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Synthesis, characterization and catalytic study of Schiff base copper(I) complexes for the amination of aryl halide

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ABSTRACT

A series of Schiff base copper(I) complexes $[Cu(L_1)(PPh_3)_2]X$ (**1a**-**d**) and $[Cu(L_2)(PPh_3)_2]X$ (**2a**-**d**) [where L₁ - (3-trifluoromethyl-phenyl)-pyridine-2-ylmethylene-amine and L₂ - 2-chloro-(5-trifluoromethyl-phenyl)-pyridine-2-ylmethylene-amine); $X = CI^-$, CN^- , CIO_4^- and BF_4^-] have been synthesized by the reaction of 3-aminobenzotrifluoride and 3-amino-4-chlorobenzotrifluoride with 2-pyridinecarboxaldehyde followed by the reaction with $[Cu(MeCN)_2(PPh_3)_2]CI$, $[Cu(MeCN)_2(PPh_3)_2]CN$, $[Cu(MeCN)_2(PPh_3)_2]CIO_4$ and $[Cu(MeCN)_2(PPh_3)_2]BF_4$. The Schiff base ligands L₁, L₂ and complexes **1a**-**d** and **2a**-**d** were then characterized by elemental analysis, IR, UV-visible and ¹H NMR spectral studies. The catalytic activity of these complexes was tested and it was found that all the complexes worked as active catalyst for the amination of iodobenzene at low temperature.

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The amination of aryl halide by transition metal catalyzed coupling methodology has been the subject of significant interest during past few decades [1-5]. This method involves production of arylamines by coupling of aryl halides and amines with stoichiometric amount of transition metal ions. Arylamines are attractive targets for chemical synthesis because of their wide utility in fine chemicals, dyes and polymers. These are important components in many biologically active natural products, medicinally important compounds as well as in materials with useful electrical and mechanical properties [6–10]. Traditionally, the most common way to access these compounds is Pd-catalyzed C-N coupling of amines and aryl halides [11-14]. However, the cost of reagents, removal of trace palladium from late stage synthetic intermediate, and difficulties in coupling of electron-rich or ortho-substituted aryl halides are the major drawbacks of this method. Copper mediated N-arylation is another choice of reaction for the production of these compounds due to cheap price and environmental friendly nature. Therefore, copper mediated Ullmann condensation is powerful method for coupling of aryl halide and amines in spite of necessity of using highly polar solvents, high temperature and large amount of copper reagents [15,16]. Many organic compounds such as 1,10-Phenanthroline [17], trans-1,2-cyclohexanediamine [18-20], diols [21,22], amino acid [23-25] and other nitrogen-oxygen containing compounds [26–29] together with copper reagents have also been studied extensively. However, only few papers have been contributed to the use of copper complexes as catalysts for this carbon-nitrogen bond forming process [30,31].

In this paper, we report synthesis of two different Schiff base ligands (3-trifluoromethyl-phenyl)-pyridine-2-ylmethylene-amine (L_1) and 2-chloro-(5-trifluoromethyl-phenyl)-pyridine-2-ylmethylene-amine (L_2). Subsequently they were coordinated to copper(I) by reaction with [Cu(MeCN)₂(PPh₃)₂]Cl, [Cu(MeCN)₂(PPh₃)₂]CN, [Cu(MeCN)₂(PPh₃)₂]ClO₄ and [Cu(MeCN)₂(PPh₃)₂]BF₄ to form eight copper(I) mixed ligand complexes **1a–d** and **2a–d** (Scheme 1). The complexes prepared were characterized on the basis of elemental analysis, IR, UV–vis and ¹H NMR spectral studies. The catalytic performance of the Schiff base copper(I) complexes in the amination of iodobenzene in solvent toluene at 90 °C (Scheme 2) have also been discussed.

The elemental analysis and spectral data of the ligands L_1 , L_2 [32] and their copper(I) complexes [34] are listed in Table 1.

The C, H, N and selected spectroscopic data presented in Table 1 confirm the assigned composition of the ligands and complexes. A strong band observed at 1620 cm⁻¹ in **L**₁ and 1624 cm⁻¹ in **L**₂ is a characteristic band of azomethine (HC=N) group. The shifting of this band towards lower frequency region by $25-30 \text{ cm}^{-1}$ in complexes indicates involvement of azomethine nitrogen in coordination with metal ion [35,36]. The characteristic band observed at around 997 cm⁻¹ in ligands L₁ and L₂ is associated with the pyridine ring breathing mode of vibrations. On complexation this band observed to higher energy at around 1020–1026 cm⁻¹ in the complexes indicating copper-nitrogen bond formation [37]. This view was further supported by appearance of a band at around 480 cm^{-1} in the complexes due to v(Cu–N) stretching mode of vibrations. The IR spectra of all the copper(I) complexes shows strong phosphine bands at around 1434, 742, 692, 506 cm⁻¹ as expected. The medium intensity band observed at around 2108 cm⁻¹ in **1b** and **2b** corresponds to CN⁻ anion. A strong band observed at

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 $R = H, Cl; X = Cl^{-}, CN^{-}, ClO_{4}^{-}, BF_{4}^{-}$

Scheme. 1. Synthetic route of Schiff base ligands and Cu(I) complexes.



R=H, Br, OMe

Scheme. 2. Amination reaction catalyzed by Cu(I) complexes.

around 1093 cm⁻¹ in complexes **1c** and **2c** indicating existence of ClO_4^- anion. However, a broad band observed at around 1094 cm⁻¹ in **1d** and **2d** corresponds to BF₄⁻anion in respective complexes [38].

The ¹H NMR spectra of the Schiff base ligands in CDCl₃ exhibit as a singlet at δ 8.10 ppm in L₁ and δ 8.60 ppm in L₂ assigned to

Microanalvtical	and	spectral	data o	f Schiff	bases	and	their	Cu(I)	complexes.

Table 1

azomethine (HC=N) proton. The downfield shift of this resonance in Cu(I) complexes relative to the free ligands can be attributed to deshielding effect resulting from coordination of the ligands [39]. The proton resonance of coordinated ligands is commonly observed in complexes **1a-d** and **2a-d**. The resonances of aromatic protons of the coordinated Ph₃P ligands overlap to some extent with those of phenyl hydrogen atoms of L₁ and L₂ in complexes. However, the ring proton peaks observed at δ 6.80–8.50 ppm in L₁ and δ 6.32–8.67 ppm in L₂ shows slight downfield shift in their respective complexes.

The electronic absorption spectra of the ligands and corresponding complexes were recorded in dichloromethane. In absorption spectra of free ligands, a band observed at 329 nm ($\epsilon = 7.6 \times 10^3 \, M^{-1} \, cm^{-1}$) in L_1 and 326 nm ($\epsilon = 7.50 \times 10^3 \, M^{-1} \, cm^{-1}$) in L_2 are due to $\pi - \pi^*$ transition of heterocyclic and its conjugate system. In the spectra of complexes, no d-d transitions are expected for d¹⁰ complexes; the UV-visible band observed at ~398 nm assigned to metal to ligand charge transfer (MLCT) or ligand centered $\pi - \pi^*$ transition [40].

The scope of copper(I) complex catalysts (1a-d, 2a-d) for the amination of aryl halide was explored by coupling reaction of iodobenzene with primary amines using KOt-Bu as base in solvent toluene at 90°C. Under this experimental condition [41], the purified product obtained was characterized by elemental analysis, IR, ¹H NMR and mass spectral studies (Table 2). When no catalyst was added, the blank reaction with solvent toluene and KOt-Bu as base exhibited extremely low reactivity towards the yield of triarylamine with many byproducts from aryl halide substrate. The effect of complex catalysts such as **1a-d** and **2a-d** on the amination of iodobenzene was investigated and it was found that the copper(I) complex catalysts significantly enhance the conversion of iodobenzene into desired amination product. The catalytic efficiency was compared with the previously reported [42] similar copper(I) complexes. It has been found that all reactions were smoothly carried out at relatively low temperature and reached the amination vield up to 45–69% (Table 3). No further increase in the vield of the amination product was observed even when the reaction time was increased for a longer time. With *p*-bromoaniline containing electron withdrawing group at para position, the amination yield was observed up to 45-62% (Table 3, entries 9-12 and 21-24). However, with *p*-anisidine containing electron donating group at *para* position, the amination reaction proceeds with considerable increase

	C, H, N found (calculated)			IR (cm ⁻¹)	UV-vis $\lambda_{max}~nm~(\epsilon\times 10^3,M^{-1}~cm^{-1})$	¹ H NMR (δ ppm)
	С	Н	N			
L ₁	62.38 (62.40)	3.65 (3.63)	11.25 (11.20)	1620, υ(HC=N)	284 (9.6), 294 (9.7), 329 (7.6)	6.80-8.50 (m, Ar-H), 8.10 (s, HC=N)
1a	67.65 (67.35)	4.48 (4.50)	3.25 (3.21)	1590, υ(HC=N); 1434, 743, 694, 516, υ(PPh ₃)	290 (13.7), 298 (9.8), 398 (1.3)	6.99–8.60 (m, Ar–H), 9.20 (s, HC=N)
1b	69.30 (69.48)	4.61 (4.55)	4.82 (4.86)	1590, υ(HC=N); 1434, 742, 693, 506, υ(PPh ₃); 2108, υ(C=N)	286 (13.7), 308 (9.7), 402 (1.1)	7.00–8.60 (m, Ar–H), 9.20 (s, HC=N)
1c	62.71 (62.76)	4.44 (4.19)	3.46 (2.98)	1590, υ(HC=N); 1435, 743, 694, 516, υ(PPh ₃); 1093, υ(ClO ₄)	290 (13.5), 300 (9.4), 394 (1.4)	6.99–8.60 (m, Ar–H), 9.20 (s, HC=N)
1d	63.71 (63.61)	4.38 (4.25)	3.10 (3.03)	1590, υ(HC=N); 1434, 742, 694, 506, υ(PPh ₃); 1094, υ(BF ₄)	288 (13.0), 310 (9.4), 392 (1.3)	7.00–8.62 (m, Ar–H), 9.20 (s, HC=N)
L ₂	54.99 (54.85)	2.81 (2.83)	9.70 (9.84)	1624, υ(HC=N)	286 (9.6), 298 (8.8), 326 (7.5)	6.32–8.67 (m, Ar–H), 8.60 (s, HC=N)
2a	64.66 (64.80)	4.52 (4.22)	3.25 (3.08)	1585, υ(HC=N); 1435, 744, 694, 517, υ(PPh ₃)	284 (12.2), 296 (9.5), 396 (1.8)	7.19–8.67 (m, Ar–H), 9.26 (s, HC=N)
2b	67.01 (66.82)	4.18 (4.26)	4.81 (4.68)	1586, υ(HC=N); 1435, 744, 694, 517, υ(PPh ₃); 2108, υ(C=N)	280 (13.0), 304 (9.5), 404 (1.1)	6.80–8.80 (m, Ar–H), 9.20 (s, HC=N)
2c	60.80 (60.53)	4.02 (3.94)	2.91 (2.88)	1586, υ(HC=N); 1435, 744, 694, 517, υ(PPh ₃); 1094, υ(ClO ₄)	294 (13.1), 304 (9.4), 398 (1.4)	6.80–8.80 (m, Ar–H), 9.30 (s, HC=N)
2d	60.87 (61.33)	4.47 (3.99)	3.89 (2.92)	1586, υ(HC=N); 1435, 744, 694, 517, υ(PPh ₃); 1093, υ(BF ₄)	284 (13.3), 308 (9.4), 394 (1.3)	6.90–8.79 (m, Ar–H), 9.20 (s, HC=N)

Table 2						
Microanalytical a	and sp	ectral	data d	of amina	tion	product

Compound	C, H, N found (calculated)		$IR (cm^{-1})$	Mass	¹ H NMR (δ ppm)	
	С	Н	Ν			
N, N-diphenyl-aniline 4-methoxy N, N- diphenyl-aniline 4-bromo-N, N- diphenyl-aniline	87.83 (88.13) 82.19 (82.88) 67.05 (66.68)	6.31 (6.16) 6.33 (6.22) 4.18 (4.35)	5.39 (5.71) 5.89 (5.09) 4.51 (4.32)	1586, 1493,1461 1586, 1490, 1461 1586, 1493, 1461	<i>m</i> / <i>z</i> 245 [(Ph) ₃ N] ⁺ , 168 [(Ph) ₂ N] ⁺ ,77 [Ph] ⁺ <i>m</i> / <i>z</i> 275 [(Ph) ₃ N–OCH ₃] ⁺ , 245 [(Ph) ₃ N] ⁺ , 168 [(Ph) ₂ N] ⁺ , 77 [Ph] ⁺ <i>m</i> / <i>z</i> 323 [(Ph) ₃ NBr] ⁺ , 245 [(Ph) ₃ N] ⁺ , 168 [(Ph) ₂ N] ⁺ , 77 [Ph] ⁺	$\begin{array}{l} \delta \ 6.09-6.39, (m, Ar-H) \\ \delta \ 3.86, (s, 3H, OMe), \delta \ 6.79- \\ 7.87, (m, Ar-H) \\ \delta \ 6.91-7.32, (m, Ar-H) \end{array}$

Table 3

Amination reaction catalyzed by Cu(I) complexes.



Reaction conditions: Ph–I, 8 mmol; aryl amine, 4 mmol; Cu(I) catalyst, 0.05 mmol; KOt–Bu, 12 mmol; Toluene, 20 ml; temperature 90 °C; reaction time 12 h.

in the yield up to 60–69% (Table 3, entries 5–8 and 17–20). These results confirmed that the variety of functional groups such as bromo and methoxy tolerated on aryl amine component under the reaction conditions and significant electronic effect was observed for substituted aryl amine containing electron donating group at *para*-position [43].

It was also observed that the efficiency of copper(I) catalyst with different counter anions exhibit different activities. It is evident that the copper(I) complex catalysts containing ClO_4^- anion shows greater activity than the complexes with Cl^- , CN^- , BF_4^- and reached the amination yield up to 60–69% (Table 3, entries 3, 7, 11, 15, 19, 23). It was also found that the catalytic activity of copper(I) complexes decreases in the order of $ClO_4^- > BF_4^- > CN^- > Cl^-$ as their counter anions. These results could be due to

difference in coordination ability of CI^- , CN^- , BF_4^- and CIO_4^- with metal ion as well as difference in solubility of the complexes in solvent during the reaction. However, the mechanism and correlation between activity and structure of copper(I) complexes could not be completely elucidated from these results; we are still in the process of studying mechanism and future scope of this reaction in our laboratory.

In conclusion, several Schiff base copper(I) complexes have been synthesized by condensation of 3-aminobenzotrifluoride and 3-amino-4-chlorobenzotrifluoride with 2-pyridinecarboxaldehyde followed by the reaction with [Cu(MeCN)₂(PPh₃)₂]Cl, [Cu(MeCN)₂(PPh₃)₂]CN, [Cu(MeCN)₂(PPh₃)₂]ClO₄, [Cu(MeCN)₂-(PPh₃)₂]BF₄. The structure of Schiff base ligands L₁ and L₂ and their copper(I) complexes (**1a–d**; **2a–d**) were confirmed by means of elemental analysis, FTIR, UV-visible and ¹H NMR spectroscopy. The copper catalyzed C–N bond forming reaction of aryl halide have been carried out and it was found that all the complexes worked as active catalyst for the amination of aryl halide. Further, the differences in the structure among these complexes significantly influence the yield of the amination product.

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dichloromethane and stirred for 2 h at room temperature. The volume of solvent was reduced to 4 ml under vacuum. The pale brown coloured complexes were developed by diffusion of diethyl ether into the filtrate.

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