Oxidative addition reaction of rhodium(I) carbonyl complexes of the pyridine-aldehyde ligands and their catalytic activity in carbonylation reaction

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Abstract

Rhodium(I) carbonyl complexes $[Rh(CO)_2ClL]$ (**1**) where L = Py-2-CHO (**a**), Py-3-CHO (**b**) and Py-4-CHO (**c**) have been synthesized and characterized by elemental analyses, IR, ^1H and ^{13}C NMR spectroscopy. The complexes **1** undergo oxidative addition reactions with different types of electrophiles such as CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2 to yield $[Rh(CO)(COCH_3)ClIL]$ (**2**), $[Rh(CO)(COC_2H_5)ClIL]$ (**3**), $[Rh(CO)(COCH_2C_6H_5)Cl_2L]$ (**4**) and $[Rh(CO)ClI_2L]$ (**5**) complexes, respectively. The kinetic study of the complexes **1** with CH_3I reveals a two-stage kinetics and the second-stage reactions are faster than that of the first stage by about 80–100 times. The rate of reaction of **1a** is higher than that of **1b** and **1c**. The catalytic activity of complexes **1** in carbonylation of methanol, in general, is higher (TON 800 – 1250) than that of the well-known species $[Rh(CO)_2I_2]^-$ (TON 650).
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Keywords: Rhodium(I) carbonyl complexes; Pyridine-aldehyde ligands; Oxidative addition; Kinetic study; Catalytic study

1. Introduction

The oxidative addition (OA) reaction is of great importance in inorganic and organometallic chemistry because of their application in carbonylation of alcohols, hydroformylation of alkenes, etc. [1–6]. The most representative example is the carbonylation of methanol to acetic acid [7–12] where the OA reaction of CH_3I with *cis*-$[Rh(CO)_2I_2]^-$ is the rate-determining step. Nucleophilicity on the metal center plays an important role on the rate of OA reaction which can be increased by increasing electron density on the metal center. Attempts are being made to modify the existing industrial catalytic species $[Rh(CO)_2I_2]^-$ for the enhancement of its activity by introducing electron-donating ligands [13–18]. Literature survey reveals that rhodium(I) complexes containing Py-2-CHO ligand have been used as active catalyst for the

transfer of hydrogen from isopropanol to acetophenone [19]. As a part of our work [20–25], i.e. the effects of different types of ligands on rhodium-catalyzed carbonylation of methanol, we report here the synthesis of rhodium(I) complexes containing Py-2-CHO, Py-3-CHO and Py-4-CHO ligands and their oxidative reactivity towards different electrophiles such as CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2. The kinetic study of OA reactions of complexes **1a**–**1c** with CH_3I and the catalytic activity of the complexes on the carbonylation of methanol are also evaluated.

2. Experimental

All the solvents used were distilled under N_2 prior to use. Elemental analyses were done on a Perkin-Elmer 2400 elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded using a Perkin-Elmer 2000 spectrophotometer in $CHCl_3$ and KBr discs. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 MHz spectrometer, and the ^1H and ^{13}C

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chemical shifts are quoted relative to SiMe$_4$ as an internal standard in CDCl$_3$. The carbonylation of methanol was carried out in a 150-cm^3 Teflon-coated pressure reactor (HR-100 Berghof, Germany) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID). RhCl$_3$·3H$_2$O was purchased from M/S Arrora Matthey Ltd., Kolkata. All the ligands were purchased from Aldrich, USA, and used as received.

2.1. Starting material

[Rh(CO)$_2$Cl]$_2$ was prepared by passing CO gas over RhCl$_3$·3H$_2$O powder at 100 °C in the presence of water [26].

2.1.1. Synthesis of the complexes [Rh(CO)$_2$ClL] (**1**), L = Py-2-CHO (**a**), Py-3-CHO (**b**) and Py-4-CHO (**c**)

[Rh(CO)$_2$Cl]$_2$ (0.0257 mmol) was dissolved in dichloromethane (10 cm^3) and to this 0.0514 mmol of the respective ligands were added. The reaction mixture was stirred at room temperature (r.t.) for about 10 min and the solvent was evaporated under vacuum. The yellowish-red color compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator.

Analytical data for the complexes **1a**–**1c** are as follows.

1a: Yield: 92%; Anal. found (calcd.) for C$_8$H$_5$ClNO$_3$Rh (%): C, 31.83 (31.87); H, 1.61 (1.66); N, 4.60 (4.65); selected IR data (CHCl$_3$): 2088, 2015 [ν(CO), cm^{-1}], 1716 [ν(CHO), cm^{-1}].

1b: Yield: 95%; Anal. found (calcd.) for C$_8$H$_5$ClNO$_3$Rh (%): C, 31.82 (31.87); H, 1.64 (1.66); N, 4.62 (4.65); selected IR data (CHCl$_3$): 2095, 2023 [ν(CO), cm^{-1}], 1714 [ν(CHO), cm^{-1}].

1c: Yield: 96%; Anal. found (calcd.) for C$_8$H$_5$ClNO$_3$Rh (%): C, 31.83 (31.87); H, 1.60 (1.66); N, 4.63 (4.65); selected IR data (CHCl$_3$): 2087, 2012 [ν(CO), cm^{-1}], 1717 [ν(CHO), cm^{-1}].

2.1.2. Synthesis of [Rh(CO)(COR)ClXL] (R = CH$_3$, X = I (**2**); R = C$_2$H$_5$, X = I (**3**); R = C$_6$H$_5$CH$_2$, X = Cl (**4**))

[Rh(CO)$_2$ClL] (0.332 mmol) was dissolved in dichloromethane (15 cm^3) and RX (5 cm^3) (RX = CH$_3$I, C$_2$H$_5$I, C$_6$H$_5$CH$_2$Cl) was added to it. The reaction mixture was then stirred at r.t. for about 2, 4 and 6 h for CH$_3$I, C$_2$H$_5$I and C$_6$H$_5$CH$_2$Cl, respectively. The color of the solution changed from yellowish-red to 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.

Analytical data for the complexes **2a**–**2c**, **3a**–**3c** and **4a**–**4c** are as follows.

2a: Yield: 92%; Anal. found (calcd.) for C$_9$H$_8$ClINO$_3$Rh (%): C, 24.35 (24.38); H, 1.75 (1.80); N, 3.14 (3.16); selected IR data (CHCl$_3$): 2071 [ν(CO), cm^{-1}], 1709 [ν(COO), cm^{-1}].

2b: Yield 94%; Anal. found (calcd.) for C$_9$H$_8$ClINO$_3$Rh (%): C, 24.31 (24.38); H, 1.72 (1.80); N, 3.11 (3.16); se-

lected IR data (CHCl$_3$): 2075 [ν(CO), cm^{-1}], 1710 [ν(COO), cm^{-1}].

2c: Yield: 95%; Anal. found (calcd.) for C$_9$H$_8$ClINO$_3$Rh (%): C, 24.33 (24.38); H, 1.75 (1.80); N, 3.17 (3.16); selected IR data (CHCl$_3$): 2077 [ν(CO), cm^{-1}], 1718 [ν(COO), cm^{-1}].

3a: Yield: 95%; Anal. found (calcd.) for C$_{10}$H$_{10}$ClINO$_3$Rh (%): C, 26.23 (26.26); H, 2.20 (2.19); N, 3.09 (3.06); selected IR data (KBr): 2065 [ν(CO), cm^{-1}], 1703 [ν(COO), cm^{-1}].

3b: Yield: 93%; Anal. found (calcd.) for C$_{10}$H$_{10}$ClINO$_3$Rh (%): C, 26.28 (26.26); H, 2.17 (2.19); N, 3.07 (3.06); selected IR data (KBr): 2072 [ν(CO), cm^{-1}], 1709 [ν(COO), cm^{-1}].

3c: Yield: 95%; Anal. found (calcd.) for C$_{10}$H$_{10}$ClINO$_3$Rh (%): C, 26.22 (26.26); H, 2.22 (2.19); N, 3.02 (3.06); selected IR data (KBr): 2072 [ν(CO), cm^{-1}], 1710 [ν(COO), cm^{-1}].

4a: Yield: 95%; Anal. found (calcd.) for C$_{15}$H$_{12}$Cl$_2$NO$_3$Rh (%): C, 42.11 (42.09); H, 2.85 (2.80); N, 3.26 (3.27); selected IR data (KBr): 2079 [ν(CO), cm^{-1}], 1657 [ν(COO), cm^{-1}].

4b: Yield: 94%; Anal. found (calcd.) for C$_{15}$H$_{12}$Cl$_2$NO$_3$Rh (%): C, 42.14 (42.09); H, 2.82 (2.80); N, 3.22 (3.27); selected IR data (KBr): 2045 [ν(CO), cm^{-1}], 1701 [ν(COO), cm^{-1}].

4c: Yield: 96%; Anal. found (calcd.) for C$_{15}$H$_{12}$Cl$_2$NO$_3$Rh (%): C, 42.12 (42.09); H, 2.84 (2.80); N, 3.232 (3.27); selected IR data (KBr): 2047 [ν(CO), cm^{-1}], 1714 [ν(COO), cm^{-1}].

2.1.3. Synthesis of [Rh(CO)ClI$_2$L] (**5**)

[Rh(CO)$_2$ClL] ((0.430 mmol) was dissolved in dichloromethane (15 cm^3) and to this solution, 0.510 mmol of I$_2$ was added. The reaction mixture was stirred at r.t. for about 4 h and the solvent was evaporated under vacuum. The brown color compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator.

Analytical data for the complexes **5a**–**5c** are as follows.

5a: Yield: 95%; Anal. found (calcd.) for C$_7$H$_5$ClI$_2$NO$_2$Rh (%): C, 15.90 (15.95); H, 0.91 (0.95); N, 2.61 (2.66); selected IR data (KBr): 2075 [ν(CO), cm^{-1}], 1707 [ν(CHO), cm^{-1}].

5b: Yield: 93%; Anal. found (calcd.) for C$_7$H$_5$ClI$_2$NO$_2$Rh (%): C, 15.92 (15.95); H, 0.91 (0.95); N, 2.63 (2.66); selected IR data (KBr): 2077 [ν(CO), cm^{-1}], 1696 [ν(CHO), cm^{-1}].

5c: Yield: 94%; Anal. found. (calcd.) for C$_7$H$_5$ClI$_2$NO$_2$Rh (%): C, 15.96 (15.95); H, 0.93 (0.95); N, 2.68 (2.66); selected IR data (KBr): 2088 [ν(CO), cm^{-1}], 1714 [ν(CHO), cm^{-1}].

2.2. Kinetic experiment

The kinetic experiments of OA reactions of complexes **1a**–**1c** with CH$_3$I were monitored by using IR spectroscopy in a solution cell (1.0 mm path length). Ten milligrams of complexes **1a**–**1c** were added to 1 cm^3 of neat CH$_3$I at r.t. An

aliquot of the reaction mixture was transferred by a syringe into the IR cell. Then kinetic measurements were made by monitoring the simultaneous decay of lower energy ν(CO) band of complexes **1a**–**1c** in the range 2010–2025 cm^{-1} and increasing the acyl ν(CO) band in the range 1705–1720 cm^{-1} of [Rh(CO)(COCH$_3$)ClIL]. A series of spectra were taken at a regular time intervals.

2.3. Carbonylation of methanol using [Rh(CO)$_2$ClL], L = Py-2-CHO, Py-3-CHO and Py-4-CHO as catalyst precursors

In the catalytic reactor a mixture of methanol (0.099 mol, 4 cm^3), CH$_3$I (0.016 mol, 1 cm^3), H$_2$O (0.055 mol, 1 cm^3) and complexes **1** (0.054 mmol) were placed. The reactor was then purged with CO for about 5 min and then pressurized with CO gas (20 bar at r.t., 0.080 mol). The carbonylation reactions were carried out at 130 ± 2 °C for 1 h. The products were collected and analyzed by GC.

3. Results and discussion

3.1. Synthesis and characterization of [Rh(CO)$_2$ClL] (1)

The dimeric complex [Rh(CO)$_2$Cl]$_2$ undergoes a bridge splitting reaction with two molar equivalent of the pyridine-aldehyde ligands to give the complex of the type [Rh(CO)$_2$ClL] (**1**), where L = Py-2-CHO (**a**), Py-3-CHO (**b**), Py-4-CHO (**c**). The IR spectra of the complexes **1a**–**1c** exhibits two equally intense ν(CO) bands in the range 2012–2095 cm^{-1} indicating *cis* disposition of the two terminal carbonyl groups [27–29]. ^{1}H NMR spectra of the complexes **1a**–**1b** exhibit a doublet in the region δ 8.93–8.98 ppm for H1 and a multiplet in the region δ 7.19–7.73 ppm and δ 7.68–8.45 ppm for H2 and H3 protons, respectively (Table 1) of the pyridine. The complex **1c** shows a doublet of doublet in the range δ 7.83–8.97 ppm for H1 and H2 of the pyridine. The complexes **1a**–**1c** exhibit a singlet in the region δ 10.07–11.05 ppm for the substituted aldehydic proton of the pyridine. ^{13}C NMR spectra of the complexes **1a**–**1c** show characteristic resonances of terminal carbonyl

CO in the range δ 180–188 ppm, aldehydic CO in the range δ 192–196 ppm and pyridine carbon in the range δ 150–159 ppm, δ 125–127 ppm, δ 135–142 ppm for C2, C3 and C4, respectively (Table 1).

3.2. Reactivity of the [Rh(CO)$_2$ClL] complexes

The complexes **1a**–**1c** are coordinatively unsaturated [30] and undergo OA reaction with different types of electrophiles such as CH$_3$I, C$_2$H$_5$I, C$_6$H$_5$CH$_2$Cl and I$_2$. The alkyl and halo groups can occupy coordination sites *trans*- or *cis*- to each other depending upon the stereochemical requirement. Thus, there may be several possible hexa-coordinated intermediates which will undergo alkyl migratory insertion reaction to yield final acyl products (Scheme 1). The OA of CH$_3$I with complexes **1** gives five-coordinated rhodium(III) acyl complexes of the type [Rh(CO)(COCH$_3$)ClIL] (**2**) which are probably formed through unisolable hexa-coordinated intermediates. The IR spectra of the complexes **2a**–**2c** show two different types of ν(CO) bands in the range 2070–2080 and 1700–1720 cm^{-1} attributable to terminal and acyl carbonyl groups, respectively [2,20–25]. The higher values of the terminal ν(CO) bands indicate the formation of the oxidized products. As most of the five-coordinated carbonyl-Rh(III)-acyl complexes reported are square-pyramidal in nature [31–33], it is likely that the acyl complexes **2a**–**2c** 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 [31]. On the other hand, the high *trans* influencing nature of the acetyl group favors strong *trans* directing iodine in its *trans* position [31,32]. Therefore, the most probable structure of the acyl complex (**2a**–**2c**) is represented by (**b'**) (Scheme 1). Chauby et al. [34] reported that cationic rhodium(III) complex in general show much higher value of ν(CO) bands for, e.g. 2118 and 2087 cm^{-1} in [Cp*Rh(CO)$_2$Me]$^+$, therefore, it is probable that the acyl complexes reported in this communication are not cationic in character.

^{1}H NMR spectra of the complexes **2a**–**2c** show a singlet in the region δ 2.67–3.44 ppm (Table 1) indicating the formation of acyl group. ^{13}C NMR spectra of the complexes of the type [Rh(CO)(COCH$_3$)ClIL] show five different types of characteristic resonances: they are terminal carbonyl CO in

Table 1
NMR (^{1}H, ^{13}C) data of the complexes

Complex/ligands	^{1}H NMR δ (ppm)					^{13}C NMR δ (ppm)						
	H$_1$	H$_2$	H$_3$	CHO	CH$_3$	C-2	C-3	C-4	CO	CHO	(CO)$_{acyl}$	CH$_3$
a	8.82 (d)	7.60–7.30 (m)	7.98–7.92 (m)	10.09	–	151	120	136	–	192	–	–
b	8.43 (d)	7.35–7.26 (m)	7.54–7.51 (m)	9.49	–	150	120	135		192	–	–
c	8.90 (d)	7.75–7.47 (m)	–	10.12	–	150	121	140		190	–	–
1a	8.93 (d)	7.67–7.19 (m)	7.88–7.68 (m)	11.05	–	150	125	135	180	196	–	–
1b	8.98 (d)	7.73–7.69 (m)	8.45–8.37 (m)	10.12	–	159	127	140	182	193	–	–
1c	8.97 (d)	7.85–7.83 (m)	–	10.07	–	153	125	142	188	192	–	–
2a	9.62(d)	7.92–7.19 (m)	8.32–8.19 (m)	10.04	2.67	153	129	139	182	194	206	52
2b	8.66 (d)	7.49–7.45 (m)	7.65–7.62 (m)	10.06	2.92	160	124	136	187	190	205	48
2c	9.01(d)	8.89 (d)	–	10.03	3.44	155	130	145	188	195	206	55

Scheme 1.
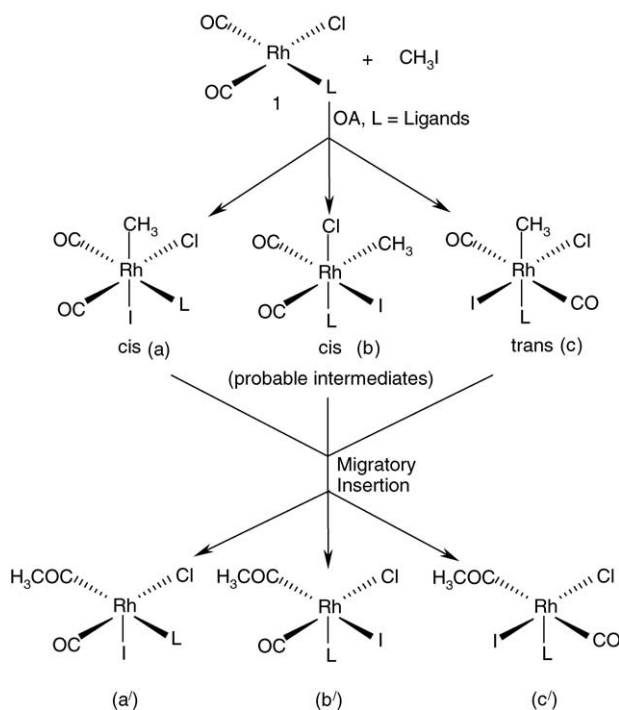
the range δ 182–188 ppm, aldehydic CO at δ 190–195 ppm, acyl CO at δ 205–206 ppm, methyl carbon in the range δ 48–55 ppm and pyridine carbon in the range δ 153–160 ppm, δ 124–130 ppm and δ 136–145 ppm for C2, C3 and C4, respectively. Similarly, complexes **1a–1c** undergo OA reactions with C_2H_5I exhibiting five-coordinated rhodium(III) acyl species $[Rh(CO)(COC_2H_5)ClIL]$ (**3**). The complexes **3a–3c** show characteristic $\nu(CO)$ bands for the terminal and acyl group in the range 2065–2072 and 1703–1710 cm^{-1}, respectively. The OA reactions with $C_6H_5CH_2Cl$ also produce a similar type of complexes $[Rh(CO)(COCH_2C_6H_5)Cl_2L]$ (**4**) which exhibit two different types of $\nu(CO)$ bands in the range 2047–2079 and 1657–1714 cm^{-1} corresponding to terminal and acyl carbonyl group. I_2 reacts oxidatively with complexes **1a–1c** to form the complexes $[Rh(CO)ClLI_2]$ (**5**) which exhibit only one terminal characteristic $\nu(CO)$ band of rhodium(III) complex in the region 2075–2088 cm^{-1}. Due to solubility problem, the NMR spectra of the complexes **3–5** were not possible to determine.

3.3. Kinetic study of OA reaction of the complexes 1 with CH₃I

The OA reaction of alkyl halide to the metal center is the key rate-determining step in the metal complex-catalyzed carbonylation of alcohol [16,20–25,35,36]. The oxidative reactivity of the metal complexes depends on the nucleophilicity of the metal center, which in turn depends upon the steric and electronic characteristics of the ligand. It is widely accepted that the OA reaction of CH₃I proceeds through two-step mechanism involving nucleophilic attack of the metal

center at the methyl carbon to displace iodide and form a metal–carbon bond and subsequently the iodide forms a co-ordination bond with the metal to form hexa-coordinated intermediate. Depending upon the stereochemical requirement of the intermediate complex, the alkyl and iodide ligands can be placed mutually *cis* or *trans* in the intermediate [34]. In order to understand the steric, electronic and the positional effects of the substituent at the pyridine ligand on the OA reactions of CH₃I with the complexes **1a–1c**, a kinetic study was carried out.

The reaction kinetics was monitored by following the simultaneous decay of the $\nu(CO)$ absorption (lower value) in the region 2010–2025 cm^{-1} for the complexes **1a–1c** and the formation of acyl $\nu(CO)$ in the region 1705–1720 cm^{-1} for the complexes **2a–2c**. During the course of the OA reactions, a series of IR spectra were recorded in a definite time intervals. Fig. 1 shows a plot of decrease in intensity of the terminal $\nu(CO)$ bands for complexes **1a–1c** against time. From the plot, it has been observed that for all the complexes **1a–1c** the OA reactions follow a two-stage kinetics, an initial slow step followed by a faster one till the end of reaction. In case of complex **1a**, the slow step proceeds up to a period of about 15 min and thereafter proceeds exponentially. However, for complexes **1b** and **1c** this slow step continues up to a period of about 310 and 295 min, respectively, and then proceeds in an exponential manner. The observed two-stage kinetics may be due to an initial equilibrium between the parent complex and a hexa coordinate unisolable Rh(III) alkyl intermediate (Scheme 1). It is worth to mention here that a similar type of kinetics was also observed from the growth of the acyl band at around 1705–1720 cm^{-1}. The kinetics of OA is complicated as revealed from IR data. The two-terminal $\nu(CO)$ bands of the parent complex **1a** at 2088 and 2014 cm^{-1} are gradually replaced by the acyl complex **2a** bands at 2073 (terminal $\nu(CO)$ band) and 1735 cm^{-1} (acyl $\nu(CO)$ band). The entire course of the OA reactions is accompanied by the formation of different types of complex intermediates as evidenced from IR data. Up to a period of 15 min of the OA reaction, there is very little change in ter-
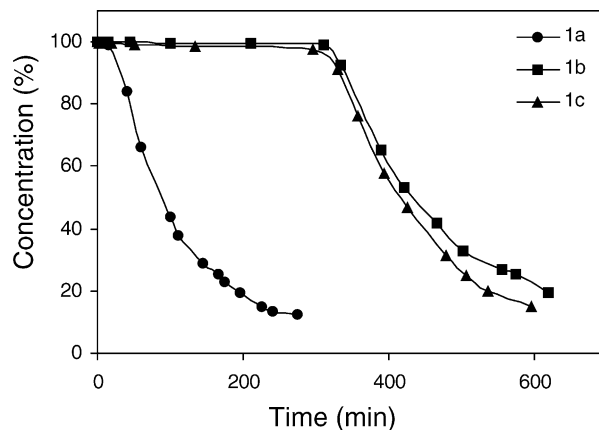

Fig. 1. The decay of the terminal $\nu(CO)$ band in the complexes **1a–1c** during the OA reaction with CH₃I against time.

minal $\nu(CO)$ bands and only the intensity of the lower $\nu(CO)$ band at 2014 cm^{-1} is slightly reduced. During 30-min reaction time, the parent $\nu(CO)$ bands shift to lower region with broad bands at 2076 and 2013 cm^{-1}, but the intensity of the former remains almost unchanged while the latter one exhibit reduced intensity along with appearance of another three new bands at 2028, 2000 and 1735 cm^{-1} which (former two) are due to terminal $\nu(CO)$ bands and the remaining one is due to acyl $\nu(CO)$ band. Thus it indicates clearly that a mixture of complex intermediates are formed. With the progress of the reaction up to about 60 min, a sharp and very strong band appears at 2075 cm^{-1} and the band at 2013 cm^{-1} shows much reduced intensity. The bands at 2028 and 2000 cm^{-1} show almost the same intensity while the acyl band at 1735 cm^{-1} exhibits higher intensity indicating the enhancement of concentration of the acyl complex in the mixture. During 75 min reaction time, the intensity of acyl band at 1735 cm^{-1} increases while the band at 2075 cm^{-1} remains unaltered. The intensity of bands at 2028, 2013 and 2000 cm^{-1} starts decreasing indicating depletion of the intermediate complexes. With the progress of the reaction, the band at 2075 cm^{-1} shows no change accompanied with increase in intensity of the acyl band at 1735 cm^{-1}, while the other bands are almost vanished indicating almost depletion of the intermediates. During 275-min reaction, only two intense bands at 2074 and 1735 cm^{-1} are observed indicating transforming all the intermediates to a single acyl complex. Thus, the above observations corroborate the formation of different unstable intermediates during the progress of the OA reactions as indicated in Scheme 1.

The reaction was found to be first order in both CH$_3$I and the complexes [7]. Kinetic measurements were done by applying pseudo-first-order condition, i.e. at high concentration of CH$_3$I. A plot is made for $\ln A_0/A_t$ versus time, where A_0 and A_t are the absorbance at time $t = 0$ and t, respectively. A two-stage linear fit, each of pseudo-first-order is observed for the entire course of OA reaction with CH$_3$I. From the slope of the plot, the rate constants for both the stages of the OA reactions were calculated and the values of k_{obs} are shown in Table 2. In general, the second-stage reactions are faster than that of the first stage by about 80–100 times.

Table 2 reveals that the overall rate of OA reaction for the complexes follows an order **1a** > **1c** > **1b**. The high reactivity of complex **1a** over **1b** and **1c** may be due to the enhancement of nucleophilicity on the metal center by the neighboring group effect [37] where the 2-substituted aldehydic group probably interacts with the metal center by some

non-conventional secondary interaction [35] and thus overcoming the sterical hindrance. To substantiate the study by X-ray crystal structure determination was not possible because no suitable crystals could be developed. The complex **1c** is sterically less hindered to be attacked by the CH$_3$I compared to that of the complex **1b** and therefore, the rate of OA reaction for the complex **1c** is higher than **1b**.

3.4. Catalytic activity

The results of carbonylation of methanol to acetic acid and its ester in the presence of the complexes **1a**–**1c** as catalyst precursors are shown in Table 3. It appears from Table 3 that the highest TON 1243 (total conversion 64.7%) and the lowest TON 626 (total conversion 32.6%) were found for the complexes **1a** and **1b**, respectively, while complex **1c** shows a moderate TON 801 (total conversion 41.7%), therefore, the efficacy follows the order **1a** > **1c** > **1b**. On the other hand, the commercial species shows TON only 653 (total conversion 34.0%). Therefore, the advantage of the complex **1a** as catalyst is obvious over the rest of the species. The efficacy trend of the complexes towards carbonylation could not be explained based on the donor capability of the ligands because the presence of electron-withdrawing –CHO group at the 2- and 4-positions of the pyridine ring of the ligands should reduce the basicity of the N-atom and consequently tend to lower the catalytic activities. In carbonylation of methanol, the OA of CH$_3$I is the rate-determining step, and the higher the rate of OA reaction, higher is the catalytic activity. From our kinetic study of OA reaction of CH$_3$I with complexes **1** it has been observed that the rate of OA reaction also follows the same order as mentioned above. Therefore, the said difference in reactivity is due to the observed difference in rate of OA reactions (vide supra).

Table 3
Result of carbonylation of methanol in the presence of complex **1** as catalyst precursors at $130 \pm 2\,^{\circ}$C and 35 ± 3 bar pressure for 1 h

Catalyst	AcOH (%)	AcOMe (%)	Total conversion (%)	TON[a]
[Rh(CO)$_2$Cl]$_2$	3.34	30.74	34.04	653
1a	12.89	51.89	64.72	1243
1b	3.9	28.7	32.6	626
1c	6.6	35.1	41.7	801

[a] TON: mole of product per mole of catalyst.

Table 2
The k_{obs} values for the OA reactions of complexes **1a**–**1c** with CH$_3$I

Complex	k_{obs} (s^{-1})	
	First stage	Second stage
1a	8.33×10^{-6}	1.5×10^{-4}
1b	0.50×10^{-6}	0.90×10^{-4}
1c	1.17×10^{-6}	1.22×10^{-4}

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