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***Research paper***



# Synthesis, Characterization and Catalytic Activity of Nano-Iron (II) Schiff Base Complex in Suzuki-Miyaura Cross Coupling Reaction

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**Abstract**

A new nano-iron (II) Schiff base complex, [Fe(L)] where L is 1-((pyridin-2-ylimino)methyl)naphthalen-2-ol with octahedral geometry has been synthesized by the sonochemical (Ultrasonic irradiation) method. This method can promote the formation of nano-sized particles in short time with improved yield toward conventional method. The complex was characterized by FTIR, UV-Vis, TGA, SEM and elemental analysis. Particle size of synthesized complex was calculated from particle size analysis. Catalytic activity of the prepared complex was studied for Suzuki-Miyaura cross-coupling reaction. The synthesized complex showed great potential in catalytic activity with less concentration.

***Keywords***: *Biphenyl; Iron Catalyst; Nano Complex; Schiff base; Suzuki-Miyaura coupling.*

## 1. Introduction

Formation of C-C bond by transition metal-catalyzed coupling reaction is understood to be a powerful tool for synthetic investigations. These complexes play a significant role in development of coordination chemistry in field of catalysis and enzymatic reactions, magnetism and molecular architectures, and liquid-crystal technology[1-4]. In addition, transition-metal nanoparticles for formation of carbon-carbon bonds are attractive to researchers[5]. Among, various catalytically active nanoparticles, palladium nanoparticles have gained considerable attention for the formation of C-C bonds[6]. Moreover, C-C coupling reaction (Suzuki and Heck) can be catalyzed by palladium nanostructures such as hollow spheres or nanoparticles of different emergence[7]. The application of transition-metal nanoparticles has been widely practiced for catalyzing the formation of carbon-carbon bond in the heterogeneous system since the last decade[8]. Nanoparticles have attained great interest in recent years as a result of their unique chemical and physical properties, which differ from their bulk materials, single atoms and can have potential applications in optoelectronics, catalysis, and ceramics etc[9-11].

Since the past decade, various alternative approaches for C-C bond formation have been reported[12]. Transition-metals like nickel, cobalt, copper, iron etc. have also been utilized for the formation of C-C bond[13]. Recently, $Fe_3O_4$ nanoparticles (NPs) have been investigated as efficient catalysts for C-C bond formation[14]. Schiff bases are considered as a very important class of organic compounds which display wide applications in biological aspects. Transition metal complexes with Schiff base ligand possess rare catalytic activity with respect to cross-coupling reaction. Moreover, Schiff base ligands and their metal complexes have been widely researched[15]. However, the functional applications of Schiff bases and their metal complexes greatly rely on several properties, such as complexation ability towards metals[16], antibacterial activity[17], anti-cancer activity, fungicidal[18] etc. On the other hand, the particle size plays important role on catalysis, so the synthesis of nano-sized compound has a basal role in many fields. In addition, the coupling of aryl halides with phenylboronic acids under mild condition is a subject of immense interest for both academicians and researchers. In the present work, we have described the synthesis of new nano-iron (II) Schiff base complex of a Schiff base ligand, namely 1-((pyridin-2-ylimino)methyl)naphthalen-2-ol using sonochemical methods. Nano-iron (II) Schiff base complex was characterized and its catalytic activity was investigated for Suzuki cross coupling reaction.

## 2. Materials and Method

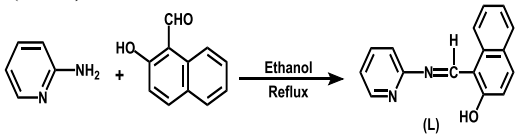
All chemicals used were of analytical reagent (AR) grade and used without any further purification. 2-aminopyridine, 2-hydroxy-1-naphthaldehyde were procured from Merck India. Ferrous chloride (hydrated) was procured from loba chemie. Acetonitrile (ACN), 1,4-dioxane, toluene, ethyl alcohol, methyl alcohol, diethyl ether, tetrahydrofuran (THF), dimethylformamide (DMF), potassium tertiary butoxide, cesium carbonate, potassium carbonate, sodium carbonate and triethylamine used in the study were purchased from Sigma-Aldrich.

$^1$H-NMR spectra were recorded in Bruker AV 400 instrument using TMS as an internal standard. The spectra of the ligand and complex were recorded in DMSO. FTIR spectra were recorded on a Bruker-Alpha FTIR spectrophotometer as KBr pellet in the frequency range 400-4000 $cm^{-1}$. Electronic spectra of ligand and complex were measured on Analytik Jena SPECORD S600 UV-Vis spectrophotometer in the 200-600 nm range. Thermogravimetric measurements were performed on (EXSTAR-6000) using nitrogen as the carrier gas (flow rate: 50 mL/min) with heating rate

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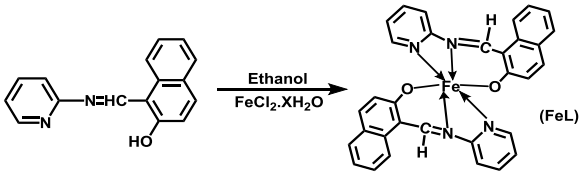
10 ˚C/min. The C, H and N contents of the ligand and metal complex was determined using microanalysis Thermoflash EA1112 series elemental analyzer. The magnetic susceptibilities of the complex was recorded at room temperature on a Sherwood UK magnetic balance, $Hg[Co(SCN)_4]$ was used as a calibrant. SEM analysis was carried out by JEOL-JSM-6360LV model to investigate the morphology of the specimen. Particle size measurement was carried out on Horiba particle size analyzer. The cross coupling product was analyzed using Gas Chromatography (GC) (Shimadzu 2014, Japan), siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector. The initial column temperature was increased from 60 ˚C to 150 ˚C at the rate of 10 ˚C/ min and then to 220 ˚C at the rate of 40 ˚C/min. Nitrogen gas was used as the carrier gas.

2-aminopyridine (0. 095 g, 1 mmol) and 2-hydroxy-1-naphthaldehyde (0.172 g, 1 mmol) were dissolved in ethanol and heated to 60 ˚C in a 50mL round bottom flask. The reaction mixture was then refluxed for 3 hours and filtered. The obtained product then washed with diethyl ether and re-crystallized from ethanol and dried. Chemical Formula: $C_{16}H_{12}N_2O$; Melting point: 180 ˚C; Yield: 80%; Color: Mehendi Yellow. Elemental Anal: Found (%): C-77.45, H-4.75, N-11.00; Calc. (%): C-77.40, H-4.80, N-11.28; FTIR (KBr) $cm^{-1}$: 1618.59 (νC=N), 1137.91 (νC-O), 3495.46 (νO-H).




**Scheme 1**: Synthesis of ligand (L)

A proper volume of ligand (0.496 gm, 2.0 mmol) solution in (ethanol) (5 mL) was added in dropwise manner under the ultrasonic irradiation to the prepared $FeCl_2.XH_2O$ (0.127 gm, 1.0 mmol) solution (5 mL) in ethanol. The mixture was irradiated under ultrasonic waves for one hour. The obtained solid was filtered, subsequently washed with cold methanol and dried. Chemical Formula: $C_{32}H_{22}FeN_4O_2$; Yield: 80%; Color: Dark brown. Elemental Anal: Found (%): C-77.45, H-4.78, N-9.72; Calc. (%): C-70.35, H-4.86, N-9.65; FTIR (KBr) $cm^{-1}$: 1561.73 (νC=N), 1124.21 (νC-O), 3448.14 (νO-H), 496.24 (νFe-N), 421.98 (νFe-O).




**Scheme 2:** Synthesis of Complex (FeL)

Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), $K_2CO_3$ (2.0 mmol), catalyst (0.04 mmol) and 1,4-dioxane (2 mL) were added to a 5 mL flask, and the mixture was stirred in parallel synthesizer for 8 hours at 110 ˚C. The progresses of the reactions were monitored by Gas chromatography. The internal standard was used and calibrated against each and every one of the cross-coupling products.

## 3. Results and Discussion

The $^1$H NMR spectrum of the ligand was recorded in DMSO solvent to confirm the number of proton present in the molecule. The -OH peak was observed around 15.21 ppm. The peak at 9.58 ppm was observed for azomethine proton (Fig. 1).

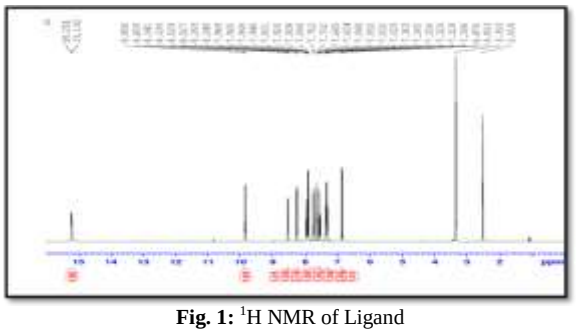


**Fig. 1:** $^1$H NMR of Ligand

FTIR spectra of ligand and the complex are shown in the Figure 2. The strong band in ligand at 1618.59 $cm^{-1}$ assignable to azomethine ν(C=N) group and and O-H peak appears at 3495.46 $cm^{-1}$. The peak in the region 1137.91 $cm^{-1}$ is indicative of phenolic ν(C-O) stretching. Moreover, for complex, the appearance of a band for ν(CH=N) in the range of 1561.73 $cm^{-1}$ indicates a shifting to the lower wave numbers compared to ligand indicating the complexion of ligand with metal atom through nitrogen atom has been formed. Phenolic ν(C-O) stretching in complex is shifted from 1137.91 $cm^{-1}$ to 1124.21 $cm^{-1}$ indicating coordination of the phenolic oxygen of ligand to the metal ion. The new band at 421.98 $cm^{-1}$ in complex, tentatively assign coordination of metal with oxygen atom ν(Fe-O). The band which appear around 496.24 $cm^{-1}$ in the spectrum of complex may be assigned to the coordination of metal with a nitrogen atom (Fe-N)[19].

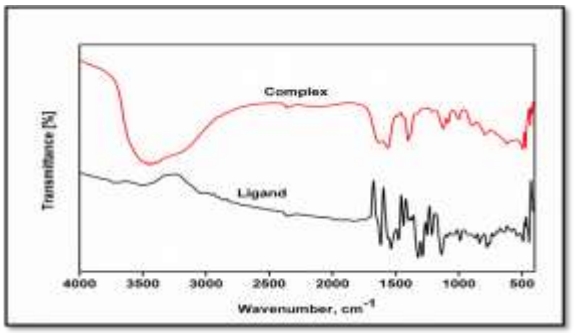



**Fig. 2:** FTIR spectrum of ligand and complex

The electronic spectra of synthesized ligand and complex were recorded in methanol solvent (Fig. 3). The ligand shows peaks at 228 nm, 282 nm and 332 nm which are due to π - π*, n - π* transitions. In case of synthesized complex, peaks at 245 nm, 299 nm, 345 nm were observed. The absorption bands which we observed in the free ligand spectrum have been shifted to lower energy region in the spectra of complex because of the ligand coordination with a metal ion. These transitions are due to intra-ligand charge transfer transitions (ILCT) and ligand to metal charge transfer transitions (LMCT). Moreover, in case of complex, peaks at 420 nm and 438 nm were observed (d-d transition)[20].

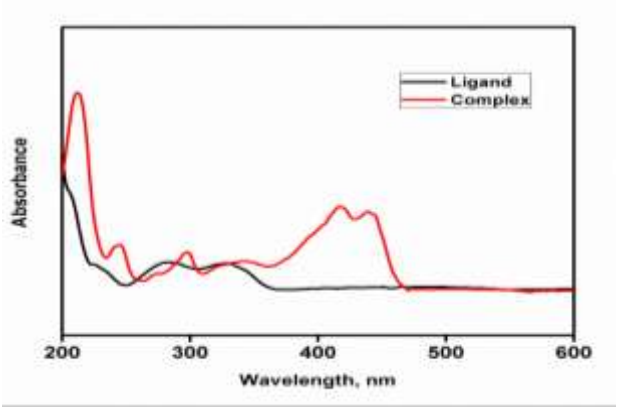



**Fig. 3:** UV-Vis spectrum of ligand and complex

The magnetic properties of the complex at room temperature have been investigated. The magnetic moment of complex was found 4.10 BM, which indicates that 4 unpaired electron is present in the complex. The paramagnetic nature revealed octahedral geometry of the synthesized complex.

The size of the nano-Fe particles was observed 47.5 nm (Fig. 4). The morphology and particle size of the nano-iron (II) complex catalyst was studied by SEM images (Fig. 5). As can be seen, the nano-Fe particles tubular nanostructure of the nanotubes (Fig. 5). The thermal behavior of the Schiff base ligand and its metal complex was studied by using thermogravimetric techniques in the range of 30–600 ˚C in a nitrogen atmosphere. The TGA curve of ligand and metal complex are given in Fig. 6. The purpose of the thermal study is to confirm the course of the degradation and the presence of the hydrated water molecules in the complex. In Figure 6, as can be seen, decomposition of the complex was completed in a single step. The remaining percentage mass loss can be assigned for iron oxide residue. The absence of the peak around 200 ˚C confirms that no water molecule present in the complex.

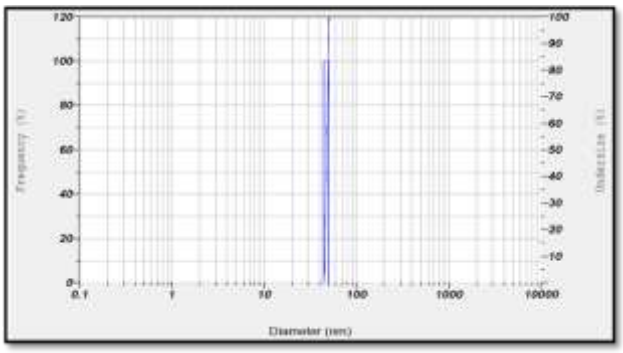


**Fig. 4:** Particle size distribution of the synthesized complex

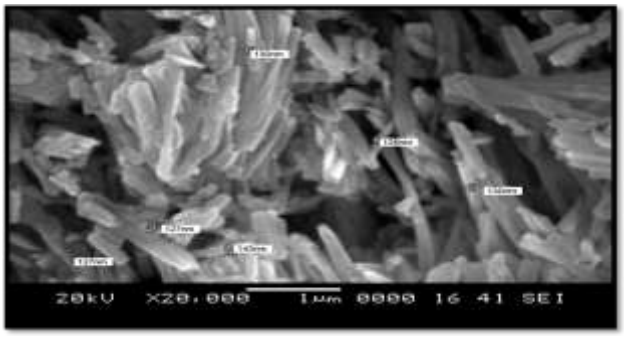



**Fig. 5:** SEM micrographs of the complex

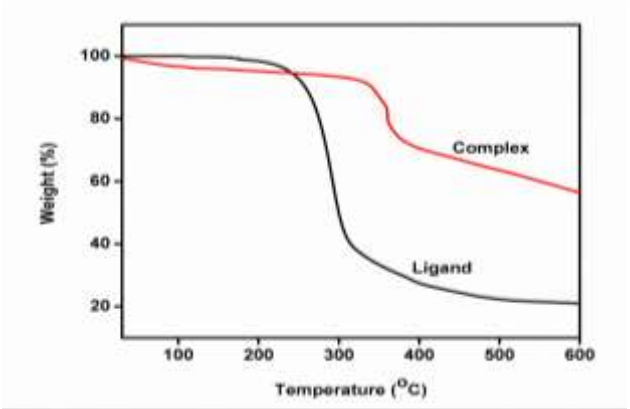



**Fig. 6:** TGA of ligand and complex

We employed the coupling of 4-bromobenzonitrile and phenylboronic acid as the model reaction to study the suzuki reaction using the nano-iron (II) Schiff base complex as a catalyst. The effects of the base, solvent, time and concentration of the catalyst on the Suzuki coupling of bromobenzonitrile and phenylboronic acid were investigated. The basic environment is essential for the Suzuki reaction. Among the bases examined (Table 1, entries 1-5), $K_2CO_3$ showed the best effect. The impact of solvents on the reaction was also investigated (Table 2, entries 1-5) and 1,4-dioxane gave the best result. Product yield dependence on the reaction time was investigated by analyzing the reaction mixture at regular intervals of time. Product conversion was observed to increase with reaction time till the completion of 8 hours. The conversion remained almost insignificant after 8 hours (Fig. 7). Hence, optimized reaction time for coupling reaction was fixed at 8 hours. Product yield dependence on the concentration of catalyst was investigated by analyzing the reaction mixture with different catalyst concentration from 0.01 mmol to 0.05 mmol (Table 3). The conversion result showed almost constant yield with 0.04 and 0.05 mmol catalyst concentrations. Hence, 0.04 mmol concentration was taken for the further catalytic studies.

**Table 1:** Effect of base on Suzuki coupling

| Entry | Bases | Solvent | Yield[a] |
|---|---|---|---|
| 1 | $Et_3N$ | 1,4-dioxane | 72 |
| 2 | $K_2CO_3$ | | 78 |
| 3 | $Cs_2CO_3$ | | 74 |
| 4 | $Na_2CO_3$ | | 68 |
| 5 | KOtBu | | 61 |

**Table 2:** Effect of solvents

| Entry | Solvents | Base | Yield[a] |
|---|---|---|---|
| 1 | Acetonitrile | $K_2CO_3$ | 70 |
| 2 | 1,4-dioxane | | 78 |
| 3 | Toluene | | 75 |
| 4 | THF | | 60 |
| 5 | DMF | | 64 |

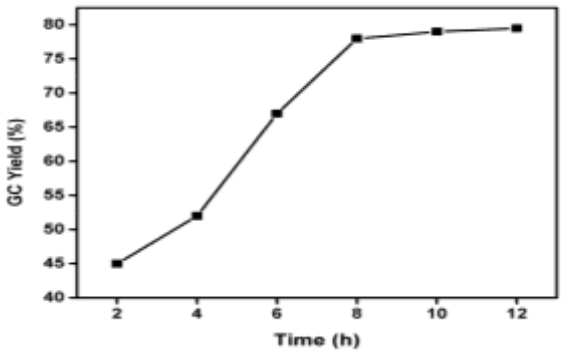


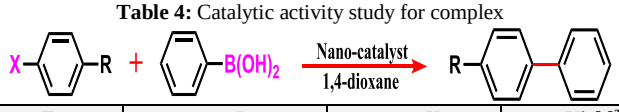

**Fig. 7:** Effect of reaction time

**Table 3:** Effect of catalyst concentration

| Entry | Concentration of catalyst | Bases | Solvent | Yield[a] |
|---|---|---|---|---|
| 1 | 0.01 | $K_2CO_3$ | 1,4-dioxane | 51 |
| 2 | 0.02 | | | 59 |
| 3 | 0.03 | | | 68 |
| 4 | 0.04 | | | 78 |
| 5 | 0.05 | | | 78.50 |

Further, different substituted aryl halides were used to extend the cross-coupling reaction with phenylboronic acid using the optimized reaction conditions. The results of different substituent are summarized in Table 4. The catalyst was found to catalyze the coupling reactions effectively. The conversion pattern with different substituents on the aryl halides was different.

**Table 4:** Catalytic activity study for complex




| Entry | R | X | Yield[a] |
|---|---|---|---|
| 1 | $OCH_3$ | | 50 |
| 2 | H | | 38 |

| | | | |
|---|---|---|---|
| 3 | CN | Br | 78 |
| 4 | $COCH_3$ | | 79 |
| 5 | $NHCOCH_3$ | | 67 |
| 6 | OH | | 50 |
| 7 | $CH_3$ | | 46 |
| 8 | F | | 57 |
| 9 | OH | I | 58 |
| 10 | CN | | 80 |

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), $K_2CO_3$ (2.0 mmol), catalyst (0.04 mmol), solvent (2.0 mL), 8 h.
[a] Yield determined by GC.

## 4. Conclusion

A new octahedral tubular nano-iron (II) Schiff base complex, [Fe(L)] where L [1-((pyridin-2-ylimino)methyl)naphthalen-2-ol] has been synthesized via Ultrasonic irradiation and characterized. Suzuki cross-coupling of different aryl halides and phenylboronic acids was catalyzed with synthesized nano-iron complex. The synthesized complex showed great potential in catalytic activity. Better result was found in 1,4-dioxane solvent with $K_2CO_3$ as a base using a catalyst load of 0.04 mmol with a reaction time of 8 hours. The yields varied on the basis of substrates having either electron-donating groups or electron-withdrawing groups. Among the halides, iodide was observed to be a better leaving group. It was concluded that the catalytic activity of the nano-iron (II) Schiff base complex could be exploited for the carbon-carbon cross coupling reaction efficiently.

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