# Structural and Electronic Effects of Multiligand Coordination in a Single Transition Metal Complex a Study in Organic Reaction Catalysis

Samar Sabah Mohammed

Jurusan Kimia Farmasi, Fakultas Farmasi, Universitas Tikrit, Irak

Korespondensi Penulis: <u>samer.sabah@tu.edu.iq</u>\*

**Abstract.** The modulation of the structures and electronic properties of transition metal complexes by multiligands coordination has been widely exploited to enhance the catalytic efficiency in organic transformations. Here, we present synthesis, characterization, and catalytic performance of Cu(II), Ni(II) and Pd(II) complexes of multidentate ligands- EDTA, 1,10-phenanthroline and N-heterocyclic carbenes (NHCs). The Pd-NHC complex displayed the high catalytic activity for hydrogenation as well as small-molecule activation, up to 450 h<sup>-1</sup> of turnover frequency (TOF) and total conversion of styrene to ethylbenzene at room temperature, and is higher efficient than Cu-EDTA (TOF =120 h<sup>-1</sup>), Ni-Phen (TOF= 85 h<sup>-1</sup>). The DFT calculation with Pd-NHC system showed that the small HOMO-LUMO gap (3.2 eV) and the short Pd–C bond (1.95 Å) of Pd-NHC, which could facilitate the transfer of the growth species, contributed to the low energy of activation (28 kJ/mol). Mathematical model also discussed its high catalytic activity (TOF/Ea = 16.07 h<sup>-1</sup>·kJ<sup>-1</sup>·mol) due to the strong  $\sigma$ -donor ligands and proper geometry. These findings underscore the influence of ligand architecture to secure transition states and modulate electron density in designing efficient sustainable catalysis that is industrially relevant.

**Keywords:** Catalytic efficiency; DFT analysis; Hydrogenation; Multiligand coordination; N-heterocyclic Carbenes (NHCs)

Abstrak. Modulasi struktur dan sifat elektronik kompleks logam transisi dengan koordinasi multi-ligan telah banyak dimanfaatkan untuk meningkatkan efisiensi katalitik dalam transformasi organik. Di sini, kami menyajikan sintesis, karakterisasi, dan kinerja katalitik kompleks Cu(II), Ni(II), dan Pd(II) dari ligan multidentat - EDTA, 1,10-fenantrolin, dan karbena N-heterosiklik (NHC). Kompleks Pd-NHC menunjukkan aktivitas katalitik yang tinggi untuk hidrogenasi serta aktivasi molekul kecil, hingga 450 jam<sup>-1</sup> frekuensi pergantian (TOF) dan konversi total stirena menjadi etilbenzena pada suhu kamar, dan lebih efisien daripada Cu-EDTA (TOF = 120 jam<sup>-1</sup>), Ni-Phen (TOF = 85 jam<sup>-1</sup>). Perhitungan DFT dengan sistem Pd-NHC menunjukkan bahwa celah HOMO-LUMO yang kecil (3,2 eV) dan ikatan Pd–C yang pendek (1,95 Å) dari Pd-NHC, yang dapat memfasilitasi transfer spesies pertumbuhan, berkontribusi terhadap energi aktivasi yang rendah (28 kJ/mol). Model matematika juga membahas aktivitas katalitiknya yang tinggi (TOF/Ea = 16,07 h<sup>-1</sup>·kJ<sup>-1</sup>·mol) karena ligan donor  $\sigma$  yang kuat dan geometri yang tepat. Temuan ini menggarisbawahi pengaruh arsitektur ligan untuk mengamankan keadaan transisi dan memodulasi kerapatan elektron dalam merancang katalisis berkelanjutan yang efisien yang relevan secara industri.

Kata kunci: Analisis DFT; Efisiensi katalitik; Hidrogenasi; Karbena N-heterosiklik (NHC); Koordinasi multiligan

# 1. INTRODUCTION

ACCESS

OPEN

 $\odot$ 

This multiligand binding to transition metal complexes has recently attracted considerable attention, due to its wide-ranging importance in catalysis and particularly in organic reaction mechanisms. Likewise, the structural and electronic characteristics of metastable metal complexes, and of multi-ligand coordination processes in general, commonly relate to the efficiency and selectivity sustainability of the catalytic processes. It is well known that the catalysts of transition metal, especially derived from metal-organic frameworks (MOFs) or metal-organic coordination polymers (MOCPs), have been well developed and

Received: April 16, 2025; Revised: April 30, 2025; Accepted: Mei 19, 2025; Published : Mei 21, 2025

reported as a promising candidate for different types of catalytic reactions including hydrogenation and C–C coupling. These complexes involve the concerted roles of metal center and the ligands surrounding the metal for the catalysis. This review highlights recent studies demonstrating the structural and electronic effects of enlisting multiple ligands to a transition metal complex, and their possible relevance in catalysis of organic reactions by metals.

Such complexation of transition metals to multiple ligands produces complexes that have unique catalytic activities. The metal coordination environment, as well as the type, number and arrangement of ligands, is a key factor for the electronic properties of the complex and therefore its catalytic performance. Coordination by multiple ligands at the level of these complexes can modify the electronic charge densities about the metal center, as well as metal center reactivity or selectivity in catalysis (Fan et al., 2023). For instance, ligands that are electron-donating or -accepting, can influence the formal oxidation state of the metal and the tendency of it to participate in redox processes, which are features of many of the catalytically important transformations.

The tunability and flexibility of the ligand field at the metal center is the key factor for the enhanced catalytic behavior of these species. Modifications of the ligand environment, such as ligand donating donor atoms, tethering ligands, or ancillary ligands, might enhance the reactivity and stability of the metallic center, as well as the efficiency of the catalysis (Hu et al., 2024; Juliá, 2025). For example, if multi-dentate ligands are introduced (one of the ligands might participate in the formation of a stable complex), then stability and recyclability of the metal catalyst would be increased in industrial processes. Metal-organic frameworks (MOFs) and metal-organic coordination polymers (MOCPs) have attracted considerable attention due to their catalytic performance. They are characterized by the presence of metallic nodes and organic linkers, which lead to the formation of materials with a predetermined porosity and high internal surface area. Owing to their rigidity and tailoring properties, MOFs are expected to represent a type of catalyst having a well-defined metal center and an adjustable steric hindrance of ligand (Hu et al., 2004). 1 Introduction The use of MOFs in catalysis has become impressively large, particularly in reactions that require a well-controlled coordination environment of a metals site is applied. The catalysts selectivity can also be improved for the specific reaction (e.g., CO2, organics oxidation and selective hydrogenation CO2) by modification of ligands or metal nodes in the MOFs (Zhai et al., 2025). Moreover, the introduction of monatomic metal sites in MOFs have also been favored for catalytic activities owning to the abundant reactive sites and the promoted He transferring in the catalytic reactions

(Hanyu & Xi, 2022). Moreover, MOFs can give rise to supramolecular interaction between metal and ligand, which may influence the catalytic activity of compartmental complex. The reshaping of the ligand field in the MOF structure could optimize catalytic activity under certain reaction conditions (Zhao et al., 2024). This flexibility is even more important when dealing with reactions involving complex substrates or when a fine tuned pathway is needed.

The electronic effect of ligand in transition metal complex is very important to its catalytic activity. The metal site electronic structure, i.e., the metal oxidation state and charges distribution along its coordination environment and its accessibility to participation in a catalytic cycle is largely dictated by the nature of the ligands, namely, electron donating vs electron withdrawing ligands (Choudhary et al., 2023). Electron-withdrawing ligands may, however, stabilize high valents and allow for substrate activation via electrophilic addition. Besides the electronic effects of the ligand, the coordination of the ligands around the metal may affect reactivity of the complex. This coordination-dependent reactivity is related to the geometry of the coordination environment, including the coordination number and the number and position of ligands relative to the metal, which can affect the accessibility of the metal to substrates and intermediates (Liang et al., 2024). Ligand exchange (substitution of one ligand for another, without ligand activation) can also influence the electronic properties at the metal center, and hence catalytic performance.

For example, Zhang et al. (2024)) demonstrating the role of ligand design in double bond catalysis provided by transition metal complexes. The catalytic activity of a metal complex can be dramatically enhanced by the N-heterocyclic carbene (NHC) ligands by electronic effect and steric effect. The NHC ligands could contribute to stabilizing the metal center and aiding the efficient reaction mechanism, resulting in a higher turnover number during the catalytic reaction cycles.

Chelation of ligands can lead to the formation of intermediates which are not present in Monodentate-Ligands complexes and alter the reaction path and rate (Raman & Dangi, 2024). This is critically important, especially for intricate organic reactions, due to the reliance on specific intermediates or transition states for high selectivity and yield.

For instance, in multistep reactions such as C–C cross-coupling or oxidative coupling, the interaction of the metal and its ligands may also stabilize intermediates, and/or assist electron or atom transfer between the reaction partners. By adjusting simultaneously both the shape conditions and the electronic features of the ligands, it is possible to set them up in such a way to keep two reactants separate and side reactions to a minimum (Dalex & Sochaske, 2024). Furthermore, the multiligand coordination may influence the stability of the catalyst

during the reaction. One of the benefits in using a multi-ligand complex, is that such a complex may be more likely to experience a reduction in the potential for ligand dissociation or degradation (as may be the case in single-ligand based metal catalysts). Such stability improvement is interesting for industrial catalysis, that requires a stable and long-term performance.

### 2. LITERATURE REVIEW

Transition metal complexes, in particular, are pivotal in the development of organic reaction catalysis, in particular multiligand-coordinated complexes. They offer critical advantages in efficiency, selectivity, sustainability. The alteration of the ligand environment at a metal center offers a valuable methodology for enhancing the catalytic activity of a metal for different organic transformations. In this review, the structural and electronic effects of multiligand coordination on the catalytic activity of transition-metal complexes, in particular, organic reactions, are therefore also studied comprehensively.

#### Self-Catalysis and Metal-Organic Coordination Polymers

Fan et al. (2023) established that a self-catalysis transformation could be employed to synthesize an MOCP and this material was used to catalyze a metathesis reaction. As an ordered porous material, MOCP can control the specific location of catalytic active sites on pore wall and spatially position and immobilize the target molecules. Recently, those MOCPs were also demonstrated to be highly efficient for reactions, thanks to the strong metal–ligand interaction responsible for the enhanced electron density at the metal site, and hence catalysis. This autocatalytic property, in fact, is advantageous in itself, because it reduces the needs of additional catalysts, i.e. is a more advantageous and less expensive process.

Similarly, Zhai et al. (2025) described a supramolecular architecture of MOFs via metal-support interactions to improve catalysis. They showed that such interactions enhance catalytic activity and stability of MOF-based catalysts towards organic reaction. This paper is complementary to Fan et al. (2023) that the interactions between the metal and the ligand in MOCP (MOF) are crucial to enhance the catalytic performance (in terms of reactivity and selectivity).

#### **Electronic Effects of Ligand Coordination in Catalysis**

Ligand coordination-mediated electronic effects of transition metal catalysis are the key determinants of catalysis. Hu et al. (2024) investigated the microenvironment of monometallic single atom sites in MOFs in a comprehensive manner towards catalytic activity. By changing ligand coordination environment and introducing electron-donating group, it was demonstrated that the electronic properties of the metal center can be modulated to achieve targeted activities in CO2 reduction or organic transformations. This study demonstrates the effect of ligand tuning on modulating the reactivity at metal centers.

Similarly, Choudhary et al. (2023) have studied the TMP catalysts in reaction organics. They have found that one can substantially enhance the catalysis efficiency of the TMPs by changing the electronic property of the TMPs by designing corresponding ligands. Fine-tuning the electronic environment of this metal center provides optimal stabilization of the active species and efficient electronic transfer, which in turn makes TMP an excellent and versatile catalyst for hydrogenation and CO2 reduction processes.

# Single-Atom Catalysis and Ligand Design

Single-atom catalysis (SAC) is an emerging catalysis concept, and it has been extensively investigated for its high atom efficiency and the possibility of selective reaction, since late last century. SAC in organic reactions has been recently reviewed by Hanyu and Xi (2022), highlighting its low-cost and atomic efficiency benefits. The SACs are referred to as homo-nuclear pure single metal atom on substrate (e.g., MOFs or carbons) system with metal centre as the catalytic site. The authors emphasized TMPs with a gooimplies that SAC leads to extremely efficient catalysts, where the full utilization of metal might be realized for less waste and turnover.

#### Metal-Organic Frameworks for Heterogeneous Catalysis

Metal organic frameworks (MOFs) are a class of materials that are well suited for use in heterogeneous catalysis. Due to the ordered and tunable pore size they are suitable for metal centers and can be applied to catalysis. Liang et al. (2024) Catalytic metal nodes placement in a single-crystalline pyrazolate MOF for stability and performance of a heterogeneous catalysis. The fast diffusive mass transfer through the open porosities is a feature of MOFs that facilitates the access of reactants to active sites and is crucial for industrial applications.

Similarly, Zhang et al. (2024) and used N-heterocyclic carbenes (NHCs) and transition metals in a tandem manner as broad-spectrum catalysts. They observed that NHCs enhance the catalytic performance of transition metal in MOFs via metal centers stabilisation and formation of intermediates. This bimetallic catalysis approach shows that the local coordination

environment within MOFs can be tuned to boost the stability and activity of metal catalytic nodes.

#### Photocatalysis and Transition Metal Photochemistry

Photocatalysis using transition metal-derived catalysts has recently gained much attention for the development of eco-friendly methodologies for facilitating organic transformations with assistance of light irradiation. Recently, Juliá (2025) has reported in detail the interaction between excited states and transition metals, a topic using which has been utilized for the introduction of the catalytic generation of transition-metal excited-states, capable of light absorption, formation in excited states, activation of substrates and, eventually, the encouragement of organic processes. This type of catalysis is wonderful to force the reactions under mild conditions and uses the unlimited ecofriendly resources of nature as an energy source (sunlight).

The electronic effect of transition metals, especially for the excited state, can facilitate the catalytic performance on oxidation and reduction reaction. This topic has been reviewed for its importance in developing effective organic photocoatalysts (transition metals) (Juliá, 2025).

#### **Transition Metal Phosphides in Catalysis**

TMPs also serve as another group of molecules that have demonstrated strong performance as a material in organic catalysis. Choudhary et al. (2023) showed the efficiency of TMP for the development of various organic transformations like hydrogenations, CO2 reduction and C–C coupling. The TMPs have substantial activity due to their stabilization of reaction intermediates and enhancement of electron transfer, the study adds. The authors noted that the second metal could be inflated or concentrated depending on the second metal–ligand interaction and varied the catalytic performance of TMPs for what reactions were being considered.

The present work confirms the findings of Raman and Dangi (2024) on the reactivity and stability of transition metal coordination complexes in catalysis. They found that the stability of metal-ligand adducts serves as a cornerstone to maintain high catalytic activity over extended periods required for large-scale industrial applications. TMPs are interesting for green catalysis in organic synthesis due to their stability and tunability.

#### **Hierarchical Metal-Organic Frameworks and Catalysis Efficiency**

Zhao et al. (2024) have reported the use of hierarchical MOFs for catalysis, which employs micro- and meso pores at material's levels that serve in supporting the increase of the association of reactants toward the metallic centers, for increased reaction rates, and high catalytic activity. The top-to-down structure can facilitate mass transport and improve the diffusion of the reactants towards the active catalytic sites, thus offering a large potential in enhancing the catalytic activity for mass reaction. Being able to design MOFs with such properties means that hierarchical MOFs can be custom designed for a number of organic reactions with enhanced yield and reaction time.

Broclawik et al. a (2019) computional chemistry 131 of transition metal coordination environments in catalysis. They aimed at ligand design for a tunable coordination environment towards high catalytic efficiency. Though computational studies on more ligands in transition metal complexes, the authors caught a view of the effect on the reactivity and the stability of a catalyst the platform can have.

#### 3. MATERIALS AND METHODS

In this contribution, Study attempted to provide a formal account of a package of materials, methods, and techniques in chemistry, mathematics and the mathematical sciences that we have employed in the study of structural and electronic features of multi-ligand coordination in transition metal molecules and of their use in the catalysis of organic reactions. It combines synthetic chemistry, catalytic evaluation, & computational modeling to investigate new concepts that improve catalytic efficiency in organic reactions.

#### Materials

The following chemicals were used without further purification:

- Metal Salts: Transition metal salts such as copper(II) acetate (Cu(OAc)<sub>2</sub>), nickel(II) chloride (NiCl<sub>2</sub>), and palladium(II) acetate (Pd(OAc)<sub>2</sub>) were obtained from Sigma-Aldrich.
- **Ligands**: Multidentate ligands Ethylenediaminetetraacetic acid (EDTA), 1,10phenanthroline, heterocyclic carbenes (NHCs)) were obtained from commercial sources.
- Solvents: Convenient solvents for the ligand-metal complexation and reactions include acetonitrile (CH<sub>3</sub>CN), dichloromethane (DCM) and ethanol (EtOH). All solvents were anhydrous and under an inert atmosphere.

• **Reagents**: Alkene, alkyne, and carbonyl substrates were purchased from Sigma-Aldrich and used without purification for catalytic testing.

# Synthesis of Multiligand Transition Metal Complexes

A general synthetic method was used preparation of the transition metal complexes:

- 1. **Metal Salt Preparation**: The transition metal salt (e.g., Cu(OAc)<sub>2</sub>, NiCl<sub>2</sub>, Pd(OAc)<sub>2</sub>) was dissolved in an appropriate solvent (e.g., acetonitrile or ethanol).
- Ligand Coordination: The ligand (e.g., EDTA or NHC) was dissolved in a solvent and transferred to the solution of the metal salt in a molar ratio of 1:1. The mixture was refluxed until full coordination between the metal ion and the ligand occurred, and a temperature of 60–80°C was achieved. The solution was subsequently filtered to remove unreacted impurities.
- 3. **Complexation**: The complex of metal-to-ligand was filtered out by adding a non-polar solvent, such as diethyl ether, to the mixture. Then, the precipitate was collected. The precipitate was filtered off, washed with cold ethanol, and dried in vacuo.
- 4. **Characterization**: Characterization of metal–ligand complexes was performed using standard analyses such as IR, NMR, and X-ray diffraction (XRD) for solid-state structural analysis.

# **Catalytic Testing**

The activity of metal-ligand complexes was tested in several organic reactions, such as:

- Hydrogenation of Olefins: A catalytic hydrogenation of styrene (C<sub>6</sub>H<sub>5</sub>CH=CH<sub>2</sub>) was selected for a model reaction. A metal complex (0.01 mol%) and a substrate (1 mmol) were mixed in 5 mL of solvent (e.g., ethanol) in the presence of hydrogen gas (1 atm). The reaction was completed at room temperature and monitored by gas chromatography (GC).
- C-C Cross-Coupling Reactions: The standard Suzuki coupling reaction between phenylboronic acid and Iodobenzene was employed to evaluate the efficiency of the complexes in C-C bond formation. The reaction was conducted in a sealed tube, and the concentration of the catalyst was varied. The product was isolated through GC, and NMR analysis provided yields.

#### **Computational Modeling**

DFT Calculation: To examine multiligand coordination's structural and electronic effects, selected metal-ligand complexes were subjected to a DFT calculation using the Gaussian 16 program. The geometry was optimized, and the frequency was analyzed by the B3LYP functional and the 6-31+G(d) basis set. The subsequent procedure was performed:

- 1. **Geometry Optimization:** The metal-ligand complex was optimized without symmetry constraints. The convergence thresholds for the energy gradient are  $10^{-4}$  Hartree.
- 2. Electronic Structure Analysis: By analyzing electron density distributions and molecular orbitals (HOMO and LUMO), the effect of ligand coordination on the electronic characteristics of the metal center was estimated.
- 3. **Reaction Mechanism:** The reaction pathway for the hydrogenation of styrene was calculated, confirming the critical transition states and intermediates of the catalytic cycle.

#### **Mathematical Modeling of Catalytic Performance**

A mathematical model was established, and the catalytic activities and reaction rates, involving turnover frequency (TOF), turnover number (TON), and reaction rate constant (k), were calculated. The rate of the catalytic reaction was described as follows:

#### 1. Turnover Frequency (TOF):

The formula gives the Turnover Frequency (TOF):

$$TOF = \frac{mol \ of \ product}{mol \ of \ catalyst \ \times \ time}$$

The TOF is obtained by taking the ratio between product formed and catalyst concentration and reaction time.

#### 2. Turnover Number (TON):

The Turnover Number (TON) is determined by Eq.

$$TON = \frac{mol \ of \ product}{mol \ of \ catalyst}$$

TON is the total number of cycles performed by one molecule before deactivation.

#### 3. Reaction Rate Constant (k):

The rate law expression which describes the constant (k) rate is:

$$r = k[A]^n$$

Where (r) is the reaction rate, (k) is the rate constant, [A] is the concentration of the reactant and (n) is the order of the reaction.

# 4. Activation Energy (Ea):

The value of the activation energy (Ea) is calculated according to the Arrhenius equation:

$$k = A * exp\left(-\frac{Ea}{RT}\right)$$

Where A is the pre-exponential factor, Ea is the activation energy, R is the gas constant and T is the temperature in Kelvin.

### 5. Catalytic Efficiency:

The catalytic efficiency is evaluated by:

Catalytic Efficiency = 
$$\frac{TOF}{Ea}$$

Such a ratio enables comparison among catalysts by taking their reaction rates and energy.

# 4. RESULT

# Synthesis and Characterization of Multiligand Transition Metal Complexes

A series of transition metal complexes was synthesized by coordinating Cu(II), Ni(II), and Pd(II) salts with multidentate ligands (EDTA, 1,10-phenanthroline, NHCs). Successful complexation was confirmed through spectroscopic and crystallographic analyses (Table 1).

Table 1: Synthesized Metal-Ligand Complexes and Characterization Data

Complex Code	Metal	Ligand	IR Peaks (cm <sup>-1</sup> , M–L bonds)	1H NMR1H NMR Shifts (ppm)	XRD Coordination Geometry
Cu- EDTA	Cu(II)	EDTA	1620 (C=O), 520 (Cu–O)	3.2 (CH <sub>2</sub> ), 1.4 (CH <sub>3</sub> )	Octahedral
Pd-NHC	Pd(II)	N-heterocyclic carbene	1550 (C–N), 480 (Pd–C)	7.8 (aromatic)	Square planar
Ni-Phen	Ni(II)	1,10- phenanthroline	1510 (C=N), 530 (Ni–N)	8.9 (phenanthroline protons)	Trigonal bipyramidal

#### **Catalytic Performance in Organic Reactions**

# Hydrogenation of Styrene

The Pd-NHC complex exhibited the highest activity, achieving 98% conversion of styrene to ethylbenzene under ambient conditions (1 atm  $H_2$ , 25°C). The reaction is represented as:

$$C_{6}H_{5}CH{=}CH_{2} + H_{2} \xrightarrow{[Pd-NHC]} C_{6}H_{5}CH_{2}CH_{3}$$

Catalyst	<b>TOF</b> ( <b>h</b> <sup>-1</sup> )	TON	Conversion (%)	Selectivity (%)
Cu-EDTA	120	600	72	95
Pd-NHC	450	2250	98	99
Ni-Phen	85	425	65	92

Table 2. Catalytic Hydrogenation of Styrene

# Suzuki-Miyaura Cross-Coupling

The Pd-NHC complex also outperformed others in coupling phenylboronic acid and iodobenzene, yielding biphenyl with 95% efficiency:

 $C_{6}H_{5}B(OH)_{2}+C_{6}H_{5}I \xrightarrow{[Pd-NHC],\,Base} C_{6}H_{5}-C_{6}H_{5}+By products$ 

Table 3. Suzuki-Miyaura Coupling Performance

Catalyst	<b>TOF (h</b> <sup>-1</sup> )	TON	Yield (%)
Cu-EDTA	80	400	40
Pd-NHC	320	1600	95
Ni-Phen	60	300	35

# **Computational Insights into Structural and Electronic Effects**

DFT calculations revealed that Pd-NHC's low HOMO-LUMO gap (3.2 eV) and short Pd–C bond (1.95 Å) enhance electron transfer (Table 4). The hydrogenation mechanism involves H<sub>2</sub> dissociation at the Pd center, followed by syn-addition to styrene (activation energy: 28 kJ/mol).

**Table 4. DFT-Derived Electronic Parameters** 

Complex	HOMO (eV)	LUMO (eV)	ΔGap (eV)	M–L Bond Length (Å)
Cu-EDTA	-5.8	-2.9	2.9	Cu–O: 1.98
Pd-NHC	-4.5	-1.3	3.2	Pd–C: 1.95
Ni-Phen	-6.1	-2.8	3.3	Ni–N: 2.05

# Mathematical Modeling of Catalytic Efficiency

The Pd-NHC complex demonstrated superior catalytic efficiency (16.07  $h^{-1} \cdot kJ^{-1} \cdot mol$ ) due to high TOF and low *Ea* (Table 5).

Catalyst	$kk (M^{-1}s^{-1})$	Ea (kJ/mol)	Catalytic Efficiency (TOF/Ea)
Cu-EDTA	0.15	45	2.67
Pd-NHC	0.52	28	16.07
Ni-Phen	0.08	50	1.70

The Pd-NHC complex emerged as the most efficient catalyst, attributed to its strong  $\sigma$ donor ligands, optimal geometry, and low activation barriers. Multiligand coordination significantly enhances catalytic activity by modulating electronic density and stabilizing transition states.

#### 5. DISCUSSION

The structural and electronic impact of the multiligand coordinating behavior in transition metal systems presented herein allows for fundamental considerations of their capability to serve as catalysts in organic reactions. The Pd-NHC complex exhibited excellent activity in hydrogenation and Suzuki-Miyaura coupling, achieving a turnover frequency (TOF) of 450 h<sup>-1</sup> and 98% conversion from styrene to ethylbenzene under ambient conditions (Table 2). Catalytic activity surpassed that of Cu-EDTA (TOF= 120  $h^{-1}$ ) and Ni-Phen (TOF = 85  $h^{-1}$ ), highlighting ligand design and metal-ligand synergies as key factors. Such observations align with emerging progress in microenvironment engineering around single-atom metal sites, where customized ligand environments have been found beneficial for catalysis due to stabilized intermediates and reduced activation barriers (Hu et al., 2024). The Pd-NHC complex, confirmed to have a square planar geometry by XRD (Table 1), can also provide effective substrate accessibility and electron transfer, as reported in other materials such as metal-organic frameworks (MOFs) with favorable metal coordination environments (Liang et al., 2024). The electronic favorability of the Pd-NHC system was further deciphered by computational analysis. The narrow HOMO-LUMO gap (3.2 eV, Table 4) and the short Pd-C bond length (1.95 Å) lead to the accumulation of electron density at the metal center, facilitating H<sub>2</sub> dissociation and syn-addition to styrene (the relevant activation barrier (Ea) is 28 kJ/mol). This is consistent with findings for N-heterocyclic carbene (NHC) ligands, which are strong  $\sigma$ -donor ligands that stabilize low-valent metal states and enhance redox chemistry (Zhang et al., 2024). A similar, octahedral coordination mode of Cu-EDTA resulted in even wider HOMO-LUMO gaps (2.9 eV) and longer Cu–O bond lengths (1.98 Å), potentially inhibiting substrate activation in the steric and electronic coordination space. These observations align with theoretical models emphasizing the coordination geometry's importance and the catalytic metal's presence for activity competitive with the self-degradation reaction mediated by the metal (Broclawik et al., 2019). A quantitative yield was obtained in Suzuki-Miyaura coupling using the Pd-NHC catalyst (95; Table 3), compared to Ni-Phen (35) and Cu-EDTA (40). This superior reactivity arises from the NHC ligand's ability to stabilize oxidative addition intermediates and facilitate Transmetallation and reductive elimination (Yong et al., 2019). A 1/TOF (320  $h^{-1}$ ) and turnover number (TON = 1600) not only indicate the system's stability, but are also attributed to the rigid, electron-rich microenvironment around Pd, which reduces the catalyst deactivation, a significant shortcoming encountered in single-atom catalysts (Hanyu & Xi, 2022). These results coincide with progress in MOF-based catalysis, where confined metal sites possess greater stability and selectivity (Zhao et al., 2024). Analyses of the catalytic efficiency through mathematical modeling (Table 5) indicate that the high TOF/Ea value (16.07  $h^{-1} \cdot kJ^{-1} \cdot mol$ ) for Pd-NHC can be attributed to its fast rate (k= 0.52) M<sup>-1</sup>s<sup>-1</sup>) and low energy barrier. This efficiency surpasses that of Cu-EDTA (2.67) and Ni-Phen (1.70), highlighting the significance of electronic effects in lowering activation energy. Similar observations were reported for TM phosphides, where electron redistribution between metal and ligands decreases Ea for H<sub>2</sub> addition (Choudhary et al., 2023). The Ea values deduced from the Arrhenius equation are also consistent with the works of MOF-embedded catalysts, in which microenvironment engineering tailors desired reaction pathways (Liang et al., 2024). However, challenges persist. Although the performance of Pd-NHC is remarkable, studies on scalability and solvent compatibility are limited. For example, acetonitrile and ethanol (Table 2) as solvents may restrict industrial application due to toxicity and cost. This series of complexes could also be incorporated into heterogeneous supports, such as electropolymerized coordination polymers (Zhang et al., 2025) or hierarchical MOFs (Zhao et al., 2024), to enhance reusability. Furthermore, one might investigate the possibility of excited-state catalysis, proposed by Juliá (2025), to exploit photochemical routes for greater efficiency. It remains to be seen how multiligand complexes perform under extended reaction conditions. Although the Pd-NHC system showed no evidence of degradation from short-term tests, follow-up studies are needed to monitor metal leaching or ligand dissociation, which plague homogeneous systems (Raman & Dangi, 2024). Operando characterization techniques, such as in situ XRD or XAFS, will enable real-time monitoring of structural dynamics during catalysis (Suremann et al., 2023).

#### CONCLUSION

The present study demonstrates the critical influence of multiligand coordination on the catalysis of MTC complexes. The Pd-NHC system was identified as the most active catalyst and achieved 98% conversion in styrene hydrogenation and 95% yield in Suzuki-Miyaura coupling due to its square planar geometry, strong  $\sigma$ -donor NHC ligands, and low activation energy (28 kJ mol-1). A comparison of the complexes with Cu-EDTA and Ni-Phen complexes emphasized the need for finely tuned ligand environments for effective modulation of electron

density and substrate accessibility. DFT calculations confirmed the electronic advantages of Pd-NHC, namely the low HOMO-LUMO gap (3.2 eV) and short metal-ligand interactions for improved reaction kinetics and stabilization of intermediates. However, there are still several issues to be addressed, including solvent resistance, mass production, and long-term stability in industrial processes. Additionally, it is highly desirable to incorporate such complexes into heterogeneous structures (e.g., electropolymerized coordination polymers and hierarchical MOFs) for recyclability, transferability, and manipulation. Furthermore, the application of excited-state catalysis or operando characterization approaches might provide additional mechanistic details. In summary, this work connects synthetic chemistry with computational design, establishing a roadmap for the future generation of catalysts in sustainable organic synthesis and energy applications.

# REFERENCES

- Broclawik, E., Borowski, T., & Radoń, M. (2019). Transition metals in coordination environments: Computational chemistry and catalysis viewpoints. In Computational chemistry and catalysis viewpoints (pp. 1–22). Springer. <u>https://doi.org/10.1007/978-3-030-11714-6</u>
- Choudhary, P., Kumar, S., & Krishnan, V. (2023). Transition metal phosphide nanoarchitectonics for versatile organic catalysis. Small, 19, Article 2207053. https://doi.org/10.1002/sml1.202207053
- Fan, F., Zhao, L., Zeng, Q., Zhang, L., Zhang, X., Wang, T., & Fu, Y. (2023). Self-catalysis transformation of metal-organic coordination polymers. ACS Applied Materials & Interfaces, 15(31), 36269–36278. <u>https://doi.org/10.1021/acsami.3c07521</u>
- Hanyu, H., & Xi, J. (2022). Single-atom catalysis for organic reactions. Chinese Chemical Letters, 34, Article 107959. <u>https://doi.org/10.1016/j.cclet.2022.107959</u>
- Hu, S., Huang, J., Gao, M.-L., Lin, Z., Yunyang, Q., Yang, W., Jiao, L., & Jiang, H.-L. (2024). Location-specific microenvironment modulation around single-atom metal sites in metal-organic frameworks for boosting catalysis. Angewandte Chemie International Edition, 64, Article e202415155. <u>https://doi.org/10.1002/anie.202415155</u>
- Hu, S., Huang, J., Gao, M.-L., Lin, Z., Yunyang, Q., Yang, W., Jiao, L., & Jiang, H.-L. (2024). Location-specific microenvironment modulation around single-atom metal sites in metal-organic frameworks for boosting catalysis. Angewandte Chemie, 137, Article e202415155. https://doi.org/10.1002/ange.202415155
- Juliá, F. (2025). Catalysis in the excited state: Bringing innate transition metal photochemistry into play. ACS Catalysis, 15(8), 4665–4680. <u>https://doi.org/10.1021/acscatal.4c07962</u>

- Liang, R.-R., Liu, Z., Han, Z., Yang, Y., Rushlow, J., & Zhou, H.-C. (2024). Anchoring catalytic metal nodes within a single-crystalline pyrazolate metal-organic framework for efficient heterogeneous catalysis. Angewandte Chemie International Edition, 64, Article e202414271. <u>https://doi.org/10.1002/anie.202414271</u>
- Liang, R.-R., Liu, Z., Han, Z., Yang, Y., Rushlow, J., & Zhou, H.-C. (2024). Anchoring catalytic metal nodes within a single-crystalline pyrazolate metal-organic framework for efficient heterogeneous catalysis. Angewandte Chemie, 137, Article e202414271. <u>https://doi.org/10.1002/ange.202414271</u>
- Raman, R., & Dangi, V. (2024). Exploring the reactivity and stability of transition metal coordination complexes in catalysis. Journal of Advances and Scholarly Researches in Allied Education, 21, Article 24. <u>https://doi.org/10.29070/wzdwjd24</u>
- Suremann, N., McCarthy, B., Gschwind, W., Kumar, A., Johnson, B., Hammarström, L., & Ott, S. (2023). Molecular catalysis of energy relevance in metal-organic frameworks: From higher coordination sphere to system effects. Chemical Reviews, 123(2), 1457– 1512. https://doi.org/10.1021/acs.chemrev.2c00587
- Yong, X., Thurston, R., & Ho, C.-Y. (2019). Electronic effects on chiral NHC–transition-metal catalysis. Synthesis, 51(05), 1021–1033. <u>https://doi.org/10.1055/s-0037-1611751</u>
- Zhai, Z., Zhu, J., Cao, S., & Van der Bruggen, B. (2025). Supramolecular engineering of metalorganic membranes with metal-support interactions for nanoconfined synergistic catalysis. Small Methods, 10, Article 202500409. <u>https://doi.org/10.1002/smtd.202500409</u>
- Zhang, C.-X., Mei, S., Cao, C., Zhang, W., Xianhe, C., He, T., Feng, Y., Long, G., Tan, G., Zhong, Y.-W., & Yao, C.-J. (2025). Regulating the metal nodes of in situ electropolymerized metal-organic coordination polymers for high performance LIBs. Small, 21, Article 202503163. <u>https://doi.org/10.1002/smll.202503163</u>
- Zhang, Z.-F., Zhang, C., & Ye, S. (2024). N-heterocyclic carbene/transition metal dual catalysis. Chemistry A European Journal, 30(22), e202402259. https://doi.org/10.1002/chem.202402259
- Zhao, B., Han, J., Liu, B., Zhang, S., & Guan, B. (2024). Hierarchical metal-organic framework nanoarchitectures for catalysis. Chemical Synthesis, 4, Article 42. https://doi.org/10.20517/cs.2024.42