

# Review on the Use of Coordination Compounds with Transition Metal

Dr. Ashish Garg

Designation Associate Prof in Chemistry, Seth R. N. Ruia Govt. College Ramgarh Shekhawati, Sikar, Rajasthan, India

## ABSTRACT

The use of coordination compounds in the chemical industry is discussed here, along with current advancements and future directions. The article examines how many physicochemical factors, including steric hindrance, electron density, complex geometry, and ligand, influence the coordination relationship and, in turn, have an impact on industrial operations. Coordination substances act as catalysts in the technological processes used for organic synthesis, including oxidation reactions, hydroformylation reactions, hydrogenation reactions, and hydrocyanation processes. In this article, the potential uses of complex compounds in catalysis were highlighted, along with the need for further research in this field.

## INTRODUCTION

A key component of scientists' work worldwide is the utilization of complicated molecules in the procedures used in the widely construed chemical industry. Global companies that produce a wide range of polymeric materials used in many areas of our lives are starting to pay attention to procedures developed on an industrial scale by scientists.

The significance of coordination compounds in catalytic reactions during industrial processes carried out on an industrial scale must be understood in terms of the particular mechanisms of the reactions that occur. By examining the workings of a representative process, we can get the conclusion that the most significant changes occur in the coordinating sphere of the overall link. This means that a number of factors, including as shape, steric hindrance, the central atom and its related ligands, and more, affect the catalytic reaction.

Increased selectivity and efficiency of processes have recently been prioritised. It has been shown that the right ligands can be selected in the metal coordination sphere to create a catalyst with the appropriate properties. Thus, the structure of the catalyst has a significant impact on the catalytic properties of the complex compound. The least amount of environmental pollution feasible, or the use of "green chemistry" concepts, is a crucial component of work on chemical technology. Supercritical liquids or ionic liquids can be used to carry out reactions instead of organic solvents. Environmentally friendly chemical technologies can be obtained by implementing microbiological and organocatalytic techniques.

The most modern methods for using coordination compounds in catalytic reactions in the chemical industry are covered in this article. We talk about how coordination molecules affect the development of processes used in the synthesis of organic compounds, such as hydroformylation, hydrogenation, oxidation, and olefin polymerization. We also go over how complex compounds and green chemistry ideas were applied in catalysis.

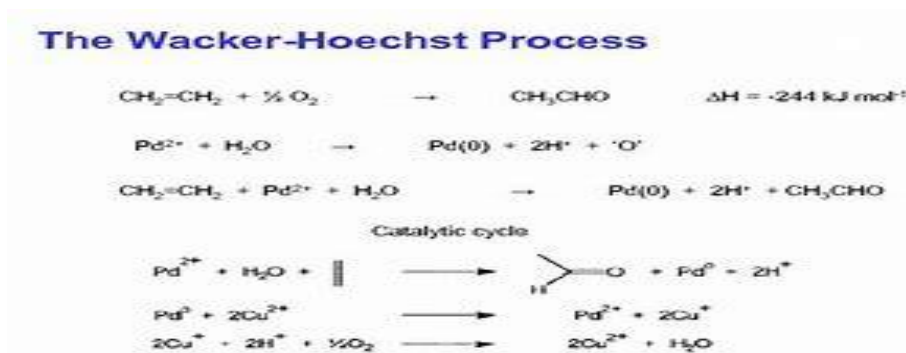
### Oxidation Processes

#### Wacker Process

Wacker and Hoechst collaborated to develop the Wacker process, published in 1959. The method is a well-known reaction for oxidizing ethene to produce acetaldehyde. PdCl<sub>2</sub> and CuCl<sub>2</sub> operate as homogeneous catalysts in an aqueous environment to carry out the reaction. Because the synthesis offered an alternative to the hydroformylation reaction, it was recognized by the chemical industry. Acetaldehyde, which is created during the process, is widely used. It primarily produces acetic acid, acetic anhydride, or chloroform. In condensation reactions with phenols and amines, it can also yield synthetic resins. The Wacker process, which combines stoichiometric processes into a single catalytic cycle, is shown in Figure 1. When palladium (II) and palladium (II) chloride mix to form a stoichiometric amount of acetaldehyde, palladium (II) is first reduced to palladium (0) in an aqueous environment. Reoxidizing palladium (0) in



the presence of copper (II)-containing molecules is the next step. This reaction yields copper (I), which is further oxidised with oxygen to form copper (II) in the final step. The entire reaction of the process is depicted in Figure 1 as reaction four.



**Figure 1 Reaction from the Catalytic Cycle of the Wacker Process**

The oxidation step is catalysed by  $[\text{PdCl}_4]^{2-}$ , which is produced in the presence of water and Cl ions. In the cycle under study, ethene and water are exchanged for two chloride ligands. The complex's ethene is then attacked by water in a nucleophilic manner, and the chloride ligand is subsequently switched out for a new water molecule. The removal of a hydrogen atom results in the production of vinyl alcohol. After this step, other processes are carried out in order to produce acetaldehyde and palladium (II) hydride. HCl and Pd (0) are produced during the reduction reaction as a result of the palladium (II) hydride's instability. The cycle is complete. Palladium (0) is oxidised to palladium (II) by  $\text{CuCl}_2$ .

Researchers conducted experiments using quantum mechanics, concluding that the anti-nucleophilic attack is the step that, under typical circumstances, determines the Wacker process. Sadly, experimental research did not support the conclusions drawn from mathematical methods. According to Keith et al., the Wacker process is controlled by a syn-nucleophilic attack.

However, the literature claims that one can carry out the Wacker process with 99% selectivity to obtain aldehydes, for example, by using 1,4-benzoquinone, t-BuOH, and  $\text{PdCl}_2(\text{MeCN})_2$ . Ketones are typically the reaction products of the Wacker oxidation. Regarding the Wacker method' selectivity, products with high selectivity can also be made while employing styrene derivatives as substrates and conducting the reaction under mild conditions.

Studies carried out over the years have demonstrated that the Wacker method generates copper trash damaging to the environment and chlorine byproducts. Solutions that influence the protection of ecosystems and the entire globe are being sought after following the principles of green chemistry. The Pd(0)/C combination was suggested as a recyclable heterogeneous catalyst by the University of Pune researchers. This made it possible to get rid of pure  $\text{CuCl}_2$ . In addition, they substituted potassium bromate ( $\text{KBrO}_3$ ) for molecular oxygen as an oxidizing agent. They created a technique that utilized cheap substrates and attained excellent process efficiency by doing so. One can conclude that the Wacker cycle's significant drawback is the by products produced during the process. Derivatives of chlorine are contaminants in the environment. The end resultant by products should therefore be tried to be deactivated by scientists.

### Hydroperoxide Epoxidation Reaction of Olefins Catalyzed by Mo (VI) Complex

Olefin oxides are epoxides. Their three-member ring structure is composed of two carbon and oxygen atoms. These substances are heterocyclic ones. High reactivity is a characteristic of these chemicals. For instance, they go through processes where the ring opens and closes, then the nucleophile attaches. Antibiotics, steroids, and hypertension medicines are all made via these reactions. Hydrogen peroxides are the most prevalent oxidants used in the olefin epoxidation processes; however,  $\text{H}_2\text{O}_2$  is rarely used due to how poorly it dissolves in hydrocarbons. Metal oxides of groups 4-6, such as Ti, V, Mo, and W, act as catalysts to speed up the process. Although there are numerous ways to make epoxides, the propene epoxidation reaction is the most well-known. The production of propene oxide worldwide is estimated to be nearly 6 million tonnes annually.

The reaction of olefin epoxidation with hydroperoxide, catalyzed by the Mo(VI) complex with a peroxide ligand, is one of the epoxidation processes that use peroxide metal complexes. Olefin is joined to the catalyst's ROO group, which is its active form. This chemical process is characterized by olefin binding to the catalyst via an oxygen atom. The metal



atom does not form any bonds, but molybdenum in the sixth degree of oxidation will break the O-O bond and help the catalyst regenerate.

The reaction produces epoxy, or propene oxide, frequently used to make polyether and polyhydric alcohols, ethers, or propylene glycols. Studies on epoxidation using molybdenum (VI) compounds have significantly increased the stereoselectivity and effectiveness of carried-out processes. Unfortunately, more research needs to be done on using epoxidation reactions without solvent.

### Sharpless System for Asymmetric Epoxidation of Olefins with Hydroperoxide with Dimeric Titanium Complex As A Catalytically Active Form

The chemistry of organometallic compounds has advanced, which has increased interest in using newly developed systems. Sharpless researched the application of organometallic catalysts in the asymmetric epoxidation reaction. A system containing titanium (IV) isopropoxide, tartaric acid derivatives, and an oxidant in the form of tert-butyl hydroperoxide participates in the epoxidation of allyl alcohol (Figure 2). The catalyst  $Ti(O-iPr)_4$  is a dimeric combination of titanium and tartaric ligands. The stereochemistry of the reaction result is impacted by the tartaric acid ethyl ester employed. When the ester and metal interact, a complex is created. Depending on the chirality of the tartrate derivative, the resultant system experiences hydrogen peroxide oxidation, and the bond breaks on the proper side of the hydrogen bond.

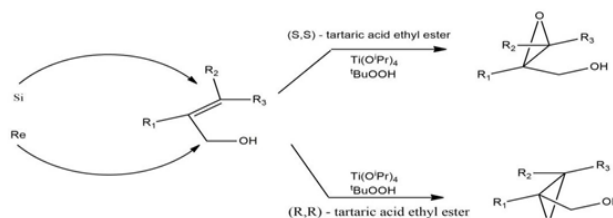


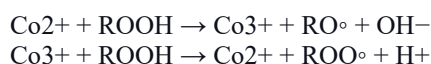
Figure 2 Sharp less System Diagram for Asymmetric Olefin Epoxidation

When using hydroperoxide and the dimeric titanium complex as a catalytically active form to asymmetrically epoxidize olefins in the Sharp less system, chlorinated solvents provide a problem. As a result, there are several problems with industrial manufacturing.

### Cyclohexyl Hydroperoxide Decomposition Reaction Catalyzed By Cobalt (II) and Cobalt (III) Complex Compounds

Many research institutes are working on improving the technology for producing polymer fibers. The great chemical synthesis relies heavily on caprolactam, which makes polyamide fibers and polymers. According to statistics, the annual production capacity of caprolactam is 5.2 million tonnes. Notably, a significant portion of caprolactam production in Poland and around the world involves the cyclohexanol-cyclohexanone mixture produced from hydrogenated benzene. This technology is thought to be used in 90% of raw material production worldwide. The Industrial Chemistry Research Institute's CYCLOPOL technology, created in collaboration with Zakady Azotowe in Tarnów and Puawy, is the main method for producing caprolactam in Poland. The CYCLOPOL technology has also been used in other nations, including Slovakia, Russia, India, Spain, and Italy. Benzene is converted to cyclohexane during the first phase of the process. In a bubble reactor, the cyclohexane oxidation reaction takes place. It occurs in the liquid phase under pressures ranging from 0.8 to 1.05 MPa and temperatures between 155 and 165 C. According to the technology, air or air that has added oxygen should be an oxidant.

In order to help in the oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone and the decomposition of hydroperoxides, a cobalt and chromium catalyst mixture is also used. The next step is to distil a combination of cyclohexanols and cyclohexanone, followed by their dehydrogenation. The critical step is the cyclohexane oxidation procedure. The various cobalt compounds, including naphthenate, serve as a catalyst in this stage. Cyclohexyl hydroperoxide breakdown is a key chemical process. What triggers the reaction is the radical mechanism. Cobalt (II) and cobalt (III) compounds are described as the catalysts in this reaction in the literature. The mechanism of catalysis is explained by the Haber-Weiss reaction.



Significant technological advancements are the result of ongoing work to enhance the Tarnów plant's cyclohexane oxidation reaction node. The brand-new CYCLOPOL-bis procedure has two steps. The creation of cyclohexyl hydroperoxides and their selective breakdown were carried out separately. The best aeration, pressure, and temperature conditions were chosen for each distinct oxidation phase. With updated CYCLOPOL-bis technology, production costs have been reduced, product quality has increased, and environmental consequences have become less harmful.

Research is still needed to increase the selectivity of decomposition reactions. It should be stressed that the CYCLOPOL-bis technology is based on a green chemistry approach.

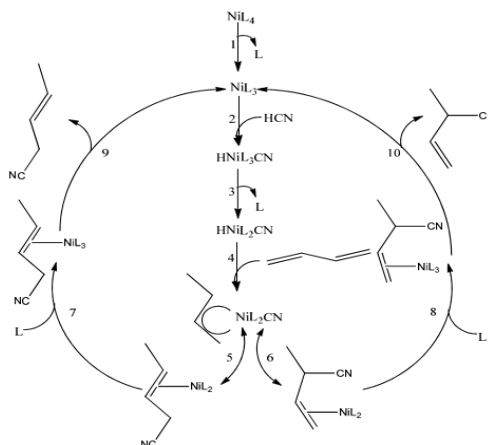
### The Hydrocyanation Reaction

The method of hydrocyanation is used to produce adipic acid nitrile for use in industry. It acts as the main starting material for the chemical reaction that results in nylon 6,6 by joining HCN to the olefin. It is commercially significant that the DuPont Company generates adipic acid nitrile using the butadiene hydrocyanation process. The technique makes use of the Ni(0) catalyst and phosphate ligands.

The process has two steps. The catalyst is essential to the whole procedure. The oxidative attachment of HCN to the NiL<sub>4</sub> catalyst first produces the hydrocyanide complex. selecting a ligand (L) that is appropriate, like a phosphorus ligand. The progression of the hydrocyanation process through each stage is influenced by electronic and steric properties. More basic ligands, on the other hand, favour the incorporation of HCN. On the other hand, less fundamental ligands with significant steric hindrance are more frequently employed. A member of this group is O-methylphenyl phosphate P(O-o-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, which facilitates the reductive elimination of the product (3-pentenitrile). When phosphine and phosphite ligands are used, steric effects have a major impact on the stability of Ni(0) complexes. The type of the ligand acceptor increases the stability of Ni(0) complexes, according to IR analyses measuring changes in the carbonyl vibration frequency (νCO) in [Ni(CO)<sub>3</sub>L] complexes (where L denotes a wide range of phosphorus ligands). The Tolman cone angle is used to illustrate the steric characteristics of the ligands. Dissociation won't happen even with highly diluted solutions for ligands with a small cone angle of about 109 degrees. [Ni[P(OEt)<sub>3</sub>]<sub>4</sub>] is an illustration of such a complex. 16-electron complexes, e.g., [Ni[P(O-o-tolyl)<sub>3</sub>]], whose Tolman cone angle was 141°, and alkene complexes [Ni(alkene)L<sub>2</sub>] were also examined. The electron effect is visible here, which leads to higher stability of the acrylonitrile complex, and Tolman also presented in his research 1H and 31P NMR studies of the complex [HNi(CN)L<sub>3</sub>] (where L is various phosphorus ligands). The addition of hydrogen cyanide to nickel(0) complexes is represented by the complex [HNi(CN)L<sub>3</sub>], and the increase in metal-alkene bond strength is affected by the replacement of the H. Because of this, [Ni(CN)<sub>2</sub>L<sub>2</sub>] is inactive throughout the hydrocyanation process.



The first stage of the research involves the HCN addition to butadiene, with the reaction occurring in the presence of a NiL<sub>4</sub> catalyst (Figure 3) and the reaction products being 3-pentene nitrile and 2-methyl-3-butene nitrile. The resulting isomer in branched form is not a substrate in the reaction to obtain adipic acid nitrile, so it is subjected to the isomerization process to 3-pentenitrile. The second stage occurs. This reaction includes the second CN group. Ethyl succinonitrile (ESN), 2-pentenitrile (AdN), and 2-methylglutaronitrile (MGN) are examples of secondary byproducts. According to studies, AlCl<sub>3</sub> has the largest hydrocyanation rate compared to isomerization, and it declines in the following order: AlCl<sub>3</sub> > ZnCl<sub>2</sub> > BPh<sub>3</sub>.



### Figure 3 Mechanism of Butadiene Hydrocyanation

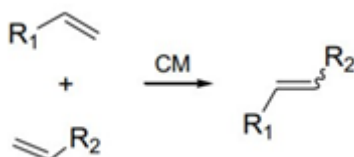
Asymmetric olefin hydrocyanation was the reaction that was mentioned. The use of bident phosphorus-based ligands in the alkene hydrocyanation process is crucial since it increases the stability of the end products produced by the process. Ruthenium (I) complexes are also employed for hydrocyanation and nickel complexes. Alkene isomerization is a crucial factor in the hydrocyanation reaction. Hydrocyanation reactions have the drawback of having low reaction yields. These problems still need to be resolved.

#### Metathesis Reaction

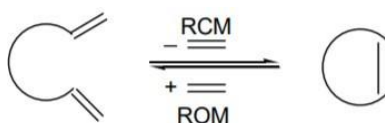
The 1930s saw the earliest investigations into the metathesis reaction. Schneider and Frolich reported that propene can be converted pyrolytically to ethene and butene without the need of a catalyst at a high temperature of about 852 °C. A fundamental idea in both academic and business research for many years has been metathesis. Using heterogeneous catalysts [Mo (CO)<sub>6</sub>/Al<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>/SiO<sub>2</sub>, Re<sub>2</sub>O<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub>] at 160 °C, Banks and Baile performed ground-breaking research on the alkylation of is alkenes with olefin in 1964. These studies uncovered new information on the linear olefin ratio and aimed to develop fuels with higher octane ratings. Using the method that had been created, Philips Petroleum began converting propylene into high-purity ethylene and but-2-ene. In a related study, Natta showed that the homogeneous catalysts [TiCl<sub>4</sub>/AlEt<sub>3</sub>, MoCl<sub>5</sub>/AlEt<sub>3</sub>, and WCl<sub>6</sub>/AlEt<sub>3</sub>] cyclobutenes and cyclopentenes allow the ring-opening metathesis polymerization (ROMP) type of polymerization to happen even at low temperatures. His studies concentrated on the copolymerization of ethylene with both linear and cyclic olefins and the polymerization of cyclic alkenes (ring-opening metathesis polymerization; ROMP). The possibility of using metal oxides on solid supports as catalysts was also known. Because of their inexpensive production and thus wide availability, they were used in the Shell higher olefin process (SHOP) and the expanded use of cutting-edge Shell technology (FEAST).

Numerous studies were being carried out concurrently, each of which was distinguished by the use of compounds with multiple bonds. The reactions as mentioned above also happened with the aid of catalysts. The study aimed to identify the precise response mechanism that may account for the observed experimental results. Researchers attempted to explain the various responses using knowledge of the transition state's structural makeup. They sought to define the catalytic center's structure and ascertain which homogeneous or heterogeneous catalysts influenced the conversion of compounds with numerous linkages. Calderon is credited with coining the word "metathesis" when he produced but-2-ene and hex-3-ene from pent-2-ene using the synthetic heterogeneous catalytic system WCl<sub>6</sub>/EtAlCl<sub>2</sub>/EtOH.

The chemists Grubbs, Schrock, and Chauvin, who shared the 2005 Nobel Prize in chemistry, precisely defined metathesis. A catalytic process called metathesis involves the exchange of double bonds between carbon atoms. Chemical compounds such as internal, terminal, and cyclic olefins, dienes, and podiums can all be affected by this reaction. High temperatures and pressure are typically not necessary for metathesis processes. All atoms are employed in the metathesis processes, and the produced by products can be processed or used again. The processes are so reversible and adhere to the principles of green chemistry. The manufacturing and processing of olefins are thought to benefit greatly from the olefin metathesis process. We categorize the following types of metathesis according to the substrate employed: Cross Metathesis—CM.



- Ring Closing Metathesis—RCM
- Ring Opening Metathesis—ROM

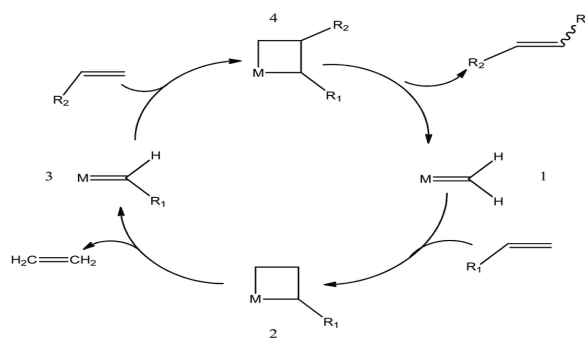


- Ring Opening Metathesis Polymerization—ROMP



• Acyclic Diene Metathesis—ADMET

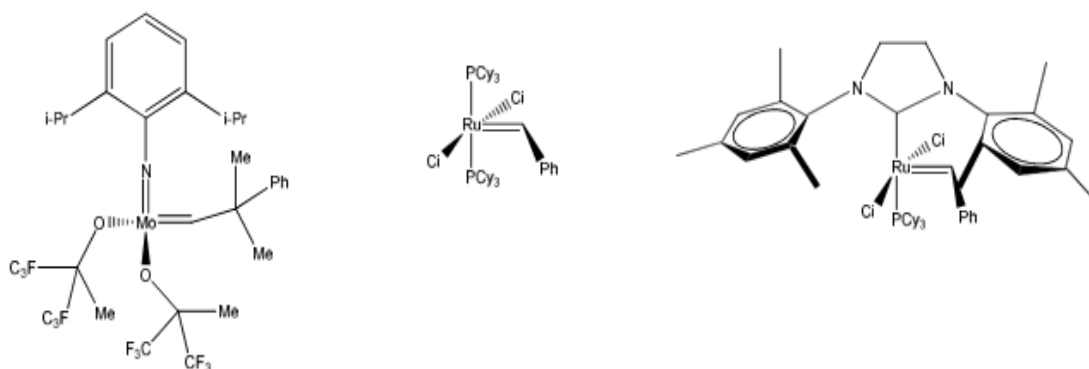
Herisson and Chauvin collaborated on the metathesis procedure. Figure 4 depicts the putative mechanism of metathesis made by these colleagues. They believed that alkylidene metal complexes catalyzed the metathesis reaction. The  $R_1-CH=CH_2$  substrate is reacted with complex I in the first step of the procedure to produce metallacyclobutane II. The resultant complex breaks down into the matching metalcarbene and the alkene, in this case, ethene. When the metalcarbene III produced combines with the olefin  $R_2-CH=CH_2$ , the following breakdown of the metalcarbene IV produces the carbene I. Carbene is a suitable catalyst for reactions when it is an alkylidene complex.



**Figure 4 The Mechanism of the Metathesis Reaction**

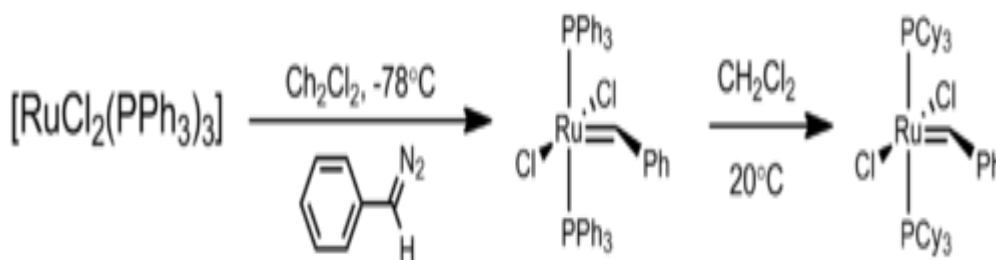
Herisson and Chauvin collaborated on the metathesis procedure. Figure 4 depicts the putative mechanism of metathesis made by these colleagues. They believed that alkylidene metal complexes catalyzed the metathesis reaction. The  $R_1-CH=CH_2$  substrate is reacted with complex I in the first step of the procedure to produce metallacyclobutane II. The resultant complex breaks down into the matching metalcarbene and the alkene, in this case, ethene. When the metalcarbene III produced combines with the olefin  $R_2-CH=CH_2$ , the following breakdown of the metalcarbene IV produces the carbene I. Carbene is a suitable catalyst for reactions when it is an alkylidene complex. Ruthenium-based complex chemicals are of particular interest. They exhibit high olefin (C-C bonds) reactivity and tolerance for the functional groups of the substrates. They are also resilient and do not react negatively with moisture and oxygen that can be present in the reaction system. The Grubbs catalyst of the first generation is an illustration of such a complex (Figure 5). Figure 5 depicts the production of a catalyst. In addition to the advantages indicated above, the resulting complex is simple to store. It is one of the most often utilized complexes in metathesis reactions because it may be used to produce macrocyclic, carbo-, and heterocyclic ring compounds.

It also catalyzes the alkene-alkyne metathesis and the engine metathesis cyclization reaction. It is frequently employed in polymerization reactions like ADMET, ROMP, and live norbornenes polymerization. Its flaw is that it cannot catalyze cross metathesis with, -unsaturated chemicals. Imidazole derivative-containing catalysts are also significant. A first-generation Grubbs catalyst is reacted with a substance that is a source of stable carbenes, such as the imidazolium salt, to produce N-heterocyclic carbenes (Figure 6). It participates in reactions with, -unsaturated olefins catalyzes ROMP cycloolefins with low ring stresses, and has significantly higher activity than the first-generation catalyst.



**Figure 5 Metathesis Catalysts, from the Left: (A) Schrock's Molybdenum Complex, (B) First-Generation Grubbs Catalyst, (C) Second-Generation Catalyst.**





**Figure 6 Grubbs Catalyst Preparation Reactions**

Metathesis reactions have been carried out in a multistage SHOP process using nickel complexes with chelate ligands. Ethene is the starting substance in this reaction. Ethene is oligomerized with the use of a nickel catalyst, producing C4-C40 olefins. Light olefins are transformed into suitable interior olefins (light C6 and heavy C18) in the isomerization process. They are transformed into medium-length olefins (C11-C14) in the subsequent stage of the metathesis process. The internal olefins that are produced are used to make surfactants. In addition, the substrates used in the synthesis of alkyl-benzenes are olefins that have undergone carbonylation and have been hydrogenated to alcohol. The separated C6-C18 portion is used to make lubricants, plasticizers, and detergents. The nickel above complexes is the oligomerization catalysts. Oxygen and phosphorus atoms cooperate to coordinate chelate ligands. Researchers are especially interested in the availability of metal-coordinated ligands. These ligands can open and close the ring, which is made possible by the various degrees of coordination between the atoms that serve as donors. With this characteristic, switching between cis- and trans-forms is possible, and the symmetry change impacts the reaction's selectivity. Numerous studies on the synthesis of catalysts affecting the preparation of sterically crowded olefins and catalysts, which regulate the stereo selectivity of reactions, are being conducted by scientists due to their selectivity.

The heterocyclic carbene-coordinated compounds of ruthenium, the salami-type bisoxime complexes of Co (II) and Ni (II), and the carboxylate, phenolate, hydroxy carboxylate, and catecholate derivatives of Ti (IV) are all olefin metathesis catalysts. It should be noted that FeCl<sub>3</sub> likewise catalyzes the metathesis reaction. According to our analysis, the metathesis process offers numerous options for the synthesis of different chemical substances. It is used in chemical investigations and the refining business. It is a potent synthesis technique. For this reason, it is worthwhile to search for new catalysts that can be employed in metathesis and adhere to the principles of green chemistry.

### Hydrosilylation Reaction

#### Reduction Pt (II) to Pt (0) in Reaction with Silane HSi(OEt)<sub>3</sub>

In the modern world, silicon compounds are frequently employed. They are added as additives to cosmetics, food, and cleaning items. They are also rapidly being used in the electronics and automotive industries. For instance, polycarbosilanes, polycarbosilane, and organ silicon polymers are utilized as precursors to ceramic materials and are chemically resistant. These substances include some that have optoelectronic, photoconductive, or electroluminescent characteristics. The hydrosilylation procedure is the basis for synthesizing silicon derivative chemicals, which are required to create the materials as mentioned above. Hydrosilylation is known as the catalytic addition reaction of organic and inorganic hydrogen silanes to unsaturated molecules. New Si-C and Si-heteroatom bonds are created depending on the substrate used in the synthesis. Platinum (II) complexes are the hydrosilylation catalysts that are most frequently utilized. However, other transition metal coordination compounds, such as Pd(II), Co(II), Ni(II), Ir(I), Rh(II), and Ru(I), are also known. According to scientific reports, numerous homogeneous catalysts are active in the hydrosilylation reaction. There are four of them: [PtCl<sub>2</sub>(cod)], [Pt(CH<sub>2</sub>=CHSiMe<sub>2</sub>)<sub>2</sub>O<sub>3</sub>], [RhCl(PPh<sub>3</sub>)<sub>3</sub>], and [Pd<sub>2</sub>(dba)<sub>3</sub>], where cod stands for cyclooctadiene and dba for dibenzoyl acetone. The reaction of [PtCl<sub>2</sub>(cod)] with (EtO)<sub>3</sub>SiH is an illustration of the reduction of platinum (II) to platinum(0). The hydrosilylation technique can potentially make use of the metal colloid that was created during the reaction.



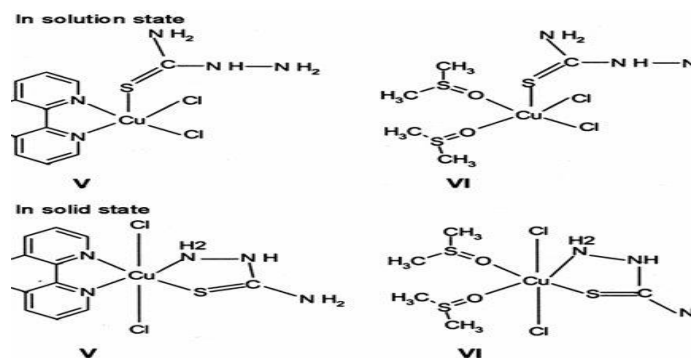


Figure 7. Example of Reducing Platinum (II) To Platinum (0)

It should be mentioned that the manufacture of siloxanes and silanes frequently uses hydroformylation. Hydroformylation's high applicability for synthesizing novel chemicals is a result of its chemoselectivity. Due to falling catalyst prices, hydroformylation catalysts are not currently reliant on platinum. Designing new transition metal compounds with catalytic capabilities in this technique is now possible because of the employment of new catalysts in the hydroformylation reaction.

#### Karstedt's Catalyst

The most frequent application of platinum complexes is the hydrosilylation of carbon-carbon double bonds. In 1973, a platinum (0) compound with divinyl siloxane ligands was identified as Karstedt's catalyst. It is produced when divinyl tetramethyl disiloxane reacts with chloroplatinic acid and has a high catalytic activity and good solubility in polysiloxane systems (Figure 8). It is useful in a variety of processes.

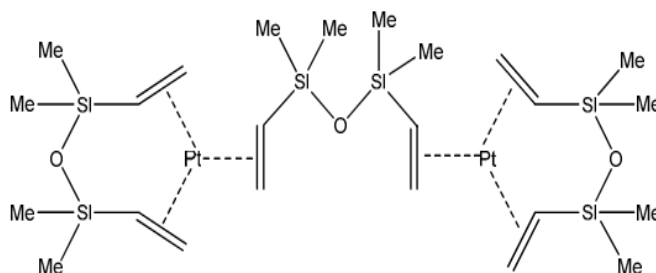


Figure 8 Karstedt's Catalyst

Therefore, Karstedt's catalyst is successfully used in industry due to its high activity and selectivity. Finding a suitable substitute for this hydroformylation catalyst will be challenging.

#### Hydrosilylation Mechanism Proposed By Chalk and Harrod and Modified Mechanism of Chal-Harrod—Catalyzed By Rhodium Complex Compounds

Free radicals may participate in reactions that enter the hydrosilylation cycle or occur in the presence of catalysts in transition metal complex molecules. Understanding the mechanisms underlying the hydrosilylation of numerous carbon-carbon bonds when transition metal complexes are present is important. The selectivity and rate of specific reactions are influenced by the use of transition metal complexes as catalysts. The production of organosilicon compounds frequently uses the hydrosilylation method. Chalk and Harrod first proposed the idea of a hydrosilylation mechanism in the 1960s. Hexachloroplatinic acid  $H_2[PtCl_6]$  served as a homogenous reaction catalyst in their study. Silane is joined to the catalyst metal in the initial stage. The transition metal employed in the catalyst is typically configured as  $d_8$  or  $d_{10}$ . A stable alkene complex is the result of the second stage. Olefin coordination occurs only after the electron cloud transfers from the double bond to the hybridized metal orbit. Utilizing extra substrate (olefin) is crucial. An M-H and M-Si bond is created due to  $HSiR_3$ 's oxidative addition to the complex. One important step is the rearranging of  $\sigma$ . A silyl-alkyl complex is produced by the migratory insertion of olefin for M-H binding. Reducing the elimination of the alkyl complex results in the formation of the reaction product.





It was also studied how the hydrosilylation process produces unsaturated compounds. The modified Chalk-Harrod process, catalyzed by complex rhodium molecules, explains this issue. Although the result of both processes is identical and unaltered, the process itself is altered. This is seen at the crucial moment of alkene insertion. The M-Si bond, not the M-H bond, is affected in the new technique. Alkenylsilane is removed in the last stage, which continues similarly. The diagram (Figure 9) depicts both procedures.

The cobalt (II) amide coordination compounds that serve as catalysts can hydrosilylate alkenes with tertiary silanes without needing a catalytic activator. It is important to note that transition metal compounds plentiful on Earth can successfully catalyze alkene hydrosilylation. Many variables, such as the solvent, catalyst, or temperature, affect the hydroformylation reaction's regio- and stereo selectivity. The difficulty of the actual structure obtained product should be recognized.

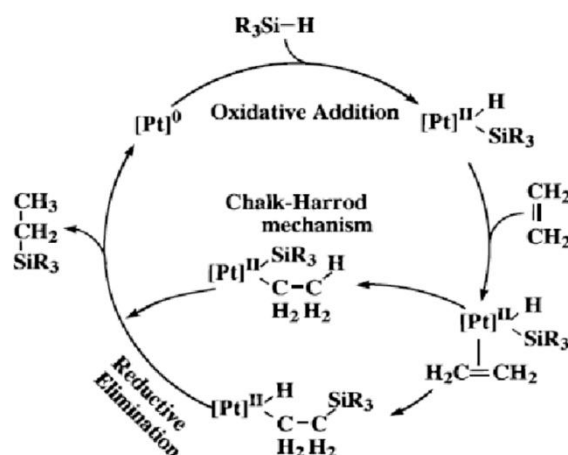
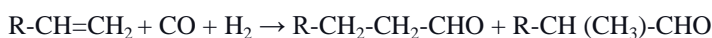


Figure 9. Hydrosilylation Mechanism and Modified Mechanism Proposed By Chalk and Harrod

### Hydroformylation Reaction

Olefins react with hydrogen and carbon monoxide (II) to generate straight-chain (n) and branched-chain (iso) aldehydes. This process is known as hydroformylation. Under the effect of the catalyst that is present during the reaction, this procedure takes place. Under the right circumstances, the products acquired as aldehydes can be transformed into alcohols, carboxylic acids, acetals, diols, or aldols. However, the goal of the reaction is typically to produce an unbranched chain aldehyde. The n/iso ratio is most frequently used to describe the catalytic system. As we can see, the catalytic system used during the hydroformylation is better the larger the numerical value of the ratio. Listed below is the reaction diagram for hydroformylation.



German chemist Roelen discovered the hydroformylation process in 1938. During the Fischer-Tropsch reaction, he made the discovery. Hydridotetracarbonyl—[HCo(CO)<sub>4</sub>] was the first catalyst utilized in the hydroformylation reaction. Then, phosphines were added to cobalt catalysts, increasing the n/iso ratio and allowing for lower pressure and temperature during the hydroformylation process.

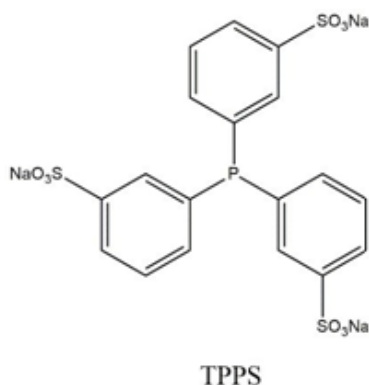
The work of English Nobel Prize laureate Sir Geoffrey Wilkinson led to a significant advancement in the quest for catalytic systems. They identified compounds made of rhodium atoms that had 1,000 times more catalytic activity than cobalt catalysts in the hydroformylation procedure.

Despite being more expensive, rhodium compounds are frequently used as catalysts in hydroformylation reactions. The British chemical business Union Carbide Davy Powergass Johnson-Matthey LPO uses hydroformylation. It involves a precursor with the formula [(acac)Rh(CO)<sub>2</sub>] and a modifying ligand called phosphine (PPh<sub>3</sub>). The active catalyst form [(acac)Rh(CO)(PPh<sub>3</sub>)] is created by adding around 10% by weight of PPh<sub>3</sub>. The following conditions are used to carry out the hydroformylation process:

Conditions: pressure between 10 and 50 bar, temperature between 60 and 120 C. The n/iso ratio for this procedure is approximately 1:5; the Zakady Azotowe in Kedzierzyn-Koz'le uses the hydroformylation procedure.



Ruhrchemie/Rhone-Poulenc's commercialization of Kuntz's industrial discovery of hydroformylation is based on utilizing a two-phase catalytic system based on a rhodium complex molecule. The hydroformylation procedure (Figure 10) made use of the chemical tris(3-sulfonylphenyl) phosphine sodium (TPPS).



**Figure 10 The Simplified Formula of Sodium Salt (Tris(3-Sulfonyl Phenyl) Phosphine)**

Because the catalyst is in the polar phase when using the catalyst above system, it can be easily separated from the desired products (aldehydes). As a result, the catalyst is utilized continuously. The hydroformylation procedure can be carried out by adopting a two-phase catalytic system while maintaining excellent selectivity and activity for creating a linear product.

The selectivity of the resultant product in the hydroformylation reaction is influenced by the electron and steric characteristics of ligands bound to the rhodium atom. A larger amount of the linear product is produced when ligands with weaker basic properties, such as pyrrolylphosphines or phosphites, in the olefin hydroformylation reaction.

The grip angle, which defines the value of the angle between the P-M-P bonds in the complex with the ligand, is used to evaluate chelate ligands. In contrast, the magnitude of the conic angle is used to determine the steric properties of the ligands. Studies on the influence of the grip angle on the reaction selectivity show that the equatorial-equatorial arrangement of donor atoms in chelating ligands observed in rhodium atom-based catalyst systems produces the optimal n/iso values. This shows that the geometry of the corresponding rhodium complexes, in this case, given grip angles, is roughly  $120^\circ$ , exhibiting the geometry of the trifocal bipyramid.

According to the most recent scientific publications, a considerably superior n/iso ratio can be obtained using carbene and phosphorus ligand catalysts connected to the rhodium atom in the coordination sphere. Such a catalyst is  $[\text{RhH}(\text{NHC})(\text{CO})\text{P}(\text{OPh})_2]$ , where NHC stands for heterocyclic carbene.

Regarding using rhodium compounds as catalysts, the catalysis of the hydroformylation process is constantly changing. Similar to the  $\text{RhCl}(\text{PPh}_3)_3$  complex, even a single rhodium atom demonstrates catalytic activity in hydroformylation. Rhodium particles' catalytic abilities can accelerate hydroformylation. Fe(II) was shown to have the capacity to catalyze the hydroformylation of alkenes in mild circumstances in 2011. The simplicity with which the catalyst and end product can be separated is the hydroformylation reaction's most significant benefit. When receiving new materials, it is crucial.

### Carbonylation Reaction

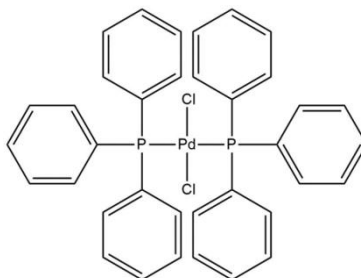
The process of joining a carbon monoxide (II) molecule to an organic substance is known as the carbonylation reaction. This method is most frequently used to create acetic acid from methanol. Or methyl acetate, an anhydrous acid from ester derivative. Transition metals, notably those in group 9, such as cobalt, rhodium, and iridium, are employed to conduct this reaction. The procedure also requires an iodide co-catalyst to activate the methanol. Acetyl iodide is created during this reaction, and when it is hydrolyzed, it yields a combination of acetic acid and hydroiodic acid.

The first commercially successful methyl alcohol carbonylation technique was carried out by BASF using a cobalt catalyst. Then Monsanto, using a rhodium catalyst, began carbonylation methanol on an industrial scale. Lower carbon



monoxide pressure and temperature were used in Monsanto's operating conditions compared to BASF's. Additionally, methyl alcohol was selected for much more effectively during this process.

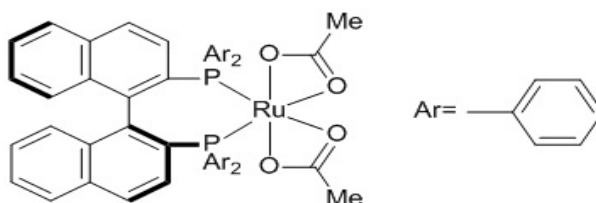
In the carbonylation procedure, the palladium complex molecule  $\text{PdCl}_2(\text{PPh}_3)_2$  is employed, and the end product is the well-known anti-inflammatory medication, ibuprofen. Boots-Hoechst-Celanese does this synthesis. A condensed version of this catalyst's formula is shown in Figure 11 below.



**Figure 11 The Simplified Formula of the Palladium Complex Used During Ibuprofen Synthesis**

Naproxen is another very well-known remedy in which production palladium complexes are used as catalysts. This drug belongs to non-steroidal inflammatory drugs obtained in a multistage synthesis. The palladium complex is a catalyst during stage 2—Heck reaction and stage 3—hydroxycarbonylation.

Both ibuprofen and naproxen synthesis can be carried out in the presence of chiral phosphine. Reactions carried out in ionic liquids, using a ruthenium coordination compound as a catalyst, and introducing a chiral phosphine, allow us to obtain the appropriate optical isomer. Below, Figure 12 shows the catalyst used to obtain (S)-ibuprofen.



**Figure 12 Ruthenium Catalyst from S-BINAP Used For the Synthesis of S-Ibuprofen**

The application of bulk Pd catalyst without using organic ligands results in the hydroaminocarbonylation of olefins, amino carbonylation of aryl iodides, and oxidative carbonylation of amines. Methanol carbonylation is catalyzed by iridium and immobilized rhodium, which results in the production of acetic acid. An intriguing feature is that membranes, such as chitosan, polyamide, and polyvinyl alcohol catalyze carbonylation processes. Membranes are involved in the carbonylation process' product separation. See the publication of  $\text{K}_2[\text{Fe}(\text{CO})_4]$  as a catalyst for the formal insertion of CO.

Therefore, iron (II) and platinum (II) complexes should be tested in the carbonylation reaction as catalysts. Palladium (II) complexes satisfactorily perform the role of catalyst carbonylation reaction; therefore, due to the similarity, analogous platinum (II) complexes should be tested.

### Olefin Polymerization

Polymerization of olefins is a process used commercially worldwide on a very large scale in the chemical industry. This is evidenced by the sum of the annual production of polyethylene and polypropylene is about 15 million tons. Another important aspect of using complex compounds such as olefin polymerization catalysts is that it is economically cheap and environmentally friendly.

The deposition of titanium (IV) tetrachloride on magnesium chloride is the most recent iteration of the Ziegler-Natta catalysts utilized in the olefin polymerization process. The grain diameter of the carrier,  $\text{MgCl}_2$ , is 50 m. A Lewis base or mechanical milling precipitates a carrier with these grain diameter properties from a soluble precursor solution. The addition of phthalic esters or silyl ethers occurs in the second stage. The comparable ionic rays of titanium (III) and

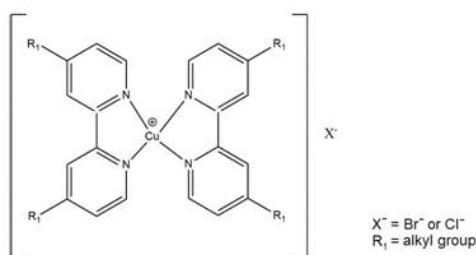


magnesium (II) ions allow for the creation of third-generation catalysts. This synthesis involves dissolving magnesium (II) ions in an alkoxide, sulfide, or carboxylate solution before adding titanium (I) tetrachloride. The catalyst is then made active by the addition of phthalates and  $\text{TiCl}_4$ .

A process known as atom transfer radical polymerization (ATRP) enables the creation of polymers and co-polymers utilized commercially worldwide. This method of polymerization was discovered and developed by Polish-American chemist Matyjaszewski. The ATRP method is inexpensive and does not harm the environment when used to manufacture polymeric materials on a large scale. Radical transfer polymerization techniques can produce polymers with the right structure and morphology. Its employment in many industrial technologies is expanding because of such control possibilities for the process being used.

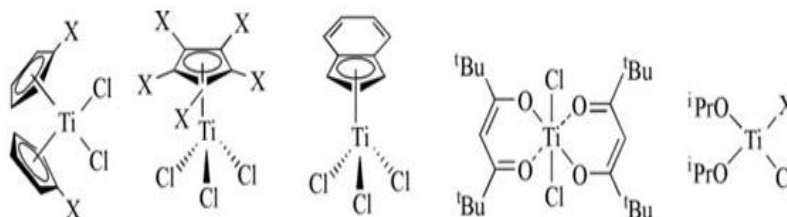
Copper and iron coordination compounds are used as catalysts during radical atomization polymerization. The application of copper compounds during the process determines the necessity of the presence of reducing agents. The polymerization process carried out in water can be inhomogeneous conditions or heterogeneous. Below, Figure 13 shows an example of a complex which is a catalyst for the ATRP process.

Producing polymers that are elements of moisturizing agents, surfactants, paints, and surfactants is possible using radical polymerization with the atom transfer process. Additionally, it is used to create polar thermoplastic elastomers. Additionally, it enables the production of polymer materials with enhanced hydrophilic, antibacterial, or conductivity properties.



**Figure 13 An Example of A Copper Complex Used As A Catalyst In Atom Transfer Radical Polymerization**

Another method for polymerization is called organometallic radical polymerization (OMRP). The polymerization of acrylates was the original application of this technique. The substrates can be acrylic acid, vinyl acetate, or another substance. Compounds of titanium, cobalt, iron, and chromium have found use in this method as catalysts. Examples of ruthenium compounds employed during OMRP are shown in Figure 14.



**Figure 14.** Titanium compounds are used as catalysts in radical polymerization using organometallic compounds.

Olefin polymerization, in our opinion, is a vast area for research since, according to recent publications, non-metallocene transition metal complexes are becoming an increasingly important catalyst for this process. Compared to conventionally utilized compounds, the new complex compounds have greater levels of catalytic activity, and their synthesis is easy and inexpensive. Chromium (III), Oxovanadium(IV), and Cobalt(II) complexes are new catalysts.

Olefin polymerization uses catalysts made of late-transition metals. One should be aware that the majority of them result in the development of atactic and amorphous polymers.  $\text{Cu}(2, 3\text{-pydc})(\text{bpp})[\text{Zn}(2,3\text{-pydc})(\text{bpp}), 2.5\text{H}_2\text{O}][\text{Cd}(2,3\text{-pydc})(\text{bpp})(\text{H}_2\text{O})]$  and  $2.5\text{H}_2\text{O}$  Metal-organic frameworks called  $3\text{H}_2\text{O}$  (2,3-pydc stands for pyridine-2,3-dicarboxylate; bpp = 1,3-bis(4-pyridyl)propane) are used in heterogeneous catalysis. N, P and S-donor-based



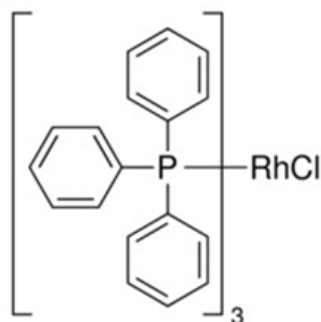
tridentate ligands provide the catalyst for ethylene trimerization and chromium (III) tetramerization. One can conclude that this field needs to be explored since new catalysts can successfully replace ones in use in the past but, regrettably, did not adhere to the principles of green chemistry.

### Hydrogenation Reaction

The hydrogenation reaction is a very important organic chemistry reaction. Hydrogen, one of the most important elements in the chemical industry, is used in almost 4% of hydrogenated carbon and hydrogen compounds. The mechanism of this reaction requires the presence of a catalyst, which is most often transition metal compound. This process is carried out to create new bonds between carbon and hydrogen.

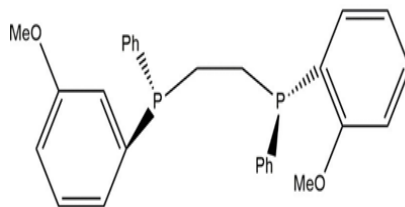
The hydrogenation reaction most frequently employs heterogeneous catalysts. Their use is justified by how simple it is to separate them from organic products. The asymmetric hydrogenation reaction, however, does not allow for the use of heterogeneous catalysts during the hydrogenation reaction. Additionally, the chemoselectivity and regioselectivity of the reaction are increased by homogeneous catalysts or those made of complex compounds based on transition metals.

It is possible to design the compound's spatial and electronic structure if a metal complex catalyzes the hydrogenation reaction. By picking the appropriate ligand, this can be accomplished. The Wilkinson catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  is an illustration of the most well-known hydrogenation reaction catalyst (Figure 15).



**Figure 15 the Simplified Formula of Wilkinson's Catalyst**

One of the phases of a very significant enantioselective synthesis, which yields the molecule L-3,4-dihydroxyphenylalanine (L-DOPA), involves an asymmetric hydrogenation process. L-DOPA is a medication used in Parkinson's disease treatment. We know that a chiral form of phosphine must be present in the catalytic system of the hydrogenation mechanism in order to obtain the proper product enantiomer. The catalytic system of the rhodium complex with 1,2-bis[(2-methoxyphenyl)phenylphosphine]ethane (DIPAMP) is employed during the synthesis reaction of L-3,4-dihydroxyphenylalanine. A simplified formula for the chiral form of phosphine, a ligand in the rhodium complex, is shown in Figure 16.



**Figure 16 Simplified Formula of The Chiral Form of Phosphine-1, 2-Bis [(2-Methoxyphenyl) Phenylphosphine] Ethane.**

It can be concluded that using phosphines as ligands in catalysts creates many opportunities to design new complexes as catalysts. These types of compounds catalyze hydrogenation of esters and amides. It is worth trying to synthesize new complexes containing other organophosphorus compounds as ligands and check the catalytic activity of phosphine-containing dual-core complexes.



## Catalysis and Green Chemistry

### Ionic Liquids—Catalytic Reactions

Green chemistry principles are given special consideration in contemporary catalysis. Environmental friendliness must be a priority in technological processes. One of the first ionic liquids was a chemical substance known as methylammonium nitrate. Walden discovered this chemical compound in 1914 due to neutralizing ethylamine with concentrated nitric acid (V). Low melting points and extremely low vapor pressure are characteristics of ionic liquids. Ionic liquids' low volatility is one of the characteristics that led to the classification of these substances as "green solvents." Imidazolium, phosphonium, imidazolium, and pyridinium salts are among the substances referred to as ionic liquids. Ionic liquids can be utilized as environmentally friendly solvents because they don't pollute the environment. Ionic liquids' ecotoxicity and biodegradability are actively being researched. Metals and chemical compounds are transported in soil by ionic liquids.

Imidazolium salts can be used in two-phase systems. Because of this, they are the ionic liquids that are utilized the most frequently as a catalyst for catalytic reactions. The production of the anti-inflammatory drugs S-Naproxen and S-Ibuprofen involves using ionic liquids. Ruthenium compounds with S-Binap chiral activity catalyze asymmetric hydrogenation. phosphine produced in systems with alcohol and ionic liquid, such as methanol.

When [PdCl<sub>2</sub> (cod)] or Pd (0)/PVP is used to catalyze the methoxycarbonylation of iodobenzene, pyridinium ionic liquids work very well as a medium. Ionic liquids were utilized in the Sonogashira process, allowing for efficient catalyst recycling [PdCl<sub>2</sub> (P (OPh)<sub>3</sub>)<sub>2</sub>]. The synthesis of alkyl derivatives is an industrial process based on the Sonogashira reaction. The pharmaceutical sector makes use of these kinds of reactions. Tetraalkylphosphonium salts are the ideal reaction media in this kind of reaction. Hexane extraction removes the end product from the catalyst-containing ionic liquid. Byproducts are eliminated through water washing.

In the Suzuki process, which uses triphenylphosphine in imidazolium ionic liquids, palladium precursors are employed. The carbene complex is the catalyst's active form in the Suzuki reaction. Ionic liquids are characterized by the production of carbene complexes, especially about imidazolium halides. Such reactions occur in complex ruthenium (I) and palladium(II) compounds. The imidazolium ring's C (2) carbon undergoes deprotonation during the process, forming an M-C bond.

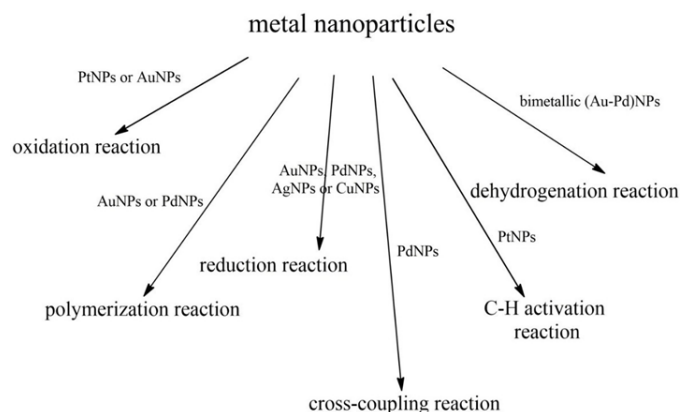
If the catalytic reaction uses the ionic liquid as a solvent, carbene complexes are created there and then.

Carbene complexes' reactivity frequently varies from that of the catalyst's precursor. Because of this, there are situations in which the ionic liquid inhibits catalytic activity. One such reaction is the methoxycarbonylation of iodobenzene. Ionic liquids can be inferred to be the reaction system's active and solvent components. Ionic liquids are involved in the synthesis of [IL]<sub>2</sub> [PdX<sub>4</sub> where IL denotes the ionic liquid's cation and X denotes the halide. In comparison to the [PdCl<sub>2</sub> (cod)] complex, [IL]<sub>2</sub> [PdX<sub>4</sub>] complex compounds are more active in the Suzuki reaction.

### Catalysts of Organic Reactions—Metal Nanoparticles

Metal nanoparticles range in size from 1 to 50 nm in diameter. The characteristics of nanotubes are significantly influenced by their size. The 1990s were when the first reports on the usage of Pd-containing metal nanoparticles in Heck's reaction appeared. This is related to interactions between butyl acrylate and iodobenzene or aryl bromides and styrene. Tetra-N-alkylammonium cations reduce metal chloride solutions to produce metal nanoparticles, which are then electrostatically stabilized. Figure 17 illustrates how metal complexes and nanoparticles are used in diverse catalytic processes.

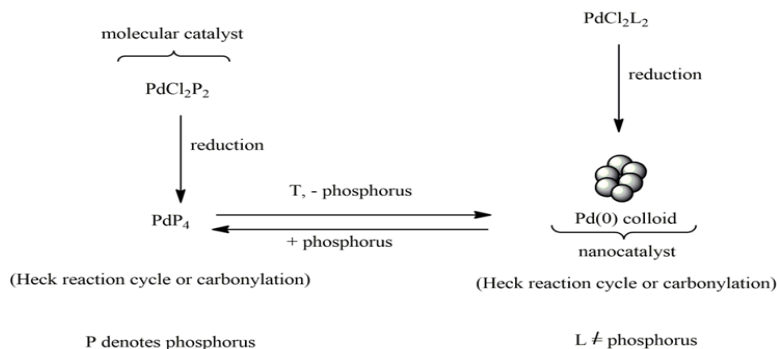




**Figure 17. The Application of Exemplary Metal Nan particles in Various Catalytic Reactions**

Some characteristics of both homogeneous and heterogeneous catalysts can be found in metal nanoparticles.

During a specific reaction, soluble metal complexes can form on nanoparticles. Nanoparticles are created when a complicated molecule undergoes a reduction reaction (Figure 18). The nanoparticles then aggregate to form a metallic framework. The method can also work in reverse. This occurs when nanoparticles are dissolved during catalytic reactions, which in turn aids in creating complex molecules. There are documented instances of palladium complexes and nanoparticle equilibria in catalytic systems. The equilibrium occurs frequently when phosphorus ligands are present in the catalytic system. Complex molecules are reduced, resulting in the formation of metal nanoparticles. The reduction can happen before and after the catalytic event, though less frequently.



**Figure 18 Transformations of Palladium Catalysts from Monomolecular To Nanoparticles. This Figure Is Adapted**

Monometallic nanoparticles are the most common type of nanoparticle. However, bimetallic nanoparticles are being studied in science more and more frequently. The inner sphere of bimetallic nanoparticles comprises less expensive base metals. A layer of precious metals, such as platinum, palladium, and ruthenium, is placed over the base metals.

Palladium and copper nanoparticle catalysis is used to create C-C and C-S bonds. The palladium nanoparticles bring about the coupling of vicinal-diiodoalkenes, acrylic esters, and nitriles. Chemoselective reduction of N-aromatic chemicals uses copper nanoparticles. It can be said that the method for future research will involve using metal nanoparticles to locate catalytic sites. Identifying the catalytic sites for oxygen reduction reactions is crucial when creating new, highly active base metal catalysts.

## CONCLUSIONS

The several chemical technology processes that use coordination compounds as catalysts are discussed in this article. The chemical industry uses various organic synthesis techniques to create polymer materials, such as the olefin polymerization process and the atom transfer radical polymerization (ATRP) process. The end results are used in the pharmaceutical sector in many aspects of our life, including the manufacturing of polyethylene and complex organic



compounds and the synthesis of medications. The broadest possible application of green chemistry principles in chemical technologies—in the case of catalytic reactions involving coordination compounds, biotechnological or organocatalytic approaches are applied—is a crucial component. The application of ultrasound to enhance solution dissolution or microwave heating illustrates the idea mentioned above.

**The following are the key findings of this evaluation:**

Modernized CYCLOPOL-bis technology for producing caprolactam allows for production costs to be reduced and product quality to be improved. Ni complexes with bidentate chelate ligands used as catalysts in SHOP allow for the separation of the C6-C18 fraction, which produces plasticizers and detergents. PdCl<sub>2</sub> participating in the Wacker process forms a stoichiometric amount of acetaldehyde. The hydrosilylation catalysts are [PtCl<sub>2</sub>(cod)], [Pt(CH<sub>2</sub>=CHSiMe<sub>2</sub>)<sub>2</sub>O<sub>3</sub>], [RhCl(PPh<sub>3</sub>)<sub>3</sub>], and [Pd<sub>2</sub>(dba)<sub>3</sub>]; the catalysts in ATRP are Cu(I) and Fe(II) complexes with ligands such as halides, 2,2'-bipyridine, or tris(2-pyridylmethyl)amine; Methoxycarbonylation is catalysed by [PdCl<sub>2</sub>(cod)], and carbonylation is catalysed by K<sub>2</sub>[Fe(CO)<sub>4</sub>]; [Cu(2,3-pydc)(bpp)][Zn(2,3-pydc)(bpp), 2.5H<sub>2</sub>O][Cd(2,3-pydc)(bpp)(H<sub>2</sub>O)] and 2.5H<sub>2</sub>O Metal-organic frameworks are used in heterogeneous catalysis; the [IL]<sub>2</sub>[PdX<sub>4</sub>] complex is more active in the Suzuki reaction than [PdCl<sub>2</sub>(cod)].

Research into the use of complex noble metal compounds as photo redox catalysts has increased in recent years. This pattern will continue long since photo redox catalysis is a particularly efficient for activating tiny molecules. Recent years have seen a growth in research into applying complicated noble metal compounds as photo redox catalysts. Because photo redox catalysis is a very effective technique for activating small molecules, this trend will last very long.

## REFERENCES

- [1]. Böhm, L.L. The Ethylene Polymerization with Ziegler catalysts: Fifty years after the discovery. *Angew. Chem. Int. Ed.* **2003**, 42, 5010–5030.[Cross Ref]
- [2]. Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. Das Mülheimer normal duck-polyethylene-verfahren. *Angew. Chem.* **1955**, 67, 541–547.[Cross Ref]
- [3]. Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. Crystalline high polymers of  $\alpha$ -olefins. *J. Am. Chem. Soc.* **1955**, 77, 1708–1710.[CrossRef]
- [4]. Cornils, B.; Herrmann, W.A. *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*; Wiley-VCH: Weinheim, Germany, 2004.
- [5]. Irie, R.; Noda, K.; Ito, Y.; Matsumoto, N.; Katsuki, T. Catalytic asymmetric epoxidation of internal olefins. *Tetrahedron Lett.* **1990**, 31, 7345–7348.[Cross Ref]
- [6]. Bhaduri, S.; Mukesh, D. *Homogeneous Catalysis: Mechanism and Industrial Applications*; A.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2000.
- [7]. Parrish, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1992.
- [8]. Seidel, W.C.; Tolman, C.A. Ethylene [bis(tri-*o*-tolyl phosphite)] nickel(0). *Inorg. Chem.* **1970**, 9, 2354–2357.[CrossRef]
- [9]. Tolman, C.A. The 16 and 18 electron rule in organometallic chemistry and homogeneous catalysis. *Chem. Soc. Rev.* **1972**, 1, 337–353.[Cross Ref]
- [10]. Tolman, C.A. Chemistry of tetrakis (triethyl phosphite) nickel hydride, HNi[P(OEt)<sub>3</sub>]<sub>4</sub>. I. Nickel hydride formation and decay. *J. Am. Chem. Soc.* **1970**, 92, 4217–4222.[CrossRef]
- [11]. Goertz, W.; Keim, W.; Vogt, D.; Englert, U.; Boele, M.D.K.; vande Veen, L.A.; Kamer, P. C. J.; van Leeuwen, P.W.N.M. Electronic effects in the nickel-catalysed hydrocyanation of styrene applying chelating phosphorus ligands with large bite angles. *J. Chem. Soc. Dalton Trans.* **1998**, 2981–2988. [Cross Ref]
- [12]. Calderon, N. Olefin metathesis reaction. *Acc. Chem. Res.* **1972**, 5, 127–132.[CrossRef]
- [13]. Calderon, N.; Chen, H.Y.; Scott, K.W. Olefin metathesis—A novel reaction for skeletal transformations of unsaturated hydrocarbons. *Tetrahedron Lett.* **1967**, 34, 3327–3329.[Cross Ref]
- [14]. Trnka, T.M.; Grubbs, R.H. The Development of L<sub>2</sub>X<sub>2</sub>RuCHR olefin metathesis catalysts: an organometallic success story. *Acc. Chem. Res.* **2001**, 34, 18–29.[Cross Ref][Pub Med]
- [15]. Grubbs, R. H. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003.
- [16]. Lutz, E.F. Shell higher olefins process. *J. Chem. Ed.* **1986**, 63, 202.[CrossRef]
- [17]. Vougioukalakis, G.C.; Grubbs, R.H. Ruthenium-based heterocyclic carbene-coordinated olefin metathesis catalysts. *Chem. Rev.* **2010**, 110, 1746–1787.[Cross Ref]
- [18]. Lewis, L.N.; Stein, J.; Gao, Y.; Colborn, R.E.; Hutchins, G. *Platinum Catalysts Used in the Silicones Industry Their Synthesis and Activity in Hydrosilylation*; GE Corporate Research & Development Center, General Electric Company, Schenectady: New York, NY, USA, 1997.





- [19]. Wilkinson, G.; Gordon, F.; Stone, A.; Abel, E.W. *Comprehensive Organometallic Chemistry*; Elsevier Science Ltd.: Amsterdam, The Netherlands, 1982.
- [20]. Trzeciak, A.M.; Ziólkowski, J.J. Perspectives of rhodium organometallic catalysis. Fundamental and applied aspects of hydroformylation. *Coord. Chem. Rev.* **1999**, 190–192, 883–900. [CrossRef]
- [21]. Van Leeuwen, P.W.N.M. *Rhodium Catalyzed Hydroformylation*; Kluwer Academic Publisher: Dordrecht, the Netherlands, 2000.
- [22]. Behr, A.; Neubert, P. *Applied Homogeneous Catalysis*; Wiley-VCH: Weinheim, Germany, 2012.
- [23]. Gil, W.; Trzeciak, A.M.; Ziólkowski, J.J. Rhodium(I) N-heterocyclic carbene complexes as highly selective catalysts for 1-hexene hydroformylation. *Organometallics* **2008**, 27, 4131–4138. [CrossRef]
- [24]. Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*; WILEY-VCH Verlag GmbH & Co.: Weinheim, Germany, 2004.
- [25]. Maitlis, P.M.; Haynes, A.; James, B.R.; Catellani, M.; Chiusoli, G.P. Iodide effects in transition metal catalyzed reactions. *Dalton Trans.* **2004**, 21, 3409–3419. [Cross Ref] [Pub Med]
- [26]. Skoda-Foldes, R.; Kollar, L. Iodide effect in transition metal catalyzed reactions. *Curr. Org. Chem.* **2002**, 6, 1097–1119. [Cross Ref]
- [27]. Kaminsky, W.; Arndt, M. *Polymerization, Oligomerization and Copolymerization of Olefins*. In *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes*; Wiley-VCH: Weinheim, Germany, 1996.
- [28]. Mathey, F.; Sevin, A. *Molecular Chemistry of the Transition Elements: An Introductory Course*; John Wiley & Sons: Chichester, UK, 1996.

