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Dicarbonylrhodium(I) complexes of benzoylpyridine ligands: Synthesis, reactivity and catalytic carbonylation reaction

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ABSTRACT

The new complexes of the type $[Rh(CO)_2ClL]$ (**1a–c**), where L = 2-Benzoylpyridine (**a**), 3-Benzoylpyridine (**b**) and 4-Benzoylpyridine (**c**) have been synthesized and characterized. Oxidative addition (**OA**) of **1a–c** with CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ afford penta coordinated Rh(III) complexes, $[Rh(CO)(COR^n)ClXL]\{R^1 = -CH_3$ (**2a–c**), $R^2 = -C_2H_5$ (**3a–c**); X = I and $R^3 = -CH_2C_6H_5$ (**4a–c**); X = Cl}. Kinetic data for the reaction of **1a–c** with CH_3I indicate a pseudo-first order reaction. The **1a–c** exhibit high catalytic activity in the carbonylation of methanol to acetic acid and its ester and show a higher turn over number (**TON** = 1529–1748) than the well known commercial species $[Rh(CO)_2I_2]^-$ (**TON** = 1000) under the reaction conditions: temperature 130 ± 2 °C, pressure 30 ± 2 bar and time 1 h.

1. Introduction

The rhodium chemistry towards the activation of small molecules like CH_3I, H_2, I_2, etc., and their direct implications in various catalytic reactions such as carbonylation of alcohols, hydroformylation of alkenes, etc., are of great importance for academic as well as industrial interest [1–3]. The well known Monsanto's species $[Rh(CO)_2I_2]^-$ is used as catalyst precursor in the industrial production of acetic acid from methanol [4–6]. Efforts are given to synthesize new rhodium complexes to improve the catalytic efficacy by incorporating different types of ligands into its coordination sphere to improve the reaction parameters for the overall production of acetic acid [7–10]. Phosphorous, being a soft donor, is used for a long time in making metal complexes in lower oxidation states like rhodium(I) for catalytic studies [7–9]. In the recent time, N-containing ligands have also gained much attention in the field of synthetic organometallic chemistry due to their binding capabilities in both high and low oxidation states [11–18]. In contrast to the P-atom, N-atom has only σ-donor (and no π-acceptor) properties due to which it imparts more ionic character to the metal ligand bond. The N-containing ligands having strong σ-donor capabilities enhance the nucleophilicity of the Rh(I) centre which in turn increases the catalytic activity of the complexes [13–15]. However, the use of rhodium complexes containing N-donor ligands and their implications in catalytic carbonylation reaction have found only limited use [13–15,19–22]. With these precedents in mind and encouraged by effectiveness of N, O donor ligands in our earlier works [13–15,21,22], we believed it of interest to explore the ability of related rhodium(I) carbonyl complexes of N,O donor ligands in catalytic carbonylation reaction. Thus, in this paper we report the synthesis and reactivity of Rh(I) complexes containing three isomeric benzoylpyridine ligands and their behavior in catalytic carbonylation reaction.

2. Experimental

All solvents were distilled under N_2 prior to use. $RhCl_3 \cdot xH_2O$ was purchased from M/S Arrora Matthey Ltd., Kolkata, India. The ligands were purchased from M/S Aldrich, USA and used without further purification. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded in KBr discs and $CHCl_3$ on a Perkin-Elmer system 2000 FT-IR spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded at room temperature (r.t.) in $CDCl_3$ solution on a Bruker DPX-300 Spectrometer and chemical shifts were reported relative to $SiMe_4$ as internal standard. The carbonylation reactions of methanol were carried out in a Parr reactor (Model: Parr - 4592, USA) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID).

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2.1. Synthesis of starting material

The starting dimeric rhodium moiety $[Rh(CO)_2Cl]_2$ was prepared by passing CO gas over $RhCl_3{\cdot}xH_2O$ powder at 100 °C in the presence of moisture [23].

2.2. Synthesis of complexes $[Rh(CO)_2Cl(L)]$ (**1a–c**) Where, L = η^1-(N) coordinated, 2-Benzoylpyridine (**a**), 3-Benzoylpyridine (**b**) and 4-Benzoylpyridine (**c**)

$[Rh(CO)_2Cl]_2$ 0.0642 mmol (25 mg) was dissolved in dichloromethane (10 cm^3) and to this solution, a stoichiometric quantity (Rh:L = 1:1) 0.1285 mmol (23.5 mg) of a particular ligand was added. The reaction mixture was stirred at r.t. (~25 °C) for about 30 min and then the solvent was evaporated under reduced pressure to obtain yellow to brick-red color solid compounds which were washed with hexane and dried over silica gel in a desiccator.

*Analytical data for the complexes **1a–c***

1a: Yield: 95%; Anal. Found (calcd.) for $C_{14}H_9ClNO_3Rh$(%): C, 44.48 (44.51); H, 2.31 (2.38); N, 3.62 (3.70); selected IR data (KBr, cm^{-1}): 2081.4, 2007.8 [νCO], 1667 $[\nu CO]_{benzoyl}$, ^{1}H NMR data (δ in ppm): δ 9.02 (H-1, d, Py), δ 8.15–8.39 (3H, m, Py), δ 7.35–7.71 (5H, m, Ph), ^{13}C NMR data (δ in ppm): δ 127–155 (Ph/Py), δ 187, 183 ($>C=O$, CO_t).

1b: Yield: 93%; Anal. Found (calcd.) for $C_{14}H_9ClNO_3Rh$(%): C, 44.23 (44.51); H, 2.35 (2.38); N, 3.68 (3.70); selected IR data (KBr, cm^{-1}): 2086, 2009 [νCO], 1665 $[\nu CO]_{benzoyl}$, ^{1}H NMR data (δ in ppm): δ 9.08 (H-1, d, Py), δ 9.16 (H-4, s, Py), δ 8.41–8.82 (2H, m, Py), δ 7.32–7.76 (5H, m, Ph), ^{13}C NMR data (δ in ppm): δ 128–154 (Ph/Py), δ 187, 185 ($>C=O$, CO_t).

1c: Yield: 92%; Anal. Found (calcd.) for $C_{14}H_9ClNO_3Rh$(%): C, 44.28 (44.51); H, 2.31 (2.38); N, 3.65 (3.70); selected IR data (KBr, cm^{-1}): 2085.3, 2010 [νCO], 1666 $[\nu CO]_{benzoyl}$, ^{1}H NMR data (δ in ppm): δ 9.11 (H-1, H-4, d, Py), δ 8.11 (H-2, H-3, d, Py), δ 7.43–7.83 (5H, m, Ph), ^{13}C NMR data (δ in ppm): δ 123–152 (Ph/Py), δ 187, 182 ($>C=O$, CO_t).

2.3. Synthesis of complexes $[Rh(CO)(COR^n)ClX(L)]$, $R^1 = -CH_3$ (**2a–c**), $R^2 = -C_2H_5$ (**3a–c**); X = I and $R^3 = -CH_2C_6H_5$ (**4a–c**); X = Cl

$[Rh(CO)_2Cl(L)]$ (**1a–c**) 0.0529 mmol (20 mg) was dissolved in dichloromethane (10 cm^3). To this solution each of R^nX (6 cm^3) ($R^nX = CH_3I$, C_2H_5I and $C_6H_5CH_2Cl$) was added. The reaction mixture was then stirred at r.t. for about 7, 12 and 15 h for CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ respectively. The color of the solution changes from yellowish red to dark reddish brown and the solvent was removed and washed with diethyl ether and stored over silica gel in a desiccator.

*Analytical data for the complexes **2a–c**, **3a–c** and **4a–c***

2a: Yield: 91%; Anal. Found (calcd.) for $C_{15}H_{12}ClINO_3Rh$(%): C, 34.58 (34.66); H, 2.23 (2.31); N, 2.59 (2.69); selected IR data (KBr, cm^{-1}): 2076 [νCO], 1750 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.07 (H-1, d, Py), δ 8.09–8.25 (3H, m, Py), δ 7.33–7.75 (5H, m, Ph), δ 3.35 (CH_3, s), ^{13}C NMR data (δ in ppm): δ 126–156 (Ph/Py), δ 186, 184.4 ($>C=O$, CO_t), δ 207.1 (CO_{acyl}), δ 47 (CH_3).

2b: Yield: 94%; Anal. Found (calcd.) for $C_{15}H_{12}ClINO_3Rh$(%): C, 34.60 (34.66); H, 2.25 (2.31); N, 2.62 (2.69); selected IR data (KBr, cm^{-1}): 2063 [νCO], 1749.4 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.10 (H-1, d, Py), δ 9.16 (H-4, s, Py), δ 8.15–8.31 (2H, m, Py), δ 7.30–7.72 (5H, m, Ph), δ 3.27 (CH_3, s), ^{13}C NMR data (δ in ppm): δ 123–152 (Ph/Py), δ 188, 185.1 ($>C=O$, CO_t), δ 206.6 (CO_{acyl}), δ 45 (CH_3).

2c: Yield: 95%; Anal. Found (calcd.) for $C_{15}H_{12}ClINO_3Rh$(%): C, 34.58 (34.66); H, 2.22 (2.31); N, 2.58 (2.69); selected IR data (KBr, cm^{-1}): 2077 [νCO], 1752 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.13 (H-1, H-4, d, Py), δ 8.15 (H-2, H-3, d, Py), δ 7.47–7.82 (5H, m, Ph) δ 3.47 (CH_3, s), ^{13}C NMR data (δ in ppm): δ 124–151 (Ph/Py), δ 185, 185.9 ($>C=O$, CO_t), δ 204.8 (CO_{acyl}), δ 43 (CH_3).

3a: Yield: 95%; Anal. Found (calcd.) for $C_{16}H_{14}ClINO_3Rh$(%): C, 35.91 (36.00); H, 2.53 (2.62); N, 2.58 (2.62); selected IR data (KBr, cm^{-1}): 2054.8 [νCO], 1749.9 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.05 (H-1, d, Py), δ 8.45–8.68 (3H, m, Py), δ 7.45–7.71 (5H, m, Ph), δ 1.53 (CH_3, t), δ 2.51 (CH_2, q), ^{13}C NMR data (δ in ppm): δ 122–159 (Ph/Py), δ 185, 184.6 ($>C=O$, CO_t), δ 204.1 (CO_{acyl}), δ 22 (CH_3), δ 57 (CH_2).

3b: Yield: 93%; Anal. Found (calcd.) for $C_{16}H_{14}ClINO_3Rh$(%): C, 35.93 (36.00); H, 2.59 (2.62); N, 2.53 (2.62); selected IR data (KBr, cm^{-1}): 2050.6 [νCO], 1754.1 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.09 (H-1, d, Py), δ 9.07 (H-4, s, Py), δ 8.39–8.58 (2H, m, Py), δ 7.46–7.74 (5H, m, Ph), δ 1.68 (CH_3, t), δ 2.71 (CH_2, q), ^{13}C NMR data (δ in ppm): δ 125–160 (Ph/Py), δ 185, 186.4 ($>C=O$, CO_t), δ 203.6 (CO_{acyl}), δ 24 (CH_3), δ 61 (CH_2).

3c: Yield: 96%; Anal. Found (calcd.) for $C_{16}H_{14}ClINO_3Rh$(%): C, 35.90 (36.00); H, 2.53 (2.62); N, 2.53 (2.62); selected IR data (KBr, cm^{-1}): 2055.8 [νCO], 1746.1 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.10 (H-1, H-4, d, Py), δ 8.70 (H-2, H-3, d, Py), δ 7.45-7.59 (5H, m, Ph), δ 1.61 (CH_3, t), δ 2.35 (CH_2, q), ^{13}C NMR data (δ in ppm) δ 125–155 (Ph/Py), δ 186, 184.9 ($>C=O$, CO_t), δ 205.2 (CO_{acyl}), δ 23 (CH_3), δ 63 (CH_2).

4a: Yield: 94%; Anal. Found (calcd.) for $C_{21}H_{16}Cl_2NO_3Rh$(%): C, 49.91 (50.00); H, 3.09 (3.17); N, 2.72 (2.77); selected IR (KBr, cm^{-1}) data: 2071 [νCO], 1744 $[\nu CO]_{acyl}$ ^{1}H NMR data (δ in ppm): δ 9.07 (H-1, d, Py), δ 8.01–8.39 (3H, m, Py), δ 7.16–7.92 (10H, m, Ph), δ 4.20 (2H, $-CH_2$, m)$_{Bz}$ (Bz stands for $C_6H_5CH_2Cl$), ^{13}C NMR data (δ in ppm): δ 127–151 (Ph/Py), δ 187, 185.3 ($>C=O$, CO_t), δ 206.2 (CO_{acyl}), δ 60 (CH_2).

4b: Yield: 96%; Anal. Found (calcd.) for $C_{21}H_{16}Cl_2NO_3Rh$(%): C, 49.87 (50.00); H, 3.11 (3.17); N, 2.72 (2.77); selected IR (KBr, cm^{-1}) data: 2076 [νCO], 1746 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.09 (H-1, d, Py), δ 9.01 (H-4, s, Py), δ 8.08–8.29 (2H, m, Py), δ 7.36–8.00 (10H, m, Ph), δ 4.31 (2H, $-CH_2$, m)$_{Bz}$ (Bz stands for $C_6H_5CH_2Cl$), ^{13}C NMR data (δ in ppm): δ 122–151 (Ph/Py), δ 185, 184.2 ($>C=O$, CO_t), δ 205.6 (CO_{acyl}), δ 63 (CH_2).

4c: Yield: 95%; Anal. Found (calcd.) for $C_{21}H_{16}Cl_2NO_3Rh$(%): C, 49.95 (50.00); H, 3.13 (3.17); N, 2.73 (2.77); selected IR (KBr, cm^{-1}) data: 2070 [νCO], 1748 $[\nu CO]_{acyl}$, ^{1}H NMR data (δ in ppm): δ 9.12 (H-1, H-4, d, Py), δ 8.60 (H-2, H-3, d, Py), δ 7.49–8.12 (10H, m, Ph), δ 4.54 (2H, $-CH_2$, m)$_{Bz}$ (Bz stands for $C_6H_5CH_2Cl$), ^{13}C NMR data (δ in ppm): δ 126–151 (Ph/Py), δ 188, 186.5 ($>C=O$, CO_t), δ 206.4 (CO_{acyl}), δ 61 (CH_2).

2.4. Kinetic experiment

The kinetic experiments of **OA** reaction of complexes **1a–c** with neat CH_3I were monitored using FT-IR spectroscopy in a solution cell (CaF_2 windows, 1.0 mm path length). In order to obtain pseudo-first-order condition excess of CH_3I relative to metal complex was used. FT-IR spectra (4.0 cm^{-1} resolution) were scanned in the ν(CO) region (2200–1650 cm^{-1}) and saved at regular time interval using spectrum software. After completion of experiment, absorbance versus time data for the appropriate ν(CO) frequencies were extracted by subtracting the solvent spectrum and analyzed off line using OriginPro 7.5 software. Kinetic measurements were made by following the decay of lower frequency ν(CO) band of the complexes **1a–c** in the region 2040–1950 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.

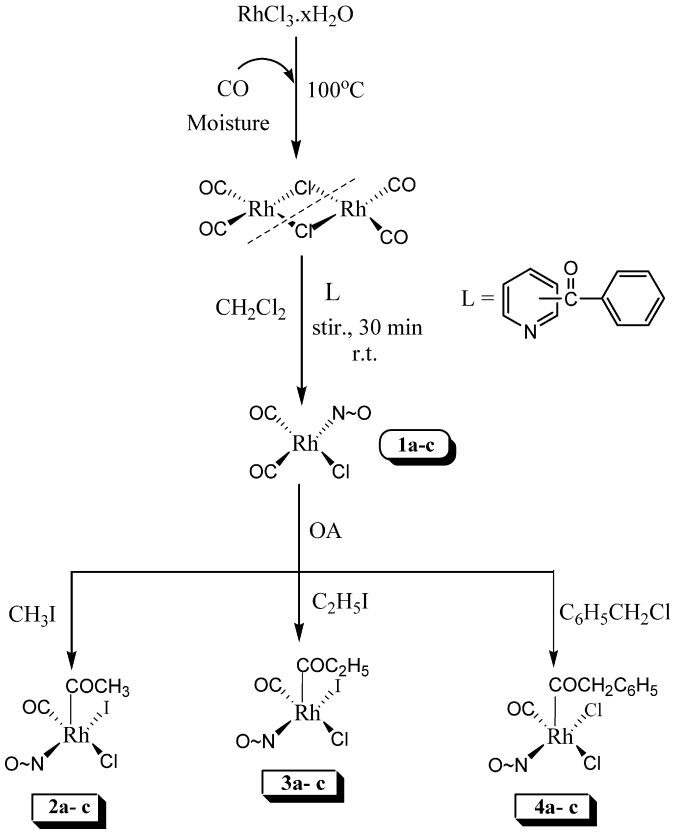
2.5. Carbonylation of methanol using *1a–c* as catalyst precursors

CH_3OH (0.099 mol, 4 cm^3), CH_3I (0.016 mol, 1 cm^3), H_2O (0.055 mol, 1 cm^3) and rhodium catalyst (0.0514 mmol) were taken into the reactor. The reactor was then purged with CO for about 5 min and then pressurized with CO gas (20 ± 1 bar) at 25 °C. The carbonylation reactions were carried out at 130 ± 2 °C for 1 h under CO pressure (30 ± 2 bar). The products were collected and analyzed by GC.

3. Results and discussion

3.1. Synthesis and characterization of Rh(I) complexes

The dimeric precursor $[Rh(CO)_2Cl]_2$ reacts with various benzoylpyridine ligands **a–c** in 1:2 mol ratio to afford the complexes of the type $[Rh(CO)_2ClL]$(**1a–c**) [Scheme 1]. The molecular composition of **1a–c** were well supported by elemental analysis data. The IR spectra of **1a–c** show two almost equally intense terminal ν(CO) bands in the range 2007–2086 cm^{-1} indicating two carbonyl groups are mutually *cis* to one another [21,22]. The ν(CO) bands of the benzoyl substituent appear almost in the same position as that of the corresponding free ligands **a–c** [ν(CO) in cm^{-1}: 1669(**a**), 1665(**b**), 1667(**c**)] and hence consistent with non coordination nature of the $\rangle C{=}O$ group of the ligands upon complexation. The ^{1}H NMR spectra of **1a–c** exhibit a doublet resonance in the range δ 9.02–9.11 ppm for H1 and multiplets in the range δ 7.32–8.83 ppm for the other protons of pyridine and benzene rings. The ^{1}H NMR spectra of the free ligands show a downfield shift when they involve in complex formation. These indicate that the coordination to the metal centre in **1a–c** takes place through N-donor site. The ^{13}C NMR spectra of **1a–c** show characteristic resonances of terminal carbonyl group in the range δ 182–185 ppm and multiplets in the region δ 123–155 ppm for carbon atoms of pyridine and benzene rings.



Scheme 1. Synthesis of Rh(I) and Rh(III) complexes of benzoylpyridine ligands.

3.2. Reactivity of *1a–c* towards various electrophiles

Carbonylation of methanol to acetic acid is considered as one of the most important industrial process utilizing homogeneous rhodium metal based catalyst. In this context, oxidative addition of alkyl halide with Rh complexes is very important reaction as it is the key step in the carbonylation reaction [2,3,13–15]. Therefore, **OA** of various electrophiles were evaluated.

The **1a–c** undergo **OA** reactions with CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ followed by migratory insertion reaction to afford five coordinate Rh(III) complexes $[Rh(CO)(COR^n)ClXL]\{R^1 = -CH_3$ (**2a–c**), $R^2 = -C_2H_5$ (**3a–c**); X = I and $R^3 = -CH_2C_6H_5$ (**4a–c**); X = Cl}. The IR spectra of the oxidized products **2a–c**, **3a–c** and **4a–c** show a single characteristics ν(CO) absorption in the range 2050–2079 cm^{-1} and a broad ν(CO) band in the range 1743–1755 cm^{-1}, indicative of Rh(III)-acyl complex, resulting from facile migratory insertion in **1a–c** after **OA** of various electrophiles. The ^{1}H NMR spectra of **2a–c** show a singlet in the region δ 3.35–3.50 ppm indicating the formation of -$COCH_3$ group including other characteristic bands of the ligands. In a similar manner, the **3a–c** show a triplet at around δ 1.53–1.68 ppm for methyl and a quartet in the region δ 2.35–2.72 ppm for methylene protons of the ethyl group. In case of complexes **4a–c**, the singlet resonances corresponding to methylene protons of $-OCH_2C_6H_5$ appears in the range δ 4.20–4.55 ppm. The presence of electron withdrawing phenyl group deshields the $-OCH_2-$ proton resonances and the peaks are obtained downfield [24]. The ^{13}C NMR spectra of **2a–c**, **3a–c** and **4a–c** exhibit two carbonyl signals in the range δ 184–188 ppm for terminal carbonyl group and a poorly resolved slightly broad signal in the range δ 203–208 ppm for acyl carbonyl group along with other characteristic peaks correspond to different carbons present in the complexes.

Depending on the stereochemical arrangement of the ligands and alkyl halides, several hexa-coordinated alkyl intermediates are possible during **OA** reactions. As most of the penta coordinated carbonyl-Rh(III)-acyl complexes reported are square pyramidal in nature [24–26], it is likely that all the acyl complexes would also have a similar geometry. The presence of a single high terminal ν(CO) value is consistent with CO group *trans* to a weak trans influencing chloride [25]. On the other hand, in view of high *trans* influencing nature, the acyl group favours apical position *trans* to the vacant coordination site [26–28]. Thus, the most probable structures of the acyl complexes are presented in Scheme 1.

The kinetic experiments of **OA** reaction of **1a–c** with CH_3I were monitored using FT-IR spectroscopy by following the decay of lower frequency ν(CO) band of **1a–c** in the region 2010–2007 cm^{-1}. A typical series of spectra of **1c** when reacts with CH_3I at 25 °C are shown in Fig. 1, in which the bands due to **1c** changes and that due to **2c** grow until equilibrium is attained. The two terminal ν(CO) bands of **1c** at 2085.3 and 2010 cm^{-1} were replaced by the terminal and acyl ν(CO) bands of **2c** at 2077 and 1752 cm^{-1}, respectively. The spectrum of the product **2c**, exhibits quite broad absorptions with shoulders, which are due to the presence of mixtures of isomers [14,24,28]. Absorbance versus time plots for the decay of lower intensity ν(CO) band (2010 cm^{-1}) of **1c** is shown in Fig. 2. A linear fit of pseudo-first-order was observed for the entire course of the reaction of CH_3I with **1a–c** as is evidenced from the plot of $\ln(A_0/A_t)$ versus time t. (Fig. 3). From the slope of the plot, the rate constants were calculated and found to be 3.56×10^{-4} s^{-1}, 2.03×10^{-4} s^{-1} and 0.719×10^{-4} s^{-1}, respectively for **1a**, **1b** and **1c**. The values of

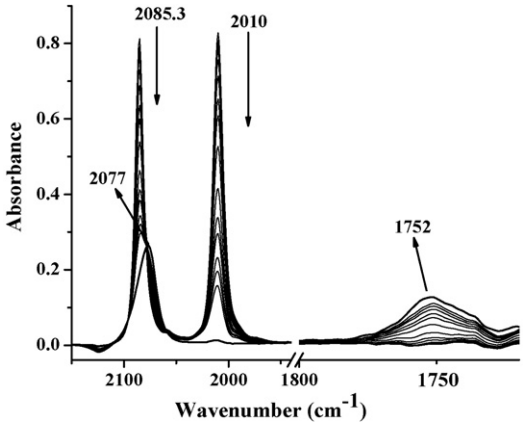


Fig. 1. Series of IR spectra {ν(CO) region} illustrating the reaction of **1c** with neat CH_3I at r.t. (~25 °C). The arrows indicate the behavior of each band as the reaction progresses.

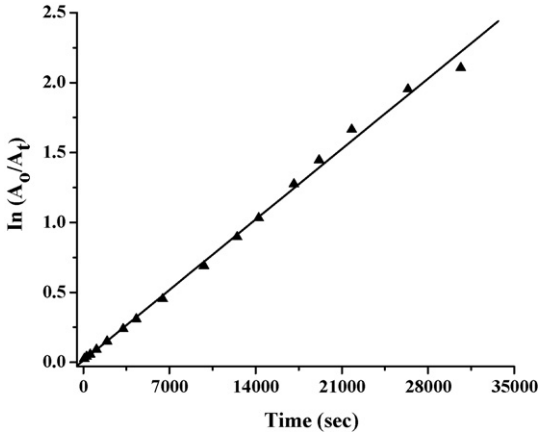


Fig. 3. Plot of $\ln(A_0/A_t)$ versus time for the **OA** reaction of **1c** with neat CH_3I at r.t. (~25 °C).

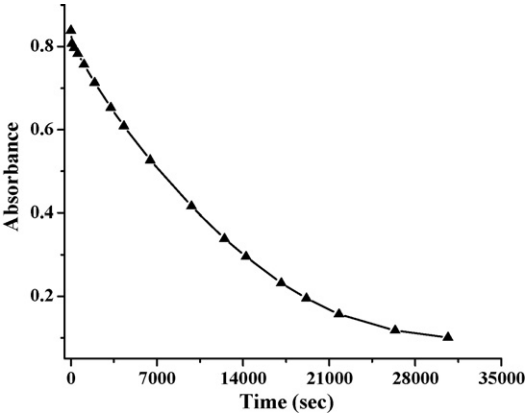
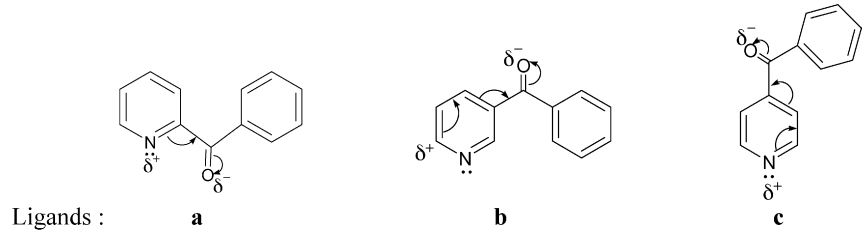


Fig. 2. Kinetic plot showing the decay of ν(CO) bands of **1c** during the reaction of **1c** with neat CH_3I at r.t. (~25 °C).

these rate constants clearly indicate that the rate of **OA** of CH_3I with **1a–c** follows the order **1a** > **1b** > **1c**. The observed trend of **OA** may be explained in terms of nucleophilicity of the metal centre which in turn depends on the electron donating capacity of the ligand around the coordination sphere. The electron donating power of the N-atom (i.e. basicity) in the ligands is affected by the presence of electron withdrawing –CO–Ph group as shown in Scheme 2. The presence of –CO–Ph group at the 2- and 4-positions of the pyridine ring in their corresponding complexes **1a** and **1c** should reduced the basicity of N-atom and consequently show higher ν(CO) frequencies and hence should have slower rate of **OA**. Thus, to explain the observed fact one must consider some other factors like neighboring group effects, field effects, etc. The appearance of lower ν(CO) frequency of **1a** over **1b** may be due to some short of interaction between the metal centre and the benzoyl group at the *ortho* position of the ligands and hence increased in nucleophilicity at the metal centre [7,29]. From the observed trend of ν(CO) frequencies of **1a–c** (**1c** > **1b** > **1a**), it is clearly observed that **1a** is highly nucleophilic and more prone towards the attack of electrophiles and shows high reactivity towards **OA**. Therefore, the rate of **OA** of CH_3I with **1a–c** substantiates the order as mentioned above.

3.3. Carbonylation of methanol to acetic acid and its ester using *1a–c* as the catalyst precursor

The results of carbonylation of methanol to acetic acid and its ester in the presence of **1a–c** and $[Rh(CO)_2Cl]_2$ as catalyst precursors are shown in Table 1. The precursor **1a–c** show a total conversion of 79.5, 90.9 and 80.5% of CH_3OH at 130 ± 2 °C and 30 ± 2 bar CO pressure with corresponding **TON** of 1529, 1748 and 1548. Under the same experimental condition, the well known catalyst precursor $[Rh(CO)_2I_2]^-$ generated *in situ* from $[Rh(CO)_2Cl]_2$, show lower **TON** 1000 only with corresponding conversion of about 52.1%. The effect of different ligands on the efficacy of catalytic carbonylation reaction is clearly reflected and follows the order **1b** > **1c** > **1a** > $[Rh(CO)_2I_2]^-$. It is well known that higher the rate of **OA** higher is the catalytic activity. However, the observed trend in activities among **1a–c** towards catalytic carbonylation reaction can not be explained by the observed trend of the rate of **OA**. The lower activity of **1a** compared to **1b** and **1c** may be due to the steric effect caused by the benzoyl substituent at 2-position of pyridine ring [7,14,29] and thus the steric effect of substituent plays a dominating role over electronic effect. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals and at the end of the catalytic reaction, multiples ν(CO) bands are obtained that matched well with the ν(CO) values of solution containing a mixture of the parent Rh(I) carbonyl complexes **1a–c** and Rh(III) acyl complexes **2a–c**. Thus, it may be inferred that the ligands remained bound to the metal centre throughout the entire course of the catalytic reactions.



Scheme 2. Effect of electron withdrawing benzoyl group on the electron donating capacity of N-donor site of the benzoylpyridine ligands.

Table 1
Results of carbonylation of methanol.

Catalysts precursor	Time (h)	Acetic acid[a] (%)	Methyl acetate[a] (%)	Total conversion (%)	**TON**[b]
$[Rh(CO)_2I_2]^-$[c]	1	10.3	41.8	52.1	1000
1a	1	32.3	47.2	79.5	1529
1b	1	58.8	32.1	90.9	1748
1c	1	46.3	34.2	80.5	1548

[a] Yield of methyl acetate and acetic acid were obtained from GC analyses.
[b] **TON** = [amount of product (mol)]/[amount of catalysts (Rh mol)].
[c] Formed from added $[Rh(CO)_2Cl]_2$ under catalytic condition.

4. Conclusions

The three new complexes **1a–c** have been synthesized and characterized. The **1a–c** undergo **OA** with electrophiles like CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ to give oxidized Rh(III) complexes **2a–c**, **3a–c** and **4a–c**. The kinetics study of **1a–c** with CH_3I follows pseudo-first order reaction. The **1a–c** exhibit high catalytic activity in the carbonylation of methanol to acetic acid and its ester and show a higher **TON** (1529–1748) than the well known Monsanto's species $[Rh(CO)_2I_2]^-$ (**TON** = 1000).

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