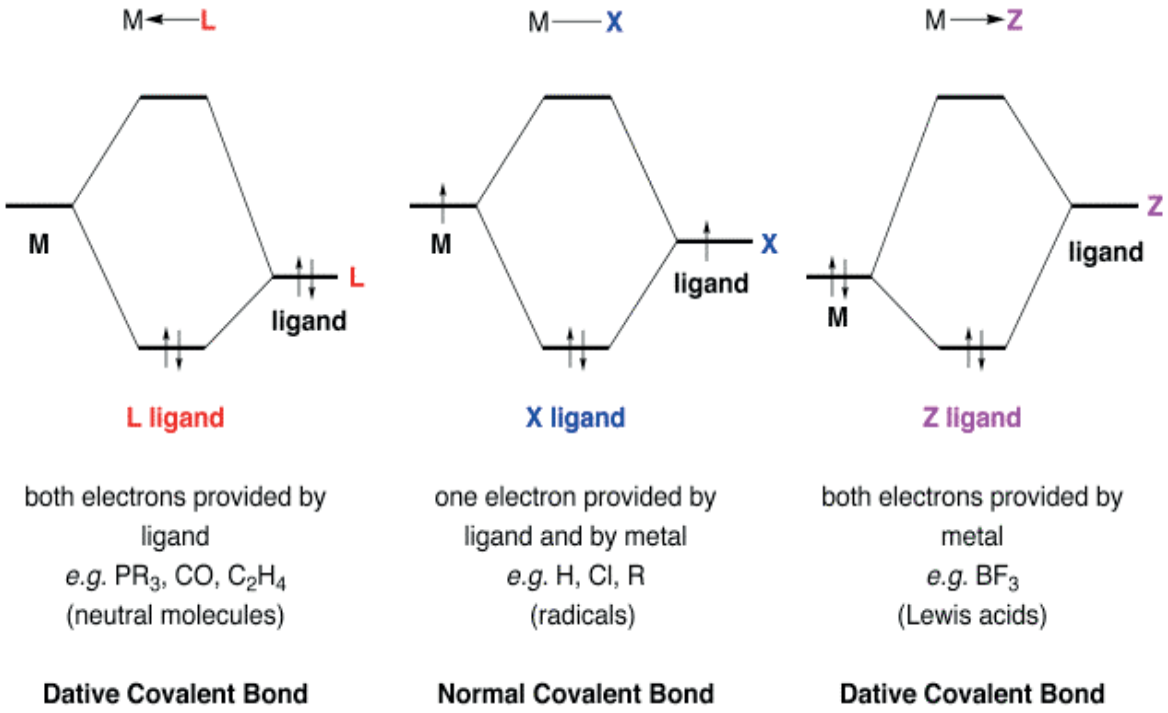
• Z- type ligand

These ligands have the ability to gain the two electrons means one electron pair from the central metal atom. Like the L- type ligands, these ligands also have the capacity to form dative or coordinate covalent bond with the central metal atoms. These are the least used ligands because of least reactivity due to nature to behave as acceptors. Examples of these ligands are mostly Lewis's acids like BR3.

• X- type ligand

These are the ligands that have the ability to undergo mutual sharing of electrons as one electron is donated to the ligand and the other electron is accepted from the central metal atom when neutral ligand method of electron counting is used. These ligands also have the capacity to donate two one electron pair means two electrons to the central metal atom when donor pair method of electron counting is used. These ligands are the most used ligands because of their reactivity and ability to lose and gain and share electrons. Normal covalent bonds are formed between central metal atom and these ligands either these ligands are anionic or neutral in its nature. Some of the examples of these ligands are halogens, hydrogen, methyl and NO (bent) (Mendoza-Ferri et al., 2009).

Following is an illustration of these ligands:



An L–function orbital is occupied by a **pair** of electrons.

An X–function orbital is filled by a **single** electron.

A Z–function orbital is **empty**.

An example of these ligands and their reactivity is discussed in the following paragraph. In modern organometallic chemistry, the C-C double bond formation is established by olefin metathesis. Stable and adjustable Grubbs, indenylidene type second generation catalysts having N-type heterocyclic carbenes (NHC) and Hoveyda-Grubbs are well-defined ruthenium complexes which play vital role in these reactions. Catalyst can be anchored both covalently and non-covalently. Covalently linked catalysts are used during these processes but still they can be moderately re-used and also their activity get decreased immensely. Non-covalently linked catalyst is dependent on the reversible pi interactions, electrostatic interactions, physio-sorption on porous materials like charcoal, wool, filter paper, cellulose, dendrimers etc. Synthesis of covalently bound analogues are quite difficult and complicated as compared to the production of non-covalently immobilized catalysts that is more straightforward and simpler. Non-tagged catalyst preparation is easy as compared to tagged catalyst according to synthetic point of view, for example, the preparation of Ru3 and Ru4 which are quaternary ammonium tagged catalysts is complicated because it involves the additional three to four steps.

Benzolyation that is ester formation is the main method for the synthesis of N-heterocyclic ligands (NHC) having Bronsted base tags. Olefin metathesis ruthenium catalysts are synthesized by using these tagged NHC ligands having 4-(dimethylamino) benzoic acids and isonicotinic agents. Basicity of these tagged fragments helps to provide a site for the non-covalent immobilization of these catalysts and the non-ionic nature helps to remove the problems that's been faced during the synthesis of quaternary ammonium-based catalysts on the basis of carbene.

Other types of ligands whose reactivity also depends on the type of bond and their structure, on the basis of their structure, are as following:

- Simple alkyl ligand
- Alkylidene ligand

- Alkylidyne ligand
- Alkene and alkyne ligands
- Polyene ligand
- Cyclic polyene ligands
- Aromatic ligands (Green, 2012).

3.2 Advances in metal catalyzed C-H activation

C-H bond activation is a process in which the whole series of mechanism takes place by which the cleavage of stable C-H bonds present in any organic compound takes place. C-O, C-N and C-C bonds are produced or synthesized which are present in more complex intermediates and product compound which is the main application of this process. This process is also used to prepare commercially beneficial complex molecules from the cheap and less toxic feedstock molecules under milder conditions by the cleavage of C-H bonds. The more commercially important compounds produced by this method are used in pharmaceuticals and also have fine chemical applications.

Different mechanisms are used for C-H activation like sigma bond metathesis, electrophilic substitution, oxidative addition, biocatalytic, photocatalytic reactions, electrocatalytic reactions and hybrid methods like photoelectrocatalysis, photobiocatalysis and all these methods are catalytic mechanisms. For more sustainable and accurate approaches to chemical synthesis, many of these techniques are used to activate C-H bonds by using metal catalysts which are abundant in earth and milder conditions are used. Transition metals like Rh, Pt, Ir etc. are used for C-H activation by catalytic oxidative addition. In this mechanism, intermediate organometallic specie is produced when transition metal coordinates with the proton attached to carbon atom present on the hydrocarbon that acts as substrate. Functionalized or active carbon atom is formed when this intermediate reacts with other species. Cleavage of C-H bond and activation of carbon atoms are done stoichiometrically. For example, transition metals are beneficial for the production of C-B bonds by borylation/ C-H activation. Electrophilic aromatic substitution is used for Friedal-Craft chemistry. Organoboron compounds are used for the formation of C-C bonds by cross-coupling reactions.

In C-H activation reactions, electron rich metals who are low valent in nature like Rh(I) and Ir(I) undergo the process of oxidative addition and high valent metals like Rh (III), Ru (II), Ir (III), Pd (II) undergo the reaction by electrophilic pathway. Functional group positional selectivity is driven by the central metal atom which is either coordinated or chelated. In ortho metalation and functionalization of aromatic hydrocarbons specific C-H bonds are targeted by directed C-H activation.

Functionalization of C-H bonds can be done as a result of Friedal- Craft's reaction which is either Friedal- Craft's acylation or Friedal- Craft's alkylation. C-M bonds are formed by the C-H activation in metalation reaction. In lithiation reactions, C-Li bond formation takes place by C-H activation/ metalation reactions.

There are multitude of variables which can affect the expected outcome in these catalytic reactions. The factors on which these catalytic reactions depend are ligands, reagents, reactants, catalytic metals, pressure, temperature, mixing, dosing rates, catalysts etc. that's why these reactions need great care in proceeding and careful control over variables during the reaction to get desired results (Raţ et al., 2018).

4. Organometallic complexes in material sciences

Polymers like homopolymers, copolymers, complexes, blends of small molecules, alloys, composites are used in microelectronics, electronics, nanoelectronic systems instead of regular metals and ceramics. These polymers are preferred because of many properties like attractive

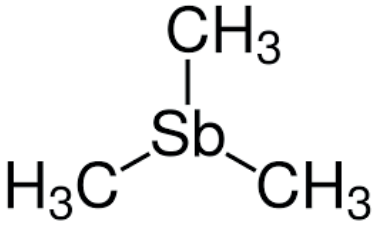
optical properties, chemical properties, physical properties, electrical and electronic properties, mechanical properties and also because of their complex mechanical properties.

Organometallic polymers are used to achieve multiple attributes and requirements in electronic systems as to get short lead time, reduced weight, can be molded into complex shapes and low cost. These above attributes are hard to get in nanoelectronics and microelectronics which is based on flexible polymeric substrates which are bendable and stretchable, 3D- PCBs that is three-dimensional printed circuit boards, MID that is molded integrated devices, integrated electronic systems like integrated circuits ICs and many other electronic components working at high temperature. Developed generations of nanoelectromechanical systems NEMS, microelectromechanical systems MEMS are the further examples in which silicone Q polymers are used in integrated circuits (Schwartz & Bernasek, 2001).

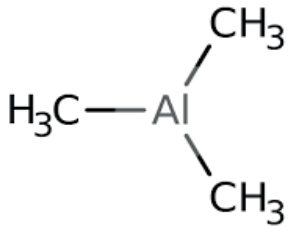
4.1 Role of organometallics in semiconductor materials

For structuring of electronic systems, organometallic compounds which are here specifically called electronic organometallics also known as hybrid organometallic polymers are used which contains organic component and also inorganic component. Ideal organometallics used for the actuators due to high piezoelectric coefficient are silicon rubber that is polydimethylsiloxane PMDS, dendrimers which are highly branched dendritic polymers, polydiphenylsilane. Organometallic polymers are also the representative of best class of stretchable electrically conductive polymers based on silicones which are used in the form of adhesives.

Electronic polymeric organometallics are used in research oriented and industrial methods as stoichiometric reagents. These organometallics are used in the manufacturing of some semiconductors and these reagents are trimethylaluminium, trimethylindium, trimethylgallium and trimethylantimony. Trimethystibine also called as trimethylantimony is an organometallic compound which is used for synthesis of semiconductor and it is synthesized by the reaction of methyl Grignard reagent along with antimony trichloride. It is a weaker Lewis base which is used for the synthesis of III-V semiconductors.



Trimethyl aluminium is also an organometallic compound having Al in the center and is tetrahedral which is surrounded by methyl groups surrounded by five neighbors. Polyethylene, polypropylene and other polyolefins are produced by using organoaluminium compounds by Ziegler-Natta catalysis. An activator of many transitions metal catalyst is methylaluminoxane synthesized from TMA. The fabrication of semiconductor is done by using trimethylaluminium which is used to deposit thin film. Atomic layer deposition or chemical vapor deposition is used for deposition of high-k dielectrics like Al2O3. For metalorganic vapor phase epitaxy (MOVPE) of aluminum containing compound semiconductors like AIN, AIAs, AISb, AllnGaN, AllnGaP, AllnGaNP, AIP, AlGaN etc use trimethylaluminium as a precursor (Weibel & Oliver, 1974).



4.2 Applications in molecular electronics and optoelectronics

The variety of organometallic polymers are used for the development of fibers, coatings, fiber matrix composites, infiltrated media, ceramic bulk parts and near net shaped manufactured ceramic components and all these are precursor- driven. Techniques and methods from polymer process engineering are used for the production of green parts. These organometallic polymers are used in the manufacturing of electronic components, polymeric electronic components, nanoelectronics and optoelectronics because of electrical conductivity of some polymers. Electronic polymers are prepared from organic polymeric electronic components.

Organic light emitting diodes OLEDs, displays in nanoelectronics and microelectronics and development of novel electronics are developed by the field of material science which helps in the development and production of small molecules, complexes and electrical conducting polymers which are actually called electronic polymers, electrically active polymers EAPs, organic electronic compounds which have inherent electrical conductivity.

Production of light emitting diode (LEDs) and other semiconductors is done by metalorganic vapor phase epitaxy (MOVPE) in which volatile compounds which are organometallics like trimethylgallium, trimethyl aluminum, trimethyl gallium and trimethylindium are degenerated or decomposed along with ammonia, arsine, phosphine and some other related hydrides on a heated substrate. Dimethylzinc is also an organometallic compound that is used for the synthesis of semiconducting films and it is a volatile pyrophoric liquid (Popczyk et al., 2019).

5. Bio- organometallic chemistry

Bio-organometallic chemistry is a branch of Chemistry which deals with the study of biomolecules, compounds containing minimum of one carbon atom which is attached to the metal and these compounds are biologically active compounds which are lying at the interface of organometallic compounds.

This new branch of Chemistry extends the study of organometallic chemistry to medicine, life, living organisms, biology and bioanalytics.

5.1 Bio-organometallic interactions and their relevance

There are many enzymes and cofactors are present in our body which are organometallic in nature and having at least one direct carbon metal bond. The naturally occurring vitamin B12 family also known as cobalamines which are actually vitamin B12 co-enzyme are actually organometallic compounds as these have dimethyl mercury that is produced by bacteria to eliminate and remove toxic metal mercury and cobalt carbon bond (Co-C).

The naturally occurring hydrogenases which helps in undergoing heterolytic splitting mechanism to catalyze the reversible conversion of molecular hydrogens to protons and electrons. CO ligand and CN- ligands are present in the center of dinuclear Ni-Fe which itself is present in

the active site of (NiFe) hydrogenase. During the catalytic or activation process, ligand sphere can be changed by the catalytic activity and active site structure of hydrogenase.

The naturally occurring bio-organometallic is the acetyl CoA synthetase (ACSs) is a vital enzyme in the anaerobic carbon dioxide fixation that is Wood- Ljungdahl pathway which is operated by a mechanism having a series of protein bound intermediates like Ni-CO, acetyl- Ni and methyl- Ni.

One of the naturally occurring organometallic compound which is CO dehydrogenase (CODH) which act as catalyst in the reversible oxidation of carbon monoxide to carbon dioxide. This bio-organometallic compound helps in the utilization of carbon monoxide as a source of energy and carbon by global carbon cycle. There are two types of CODH exists:

- Ni-CODH
- Molybdopterin/Cu/Fe-S cluster

The nickle containing enzyme (Ni-CODH) is used in anaerobes and present as a component of large complex with acetyl- coenzyme or can exist as an independent enzyme. The molybdopterin/Cu/Fe-S cluster is found in aerobic microorganisms.

Methyl coenzyme M reductase (MCR, F430 cofactor) is also a bio-organometallic compound is used in the terminal step of methanogenesis as a catalyst by using co enzyme B (CoBSH). Heterodisulphide, methane and CoBS-SCoM are produced when methyl coenzyme M (methyl-SCoM) is reduced when two electrons are donated by CoBSH. Many catalytic mechanisms are proposed to understand the method of production of methane which are different from each other because of the unclear understanding of production of either methyl radical or methyl- Ni (II) as the first catalytic intermediate. Hemolysis of methyl-Ni (II) can produce methyl radical which is suggested by the most recent proposal (Jaouen & Metzler-Nolte, 2010).

5.2 Medicinal applications of organometallic complexes

- Following are the few medicinal applications of organometallic compounds:
- Technetium sestamibi is used to image the heart muscle in nuclear medicine.
- Several crucial enzymatic reactions take place in human body in which an organometallic compound is used that can act as a cofactor named Adenosylcobalamin which is found rarely in the body as it's a metal (cobalt) and alkyl.
- Industrial production of alcohols is done by using an organometallic compound which is trimethylaluminium having a bridging methyl group.
- Before the invention of modern antibiotics, organometallic compounds containing mercury like thiomersal was used as an antibiotic.
- A nonselective antimicrobial organometallic is used in medicine that contains arsenic like salvarsan.
- Anti-cancer activity is displayed by an organometallic compound named Titanocene dichloride.
- Current anticancer medicine is also an organometallic compound which is dichloridobis [(p- methoxybenzyl) cyclopentadienyl] titanium.
- For the design of new radiopharmaceuticals, arene and cyclopentadienyl complexes provide kinetically inert platform.
- As carbon monoxide is gasotransmitter so many organometallic compounds have been used and studied which has the ability to release carbon monoxide.

- Incentive salience and habituation are efficiently increased by using dopamine transporter which are actually created by using semi-synthetic ligands namely with the phenyltropane compound named as [n6- (2beta-carbomethoxy-3beta-phenyl) tropane] tricarbonylchromium.
- Organometallic compounds are used as biosensors.
- Organometallic compounds are used in the peptide synthesis (Martins et al., 2014).

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To Cite This Chapter:

Arif Z. (2024). Advances in Organometallic Chemistry Synthesis. In Y. Junejo (Ed.), Chemistry: The Modern Approach (pp. 141-160). ISRES Publishing.