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Synthesis of homo and heteroleptic Cu(I) complexes with chelating N and P donor ligands

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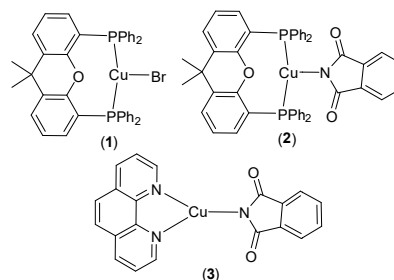
ABSTRACT

Reaction of 6,6'-dimethyl-2,2'-bipyridine (6,6'-Me₂bpy) with [Cu(NCMe)₄]PF₆ in the 2:1 molar-ratio afforded [Cu(6,6'-Me₂bpy)₂]PF₆ (**8**) as a red solid. [Cu(Ph₄bpy)₂]PF₆ (**9**) (Ph₄bpy = 3,4,5,6-tetraphenyl-2,2'-bipyridine) was prepared in a similar manner. Treatment of 4,5-bis(diphenylphosphino)-9,9'-dimethylxanthene (xantphos) with [Cu(NCMe)₄]PF₆ in the 2:1 molar-ratio gave the four-coordinate homoleptic complex [Cu(xantphos)₂]PF₆ (**10**) as a white solid. The four-coordinate heteroleptic copper(I) complex [Cu(6,6'-Me₂bpy)(xantphos)]PF₆ (**1**) containing both N and P donor ligands was prepared by treating [Cu(NCMe)₄]PF₆ with a (1:1) mixture of 6,6'-Me₂bpy and xantphos. [Cu(Ph₄bpy)(xantphos)]PF₆ (**12**) was prepared in a similar manner. Treatment of [Cu(NCMe)₄]PF₆ with one mole of xantphos in acetonitrile gave a tri-coordinate copper(I) complex [Cu(NCMe)(xantphos)]PF₆ (**13**) as a white solid. Treatment of (**13**) with one mole of 6,6'-Me₂bpy gave the mixed-ligand complex [Cu(6,6'-Me₂bpy)(xantphos)]PF₆ (**11**) in 96% yield. Reaction of [Cu(NCMe)₄]PF₆ and bis(diphenylphosphino) methane (dppm) in the 1:1 molar-ratio resulted in [Cu(NCMe)₂(μ-dppm)₂Cu(NCMe)₂][PF₆]₂ (**14**) as a white solid. Reaction of (**14**) with 3,6-di(2'-pyridyl)tetrazine (dptz) in the 1:1 molar-ratio gave dark purple crystals of [Cu₂(μ-dptz)(μ-dppm)₂][PF₆]₂ (**15**). Above complexes were characterized by elemental analysis, IR, Mass and NMR spectroscopy.

1. Introduction

The stereochemistry of copper(I) complexes show number of coordination modes depending on the nature of the ligands. Four-coordination is preferred with planar chelating N-donor ligands and triarylphosphines with small cone angles. The ligands 1,10-phenanthroline (phen) or 4,7-substituted-1,10-phenanthroline associated with CuI (or Cu₂O, CuBr, CuOTf, [Cu(MeCN)₄]PF₆) have been used to catalyse C-C, C-O or C-N cross-coupling reactions [1]. Molecular and supramolecular architectures (e.g. catenanes, rotaxanes, knots, helices, dendrimers, cages, etc) containing Cu(I) centres are known to exhibit photo and electroluminescence [2]. Electron transfer reactions involving Cu(II)/(I) centres have attracted attention of many researchers since these reactions are strongly related to the biologically important catalytic processes [3]. The 1:1 molar-ratio reaction between copper(I) bromide and xantphos in acetonitrile results in the formation of neutral tri-

coordinate [CuBr(xantphos)] (**1**), which displays luminescent emission at room temperature.

**Figure 1.** Structures of compounds (**1**) - (**3**)

The high rigidity and steric requirements of the xanthene unit has influenced the trigonal planar geometry around Cu(I) centre where the diposphine acting as a chelate [4]. Neutral tri-coordinate Cu(I) phthalimide complexes (**2**) and (**3**) contain xantphos and phen ligands, respectively [5]. The interest on Cu(I) complexes has risen recently as an alternative to many other expensive light

harvesting complexes based on transition metals such as ruthenium, platinum and iridium [2]. The copper(I) complex of the type $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ (**4**) containing mixed-ligands 2,9-Me₂phen and bis[2-diphenylphosphino]phenyl ether has shown unusually efficient, long-lived photoluminescence [6]. Analogous Cu(I) complex (**5**) containing 1,1'-bis(diphenylphosphino)ferrocene is not luminescent under any condition due to photoinduced energy transfer from Cu(I) unit to the ferrocene moiety [7].

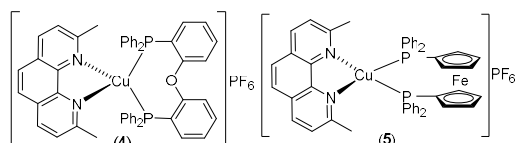


Figure 2. Structures of compounds (**4**) and (**5**)

Luminescent binuclear and polynuclear Cu(I) complexes have been prepared from 4,4'-bis(diphenylphosphino) biphenylene (**6**), which contains two PPh₂ groups attached to a rigid aromatic spacer [8]. Methanol drives the blue emissive complex $[\text{Cu}_2(\text{dppy})_3(\text{MeCN})][\text{BF}_4]_2$ (**7**) (dppy = diphenylphosphino pyridine) with a head-to-tail arrangement of the three bridging phosphine ligands. In the solid state, it has converted to its linkage isomer (head-to-head, green emissive) [9].

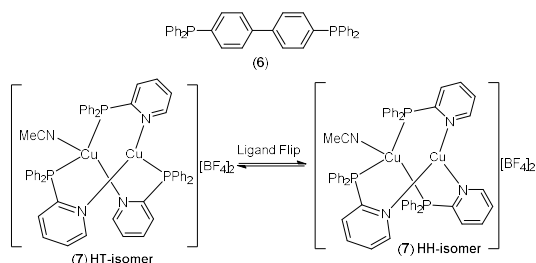


Figure 3. Structures of compounds (**6**) and (**7**)

In 2017, Zeng *et al.*, synthesized several Cu(I) complexes using 1,2-phenyl-bridged P[^]N, P[^]N[^]P, and N[^]P[^]N ligands. Some of these complexes display phosphorescence with emission color ranging from blue to red [10]. Recently, triply bridged binuclear copper(I) complexes of the type $[\text{Cu}_2(\mu\text{-rac-dpmpm})(\text{N}^{\wedge}\text{N})_2]^{2+}$, containing $\text{rac-dpmpm} = \text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{PPh}_2$ and N[^]N = phen, 4-Mephen, 4,7-Me₂phen, 5,6-Me₂phen, 2,9-Me₂phen, 3,4,7,8-Me₄phen, 4,7-Ph₂phen, bipy, 4,4'-Me₂bipy, and 1,8-naphthyridine were prepared [11].

Copper is a cheap metal. In addition to its huge contribution made in organic synthesis, copper complexes may find applications in OLED and other optical devices due to their interesting photo-physical and electrochemical properties, which depend on the number and nature of the attached ligands [1-11]. Therefore, it is of interest to explore

the chemistry of copper(I) centres with chelating (N[^]N) donors, (P[^]P) donors, and mixed (N[^]N) and (P[^]P) donors. Here we report studies carried out to devise synthetic routes to such complexes using ligands such as 6,6'-dimethyl-2,2'-bipyridine (6,6'-Me₂bpy), 3,4,5,6-tetraphenyl-2,2'-bipyridine (Ph₄bpy), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos), bis(diphenylphosphino) methane (dppm) and 3,6-di(2'-pyridyl)tetrazine (dptz). 6,6'-Me₂bpy is a planar symmetrical ligand whilst Ph₄bpy is a bulky unsymmetrical ligand with two nitrogen donors. 3,6-Di(2'-pyridyl)tetrazine has six nitrogen donors which can bridge two metal centres or produce polynuclear complexes.

2. Methodology

All the experiments were carried out in an inert atmosphere (dinitrogen or argon). Elemental analysis was carried out on a Carlo Erba 1006 automatic analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer fitted with a Universal-ATR sampling accessory. Mass spectral data were obtained using a micromass LCT electrospray mass spectrometer. MALDI-TOF mass spectra were recorded on a Waters Premier spectrometer using α -cyano-4-hydroxy cinnamic acid matrix. Accurate mass spectra were referenced against Leucine Enkephalin. NMR spectra were recorded on a DPX 400 spectrometer operating at 400.13 MHz for ¹H, and 100.62 MHz for ¹³C, and were standardized with respect to TMS. ³¹P NMR spectra were recorded at 161 MHz and were standardized with respect to phosphoric acid. 6,6'-Dimethyl-2,2'-bipyridine (6,6'-Me₂bpy), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos), bis(diphenylphosphino)methane (dppm) and $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$, were purchased from Aldrich. 3,4,5,6-Tetraphenyl-2,2'-bipyridine and 3,6-di(2'-pyridyl)tetrazine (dptz) were prepared according to literature procedures [12, 13].

$[\text{Cu}(6,6'\text{-Me}_2\text{bpy})_2]\text{PF}_6$ (**8**)

6,6'-Dimethyl-2,2'-bipyridine (13 mg, 0.070 mmol) and $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ (12 mg, 0.032 mmol) were dissolved in dichloromethane (4 mL). The resulting red solution was stirred at room temperature for 2 h. It was concentrated to a low volume and diethyl ether was added to give red crystals (15 mg, 81%). IR (neat, cm⁻¹): 2963, 1599, 1463, 1404, 835 and 786. MS ESI (MeCN, m/z): Found: 431.1294; calcd. 431.1297 for C₂₄H₂₄N₄Cu, $[\text{M-PF}_6]^+$. ¹H NMR (400 MHz, CD₃CN): δ 8.28 (d, 4H, ³J(HH) 8.0 Hz, H^{Pv}), 8.04 (t, 4H, ³J(HH) 7.5 Hz, H^{Pv}), 7.52 (d, 4H, ³J(HH) 7.5 Hz, H^{Pv}) and 2.24 (s, 12H, Me).

[Cu(Ph₄bpy)₂]PF₆ (9)

[Cu(NCMe)₄]PF₆ (12.1 mg, 0.0325 mmol) was added to a solution of 3,4,5,6-tetraphenyl-2,2'-bipyridine (30 mg, 0.065 mmol) in dichloromethane (1 mL) to give a dark solution. The reaction mixture was warmed at 50 °C for 1 min. After 1 h, the solvent was removed under reduced pressure and the residue was triturated with methanol to give a dark brown solid, (28 mg, 78%). Found: C, 71.98; H, 4.28; N 4.79, calcd. (%) for C₆₈H₄₈N₄PF₆Cu: C, 72.3; H, 4.28; N 4.96. IR (neat, cm⁻¹): 3057, 1599, 1468, 1443, 1401, 834, 759 and 697.ESI-MS (acetonitrile, m/z): Found: 983.3201; calcd. 983.3175 for C₆₈H₄₈N₄Cu, [M-PF₆]⁺. ¹H NMR (400 MHz, CDCl₃): δ 8.37 (d, br, 1H, J = 3.5 Hz, H^{6'}), 7.54-7.42 (m, 2H, H^{4'} & H^{5'}) 7.31-7.15 (m, 6H, H^{Ph}), 7.07-6.88 (m, 10H, H^{Ph}), 6.75 (d, br, 1H, J = 8.0 Hz, H^{3'}) and 6.72-6.62 (m, 4H, H^{Ph}).

[Cu(xantphos)₂]PF₆ (10)

4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos) (19 mg, 0.0328 mmol) and [Cu(NCMe)₄]PF₆ (6 mg, 0.016 mmol) were dissolved in degassed dichloromethane (4 mL). The resulting clear solution was stirred at room temperature for 2 h. It was concentrated to a low volume and diethyl ether was added to give a white solid (19 mg, 86%). Found: C, 67.62; H, 4.79, calcd. (%) for C₇₈H₆₄F₆O₂P₅Cu·0.25CH₂Cl₂: C, 67.76; H, 4.68. IR (neat, cm⁻¹): 2965, 1602, 1406, 1231, 833, 742 and 694. MS ESI (MeCN, m/z): Found: 1219.2469; calcd. 1219.3153 for C₇₈H₆₄O₂P₄Cu, [M-PF₆]⁺. ¹H NMR (400 MHz, CD₃CN): 7.79-6.06 (broad, 52H, H^{Ph/Ar}) and 1.64 (broad, 12H, Me). ³¹P NMR (161 MHz, CD₃CN): -17.6 ppm (broad).

[Cu(6,6'-Me₂bpy)(xantphos)]PF₆ (11)

[Cu(NCMe)₄]PF₆ (12 mg, 0.0322 mmol) was added to a degassed solution containing 6,6'-dimethyl-2,2'-bipyridine (5.9 mg, 0.0322 mmol) and xantphos (18.6 mg, 0.0322 mmol) in dichloromethane (3 mL). The reaction mixture was stirred at room temperature for 2 h. It was concentrated to a low volume and diethyl ether was added to give yellow crystals (22 mg, 88%). Found: C, 61.45; H, 4.48; N 2.52, calcd. (%) for C₅₁H₄₄CuF₆N₂OP₃·0.5CH₂Cl₂: C, 61.00; H, 4.47; N 2.76. IR (neat, cm⁻¹): 2964, 1600, 1404, 1224, 1096, 835, 742 and 695. MS ESI (MeCN, m/z): Found: 825.2219; calcd. 825.2225 for C₅₁H₄₄N₂OP₂Cu, [M-PF₆]⁺. ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, 2H, ³J(HH) 8.0 Hz, H^{Py}), 7.89 (t, 2H, ³J(HH) 7.5 Hz, H^{Py}), 7.63 (dd, 2H, ³J(HH) 7.5 Hz, ³J(HH) 1.0 Hz, H^{Ar}), 7.36 (t, 4H, ³J(HH) 7.5 Hz, H^{Ph}), 7.24-7.13 (m, 12H, H^{Ph}, H^{Py}&H^{Ar}), 7.10-7.05 (m, 8H, H^{Ph}), 6.89 (m, 2H, H^{Ar}), 2.01 (s, 6H, Me), and 1.74 (s, 6H, Me). ¹³C NMR (100 MHz, CD₃CN): δ 157.6, 155.0, 152.1, 139.2 (C^{Ph}), 133.7, 133.0 (t, J(PC) = 7.7 Hz, C^{Ph}), 131.3 (t, J(PC) = 7.7

Hz, C^{Ph}), 130.4 (C^{Ar}), 130.4 (C^{Ph}), 128.8 (t, J(PC) = 4.4 Hz, C^{Ph}), 127.2 (C^{Ar}), 125.6 (C^{Py}), 125.3 (C^{Ar}), 121.9 (t, J(PC) = 13.2 Hz, C^{Ar}), 120.5 (C^{Py}), 65.8, 36.1, 28.3, 26.5 (Me), 15.2 (Me). ³¹P NMR (161 MHz, CD₃CN): -11.7 ppm.

[Cu(6,6'-Me₂bpy)(xantphos)]PF₆ (11) from (13)

[Cu(NCMe)(xantphos)]PF₆ (13) (20 mg, 0.024 mmol) and 6,6'-Me₂bpy (4.6 mg, 0.025 mmol) were dissolved in dichloromethane (2 mL) to give a pale yellow solution. After one hour, the solution was concentrated to a low volume and diethyl ether was added to give (11) as a yellow solid, (22 mg, 96%). Characterizing data are same as above.

[Cu(Ph₄bpy)(xantphos)]PF₆ (12)

[Cu(NCMe)₄]PF₆ (12 mg, 0.0322 mmol) was added to a degassed solution containing 3,4,5,6-tetraphenyl-2,2'-bipyridine (14.8 mg, 0.0322 mmol) and xantphos (18.6 mg, 0.0322 mmol) in CH₂Cl₂ (3 mL). Reaction mixture was stirred at room temperature for 2 h and concentrated to a low volume; methanol was added to give a yellow solid, (18 mg, 53%). IR (neat, cm⁻¹): 3057, 1596, 1436, 1403, 1228, 1097, 834, 746 and 695. Maldi (MeCN, m/z): Found: 1101.3213; calcd. 1101.3164 for C₇₃H₅₆N₂OP₂Cu, [M-PF₆]⁺. ¹H NMR (400MHz, CD₃CN at 20 °C): 7.67-6.41 (broad, 50H, H^{Ph/Ar/Py}), 2.05 (broad, 3H, Me) and 1.45 (broad, 3H, Me). ¹H NMR (400MHz, CD₃CN at 60 °C): 7.75 (d, 1H, ³J(HH) 6.6 Hz, H^{Py}), 7.55-6.51 (broad, 49H, H^{Ph/Ar/Py}) and 1.70 (broad, 6H, Me). ³¹P NMR (400MHz, CD₃CN): -14.2 ppm (broad).

[Cu(Ph₄bpy)(xantphos)]PF₆ (12) from (13)

[Cu(NCMe)(xantphos)]PF₆ (13) (10 mg, 0.012 mmol) and 3,4,5,6-tetraphenyl-2,2'-bipyridine (6 mg, 0.013 mmol) were dissolved in dichloromethane (2 mL) to give a pale yellow solution. After 1 h, the solution was concentrated to a low volume and diethyl ether was added to give (12) as a yellow solid, (11 mg, 77%). Maldi (MeCN, m/z): Found: 1101.3130; calcd. 1101.3164 for C₇₃H₅₆N₂OP₂Cu, [M-PF₆]⁺. ¹H NMR in CD₃CN is broad at RT, ³¹P NMR (400MHz, CD₃CN): -14.2 ppm (broad).

[Cu(NCMe)(xantphos)]PF₆ (13)

4,5-Bis(diphenylphosphino)-9,9'-dimethylxanthene (19 mg, 0.032 mmol) and [Cu(NCMe)₄]PF₆ (12 mg, 0.032 mmol) were dissolved in degassed acetonitrile (3 mL). The resulting solution was heated to 60 °C for 1 h. It was concentrated to a low volume and diethyl ether was added to give a white solid (18 mg, 64%). Found: C, 59.72; H, 3.97; N, 1.49 calcd.(%) for C₄₁H₃₅F₆NOP₃Cu, C, 59.46; H, 4.26; N, 1.69. IR (neat): 3056, 2954, 2273, 1607, 1480, 1435, 1405, 1233, 1097, 835, 749, 738 and 691 cm⁻¹. MS ESI (acetone, m/z): found: 641.1255;

calcd. 641.1224 for $C_{39}H_{32}OP_2Cu$, $[M-MeCN-PF_6]^+$. 1H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, 2H, $^3J(HH)$ 8.0 Hz, $^4J(HH)$ 1.5 Hz, H^{Ar}), 7.40 (t, 4H, $^3J(HH)$ 7.0 Hz, H^{Ph}), 7.33 (t, 6H, $^3J(HH)$ 7.5 Hz, H^{Ph}), 7.29-7.24 (m, 10H, H^{Ph}), 7.19 (t, 2H, $^3J(HH)$ 8.0 Hz, H^{Ar}), 6.67 (m, 2H, H^{Ar}), 2.21 (s, 3H, Me), and 1.62 (s, 6H, Me). ^{31}P NMR (161 MHz, CD_3CN): -12.9 ppm (s).

$[Cu(NCMe)_2(\mu-dppm)_2Cu(NCMe)_2][PF_6]_2$ (**14**)

Bis(diphenylphosphino)methane (dppm) (37 mg, 0.0963 mmol) and $[Cu(NCMe)_4]PF_6$ (36 mg, 0.096 mmol) were refluxed in degassed acetonitrile (6 mL) for 1 hour. The solution was filtered and the filtrate was concentrated to a low volume (ca. 1.5 mL) and diethyl ether was added to give a white solid (56 mg, 86%). IR (neat): 3058, 2263, 1575, 1484, 1436, 1371, 1099, 828, 770, 739 and 693 cm^{-1} . MS MALDI-TOF (MeCN, m/z): Found: 831.1668; calcd. 831.1690 for $C_{50}H_{44}P_4Cu$, $[Cu(dppm)_2]^+$. 1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 40H, H^{Ph}), 3.53 (m, 4H, CH_2) and 2.19 (s, 12H, Me). ^{31}P NMR (161 MHz, $CDCl_3$): -6.4 ppm.

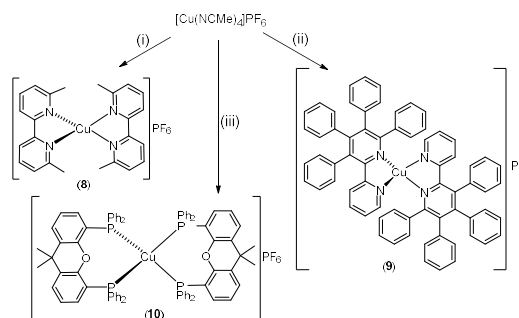
$[Cu_2(\mu-dptz)(\mu-dppm)_2][PF_6]_2$ (**15**)

$[Cu(NCMe)_2(\mu-dppm)_2Cu(NCMe)_2][PF_6]_2$ (22 mg, 0.0169 mmol) was added to a solution of 3,6-di(2-pyridyl)tetrazine (dptz) (4 mg, 0.0169 mmol) in dichloromethane (2 mL) and the reaction mixture was stirred for 3 h. It was filtered, and the filtrate was concentrated to a low volume (ca. 0.5 mL). Addition of diethyl ether gave dark purple crystals which was filtered off and washed with diethyl ether (21 mg, 88%). IR (neat, cm^{-1}): 2961, 1605, 1481, 1436, 1395, 1097, 831, 733 and 687. Found: C, 51.95; H, 4.10; N 6.15, calcd. (%) for $C_{62}H_{52}N_6PF_2Cu_2$: C, 52.37; H, 3.69; N 5.91. 1H NMR (400 MHz, $CDCl_3$): δ 9.26 (d, 2H, $^3J(HH)$ 8.0 Hz), 8.29 (d, 2H, $^3J(HH)$ 4.5 Hz), 8.23 (t, 2H, $^3J(HH)$ 7.5 Hz), 7.53 (m, 2H, $^3J(HH)$ 7.5 Hz), 7.39-7.38 (s, br, 6H, H^{Ph}), 7.34-7.20 (m, 18H, H^{Ph}), 6.74-6.67 (s, br, 6H, H^{Ph}), 3.94 (m, 2H, CH_2) and 3.44 (m, 2H, CH_2). ^{31}P NMR (161 MHz, $CDCl_3$): -8.2 ppm.

3. Results and Discussion

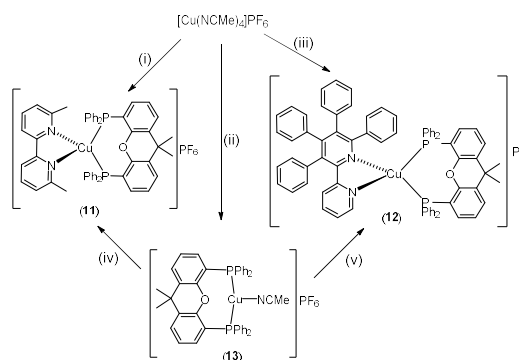
The coordination chemistry of the copper(I) centre with bidentate nitrogen donor ligands was studied first, and the four-coordinate homoleptic Cu(I) complex (**8**) of the type $[Cu(N^{\wedge}N)_2]^+$ was prepared by reacting the labile copper(I) salt $[Cu(NCMe)_4]PF_6$ with two moles of 6,6'-Me₂bpy in dichloromethane. $[Cu(6,6'-Me_2bpy)_2]PF_6$ (**8**) was isolated as a red solid in 81% yield (see scheme 1). All complexes were adequately characterized by a combination of elemental analysis, IR, Mass and NMR spectroscopy. The 1H -NMR spectrum of (**8**) showed two doublets and a triplet for the pyridyl

moiety whilst the methyl protons appeared as a singlet at 2.24 ppm. Accurate mass value (m/z, 431.1294) is in good agreement with the cation $[Cu(6,6'-Me_2bpy)_2]^+$ containing two bipyridyl ligands.



Scheme 1. Synthetic routes to compounds (**8**) - (**10**). (i) 6,6'-Me₂bpy; (ii) Ph₄bpy; (iii) xantphos

In a similar manner, homoleptic Copper(I) complex $[Cu(Ph_4bpy)_2]PF_6$ (**9**) was prepared as a dark brown solid in 78% yield using the bulky ligand 3,4,5,6-tetraphenyl-2,2'-bipyridine (Ph₄bpy). In the proton NMR spectrum, the H6' proton of the pyridyl group appeared as a broad doublet at 8.37 ppm. Treatment of two moles of the bulky diphosphinexantphos with $[Cu(NCMe)_4]PF_6$ gave the hoped for four-coordinate homoleptic Cu(I) complex $[Cu(xantphos)_2]PF_6$ (**10**) as a white solid in 86% yield. The ^{31}P -NMR spectrum of (**10**) showed a broad singlet at -17.6 ppm. 1H -NMR spectrum of (**10**) showed broad signals suggesting the fluxionality of the molecule.

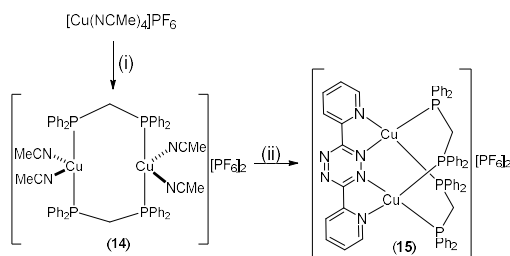


Scheme 2. Synthetic routes to compounds (**11**) - (**13**). (i) 6,6'-Me₂bpy and xantphos (1:1); (ii) xantphos; (iii) Ph₄bpy and xantphos (1:1); (iv) 6,6'-Me₂bpy; (v) Ph₄bpy

The four-coordinate heteroleptic copper(I) complexes of the type $[Cu(N^{\wedge}N)(P^{\wedge}P)]^+$ containing both N and P donor ligands can be prepared by treating $[Cu(NCMe)_4]PF_6$ with a mixture of N[∧]N donor ligand and xantphos in (1:1) molar-ratio (see scheme 2). The $[Cu(6,6'-Me_2bpy)(xantphos)]PF_6$ (**11**) was isolated as a yellow solid in 88% yield which indicates that the formation of mixed-ligand complex $[Cu(N^{\wedge}N)(P^{\wedge}P)]^+$ is more stable than the

other possible coordination modes leading to $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ and $[\text{Cu}(\text{P}^{\wedge}\text{P})_2]^+$. The ^{31}P -NMR spectrum of (**11**) showed a singlet at -11.7 ppm. In the ^1H -NMR spectrum of (**11**), the methyl proton resonance of 6,6'-Me₂bpy appeared as a singlet at 2.01 ppm. Analogous complex (**12**) was prepared in a similar manner as a yellow solid in moderate yield. The ^{31}P -NMR spectrum of (**11**) showed a broad singlet at -14.2 ppm. At 20 °C, the methyl groups of xantphos were not equivalent and gave two broad singlets at 2.05 and 1.45 ppm. At 60 °C, they coalescence to a broad singlet at 1.70 ppm.

The possibility of stepwise introduction of P donors and N donors to prepare complexes of the type $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ via a complex $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{labile ligand})]^+$ was explored by replacing the labile ligand with a bidentate ligand N[∧]N as shown in the scheme 2. Treatment of $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ with one equivalent xantphos in acetonitrile gave a white solid in 64% yield. It showed a phosphorus-31 resonance at -12.9 ppm. Characterizing data including elemental analysis suggests it to be a three-coordinate copper(I) complex $[\text{Cu}(\text{NCMe})(\text{xantphos})]\text{PF}_6$ (**13**). Treatment of this copper(I) complex (**13**), containing a labile acetonitrile ligand, with one equivalent of 6,6'-Me₂bpy gave bis(diphenylphosphino)methane (dppm) was then studied. The diphosphined ppmis known to bridge two metal centres than forming 4-membered chelate rings.



Scheme 3. Synthetic routes to compounds (**14**) and (**15**). (i) dppm; (ii) dptz.

Treatment of $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ with one equivalent of dppm in acetonitrile resulted in the formation of a white solid in 86% yield (see scheme 3). The phosphorus-31 resonance of (**15**) appeared at -6.4 ppm. The proton resonances at 3.53 (multiplet) and 2.19 (singlet) ppm are assigned to the CH₂ groups and coordinated acetonitrile ligands. We tentatively suggest it has the structure as shown in (**14**) with two dppm ligands bridging two copper(I) centres, as its crystal structure was determined by Wu, *et al.* [14].

It is interesting to replace all four acetonitrile ligands with a ligand containing four nitrogen donor atoms; thus, we studied the reaction of (**14**) with 3,6-di(2-pyridyl)tetrazine (dptz) which has the

capability to bind two metal centres. Treatment of complex (**14**) with one equivalent of dptz gave dark purple crystals of $[\text{Cu}_2(\mu\text{-dptz})(\mu\text{-dppm})_2][\text{PF}_6]_2$ (**15**) in 88% yield. The ^1H -NMR spectrum of (**15**) showed two doublets and a triplet at 9.26 (d, $^3\text{J}(\text{HH})$ 8.0 Hz), 8.29 (d, $^3\text{J}(\text{HH})$ 4.5 Hz), 8.23 (t, $^3\text{J}(\text{HH})$ 7.5 Hz) for the protons of dptz ligand. It is clear that the CH₂ protons of dppm are not chemically equivalent and appeared as two broad multiplets at 3.94 and 3.44 ppm. Recently, the crystal structure of a similar heteroleptic Cu(I) complex with the ligand 3,6-bis(2-pyridyl)-4,5-diphenyl-pyridazine was determined [15].

4. Conclusions

Synthetic routes were developed to homoleptic copper(I) complexes such as $[\text{Cu}(\text{N}^{\wedge}\text{N})_2]^+$ and $[\text{Cu}(\text{P}^{\wedge}\text{P})_2]^+$. Heteroleptic complexes of the type $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ can be prepared by mixing both P[∧]P and N[∧]N with $[\text{Cu}(\text{NCMe})_4]\text{PF}_6$ in a one-pot reaction or by a two-step process in which the complex $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{labile ligand})]^+$ is made first and then by replacing the labile ligand with a bidentate ligand N[∧]N. A binuclear heteroleptic Cu(I) complex containing bridging ligands 3,6-di(2'-pyridyl) tetrazine and dppm was also prepared.

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