

**COORDINATION COMPOUNDS WITH TRANSITION METAL IONS & ITS
APPLICATION IN THE INDUSTRY**

N. A. Kedar*

Department of Chemistry Dayanand Science College, Latur-413512 Tq. & Dist. Latur.

*Corresponding Author: Dr. N. A. Kedar

Department of Chemistry Dayanand Science College, Latur-413512 Tq. & Dist. Latur.

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ABSTRACTS

Coordination Compounds With Transition Metal Ions & Its Application in the Industry describes the influence of various physicochemical factors regarding the coordination relationship (for example, steric hindrance, electron density, complex geometry, ligand), which condition technological processes. Coordination compounds are catalysts in technological processes used during organic synthesis, for example: Oxidation reactions, hydroformylation process, hydrogenation reaction, hydrocyanation process. In this article, we pointed out the possibilities of using complex compounds in catalysis, and we noticed what further research should be undertaken for this purpose.

KEYWORDS: Coordination compounds; Technological processes, Polymer materials; Chemical industry.

INTRODUCTION

Processes carried out on an industrial scale and conducted by scientists are enjoying the growing recognition of global corporations dealing in the production of various polymeric materials used in many aspects of our lives.

In order to understand the important function of coordination compounds in catalytic reactions during industrial processes carried out on an industrial scale, it is necessary to learn the exact mechanisms of the reactions carried out. This means that many factors related to geometry, steric hindrance,^[1] or the used central atom and attached ligands of the complex compound affect the catalytic reaction.

A very important aspect of work on chemical technologies is the smallest possible pollution of the environment, i.e., the application of the principles of green chemistry. Conducting reactions in organic solvents is replaced by supercritical liquids.^[2,3]

Latest methods of using coordination compounds in catalytic reactions used in the chemical industry. We present the influence of coordination compounds on the course of reactions taking place in organic synthesis e. g. Hydroformylation process,^[6] hydrogenation reaction, oxidation processes, olefin polymerization processes. We also describe the application of green chemistry principles in a catalysis with the participation of complex compounds.

Oxidation processes

The Wacker process was developed in cooperation of two concerns, Wacker and Hoechst, and then published in 1959. The process is a well-known reaction for obtaining acetaldehyde by oxidation of ethene. The reaction is carried out in an aqueous environment using a homogeneous catalyst (PdCl₂ · CuCl₂). The synthesis was recognized^[7] by the chemical industry, due to the fact that it was an alternative to the hydroformylation reaction. The acetaldehyde obtained in the synthesis is widely used. It is mainly applied for production of acetic acid, acetic anhydride or chloroform. In addition, it can form synthetic resins in condensation reactions with phenols and amines. The Wacker process is shown in Figure 1, in which stoichiometric reactions^[8] combine in one catalytic cycle. In the first stage, in an aqueous environment, it reacts with palladium (II) chloride, forming a stoichiometric amount of acetaldehyde, and palladium (II) is reduced to palladium (0). In the next stage, palladium (0) undergoes reoxidation in the presence of copper (II) compounds. Copper (I) is formed as the product of this reaction while in the last stage copper (I) is oxidized with oxygen to copper (II). Reaction 4 in Figure 1 represents the overall reaction of the process.^[11]

According to research recommendations, the oxidation stage is actually catalyzed by [PdCl₄]²⁻, which is formed under the conditions of water and Cl⁻ ions. In the analyzed cycle, two chloride ligands are replaced by ethene and water. In the next stage, there is a

nucleophilic attack of water on ethene in the complex, followed by substitution of the chloride ligand by another water molecule. β -elimination of a hydrogen atom leads to the formation of vinyl alcohol. This stage is followed by a series of processes leading to the production of acetaldehyde and palladium (II) hydride. Due to the fact that palladium (II) hydride is unstable, Pd (0) and HCl are formed as a result of the reduction reaction. The cycle is closed. Palladium (0) is oxidized to palladium (II) with CuCl_2 .^[2]

Quantum mechanical tests that the anti-nucleophilic attack is the step determining the Wacker process.

The Wacker oxidation usually gives ketones as reaction products, but the literature reports that one can carry out the Wacker process that will give 99% selectivity in obtaining aldehydes, e.g., using 1,4-benzoquinone, *t*-BuOH, and $\text{PdCl}_2(\text{MeCN})_2$. Regarding the selectivity of the Wacker process, products with high selectivity are also obtained using styrene derivatives as substrates with the reaction carried out under mild conditions.

Wacker process produces environmentally hazardous, chlorinated by-products, as well as harmful copper waste.

According to the principles of green chemistry, solutions are being sought that affect the protection of ecosystems and the whole world. Researchers at the University of Pune proposed the Pd(0)/C system as a heterogeneous catalyst that can be recycled. This allowed the elimination of pure CuCl_2 . In addition, they used potassium bromate KBrO_3 as an oxidizing agent instead of molecular oxygen. By that, they developed a method using inexpensive substrates and achieved high process efficiency.

One may conclude that the by-products formed during the Wacker process are a major disadvantage of this cycle. Chlorine derivatives are environmental pollutants. Therefore, scientists should attempt to deactivate the resulting by-products.

The hydrocyanation reaction

Hydrocyanation is used in the industry in the production of adipic acid nitrile. It is the basic raw material for the production of nylon 6,6, the reaction of which consists of attaching HCN to the olefin. DuPont company processes possess an economic significance, where adipic acid nitrile is obtained in the process of butadiene hydrocyanation. The process uses the Ni(0) catalyst with phosphateligands.

The process consists of two stages. The catalyst plays a key role in the whole process. At first, the oxidative attachment of HCN to the NiL_4 catalyst occurs and the hydrocyanide complex is formed. At this stage, the selection of a suitable ligand (L), e.g., a phosphorus ligand, is particularly important. Electronic and steric

properties are taken into account, which have an impact on the course of individual stages of the hydrocyanation reaction. On the one hand, more basic ligands favor the addition of HCN. On the other hand, less basic ligands, which are characterized by high steric hindrance, are more popular. Representative of this group is *o*-methylphenyl phosphate $\text{P}(\text{O}-\text{o}-\text{MeC}_6\text{H}_4)_3$, which facilitates the reductive elimination of the product (3-pentenitrile). According to the research, steric effects in the case of phosphine and phosphite ligands have a significant impact on the stability of Ni(0) complexes. IR analyses determining changes of carbonyl vibration frequency (ν_{CO}) in $[\text{Ni}(\text{CO})_3\text{L}]$ (where L denotes a broad variety of phosphorus ligands) complexes have shown that the nature of the ligand π acceptor increases the stability of Ni(0) complexes. The steric properties of the ligands are represented using the Tolman cone angle. For ligands with a small cone angle of approximately 109° , dissociation will not occur even if we use high dilution solutions. An example of such a complex is $[\text{Ni}[\text{P}(\text{OEt})_3]_4]$. 16-electron complexes, e.g., $[\text{Ni}[\text{P}(\text{O}-\text{o}-\text{tolyl})_3]]$, whose Tolman cone angle was 141° , and alkene complexes $[\text{Ni}(\text{alkene})\text{L}_2]$ were also examined. Subsequent studies have determined that the increase in metal-alkene bond strength is affected by the replacement of the H-alkene atom by a more electronegative CN. The electron effect is visible here, which results in higher stability of the acrylonitrile complex. Tolman also presented in his researches ^1H and ^{31}P NMR studies of the complex $[\text{HNi}(\text{CN})\text{L}_3]$ (where L is various phosphorus ligands). The addition of hydrogen cyanide to nickel(0) complexes is represented by the following reactions, where protonation is preceded by the dissociation of the ligand. The scientist pointed out that the addition of excess HCN may result in the formation of an undesirable complex $[\text{Ni}(\text{CN})_2\text{L}_2]$ (where L is a phosphorus donor ligand), which deactivates the catalyst. For this reason, $[\text{Ni}(\text{CN})_2\text{L}_2]$ is not active in the process of hydrocyanation.^[10,11]



Research concerns the HCN addition to butadiene at the first stage and the reaction taking place in the presence of a NiL_4 catalyst. The reaction products are 3-pentenitrile and 2-methyl-3-butenitrile. The resulting isomer in branched form is not a substrate in the reaction of obtaining adipic acid nitrile; therefore, it is subjected to the process of isomerization to 3-pentenitrile. The next stage takes place using the same catalyst with addition of Lewis acid. The Lewis acids used can be ZnCl_2 , ZnBr_2 , AlCl_3 , BPh_3 . It works with a free electron pair on the nitrogen of the CN group, which facilitates the creation of C-C connections.

Isomerization of the double bond occurs and the 3-pentenitrile is structured to an alkene (4-pentenitrile). The second CN group is joined in this reaction. Secondary by-products include 2-methylglutaronitrile (MGN), ethylsuccinonitrile (ESN), and 2-pentenitrile

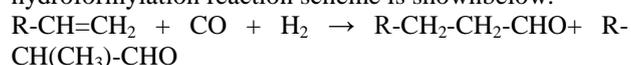
(AdN). Studies show that the hydrocyanation rate relative to isomerization is the highest for AlCl_3 and decreases in the order of $\text{AlCl}_3 > \text{ZnCl}_2 > \text{BPh}_3$.^[12,13,14]

In 2019 it was confirmed that hydrocyanation can run without cyanide. The mentioned reaction was asymmetric olefin hydrocyanation. In the alkenic hydrocyanation process, the use of bident phosphorus-based ligands is of great importance, which contributes to increasing the stability of the products obtained during hydrocyanation. In addition to nickel complexes, ruthenium (I) complexes for hydrocyanation are used.

The important issue regarding the hydrocyanation reaction is alkene isomerization. Low reaction yields are a disadvantage of hydrocyanation reactions. These issues remain to be improved.

Hydroformylation reaction

Hydroformylation is the reaction of olefins with hydrogen and carbon monoxide (II), where the products are straight chain (n) and branched chain (iso) aldehydes. This process occurs under the influence of the catalyst present during the reaction.^[21] The products obtained in the form of aldehydes can be converted into alcohols, carboxylic acids, acetals, diols, or aldols under appropriate conditions. Most often, however, the intention of the reaction is to obtain an unbranched chain aldehyde. The catalytic system is most often characterized by the n/iso ratio. As we can see, the higher the numerical value of the ratio, the better the catalytic system used during the hydroformylation. The hydroformylation reaction scheme is shown below.



The hydroformylation process was discovered by German chemist, Roelen, in 1938. He made the discovery during the Fischer–Tropsch reaction. The first catalyst used during the hydroformylation reaction was hydridotetracarbonyl— $[\text{HCo}(\text{CO})_4]$. Then, the addition of phosphines to cobalt catalysts was applied, which resulted in a higher n/iso ratio and the hydroformylation process was carried out at a lower pressure and temperature.

A great breakthrough in the search for catalytic systems was made thanks to the work of the English Nobel Prize winner Sir Geoffrey Wilkinson. They allowed the discovery of compounds based on rhodium atoms that showed a thousand-fold higher catalytic activity in the hydroformylation reaction compared to cobalt catalysts.

Rhodium compounds, despite a higher price, are commonly used as catalysts for hydroformylation reactions. Union Carbide Davy Powergass Johnson–Matthey LPO—a British chemical company—uses a hydroformylation process using a precursor of formula $[(\text{acac})\text{Rh}(\text{CO})_2]$ and a modifying ligand, phosphine (PPh_3). The addition of approximately 10% by weight

PPh_3 produces the active catalyst form— $[(\text{acac})\text{Rh}(\text{CO})(\text{PPh}_3)]$. The hydroformylation process is carried out under the following conditions: At a temperature from 60 °C to 120 °C, pressure in the range of 10–50 bar. This process has a n/iso ratio of around 1:5. The hydroformylation process in Ke,dzierzyn–Koz'le at Zakłady Azotowe is used in Poland.^[22] Kuntz's discovery of the industrial conduct of the hydroformylation process and its commercialization by Ruhrchemie/Rhone-Poulenc is based on the use of a two-phase catalytic system based on a rhodium complex compound. Tris(3-sulfonylphenyl)phosphine sodium (TPPS) was used in the hydroformylation process

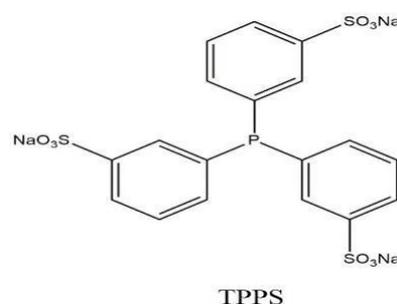


Figure 1: Simplified formula of sodium salt (tris(3-sulfonylphenyl)phosphine).

The use of the aforementioned catalyst system allows easy separation of the catalyst from the desired products (aldehydes) because it is in the polar phase. Therefore, the catalyst is used in a continuous process. Conducting the hydroformylation process using a two-phase catalytic system allows for high selectivity and activity for the production of a linear product to be maintained.^[23]

The electron and steric properties of ligands attached to the rhodium atom influence the selectivity of the obtained product in the hydroformylation reaction. A larger amount of the linear product in the olefin hydroformylation reaction is obtained by using ligands with weaker basic properties—for example, pyrrolylphosphines or phosphites.

The steric properties of the ligands are evaluated based on the size of the conic angle, while for chelate ligands they are based on the grip angle, which determines the value of the angle between the P–M–P bonds present in the complex with the ligand. Studies on the impact of the grip angle on the selectivity of the reaction have shown that the equatorial–equatorial location of donor atoms in chelating ligands found in rhodium atom-based catalyst systems results in obtaining the best n/iso values. This means that the geometry of the respective rhodium complexes, in this case, for grip angles, is about 120°, exhibiting the geometry of the trigonal bipyramid.^[24]

The newest reports from scientists inform that the use of carbene and phosphorus ligand catalysts simultaneously attached to the rhodium atom in the coordination sphere results in obtaining a much better n/iso ratio.^[25]

$[\text{RhH}(\text{NHC})(\text{CO})\text{P}(\text{OPh})_3]_2$, where NHC denotes heterocyclic carbene, is an examples of such a catalyst.

The catalysis of the hydroformylation process is constantly evolving with regard to the use of rhodium compounds as catalysts. Even a rhodium single-atom exhibits catalytic activity in hydroformylation similar to the $\text{RhCl}(\text{PPh}_3)_3$ complex. Rhodium particles also have catalytic properties in hydroformylation.^[25]

In 2018 it was published that Fe(II) has the ability to catalyze hydroformylation of alkenes under mild conditions.

The most important advantage of the hydroformylation reaction is the ease of separation of the resulting product and catalyst. It is very important when receiving new materials.

Carbonylation reaction

The carbonylation reaction is the process of attaching a carbon monoxide (II) molecule to an organic compound. Most often, this process is used to produce acetic acid from methanol or an anhydrous derivative of the acid from the ester—methyl acetate. This reaction is carried out in the presence of transition metals, specifically metals in group 9, cobalt, rhodium, and iridium are used primarily. In addition, an iodide co-catalyst is needed during the process to activate methanol. This reaction produces acetyl iodide, which in subsequent hydrolysis produces a mixture of acetic acid and hydroiodic acid.^[27]

BASF carried out the first commercially conducted process of carbonylation of methyl alcohol with a cobalt catalyst. Then, industrial scale carbonylation of methanol was started by Monsanto, which applied a rhodium catalyst. The conditions operated by Monsanto compared to BASF differed in the use of lower carbon monoxide pressure and temperature. This process was also carried out with much better selectivity for methyl alcohol.

Studies on the mechanism of methanol carbonylation were conducted very thoroughly. Maitlis' group examined the reaction using infrared spectroscopy and found that the mechanism of methanol carbonylation contains two catalytic cycles. The first cycle, rhodium, involves organometallic compounds and an iodide cycle containing organic reactions. The catalyst for this carbonylation reaction was the rhodium complex compound, *cis*- $[\text{Rh}(\text{CO})_2\text{I}_2]$.

The methanol carbonylation process proposed by BP Chemicals, called the Cativa process, was carried out using an alternative iridium catalyst. The main difference of this process compared to the mechanism proposed by Monsanto is that it has about 100 times faster oxidation caused by the addition of CH_3I to $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ than to $[\text{Rh}(\text{CO})_2\text{I}_2]$.

However, a different type of catalyst is used when carbonylation of higher alcohols is carried out. This is caused by too slow a reaction using a rhodium catalyst. Therefore, palladium catalysts are applied that simultaneously also catalyze the olefin hydroxycarbonylation.^[28]

The palladium complex compound- $\text{PdCl}_2(\text{PPh}_3)_2$ is used in the carbonylation reaction, where the product is the known anti-inflammatory drug, ibuprofen. This synthesis is carried out by Boots–Hoechst–Celanese.^[17]

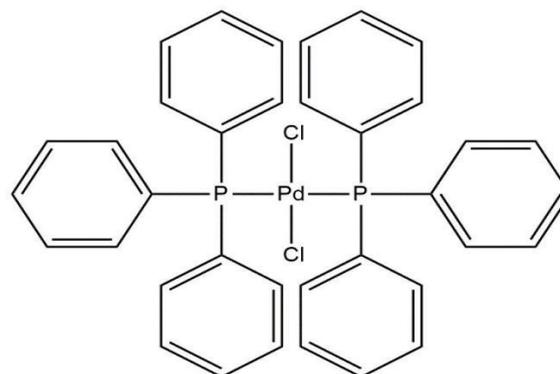


Figure 2: Simplified formula of the palladium complex used during ibuprofen synthesis.

Naproxen is another very well-known remedy in which production palladium complexes are used as catalysts. This drug belongs to non-steroidal inflammatory drugs, which are obtained in a multistage synthesis. The palladium complex is a catalyst during stage 2—Heck reaction, and during stage 3—hydroxycarbonylation.^[25]

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 with the introduction of a chiral phosphine allows us to obtain the appropriate optical isomer.

Hydroaminocarbonylation of olefins, aminocarbonylation of aryl iodides, and oxidative carbonylation of amines occurs with the application of bulk Pd catalyst without the use of organic ligands. Iridium and immobilized-rhodium catalyze the methanol carbonylation process, leading to the formation acetic acid. An interesting fact is that membranes, e.g., chitosan, polyamide, polyvinyl alcohol, are used to catalyze carbonylation reactions.¹⁹ Membranes take part in the product separation of carbonylation. In 2019 $\text{K}_2[\text{Fe}(\text{CO})_4]$ as a catalyst promoting the formal insertion of CO was published.

Therefore, in the carbonylation reaction, iron (II) and platinum (II) complexes should be tested 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 that is used commercially around the world on a very large scale in the chemical industry. This is evidenced by the fact that the sum of the annual production of polyethylene and polypropylene is about 15 million tons.^[27] Another important aspect of using complex compounds such as olefin polymerization catalysts is the fact that it is economically cheap and environmentally friendly.

The newest version of the Ziegler–Natta catalysts used in the olefin polymerization process is the deposition of titanium (IV) tetrachloride on magnesium chloride. The $MgCl_2$, the carrier, has a grain diameter of about 50 μm . A carrier with such grain diameter characteristics is obtained by precipitation from a soluble precursor solution with the addition of a Lewis base or by mechanical milling.^[29] The second stage is the addition of phthalic esters or silyl ethers.^[30] Magnesium(II) ions and titanium(III) ions have similar ionic radii, which make it possible to obtain a third-generation catalyst. This synthesis consists of adding titanium (I) tetrachloride to a solution of alkoxide, sulfide, or carboxylate containing magnesium (II) ions. Then the addition of $TiCl_4$ and phthalates activates the catalyst.^[17]

Atom transfer radical polymerization (ATRP) is a technique that allows the production of polymers and copolymers used commercially around the world. Polish chemist Matyjaszewski, working in the United States, discovered and developed this method of polymerization. The technique is cheap and does not pollute the environment in the production of polymeric materials on an industrial scale. The application of radical transfer polymerization techniques^[31] allows for polymers with the appropriate structure and morphology to be obtained. Thanks to such control possibilities of the process being carried out, its application in various industrial technologies is becoming wider.

Copper and iron coordination compounds are used as catalysts during radical atomization polymerization. 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 in homogeneous conditions or heterogeneous.

The technique of radical polymerization with atom transfer allows for the production of polymers that are components of moisturizing agents, surfactants, paints, and surfactants. It is also used in the synthesis of polar thermoplastic elastomers. It also allows the improvement of hydrophilic, antibacterial, or conductivity properties in the polymer materials produced.^[32]

Radical polymerization using organometallic compounds is another technique used in polymerization. This method was initially proposed for the polymerization of acrylates. Acrylic acid, vinyl acetate, or other substrates are the monomers. Titanium, cobalt, iron, and chromium

compounds have found application in this technique as catalysts.

In our view, olefin polymerization is a wide field for research, because nowadays there are reports of ever-increasing catalysts of this reaction being non-metallocene transition metal complexes. The new complex compounds have higher values of catalytic activities than those traditionally used, and their synthesis is simple and cheap. New catalysts are chromium (III), oxovanadium (IV), and cobalt (II) complexes.

Late transition-metal catalysts are used in olefin polymerization. However, one should bear in mind that most of them cause the formation of amorphous and atactic polymers. $[Cu(2,3\text{-pydc})(bpp)] \cdot 2.5H_2O$, $[Zn(2,3\text{-pydc})(bpp)] \cdot 2.5H_2O$, and $[Cd(2,3\text{-pydc})(bpp)(H_2O)] \cdot 3H_2O$ (2,3-pydc denotes pyridine-2, 3-dicarboxylate, $bpp = 1, 3\text{-bis}(4\text{-pyridyl})\text{propane}$) are metal–organic frameworks which are applied in heterogeneous catalysis. Tridentate ligands based on N-, P-, and S-donors are used to synthesize the chromium (III) catalyst for ethylene trimerization and tetramerization. One may conclude that this field must be developed because new catalysts can successfully replace traditionally used ones, which, unlike new catalysts, unfortunately did not meet the principles of green chemistry.^[33]

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 hydrogenate carbon and hydrogen compounds. The mechanism of this reaction requires the presence of a catalyst, which is most often transition metal compounds. This process is carried out to create new bonds between carbon and hydrogen.^[34]

Heterogeneous catalysts are most often used during the hydrogenation reaction. The reason for their application is the ease of separation from organic products. However, the exploit of heterogeneous catalysts during the hydrogenation reaction is not possible in the asymmetric hydrogenation reaction. In addition, homogeneous catalysts^[18], i.e., those made of complex compounds that are based on transition metals, increase chemoselectivity and regioselectivity^[35] of the reaction.

If we use a metal complex as a catalyst during the hydrogenation reaction, this gives the opportunity to create a spatial and electronic structure of the compound. This can be achieved by choosing the right ligand. An example of the best-known hydrogenation reaction^[19] catalyst is the Wilkinson catalyst— $[RhCl(PPh_3)_3]$.

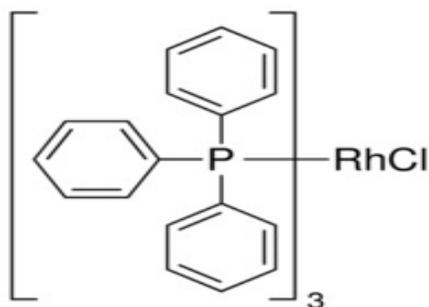


Figure 3: Simplified formula of Wilkinson's catalyst.

A very important enantioselective synthesis, during which the L-3,4-dihydroxyphenylalanine compound is obtained (L-DOPA), in one of the stages uses an asymmetric hydrogenation reaction. L-DOPA is a medicine applied during therapy against Parkinson's disease. The need to obtain the appropriate product enantiomer informs us that the catalytic system of the hydrogenation mechanism must contain a chiral form of phosphine. During the synthesis reaction of L-3,4-dihydroxyphenylalanine, the catalytic system of the rhodium complex with 1,2-bis[(2-methoxyphenyl)phenylphosphine]ethane (DIPAMP) is used. Shows a simplified formula of the chiral form of phosphine, which is a ligand in the rhodium complex.

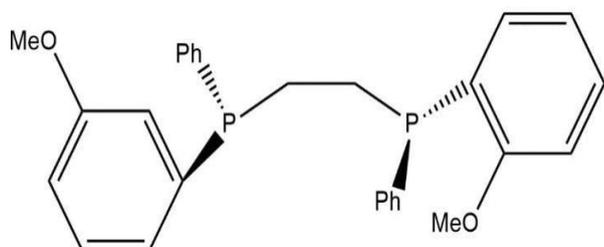


Figure 4: Simplified formula of the chiral form of phosphine-1, 2-bis[(2-methoxyphenyl)phenylphosphine] ethane.

It can be concluded that the use of phosphines as ligands in catalysts creates many opportunities to design new complexes as catalysts. Hydrogenation of esters and amides are catalyzed by these types of compounds. It is worth trying to synthesize new complexes containing other organophosphorus compounds as ligands, as well as trying to check the catalytic activity of phosphine-containing dual-core complexes.^[20]

Catalysis and Green chemistry

Ionic Liquids—Catalytic reactions

In modern catalysis, particular attention is paid to the principles of green chemistry. Technological processes must be as environmentally friendly as possible. Ethylammonium nitrate is a chemical compound recognized as one of the first ionic liquids. As a result of the neutralization of ethylamine with the help of concentrated nitric acid. Ionic liquids are characterized by very low vapor pressure and low melting points. The low volatility of ionic liquids is a property that caused these chemicals to be classified as green solvents.^[21]

Compounds called ionic liquids include: Pyridinium, tetraalkylammonium, imidazolium, and phosphonium salts. Ionic liquids can be used as solvents friendly to the environment because it does not cause environmental load. Ionic liquids are involved in the transport of metals and chemical compounds in soil.

Pyridinium ionic liquids are a very good medium for the methoxycarbonylation reaction of iodobenzene catalyzed by $[\text{PdCl}_2(\text{cod})]$ or $\text{Pd}(0)/\text{PVP}$. In the Sonogashira reaction, ionic liquids were used, and thus effective catalyst recycling was possible $[\text{PdCl}_2(\text{P}(\text{OPh})_3)_2]$. Processes based on the Sonogashira reaction that applies in industries are the synthesis of alkyl derivatives. These types of reactions are used in the pharmaceutical industry. In this type of reaction tetraalkylphosphonium salts are the best reaction medium. The resulting product is separated from the ionic liquid containing the catalyst using hexane extraction. By-products are removed by washing with water.^[22]

Carbene complexes are formed in situ if the ionic liquid is a solvent in the catalytic reaction. The reactivity of carbene complexes often differs from the catalyst precursor. For this reason, there are cases where the ionic liquid is an inhibitor of catalytic activity. Iodobenzene methoxycarbonylation is an example of such a reaction. It can be concluded that ionic liquids are not only solvents, but are also active components of the reaction system.

The application of catalysts which are coordination compounds containing ionic liquids (as ligands) was implemented in the technological²³ process of obtaining S-naproxen and S-ibuprofen. Therefore, we conclude that it is necessary to examine the influence of geometric isomerism of catalysts on their catalytic activity and the type of reaction product obtained.

Metal nanoparticles

Metal nanoparticles have diameters in the range from 1 to 50 nm. The size of the nanotube has a very large impact on their properties. First information on the use of metal nanoparticles of Pd in Heck's reaction comes from the 90s. This concerned reactions between aryl bromides and styrene, or butyl acrylate and iodobenzene. Metal nanoparticles obtained by reducing metal chloride salts in the presence of tetra-N-alkylammonium cations are electrostatically stabilized.

Metal nanoparticles have some features of both homogeneous and heterogeneous catalysts. Nanoparticles can be a source of soluble metal complexes formed during a given reaction. The complex compound undergoing a reduction reaction generates nanoparticles. Then the nanoparticles form a metallic structure because they agglomerate. The reverse process is also possible. This happens in the case of catalytic reactions during which nanoparticles are dissolved, which in turn contributes to the formation of complex compounds. The equilibrium is

particularly common when phosphorus ligands are present in the catalytic system. Metal nanoparticles are formed as a result of a reduction of complex compounds. Reduction may occur during the catalytic reaction, but it is also possible before catalysis.^[24]

Among the nanoparticles, monometallic nanoparticles are the most popular. However, bimetallic nanoparticles are becoming the subject of more and more frequent scientific research. Cheaper base metals are part of the inner sphere of bimetallic nanoparticles. The base metals are covered with a layer of precious metals, e.g., platinum, palladium, and ruthenium.

Catalysis with palladium and copper nanoparticles is applied to form C–C and C–S bonds. The palladium nanoparticles cause coupling of vicinal–diiodoalkenes and acrylic esters and nitriles. The copper nanoparticles are used in chemoselective reduction of N- aromatic compounds.

It can be stated that the future research approach is the application of metal nanoparticles to identify catalytic sites. The identification of catalytic sites for oxygen reduction reactions is extremely important when designing new highly active catalysts containing base metals.

CONCLUSIONS

A very important aspect in chemical technologies is the widest possible application of the principles of green chemistry—in the case of catalytic reactions involving coordination compounds, biotechnological, or organocatalytic methods are applied. An example of the described principle can be use of ultrasound to better dissolve solutions or microwave radiation for heating. Chemical technology processes that involve coordination compounds as catalysts. Many organic synthesis processes in the chemical industry, including the olefin polymerization process and atom transfer radical polymerization process, are used to produce polymer materials. The resulting products are used in many areas of our lives in the pharmaceutical industry—for the synthesis of drugs, polyethylene production, or for the synthesis of complex organic compounds.

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