Copper(I) complexes with Schiff base and 1,2-bis(diphenylphosphino)ethane as ligands: Synthesis, structure and catalytic properties for the amination of aryl halide

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ABSTRACT

Some copper(I) complexes of the type [Cu(**L**)(dppe)]X (**1–4**) [where **L** = (3-trifluoromethylphenyl)pyridine-2-ylmethylene-amine; dppe = 1,2-bis(diphenylphosphino)ethane; X = Cl^-, CN^-, ClO_4^- and BF_4^-] have been synthesized by the condensation of 3-aminobenzotrifluoride with 2-pyridinecarboxaldehyde followed by the reaction with CuCl, CuCN, [Cu(MeCN)$_4$]ClO$_4$ and [Cu(MeCN)$_4$]BF$_4$ in presence of dppe. The complexes **1–4** were then characterized on the basis of elemental analysis, IR, UV–Vis and ^{1}H NMR spectral studies. The representative complex of the series **4** has been characterized by single crystal X-ray diffraction which reveal that in complex the central copper(I) ion assumes the irregular pseudo-tetrahedral geometry. The catalytic activity of the complexes was tested and it was found that all the complexes worked as effective catalyst in the amination of aryl halide.

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1. Introduction

The catalytic amination of aryl halide by transition metal ion is subject of growing interest in past few decades. This method involves production of arylamines by coupling of aryl halide with amines in presence of stoichiometric amount of transition metal ion. Arylamines are prevalent in organic compounds, shows wide utility in fine chemicals, dyes and polymers [1]. These are important components in many biological active natural products, medicinally important compounds as well as in materials with useful electrical and mechanical properties [2–4]. High purity triarylamines find applications in xerographic photoreceptors as constituents of non linear optical chromophores useful in design of integrated electro-optic switches and modulators [5]. This wide spread importance of arylamines has led to the development of many synthetic methodologies for the production of arylamines. Amongst them, the classical copper mediated Ullman coupling and the recently developed Pd(0) catalyzed aryl coupling are more commonly used methods [6–9]. Although the Pd-catalyzed amination of aryl halide has recently become the most important method for laboratory scale synthesis of arylamines; the copper mediated coupling is still the reaction of choice due to its cheap price and environmentally friendly nature. Many ligand systems such as amino acid [10], diamines [11], di-imines [12], diols [13], 1,10-phe-

nanthroline [14] and other nitrogen, oxygen containing ligands [15,16] together with copper(I) reagents have been applied for the production of arylamine under mild condition. More recently Cu(PPh$_3$)$_3$Br [17] and Cu(phen)$_2$Cl [18] have also been reported for the amination of aryl halides.

In this paper we report synthesis of some copper(I) complexes **1–4** by the reaction of Schiff base ligand (3-trifluoromethylphenyl)-pyridine-2-ylmethylene-amine (**L**) with CuCl, CuCN, [Cu(MeCN)$_4$]ClO$_4$ and [Cu(MeCN)$_4$]BF$_4$ in presence of 1,2-bis(diphenylphosphino)ethane as a coligand. All the complexes were characterized on the basis of elemental analysis, IR, UV–Vis, ^{1}H NMR spectral studies and compound **4** also by X-ray crystallography. The catalytic performance of all the copper(I) complexes in the amination of aryl halide has also been discussed.

2. Experimental

2.1. Materials and methods

The reagents used in synthesis of copper(I) complexes were 2-pyridinecarboxaldehyde (Alfa Aesar), 3-aminobenzotrifluoride (Alfa Aesar), 1,2-bis(diphenylphosphino)ethane (Aldrich, USA) were of reagent grade used without further purification. The Schiff base ligand (3-trifluoromethylphenyl)-pyridine-2-ylmethylene-amine (**L**) was prepared as previously reported [19]. Other reagents included bromobenzene, iodobenzene, aniline, p-bromoaniline, p-anisidine and KOt–Bu. The copper(I) compounds CuCl [20],

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[Cu(MeCN)$_4$]ClO$_4$ [21] and [Cu(MeCN)$_4$]BF$_4$ [21] were prepared according to the literature procedure. Elemental analysis (C, H and N) of the copper(I) complexes were conducted on Thermo Finnigan FLASH EA-1112 CHNS analyzer. IR spectra were recorded on a Perkin–Elmer-100 FTIR spectrometer. ^{1}H NMR spectra of the samples dissolved in CDCl$_3$ were measured on a AMX 400 MHz instrument using TMS[(CH$_3$)$_4$Si] as an internal standard of chemical shifts (ppm). Electronic spectra were recorded in dichloromethane (10^{-4} M) on Shimadzu 3600 UV–Vis-NIR spectrophotometer. Mass spectra were measured on GCMS Shimadzu-2010.

2.2. Synthesis

2.2.1. Preparation of [Cu(**L**)(dppe)]Cl (**1**)

To a solution of Schiff base ligand **L** (1 mmol, 0.250 g) was added a solution of 1,2-bis(diphenylphosphino)ethane (1 mmol, 0.397 g) and CuCl (1 mmol, 0.0989 g) in 10 ml dichloromethane. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 2 h and then the solution was evaporated to small volume under vacuum. The pale yellow coloured complex was developed by diffusion of diethyl ether into the solution.

Complex **1**: Yield 85%; m.p. 130 °C; elemental analysis (C, H and N, wt.%) *Anal.* Calc. for C$_{39}$H$_{33}$ClCuF$_3$N$_2$P$_2$: C, 62.65; H, 4.45; N, 3.75. Found: C, 62.75; H, 4.47; N, 3.78%. IR (KBr) (cm^{-1}): 1590, υ(HC=N); 1483, 1435, 1165, 693, υ(dppe); UV–Vis (CH$_2$Cl$_2$) λ_{max} (nm)($\varepsilon \times 10^3$, M^{-1} cm^{-1}): 278 (13.7), 298 (9.8), 396 (0.53); ^{1}H NMR (CDCl$_3$) (400 MHz), δ 9.45 (s, HC=N), 7.18–8.75 (m, Ar-H), δ 2.67 (s, PCH$_2$CH$_2$P).

2.2.2. Preparation of [Cu(**L**)(dppe)]CN (**2**)

The complex **2** was prepared similar to the procedure performed in the preparation of **1** except that CuCl was replaced by CuCN (1 mmol, 0.0895 g).

Complex **2**: Yield 85%, m.p. 122 °C; elemental analysis (C, H and N, wt.%) *Anal.* Calc. for C$_{40}$H$_{33}$CuF$_3$N$_3$P$_2$: C, 65.08; H, 4.51; N, 5.69. Found: C, 65.25; H, 4.54; N, 5.72%. IR (KBr) (cm^{-1}): 1585, υ(HC=N); 1483, 1435, 1168, 693, υ(dppe); 2110, υ(C≡N); UV–Vis (CH$_2$Cl$_2$) λ_{max} (nm)($\varepsilon \times 10^3$, M^{-1} cm^{-1}): 288 (13.7), 308 (9.7) 402 (1.2); ^{1}H NMR (CDCl$_3$) (400 MHz): δ 9.47 (s, HC=N), 7.18–8.75 (m, Ar-H), δ 2.66 (s, PCH$_2$CH$_2$P).

2.2.3. Preparation of [Cu(**L**)(dppe)]ClO$_4$ (**3**)

The complex **3** was prepared similar to the procedure performed in the preparation of **1** except that CuCl was replaced by [Cu(MeCN)$_4$]ClO$_4$ (1 mmol, 0.327 g).

Complex **3**: Yield 89%, m.p. 171 °C; elemental analysis (C, H and N, wt.%) *Anal.* Calc. for C$_{39}$H$_{33}$ClCuF$_3$N$_2$O$_4$P$_2$: C, 57.71; H, 4.11; N, 3.45. Found: C, 57.83; H, 4.37; N, 3.48%. IR (KBr) (cm^{-1}): 1590, υ(HC=N); 1483, 1435, 1168, 693, υ(dppe); 1096, 621 υ(ClO$_4$); UV–Vis (CH$_2$Cl$_2$) λ_{max} (nm)($\varepsilon \times 10^3$, M^{-1} cm^{-1}): 287 (13.5), 300 (9.4), 397 (1.4); ^{1}H NMR (CDCl$_3$) (400 MHz) δ 9.49 (s, HC=N), 7.22–8.78 (m, Ar-H), δ 2.67 (s, PCH$_2$CH$_2$P).

2.2.4. Preparation of [Cu(**L**)(dppe)]BF$_4$ (**4**)

The complex **4** was prepared similar to the procedure performed in the preparation of **1** except that CuCl was replaced by [Cu(MeCN)$_4$]BF$_4$ (1 mmol, 0.314 g).

Complex **4**: Yield 84%, m.p. 174 °C; elemental analysis (C, H and N, wt.%) *Anal.* Calc. for C$_{39}$H$_{33}$ BCuF$_7$N$_2$P$_2$: C, 58.63; H, 4.16; N, 3.51. Found: C, 58.62; H, 4.47; N, 3.54%. IR (KBr) (cm^{-1}) 1587, υ(HC=N); 1483, 1435, 1168, 693, υ(dppe); 1071, υ(BF$_4$); UV–Vis (CH$_2$Cl$_2$) λ_{max} (nm)($\varepsilon \times 10^3$, M^{-1} cm^{-1}): 288 (13.0), 300 (9.4), 392 (1.3); ^{1}H NMR (CDCl$_3$) (400 MHz): δ 9.49 (s, HC=N), δ 7.20–8.67 (m, Ar-H), δ 2.67 (s, PCH$_2$CH$_2$P).

2.3. Catalytic activity for the amination of aryl halide

The amination of bromobenzene and iodobenzene catalyzed by copper(I) complexes was carried out according to the procedure (Scheme 1): 0.05 mmol of copper(I) catalyst was added to 4 mmol of respective arylamine, 8 mmol of bromobenzene or iodobenzene, 12 mmol of KOt–Bu in toluene and the reaction mixture was stirred for 12 h at 90 °C under nitrogen. The reaction mixture was then cooled to room temperature and the solution was filtered to re-

Table 1
Crystal data and structure refinements details for [Cu(**L**)(dppe)]BF$_4$(**4**).

Empirical formula	C$_{39}$H$_{33}$BCuF$_7$N$_2$P$_2$
Formula weight	798.96
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.3579(4)
b (Å)	13.2014(5)
c (Å)	14.5780(5)
α (°)	92.805(3)
β (°)	102.438(3)
γ (°)	111.747(4)
V (Å^3)	1789.75(11)
Z	2
D_{calc} (mg m^{-3})	1.483
μ (Mo Kα)(mm^{-1})	0.768
F (0 0 0)	816
Data collection	
Temperature (K)	150(2)
θ Minimum–maximum (°)	3.46–25.00
Dataset [h, k, l]	−12/12, −15/15, −17/16
Total, unique data, R_{int}	13146, 6271, 0.0214
Observed data	$I > 2\sigma(I)$
Refinement	
Number of reflection, number of parameters	16172, 1155
R_1, R_1	0.0313, 0.0392
wR_2, wR_2	0.0823, 0.0843
Goodness-of-fit (GOF)	1.078
Largest difference in peak and hole (e A^{-3})	0.446, −0.339
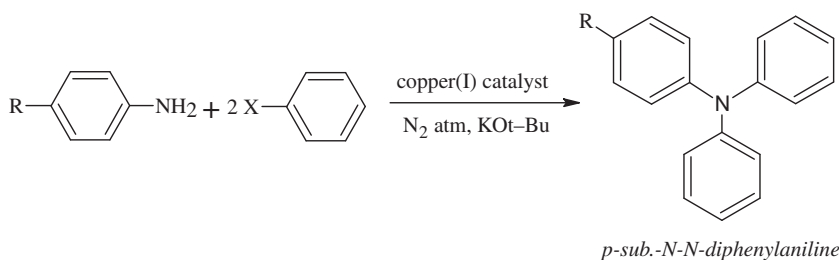
X= Br, I; R= H, Br, OMe

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

move the precipitated base and washed with toluene. The solvent was removed by rotary evaporator and the crude product obtained was isolated by silica gel chromatography using (9:1) ether:chloroform system. The purified product was then characterized by elemental analysis, IR, ^{1}H NMR and mass spectral studies.

2.4. X-ray crystallography

A single crystal of complex **4** suitable for X-ray analysis was obtained by slow diffusion of diethyl ether into solution of complex in dichloromethane. The intensity data were collected on a Nonius MACH-3 four-circle diffractometer with graphite-monochromatized Mo Kα radiation. The details of crystal data, data collection and the refinement are given in Table 1. The structure was solved by direct methods using the SHELXS 93 program and refined by using SHELXTL 97 software [22]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All of the hydrogen atoms were geometrically fixed and refined using a riding model.

3. Results and discussion

The reaction of equimolar quantities of copper(I) salt with Schiff base ligand **L** in presence of cis-1,2-bis(diphenylphosphino)ethane (dppe) in dichloromethane solution at room temperature afforded monomeric mixed ligand complexes of the type [Cu(**L**)(dppe)]X. All the complexes are microcrystalline solids that are soluble in common organic solvents like dichloromethane, chloroform, acetonitrile, THF, methanol, ethanol, etc. The results of elemental analysis (C, H and N) of all copper(I) complexes which are given in Section 2 confirmed that their stoichiometry and physical properties are in accordance with the proposed formula. At room temperature all the complexes are diamagnetic, which is characteristic of the presence of Cu(I) (d^{10}).

3.1. Spectroscopic properties

The IR spectra of ligands and their complexes are found to be quite complex as they are in general exhibit large number of bands on varying intensities. However, a strong band observed at 1620 cm^{-1} in the spectrum of free ligand **L** corresponds to v(HC=N) group shifted to the lower frequency region by 25–30 cm^{-1} in the complexes indicate involvement of imine (HC=N) nitrogen in coordination with metal ion [23]. 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 was further supported by the appearance of a band corresponding to the metal–nitrogen v(Cu–N) stretching vibration at ~482 cm^{-1} in the complexes [24]. The spectra of all the copper(I) complexes exhibit the expected bands due to the dppe ligand at around 1483, 1435, 1168 and 693 cm^{-1}. The stretching frequency v(C≡N) of the cyanide ion in complex **2** occurs at 2110 cm^{-1}. The perchlorate complex **3** exhibit broad band at 1095 cm^{-1} (v_3) and strong band at 621 cm^{-1} (v_4), is devoid of any splitting suggesting that the ClO$_4^-$ anion is not coordinated to the copper atom. However, a broad band at 1071 cm^{-1} in **4** corresponds to presence of BF$_4^-$ anion in the complex [25].

The electronic spectra of all copper(I) complexes (**1–4**) in dichloromethane (10^{-4} M) were measured at room temperature. The electronic spectra of all the complexes are noticeably different from the spectrum of the free ligand **L** and also give information concerning copper–ligand binding in the complexes. In the spectra of complexes, no d–d transitions are expected for d^{10} complexes, the UV–Vis band observed at ~396 nm is assigned to metal to li-

gand charge transfer (MLCT) or ligand centered π–π* transition [26]. The high energy transitions located in the UV region of the complexes in the range 260–280 and 290–320 nm are from intraligand π–π* transition.

The ^{1}H NMR spectral data of all copper(I) complexes (**1–4**) in CDCl$_3$ are given in the Section 2. Comparison of chemical shift of uncomplexed ligands with those of copper(I) complexes show that some of the resonance is shifted up on complexation in each case. The ^{1}H NMR spectrum of Schiff base ligand **L** in CDCl$_3$ exhibit a singlet at δ 8.10 ppm assigned to imine (HC=N) proton. The downfield shift of imine proton relative to the corresponding signals in the free ligand **L** can be attributed to the deshielding effect resulting from the coordination of the imine nitrogen [27]. The resonances of phenyl protons of the coordinated dppe ligand overlap to some extent with those of phenyl hydrogen atoms of **L** in the complexes. However, the broad multiplet observed in the range δ 7.18–8.78 ppm for all the complexes were assigned to the phenyl group of dppe together with ring proton of Schiff base ligand **L**. The ^{1}H NMR spectra of all the complexes exhibit a broad singlet at approximately δ 2.67 ppm due to CH$_2$ protons in the dppe ligand.

3.2. Crystal structure

The crystals of [Cu(**L**)(dppe)]BF$_4$ were grown by slow diffusion of diethyl ether into solution of complex in dichloromethane and structure was determined by X-ray crystallography. X-ray analysis revealed that complex crystallizes in triclinic system in an asymmetric unit cell. The crystallographic data are summarized in Table 1 and selected bond angles are given in Table 2. No classical H-bonding occurs in the crystal structure.

A view of the cation of complex **4**, including the atom numbering scheme is illustrated in Fig. 1. In the monomeric complex copper(I) exhibits highly distorted tetrahedral coordination geometry, with the metal atom being surrounded by two nitrogen atoms of Schiff base (imine nitrogen and pyridine nitrogen) and two phosphorous atoms of dppe. The largest deviation from the ideal tetrahedral geometry is reflected by the restricting bite angles of the chelating ligands. The intraligand N(1)–Cu(1)–N(2) and N(2)–

Table 2
Selected bond lengths (Å) and bond angles (°) for [Cu(**L**)(dppe)]BF$_4$ (**4**).

Cu(1)–N(1)	2.0529(17)
Cu(1)–N(2)	2.0745(17)
Cu(1)–P(2)	2.2602(6)
Cu(1)–P(1)	2.2658(6)
P(1)–C(22)	1.821(2)
P(1)–C(16)	1.822(2)
P(1)–C(14)	1.841(2)
P(2)–C(34)	1.822(2)
P(2)–C(28)	1.826(2)
P(2)–C(15)	1.852(2)
N(1)–Cu(1)–N(2)	80.52(7)
N(1)–Cu(1)–P(2)	121.64(5)
N(2)–Cu(1)–P(2)	125.39(5)
N(1)–Cu(1)–P(1)	120.63(5)
N(2)–Cu(1)–P(1)	121.37(5)
P(2)–Cu(1)–P(1)	91.16(2)
C(22)–P(1)–Cu(1)	121.69(7)
C(16)–P(1)–Cu(1)	117.02(7)
C(14)–P(1)–Cu(1)	103.02(7)
C(34)–P(2)–Cu(1)	117.19(7)
C(28)–P(2)–Cu(1)	125.05(7)
C(15)–P(2)–Cu(1)	101.17(7)
C(1)–N(1)–Cu(1)	130.71(15)
C(5)–N(1)–Cu(1)	112.47(13)
C(6)–N(2)–C(7)	118.71(18)
C(7)–N(2)–Cu(1)	128.94(14)
C(6)–N(2)–Cu(1)	112.35(14)
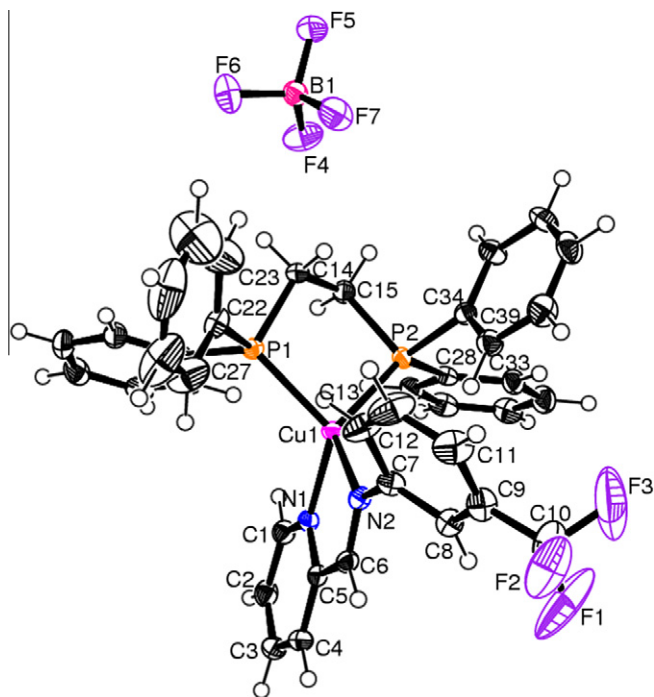
Fig. 1. Molecular structure of [Cu(**L**)(dppe)]BF$_4$ (**4**).

Cu(1)–P(1) angles are much less than 109.4°, being 80.52(7)° and 91.16(2)°, respectively. However, the N(1)–Cu(1)–P(2), N(2)–Cu(1)–P(2), N(1)–Cu(1)–P(1) and P(2)–Cu(1)–P(1) angles are 121.64(5)°, 125.39(5)°, 120.63(5)° and 121.37(5)°, respectively are much larger than those of a tetrahedral complex. The average Cu–N bond distance (2.0632 Å) is comparable to those reported for [Cu(A)(PPh$_3$)$_2$]ClO$_4$ pseudo-tetrahedral complexes [28]. All of the Cu–P bond lengths are as one would expect, i.e. close to the average value (2.253 Å) found for bonds between copper and different phosphines such as those found in complex [Cu(dppe)(NO$_3$)(CH$_3$CN)]$_n$ [29]. The quality of data permits to distinguish be-

tween P–C (sp^2) and P–C (sp^3) bond lengths, which are 1.821–1.826 and 1.841–1.852 Å, respectively.

Torsion angles in the chelating rings, the pyridine group and aromatic rings of each PPh$_2$ are listed in Table 3. This result demonstrates that the chelating ring Cu(1)–N(1)–C(5)–N(2) is nearly planar and the pyridine groups are coplanar with the chelate ring. Despite of the fact that the chelate ring is planar, the sum of three N atom bond angles is 359.94° N(1) and 360° N(2), however, some strain in the chelate ring is suggested by the deviation from the 120° angle about the N atom (Cu(1)–N(1)–C(1), 130.71(15)° and C(7)–N(2)–Cu(1), 128.94(14)°). Moreover, the planes of the two aromatic rings of each PPh$_2$ moiety are essentially perpendicular to one another.

3.3. Catalytic properties

Catalytic role of all the copper(I) complexes (**1**–**4**) in the amination of aryl halide was investigated. The system chosen for study is the coupling of bromobenzene or iodobenzene with different amines by using 0.05 mmol copper(I) catalyst and KOt–Bu as base in toluene at 90 °C (Scheme 1). Under this experimental condition the purified product obtained was characterized by elemental analysis, IR, ^{1}H NMR and mass spectral studies (Table 4). In order to check the catalytic effect of Schiff base copper(I) complexes, it was observed that, 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 by-products from aryl halide substrate. The effect of complex catalysts (**1**–**4**) on the amination of bromobenzene and iodobenzene was investigated and it was found that copper(I) complexes significantly enhance the conversion of bromobenzene and iodobenzene into desired amination product in moderate to good yield. All the reactions were smoothly carried out at relatively low temperature and reached the amination yield up to 48–80% (Table 5). 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 and iodobenzene with aniline reached the amination yield up to 48–69% and 60–72%, respectively. With *p*-bromoaniline containing electron withdrawing group at *para*-position, the amination reaction yield was observed up to 44–64% for bromobenzene and 55–70% for iodobenzene. However, with *p*-anisidine containing electron donating group at *para*-position, the amination reaction proceeds with considerable increase in the yield up to 58–74% and 65–80% for bromobenzene and iodobenzene, respectively. 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 with electron donating –OCH$_3$ group at *para*-position while lower yield was obtained for electron withdrawing group at *para*-position of substituted arylamine [30].

It was also observed that the efficiency of copper(I) catalyst with different counter anions exhibit different activities. It is evi-

Table 3
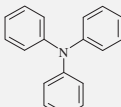Torsion angles for chelating ring.
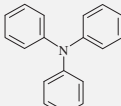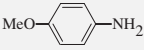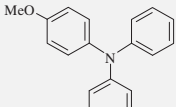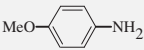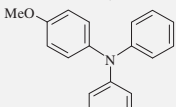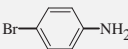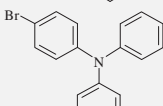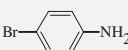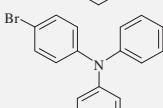
N(2)–Cu(1)–N(1)–C(5)	2.64(13)
Cu(1)–N(1)–C(5)–C(6)	−3.7(2)
C(3)–C(4)–C(5)–N(1)	−0.5(3)
C(3)–C(4)–C(5)–C(6)	179.34(19)
Cu(1)–N(2)–C(6)–C(5)	−0.7(2)
N(1)–C(5)–C(6)–N(2)	3.0(3)
C(4)–C(5)–C(6)–N(2)	−176.87(19)
C(7)–C(8)–C(9)–C(10)	−177.7(2)
P(1)–C(14)–C(15)–P(2)	−55.05(18)
Cu(1)–P(2)–C(15)–C(14)	45.49(16)

Table 4
Microanalytical and spectral data of amination product.

Compound	C, H, N found (calculated)			IR (cm^{-1})	Mass	^{1}H NMR (δ ppm)
	C	H	N			
N, N-diphenyl-aniline	87.72 (88.13)	6.05 (6.16)	5.87 (5.71)	1587, 1493, 1461	*m/z* 245 [(Ph)$_3$N]$^+$, 168 [(Ph)$_2$N]$^+$, 77 [Ph]$^+$	δ 6.09–6.39, (m, Ar-H)
4-Methoxy-N, N-diphenyl-aniline	82.63 (82.88)	6.17 (6.22)	5.68 (5.09)	1586, 1490, 1462	*m/z* 275 [(Ph)$_3$N–OMe]$^+$, 245 [(Ph)$_3$N]$^+$, 168 [(Ph)$_2$N]$^+$, 77 [Ph]$^+$	δ 3.86, (s, 3H, OMe), δ 6.79–7.87, (m, Ar-H)
4-Bromo-N, N-diphenyl-aniline	67.40 (66.68)	4.23 (4.35)	4.51 (4.32)	1586, 1493, 1461	*m/z* 323 [(Ph)$_3$NBr]$^+$, 245 [(Ph)$_3$N]$^+$, 168 [(Ph)$_2$N]$^+$, 77 [Ph]$^+$	δ 6.91–7.32, (m, Ar-H)

Table 5
Animation reaction catalyzed by copper(I) complexes.

Entry	Aryl halide	Arylamine	Product	Complex	Yield (%)
1	Br	NH₂		**1**	48
2				**2**	55
3				**3**	69
4				**4**	62
5	I	NH₂		**1**	60
6				**2**	63
7				**3**	72
8				**4**	65
9	Br	MeO–NH₂	MeO	**1**	58
10				**2**	65
11				**3**	74
12				**4**	68
13	I	MeO–NH₂	MeO	**1**	65
14				**2**	66
15				**3**	80
16				**4**	72
17	Br	Br–NH₂	Br	**1**	44
18				**2**	51
19				**3**	64
20				**4**	55
21	I	Br–NH₂	Br	**1**	55
22				**2**	59
23				**3**	70
24				**4**	60

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

dent that the copper(I) complex catalyst with ClO_4^- anion shows greater activities than the complexes with Cl^-, CN^-, BF_4^- and reached the amination yield up to 64–80% (Table 5, entries 3, 7, 11, 15, 19 and 23). 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 due 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.

4. Conclusions

Some mixed ligand copper(I) complexes have been synthesized by the reaction of (3-trifluoromethylphenyl)pyridine-2-ylmethyl-ene-amine with CuCl, CuCN, [Cu(MeCN)₄]ClO₄ and [Cu(MeCN)₄]BF₄ in presence of *cis*-1,2-bis(diphenylphosphino)ethane as coligand. The structure of all the copper(I) complexes (**1–4**) were confirmed on the basis of elemental analysis, FTIR, UV–Vis and ¹H NMR spectroscopy. The single crystal X-ray diffraction which reveals that in complex **4** the central copper(I) ion assumes the irregular pseudo-tetrahedral geometry. The catalytic activity of all the copper(I) complexes in the amination of aryl halide have been tested and it was found that all the complexes significantly enhance the conversion of aryl halide into desired triarylamine product in moderate to good yield.

Appendix A. Supplementary material

CCDC 762585 contains the supplementary crystallographic data for [Cu(**L**)(dppe)]BF₄ (**4**). 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 associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.06.023.

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