

Catalytic activity of dicarbonylrhodium complexes of aminobenzoic acid ligands on carbonylation of alcohol

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Abstract

Rhodium(I) complexes of the type, $[\text{Rh}(\text{CO})_2\text{CIL}]$ (**1**), where L = 2-aminobenzoic acid (**a**), 3-aminobenzoic acid (**b**) and 4-aminobenzoic acid (**c**), have been synthesised. Oxidative addition (OA) of complexes **1** with electrophiles like RI (R = CH_3 , C_2H_5) produce Rh(III) complexes of the type $[\text{Rh}(\text{CO})(\text{COCH}_3)\text{ICIL}]$ (**2**) and $[\text{Rh}(\text{CO})(\text{COC}_2\text{H}_5)\text{ICIL}]$ (**3**). The OA reactions of complexes **1** with RI follow a two stage kinetics and the observed rate constants are in the order **1b** > **1c** > **1a** irrespective of stages. The complexes **1** show higher catalytic activity for carbonylation of methanol and ethanol than that of the well known species $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

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1. Introduction

Transition metal complex catalysed carbonylation is one of the most useful methods for the direct introduction of carbonyl group into alcohol molecules to produce acid and its esters. Recently, rhodium complexes have gained much importance as efficient catalyst in carbonylation reactions [1–6]. One of the most important species, $[\text{Rh}(\text{CO})_2\text{I}_2]^-$, has been still considered as a preferred catalyst in the industrial application of carbonylation of methanol [7]. Research activities are continued to modify the catalyst either by simple ligand tailoring or by changing the central metal atom [3–6,8–10]. Literature survey reveals that rhodium(I) complexes containing aminobenzoic acids

as ligands, particularly 2-aminobenzoic acid [11,12], have been used as efficient catalyst for the reductive carbonylation of nitroaromatics as well as in hydrogenation [13,14]. This prompted us to undertake an investigation on the catalytic activity of rhodium complexes containing aminobenzoic acid of the type $[\text{Rh}(\text{CO})_2\text{CIL}]$ (**1**), where L = 2-aminobenzoic acid (**a**), 3-aminobenzoic acid (**b**), 4-aminobenzoic acid (**c**) towards the carbonylation of alcohols, like methanol and ethanol. As a part of our continuing work [15–17], i.e. effect of various ligands on rhodium catalysed carbonylation of alcohol, we have reported in the present communication the positional effect of substituent of the ligands **a–c** on oxidative reactivity of the complexes **1** towards the electrophiles RI (where R = CH_3 , C_2H_5), which is a key step in the metal catalysed carbonylation reaction [18], and the catalytic activity in the carbonylation of methanol and ethanol.

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2. Experimental

All the solvents used were distilled under N₂ prior to use. Elemental analyses were done on a Perkin-Elmer 2400 elemental analyser. FT-IR spectra (4000–400 cm⁻¹) were recorded using a Perkin-Elmer 2000 spectrophotometer in CHCl₃ and as KBr discs. The ¹H NMR (300 MHz) spectra were recorded in CDCl₃ solution on a Bruker DPX-300 Spectrometer and chemical shifts were reported relative to SiMe₄ as an internal reference. The carbonylation of alcohols were carried out in a 100 cm³ teflon coated high pressure reactor (HR-100 Berghof, Germany) fitted with a pressure gauge and the reaction products were analysed by GC (Chemito 8510, FID). RhCl₃·3H₂O was purchased from M/S Arora Matthey Ltd., Kolkata, India. All the ligands were purchased from Aldrich, USA and used as received.

2.1. Starting material

All the complexes were synthesised from [Rh(CO)₂Cl]₂ which was prepared by passing CO gas over RhCl₃·3H₂O at 100 °C [19].

2.1.1. General procedure for the synthesis of the complexes [Rh(CO)₂ClL] (**1**) (L = 2-aminobenzoic acid (**a**), 3-aminobenzoic acid (**b**) and 4-aminobenzoic acid (**c**))

An amount of 0.0257 mmol of [Rh(CO)₂Cl]₂ was dissolved in 10 cm³ CH₂Cl₂ and to this 0.0514 mmol of the respective ligands, **a–c**, in 10 cm³ acetone solution, was added. The reaction mixture was stirred at room temperature (RT) for about 10 min and the solvent was evaporated under vacuum. The compound so obtained was washed with diethyl ether and stored over silica gel in a desiccator.

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

1a: Colour: light yellow; yield: 95%; anal. calcd. for C₉H₇ClNO₄Rh (%): C, 32.59; H, 2.11; N, 4.22; found: C, 32.42; H, 2.10; N, 4.25.

1b: Colour: reddish brown; yield: 93%; anal. calcd. for C₉H₇ClNO₄Rh (%): C, 32.59; H, 2.11; N, 4.22; found: C, 32.45; H, 2.12; N, 4.20.

1c: Colour: deep violet; yield: 97%; anal. calcd. for C₉H₇ClNO₄Rh (%): C, 32.59; H, 2.11; N, 4.22; found: C, 32.51; H, 2.10; N, 4.21.

2.1.2. Synthesis of [Rh(CO)(COR)ICIL], where R = CH₃ (**2**), R = C₂H₅ (**3**)

A total of 0.3017 mmol of complex **1a–c** was dissolved in 10 cm³ acetone and to this 6 cm³ RI (R = CH₃, C₂H₅) was added. The reaction mixture was then stirred at RT for about 4 and 24 h for CH₃I and C₂H₅I, respectively and the solvent was evaporated under vacuum. Yellow-reddish coloured compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

Analytical data for the complexes **2a–c** and **3a–c** are as follows:

2a: Colour: reddish brown; yield: 93%; anal. calcd. for C₁₀H₁₀ClINO₄Rh (%): C, 25.35; H, 2.11; N, 2.96; found: C, 25.30; H, 2.10; N, 2.92.

2b: Colour: reddish brown; yield: 94%; anal. calcd. for C₁₀H₁₀ClINO₄Rh (%): C, 25.35; H, 2.11; N, 2.96; found: C, 25.32; H, 2.12; N, 2.90.

2c: Colour: reddish brown; yield: 92%; anal. calcd. for C₁₀H₁₀ClINO₄Rh (%): C, 25.35; H, 2.11; N, 2.96; found: C, 25.37; H, 2.13; N, 2.96.

3a: Colour: brown; yield: 92%; anal. calcd. for C₁₁H₁₂ClINO₄Rh (%): C, 27.09; H, 2.46; N, 2.87; found: C, 27.12; H, 2.44; N, 2.92.

3b: Colour: brown; yield: 92%; anal. calcd. for C₁₁H₁₂ClINO₄Rh (%): C, 27.09; H, 2.46; N, 2.87; found: C, 27.21; H, 2.50; N, 2.91.

3c: Colour: brown; yield: 92%; anal. calcd. for C₁₁H₁₂ClINO₄Rh (%): C, 27.09; H, 2.46; N, 2.87; found: C, 27.19; H, 2.48; N, 2.90.

2.2. Carbonylation of methanol and ethanol using complexes **1** as the catalyst precursors

A total of 0.099 mol of ROH (R = CH₃, C₂H₅), 0.016 mol of RI, 0.055 mol of H₂O, 0.054 mmol of complexes **1** were taken in the reactor and then pressurised with CO gas (20 bar at RT, 0.080 mol). The reaction vessel was then placed into the heated jacket of the autoclave and the reactions were carried out at 130 ± 5 °C (corresponding pressure 35 ± 2 bar) with variation of reaction time. The products were collected and analysed by GC. The recycle experiments were done by maintaining the same experimental conditions as described above with the dark brown solid mass as catalyst obtained by evaporating the carbonylation reaction mixture under reduced pressure.

Table 1
IR and ¹HNMR spectral data of the rhodium carbonyl complexes

Complex/free ligand	IR spectra (cm ⁻¹)			¹ HNMR δ (ppm)
	ν(CO)	ν(COO) _{asy}	ν(NH ₂)	
a	–	1670	3494, 3379	7.25 (s, NH ₂), 6.12–6.83 (m, C ₆ H ₅)
b	–	1633	3428	7.14 (s, NH ₂), 6.21–6.84 (m, C ₆ H ₅)
c	–	1665	3463, 3364	7.26 (s, NH ₂), 6.02–6.44 (m, C ₆ H ₅)
1a	2096, 2027	1673	3290, 3212	7.73 (s, NH ₂), 6.54–7.26 (m, C ₆ H ₅)
1b	2082, 2011	1672	3216	7.52 (s, NH ₂), 6.75–7.33 (m, C ₆ H ₅)
1c	2090, 2018	1683	3276, 3196	7.47 (s, NH ₂), 6.28–6.69 (m, C ₆ H ₅)
2a	2077, 1718 ^a	1698	3288, 3211	7.81 (s, NH ₂), 6.45–7.12 (m, C ₆ H ₅), 3.12 (s, COCH ₃),
2b	2076, 1714 ^a	1688	3202	7.66 (s, NH ₂), 6.65–7.23 (m, C ₆ H ₅), 3.22 (s, COCH ₃)
2c	2077, 1719 ^a	1687	3256, 3165	7.58 (s, NH ₂), 6.37–6.81 (m, C ₆ H ₅), 3.02 (s, COCH ₃)
3a	2084, 1723 ^a	1684	3286, 3206	7.77 (s, NH ₂), 6.34–7.22 (m, C ₆ H ₅), 2.27 (q, CH ₂), 1.88 (t, CH ₃)
3b	2077, 1715 ^a	1680	3200	7.71 (s, NH ₂), 6.59–7.20 (m, C ₆ H ₅), 2.47 (q, CH ₂), 1.68 (t, CH ₃)
3c	2078, 1717 ^a	1683	3255, 3162	7.69 (s, NH ₂), 6.20–6.77 (m, C ₆ H ₅), 2.14 (q, CH ₂), 1.58 (t, CH ₃)

^a Acyl ν(CO).

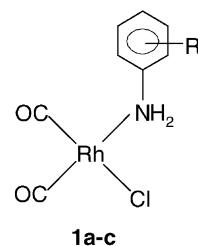
3. Result and discussion

3.1. Synthesis and characterisation of complexes **1**

One equivalent of the chlorobridged dimeric complex [(CO)₂Rh(μ-Cl)₂Rh(CO)₂] undergoes a bridge splitting reaction with two equivalent of the ligands **a–c** to yield complexes of type [Rh(CO)₂CIL], where L = 2-aminobenzoic acid, 3-aminobenzoic acid and 4-aminobenzoic acid. The complexes exhibit colours ranging from light yellow to deep violet. The IR spectra of the complexes **1a–c** (Table 1) show two almost equal intense terminal ν(CO) bands in the range 2010–2100 cm⁻¹, attributable to the *cis*-disposition of the carbonyl groups [20–22]. The ν(NH₂) bands in the complexes **1** show an appreciable shift towards the lower wave number compared to that of the free ligands (Table 1) indicating coordination occurs through N-donor [23–25]. Further, the positions of ν(COO)_{asy} bands in the complexes **1** indicate the COO group is not involved in coordination [26]. The probable structure of the complexes **1** is shown in Fig. 1. It is interesting to note that the ligands **a–c** show intra/inter-molecular hydrogen bonding in the free state [27] and the ν(COO)_{asy} bands occur in the range 1630–1670 cm⁻¹ which shifts to a slightly higher value (Table 1) upon complexation suggesting minimisation of hydrogen bonding [28]. From Table 1, it has been observed that the positions of the ν(CO) bands in these complexes **1** follow the

order **1a** > **1c** > **1b** which can be explained by the electron donating capacity of the ligand. The electron donating capacity of the –NH₂ group influenced by the presence of electron withdrawing –COOH group at different positions in the benzene ring is well understood from Fig. 2. This is further corroborated by the calculated data (Semiempirical MNDO approximation method [29]) of electron density on the N-atom i.e. –0.3829, –0.4084, –0.3951 for **a**, **b** and **c** ligands, respectively. High electron density on the N-atom will in turn increase the electron density on the central metal atom which may donate more d_π-electron to the antibonding π*-orbital of the CO and consequently decrease the C–O bond order resulting in a lowering the ν(CO) frequency [15].

The ¹HNMR values of the free ligands and the complexes **1a–c** are shown in Table 1. The –NH₂ protons



(**a**, R = 2-COOH; **b**, R = 3-COOH; **c**, R = 4-COOH)

Fig. 1. Structure of complex **1a–c**.

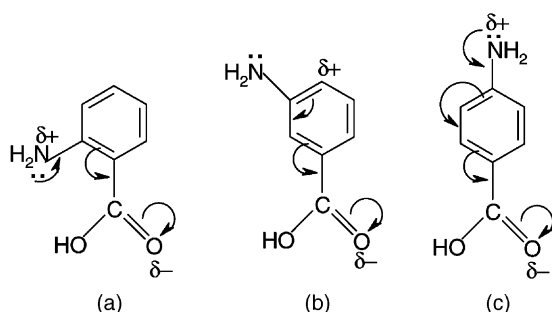


Fig. 2. Effect of electron withdrawing $-\text{COOH}$ group on nitrogen atom of the aminobenzoic acid ligand.

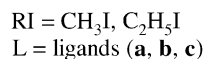
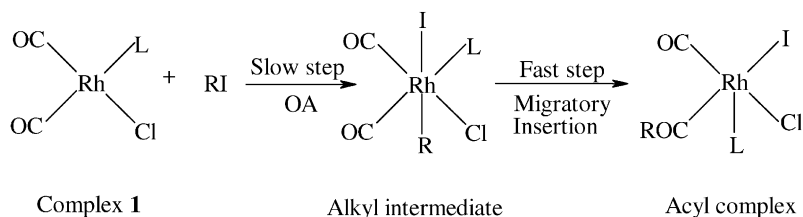
show a downfield shift compared to that of the free ligands, which is due to the partial shift of electron cloud from N-atom to the metal centre. This interaction also causes the phenylic protons a downfield shift.

3.2. Reactivity of the complexes **1** towards various electrophiles

The complexes **1** undergo OA reactions with electrophiles (RI), like CH_3I and $\text{C}_2\text{H}_5\text{I}$ followed by a migratory insertion reaction to form five-coordinated rhodium(III) acyl complexes of the type $[\text{Rh}(\text{CO})(\text{COR})\text{IClL}]$, where $\text{R} = \text{CH}_3$ (**2**), C_2H_5 (**3**). The acyl species is believed to form through an unstable six-coordinated intermediate (Scheme 1). The IR spectra of the oxidised products (**2** and **3**) show a single characteristic terminal $\nu(\text{CO})$ band in the range $2070\text{--}2085\text{ cm}^{-1}$ and a broad $\nu(\text{CO})$ band in the range $1714\text{--}1725\text{ cm}^{-1}$ due to the acyl carbonyl group (Table 1). Similar to complexes **1**, the $\nu(\text{COO})_{\text{asy}}$

bands of these complexes (**2** and **3**) occur in the higher range compared to free ligands and thus nullifies the coordination through O-donor. The $^1\text{H NMR}$ spectra of the complexes **2a–c** show a singlet in the region δ 3.00–3.25 ppm apart from other characteristics resonance of ligands indicating the formation of $-\text{COCH}_3$. In a similar manner, the $^1\text{H NMR}$ spectra of complexes **3a–c** show a triplet at around δ 1.55–1.90 ppm and a quartet at around δ 2.14–2.50 ppm corresponding to the methyl and methylene protons of the $-\text{COOCH}_2\text{CH}_3$ group (Table 1). As most of the five-coordinated carbonyl–Rh(III)–acyl complexes reported are square pyramidal in nature [30,31], it is likely that the acyl complexes **2** and **3** would also have a similar geometry. The presence of a single high terminal $\nu(\text{CO})$ value is consistent with CO group *trans* to a weak *trans* influencing chloride [32]. On the other hand, the high *trans* influencing nature of the acetyl group favours strong *trans* directing iodine in its *trans* position [31,33] which facilitate the elimination of RCOI molecule from the Rh(III) acyl complex to generate the parent Rh(I) complex, during the course of catalytic cycle. It is obvious that the site *trans* to aminobenzoic acid ligand (L) lies vacant. Thus, the most probable structure of the acyl complex is represented in Scheme 1.

The oxidative reactivities of the complexes **1** towards electrophiles CH_3I and $\text{C}_2\text{H}_5\text{I}$ are different. The reaction kinetics are monitored by following the simultaneous decay of the lower $\nu(\text{CO})$ absorption of the complexes **1** in the region $2010\text{--}2027\text{ cm}^{-1}$ and the formation of acyl $\nu(\text{CO})$ in the region $1710\text{--}1725\text{ cm}^{-1}$. During the course of the OA reactions of complexes **1** with CH_3I , a series of IR



Scheme 1. OA reaction of complexes with RI.

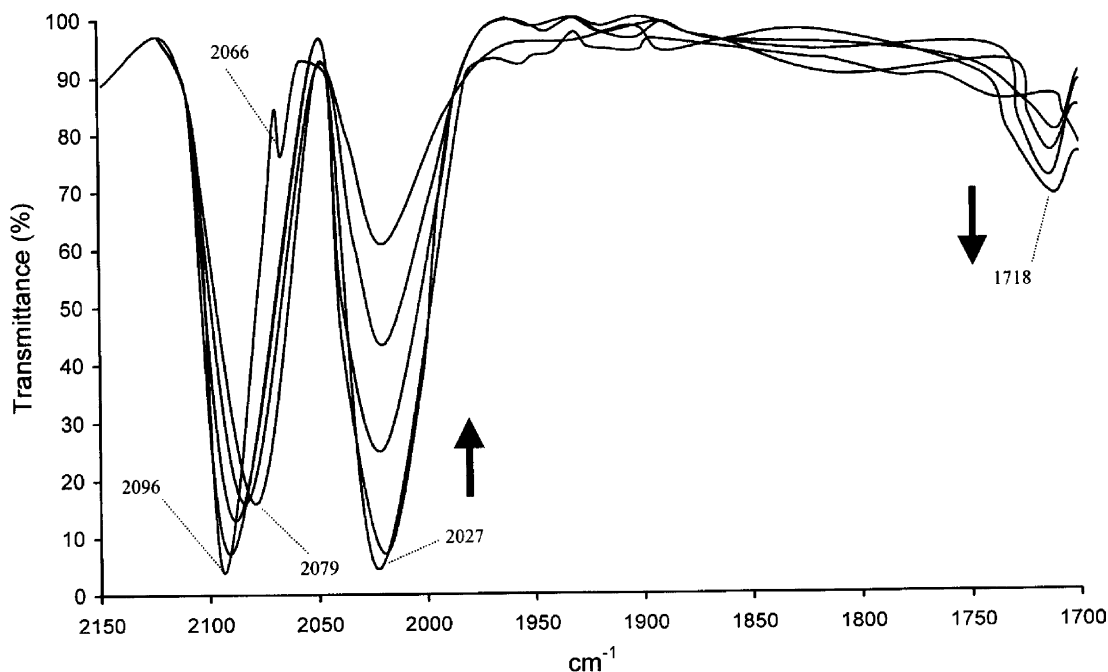


Fig. 3. Series of IR spectra ($\nu(\text{CO})$ region) showing the OA reaction of $[\text{Rh}(\text{CO})_2\text{CIL}]$ ($\text{L} = 2\text{-aminobenzoic acid}$) with CH_3I at room temperature. The arrows (\uparrow) and (\downarrow) indicate the decrease and increase in intensity of the terminal and acyl $\nu(\text{CO})$ bands, respectively with the progress of the reaction.

spectra were recorded with different time intervals and a typical set of spectral pattern for complex **1a** is shown in Fig. 3. It reveals that out of the two terminal $\nu(\text{CO})$ bands, the intensity of the $\nu(\text{CO})$ band occurring at 2027 cm^{-1} decreases while the higher $\nu(\text{CO})$ band at 2096 cm^{-1} shifts to a slightly lower region at 2079 cm^{-1} with little decrease in intensity. During the initial period of the OA reaction, a number of spectra show an additional weak terminal $\nu(\text{CO})$ band at 2066 cm^{-1} which disappears within a few minutes. It is most likely that this weak band is due to the lower $\nu(\text{CO})$ absorption of the dicarbonyl alkyl intermediate (Scheme 1, $\text{R} = \text{CH}_3$). The other higher $\nu(\text{CO})$ absorbance is probably enveloped by the $\nu(\text{CO})$ band of complexes **1** at 2096 cm^{-1} . Similar type of observation was also reported earlier [34,35].

The rate of the OA reaction was found to be dependent on both the concentration of complexes **1** and RI . To find out the concentration dependence on reaction rate, the OA reaction was carried out with a varying concentration of CH_3I (2.0×10^{-5} to $6.4 \times 10^{-5}\text{ M}$) in dichloromethane solution of complexes **1** (10 mg) at

35°C . The kinetics measurements were made by monitoring the decay of the absorbance of the $\nu(\text{CO})$ band occurring at around 2027 cm^{-1} for the complexes **1**. It is worth to mention here that same kinetics is observed if it is measured from the growth of the acyl band at around 1716 cm^{-1} .

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, as shown in Fig. 4. A two stage linear fit, each of pseudo-first order, is observed for the entire course of the OA reaction with CH_3I . During the OA reaction with $2.0 \times 10^{-5}\text{ M}$ CH_3I (Fig. 4A), a slow first stage was observed up to a period of about 160, 70 and 150 min for the complexes **1a–c**, respectively indicating an induction period and thereafter the reactions become very fast for second stage. It is obvious from Fig. 4 that as the concentration of CH_3I increases, the time required for the completion of first and second stage, in general, decreases. During the induction period, the concentration of the intermediate is likely to increase to a certain value which might be responsible for the sharp enhancement of the rate of the second

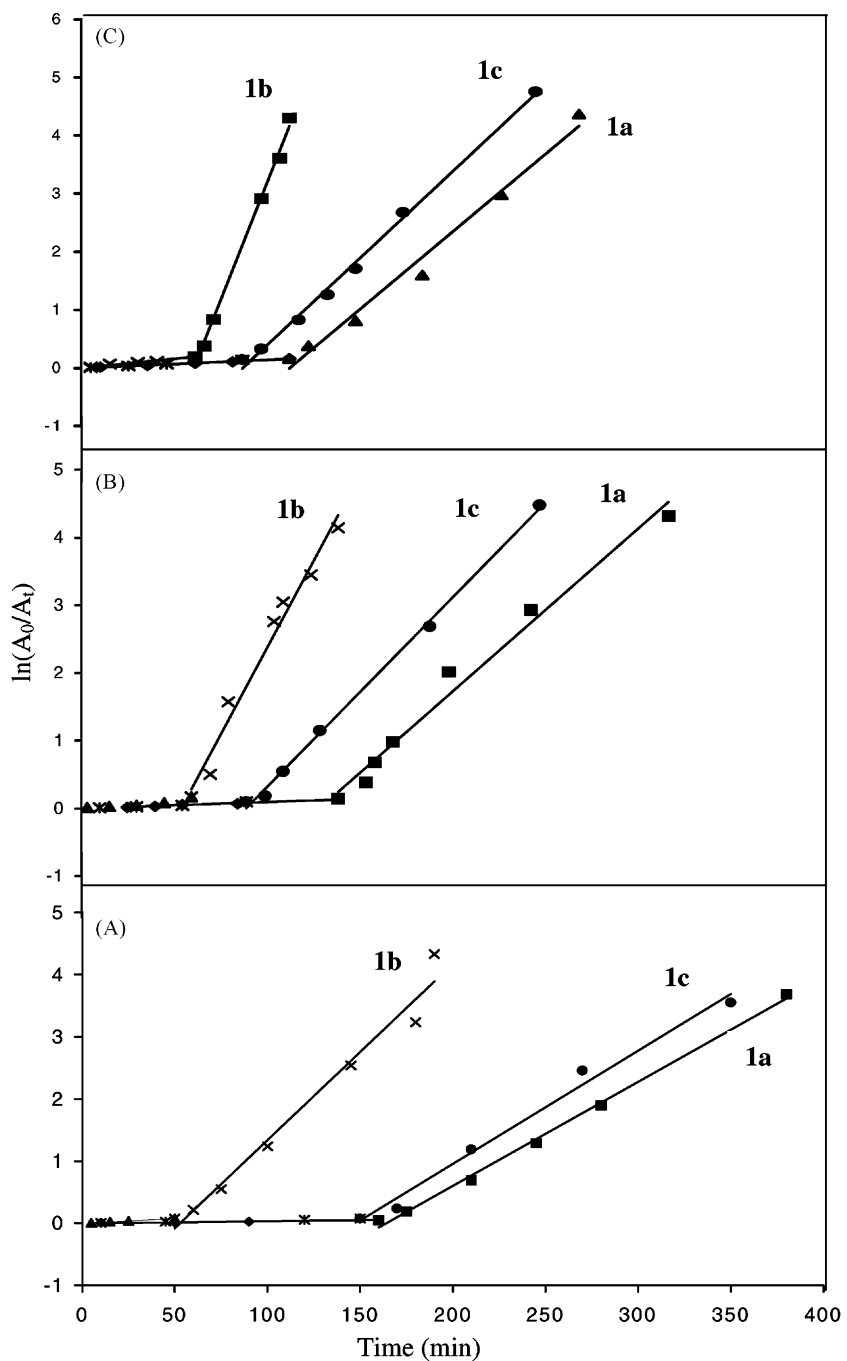


Fig. 4. Plot of $\ln A_0/A_t$ against t (time) of the OA of complexes 1 with: (A) 2.0×10^{-5} M; (B) 3.6×10^{-5} M; (C) 6.4×10^{-5} M of CH_3I .

Table 2

The k_{obs} values for the OA reactions of complexes **1** with RI

RI	[RI] (M)	k_{obs} (s^{-1})					
		1a		1b		1c	
		First stage	Second stage	First stage	Second stage	First stage	Second stage
CH ₃ I	2.0×10^{-5}	0.5×10^{-5}	2.8×10^{-4}	2.0×10^{-5}	4.8×10^{-4}	0.8×10^{-5}	3.0×10^{-4}
	3.6×10^{-5}	1.5×10^{-5}	4.0×10^{-4}	3.2×10^{-5}	8.5×10^{-4}	1.7×10^{-5}	4.6×10^{-4}
	6.4×10^{-5}	2.3×10^{-5}	4.5×10^{-4}	5.3×10^{-5}	14.0×10^{-4}	2.7×10^{-5}	5.0×10^{-4}
C ₂ H ₅ I	6.2×10^{-5}	1.3×10^{-5}	1.1×10^{-4}	1.8×10^{-5}	2.0×10^{-4}	1.5×10^{-5}	1.6×10^{-4}

stage. The rate of formation of the acyl complex from the intermediate may be represented by the following rate equation:

$$\frac{d[\text{acyl complex}]}{dt} = k_{\text{obs}}[\text{intermediate}]$$

where k_{obs} is the observed first order rate constant. From the slope of the plot of $\ln A_0/A_t$ versus t , the rate constants (k_{obs}) for both the stages of the reaction were calculated. The values of k_{obs} measured in various concentrations of CH₃I are given in Table 2. It reveals that, in general, the second stage reaction is faster than that of the first stage and as the concentration of CH₃I increases the rate of the OA reaction also increases accordingly irrespective of reaction stages. When k_{obs} was plotted against the concentration of CH₃I, a good linear fit was observed revealing that the reactions are of first order in CH₃I.

The OA of complexes **1** with C₂H₅I was found to be slower than that of CH₃I. Therefore, to find out the k_{obs} , a typical OA reaction was carried out with 6.2×10^{-5} M of C₂H₅I and 10 mg of complexes **1**. Such reactions follow a two stage kinetics like that of CH₃I addition. The slow first stage continue up to a period of about 910, 680 and 840 min and thereafter the reactions follow the fast second stage up to a period of about 1420, 1020 and 1240 min for the complexes **1a–c**, respectively (Fig. 5). Similar to OA of CH₃I, the C₂H₅I reactions also show that the second stage is faster than that of the first stage irrespective of complexes **1a–c** (Table 2). It may be worth to mention here that no additional weak terminal $\nu(\text{CO})$ band was observed for the proposed alkyl intermediate (Scheme 1, R = C₂H₅) during the course of the reaction. In this case also, a concentration factor of the undetectable intermediate is

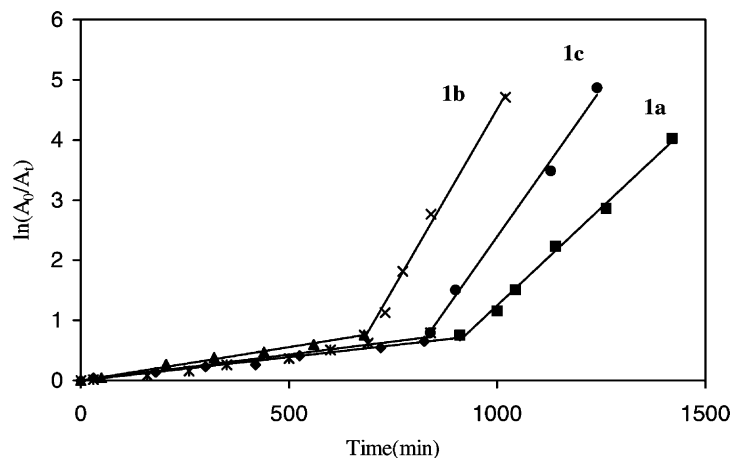


Fig. 5. Plot of $\ln A_0/A_t$ against t (time) of the OA of complexes **1** with 6.2×10^{-5} M of C₂H₅I.

Table 3

Results of carbonylation of methanol^a in presence of complexes **1** as catalyst precursors

Catalyst	Duration (min)	Methyl acetate (%)	Acetic acid (%)	Total conversion (%)	TON ^b
1a	30	33.60	4.51	38.11	588
	45	37.64	9.3	46.99	725
	60	44.27	16.46	60.37	937
	75	48.12	26.93	75.05	1158
	90	51.56	35.86	87.42	1349
	120	36.14	59.48	95.62	1475
	120 ^c	37.55	55.39	92.94	1434
1b	30	39.49	2.22	41.71	644
	45	42.29	13.58	55.87	862
	60	42.59	27.14	69.73	1075
	75	44.23	40.28	84.51	1304
	90	41.35	54.56	95.91	1480
	120	40.17	57.83	98.00	1512
	120 ^c	41.06	55.25	96.31	1486
1c	30	33.31	4.98	38.29	590
	45	37.97	9.21	47.18	728
	60	42.32	18.54	60.86	939
	75	49.37	25.81	75.18	1160
	90	48.31	39.60	87.91	1356
	120	40.62	55.71	96.33	1486
	120 ^c	51.68	45.69	97.37	1510

^a Reaction conditions: catalyst:substrate = 1:1600; temperature, 130 ± 5 °C; pressure, 35 ± 2 bar.^b TON = mole of product per mole of catalyst.^c Recycled; TON obtained by using precursor [Rh(CO)₂Cl]₂ are 460, 572, 648, 788, 951 and 1159 with corresponding reaction time 30, 45, 60, 75, 90 and 120 min.

Table 4

Results of carbonylation of ethanol^a in presence of complexes **1** as catalyst precursors

Catalyst	Duration (min)	Ethylpropanoate (%)	Propanoic acid (%)	Total conversion (%)	TON ^b
1a	60	33.36	3.06	36.42	562
	90	41.96	4.31	46.27	714
	120	45.98	16.04	62.02	957
	150	60.34	27.67	88.01	1358
	150 ^c	57.19	26.87	84.06	1297
1b	60	37.36	4.19	41.54	641
	90	49.57	5.06	54.63	843
	120	51.45	18.22	69.67	1075
	150	60.91	29.11	90.02	1389
	150 ^c	57.01	28.67	85.68	1322
1c	60	34.28	3.24	37.52	579
	90	42.33	4.79	47.12	727
	120	45.82	17.11	62.93	971
	150	63.62	25.23	88.85	1371
	150 ^c	61.78	23.12	84.90	1310

^a Reaction conditions: catalyst:substrate = 1:1600; temperature, 130 ± 5 °C; pressure 35 ± 2 bar.^b TON = mole of product per mole of catalyst.^c Recycled; TON obtained by using precursor [Rh(CO)₂Cl]₂ are 387, 564, 748 and 921 with corresponding time 60, 90, 120 and 150 min.

likely to be responsible for such two stage kinetic behaviour.

It appears from Table 2 that the rate of OA reactions of the complexes **1** follow the order **1b** > **1c** > **1a** irrespective of the electrophiles. As the OA reaction is believed to occur via nucleophilic attack by the Rh-centre at the carbon atom of RI [36,37], the observed trend is obvious from the electron donating capacity of the ligands **a–c** (vide supra).

3.3. Carbonylation of methanol and ethanol in the presence of complexes **1** as the catalyst precursors

The carbonylation of methanol and ethanol to ethanoic and propanoic acid and their esters in presence of complexes **1** as catalyst precursors were

studied and the results are shown in Tables 3 and 4, respectively. It has been observed from Table 3, that as the reaction time increases from 30 to 120 min for the complex **1a**, the total conversion percentage increases from 38.11 to 95.62% with corresponding increase in turn over number (TON) from 588 to 1475. Like **1a**, the complexes **1b** and **1c** also show a similar increasing trend in TON with the increase in reaction time and maximum TON of 1512 (**1b**) and 1486 (**1c**) with corresponding conversion of 98.00 and 96.33% have been obtained at 120 min of reaction time. It is interesting to note that with the progress of reaction time, the selectivity of the catalyst changes, i.e. initially the major product was methyl acetate but near the end of the reaction acetic acid was the major yield (Fig. 6). It has been observed (Fig. 6) that for

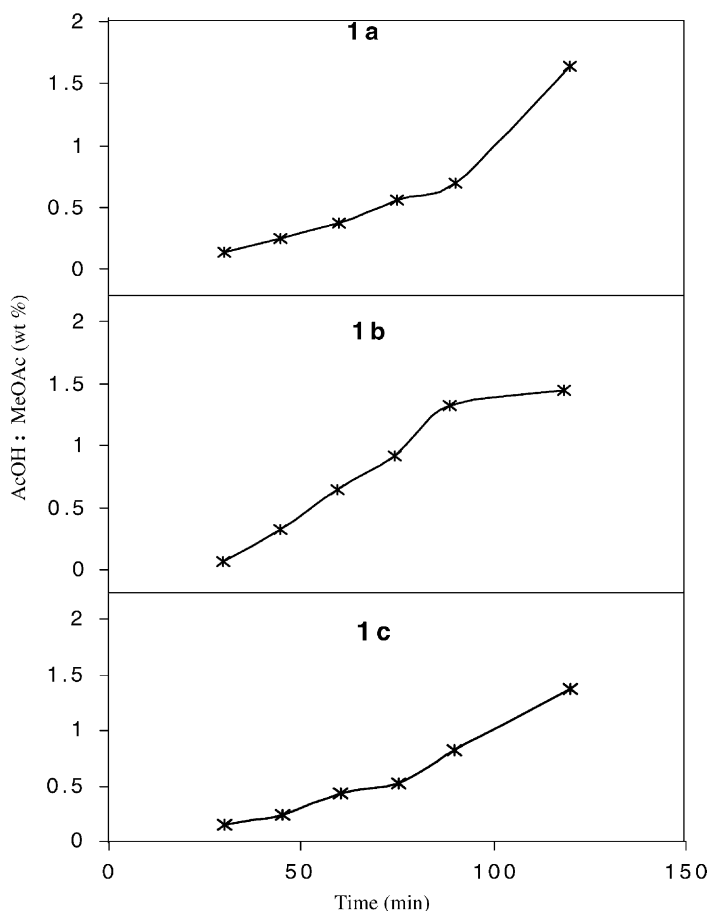


Fig. 6. Distribution of products ratio of acetic acid and methyl acetate against reaction time of carbonylation of methanol.

the complexes **1a** and **1c**, a 50:50 (wt.%) product ratio of acetic acid and its esters can be obtained at around 100 min of reaction time, while in case of complex **1b**, the said ratio can be obtained at relatively lower time, i.e. around 80 min.

Similar to carbonylation of methanol, the carbonylation of ethanol also shows an increase in TON with increase in the reaction time (Table 4). At 150 min, maximum TON of 1358, 1389 and 1371 with corresponding conversion 88.01, 90.02 and 88.85% have been obtained for the complexes **1a–c**, respectively. It may be mentioned here that throughout the reaction (Table 4) the major product obtained was ethylpropanoate. The efficacy of the complexes **1** towards the carbonylation of ethanol is found to be lower than that of methanol. In both the carbonylation reactions, for a particular reaction time and condition, the complexes **1** show higher TON over the well known catalyst precursor $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ generated in situ from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [38]. The efficacy of the complexes **1** towards the carbonylation of alcohols is different (Tables 3 and 4) and is found to follow an order **1b** > **1c** > **1a**. It is well known that in catalytic carbonylation of alcohol, the OA of the complexes **1** with alkyl halide is the rate determining step [39], therefore, higher the rate of OA reaction higher is the catalytic activity. Thus, the said difference in reactivity is due to the observed difference in rate of OA reaction of the complexes **1** with RI (Table 2). After completion of carbonylation reaction of methanol (120 min run) and ethanol (150 min run) the catalytic solution have been evaporated to dryness to get a solid mass which show a multiple $\nu(\text{CO})$ bands that matched well with the spectra of a mixture of parent rhodium(I) carbonyl complexes and rhodium(III) acyl complexes. On recycling the solid mass as catalysts for the second time, nearly the same amount of conversion have been found (Tables 3 and 4) indicating longer durability as well as stability of the catalysts.

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