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Mixed-ligand complexes of copper(I) with Schiff base and triphenylphosphine: Effective catalysts for the amination of aryl halide

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ABSTRACT

Some copper(I) complexes of the type $[Cu(\mathbf{L})(PPh_3)_2]X$ (**1**–**4**) [where **L** = 2-chloro-(5-trifluoromethyl-phenyl)-pyridine-2-ylethylene-amine; $X = Cl^-$, CN^-, ClO_4^- and BF_4^-] have been prepared by the condensation of 3-amino-4-chloro-benzotrifluoride with 2-acetylpyridine followed by the reaction with $[Cu(MeCN)_2(PPh_3)_2]Cl$, $[Cu(MeCN)_2(PPh_3)_2]CN$, $[Cu(MeCN)_2(PPh_3)_2]ClO_4$ and $[Cu(MeCN)_2(PPh_3)_2]BF_4$. All the complexes **1**–**4** were characterized on the basis of elemental analysis, IR, UV–visible and ^1H NMR spectral studies. The representative complex of the compound **3** has been characterized by single crystal X-ray diffraction which reveals that the central copper(I) ion assumes highly distorted tetrahedral geometry. All the complexes worked as effective catalyst for the amination of aryl halide.

Aryl amines are attractive targets for chemical synthesis because of their prevalence and wide utility in fine chemicals, dyes and polymers [1–3]. These are important components in many biological active natural products, medicinally important compounds as well as in materials with useful electrical and mechanical properties [4–6]. High purity triarylamines find applications in xerographic photoreceptors as constituents of non linear optical chromophores useful in the design of integrated electro-optic switches and modulators, and as hole-transport materials for organic electroluminescent (EL) display devices [7]. They are found in biologically active compounds such as pharmaceuticals [8] and agrochemicals [9]. Aryl amines have also been employed as ligands for transition metals, and in design of conducting polymers and other electrochemically interesting materials [7]. This wide spread importance of arylamines has led to the development of many synthetic methodologies for the production of arylamines. Although the Pd-catalyzed amination of aryl halide has recently become the most important method for laboratory scale synthesis of arylamines; copper stands out as a convenient alternative to palladium catalysts, because copper salts are often cheap and environmentally benign. Many ligand systems such as amino acid [10], diamines [11], di-imines [12], aminoarenethiolate [13], phosphine [14,15] and other nitrogen, oxygen containing ligands [16–19] together with copper(I) reagents have been applied for the production of arylamines under mild condition.

As a continuation of our research on copper(I) catalyzed amination of aryl halide [20], we report herein synthesis of four mixed ligand copper(I) complexes **1**–**4** by the reaction of Schiff base ligand 2-chloro-(5-trifluoromethyl-phenyl)-pyridine-2-ylethylene-amine (**L**) with $[Cu(MeCN)_2(PPh_3)_2]Cl$, $[Cu(MeCN)_2(PPh_3)_2]CN$, $[Cu(MeCN)_2(PPh_3)_2]ClO_4$ and $[Cu(MeCN)_2(PPh_3)_2]BF_4$. All the compounds were characterized on the basis of elemental analysis, IR, UV–vis, ^1H NMR spectral studies and compound **3** also by X-ray crystallography. The catalytic performance of all the copper(I) complexes in the amination of bromobenzene has also been discussed.

The elemental analysis and spectral data of the ligand **L**[21] and its copper(I) complexes [23] are listed in Table 1. The CHN and spectral data presented in Table 1 confirm the assigned composition of the complexes. The IR spectrum of ligand **L** shows a strong band at $1622\ cm^{-1}$, which is a characteristic band of azomethine (>C=N) group. The shifting of this band towards the lower frequency region by $20–30\ cm^{-1}$ in complexes indicates involvement of azomethine (>C=N) nitrogen in coordination with metal ion [24]. Another characteristic band observed at $997\ cm^{-1}$ in **L** is associated with pyridine ring breathing mode of vibration. On complexation, this band observed to higher energy at around $1024–1028\ cm^{-1}$ in the complexes indicates copper–nitrogen bond formation. This view is further supported by the appearance of a band corresponding to the metal–nitrogen $\nu(Cu-N)$ stretching vibration at $\sim 482\ cm^{-1}$ in the complexes [25]. The spectra of all the copper(I) complexes show strong phosphine bands at around 1480, 1434, 669, $517\ cm^{-1}$ as expected. The medium intensity band observed at $2110\ cm^{-1}$ in **2** corresponds to CN^- anion. A strong band observed at $1095\ cm^{-1}$ in complex **3** indicates existence of ClO_4^- anion. However, a broad band at $1094\ cm^{-1}$ in **4** corresponds to presence of BF_4^- anion in the complex.

The electronic spectral data of copper(I) complexes (**1**–**4**) were recorded in CH_2Cl_2 (10^{-4} M). In the spectra of complexes, no d–d

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Table 1
Microanalytical and spectral data of Schiff base and its copper(I) complexes.

	C, H, N found (calculated)			IR (cm^{-1})	UV–vis λ_{max}/nm ($\varepsilon \times 10^3$/M^{-1}cm^{-1})	^{1}H NMR (δ ppm)
	C	H	N			
L	56.51 (56.29)	3.39 (3.37)	9.45 (9.38)	1622, υ(C═N)	261 (9.1), 290 (9.4), 329 (7.1)	2.24 (s, CH$_3$), 6.32–8.80 (m, Ar-H), 8.98(s, HC═N)
1	65.44 (65.12)	4.36 (4.37)	3.08 (3.04)	1590, υ(C═N); 1480, 1434, 669, 516, υ(PPh$_3$)	264 (15.66), 249 (9.70), 326 (0.83), 400 (0.53)	2.50 (s, CH$_3$), 6.38–8.85 (m, Ar-H), 9.18(s, HC═N)
2	67.53 (67.10)	4.39 (4.42)	4.62 (4.60)	1594, υ(C═N); 1480, 1434, 669, 517, υ(PPh$_3$); 2110, υ(C≡N)	262 (16.02), 288 (10.65), 319 (0.99), 402 (0.64)	2.52 (s, CH$_3$), 6.40–8.87 (m, Ar-H), 9.18(s, HC═N)
3	61.25 (60.89)	4.55 (4.09)	2.72 (2.84)	1595, υ(C═N); 1480, 1435, 669, 517, υ(PPh$_3$); 1095, υ(ClO$_4$)	264 (15.66), 294 (9.73), 326 (0.83), 400 (0.53)	2.50 (s, CH$_3$), 6.36–8.90 (m, Ar-H), 9.17(s, HC═N)
4	61.92 (61.68)	4.16 (4.14)	2.88 (2.87)	1603, υ(C═N); 1480, 1434, 669, 517, υ(PPh$_3$); 1094, υ(BF$_4$)	269 (16.45), 283 (9.32), 315 (1.13), 404 (0.84)	2.50 (s, CH$_3$), 6.38–8.84 (m, Ar-H), 9.18(s, HC═N)

Table 2
Selected bond lengths (Å) and bond angles (°) for [Cu(L)(PPh$_3$)$_2$]ClO$_4$ (**3**).

Bond lengths (Å)		Bond angles (°)	
Cu(1) – N (1)	2.053(6)	N(1) – Cu(1) – N(2)	78.5(2)
Cu(1) – N (2)	2.106(5)	N(1) – Cu(1) – P(1)	111.54(16)
Cu(1) – P (1)	2.259(19)	N(2) – Cu(1) – P(1)	119.24(16)
Cu(1) – P (2)	2.269(19)	N(1) – Cu(1) – P(2)	120.75(17)
Cu(2) – N (3)	2.051(6)	N(2) – Cu(1) – P(2)	106.36(15)
Cu(2) – N (4)	2.090(5)	P(1) – Cu(1) – P(2)	115.37(7)
Cu(2) – P (3)	2.228(2)	N(3) – Cu(2) – N(4)	78.4(2)
Cu(2) – P (4)	2.252(18)	N(3) – Cu(2) – P(3)	113.79(16)
		N(4) – Cu(2) – P(3)	120.11(16)
		N(3) – Cu(2) – P(4)	108.17(15)
		N(4) – Cu(2) – P(4)	110.09(15)
		P(3) – Cu(2) – P(4)	118.90(8)

transitions are expected for d^{10} complexes, the UV–visible band observed at 402 nm assigned to metal to ligand charge transfer (MLCT) or ligand centered π–π* transition [26]. The absorption bands observed below 400 nm in all the complexes are attributed to ligand-centered π–π* and n–π* transitions.

The ^{1}H NMR spectra of all the complexes (Table 1) indicate that the resonances of aromatic protons of the coordinated PPh$_3$ ligands overlap to some extent with those of phenyl hydrogen atoms of **L** in the complexes. However, the ring proton peaks observed at δ 6.32–8.80 ppm in **L** show slight downfield shift in its complexes. The methyl proton of azomethine group appears as a singlet at δ 2.50–2.52 ppm in all the complexes. The downfield shift of imine protons relative to free ligand **L** can be assigned to deshielding effect resulting from the coordination of azomethine nitrogen [27].

The structure of the complex **3** was determined by X-ray single crystal analyses at room temperature [28]. The selected bond lengths and bond angles are given in Table 2. However, more details including those of crystal data and structural refinements are available on-line as supplementary material. The complex **3** crystallizes in triclinic system with two molecules per asymmetric unit probably due to some small conformational differences and is shown in Fig. 1.

The structure can be described as formed by a cationic complex molecule with a perchlorate as a counter ion and the copper(I) ion coordinates to two triphenylphosphine and a bidentate Schiff base ligand **L** in its neutral form. In the monomeric complex, the copper(I) exhibits highly distorted tetrahedral geometry arising from the intra-ligand chelate angles N(1) – Cu(1) – N(2) in I and N(3) – Cu(2) – N(4) in II, are much less than 109.4°, being 78.5(2) and 78.4(2)°, respectively. However, the P(1) – Cu(2) – P(2) angle 115.37(7)° in I and the P(3) – Cu(2) – P(4) angle 118.90(8)° in II, have opened up due to the steric effects from the bulky PPh$_3$ ligands. The average Cu – N (2.052 Å) and Cu – P (2.251 Å) bond distances are comparable to those reported for [Cu(A)(PPh$_3$)$_2$]ClO$_4$ (2.098 and 2.251 Å) [30].

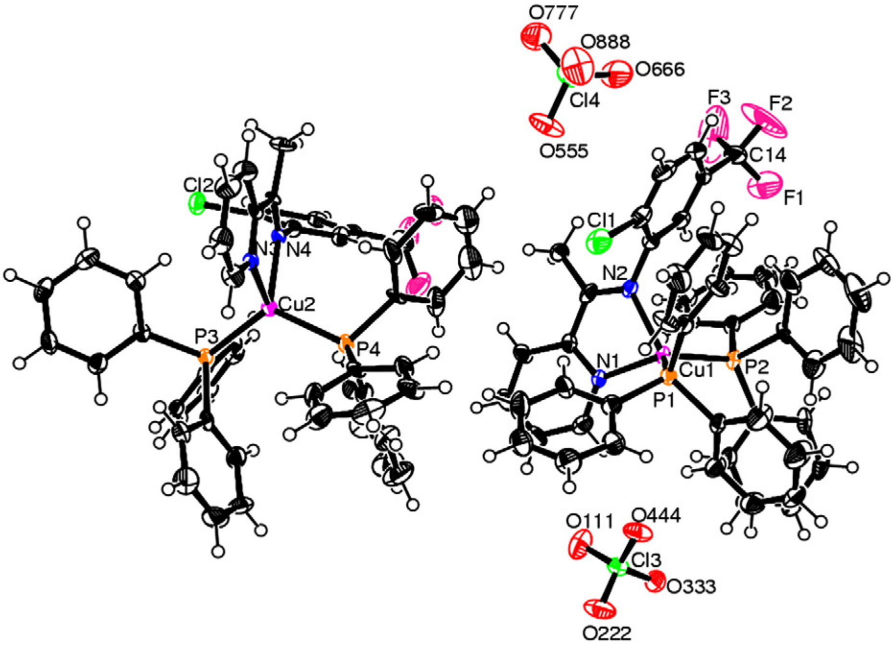
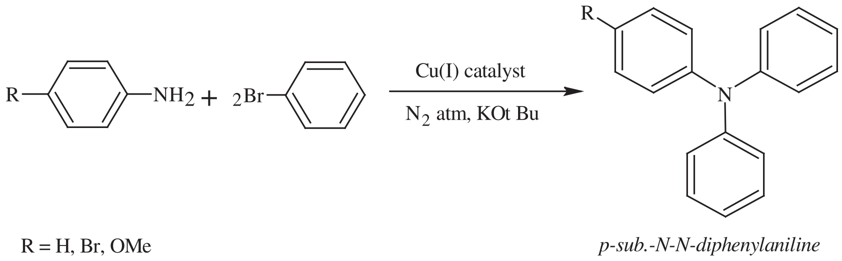


Fig. 1. Single crystal X-ray diffraction structure of [Cu(L)(PPh$_3$)$_2$]ClO$_4$ (**3**).



Scheme 1. Amination reaction catalyzed by copper(I) complexes.

The copper(I) complexes (**1**–**4**) have been found promising for catalyzing the amination of bromobenzene [31] by coupling reaction with different primary amines in toluene at 90 °C in presence of KOt – Bu as base (Scheme 1). The effect of complex catalysts (**1**–**4)** on the amination of bromobenzene was investigated and it was found that copper(I) complexes significantly enhance the conversion of bromobenzene into desired amination product in moderate to good yield. The catalytic efficiency was compared with the previously reported [20] similar copper(I) complexes and it has been found that all reactions were smoothly carried out at relatively low temperature and reached the amination yield up to 45–69% (Table 3). No further increase in the yield of the product was observed even when the reaction time was increased for a longer time.

It was observed that the catalytic amination of bromobenzene with aniline reached the amination yield up to 52–71% (Table 3, entries 1–4). With *p*-bromoaniline containing electron withdrawing group at *para* position, the amination reaction yield was observed up to 48–65% (Table 3, entries 5–8). However, with *p*-anisidine containing electron donating group at *para*-position, the amination reaction proceeds with considerable increase in the yield up to 60–75% (Table 3, entries 9–12). These results confirm that the variety of functional group such as bromo and methoxy tolerated on arylamine component under the reaction condition. A marginal increase in the yield was observed for substituted aryl amine containing electron donating – OCH_3 group at *para*-position.

The efficiency of all the copper(I) complex catalysts (**1**–**4**) with different counter anions exhibit different activities. The copper(I) complex **3** with ClO_4^- anion shows greater activities than the complexes with Cl^-, CN^-, and BF_4^- as anions and reached the amination yield up to 65–75% (Table 3, entries 3, 7 and 11). It was also found that the catalytic activity of these complexes decreases in the order of $ClO_4^- > BF_4^- > CN^- > Cl^-$ as their counter anions. These results could be attributed to difference in coordination ability of Cl^-, CN^-, BF_4^- and ClO_4^- with metal ion as well as difference in solubility of complexes in solvent during the reaction.

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Appendix A. Supplementary material

CCDC 753005 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.05.025.

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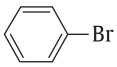
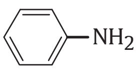
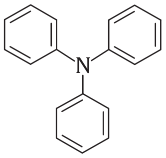
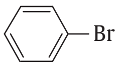
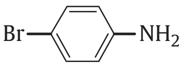
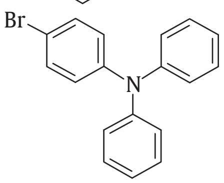
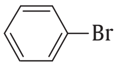
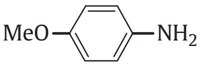
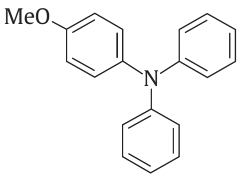
Table 3
Amination reaction catalyzed by copper(I) complexes.

Entry	Aryl halide	Aryl amine	Product	Complex	% yield
1.				1	52
2.				2	57
3.				3	71
4.				4	64
5.				1	48
6.				2	55
7.				3	65
8.				4	57
9.				1	60
10.				2	65
11.				3	75
12.				4	70

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

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