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Copper(I) complexes with N-(2-quinolinylmethylene)-1, 5-dimethyl- 2-phenyl-1-pyrazole-3-(2H)-one and phosphine as ligands: Effective catalyst for Sonogashira cross-coupling reaction

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A new series of copper(I) complexes of the type $[Cu(\mathbf{L})(PPh_3)_2]X$ (**1a-c**) and $[Cu(\mathbf{L})(dppe)]X$ (**2a-c**) have been prepared by the reaction of $Cu(MeCN)_4]X$ (where X = ClO_4^-, BF_4^- and PF_4^-) with N-(2-quinolinylmethylene)-1,5-dimethyl-2-phenyl-1-pyrazole-3-(2H)-one (**L**) in presence of triphenylphosphine (PPh_3) or 1,2-bis(diphenylphosphino)ethane (dppe) as an ancillary ligand. The UV-visible spectra indicate that, the ancillary phosphine ligands significantly perturb the MLCT state of copper(I) complexes. The thermally stable **1a-c** and **2a-c** complexes exhibit quasireversible redox behaviour corresponding to Cu(I)/Cu(II) couple. All complexes are tested as catalyst for Sonogashira cross-coupling of phenylacetylene with aryl iodide. The results show that all complexes worked as an effective catalyst at low temperature yielding substituted aryl alkynes as a product. The nature of phosphine ligands and size of counter anions shows marked effect on catalytic properties of all the complexes.

Keywords: Copper complexes, Copper catalyst, Arylated alkynes, Sonogashira coupling

The catalytic Sonogashira cross-coupling reaction is a valuable transformation in organic synthesis. This reaction involve formation of C(sp)-C(sp^2) bonds between aryl halides and terminal aryl or alkyl-alkynes to afford corresponding substituted alkynes. Alkynes are prevalent in organic compounds shows wide utility in synthesis of pharmaceuticals, natural products, biological active molecules, conducting polymers, nonlinear optical and liquid crystal materials.[1-5] Traditionally, Sonogashira coupling reactions are carried out by Pd-based catalyst and copper(I) salt as a co-catalyst.[6,7] The role of copper co-catalyst is to produce a copper-acetylide intermediate that subsequently transmetallates to the palladium center. Many different catalytic systems including copper free palladium based catalyst such as $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$ have been applied for the reaction. But, the removal of trace palladium from late stage synthetic intermediate, cost of reagents, impossibility to reuse it in consecutive reactions, difficulties in coupling of electron-rich or ortho-substituted aryl iodide are the major drawbacks of this method. Thus the development of new catalytic system that is eco-friendly, readily available, mild and easily separable would be useful in modern synthesis. Numerous catalytically active metals were used to catalyze this coupling reaction including iron[8], cobalt[9], nickel[10] and copper[11]. Among these, copper-catalyzed Sonogashira cross-coupling reaction is highly attractive due to relatively low cost advantage and environmental friendly nature. Many organic compounds as well as phosphine and non-phosphine ligands such as triphenylphosphine, 1,10-phenanthroline, ethylenediamine, N,N-dimethylglycine, 1,4-diazabicyclo-[2.2.2]-octane (DABCO), 1,1'-binaphthyl-2,2'-diamine (BINAM) and its derivatives, 1,1'-binaphthyl-2,2'-diol (rac-BINOL), β-diketones, pyrimidines, salicylic acid, 8-hydroxyquinoline and N,N'-dimethyl ethylenediamine (DMEDA) have been examined for copper-catalyzed Sonogashira type cross-coupling reactions.[12-17] More recently highly dispersed copper metal on alumina[18] and choline chloride/CuCl[19] has also been reported for the coupling of aryl iodide with phenylacetylene. However, to the best of our knowledge, only few papers have been contributed to use of copper complexes as a catalysts for sp^2-sp carbon-carbon bond forming process under mild condition.[20, 21]

Recently, we have reported a series of mononuclear copper(I) complexes of the type $[Cu(\mathbf{L})(PPh_3)_2]X$ (where **L**= N-(2-quinolinylmethylene)-1H-benzimidazole, PPh_3 = triphenylphosphine;

X = ClO_4^-, BF_4^- and PF_4^-)[22]. All the complexes worked as an active catalyst in the Sonogashira cross-coupling reactions. As a continuation of our research, we report herein synthesis, spectroscopic characterization and catalytic activity of copper(I) complexes derived from the reaction of N-(2-quinolylmethylene)-1,5-dimethyl-2-phenyl-1-pyrazol-3-(2H)-one (**L**) and $[Cu(MeCN)_4]ClO_4$, $[Cu(MeCN)_4]BF_4$ and $[Cu(MeCN)_4)]PF_6$ in presence of triphenylphosphine (PPh_3) or 1,2-bis(diphenylphosphino)ethane (dppe) as an ancillary ligand. All the complexes were characterized on the basis of elemental analysis and spectroscopic (IR, UV–visible, ^1H NMR, ^{13}C NMR, ^{31}P NMR and ESI-MS) techniques. The influence of phosphine ligands on catalytic performance of copper(I) complexes have been studied.

Materials and Methods

The reagent used in synthesis of copper(I) complexes are 2-quinolinecarboxaldehyde (Alfa Aesar), 4-aminoantipyrine (Aldrich, USA), triphenylphosphine and 1,2-bis(diphenylphosphino) ethane were of reagent grade and used without further purification. Other reagents included iodobenzene, 4-iodoaniline, 1-bromo-4-iodobenzene, phenylacetylene and potassium carbonate were purchased from Aldrich, USA. The copper(I) compounds $[Cu(MeCN)_4]ClO_4$[23], $[Cu(MeCN)_4]BF_4$[26] and $[Cu(MeCN)_4]PF_6$ [25] were prepared according to literature procedure.

Elemental analysis (C, H and N) of all copper(I) complexes were conducted on Thermo Finnegan FLASH EA-1112 CHNS analyzer. IR spectra were recorded on Perkin-Elmer-100 FTIR Spectrometer, ^1H NMR and ^{13}C NMR spectra of the samples were measured in $CDCl_3$ on Bruker 300 MHz instrument using TMS[$(CH_3)_4Si$] as an internal standard. ^{31}P NMR spectra were recorded using a Varian Mercury-300 FTNMR Spectrometer relative to H_3PO_4. Electronic spectra were recorded on Shimadzu 3600 UV-Vis-NIR spectrophotometer in dichloromethane (10^{-4} M). Electrochemical measurements were performed with a CH-400 electrochemical analyzer. Tetrabutyl ammonium perchlorate (TBAP) was used as a supporting electrolyte and all measurements were carried out in dichloromethane solution (10^{-4} M) at room temperature with scan rate 100 mVs^{-1}.

Synthesis of ligand L

N-(2-quinolylmethylene)-1,5-dimethyl-2-phenyl-1-pyrazol-3-(2H)-one (**L**) was prepared by adopting and modifying the method described in the literature[26]. To a solution of 4-amino antipyrine (0.640 g, 3.142 mmol) in methanol (10 ml), a solution of 2-quinoline carboxaldehyde (0.5 g, 3.142 mmol) in MeOH (10 ml) was added with constant stirring. The resulting reaction mixture was refluxed at 80 °C until the completion of reaction (checked by TLC). The product obtained was filtered, washed with ethanol: water (1:1) mixture and recrystalized from EtOH.

Yield: 87% (0.991 g, 2.89 mmol); Colour: Pale yellow; Elemental analyses (C, H and N, wt %) Anal. Calc. for $C_{21}H_{18}N_4O$: C, 73.67; H, 5.30; N, 16.36; found: C, 73.59; H, 5.27; N, 16.43%; IR (KBr; cm^{-1}); 1649, υ(C=O); 1614, υ(HC=N); 1382, υ(C-N); 1436, υ(N-CH_3); 3055, υ(Ar-CH); UV-visible (CH_2Cl_2) λ_{max} (nm) (ε x 10^4 M^{-1} cm^{-1}): 242(0.92), 280(0.51); ^1H NMR ($CDCl_3$; 300 MHz): 9.22 (s, 1H, HC=N), 7.27-8.29 (m, 11H, Ar-H), 3.22 (s, 3H, N-CH_3), 2.57 (s, 3H, C-CH_3); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 160.39(>C=O), 152.91(quin-C), 149.79(HC=N), 134.66 (CH_3C=CN), 132.72((quin-C), 131.61(quin-C), 129.70(quin-C), 128.81(quin-C), 127.12(quin-C), 127.10 (Ph-C), 126.89(quin-C), 124.73(Ph-C), 123.95(Ph-C), 123.81(quin-C), 121.51(Ph-C), 118.13(NC=CCH_3), 35.59(N-CH_3), 10.26(C-CH_3); ESI(MS): 364 $[M+Na]^+$.

Synthesis of $[Cu(L)(PPh_3)_2]ClO_4$ (1a)

To 10 ml acetonitrile solution of $[Cu(MeCN)_4]ClO_4$ (0.258 g, 0.789 mmol), a solution of two equivalent of triphenylphosphine (0.413 g, 1.57 mmol) in 10 ml of acetonitrile was added. The reaction mixture was stirred for 30 min under N_2 atmosphere at room temperature and allowed to evaporate slowly. The crystalline product $[Cu(MeCN)_2(PPh_3)_2]ClO_4$ obtained was subsequently added to a stirring solution of **L** (0.27 g, 0.789 mmol) in 10 ml dichloromethane. The mixture was stirred for 4 h at room temperature and the solution was evaporated to a small volume under vacuum. The product obtained was filtered, washed with diethyl ether and dried under vacuum.

Yield: 83% (0.781 g, 0.759 mmol); Colour: Yellow; Elemental analyses (C, H, N, wt %) Anal. Calc. for $C_{57}H_{48}N_4P_2O_5ClCu$: C, 66.47; H, 4.70, N, 5.44; found: C, 66.41; H, 4.69; N, 5.51%; IR (KBr; cm^{-1}): 1652, υ(C=O); 1595, υ(HC=N); 1435, υ(N-CH_3); 1385, υ(C-N); 3064, υ(Ar-CH); 487 υ(Cu-N); 1481, 1436, 693, 519, υ(PPh_3); 1094, 621 υ(ClO_4); UV-visible (CH_2Cl_2) λ_{max} (nm)

(ε x 10^4 M^{-1} cm^{-1}): 253 (0.95), 286 (0.66), 390 (0.31); ^{1}H NMR ($CDCl_3$; 300 MHz): 9.92 (s, 1H, HC=N), 7.19-8.40 (m, 41H, Ar-H), 3.21 (s, 3H, N-CH_3), 2.57 (s, 3H, C-CH_3); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 159.12 (>C=O), 152.84(quin-C), 149.55(HC=N), 134.61 (CH_3C=CN), 133.13(PPh_3-C), 132.22 ((quin-C), 131.58 (quin-C), 131.51(PPh_3-C), 130.73(PPh_3-C), 129.68(quin-C), 129.55(PPh_3-C), 129.11 (PPh_3-C), 128.74(quin-C), 126.96(quin-C), 126.99(Ph-C), 126.81(quin-C), 124.62 (Ph-C), 123.88(Ph-C), 123.79(quin-C), 121.48(Ph-C), 118.10(NC=CCH_3), 35.43(N-CH_3), 10.19(C-CH_3); ^{31}P NMR: δ 1.76 (s, PPh_3); ESI(MS): 929 $[M\text{-}ClO_4]^+$.

Synthesis of $[Cu(L)(PPh_3)_2]BF_4$ (1b)

Complex **1b** was prepared by a procedure similar to that used for the preparation of **1a** except that, $[Cu(MeCN)_4]ClO_4$ was replaced by $[Cu(MeCN)_4]BF_4$ (0.248 g, 0.789 mmol).

Yield: 85% (0.792 g, 0.778 mmol); Colour: Yellow; Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{57}H_{48}N_4P_2OF_4BCu$: C,67.30; H, 4.76, N, 5.51; found: C, 67.23; H, 4.71; N, 5.63%; IR (KBr; cm^{-1}); 1650, υ(C=O); 1592, υ(HC=N); 1435, υ(N-CH_3); 1385, υ(C-N); 3066, υ(Ar-CH); 488, υ(Cu-N); 1482, 1435, 694, 519, υ(PPh_3); 1056, 597 υ(BF_4); UV-visible (CH_2Cl_2) λ_{max} (nm) (ε x 10^4 M^{-1} cm^{-1}): 253 (0.98), 288(0.69), 393(0.37); ^{1}H NMR ($CDCl_3$; 300 MHz): 9.93 (s, 1H, HC=N), 7.22-8.36 (m, 41H, Ar-H), 3.21 (s, 3H, N-CH_3), 2.58 (s, 3H, C-CH_3); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 159.15(>C=O), 152.81(quin-C), 149.57(HC=N), 134.61(CH_3C=CN), 133.13(PPh_3-C), 132.23 (quin-C), 131.60 (quin-C), 131.52(PPh_3-C), 130.73(PPh_3-C), 129.69(quin-C), 129.55(PPh_3-C), 129.12(PPh_3-C), 128.76(quin-C), 126.97(quin-C), 126.99(Ph-C), 126.83(quin-C), 124.60 (Ph-C), 123.87(Ph-C), 123.79(quin-C), 121.50(Ph-C), 118.10(NC=CCH_3), 35.44(N-CH_3), 10.17 (C-CH_3); ^{31}P NMR: δ 1.72 (s, PPh_3); ESI(MS): 929 $[M\text{-}BF_4]^+$.

Synthesis of $[Cu(L)(PPh_3)_2]PF_6$ (1c)

Complex **1c** was prepared by a procedure similar to that used for the preparation of **1a** except that, $[Cu(MeCN)_4]ClO_4$ was replaced by $[Cu(MeCN)_4]PF_6$ (0.294 g, 0.789 mmol).

Yield: 82% (0.802 g, 0.745 mmol); Colour: Dark yellow; Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{57}H_{48}N_4P_3OF_6Cu$: C,63.66; H, 4.50, N, 5.21; found: C, 63.60; H, 4.47; N, 5.29%; IR (KBr; cm^{-1}); 1651, υ(C=O); 1591, υ(HC=N); 1432, υ(N-CH_3); 1388, υ(C-N); 3061, υ(Ar-CH); 488 υ(Cu-N); 1482, 1435, 694, 518, υ (PPh_3); 842, 558, υ(PF_6); UV-visible (CH_2Cl_2) λ_{max} (nm) (ε x 10^4 M^{-1} cm^{-1}): 249(0.88), 278(0.62), 390(0.28): ^{1}H NMR ($CDCl_3$; 300 MHz): 9.92 (s, 1H, HC=N), 7.19-8.40(m, 41H, Ar-H), 3.22 (s, 3H, N-CH_3), 2.57 (s, 3H, C-CH_3); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 159.19 (>C=O), 152.87(quin-C), 149.59(HC=N), 134.61(CH_3**C**=CN), 133.13(PPh_3-C), 132.23 (quin-C), 131.62(quin-C), 131.52(PPh_3-C), 130.75(PPh_3-C), 129.69(quin-C), 129.55 (PPh_3-C), 129.13 (PPh_3-C), 128.76(quin-C), 126.97(quin-C), 126.97(Ph-C), 126.83(quin-C), 124.60(Ph-C), 123.89 (Ph-C), 123.77(quin-C), 121.50(Ph-C), 118.12(NC=CCH_3), 35.44(N-CH_3), 10.17(C-CH_3): ^{31}P NMR: δ 1.78 (s, PPh_3); -144.6 (septet, PF_6); ESI(MS): 929 $[M\text{-}PF_6]^+$.

Synthesis of $[Cu(L)(dppe)]ClO_4$ (2a)

To a 10 ml acetonitrile solution of $[Cu(MeCN)_4]ClO_4$ (0.258 g , 0.789 mmol), a solution of one equivalent of 1,2-bis(diphenylphosphino) ethane (0.314 g, 0.789 mmol) in 10 ml acetonitrile was added and the reaction mixture was stirred for 30 min under N_2 atmosphere at room temperature. To a stirring mixture, a solution of **L** (0.27 g, 0.789 mmol) in dichloromethane (10 ml) was added. The resulting solution was stirred for 4 h at room temperature and solution was evaporated to a small volume under vacuum. The product obtained was filtered, washed with diethyl ether and dried under vacuum.

Yield: 83% (0.699 g, 0.773 mmol); Colour: Brick red; Elemental analyses (C, H, N, wt %) Anal. Calc. for $C_{47}H_{42}N_4P_2O_5$ ClCu: C, 62.46; H, 4.68, N, 6.20; found: C, 62.41; H, 4.62; N, 6.28%; IR (KBr; cm^{-1}); 1650, υ(C=O); 1594, υ(HC=N); 1438, υ(N-CH_3); 1384, υ(C-N); 3066, υ(Ar-CH); 489 υ(Cu-N); 1478, 1434, 1175, 694, υ(dppe); 1094,621 υ(ClO_4); UV-visible (CH_2Cl_2) λ_{max} (nm) (ε x 10^4 M^{-1} cm^{-1}): 256(0.84), 298(0.55), 408(0.20); ^{1}H NMR ($CDCl_3$; 300 MHz): 10.04 (s, 1H, HC=N), 7.10-8.43 (m, 31H, Ar-H), 3.22 (s, 3H, N-CH_3), 2.57 (s, 3H, C-CH_3); 2.61 (s, 4H, P-CH_2-CH_2-P); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 159.21(>C=O), 152.81(quin-C), 149.57(HC=N), 138.41(dppe-C), 134.59(CH_3C=CN), 132.31((quin-C), 131.61(quin-C), 129.62(quin-C), 129.13 (dppe-C), 128.74 (quin-C), 128.71(dppe-C), 126.92(quin-C), 126.89(Ph-C), 126.77(quin-C), 125.81 (dppe-C), 124.61(Ph-C), 123.85(Ph-C), 123.76(quin-C), 121.51(Ph-C), 118.13 (NC=CCH_3), 35.41(N-CH_3), 23.93(-CH_2), 16.52(-CH_2), 10.22(C-CH_3); ^{31}P NMR: δ -4.7 (s, dppe); ESI(MS): 803 $[M\text{-}ClO_4]^+$.

Synthesis of [Cu(L)(dppe)]BF_4 (2b)

Complex **2b** was prepared by a procedure similar to that used for the preparation of **2a** except that, $[Cu(MeCN)_4]ClO_4$ was replaced by $[Cu(MeCN)_4]BF_4$ (0.248 g, 0.789 mmol).

Yield: 82% (0.682 g, 0.766 mmol); Colour: Brick red; Elemental analyses (C, H, N, wt%) Anal. Calc. for $C_{47}H_{42}N_4P_2OF_4BCu$: C, 63.34; H, 4.75; N, 6.29; found: C, 62.41; H, 4.62; N, 6.28%; IR (KBr; cm^{-1}); 1650, υ(C=O); 1587, υ(HC=N); 1434, υ(N-CH_3); 1386, υ(C-N); 3067, υ(Ar-CH); 488, υ(Cu-N); 1478, 1434, 1175, 694, υ(dppe); 1056, 597 υ(BF_4); UV-visible (CH_2Cl_2) λ_{max} (nm) (ε x 10^4 M^{-1} cm^{-1}): 259(0.90), 298(0.59), 419(0.25); ^{1}H NMR ($CDCl_3$; 300 MHz): 10.03 (s, 1H, HC=N), 7.13-8.45 (m, 31H, Ar-H), 3.22 (s, 3H, N-CH_3), 2.58 (s, 3H, C-CH_3); 2.61 (s, 4H, P-CH_2-CH_2-P); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 159.23(>C=O), 152.78(quin-C), 149.56 (HC=N), 138.41(dppe-C), 134.59(CH_3C=CN), 132.33(quin-C), 131.61(quin-C), 129.62(quin-C), 129.11(dppe-C), 128.74(quin-C), 128.71(dppe-C), 126.95(quin-C), 126.89(Ph-C), 126.76(quin-C), 125.81(dppe-C), 124.62(Ph-C), 123.85(Ph-C), 123.77(quin-C), 121.53(Ph-C), 118.13(NC=CCH_3), 35.41(N-CH_3), 23.95(-CH_2), 16.52(-CH_2), 10.24(C-CH_3); ^{31}P NMR: δ -4.4 (s, dppe); ESI(MS): 803 $[M\text{-}BF_4]^+$.

Synthesis of [Cu(L)(dppe)]PF_6 (2c)

Complex **2c** was prepared by a procedure similar to that used for the preparation of **2a** except that, $[Cu(MeCN)_4]ClO_4$ was replaced by $[Cu(MeCN)_4]PF_6$ (0.294 g, 0.789 mmol,).

Yield: 84% (0.738 g, 0.778 mmol); Colour: Red; Elemental analyses (C, H, N, wt%) Anal. Calc.for $C_{47}H_{42}N_4P_3OF_6Cu$: C,59.42; H, 4.41, N, 5.97; found: C, 59.46; H, 4.46; N, 5.90%; IR (KBr; cm^{-1}); 1651, υ(C=O); 1589, υ(HC=N); 1433, υ(N-CH_3); 1387, υ(C-N); 3063, υ(Ar-CH); 488 υ(Cu-N); 1478, 1435, 1176, 694, υ (dppe); 842, 558, υ(PF_6); UV-visible (CH_2Cl_2) λ_{max} (nm) (ε x 10^4 M^{-1} cm^{-1}): 257(0.96), 296(0.62), 421(0.22); ^{1}H NMR ($CDCl_3$; 300 MHz): 10.05 (s, 1H, HC=N), 7.11-8.43 (m, 31H, Ar-H), 3.21 (s, 3H, N-CH_3), 2.57 (s, 3H, C-CH_3); 2.61 (s, 4H, P-CH_2-CH_2-P); ^{13}C NMR ($CDCl_3$; 300 MHz): δ 159.21(>C=O), 152.77(quin-C), 149.59(HC=N), 138.41(dppe-C), 134.60(CH_3C=CN), 132.34(quin-C), 131.61(quin-C), 129.63(quin-C), 129.13 (dppe-C), 128.74(quin-C), 128.71(dppe-C), 126.95(quin-C), 126.89(Ph-C), 126.79(quin-C), 125.82 (dppe-C), 124.62(Ph-C), 123.88(Ph-C), 123.76(quin-C), 121.53(Ph-C), 118.15(NC=CCH_3), 35.40(N-CH_3), 23.98(-CH_2), 16.53(-CH_2), 10.24(C-CH_3); ^{31}P NMR: δ -4.5 (s, dppe), -144.3 (septet, PF_6); ESI(MS): 803 $[M\text{-}PF_6]^+$.

General procedure for catalytic reaction of Sonogashira cross-coupling reaction

The Sonogashira coupling reaction of phenylacetylene with aryl halides catalyzed by copper(I) complexes was carried out according to the procedure: 10 mol% of copper(I) complex catalyst was added to 2 mmol of respective aryl halide, 2.5 mmol of phenylacetylene, 2 mmol of K_2CO_3 in toluene and the reaction mixture was stirred for 16 h at 90 ºC under nitrogen. The reaction mixture was then cooled to room temperature and solution was filtered to remove the precipitated solid. The filtrate was concentrated and crude product was purified by column chromatography using ether:chloroform (9:1) mixture. The purified product was then characterized by elemental analysis, IR, ^{1}H NMR and mass spectral studies.

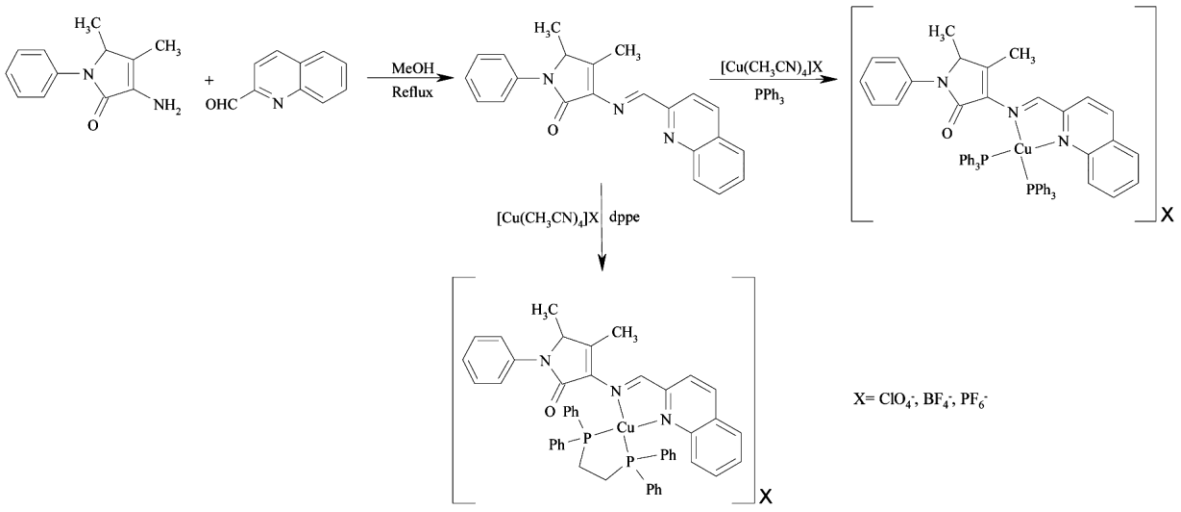
Results and Discussion

Synthesis

Initially, N-(2-quinolinylmethylene)-1,5-dimethyl-2-phenyl-1-pyrazole-3-(2H)-one (**L**) was synthesized by the reaction of 4-aminoantipyrine with 2-quinolinecarboxaldehyde at 80 °C in high yield. The copper(I) complexes of the formula [Cu(**L**)(PPh_3)$_2$]X (X = ClO_4 (**1a**), BF_4 (**1b**), PF_6 (**1c**)) and [Cu(**L**)(dppe)]X (X = ClO_4 (**2a**), BF_4 (**2b**), PF_6 (**2c**)) were prepared by the reaction of two equivalent of triphenylphosphine (PPh_3) or one equivalent of 1,2-bis(diphenylphosphino)ethane (dppe) with $[Cu(CH_3CN)_4]ClO_4$, $[Cu(CH_3CN)_4]BF_4$ or $[Cu(CH_3CN)_4]PF_6$ followed by addition of one equivalent of N-(2-quinolinylmethylene)-1,5-dimethyl-2-phenyl-1-pyrazole-3-(2H)-one (**L**) in dichloromethane solution (Scheme 1). The complexes prepared were soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, THF, MeOH, and EtOH. Composition and identity of all complexes were deduced from the satisfactory elemental analysis, FTIR, UV-visible, ^{1}H NMR and mass spectral studies. At room temperature all complexes were diamagnetic which is characteristic of presence of copper(I) (d^{10}).

Spectroscopic characterization

The IR spectra of **L** and its copper(I) complexes **1a-c** and **2a-c** exhibit a strong band in the region 1649-1652 cm^{-1} is a characteristic of >C=O group. This indicate >C=O group is in a similar environment



Scheme 1 — Synthesis of copper(I) complexes (**1a-c** and **2a-c)**

in ligand **L** and the complexes and thus free from coordination with metal ion. Another characteristic band observed at 1614 cm^{-1} in **L** assigned to υ(HC=N) vibration shifted to lower frequency by 19–23 cm^{-1} in **1a-c** and 20–27 cm^{-1} in **2a-c** indicating decrease in HC=N bond order due to π-back bonding from the electron rich copper(I) center to vacant π*-orbital of the ligand[27]. The spectra of **1a-c** exhibit an expected band due to coordinated PPh_3 at around 1482, 1436, 693 and 519 cm^{-1} whereas; **2a-c** shows band at around 1478, 1435, 1176 and 694 cm^{-1} due to presence of dppe ligand in the complexes. The perchlorate complexes **1a** and **2a** exhibit a broad band at 1094 cm^{-1} (υ_3) and the unsplit band at 621 cm^{-1} (υ_4), which are assigned to the non-coordinated ClO_4^- anion[28]. For tetrafluroborate complexes **1b** and **2b** an intense band at 1056 cm^{-1} and 597 cm^{-1} are attributed to anti-symmetric υ(B-F) stretching and bending mode[29] whilst, strong bands at 842 cm^{-1} and 558 cm^{-1} in **1c** and **2c** are consistent with presence of PF_6^- anion in the complexes[30].

^{1}H NMR spectrum of free ligand **L** in $CDCl_3$ displayed a single resonance at δ 9.22 ppm is assigned to imine (HC=N) proton (Fig. 1). In the spectra of **1a-c** and **2a-c**, the signal of imine proton is shifted to downfield region and appeared as a singlet at around δ 9.92 ppm for **1a-c** and δ 10.04 ppm for **2a-c** due to decrease in electron density caused by coordination of ligands to metal ion[31]. However, a broad multiplet is observed in the range δ 7.19–8.40 ppm for **1a-c** and 7.10–8.45 ppm for **2a-c** is assigned to phenyl protons of phosphine ligand together with ring protons of **L**. The ^{1}H NMR spectra of all copper(I) complexes showed signals at δ 2.57 and δ 3.22 ppm with an integration equivalent to three protons due to C-CH_3 and N-CH_3 group, respectively. In addition to these signals, **2a–c** exhibit a broad singlet at approximately δ 2.61 ppm is attributed to ethylene (CH_2) protons of the dppe ligand[32].

The ^{31}P NMR spectra of **1a-c** exhibit single resonance in the range 1.72–1.78 ppm relative to H_3PO_4 indicative of two phosphorus nuclei of PPh_3 are equivalent in nature[33]. In the chelating diphosphine complexes **2a-c**, two phosphorus nuclei must be *cis* to each other and therefore singlet is observed at -4.5 ppm. The presence of only one signal in the ^{31}P NMR spectrum of the complex confirmed that the chemical environment of two P atom is similar and the geometry around copper(I) ion must be tetrahedral, not square planar[34]. The complexes **1c** and **2c** contain PF_6^- as a counter ion, which appeared as a septet at around -144.3 ppm [35].

UV-visible absorption spectra of **L** shows two absorption bands at $\lambda_{max} \approx 242$ and 280 nm attributed to π-π* ligand centered (LC) transitions in near UV region. The copper(I) complexes exhibit a several maxima in the range 249–253 and 278–288 nm for **1a-c** and 256–259 and 297–302 nm for **2a-c** (Fig. 2) most likely originating from the ligand **L** and phosphine. The red shift of π-π* absorption in **1a-c** and **2a-c** are consistent with better conjugation of the ligands upon coordination resulting in a smaller π-π* energy gap. In addition to high energy absorptions, a comparatively weak, low energy absorptions observed at 389-393 nm for **1a-c** and 408-421 nm for **2a-c** can be assigned to a metal-to-ligand charge transfer

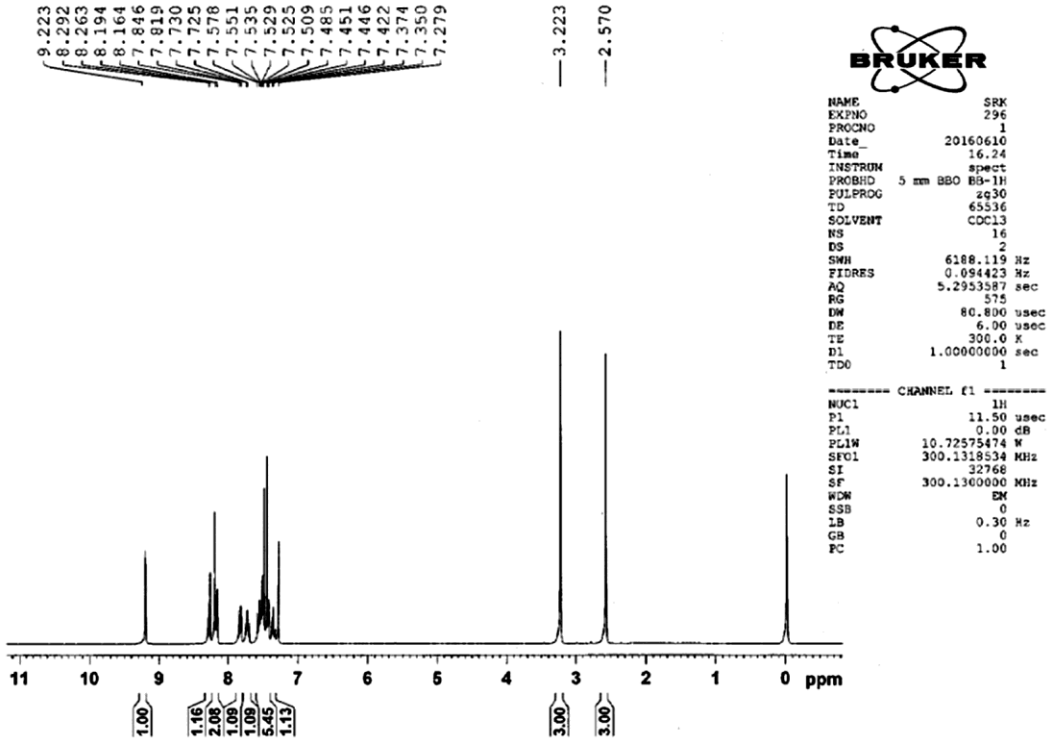


Fig. 1 — ^{1}H NMR spectra of **L**

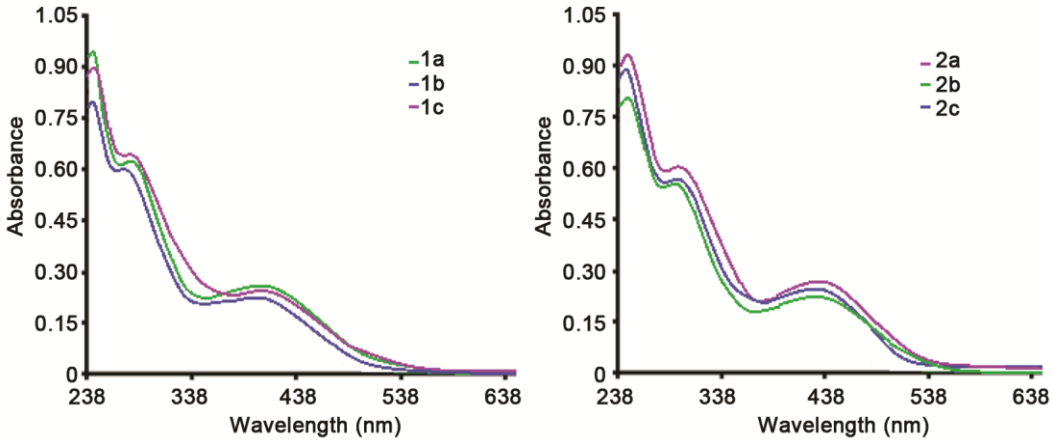


Fig. 2 — UV-visible spectra of **1a-c** and **2a-c**

(MLCT) transition involving mainly the 3d orbitals of copper(I) centre and π* orbital of the ligand **L**[36].

Thermogravimetric analysis

In order to examine the thermal stability of **1a-c** and **2a-c**, the thermal decomposition studies of all copper(I) complexes were carried out between 25–800 °C under nitrogen atmosphere. The perchlorate complexes (**1a** and **2a**) are potentially explosive and hence were not studied for safety reason. The thermal decomposition process of **1b, 1c**, **2b** and **2c** involves two decomposition processes. The TGA curve of **1b** and **1c** shows that, the first decomposition stage in the region 232-328 °C (**1b**) and 222-318 °C (**1c**) is assigned to decomposition of coordinated triphenylphosphine which corresponds to mass loss of 58.11 and 54.76% (theoretical mass loss 58.21% (**1b**), and 54.91% (**1c**). The second stage keeps losing weight from 334–465 °C and 318–457 °C accompanied by a mass loss of 32.12% (**1b**), 29.60% (**1c**) attributed to decomposition of ligand **L** leaving $CuBF_4$ and $CuPF_6$ as a residue

(theoretical mass loss 31.33 and 29.33%, respectively). The complexes **2b** and **2c** show very similar behaviour to the above, once again the complexes undergo a rapid and significant weight loss of 36.33 (**2b**) and 33.79 (**2c**) in the temperature range 201-342 (**2b**) and 193–318 °C (**2c**) corresponding to decomposition of dppe ligands (theoretical mass loss 36.47 and 33.80%). While the second stage occurs in the temperature range 323–513 °C (**2b**) and 318–561 °C (**2c**) indicative of gradual breakdown of coordinated ligand **L** (observed weight loss of 51.72 and 47.90% theoretical mass loss 51.86% (**2b**) and 48.05% (**2c**) leaving $CuBF_4$ and $CuPF_6$ as the end product.

Electrochemistry

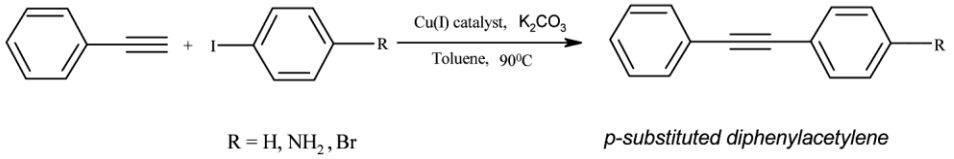
In order to study the electrochemical properties of **1a-c** and **2a-c**, cyclic voltammetry was carried out in 10^{-3} M CH_2Cl_2 solution containing 0.05 M *n*-Bu_4NClO_4 as a supporting electrolyte. All the measurements were carried out in the potential range ±1.5 V with scan rate of 100 mVs^{-1} and are presented in Table 1. The cyclic voltammogram of **1a-c** and **2a-c** shows an anodic peak (E_{pa}) at 0.769–0.781 V and 0.751–0.758 V corresponding to oxidation of Cu(I) to Cu(II). In reverse scan, cathodic peak (E_{pc}) at 0.619–0.626 V and 0.614–0.621 V for complexes **1a-c** and **2a-c** associated with reduction of Cu(II) to Cu(I). The current peak ratio (I_{pc}/I_{pa}) is not equal to 1 and ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) value is >60 mV indicate quasireversible one electron transfer process. Electrochemical data also reveals that the metal centered redox potential is sensitive to coordinated phosphine ligand. Compared to **2a-c** the redox process for **1a-c** appeared at more positive potential which is might be due to better π-acceptability character of PPh_3 than that of dppe ligand. These results are in good agreement with those values reported in the literature[37].

Table 1 — Electrochemical data of copper(I) complexes (1a-c and 2a-c)

Complex	E_{pa}(V)	E_{pc}(V)	ΔE_p (mV)	$E_{1/2}$ (V)
1a	0.769	0.619	150	0.694
1b	0.781	0.626	155	0.703
1c	0.771	0.622	149	0.696
2a	0.753	0.614	139	0.683
2b	0.751	0.621	130	0.686
2c	0.758	0.617	141	0.687

Sonogashira cross-coupling reaction

The scope of copper(I) complexes **1a-c** and **2a-c** as a catalysts for the Sonogashira cross-coupling reaction was examined. The system chosen for study is the coupling of phenylacetylene with different aryl iodides by using K_2CO_3 as a base in toluene at 90 ºC (Scheme 2). Under this optimized reaction condition the coupling of iodobenzene, 4-iodoaniline and 1-bromo-4-iodoaniline with phenylacetylene led to formation of substituted aryl alkynes in good to excellent yield. The purified product obtained was characterized by elemental analysis, IR, ^{1}H NMR and mass spectra (Table 2). In order to check catalytic efficiency of **1a-c** and **2a-c** it was observed that, when $[Cu(CH_3CN)_4]X$ (where X = ClO_4^-, BF_4^- and PF_4^-) was added in toluene and K_2CO_3 as a base, the catalytic reaction exhibited extremely low reactivity towards the yield of diphenylacetylene with many by-products from aryl iodide substrate. The catalytic efficiency of **1a-c** and **2a-c** was compared with the previously reported copper(I) compounds[22] and it was found that, all of the reactions proceeded smoothly relatively at low temperature for 16 h and attained the coupling yield up to 66-89% (Table 3). We examined the effects of substituted group on the yield of the products and we found that, the catalytic system was compatible with different functional groups such as amino and bromo on aryl iodide substrates. on aryl iodide It was observed that the catalytic coupling of phenylacetylene with iodobenzene proceed the coupling yield up to 66–79% for **1a-c** and 73–82% for **2a-c** (Table 3, entries 1-3 and 4-6). With 4-iodoaniline containing electron donating NH_2 group at a *para* position, the yield reached up to 76–85% for **1a-c** and 78–89% for **2a-c** (Table 3, entries 7–9 and 10–12). However, with 1-bromo-4-iodoaniline containing electron withdrawing group at *para* position, the coupling reaction continued with

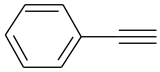
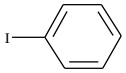
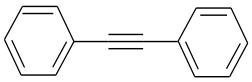
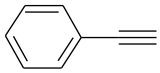
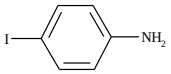
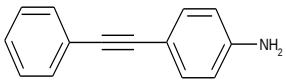
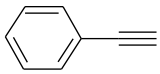
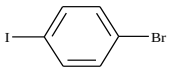
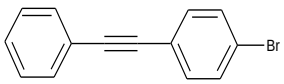


Scheme 2 — Sonogashira coupling reaction of phenylacetylene with aryl halides catalyzed by copper(I) complexes

Table 2 — Microanalytical and spectral data of coupling product

Compound	C, H, N found (calculated)			IR (cm^{-1})	Mass	^{1}H NMR (δ ppm)
	C	H	N			
Diphenylacetylene	94.30 (94.35)	5.48 (5.66)	- -	2151	m/z 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.41-7.59, (m, Ar -H)
4- Amino-diphenylacetylene	86.76 (87.02)	5.71 (5.76)	7.27 (7.24)	3414, 3294, 2152	m/z 193 $[C_6H_5C{\equiv}CC_6H_4NH_2]^+$, 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.41-7.65, (m, Ar-H) δ 3.86, (s, 2H, NH_2)
4-Bromo- diphenylacetylene	65.12 (65.39)	3.55 (3.54)	- -	2152	m/z 257 $[C_6H_5C{\equiv}CC_6H_4Br]^+$, 178 $[C_6H_5C{\equiv}CC_6H_5]^+$, 77 $[C_6H_5]^+$	δ 7.39-7.59, (m, Ar -H)

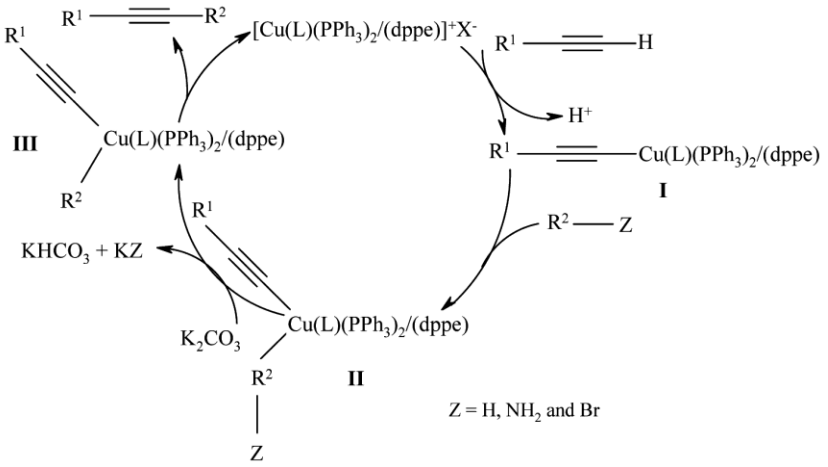
Table 3 — Sonogashira cross-coupling of phenylacetylene with aryl halides

Entry	Phenylacetylene	Aryl halide	Product	Complex	% yield
1.				1a	68
2.				1b	74
3.				1c	79
4.				2a	73
5.				2b	78
6.				2c	82
7				1a	76
8				1b	79
9				1c	85
10.				2a	78
11.				2b	83
12.				2c	89
13.				1a	66
14.				1b	70
15.				1c	76
16.				2a	70
17.				2b	73
18.				2c	79

Reaction conditions: phenylacetylene, 2.5 mmol; aryl halide, 2 mmol; copper(I) catalyst (10 mol%); K_2CO_3 (2 mmol); Toluene, 20 ml; temperature 90°C; reaction time 16 h.

increase in yield up to 66–76% for **1a-c** and 70–79 % for **2a-c** (Table 3, entries 13–15 and 16–18). These results confirm that variety of functional groups such as amino or bromo substituents were tolerated on aryl halide component, whilst significant electronic effects were observed for substituted aryl halide containing an electron donating NH_2 group at the *para*-position. Compared to **1a–c**, complexes **2a–c** shows greater activity for coupling of phenylacetylene with aryl halides. These results could be attributed to steric strain caused by dppe ligand is less than PPh_3 ligand which is more susceptible to the structural relaxation during the catalytic reaction[38]. The copper(I) complexes with different counter ions also exhibit different activities, especially the copper(I) complexes with PF_6^- counter ion returned slightly greater catalytic activities than the complexes' with ClO_4^-, BF_4^- and follow the order of PF_4^- > ClO_4^- > BF_4^- as their counter anions. These results might be due to the difference in binding ability of ClO_4^-, BF_4^- and PF_4^- to copper(I) ion which causes difference in solubility of the complexes in solvent during the reaction[39].

The probable mechanistic route and correlation between activity and structure of **1a–c** and **2a–c** could be completely elucidated from the results and is shown in Scheme 3. Initially, the copper(I) catalysts **1a-c** and **2a-c** activates terminal C-H bond of phenylacetylene to give a copper-acetylide intermediate (species I), which on oxidative addition of aryl iodide leads to formation of species II. This species is activated in presence of base to give *pi*-alkyne complex (species III), which makes terminal proton on alkyne more acidic and undergoes reductive elimination to give desired



Scheme 3 — Probable mechanistic route for the coupling of phenylacetylene with aryl halides using **1a-c** and **2a-c**.

diphenylacetylene and regenerate corresponding copper(I) complex.

Conclusions

A series of copper(I) complexes of the type [Cu(**L**)$(PPh_3)_2$]X(**1a-c**) and [Cu(**L**)(dppe)]X (**2a-c**) [where **L** = N-(2-quinolinylmethylene)-1,5-dimethyl-2-phenyl-1-pyrazole-3-(2H)-one; PPh_3= triphenyl-phosphine; dppe = 1,2-bis(diphenylphosphino)ethane; X = ClO_4^-, BF_4^- and PF_4^-] have been prepared and characterized by elemental analysis and spectroscopic techniques. All complexes displayed a weak MLCT that varies considerably with coordinated phosphine ligands. Thermogravimetric analysis reveals that copper(I) complexes based on PPh_3 ligand are thermally more stable than the dppe complexes. Quasireversible redox behavior is observed for all complexes corresponding to Cu(I)/Cu(II) couple. Moreover, compared to **2a-c** the redox process for **1a-c** appears at more positive potential which might be due to better π-acceptability character of PPh_3 than that of dppe ligand. All complexes worked as an efficient catalyst in Sonogashira cross-coupling reaction of phenylacetylene with aryl iodides in excellent yield. Complexes **2a–c** shows greater catalytic activity as compared to **1a–c** which is might be due to less steric strain caused by dppe ligand than PPh_3 ligand which is more susceptible to the structural relaxation during the catalytic reaction.

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