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A New 2-[2-(Diphenylphosphino)ethyl]pyridine-Ruthenium(II) Complex as an Efficient Pre-catalyst for Oxidation of Alcohol at Room Temperature in Aqueous Medium

Devajani Boruah

Department of Chemistry, Silapathar Science College, Silapathar-787059, India

Corresponding author: E-mail: dr.devajani5@gmail.com

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A ruthenium(II) complex [$RuCl_2\{\eta^2$-(P,N)$PPh_2Etpy\}(PPh_3)_2$] (**1**) was synthesized by reacting $RuCl_2(PPh_3)_3$ with ligand 2-[2-(diphenylphosphino)ethyl]pyridine (PPh_2Etpy) in 1:1 molar ratio in dichloromethane under refluxing condition. The complex was characterized by FT-IR, UV-vis, ^1H and $^{31}P\{^1H\}$ NMR, ESI(+) mass spectrometry, elemental analysis, conductivity measurement, TGA-DTG and cyclic voltammetry. Complex **1** was found to exhibit good catalytic activity towards the oxidation of aromatic alcohols to corresponding carbonyl compounds with H_2O_2/NaOCl as an oxidant in water. The maximum conversion of 89% can be achieved under mild reaction conditions.

Keywords: Ruthenium complex, Alcohol, Oxidation, Catalysis.

INTRODUCTION

A variety of ruthenium complexes featuring various bifunctional ligands with phosphorus and nitrogen donor sites has gained significant attention in recent years due to their structural uniqueness, reactivity and catalytic properties [1-7]. These P–N donor ligands exhibit hemilabile behaviours which can be attributed to their distinct σ and π donor/acceptor properties, alongside the "hard" and "soft" interactions that occur between the ligand and the metal [8]. Several articles have been documented on these complexes as catalyst precursors for various chemical reactions [9,10] such as transfer hydrogenation of acetophenone [11-13], hydrogenation [14,15], oxidation of aromatic and primary aliphatic alcohols under mild reaction conditions [16-21], hydroformylation reaction [3,22], methanol and alkynes carbonylation, olefin oligomerizations and polymerization [23]. In the catalytic process, the ligand backbone plays important role [24,25]. In order to improve the catalysts, researchers have continuously designed different complexes by incorporating various ligands to their coordination sphere [26].

The metal catalyzed selective oxidation of alcohols into aldehyde and ketones is one of the most fundamental reactions in synthetic organic chemistry [27]. They play an important role in the pharmaceutical and fine chemical industries as both precursors and synthesis intermediates [28-33]. Also in the production of biologically important active compounds, different flavours and fragrances [34]. Unfortunately, such conversion had been performed using stoichiometric quantities of costly inorganic oxidants such as CrO_3, $KMnO_4$, SeO_2, MnO_2 [35,36], hypervalent iodines [37], oxalyl chloride [38], *etc.* However, use of these reagents has many drawbacks, mainly large quantities of undesired toxic byproducts are formed during the reaction, which create problem to isolate the pure product after completion of a reaction and also for environmental safety these are not catalyst of choice [39]. In addition to this, there are limitations to choose the substrates, as these types of systems require acidic condition, which do not allow the complete conversion [40]. Therefore, from the environmental point of view, there is a strong need to develop new catalytic systems for oxidation, which are green and atom-efficient. Generally, molecular oxygen, H_2O_2 and NaOCl are eco-friendly and waste avoiding oxidants [17,18,41].

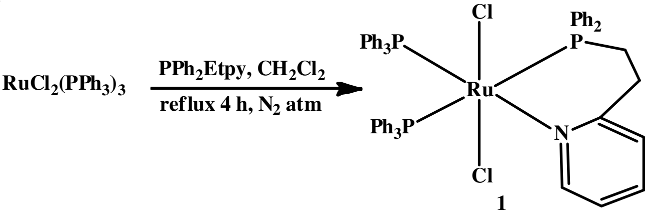
Several literature describes the catalytic systems that use molecular oxygen or free oxygen (air) as an oxidant along with various platinum group metals [42,43]. Because of its greater amount of atom efficiency, active oxygen, low cost and eco-friendly qualities, H_2O_2 has emerged as one of the most promising oxidants for application in laboratory and commercial production. The release of the active oxidative species and the generation of water as the only byproduct make H_2O_2 desirable in aqueous solutions [19,20]. For liquid-phase oxidation reaction H_2O_2 is used as oxidant, typically for the preparation of agrochemicals and pharmaceuticals, as it is easier to handle. In case of application of O_2, there arises some problems to control which lead to combustion and in almost all oxidation reactions, only one oxygen atom is utilized due to which an over stoichiometric amount of co-reductant is required for such processes [44]. Ruthenium catalyst having high oxidation states have been found to be the best catalyst for oxidation of alcohols. During the reaction of such system produces very low or no over oxidation products [45]. Yang *et. al.* [46] reported the oxidation of aromatic alcohols such as benzyl alcohol and its derivatives, benzhydrol and its derivatives and long-chained aliphatic alcohols catalyzed by ruthenium complexes in presence of iodosylbenzene as oxidant at room temperature. The Ru catalyzed oxidation of both aromatic and aliphatic alcohols, Lei *et. al.* [47] found that aliphatic alcohols can be converted to their corresponding carbonyl compound in their reaction system, which are generally difficult to oxidize in other oxidation system.

Herein, we have reported the synthesis of a neutral Ru(II) complex with 2-[2-(diphenylphosphino)ethyl]pyridine. The complex was characterized by using IR, UV-vis, TGA-DTG, ESI(+)MS and ^1H and $^{31}P\{^1H\}$ NMR spectroscopic methods. The catalytic efficiency of Ru(II) complex have been explored for the oxidation of aromatic alcohols to corresponding carbonyl compounds with H_2O_2/NaOCl as oxidant in water.

EXPERIMENTAL

Ruthenium(III) chloride ($RuCl_3 \cdot xH_2O$) was purchased from Arora-Matthey Ltd., India. Ligand 2-[2-(diphenylphosphino)ethyl]pyridine (PPh_2Etpy) was purchased from Aldrich (USA). The precursor complex, $RuCl_2(PPh_3)_3$, was synthesized according to the published procedure [48]. All other chemicals used were of AR grade purchased from different Indian firms and used as received. The solvents used were of analytical grade, distilled and dried over 4 Å molecular sieves before use. The reactions were performed in inert atmosphere of nitrogen.

Synthesis of [$RuCl_2\{\eta^2$-(P,N)$PPh_2Etpy\}(PPh_3)_2$] (1): A solution of 2-[2-(diphenylphosphino)ethyl]pyridine (PPh_2-Etpy) (0.070 g, 0.241 mmol) in dichloromethane was added to a dichloromethane solution (20 mL) of $RuCl_2(PPh_3)_3$ (0.230 g, 0.240 mmol). The reaction mixture was refluxed under nitrogen for about 4 h, during which colour of the solution changed from chocolate brown to green. The solvent was removed under reduced pressure to afford a dirty green residue, which was then dissolved in a minimum amount of CH_2Cl_2 and was chromatographed on a silica gel column with 20% acetone in CH_2Cl_2 as eluting solvent. After evaporation, the solid product was isolated as green solid (**Scheme-I**). Yield: 84%; m.p.: 163 ºC; $\Lambda = 10\ \Omega^{-1}\ cm^2\ mol^{-1}$; Anal. analysis of $C_{55}H_{48}N_1P_3Cl_2Ru$, calcd. (found) %: C, 66.87 (66.10); H, 4.86 (4.12); N, 1.42 (1.22); IR (KBr, ν_{max}, cm^{-1}): 3055(m) (=C-H), 2922(w) (C-H), 1607(m) (py-C=N), 538(s) (Ru-P), 417(w) (Ru-N), 328 (ms) (Cl-Ru-Cl); UV-vis (CH_2Cl_2), Λ_{max} (nm): 351, 223; ^1H NMR ($CDCl_3$, RT) δ ppm: 9.02 (d, $^3J_{HH} = 5.52$ Hz, 1H, py, H^6), 7.98 (t, 1H, py, H^4), 7.39 (m, 1H, py, H^5), 7.26 (m, 1H, py, H^3), 6.42-7.80 (m, 40H, Ph), 3.40 (m, 2H, Py-CH_2), 2.18 (m, 2H, PPh_2-CH_2); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 300 K) δ ppm: 51.21 (t, 1P, $J_{PP} = 34.88$ Hz, PPh_3), 48.81(d, 1P, $J_{PP} = 34.88$ Hz, PPh_2), 39.17(d, 1P, $J_{PP} = 34.88$ Hz, PPh_3); ESI/MS (*m/z*): 1005 $[M + NH_4]^+$ (base peak), 968 $[M + NH_4\text{-}Cl^{35.5}]^+$, 934 $[M + NH_4\text{-}2Cl^{35.5}]^+$, 742 $[M + NH_4\text{-}PPh_3]^+$, 720 $[M+Na\text{-}PPh_2Etpy]^+$], 464 $[M+1\text{-}PPh_2Etpy]^+$.



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Scheme-I: Synthesis of [$RuCl_2\{\eta^2$-(P,N)$PPh_2Etpy\}(PPh_3)_2$] (**1**)

General procedures for oxidation of alcohols: The alcohol, 1-phenylethanol (4.50 g, 36.9 mmol) and oxidant (air/H_2O_2/NaOCl; H_2O_2/NaOCl: 3.00 g, 88.2 mmol/6.55 g, 87.9 mmol) in CH_2Cl_2 (6 mL) were taken in a glass reactor and the amount of synthesized catalyst [$RuCl_2\{\eta^2$-(P,N)$PPh_2Etpy\}$-$(PPh_3)_2$] (**1**) was changed from 0.025 g (0.038 mmol) to 0.0003 g (0.000289 mmol). The solution was stirred for 23 h at room temperature in a 25 mL glass reactor. A set of reactions were also conducted without the catalyst, using the same quantity of substrate and oxidant for the corresponding period of time. Another set of reactions were carried out using [$RuCl_2(PPh_3)_3$] as catalyst (substrate:catalyst = 10,000:1) to compare the catalytic activity of complex **1** with the starting compound [$RuCl_2(PPh_3)_3$]. The progress of the reactions was monitored by TLC. After 23 h of reaction time, the reaction mixture was diluted with water (23 mL) and extracted with Et_2O (3 × 25 mL). The combined extract was washed with brine (2 × 20 mL) and dried over Na_2SO_4. After the evaporation of solvent under reduced pressure, the residue was chromatographed (silica gel, 3.5-4.1% ethylacetate in hexane) to obtain the desired products.

Physical measurements: The melting point of the complex **1** was determined using BuchiB450 melting point apparatus. IR spectra (4000-250 cm^{-1}) were recorded on a Shimadzu Prestige-21 FTIR spectrophotometer using KBr disks. The UV-vis spectra were recorded in dichloromethane solution using 1 cm^3 quartz cell in the range 800-200 nm on a Shimadzu-Graphicord UV-1700 spectrometer. The conductivity of the complex was measured in dichloromethane (10^{-2} M) by using a digital conductivity bridge (type ELICO-CM-180) at 25 ºC. ^1H and $^{31}P\{^1H\}$NMR spectra were recorded in $CDCl_3$ operating at 300.13 and 161.97 MHz, respectively, on a Bruker DRX-300 spectrometer. The ESI(+) mass spectra were recorded on a THERMO Finnigan LCQ Advantage max ion trap mass spectrometer. The thermogravimetric analyses (900-40 ºC) were done on a Perkin-Elmer TGA-DTA instrument (model: Pyris Diamond) under nitrogen at a heating rate of 10 ºC min^{-1}. A cyclic voltammetry study was carried out in acetonitrile solution with a CH Instrument (model 600C) using platinum as working electrode and Ag/AgCl as reference electrode with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at a scan rate of 50 mV/s.

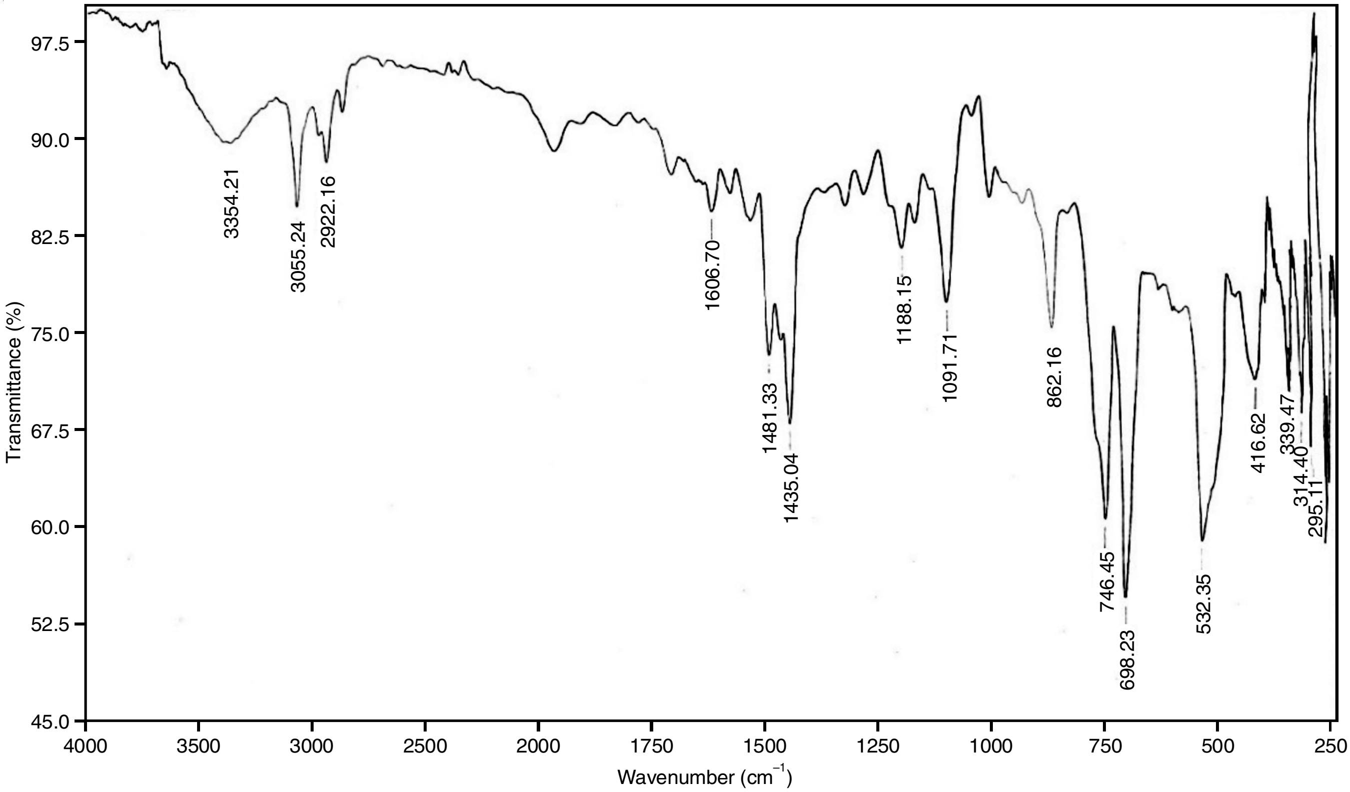


Fig. 1. FTIR spectrum of complex **1**

RESULTS AND DISCUSSION

The reaction of starting compound $RuCl_2(PPh_3)_3$ with equimolar amount of ligand 2-[2-(diphenylphosphino)ethyl]-pyridine (PPh_2Etpy) in dichloromethane solution under refluxing condition led to the formation of green solid P,N-chelated complex $[RuCl_2\{\eta^2\text{-(P,N)}PPh_2Etpy\}(PPh_3)_2]$ (**1**) with 84% yield.

The conductivity data indicate that complex **1** is a neutral molecule [49]. The FTIR spectrum of complex **1** shows the ν_{py}(C=N) at 1607 cm^{-1} with a shift of 17 cm^{-1} as compared to the free ligand (1589 cm^{-1}) indicating coordination of PPh_2Etpy through pyridyl N-atom [50,51]. The presence of a medium-strong absorption band at 328 cm^{-1} for ν(Ru-Cl) confirms the presence of *trans*-$RuCl_2$ unit in complex **1** [52,53]. Complex **1** also exhibits a new band at 538 cm^{-1}, which is the characteristic region of M-P stretching [54]. In the far-IR region of the spectrum, a weak band at ~ 417 cm^{-1} is observed, may be assigned to ν(Ru-N) stretching. It also supported the presence of N-coordinated ligand (Fig. 1).

The UV-vis spectrum of complex **1** in CH_2Cl_2 shows two intense bands at 223 and 351 nm, presumably due to intraligand π→π* and n→π* transitions, respectively (Fig. 2). Compared to the free ligand (230 nm) and starting metal precursor (416 nm) these bands are blue shifted [5]. The ESI(+) mass spectrum of complex **1** shows molecular ion peak at *m/z* 1005 $[M+NH_4]^+$. The fragmented ions with peaks at *m/z* 968, 934, 742, 720 and 464 are assignable to $[M+NH_4\text{-}Cl^{35}]^+$, $[M+NH_4\text{-}2Cl^{35}]^+$, $[M+NH_4\text{-}PPh_3]^+$, $[M+Na\text{-}PPh_2Etpy]^+$ and $[M+1\text{-}PPh_2Etpy]^+$, respectively, indicating mononuclear nature of the complex (Fig. 3).

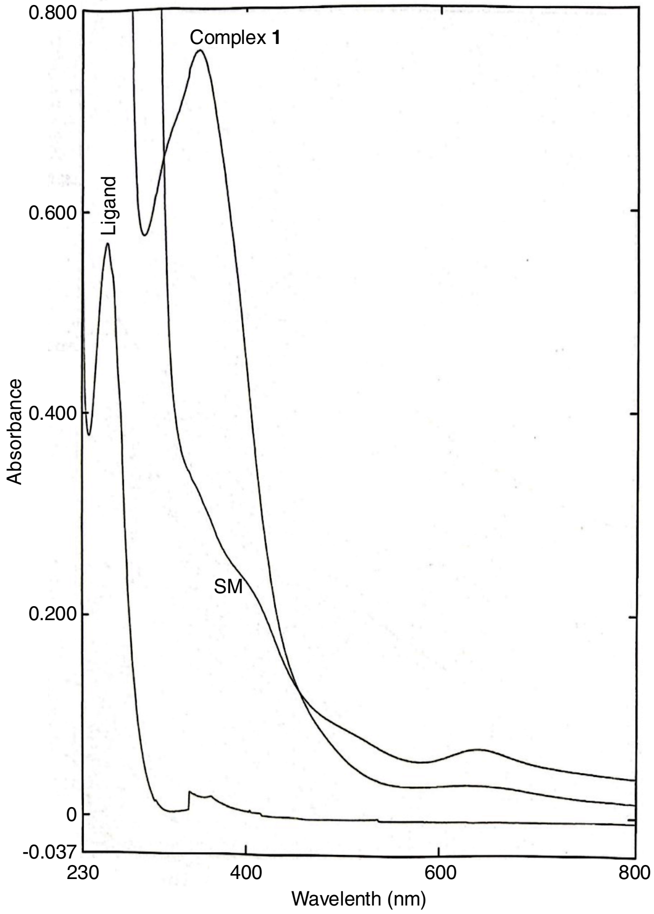


Fig. 2. UV-vis spectrum of complex **1**

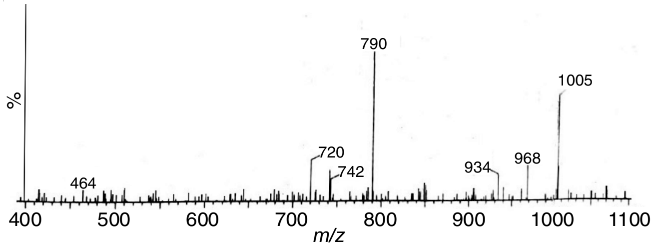
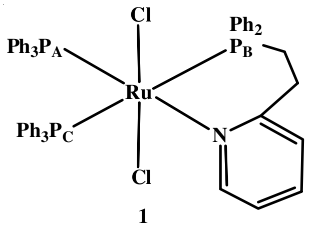


Fig. 3. ESI(+) mass spectrum of complex **1**

The ^{31}P{^{1}H} NMR spectrum of complex **1** in $CDCl_3$ solution at 299 K shows a triplet at $\delta = 51.21$ ppm, ($J_{P-P} = 34.88$ Hz) could be assigned to the resonance of P_A (**Scheme-II**). The large downfield shift suggests that the P_A atom in complex **1** is *trans* to the N atom of the chelated PPh_2Etpy. The corresponding coupling constant value is indicative of *cis*-coordination of the three phosphorus atoms. Another two doublets at $\delta = 48.81$ ppm, ($J_{P-P} = 34.88$ Hz) and $\delta = 39.17$ ppm, ($J_{P-P} = 34.88$ Hz) are associated with the resonance of P_B and P_C atoms respectively, which indicated that both phosphorus atoms are present in *trans* to each other. The ^{31}P{^{1}H} NMR spectrum of complex is consistent with the ABC spin system [52] (A = C = ^{31}P of PPh_3 and B = ^{31}P of PPh_2Etpy) of complex (Fig. 4).



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Scheme-II: Labeling of phosphorus atoms of $[RuCl_2\{\eta^2\text{-(P,N)}PPh_2Etpy\}(PPh_3)_2]$ (**1**)

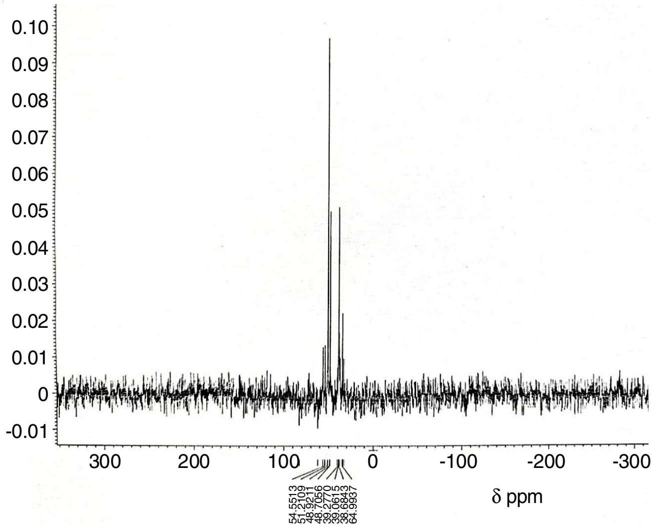


Fig. 4. ^{31P}\{^{1}H\} NMR spectrum of complex **1**

Moreover, the significant downfield shift of phosphorus (P_B) resonance of PPh_2Etpy compared to free ligand ($\delta = -14.9$ ppm) [55] clearly indicates the formation of six-membered ring by P,N-chelation of the ligand to the Ru^{2+} ion [56]. In the ^{1}H NMR spectrum, the resonances associated with pyridine ring and methylene protons show considerable downfield shift. This is consistent with η^2-coordination mode of the P,N-ligand. The multiplet in the range δ 6.42-7.80 ppm is clearly assigned to forty aromatic protons. The complex shows the signal for py-H^6 as a doublet with a significant downfield shift at δ 9.02 ppm with $J_{H-H} = 5.52$ Hz, indicating the coordination of PPh_2-Etpy through pyridyl nitrogen. In addition to this, two multiplets at δ 2.18 ppm and δ 3.40 ppm are attributed to the methylene protons of PPh_2-CH_2 and py-CH_2, respectively. The resonances for the protons py-H^3, py-H^4 and py-H^5 are observed as multiplet in the range δ 7.26-7.98 ppm (Fig. 5).

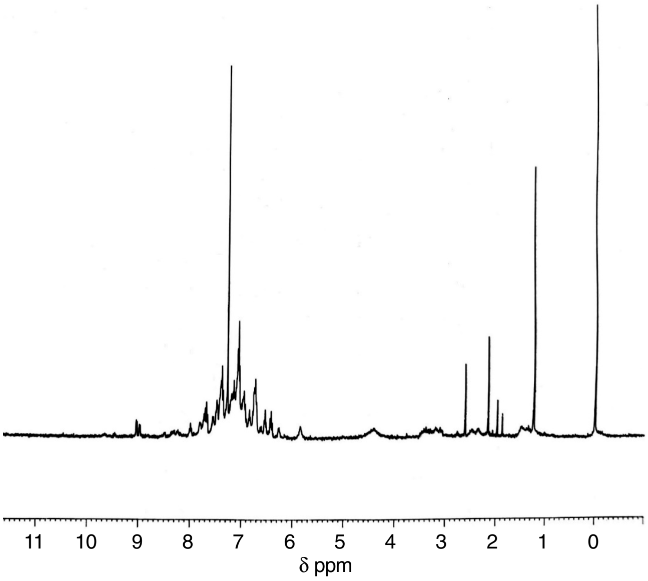


Fig. 5. ^{1}H NMR spectrum of complex **1**

Thermal studies: The TGA analysis of complex **1** displays gradual weight loss of 2% (calc. 1.8%) in the temperature range 88.8-133.5 °C, which corresponds to the removal of surface water. This is followed by a major weight loss of 56.1% (calc. 56.0%) in the temperature range 180.3-513.9 °C, assigned to the loss of PPh_2Etpy and PPh_3 ligands. After that, the weight loss occurs gradually up to 1119 °C. The cyclic voltammetry study of complex **1** in acetonitrile exhibits an oxidative response at -0.11 V and 0.58 V with no peak reversal, may be assigned to ligand-based redox process by comparing with the CV of free ligand PPh_2Etpy. This is followed by a quasi-reversible electron-transfer wave at 1.12 V ($\Delta E_p = 72$ mV, $i_{pa} = i_{pc}$), could be attributed to Ru(II)/Ru(III) couple [55]. The reduction peaks at 0.06 V and -0.91 V with no peak reversal may be assigned to ligand-based origin (Fig. 6).

Catalytic studies: Compared to the activity of precursor complex $[RuCl_2(PPh_3)_3]$, complex **1** has more catalytic activity for the oxidation of alcohols, 1-phenylethanol, benzyl alcohol and its derivatives to the corresponding aldehydes and ketones. In this oxidation system, the catalyst did not effectively oxidize aliphatic alcohols. All the oxidations produced the desired products without additional oxidation. Furthermore, utilizing NaOCl as an oxidant with these catalysts resulted in a greater conversion %, but the aerial oxidation procedure did not extract any oxidized product (Table-1).

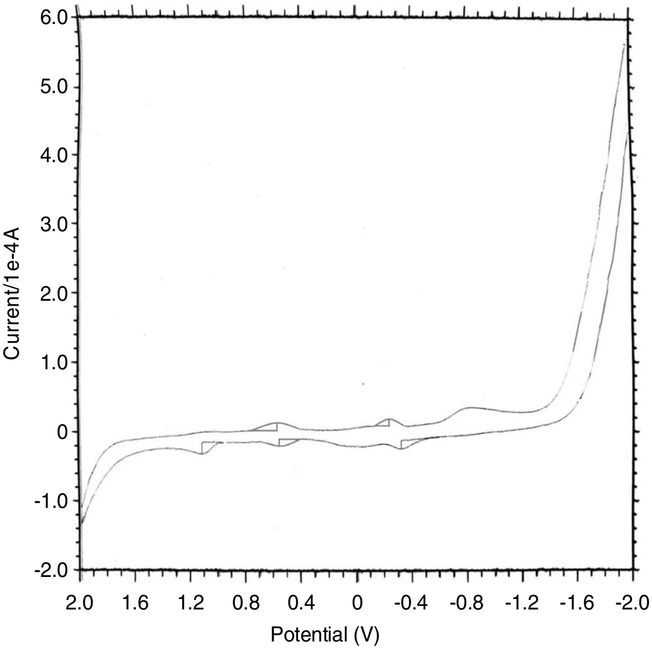
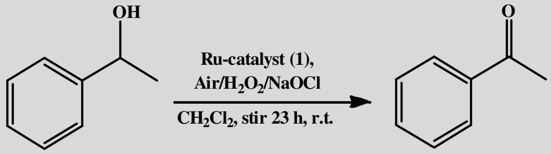


Fig. 6. Cyclic voltammogram of complex **1** in acetonitrile solution

TABLE-1
CATALYTIC OXIDATION OF 1-PHENYLETHANOL WITH VARYING AMOUNTS OF CATALYST
[RuCl$_2${η^2-(P,N)PPh$_2$Etpy}(PPh$_3$)$_2$] (**1**)

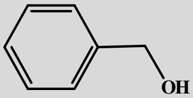
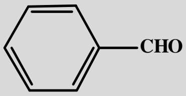
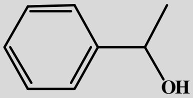
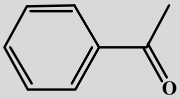
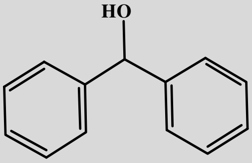
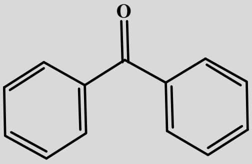
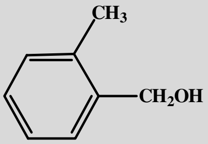
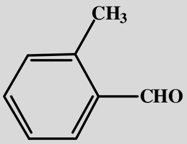
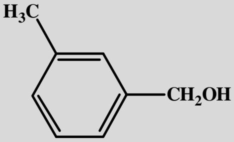
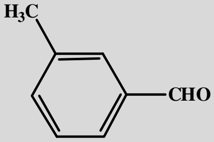
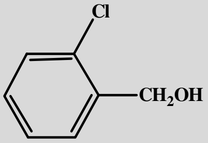
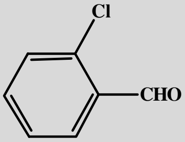


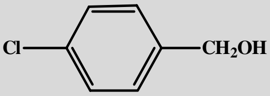
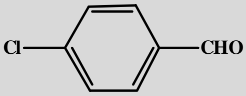
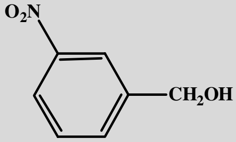
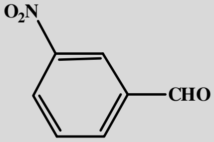
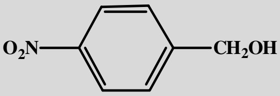
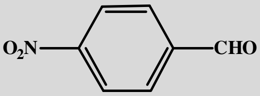
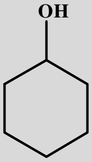
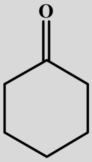
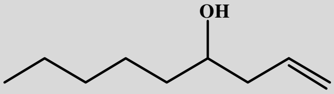
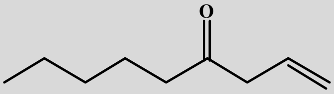
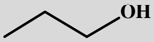
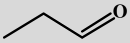
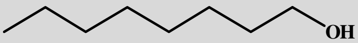
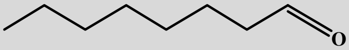
Entry	Oxidant	S:C	Catalytic (non-catalytic); Yield (%)[a]
1	Air	1,000:1	Nil (Nil)
2		10,000:1	Nil
3		80,000:1	Nil
4	H_2O_2	1,000:1	78(15)
5		10,000:1	73
6		50,000:1	70
7		80,000:1	56
8	NaOCl	1,000:1	89(19)
9		10,000:1	78, 22[b]
10		50,000:1	75
11		80,000:1	73

[a]All yields refer to isolated yield; [b]Yield (%) obtained using precursor complex, [RuCl$_2$(PPh$_3$)$_3$] as catalyst.

Complex **1** catalyzes a variety of benzylic alcohols to practically quantitative yields (Table-2, entries 1-10) and its catalytic efficiency increases significantly in comparison to the starting compound [RuCl$_2$(PPh$_3$)$_3$] due to the incorporation of hemilabile P,N-donor ligand into the metal center. None of the studied alcohols produced any over-oxidized compounds. The catalyst was found to be ineffective for oxidation of both short and long chain aliphatic alcohols (entry 11, 12 and 13). The position of the substituent and its electronic nature had minimal impact on the oxidation reaction. More the desired products were obtained by the electron-donating substituent (entries 4-7) than by the electron-withdrawing one (entries 8 and 9).

TABLE-2
CATALYTIC OXIDATION OF ALCOHOLS USING NaOCl BY THE CATALYST **1**

Entry	Substrate	Product	Catal. (non-catal) yield (%)[a]
1			79(30), 35[b]
2			77(16), 27[b]
3			78(21), 23 [b]
4			84(20), 30[b]
5			83(20), 30[b]
6			89(30)

7			88(30)
8			72(20), 24^b
9			74(19), 27^b
10			69(13)
11			33(10)
12			30
13			20

Reaction condition: Alcohol 30 mmol, NaOCl 90 mmol, catalyst 0.003 mmol, CH_2Cl_2 5 mL, stirring for 23 h at r.t. The products were identified by FTIR and ^{1}H NMR. ^{a}All yields refer to isolated yields. ^{b}Yield (%) obtained using precursor complex, [$RuCl_2(PPh_3)_3$] as catalyst.

Conclusion

A new ruthenium(II) complex [$RuCl_2\{\eta^2$-(P,N)PPh_2Etpy}-$(PPh_3)_2$] (**1**) was synthesized with 2-[2-(diphenylphosphino)-ethyl]pyridine ligand and characterized by FT-IR, ^{1}H and ^{31}P{^{1}H}-NMR and mass spectroscopy. The complex was found to be mononuclear, neutral, low-spin and diamagnetic. The multi-functionalized 2-[2-(diphenylphosphino)ethyl]pyridine ligand form a chelate ring with the metal center. The efficiency of the new complex **1** was evaluated as catalyst for oxidation of alcohols to carbonyl groups with NaOCl/H_2O_2 as oxidant at room temperature and found to exhibit higher catalytic activity in comparison to the activity of [$RuCl_2(PPh_3)_3$]. In addition to this, the catalyst was efficient for the oxidation of aromatic alcohols in this oxidation system.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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