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Structural characterization and catalytic activities of copper complexes with pyridine-amine-phosphine-oxide ligand

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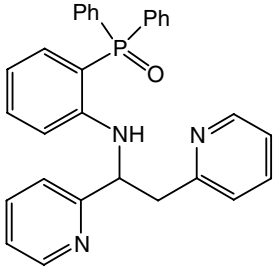
Abstract

A new tetradentate containing pyridine, amine and phosphine oxide donor systems (**1**) was synthesized by the condensation of *o*-diphenylphosphinoaniline with 2-pyridinecarbaldehyde. Reaction of **1** with equal molar amount of $CuCl_2$ and $Cu(ClO_4)_2$ provided the formation of $[CuCl_2(\mathbf{1})]$ (**4**) and $[[Cu(\mathbf{1})(H_2O)](ClO_4)_2]$ (**5**), respectively. The ligand **1** behaves as a tridentate in **4**, while as a tetradentate in **5**. Both complexes were characterized by EPR, UV–Vis spectroscopy and X-ray diffraction. Both copper(II) complexes are in a square-pyramidal geometry. Single crystal structure of the copper complex reveals that the copper center is surrounded by three nitrogen donors and two chloride for **4**; three nitrogen donors, water and oxygen donor from the moiety of phosphine oxide for **5**. Complexation of **1** with CuCl in dichloromethane resulted in the formation of the corresponding copper(I) species, which catalyzed the oxidation of benzylic alcohols under aerobic conditions.

Keywords: Phosphine-oxide; Amine; Catalysis; Copper; Oxidation

1. Introduction

There is a considerable interest in the design of multiple mixed donors, which can offer both hard and soft donor environment in these ligands for their coordination behavior toward transition metal ions. It is believed that the properly designed ligand systems would provide new property and reactivity of the resulting metal complexes [1]. Thus, developments of new copper complexes for their potential as catalysts in oxidation of organic substrates continue to be attractive [1–9]. Among various coordination modes for copper(II), complexes with five-coordinate adopting in a square-pyramidal geometry were found in natural occurring metalloproteins such as galactose oxidase [9]. In this context a great number of copper(II) complexes containing chelating nitrogen donors including pyridinyl, imidazoyl and polyamino ligands in model studies were reported [1–8]. In such pursuit, we synthesized a designed tetradentate **1** involving two pyridine nitrogens, one secondary amine group as well as a phosphine-oxide moiety in its ligand set and studied its coordination behavior toward copper ions.



1

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2. Results and discussion

2.1. Preparation of ligands

The desired ligand was prepared through the reaction of 2-diphenylphosphinoaniline with 2-pyrdinecarbaldehyde followed by the hydrogenation (Scheme 1, path a). Without any acid catalyst, the condensation reaction took place immediately in methanol at 50 °C and quantitatively provided the formation of enamine product **2**. Upon the recrystallization, this compound appears to be a clear, colorless single crystal. This reaction has also been investigated by Doherty et al. (Scheme 1, path b) [10]. In the presence of formic acid, the adduct **3** from imine and aldehyde was obtained at ambient temperature in toluene. Presumably, the reaction at higher temperature in the polar solvent readily facilitates the dehydration to form **2**. Metal catalyzed hydrogenation of **2** in the presence of atmospheric hydrogen gave the desired ligand **1**.

Compound **2** was characterized by both spectroscopic and X-ray crystallographic methods. A shift at 30.7 ppm in the ^{31}P NMR spectrum of **2** shows the existence of tertiary-phosphine oxide in the molecule. In addition to the aromatic protons, the appearance of one singlet absorption at 6.23 ppm in ^{1}H NMR, which is in the typical range for olefinic protons, suggests the formation of carbon–carbon double bond functionality. Although the spectral data of **2** are consistent with the proposed structure, the confirmation comes from the single crystal analysis. Fig. 1 shows its ORTEP plot with 30% ellipsoid. All bond lengths and angles are in agreement with the reported values. The C(19)–C(20) bond length of 1.356(4) Å is a typical distance for C=C, whereas the distance of 1.379(3) Å for C(19)–N(1) clearly illustrates the single bond nature between two atoms. These observations also confirm the enamine moiety in the presence of the molecule. As for the hydrogenated product **1** is easily characterized by both NMR spectroscopy and elemental analysis.

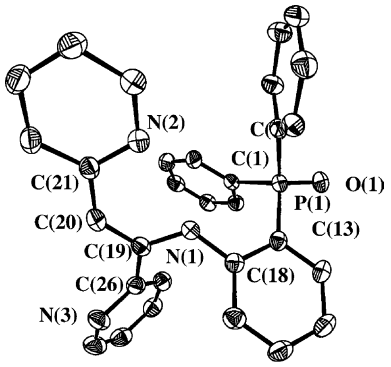
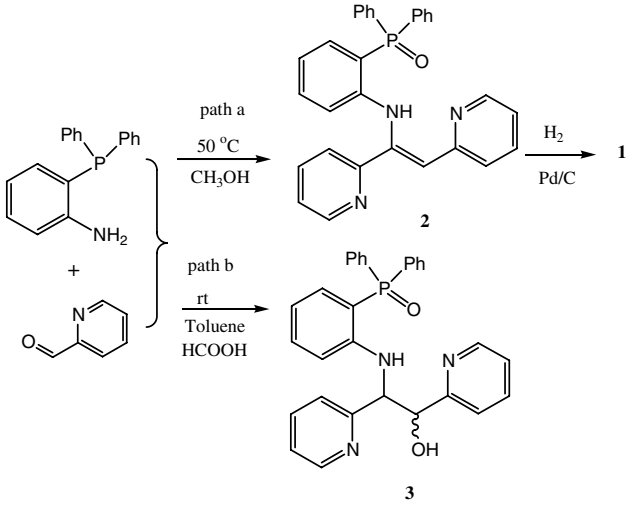


Fig. 1. ORTEP plot of **2**. Selected bond distances and angles: P(1)–C(1) 1.806(3) Å; P(1)–O(1) 1.483(2) Å; P(1)–C(13) 1.811(3) Å; C(18)–N(1) 1.412(3) Å; N(1)–C(19) 1.379(3) Å; C(19)–C(20) 1.356(4) Å; C(18)–N(1)–C(19) 125.3(2)°; N(1)–C(19)–C(20) 122.8(3)°; N(1)–C(19)–C(20) 118.2(2)°.

2.2. Copper complexes

Under refluxing conditions, reaction of $CuCl_2$ with equimolar amount of **1** in absolute ethanol for 3 h provided the green complex [$CuCl_2$(**1**)] (**4**), whereas complexation of **1** with $Cu(ClO_4)_2 \cdot 6H_2O$ gave the ionic complex [$Cu(H_2O)$(**1**)]$(ClO_4)_2$ (**5**) in green solids. By the recrystallization, X-ray suitable crystals for both complexes can be accomplished. ORTEP plots of both complexes **4** and **5** are deposited in Figs. 2 and 3, respectively. The copper(II) center in both complexes has the distorted square-pyramidal geometry with one nitrogen donor [N(2)] from the ligand seated in the apical position. The basal plane in complex **4** was formed by two chloride donors and two nitrogen atoms [N(1) and N(3)] from the ligand. The formation of a stable five-member chelate ring by the secondary amine N(3) and pyridine nitrogen N(1) is presumably an explanation for these two donors in the equatorial direction. The



Scheme 1. Ligand preparation.

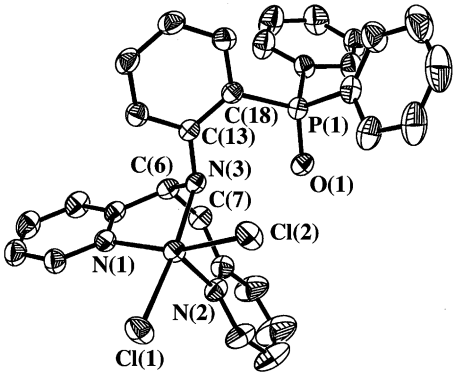


Fig. 2. Molecular structure of copper complex **4**.

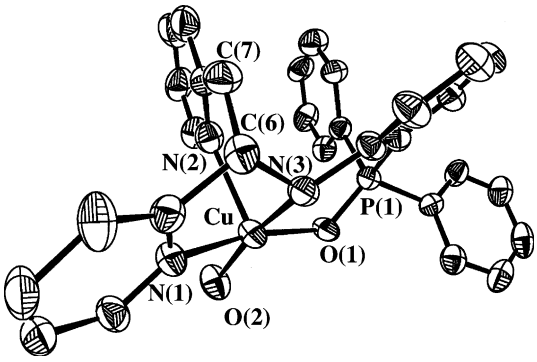


Fig. 3. ORTEP drawing of the cationic part of **5**.

coordination mode of nitrogen donors in complex **5** is similar to those in **4**, but the oxygen atom [O(1)] of phosphine-oxide moiety of the ligand is bounded to metal center. Thus donor atoms of N(1), N(3), and O(1) as well as a water molecule formed the basal plane in **5**.

The bond distances and bond angles of basal plane of both complexes are summarized in the Fig. 4. A significant difference in the structure of **4** compared to that of **5** is that all Cu–N lengths in **4** are longer those in **5** particularly the apical one [Cu–N(2) = 2.334(3) Å in **4**; 2.254(8) Å in **5**]. Also, bond lengths of Cu–N(1) are somewhat shorter than those of Cu–N(3), which is attributed to the different hybridization of nitrogen donors; the N(1) is a pyridinyl nitrogen, whereas N(3) is a secondary amine group. In both complexes, the distance of the apical nitrogen to copper center is longer by ca. 0.3 Å than those of equatorial ones, indicating a weak interaction in the apical orientation. All bond distance and bond angles in both complexes lie within normal ranges except N(2)–Cu–N(3) [80.8(1)°]. However, it is noticed that the angles Cl(1)–Cu–Cl(2) in **4** [96.36(4)°] much derived from the 90° as compared to the smaller derivation of O(1)–Cu–O(2) [87.9(2)°].

N(1)-Cu-N(3)	81.1(1)°
N(3)-Cu-Cl(2)	89.30(9)°
Cl(2)-Cu-Cl(1)	96.36(4)°
Cl(1)-Cu-N(1)	92.80(9)°
N(3)-Cu-Cl(1)	173.80(9)°
N(1)-Cu-Cl(2)	161.74(9)°
N(2)-Cu-N(1)	91.6(1)°
N(2)-Cu-N(3)	80.8(1)°
N(2)-Cu-Cl(1)	100.36(9)°
N(2)-Cu-Cl(2)	102.22(9)°

N(1)-Cu-N(3)	81.8(3)°
N(3)-Cu-O(2)	93.7(3)°
O(2)-Cu-O(1)	87.9(2)°
O(2)-Cu-N(1)	94.3(3)°
N(3)-Cu-O(2)	169.3(3)°
N(1)-Cu-O(1)	166.3(3)°
N(2)-Cu-N(1)	90.6(3)°
N(2)-Cu-N(3)	88.6(3)°
N(2)-Cu-O(1)	102.2(2)°
N(2)-Cu-O(2)	101.4(3)°

Fig. 4. Comparison of bond distances (Å) and angles around the metal centers between **4** and **5**.

Five-coordinate Cu(II) complexes are quite common and their stereochemistry are adopted ranging between square-pyramidal (SP) and trigonal-bipyramidal (TBP). In complexes **4** and **5**, the preference in SP is presumably due to the geometrical arrangement of donors in **1**. This type of geometry was also observed for the related species $[CuCl_2(\mathbf{N_3})]$ [12]. The coordination of phosphine-oxide toward metal center is readily through the assistance of the chelate effect of this multidentate **1**. All the distances of Cu–N in **4** appear to be longer than those in **5**, which might be the results of the steric relief of ligand interaction. The free phosphine-oxide in **4** may cause the steric strain between substituents on phosphorus and chloride ligands, which causes the elongation of the distances between metal center and nitrogen donors.

In addition to crystallography, both EPR spectroscopic data and electronic absorption are in agreement with the structure. The X-band EPR spectra of **4** and **5** in methanol glass (80 K) were determined and their data were collected in Table 3. It appears that both complexes with the parameters $g_{\|} > g_{\perp}$ are typical monomeric square-pyramidal copper(II) complexes with $d_{x^2-y^2}$ ground state [11]. The spectra of **4** and **5** recorded as mulls show a broad band centered at 540 and 567 nm, respectively, which are in agreement of the d–d transitions for a square-pyramidal copper(II) complex with pyridine donors [13]. Table 1 also includes the electronic absorptions in methanol of both complexes. The absorptions in UV region are assigned as the transition from the ligand itself, whereas the λ_{max} around 370 nm is believed due to the LMCT band. In addition, complex **4** in methanol exhibits a d–d band around 740 nm with a shoulder to lower wave-numbers, a characteristic profile for the copper(II) species in square-pyramidal geometry. This outcome also indicates that the complexes remain the same structural feature in solution.

For the copper(I) complex [CuCl(1)] (**6**) was prepared by simple mixing the ligand **1** and CuCl in acetonitrile under nitrogen atmosphere. The un-coordination of phosphine oxide moiety toward metal center was suggested by the observation of ^{31}P NMR shift at 36.3 ppm, which was essentially similar to that for free ligand. The ^{1}H NMR splitting pattern and chemical shifts for the complex were different from the ligand **1** itself, indicating the coordination of nitrogen donors to the copper center. Unfortunately, we were not able to obtain the single crystal of this complex for the confirmation of its detail coordination environments.

2.3. Catalytic oxidation of alcohols

In the catalytic oxidation, both complexes **4** and **5** did not show much activity for the conversion of benzyl alcohol into benzaldehyde. However, the copper(I) complex can act as a catalyst for the oxidation of benzylic

Table 1
EPR spectroscopic data[a] and electronic absorptions of **1**, **4** and **5**[b]

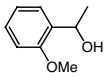
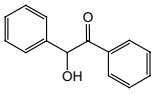
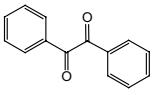
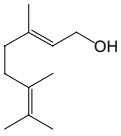
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (G)	λ_{max}[b]					
1	–	–	–	210(41.93)	260(13.06)	326(5.05)			
4	2.284	2.071	144	211(21.68)	261(15.01)	321(1.91)	371(0.85)	421(0.62)	743(0.11)
5	2.311	2.078	173	211(31.78)	261(10.79)	324(2.98)	369(2.13)	516(0.18)	700(0.07)
6	–	–	–	207(54.3)	260(14.7)	325(4.99)	372(1.09)	432(0.18)	514(0.16)

[a] In methanol glass (80 K).
[b] In methanol, ε is given in the parenthesis ($\times 10^3$ M^{-1} cm^{-1}), but **6** in acetonitrile.

alcohol into the corresponding carbonyl compound. In a typical experiment for the reaction, a mixture of benzyl alcohol, copper(I) chloride, ligand **1** and base in a freshly distilled N-methylprolidinone (NMP) solution was heated in a oil bath at 110 °C in the presence of air or oxygen gas for a specified time. The reaction product was monitored by ^{1}H NMR and the yield was based on the integration. All results are summarized in Table 2.

Complete conversion of benzyl alcohol into benzaldehyde was observed with the catalytic system of Cu(I)/ligand **1** or complex **6** in the presence of dioxygen at 110 °C (entries 1–2). For other substrates, various kind of benzylic alcohols can be oxidized into the corresponding carbonyl compound by Cu(I)/ligand **1** under oxygen atmosphere. Complete oxidation of benzoin into benzil was accomplished within 2.5 h (entry 10, Table 2). Similarly, the yield of the oxidation of diphenylmethanol to give benzophenone could be reached up to 100% within 12 h. This catalytic system also provided reasonable conversion with other substrates except the steric bulky alcohol (entry 8, Table 2). It was noticed that this copper complex did not have activity in the oxidation of diphenylmethane and allylic alcohol (entries 12–13). However, the oxidation of (E)-3-phenyl-2-propenol could be converted into cinnamaldehyde presumably due to its conjugation.

Table 2
Catalytic oxidation of alcohols[a]

Entry	Substrates	Product	t (h)	Conversion[c] (%)
1	$C_6H_5CH_2OH$	C_6H_5CHO	60	100
2[b]	$C_6H_5CH_2OH$	C_6H_5CHO	60	100
3	3-$(NO_2)C_6H_4CH_2OH$	3-$(NO_2)C_6H_4CHO$	12	85
4	4-$(MeO)C_6H_4CH_2OH$	4-$(MeO)C_6H_4CHO$	12	59
5	2-$IC_6H_4CH_2OH$	2-IC_6H_4CHO	17	72
6	2-Pyridinylmethanol	2-Pyridinecarbaldehyde	14	64
7	$C_6H_5CH(CH_3)OH$	Acetophenone	14	50
8			14	38
9	$(C_6H_5)_2CHOH$	$(C_6H_5)_2C{=}O$	12	100
10			2.5	100
11	$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	14	64
12	$(C_6H_5)_2CH_2$	–	45	N.R.[d]
13		–	45	N.R.[d]

[a] Reaction conditions: substrate (1 mmol), catalyst (0.1 mmol), K_2CO_3 (2 mmol), in 2.5 ml NMP at 110 °C, under O_2 (1 atm); catalyst was in situ prepared by mixing **1** and CuCl.
[b] Complex **6** as catalyst.
[c] Based on NMR integration.
[d] No reaction.

3. Conclusion

In summary, this new polydentate ligand gave the formation of square-pyramidal copper(II) complexes with all three nitrogen donors in facial arrangement. These copper(II) complexes showed no catalytic activity in oxidation of alcohols, but the copper(I) complex may oxidize benzylic alcohols into the corresponding carbonyl compounds.

4. Experimental

4.1. General

All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried with CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on either a Bruker AM-300 or AVANCE-400 spectrometer. Chemical shifts are given in parts per million relative to Me_4S for ^1H and relative 85% H_3PO_4 for ^{31}P NMR. Infrared spectra were measured on a BioRad FTS-40 spectrometer (Series-II) as KBr pallets, unless otherwise noted. UV–Vis spectra were determined on a U-3010 spectrophotometer. EPR spectra at X-band frequency were recorded with a Brucker ESP 300 spectrometer.

4.2. Synthesis and characterization

4.2.1. Compound **2**

To a 50 ml round bottom flask was placed *o*-(diphenylphosphinyl)aniline [14] (1.21 g, 4.4 mmol) and 2-pyridinecarbaldehyde (1.0 g, 9.3 mmol) in methanol (15 ml) under the degassed conditions. The mixture was heated in the oil bath at 55 °C for 5 h. After the completion of the reaction, the mixture was concentrated and dissolved in dichloromethane. Upon the addition of hexane to the solution, the desired product was precipitated as a white solid (1.88 g, 91%): m.p. 200–201 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 11.56 (s, 1H, –*H*N–C), 8.55 (d, $J = 4.8$ Hz, 1H, Ar*H*), 8.32 (d, $J = 4.8$ Hz, 1H, Ar*H*), 7.86–7.81 (m, 4H, –Ar*H*), 7.54–7.45 (m, 7H, Ar*H*), 7.27 (td, $J = 6.9$, 1.4 Hz, 1H, Ar*H*), 7.20 (td, $J = 7.6$, 1.7 Hz, 1H, Ar*H*), 7.11 (d, $J = 8.0$ Hz, 1H, Ar*H*), 7.04–7.01 (m, 2H, Ar*H*), 6.92 (dd, $J = 7.4$ Hz, 5.0 Hz, 1H, Ar*H*), 6.78 (td, $J = 7.4$, 1.4 Hz, 1H, Ar*H*), 6.39 (dd, $J = 8.1$, 4.9 Hz, 1H, Ar*H*), 6.25 (d, $J = 7.8$ Hz, 1H, Ar *H*), 6.23 (s, 1H, –*H*C═C–); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 155.8, 149.3, 148.0, 146.8, 146.7, 144.1, 135.8, 135.7, 133.6, 133.5, 132.7, 132.3, 132.2, 131.7, 131.7, 131.6, 128.4, 128.3, 123.3, 123.1, 123.0, 122.4, 122.3, 122.0, 121.0, 120.3, 120.2, 119.6, 110.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.9. Anal. Calc. for $C_{30}H_{24}N_3OP$: C, 76.10; H, 5.11; N, 8.87. Found: C, 75.59; H, 5.10; N, 8.66%.

4.2.2. Ligand **1**

A mixture of **2** (4.58 g, 9.67 mmol), 10% Pd/C (1.03 g, 0.97 mmol) in 30 ml methanol was pressurized with hydrogen gas (20 psi). After stirring for 48 h at rt, the reaction mixture was filtered through celite, concentrated and re-dissolved in dichloromethane. The hydrogenated product was obtained as a white solid (4.4 g, 96%) by addition of diethyl ether; m.p. 101–102 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, $J = 4.4$ Hz, 1H, Ar*H*), 8.40 (d, $J = 4.4$ Hz, 1H, Ar*H*), 7.71 (d, $J = 6.0$ Hz, 1H, Ar*H*), 7.64–7.41 (m, 11H, Ar*H*), 7.31 (t, $J = 7.6$ Hz, 1H, Ar*H*), 7.06–6.92 (m, 3H, Ar*H*), 6.71 (dd, $J = 14.6$, 7.5 Hz, 1H, Ar*H*), 6.46–6.41 (m, 2H, Ar*H*), 4.99 (br, 1H, –C*H*–), 3.32 (dd, $J = 13.6$, 4.6 Hz, 1H, –CH_2–), 3.13 (dd, $J = 13.6$, 8.8 Hz, 1H, –CH_2–), 2.75 (s, 1H, –N*H*–); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 157.8, 151.9, 149.1, 148.9, 136.7, 136.1, 133.5, 133.3, 132.3, 132.2, 132.1, 132.0, 131.8, 128.5, 128.4, 128.4, 128.3, 124.0, 121.9, 121.3, 120.4, 115.4, 115.3, 112.5, 112.4, 59.4, 45.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.1; HRMSFAB Calc. for $C_{30}H_{26}N_3OP$: $m/z = 475.1813$. Found: 475.1825; Anal. Calc. for $C_{30}H_{26}N_3OP$: C, 75.77; H, 5.51; N, 8.84. Found: C, 75.58; H, 5.15; N, 8.38%.

4.2.3. Complex **4**

A solution of $CuCl_2$ (30 mg, 0.22 mmol) in absolute ethanol (1 ml) was added to a solution of ligand **1** (106 mg, 0.22 mmol) in absolute ethanol (2 ml) under nitrogen atmosphere. The resulting mixture was heated to reflux for 3 h. The volume of the solvent was reduced down to 0.5 ml under vacuum. Addition of ether to the solution gave the complex as a green precipitates (40.1 mg, 29.5%). Anal. Calc. for $C_{34}H_{36}Cl_2CuN_3O_2P$(**4** + ether): C, 59.69; H, 5.30; N, 6.14. Found: C, 59.28; H, 4.98; 5.97%.

4.2.4. Complex **5**

A solution of ligand **1** (75 mg, 0.16 mmol) in methanol (2 ml) was slowly added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (58.5 mg, 0.16 mmol) in methanol (1 ml) with stirring. After stirring 2 h, the reaction mixture was concentrated to a volume of 0.5 ml. Upon addition of ether, the desired complex was precipitated as a green solid (92 mg, 77%). Anal. Calc. for $C_{34}H_{38}Cl_2CuN_3O_{11}P$(**5** +ether): C, 49.19; H, 4.61; N, 5.06. Found C, 49.01; H, 4.22; N, 4.87%.

Table 3
Crystal data of **1**, **4** and **5**

Compound	**1**	**4**	**5**
Formula	$C_{30}H_{24}N_3OP$	$C_{34}H_{36}Cl_2CuN_3O_2P$	$C_{34}H_{38}Cl_2CuN_3O_{11}P$
Formula weight	473.49	684.07	830.08
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a (Å)	9.9070(1)	14.2250(2)	10.0940(3)
b (Å)	16.3410(2)	15.3980(2)	17.608(1)
c (Å)	29.8970(4)	15.4600(2)	21.288(1)
α (°)	90	90	90
β (°)	99.057(1)	91.489(1)	90
γ (°)	90	90	90
V (Å^3)	4779.7(1)	3385.16(8)	3783.6(3)
Z	8	4	4
D_{calc} (Mg/m^3)	1.316	1.342	1.457
$F(000)$	1984	1420	1716
Crystal size (mm)	$0.25 \times 0.20 \times 0.20$	$0.30 \times 0.25 \times 0.10$	$0.25 \times 0.20 \times 0.10$
θ Range	1.38–27.50	4.94–27.43	2.78–25.01
Reflection collected	60,745	26,525	18,991
Independent reflection (R_{int})	10,960 (0.0710)	7642 (0.0535)	6592 (0.1152)
Refined method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
R [$I > 2\sigma(I)$]	$R_1 = 0.0645$; $wR_2 = 0.1648$	$R_1 = 0.0543$; $wR_2 = 0.0912$	$R_1 = 0.0682$; $wR_2 = 0.1385$
Goodness-of-fit on F^2	1.092	1.012	1.024

4.2.5. Complex **6**

To a solution of CuCl (37 mg, 0.37 mmol) in anhydrous acetonitrile was added a solution of ligand **1** (178 mg, 0.37 mmol) in acetonitrile. The resulting solution was stirred at room temperature for 1 h. The desired complex was obtained in brown-red color solid,which was further purified by precipitation from dichloromethane/ether (185 mg, 86%); m.p. 118 °C (dec.); ^{1}H NMR δ 8.50 (br, 1H, Ar*H*), 8.40 (br, 1H, Ar*H*), 7.73–7.44 (m, 11H, Ar*H*), 7.12–6.99 (br, 6H, Ar*H*), 6.71 (dd, $J = 14.6$ Hz, 7.5 Hz, 1H, Ar*H*), 6.46–6.41 (m, 2H, Ar*H*), 4.98 (br, 1H, –C*H*–), 3.30 (br, 1H, –CH_2–), 3.12 (br, 1H, –CH_2–), 2.54 (s, 1H, –N*H*–); ^{31}P NMR δ 36.3. Anal. Calc. for $C_{30}H_{26}ClCuN_3OP$: C, 62.72; H, 4.56; N, 7.31. Found: C, 62.45; H, 4.22; N, 7.02%.

4.3. X-ray crystallographic analysis

Crystals suitable for X-ray determination were obtained for **1**, **4** · ether and **5** · ether by slow diffusion of diethyl ether into a methanol solution at room temperature. Cell parameters were determined either by a Siemens SMART CCD diffractometer. Crystal data of these complexes are listed in Table 3 and ORTEP plots of **1**, **4** and cationic part of **5** are shown in Figs. 1–3, respectively (Labels of phenyl groups are omitted for clear view). Other crystallographic data have been deposited with the Cambridge Crystallographic Data Center: CCDC 233664–233666 for **1**, **4** and **5**, respectively. Copies of this information can be obtained free of charge and by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44 1223/336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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