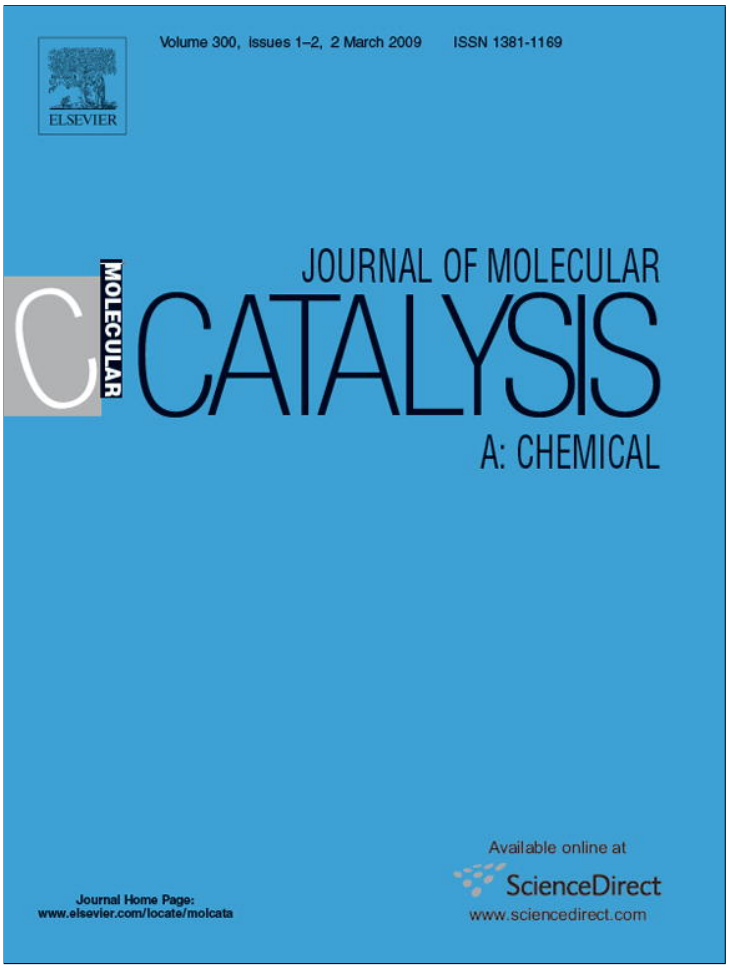

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Rhodium carbonyl complexes containing pyridine carboxylic acid ligands: Reactivity towards various electrophiles and catalytic activity

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ABSTRACT

The complex $[Rh(CO)_2Cl]_2$ reacts with two molar equivalent of pyridine carboxylic acids ligands Py-2-COOH(**a**), Py-3-COOH(**b**) and Py-4-COOH(**c**) to yield rhodium(I) dicarbonyl chelate complex $[Rh(CO)_2(L^{/})]$(**1a**) {$L^{/} = \eta^2$-(N,O) coordinated Py-2-COO^-(**a**$^{/}$)} and non-chelate complexes $[Rh(CO)_2ClL^{//}]$(**1b,c**) {$L^{//} = \eta^1$-(N) coordinated Py-3-COOH(**b**), Py-4-COOH(**c**)}. The complexes **1** undergo oxidative addition (**OA**) reactions with different electrophiles such as CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2 to give penta coordinated Rh(III) complexes of the types $[Rh(CO)(COR^n)XL^{/}]$, {n = 1,2,3; R^1 = —CH_3(**2a**); R^2 = —C_2H_5(**3a**); X = I and R^3 = —$CH_2C_6H_5$ (**4a**); X = Cl}, $[Rh(CO)I_2L^{/}]$(**5a**), $[Rh(CO)(COR^n)ClXL^{//}]$ {R^1 = —CH_3(**6b,c**); R^2 = —C_2H_5(**7b,c**); X = I and R^3 = —$CH_2C_6H_5$ (**8b,c**); X = Cl} and $[Rh(CO)ClI_2L^{//}]$(**9b,c**). The complexes have been characterized by elemental analysis, IR and ^{1}H NMR spectroscopy. Kinetic data for the reaction of **1a–b** with CH_3I indicate a first order reaction. The catalytic activity of **1a–c** for the carbonylation of methanol to acetic acid and its ester is evaluated and a higher turn over number (TON = 810–1094) is obtained compared with that of the well-known commercial species $[Rh(CO)_2I_2]^-$ (TON = 653) at mild reaction conditions (temperature 130 ± 5 °C, pressure 35 ± 5 bar).

1. Introduction

The catalytic carbonylation of methanol to acetic acid and its ester is of great importance for academic as well as industrial interest [1]. Since the invention of Monsanto's catalytic species for carbonylation of alcohols, considerable efforts have been devoted to improve the catalyst by incorporating different ligands into its coordination sphere where the phosphine ligands are preferentially chosen in most of the cases [1b,2–4]. Phosphorus containing ligands dominated the coordination chemistry of transition metals in lower oxidation states for a long time because of the softness of P-atom due to which they are considered to be more suitable for binding to soft metal atoms. But, recently it is becoming recognized that many N-containing ligands, in particular bi-, ter- and tetradentate systems can bind strongly to transition metals stabilizing both high and low oxidation states [5–8]. Nitrogen containing ligands are classified based on hybridizations of the N-atom: sp^3, sp^2 and sp. Ligands containing sp^2-hybridized nitrogen atoms, especially when the nitrogen atom is part of an aromatic system, have extensive coordination chemistry. In contrast to the P-atom, N-atom has only σ-donor (and no π-acceptor) properties due to which M—N bond has more prominent ionic character compared to the M—P bond. The σ-donor character of nitrogen makes the metal more susceptible to oxidative addition reactions which are part of the carbonylation catalytic cycle. Chelating ligands containing N—O donors are also reported. Picolinic acid is known to bind with metal ions as a bidentate N,O-donor forming a stable five membered chelate ring [9–12]. Interestingly, both the donor sites bear significantly different bonding nature. The N-atom which is a part of benzene ring and the O-atom of the side chain of the benzene ring are hard donors having different hardness stabilize metal centers in their higher oxidation states. The combination of atoms of unequal hardness in the same ligand framework may offer the advantage of providing free coordination sites by being detaching reversibly from the coordinating site and make space for the incoming substrate.

Thus, N-containing ligands are getting in significance relative to complexes of P-based ligands. Due to strong σ-donor capabilities, such N-donor ligands enhance the nucleophilicity of the Rh(I) center which in turn increases the catalytic activity of the complexes. However, in rhodium based catalytic reactions, N-containing ligands have found only limited use [6,7,13–18]. This prompted us to undertake an investigation into the catalytic activity of rhodium complexes containing Py-2-COOH, Py-3-COOH and Py-4-COOH ligands towards the carbonylation of methanol. As a part of our

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continuing work [2,6,7,13,14,19,20], i.e. effect of various ligands on rhodium catalyzed carbonylation of alcohols, we report in the present communication the positional effect of substituent of the ligands on the nucleophilicity of the metal center which in turn affects the catalytic activity of the complexes.

2. Experimental

Reactions were conducted under an inert atmosphere of dry nitrogen. The solvents used in various purposes were distilled under nitrogen prior to use. FTIR spectra of range 400–4000 cm^{-1} were recorded using a Perkin Elmer 2000 spectrophotometer on KBr discs. Elemental analyses were done on a Perkin Elmer 2400 elemental analyzer. ^1H NMR data were recorded on a Bruker DPX 300 MHz spectrometer and chemical shifts are quoted relative to $SiMe_4$ as internal standard respectively using $CDCl_3$ and d_6-acetone as solvent. The carbonylation reactions of methanol were carried out in a 100 cm^3 teflon coated high pressure reactor (HR-100 Berghof, Germany) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID). The hydrated rhodium complex $RhCl_3{\cdot}3H_2O$ was purchased from M/s Arrora Matthey Ltd., Kolkata, India. All the ligands and other chemicals like CH_3I, C_2H_5I, $C_6H_5CH_2Cl$, I_2, etc. were supplied by M/s Lancaster, UK and were used without further purification. The carbon monoxide and nitrogen gases used were of 99+% purity.

2.1. Starting material

The starting dimeric rhodium moiety $[Rh(CO)_2Cl]_2$ was prepared by passing CO gas over $RhCl_3{\cdot}3H_2O$ powder at 100 °C in the presence of water [21].

2.2. Synthesis of complexes $[Rh(CO)_2L^{/}]$(**1a**) and $[Rh(CO)_2ClL^{//}]$(**1b,c**); $L^{/} = \eta^2$-(N,O) coordinated Py-2-COO^-(**a′**); $L^{//} = \eta^1$-(N) coordinated Py-3-COOH(**b**), Py-4-COOH(**c**)

0.0514 mmol (6.33 mg) of the ligands Py-2-COOH (**a**), Py-3-COOH(**b**) and Py-4-COOH(**c**) were dissolved in a warm mixture of dichloromethane, methanol and acetone (15 cm^3) and as added to a 10 cm^3 dichloromethane solution of 0.0257 mmol (10 mg) $[Rh(CO)_2Cl]_2$ with stirring. The addition of ligand solutions were completed within 5 min. The reaction mixture was stirred at room temperature (r.t.) for about 10 min and then the solvent was evaporated under reduced pressure to obtain deep violet to brick-red coloured solid compounds which were washed with hexane and dried over silica gel in a desiccator.

2.3. Synthesis of complexes $[Rh(CO)(COR^n)XL^{/}]$, n = 1,2,3; $R^1 = -CH_3$ (**2a**); $R^2 = -C_2H_5$ (**3a**); X = I and $R^3 = -CH_2C_6H_5$ (**4a**); X = Cl; $L^{/} = \eta^2$-(N,O) coordinated **a′**

0.0356 mmol (10 mg) aliquot of complex $[Rh(CO)_2L^{/}]$(**1a**) was dissolved in 20 cm^3 methanol. To this solution, 6 cm^3 of R^nX (CH_3I, C_2H_5I and $C_6H_5CH_2Cl$) were added. The reaction mixtures were then stirred at r.t. for about 4, 12 and 18 h for CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ respectively, and the solvent was evaporated under vacuum. The black compounds so obtained were washed with diethyl ether and stored in a desiccator.

2.4. Synthesis of complexes $[Rh(CO)I_2L^{/}]$(**5a**); $L^{/} = \eta^2$-(N,O) coordinated **a′**

To a solution of complex **1a** (10 mg, 0.0356 mmol) methanol (20 mL), I_2 (9.04 mg 0.0712 mmol) was added and stirred for about 4 h. The black compound obtained after evaporation of the resulting solution was washed with diethyl ether and stored over silica gel in a desiccator.

2.5. Synthesis of complexes $[Rh(CO)(COR^n)ClXL^{//}]$, n = 1,2,3; $R^1 = -CH_3$(**6b,c**); $R^2 = -C_2H_5$(**7b,c**); X = I and $R^3 = -CH_2C_6H_5$(**8b,c**); X = Cl; $L^{//} = \eta^1$-(N) coordinated **b** and **c**

0.063 mmol (20 mg) of complexes $[Rh(CO)_2ClL^{//}]$(**1b,c**) were dissolved in 10 cm^3 methanol and to this 6 cm^3 R^nX (CH_3I, C_2H_5I and $C_6H_5CH_2Cl$) was added. The reaction mixtures were then stirred at r.t. for about 4, 12 and 18 h for CH_3I, C_2H_5I and $C_6H_5CH_2Cl$ respectively, and the solvent was evaporated under vacuum. Deep violet compounds so obtained were washed with diethyl ether and stored over silica gel.

2.6. Synthesis of complexes $[Rh(CO)ClI_2L^{//}]$(**9b,c**); $L^{//} = \eta^1$-(N) coordinated **b** and **c**

0.0315 mmol (10 mg) of $[Rh(CO)_2ClL^{//}]$(**1b,c**) and I_2 (8.00 mg, 0.063 mmol) were treated similarly as described for the complex **5a** to give black compounds which were washed with diethyl ether and stored over silica gel in a desiccator.

2.7. Kinetic experiment

The kinetic experiments of **OA** reaction of complexes **1a** and **1b** with CH_3I were monitored using FTIR spectroscopy in a solution cell (CaF_2 windows, 1.0 mm path length). In order to obtained pseudo-first order condition excess of CH_3I relative to metal complex was used. FTIR spectra (4.0 cm^{-1} resolution) were scanned in the ν(CO) region (2200–1600 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 in the region 2024–2013 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.

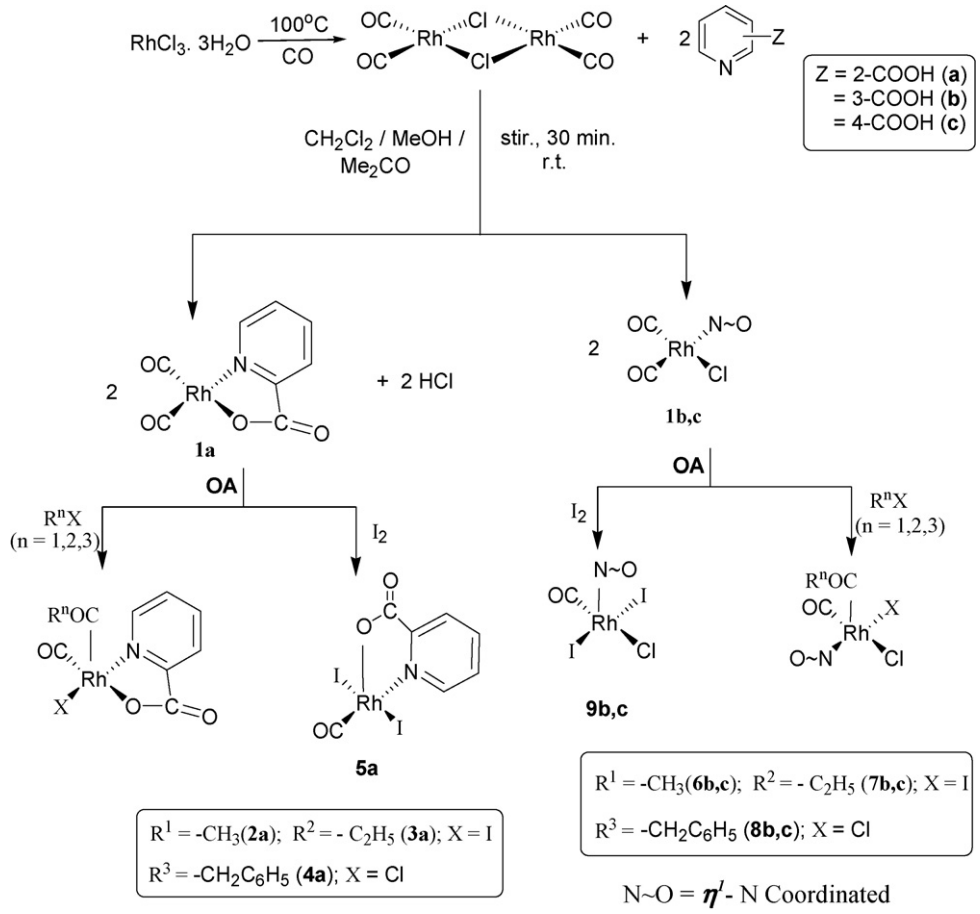
2.8. Carbonylation of methanol using complexes **1a–c** as catalyst precursors

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 complexes **1** (0.054 mmol) were taken into the reactor. The reactor was then purged with CO for about 5 min and then pressurized with CO gas (30 ± 5 bar). The carbonylation reactions were carried out at 130 ± 5 °C for 1 h. The products were collected and analyzed by G.C.

3. Results and discussion

3.1. Synthesis and characterization of Rh(I) complexes

The dimeric complex $[Rh(CO)_2Cl]_2$ undergoes bridge splitting reaction with two molar equivalent of the ligand Py-2-COOH (**a**) to produce the complex $[Rh(CO)_2(L^{/})]$(**1a**) {$L^{/} = \eta^2$-(N,O) coordinated Py-2-COO^-(**a′**)} (Scheme 1). The molecular composition of the complex was supported by elemental analysis data (Table 1). The IR spectra of the complex show two almost equal intense terminal ν(CO) bands at 2024 and 2087 cm^{-1} (Table 1) reflecting to the *cis*-disposition of the two carbonyl groups [22,23]. The IR spectra clearly indicates that the $\nu(COO)_{asy}$ band at 1719 cm^{-1} in the ligand



Scheme 1. Synthesis of Rh(I) and Rh(III) complexes and spatial arrangements of the different atoms, groups and ligands.

(**a**) is shifted to 1669 cm^{-1} in the complex (**1a**). This remarkable shift of 50 cm^{-1} towards the lower region suggests that the —COOH group is involved in bonding with the metal to produce a five membered chelate ring (Scheme 1) [9]. The ligand Py-2-COOH (**a**) in free state shows hydrogen bond which minimizes on complexation [24]. It is worth noting that, despite the reduction in hydrogen bonding, the $\nu(COO)_{asy}$ band is shifted towards the lower region because of chelate formation. The ^1H NMR values of the free ligand (**a**) and the complex **1a** are shown in Table 2. The complex **1a** exhibits a singlet at δ 9.01 ppm for H_1, a doublet at δ 8.34 ppm for H_2 and two multiplet resonances at δ 7.93–7.99 ppm and δ 8.23–8.27 ppm for H_3 and H_4 proton respectively of the pyridine ring.

In contrast to the ligand **a**, the ligands **b** and **c** produce the non-chelate complexes $[Rh(CO)_2ClL^{//}]$(**1b,c**) {$L^{//} = \eta^1$-(N) coordinated Py-3-COOH(**b**), Py-4-COOH(**c**)} with the dimeric complex $[Rh(CO)_2Cl]_2$ in 1:2 molar ratio reaction. The ν(CO) values of the two terminal carbonyl groups are observed in the range 2012–2106 cm^{-1} (Table 1). The $\nu(COO)_{asy}$ bands appear almost in

Table 1
Analytical data and IR bands of complexes **1–9**.

Complexes	Yield (%)	Found (Calcd.)(%)			IR (cm^{-1})	
		C	H	N	ν(CO)	$\nu(COO)_{asy}$
1a	89	34.10 (34.16)	1.37 (1.42)	4.96 (4.98)	2024, 2087	1669
1b	95	30.26 (30.23)	1.60 (1.57)	4.39 (4.41)	2013, 2106	1710
1c	92	30.21 (30.23)	1.62 (1.57)	4.37 (4.41)	2012, 2075	1716
2a	91	25.50 (25.53)	1.61 (1.65)	3.35 (3.31)	2075, 1716	–
3a	96	27.41 (27.46)	2.03 (2.06)	3.17 (3.20)	2069, 1712	–
4a	90	44.13 (44.17)	2.73 (2.70)	3.41 (3.44)	2074, 1723	–
5a	88	16.59 (16.57)	0.83 (0.79)	2.71 (2.76)	2078	1670
6b	91	23.55 (23.50)	1.72 (1.74)	3.01 (3.05)	2080, 1701	–
6c	92	23.53 (23.50)	1.77 (1.74)	3.08 (3.05)	2070, 1710	–
7b	95	25.30 (25.34)	2.15 (2.11)	3.00 (2.96)	2040, 1715	–
7c	88	25.31 (25.34)	2.08 (2.11)	2.95 (2.96)	2045, 1716	–
8b	90	40.51 (40.54)	2.73 (2.70)	3.20 (3.15)	2065, 1724	–
8c	93	40.56 (40.54)	2.73 (2.70)	3.12 (3.15)	2086, 1728	–
9b	95	15.40 (15.45)	0.88 (0.92)	2.60 (2.57)	2089	1716
9c	89	15.43 (15.45)	0.90 (0.92)	2.62 (2.57)	2087	1717

Free ligand $\nu(COO)_{asy}$ in cm^{-1}: Py-2-COOH(**a**), 1719; Py-3-COOH(**b**), 1709; Py-4-COOH(**c**), 1712.

Table 2
^{1}H NMR data of different types of rhodium complexes containing N-donor ligands.

Complexes/ligands	H_1	H_2	H_3	H_4	COOH	—CH_3	—CH_2—	C_6H_5
a	8.81s	8.30 (d, J_{HH} = 9.0 Hz)	7.61–7.66m	7.98–8.03m	9.89s	–	–	–
b	8.78 (d, J_{HH} = 6.8 Hz)	7.51–7.54 m	8.24–8.27m	–	9.06s	–	–	–
c	8.76 (d, J_{HH} = 7.6 Hz)	7.80 (d, J_{HH} = 7.6 Hz)	–	–	9.03s	–	–	–
1a	9.01s	8.34 (d, J_{HH} = 8.6 Hz)	7.93–7.99m	8.23–8.27m	–	–	–	–
1b	8.83 (d, J_{HH} = 6.9 Hz)	7.65–7.77 m	8.47–8.65m	–	9.34s	–	–	–
1c	8.93 (d, J_{HH} = 7.7 Hz)	8.06 (d, J_{HH} = 7.7 Hz)	–	–	9.30s	–	–	–
2a	8.37s	8.00 (d, J_{HH} = 9.1 Hz)	7.66–7.79m	8.28–8.30m	–	2.78s	–	–
3a	8.37s	8.00 (d, J_{HH} = 8.3 Hz)	7.66–7.79m	8.28–8.30m	–	1.97t	2.80q	–
4a	8.31s	7.98 (d, J_{HH} = 7.8 Hz)	7.62–7.77m	8.22–8.24m	–	–	3.88s	–
5a	8.33s	7.97 (d, J_{HH} = 8.9 Hz)	7.60–7.78m	8.24–8.26m	–	–	–	–
6b	8.85 (d, J_{HH} = 6.9 Hz)	7.63–7.78 m	8.46–8.67m	–	9.39s	2. 82s	–	–
6c	8.98 (d, J_{HH} = 7.3 Hz)	8.09 (d, J_{HH} = 7.3 Hz)	–	–	9.35s	2.98s	–	–
7b	8.83 (d, J_{HH} = 7.1 Hz)	7.62–7.79m	8.47–8.68m	–	9.51s	1.95t	2.85q	–
7c	8.85 (d, J_{HH} = 7.5 Hz)	8.12 (d, J_{HH} = 7.5 Hz)	–	–	9.46s	1.98t	3.01q	–
8b	8.87 (d, J_{HH} = 7.4 Hz)	7.69–7.80m	8.45–8.68m	–	10.07s	–	3.58s	–
8c	8.90 (d, J_{HH} = 7.7 Hz)	8.18 (d, J_{HH} = 7.7 Hz)	–	–	9.50s	–	3.54s	–
9b	8.77 (d, J_{HH} = 8.3 Hz)	7.65–7.78m	8.40–8.65m	–	10.02s	–	–	–
9c	8.92 (d, J_{HH} = 7.4 Hz)	8.20 (d, J_{HH} = 7.4 Hz)	–	–	9.48s	–	–	–

s = singlet; d = doublet, t = triplet, m = multiplet.

the same position as that of the corresponding free ligands **b** and **c** and hence consistent with non-coordination nature of the —COOH group of the ligands upon complexation. In ^{1}H NMR spectroscopy, the complex **1b** exhibits a doublet at δ 8.83 ppm for H_1 and two multiplet resonances at δ 7.65–7.77 and δ 8.47–8.65 ppm for H_2 and H_3 protons respectively of the pyridine ring. In the complex **1c**, two doublet resonances are observed at δ 8.93 and δ 8.06 ppm for H_1 and H_2 protons respectively. The acidic proton of the —COOH group appears as a singlet at δ 9.34 δ 9.30 ppm for the complexes **1b** and **1c** respectively.

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

One of the most important industrial processes utilizing homogeneous transition-metal catalysis is the rhodium and iodide promoted carbonylation of methanol to acetic acid. In this respect, **OA** reaction of alkyl halides with metal complexes is a very important reaction as it is the key step in the carbonylation catalysis [25]. Therefore, oxidative reactivities of **1a–c** towards various electrophiles were evaluated.

The complex **1a** undergoes **OA** reactions with CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2 followed by migratory insertion reaction to afford five coordinate Rh(III) complexes [Rh(CO)(COR^n)XL$^/$], {where, n = 1,2,3; R^1 = —CH_3(**2a**); R^2 = —C_2H_5(**3a**); X = I and R^3 = —$CH_2C_6H_5$(**4a**); X = Cl} and [Rh(CO)I_2L$^/$](**5a**) respectively. Similarly, the complexes [Rh(CO)$_2$ClL$^{//}$](**1b,c**) {L$^{//}$ = η^1-(N) coordinated Py-3-COOH(**b**), Py-4-COOH(**c**)} undergo oxidative addition reactions with various alkyl halides to yield their corresponding acyl complexes, [Rh(CO)(COR^n)ClXL$^{//}$] {where, n = 1,2,3; R^1 = —CH_3(**6b,c**); R^2 = —C_2H_5 (**7b,c**); X = I and R^3 = —$CH_2C_6H_5$(**8b,c**); X = Cl} and [Rh(CO)ClI_2L$^{//}$](**9b,c**) under slightly different reaction conditions. The IR spectra of the oxidized products show a single characteristics ν(CO) band in the range 2040–2090 cm^{-1} and a broad ν(CO) band (except **5a** and **9b,c** where the electrophiles are iodines) in the range 1700–1730 cm^{-1} due to acyl carbonyl group (Table 1). The $\nu(COO)_{asy}$ band in the complexes **2a–4a** and **6b,c–8b,c** was not observed, probably due to the merging of the band with the new acyl band. As a typical example, the solution spectra (chloroform) of the complex **2a** clearly indicates the presence of both acyl and $\nu(COO)_{asy}$ band at 1715 and 1677 cm^{-1} respectively. The solid state spectra exhibits only the acyl peak at 1716 cm^{-1} and hence the $\nu(COO)_{asy}$ band is obscured. This $\nu(COO)_{asy}$ bands for the complex **5a** was observed at 1670 cm^{-1} which suggests the involvement of the —COOH group in bond formation. In the complexes **9b** and **9c** the corresponding $\nu(COO)_{asy}$ bands were observed at 1716 and 1717 cm^{-1} which indicate that the —COOH groups are "free" as their corresponding parent complexes. The ^{1}H NMR (Table 2) spectra of the complexes **2a** and **6b,c** display singlet resonances in the range δ 2.78–2.98 ppm suggesting the formation of —OCH_3 group including other characteristic bands of the ligands. Similarly, the complexes **3a**, **6b,c** and **7c** show the bands for methylene and methyl protons of —OCH_2CH_3 group as quartet and triplet in addition to characteristic bands for the ligands. The singlet resonances corresponding to methylene protons of —$OCH_2C_6H_5$ group in the complexes **4a**, **8b** and **8c** were appeared in the range δ 3.54–3.88 ppm. The presence of electron withdrawing phenyl group deshields the —OCH_2— proton resonances and the peaks are obtained downfield [26]. **9b** and **9c** show peaks characteristic for N-heterocylic ring as well as acidic protons.

Depending on the stereochemical arrangement of the ligands **R** and **X** of the alkyl halides R^{n}X, 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 [27,28], 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 [27]. On the other hand, in view of high *trans* influencing nature, the acyl group favours apical position *trans* to the vacant coordination site [29,30]. Thus, the most probable structure of the intermediates as well as the acyl complexes are represented in Scheme 1. In the complexes **5a** and **9b,c** iodine prefers to coordinate to the metal center *trans* to each other [31].

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 developed in spite of several attempts.

Kinetic measurements for the **OA** reaction of the complexes **1a** and **1b** with methyl iodide were carried out using IR spectroscopy by monitoring the changes in the ν(CO), but due to solubility problem kinetic study of the complex **1c** with methyl iodide could not be performed. Fig. 1 shows a typical series of spectra, in which the bands due to **1a** decay and that due to **2a** grow until equilibrium is attained. The two terminal ν(CO) bands of the reactant **1a** at 2087 and 2024 cm^{-1} were replaced by the terminal ν(CO) band at 2074 cm^{-1} and acyl ν(CO) band at 1716 cm^{-1} (not shown for clarity

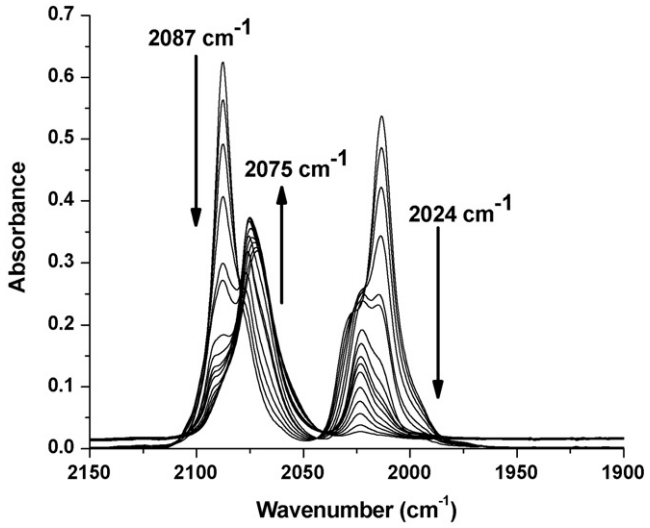


Fig. 1. Series of IR spectra {ν(CO) region} illustrating the reaction of **1a** with MeI at 25 °C.

of the Fig. 1) of the product **2a**. Absorbance versus time plots for the decay of lower intensity ν(CO) bands at 2024 and 2013 cm^{-1} of **1a** and **1b** respectively are shown in Fig. 2. A linear fit of pseudo-first order was observed for the entire course of the reaction of CH_3I with the complexes **1a–b** 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. 3). From the slopes of the plots, the rate constants were calculated and found to be 5.00×10^{-4} and 3.90×10^{-4} s^{-1} respectively for the complexes **1a** and **1b**.

Table 3
Results of carbonylation of methanol in the presence of complexes **1a–c** catalyst precursors at 130 ± 5 °C and 35 ± 5 bar CO pressure for 1 h.

Catalysts	Acetic acid[a] (%)	Methyl acetate[a] (%)	Total conversion (%)	TON[b]
$[Rh(CO)_2I_2]^-$[c]	3.30	30.74	34.04	653
1a	6.20	41.80	48.0	923
1b	9.40	47.50	56.90	1094
1c	6.55	35.55	42.10	810

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

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

The results of carbonylation of methanol to acetic acid and methyl acetate in the presence of complexes $[Rh(CO)_2L^{/}]$(**1a**) and $[Rh(CO)_2ClL^{//}]$(**1b,c**) {where $L^{/} = \eta^1$-(N) coordinated Py-2-COO^-, $L^{//} = \eta^1$-(N) coordinated Py-3-COOH, Py-4-COOH} as catalyst precursors are shown in the Table 3. In addition to the above-mentioned products, trace amount of other compounds are also observed as byproducts which could not be identified. The catalytic efficacies of the complexes are expressed by turn over number (TON) which indicates moles of product per moles of catalyst. The precursor complexes **1a–c** show a total conversion of 48, 56.9 and 42.1% of CH_3OH at 130 ± 5 °C and 35 ± 5 bar CO pressure with corresponding TON of 923, 1094 and 810. Under the same experimental conditions, the well known precursor $[Rh(CO)_2I_2]^-$ generated *in situ* from $[Rh(CO)_2Cl]_2$ [32] shows only 34.04% total conversion with a TON of 653. Thus, the efficacy of the complexes depends on the nature of the ligands and follows the order $[Rh(CO)_2Cl(Py\text{-}3\text{-}COOH)]$(**1b**) > $[Rh(CO)_2$(Py-

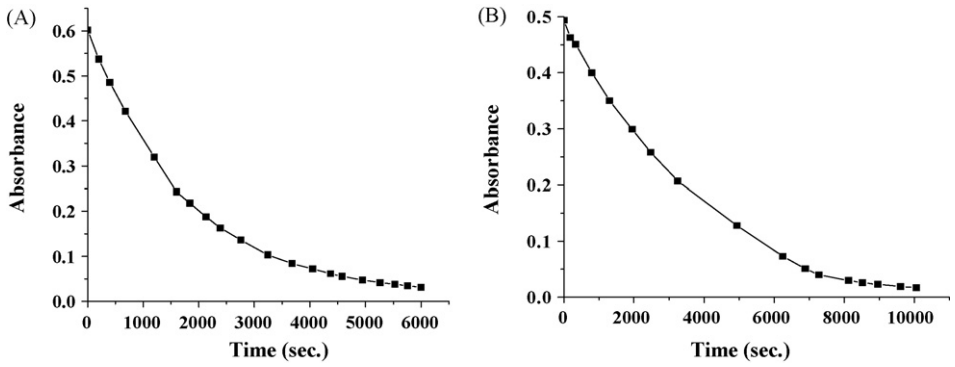


Fig. 2. Kinetic plot showing the decay of ν(CO) bands of **1a** (A) and **1b** (B) during the reaction with neat MeI at 25 °C.

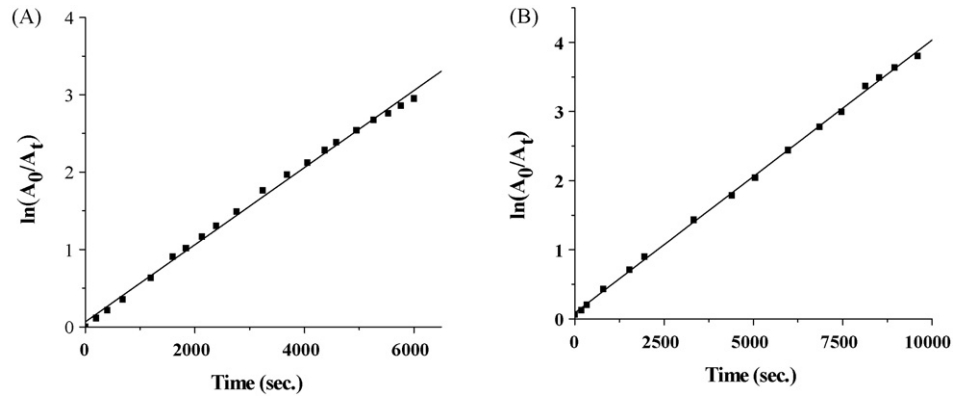
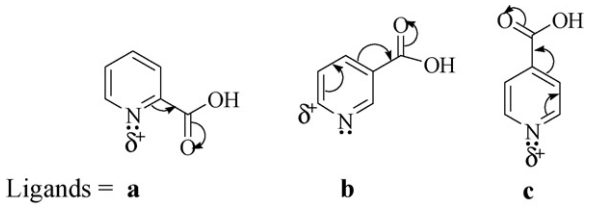


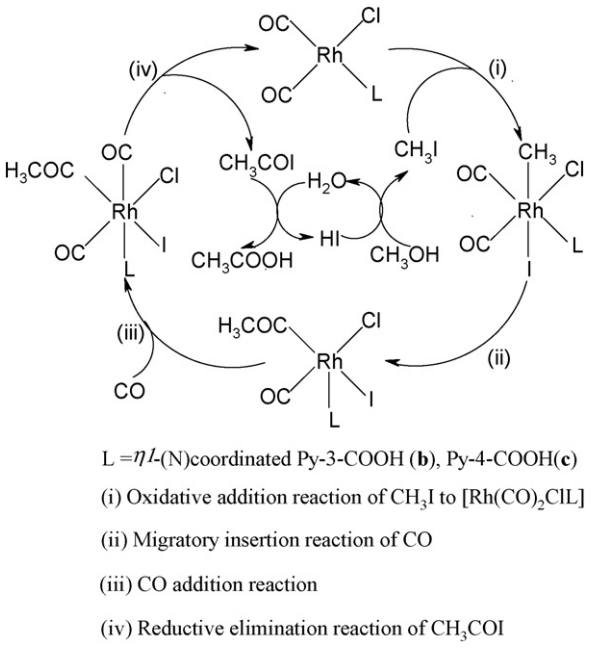
Fig. 3. Plot of $\ln(A_0/A_t)$ versus time for the **OA** reaction of the complex **1a** (A) and **1b** (B) with neat MeI at 25 °C.



Scheme 2. Effect of electron withdrawing —COOH group on the electron donating capacity of N-donor site of the pyridine carboxylic acid ligands.

2-COO^-)]([**1a**) > [$Rh(CO)_2Cl$(Py-4-COOH)]([**1c**) > [$Rh(CO)_2Cl]_2$. The complexes **1a–c** are more efficient as catalysts over the Monsanto's species, $[Rh(CO)_2I_2]^-$ and even better than certain conventional phosphine based Rh(I) carbonyl complexes [4a]. Recently, Lamb et al. [4a] reported the carbonylation of methanol using Rh(I)-diphosphine complexes which showed, in general, lower catalytic activity than the present study. However, the catalytic conversions of methanol by **1a–c** are slightly lower than those reported earlier by us [6] where analogous alkoxycarbonyl pyridine derivatives were used. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals and at the end of the catalytic reaction, multiple ν(CO) bands are obtained that matched well with the ν(CO) values of solution containing a mixture of the parent rhodium(I) carbonyl complexes **1a–c** and rhodium(III) acyl complexes **2a** and **6b,c**. Thus, it may be inferred that the ligands remained bound to the metal center throughout the entire course of the catalytic reactions.

It is well known that the higher the nucleophilicity of the metal center the higher is the catalytic activity of the corresponding complexes. The nucleophilicity depends on the electron donating capacity of the ligands. The electron donating capacity of the N-atom (i.e. basicity) in the ligands is affected by the presence of electron withdrawing —COOH group as shown in the Scheme 2. Therefore, the efficacy trend of the complexes towards the carbonylation could be explained based on the electron donating capacity of the ligands because the presence of —COOH group at the 2- and 4-positions (respective ligands **a** and **c**) of the pyridine ring in their



Scheme 3. Catalytic cycle for carbonylation of methanol in presence of catalyst precursors **1b,c**.

corresponding complexes **1a** and **1c** should reduce the basicity of N-atom and consequently tend to lower the catalytic activity compared to the complex **1b**. The higher activity of **1a** over **1c** may be attributed to the higher stability of the complex due to formation of five-member chelate ring.

A possible mechanism (Scheme 3) of the carbonylation reaction for the precursor **1b** and **1c** is proposed in which the penta coordinated Rh(III) complex $[Rh(CO)(COCH_3)ClIL]$ acts as an intermediate. Under CO pressure, the sixth position is occupied by carbon monoxide molecule forming a hexa coordinate Rh(III) complex $[Rh(CO)_2(COCH_3)ClIL]$ which on subsequent reductive elimination of CH_3COI molecule gives back the parent rhodium(I) complex. Further, the CH_3COI molecule reacts with H_2O to generate CH_3COOH and HI which reacts with CH_3OH to yield CH_3I and H_2O and thus the cycle is maintained. The CH_3COOH then reacts with unreacted CH_3OH to generate CH_3COOCH_3. The mechanism is similar to the cycle proposed for catalysis by $[Rh(CO)_2I_2]^-$ [33].

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