



## Cobalt complexes in [EMIM]Cl – A catalyst for oxidation of alcohols to carbonyls

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### ABSTRACT

A coordination complex system consisting of Cobalt (II)-Schiff bases with triphenylphosphine were synthesized and characterized. These catalysts were effective in the oxidation of primary and secondary alcohols. The oxidation reactions were carried out in ethyl-methyl-imidazolium ionic liquid in presence of NaOCl. Higher catalytic activity was observed for **CoL1**.

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The selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones plays a central role in the synthetic organic chemistry. This represents an important entry to essential functional groups, such as ketones, aldehydes, and carboxylic acids [1]. Use of some homogeneous metal complexes of Ru [2–7], Pd [8,9], Co [10,11], Os [12] and Cu [13,14] has achieved high catalytic activity and selectivity. Hence a wide variety of methods have been developed [15]. Stoichiometric reactions include Swern oxidation [16], Dess–Martin oxidation [17] and various metal oxidants [18], whereas catalytic reactions involve transition metal complexes in combination with oxidants, used as sacrificial reagents (N-oxides, S-oxides, NaIO<sub>4</sub>, NaOCl, etc.) [19–22]. Thus, it is not surprising that transition metal complexes have attracted a considerable interest in recent years. It is well-known that the wide spread use of traditional organic solvents in many chemical processes is an issue of great environmental concern. Hence, the use of ionic liquids as reaction medium is a topic of much current interest in the context of environmentally friendly chemical reactions [23].

Cobalt species have been extensively studied as catalysts for a wide range of oxidation reactions [24,25]. Cobalt-catalyzed oxidation of alcohols has been studied by different groups. Sharma et al. studied oxidation of secondary alcohols in acetonitrile catalyzed by Cobalt (II)-Schiff base [26] and cobalt (II) acetylacetonate [27] with O<sub>2</sub> and N-bromosuccinimide as oxidants, respectively. Das and Punniyamurthy used cobalt (II) complex to catalyze oxidation of alcohols into carboxylic acids and ketones in acetonitrile with H<sub>2</sub>O<sub>2</sub> as oxidant [28]. N-bromosuccinimide, t-Butyl hydroperoxide and H<sub>2</sub>O<sub>2</sub> have also been used as oxidants in many cases for cobalt

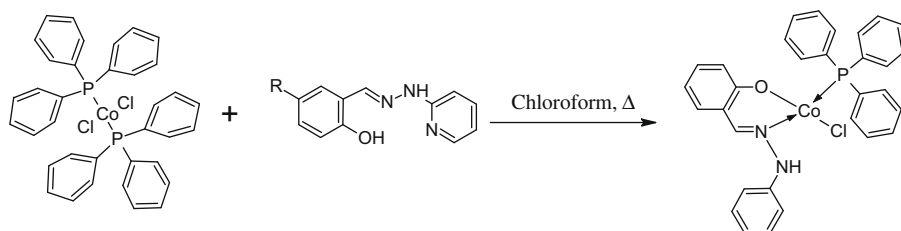
catalyzed systems. However, the long reaction time reported in the above systems makes it unfriendly for the industries. The green solvent system for the catalytic oxidation of alcoholic to carbonyl using the metal complexes has not been studied extensively.

We are reporting our attempts to synthesize a series of Cobalt triphenylphosphine complexes (**CoL1–CoL5**) containing N-(2-pyridyl)-N'-(salicylidene) hydrazine with its derivatives (Scheme 1) and their application as catalysts for the oxidation of alcohols to carbonyl compounds in ionic liquid.

The starting complex [CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] was prepared by the reaction between CoCl<sub>2</sub>·6H<sub>2</sub>O and triphenylphosphine in glacial acetic acid [29]. The Schiff bases were prepared in 70–80% yield by condensation reactions of 2-hydrazinopyridine with the corresponding 5-substituted salicylaldehyde in methanol [30]. Complexes **CoL1–CoL5** were prepared by refluxing a dichloromethane solution of [CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and ligand in a 1:1 molar ratio for 3 h [31]. All the complexes are dark green. They were found to be soluble in CH<sub>3</sub>OH, CH<sub>3</sub>CN, C<sub>6</sub>H<sub>6</sub>, DMSO and DMF. The analytical data for these complexes are in good agreement with the above molecular formula. The process is on to get single crystals suitable for X-ray diffraction.

The electronic spectra of the complexes showed many bands in the region 250–490 nm. The bands appeared in the region 250–350 nm have been assigned to intraligand transitions. A less intense band in range 390–490 nm corresponds to forbidden d → d transition. The IR spectra of the ligands exhibit a strong band around 1610–1620 cm<sup>-1</sup>, which is assigned to ν(C=N) vibration. As a result of coordination, this band is altered in complexes. The band in the region 1315–1330 cm<sup>-1</sup> which is assigned to phenolic ν(C–O) in the free ligand, is shifted to higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion. The N–H stretching frequency occurs around 3100 cm<sup>-1</sup> in

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Scheme 1. Synthesis of cobalt (II) complexes.

ligands is unaltered in complexes. The pyridine vibrations around  $610\text{ cm}^{-1}$  (in-plane ring deformation) and  $490\text{ cm}^{-1}$  (out of plane ring deformation) were also unchanged in complexes. These factors reveal the non participation of  $\text{-NH}$  group and pyridine-N in coordination. The bands around  $550\text{ cm}^{-1}$  and  $470\text{ cm}^{-1}$  in the complex is assigned to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$ , respectively. Bands due to triphenylphosphine are also appeared in the expected region [32].  $^1\text{H}$  NMR spectra of the complexes exhibit a multiplet around 6.9–7.9 ppm which has been assigned to the protons of phenyl groups present in Schiff base ligand and triphenylphosphine. A peak observed at 8.5 ppm in the complexes has been assigned to azomethine proton ( $\text{-CH=N-}$ ). The absence of a resonance at 10.3 ppm due to phenolic hydrogen indicates the deprotonation of the Schiff base [33]. In the  $^{13}\text{C}$  NMR spectra of all the complexes, azomethine carbon resonances are observed in the 151.12–154.49 ppm range. The resonances for C–N, C–O and C–P are observed in the regions 149.32–149.99, 162.44–164.93 and 142.96–144.48 ppm, respectively. The  $^{13}\text{C}$  NMR spectra of complexes revealed the presence of six different carbons (119.30, 129.46, 143.85, 143.98, 149.82 and 163.98 ppm). This indicates that the three quaternary carbons arising from triphenylphosphine aromatic units are in different magnetic environments.  $^{31}\text{P}$  NMR spectra exhibits a singlet at 22.3–22.8 ppm suggesting the presence of one coordinated triphenylphosphine in the complexes. In order to obtain further structural information, the magnetic moments of the complexes were measured. All cobalt (II) complexes show magnetic moments in the 2.33–2.49 B.M. range indicating that these complexes have a low spin square planar geometry [34].

The optimization of the reaction conditions was studied by taking benzyl alcohol as substrate with CoL1 in EMIM–NaOCl system (Table 1). The benzaldehyde formed was quantified by GC [35]. 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 observed that the total reaction time was only 15 min even at room temperature. The experiments were conducted at regular intervals of time beyond 30 min. The results show that the conversion remains constant at about 90% after a

**Table 1**  
Optimization of reaction conditions for oxidizing benzyl alcohol to benzaldehyde.<sup>a</sup>

Entry	Amount of CoL1 (mmol)	Amount of NaOCl (mmol)	Conversion <sup>b</sup> (%)
1	0	1.0	1.2
2	0.01	1.0	60.2
3	0.02	1.0	89.2
4	0.03	1.0	89.3
5	0.04	1.0	89.8
6	0.05	1.0	89.7
7	0.02	0	27.6
8	0.02	0.5	68.6
9	0.02	1.0	89.2
10	0.02	1.5	89.6
11	0.02	2.0	89.4

<sup>a</sup> 1 mmol Benzyl alcohol, 0.2 mL EMIM, 15 min, room temperature.

<sup>b</sup> Average of 3 trials.

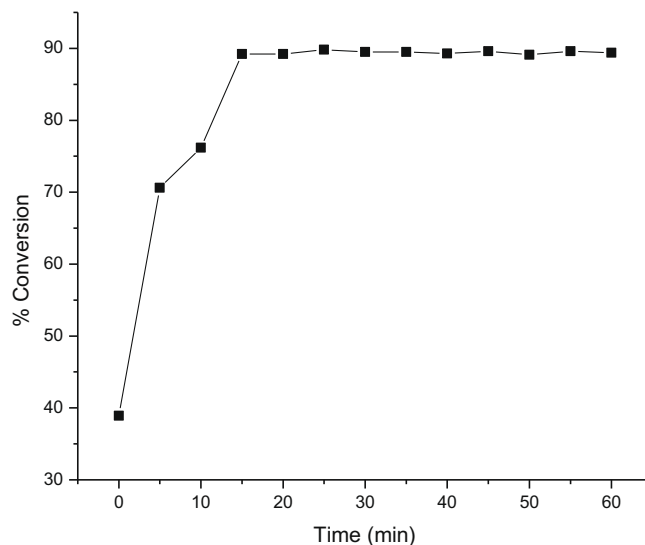
































Fig. 1. Effect of time on conversion of benzyl alcohol to benzaldehyde.

reaction time of 15 min. This implies that CoL1 in EMIM–NaOCl system showed good efficiency (Table 1, entries 3 and 9). The catalytic activities of CoL2–CoL5 in EMIM–NaOCl were carried out [36] (Table 2). The catalytic activity varies with the size of the substituent. It was observed that the activity decreased with increase in the bulkiness of the substituents. This may probably be due to steric hindrance caused by the substituent which can affect the planarity of the ligand in the complexes.

The effect of the concentration of catalyst with respect to substrate was carried out at different substrate to catalyst ratios. A 0.02 mmol of catalyst was sufficient for the effective transformation of benzyl alcohol to benzaldehyde (Table 1, entry 3). The reaction was also studied in the absence of catalyst. The yield was insignificant in this case (Table 1, entry 1). This observation reveals the catalytic role of cobalt (II) complexes. The reaction was studied at various substrate to oxidant ratios (Table 1). A minimum quantity of 1 mmol of the oxidant was sufficient for the effective oxidation of benzyl alcohol to benzaldehyde (Table 1, entry 9). All the alcohols were oxidized in good to excellent yields. All the synthesized cobalt (II) complexes were found to catalyze the oxidation of alcohols (both aliphatic and aromatic) to corresponding carbonyl compounds in 60–96% yield. Benzylic primary and secondary alcohols oxidize smoothly to give aldehydes and ketones respectively. All the experiments are carried out in air atmosphere since there is no change in conversion if reaction is carried out in inert atmosphere. From this it is clear that air is not a significant co-oxidant in the oxidation process and cobalt (II) complexes are air stable.

In conclusion, the series of experiments described represents a useful method for the oxidation of alcohols to carbonyl compounds at room temperature. The catalyst can be easily prepared and is

**Table 2**  
Oxidation of alcohols catalyzed by Co(II) complexes.<sup>a</sup>

Entry	Alcohols	Product	% Conversion of carbonyl compound <sup>b</sup>				
			CoL1 <sup>c</sup>	CoL2 <sup>c</sup>	CoL3 <sup>d</sup>	CoL4 <sup>e</sup>	CoL5 <sup>e</sup>
1			89.2	82.8	83.5	80.9	84.1
2			90.2	90.6	89.2	79.5	81.6
3			87.3	91.1	81.4	76.0	80.4
4			87.6	90.2	87.0	79.0	80.8
5			87.5	77.5	85.2	71.3	78.1
6			94.8	91.3	80.1	78.6	81.2
7			93.7	90.9	87.2	79.0	81.1
8			90.5	91.7	86.0	73.4	76.4
9			94.8	91.5	86.3	73.4	78.6
10			83.0	88.6	81.2	79.1	77.4
11			81.3	79.6	76.8	80.1	71.4
12			82.6	76.8	78.6	79.3	75.6
13			75.4	71.2	74.6	72.0	73.4
14			76.7	74.7	73.4	75.2	75.9
15			72.6	69.1	67.1	66.5	64.3

<sup>a</sup> 1 mmol Alcohol, 1 mmol NaOCl, 0.2 mmol Co(II) complex, 0.1 mL EMIM, stirring at room temperature.

<sup>b</sup> GC yield, average of 3 trials.

<sup>c</sup> Reaction time, 15 min.

<sup>d</sup> Reaction time, 20 min.

<sup>e</sup> Reaction time, 25 min.

therefore extremely cost effective. The rapid reaction times for the substrates means a large number of materials may be screened in parallel over a short time period. EMIM ionic liquid as a solvent will exhibit real advantages by providing a 'green' process with safer operation, easier separation, high catalytic activity and with no loss of solvent by oxidation.

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- [31] Procedure: To a solution of  $[\text{CoCl}_2(\text{PPh}_3)_2]$  (0.2 mmol) in Chloroform (20 mL) the corresponding Schiff base ligand (0.2 mmol) was added. The mixture was refluxed for 3 h. After the completion of reaction, the solvent was removed under vacuum. The residue was washed with diethyl ether and dried in vacuo to form dark green color complexes. **CoL1**: Yield: 69%. IR (KBr,  $\text{cm}^{-1}$ ): 3106, 1592, 1446, 1345, 1095, 697, 609, 550, 490, 470.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 6.6–7.3 (m, 15H, Ar–H), 7.4–7.7 (m, 8H, Ar–H),  $\delta$  8.5 (d, 1H, CH=N).  $^{13}\text{C}$  NMR (ppm): 163.98, 154.51, 143.98, 143.85, 134.84, 134.72, 133.98, 133.00, 130.59, 130.57, 129.00, 128.62, 128.60, 128.21, 128.11, 126.70, 121.88, 121.63, 119.30, 115.44, 114.84.  $^{31}\text{P}$  NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$  ppm): 22.4. CHN found (calc.) for  $\text{C}_{30}\text{H}_{25}\text{ClN}_3\text{OPCo}$ : C: 67.13(67.55), H: 4.65(4.72), N: 7.67(7.88); UV–Vis:  $\lambda_{\text{max}}$  (nm) intraligand interactions: 253, 322, 359, d  $\rightarrow$  d forbidden transition: 442.  $\mu_{\text{eff}}$ : 2.41. **CoL2**: Yield: 65%. IR (KBr,  $\text{cm}^{-1}$ ): 3104, 1597, 1435, 1330, 1101, 690, 610, 545, 493, 472.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 6.6–7.3 (m, 15H, Ar–H), 7.4–7.8 (m, 7H, Ar–H), 8.5 (d, 1H, –CH=N–);  $^{13}\text{C}$  NMR (ppm): 162.44, 154.25, 144.46, 144.32, 135.95, 134.86, 134.72, 132.73, 130.55, 130.42, 129.69, 128.63, 128.20, 128.07, 128.02, 126.52, 124.23, 121.83, 121.35, 118.84, 114.76, 20.23.  $^{31}\text{P}$  NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$  ppm): 22.3. CHN found (calc.) for  $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_3\text{OPCo}$ : C: 63.19(63.45), H: 4.14(4.26), N: 7.01(7.20); UV–Vis:  $\lambda_{\text{max}}$  intraligand interactions: 256, 325, 369, d  $\rightarrow$  d forbidden transition: 443.  $\mu_{\text{eff}}$ : 2.33. **CoL3**: Yield: 62%. IR (KBr,  $\text{cm}^{-1}$ ): 3109, 1585, 1439, 1340, 1093, 698, 615, 552, 495, 475.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 6.7–7.3 (m, 15H, Ar–H), 7.8–7.9 (m, 7H, Ar–H), 8.5 (d, 1H, –CH=N–);  $^{13}\text{C}$  NMR (ppm): 162.53, 153.46, 144.48, 144.33, 134.79, 134.66, 133.94, 131.84, 130.70, 130.67, 128.74, 128.66, 128.28, 128.14, 127.06, 123.07, 122.03, 119.90, 119.54, 114.95.  $^{31}\text{P}$  NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$  ppm): 22.5. CHN found (calc.) for  $\text{C}_{30}\text{H}_{24}\text{BrClN}_3\text{OPCo}$ : C: 57.97(58.34), H: 3.89(3.95), N: 6.25(6.86); UV–Vis:  $\lambda_{\text{max}}$  intraligand interactions: 253, 319, 369, d  $\rightarrow$  d forbidden transition: 449.  $\mu_{\text{eff}}$ : 2.44. **CoL4**: Yield: 72%. IR (KBr,  $\text{cm}^{-1}$ ): 1595, 1429, 1351, 1087, 695, 610, 549, 489, 479.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 6.6–7.4 (m, 15H, Ar–H), 7.4–7.8 (m, 7H, Ar–H), 8.6 (d, 1H, –CH=N–);  $^{13}\text{C}$  NMR (ppm): 162.83, 153.39, 144.42, 144.24, 136.46, 135.06, 134.79, 134.66, 130.72, 130.67, 128.73, 128.66, 128.29, 128.16, 127.09, 123.50, 122.05, 120.83, 114.97, 106.28.  $^{31}\text{P}$  NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$  ppm): 22.8. CHN found (calc.) for  $\text{C}_{30}\text{H}_{24}\text{ClN}_4\text{O}_3\text{PCo}$ : C: 62.13(62.29), H: 4.16(4.18), N: 9.50(9.69); UV–Vis:  $\lambda_{\text{max}}$  intraligand interactions: 252, 320, 358, d  $\rightarrow$  d forbidden transition: 440.  $\mu_{\text{eff}}$ : 2.49. **CoL5**: Yield: 55%. IR (KBr,  $\text{cm}^{-1}$ ): 1586, 1428, 1346, 1105, 695, 608, 550, 495, 476.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 6.6–7.3 (m, 15H, Ar–H), 7.4–7.8 (m, 7H, Ar–H), 8.5 (d, 1H, –CH=N–);  $^{13}\text{C}$  NMR (ppm): 164.93, 151.12, 143.23, 142.96, 134.84, 134.63, 134.19, 130.64, 130.60, 129.70, 128.80, 128.32, 128.10, 127.58, 127.06, 126.03, 124.24, 122.77, 121.98, 118.94, 114.85, 110.29.  $^{31}\text{P}$  NMR ( $\text{H}_3\text{PO}_4$ ,  $\delta$  ppm): 22.6. CHN found (calc.) for  $\text{C}_{31}\text{H}_{27}\text{ClN}_3\text{O}_2\text{PCo}$ : C: 65.97(66.08), H: 4.36(4.83), N: 7.21(7.46); UV–Vis:  $\lambda_{\text{max}}$  intraligand interactions: 251, 320, 365, d  $\rightarrow$  d forbidden transition: 440.  $\mu_{\text{eff}}$ : 2.36.
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- [35] 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 °C to 150 °C at the rate of 10 °C/min and then to 220 °C at the rate of 40 °C/min Nitrogen gas was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 150 °C and 250 °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.
- [36] A solution of cobalt (II) complex (0.02 mmol) in 0.1 mL ethyl-methyl-imidazolium (EMIM) ionic liquid was added to the solution of substrate (1 mmol) and NaOCl (1 mmol). 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 GC.