



## Green conversion of alcohols to carbonyls catalyzed by novel ruthenium-Schiff base-triphenylphosphine complexes

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### ABSTRACT

A series of new Ru<sup>II</sup>-Schiff base complexes of containing Ph<sub>3</sub>P has been prepared and characterized. The complexes have been used as catalysts for the oxidation of alcohols in [EMIM]Cl ionic liquid–NaOCl system. Higher catalytic activity was found for **RuL1**. A plausible mechanism has been proposed.

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Ru-based oxidation catalysis is a powerful and extremely versatile synthetic tool to afford selectively oxygenated products both in homogeneous and in heterogeneous conversions [1,2]. The ability of ruthenium to assume a wide range of oxidation states and coordination geometries provides unique opportunities for catalysis. The oxidation of alcohols by ruthenium complexes along with primary oxidants like iodobenzene [3], alkyl hydroperoxides [4], NMO [5] and molecular oxygen [6] is well established. Issues such as product separation from the catalyst and catalyst recovery remain problematic. One of the alternative approaches for tackling these problems is the use of ambient temperature ionic liquids (ILs) as solvents. This is because of their solvating ability, negligible vapor pressure, easy recyclability and reusability. Over the last several years, many transition metals such as nickel [7], cobalt [8], ruthenium [9], manganese [10], tungsten [11], rhenium [12], iron [13] and vanadium [14] have been used as catalysts for alcohol oxidation with ILs as green solvents [15]. The present work reports the synthesis of a series of ruthenium triphenylphosphine complexes (**RuL1–RuL5**) containing N-(2-pyridyl)-N'-(5-Sub-salicylidene) hydrazine (Scheme 1) and their application as catalysts for the oxidation of alcohols to carbonyl compounds in ethyl-methyl imidazolium chloride [EMIM] ionic liquid media with NaOCl as co-oxidant.

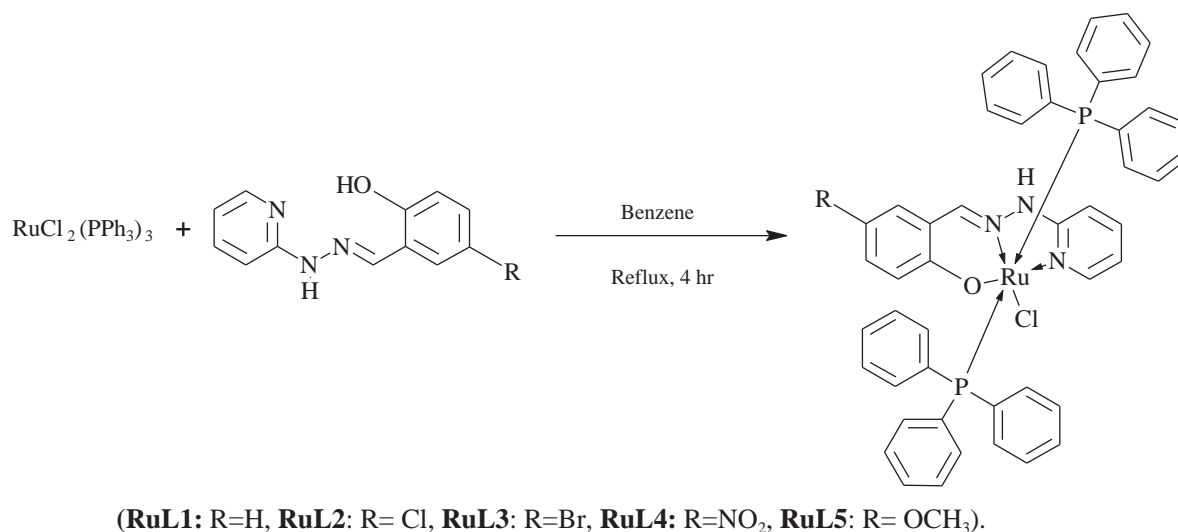
[RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] was prepared by refluxing RuCl<sub>3</sub>·3H<sub>2</sub>O and triphenylphosphine in methanol for 4 h [16–18]. The Schiff bases were prepared in 70–80% yield by condensation reactions of 2-hydrazinopyridine with the corresponding 5-substituted salicylaldehyde in methanol [19]. Complexes

**RuL1–RuL5** were prepared by refluxing a benzene solution of [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>] and ligand in a 1:1 molar ratio for 3 h [20].

All the complexes were greenish-black in colour and found to be air stable at room temperature, and non-hygroscopic in nature. The synthesized ruthenium (II) complexes are highly soluble in common organic solvents.

The IR spectra of all the ligands exhibit significant bands around 1561–1579 and 1268–1278 cm<sup>-1</sup> which are tentatively assigned to  $\nu_{\text{CH}=\text{N}}$  and phenolic  $\nu_{\text{C}-\text{O}}$  stretching, respectively. On complexation  $\nu_{\text{CH}=\text{N}}$  appears at 1590–1610 cm<sup>-1</sup> and the red shift corroborates the N (azomethine) coordination. In the spectra of complexes the coordination through phenolic oxygen is confirmed by the increase in C–O at higher frequencies in the region 1275–1296 cm<sup>-1</sup>. The positive shift is further supported by the disappearance of the  $\nu_{\text{OH}}$  band in the range 3430–3454 cm<sup>-1</sup> in all the complexes. Further, these complexes show a strong band near 1440, 1100, and 690 cm<sup>-1</sup> indicating the presence of coordinated PPh<sub>3</sub> ligands. Besides, all the complexes show strong bands corresponding to  $\nu_{\text{M}-\text{N}}$  and  $\nu_{\text{M}-\text{O}}$  in the region 437–451 and 516–525 cm<sup>-1</sup>, respectively [21–23]. All the complexes show multiplets at  $\delta$  6.75–8.60 ppm due to the coordinated PPh<sub>3</sub> ligands. Among the expected aromatic proton signals for the coordinated ligand, most have been clearly observed while a few could not be detected due to their overlap with their PPh<sub>3</sub> signals. Additional methoxy signals are observed as singlet for complex **RuL5** at  $\delta$  2.24 ppm. A sharp singlet appeared for OH proton of all ligands in the region  $\delta$  13.0 ppm is absent in all the complexes. A peak observed at 8.5 ppm in the complexes has been assigned to azomethine proton (–CH=N–). <sup>31</sup>P NMR spectra exhibit a singlet at 33.5–34.6 ppm suggesting that triphenylphosphine groups must be *trans* to each other [24,25]. Electronic spectra of the complexes have been recorded in dichloromethane solution. All the ruthenium complexes show four intense absorptions in the visible and ultraviolet region 450–280 nm.

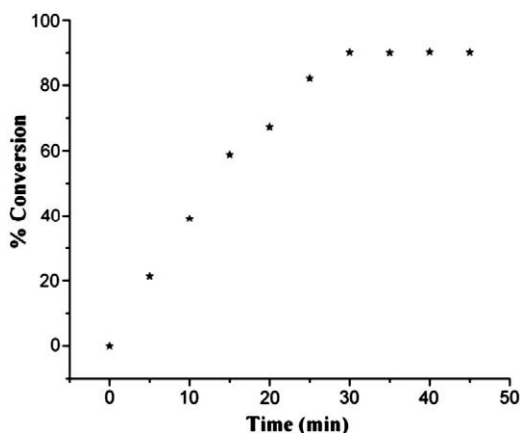
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**Scheme 1.** Synthesis of ruthenium (II) complexes.

The intense absorption in the visible region at 437–442 nm is probably due to metal-to-ligand charge transfer transitions [26]. In addition, the other high intensity bands in the 300–305 nm regions were characterized by ligand-centered transitions taking place in the three coordinated ligand. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around ruthenium (II) ion, similar to that of other ruthenium complexes [27].

Benzylalcohol was selected as a model substrate for optimization of the reaction conditions [28,29]. In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig 1). It was found that the total reaction time required was 30 min in EMIM-NaOCl. The oxidation occurred only in poor yield by simply bubbling molecular oxygen through reaction mixture under similar reaction conditions (Table 1, entry 2). To evaluate the catalytic effect of **RuL1**, the oxidation of benzylalcohol was carried out under similar reaction conditions in the absence of catalyst and no conversion was observed (Table 1, entry 3). The reaction was complete at 30 min at room temperature (Table 1, entry 1). Further, when the oxidation of benzylalcohol was carried out using less amount of **RuL1**, the yield was low (Table 1, entry 5). Also the reaction was carried out using low



**Fig 1.** Effect of time with conversion. (1 mmol alcohol, 1 mmol NaOCl, 0.01 mmol **RuL1**, 0.1 mL EMIM, RT).

amount of oxidant under same conditions and was observed that the yield was low (Table 1, entry 6).

The oxidation of other benzylic and allylic alcohols was then examined using the optimized reaction conditions. All the synthesized complexes were found to catalyze the oxidation of alcohols to corresponding carbonyl compounds. **RuL1** showed better results than all the other complexes. This may be due to the fact that the catalytic activity of complexes varies with the size of substituent. It was observed that the activity decreases with increase of bulkiness of the substituents. This may be due to steric hindrance caused by the substituent, which can affect the planarity of the ligand in the complexes [7]. The results for the oxidation of a variety of alcohols are summarized in Table 2. Further oxidation to acids was ruled out. The GC results showed no extra peak confirming the absence of carboxylic acid formation. In spite of IL being non-volatile and non-flammable, its improper disposal would still lead to new pollution of environment (because of minimal degradation in the environment). At the same time ILs are also expensive reagents. Thus, attention needs to be paid to recycling and re-use of ILs.

Fig. 2 shows the efficiency of the reaction in [EMIM]Cl till 7 runs with benzylalcohol as substrate. It is clear from the figure that recycling of ionic liquid slightly affects the conversion of the product.

Results of the present investigation suggest that the complexes are able to react efficiently with NaOCl to yield high valent ruthenium-

**Table 1**  
Oxidation of benzylalcohol to benzaldehyde<sup>a</sup> in EMIM-NaOCl system.

Entry	Reaction time (min)	% conversion
1	30	92.1
2 <sup>b</sup>	360	<15
3 <sup>c</sup>	360	NR <sup>d</sup>
4 <sup>e</sup>	30	59.0
5 <sup>f</sup>	30	56.3

<sup>a</sup> Unless otherwise indicated, all reactions were carried out with 1 mmol of benzylalcohol with 0.01 mmol of **RuL1** catalyst, 1 mmol of NaOCl.

<sup>b</sup> The reaction was carried out under oxygen instead of NaOCl.

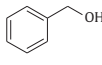
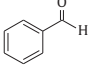
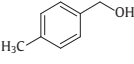
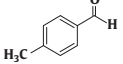
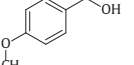
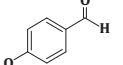
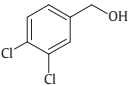
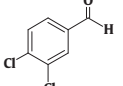
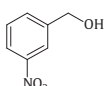
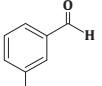
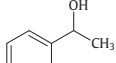
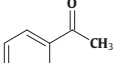
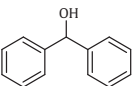
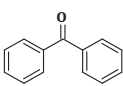
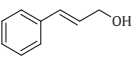
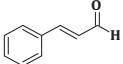


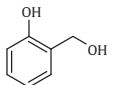
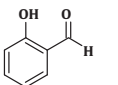
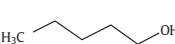
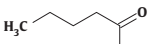
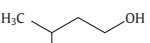
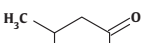

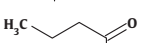



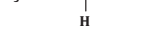
<sup>c</sup> Reaction without catalyst.

<sup>d</sup> NR: No reaction.

<sup>e</sup> 0.005 mmol of catalyst.

<sup>f</sup> 0.5 mmol of NaOCl.

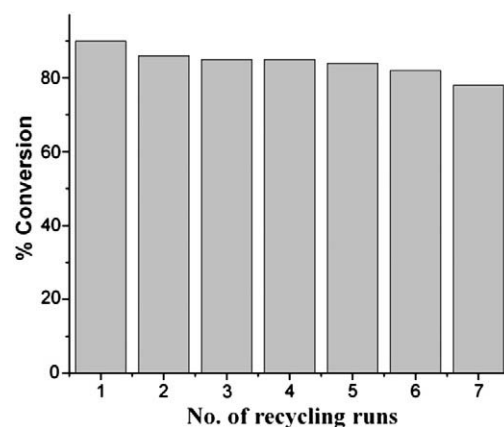
**Table 2**  
Oxidation of alcohols catalyzed by **RuL1**<sup>a</sup> in EMIM-NaOCl system.

Alcohols	Product	% conversion of carbonyl compound <sup>b</sup>				
		<b>RuL1</b>	<b>RuL2</b>	<b>RuL3</b>	<b>RuL4</b>	<b>RuL5</b>
		90	89	87	87	83
		88	88	85	85	82
		89	88	87	87	82
		86	85	84	84	81
		86	86	85	85	83
		95	92	91	88	81
		90	89	88	87	80
		86	85	84	84	80
		81	90	88	87	80
		84	84	83	80	81
		78	77	77	72	70
		79	78	78	74	72
		78	78	78	75	70
		70	70	69	69	68
		72	72	71	71	68

<sup>a</sup> 1 mmol alcohol, 1 mmol NaOCl, 0.01 mmol **RuL1**, 0.1 mL EMIM, RT.

<sup>b</sup> GC yield.

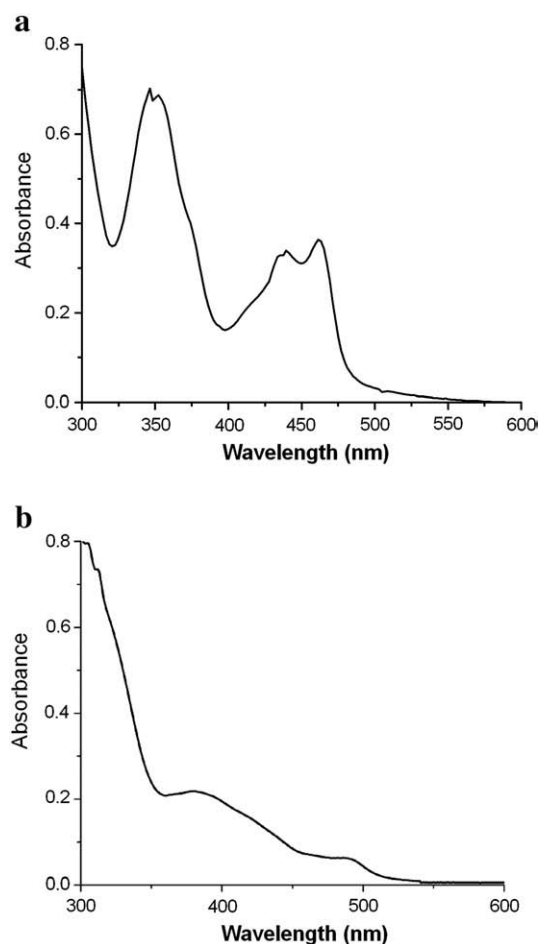
oxo species responsible for dehydrogenation of alcohols. This was further supported by spectral changes that occur by addition of NaOCl to an ionic liquid solution of the ruthenium (II) complexes. The appearance of peak at 390 nm is attributed to the formation of oxoruthenium (IV) species (Fig. 3), which is in conformity with other oxo ruthenium (II) complexes [30–32]. Further support in favor of the formation of such species is identified by the IR spectrum of the solid



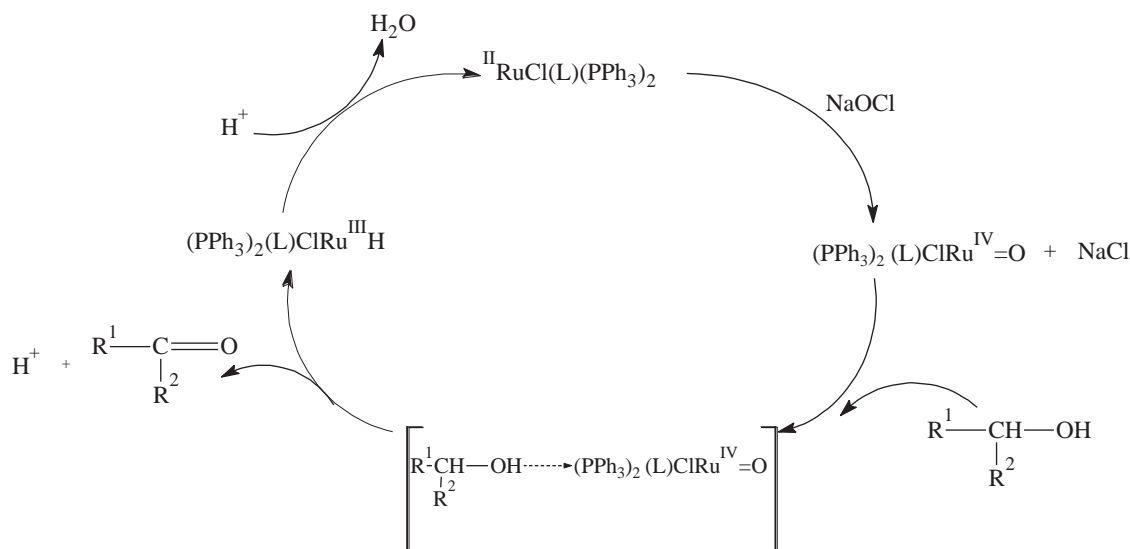
**Fig 2.** Effect of recycling on conversion of benzylalcohol.

mass (obtained by evaporation of the resultant solution to dryness), which shows a band at  $820\text{ cm}^{-1}$ , characteristic of oxoruthenium (IV) species [30,31]. The proposed mechanism with NaOCl as co-oxidant is shown in Scheme 2.

In conclusion, the ruthenium (II) complexes in ionic liquid provides a greener route for the catalytic oxidation of alcohols to carbonyls using NaOCl as a green oxidant. A smaller reaction time, higher catalytic activity of the complexes, reasonable time and recycling make this catalytic system a cheaper, easier and environmental friendly process.



**Fig 3.** UV-Vis spectra of (a) **RuL1** (b) **RuL1** + NaOCl (spectra taken after 30 min of mixing).



Scheme 2. Proposed mechanism for the oxidation of alcohols using Ru/NaOCl.

## References

- [1] I.W.C.E. Arends, T. Kodama, R.A. Sheldon, Topics in organometallic chemistry, Springer, Berlin, 2004.
- [2] M. Pagliaro, S. Campestrini, R. Ciriminna, Chem. Soc. Rev. 34 (2005) 837.
- [3] D.M. Ziegler, Ann. Rev. Biochem. 54 (1985) 305.
- [4] A.G. Lappins, A. McAuley, J. Chem. Soc. (1975) 1560, (A).
- [5] R. Ramesh, Inorg. Chem. Commun. 7 (2004) 274.
- [6] M. Hasan, M. Musawir, P.N. Davey, I.V. Kozhevnikov, J. Mol. Catal. A 180 (2002) 77.
- [7] D. Ramakrishna, B. Ramachandra Bhat, R. Karvembu, Catal. Commun. 11 (2010) 498.
- [8] D. Ramakrishna, B. Ramachandra Bhat, Inorg. Chem. Commun. 13 (2010) 195.
- [9] A. Wolfson, S. Wuyts, D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs, Tetrahedron Lett. 43 (2002) 8107.
- [10] J.W. Li, W. Sun, L.W. Xu, C.G. Xia, H.W. Wang, Chin. Chem. Lett. 15 (2004) 1437.
- [11] B.S. Chhikara, S. Tehlan, A. Kumar, Synlett. (2005) 63.
- [12] G. Bianchini, M. Crucianelli, F. de Angelis, V. Neri, R. Saladino, Tetrahedron Lett. 46 (2005) 2427.
- [13] A. Kumar, N. Jain, S.M.S. Chauhan, Synlett. (2007) 411.
- [14] J. Nan, J.R. Arthur, Lett. 48 (2007) 273.
- [15] J. Muzart, Adv. Synth. Catal. 348 (2006) 275.
- [16] J. Chatt, G.J. Leigh, D.M.P. Mingos, R.J. Paske, J. Chem. Soc. (1968) 2636, (A).
- [17] R.K. Poddar, I.P. Khullar, U. Agarwala, Inorg. Nucl. Chem. Lett. 10 (1974) 221.
- [18] K. Natarajan, R.K. Poddar, U. Agarwala, J. Inorg. Nucl. Chem. 39 (1977) 431.
- [19] A. Sarkar, S. Pal, Polyhedron 25 (2006) 1689.
- [20] The ruthenium complex  $\text{RuCl}_2(\text{PPh}_3)_3$  [0.16 mmol; 0.150 g] and *N*-(2-pyridyl)-*N'*-(5-*R*-salicylidene) hydrazine ligands (where *R* = -H, -Cl, -Br, -NO<sub>2</sub>, -OMe) (0.16 mmol; 0.033–0.041 g) were taken in 20 ml benzene. The mixture was refluxed for 3 h and was monitored by TLC. The solvent was partially evaporated and light petroleum (600–800 C, 5 ml) was added to the reaction mixture to separate the solid.
 

**RuL1.** Calcd. Anal. For  $\text{C}_{48}\text{H}_{40}\text{ClN}_3\text{O}_2\text{P}_2\text{Ru}$ : C, 66.01; H, 4.62; N, 4.81; found: C, 65.87; H, 4.56; N, 4.79. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3244, 1564, 1444, 1296, 1096, 612, 520, 489, 451. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.55 (s, -CH=N-), 6.75–8.15 (m, Ar-H), 3.85 (s, -N-H). <sup>31</sup>P NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$ , ppm): 34.1. UV  $\lambda_{\text{max}}$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 442 (6126), 350 (12603), 301 (18250).

**RuL2.** Calcd. Anal. For  $\text{C}_{48}\text{H}_{39}\text{Cl}_2\text{N}_3\text{O}_2\text{P}_2\text{Ru}$ : C, 63.51; H, 4.33; N, 4.63; found: C, 63.47; H, 4.26; N, 4.57. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3225, 1579, 1440, 1289, 1097, 611, 516, 491, 441. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.50 (s, -CH=N-), 6.75–8.15 (m, Ar-H), 3.85 (s, -N-H). <sup>31</sup>P NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$ , ppm): 34.6. UV  $\lambda_{\text{max}}$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 439 (6084), 356 (12818), 305 (18493).

**RuL3.** Calcd. Anal. For  $\text{C}_{48}\text{H}_{39}\text{BrClN}_3\text{O}_2\text{P}_2\text{Ru}$ : C, 60.54; H, 4.13; N, 4.41; found: C, 60.49; H, 4.06; N, 4.37. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3235, 1565, 1437, 1285, 1096, 620, 521, 492, 437. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.55 (s, -CH=N-), 6.75–8.15 (m, Ar-H), 3.85 (s, -N-H).

<sup>31</sup>P NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$ , ppm): 34.2. UV  $\lambda_{\text{max}}$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 437 (6056), 349 (12566), 302 (18310).

**RuL4.** Calcd. Anal. For  $\text{C}_{48}\text{H}_{39}\text{ClN}_4\text{O}_3\text{P}_2\text{Ru}$ : C, 62.78; H, 4.28; N, 6.10; found: C, 62.49; H, 4.16; N, 5.98. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3245, 1568, 1439, 1275, 1099, 615, 525, 499, 446. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.45 (s, -CH=N-), 6.75–8.15 (m, Ar-H), 3.85 (s, -N-H). <sup>31</sup>P NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$ , ppm): 33.8. UV  $\lambda_{\text{max}}$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 440 (6098), 345 (12422), 308 (18674).

**RuL5.** Calcd. Anal. For  $\text{C}_{48}\text{H}_{42}\text{ClN}_3\text{O}_2\text{P}_2\text{Ru}$ : C, 65.15; H, 4.69; N, 4.65; found: C, 65.01; H, 4.56; N, 4.58. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3238, 1561, 1449, 1281, 1102, 610, 520, 495, 449. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.50 (s, -CH=N-), 6.75–8.15 (m, Ar-H), 3.85 (s, -N-H), 2.1 (s, -OCH<sub>3</sub>). <sup>31</sup>P NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$ , ppm): 33.5. UV  $\lambda_{\text{max}}$  (nm) ( $\epsilon$  ( $\text{M}^{-1}\text{cm}^{-1}$ )): 437 (6056), 353 (12710), 303 (18370).
- [21] P. Byabartta, P.K. Santra, T.K. Misra, C. Sinha, C.H.L. Kennard, Polyhedron 20 (2001) 905.
- [22] S. Goswami, R. Mukherjee, A. Chakravorty, Inorg. Chem. 22 (1983) 2825.
- [23] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York, 1971.
- [24] N. Dharmaraj, P. Viswanathamurthi, K. Natarajan, Transit. Met. Chem. 26 (2001) 105.
- [25] V. Chinnusamy, K. Natarajan, Synth. React. Inorg. Met. Org. Chem. 23 (1993) 889.
- [26] A. Ceulemans, L.G. Vanquickenborne, J. Am. Chem. Soc. 103 (1981) 2238.
- [27] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed. Elsevier, New York, 1984.
- [28] A solution of ruthenium complex (0.01 mmol) in 0.1 mL EMIM ionic liquid was added to the solution of substrate (1 mmol) and NaOCl (1 mmol- 0.1 mL of 15% Solution). The mixture was stirred at room temperature. At the requisite times aliquots of the reaction mixture were removed and the alcohol and aldehyde / ketone extracted with ether. The ether solution was then analyzed by gas chromatography using an internal standard method. The aqueous layer, the ionic liquid with the catalyst dispersed within was then separated and tested for its reusability.
- [29] The reaction product analysis was carried out using gas chromatography (GC) (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane Restek capillary column (30 m length and 0.25 mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 60<sup>o</sup> C to 150<sup>o</sup> C at the rate of 10<sup>o</sup> C/min and then to 220<sup>o</sup> C at the rate of 40<sup>o</sup> C/min Nitrogen gas was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 150<sup>o</sup> C and 250<sup>o</sup> C respectively during product analysis. The retention times for different compounds were determined by injecting commercially available compounds under identical gas chromatography conditions. The oxidation products are commercially available, and were identified by GC co-injection with authentic samples.
- [30] M.M.T. Khan, Ch. Sreelatha, S.A. Mizra, G. Ramachandraiah, S.H.R. Abdi, Inorg. Chim. Acta 154 (1988) 103.
- [31] W.H. Leung, C.M. Che, Inorg. Chem. 28 (1989) 4619.
- [32] A.S. Goldstein, R.S. Drago, J. Chem. Soc. Chem. Commun. (1991) 21.