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# Ruthenium(II) carbonyl complexes with N-[di(alkyl/aryl) carbamothioyl]benzamide derivatives and triphenylphosphine as effective catalysts for oxidation of alcohols

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Ruthenium(II) complexes,  $[RuCl(L)(CO)(PPh_3)_2]$  {where L = N-[di(alkyl/aryl)carbamothioyl] benzamide derivatives}, are prepared from reaction between  $[RuHCl(CO)(PPh_3)_3]$  and N-[di(alkyl/aryl)carbamothioyl]benzamide derivatives in toluene and characterized by elemental analysis and spectral data (electronic, infrared, <sup>1</sup>H NMR, and <sup>31</sup>P NMR). The combination of  $[RuCl(L)(CO)(PPh_3)_2]$  (0.01 mmol) and *N*-methylmorpholine-*N*-oxide (NMO) (3 mmol) is an active catalyst for the oxidation of primary, secondary, cyclic, allylic, aliphatic, and benzylic alcohols to their corresponding aldehydes and ketones at room temperature. The oxidation protocol is simple to operate and gives the corresponding carbonyl compounds good to excellent yields.

Keywords: Ruthenium(II); Thiourea derivatives; Triphenylphosphine; Catalytic oxidation; NMO

# 1. Introduction

Oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones is a very important transformation that is used in the manufacture of a wide range of products [1–4]. Traditionally, such transformations have been performed with stoichiometric quantities of inorganic oxidants such as chromium(VI) compounds. The quest for effective catalytic systems that use clean and inexpensive oxidants, such as molecular oxygen, hydrogen peroxide, NMO, *tert*-butylhydroperoxide, or TEMPO, for converting alcohols to carbonyl products, remains an important challenge. Thiourea derivatives are versatile ligands due to their coordination ability to a wide range of metal centers as either neutral ligands [5], monoanions [6], or dianions [7, 8]. *N*-[Di(alkyl/aryl)carbamothioyl]benzamide derivatives readily coordinate with metal ions through O, S donors [9–13] and these ligands can alter the catalytic property of complexes due to steric and electronic properties provided by various substituents.

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Recently we developed an active and selective ruthenium(III)–PPh<sub>3</sub>/NMO catalytic system for the oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones [14]. This catalytic system did not give satisfactory results for the oxidation of linear and cyclic aliphatic alcohols even at elevated temperature. In the present work, ruthenium(II) carbonyl complexes containing N-[di(alkyl/aryl)carbamothioyl]benzamide derivatives and triphenylphosphine are improved and highly efficient catalysts for the oxidation of various alcohols to carbonyl compounds in the presence of NMO as oxidant at room temperature. The present catalytic system exhibited high activity for the oxidation of linear and cyclic aliphatic alcohols. The structures of the ligands used in this work are given in figure 1.

# 2. Experimental

# 2.1. Materials and methods

All solvents were dried and purified by standard methods. Infrared (IR) spectra were recorded as KBr pellets with a Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer from 4000 to  $400 \,\mathrm{cm}^{-1}$ . Electronic spectra of the complexes were recorded in ethanol solutions using a PG Instruments Ltd. T90+ spectrophotometer from 800 to 200 nm. Magnetic susceptibility measurements were made with a Sherwood Scientific Auto Magnetic Susceptibility Balance. Microanalyses were carried out with a Vario EL AMX-400 elemental analyzer. <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were recorded with a Bruker Avance 400 MHz instrument in CDCl<sub>3</sub> using TMS and H<sub>3</sub>PO<sub>4</sub> as internal standards, respectively. Melting points were recorded with a Veego VMP-D melting



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Figure 1. Structure of ligands.

point apparatus and were uncorrected. Capillary gas chromatography was performed on a Shimadzu GC-2010 gas chromatograph.

# 2.2. Synthesis of Ru(II) complexes

All the complexes are prepared by the following general procedure. Ligand (HL) (0.062-0.084 g, 0.26 mmol) dissolved in toluene (15 mL) was added to  $[\text{RuHCl(CO)(PPh}_3)_3]$  (0.25 g, 0.26 mmol) in toluene (10 mL). The mixture was heated in an oil bath at 80°C. After 24 h, the reaction mixture was concentrated to 3 mL and 20 mL of *n*-hexane was added. The precipitate formed was filtered, recrystallized from dichloromethane/*n*-hexane, and dried *in vacuo*.

**[RuCl(L1)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (1)** is prepared from [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.25 g, 0.26 mmol) and HL1 (0.081 g, 0.26 mmol). Yield: 88%, decomposition point 125°C, Anal. Calcd for C<sub>57</sub>H<sub>48</sub>ClN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>RuS (%): C, 66.89; H, 4.73; N, 2.74; S, 3.13. Found (%): C, 66.29; H, 4.20; N, 2.50; S, 3.00. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (N–H) disappeared;  $\nu$ (C === O) 1485;  $\nu$ ((C === S)) 1187;  $\nu$ (C ==O) 1943; bands due to PPh<sub>3</sub> 1435, 1093, 744. UV [ethanol,  $\lambda$  in nm ( $\varepsilon$  in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 226 (45,685), 271 (13,971), 414 (1771). <sup>1</sup>H NMR (ppm): 6.6–7.7 (m, 45H, aromatic). <sup>31</sup>P NMR (ppm): 30.9 (s).

**[RuCl(L2)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (2)** is prepared from [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.25 g, 0.26 mmol) and HL2 (0.062 g, 0.26 mmol). Yield: 78%, decomposition point 105°C, Anal. Calcd for C<sub>55</sub>H<sub>60</sub>ClN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>RuS (%): C, 65.30; H, 5.98; N, 2.77; S, 3.16. Found (%): C, 65.21; H, 5.90; N, 2.67; S, 3.07. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (N–H) disappeared;  $\nu$ (C == O) 1483;  $\nu$ (C == S) 1190;  $\nu$ (C=O) 1935; bands due to PPh<sub>3</sub> 1436, 1094, 747. UV [ethanol,  $\lambda$  in nm ( $\varepsilon$  in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 226 (63,085), 265 (11,285). <sup>1</sup>H NMR (ppm): 7.0–7.6 (m, 35H, aromatic), 3.0–3.4 (q, 4H, methylene), 0.6–0.9 (t, 6H, methyl). <sup>31</sup>P NMR (ppm): 31.4 (s).

**[RuCl(L3)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (3)** is prepared from [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.25 g, 0.26 mmol) and HL3 (0.069 g, 0.26 mmol). Yield: 80%, decomposition point 107°C, Anal. Calcd for C<sub>59</sub>H<sub>68</sub>ClN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>RuS (%): C, 66.37; H, 6.42; N, 2.62; S, 3.00. Found (%): C, 66.29; H, 6.35; N, 2.56; S 2.93. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (N–H) disappeared;  $\nu$ (C === O) 1472;  $\nu$ (C === S) 1187;  $\nu$ (C ==O) 1954; bands due to PPh<sub>3</sub> 1435, 1093, 743. UV [ethanol,  $\lambda$  in nm ( $\varepsilon$  in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 225 (42,800), 275 (19,971), 410 (3142). <sup>1</sup>H NMR (ppm): 7.5–7.7 (m, 35H, aromatic), 3.0–3.3 (t, 4H, methylene), 2.9 (s, 8H, methylene), 0.7–1.0 (q, 6H, methyl). <sup>31</sup>P NMR (ppm): 31.5 (s).

**[RuCl(L4)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (4)** is prepared from [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.25 g, 0.26 mmol) and HL4 (0.084 g, 0.26 mmol). Yield: 78%, decomposition point 102°C, Anal. Calcd for C<sub>59</sub>H<sub>52</sub>ClN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>RuS (%): C, 67.39; H, 4.98; N, 2.66; S, 3.04. Found (%): C, 67.29; H, 4.89; N, 2.55; S, 2.97. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (N–H) disappeared;  $\nu$ (C==O) 1482;  $\nu$ (C==S) 1190;  $\nu$ (C=O) 1962; bands due to PPh<sub>3</sub> 1435, 1093, 746. UV [ethanol,  $\lambda$  in nm ( $\varepsilon$  in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 226 (60,457), 271 (16,942). <sup>1</sup>H NMR (ppm): 7.4–7.7 (m, 45H, aromatic), 0.8–1.3 (m, 4H, methylene). <sup>31</sup>P NMR (ppm): 29.5 (s).

[RuCl(L5)(CO)(PPh<sub>3</sub>)<sub>2</sub>] (5) is prepared from [RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>] (0.25 g, 0.26 mmol) and HL5 (0.077 g, 0.26 mmol). Yield: 88%, decomposition point 176°C, Anal. Calcd for  $C_{51}H_{52}ClN_2O_2P_2RuS$  (%): C, 64.11; H, 5.49; N, 2.93; S, 3.36. Found (%): C, 68.70; H, 5.41; N, 2.85; S, 3.28. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$ (N–H) disappeared;  $\nu$ (C==O) 1481;  $\nu$ (C==S) 1188;  $\nu$ (C=O) 1956; bands due to PPh<sub>3</sub> 1435, 1093, 744. UV [ethanol,

λ in nm (ε in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>)]: 227 (64,885), 271 (30,371), 406 (4570). <sup>1</sup>H NMR (ppm): 7.3–7.7 (m, 35H, aromatic), 3.3–3.6 (s, 1H, methine), 1.4 (d, 6H, methyl). <sup>31</sup>P NMR (ppm): 29.5 (s).

## 2.3. Procedure for catalytic oxidation

To a solution of alcohol (1 mmol) in solvent (20 mL), *N*-methylmorpholine-*N*-oxide (3 mmol) and the ruthenium complex (0.01 mmol) were added. The solution was stirred for 12 h at room temperature. At the requisite time aliquots of the reaction mixture were removed and the alcohol and aldehyde/ketone were extracted with *n*-hexane. The *n*-hexane extract was then analyzed by GC.

#### 3. Results and discussion

The bidentate ligands (HL1, HL2, HL3, HL4, and HL5) are synthesized from benzoyl chloride, potassium thiocyanate, and the corresponding secondary amine [15]. New six-coordinate ruthenium(II) carbonyl complexes,  $[RuCl(L)(CO)(PPh_3)_2]$ , are synthesized by reacting  $[RuHCl(CO)(PPh_3)_3]$  [16] with *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives (HL) (scheme 1). Spectral analysis revealed monoanionic bidentate coordination of *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives replacing one triphenylphosphine and one hydride from the starting complex. All the complexes are air stable, non-hygroscopic, insoluble in water and highly soluble in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>OH, DMF, and DMSO. The analytical data obtained are in good agreement with the proposed molecular formulae.

# 3.1. IR spectroscopic analysis

In IR spectra of free carbamothioyl ligands, a very strong absorption band is at  $3174-3329 \text{ cm}^{-1}$  for N–H, which disappears on complexation with ruthenium, indicating deprotonation of the ligands prior to coordination through enolization. The free ligands exhibit a strong band corresponding to C=O at  $1652-1692 \text{ cm}^{-1}$ . In complexes, this band is at  $1472-1485 \text{ cm}^{-1}$  indicating coordination of C==O to ruthenium. A medium intensity band at  $1243-1314 \text{ cm}^{-1}$  due to C=S of the ligands undergoes a shift to lower frequency ( $1187-1190 \text{ cm}^{-1}$ ) after complexation, revealing bonding through sulfur [15]. These complexes show new bands at 1410, 1100, and 750 cm<sup>-1</sup>, which are due to triphenylphosphine ligand. All the new complexes show a strong absorption band around  $1935-1962 \text{ cm}^{-1}$  due to terminally coordinated carbonyl [17].

#### 3.2. Electronic spectroscopic analysis

All the new ruthenium complexes are diamagnetic ( $\mu_{eff}=0$ ), indicating ruthenium in +2 oxidation state. The ground state of ruthenium(II) is  ${}^{1}A_{1g}$  arising from the  $t_{2g}^{6}$  configuration in an octahedral environment. The excited states corresponding to the  $t_{2g}^{5}e_{g}^{1}$  configuration are  ${}^{3}T_{1g}$ ,  ${}^{3}T_{2g}$ ,  ${}^{1}T_{1g}$ , and  ${}^{1}T_{2g}$ . Hence, four bands corresponding to



Scheme 1. Formation of Ru(II) complexes.

 ${}^{1}A_{1g} \rightarrow {}^{3}T_{1g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{3}T_{2g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ , and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  are possible in order of increasing energy. Electronic spectra of all the complexes in ethanol showed two to three bands in the region 414–225 nm. On the basis of high extinction coefficients ( $\varepsilon = 11,285-64,885 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^{3}$ ), the bands appearing at 275–225 nm have been assigned to charge transfer transitions arising from the excitation of an electron from the metal  $t_{2g}$  level to an unfilled molecular orbital derived from the  $\pi^*$  level of the ligands. The other bands around 414–406 nm have been assigned to the d–d transition ( ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ). The nature of electronic spectra are similar to those observed for other octahedral ruthenium(II) complexes [18, 19].

# 3.3. NMR spectroscopic analysis

<sup>1</sup>H NMR spectra of all the complexes have been recorded in  $CDCl_3$  solution. All the Ru(II) complexes exhibit a multiplet around 6.6–7.7 ppm, which has been assigned to the protons of the phenyl groups present in triphenylphosphine and the ligand. The characteristic signal at 11–12 ppm for N–H disappeared in NMR spectra of the complexes indicating deprotonation of the ligands prior to coordination through enolization [20]. Complex **2** exhibits a quartet at 3.0–3.4 ppm corresponding to methylene and a triplet around 0.6–0.9 ppm corresponding to methyl. Complex **3** 





Entry	Complex	Solvent	Oxidant	Yield (%) <sup>b</sup>
1	1	CH <sub>2</sub> Cl <sub>2</sub>	NMO	94
2	2	CH <sub>2</sub> Cl <sub>2</sub>	NMO	95
3	3	CH <sub>2</sub> Cl <sub>2</sub>	NMO	94
4	4	CH <sub>2</sub> Cl <sub>2</sub>	NMO	92
5	5	CH <sub>2</sub> Cl <sub>2</sub>	NMO	97
6	5	CH <sub>3</sub> CN	NMO	98
7	5	C <sub>6</sub> H <sub>6</sub>	NMO	93
8	5	DMF	NMO	97
9	5	CH <sub>3</sub> CN	NMO	98
10	5	CH <sub>3</sub> CN	$H_2O_2$	94
11	5	CH <sub>3</sub> CN	t-BuOOH	97

<sup>a</sup>Reaction conditions: 1-phenylethanol (1 mmol), oxidant (3 mmol), catalyst (0.01 mmol), solvent (20 mL), stirring for 12 h, 27° C. <sup>b</sup>Yield is determined by GC with area normalization; GC conditions: RTX-5

"Yield is determined by GC with area normalization; GC conditions: RTX-5 column,  $60 \text{ m} \times 0.32 \text{ mm}$ ,  $250^{\circ}\text{C}$ ; FID detector,  $280^{\circ}\text{C}$ ; injector,  $250^{\circ}\text{C}$ ; carrier gas: N<sub>2</sub>; rate:  $1.39 \text{ mL min}^{-1}$ .

exhibits a triplet around 3.0–3.3 ppm corresponding to methylene protons near nitrogen and a broad signal around 2.9 ppm attributed to remaining methylene protons of the aliphatic carbon chain. Two triplets at 0.7–1.0 ppm in **3** have been assigned to methyls. Complex **4** exhibits two multiplets at 0.8–1.3 ppm corresponding to methylene protons attached to phenyl. In **5**, two doublets at 1.2–1.4 ppm are due to methyls and two broad singlets at 3.3 and 3.6 ppm are from methine protons attached to nitrogen. <sup>31</sup>P NMR spectra of all the complexes in CDCl<sub>3</sub> confirm the presence of triphenylphosphine in Ru(II) complexes. All complexes exhibit one signal at 29.5–31.5 ppm, indicating that both phosphorus atoms are magnetically equivalent and hence, *trans* triphenylphosphines were assigned [21, 22].

## 3.4. Catalytic oxidation

In order to explore the catalytic activity of ruthenium(II) complexes, 1–5 were tested as catalysts for the oxidation of 1-phenylethanol (table 1, entries 1, 2, 3, 4, and 5) in the presence of NMO as oxidant and dichloromethane as solvent at 27°C. Although all the complexes exhibit good catalytic activity, the yield of acetophenone (table 1, entry 5) was highest when 5 was used as a catalyst. Hence, 5 was chosen as catalyst for optimization and extending the scope of substrates. In no case was there detectable oxidation of alcohols in the presence of NMO alone [23]. The catalytic oxidation of 1-phenylethanol (table 1, entries 5, 6, 7, and 8) was carried out in dichloromethane, acetonitrile, benzene, and dimethylformamide in order to optimize the solvent. Among these, acetonitrile (table 1, entry 6) was a better solvent as the yield of carbonyl compound was 98%. The catalytic oxidation of 1-phenylethanol

Table 2. Oxidation of alcohols by 5a.

$$\begin{array}{c} \begin{array}{c} \mathsf{OH} \\ \mathsf{R}_1 \\ \mathsf{R}_2 \end{array} \xrightarrow[]{\text{Ru}} (0.01 \text{ equiv}), \\ \begin{array}{c} \mathsf{Oxidant} (3 \text{ equiv}), \mathsf{CH}_3\mathsf{CN} \\ \hline \\ \text{Stirring, } 27^\circ\mathsf{C}, 12 \text{ h} \end{array} \xrightarrow[]{\text{Ru}} \\ \begin{array}{c} \mathsf{R}_1 \\ \mathsf{R}_2 \end{array} \xrightarrow[]{\text{Ru}} \\ \begin{array}{c} \mathsf{R}_1 \\ \\ \end{array} \xrightarrow[]{\text{Ru}} \\ \begin{array}{c} \mathsf{R}_1 \\ \\ \\ \end{array} \xrightarrow[]{\text{Ru}} \end{array} \xrightarrow[]{\text{Ru}} \\ \\begin{array}{c} \mathsf{R}_1 \\ \\ \end{array} \xrightarrow[]{\text{Ru}} \\ \end{array} \xrightarrow[]{\text{Ru}} \\\[]{\text{Ru}} \end{array} \xrightarrow[]{\text{Ru}} \\\[]{\text{Ru}} \\\[]{\text{Ru}} \end{array} \xrightarrow[]{\text{Ru}} \\\[]{\text{Ru}} \\\[$$

Entry	Substrate	Product	Yield (%) <sup>b</sup>
1	OH	O C C	98 (94) <sup>c</sup>
2	OH	° C	99 (95) <sup>c</sup>
3	OH	°	97
4	CI	CI	98
5	CIOH	CIO	94
6	OH O		88
7	ОН	O H	94
8	ОН	H	94

Entry	Substrate	Product	Yield (%) <sup>b</sup>
9	OH	°	94
10	OH	O C	96
11	ОН	O O	95
12	ОН		93
13	ОН	0	98

Table 2. Continued.

<sup>a</sup>Reaction conditions: alcohol (1 mmol), NMO (3 mmol), catalyst (0.01 mmol), acetonitrile (20 mL), stirring for 12 h, 27°C. <sup>b</sup>Yield (average of two trials) is determined by GC with area normalization.

<sup>c</sup>Isolated yield is given in parenthesis.

(table 1, entries 9, 10, and 11) was carried out using NMO, hydrogen peroxide or tertbutylhydroperoxide as oxidant in order to select the suitable oxidant for the present catalyst. With NMO (table 1, entry 9), the yield of acetophenone was 98%; 0.01 mmol of catalyst and 3 mmol of NMO were sufficient for oxidation. Acetonitrile was used as solvent, NMO as oxidant, and 5 as catalyst for extending the scope of substrates. Table 2 shows the results for the oxidation of various alcohols. Virtually every alcohol investigated was converted to the corresponding carbonyl compound with  $\sim 90\%$  yield at room temperature. The yield of carbonyl compounds obtained is significantly higher than those obtained from recently reported Ru(III)-PPh<sub>3</sub>/NMO catalytic system [14]. Benzylic primary (table 2, entry 7) and secondary alcohols (table 2, entries 1, 2, 3, 4, and 5) are smoothly oxidized to the corresponding carbonyl compounds with excellent yields. The efficiency of oxidation of benzylic alcohols is comparable with already reported [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>]/hydroquinone/air [24] and [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub>/Cs<sub>2</sub>CO<sub>3</sub>/O<sub>2</sub> [25] catalytic systems, and higher than Ru(III)-PPh<sub>3</sub>/NMO [26], Ru(II)-PPh<sub>3</sub>/NMO [27], and  $[Ru(acac)_2(CH_3CN)_2]PF_6/H_5IO_6$  [28] catalytic systems. The catalytic oxidation of 1-phenoxy-2-propanol (table 2, entry 6) gave corresponding ketone with 88% yield at room temperature, whereas oxidation of the same substrate by similar Ru(III) complexes with NMO gave the product with 75% yield after stirring for 12 h at 70°C [14]. The present catalytic system exhibits better efficiency for the oxidation of cinnamylalcohol (table 2, entry 8) when compared with earlier reports on ruthenium



Scheme 2. Proposed mechanism for oxidation of alcohols.

complexes as catalysts and NMO/t-BuOOH as oxidant [29-31]. 1-Indanol (table 2, entry 9) was readily converted into 1-indanone with 94% yield and the yield of product is higher than  $K_3$ [Fe(CN)<sub>6</sub>] or Shvo complex-catalyzed oxidation of the same substrate with TEMPO or molecular oxygen, respectively [32, 33]. Oxidation of 1-cyclohexylethanol (table 2, entry 10) was carried out at 27°C to give corresponding ketone with 96% yield. Cyclohexanol (table 2, entry 11) and cyclopentanol (table 2, entry 12) are converted into cyclohexanone (95% yield) and cyclopentanone (93% yield), respectively. Oxidation of these substrates was found to be difficult due to the fact that  $\alpha$ -CH unit is less acidic than aromatic substrates [29]. Interestingly, the present catalytic system is highly efficient for these substrates and yield of products is higher than those obtained from [RuCl<sub>2</sub>(p-cymene)]<sub>2</sub>/Cs<sub>2</sub>CO<sub>3</sub>/O<sub>2</sub> [25] and Ru-SiO<sub>2</sub>/t-BuOOH [34] catalytic systems. Our catalyst is very active toward the oxidation of linear aliphatic alcohol viz 2-octanol (table 2, entry 13) to 2-otanone (98% yield). The present catalytic system is more efficient in the oxidation of linear aliphatic alcohols compared to Ru(II)/Ru(III)-NMO catalytic systems [35–38]. It is found that cycloruthenated carbonyl complexes [37] and Ru(II) half sandwich complexes [38] are equally efficient compared with our system, but they require high temperature. The present catalytic system oxidizes 2octanol with excellent yield at room temperature. Recently, the catalytic oxidation of alcohols by Ru(II) and Ru(III) complexes containing Schiff-base ligand and PPh<sub>3</sub>/ AsPh<sub>3</sub> have been reported [39-41]. Compared to these systems, the present catalytic system is better in terms of yield of products and mild reaction conditions.

A characteristic peak at  $850 \text{ cm}^{-1}$  in the IR spectrum of reaction mixture supports the fact that the catalytic cycle passes through a Ru(IV) = O species [42]. The proposed mechanism is given in scheme 2.

## 4. Conclusion

We have synthesized Ru(II) carbonyl complexes containing *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives and triphenylphosphine. These complexes are employed as catalysts in combination with NMO for oxidation of various alcohols at room temperature. The catalytic procedure is simple and easy to implement.

#### Supplementary material

Electronic spectra, representative <sup>1</sup>H and <sup>31</sup>P-NMR spectrum of ruthenium(II) complexes, GC chromatogram, and GC conditions for catalytic studies have been provided as supplementary materials.

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