

Air-Stable Cobalt(II) and Nickel(II) Complexes with Schiff Base Ligand for Catalyzing Suzuki–Miyaura Cross-Coupling Reaction¹

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Abstract—The Co(II) complex [Co{C₆H₄-1,2-(N=CH-C₆H₄O)₂}] (I) and Ni(II) complex [Ni{C₆H₄-1,2-(N=CH-C₆H₄O)₂}] (II) with Schiff base of *o*-phenylenediamine and salicylaldehyde have been synthesized. The structure of the ligand and its complexes were derived on the basis of various techniques such as elemental analysis, mass, FT-IR, electronic spectra and magnetic susceptibility. From the Single crystal X-ray diffraction (SCXRD) analysis techniques (CIF file CCDC no. 1498772 (II)), it has been confirmed that the Schiff base ligand (L), coordinates to the metal ion in a tetradentate fashion through the nitrogen and oxygen atom. In addition, the square planar geometry of Ni(II) complex also has been confirmed from SCXRD. Electronic spectra, mass spectra, and magnetic susceptibility measurements reveal square planar geometry for the Co(II) complex. Synthesized complexes were used in cross-coupling of arylhalides with phenylboronic acid. The transformation offers products in good yields using 0.02 mmol catalysts loading, thereby proving the efficiency of the complexes as catalysts for Suzuki–Miyaura reaction.

Keywords: Suzuki–Miyaura cross coupling, transition metal complex, Schiff base, biphenyl

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INTRODUCTION

A Schiff base is described as a compound with an imine group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an alkyl or aryl group [1, 2]. Schiff bases and their complexes have been reported to be widely employed for carrying out ample reactions in synthetic chemistry [3]. Schiff bases have the ability to bind with various metals to form stable complexes [4, 5] and also pose to be intermediates in several organic reactions. Schiff base complexes have proven to be superior when used as a catalyst for various kinds of reactions [6]. In addition, various Schiff bases have also been examined for their biological activities by researchers [7–9]. Basically, C–C bonds are crucial as an intermediate for both organic synthesis and pharmaceutical industry. Chemical reactions that generate new C–C bonds are more fundamental and important tool for the formation of man-made chemicals such as fine chemicals, agrochemicals, pharmaceuticals, polymers etc. [10–12]. From the past few decades, several catalytic methods have been developed for the formation of C–C bonds, and among various catalysts reported palladium catalyzed cross coupling reaction have proven to

be promising chemical tool for the formation of C–C bonds [13, 14]. Palladium has been extensively applied for the synthesis of natural products and biologically relevant organic molecules [15, 16]. Conventionally used complexes with palladium-phosphine ligand are efficient in C–C coupling reactions like Suzuki–Miyaura cross-coupling reactions. However, they do not adhere firmly to the principles of Green Chemistry by being highly expensive and less eco-friendly due to their leaching into the reaction and causing impurities in the product. Catalysis using low cost and less toxic metals makes an appreciable and prolific attempt of overcoming the limitations posed by Pd-catalyzed reactions. In presented research work, we provide contemporary catalysts which could efficiently complement the coupling reaction with their high catalytic activity. The proposed catalysts possess sufficient thermal stability to react at elevated reaction temperatures. We report the synthesis of cobalt(II) and nickel(II) complexes with a Schiff base ligand (L) which has been successfully employed to study their C–C coupling efficiency in cross-coupling between phenylboronic acid and *para*-substituted aryl halides.

¹ The article is published in the original.

EXPERIMENTAL

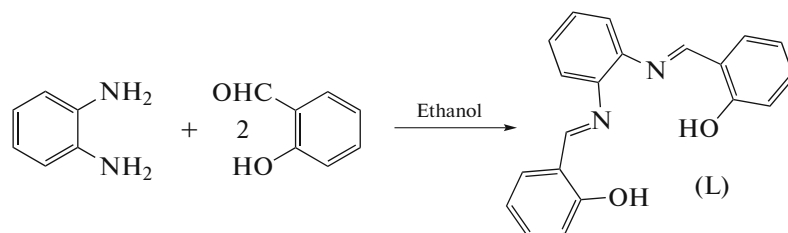
Materials and methods. All chemicals used were of analytical reagent (AR) grade without further any purification. *o*-Phenylenediamine, salicylaldehyde, nickel acetate tetrahydrate, cobalt acetate tetrahydrate potassium carbonate and sodium carbonate were procured from Merck India and used as received. Acetonitrile (ACN), 1,4-dioxane, dimethylformamide (DMF), tetrahydrofuran (THF), toluene, ethyl alcohol, diethyl ether, potassium tertiary butoxide, cesium carbonate and triethylamine used in the study were purchased from Sigma-Aldrich. The C, H, and N contents of the ligand and metal complexes were examined using microanalysis Thermoflash EA1112 series elemental analyzer. Electronic spectra of ligand and complexes were measured on Analytik Jena SPECORD S600 UV-Vis spectrophotometer in the 200–800 nm range. FT-IR results were obtained on a Bruker-Alpha ECO-ATR FT-IR spectrophotometer. The magnetic susceptibilities of the complexes were recorded at room temperature on a Sherwood UK magnetic balance, mercury(II) tetrathiocyanatocobaltate(II) ($\text{Hg}[\text{Co}(\text{SCN})_4]$) was used as a calibrant. The ^1H NMR (400 MHz) spectrum of the ligand was

recorded in Bruker AV 400 instrument using tetramethylsilane (TMS) as an internal standard. Molecular mass was determined using a Waters Q-ToF micro mass spectrometer with an ESI source. Thermogravimetric (TG) measurements were performed on (EXSTAR-6000) using nitrogen as the carrier gas (flow rate: 50 mL/min) with a heating rate of $10^\circ\text{C}/\text{min}$.

Synthesis of the Schiff base (Scheme 1). A solution of *o*-phenylenediamine (0.108 g, 1.0 mmol) and salicylaldehyde (0.244 g, 2.0 mmol) in 10 mL ethanol was taken in a round bottom flask and refluxed for 3 h. The reaction mixture was monitored by thin layer chromatography. The completed reaction was filtered and crude solid product obtained was washed with diethyl ether several times till no impurities were observed and this purified product was dried in a vacuum oven for 5 h at 60°C . The Schiff base obtained was turmeric yellow in colour with 82% of yield.

For $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$

anal. calcd., %	C, 75.93	H, 5.10	N, 8.86
Found, %	C, 75.22	H, 4.90	N, 8.74



Scheme 1.

Synthesis of metal complexes (Scheme 2). Cobalt-Schiff base complex was prepared by refluxing ethanolic solutions of $\text{Co}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol, 5 mL) and the Schiff base (0.316 g, 1.0 mmol, 10 mL) under constant stirring for 2 h. The reaction was monitored for the change in colour and precipitate formation. The obtained brown colored precipitate was filtered, washed with ethanol and diethyl ether to remove unreacted Schiff base. The product was dried in a vacuum oven at 60°C for 5 h (the yield was 64%). Similarly, the nickel Schiff base complex was prepared by

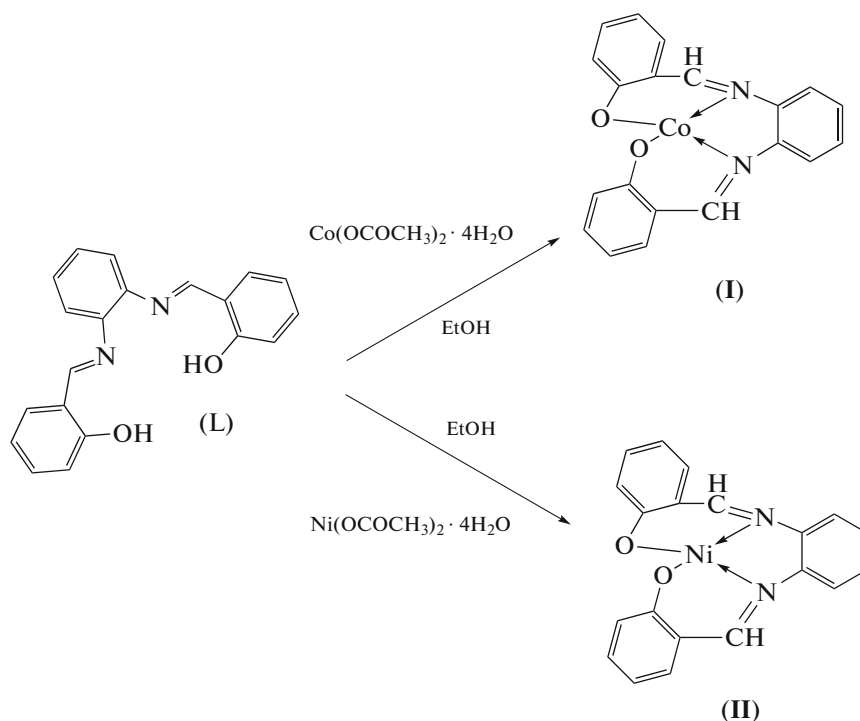
using $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (the yield was 78%). Crystals for complex **II** crystal were obtained by a slow evaporation method using ethanol.

For $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2\text{Co}$ (**I**)

anal. calcd., %	C, 64.35	H, 3.78	N, 7.50
Found, %	C, 64.30	H, 3.67	N, 7.50

For $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_2\text{Ni}$ (**II**)

anal. calcd., %	C, 64.40	H, 3.78	N, 7.51
Found, %	C, 64.20	H, 3.55	N, 7.40



Scheme 2.

X-ray crystallography. The X-ray diffraction studies for crystal **II** was performed on a Bruker APEX-II CCD diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using ω scan technique at 296 K. The structure was solved by the direct method using SHELXL-2007/2014 [17] software and refined by full matrix least square methods. Anisotropic displacement parameters were calculated for all non-hydrogen atoms. The crystallographic data for complex **II** are listed in Table 1. Selected bond lengths and angles for complex **II** are given in Table 2.

The atomic coordinates and other parameters of the complex have been deposited with the Cambridge Crystallographic Data Center (CCDC no. 1498772; deposit@ccdc.cam.ac.uk).

General procedure for the Suzuki coupling reaction.

The synthesized catalyst (0.02 mmol), aryl halides (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), and 1,4-dioxane (2.0 mL) were heated to 110°C for 8 h. The reaction mixture was cooled to room temperature and the organic phase was examined by gas chromatography. The yield was calculated with the help of GC results.

RESULTS AND DISCUSSION

The crystallographic analysis of complex **II** reveals that the unit cell contains one complex molecule (Fig. 1). Here, nickel(II) atom is four-coordinated via

two oxygen atoms and two nitrogen atoms from the deprotonated Schiff base ligand, forming a perfectly square planar geometry with the smallest angle of $\text{O}(2)\text{Ni}(1)\text{O}(1) 84.34(7)^\circ$ and the biggest angle of $\text{O}(2)\text{Ni}(1)\text{N}(1) 179.03(7)^\circ$. The $\text{N}(2)\text{Ni}(1)\text{N}(1)$ angle is found to be $86.20(7)^\circ$. The bifurcated $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond with bond distance 3.330 and 3.308 \AA was observed in the molecular crystal. Moreover, $\text{C}-\text{H}\cdots\pi$ interaction with bond distance 3.506 \AA was observed between the neighboring molecular units. Each unit is interconnected to the adjoining units through a $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond where phenyl ring hydrogen of one unit links with oxygen of another unit to form one-dimensional structure. The complex molecules are regularly arranged by weak van der Waals forces to construct three dimensional structures.

The synthesized Schiff base ligand was characterized by ^1H NMR analysis in DMSO. The ^1H NMR spectrum of ligand portrays the well characteristic singlet peaks at $\delta 12.90$ which corresponds to the phenolic proton. Similarly, the peak at $\delta 8.9-9.0$ represents the characteristic peak of azomethine protons. The presence of a multiplet at $\delta 6.95-7.65$ is due to the aromatic protons ($\text{Ar}-\text{H}$). Moreover, the peak at $\delta 12.90$ in Schiff base ligand due to phenolic proton was not visible in the spectrum of nickel complex, which confirmed the bonding between phenolic oxygen with nickel ions. The spectrum displays all the characteris-

Table 1. Crystallographic data and structure refinements for complex **II**

Parameter	Value
Empirical-formula	C ₂₀ H ₁₄ N ₂ NiO ₂
Colour	Maroon
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁
Unit cell dimensions	
<i>a</i> , Å	5.4430(3)
<i>b</i> , Å	16.6157(7)
<i>c</i> , Å	17.2995(8)
<i>V</i> , Å ³	1564.55
<i>Z</i>	4
ρ _{calcd} , g/cm ³	1.592
Crystal size, mm	0.32 × 0.24 × 0.20
μ, mm ⁻¹	1.256
<i>F</i> (000)	776
Scan mode	ω
θ Range, deg	1.699–25.997
Limiting indices <i>h</i> , <i>k</i> , <i>l</i>	–6 ≤ <i>h</i> ≤ 6, –20 ≤ <i>k</i> ≤ 20, –21 ≤ <i>l</i> ≤ 21
Reflection collected	29500
Independent reflections (<i>R</i> _{int})	3093 (0.0189)
Reflections with <i>I</i> > 2σ(<i>I</i>)	2987
Number of parameters	226
Goodness-of-fit	1.012
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))*	0.0230
<i>R</i> ₁ (all data)**	0.0699
Δρ _{min} /Δρ _{max} , e Å ⁻³	0.156/–0.159

* $R = \sum(F_o - F_c) / \sum(F_o)$.

** $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum(F_o^2)^2\}^{1/2}$.

tic peaks without any impure peak confirming the prepared Schiff base ligand and complex.

The synthesized ligand and the complex molecules were examined by the FT-IR analysis. The FT-IR spectra of the ligand exhibited strong band at 1615 cm⁻¹ assignable to azomethine ν(C=N) group. The peak in the region 1275 cm⁻¹ is indicative of phenolic ν(C–O) stretching. The appearance of a band for ν(CH=N) in the range of 1608–1599 cm⁻¹ indicates a shift to the lower frequencies compared to ligand (L) indicating the complexation of the ligand with metal atom through nitrogen atom [18]. Phenolic ν(C–O) stretching is shifted to 1251–1245 cm⁻¹ in complexes from 1275 cm⁻¹ seen in the ligand spectra. The shift towards lower wavenumbers indicates coordination of the phenolic oxygen of ligand to the metal ion. The new bands in the range 534–541 cm⁻¹ in complexes, can be tentatively assigned to coordination of metal with an oxygen atom. The coordination through azomethine N is further supported by the appearance of the band at 420–455 cm⁻¹ in metal complexes which can be assigned to ν(M–N) [19].

The prepared M–L complexes were confirmed by using UV-Vis absorption measurements in ethanol solvent as a media. Figure 2 shows the UV-Vis spectra of L, complexes **I** and **II**. In the UV-Vis absorption spectrum of free ligand, the molecule shows maximum wavelength values at 212 and 257 nm which are attributed to ?? – ??* transition. Similarly, 325 and 387 nm can be assigned to imino *n* – ??* transitions in ligand. Compared to the free L, the imine *n* – ??* transitions of the complexes were shifted to some extent, possibly the coordination of nitrogen atom of the ligand imine group to the metal ion [20]. Moreover, quite higher absorption intensity band at 484 nm (20661.2 cm⁻¹) for complex **I** was observed, which confirms the square planar geometry of the cobalt(II) complex. Similarly, absorption at 470 nm (21276.5 cm⁻¹) in complex **II** indicates the square planar geometry of nickel(II) complex [21].

Table 2. Selected interatomic distances (*d*) and bond angles (ω) in complex **II**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ni(1)–O(1)	1.840	Ni(1)–N(1)	1.858
Ni(1)–O(2)	1.836	Ni(1)–N(2)	1.859
Angle	ω, deg	Angle	ω, deg
O(2)Ni(1)O(1)	84.34(7)	N(2)Ni(1)N(1)	86.20(7)
O(2)Ni(1)N(2)	94.74(7)	O(1)Ni(1)N(2)	178.43(7)
O(1)Ni(1)N(1)	94.72(7)	O(2)Ni(1)N(1)	179.03(7)

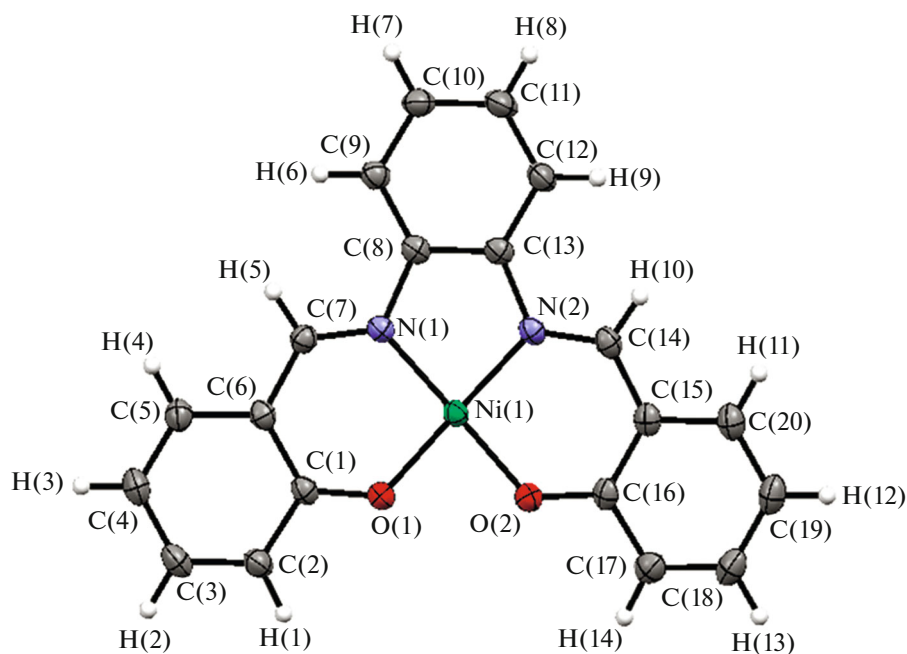


Fig. 1. Molecular structure of **II** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

The purpose of the thermal study is to confirm the course of the degradation and the presence of the hydrated water molecules in the complexes. The thermal decomposition curves for both the complexes at a temperature range from 50 to 700°C are given in Fig. 3. TG analysis of the complexes indicates that removal of ligand proceeds in a single step with 84.98% mass loss and remaining 15.02% residual mass, which can be attributed to the formation of metal oxides. Complexes showed complete decomposition at $\geq 450^\circ\text{C}$. The absence of peak from 100 to

200°C confirms that no coordinated water molecules are present in both the complexes [22, 23]. Losses of weight are in agreement with the calculated values.

The magnetic moment for complex **I** was found to be $1.23 \mu_{\text{B}}$, which indicates that one unpaired electron is present in the complex. Hence cobalt complex is paramagnetic in nature and geometry of the complex is square planar. The effective magnetic moment ($0.0 \mu_{\text{B}}$) of complex **II** clearly confirms the absence of unpaired electrons and indicates the complex to be square planar [21].

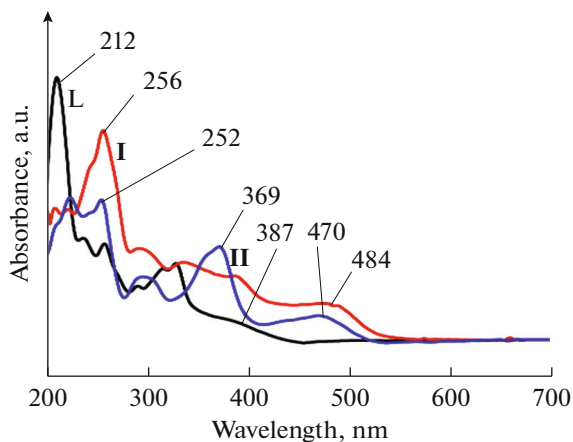


Fig. 2. UV-Vis spectra of ligand and complexes **I**, **II**.

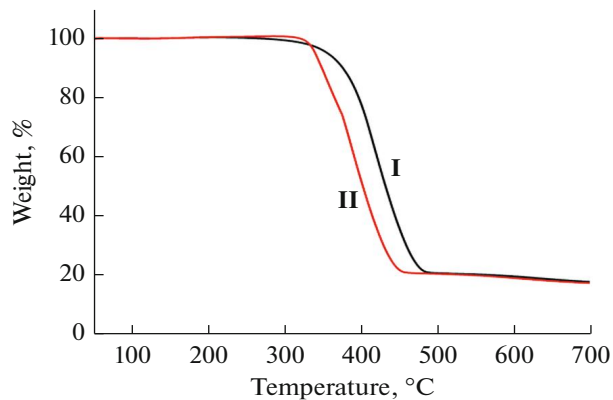


Fig. 3. TG curve of complexes **I** and **II**.

Table 3. Effect of solvent on Suzuki coupling 4-bromobenzonitrile with phenylboronic acid*

Entry	Solvent	Base	Time, h	Conversion, %**	
				I	II
1	DMF	K ₂ CO ₃	8	52	60
2	Toluene			67	80
3	THF			65	76
4	CH ₃ CN			80	81
5	1,4-Dioxane			82	88

* Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (2.0 mmol), catalyst (0.02 mmol), solvent (2 mL), 8 h.

** Yield determined by GC.

Table 4. Effect of various base on Suzuki coupling of 4-bromobenzonitrile with phenylboronic acid in 1,4-dioxane*

Entry	Base	Solvent	Time, h	Conversion, %**	
				I	II
1	K ₂ CO ₃	1,4-Dioxane	8	82	88
2	Na ₂ CO ₃			75	78
3	Cs ₂ CO ₃			70	72
4	KO ^t Bu			71	76
5	Et ₃ N			60	63

* Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (0.02 mmol), solvent (2 mL), 8 h.

** Yield determined by GC.

Table 5. Effect of catalyst concentration on Suzuki coupling of 4-bromobenzonitrile with phenylboronic acid*

Entry	Amount of catalyst (mmol)	Solvent	Base	Time, h	Conversion, %**	
					I	II
1	0.01	1,4-Dioxane	K ₂ CO ₃	8	60	62
2	0.02				82	88
3	0.03				80	88

* Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (2.0 mmol), solvent (2 mL), 8 h.

** Yield determined by GC.

ESI MS data of ligand and complexes **I** and **II** are given below:

Compound	Observed mass	Expected mass
L	317.10	316.12
I	373.00	373.04
II	373.10	372.04

The reaction between 4-bromobenzonitrile and phenylboronic acid were chosen for the optimization studies. Significant parameters affecting the reaction such as solvent, alkalinity, catalyst loading and the reaction time were screened for optimization.

(i) *effect of solvent.* The activities of the synthesized complex (**I** and **II**) for the coupling of 4-bromobenzonitrile with phenylboronic acid was studied using different solvents such as DMF, toluene, THF, CH₃CN, and 1,4-dioxane (Table 3). Reaction temperatures were set at the reflux temperature of the chosen solvent respectively. K₂CO₃ was used as the base and 0.02 mmol catalyst **I/II** were used for the reaction. Dioxane as a solvent media showed increased catalytic activity with the yield output 82% for **I** and 88% for **II**, followed by acetonitrile which also showed a considerable yield output. Other solvents supported the coupling reaction to a substantially lesser extent. Dioxane was chosen as an ideal solvent for carrying out the reactions owing to its involvement in enhancing the coupling yield.

(ii) *effect of base.* Alkalinity of the reaction media for a Suzuki coupling reaction is significant as the base plays an important role in the catalytic cycle by initially reducing the precatalyst to its active form and further replacing the halide ion in the oxidative addition step. We investigated the effect of various bases for our reaction by carrying out the chosen reaction using different bases like K₂CO₃, Na₂CO₃, Et₃N, Cs₂CO₃, and KO^tBu. Highest yield obtained was with K₂CO₃ (Table 4, entry 1) whereas the other bases were less effective in enhancing the catalytic conversion. K₂CO₃ was chosen as the optimal base for all further reactions.

(iii) *effect of catalyst concentration.* To study the effect of catalyst concentration on the reaction, catalyst ratio was varied from 0.01 to 0.03 mmol (Table 5). The increase in the catalytic yield was observed up to 0.02 mmol of the respective catalyst. The further increase at 0.03 mmol showed a slightly reduced yield for **I**, and a constant yield for **II** (Table 5, entries 2 and 3). Optimum catalyst loading was therefore finalized as 0.02 mmol of catalyst **I/II**.

(iv) *effect of reaction time.* The dependence of product yield on reaction time for the coupling of 4-bromobenzonitrile with phenylboronic acid was checked by analyzing the reaction mixture at regular intervals of the time under same reaction condition. The apparent increase in the product yields using both catalysts **I** and **II** were noticeable until 8 h of the reaction after which there was negligible change in the yield (Fig. 4).

All further cross-coupling reactions between phenylboronic acid and different aryl halides were carried

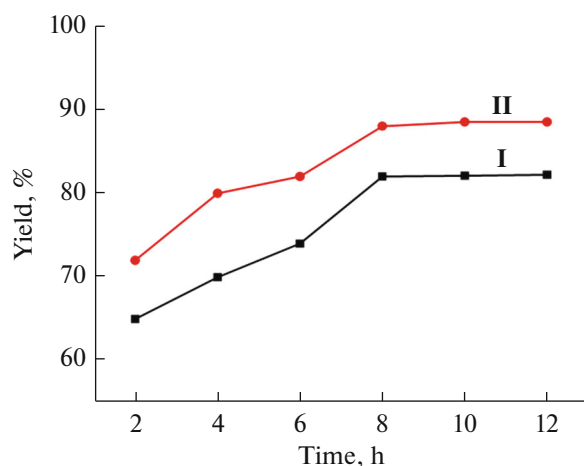


Fig. 4. Effect of reaction time on the yield of 4-cyanobiphenyl.

out with the optimized reaction conditions i.e, using dioxane as a solvent and K_2CO_3 as a base with a catalyst load of 0.02 mmol of catalyst I/II for a period of 8 h (Table 6).

The proposed mechanism for cross coupling is depicted in Fig. 5 for the synthesized metal–Schiff base complex catalyzed reaction. The catalytic metal M(II) Schiff base complex (a) which is the catalyst precursor gets reduced to its catalytically active M(0) form (b) initially in the presence of phenylboronic acid and base (K_2CO_3). The oxidative addition of metal complex to the aryl halide forms the organometal species (c). Reductive elimination of the coupled product (f) from (c) brings back the original catalyst (b) which completes the catalytic cycle.

Table 6. Effect of catalyst on Suzuki coupling of aryl halide with phenylboronic acid*

Entry	R	X	Yield**	
			I	II
1	OCH ₃	Br	60	64
2	H		35	45
3	CN		82	88
4	COCH ₃		80	82
5	NHCOCH ₃		70	71
6	OH		51	55
7	CH ₃		44	44
8	F		50	58
9	OH	I	68	72
10	CN		85	90

* Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (0.02 mmol), solvent (2 mL), 8 h.

** Yield determined by GC.

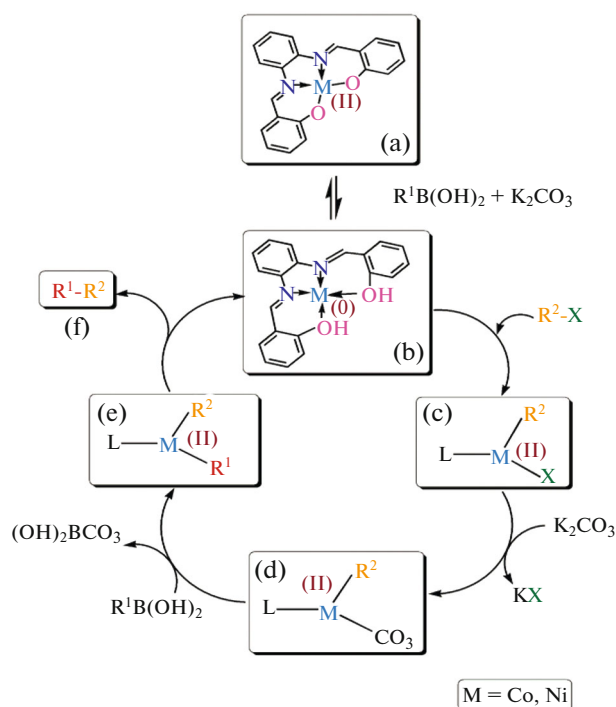


Fig. 5. Proposed mechanism for cross coupling using pre-prepared complexes.

halide ion and replace it with the anion of the base. The forming intermediate (d) will further undergo transmetalation with the phenylboronic acid to produce the organometal species (e). Reductive elimination of the coupled product (f) from (e) brings back the original catalyst (b) which completes the catalytic cycle.

Thus, we have synthesized nickel and cobalt Schiff base complexes in a simple method to act as catalysts for Suzuki–Miyaura coupling reaction. Characterization disclosed the formation of the complexes. The synthesized catalysts were successful in carrying out Suzuki–Miyaura coupling reaction with only 0.02 mmol catalyst being sufficient for the coupling reaction. Type of substituent on the aryl halide highly influenced the catalytic yield. The presence of electron withdrawing groups enhanced the catalytic output, while the electron donating groups ended with low yield. The simple ligand and the low cost of nickel and cobalt salts make these complexes complementary to existing Pd catalysts and serve as potential non-noble metal catalysts for organic transformations.

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