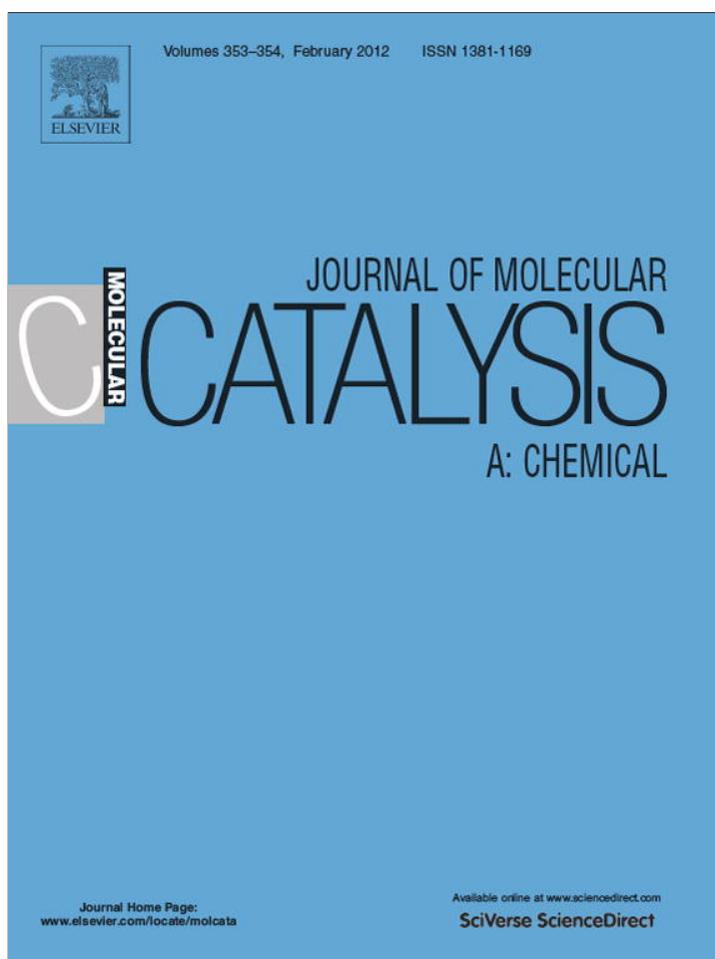


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## Journal of Molecular Catalysis A: Chemical

journal homepage: [www.elsevier.com/locate/molcata](http://www.elsevier.com/locate/molcata)Chelate and *trans* effect of P,O donor phosphine ligands on rhodium catalyzed carbonylation of methanolDipak Kumar Dutta<sup>a,\*</sup>, Biswajit Deb<sup>a</sup>, Guoxiong Hua<sup>b</sup>, J. Derek Woollins<sup>b</sup><sup>a</sup> Materials Science Division, Council of Scientific and Industrial Research, North East Institute of Science and Technology, Jorhat 785006, Assam, India<sup>b</sup> EaStCHEM School of Chemistry, University of St. Andrews, St. Andrews, UK KY16 9ST, UK

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## ABSTRACT

Four complexes of the type  $[\text{Rh}(\text{CO})\text{Cl}(\eta^2\text{-P,O-L})](\mathbf{1a}, \mathbf{1b})$  and  $[\text{Rh}(\text{CO})\text{Cl}(\eta^1\text{-P-L})_2](\mathbf{2a}, \mathbf{2b})$ , where  $\text{L} = \text{Ph}_2\text{PC}_6\text{H}_4\text{-2-OCH}_3(\mathbf{a})$  and  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3(\mathbf{b})$ , have been synthesized by the reaction of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  with appropriate mol equivalents of the ligands in  $\text{CH}_2\text{Cl}_2$ . The complexes show single intense  $\nu(\text{CO})$  bands in the range  $1965\text{--}1989\text{ cm}^{-1}$  indicating the presence of terminal carbonyl groups. All the complexes have been characterized by elemental analyses, mass spectrometry, IR and multinuclear NMR ( $^1\text{H}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$ ) spectroscopy, and the molecular structure of the ligand  $\mathbf{b}$  is determined by single crystal X-ray diffraction. The complexes undergo oxidative addition ( $\text{OA}$ ) with excess  $\text{CH}_3\text{I}$  to afford  $\text{Rh}(\text{III})$ -acyl complexes of the type  $[\text{RhCl}(\text{COCH}_3)(\text{L})](\mathbf{3a}, \mathbf{3b})$  and  $[\text{RhCl}(\text{COCH}_3)(\text{L})_2](\mathbf{4a}, \mathbf{4b})$ . The kinetic data for the  $\text{OA}$  reactions with  $\text{CH}_3\text{I}$  indicate a first order reaction and also exhibit that the rate of  $\text{OA}$  for the chelate complexes ( $\mathbf{1a}$  and  $\mathbf{1b}$ ) is higher than those of *trans*-complexes ( $\mathbf{2a}$  and  $\mathbf{2b}$ ). The catalytic efficiencies of  $\mathbf{1a}$ ,  $\mathbf{1b}$ ,  $\mathbf{2a}$  and  $\mathbf{2b}$  in carbonylation of methanol exhibit higher Turn Over Frequency (TOF)  $689\text{--}1808\text{ h}^{-1}$  than the well-known Monsanto's species  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  (TOF =  $464\text{--}1000\text{ h}^{-1}$ ) under similar experimental conditions. The catalytic activities vary in the order as  $\mathbf{1a} > \mathbf{1b} > \mathbf{2a} > \mathbf{2b}$ .

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## 1. Introduction

The coordination chemistry of unsymmetrical phosphine-phosphineoxide (P,O) ligands is of considerable interest because of their structural novelty, reactivity and catalytic activity [1–5]. Due to the presence of two different types of donor sites in the ligands, they are capable of coordinating either as a mono-dentate ( $\eta^1\text{-P}$  coordinated) or bi-dentate chelating ( $\eta^2\text{-P,O}$  coordinated) fashion depending upon the central metal atom and its environment [3,6]. However, the chemistry of these ligands is more fascinating as they can confer extra stability to the metal centre by chelate formation and may create vacant coordination sites by the cleavage of the relatively weaker metal–oxygen bond. Thus, such ligands have great impact on  $\text{OA}$  reactions [1b,2d,7,8], which is a key step in many catalytic reactions like the carbonylation of methanol. Since the first introduction of the commercial species, i.e.  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  as an efficient catalyst for the carbonylation of methanol to acetic acid [7a–d], considerable efforts have been devoted to improve the catalyst by incorporating different ligands [2,7,9–11] into its coordination sphere. As a part of our ongoing research activity [2,10], herein, we

have selected two typical P,O ligands viz.  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-OCH}_3$  and  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$  for the synthesis of rhodium complexes. In this paper, we report the synthesis of chelate ( $\eta^2\text{-P,O}$ ) and *trans*-( $\eta^1\text{-P}$ ) rhodium(I) carbonyl complexes and their activity in catalytic carbonylation of methanol. The effect of chelate and *trans*-complexes on the methanol carbonylation has also been demonstrated.

## 2. Experimental

## 2.1. General

All solvents were distilled under  $\text{N}_2$  prior to use.  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  was purchased from M/S Arrora Matthey Ltd., Kolkata, India.

Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. IR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded as thin film using NaCl cell on a Shimadzu IR Affinity-1 spectrophotometers. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded at room temperature in  $\text{CDCl}_3$  solution on a Bruker DPX-300 Spectrometer and chemical shifts were reported relative to  $\text{SiMe}_4$  and  $85\% \text{H}_3\text{PO}_3$  as internal and external standards respectively. Mass spectra of the complexes were recorded on ESQUIRE 3000 Mass Spectrometer. The carbonylation reactions of methanol were carried out in a high pressure reactor (Parr-4592, USA) fitted with a pressure gauge and the reaction products were analysed by GC (Chemito 8510, FID).

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## 2.2. Synthesis of ligands

### 2.2.1. Synthesis of $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-OCH}_3$ (**a**)

The ligand **a** was prepared by literature method [12].

Analytical data for **a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  3.71 (s, 3H,  $\text{CH}_3$ ),  $\delta$  7.28–7.36, 6.8–6.9 (m, 14H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  61.2 ( $\text{CH}_3$ ),  $\delta$  125–139 (Ph),  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  –16.09 [s,  $\text{P}^{\text{III}}$ ]. Elemental analyses; Found (Cald. for  $\text{C}_{19}\text{H}_{17}\text{OP}$ ): C, 77.96 (78.08), H, 5.78 (5.82). Mass: 292 ( $m/z^+$ ).

### 2.2.2. Synthesis of $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$ (**b**)

1.0 M solution of  $\text{NaOCH}_3$ , prepared from 0.60 g of metal sodium (25.0 mmol, 1.20 equiv.) in  $15\text{ cm}^3$  of  $\text{CH}_3\text{OH}$ , was added to 5.22 g of 2-bromobenzyl bromide (20.9 mmol) and heated to reflux for 5 h. The mixture was then cooled to room temperature and dried. The residue was taken up with water/ethyl acetate. The organic layer was washed with water and brine for three times and dried over  $\text{MgSO}_4$ . The organic solvent was removed to produce a colourless oil 1-bromo-2-(methoxymethyl)benzene in 92% yield (3.70 g).

*n*-Butyllithium solution ( $7.5\text{ cm}^3$ , 2.5 M in hexane, 18.5 mmol) was added to a mixture of 1-bromo-2-(methoxymethyl)benzene (3.70 g, 18.5 mmol) in  $40\text{ cm}^3$  of THF at  $-78^\circ\text{C}$  for a period of 1 h. The mixture was stirred for another 1 h. Then chlorophenylphosphine ( $3.2\text{ cm}^3$ , 18.5 mmol) was added to the mixture at  $-78^\circ\text{C}$  within 30 min. The mixture was further stirred at  $-78^\circ\text{C}$  for 2 h and kept for 3 h to reach upto room temperature. The solvent was removed in vacuum and the residue was taken up with water/ethyl acetate. The organic layer was washed with water and brine and dried over  $\text{MgSO}_4$ . Concentrated the organic layer to  $5\text{ cm}^3$  and purified by silica gel (eluent by  $\text{CH}_2\text{Cl}_2$ ) gave 2.72 g as colourless crystals after crystallization from  $\text{CH}_2\text{Cl}_2$  solution.

Analytical data for **b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  3.26 (s, 3H,  $\text{CH}_3$ ),  $\delta$  4.64 (s, 2H,  $\text{CH}_2$ ),  $\delta$  7.17–7.32, 7.52–7.68 (m, 14H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  53.8 ( $\text{CH}_3$ ),  $\delta$  74.3 ( $\text{CH}_2$ ),  $\delta$  128–142 (Ph),  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  –15.08 [s,  $\text{P}^{\text{III}}$ ]. Elemental analyses; Found (Cald. for  $\text{C}_{20}\text{H}_{19}\text{OP}$ ): C, 78.43 (78.11), H, 6.20 (6.08). Mass: 306 ( $m/z^+$ ).

## 2.3. Starting materials

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$  was prepared by passing CO gas over  $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$  at  $100^\circ\text{C}$  in the presence of moisture [13].

### 2.4. Synthesis of the complexes $[\text{Rh}(\text{CO})\text{Cl}(\eta^2\text{-P,O-L})]$ (**1a, 1b**), $L = \text{Ph}_2\text{PC}_6\text{H}_4\text{-2-OCH}_3$ (**a**), $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$ (**b**)

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$  [0.128 mmol, 50 mg] was dissolved in dichloromethane ( $10\text{ cm}^3$ ) and to this solution, a stoichiometric quantity of the respective ligands [0.256 mmol, 74.75 mg (**a**), 78.35 mg (**b**)] were added. The reaction mixture was stirred at room temperature ( $25^\circ\text{C}$ ) for about 20 min and the solvent was evaporated under vacuum. The yellowish to reddish brown coloured compounds so obtained were washed with pentane as well as diethyl ether and also recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane and stored over silica gel in a desiccator.

Analytical data for the complexes **1a, 1b** are as follows:

**1a**: Yield: 81%; IR (Thin film, NaCl): 1979 [ $\nu(\text{CO})$ ],  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.54 (s, 3H,  $\text{CH}_3$ ),  $\delta$  6.9, 7.27–7.43, 7.55–7.68, 7.81–7.93 (m, 14H, Ph) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  58.5 ( $\text{CH}_3$ ),  $\delta$  114–137 (Ph),  $\delta$  168 (C–O),  $\delta$  184.8 (CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  27.96 [ $\text{P}^{\text{V}}$ , d,  $J_{\text{P-Rh}} = 128\text{ Hz}$ ]. Elemental analyses; Found (Cald. for  $\text{C}_{20}\text{H}_{17}\text{ClO}_2\text{PRh}$ ): C, 51.89 (52.35), H, 3.63 (3.70). Mass: 458.41 ( $m/z^+$ ).

**1b**: Yield: 74%. IR (Thin film, NaCl): 1989 [ $\nu(\text{CO})$ ],  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  3.14 (s, 3H,  $\text{CH}_3$ ),  $\delta$  4.54 (s, 2H,  $\text{CH}_2$ ),  $\delta$  7.42–7.62 (m, 14H, Ph).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  53.5 ( $\text{CH}_3$ ),  $\delta$  74.2

( $\text{CH}_2$ ),  $\delta$  127–143 (Ph),  $\delta$  183 (CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  28.5 [ $\text{P}^{\text{V}}$ , d,  $J_{\text{P-Rh}} = 125.3\text{ Hz}$ ]. Elemental analyses; Found (Cald. for  $\text{C}_{21}\text{H}_{19}\text{ClO}_2\text{PRh}$ ): C, 53.02 (53.34), H, 3.89 (4.02). Mass: 472.41 ( $m/z^+$ ).

### 2.5. Synthesis of the complexes $[\text{Rh}(\text{CO})\text{Cl}(\eta^1\text{-P-L})_2]$ (**2a, 2b**) $L = \text{Ph}_2\text{PC}_6\text{H}_4\text{-2-OCH}_3$ (**a**), $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$ (**b**)

$[\text{Rh}(\text{CO})_2\text{Cl}]_2$  [0.128 mmol, 50 mg] was dissolved in dichloromethane ( $10\text{ cm}^3$ ) and to this solution, a stoichiometric quantity of the respective ligands [0.512 mmol, 149.5 (**a**), 156.7 (**b**) mg] were added. The reaction mixture was stirred at room temperature ( $25^\circ\text{C}$ ) for about 30 min and the solvent was evaporated under vacuum. The yellowish to reddish brown coloured compounds so obtained were washed with pentane as well as diethyl ether and also recrystallized from DCM/hexane and stored over silica gel in a desiccator.

Analytical data for the complexes **2a, 2b** are as follows:

**2a**: Yield: 72%; IR (Thin film, NaCl): 1970 [ $\nu(\text{CO})$ ],  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.68 (s, 6H,  $\text{CH}_3$ ),  $\delta$  6.85–6.95, 7.27–7.45, 7.65–7.91 (m, 28H, Ph) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  57.5 ( $\text{CH}_3$ ),  $\delta$  118–135 (Ph),  $\delta$  165 (C–O),  $\delta$  187.4 (CO) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  22.8 [ $\text{P}^{\text{V}}$ , d,  $J_{\text{P-Rh}} = 135\text{ Hz}$ ] ppm. Elemental analyses; Found (Cald. for  $\text{C}_{39}\text{H}_{34}\text{ClO}_3\text{P}_2\text{Rh}$ ): C, 61.86 (62.36), H, 4.25 (4.53). Mass: 750.41 ( $m/z^+$ ).

**2b**: Yield: 71%. IR (Thin film, NaCl): 1965 [ $\nu(\text{CO})$ ],  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  3.18 (s, 6H,  $\text{CH}_3$ ),  $\delta$  4.72 (s, 4H,  $\text{CH}_2$ ),  $\delta$  7.39–7.63 (m, 28H, Ph) ppm.  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  54.7 ( $\text{CH}_3$ ),  $\delta$  74.8 ( $\text{CH}_2$ ),  $\delta$  126–142.3 (Ph),  $\delta$  184.3 (CO) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  24.6 [ $\text{P}^{\text{V}}$ , d,  $J_{\text{P-Rh}} = 127.2\text{ Hz}$ ] ppm. Elemental analyses; Found (Cald. for  $\text{C}_{41}\text{H}_{38}\text{ClO}_3\text{P}_2\text{Rh}$ ): C, 62.88 (63.20), H, 4.78 (4.88). Mass: 778.41 ( $m/z^+$ ).

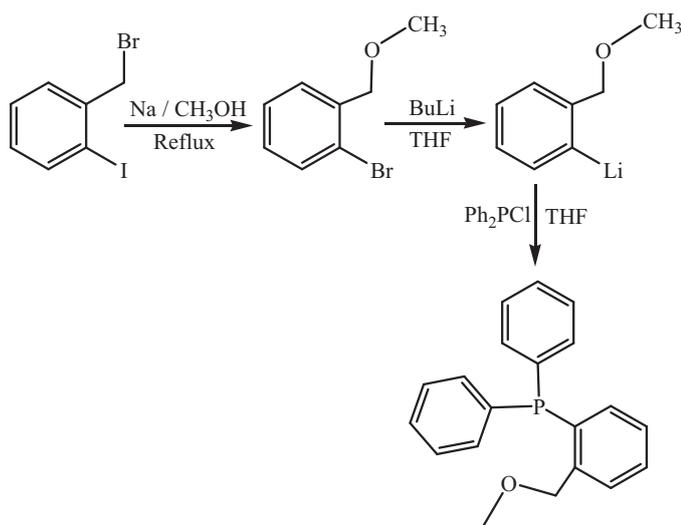
### 2.6. Reactivity of $[\text{Rh}(\text{CO})\text{Cl}(\eta^2\text{-P,O-L})]$ and $[\text{Rh}(\text{CO})\text{Cl}(\eta^1\text{-P-L})_2]$ with $\text{CH}_3\text{I}$

Synthesis of  $[\text{RhCl}(\text{COCH}_3)(\text{I})(\eta^2\text{-P,O-L})]$  (**3a, 3b**) and  $[\text{RhCl}(\text{COCH}_3)(\text{I})(\eta^1\text{-L})_2]$  (**4a, 4b**), where  $L = \text{Ph}_2\text{PC}_6\text{H}_4\text{-2-OCH}_3$  (**a**),  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$  (**b**)

$[\text{Rh}(\text{CO})\text{Cl}(\eta^2\text{-P,O-L})]$  or  $[\text{Rh}(\text{CO})\text{Cl}(\eta^1\text{-P-L})_2]$  (50 mg) was dissolved in  $\text{CH}_2\text{Cl}_2$  ( $10\text{ cm}^3$ ) and each of  $\text{CH}_3\text{I}$  ( $3\text{ cm}^3$ ) was added to it. The reaction mixture was then stirred at r.t. for about 0.5–2 h. The colour of the solution changed from yellowish red to dark reddish brown and the solvent was evaporated under vacuum. The compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

## 2.7. Kinetic experiment

The kinetic experiments of **OA** reactions of the complexes **1a, 1b, 2a** and **2b** with  $\text{CH}_3\text{I}$  were monitored using FTIR spectroscopy in a solution cell (NaCl windows, 0.5 mm path length). In order to obtain pseudo-first-order condition, excess of  $\text{CH}_3\text{I}$  relative to metal complex was used. FTIR spectra ( $4.0\text{ cm}^{-1}$  resolution) were scanned in the  $\nu(\text{CO})$  region ( $2200\text{--}1600\text{ cm}^{-1}$ ) and saved at regular time interval using spectrum software. After completion of experiment, absorbance versus time data for the appropriate  $\nu(\text{CO})$  frequencies were extracted by subtracting the solvent spectrum and analysed off line using OriginPro 7.5 software. Kinetic measurements were made by following the decay of lower frequency  $\nu(\text{CO})$  band of the complexes in the region  $1965\text{--}1989\text{ cm}^{-1}$ . The pseudo-first-order rate constants were found from the gradient of the plot of  $\ln(A_0/A_t)$  versus time, where  $A_0$  is the initial absorbance and  $A_t$  is the absorbance at time  $t$ .



Scheme 1. Synthesis of  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$  (**b**).

### 2.8. Carbonylation of methanol using complexes **1a**, **1b**, **2a** and **2b** as catalyst precursors

$\text{CH}_3\text{OH}$  (0.099 mol,  $4\text{ cm}^3$ ),  $\text{CH}_3\text{I}$  (0.016 mol,  $1\text{ cm}^3$ ),  $\text{H}_2\text{O}$  (0.055 mol,  $1\text{ cm}^3$ ) and catalyst (0.0514 mmol) were placed in a  $50\text{ cm}^3$  reaction vessel. The reaction mixture was then purged with CO for about 5 min and then pressurized with CO gas (5, 10 and 20 bar) at  $25^\circ\text{C}$ . The carbonylation reactions were carried out at  $130 \pm 2^\circ\text{C}$  for 1 h with corresponding gas pressure at around  $15 \pm 2$ ,  $20 \pm 2$  and  $33 \pm 2$  bar. The products were collected and analysed by G.C.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the ligands **a** and **b**

The ligand **a** was synthesized by literature method [12] and **b** was prepared according to Scheme 1. The ligands were characterized by elemental analyses, mass spectrometry and multinuclear NMR spectroscopic techniques. The  $^1\text{H}$  NMR spectra of **a** and **b** show characteristic phenylic multiplets in the region  $\delta$  6.8–7.68 ppm and methyl and methylene singlets in the range  $\delta$  3.26–4.64 ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **a** and **b** show characteristic resonances at  $\delta$  –16.09 and –15.08 ppm, respectively corresponding to the trivalent phosphines. In their  $^{13}\text{C}$  NMR spectra, the chemical shifts due to the phenylic and methyl carbons of **a**, **b** are found in the range 125–142 and 53.8–61.2 ppm respectively, and the methylene carbon of the ligand **b** is found at around 74.3 ppm. All the spectroscopic studies as well as the elemental and mass spectrometric results substantiate the formation of the desired ligands. The ligand **b** was also structurally characterized by single crystal X-ray structure determination (Fig. 1).

#### 3.1.1. Synthesis and characterization of **1a**, **1b**, **2a** and **2b**

The reaction of the chloro-bridged dimer  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in  $\text{CH}_2\text{Cl}_2$  with two mol equivalents of ligands (**a**, **b**) proceeds rapidly with the evolution of CO gas to yield the yellow chelated monocarbonyl complex of the type  $[\text{Rh}(\text{CO})\text{Cl}(\eta^2\text{-P,O-L})]$  (**1a**, **1b**), where  $\text{L} = \text{Ph}_2\text{PC}_6\text{H}_4\text{-2-OCH}_3$  (**a**) and  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$  (**b**) (Scheme 2). Elemental analyses of the complexes support the observed molecular composition of **1a** and **1b**. The IR spectra of **1a** and **1b** exhibit single intense  $\nu(\text{CO})$  bands at around 1979 and  $1989\text{ cm}^{-1}$  respectively, indicating the presence of a terminal carbonyl group. **1a** and **1b** show characteristic  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra with doublets

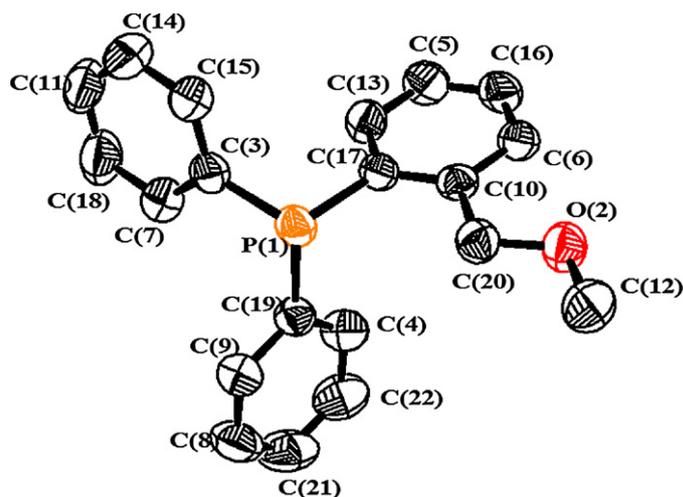
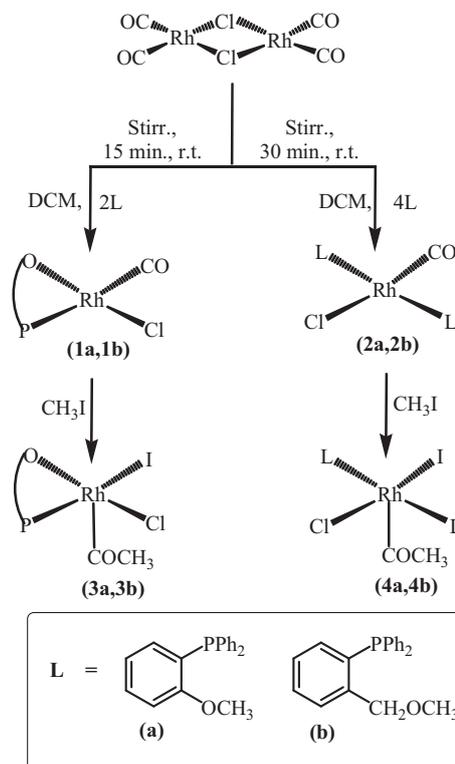


Fig. 1. X-ray crystal structure of  $\text{Ph}_2\text{PC}_6\text{H}_4\text{-2-CH}_2\text{OCH}_3$  (**b**). Hydrogen atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ): P(1)–C(17) 1.836(2), P(1)–C(19) 1.831(2), P(1)–C(3) 1.832(2), C(10)–C(20) 1.511(3), C(20)–O(2) 1.404(3), C(12)–O(2) 1.422(3).

at  $\delta$  28.0 (d,  $J_{\text{P-Rh}} = 128\text{ Hz}$ ) and 28.5 (d,  $J_{\text{P-Rh}} = 125\text{ Hz}$ ) ppm respectively, which show downfield shifts compared to the free ligands [ $\delta$  –16.09 (**a**) and –15.08 (**b**) ppm] indicating the formation of Rh–P bonds. The  $^1\text{H}$  NMR spectrum of **1a** shows characteristic phenylic multiplet in the region  $\delta$  6.90–7.93 ppm and methyl singlet at  $\delta$  3.54 ppm. However, **1b** shows the phenylic multiplet in the range  $\delta$  7.52–7.68 ppm, methylene and methyl singlet at around  $\delta$  4.54 and 3.14 ppm respectively. The appearance of upfield shifts of  $\text{CH}_3$  and  $\text{CH}_2$  protons in  $^1\text{H}$  NMR spectra and the downfield shift of phosphorus in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra compared to free ligands substantiate the formation of chelate  $\eta^2\text{-P,O}$  complex. On the other hand, the dimeric precursor  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in  $\text{CH}_2\text{Cl}_2$  reacts with four



Scheme 2. Syntheses and reactivity of **1a**, **1b**, **2a** and **2b**.

**Table 1**  
Significant IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for the OA adducts.

OA adducts	IR ( $\text{cm}^{-1}$ )	$^1\text{H}$ NMR (ppm)	$^{13}\text{C}$ NMR (ppm)
	$\nu(\text{CO})_{\text{acyl}}$	$\text{COCH}_3$	$(\text{CO})_{\text{acyl}}$
<b>3a</b>	1694	2.58(s)	206(s)
<b>3b</b>	1690	2.51(s)	205.6(s)
<b>4a</b>	1698	2.61(s)	203.4(s)
<b>4b</b>	1692	2.67(s)	204.1(s)

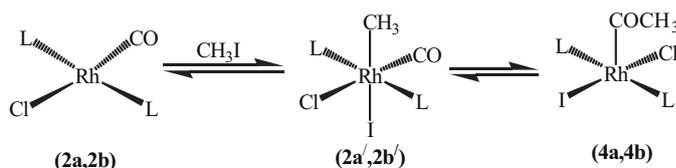
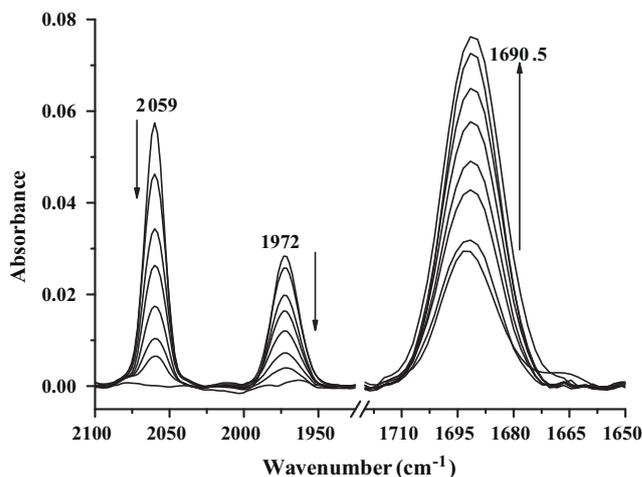
mol equivalents of ligands (**a**, **b**) to yield *trans*-[Rh(CO)Cl( $\eta^1$ -P-L) $_2$ ] (**2a**, **2b**) (Scheme 2). The synthesis and structural characterization of **2a** was already reported [14], however, **2b** is newly synthesized in this report. Elemental analyses and mass spectrometric results of the complexes support the expected molecular composition of **2a** and **2b**. The IR spectra of **2a** and **2b** exhibit single intense  $\nu(\text{CO})$  bands at 1970 and 1965  $\text{cm}^{-1}$  respectively, indicating the presence of terminal carbonyl groups. The  $^1\text{H}$  NMR spectrum of **2a** shows a characteristic phenylic multiplet in the region  $\delta$  6.85–7.91 ppm and methyl singlet at  $\delta$  3.68 ppm. However, **2b** shows the phenylic multiplet in the range  $\delta$  7.39–7.63 ppm, methylene and methyl singlet at around  $\delta$  4.72 and 3.18 ppm respectively. **2a** and **2b** show characteristic  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra with doublet at around  $\delta$  22.8 (d,  $J_{\text{P-Rh}} = 135$  Hz) and 24.6 (d,  $J_{\text{P-Rh}} = 128$  Hz) ppm respectively, which show downfield shift compared to the free ligands, indicating the formation of Rh-P bond. The appearance of almost similar shifts of  $\text{CH}_3$  and  $\text{CH}_2$  protons in  $^1\text{H}$  NMR spectra and the downfield shift of phosphorus in  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in the complexes compared to free ligands substantiate the formation of  $\eta^1$ -P coordinated complex. The  $^{13}\text{C}$  NMR spectra of **1a**, **1b**, **2a** and **2b** show characteristic resonances in the range  $\delta$  183.0–187.4 ppm respectively for the carbonyl carbons. The phenyl and other carbons in the complexes are found in their respective ranges.

### 3.2. Reactivity of **1a**, **1b**, **2a** and **2b** with $\text{CH}_3\text{I}$

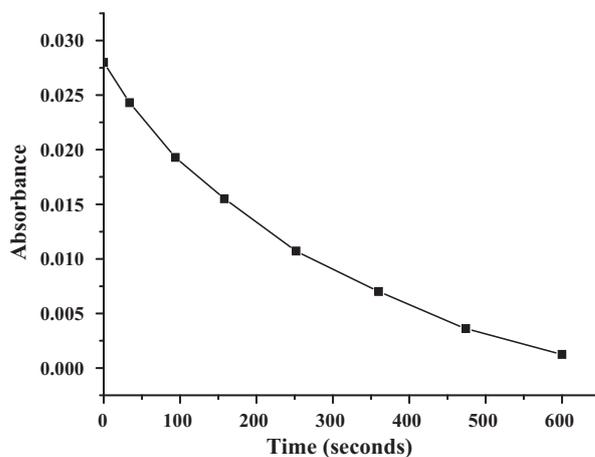
The complexes **1a**, **1b**, **2a** and **2b** undergo OA reactions with  $\text{CH}_3\text{I}$  followed by migratory insertion reaction to generate Rh(III)-acyl complexes of the type [RhCl(COCH $_3$ )]( $\eta^2$ -P,O-L) (**3a**, **3b**) and [RhCl(COCH $_3$ )]( $\eta^1$ -P-L) $_2$ ) (**4a**, **4b**) (Scheme 2). The IR spectra of the oxidized products show broad  $\nu(\text{CO})$  bands in the range 1690–1698  $\text{cm}^{-1}$  characteristic of acyl carbonyl groups (Table 1). The  $^1\text{H}$  NMR spectra of **3a**, **3b**, **4a** and **4b** display singlet resonances in the range 2.58–2.67 ppm suggesting the formation of  $-\text{OCCCH}_3$  group including other characteristic bands of the ligands. Similarly, the  $^{13}\text{C}$  NMR spectra of the OA adduct exhibit bands in the range 203–206 ppm due to the formation of  $-\text{COCH}_3$  group (Table 1).

Attempts to substantiate the structures of different rhodium(I) and rhodium(III) carbonyl complexes by X-ray crystal structure determination was not possible because no suitable crystals could be obtained after numerous attempts.

Kinetic measurements for the OA reaction of **1a**, **1b**, **2a** and **2b** with excess methyl iodide were carried out using IR spectroscopy by monitoring the changes in the lower  $\nu(\text{CO})$  bands. The reaction of **1a** and **1b** with methyl iodide leads smoothly to the acetyl product, however, when the reactions of **2a** and **2b** were performed with methyl iodide, a strong  $\nu(\text{CO})$  band at around 2058–2062  $\text{cm}^{-1}$  was observed in the IR spectrum in addition to the bands in **2a**, **4a** and **2b**, **4b**; which are consistent with the presence of intermediate methyl complexes **2a'** and **2b'** (Scheme 3). A typical series of IR spectra is shown in Fig. 2. When the complex **2a** reacts with  $\text{CH}_3\text{I}$  at 25  $^\circ\text{C}$ , immediately two new bands grow at around 1690 and 2059  $\text{cm}^{-1}$  along with the shifted parent  $\nu(\text{CO})$  band of **2a** at 1972  $\text{cm}^{-1}$ . As the reaction progresses, the bands around 1972 and 2059  $\text{cm}^{-1}$  decay and the band at 1690  $\text{cm}^{-1}$  grows continuously. Finally, the former two  $\nu(\text{CO})$  bands vanish and a new broad acyl  $\nu(\text{CO})$  band appears

**Scheme 3.** Reaction of **2a** and **2b** with  $\text{CH}_3\text{I}$ .**Fig. 2.** Series of IR spectra  $\{\nu(\text{CO})$  region} illustrating the reaction of **2a** with  $\text{CH}_3\text{I}$  at 25  $^\circ\text{C}$ . The arrows indicate the behaviour of each band as the reaction progresses.

at 1690.5  $\text{cm}^{-1}$ . Absorbance versus time plots for the decay of lower intensity  $\nu(\text{CO})$  bands at 1972  $\text{cm}^{-1}$  of **2a** is shown in Fig. 3. A linear fit of pseudo-first order was observed for the entire course of the reaction of  $\text{CH}_3\text{I}$  with the complex **2a** as is evidenced from the plot of  $\ln(A_0/A_t)$  versus time, where  $A_0$  and  $A_t$  are the absorbance at time  $t = 0$  and  $t$ , respectively (Fig. 4). The rate constants for the OA reaction of  $\text{CH}_3\text{I}$  towards **1a**, **1b**, **2a** and **2b** are  $3.51 \times 10^{-3}$ ,  $9.14 \times 10^{-4}$ ,  $1.12 \times 10^{-4}$  and  $9.44 \times 10^{-5} \text{ s}^{-1}$ , which varies as **1a** > **1b** > **2a** > **2b**. The observed values of the rate constants indicate that the rate of OA is higher in case of chelate  $\eta^2$ -P,O complexes than those of *trans*- $\eta^1$ -P complexes. This may be due to the presence of bulky  $\text{OCH}_3/\text{CH}_2\text{OCH}_3$  groups at the *ortho* position of one of the phenyl rings of the phosphine ligands which may sterically restrict the path of OA reaction of  $\text{CH}_3\text{I}$  to the Rh centre of **2a** and **2b**. However, such steric hindrance is absent in the chelate complexes (**1a** and **1b**) resulting in faster reaction kinetics.

**Fig. 3.** Kinetic plot of showing the decay of  $\nu(\text{CO})$  bands of **2a** during the reaction with neat  $\text{CH}_3\text{I}$  at room temperature ( $\sim 25$   $^\circ\text{C}$ ).

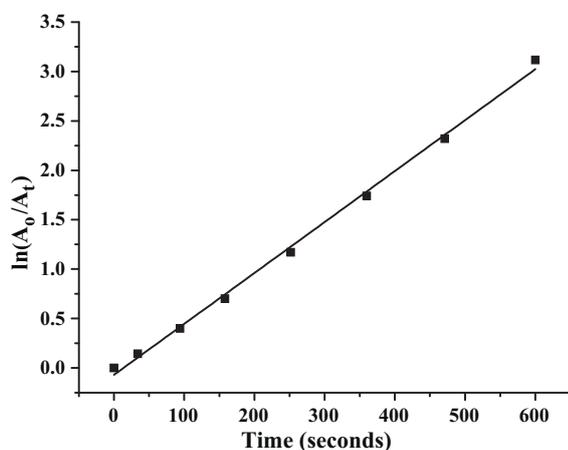
**Table 2**  
Results of methanol carbonylation.

Catalyst precursor	CO pressure at 25 °C (±1 bar)	Total conv. (%)	Acetic acid <sup>a</sup> (%)	Methyl acetate <sup>a</sup>	TOF <sup>b</sup> (h <sup>-1</sup> )
[Rh(CO) <sub>2</sub> I <sub>2</sub> ] <sup>-c</sup>	5	24.1	4.0	20.1	463
	10	41.4	12.3	29.1	796
	20	52.1	10.3	41.8	1000
<b>1a</b>	5	46.9	10.1	36.8	902
	10	68.8	26.1	42.7	1323
	20	94.0	62.1	31.9	1808
<b>1b</b>	5	45.8	17.7	28.1	881
	10	58.3	23.5	34.8	1121
	20	90.8	52.1	38.7	1747
<b>2a</b>	5	35.8	8.7	27.1	689
	10	50.2	21.3	28.9	966
	20	87.4	53.7	33.7	1681
<b>2b</b>	5	39.8	12.7	27.1	766
	10	52.3	25.1	27.2	1006
	20	86.5	50.0	36.5	1660

<sup>a</sup> Yield of methyl acetate and acetic acid were obtained from GC analyses after 1 h reaction time.<sup>b</sup> TOF = [amount of product (mol)]/[amount of catalyst (Rh mol)]/time (h).<sup>c</sup> Formed from added [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> under catalytic condition [15].

### 3.3. Carbonylation of methanol to acetic acid and ester using the complexes **1a**, **1b**, **2a** and **2b** as the catalyst precursors

The results of carbonylation of methanol to acetic acid and methyl acetate in the presence of **1a**, **1b**, **2a** and **2b** as catalyst precursors are shown in Table 2. The precursor complexes **1a**, **1b**, **2a** and **2b** show total conversion of CH<sub>3</sub>OH in the range 35.8–94.0% at 130 ± 2 °C under initial CO pressure 5–20 bar (at ~25 °C) for 1 h reaction time with corresponding TOF 689–1808 h<sup>-1</sup>. From Table 2 it can be noted that as the applied CO pressure increases from 5 to 20 bar for **1a**, total conversion increases from 46.9 to 94.0% with corresponding increase in TOF from 689 to 1808 h<sup>-1</sup>. Likewise, the complexes **1b**, **2a** and **2b** also show a similar increasing trend with the increase in CO pressure and maximum TOF of about 1747 (**1b**), 1681 (**2a**), and 1660 (**2b**) with corresponding conversions of 90.8, 87.4, and 86.5% have been obtained at 20 bar initial CO pressure (~25 °C). Under the similar experimental conditions, the well known precursor [Rh(CO)<sub>2</sub>I<sub>2</sub>]<sup>-</sup> generated *in situ* from [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> [15] shows lower TOF compared to **1a**, **1b**, **2a** and **2b**. Thus, the efficiency of the complexes depends on the nature of the ligands and follows the order **1a** > **1b** > **2a** > **2b** > [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>. The observed trend is also well supported by their kinetic experiments. The chelate complexes **1a** and **1b** undergo OA of methyl iodide with higher rate than those of *trans*-complexes **2a** and **2b**, and hence the former complexes show higher TOF compared to latter ones.

**Fig. 4.** ln(A<sub>0</sub>/A<sub>t</sub>) versus time plot for the OA reaction of **2a** with neat CH<sub>3</sub>I at ~25 °C.

## 4. Conclusions

Chelate and *trans*-complexes of the type [Rh(CO)Cl(L)](**1a**, **1b**) and [Rh(CO)Cl(L)<sub>2</sub>](**2a**, **2b**) respectively, have been synthesized and characterized, and the structure of the ligand **b** was determined by single crystal X-ray diffraction. The complexes undergo oxidative addition with CH<sub>3</sub>I to afford acyl Rh(III) complexes. The kinetic data for the OA reactions with CH<sub>3</sub>I indicate a first order reaction and also exhibit that the rate of OA for the chelate complexes **1a**, **1b** is higher than those of *trans*-complexes. The catalytic activities of **1a**, **1b**, **2a** and **2b** in carbonylation of methanol to produce acetic acid and its ester exhibit higher TOF (689–1808 h<sup>-1</sup>) than that of the well-known commercial species [Rh(CO)<sub>2</sub>I<sub>2</sub>]<sup>-</sup> (TOF = ~464–1000 h<sup>-1</sup>) under similar experimental conditions.

## Supplementary data

CCDC 795222 contains the supplementary crystallographic data for the ligand **b**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44 1223 336 033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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