# KİMYA ÇALIŞMALARI

Editör: Doç.Dr. Güzide PEKCAN

yaz

yayınları

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# İÇİNDEKİLER

# 2,3-PİRİDİNDİKARBOKSİLİK ASİT VE METAL KOMPLEKSLERİ

**Zeynep ALKAN ALKAYA**[1]

## 1. GİRİŞ

Piridindikarboksilik asitler, organik asitlerin önemli bir kısmını oluşturan karboksilik asitler grubuna aittir. Hayvanların metabolik yollarında bulunmakta olup, metal iyonlarının vücut tarafından taşınması, temizlenmesi için kullanılmaktadır [1]. Ayrıca, bu ligandın daha etkili anti-HIV ajanları geliştirmek için kullanıldığı çalışmalar da mevcuttur [2-4]. Piridindikarboksilik asitler, organik-inorganik hibrid malzemelerin oluşturulmasında oldukça yaygın bir şekilde kullanılmıştır [5-6]. Bu asitler, çoklu proton verici ve alıcı olarak hareket edebilir, karboksilik asit ve aromatik bileşiklerin avantajlarını da birleştirebilirler [5-7]. Ayrıca çeşitli koordinasyon modları kullanarak birden fazla metal iyonunu birleştirebilmeleri sayesinde metal-organik komplekslerin tasarımında fazlaca kullanılmıştır, bu modlar arasında monodentat koordinasyon ve bidentat şelasyon bulunmaktadır [8]. Sahip oldukları tüm bu özellikler sayesinde piridindikarboksilik asit bileşikleri, çeşitli endüstriyel ve farmasötik araştırma alanlarında önemli uygulamalara sahiptirler. Bu uygulama alanlarına, antioksidan, antifungal, antimikrobiyal, antitümor, antikanser, antiinflamatuar, antiülser, antidiyabetik, antimütajen, süperoksit giderici ve radyoprotektif aktivite gibi biyolojik özellikler sayılabilir [9-14]. Metal kompleksleri de farklı yapıları ve mükemmel özellikleri nedeniyle kataliz [14],

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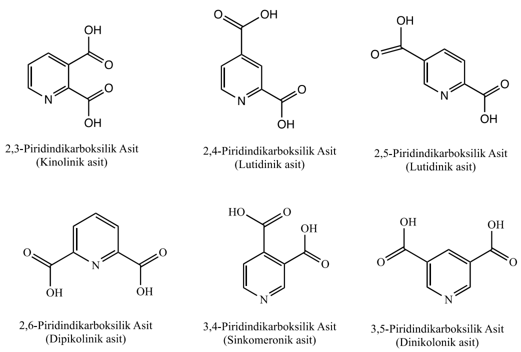
biyoalgılama [15], gaz depolama [16] ve yakalama [17], moleküler tanıma ve ayırma [18] gibi alanlarda yaygın olarak kullanılmakta ve antifungal [19], antitüberküloz [20], analjezik [21] ve antikanser [22] gibi aktiviteler sergilemektedir.

## 2. GENEL ÖZELLİKLERİ VE KULLANIM ALANLARI

2,3-Piridindikarboksilik asit bir diğer ismiyle kinolinik asit, kimyasal ve fiziksel özelliklerine bağlı olarak birçok farklı uygulamada kullanılan çok yönlü bir bileşiktir ve koordinasyon kimyasında da önemli bir rol oynar. Yapısı piridin halkası ve iki karboksilik asit grubundan oluşur. Metal iyonları ile çeşitli özelliklere sahip kompleksler oluşturabilir. Özellikle malzeme bilimi, ilaç araştırmaları ve organik sentez gibi alanlarda büyük potansiyele sahip bir bileşiktir [23]. Daha önce yapılmış çalışmalara göre, elde edilen metal komplekslerinde merkezi metalinin türü, bileşiğin antikanser ilacı olarak inhibisyon etkisini etkileyebilir, metal iyonlarıyla koordine olan organik ligand da biyolojik aktivitesi üzerinde önemli bir etkiye sahip olabilir [24]. Metallerin olumsuz etkileri, organik ligandlarla koordinasyon sağlanarak azaltılabilir [25-26]. Bu ligandın daha etkili anti-HIV ajanlarını geliştirmek için kullanıldığı çeşitli çalışmalarla da bilinmektedir [27–29].

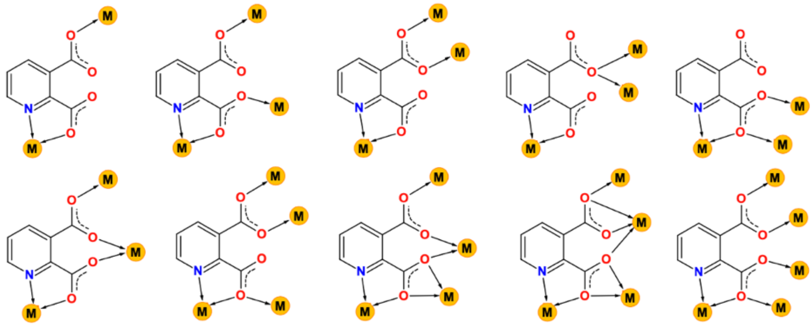
**Şekil 1. Piridindikarboksilik Asitlerin İzomer Yapıları**



Piridindikarboksilik asitler, 2,3-piridindikarboksilik asit (kinolinik asit), 2,4-piridindikarboksilik asit (lutidinik asit), 2,5-piridindikarboksilik asit (izosinomeronik asit), 2,6-piridindikarboksilik asit (dipikolinik asit), 3,4-piridindikarboksilik asit (sinkomeronik asit) ve 3,5-piridindikarboksilik asit (dinotinik asit) olmak üzere altı farklı izomere sahiptir (Şekil 1).

Genel olarak bu asidin metal-organik koordinasyon kompleksleri üç kategoriye ayrılabilir; geçiş metali motiflerine dayalı olanlar, lantanit motiflerine dayalı olanlar ve lantanit-geçiş metali-heterometalik koordinasyon polimerlerine dayalı olanlar. Komplekslerin her tipinde bağlayıcı olarak bir tip ligand içerenler ve metal iyonlarını bağlayan iki veya daha fazla farklı tipte ligand içeren kompleksler bulunmaktadır [30-31]. 2,3-Piridindikarboksilik asitin metal kompleks bileşiklerinde bağlanma şekillerine şekil 2'de ki modeller örnek verilebilir [32].

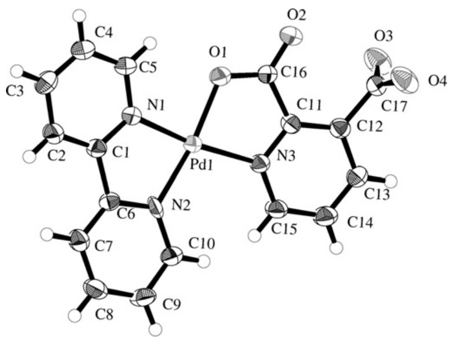
**Şekil 2. 2,3-Piridindikarboksilik Asitin Metal Kompleks Bileşiklerinde Bağlanma Şekilleri**



## 3. METAL KOMPLEKSLERİ

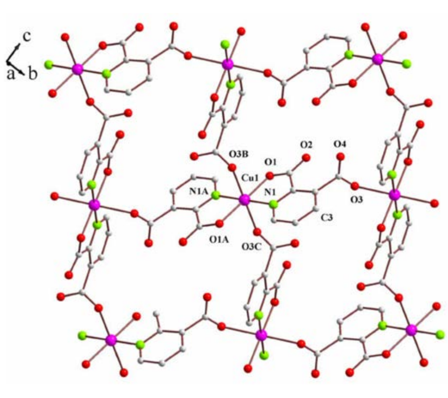
Wang ve arkadaşları (2005), 2,3-piridindikarboksilik asit ve 2,2'-bipiridin kullanarak Pd (II) metali ile metal kompleksi elde etmişlerdir. Kompleksi X-ışınları tek kristal analizi ile aydınlatmışlardır [33] (Şekil 3).

**Şekil 3. Wang ve Arkadaşlarının (2005) Elde Ettiği Pd(II) Kompleksi**



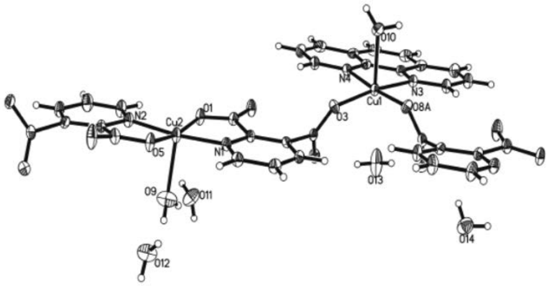

Yin ve Liu (2009) 2,3-piridindikarboksilik asit, 2,2’-bipiridin, 4,4’-bipiridin, 1,10-phenanthroline ligantlarını ve Cu/Zn metallerini kullanarak karışık ligantlı metal kompleksleri elde etmişler, kompleksleri X-ışınları tek kristal analizi ile aydınlatmışlardır. Ayrıca çalışmalarında komplekslerin manyetik özellikleri ve fotolüminesans özelliklerini tartışmışlardır. Çalışmada yer alan 2,3-piridindikarboksilik asit-Cu kompleksi şekil 4’te verilmiştir [34].

**Şekil 4. Yin Ve Liu’nun Elde Etmiş Olduğu Metal Komplekslerinden {[Cu(pydcH)$_2$].4H$_2$O}n**



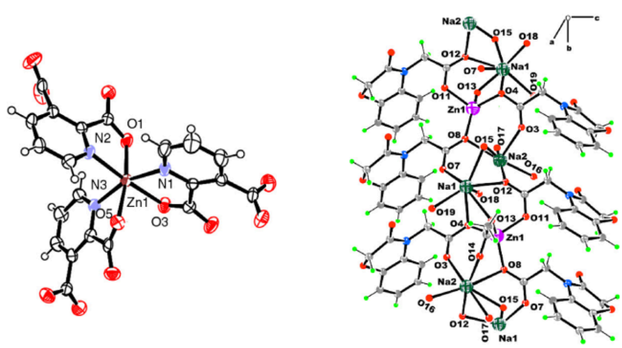
Yan ve arkadaşları (2009) çalışmalarında, 2,3-piridindikarboksilik asit ile 1,10-phenanthroline ligantlarını ve Cu metalini kullanarak karışık ligantlı metal kompleksleri elde etmiş, yapılarını X-ışınları tek kristal analizi ile aydınlatmışlardır [35] (Şekil 5).

**Şekil 5. Yan ve Arkadaşlarının Elde Etmiş Olduğu 2,3-Piridindikarboksilik Asit İle 1,10-Phenanthroline Cu Kompleksi**




Singh ve arkadaşları (2011) 2,3-piridindikarboksilik asit ile Zn metali içeren iki metal kompleksi elde etmiş, yapılarını X-ışınları tek kristal analizi ile aydınlatmışlardır [36] (Şekil 6).

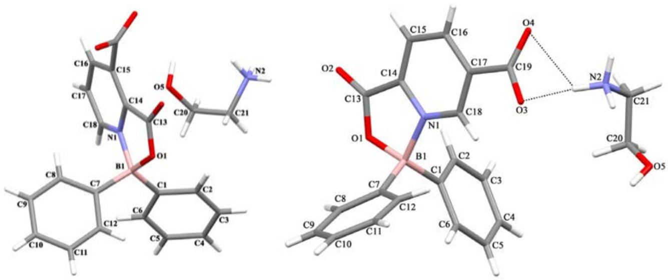
**Şekil 6. Singh ve Arkadaşlarının Elde Etmiş Olduğu 2,3-Piridindikarboksilik Asit-Çinko Kompleksleri**




**a.** **b.**

Çolak ve arkadaşları (2012) 2,3 ve 2,5-piridindikarboksilik asit ile Bor içeren üç yeni kompleks elde etmiş, komplekslerin karakterizasyonunu X-ışınları tek kristal analizi ile aydınlatmışlardır. Ayrıca iki kompleksin in vitro antibakteriyel ve antikandidal aktiviteleri incelenmiş, her iki kompleksin de MRSA, klinik ve standart maya izolatlarına karşı antimikrobiyal aktivite gösterdiği tespit edilmiştir [37] (Şekil 7).

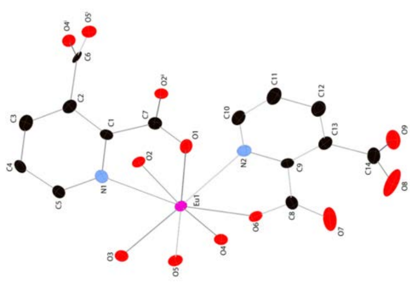
**Şekil 7. Çolak ve Arkadaşlarının Elde Etmiş Olduğu 2,3 Ve 2,5-Piridindikarboksilik Asit İçeren Bor Kompleksleri**



a. b.

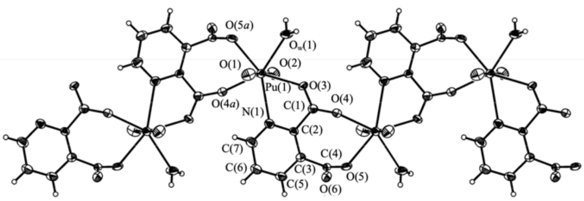
Ramirez ve arkadaşları (2012) 2,3-piridindikarboksilik asit içeren iki-boyutlu lantanit koordinasyon polimeri $[Ln(C_7H_3NO_4)(C_7H_4NO_4)(H_2O)]_n$ (Ln = üç değerlikli Pr, Nd, Sm, Eu ve Tb) sentezlemişlerdir. Bileşiğin yapısını X-ışınları tek kristal analizi ile aydınlatmışlardır [38] (Şekil 8).

**Şekil 8. Ramirez ve Arkadaşlarının Elde Etmiş Olduğu 2,3-Piridindikarboksilik Asit İçeren İki-Boyutlu Koordinasyon Polimeri**

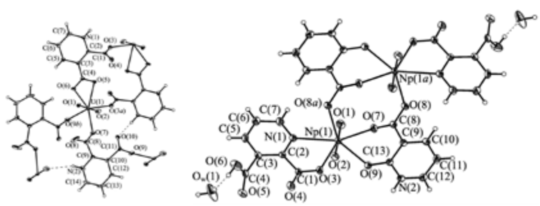


Yusov ve arkadaşları (2012) 2,3-piridindikarboksilik a sit ile U, Np, Pu metallerini içeren üç metal kompleksi elde etmiş, yapılarını X-ışınları tek kristal analizi ile aydınlatmışlardır [39] (Şekil 9).

**Şekil 9. Yusov ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik Asit İçeren Metal Kompleksleri**



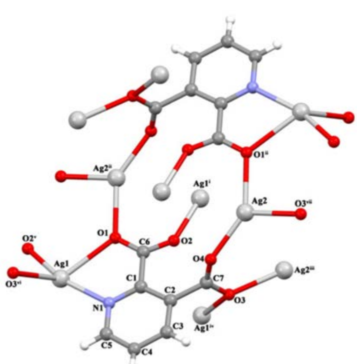
a.



b. c.

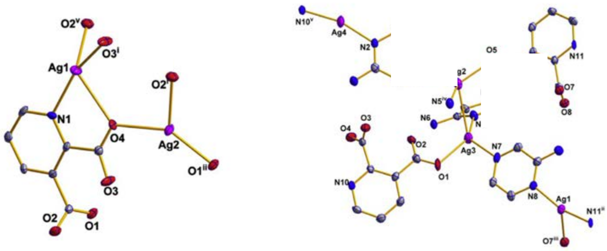
Colak ve arkadaşları (2013) çalışmalarında 2,3-piridindikarboksilat-Ag(I) içeren bir kompleks elde etmiş, yapısını X-ışınları tek kristal analizi ile aydınlatmış ve fotolüminesans özelliğini araştırmışlardır [40] (Şekil 10).

**Şekil 10. Colak ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik Asit İçeren Ag Kompleksi**



Wang ve arkadaşları (2014) çalışmalarında 2,3-piridindikarboksilik asit ve Ag içeren iki yeni bileşik elde etmiş, bileşiklerin yapıları X-ışınları tek kristal analizi ile aydınlatmış, fotolüminesans özellikleri incelemişlerdir [41] (Şekil 11).

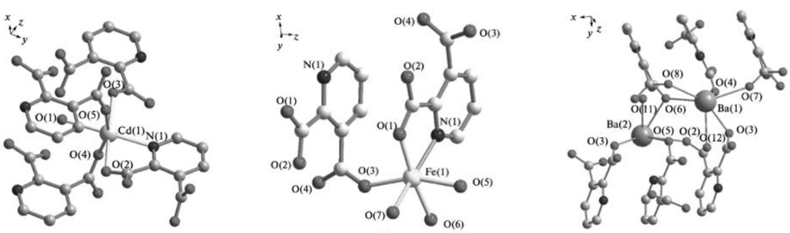
**Şekil 11. Wang ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik İçeren Ag Kompleksleri**



a. b.

Huang ve arkadaşları (2014) çalışmalarında 2,3-piridindikarboksilik asit ile Cd, Fe ve Ba metallerini kullanarak 3 yeni metal kompleksi elde etmiş, X-ışınları tek kristal analizi ile yapısını tanımlamışlardır [42] (Şekil 12).

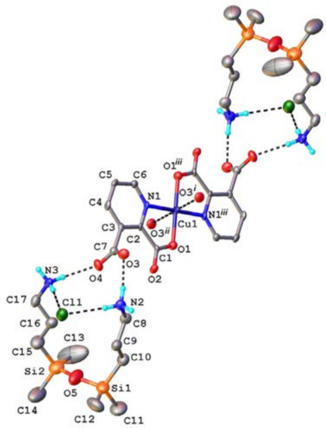
**Şekil 12. Wang ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik İçeren Cd (a), Fe (b) ve Ba (c) Kompleksleri**



**a.** **b.** **c.**

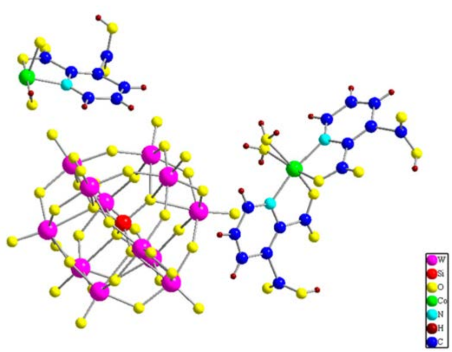
Soroceanu ve arkadaşlarının (2015) makalesinde, 2,3-piridindikarboksilik asit, 1,3-bis(3-aminopropil) tetrametildisiloksan ve Cu içeren kompleks elde edilmiş, X-ışınları tek kristal analizi ile aydınlatılmış, ayrıca kompleksin termal ve nem davranışları termogravimetrik analiz ve dinamik buhar sorpsiyonu ile incelenmiştir [43] (Şekil 13).

**Şekil 13. Soroceanu ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik İçeren Cu Kompleksi**



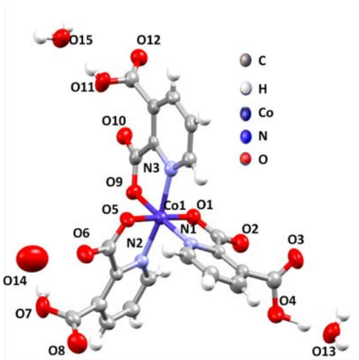

Xiao ve arkadaşları (2015) çalışmalarında 2,3-piridindikarboksilik asit bileşiği ile Co ve Si içeren organik-inorganik hibrit bir supramoleküler kompleks elde etmiş, yapısını X-ışınları tek kristal analizi ile karakterize etmişlerdir. Ayrıca kompleksin termal kararlılığı, floresans (FL) ve oksidasyon-indirgeme özellikleri, metanolün eliminasyonu için katalitik performansı araştırılmıştır [44] (Şekil 14).

**Şekil 14. Xiao ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik İçeren Supramoleküler Kompleks**



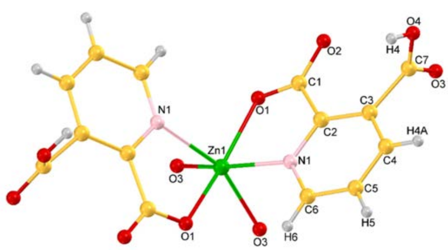
Terenti ve arkadaşları (2018) çalışmalarında, 2,3-piridindikarboksilik asit ve Co içeren metal kompleksi elde etmişlerdir. Kompleks X-ışınları tek kristal analizi ile aydınlatmışlardır [45] (Şekil 15).

**Şekil 15. Terenti ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik İçeren Co Kompleksi**



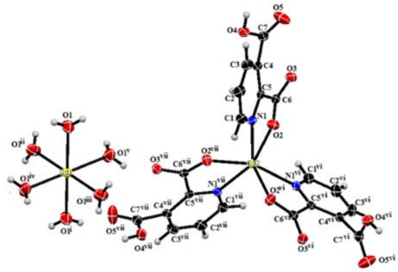

Ashafaq ve arkadaşları (2020) çalışmalarında 2,3-piridindikarboksilik asit ve Zn içeren metal kompleksi elde etmişler ve kompleksi X-ışınları tek kristal analizi ile aydınlatmışlardır. Ayrıca elde edilen metal kompleksin floresan özelliği araştırılmıştır [46] (Şekil 16).

**Şekil 16. Ashafaq ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik İçeren Zn Kompleksi**



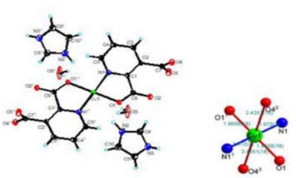

Soudani ve arkadaşları (2021) çalışmalarında, 2,3-piridindikarboksilik asit ve Cd içeren metal kompleksi elde etmiş, kompleksi X-ışını kristalografisi ve teorik kimya hesaplamaları ile aydınlatmışlardır [47] (Şekil 17).

**Şekil 17. Soudani ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik İçeren Cd Kompleksi**

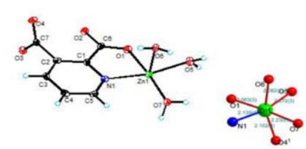


Zhang ve arkadaşları (2023) 2,3-piridindikarboksilik asit ile çeşitli geçiş metallerini içeren 6 metal kompleksi elde etmiş, komplekslerin yapılarını X-ışınları tek kristal analizi ile aydınlatmış ve antikanser aktivitelerini incelemişlerdir. [8] (Şekil 18).

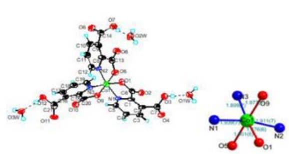
**Şekil 18. Zhang ve Arkadaşlarının Sentezlemiş Olduğu 2,3piridindikarboksilik İçeren Cu (a), Zn (b ve f), Co (c ve d) Ni (e) Kompleksleri**



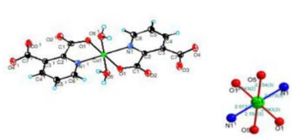
a.



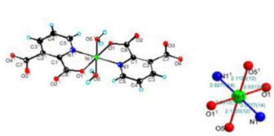
b.



c.



d.

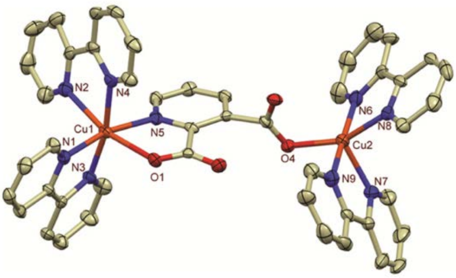


e.

f.

Mondal ve arkadaşları (2023), 2,3-piridindikarboksilik asit ve 2,2'-bipiridin kullanarak Cu kompleksi elde etmiş, yapısını X-ışınları tek kristal analizi ile aydınlatmışlardır. Ayrıca kompleksin katalizör olarak uygulamasını deneyerek, %90 verimle başarılı bir sonuç elde ettiklerini çalışmalarına eklemişlerdir [48] (Şekil 19).

**Şekil 19. Mondal ve Arkadaşlarının Sentezlemiş Olduğu 2,3-Piridindikarboksilik ve 2,2-Bipiridin İçeren Cu Kompleksi**




## 4. SONUÇ

Geçiş metali ve multikarboksilat ligandları kullanılarak oluşturulan koordinasyon bileşikleri, geniş potansiyel uygulamaları nedeniyle yoğun olarak çalışılmaktadır. İstenilen yapının tasarlanmasında anahtar nokta metal iyonu ve ligandın doğru seçimidir. Polikarboksilik ligandlar bu tür bileşikler için oldukça iyi adaylardır çünkü protondan arındırılmış karboksilik grupların sayısına bağlı olarak, hidrojen bağında hem proton verici hem de alıcı olarak görev üstlenebilirler. Bu bağlamda piridindikarboksilik asitlerin ilginç ve önemli bir ligand olduğu da birçok çalışmada yer alan çeşitli koordinasyon modlarıyla kanıtlanmıştır [49-54] Piridindikarboksilik asit ligandları, N- ve O- donörleri sayesinde metallerle çok yönlü yapısal motifler oluşturabilir ve sonuçta ilginç özelliklere sahip çeşitli moleküller elde edilebilmektedir [34].

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# CHEMICAL SYNTHESIS METHODS AND PROMISING AGRICULTURAL SOLUTIONS OF METAL OXIDE NANOPARTICLES

**Hakan ŞAHAL[1]**

## 1. INTRODUCTION

One of the world's oldest and most significant industries for both human and animal survival is agriculture. Ensuring sustainable agriculture and global food security while limiting the detrimental impacts of agricultural techniques on the environment is one of the most significant concerns of the twenty-first century (Van Dijk vd. 2021). According to data released by the Food and Agriculture Organization of the United Nations (FAO), the amount of arable land area worldwide per person fell from roughly 0.45 hectares in 1961 to 0.21 hectares in 2016. This implies that the issue of inadequate cultivated land area for the production of food, fiber, and fuel is one that the agricultural industry is tackling on a global scale. Therefore, efforts to increase production per area will become critical for reliable and efficient food production in the coming years. (Sun vd. 2024). As a result, there is a pressing need to solve these complex issues with ecologically friendly and sustainable solutions. However, excessive greenhouse gas emissions have led to global warming and increased the susceptibility of plants to diseases and epidemics. Moreover, climate change will reduce the effectiveness of traditional disease control methods, directly harm crop growth, and pose a significant threat to the already weak global food security system (Gilbertson vd. 2020). The goal of

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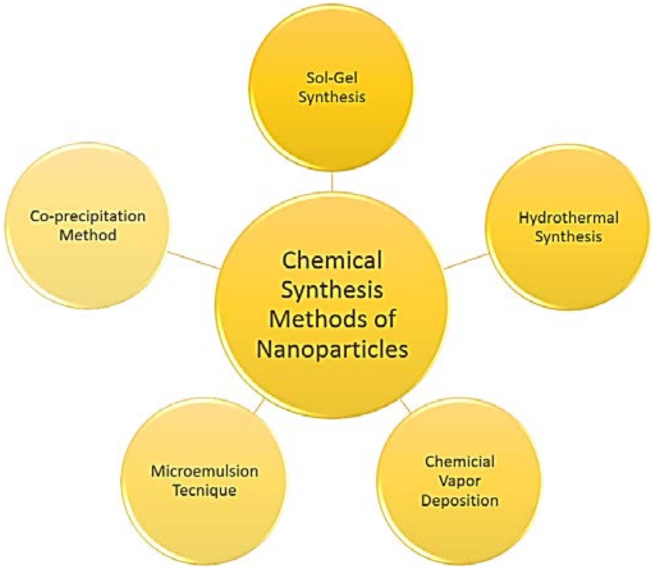
current research is to put ecologically friendly farming methods into practice so that food production may be sustained throughout time without degrading the environment or squandering resources (Islam et al., 2017).

Biological stresses such as drought, pests and diseases, together with losses, lead to low-profit production or expensiveness, that is, large product losses that directly affect profits (Terra et al; 2019). In this regard, nanotechnology has become a potentially useful tool for farming. Several investigations have been carried out to examine the efficacy of novel approaches against biotic and abiotic stress factors, such as the utilization of nanomaterials, living organisms, and their metabolic byproducts (Hassanisaadi et al., 2022). Protecting the environment and ensuring sustainable food production depend on the use of innovative technologies like nanotechnology. Dr. Richard Feynman initially discussed nanosurgeons and nanomaterials that can enter the body and interact with the surrounding environment at the cellular level in his paradigm-shifting lecture titled "there's plenty of room at the bottom." Since then, numerous new and improved classes of nanomaterials that can help with illness detection and therapy and enhance patient management have been investigated in the constantly developing biomedical sciences (Feynman. 1960). These researches have produced positive results for both us and plants. Numerous uses for nanomaterials exist, particularly in the agricultural sector, where they are employed in the production, processing, storage, packaging, and transportation of agricultural goods (Baker et al., 2017).

Research on nanoparticles (NPs) primarily concentrate on their phytotoxicity, absorption, and the physiological and biochemical reactions of plants that come into contact with them. Because NPs can contact plants in both underground and aboveground environments, they can affect a plant even before germination in the soil through penetration into the seed coat. This is a phenomenon exploited using the method of coating seeds with nanomaterials (Tondey vd, 2021). When the literature is examined, it has been reported in many studies that nanoparticles are used as fertilizers and pesticides in agriculture.

**Figure 1. Chemical Synthesis Methods of Nanoparticles**




## 2. CHEMICAL SYNTHESIS METHODS OF METAL OXIDES NANOPARTICLES

For the synthesis of metal oxide nanoparticles; Chemical synthesis methods, including sol–gel, hydrothermal, co-precipitation, microemulsion, and chemical vapor deposition approaches, are often preferred due to their ability to produce smaller nanoparticles with precise control over their size, shape, and uniformity. (Figure 1).

### 2.1. Sol-gel Method

A quick and efficient synthetic method for creating high-purity metal oxide nanoparticles and hybrid oxide composites is the sol-gel process. In general, the sol-gel method is applied in five basic steps: hydrolysis, polycondensation, aging, drying and thermal decomposition. The sol-gel method has advantages such as using more limited precursor materials, producing stable surfaces with high surface area, low processing temperature, excellent homogeneity, high purity, ability to control the composition and morphology of the obtained materials, low cost advantage, scalability and green energy saving (Mabuea et al., 2024).

Photoluminescent products (Ali et al., 2024), biomedical applications (Tahir et al., 2024), supercapacitors (Selvanathan et al., 2024;), magnetic materials (Zayakhanov et al., 2024), gas sensors (Singh et al., 2024). ), functional materials such as superparamagnetics (Girardet et al., 2024), antimicrobial, antioxidant and anticancer materials (Zagloul et al., 2024), photocatalysts (Fardood et al., 2024), superconductors (Mary et al., 2024) have controlled porosity and microstructure. Processes such as the synthesis of high-purity ceramic and glass materials with a structured structure (Chowdhury et al., 2024) and the development of thin films and coatings with specific optical, electrical or protective properties (Prasad et al., 2024) can be performed using the sol-gel method.

The process of going from a liquid "sol" (a colloidal dispersion of particles) to a solid "gel" phase is called the sol-gel process. This method is versatile and can be used to synthesize a wide variety of materials, including oxides, hybrid materials, and composites. Steps in the Sol-Gel process; (Figure 2);

**Preparation of Sol:** The process begins by selecting appropriate precursors, typically metal alkoxides (e.g. tetraethyl orthosilicate (TEOS) for silica, titanium isopropoxide for titania) or metal salts (e.g. nitrates, chlorides). The precursors are dissolved in a solvent, typically methanol or ethanol, which are alcohols. Acidic (e.g. HCl) or basic (e.g. NH3) catalysts are added to the solution to control hydrolysis and condensation reactions.

**Hydrolysis:** Metal alkoxides react with water to form metal hydroxides. The reaction can be described as follows:

$$M(OR)_x + xH_2O \rightarrow M(OH)_x + xROH$$

(M) metal/(OR) alkoxy group/(ROH) alcohol byproduct.

**Condensation:** Hydroxyl groups formed during hydrolysis undergo polycondensation reactions to form metal-oxygen-metal (M-O-M) bonds, leading to the formation of a three-dimensional network. This process causes the particles to grow and eventually gel:

$$M(OH)_x \rightarrow M\text{-}O\text{-}M + H_2O$$

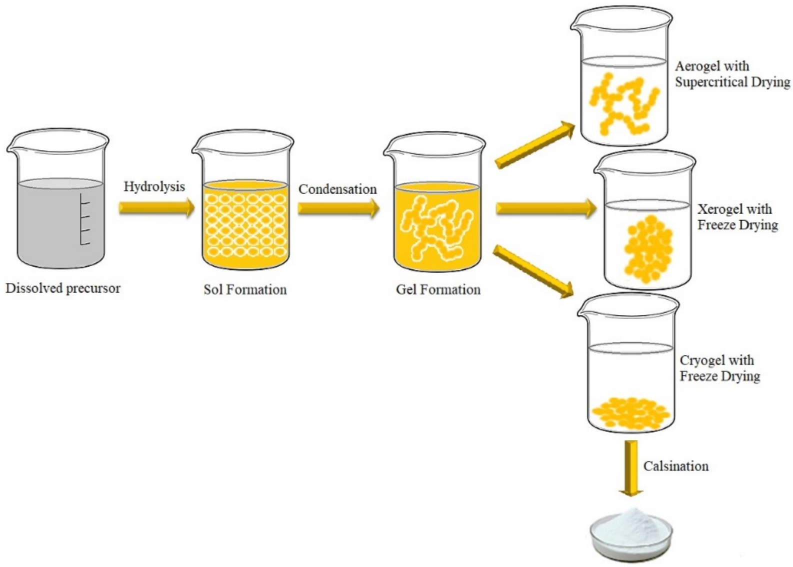
**Development:** The sol gradually turns into a gel, a solid network containing a significant amount of solvent. The gel consists of interconnected nanoparticles that form a porous structure.

**Aging:** The gel undergoes aging, during which further condensation and syneresis (shrinkage and expulsion of solvent) occur. This process strengthens the gel network and reduces its porosity.

**Drying:** The gel is dried to remove the remaining solvent, resulting in airgel, xerogel or cryogel, depending on the drying method. Careful drying is necessary to prevent cracking and maintain the desired structure.

**Thermal Processing:** Airgel, xerogel, or cryogel is often subjected to calcination or sintering at high temperatures to increase crystallinity, remove residual organic compounds, and improve the mechanical and thermal properties of the material.

**Figure 2. Sol-Gel Process in Production of Metal Oxide Nanoparticle [21,22, 23, 24]**




### 2.2. Hydrothermal Synthesis Method

Hydrothermal synthesis is a method in which nanoparticles are obtained by mixing metal salts with a reducing agent and subjecting them to high temperature and high pressure conditions in an aqueous solution. This is a versatile and cost-effective method that allows adjustment of particle size, crystallinity, temperature of the solution, pressure, pH and surface properties (Machakanti vd. 2024). This method mimics natural geological processes and can be used to produce high-quality crystalline materials. Depending on the desired qualities and materials, hydrothermal synthesis is performed at temperatures between 100°C and 300°C and pressures between a few bars and several hundred bars. Water is the most commonly used solvent here. However, other solvents or a mixture of solvents can also be used. The reaction takes place in closed vessels called autoclaves that can withstand high temperatures and pressures. (Figure 3).

Hydrothermal synthesis is carried out in several steps (Figure 3);

**Preparation of Precursors:** To prepare the precursor solution, metal salts (such as chlorides, nitrates, and acetates) or organometallic compounds are dissolved in water or other solvents. The pH of the solution is usually adjusted using acids or bases to influence the growth and morphology of the nanoparticles.

**Loading the Autoclave:** The precursor solution is placed in an autoclave and then closed. Autoclaves are typically made of stainless steel. This material may be coated with Teflon or other materials to prevent contamination and corrosion.

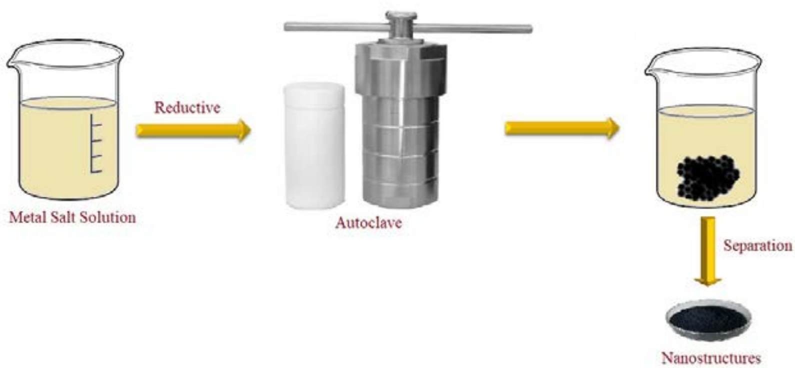
**Heating:** The autoclave is heated to the desired temperature, usually between 100°C and 300°C. Temperature and pressure conditions promote the dissolution of precursors and subsequent nucleation and growth of nanoparticles. Depending on the material and desired properties, heating time can vary from a few hours to several days.

**Cooling and Collection:** After the reaction period, the autoclave is slowly cooled to room temperature. Next, the resultant nanoparticles are gathered, typically by centrifugation or filtration. Nanoparticles are washed with water or other solvents to remove residual precursors or byproducts.

**Drying:** The collected nanoparticles are usually dried under vacuum or in an oven to obtain the final product. Additional post-treatments such as calcination or annealing may be performed to improve crystallinity and phase purity.

Compared to other methods that require high temperatures, hydrothermal synthesis allows obtaining the desired crystal at relatively lower temperatures. Simultaneously, this process yields high-quality nanoparticles in a low-stage, eco-friendly manner that eliminates the need for hazardous chemicals and enables scalable, ecologically friendly product production. (Awan et al., 2024). Hydrothermally synthesized nanoparticles are used in water purification, degradation of pollutants, and other environmental applications (Deepika et al., 2024).

**Figure 3. Hydrothermal Synthesis Process in Production of Metal Oxide Nanoparticle**




### 2.3. Co-precipitation Method

This method involves the simultaneous precipitation of multiple components from a single solution, leading to the formation of mixed metal nanoparticles or composite materials. The co-precipitation method is used to prepare nano or sub-micro structures of various metal oxides, starting from inorganic salts as precursors (Liang et al., 2024). This method is particularly useful for synthesizing complex oxides, hydroxides and other mixed metal compounds.

Steps in the co-precipitation method (Figure 4);

**Preparation of Precursors:** Metal salts (e.g., chlorides, nitrates, sulfates) are selected as precursors. These salts are dissolved in water or other suitable solvents to form a homogeneous solution. The ratio of metal precursors is carefully controlled to obtain the desired composition of the final nanoparticles.

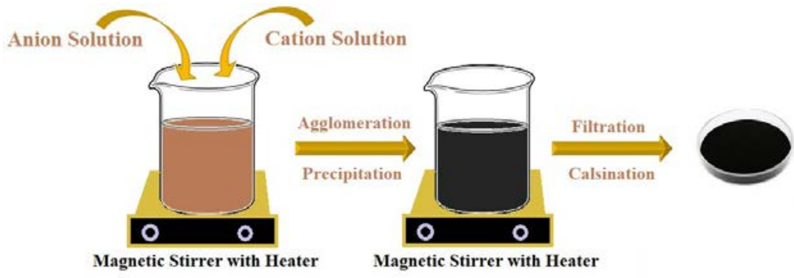
**Precipitation:** Under constant stirring, a precipitating agent—such as a reducing agent or a base—is gradually added to the precursor solution. This results in the formation of insoluble metal hydroxides or oxides. The pH, temperature and rate of addition of the precipitant are carefully controlled to ensure proper precipitation and prevent the formation of undesirable phases.

**Aging:** The precipitate is typically allowed to age with continuous stirring to promote the growth and crystallization of nanoparticles. Aging helps achieve the desired particle size and morphology.

**Filtration and Washing:** Filtration or centrifugation are used to extract the precipitated nanoparticles from the solution. The particles are then washed with water or other solvents to remove any residual precursors, byproducts, or impurities.

**Drying:** The washed nanoparticles are usually dried under vacuum or in an oven to remove any remaining solvent. Depending on the desired application, nanoparticles can be subjected to additional processes such as calcination to improve crystallinity, phase purity, and other properties.

**Figure 4. Co-Precipitation Method in Production of Metal Oxide Nanoparticle**




## 2.4. Chemical Vapor Deposition Method (CVD)

With this process, the desired material is created by the chemical reactions of gaseous precursors on a substrate's surface. Volatile precursors are moved in the gas phase to a heated substrate during the CVD process, where they react or decompose to generate a solid substance. Many different types of materials, such as metals, semiconductors, oxides, and nitrides, can be deposited using this method (Chen et al., 2024). Protective and functional coatings such as anti-reflective, wear-resistant and corrosion-resistant layers are produced by CVD (Ramalho et al., 2024). CVD is used to synthesize materials for batteries and supercapacitors, improving their performance and stability (Pahlavani et al., 2024). Materials for LEDs, solar cells and photodetectors are produced using CVD techniques (Darekar et al., 2024).

Steps in the Chemical Vapor Deposition Process (Figure 5);

**Preparation of Precursors:** The choice of gaseous precursors depends on the material to be synthesized. Common precursors include metal-organic compounds, halides, and hydrides. Inert gases such as nitrogen, argon or hydrogen are used as carrier gas to transport the precursors to the reaction chamber.

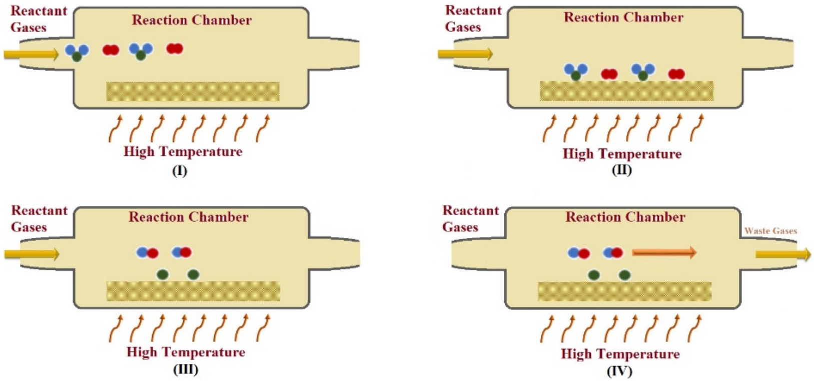
**Transport to Reaction Chamber:** The substrate is placed in a reaction chamber and gaseous precursors and carrier gases are added.

**Reaction and Deposition:** The substrate is heated to a temperature at which the precursors decompose or react. This temperature varies depending on the material and precursors used. The precursors undergo chemical reactions on the substrate surface, resulting in the deposition of a thin film or nanoparticles. Reactions may include pyrolysis, reduction, oxidation or hydrolysis.

**Formation of Nanoparticles:** Nanoparticles are formed either directly on the substrate or in the gas phase, depending on the specific conditions and setup. These particles can nucleate and grow to reach the desired size and morphology.

**Byproduct Removal:** Gaseous byproducts of the reaction are removed from the reaction chamber by the carrier gas flow and expelled through a vacuum system.

**Figure 5. Chemical Vapor Deposition Method in Production of Metal Oxide Nanoparticle**



### 2.5. Microemulsion Technique

This technique provides precise control over nanoparticle size by adjusting the microemulsion droplet size. Microemulsions are transparent, isotropic, thermodynamically stable mixes of water, oil, and surfactant; co-surfactants may also be added. However, microemulsions can be prepared directly by combining oil, water, and amphisolvent without conventional surfactants. Water and oil can both be dissolved by amphisolvents (Tarkas et al., 2024). Nanometer-sized droplets in the microemulsion serve as small reaction vessels where the synthesis of nanoparticles takes place (Rahaman et al., 2024). This method is widely used due to its ability to produce monodisperse nanoparticles with well-defined properties. Water droplets distributed in a continuous oil phase (Water in Oil (W/O)), oil droplets scattered in a continuous aqueous phase (Oil in Water (O/W)), and both water and oil in the microemulsion as linked networks (Bi-continuous) are the three forms of the microemulsion method. (Hu et al., 2024).

Steps in the Microemulsion Process (Figure 6);

**Preparation of microemulsion:** The selection of oil, water, surfactant and co-surfactant is very important. Sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and Tween are examples of common surfactants. The components are mixed in appropriate proportions to form a clear and stable microemulsion. The specific ratios depend on the type of microemulsion desired and the nature of the nanoparticles synthesized.

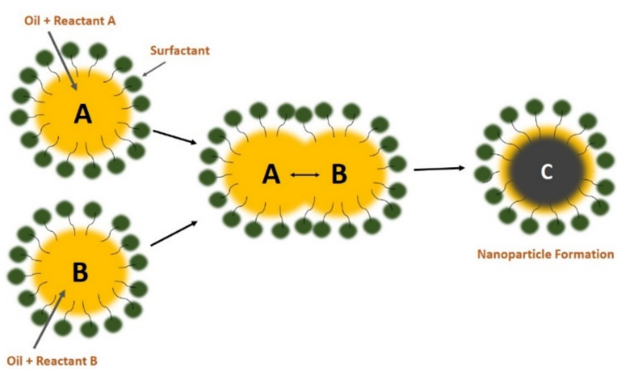
**Addition of Precursors:** Metal salts or other precursor compounds are dissolved in the appropriate phase (water or oil). For example, in a W/O microemulsion the metal precursor is usually dissolved in water droplets.

**Nanoparticle Formation:** A reducing agent or other reactants are added to the microemulsion to initiate nanoparticle formation. This can be done by mixing two microemulsions containing different reactants or by adding the reactant directly to the microemulsion. Nanometer-sized droplets act as nanoreactors, restricting the growth of nanoparticles and allowing equal size distribution. By modifying the size of the microemulsion droplets, which is influenced by the concentration of surfactant and the oil to water ratio, the size of the nanoparticles may be regulated.

**Isolation and Purification:** The formed nanoparticles are extracted from the microemulsion, typically by adding a solvent that breaks up the microemulsion followed by centrifugation or filtration. The nanoparticles are washed to remove any remaining surfactant and byproducts.

**Drying and Post-Treatment:** Purified nanoparticles are usually dried under vacuum or in an oven to remove any remaining solvent. Additional post-treatments such as annealing or calcination may be applied to improve crystallinity and phase purity.

**Figure 6. Microemulsion Technique (Identical Composition) in Production of Metal Oxide Nanoparticle**



## 3. PROMISING AGRICULTURAL SOLUTIONS OF METAL-OXIDE NANOPARTICLES

Nanotechnology introduced nanoparticles used in agricultural products in areas such as antimicrobial agent, pesticide, nutrient source, soil improvement, nano fertilizer, growth enhancer in plants, water purification, drought resistance, food preservation, gene flow, increasing genetic diversity, improving crop quality and controlled release. (Meydan et al., 2022;). Because of their special physicochemical characteristics, metal oxide nanoparticles (MONPs) have garnered a lot of interest in the agricultural community. These qualities can enhance a variety of agricultural operations and support sustainable agriculture. Common metal oxides used in agriculture include zinc oxide (ZnO), titanium dioxide ($TiO_2$), iron oxide ($Fe_2O_3$), and copper oxide (CuO). Zinc oxide and copper oxide nanoparticles (ZnONP and CuONP) with biological activity have attracted great attention due to their effectiveness against plant pathogens. Size, shape, and reactivity all affect ZnONP and CuONP antibacterial properties. The antiviral, antibacterial, and antimycotic actions of ZnONPs and CuONPs against a variety of pathogenic microorganisms boost agricultural output. They also exhibit low phytotoxicity and promise targeted antimicrobial characteristics (Rehman et al., 2024).

ZnONP and CuONPs are promising for the health of agriculture due to their properties such as anticancer against citrus canker caused by *Xanthomonas citri subsp.* (Rao et al., 2024), termiticidal against *Odontotermes formosanus* termite (Nasser et al., 2024), antifungal against Fusarium *Oxysporum fungus*, which causes wilt in vegetables (Jomeyazdian et al., 2024), pesticide against *Oligonychus coffeae*, that results in red spider illness, fungicidal against pestalotiopsis theae fungus that causes gray blight (Jayaseelan et al., 2024).

However, there are also noteworthy studies on ZnONP and CuONPs on pest control. This shows that nanoparticles can be an alternative to ordinary chemicals for reasons such as the insecticidal activity (Aisvarya et al., 2024) against *Sitophilus oryzae (L.)*, which attacks the seeds of crops such as wheat, rice and corn, (Agredo- Gomez et al., 2024) against the phytophage *Puto barberi ("mealybug")*, which causes tree weakening, insecticidal activity against *Polyphagotarsonemus latus* and acaricidal action of Tetranychus urticae Koch, a two-spotted spider mite (Al-Azzazy et al., 2024) against the mite predators *Neoseiulus cucumeris* and *Euseius scutalis*, damage to stored grains and grain products. Insecticidal activity (Solorzano et al., 2024) against *Tribolium castaneum*, an important agricultural pest that causes disease, larvicidal activity (Narayanan et al., 2024) against *Anopheles stephensi* and *Aedes aegypti*, which are in charge of spreading illnesses including chikungunya, dengue fever, malaria, and the Zika virus (Anopheles stephensi).

Micronutrients, which are vital nutrients for plant growth, are currently in short supply for soil and crops. This deficiency both endangers food security and causes malnutrition worldwide. Research shows that metal and metal oxide nanoparticles (NPs) have great potential in solving this problem. However, researchers report that these nanoparticles can provide resistance to drought, diseases, and pests even in the absence of fertilizers. Plants get their nutrients from the soil and, if necessary, from conventional fertilizers. However, nanofertilizers designed to prevent low efficiency and major environmental impacts are relatively more competent and target-oriented. Because of their microscopic size and unique surface characteristics, these nanoparticles are more easily absorbed by plants and have a longer effective period than chemical fertilizers (Parashar et al., 2024). However, soil contaminated by heavy metals, organic contaminants, fertilizer residues, and other sources can also be cleaned up using metal and metal oxide nanoparticles (Umair et al., 2024). Research continues every day to produce more natural foods. In this sense, investigating the use of bacteria as biopesticides and biofertilizers is one of them. Additionally, natural products' current efficacy is increased by the usage of nanoparticles (Benedetti et al., 2024).

Due to the increasing population density and excessive food demand, researchers are making various initiatives on post-harvest food management. It has become possible to extend the shelf life of products by improving the properties of metaloxide nanoparticle-added packages such as mechanical strength, permeability and antibacterial activity (López-Alcántara et al., 2024).

## 4. CONCLUSION

Nanotechnology and metal oxide nanoparticles include future technologies to increase crop production, improve soil quality and reduce environmental impacts in agriculture. It enables the development of nanosensors, nanofertilizers, nanopesticides to improve nutrient uptake, pest management in soil and plants, and monitoring of plant development and health. It is clear that the use of nanoparticles in future agricultural applications will gradually increase. Research shows that nanotechnological developments are likely to change humanity's traditional perspective in every field.

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# KÖPRÜLÜ N-HETEROSİKLİK KARBEN LİGANTLI PALLADYUM KOMPLEKSLERİ VE ÖZELLİKLERİ

**Serpil DEMİR DÜŞÜNCELİ[1]**

## 1. GİRİŞ

### 1.1.Köprülü N-Heterosiklik Karben

N-Heterosiklik karbenler (NHC), dört ile sekiz halka atomuna sahip, en az bir azot atomu içeren heterosiklik karben türleridir. NHC'ler azot atomu üzerindeki sübstitüyentlerin değiştirilmesi ile sterik, elektronik ve kimyasal açıdan en uygun yapının hazırlanmasına imkân verir. Aynı zamanda NHC'ler, güçlü σ-donör ve zayıf π-akseptör özellikleri sayesinde koordine olduğu metal ile güçlü bir etkileşime girerek metal merkezinden kolaylıkla dissossiye olmazlar. Tüm bu özellikleri sayesinde benzerleri olan fosfin ligandlarına alternatif olarak yaygın bir şekilde kullanıldıkları gibi, fosfin ligandlarına kıyasla birtakım avantajlara da sahiptirler. NHC'lerin halka büyüklüğü açısından dört, beş, altı, yedi ve sekiz üyeli pek çok türü olmasına rağmen en yaygın kullanılan NHC'ler beş üyeli olanlardır. NHC'lerin keşfinden bu güne kadar farklı halka büyüklüğüne sahip çok sayıda NHC ligandı sentezlenmiştir. N-Heterosiklik karbenlerin çok sayıda türü olmasının yanı sıra, poly-NHC'ler birden fazla NHC birimi içeren çok dişli ligandlar olarak bilinirler ve bu tür ligandlar farklı geometrilere sahip çeşitli organometalik bileşiklerin sentezine imkân sağladığı için son yıllarda oldukça dikkat çekmektedir [1]. Köprülü NHC lerin bazı avantajları

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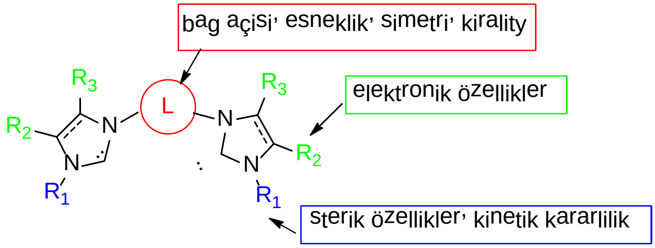
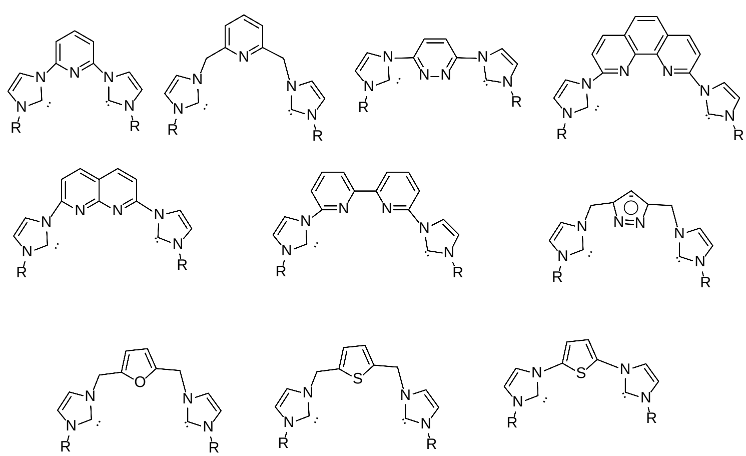
vardır. Bunlar arasında kelat etki ile birlikte artan entropik kararlılık, sterik engel, köprü ya da azota bağlı sübstitüyentlerin modifikasyonuyla iki NHC biriminin bağ açısı gibi parametreler verilebilir. Bis NHC lerin elektronik ve sterik özelliklerinin belirlenmesinde köprü olarak kullanılan molekül, azot atomuna bağlı sübstitüyentlerin özellikleri ve NHC iskeletinin doymuş ya da doymamış olması gibi özellikler rol alır. Bu etkiler genel bir yapı üzerinde aşağıda verilmiştir [2].



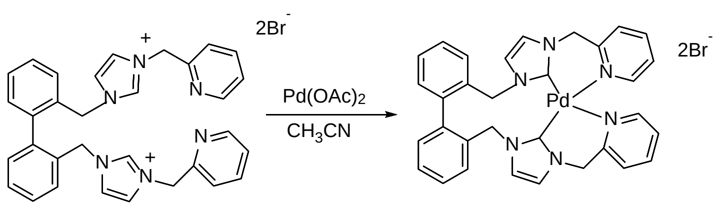

NHC ligantının köprülü bileşikleri arasında heteroaren içeren yapılar da pekçok araştırmacı tarafından çalışılmıştır. Bunlar arasında pridin ve lutidin köprülü olanlar [3, 4] , pridazin köprülü olanlar [5-7], naftiridin köprülü olanlar [8, 9], bipridin ya da fenentrolin köprülü olanlar [10-13], pirazol köprülü olanlar [14-19] ve tiyofen ve furan köprülü olanlar [20] olmak üzere pekçok köprülü bileşik farklı araştırma grupları tarafından sentezlenmiştir.

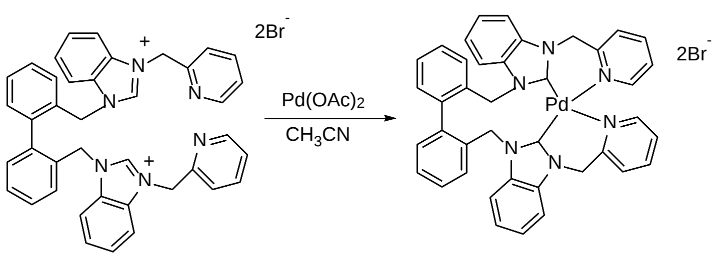


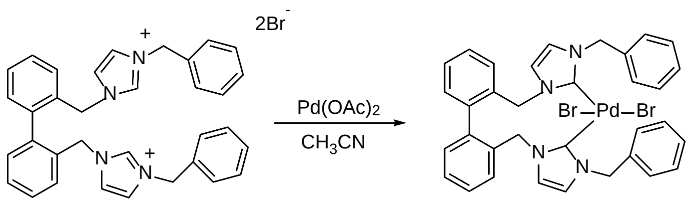
Poly-NHC'ler kelatlayıcı özellikleri sayesinde kompleksin kararlılığını arttırmanın yanı sıra, kompleksin kirallik ve sterik engel gibi önemli yapısal özelliklere sahip olmasında da etkin rol oynamaktadır. Diğer yandan, poly-NHC'ler köprü oluşturma özellikleri sayesinde çok merkezli homo- veya hetero-metalik komplekslerin oluşumuna da imkân vermektedir. Bu özelliklerinden dolayı poly-NHC'ler son zamanlarda araştırmacıların ilgisini yoğun bir şekilde çekmektedir ve özellikle 2000'li yılların başlarından beri poly-NHC'ler üzerinde yapılan çalışmaların sayısı büyük bir hızla artmaktadır.

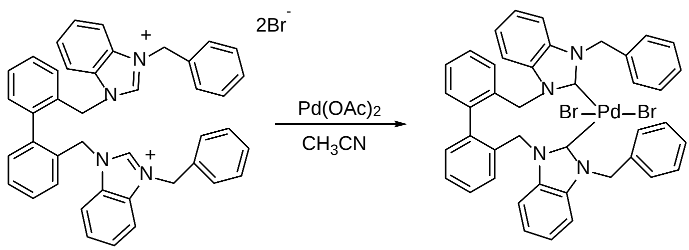
### 1.2.Köprülü NHC Ligantlı Palladyum Kompleksleri ve Uygulamaları

Sabiah ve grubu sübstitüyent olarak pikolil ve benzil grubu içeren 2,2'-bifenil köprülü imidazolin-2-iliden ve benzimidazol-2-iliden ligantlı palladyum komplekslerini sentezleyerek Suzuki eşleşme tepkimesindeki katalizör etkisini belirtmişlerdir [21].

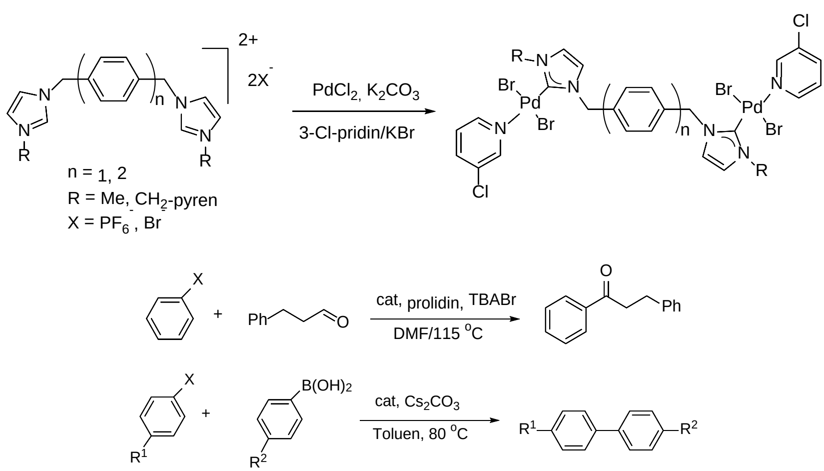


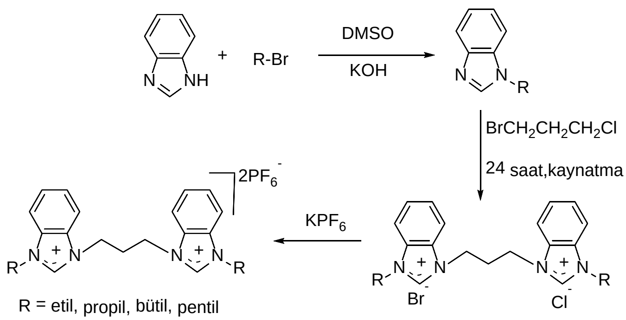


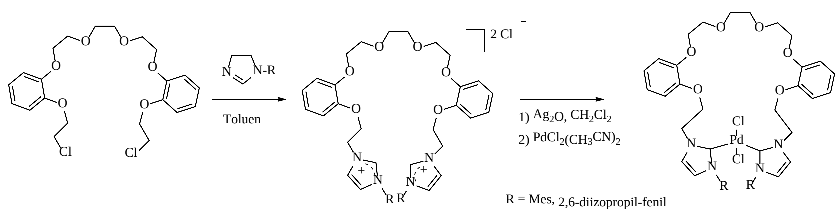

2014 yılında Peris ve grubu imidazol iskeleti içeren bifenil köprülü NHC öncülünün sentezini yaparak Palladyum PEPPSI tipi komplekslerini sentezlemişlerdir. Sentezlenen bu bimetalik Pd komplekslerinin hidrosinamaldehitlerle aril halojenürlerin açilasyon tepkimesinde ve aril halojenür ve aril boronik asitlerle Suzuki eşleşme tepkimesindeki katalitik özelliklerini araştırmışlardır [22].



İki benz/imidazolyum grubunun birbirine köprü bağlanmasında köprü olarak kullanılan örneğin alkilen [23], ksililen [24] veya piridil [25] ile yapılan çalışmalar da mevcuttur. Razali ve grubu da bu tür yapılara benzer olarak alifatik zincir içeren propilen köprülü bis benzimidazolyum tuzlarının sentezini belirtmişlerdir [26].

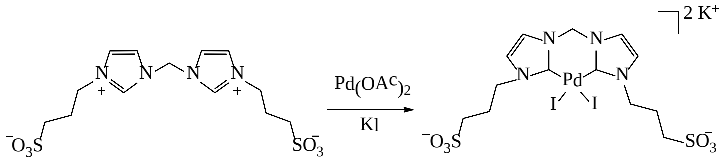


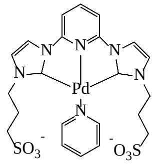

Taç eter köprülü bis-NHC ligandı, iki eşdeğer N-sübstitüye imidazol halkasının bir eşdeğer dihalojenür ile etkileşmesinden hazırlanıp bu bileşiğin Pd kompleksleri Ag-NHC kompleksinden transmetallasyon yoluyla sentezlendiği belirtilmiştir. XRD analizinden, Pd'deki koordinasyon geometrisinin neredeyse kare düzlemsel olduğu bulunmuştur [27-29].



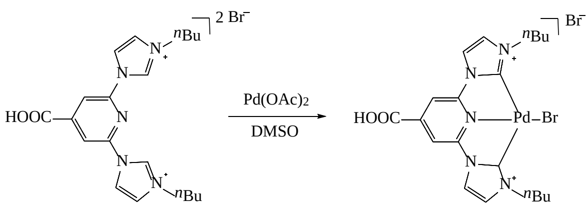

2011 Yılında Peris ve arkadaşları bir dizi suda çözünür Pd-(bis-NHC) kompleksi sentezlemiştir. Zwitteriyonik yapıdaki bileşiği bis(imidazolil)metanın 1,3-propansülton ile tepkimesi sonucu hazırlanmıştır [30]. Bu ligand daha sonra palladyum kompleksi elde etmek amacıyla $Pd(OAc)_2$ ile etkileştirilmiş ve

%29 verimle palladyum kompleksi elde edilmiştir. Aynı çalışmada bildirilen diğer iki Pd-(bis-NHC) kompleksi, CNC kıskaç tipi komplekslerdir. Burada ligand, $Pd(OAc)_2$ ve KI ile etkileştirilerek palladyum kompleksi hazırlanmıştır [30].

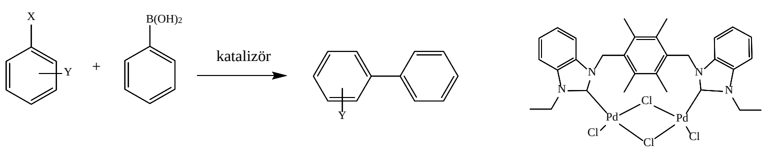


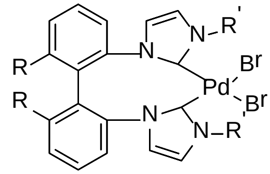
CNC kıskaç tipi bir Pd-(bis-NHC) kompleksinin sentezi de Churruca ve arkadaşları tarafından ligantın DMSO içerisinde $Pd(OAc)_2$ ile etkileştirilmesi sonucu gerçekleştirilmiştir [31].



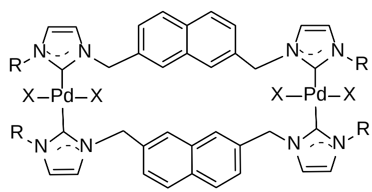

Liu ve arkadaşları, Ag-NHC kompleksinden yola çıkarak transmetalasyon yöntemi ile dinükleer palladyum kompleksini sentezleyerek Suzuki tepkimesindeki katalizör özelliklerini araştırmışlardır [32].



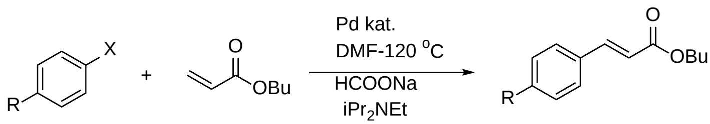

Luo ve grubu 2,2'-bifenil köprülü bis-imidazolin-2-iliden ligantlı cis-kelat palladyum(II) kompleksinin sentezini belirterek Suzuki Miyaura tepkimesindeki katalizör özelliğini araştırmışlardır [33].



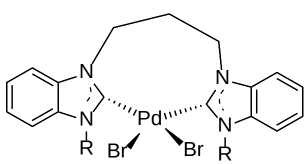
Saito ve grubu metal-bis NHC kompleksleri içerisinde 2011 yılında N-sübstitüye imidazol grubunun 2,7-dimetilnaftalen ile köprü oluşturduğu gümüş ve palladyum komplekslerinin sentezini belirtmişlerdir. Elde ettikleri gümüş bileşiklerini palladyum kompleksinin sentezinde kullanmışlardır. Gümüş transfer yöntemi ile hazırladıkları palladyum komplekslerinin bütil akrilat ile aril bromürlerin Heck tepkimesindeki katalitik özelliklerini belirtmişlerdir [34].



R = 2,6-*i*-$Pr_2C_6H_3$, Cy, *n*-Bu
X = Cl, Br, I

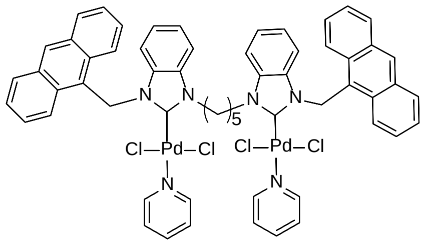



1,3-propandiil köprülü bis(NHC) palladyum(II) kompekslerinin sentezi de 2021 yılında verilmiş olup bu komplekslerin aril bromürlerle stiren ve akrilat türevlerinin Heck eşleşme tepkimesindeki katalitik aktiviteleri belirtilmiştir [35].

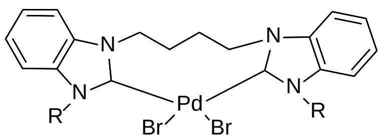


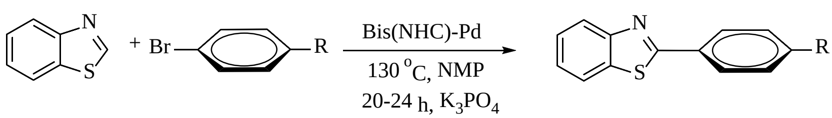
R = $CH(CH_3)_2$, $CH_2Ph$, p-Ph-$OCH_3$

Karataş, 2020 yılında benzimidazol çekirdeği içeren antrasen sübstitüye bimetalik köprülü palladyum PEPPSI tipi kompleks sentezini yapıp bu kompleksin Suzuki eşleşme tepkimesindeki katalitik özelliklerini belirtmiştir [36].

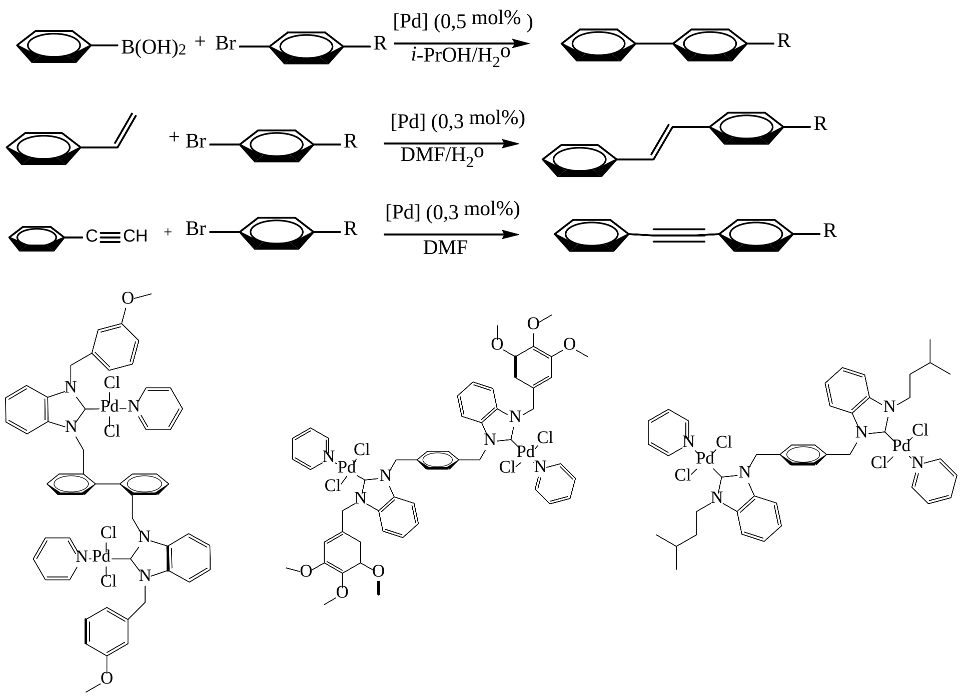



2011 yılında Özdemir ve araştırma grubu, poly-NHC öncülleri olarak bütilen köprülü bis-benzimidazolyum tuzlarından yola çıkarak bir dizi Pd-(bis-NHC) kompleksleri sentezlemiş ve yapılarını karakterize etmiştir. Sentezlenen Pd-(bis-NHC) kompleksleri benzotiyazol ve aril bromürler arasındaki direkt arilasyon tepkimelerinde katalizör olarak kullanılmıştır [37].

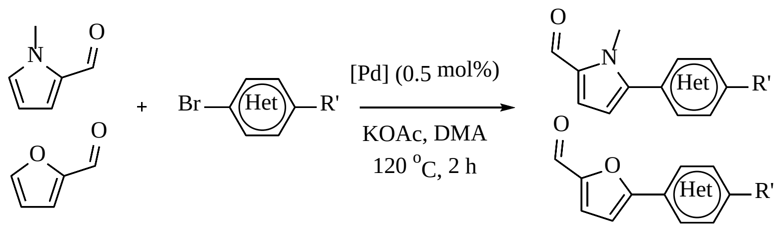


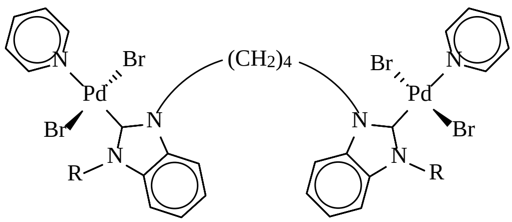




2019 yılında Özdemir ve arkadaşları tarafından köprülü bis-benzimidazolyum tuzlarından yola çıkarak bir dizi PEPPSI tipi palladyum kompleksi sentezlenmiş ve yapıları karakterize edilmiştir. Sentezlenen PEPPSI tipi palladyum kompleksi Suzuki-Miyaura, Mizoroki-Heck ve Sonogashira-Hagihara çapraz-eşleşme tepkimelerinde kullanılmıştır [38, 39].

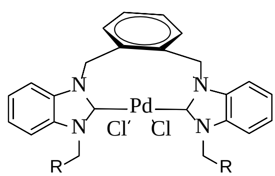


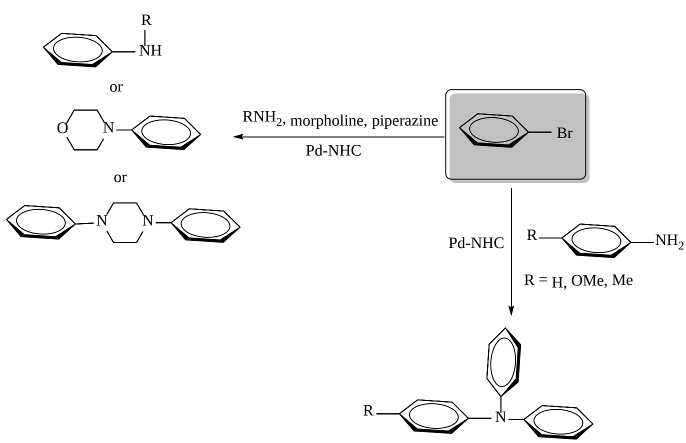

2020 yılında Özdemir ve arkadaşları tarafından bütilen köprülü bis-benzimidazolyum tuzlarından yola çıkarak bir dizi PEPPSI tipi palladyum kompleksi sentezlenmiş ve yapıları karakterize edilmiştir. Sentezlenen PEPPSI tipi palladyum kompleksi 2-sübstitüye pirol ve furan bileşiklerinin aril bromürlerle direkt C5 arilasyonunda kullanılmıştır [40].



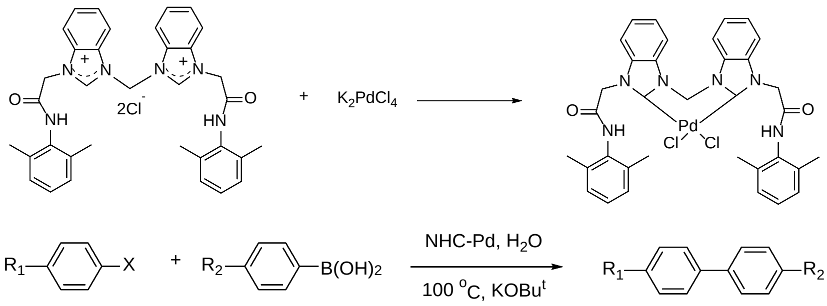




2011 yılında Özdemir ve arkadaşları, poly-NHC öncülleri olarak o-ksilil köprülü bis-imidazolinyum tuzlarından yola çıkarak bir dizi Pd-(bis-NHC) kompleksleri sentezlemiş ve yapılarını karakterize etmiştir. Sentezlenen Pd-(bis-NHC) kompleksleri aril aminler ve brombenzen arasındaki Buchwald-Hartwig aminasyonunda katalizör olarak kullanılmıştır [41].



2024 yılında Ding ve grubu amit fonksiyonalize olmuş bidentat NHC komplekslerinin palladyum komplekslerini sentezleyerek Suzuki Miyaura eşleşme tepkimesindeki katalizör özelliklerini araştırmışlardır [42].



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