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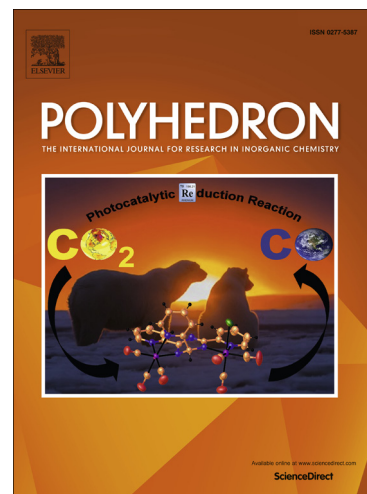
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Synthesis, characterization and catalytic oxidation property of copper(I) complexes containing monodentate acylthiourea ligands and triphenylphosphine

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ABSTRACT

The reactions between $[\text{CuCl}_2(\text{PPh}_3)_2]$ and 3,3-diphenyl-1-(2,4-dichlorobenzoyl)thiourea (HL1), 3,3-diisobutyl-1-(2,4-dichlorobenzoyl)thiourea (HL2) or 3,3-diethyl-1-(2,4-dichlorobenzoyl)thiourea (HL3) in benzene gave new four-coordinated tetrahedral copper(I) complexes of the type $[\text{CuCl}(\text{HL})(\text{PPh}_3)_2]$ (**1-3**) [HL = 3,3-dialkyl/aryl-1-(2,4-dichlorobenzoyl)thiourea derivatives]. These complexes were then characterized by analytical and spectroscopic (IR, UV/Vis, ^1H , ^{13}C and ^{31}P NMR) techniques. The molecular structure of a representative complex, $[\text{CuCl}(\text{HL1})(\text{PPh}_3)_2]$ (**1**), was determined by the single crystal X-ray diffraction method which reveals a distorted tetrahedral geometry around the Cu(I) ion. The complexes **1-3** (0.007 mmol) were found to be active catalysts for the oxidation of primary and secondary alcohols (5 mmol) to their corresponding acids and ketones, respectively, in the presence of hydrogen peroxide (6.0 mmol) in 1-butyl-3-methylimidazolium hexafluorophosphate $\{[\text{bmim}][\text{PF}_6]\}$ (0.1 mL) without any additive and base, at 70 °C.

Keywords: Copper(I), Thiourea derivatives, Catalytic oxidation, H_2O_2 , Ionic liquids

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1. Introduction

The selective oxidation of alcohols is among the most important reactions in synthetic chemistry and offers a significant methodology for the introduction and alteration of functional groups [1-4]. Several catalytic oxidation reactions occurring with stoichiometric amounts of hazardous inorganic oxidants (CrO_3 , KMnO_4 , MnO_2 , etc.) bring considerable amounts of environmentally harmful waste [5]. Hence the discovery of new environmental friendly methods for the selective oxidation of alcohols is an important goal in modern chemistry. In recent years, there has been a growing interest in the development of new transition metal catalytic systems for the oxidation of alcohols that work with hydrogen peroxide [6,7] or dioxygen [8,9] as the ultimate stoichiometric oxidant, due to their obvious cost-effectiveness and conservation advantages.

Ionic liquids (ILs) are now gaining appreciation as greener solvents in organic synthesis and catalysis because of their unique properties, such as high thermal stability, non-volatility, good ionic conductivity and high polarity [10,11]. Though ILs are considered relatively recent supernatural chemicals, due to their diverse applications such as sensors [12], fuel cells [13], batteries [14], capacitors [15], thermal fluids [16], plasticizers [17], lubricants [18], ionogels [19], extractants [20] and solvents in analysis [21], synthesis [22], catalysis [22] and separation [23] etc., today they are centenarian [24]. Structural modifications of the anionic and cationic parts of the ILs provide an opportunity to tune their physical and chemical properties. So ILs can be utilized as good alternatives to the traditional organic solvents for inorganic, organic and polymeric materials [25-27].

N-(Alkyl/aryl)-*N'*-acylthiourea and *N*-di(alkyl/aryl)-*N'*-acylthiourea derivatives act as versatile ligands with various coordination modes towards transition metal ions as they have

oxygen, nitrogen and sulfur donor atoms. Although these ligands exhibit common monoanionic O,S-bidentate coordination towards a variety of transition metal ions [28,29], the unusual neutral monodentate coordination through the sulfur atom is reported in some Au(I) [30], Ag(I) [31], Hg(II) [32], Pt(II) [33], Cu(I) [34] and Ru(II) [35] complexes. In addition, exceptional coordination modes, such as neutral bidentate [36] and monobasic bridging [37], are also showed by the acylthiourea ligands in some complexes. These types of ligands and their transition metal complexes have long been known not only for their biological applications but also for their role in analytical sciences [38-40]. For instance, acylthiourea derivatives and their Co(III) complexes have shown antibacterial [41] and antifungal [42] activities. Ni(II) complexes containing 3-dialkyl/aryl-1-benzoylthiourea ligands exhibit cytotoxicity against T47D cell lines [43]. Water soluble (2,2'-bipyridyl)- and (1,10-phenanthroline)-platinum(II) benzoylthiourea complexes have shown significant antimalarial activity [44]. Further, acylthiourea derivatives are utilized as effective ligands for the extraction of some transition metal and post transition metal ions [45,46].

Though the use of transition metal complexes bearing acylthiourea ligands have been explored in a range of fields, their utility in catalysis is relatively less studied. In recent years, we have tested *N*-[di(alkyl/aryl)carbamothioyl]benzamide complexes of Ru(II) [47], Ru(III) [48], Cu(I) [49] and Co(III) [50] as catalysts for the oxidation of alcohols in the presence of oxidants such as *N*-methylmorpholine-*N*-oxide(NMO)/hydrogen peroxide/*tert*-butyl hydroperoxide (TBHP) in organic solvents such as CH₂Cl₂/CH₃CN. As all these catalytic systems exhibited effective yields under mild reaction conditions, we are interested to investigate the catalytic oxidation property of transition-metal complexes containing acylthiourea ligands in an IL solvent. As a part of our research, we report herein the synthesis and characterization of

copper(I) complexes containing 3,3-dialkyl/aryl-1-(2,4-dichlorobenzoyl)thiourea and their enhanced catalytic activity for the oxidation of primary and secondary alcohols to the corresponding carboxylic acids and ketones, respectively, in the presence of H₂O₂ in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) solvent. Our report describes the first catalytic oxidation property of Cu(I) complexes incorporating acylthiourea ligands in an ionic liquid solvent. The structures of the ligands used in this study are given in Fig. 1.

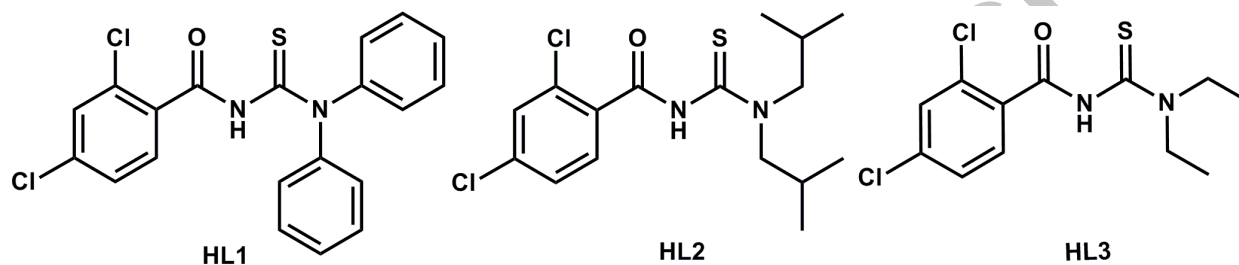


Fig. 1. Chemical structure of the ligands investigated herein.

2. Experimental section

2.1. Materials and reagents

All chemicals, including the ILs, used in this work were purchased from commercial sources and utilized without further purification. The organic solvents were distilled and purified according to the literature procedures. The precursor [CuCl₂(PPh₃)₂] was prepared in accordance with the literature method [51]. For the preparation of the ligands HL1, HL2 and HL3, a previously described procedure was followed [52].

2.2. Physical measurements

Elemental analyses were performed on a Vario EL AMX-400 elemental analyzer. Melting points are uncorrected and were obtained in open capillary tubes on a Sigma melting point apparatus. FT-IR spectra in the mid-IR region (4000–600 cm⁻¹) were recorded on a Nicolet iS5 FT-IR spectrophotometer with KBr pellets. UV-vis spectra of the complexes in the 800 to 200 nm range were recorded in ethanol solutions using a PG Instruments double-beam UV-vis

spectrophotometer (Model T90+) with a quartz cell of 1 cm path length. Magnetic susceptibility measurements were taken on a Sherwood scientific auto magnetic susceptibility balance. NMR (^1H , ^{13}C and ^{31}P) spectra were recorded on a Bruker Avance 400 MHz instrument in CDCl_3 . ^1H and ^{13}C NMR spectra were referenced to TMS as an internal standard and H_3PO_4 was used as an internal standard for the ^{31}P NMR spectra. The course of the reactions was analyzed with a Shimadzu GC-2014 gas chromatograph equipped with a RTX-5 column (60 m length, 0.32 mm inner diameter) and flame ionization detector.

2.3. Synthesis of the Cu(I) complexes

The following general procedure was used to prepare all the new Cu(I) complexes. A solution of the ligand (HL) (0.1373-0.1806 g, 0.45 mmol) in 10 mL of benzene was added to $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.3 g, 0.45 mmol) dissolved in benzene (20 mL). The reaction mixture was stirred for 48 h at room temperature and then the solution was concentrated to 3 mL under vacuum. An orange precipitate was developed by the addition of 25 mL of ethyl acetate/*n*-hexane mixture (1:9), filtered and recrystallized from dichloromethane/*n*-hexane and dried in *vacuo*.

$[\text{CuCl}(\text{HL1})(\text{PPh}_3)_2]$ (**1**) was prepared from $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.3 g, 0.45 mmol) and HL1 (0.1806 g, 0.45 mmol). Yield: 90%. Orange solid. Decomposition point: 164 °C. $\text{C}_{56}\text{H}_{44}\text{Cl}_3\text{CuN}_2\text{OP}_2\text{S}$ (1024.82): calcd. C 65.62, H 4.32, N 2.73, S 3.12; found C 65.58, H 4.27, N 2.67, S 3.06%. $\mu_{\text{eff}} = 0$. FT-IR (KBr, cm^{-1}) ν : 3364 (N-H), 1703 (C=O), 1222 (C=S), 1434, 1093, 743 (PPh_3). UV [Ethanol, λ in nm (ϵ in $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)]: 240 (27,954), 252 (23,693). ^1H NMR (CDCl_3) δ , ppm: 11.78 (s, 1H, N-H), 7.30-7.77 (m, 30H, phenyl from PPh_3), 7.17-7.22 (m, 13H, phenyl from HL1). ^{13}C NMR (CDCl_3) δ , ppm: 183.59 (C=S), 161.41 (C=O), 128.07,

129.05, 129.70, 129.79, 130.45, 130.99, 131.61, 132.11, 132.80, 133.31, 133.37, 133.57, 133.91, 134.77, 135.01, 135.15, 139.00, 146.43 (aromatic). ^{31}P NMR (CDCl_3) δ , ppm: 30.1 (s).

$[\text{CuCl}(\text{HL}2)(\text{PPh}_3)_2]$ (**2**) was prepared from $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.3 g, 0.45 mmol) and HL2 (0.1626 g, 0.45 mmol). Yield: 85%. Orange solid. Decomposition point: 115 °C. $\text{C}_{52}\text{H}_{52}\text{Cl}_3\text{CuN}_2\text{OP}_2\text{S}$ (984.90): calcd. C 63.41, H 5.32, N 2.84, S 3.26; found C 63.33, H 5.27, N 2.78, S 3.17%. $\mu_{\text{eff}} = 0$. FT-IR (KBr, cm^{-1}) ν : 3172 (N-H), 1696 (C=O), 1138 (C=S), 1432, 1102, 745 (PPh_3). UV [Ethanol, λ in nm (ϵ in $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)]: 241 (18,230), 252 (16,700). ^1H NMR (CDCl_3) δ , ppm: 11.44 (s, 1H, N-H), 7.31-7.67 (m, 30H, phenyl from PPh_3), 7.16-7.25 (m, 3H, phenyl from HL2), 3.71 (d, 2H, CH_2), 3.39 (d, 2H, CH_2), 2.21-2.31 (m, 1H, CH), 2.01-2.11 (m, 1H, CH), 0.96 (d, 6H, CH_3), 0.83 (d, 6H, CH_3). ^{13}C NMR (CDCl_3) δ , ppm: 180.62 (C=S), 163.64 (C=O), 128.38, 129.48, 129.72, 129.81, 131.01, 131.37, 132.42, 133.32, 133.51, 133.83, 134.18, 135.00, 135.15, 138.72 (aromatic), 61.57, 63.63 (CH), 27.92, 28.90 (CH_2), 21.17, 21.32 (CH_3). ^{31}P NMR (CDCl_3) δ , ppm: 32.1 (s).

$[\text{CuCl}(\text{HL}3)(\text{PPh}_3)_2]$ (**3**) was prepared from $[\text{CuCl}_2(\text{PPh}_3)_2]$ (0.3 g, 0.45 mmol) and HL3 (0.1373 g, 0.45 mmol). Yield: 82%. Orange solid. Decomposition point: 196 °C. $\text{C}_{48}\text{H}_{44}\text{Cl}_3\text{CuN}_2\text{OP}_2\text{S}$ (931.82): calcd. C 61.87, H 5.08, N 3.01, S 3.44; found C 61.80, H 5.02, N 2.93, S 3.39%. $\mu_{\text{eff}} = 0$. FT-IR (KBr, cm^{-1}) ν : 3168 (N-H), 1686 (C=O), 1132 (C=S), 1434, 1095, 744 (PPh_3). UV [Ethanol, λ in nm (ϵ in $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)]: 241 (13,641), 252 (9,926). ^1H NMR (CDCl_3) δ , ppm: 10.81 (s, 1H, N-H), 7.39-7.71 (m, 30H, phenyl from PPh_3), 7.16-7.25 (m, 3H, phenyl from HL3), 2.95-4.04 (m, 4H, CH_2), 1.19 (t, 3H, CH_3), 0.78 (t, 3H, CH_3). ^{13}C NMR (CDCl_3) δ , ppm: 179.08 (C=S), 164.32 (C=O), 128.30, 129.62, 129.74, 129.82, 131.18, 131.44, 132.50, 133.14, 133.28, 133.53, 135.12, 138.85 (aromatic), 49.04, 50.11 (CH_2), 12.76, 14.16 (CH_3). ^{31}P NMR (CDCl_3) δ , ppm: 29.4 (s).

2.4. Single crystal X-ray diffraction study

Recrystallization of [CuCl(HL1)(PPh₃)₂] (**1**) in an ethyl acetate and dichloromethane (4:1) mixture yielded yellow crystals at room temperature, and a plate having dimensions 0.57 × 0.441 × 0.308 mm was chosen for the study. Intensity data were measured at 110 K on a BRUKER APEX 2 X-ray (three-circle) diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). For each reflection, integrated intensity information was obtained by reduction of data frames with APEX2 [53]. SADABS was employed to correct the data for absorption effects [54]. The structure was solved by direct methods and refined using SHELXT, with full-matrix least squares on F^2 and using all the unique data [55,56]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The absence of additional symmetry and/or voids was verified with PLATON [57]. The crystallographic data and the results of the refinements are summarized in Table 1.

2.5. Procedure for catalytic oxidation

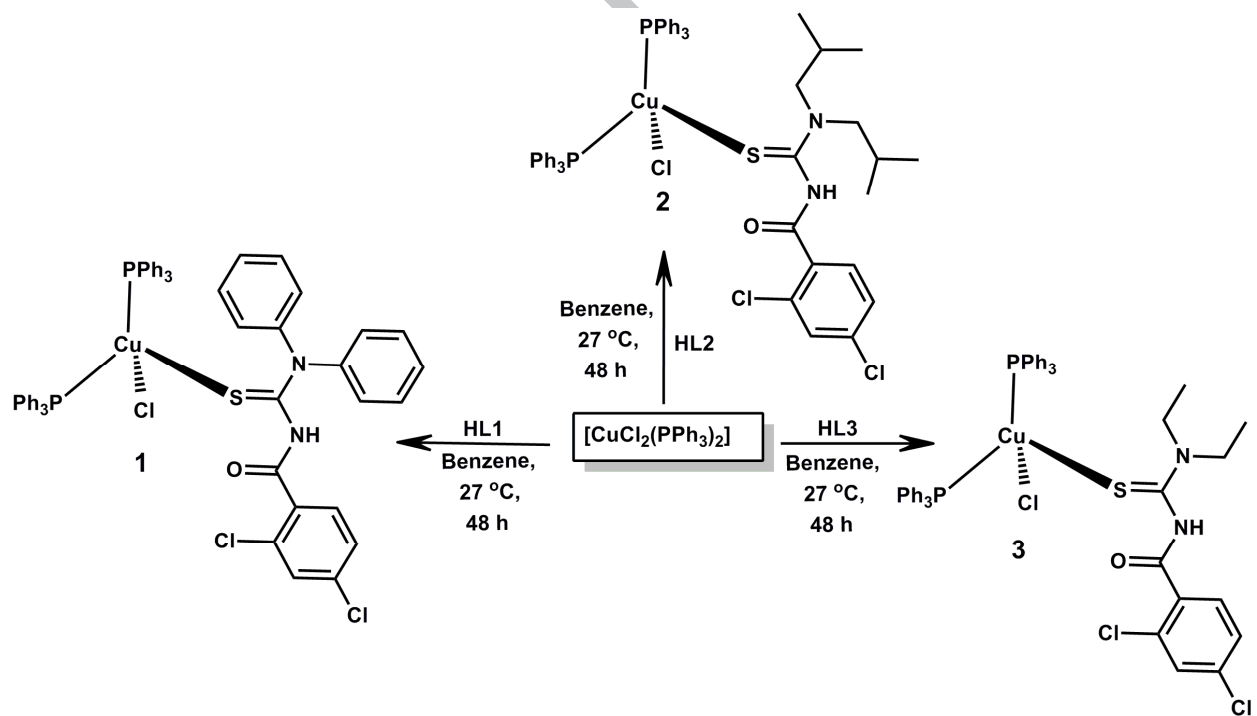
To a mixture of alcohol (5 mmol) and complex **1** (7 mg, 0.007 mmol) in [bmim][PF₆] (0.1 mL), hydrogen peroxide (6 mmol, 0.678 mL) was added. The reaction mixture was stirred for 48 h at 70 °C. After the appropriate time, the resulting mixture was extracted with *n*-hexane and then the extract was analyzed by GC. To identify the reaction products and determine their percentage yields, the retention times and corresponding peak areas were compared with authentic commercial samples under identical experimental conditions. To calculate the percentage yields of the formed products the area normalization method was used. To determine the isolated yields of acetophenone and benzoic acid, their crude mixture was purified by column chromatography. To investigate the recyclability of the IL and the catalyst, [bmim][PF₆] with complex **1** was recovered by overnight drying in *vacuo*. For the five consecutive cycles, the

recovered complex **1** in [bmim][PF₆] was used by adding fresh 1-phenylethanol (5 mmol) and hydrogen peroxide (6 mmol) under the same experimental conditions.

3. Results and discussion

3.1. Synthesis

The reactions of equimolar quantities of [CuCl₂(PPh₃)₂] with 3,3-diphenyl-1-(2,4-dichlorobenzoyl)thiourea (HL1), 3,3-diisobutyl-1-(2,4-dichlorobenzoyl)thiourea (HL2) or 3,3-diethyl-1-(2,4-dichlorobenzoyl)thiourea (HL3), respectively, in benzene at room temperature afforded the new Cu(I) complexes [CuCl(HL1)(PPh₃)₂] (**1**), [CuCl(HL2)(PPh₃)₂] (**2**) or [CuCl(HL3)(PPh₃)₂] (**3**) (Scheme 1). While the reactions were carried out, the Cu(II) ion was reduced to the Cu(I) ion with the oxidation of the ligand [58]. According to analytical, spectral and single crystal X-ray diffraction studies, the new copper(I) complexes (**1**, **2** and **3**) have a four coordinated distorted tetrahedral geometry with one molecule of HL1, HL2 and HL3,



Scheme 1. Synthesis of the Cu(I) complexes.

respectively, and two molecules of PPh_3 . In all the new complexes, the ligands HL1, HL2 and HL3 show an unusual neutral monodentate coordination through the sulfur atom to the Cu(I) ion. As the new Cu(I) complexes are air stable in nature, they are fit for catalytic oxidation reactions. The analytical data obtained were in excellent agreement with the proposed molecular formulae.

3.2. Spectroscopy

A medium intensity band was observed around $1210\text{--}1371\text{ cm}^{-1}$ in the FT-IR spectra of the free acylthiourea ligands, which is characteristic of the C=S group [59]. The bands at 1132 , 1138 and 1222 cm^{-1} in the IR spectra of **1**, **2** and **3**, respectively could be assigned to the C=S stretching mode of the thiocarbonyl group. In the IR spectra of the complexes, the band due to the C=S group appeared in the lower frequency region, indicating that the sulfur atom of the thiocarbonyl group is involved in coordination. The ligands and their copper complexes exhibited a strong band in the region $1703\text{--}1686\text{ cm}^{-1}$, which is characteristic of the C=O group. This indicates that the C=O group is in a similar environment in the ligands and the complexes, and thus is free from coordination. A characteristic broad band corresponding to the N-H group was observed in the region $3168\text{--}3364\text{ cm}^{-1}$ in the spectra of the copper complexes. In addition, bands (around 1435 , 1100 and 750 cm^{-1}) of the triphenylphosphine ligand also appeared in the IR spectra of the complexes [49].

Magnetic susceptibility measurements ($\mu_{\text{eff}} = 0$) of the Cu(I) complexes (**1**, **2** and **3**) showed that they are diamagnetic in nature and the copper center is in the +1 oxidation state. The room temperature electronic spectra of complexes **1**, **2** and **3** in ethanol solution clearly revealed copper-ligand binding in the complexes as they are different from those of the corresponding free ligands. The d^{10} configuration of the copper center was also confirmed by the electronic spectra of the Cu(I) complexes, which had no d-d transitions. UV-vis bands appeared in the

region 240-252 nm ($\epsilon = 9929-27954 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$) due to metal to ligand charge transfer (MLCT) or ligand centered $\pi-\pi^*$ transitions [60].

For the new Cu(I) complexes (**1**, **2** and **3**) the ^1H , ^{13}C and ^{31}P NMR spectra were recorded in CDCl_3 solution. All the complexes exhibited multiplets around δ 7.13-7.25 and 7.30-7.77 ppm in their ^1H NMR spectra, which are attributed to the phenyl protons present in the triphenylphosphine and 3,3-diphenyl/isobutyl/ethyl-1-(2,4-dichlorobenzoyl)thiourea ligands. In the ^1H NMR spectra of the complexes the characteristic signal for the N-H group appeared in the region δ 10.81–11.78 ppm, which was about 0.5 ppm less than that found in the spectra of the ligands. This is due to the intramolecular hydrogen bonding between the N-H group and the coordinated chloride ligand [58]. Complex **2** exhibited two doublets at δ 3.39 and 3.71 ppm, corresponding to the $-\text{CH}_2-$ protons, and two more doublets at δ 0.83 and 0.96 ppm, corresponding to the $-\text{CH}_3$ protons, in its ^1H NMR spectrum. Complex **2** also showed two multiplets at δ 2.01-2.11 and 2.21-2.31 ppm which were assigned to the methine protons in the aliphatic chain. In the ^1H NMR spectrum of complex **3**, a multiplet (merging of two quartets) in the region δ 2.95-4.05 ppm and two triplets at δ 0.78 and 1.19 ppm were observed, which were attributed to the methylene protons proximate to the nitrogen atom and terminal methyl protons, respectively. In the ^{13}C NMR spectra of complexes **1**, **2** and **3**, the signals observed around δ 128.3-146.4 ppm were assigned to the aryl carbon atoms of the triphenylphosphine and coordinated acythiourea ligands. The ^{13}C NMR spectra of the complexes showed signals in the regions δ 179.0-183.5 and 161.4-164.3 ppm due to the C=S and C=O carbon atoms, respectively. Complexes **2** and **3** exhibited resonances for the aliphatic carbons in the expected regions. Only one signal, obtained at δ 30.1, 32.1 and 29.4 ppm, in ^{31}P NMR spectra of complexes **1**, **2** and **3**

respectively confirmed the presence of the coordinated triphenylphosphine ligand in the Cu(I) complexes.

3.3. Crystallography

A view of the molecular structure for complex **1** is illustrated in Fig. 2, and selected geometric parameters are listed in Table 2. In the monomeric complex, the Cu(I) ion consists of two triphenylphosphine ligands coordinated by phosphorus atom, a coordinated chloride ion and a 3,3-diphenyl-1-(2,4-dichlorobenzoyl)thiourea ligand (HL1) coordinated solely through the sulfur atom, with the bond angles around the copper ion in the range *ca.* 99-124°. The bond angles around the copper ion are slightly distorted from those of an ideal tetrahedral geometry,

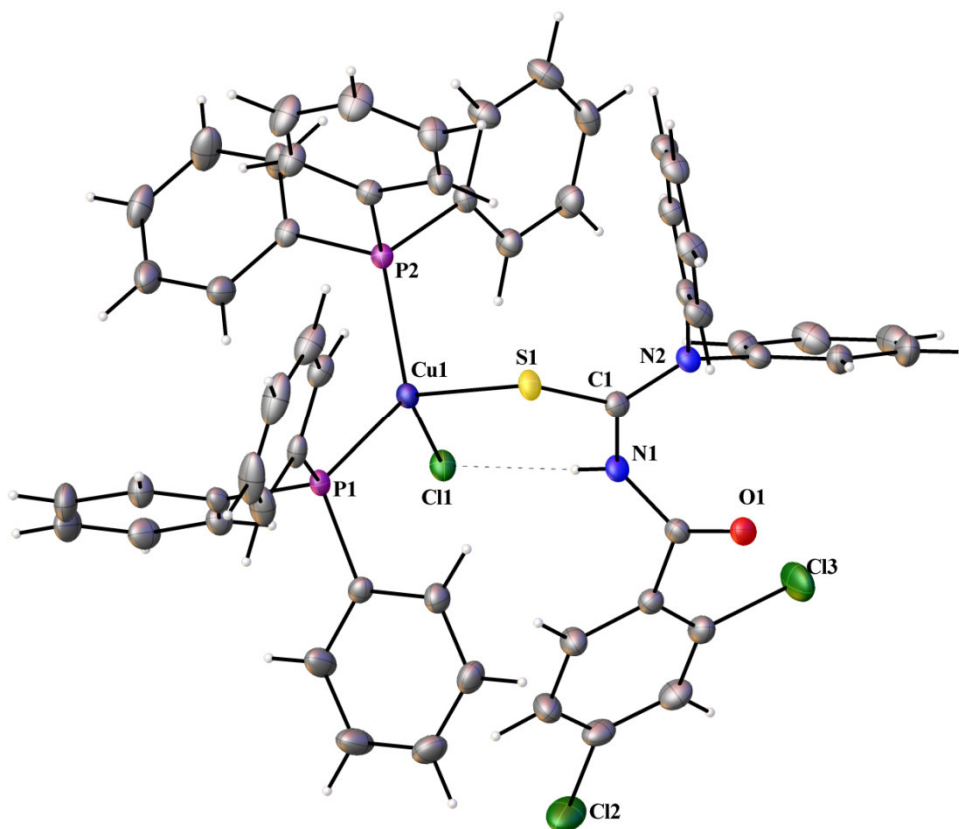


Fig. 2. Molecular structure of complex **1**. Only selected atoms are labelled in the thermal ellipsoid plot for clarity.

noticeably a narrow $99.054(17)^\circ$ for P(2)-Cu(1)-S(1) to a wide $124.150(18)^\circ$ for P(1)-Cu(1)-P(2), due to the presence of two bulky triphenylphosphine ligands in the coordination sphere. The distortion might also be associated with the presence of an intramolecular hydrogen bond between the thiourea N-H group and the coordinated chloride ion. In complex **1**, the Cu-S bond length of $2.3859(5) \text{ \AA}$ was analogous to that ($2.2668\text{-}2.4226 \text{ \AA}$) of Cu(I) tetrahedral complexes containing monodentate acylthiourea ligands [61,62]. The Cu-Cl bond length [$2.3181(4) \text{ \AA}$] in complex **1** was less than the sum of the ideal ionic radii of the Cu^+ and Cl^- ions (2.58 \AA) [63].

3.4. Catalytic oxidation

Investigations were initially conducted on the oxidation of 1-phenylethanol (Table 3, entries 1-3) with the new Cu(I) complexes **1-3** in [bmim][PF₆] in the presence of H₂O₂ oxidant at 70 °C for 48 h. Though the yields of acetophenone were good with all the new Cu(I) complexes, the catalytic activity of complex **1** (Table 3, entry 1) was slightly higher (90%) and hence it has been chosen as a catalyst for optimizing the reaction conditions and extending the scope of the substrates. To select a suitable ionic liquid as the solvent, the oxidation of 1-phenylethanol was studied in 0.1 mL of [bmim][PF₆] and [bmim][BF₄] (Table 3, entry 4). Among these ILs, [bmim][PF₆] was chosen as the best solvent as the yield of acetophenone was higher when it was used for the oxidation reaction (Table 3, entry 1). In order to find the optimum amount of catalyst, oxidant and temperature, the catalytic oxidation of 1-phenylethanol (Table 3, entries 5-10) was carried out with various amounts of catalyst and oxidant in a range of temperatures. The results of the reaction confirmed that a better yield of acetophenone was obtained with 0.007 mmol of catalyst and 6 mmol of oxidant at 70 °C (Table 3, entry 1). The oxidation did not occur in the absence of complex **1** under identical conditions and an extremely low yield (8-9%) of acetophenone was observed when copper salts such as CuCl₂ (Table 3, entry

11) and CuCl (Table 3, entry 12) were added as the catalyst in the place of complex **1**. In a control experiment under identical conditions, no reaction was observed in the oxidation of 1-phenylethanol when complex **1** was replaced by the ligand HL1 (Table 3, entry 13). To confirm that H₂O₂ acted solely as the oxidant, and not added O₂, the oxidation of 1-phenylethanol (Table 3, entry 14) was conducted with complex **1** under a nitrogen atmosphere, which also gave 90% of acetophenone.

The results of the test reactions established 0.1 mL of [bmim][PF₆], 6 mmol of H₂O₂ and 0.007 mmol of complex **1** were sufficient for the oxidation of 5 mmol of 1-phenylethanol and these optimal conditions were utilized for the scope extension to various primary and secondary alcohols. Further oxidation did not occur after 48 h. The results obtained are summarized in Table 4. Interestingly, benzylic primary alcohols (Table 4, entries 1-3) were oxidized to form the corresponding carboxylic acids at 70 °C in fair to good yields by using 1.2 equivalents of H₂O₂, whereas Cu(II) catalyzed oxidation of primary alcohols to carboxylic acids in acetonitrile solvent required 10 equivalents of H₂O₂ at the same temperature [64]. Even our previous Cu(I)-acylthiourea/H₂O₂ catalytic system in CH₃CN solvent required 5 equivalents of H₂O₂ for the oxidation of alcohol substrates (1 mmol) at room temperature [49]. Our present catalytic system is very active towards the oxidation of allylic alcohol *viz* cinnamyl alcohol (Table 4, entry 4) to cinnamic acid (92% yield), whereas oxidation of cinnamyl alcohol was not catalyzed by our earlier Cu(I)-thiourea/H₂O₂ catalytic [49] and Cu(II)/H₂O₂ catalytic [64] systems. The benzylic secondary alcohols 1-phenylethanol, α -methyl-2-naphthalenemethanol and 1-phenoxy-2-propanol (Table 4, entries 5, 7 and 8) on oxidation gave the corresponding ketones in 90, 57 and 97% yield, respectively. Even though these results are comparable with the Cu(I)-thiourea/H₂O₂ catalytic system in CH₃CN solvent, the present catalytic system worked

with 1.2 equivalents of H_2O_2 . However, the oxidation of 4-chlorophenylethanol (Table 4, entry 6) did not give a satisfactory result. Very interestingly, the oxidation of 1-indanol to 1-indanone (Table 4, entry 9) proceeded to give 97% of the product, while our previous system exhibited only a 40% yield of 1-indanone [49]. The present catalytic system did not work for the oxidation of cyclic alcohol, *viz* cyclohexanol (Table 4, entry 10). Unfortunately, and despite extensive efforts, aliphatic alcohols could not be oxidized by the present catalytic system.

Additional experiments were conducted to analyze the recyclability and reusability of both [bmim][PF₆] and the catalyst (complex **1**) for the same reaction. For the catalytic oxidation of 1-phenylethanol to acetophenone, the catalytic phase (complex **1** in [bmim][PF₆]), recovered from overnight drying (in *vacuo*), maintained its good level catalytic activity even after being recycled 5 times in consecutive runs. This indicated the viability of both the ionic liquid and catalyst.

In order to understand the reactive species involved in the reaction, complex **1** in ethanol (10^{-5} M) was treated with H_2O_2 (dissolving five drops in 5 mL of methanol) and the progress of the reaction was monitored by electronic absorption spectroscopy. The titration was carried out by the addition of two drops of H_2O_2 for each addition to the solution of complex **1** in ethanol. The results showed that the intensities of the bands at 240 and 252 nm increased considerably, but no other new bands were formed. The data suggest the interaction of complex **1** with H_2O_2 and hence, presumably a Cu(I)-peroxo complex was formed and acted as an active intermediate in the oxidation reaction [65].

4. Conclusions

In summary, new four-coordinated tetrahedral copper(I) complexes incorporating 3,3-dialkyl/aryl-1-(2,4-dichlorobenzoyl)thiourea derivatives (HL1, HL2 and HL3) and

triphenylphosphine have been prepared and characterized. An unusual neutral monodentate coordination was exhibited by the 3,3-dialkyl/aryl-1-(2,4-dichlorobenzoyl)thiourea derivatives through the S atom to the Cu(I) ion. Both the ligands and complexes were synthesized at room temperature. The complexes were used as catalysts in 1-butyl-3-methylimidazolium hexafluorophosphate medium in the presence of H₂O₂ for the oxidation of various alcohols at 70 °C. Interestingly, the present catalytic system worked for the oxidation of alcohols without any additive and base.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article (electronic spectra, representative ¹H, ¹³C and ³¹P-NMR spectra of the Cu(I) complexes, GC chromatogram, and GC conditions for catalytic studies) can be found in the online version. Crystallographic data (excluding structure factors) for the structure described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1473182. Copies of the data can be obtained free of charge on application to The Director, 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>).

References

- [1] R.A. Sheldon and J.K. Koch, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- [2] S.D. Burke, in: R.L. Danheiser (Ed.), *Handbook of Reagents for Organic Synthesis: Oxidizing and Reducing Agents*, John Wiley & Sons, New York, 1999.
- [3] M. Beller and C. Bolm, 2nd Ed., *Transition Metals for Organic Synthesis*, Wiley-VCH, Weinheim, 2004.
- [4] G.-J. Brink, I.W.C.E. Arends, R.A. Sheldon, *Science* 287 (2000) 1636–1639.
- [5] L. Delaude, P. Laszlo, *J. Org. Chem.* 61 (1996) 6360–6370.
- [6] H.R. Mardani, H. Golchoubian, *Tetrahedron Lett.* 47 (2006) 2349–2352.
- [7] S.E. Martin, A. Garrone, *Tetrahedron Lett.* 44 (2003) 549–552.
- [8] I.E. Marko, P.R. Giles, M. Tsukazaki, I. Chelle-Regnaut, C.J. Urch, S.M. Brown, *J. Am. Chem. Soc.* 119 (1997) 12661–12662.
- [9] C.Y. Lorber, S.P. Smidt, J.A. Osborn, *Eur. J. Inorg. Chem.* (2000) 655–658.
- [10] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772–3789.
- [11] N. Gunasekaran, *Adv. Synth. Catal.* 357 (2015) 1990–2010.
- [12] D.S. Silvester, *Analyst* 136 (2011) 4871–4882.
- [13] M. Díaz, A. Ortiz, I. Ortiz, *J. Membr. Sci.* 469 (2014) 379–396.
- [14] A. Lewandowski, A.Š. Mocek, *J. Power Sources* 194 (2009) 601–609.
- [15] E. Uesugi, H. Goto, R. Eguchi, A. Fujiwara, Y. Kubozono, *Sci. Rep.* 3:1595 (2013) 1–5.
- [16] E.A. Chernikova, L.M. Glukhov, V.G. Krasovskiy, L.M. Kustov, M.G. Vorobyeva, A.A. Koroteev, *Russ. Chem. Rev.* 84 (2015) 875–890.
- [17] B. Zhang, D. A. Hoagland, Z. Su, *J. Phys. Chem. B* 119 (2015) 3603–3607.
- [18] T. Bartels, *Encyclopedia of Lubricants and Lubrication: Ionic Liquids as Lubricants*, Springer-Verlag Berlin Heidelberg, 2014.
- [19] J. Le Bideau, L. Viau, A. Vioux, *Chem. Soc. Rev.* 40 (2011) 907–925.
- [20] R. Liang, Z. Bao, B. Su, H. Xing, Q. Yang, Y. Yang, Q. Ren, *J. Agric. Food Chem.* 61 (2013) 3479–3487.

- [21] M. Koel, *Crit. Rev. Anal. Chem.* 35 (2005) 177–192.
- [22] J.P. Hallett, T. Welton, *Chem. Rev.* 111 (2011) 3508–3576.
- [23] K. Nakashima, F. Kubota, T. Maruyama, M. Goto, *Ind. Eng. Chem. Res.* 44 (2005) 4368–4372.
- [24] P. Walden, *Bull. Acad. Sci. St Petersburg* (1914) 405–422.
- [25] R.D. Rogers, K.R. Seddon, *Science* 302 (2003) 792–793.
- [26] T.L. Greaves, C.J. Drummond, *Chem. Rev.* 107 (2007) 2615–2665.
- [27] R. Giernoth, *Angew. Chem., Int. Ed.* 49 (2010) 2834–2839.
- [28] R.A. Bailey, K.L. Rothaupt, *Inorg. Chim. Acta* 147 (1988) 233–236.
- [29] A.N. Westra, S.A. Bourne, C. Esterhuysen, K.R. Koch, *Dalton Trans.* (2005) 2162–2172.
- [30] A. Molter, F. Mohr, *Coord. Chem. Rev.* 254 (2010) 19–45.
- [31] U. Braun, R. Richter, J. Sieler, A.I. Yanovski, Y.T. Struchkov, *Z. Anorg. Allg. Chem.* 529 (1985) 201–208.
- [32] R. Richter, J. Sieler, I. Beyer, O. Lindqvist, L. Anderson, *Z. Anorg. Allg. Chem.* 522 (1985) 171–183.
- [33] K.R. Koch, S. Bourne, *J. Mol. Struct.* 441 (1998) 11–16.
- [34] J. Cernak, J. Chomic, P. Kutschy, D. Svrčinova, M. Dzurilla, *Inorg. Chim. Acta* 181 (1991) 85–92.
- [35] M.M. Sheeba, M.M. Tamizh, L.J. Farrugia, A. Endo, R. Karvembu, *Organometallics* 33 (2014) 540–550.
- [36] D.J. Che, G. Li, X.L. Yao, Q.J. Wu, W.L. Wang, Y. Zhu, *J. Organomet. Chem.* 584 (1999) 190–196.
- [37] G. Kemp, A. Roodt, W. Purcell, K.R. Koch, *J. Chem. Soc., Dalton Trans.* (1997) 4481–4484.
- [38] K.R. Koch, *Coord. Chem. Rev.* 216–217 (2001) 473–488.
- [39] M.K. Rauf, Imtiaz-ud-Din, A. Badshah, M. Gielen, M. Ebihara, D. de Vos, S. Ahmed, *J. Inorg. Biochem.* 103 (2009) 1135–1144.
- [40] M. Kalhor, M. Salehifar, I. Nikokar, *Med. Chem. Res.* 23 (2014) 2947–2954.

- [41] W. Yang, H. Liu, M. Li, F. Wang, W. Zhou, J. Fan, *J. Inorg. Biochem.* 116 (2012) 97–105.
- [42] Z. Weiqun, Y. Wen, X. Liqun, C. Xianchen, *J. Inorg. Biochem.* 99 (2005) 1314–1319.
- [43] N. Selvakumaran, A. Pratheepkumar, S.W. Ng, E.R.T. Tiekink, R. Karvembu, *Inorg. Chim. Acta* 404 (2013) 82–87.
- [44] T.J. Egan, K.R. Koch, P.L. Swan, C. Clarkson, D.A. Van Schalkwyk, P.J. Smith, *J. Med. Chem.* 47 (2004) 2926–2934.
- [45] R.C. Luckay, F. Mebrahtu, C. Esterhuysen, K.R. Koch, *Inorg. Chem. Commun.* 13 (2010) 468–470.
- [46] M.M. Habtu, S.A. Bourne, K.R. Koch, R.C. Luckay, *New J. Chem.* 30 (2006) 155–1162.
- [47] N. Gunasekaran, N. Remya, S. Radhakrishnan, R. Karvembu, *J. Coord. Chem.* 64 (2011) 491–501.
- [48] N. Gunasekaran, R. Karvembu, *Inorg. Chem. Commun.* 13 (2010) 952–955.
- [49] N. Gunasekaran, P. Ramesh, M. N. Ponnusamy, R. Karvembu, *Dalton Trans.* 40 (2011) 12519–12526.
- [50] N. Gunasekaran, P. Jerome, S.W. Ng, E.R.T. Tiekink, R. Karvembu, *J. Mol. Catal. A: Chem.* 353–354 (2012) 156–162.
- [51] J. Venanzi, *J. Chem. Soc.* (1958) 719–724.
- [52] N. Selvakumaran, N.S.P. Bhuvanesh, A. Endo, R. Karvembu, *Polyhedron* 75 (2014) 95–109.
- [53] APEX2 “Program for Data Collection and Integration on AreaDetectors”, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.
- [54] G.M. Sheldrick, SADABS, (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames, University of Göttingen, 2008.
- [55] G.M. Sheldrick, *Acta Cryst. A* 71 (2015) 3–8.
- [56] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 42 (2009) 339–341.
- [57] A.L. Spek, *J. Appl. Crystallogr.* 36 (2003) 7–13.
- [58] Y.F. Yuan, J.T. Wang, M.C. Gimeno, A. Laguna P.G. Jones, *Inorg. Chim. Acta* 324 (2001) 309–317.
- [59] G. Binzet, N. Kulcu, U. Florke, H. Arslan, *J. Coord. Chem.* 62 (2009) 3454–3462.

- [60] S. Dehghanpour, N. Bouslimani, R. Welter, F. Mojahed, *Polyhedron* 26 (2007) 154–162.
- [61] N. Gunasekaran, S.W. Ng, E.R.T. Tiekink, R. Karvembu, *Polyhedron* 34 (2012) 41–45.
- [62] Y.-M. Zhang, H.-X. Pang, C. Cao, T.-B. Wei, *J. Coord. Chem.* 61 (2008) 1663–1670.
- [63] J.E. Huheey, E.A. Keiter, R.L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th Edition, Harper Collins, New York, 1993.
- [64] S. Velusamy, T. Punniyamurthy, *Eur. J. Org. Chem.* (2003) 3913–3915.
- [65] S. Goldstein, G. Czapski, *J. Free Radicals Bio. Med.* 1 (1985) 373–380.

ACCEPTED MANUSCRIPT

Table 1Summary of crystallographic data for **1**

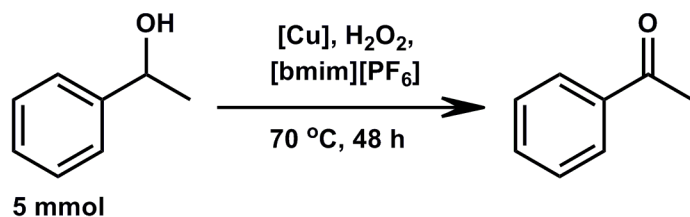
Empirical formula	C ₅₆ H ₄₄ Cl ₃ CuN ₂ OP ₂ S
Formula weight	1024.82
Crystal color	Brown
Crystal dimensions (mm ³)	0.57 × 0.441 × 0.308
Crystal system	Triclinic
Space group	<i>P</i> -1
a (Å)	11.4077(8)
b (Å)	14.4196(11)
c (Å)	17.4337(13)
α (°)	74.1040(10)
β (°)	71.7640(10)
γ (°)	67.7780(10)
V (Å ³)	2481.6(3)
Z	2
D _x (g cm ⁻³)	1.371
F(000)	1056
μ(Mo Kα) (mm ⁻¹)	0.750
Reflections collected	35827
Independent reflections (R _{int})	11338 (0.0259)
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6443
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11338 / 0 / 595
Goodness-of-fit on F ²	1.041
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	R ₁ = 0.0337, wR ₂ = 0.0866
R indices (all data)	R ₁ = 0.0404, wR ₂ = 0.0910
Extinction coefficient	n/a
Largest diff. peak and hole (e Å ⁻³)	0.896 and -0.464

Table 2Selected bond lengths [Å] and angles [°] for **1**

Cu(1)-Cl(1)	2.3181(4)
Cu(1)-S(1)	2.3859(5)
Cu(1)-P(1)	2.2675(5)
Cu(1)-P(2)	2.2771(5)
S(1)-C(1)	1.6779(17)
O(1)-C(2)	1.215(2)
N(1)-C(1)	1.398(2)
N(2)-C(1)	1.348(2)
Cl(2)-C(6)	1.7432(19)
Cl(3)-C(8)	1.7352(19)
Cl(1)-Cu(1)-S(1)	108.956(17)
P(1)-Cu(1)-Cl(1)	105.448(17)
P(2)-Cu(1)-Cl(1)	113.238(17)
P(1)-Cu(1)-S(1)	104.782(16)
P(2)-Cu(1)-S(1)	99.054(17)
P(1)-Cu(1)-P(2)	124.150(18)
C(5)-C(6)-Cl(2)	119.40(16)
C(7)-C(6)-Cl(2)	118.71(15)
C(3)-C(8)-Cl(3)	120.61(14)
C(7)-C(8)-Cl(3)	118.14(14)
C(1)-N(1)-H(1)	117.4
C(2)-N(1)-H(1)	117.4

Table 3

Optimization of catalytic oxidation.



Entry	Complex/Compound	Complex/Compound Amount (mmol)	Oxidant Amount (mmol)	Yield (%) ^a
1	1	0.007	3.0	90
2	2	0.007	3.0	88
3	3	0.007	3.0	85
4	1	0.007	3.0	78 ^b
5	1	0.010	3.0	79
6	1	0.005	3.0	80
7	1	0.007	2.5	80
8	1	0.007	3.5	83
9	1	0.007	3.0	82 ^c
10	1	0.007	3.0	81 ^d
11	CuCl₂	0.007	3.0	9
12	CuCl	0.007	3.0	8
13	HL1	0.007	3.0	No reaction
14	1	0.007	3.0	90 ^e

^a Yield is determined by GC with area normalization; GC conditions: RTX-5 Column, 60 m × 0.32 mm, initial column temperature was increased from 130 to 250 °C at a rate of 7 °C/min; FID detector, 290 °C; Injector, 260 °C; Carrier Gas: N₂; Rate: 2.00 mL/min.

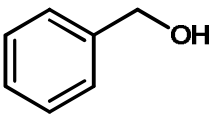
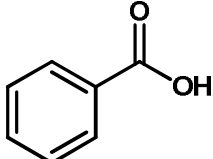
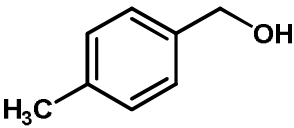
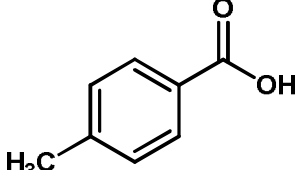
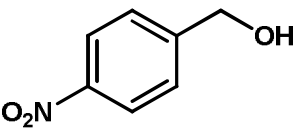
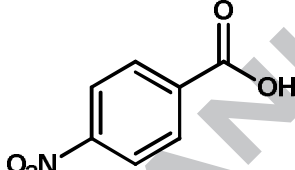
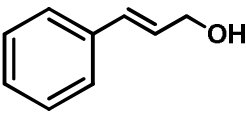
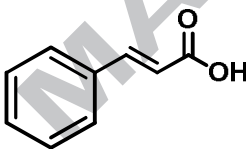
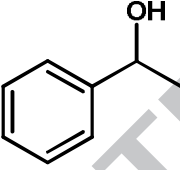
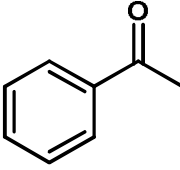
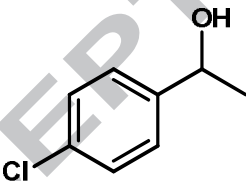
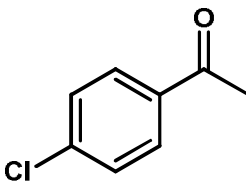
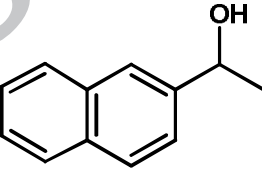
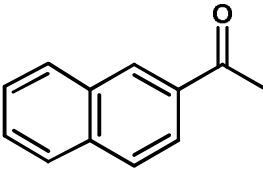
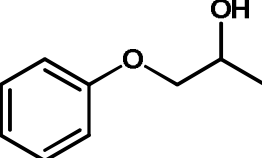
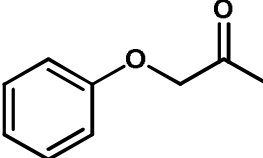
^b [bmim][BF₄] was used as the solvent

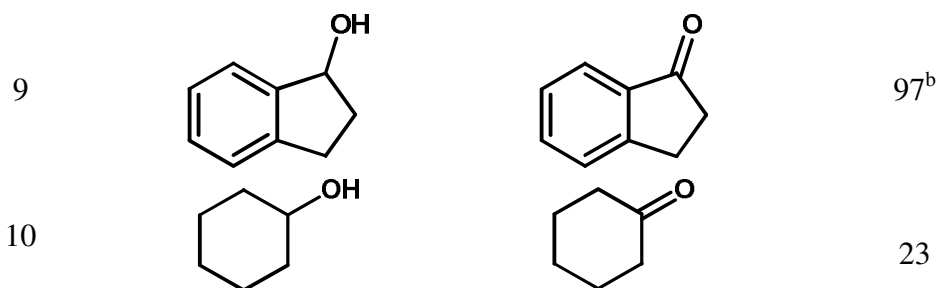
^c Reaction occurred at 75 °C

^d Reaction occurred at 65 °C

^e Reaction conditions: 1-phenylethanol (5.0 mmol), oxidant (6.0 mmol), catalyst (0.007 mmol), solvent (0.1 mL), stirring for 48 h at 70 °C under a nitrogen atmosphere.

Table 4Oxidation of alcohols^a by **1**.

Entry	Substrate	Product	Yield ^c (%)
1			75 (72) ^d
2			67
3			53 ^b
4			92
5			90 (86) ^d
6			16
7			57 ^b
8			97



^a Reaction conditions: alcohol (5 mmol), H₂O₂ (6.0 mmol), catalyst (0.007 mmol), [bmim][PF₆] (0.1 mL), stirring for 48 h, 70°C.

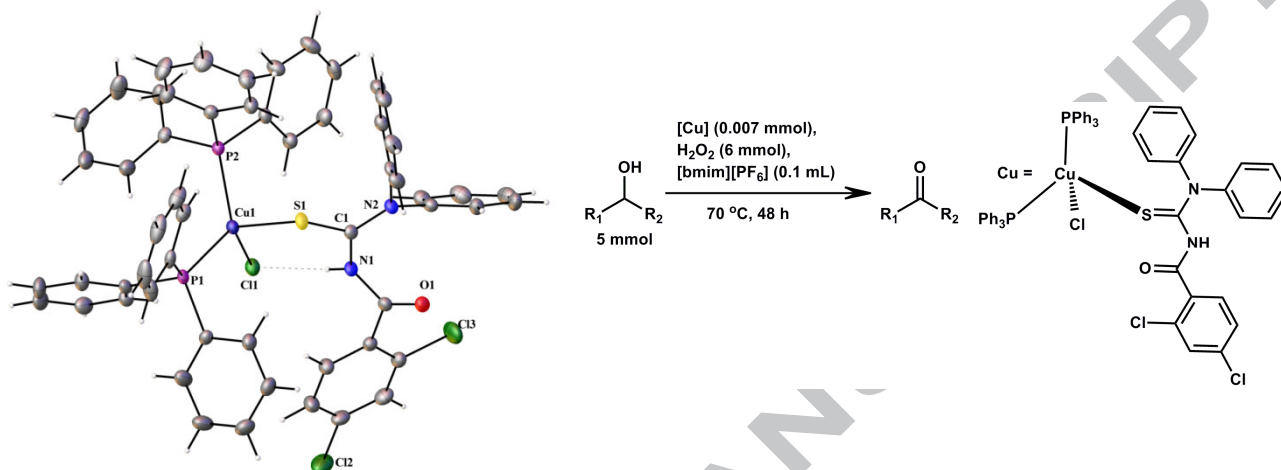
^b Reaction conditions: alcohol (5 mmol), H₂O₂ (3.0 mmol), catalyst (0.007 mmol), [bmim][PF₆] (0.4 mL), stirring for 48 h, 70°C.

^c Yield is determined by GC with area normalization.

^d Isolated yield is given in parenthesis.

Synthesis, characterization and catalytic oxidation property of copper(I) complexes containing monodentate acylthiourea ligands and triphenylphosphine

N. Gunasekaran, N.S.P. Bhuvanesh, R. Karvembu



Synthesis, characterization and catalytic oxidation property of copper(I) complexes containing monodentate acylthiourea ligands and triphenylphosphine

N. Gunasekaran, N.S.P. Bhuvanesh, R. Karvembu

A rare monodentate coordination mode has been observed for 3,3-dialkyl/aryl-1-(2,4-dichlorobenzoyl)thiourea ligands with the Cu(I) ion. The resulting four-coordinated tetrahedral copper(I) complexes were found to be active catalysts in 1-butyl-3-methylimidazolium hexafluorophosphate medium in the presence of H₂O₂ for the oxidation of various alcohols at 70 °C. Interestingly, the present catalytic system worked for the oxidation of alcohols without any additive and base.