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Cite this: DOI: 10.1039/c0xx00000x

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FULL PAPER

# Syntheses, Characterization, and Structural studies of Copper(I) complexes containing 1,1'-bis(di-*tert*-butylphosphino) ferrocene (dtbpf) and their Application in Palladium-Catalyzed Sonogashira Coupling of Aryl halides

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Four copper(I) complexes [Cu<sub>4</sub>(μ<sub>3</sub>-Cl)<sub>4</sub>(μ-dtbpf)<sub>2</sub>] (**1**), [Cu<sub>6</sub>(μ<sub>3</sub>-Br)<sub>4</sub>(μ<sub>2</sub>-Br)<sub>2</sub>(μ-dtbpf)<sub>3</sub>] (**2**), [Cu<sub>4</sub>(μ<sub>2</sub>-I)<sub>2</sub>(μ<sub>3</sub>-I)<sub>2</sub>(μ-dtbpf)<sub>2</sub>] (**3**) and [Cu<sub>2</sub>(μ<sub>1</sub>-CN)<sub>2</sub>(κ<sup>2</sup>-dtbpf)<sub>2</sub>] (**4**) were prepared using CuX (X=Cl, Br, I, CN) and 1,1'-bis(di-*tert*-butylphosphino) ferrocene (dtbpf) in 2:1 molar ratio in DCM-MeOH (50:50 V/V) at room temperature. These complexes have been characterized by elemental analyses, IR, <sup>1</sup>H and <sup>31</sup>P NMR, ESI<sup>+</sup>-MS and electronic absorption spectroscopy. Molecular structures of the complexes **1**, **2** and **3** were determined crystallographically. Complexes **1** and **3** are tetrameric Cu(I) *pseudo*-cubane like structures with Cu<sub>4</sub>Cl<sub>4</sub> core, and stepped cubane-like structure with Cu<sub>4</sub>I<sub>4</sub> core, respectively, whereas complex **2** show trimeric copper(I) framework containing two [Cu<sub>3</sub>(μ<sub>3</sub>-Br)<sub>2</sub>(μ<sub>2</sub>-Br)] units that are bridged by three bidentate μ-dtbpf ligands. Each [Cu<sub>3</sub>(μ<sub>3</sub>-Br)<sub>2</sub>(μ<sub>2</sub>-Br)] units form a pyramid with one copper atom at the apex and one of the triangular faces capped by one bromine atom. All the complexes were found to be efficient catalysts for Sonogashira reaction. The coupling products were obtained in moderate to good yields (58-99%) by using Pd loadings to 0.2 mol% as well as complex loading to 0.1 mol%. The <sup>31</sup>P NMR studies show that all the complexes are unstable during the course of tandem catalytic reaction and dtbpf ligand migrates from copper(I) to palladium(II), which promotes palladium Sonogashira cross-coupling of activated and non-activated aryl halides.

## Introduction

During the last four decades, ferrocenyl diphosphines have received significant research interest because of their extensive applications as ligands for a wide variety of transition metal catalysed transformations.<sup>1</sup> Although there are many different types of ferrocenyl diphosphines, the most common are 1,1'-bis(diphenylphosphino) ferrocene (dppf)<sup>2</sup> and 1,1'-bis(di-*tert*-butylphosphino) ferrocene (dtbpf).<sup>2i,3</sup> These ligands have significant advantages over other diphosphines which contain alkyl rather than metallocene-backbones.<sup>4</sup> Recently it has been reported that dtbpf is superior to dppf for the Pd-catalyzed  $\alpha$ -arylation of ketones and for certain Pd-catalyzed Suzuki couplings.<sup>5,6</sup> The tetraphosphine ligand Fc(P)<sub>4</sub><sup>i</sup>Bu<sub>1,1',2,2'</sub>-tetrakis(diphenylphosphino)-4,4'-di-*tert*-butylferrocene, acts as an efficient auxiliary in Sonogashira reaction in the presence of [Pd( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> and copper.<sup>7</sup> Various Cu(I) complexes containing phosphine, *N*-heterocyclic carbene, imidazole, triazole, hybrid nitrogen-sulfur ligands have been found to be versatile catalysts in catalytic reactions.<sup>8</sup> We were interested in the structural properties of dtbpf complexes with simple salts, particularly copper(I) and their applications in cross-coupling reactions.<sup>9</sup> As compared to the previously mentioned 1,1'-

bis(phosphino)metallocene ligands, dtbpf has not been studied extensively. To date, most of the work with dtbpf had focused on catalytic systems in which dtbpf is used as a ligand for the palladium catalyst.<sup>10</sup> With these viewpoints and to explore other less expensive metal centre recently, our group<sup>11</sup> has explored the interaction of copper(I) thiocyanate with dtbpf for the construction of a tetranuclear copper(I) complex with a cubane-like structure and its application in palladium-catalyzed Sonogashira coupling reaction. To the best of our knowledge no structural report has been published on CuX: dtbpf (X=Cl, Br, I, CN). We decided to extend our studies in order to have a better understanding regarding the Cu(I) species present in the solid state as well as in solution. Herein we report the first syntheses, spectroscopic characterization, and catalytic properties of four copper(I) complexes [Cu<sub>4</sub>(μ<sub>3</sub>-Cl)<sub>4</sub>(μ-dtbpf)<sub>2</sub>] (**1**), [Cu<sub>6</sub>(μ<sub>3</sub>-Br)<sub>4</sub>(μ<sub>2</sub>-Br)<sub>2</sub>(μ-dtbpf)<sub>3</sub>] (**2**), [Cu<sub>4</sub>(μ<sub>2</sub>-I)<sub>2</sub>(μ<sub>3</sub>-I)<sub>2</sub>(μ-dtbpf)<sub>2</sub>] (**3**) and [Cu<sub>2</sub>(μ<sub>1</sub>-CN)<sub>2</sub>(κ<sup>2</sup>-dtbpf)<sub>2</sub>] (**4**), respectively.

## Experimental Section

### Materials and Physical Measurements

All the synthetic manipulations were performed under nitrogen atmosphere. The solvents were dried and distilled before use by following the standard procedures.<sup>12</sup> Copper(I) chloride,

Copper(I) bromide, Copper(I) iodide, Copper(I) cyanide and 1,1'-bis(di-*tert*-butylphosphino) ferrocene (all from Aldrich) were used as received. Elemental analyses were performed on a Carlo Erba Model EA-1108 elemental analyzer and data for C, H and N analyses were within  $\pm 0.4\%$  of calculated values. IR(KBr) was recorded using Perkin-Elmer FT-IR spectrophotometer. Electronic and emission spectra for **1-4** were obtained on a Perkin Elmer Lambda-35 and Horiba Jobin Yvon Fluorolog 3 spectrofluorometer, respectively.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a JEOL AL-400 FTNMR instrument using tetramethylsilane and phosphoric acid as an internal standard, respectively. Mass spectral data were recorded using a Waters micromass LCT Mass Spectrometer/Data system. Thermogravimetric analysis was carried out in air using TA DSC Q 200 instrument with a heating rate of  $10^\circ\text{C min}^{-1}$ . Powder X-ray diffraction data were collected on Bruker D8 Discover X-ray diffractometer, with Cu-K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). Electrochemical properties of the complexes **1-4** were measured by cyclic voltammetry using platinum as the working electrode and the supporting electrolyte used was [NBu<sub>4</sub>]ClO<sub>4</sub> (0.1 M) in 0.001 M dichloromethane solution of complexes **1-4** versus Ag/AgCl at a scan rate of  $100 \text{ mVs}^{-1}$ . GCMS studies were done with the Shimadzu-2010 instrument containing a DB-5/RtX-5MS-30Mt & 60Mt column of 0.25mm internal diameter.  $M^+$  is the mass of the cation.

#### Syntheses of the complexes

**Synthesis of [Cu<sub>4</sub>( $\mu_3$ -Cl)<sub>4</sub>( $\mu$ -dtbpf)<sub>2</sub>] (1).** 1,1'-bis(di-*tert*-butylphosphino) ferrocene (474 mg, 1 mmol) was added slowly to a solution of CH<sub>3</sub>OH (15 mL), and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) containing copper(I) chloride (198 mg, 2 mmol). The resulting solution was refluxed for 24 hours. Slowly, color of the solution changed from orange to yellowish orange. The resulting solution was filtered and saturated with hexane and left for slow evaporation. Orange colored crystals suitable for X-ray studies were obtained after two days. Yield: (1.075 g, 80%). Anal. Calc. for C<sub>52</sub>H<sub>88</sub>Cl<sub>4</sub>P<sub>4</sub>Cu<sub>4</sub>Fe<sub>2</sub>: C, 46.40; H, 6.54. Found: C, 46.43; H, 6.85. IR( $\text{cm}^{-1}$ , KBr):  $\nu = 3448, 3356, 3094, 2941, 2895, 2862, 1637, 1475, 1458, 1389, 1365, 1178, 1157, 1037, 932, 831, 815, 741, 606, 581, 547, 494, 471$ .  $^1\text{H}$  NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298K):  $\delta$  4.63 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 4.44 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 1.32 (d,  $^3J_{\text{H-P}} = 13.5 \text{ Hz}$ , 72H, CH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  31.14 (s) (sharp). UV/Vis:  $\lambda_{\text{max}}$  ( $\epsilon[\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}]$ ) = 390(14770), 288(34421). ESI<sup>+</sup>-MS ( $m/z$ ): 1344.9 ( $M^+$ ).

**Synthesis of [Cu<sub>6</sub>( $\mu_3$ -Br)<sub>4</sub>( $\mu_2$ -Br)<sub>2</sub>( $\mu$ -dtbpf)<sub>3</sub>] (2).** 1,1'-bis(di-*tert*-butylphosphino) ferrocene (474 mg, 1 mmol) was added slowly to a solution of CH<sub>3</sub>OH (15 mL), and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) containing copper(I) bromide (286 mg, 2 mmol). The resulting solution was refluxed for 24 hours, and color of the solution changed from orange to yellowish orange over this period. The resulting solution was filtered and saturated with hexane and left for slow evaporation. Yellow color crystals suitable for X-ray studies were obtained after four days. Yield: (1.485 g, 65%). Anal. Calc. for C<sub>78</sub>H<sub>132</sub>Br<sub>6</sub>P<sub>6</sub>Cu<sub>6</sub>Fe<sub>3</sub>: C, 40.98; H, 5.78. Found: C, 41.12; H, 5.95. IR ( $\text{cm}^{-1}$ , KBr):  $\nu = 3422, 3106, 3082, 2945, 2922, 2895, 2864, 2714, 2368, 2345, 2125, 1718, 1475, 1458, 1390, 1365, 1307, 1177, 1155, 1061, 1037, 934, 890, 850, 830, 813, 745, 629, 604, 577, 547, 492, 473, 438$ .  $^1\text{H}$  NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298K):  $\delta$  4.44 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 4.29 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 1.35 (d,  $^3J_{\text{H-P}} = 13.92 \text{ Hz}$ , 72H, CH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  37.39 (s) (sharp). UV/Vis:  $\lambda_{\text{max}}$  ( $\epsilon[\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}]$ ) = 467 (40838),

299(9930). ESI<sup>+</sup>-MS ( $m/z$ ): 2283.5 ( $M^+$ ).

**Synthesis of [Cu<sub>4</sub>( $\mu_2$ -I)<sub>2</sub>( $\mu_3$ -I)<sub>2</sub>( $\mu$ -dtbpf)<sub>2</sub>] (3).** 1,1'-bis(di-*tert*-butylphosphino) ferrocene (474 mg, 1 mmol) was added slowly to a solution of CH<sub>3</sub>OH (15 mL), and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) containing copper(I) iodide (380 mg, 2 mmol). The resulting solution was refluxed for 24 hours. Solution color changed slowly from orange to reddish orange color. The resulting solution was filtered and saturated with hexane and left for slow evaporation. Orange color crystals suitable for X-ray studies were obtained after three days. Yield: (1.197 g, 70%). Anal. Calc. for C<sub>52</sub>H<sub>88</sub>P<sub>4</sub>I<sub>4</sub>Cu<sub>4</sub>Fe<sub>2</sub>: C, 36.49; H, 5.15. Found: C, 36.63; H, 5.20. IR( $\text{cm}^{-1}$ , KBr):  $\nu = 3430, 3097, 2942, 2894, 2862, 1637, 1458, 1389, 1364, 1175, 1157, 1035, 936, 817, 580, 544, 493, 470, 439$ .  $^1\text{H}$  NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298K):  $\delta$  4.45 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 4.40 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 1.34 (d,  $^3J_{\text{H-P}} = 8.8 \text{ Hz}$ , 72H, CH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  28.31 (s) (sharp). UV/Vis:  $\lambda_{\text{max}}$  ( $\epsilon[\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}]$ ) = 484(48568), 272 (12832). ESI<sup>+</sup>-MS ( $m/z$ ): 1710.8 ( $M^+$ ).

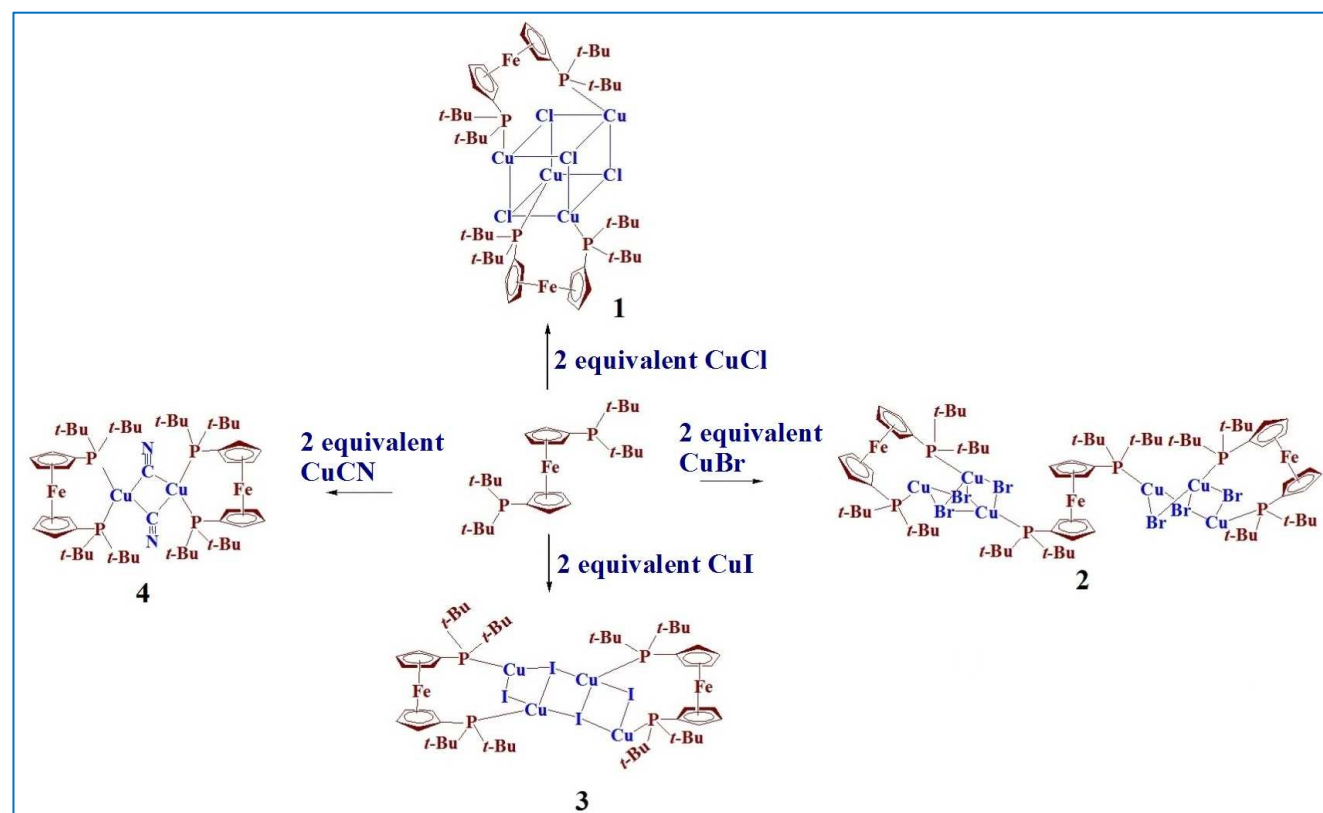
**Synthesis of [Cu<sub>2</sub>( $\mu$ -CN)<sub>2</sub>( $\kappa^2$ -dtbpf)<sub>2</sub>] (4).** 1,1'-bis(di-*tert*-butylphosphino) ferrocene (474 mg, 1 mmol) was added slowly to a solution of CH<sub>3</sub>OH (15 mL), and CH<sub>2</sub>Cl<sub>2</sub> (15 mL) containing copper(I) cyanide (179 mg, 2 mmol). The resulting solution was refluxed for 24 hours. Color of the solution changed slowly from orange to reddish orange. The resulting solution was filtered and saturated with hexane. In a couple of days reddish orange powder was precipitated which was washed several times with diethyl ether, and vacuum-dried. Yield: (0.789 g, 70%). Anal. Calc. for C<sub>54</sub>H<sub>88</sub>N<sub>2</sub>P<sub>4</sub>Cu<sub>2</sub>Fe<sub>2</sub>: C, 57.49; H, 7.81. Found: C, 57.64; H, 7.85. IR( $\text{cm}^{-1}$ , KBr):  $\nu = 3407, 2925, 2225, 2138, 1541, 1366, 1143, 1157, 1020, 813, 656, 602, 493$ .  $^1\text{H}$  NMR ( $\delta$  ppm, 400 MHz, CDCl<sub>3</sub>, 298K):  $\delta$  4.30 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 4.04 (s, 8H, C<sub>5</sub>H<sub>4</sub>), 1.36 (d,  $^3J_{\text{H-P}} = 8.8 \text{ Hz}$ , 72H, CH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  66.78 (s) (sharp). UV/Vis:  $\lambda_{\text{max}}$  ( $\epsilon[\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}]$ ) = 374 (11159), 284 (9565). ESI<sup>+</sup>-MS ( $m/z$ ): 1127.2 ( $M^+$ ).

#### X-ray structure determination

Intensity data sets for **1**, **2** and **3** were collected on Bruker APEX II and Oxford X-calibur S CCD area detector diffractometers using graphite monochromatized Mo-K $\alpha$  radiation at 100(2) and 293(2) K. ApexII, SAINT and CrysAlisPro RED software packages were used for data collection and data integration for **1** to **3**.<sup>13</sup> The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on  $F^2$ .<sup>13</sup> The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atoms were treated using appropriate riding models. Structures **1** and **2** were refined using solvent masking routine, SQUEEZE (Platon) as it was difficult to identify and model the solvent present in the lattice. Despite several attempts, we are not able to get better quality crystals for complex **3**. This resulted in poor crystal data with higher R-factor. The crystal undergoes decomposition/solvent loss during data collection adding to the problem. PLATON was also used for analyzing the interaction and stacking distances.<sup>14</sup>

#### Sonogashira Catalytic Reactions

The reaction of aryl halides ( $3.38 \times 10^{-3}$  mol, 1 equivalent), phenylacetylene (0.75 mL,  $6.76 \times 10^{-3}$  mol, 2 equivalent), and K<sub>2</sub>CO<sub>3</sub> (0.935 g,  $6.76 \times 10^{-3}$  mol, 2 equivalent) with 0.001 equivalent of complex **1/2/3/4** and 0.002 equivalent [PdCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (0.73 mg), at 120°C for 20 h in DMF (10 mL), under nitrogen, formed the coupling products. The progress of the



Scheme 1. Synthetic routes for the complexes 1-4.

reaction was monitored by TLC using EtOAc and hexane as eluent. After completion, the reaction mixture was treated with EtOAc (10 mL) and water (3 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic solution was washed with brine (3 × 5 mL) and water (1 × 5 mL). Drying (anhydrous Na<sub>2</sub>SO<sub>4</sub>) and evaporation of the solvent provided a residue, which was purified on short pad of silica gel using EtOAc and hexane as eluent.

## Results and Discussion

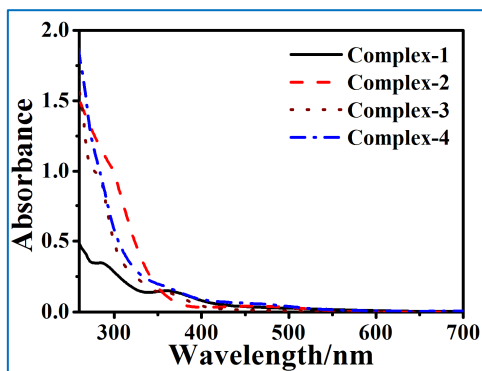
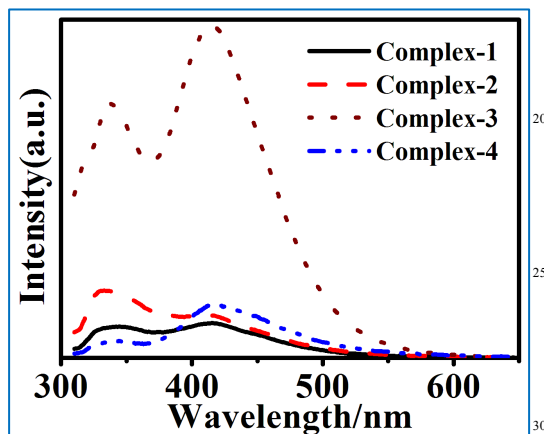
### Synthesis

All the complexes [Cu<sub>4</sub>(μ<sub>3</sub>-Cl)<sub>4</sub>(μ-dtpbf)<sub>2</sub>] (**1**), [Cu<sub>6</sub>(μ<sub>3</sub>-Br)<sub>4</sub>(μ<sub>2</sub>-Br)<sub>2</sub>(μ-dtpbf)<sub>3</sub>] (**2**), [Cu<sub>4</sub>(μ<sub>2</sub>-I)<sub>2</sub>(μ<sub>3</sub>-I)<sub>2</sub>(μ-dtpbf)<sub>2</sub>] (**3**) and [Cu<sub>2</sub>(μ<sub>1</sub>-CN)<sub>2</sub>(κ<sup>2</sup>-dtpbf)<sub>2</sub>] (**4**) were prepared in high yield by the reaction of CuX (X = Cl, Br, I, CN) with 1,1'-bis(di-*tert*-butylphosphino)ferrocene ligand in a dichloromethane: methanol mixture (50:50 V/V) in 2:1 ratio under refluxing condition (Scheme 1). Complexes **1-4** were found to be air stable, non-hygroscopic solids and soluble in dimethylformamide, dimethylsulfoxide and halogenated solvents but insoluble in petroleum ether and diethyl ether. The elemental analyses were consistent with their chemical formula. More information about composition of the complexes was also obtained from ESI<sup>+</sup>-MS. The positions of different peaks and overall fragmentation patterns in the ESI<sup>+</sup>-MS of the respective complexes are consistent with their formulations. The IR spectrum of complex **4** exhibited characteristic band corresponding to ν<sub>C≡N</sub> of the bridging cyanide group at 2138 cm<sup>-1</sup> (See F4, supporting material). However, only one ν<sub>C≡N</sub> band

agreed well with the presence of only one type of cyanide bridge between copper(I) atom<sup>15</sup>, which is in accordance with those reported in literature for bridging pseudohalide groups.<sup>16</sup> <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectral data of the complexes are presented in the experimental section along with the other data. In <sup>1</sup>H NMR spectra of the complexes **1**, **2**, **3** and **4**, η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub> protons of dtpbf ligand resonated as a two broad singlets in the range of δ 4.63-4.04 ppm (See F-5 supporting material). The *tert*-butyl protons of dtpbf were observed as a doublet at 1.32-1.36 ppm. The <sup>31</sup>P NMR spectra of the complexes **1-4** showed a single resonance (δ 31.14(**1**), 37.39(**2**), 28.31(**3**), 66.78 (**4**) ppm) for the dtpbf ligand which suggested that all the phosphorus atoms were chemically equivalent (See F-6-F-9 supporting material). These chemical shifts were within the accepted range and are comparable to that of the chelating dtpbf ligands.<sup>10c,17</sup> All the complexes exhibited two bands at 374-484 nm and 272-299 nm in dichloromethane solution (Fig. 1; Table 1). The lower-energy band in the range 374-484 nm can be assigned to the d-d transition. The higher-energy band at 259-275 nm has been assigned to intraligand charge transfer. All the complexes upon excitation at their respective lowest energy band maximum (374-484 nm) were non-emissive, however, on excitation at 272-299 nm exhibited two broad emission at 334-341 nm and 415-419 nm, respectively (Fig. 2; Table 1). We tentatively assigned the emission of these complexes to XLCT, CC, and LC transitions as dtpbf ligand does not show luminescence in the range of 495-900 nm.

**Table 1.** Electronic and emission spectral data for complexes 1-4.

Complexes	Absorbance	Emission
	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )	$\lambda_{\text{max}}/\text{nm}$
$[\text{Cu}_4(\mu_3\text{-Cl})_4(\mu\text{-dtbpf})_2]$ (1)	390, 288	341, 417
$[\text{Cu}_6(\mu_3\text{-Br})_4(\mu_2\text{-Br})_2(\mu\text{-dtbpf})_3]$ (2)	467, 299	337, 415
$[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$ (3)	484, 272	334, 417
$[\text{Cu}_2(\mu_1\text{-CN})_2(\kappa^2\text{-dtbpf})_2]$ (4)	374, 284	338, 419

**Fig. 1.** Electronic spectra for 1-4 in  $\text{CH}_2\text{Cl}_2$ .**Fig. 2.** Emission spectra for 1-4 in  $\text{CH}_2\text{Cl}_2$ .

The electrochemical redox behavior of the complexes 1-4 were studied through cyclic voltammetry (CV) at the Pt electrode in dichloromethane solution (1mM) containing 0.1M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte (Fig. 3). The  $\text{Ag}/\text{Ag}^+$  in acetonitrile was used as reference electrode. The electrochemical parameters derived from these voltammograms ( $E_{\text{p,a}}$ ,  $E_{\text{p,c}}$ ,  $\Delta E$ ) are given in Table 2. It is to be noted that the peak potential separation ( $\Delta E = E_{\text{p,a}} - E_{\text{p,c}}$ ) is larger than the expected value for one electron transfer process ( $\sim 60$  mV,  $I_{\text{p,a}}/I_{\text{p,c}} = 1$ ) for these complexes so, one can conclude that these complexes exhibit *quasi*-reversible redox behavior coupled with some chemical reaction. In comparison to the ferrocene standard ( $E^\circ = 0.19\text{V}$ ), the potentials for these complexes are anodically shifted due to the electron withdrawing effect of the linker groups between the ferrocene units. In complexes 1 and 3, single cathodic peak are present at -173 and -714 mV, respectively.

#### Description of the Crystal Structures

Three X-ray structures emerged from the current study. Refinement details for all the structures are summarized in

**Table 2.** Electrochemical data for 1-4 in dichloromethane solution/0.1M  $[\text{NBu}_4]\text{ClO}_4$  at 298K.

	$E_{\text{p,a.1}}$ (mV)	$E_{\text{p,c.1}}$ (mV)	$E_{\text{p,c.2}}$ (mV)	$\Delta E$ (mV)	$I_{\text{p,a}}/I_{\text{p,c}}$
<b>Complex-1</b>	+258	+170	-173	88	1.11
<b>Complex-2</b>	+431	+320	-	111	1.69
<b>Complex-3</b>	+72	+12	-714	60	0.84
<b>Complex-4</b>	+39	-37	-	76	0.61

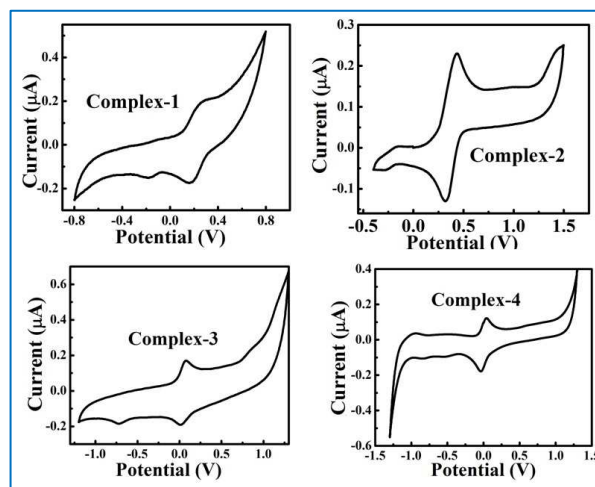
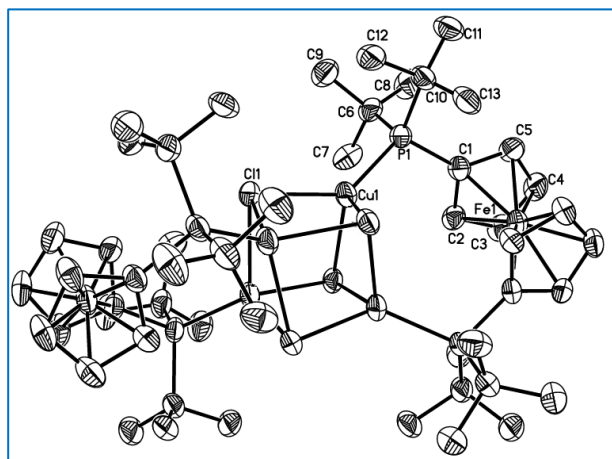
**Fig. 3.** Cyclic voltammogram for the complexes 1-4 in  $\text{CH}_2\text{Cl}_2/0.1$  M  $[\text{NBu}_4]\text{ClO}_4$  at  $100$   $\text{mV}/\text{s}^{-1}$  scan rate.

Table 1 in the SI, and selected bond lengths and angles and hydrogen bond parameters are presented in Table 2 and Table 3 in the SI, respectively. Complex 1 crystallizes in the orthorhombic crystal system, and the structure was solved in space group  $Fddd$ . The molecular structure of 1 is depicted in Fig. 4. Complex 1 reveals the tetranuclear copper(I) complex, which produces an 18-electron configuration at each copper without the need for any metal-metal bonds. The  $\text{Cu}_4\text{Cl}_4$  core of the molecule defines a rather distorted “cubane-like” framework, with the phosphorus atoms being approximately apical, thereby completing a *pseudo*-tetrahedral coordination provided by the bidentate dtbpf ligands in  $\kappa^1$ -manner and the four bridging chloro groups in  $\mu_3$ -manner about each Cu(I) atom. The Cu-Cl bond lengths vary appreciably, ranging from  $2.3747(16)$  Å to  $2.5269(16)$  Å [ $\text{Cu}(1)\text{-Cl}(1)^{\#1} = 2.4315(17)$  Å;  $\text{Cl}(1)\text{-Cu}(1)^{\#2} = 2.5269(16)$  Å;  $\text{Cu}(1)\text{-Cl}(1) = 2.3747(16)$  Å]. The tetramer is irregular with respect to the  $\text{Cu}\cdots\text{Cu}$  separations ( $2.936\text{-}3.424$  Å) and the  $\text{Cl}\cdots\text{Cl}$  separations ( $3.378\text{-}3.953$  Å). The six  $\text{Cu}\cdots\text{Cu}$  distances; are in the range of  $2.936\text{-}3.424$  Å, (average value =  $3.200$  Å). All these distances are sufficiently large to preclude the possibility of any significant direct  $\text{Cu}\cdots\text{Cu}$  interaction. The  $\text{Cl}\cdots\text{Cl}$  distances within the  $[\text{Cu}_4(\mu_3\text{-Cl})_4(\mu\text{-dtbpf})_2]$  molecule spread over a slightly larger range than the  $\text{Cu}\cdots\text{Cu}$  distances. Angles within the  $\text{Cu}_4\text{Cl}_4$  cube vary significantly from the idealized value of  $90^\circ$ . The Cu-Cl, and Cu-P bond distances are  $2.3747(16)\text{-}2.5269(16)$  Å, and  $2.1950(17)$  Å, respectively and are comparable with other copper derivatives with ferrocenyl diphosphines.<sup>8,9,17,18</sup> The two substituted Cp rings in the dtbpf ligand in 1 adopt the antiperiplanar staggered conformation. Crystal packing in complex 1 is stabilized by  $\text{C-H}\cdots\text{Cl}$  hydrogen bond interactions (See F-11 supporting material). The contact distances for  $\text{C-H}\cdots\text{Cl}$  interactions are in the range of  $2.74\text{-}2.90$  Å.

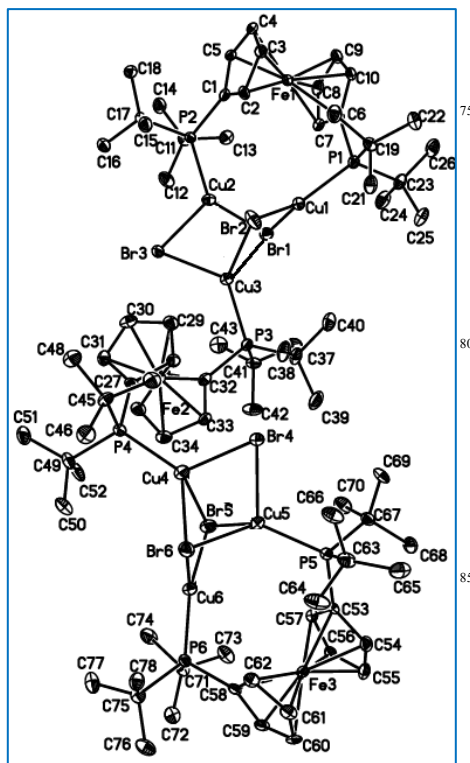
Complex **2** crystallized in the triclinic space group *P*-1. The molecular structure of **2** is depicted in Fig. 5. The structure of complex **2** exhibits a triangular copper(I) frameworks, where two [Cu<sub>3</sub>(μ<sub>3</sub>-Br)<sub>2</sub>(μ<sub>2</sub>-Br)] units are bridged by three bidentate dtbpf ligands in κ<sup>1</sup>-manner. Each [Cu<sub>3</sub>(μ<sub>3</sub>-Br)<sub>2</sub>(μ<sub>2</sub>-Br)] units to form a pyramid with one copper atom at the apex and one of the



**Fig. 4.** Projection view of **1** (ellipsoids with 50% probability; hydrogen atoms are omitted for clarity).

triangular faces capped by one bromine atom. Atoms Cu(4) and Cu(5) are tetrahedrally coordinated to the phosphorus donor [P(4), P(5)] of two bridging dtbpf ligands [Cu(5)-P(5)= 2.2088(12) Å; Cu(4)-P(4)= 2.2216(13) Å; P(5)-Cu(5)-Br(4)= 113.56(4)°; P(5)-Cu(5)-Br(6)= 124.58(4)°; P(5)-Cu(5)-Br(5)= 123.64(4)°; P(4)-Cu(4)-Br(4)= 121.59(4)°; P(4)-Cu(4)-Br(6)= 121.15(4)°; P(4)-Cu(4)-Br(5)= 124.34(4)°] in κ<sup>1</sup>-manner, one double-bridging bromine atom [Br(4)] and two triple-bridging bromine atoms [Br(5) and Br(6)] whereas, the second phosphorus atom [P(6)] of the same dtbpf donor additionally coordinates in κ<sup>1</sup>-manner to Cu(6) atom in trigonal fashion [Cu(6)-P(6)= 2.2059(13) Å; P(6)-Cu(6)-Br(5)= 128.84(4)°, P(6)-Cu(6)-Br(6)= 131.86(4)°, and two triple-bridging bromine atoms [Br(5) and Br(6)]. The Cu(2) and Cu(3) of other [Cu<sub>3</sub>(μ<sub>3</sub>-Br)<sub>2</sub>(μ<sub>2</sub>-Br)] unit are coordinated tetrahedral to the phosphorus donor [P(2), P(3)] of bridging dtbpf ligands [Cu(2)-P(2)= 2.2134(12) Å; Cu(3)-P(3)= 2.2048(13) Å; P(2)-Cu(2)-Br(3)= 121.51(4)°; P(2)-Cu(2)-Br(1)= 119.23(4)°; P(2)-Cu(2)-Br(3)= 121.51(4)°, P(3)-Cu(3)-Br(3)= 127.09(4)°, P(3)-Cu(3)-Br(2)= 129.12(4)°, P(3)-Cu(3)-Br(1)= 108.39(15)°] in κ<sup>1</sup>-manner, one double bridging bromine atom [Br(3)] and two triple-bridging bromine atoms [Br(1) and Br(2)], while the remaining Cu(1) atom is trigonally bonded to phosphorus donor [P1] of bridging dtbpf in κ<sup>1</sup>-manner [Cu(1)-P(1)= 2.1998(13) Å; P(1)-Cu(1)-Br(2)= 124.71(4)°, P(1)-Cu(1)-Br(1)= 128.83(4)°, Br(2)-Cu(1)-Br(1)= 106.06(3)°] and two triple-bridging bromine atoms [Br(1) and Br(2)]. The Cu(I) ions thus come as tetra- and tricoordinate pairs with distorted tetrahedral or trigonal planar coordination. As expected, the Cu-P [Cu(6)-P(6)= 2.2059(13) Å, Cu(1)-P(1)= 2.1998(13) Å] and Cu-Br [Cu(6)-Br(5)= 2.4232(7) Å, Cu(6)-Br(6)= 2.4413(8) Å, Cu(1)-Br(1)= 2.4064(8) Å, Cu(1)-Br(2)= 2.3884(8) Å] bond distances of the tricoordinate copper ions are appreciably shorter than those of the tetrahedrally coordinated Cu-P bond distances

[Cu(4)-P(4)= 2.2216(13) Å, Cu(5)-P(5)= 2.2088(12) Å, Cu(3)-P(3)= 2.2048(13) Å, Cu(2)-P(2)= 2.2134(12) Å] and Cu-Br [Br(4)-Cu(4)= 2.4592(8) Å, Br(5)-Cu(4)= 2.6900(9) Å, Br(6)-Cu(4)= 2.7471(8) Å, Br(4)-Cu(5)= 2.4740(8) Å, Br(5)-Cu(5)= 2.6883(8) Å, Br(6)-Cu(5)= 2.5669(8) Å, Br(2)-Cu(3)= 2.4759(8) Å, Br(3)-Cu(3)= 2.4308(7) Å, Br(1)-Cu(3)= 3.054(9) Å, Br(1)-Cu(2)= 2.4763(7) Å, Br(3)-Cu(2)= 2.4311(7) Å, Br(2)-Cu(2)= 3.027(7) Å]. Such types of copper(I) complexes involving tetrahedral and trigonal chromophores and both triple- and double-bridging halides have been found in the tetranuclear ‘step’ [Cu(PPH<sub>3</sub>)X]<sub>4</sub><sup>18b,19</sup>, [CuX<sub>2</sub>(dppm)]<sub>2</sub> (X = I, Br or Cl)<sup>20</sup> and ‘three-runged ladder’ [Cu<sub>3</sub>(μ<sub>3</sub>-X)(μ-X)<sub>2</sub>(μ-dpmt)]<sub>2</sub> (X = I, Br, Cl), where dpmt = 2,5-bis[(diphenylphosphino)methyl]thiophene.<sup>21</sup> The structure of complex **2** has some similarities with these open ‘step’ molecules, but differ from them by the virtual planarity of the Cu<sub>3</sub>X<sub>3</sub> framework. The copper-copper distances are in the range of 2.6980(8) Å–2.9789(8) Å in **2**, shorter than those found in ‘cubane’ [Cu<sub>4</sub>X<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>] (X = I, Br or Cl) [2.874(5)–3.164(4) Å]<sup>18a,18b,22</sup> and ‘step’ [Cu<sub>4</sub>X<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>] (X = I or Br) [2.835(3)–3.448(3) Å]<sup>18b,19</sup> and are comparable to those found in ‘step’ [CuX<sub>2</sub>(dppm)]<sub>2</sub> (X = I, Br or Cl) [2.682(7)–3.180(2) Å]<sup>22</sup>, indicating that there are no direct Cu...Cu interactions. The sum of all bonding angles of 359.8° and 343.2° for the tricoordinate and tetracoordinate copper ions in **2** indicates pyramid formation. The two substituted Cp rings in the dtbpf ligand in **2** adopt the antiperiplanar staggered conformation as well. Crystal packing in complex **2** is stabilized by C-H...Br hydrogen bond interactions (See F-15 supporting material). The contact distances for C-H...Br interactions are in the range of 2.90–3.14 Å.



**Fig. 5.** Projection view of **2** (ellipsoids with 50% probability; hydrogen atoms are omitted for clarity).

Complex **3** crystallized in the orthorhombic space group Pca21. The molecular structure of **3** is depicted in Fig. 6. Complex **3** shows the tetranuclear copper(I) complex, which produces an 18-electron configuration at each copper without the need for any metal-metal bonds. The  $\text{Cu}_4\text{I}_4$  core for this molecule has a step structure, rather than a cubane-like configuration. The step structure of  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  is defined by three four-membered systems: Cu(1)-I(1)-Cu(2)-I(2) [plane I], Cu(1)-I(1)-Cu(4)-I(3), and Cu(3)-I(3)-Cu(4)-I(4) (plane II). The dihedral angle between planes I and II is  $101.31^\circ$ - $102.23^\circ$ , which is lower

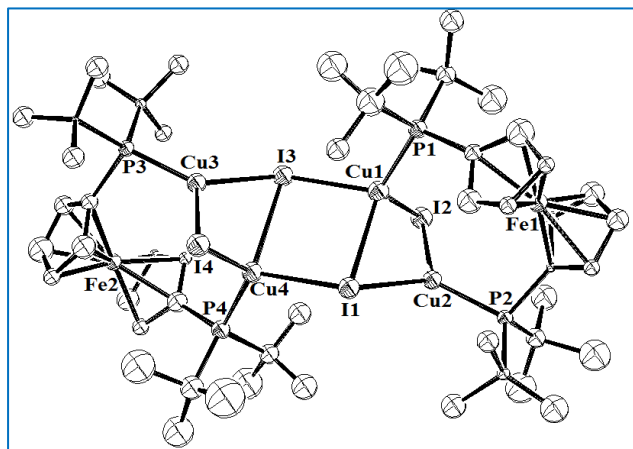


Fig. 6. Projection view of **3** (ellipsoids with 50% probability; hydrogen atoms are omitted for clarity).

than that of  $[\text{PPh}_3\text{Cu}]_4$ .<sup>19</sup> Atoms Cu(1), I(1), Cu(4), and I(3) are crystallographically coplanar. Atoms Cu(2), I(2), Cu(1), and I(1) are not precisely coplanar. The nonplanarity of this four-membered motif is conveniently described in terms of the dihedral angles of  $135.09^\circ$  [between I(2)-Cu(2)-I(1) and I(2)-Cu(1)-I(2)] and  $133.27^\circ$  [between Cu(1)-I(2)-Cu(2) and Cu(1)-I(1)-Cu(2)]. Atoms in the step-like  $\text{Cu}_4\text{I}_4$  core of the  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  molecule have variable coordination numbers. Thus, Cu(1) and Cu(2) are of trigonal coordination (CN = 3), while Cu(3) and Cu(4) each have an essentially tetrahedral coordination environment (CN = 4). Atoms I(2) and I(4) have an angular geometry (CN = 2), while I(1) and I(3) are in pyramidal sites (CN = 3). As was previously seen for  $\text{Cu}_4\text{I}_4$  core by Churchill et al.,<sup>19</sup> the copper-halogen distances show significant differences and increase systematically as the CN of the component atoms increases. In the present case, we have observed a similar pattern. The four copper atoms are exactly coplanar and show a parallelogram. These distances in “ $\text{Cu}_4$  parallelogram” are comparable to the reported values. The four iodine atoms of  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  are precisely coplanar. Individual I...I distances show considerably less variation than do the Cu...Cu distances; these are I(1)...I(2) =  $4.251 \text{ \AA}$ , I(2)...I(3) = I(1)...I(4) =  $4.115 \text{ \AA}$ , and I(1)...I(3) =  $3.974 \text{ \AA}$ . These distances are within the range reported for iodo derivatives of phosphine complexes.<sup>18,23</sup> Angles within the four-membered rings defined by Cu(2)-I(2)-Cu(1)-I(1) and Cu(3)-I(4)-Cu(4)-I(3) vary grossly from  $90^\circ$ . Angles at the copper atoms are close to the ideal trigonal or tetrahedral values [I(2)-Cu(2)-I(1) =  $111.9(2)^\circ$ , I(1)-Cu(1)-I(2) =  $102.30(2)^\circ$ , I(3)-Cu(4)-I(4) =  $100.62(19)^\circ$ , and I(4)-Cu(3)-I(3) =  $113.0(2)^\circ$ , respectively] while angles at the iodine atoms are quite acute

[Cu(2)-I(2)-Cu(1) =  $63.14(18)^\circ$ , Cu(2)-I(1)-Cu(1) =  $60.90(17)^\circ$ , Cu(3)-I(3)-Cu(4) =  $60.30(17)^\circ$ , Cu(3)-I(4)-Cu(4) =  $63.70(18)^\circ$ . Angles between atoms in different planes of the step are not dependent upon the nature of the central atom. Small angles at the iodine atoms are common to species with a  $\text{Cu}_4\text{I}_4$  core, irrespective of the gross geometry of the molecule. The Cu-I-Cu angles are comparable to those in the other similarly related complexes with step and cubane-like structures. The reason for small Cu-I-Cu angles could be due to van der Waals repulsions between the halogen atoms. The Cu(trigonal)-P distance of  $2.176(12) \text{ \AA}$ - $2.252(12) \text{ \AA}$  is slightly shorter than the Cu(tetrahedral)-P distance of  $2.230(12) \text{ \AA}$ - $2.279(11) \text{ \AA}$ . The two substituted Cp rings in the dtbpf ligand in **3** adopt the antiperiplanar staggered conformation. Crystal packing in complex **3** is stabilized by C-H...I hydrogen bond interactions (See F-19 supporting material). The contact distances for C-H...I interactions are in the range of  $3.00$ - $3.16 \text{ \AA}$ .

#### Powder X-ray diffraction and thermal gravimetric analysis

All the four complexes (**1**, **2**, **3** and **4**) have been further studied by powder X-ray diffraction (PXRD) (See F-22 to F-25 supporting material) and thermogravimetric analysis (TGA) (See F-26 to F-29 supporting material). There is good agreement between the experimental and calculated powder XRD patterns for the complexes **1**, **2**, and **3**, thus supporting phase purity. The thermogravimetric (TG) curves over  $30$ - $800^\circ\text{C}$  indicates that in complex **1**, weight loss takes place in four close and consecutive steps from  $30^\circ\text{C}$  to  $784^\circ\text{C}$ . Weight loss occurred in two steps in complex **2**. The first weight loss is between  $30^\circ\text{C}$  to  $425^\circ\text{C}$  whereas the second weight loss is finished around  $700^\circ\text{C}$ . There are two weight loss steps in complex **3**. The first one is from  $32^\circ\text{C}$  to  $533^\circ\text{C}$ , the second one is finished around  $600^\circ\text{C}$ . Complex **4** is stable up to  $\sim 250^\circ\text{C}$  but after that there is a slight weight increase till  $280^\circ\text{C}$ . Followed by that, there is a weight loss from  $410^\circ\text{C}$  to  $745^\circ\text{C}$ .

#### Catalytic Performances in Sonogashira Alkynylation Reactions

The comparative catalytic activities of the CuI and newly synthesized copper(I) complexes were investigated in Sonogashira alkynylation of activated and non-activated aryl halides according to the previously established method developed by Hierso et al.<sup>24</sup> The comparative catalytic performances for the coupling of the activated and non-activated aryl halides with phenylacetylene are presented in Table 4. It can be seen that, without palladium, the system incorporating only either complex **1-4** or CuI were inefficient (Table 4, entry 1 & 2). We have also found that no reaction occurred in the absence of a copper source and dtbpf (Table 4, entry 3). As shown in Table 4, we isolated 10-11% yield of coupling product in the presence of  $[\text{Pd}(\text{allyl})\text{Cl}]_2/\text{dtbpf}$  (Table 4, entry 4) with no formation of homocoupling products under these conditions indicating that dtbpf and copper source are crucial to the cross-coupling reaction. Actually, as shown in Table 4, we observed a difference in catalytic activity, that is, complexes **1-4** exhibited higher catalytic activity compared to CuI. In the case of coupling between bromobenzene and phenylacetylene in the presence of either 0.4 mol% of CuI or CuI/dtbpf and 0.2 mol% of  $[\text{Pd}(\text{allyl})\text{Cl}]_2$ , the isolated yield of alkynylation product was 20-25%, while alkylne

**Table 4.** Sonogashira Coupling of activated and non-activated aryl halides with Alkynes  $\text{RC}\equiv\text{CH}^a$  in the presence of complexes **1-4**.

Entry	R	X	Copper source	Palladium source ([Pd(allyl)Cl] <sub>2</sub> )	Alkynylation product yield [%] <sup>b</sup>				Alkyne dimerization yield [%] <sup>b</sup>				
					1	2	3	4	1	2	3	4	
1.	H	Br	0.1 mol% complexes 1-4		0	0	0	0	0	0	0	0	0
2.	H	Br	0.4 mol% CuI		0	0	0	0	0	0	0	0	0
3.	H	Br		0.2 mol%	0	0	0	0	0	0	0	0	0
4.	H	Br		0.2 mol%/dtbpf	10	10	11	10	No	No	No	No	No
5.	H	Br	0.4 mol% CuI	0.2 mol%	20	20	20	21	50	50	50	50	50
6.	H	Br	0.4 mol% CuI	0.2 mol%/dtbpf	25	25	25	25	60	60	60	60	60
7.	H	Br	0.1 mol% complexes 1-4	0.2 mol%	70	78	85	70	traces	traces	traces	traces	traces
8.	H	I	0.1 mol% complexes 1-4	0.2 mol%	85	86	95	75	No	No	No	No	No
9.	H	Cl	0.1 mol% complexes 1-4	0.2 mol%	60	66	70	61	25	20	25	30	30
10.	CH <sub>3</sub>	Br	0.1 mol% complexes 1-4	0.2 mol%	68	75	84	72	traces	traces	traces	traces	traces
11.	CH <sub>3</sub>	I	0.1 mol% complexes 1-4	0.2 mol%	85	88	99	77	No	No	No	No	No
12.	CH <sub>3</sub>	Cl	0.1 mol% complexes 1-4	0.2 mol%	62	62	75	58	traces	traces	traces	traces	traces

<sup>a</sup>All reactions were carried out using  $3.38 \times 10^{-3}$  mol activated and non-activated aryl halides, phenylacetylene (2 equivalent),  $\text{K}_2\text{CO}_3$  (2 equivalent), 0.1 mol% of the complexes **1-4**/0.4 mol% of CuI with 0.2 mol% of  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  and the catalytic system stirred at  $120^\circ\text{C}$  over 20 h in 10 mL of DMF under nitrogen.

<sup>b</sup>Isolated yield.

dimerization products were formed in appreciable amounts (entry 5 & 6) so the use of complexes **1-4** in the presence of  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  was more efficient for this coupling. The use of the complexes **1-4** confirmed that the pre-stabilization of copper(I) structures with a bidentate ferrocenyl phosphine ligand promotes the palladium cross-coupling of activated and non-activated aryl halides with phenylacetylene. The desired coupled product in 60-95% yield was obtained (75-85%, 75-95% and 60-70%, respectively, Table 4 entries 7, 8, and 9) by employing 0.1 mol% of **1** to **4**, 0.2 mol% of the palladium source, and the non-activated bromo, iodo or chlorobenzene. Under the same catalytic conditions the electron-rich 4-bromotoluene, 4-iodotoluene and 4-chlorotoluene were efficiently coupled resulting in yields of over 58-99% (68-84%, 77-99% and 58-75%, respectively, Table 4 entries 10, 11, and 12). The catalytic activities of various copper(I) complexes such as  $[\text{Cu}_4(\mu_3\text{-SCN})_4(\kappa^1\text{-P},\text{P-dtbpf})_2]$ ,<sup>11</sup>  $[\text{Cu}_4(\mu_3\text{-Cl})_4(\mu\text{-dtbpf})_2]$ ,  $[\text{Cu}_6(\mu_3\text{-Br})_4(\mu_2\text{-Br})_2(\mu\text{-dtbpf})_3]$ ,  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  and  $[\text{Cu}_2(\mu_1\text{-CN})_2(\kappa^2\text{-dtbpf})_2]$  were tested in Sonogashira alkynylation reactions. Among them,  $[\text{Cu}_4(\mu_3\text{-SCN})_4(\kappa^1\text{-P},\text{P-dtbpf})_2]$  and  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  are more efficient copper source as compared to others in catalyzing this reaction.

#### Interactions of Copper(I) complexes **1-4** with Palladium(II)

The stability of all the complexes **1-4** were checked by <sup>31</sup>P and <sup>1</sup>H NMR experiments with palladium allyl chloride during the course of tandem catalytic reaction. Upon mixing the complex **1** with 0.5 equivalent of the  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  and heating for 2 h at  $120^\circ\text{C}$ , a portion of the dtbpf ligand is transferred to palladium, giving rise to the palladium complex  $[\text{PdCl}(\mu^1\text{-C}_3\text{H}_5)(\kappa^2\text{-P},\text{P-dtbpf})]$ , clearly characterized in the <sup>31</sup>P NMR by two sharp singlets at 31.14 ppm (complex **1**) and 57.27 ppm (palladium complex) of equal intensity (See F-30 supporting material). Further heating the mixture for 4 h at  $120^\circ\text{C}$ , the equilibrium is not modified. Upon heating the mixture for 20 h at  $120^\circ\text{C}$ , the total transfer of the

ligand from copper to palladium centre has been observed in complex **1** (See F-31 supporting material). The same kind of experiments was conducted with the complexes **2-4** in  $\text{CDCl}_3$ . Analogous behaviour was observed with the complexes **2-4** in  $\text{CDCl}_3$  (Figure F32-F34), showing the total transfer of the ligand from copper to palladium (See F-35 to F-37 supporting material). Similar type of finding has been found in copper(I) iodide triphosphine adducts used at low loading for Sonogashira alkynylation of demanding halide substrates, for which ligand exchange study between copper and palladium have been reported.<sup>24</sup> The generalized results of Pd/Cu ligand exchange has been summarized in a scheme 2. The ligand transfer from the complexes **1-4** might takes place due to the relatively soft nature of Pd(II) precursor which results in the transmetalation reaction to form  $[\text{PdCl}(\mu_1\text{-C}_3\text{H}_5)(\kappa^2\text{-P},\text{P-dtbpf})]$  (See F-38 to F-39 supporting material) when the palladium precursor is simply mixed.

## CONCLUSIONS

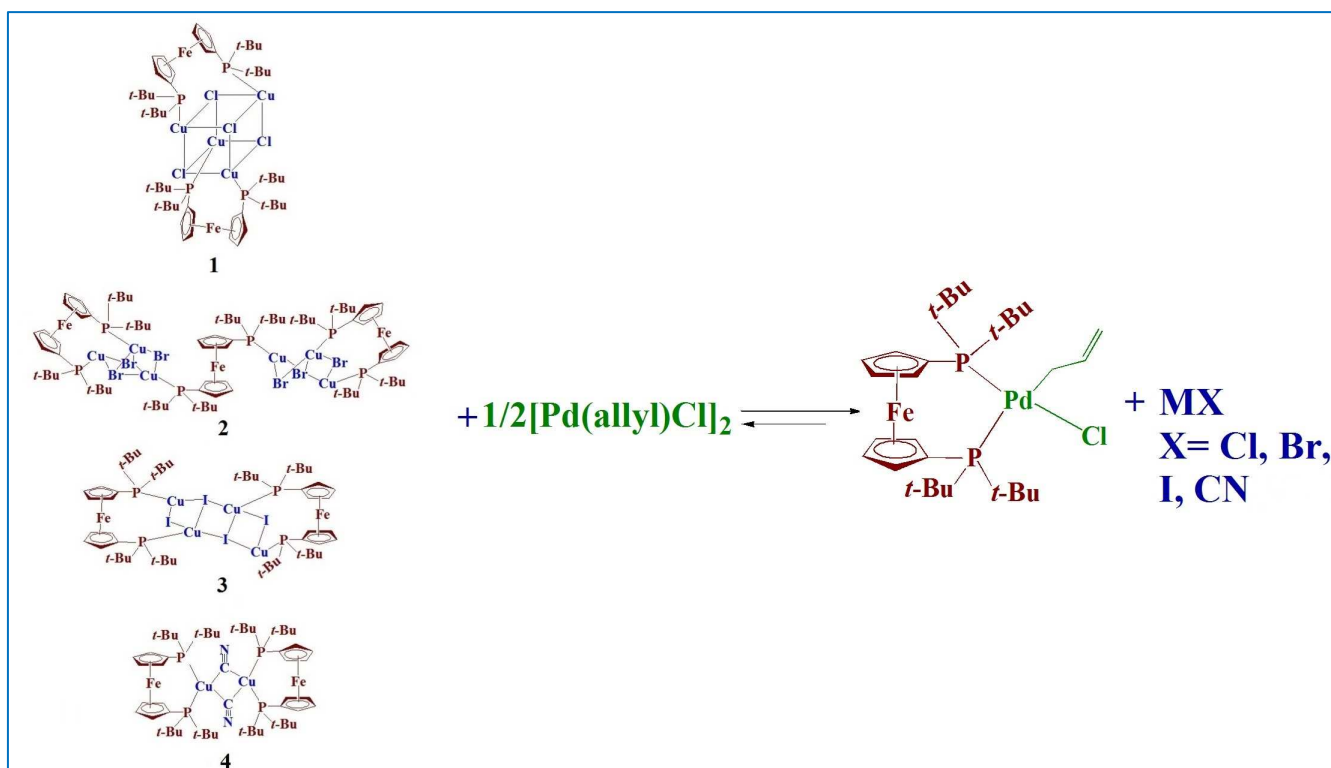
We have synthesized and structurally characterized a series of copper(I) complexes  $[\text{Cu}_4(\mu_3\text{-Cl})_4(\mu\text{-dtbpf})_2]$  (**1**),  $[\text{Cu}_6(\mu_3\text{-Br})_4(\mu_2\text{-Br})_2(\mu\text{-dtbpf})_3]$  (**2**),  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  (**3**), and  $[\text{Cu}_2(\mu_1\text{-CN})_2(\kappa^2\text{-dtbpf})_2]$  (**4**) in both solid state and solution. The interesting features of complex **1** and **2** are Cu(I) pseudo-cubane with  $\text{Cu}_4\text{Cl}_4$  core and stepped cubane-like structure with  $\text{Cu}_4\text{I}_4$  core, whereas complex **3** shows a triangular copper(I) frameworks, where each  $[\text{Cu}_3(\mu_3\text{-Br})_2(\mu_2\text{-Br})]$  units forms a pyramid with one copper atom at the apex and one of the triangular faces capped by one bromine atom. The newly synthesized complexes were successfully used in the Sonogashira cross-coupling of activated and non-activated aryl halides with phenylacetylene. While all the complexes screened were found to be catalytically active, the best results were obtained for the complexes  $[\text{Cu}_4(\mu_3\text{-SCN})_4(\kappa^1\text{-P},\text{P-dtbpf})_2]$  and  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  in comparison to CuI. The <sup>31</sup>P NMR studies show



Cite this: DOI: 10.1039/c0xx00000x

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Scheme 2. The generalized results of Pd/Cu ligand exchange in complexes 1-4.

that complexes 1-4 are unstable during the course of tandem catalytic reaction and dtbpf ligand migrates to palladium(II) from copper(I), which promotes palladium Sonogashira cross-coupling of activated and non-activated aryl halides. Further works towards development of new copper(I) complexes containing various chiral and achiral ferrocene phosphine ligands and their catalytic properties is in progress in our laboratory.

### Acknowledgements

Thanks are due to Department of Science and Technology, New Delhi for financial assistance (Grant No. SR/FT/CS-104/2011). We also thank to the Director, USIC, and Dr. R. Nagarajan, University of Delhi, Delhi, for providing analytical, spectral, PXRD and Single Crystal X-ray Diffraction facilities and GC-MS facility from AIRF center of JNU, New Delhi. Special thanks are due to Professor P.J. Sadler, University of Warwick, UK and Professor Josef Michl, University of Colorado, USA for their kind encouragement. We acknowledge funding from the National Science Foundation (CHE0420497) for the purchase of the APEX II diffractometer.

### Notes and references

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30 † Electronic Supplementary Information (ESI) available: CCDC reference numbers 1002754(1), 1002756 (2), 924712 (3). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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***Graphical Abstract: Synopsis and Pictogram***

The syntheses and characterization of copper(I) complexes  $[\text{Cu}_4(\mu_3\text{-Cl})_4(\mu\text{-dtbpf})_2]$  (**1**),  $[\text{Cu}_6(\mu_3\text{-Br})_4(\mu_2\text{-Br})_2(\mu\text{-dtbpf})_3]$  (**2**),  $[\text{Cu}_4(\mu_2\text{-I})_2(\mu_3\text{-I})_2(\mu\text{-dtbpf})_2]$  (**3**) and  $[\text{Cu}_2(\mu_1\text{-CN})_2(\kappa^2\text{-dtbpf})_2]$  (**4**) are reported. These complexes were shown to exhibit efficient catalytic activity compared to CuI in Sonogashira reaction by using Pd loadings to 0.2 mol% as well as complexes **1/2/3/4** to 0.1 mol%.

