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

Dipak Kumar Dutta a,∗, Prapat Chattia, Bhaskar J. Sarmah a, Bibeck J. Boraha a, Biswajit Deb a, J. Derek Woollins b

a Materials Science Division, North East Institute of Science and Technology (CSIR), Jorhat 785006, Assam, India
b Head of School, Department of Chemistry, University of St. Andrews, St. Andrews, UK KY16 9ST, UK

A R T I C L E   I N F O
Article history:
Received 15 August 2008
Received in revised form 19 September 2008
Accepted 23 September 2008
Available online 5 October 2008

Keywords:
Rhodium carbonyl complexes
Pyridine carboxylic acids
Oxidative addition reactions (OA)
Carbonylation of methanol

A B S T R A C T
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/ = R2+−(N,O) coordinated Py-2-COOH(a)) and non-chelate complexes [Rh(CO)2Cl(L//)]1b,c (L// = R3+−(N) coordinated Py-3-COOH(b), Py-4-COOH(c)). The complexes 1 undergo oxidative addition (OA) reactions with different electrophiles such as CH3I, C2H5I, C6H5CH2Cl and I2 to give penta coordinated Rh(III) complexes of the types [Rh(CO)(COR n)XL//]5a,b,c (R1 = −CH3; R2 = −C6H5; R3 = −C6H5CH2Cl and L = H2O); [Rh(CO)ClR 3−DC1](L//)1−a,b,c (R1 = −CH3; R2 = −C6H5; R3 = −C6H5CH2Cl and L = H2O); [Rh(CO)2Cl2(L/)]5a,b,c (L/ = −CH3; R2 = −C6H5; R3 = −C6H5CH2Cl). The complexes have been characterized by elemental analysis, IR and 1H NMR spectroscopy. Kinetic data for the reaction of 1a–b with CH3I 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 turnover number (TON = 810–1094) is obtained compared with that of the well-known commercial species [Rh(CO)2I2] (TON = 653) at mild reaction conditions (temperature 130 ± 5 °C, pressure 35 ± 5 bar).

© 2008 Elsevier B.V. All rights reserved.

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 bidentate N,N-donor capabilities, 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

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 detachable 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

* Corresponding author. Tel.: +91 376 2370081; fax: +91 376 2370011.
E-mail address: dipak@du.ac.in (D.K. Dutta).

1381-1169/– see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2008.09.024
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 1000 commercial 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 SiMe₄ as internal standard respectively using CDCl₃ and d₆-acetone as solvent. The carbonylation reactions of methanol 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 analyzed by GC (Chemito 8510, FID). The hydrated rhodium complex RhCl₃·3H₂O was purchased from M/s Asrara Matthey Ltd., Kolkata, India. All the ligands and other chemicals like CH₃I, C₂H₅I, C₆H₅CH₂Cl, I₂, 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 RhCl₃·3H₂O 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 = n=⁻¹(N,O) coordinated Py-2-COO⁻ (a); L = n=⁻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 cm³) and as added to a 10 cm³ dichloromethane solution of 0.0257 mmol (10 mg) [Rh(CO)₂Cl₂] 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 products which were washed with diethyl ether and stored over silica gel in a desiccator.

2.3. Synthesis of complexes [Rh(CO)(COR)X]L [1]; n = 1,2,3; R¹ = CH₃ (2a); R² = CH₂ (3a); X = 1 and R¹ = CH₂ (4a); X = Cl; L = n=⁻¹(N,O) coordinated a¹

0.0356 mmol (10 mg) aliquot of complex [Rh(CO)₂L] [1a] was dissolved in 20 cm³ methanol. To this solution, 6 cm³ of R¹X (CH₃I, C₂H₅I and C₆H₅CH₂Cl) were added. The reaction mixtures were then stirred at r.t. for about 4, 12 and 18 h for CH₃I, C₂H₅I and C₆H₅CH₂Cl respectively, and the solvent was evaporated under vacuum. Deep violet compounds so obtained were washed with diethyl ether and stored over silica gel.

2.4. Synthesis of complexes [Rh(CO)₂L] [5a]; L = n=⁻¹(N,O) coordinated a¹

To a solution of complex 1a (10 mg, 0.0356 mmol) methanol (20 mL), I₂ (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)₂ClL] [6b,c]; R² = CH₃ (6b,c); R² = CH₂ (7b,c); X = 1 and R¹ = CH₂ (8b,c); X = Cl; L = n=⁻¹(N) coordinated b and c

0.063 mmol (20 mg) of complexes [Rh(CO)₂ClL] [1b,c] were dissolved in 10 cm³ methanol and to this 6 cm³ R¹X (CH₃I, C₂H₅I and C₆H₅CH₂Cl) was added. The reaction mixtures were then stirred at r.t. for about 4, 12 and 18 h for CH₃I, C₂H₅I and C₆H₅CH₂Cl 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)₂ClL] [9b,c]; L = n=⁻¹(N) coordinated b and c

0.0315 mmol (10 mg) of [Rh(CO)₂ClL] [1b,c] and I₂ (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 with CH₃I and 1b with CH₃Cl were monitored using FTIR spectroscopy in a solution cell (CaF₂ windows, 1.0 mm path length). In order to obtained pseudo-first order condition excess of CH₃I 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 2043–13 cm⁻¹. The pseudo-first order rate constants were found from the gradient of the plot of ln(A₀/A₁) versus time, where A₀ is the initial absorbance and A₁ is the absorbance at time t.

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

CH₃OH (0.099 mol, 4 cm³), CH₃I (0.016 mol, 1 cm³), H₂O (0.055 mol, 1 cm³) 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(1) complexes

The dimeric complex [Rh(CO)₂Cl] undergoes bridge splitting reaction with two molar equivalent of the ligand Py-2-COO⁻ (a) to produce the complex [Rh(CO)₂L] [1a] L = n=⁻¹(N,O) coordinated Py-2-COO⁻ (a¹) (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 ν(CO)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 $^1$H NMR values of the free ligand (a) and the complex 1a are shown in Table 2. The complex 1a exhibits a singlet at $\delta$ 9.01 ppm for H$_1$, a doublet at $\delta$ 8.34 ppm for H$_2$ and two multiplet resonances at $\delta$ 7.93–7.99 ppm and $\delta$ 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)$_2$ClL]$_n$ (1b,c) ($L^\equiv =\eta^1-(N)$ coordinated Py-3-COOH(b), Py-4-COOH(c)) with the dimeric complex [Rh(CO)$_2$Cl]$_2$ in 1:2 molar ratio reaction. The $\nu$(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

![Scheme 1](image-url)

Table 1

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Yield (%)</th>
<th>Found (Calcd, %)</th>
<th>IR (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>1a</td>
<td>89</td>
<td>34.10 (34.16)</td>
<td>1.37 (1.42)</td>
</tr>
<tr>
<td>1b</td>
<td>95</td>
<td>30.26 (30.23)</td>
<td>1.60 (1.57)</td>
</tr>
<tr>
<td>1c</td>
<td>92</td>
<td>30.21 (30.23)</td>
<td>1.62 (1.57)</td>
</tr>
<tr>
<td>2a</td>
<td>91</td>
<td>25.50 (25.53)</td>
<td>1.61 (1.65)</td>
</tr>
<tr>
<td>3a</td>
<td>96</td>
<td>27.41 (27.46)</td>
<td>2.03 (2.06)</td>
</tr>
<tr>
<td>4a</td>
<td>90</td>
<td>44.13 (44.17)</td>
<td>2.73 (2.70)</td>
</tr>
<tr>
<td>5a</td>
<td>88</td>
<td>16.59 (16.57)</td>
<td>0.83 (0.79)</td>
</tr>
<tr>
<td>6a</td>
<td>91</td>
<td>23.55 (23.50)</td>
<td>1.72 (1.74)</td>
</tr>
<tr>
<td>6b</td>
<td>92</td>
<td>23.53 (23.50)</td>
<td>1.77 (1.74)</td>
</tr>
<tr>
<td>7a</td>
<td>95</td>
<td>25.30 (25.34)</td>
<td>2.15 (2.11)</td>
</tr>
<tr>
<td>7b</td>
<td>95</td>
<td>25.30 (25.34)</td>
<td>2.15 (2.11)</td>
</tr>
<tr>
<td>7c</td>
<td>88</td>
<td>25.31 (25.34)</td>
<td>2.08 (2.11)</td>
</tr>
<tr>
<td>8a</td>
<td>90</td>
<td>40.51 (40.54)</td>
<td>2.73 (2.70)</td>
</tr>
<tr>
<td>8b</td>
<td>90</td>
<td>40.51 (40.54)</td>
<td>2.73 (2.70)</td>
</tr>
<tr>
<td>8c</td>
<td>93</td>
<td>40.56 (40.54)</td>
<td>2.73 (2.70)</td>
</tr>
<tr>
<td>9a</td>
<td>95</td>
<td>15.40 (15.45)</td>
<td>0.88 (0.92)</td>
</tr>
<tr>
<td>9b</td>
<td>89</td>
<td>15.43 (15.45)</td>
<td>0.90 (0.92)</td>
</tr>
</tbody>
</table>

Free ligand $\nu$(COO)asy in cm$^{-1}$: Py-2-COOH(a), 1719; Py-3-COOH(b), 1709; Py-4-COOH(c), 1712.
the same position as that of the corresponding free ligands b and c and hence consistent with non-coordination nature of the \(-\text{COOH}\) group of the ligands upon complexation. In \(^1\)H NMR spectroscopy, the complex 1b exhibits a doublet at \(8.83\) ppm for \(H_1\) and two multiplet resonances at \(\delta 7.65–7.77\) and \(8.47–8.65\) ppm for \(H_2\) and \(H_3\) protons respectively of the pyridine ring. In the complex 1c, two doublet resonances are observed at \(\delta 8.90\) and \(8.97\) ppm for \(H_1\) and \(8.06\) ppm for \(H_2\) and \(H_3\) protons respectively. The acidic proton of the \(-\text{COOH}\) group appears as a singlet at \(\delta 9.34\) 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 activities of 1a–c towards various electrophiles were evaluated.

The complex 1a undergoes OA reactions with \(\text{CH}_3\text{I}, \text{C}_2\text{H}_5\text{I}, \text{C}_6\text{H}_5\text{CH}_2\text{Cl}\) and \(\text{I}_2\) followed by migratory insertion reaction to afford five coordinate Rh(III) complexes \([\text{Rh(CO)(COR)}_n\text{XL}]_\parallel\), where, \(n = 1, 2, 3; R = \text{CH}_3, \text{C}_2\text{H}_5; X = \text{Cl}^–\) and \(R^3 = \text{Cl}^–\), \(\text{Py}^–\), \(\text{COM}^–\) and \([\text{Rh(CO)I}_2\text{L}]_\parallel\) respectively. Similarly, the complexes \([\text{Rh(CO)}_3\text{Cl}]^\parallel\) and \([\text{Rh(CO)}_3\text{I}]^\parallel\) undergo oxidative addition reactions with various alkyl halides to yield their corresponding acyl complexes, \([\text{Rh(CO)}_3\text{COR}]^\parallel\) \ ([\text{Rh(CO)}_3\text{Cl}]^\parallel\) and \([\text{Rh(CO)}_3\text{I}]^\parallel\) under slightly different reaction conditions. The IR spectra of the oxidized products show a single characteristic \(\nu\text{(CO)}\) band in the range \(2040–2090\) cm\(^{-1}\) and a broad \(\nu\text{(CO)}\) 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 \(\nu\text{(CO)}\) bands in the complexes 2a–4a and 6b–c, 9b–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 \(\nu\text{(CO)}\) band at \(1715\) and \(1677\) cm\(^{-1}\) respectively. The solid state spectra exhibits only the acyl peak at \(1716\) cm\(^{-1}\) and hence the \(\nu\text{(CO)}\) band is obscured. This \(\nu\text{(CO)}\) bands for the complex 5a was observed at \(1670\) cm\(^{-1}\) which suggests the involvement of the \(-\text{COOH}\) group in bond formation.

### Table 2

<table>
<thead>
<tr>
<th>Complexes/ligands</th>
<th>(H_1)</th>
<th>(H_2)</th>
<th>(H_3)</th>
<th>(H_4)</th>
<th>(\text{COOH})</th>
<th>(-\text{CH}_3)</th>
<th>(-\text{CH}_2)</th>
<th>(\text{C}_6\text{H}_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>8.81s</td>
<td>8.30 (d, (J_{	ext{H1-H2}} = 9.0) Hz)</td>
<td>7.81–7.66</td>
<td>7.98–8.03</td>
<td>9.89s</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>b</td>
<td>8.78 (d, (J_{	ext{H1-H2}} = 6.8) Hz)</td>
<td>7.51–7.54</td>
<td>8.24–8.27m</td>
<td>–</td>
<td>9.06s</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>c</td>
<td>8.76 (d, (J_{	ext{H1-H2}} = 7.6) Hz)</td>
<td>7.80 (d, (J_{	ext{H1-H2}} = 7.6) Hz)</td>
<td>–</td>
<td>9.03s</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1a</td>
<td>9.01s</td>
<td>8.34 (d, (J_{	ext{H1-H2}} = 8.6) Hz)</td>
<td>7.93–7.99m</td>
<td>8.23–8.27m</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1b</td>
<td>8.83 (d, (J_{	ext{H1-H2}} = 6.9) Hz)</td>
<td>7.65–7.77m</td>
<td>8.47–8.65m</td>
<td>9.34s</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1c</td>
<td>8.91 (d, (J_{	ext{H1-H2}} = 7.7) Hz)</td>
<td>8.06 (d, (J_{	ext{H1-H2}} = 7.7) Hz)</td>
<td>–</td>
<td>9.30s</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2a</td>
<td>8.37s</td>
<td>8.00 (d, (J_{	ext{H1-H2}} = 9.1) Hz)</td>
<td>7.66–7.79m</td>
<td>8.28–8.30m</td>
<td>2.78s</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3a</td>
<td>8.37s</td>
<td>8.00 (d, (J_{	ext{H1-H2}} = 9.1) Hz)</td>
<td>7.66–7.79m</td>
<td>8.28–8.30m</td>
<td>–</td>
<td>1.97t</td>
<td>2.80q</td>
<td>–</td>
</tr>
<tr>
<td>4a</td>
<td>8.31s</td>
<td>7.98 (d, (J_{	ext{H1-H2}} = 7.8) Hz)</td>
<td>7.62–7.77m</td>
<td>8.22–8.24m</td>
<td>–</td>
<td>–</td>
<td>3.88s</td>
<td>–</td>
</tr>
<tr>
<td>5a</td>
<td>8.33s</td>
<td>7.97 (d, (J_{	ext{H1-H2}} = 8.9) Hz)</td>
<td>7.60–7.78m</td>
<td>8.24–8.26m</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6b</td>
<td>8.85 (d, (J_{	ext{H1-H2}} = 6.9) Hz)</td>
<td>7.63–7.78m</td>
<td>8.46–8.67m</td>
<td>9.39s</td>
<td>2.82s</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>6c</td>
<td>8.98 (d, (J_{	ext{H1-H2}} = 7.3) Hz)</td>
<td>8.09 (d, (J_{	ext{H1-H2}} = 7.3) Hz)</td>
<td>–</td>
<td>9.35s</td>
<td>2.98s</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7b</td>
<td>8.83 (d, (J_{	ext{H1-H2}} = 7.1) Hz)</td>
<td>7.62–7.79m</td>
<td>8.47–8.68m</td>
<td>9.51s</td>
<td>1.95t</td>
<td>2.85q</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>7c</td>
<td>8.85 (d, (J_{	ext{H1-H2}} = 7.5) Hz)</td>
<td>8.12 (d, (J_{	ext{H1-H2}} = 7.5) Hz)</td>
<td>–</td>
<td>9.46s</td>
<td>1.98t</td>
<td>3.01q</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8b</td>
<td>8.87 (d, (J_{	ext{H1-H2}} = 7.4) Hz)</td>
<td>7.69–7.80m</td>
<td>8.45–8.68m</td>
<td>10.07s</td>
<td>3.58s</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>8c</td>
<td>8.90 (d, (J_{	ext{H1-H2}} = 7.7) Hz)</td>
<td>8.18 (d, (J_{	ext{H1-H2}} = 7.7) Hz)</td>
<td>–</td>
<td>9.50s</td>
<td>3.54a</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9b</td>
<td>8.77 (d, (J_{	ext{H1-H2}} = 8.3) Hz)</td>
<td>7.65–7.78m</td>
<td>8.40–8.65m</td>
<td>10.02s</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>9c</td>
<td>8.92 (d, (J_{	ext{H1-H2}} = 7.4) Hz)</td>
<td>8.20 (d, (J_{	ext{H1-H2}} = 7.4) Hz)</td>
<td>–</td>
<td>9.48s</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(s = \text{singlet}; d = \text{doublet}; t = \text{triplet}; m = \text{multiplet.}\)
of the Fig. 1) of the product 2a. Absorbance versus time plots for the decay of lower intensity \(\nu(CO)\) 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 CH3I with the complexes 1a–b as is evidenced from the plot of \(\ln(A_0/At)\) versus time, where \(A_0\) and \(At\) 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 \(5.00 \times 10^{-4}\) and \(3.90 \times 10^{-4}\) s\(^{-1}\) respectively for the complexes 1a and 1b.

The results of carbonylation of methanol to acetic acid and ester using the complexes 1a–c as the 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 CH3OH at 130 ± 5 \(^\circ\)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)\(_2\)I\(_2\)] \(^-\) generated in situ from [Rh(CO)\(_2\)Cl\(_2\)] \([32]\) 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)\(_2\)(Py-3-COOH)](1b) > [Rh(CO)\(_2\)(Py-4-COOH)](1c) > [Rh(CO)\(_2\)(Py-2-COO\(^-\))](1a).

Table 3

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Acetic acid(^a) (%)</th>
<th>Methyl acetate(^a) (%)</th>
<th>Total conversion (%)</th>
<th>TON(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(CO)(_2)I(_2)] (^-)</td>
<td>3.30</td>
<td>30.74</td>
<td>34.04</td>
<td>653</td>
</tr>
<tr>
<td>1a</td>
<td>6.20</td>
<td>41.80</td>
<td>48.0</td>
<td>923</td>
</tr>
<tr>
<td>1b</td>
<td>9.40</td>
<td>47.50</td>
<td>56.90</td>
<td>1094</td>
</tr>
<tr>
<td>1c</td>
<td>6.55</td>
<td>35.55</td>
<td>42.10</td>
<td>810</td>
</tr>
</tbody>
</table>

\(^a\) 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)\(_2\)Cl\(_2\)] under catalytic condition.

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

![Fig. 1. Series of IR spectra (\(\nu(CO)\) region) illustrating the reaction of 1a with Mel at 25 \(^\circ\)C.](image1)

![Fig. 2. Kinetic plot showing the decay of \(\nu(CO)\) bands of 1a (A) and 1b (B) during the reaction with neat Mel at 25 \(^\circ\)C.](image2)

![Fig. 3. Plot of \(\ln(A_0/At)\) versus time for the OA reaction of the complex 1a (A) and 1b (B) with neat Mel at 25 \(^\circ\)C.](image3)
2-COOH −)[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)2Cl2]− and even better than certain conventional phosphine based Rh(I) carbonyl complexes [4a]. Recently, Lamb et al. [4a] reported the carbylation 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 alkoxy carbonyl pyridine derivateives 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 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 corresponding complexes 1a and 1c should reduce the basicity of N-atoms 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)(COCH3)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)5(COCH3)ClIL] which on subsequent reductive elimination of CH3COI molecule gives back the parent rhodium(I) complex. Further, the CH3COI molecule reacts with H2O to generate CH3COOH and HI which reacts with CH3OH to yield CH3I and H2O and thus the cycle is maintained. The CH3COOH then reacts with unreacted CH3OH to generate CH3COOC2H5. The mechanism is similar to the cycle proposed for catalysis by [Rh(CO)2I2]− [33].

Acknowledgements

The authors are grateful to Dr. P.G. Rao, Director, North East Institute of Science and Technology (CSIR), Jorhat-785006, Assam, India for his kind permission to publish the work. The Department of Science and Technology (DST), New Delhi (Grant: SR/S1/IC-05/2006) and Royal Society (UK) International Joint Project 2007/R2-CSR (India) joint research scheme are acknowledged for the partial financial grant. The authors P.C., B.J.S. and B.B.D. thank CSIR, New Delhi, for the award of Senior Research Fellowship (SRF) and Junior Research Fellowship (JRF).

References