Original Article: Mechanistic Studies of Organic-Metallic Catalysts in Cross-Coupling Reactions

Mehdi Imanzadeh
Department Of Chemistry, Parsabad Moghan Branch, Islamic Azad University, Parsabad, Iran

Use yor device to scan and read the article online

Citation *M Imanzadeh,* ***Mechanistic Studies of Organic-Metallic Catalysts in Cross-Coupling Reactions,*** *EJCMPR.* 2025; 3(5): 86-93.

https://doi.org/EJCMPR/202786392

Article info:
Received: 10 September 2024
Accepted: 16 November 2024
Available Online:
ID: EJCMPR-2410-1256
Checked for Plagiarism: Yes
Peer Reviewers Approved by:
Dr. Frank Rebout
Editor who Approved Publication:
Dr. Frank Rebout

Keywords:
Catalyst Mechanism, Organic-Metallic, Cross-Linking Reaction, Kinetic Model, Carbon Tetrachloride Solvent.

ABSTRACT

In many industrial applications, the presence of selectable catalysts in terms of molecular shape and size is of particular importance. The most significant feature of metal-organic structures, which has made their application important in the catalytic discussion, is the absence of dead space that cannot be accessed. Organometallic compounds are materials that have at least one carbon-metal bond in their structure and contain pseudo metals such as B, As, Si and real metals. Organic compounds are widely used in industry and environment. They play a role as cleaners and catalysts in industrial processes and are used in the environment because of their compatibility with it. Characterization was done in a similar way for new catalysts. The maximum catalytic activity was related to 12Mn-BTCarg/Al5,0.4 calcined in argon atmosphere. The activity of the optimal catalysts of each part was investigated in the activation of hydrogen peroxide to remove the drug azithromycin in aqueous solution. The catalytic elimination reaction of azithromycin followed a pseudo-first-order kinetic model. For V-DETA-MIL-101 catalyst, the amount of 15 mg of catalyst, 1.12 mmol of tertiobutyl hydrogen peroxide and 1 ml of carbon tetrachloride solvent at 80°C temperature were selected as optimal conditions.

Corresponding Author:* ***Mehdi Imanzadeh* *(Imanzade.m@gmail.com)*

Introduction

Organic-metallic compounds are a new generation of nano adsorbents with high absorption capacity due to their unique characteristics such as very high porosity (more than 90% void volume), very high specific surface area (more than 4000 m^2/g), various methods and the simple synthesis, the ability to adjust the pore size, low density [1], high biocompatibility, high mechanical and thermal stability, as well as low energy consumption during the regeneration process, have attracted the attention of researchers. These structures are

used in many fields, including surface adsorption and catalyst, due to the mentioned exceptional features. Because one of the most important and widely used industrial processes is the process of dehumidification and absorption of moisture in gases and liquids. In this article, nano adsorbents that have basic criteria such as high absorption capacity and operational stability against water have been introduced and compared with other commercial adsorbents such as zeolites and silica gel [2-4].

The results of this research showed that organic-metallic adsorbents have a high absorption capacity for dehumidification due to their high stability in aqueous environment and suitable surface characteristics and porosity. Organic catalyst or organo catalyst is a type of catalyst in which the rate of chemical reaction is increased by organic catalyst. These materials are created from carbon, hydrogen, sulfur and other non-metallic elements found in organic compounds. Due to their similarity in composition and description, they are usually mistakenly called enzymes because they have similar effects on reaction rates and forms of catalyst involvement. Organo catalysts that perform the secondary amine function can be described as enamine catalysts or imine catalysts [5].

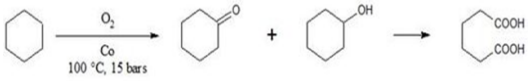
Some important reactions carried out by metal nano catalyst

Hydrosilylation reactions

Reduction of metal aggregation of gold, cobalt, nickel, palladium or platinum with silane produces metal nanoparticles that catalyze the hydrosilylation reaction. BINAP-functionalized pd nanoparticles and gold nanoparticles have been used for hydrosilylstyrene under mild conditions, and it was found that metal nanoparticles are more active and stable catalysts than non-nanoparticle pd-BINAP aggregates.

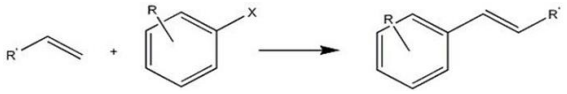
Organic redox reaction (Oxidation reduction)

The oxidation reaction of cyclohexane for the synthesis of adiapic acid can be catalyzed by cobalt nanoparticles, which are usually used on an industrial scale to produce polymers (nylon 6 and 6). Other examples of oxidation reactions carried out by metal nano catalysts include: Ethene oxidation, cyclooctane oxidation, and glucose oxidation.



Heck coupling reaction (pairing) carbon-carbon (c-c coupling reactions)

Metal nanoparticles can catalyze c-c coupling reactions such as hydro formylation of olefins, vitamin E synthesis, and Heck coupling and Suzuki coupling reactions. Palladium nanoparticles efficiently catalyze Heck coupling reactions. It was found that increasing the negative electric charge of ligands on palladium nanoparticles increases their catalytic activity [6].



Advantages of metal nanoparticles

- ✓ They are more stable than solvents;
- ✓ Metal nanoparticles in liquids are affected by van der Waals force;
- ✓ By combining nanoparticles with polymers or oligomers, nanoparticles can be activated. As a result, the interaction of nanoparticles can be prevented by creating a protective layer;

- ✓ Alloys of two metals, called bimetallic nanoparticles, are used to create synergistic effects in catalysis between two metals [7].

Production of nano catalysts

Heterogeneous metal nano catalysts are prepared by adsorbing nanoparticles on supports, which involves using supports to adsorb nanoparticles on them by lithography technique. Today, most nano catalysts are produced commercially, and most commercial catalysts are still produced by mixing, shaking, and baking a mixture of several components. For economic savings and optimal use of nano catalyst, it is usually made as a composite and chemical modification is applied on its surface. One of the disadvantages of the commercial method is that the nano scale is not well controlled in this method. As a result, it has poor performance [8].

Designing mesoporous MOFs with suitable pore size is very important. If the size of the pores is small, the drug loading and release will be limited. Harkajada and his colleagues designed MOFs called MIL-100 and MIL-101 for the release of ibuprofen. This category of MOFs has a suitable structure and their porosity is also suitable. The diameter of the pores of MIL-100 is in the range of 25 to 29 angstroms and the diameter of the pores of MIL-101 is in the range of 29 to 34 angstroms. MIL-100-unit cell structure is pentagonal and MIL-101 cell structure is pentagonal and hexagonal. The results showed that the amount of drug loading in MIL-100 is 0.35 grams of ibuprofen for each gram of MIL-100 and the amount of drug loading in MIL-100 is 1.4 grams of ibuprofen for each gram. These results are due to the fact that ibuprofen can be loaded in MIL-101 due to higher porosity and network type. Regarding this category of MOFs, no loss of crystallinity and destruction of the structure was observed after drug loading [9-11].

Another notable biomedical application of MOFs is in the case of structures in which certain molecules such as biocompatible metal cations exist which are called Bio MOF. These stable structures are made of hard biomolecules that are its blocks and have stable crystal structures in biological buffers for a long time. Recently, McKinley and his colleagues investigated the possibility of using biomolecules as binders and bioactive metals as inorganic parts to make Bio MOFs. The anionic nature of MOFs causes the absorption of cationic drugs [12].

Also, the cations in biological buffers control the drug release. Rasin and his colleagues investigated a number of MOFs that included zinc ions, adenine and para-diphenyldicarboxylic acid. The anionic nature of MOF was used to absorb the cationic drug (procainamide hydrochloride salt) and the release of the drug was observed due to cationic exchange in the biological fluid.

Despite the high potential of MOF in terms of drug release, one of the challenges of using these materials is that they are not suitable for systemic circulation due to their size. Therefore, it is necessary that the size of these substances reach nano so that they can easily circulate in the blood. The size, porosity and surface of MOFs can be engineered for optimization. Also, they can be used to maintain the stability of all kinds of hydrophobic and hydrophilic drugs. In biomedical applications, MOFs can be obtained from aqueous and alcoholic solutions. These materials are also referred to as molecular sponges because it is possible to encapsulate drugs with different polarity, size and functional groups after immersion in the solution containing them [13].

History of organometallic compounds

In 1849, an English chemist named Frankland synthesized diethyl zinc for the first time. Then

he expanded the use of organic zinc compounds for the synthesis of organic materials. For this reason, organometallic chemistry has been attributed to this great English scientist. In the early 1900s, the French Chemist Victor Grignard developed a new method for preparing organo magnesium halide. So that it was used as an intermediate in the synthesis of organic zinc compounds. In 1951, with the accidental synthesis of ferrocene and the identification of its molecular structure, the field of research in the direction of chemical bonds became easy [14].

Properties of organometallic compounds

In terms of physical properties, organometallic compounds are more similar to organic compounds than inorganic compounds. These compounds have an isolated molecular structure that can be seen as liquids, gases and crystals with a low melting point at normal temperatures. The mentioned compounds are soluble in low polar organic solvents, such as dichloromethane, toluene and ethers. There is a significant difference between organometallic compounds chemically. For example, tetramethylsilane remains unchanged at 500 degrees Celsius after a few days, but tetramethyltitanium decomposes quickly at room temperature. This shows that the thermal stability of these compounds depends on their chemical composition [15].

Properties of organometallic compounds

These types of compounds can act as reducing agents. This role is played by those compounds produced by metals with low electronegativity. Compounds that have low electronegativity atoms such as sodium and lithium participate in spontaneous combustion reactions because they are highly volatile. Compounds whose structure is cyclic or hydrocarbon groups are aromatic are solid. Most organometallic compounds, especially volatile compounds, are toxic [16].

Stability against waterlogging

The rate of hydrolysis of organometallic compounds depends on the polarity of the carbon-metal bond. For example, in trimethyl aluminum, the molecular attack is fast, because it has a high bond polarity. While trimethylboraba has an empty P2 orbital on the boron atom at room temperature, it is not affected by the water molecule. Likewise, it can be said that the rate of desorption depends on the polarity of the bond, the presence of a large number of empty orbitals with low energy and the large size of the central atom. For example, organic lanthanides are hydrolyzed quickly, but most organic derivatives of neutral transition metals are not susceptible to the hydrolysis process [17].

Stability against the oxidation process

Thermodynamically, all organometallic compounds are unstable against oxidation. The formation of metal oxide, carbon dioxide and water, which have negative free energy, are the stimulating force required for the oxidation of organometallic compounds. Most of these compounds are kinetically unstable against oxidation at room temperature or below. Most of these compounds such as trimethyl tin, trimethyl indium and dimethyl zinc are flammable (Figure 1). Most transition metal derivatives of these compounds are sensitive to oxygen and it is necessary to research and study them in inert atmospheres of nitrogen and argon gas [18].

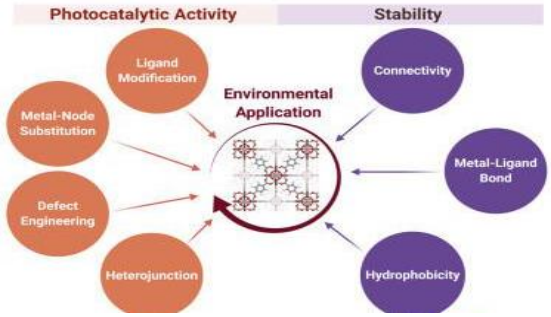


Figure 1. Stability against the oxidation process

Application of organometallic compounds

The use of discussed compounds as catalysts in oligomers and polymerization of olefins is widely used. Also, tetraethyl lead and tetramethyl lead can be used to increase the octane level of gasoline. Production of acetic acid is done by carbonylation of methanol, acetic acid is widely used in industry. Among other things, acetic acid is used for the preparation of industrial solvents such as acetate esters, for the production of polyvinyl acetate and its dehydration product, polyvinyl alcohol (Figure 2), as well as in the industries that produce cellulose acetate fibers and plastics for the production of acetic anhydride. In the pharmaceutical industry, the use of organic derivatives of transition metals and the use of organic compounds of ruthenium and iridium in dealing with drug resistance are other applications of these compounds. They can also be used as pesticides [19].

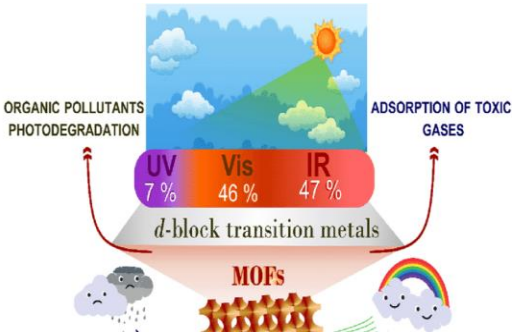


Figure 2. Application of organometallic compounds

Adhesion improvers in polymer

Polymer composites and resins are without polar functional groups and have low surface energy, so they have poor adhesive properties. Therefore, to increase their adhesion, they use materials known as adhesion improvers. In these compounds, active functional groups cause the adhesion of incompatible components. Among the adhesion improvers, we can mention organometallic compounds, silanes and polymer improvers. When mixing polymers with other components, which can be another polymer for example, there are often cases of poor adhesion or the components may repel each other. In these cases, adhesion improvers and polymer improvers that are easy to work with are used. These substances are known as binding agents, compatibilizers, or coupling agents, which are surface active agents [20].

Types of adhesion improvers in polymer

Adhesion improvers are divided into two categories according to their type of action. In situations where adhesion improvers are used between two incompatible polymers to increase miscibility, they are called compatibilizers. Also, in situations where adhesion improvers are used to create adhesion between a filter and a polymer system, they are referred to as coupling agents or binding agents. Being active or inactive depends on having a functional group in the reaction with other components, and the result is that the adhesion between the two layers occurs by reducing the surface tension [21].

The mechanism of action of the coupling or binding agent

A polymer that binds an inorganic filler to a polymer matrix is a coupling agent. Common fillers include glass fibers, calcium carbonate, talc or flame retardants such as aluminum trihydrate or magnesium hydroxide. The

purpose of adding filler is to delay the flame, reduce the price of polymer and increase the toughness and hardness of glass fibers. Because there are a lot of fillers in the composition. This causes the reduction of flexibility, reduction of toughness and increase in length at the time of failure. In most cases, fillers repel polymers and do not like them very much and are not compatible with polymers. To deal with this problem, bonding agents are used to reduce the repulsion between polymers and fillers. Therefore, the filler adheres much better to the polymer matrix and increases the properties of the mixture [22].

Discussion

Metal-Organic Frameworks are an important and new group of porous nanomaterials that, due to their unique structural properties such as high surface area, wide structural diversity, suitable physical and chemical stability, and porous and crystalline structure, have wide applications in different fields such as adsorption, catalytic degradation, gas sensor. Among the most important advantages of organic-metallic frameworks compared to common nanomaterials in the mentioned applications, we can mention the wide structural diversity and the possibility of determining the performance by choosing different metal groups and organic ligands. Based on this, this group of nanomaterials has a high potential for use in various industries, such as water/wastewater treatment, oil/gas refining, as well as identifying and making sensors for toxic, flammable and polluting gases at ambient temperature. Different methods such as hydrothermal, solvothermal, sol-gel, mechanical-chemical methods can be used in the construction of metal-organic frameworks. The existence of some structural properties such as active metal adsorption sites, high surface area that provides more active adsorption sites for the absorption of pollutant molecules, and changeable cavities that are capable of various interactions such as electrostatic interactions, hydrophobic interactions, and hydrogen bonds with the presence of organic ligands different molecules in the liquid and gas phase, causing better performance of metal-organic frameworks compared to common industrial materials such as Zeolites and carbon materials. However, despite the mentioned advantages, this group of nanomaterials has a higher production cost compared to zeolites or carbon materials, and in some environments, especially in the liquid phase, they are sometimes less stable [23].

To solve these disadvantages, the manufacturing and evaluation of nanomaterials based on organic-metallic frameworks such as various composites, doping metals and metal oxides in their structure, carbonizing these compounds and inventing green synthesis techniques seem to be appropriate solutions. Also, due to the variety of metals and organic ligands used in this group of materials and the effect of various factors on their final performance as absorbers or catalysts, unlike common industrial nanomaterials, it is not possible to use common scientific propositions such as improving performance by increasing surface area and crystallinity [24]. To put it better, in this group of materials, it is necessary to optimize the method and conditions of adsorbent or catalyst manufacturing for the purpose of a specific process. Based on this, it seems that in order to take advantage of the benefits of this group of materials in industries along with adjusting costs, improving stability and optimizing the manufacturing method, the need for more studies on a laboratory and semi-industrial scale is necessary [25].

Conclusion

The presence of selective catalysts in terms of shape and molecular size is of particular

importance in many catalytic reactions in various industries. The most prominent feature of metal-organic structures is the absence of dead space that cannot be accessed. In metal-organic frameworks with a regular structure, the active sites are well separated from each other, and on the other hand, the very high surface area of these structures make it possible to have a high density of active sites per unit volume of the catalyst. In the last few decades, extensive studies have been conducted on porous organic-inorganic hybrid materials that refer to organic coordination networks. Porous organic coordination networks can be formed through the process of spontaneous assembly of metal and linkers (ligands), which connect metal-ligand bonds to create porous crystal structures. Metal-organic frameworks (MOFs) are porous materials synthesized from the reaction between inorganic polymers and organic linkers.

Metal-organic frameworks are coordination polymer compounds composed of metal as nodes and organic ligands as linkers. These compounds are crystalline and porous and the size and shape of their holes can be engineered. These features, along with a very high surface to volume ratio (up to 14,800 m^2/g in some cases), make them suitable for various applications, such as heterogeneous catalysts, absorbents, gas separation and storage agents, sensors, fuel cells, solar cells, and pollutant removal.

References

[1]Liu, J.; Song, Y.; Ma, L. Earth-Abundant Metal-Catalyzed Reductive Amination: Recent Advances and Prospect for Future Catalysis. Chem. Asian J. **2021**, 16, 2371–2391. [Google Scholar] [CrossRef] [PubMed]

[2]Ott, J.C.; Bürgy, D.; Guan, H.; Gade, L.H. 3d Metal Complexes in T-Shaped Geometry as a Gateway to Metalloradical Reactivity. Accounts Chem. Res. **2022**, 55, 857–868. [Google Scholar] [CrossRef] [PubMed]

[3]Arora, V.; Narjinari, H.; Nandi, P.G.; Kumar, A. Recent Advances in Pincer-Nickel Catalyzed Reactions. Dalton Trans. **2021**, 50, 3394–3428. [Google Scholar] [CrossRef]

[4]Rufino-Felipe, E.; Valdés, H.; Morales-Morales, D. C–S Cross-Coupling Reactions Catalyzed by Well-Defined Copper and Nickel Complexes. Eur. J. Org. Chem. **2022**, 2022, e202200654. [Google Scholar] [CrossRef]

[5]Junge, K.; Papa, V.; Beller, M. Cobalt–Pincer Complexes in Catalysis. Chem. Eur. J. **2019**, 25, 122–143. [Google Scholar] [CrossRef] [PubMed]

[6]González-Sebastián, L.; Reyes-Sanchez, A.; Morales-Morales, D. Hydrogenation and Cross-Coupling Reactions Catalyzed by Mn, Fe, and Co Aromatic Pincer Complexes. Organometallics **2023**, 42, 2426–2446. [Google Scholar] [CrossRef]

[7]Valdés, H.; Rufino-Felipe, E.; van Koten, G.; Morales-Morales, D. Hybrid POCZP Aryl Pincer Metal Complexes and Their Catalytic Applications. Eur. J. Inorg. Chem. **2020**, 2020, 4418–4424. [Google Scholar] [CrossRef]

[8]Farrell, K.; Albrecht, M. Late Transition Metal Complexes with Pincer Ligands That Comprise N-Heterocyclic Carbene Donor Sites. Privil. Pincer-Metal. Platf. Coord. Chem. Appl. **2015**, 54, 45–92. [Google Scholar] [CrossRef]

[9]Kuwabara, J.; Kanbara, T. Synthesis and Optical Properties of Pincer Palladium and Platinum Complexes Having Thioamide Units. J. Photopolym. Sci. Technol. **2008**, 21, 349–353. [Google Scholar] [CrossRef]

[10] Kocherga, M.; Boyle, K.M.; Merkert, J.; Schmedake, T.A.; Walter, M.G. Exploring the Molecular Electronic Device Applications of Synthetically Versatile Silicon Pincer Complexes as Charge Transport and Electroluminescent Layers. Mater. Adv. **2022**, 3, 2373–2379. [Google Scholar] [CrossRef]

[11] Hegde, V.; Kulkarni, N.V.; Mathew, J. Synthesis and Characterization of Cobalt (II) Pincer Complexes and Their Application as Dyes in Dye-Sensitized Solar Cells. J. Mol. Struct. **2023**, 1286, 135508. [Google Scholar] [CrossRef]

[12] Qu, J.-J.; Bai, P.; Liu, W.-N.; Liu, Z.-L.; Gong, J.-F.; Wang, J.-X.; Zhu, X.; Song, B.; Hao, X.-Q. New NNN Pincer Copper Complexes as Potential Anti-Prostate Cancer Agents. Eur. J. Med. Chem.

2022, 244, 114859. [Google Scholar] [CrossRef]
[13] El-Sayed, N.M.A.; Elsawy, H.; Adam, M.S.S. Polar and Nonpolar Iron (II) Complexes of Isatin Hydrazone Derivatives as Effective Catalysts in Oxidation Reactions and Their Antimicrobial and Anticancer Activities. Appl. Organomet. Chem. **2022**, 36, e6662. [Google Scholar] [CrossRef]
[14] Aragón-Muriel, A.; Reyes-Márquez, V.; Cañavera-Buelvas, F.; Parra-Unda, J.R.; Cuenú-Cabezas, F.; Polo-Cerón, D.; Colorado-Peralta, R.; Suárez-Moreno, G.V.; Aguilar-Castillo, B.A.; Morales-Morales, D. Pincer Complexes Derived from Tridentate Schiff Bases for Their Use as Antimicrobial Metallopharmaceuticals. Inorganics **2022**, 10, 134. [Google Scholar] [CrossRef]
[15] Aleksanyan, D.V.; Konovalov, A.V.; Churusova, S.G.; Rybalkina, E.Y.; Peregudov, A.S.; Aksenova, S.A.; Gutsul, E.I.; Klemenkova, Z.S.; Kozlov, V.A. Modulation of the Cytotoxic Properties of Pd(II) Complexes Based on Functionalized Carboxamides Featuring Labile Phosphoryl Coordination Sites. Pharmaceutics **2023**, 15, 1088. [Google Scholar] [CrossRef] [PubMed]
[16] Liu, W.; Sahoo, B.; Junge, K.; Beller, M. Cobalt Complexes as an Emerging Class of Catalysts for Homogeneous Hydrogenations. Accounts Chem. Res. **2018**, 51, 1858–1869. [Google Scholar] [CrossRef]
[17] Roy, D.; Uozumi, Y. Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at Ppm to Ppb Molar Catalyst Loadings. Adv. Synth. Catal. **2018**, 360, 602–625. [Google Scholar] [CrossRef]
[18] Christoffel, F.; Ward, T.R. Palladium-Catalyzed Heck Cross-Coupling Reactions in Water: A Comprehensive Review. Catal. Lett. **2018**, 148, 489–511. [Google Scholar] [CrossRef]
[19] Salih, K.S.M. Modern Development in Copper- and Nickel-Catalyzed Cross-Coupling Reactions: Formation of Carbon-Carbon and Carbon-Heteroatom Bonds under Microwave Irradiation Conditions. Asian J. Org. Chem. **2022**, 11, 244–269. [Google Scholar] [CrossRef]
[20] Andrade, M.A.; Martins, L.M.D.R.S. New Trends in C–C Cross-Coupling Reactions: The Use of Unconventional Conditions. Molecules **2020**, 25, 5506. [Google Scholar] [CrossRef] [PubMed]
[21] Durandetti, M. Synthetic Applications of Nickel-Catalyzed Cross-Coupling and Cyclisation Reactions. Chem. Rec. **2021**, 21, 3746–3757. [Google Scholar] [CrossRef]
[22] Cooper, A.K.; Leonard, D.K.; Bajo, S.; Burton, P.M.; Nelson, D.J. Aldehydes and Ketones Influence Reactivity and Selectivity in Nickel-Catalysed Suzuki-Miyaura Reactions. Chem. Sci. **2020**, 11, 1905–1911. [Google Scholar] [CrossRef] [PubMed]
[23] Favela-Mendoza, R.; Rufino-Felipe, E.; Valdés, H.; Toscano, R.A.; Hernandez-Ortega, S.; Morales-Morales, D. Synthesis and Characterization of Non-Symmetric Ni(II)- and Pd(II)-POCOP Pincer Complexes Derived from 1,7-Naphthalenediol. Evaluation of Their Catalytic Activity in Suzuki-Miyaura Couplings. Inorganica Chim. Acta **2020**, 512, 119920. [Google Scholar] [CrossRef]
[24] Kumar, L.M.; Bhat, B.R. Iron Pincer Complexes as Catalysts in Cross-Coupling of Aryl Halides and Phenylboronic Acid. Int. J. Eng. Technol. **2018**, 7, 428–430. [Google Scholar] [CrossRef]
[25] Keskin, E.; Arslan, H. Palladium Complexes Containing NNN Pincer Type Ligands and Their Activities in Suzuki-Miyaura Cross Coupling Reaction. Heliyon **2023**, 9, e17608. [Google Scholar] [CrossRef] [PubMed]