FULL PAPER



Catalytic activity of Fe(II) and Cu(II) PNP pincer complexes for Suzuki coupling reaction

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Badekai Ramachandra Bhat, Catalysis and Materials Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasanagar-575025, India. Email: ram@nitk.edu.in Iron and copper PNP pincer complexes of the type $[Fe(L)SO_4]$ and $[Cu(L) OCOCH_3]$ are reported and represented as C-1 and C-2 catalyst. Both the complexes were synthesized using bis(diphenylphosphino)pyridine-2,6-diamine [L], and salts of 'Fe' and 'Cu' by direct coordination method. The as synthesized complexes were characterized using FTIR, UV–Vis, mass analysis and TGA. The effect of reaction time, catalyst load, solvent and base on the reaction between phenylboronic acid and para substituted bromobenzenes in the presence of the catalysts were investigated for evaluating the catalytic efficiency of the complexes. The results obtained highlight the enhanced C-C coupling reactions with the use of 0.4 mol% of the catalyst C-1 in 14 h and 0.6 mol% of C-2 in 16 h respectively with Cs₂CO₃ base and ACN as solvent media. Of the two complexes reported, C-1 with iron as catalytically active metal is more stable and active towards coupling which is reflected in its better coupling yields in lesser reaction time compared to copper bearing C-2 complex.

KEYWORDS

pincer ligand, PNP, Suzuki-Miyaura cross-coupling

1 | INTRODUCTION

Transition metals have displayed excellent catalytic activity enabling several unfeasible chemical processes both viable as well as productive. Process viability depends majorly on the overall cost and ease of preparation of the pre-catalysts which needs to be based on abundant metals and inexpensive ligands.^[1] Complexes bearing pincer ligands are among the organometallic complexes that have been established and recognized as effective pre-catalysts for various reactions. Their unique metal bound structures, high thermal stability, and process viability makes them the most active catalysts for organic transformations involving the activation of bonds.^[2] Pincer complexes are also well known to catalyze Suzuki-Miyaura cross-coupling reaction with high catalytic activity and selectivity.^[3-6] However, the most emphasized complexes catalyzing this coupling reaction are with palladium,^[3–12]

which despite having unsurpassed catalytic activity is less abundant and expensive. The metals like nickel^[13-15] and ruthenium^[16,17] are also employed which show good activity, but deters the green motive of catalysis by being environmentally less benevolent. In this context, the study and development of catalytic reactions promoted by inexpensive and environmentally benign metals is significant and perpetual research activity in the field of catalysis. In present work, we have considered the price of metals and cost of ligand synthesis which led us to focus our studies on the first-row transition metal complexes with a PNP-pincer ligand. Among the first-row transition metals, iron [18-29] and copper[30-35] are widely studied for their catalytic potential. The importance of these metals for developing catalysts is majorly due to their low cost and toxicity. Iron (II) PNP pincer complexes were synthesized and utilized for heterolytic cleavage of dihydrogen via metal-ligand cooperation.^[27] A new class

of iron hydride complexes bearing phosphinite-based pincer ligands was demonstrated as competent catalysts for the hydrosilylation of aldehydes and ketones with different functional groups.^[28] Copper and copper/noble metal combination nanoclusters were found to be active catalysts in the Suzuki cross-coupling of various aryl halides with phenylboronic acid.^[31] Iron(II) complexes bearing tridentate PNP pincer ligands were employed as catalysts for the selective formation of 3-hydroxyacrylates from aromatic aldehydes and ethyldiazoacetate.^[36] Iron(II) complexes of the types [Fe(PNP)Br₂] and [Fe(PNP)(CO)Br₂] with PNP pincer ligands based on triazine and pyridine backbones were tested as catalysts for the alkylation of amines by alcohols.^[37] Fe(II) complexes stabilized by a PNP ligand based on the 2.6-diaminopyridine scaffold were reported to efficiently couple the alcohols and amines.^[38] An air-stable, thermally robust, and well-defined Cu(I) PNP pincer complex based on 2.6-diaminopyridine which actively catalyzed the crosscouplings of a range of aryl and heteroaryl halides with different organomagnesium reagents, alkynes, and arylamines giving excellent to good isolated yields was also reported by the same group.^[39] However, PNP pincer complex with iron or copper as active metal center have not been reported for Suzuki coupling reactions. Therefore, here we report the catalytic activity of iron and copper based PNP pincer complexes in Suzuki coupling reactions.

2 | EXPERIMENTAL

2.1 | Materials

Iron(II) sulphate heptahydrate and copper(II) acetate monohydrate were purchased from Merck, India and used as received. 2,6-diaminopyridine, chlorodiphenylphosphine, phenylboronic acid, and aryl halides were purchased from Sigma-Aldrich and tetrahydrofuran (THF), triethylamine (Et₃N), acetonitrile (ACN) were purchased from Alfa-Aesar and used without further purification.

2.2 | Synthesis of $(N^2, N^6$ bis(diphenylphosphino)pyridine-2,6diamine) (ligand = L)

The ligand was synthesized as per the reported procedure ^[40] with certain modifications. In a typical synthesis process, triethylamine (1.85 g, 18.3 mmol) was dissolved in THF (20 ml) with 2,6-diaminopyridine (1 g, 9.2 mmol). The mixture was cooled to 0 °C followed by drop wise addition of chlorodiphenylphosphine (4.04 g, 18.3 mmol) under stirring. The solution was brought to room

temperature and refluxed overnight. The solution was then filtered, washed with anhydrous hexane $(2 \times 10 \text{ ml})$, and the solvent was removed under vacuum to afford orange colored crude ligand. The crude compound was purified by column chromatography and pure ligand (**L**) was obtained as white solid (Figure 1).

Yield: 87.2%. Melting point: 152°C.

¹H NMR (400 MHz, CDCl₃) δ 7.82–7.62 (m, 9H), 7.61–7.54 (m, 3H), 7.53–7.40 (m, 8H), 7.40–7.27 (m, 3H), 3.78–3.49 (br s, 2H, NH) (Supplementary Information Figure S1).

 $^{31}P{^{1}H}MR$ (161.8 MHz, DMSO): δ (ppm) 25.46 (s, PN) (Supplementary Information Figure S2).

MS-ESI: (m/z): 478.4 (Supplementary Information Figure S3).

Elemental analysis calculated for $C_{29}H_{25}N_3P_2$ ($M_r = 477.1$): C, 72.95; H, 5.28; N, 8.80. Found: C, 72.15; H, 5.03; N, 8.56%.

2.3 | Synthesis of [Fe(L)SO₄]and [Cu(L) OCOCH₃] pincer complexes (C-1 and C-2)

The prepared ligand (0.5 mmol) was taken in dry THF and refluxed with 0.5 mmol of $FeSO_4.(H_2O)_7$ (0.5 mmol) and $Cu(OCOCH_3)_2.H_2O$ (0.5 mmol) in separate round bottom flasks for 4 h, respectively. The obtained precipitates were decanted and washed with dry ether followed by filtration and drying at 50 °C in a vacuum oven for 4 h to obtain complexes C-1 and C-2, respectively (Figure 2).

2.3.1 | $[Fe(SO_4){C_5H_3N-2,6-(NHPPh_2)_2}](C-1)$

Yield: 80.9%.

MS-ESI: (m/z): 630.3 $[M]^+$ ((Supplementary Information Figure S4).



FIGURE 1 Synthesis of ligand, L





Elemental analysis calculated for $C_{29}H_{25}FeN_3O_4P_2S$ (M_r = 629.1): C, 55.34; H, 4.00; N, 6.68. Found: C, 55.15; H, 3.92; N, 6.51%.

2.3.2 | [Cu(OCOCH₃)₂{C₅H₃N-2,6-(NHPPh₂)₂]](C-2)

Yield: 75.3%.

MS-ESI: (m/z): 659.5 $[M]^+$ (Supplementary Information Figure S5).

Elemental analysis calculated for $C_{33}H_{31}CuN_3O_4P_2$ ($M_r = 658.1$): C, 60.13; H, 4.74; N, 6.38. Found: C, 59.85; H, 4.47; N, 6.12%.

2.4 | General procedure for the Suzuki reaction

The prepared pincer complex (C-1/C-2) were added to the mixture of phenylboronic acid (1.3 mmol) and a base in a dry solvent (5 ml) and allowed to stir for 30 min. Aryl halide (1.0 mmol) was added slowly to the mixture and refluxed for the reaction to complete. The progress of the reaction was monitored by thin layer chromatography and gas chromatography. The completed reaction was cooled to room temperature and the organic phase was decanted and washed with 1.5 N HCl and brine solution followed by drying with sodium sulphate, and concentrated to obtain a crude product. The crude product obtained was purified using column chromatography.

2.5 | Characterization methods

The C, H and N contents of the compounds were determined by Thermoflash EA1112 series elemental analyzer. Magnetic susceptibility measurement was recorded on a Sherwood Scientific magnetic susceptibility balance (UK). TGA was carried out from room temperature to 700 °C at a heating rate of 10 °C/min on EXSTAR-6000. The UV-Vis spectrum of the complex was recorded using Analytik Jena SPECORD S600. FT-IR spectra were recorded on a Bruker-Alpha ECO-ATR FTIR spectrometer. ¹H NMR (400 MHz) spectrum was recorded in Bruker AV 400 using TMS as an internal standard. ³¹P{¹H} NMR (161.8 MHz) spectrum was recorded in VARIAN using H₃PO₄ as an internal standard. The molecular mass of the compounds was determined using a Waters Q-TOF micro mass spectrometer with an ESI source. The coupling reaction product analysis was carried out using Gas Chromatography (GC) (Shimadzu 2014, Mangalore, Japan) with siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector. Nitrogen was used as the carrier gas.

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3 | RESULTS AND DISCUSSION

3.1 | Characterization studies

The following section describes the confirmation of the prepared pincer complexes by using different analytical techniques like FTIR, UV-Vis, magnetic susceptibility and TGA. Figure 3 (a) represents the FTIR spectra of the complexes C-1 and C-2 in comparison with the ligand and 2,6-diaminopyridine (precursor for ligand synthesis). The significant decrease in the characteristic N-H stretching peak from the starting material to the ligand indicates the formation of N-P bond at the expense of N-H bond. It is further confirmed by the presence of doublet in the 690-740 cm⁻¹ region of spectra of ligand and complexes which is characteristic to the P-N stretching^[41] and P-C stretching^[42], respectively. Figure 3 (b) is the fingerprint region of the spectra within 1600–400 cm^{-1} and shows the evidence of metal-N bond formation. Stretching peak at 491 cm⁻¹ in C-1 is due to the Fe-N bond stretching and at 479 cm^{-1} in C-2 is because of the Cu-N bond stretching.^[43]

To further confirm the complex formation, UV–Vis spectra was examined for the complexes, C-1 and C-2 in comparison to the ligand (L) as shown in Figure 4. From



FIGURE 3 FTIR spectra of ligand and complexes C-1 and C-2: (a) at 4000–400 cm⁻¹ (b) 1600–400 cm⁻¹



FIGURE 4 12UV-vis spectrum of ligand and complexes C-1 and C-2

the spectra, it is observed that the ligand has broad absorption bands at 204 nm, 264 nm, and 289 nm. On complexation, the spectra showed a red shift in absorption peak from 204 nm to 213 nm in C-1 and to 208 nm in C-2. Also a decrease in intensity of ligand peak at 264 nm is observed for both C-1 and C-2 and the absorption at 289 nm in the ligand have intensified with red shifts in both the complexes. New peaks appear for the complexes, C-1 and C-2 at 331 nm and 338 nm respectively. Bathochromic shift observed from the free ligand to the complexes indicates a charge transfer phenomenon and it can be inferred that the transitions observed in the spectra are majorly due to intra-ligand charge transfer transitions (ILCT) and ligand to metal charge transfer transitions (LMCT). A small and broad peak at 655 nm in C-2 spectra signifies a possible d-d transition for the Cu complex.

The magnetic susceptibility measurement shows that the complex C-1 is paramagnetic at room temperature with magnetic moment value of 2.97 BM supporting the formation of Fe(II) complex.^[44] Complex C-2 also showed paramagnetic behavior with the magnetic moment of 1.77 BM indicating a Cu(II) complex.

To determine the thermal behavior and stability of the complexes, TGA analysis was performed from room temperature to 700 °C at a heating rate of 10 °C/min. The TGA results of C-1 and C-2 complex are represented in Figure 5. Thermogram of C-1 shows the thermal decomposition around 500 °C in a single step process which is attributed to the excellent thermal stability expected of a pincer complex. Thermogram of C-2 represents a two-step dissociation, wherein the first dissociation begins at 130°C and continues up to 230°C showing a cumulative weight loss of about 22%, constituting the dissociating acetate ligands along with water of crystallization. The dissociating pattern infers that among the



FIGURE 5 TGA curves of the complexes C-1 and C-2

two complexes, C-1 (Fe pincer complex) is stable at relatively lower temperature and likely to possess better efficiency as a catalyst.

3.2 | Catalytic activity studies

The catalytic efficiency of the prepared complexes was examined for the Suzuki coupling reaction. The study included the reaction between aryl halides with phenyl boronic acid in presence of a base, solvent and prepared C-1 and C-2 pincer complex as catalyst. To achieve high catalytic efficiency, yield and optimized reaction conditions, various factors including solvent, catalyst loading, alkalinity, temperature, and time were optimized. The reaction between 4-bromobenzonitrile and phenyl boronic acid was selected as a model reaction to evaluate the catalytic activity of the pincer complexes.

The solvent effect was examined for the reaction. The most commonly used solvents in Suzuki coupling reactions like ethanol, 1,4-dioxane, toluene, and acetonitrile were screened for the selection of optimized solvent. The time taken for the completion of reaction with selected solvents are represented in Figure 6 (a, b) for C-1 and C-2 complexes respectively. From the figure, it is observed that the pincer complex with ACN shows greater catalytic efficiency and higher reaction yield than toluene and ethanol, which can be attributed to the coordinating nature of the ACN in the reaction process and easy miscibility of reactants and the catalyst ^[45]. Even though there is no significant difference observed in the reaction yield and reaction time for ACN and dioxane as a solvent, the lower reflux temperature of ACN makes it suitable solvent for the catalyzed reaction.

The reaction was also optimized for efficient usage of the base in the reaction. In this context, we investigated the Suzuki coupling reaction with the use of Cs_2CO_3 .



FIGURE 6 Effect of solvent on (a) C-1, (b) C-2

Et₃N, K₂CO₃, Na₂CO₃ and KO^tBu in ACN solvent. The different bases produced different yields as represented in Table 1. From the results, it is observed that Cs₂CO₃ provide better yield than other bases used in the study which can be attributed to the ability of the base to easily donate its carbonate ion for replacement of the halide ion in the oxidative addition step of the catalytic cycle ^[46]. The C-1

TABLE 1 Study of effect of base on Suzuki coupling of 4-bromobenzonitrile and phenyl boronic acid using catalyst C-1 andC-2

			Yield (%) ^a	
Entry	Solvent	Base	C-1	C-2
1	ACN	Na ₂ CO ₃	74.8	65.1
2		K ₂ CO ₃	81.8	71.2
3		Cs_2CO_3	89.9	76.1
4		KO ^t Bu	66.7	58.0
5		Et ₃ N	82.4	71.7

Reaction conditions: 4-bromobenzonitrile (1.0 mmol), phenylboronic acid (1.3 mmol), base (2.0 mmol), catalyst (0.5 mol %), solvent (5.0 ml), 16 h. ^aGC yields



catalyzed reaction yields 89.9%, whereas C-2 yields 76.1% of the product. Hence among the different bases employed in the Suzuki reaction, Cs_2CO_3 was considered as a suitable base to achieve enhanced catalytic efficiency and greater yield.

To study the effect of the concentration of catalyst, the reaction was studied under optimized conditions of ACN as solvent and Cs_2CO_3 as a base, in the presence of different amount of catalyst. Figure 7 shows the yield vs. catalyst load study where the catalyst loads was varied from 0.1 mol% to 1.0 mol%. From the figure, it is observed that the increase in catalyst loading linearly increases the coupling yield, suggesting that the amount of catalyst plays a crucial role in yield of the reaction. When the catalyst load reaches 0.4 mol% and 0.6 mol% for C-1 and C-2 respectively, the maximum conversion was observed. However, with further raise in the catalyst load, there was no significant contribution to the product yield. Thus, from the obtained results, we considered 0.4 mol% of the catalyst load.

Effect of reaction time on the catalytic activity was studied by analyzing the reaction aliquots at regular intervals of time. Figure 8 shows GC yield vs. time taken to complete the reaction in presence of C-1 and C-2 catalyst. From the figure, it is observed that with optimized conditions like catalyst concentration, alkalinity, and solvent, the C-1 shows maximum yield after 14 h as compared to 16 h for C-2. However, further raise in the reaction time does not contribute much to the increase in product yield and the graph shows almost steady-state yield. Thus, 14 h and 16 h are the optimized reaction time for C-1 and C-2 catalysts respectively.

Further, all reactions between substituted aromatic halides and phenylboronic acid were carried out with the optimized conditions like Cs_2CO_3 base, ACN solvent, 0.4 mol% of C-1 with a reaction time of 14 h and



FIGURE 7 Effect of catalyst loading on reaction



FIGURE 8 Effect of reaction time on C-1 and C-2

0.6 mol% of C-2 with a reaction time of 16 h respectively. The coupling reaction results are summarized in Table 2. From the tabulated results, it is observed that electron donating substituents rather slowed the cross-coupling process, whereas the electron withdrawing substituents were found to significantly increase the coupling efficiency. Among the aryl halides, 4-iodobenzonitrile showed maximum GC conversion of 96.0% for C-1 and 83.0% for C-2. The result conveys that the leaving capacity of iodide group is better among the halides.

Within the two catalysts employed in this study, observed conversion rate was relatively high for C-1 which is a Fe-based complex. The enhanced and ready

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R - K + B(OH)2 catalyst C-1 / C-2 Acetonitrile							
			Yield (%) ^a	Yield (%) ^a			
Entry	Х	R	C-1	C-2			
1	Br	Н	64 (56.5)	51			
2		CN	92 (84.4)	79			
3		OCH ₃	79 (69.3)	69			
4		$COCH_3$	89 (76.3)	76			
5		NHCOCH ₃	87 (80.2)	77			
6		F	42 (34.0)	37			
7		CH_3	65 (56.4)	53			
8	Ι	ОН	78 (70.0)	69			
9		CN	96 (89.6)	83			
10	Cl	СНО	74 (66.8)	64			

Reaction conditions: Aryl halide (1.0 mmol), Phenylboronic acid (1.3 mmol), Cs₂CO₃ (2.0 mmol), catalyst (C-1 - 0.4 mol%, 14 h / C-2 - 0.6 mol%, 16 h), solvent (5.0 ml),

^aGC yields, average of 3 trials (Isolated yield).

participation of the Fe in the rate determining oxidative addition step can result in the formation of a more stable intermediate compared to that in the case of Cu based C-2 catalyst. This is because, during reduction of the precatalyst to its catalytically active form, C-1 will lose its sulphate group, and in the oxidative addition step it further acquires Fe(II) state which is a stable oxidation state of iron. Thus, a stable intermediate is formed by the oxidative addition process. However, Cu in C-2 may lose a single acetate ion to form Cu(I) state or both the acetate ions to form active Cu(0) species ^[47]. Considering this, the formation of less stable Cu(III) intermediate in the oxidative addition cycle along with the stable Cu(II) intermediate state is possible. This largely explains the lower coupling yield shown by the C-2 complex in this study.



FIGURE 9 Proposed mechanism for the coupling reaction with C-1 and UV-vis spectra supporting the formation of active catalyst (b)

3.3 | Proposed mechanism

Inference of catalysis mechanism for metal catalyzed C-C coupling reaction needs a thorough understanding of the process. In Figure 9, we attempt to provide a mechanistic insight of the catalysis cycle for complex C-1 which is showing enhanced coupling activity among the two complexes reported. Catalytically active Fe(II) metal component (a) complex gets reduced to Fe(0) in the presence of a base and phenylboronic acid (**b**). This is followed by the oxidative addition to aryl halide which leads to the formation of R^2 -Fe(II) intermediate (c). Further, in presence of the base Cs₂CO₃, the nucleophilic substitution of the halide group and transmetallation takes place between phenylboronic acid and R^2 -Fe(L)-CO₃(**d**) which would result in the formation of biaryl R^1 -Fe(L)- $R^2(\mathbf{e})$ species. Finally, there is the reductive elimination of biaryl as product, and Fe(0) species is regenerated to continue the catalytic cycle.

The conversion of pre-catalyst (a) to the active catalyst (b) via a reduction process in the reaction condition is further confirmed by the UV–Vis spectroscopy. Absorption spectra were obtained with the reaction mixture as a reference. The spectra were recorded when the catalyst was added to the reaction and at an intermediate stage i.e.7 h of reaction. A sharp peak at 280 nm appears on both the spectra is associated to Fe(II) state of precatalyst (a). Additionally, a small and broad peak is observed in the spectrum of the intermediate stage at 352 nm which corresponds to the formation of Fe(0) state (b) that is the active catalyst in the coupling reaction.

4 | CONCLUSIONS

In view of the current use of expensive Pd catalyst for cross-coupling reactions, an attempt was made to synthesize more economical transition metal (Fe and Cu) based pincer complexes as an alternative catalyst. Various molecular characterizations showed the successful synthesis of the desired pincer complexes and TGA reflected upon their excellent thermal stability. Moreover, the effect of reaction parameters like solvent, alkalinity, reaction time, and catalyst loading suggested that among the tested factors, the cross-coupling reaction showed better performance in ACN solvent with Cs₂CO₃ base and a reaction time of 14 h and 16 h for 0.4 mol% C-1 and 0.6 mol% C-2 catalysts respectively. Fe-based C-1 pincer complex shows superior catalytic activity over Cu-based C-2 complex because, in the rate determining oxidative addition step, more stable Fe(II) coordinated intermediate is formed in C-1 as compared to the less stable Cu(III) interfering in the metal coordinated intermediate in case of C-2 as catalyst. We further conclude that synthesized transition metal PNP pincer complex can be a viable alternative to the more commonly used Pd catalysts in the cross-coupling reactions.

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SUPPORTING INFORMATION

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