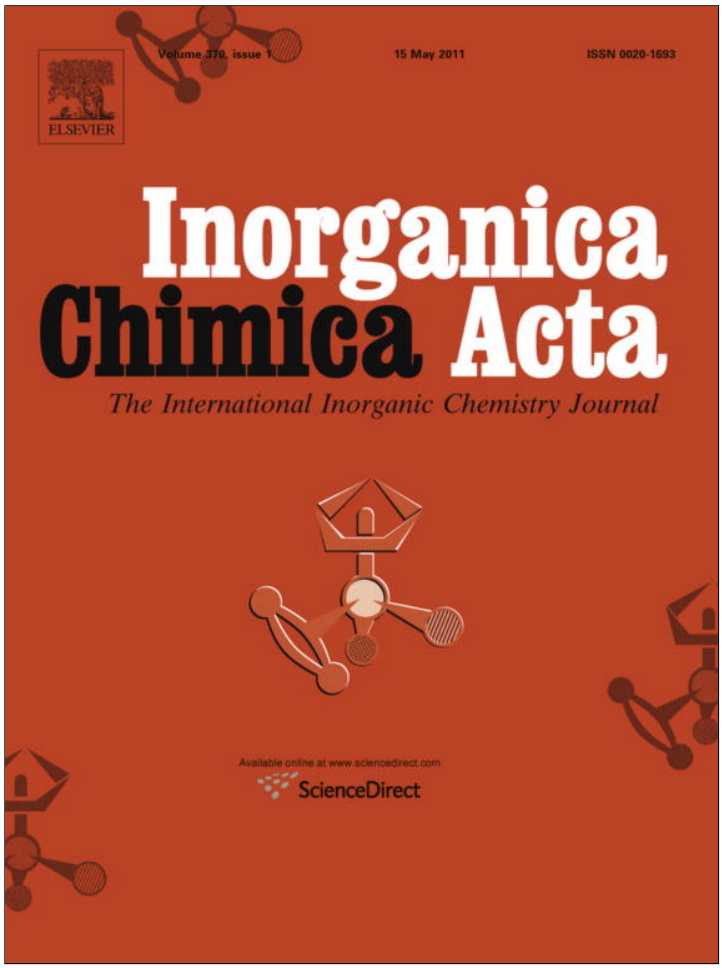

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Synthesis, reactivities and catalytic carbonylation of rhodium(I) carbonyl complexes containing isomeric acetylpyridine ligands

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ABSTRACT

$[Rh(CO)_2Cl]_2$ reacts with two mole equivalent of 2-acetylpyridine (**a**), 3-acetylpyridine (**b**) and 4-acetylpyridine (**c**) to afford chelate $[Rh(CO)Cl(\eta^2\text{-}N\cap O)]$ (**1a**) and non-chelate $[Rh(CO)_2Cl(\eta^1\text{-}N\sim O)]$ (**1b, 1c**) complexes, where, N∩O = **a**, N∼O = **b**, **c**. Oxidative addition (**OA**) of **1a–1c** with CH_3I and C_2H_5I yields penta coordinate rhodium(III) complexes, $[Rh(COR)CII(\eta^2\text{-}N\cap O)]$ {R = $-CH_3$ (**2a**); $-C_2H_5$ (**3a**)} and $[Rh(COR)(CO)CII(\eta^1\text{-}N\sim O)]$ {R = $-CH_3$ (**2b, 2c**); $-C_2H_5$ (**3b, 3c**)}. Kinetic study for the reaction of **1a–1c** with CH_3I indicates a pseudo-first order reaction. The catalytic activity of **1a–1c** for the carbonylation of methanol to acetic acid and its ester was evaluated at different initial CO pressures 5, 10 and 20 bar at ∼25 °C and higher turn over numbers (**TON** = 1581–1654) were obtained compared to commercial Monsanto's species $[Rh(CO)_2I_2]^-$ (**TON** = 1000) under the reaction conditions: temperature = 130 ± 1 °C, pressure = 15–32 bar, rpm = 450, time = 1 h and catalyst: substrate = 1: 1900.

1. Introduction

The famous Monsanto's species $[Rh(CO)_2I_2]^-$, is one of the most successful homogeneous catalyst in industry for the production of acetic acid [1–3]. As the rate-determining step of the catalytic cycle is the oxidative addition (**OA**) of MeI to $[Rh(CO)_2I_2]^-$ [4,5], electron enrichment at the metal center is expected to facilitate this step. Therefore, to improve the overall rate of acetic acid formation, considerable efforts are given to synthesize new electron rich rhodium(I) complexes by incorporating different types of ligands into its coordination sphere [6–9].

Recently, nitrogen containing aromatic heterocyclic ligands like pyridine and related compounds offer the possibilities for the synthesis of transition metal complexes with application in catalysis [9,10]. N-donor ligands are classified as "Hard" donors in the R.G. Pearson, "Hard Soft (Lewis) acid base" (HSAB) principle [11,12] and they can stabilize both high and low metal oxidation states. In contrast to phosphorous atom, N-atom has no low lying d-orbitals available and therefore N-containing ligands have only σ-donor properties due to which the metal-N bond has more pronounced ionic character than the metal-P bond [13–17]. Such characteristic of N-donor ligands makes the metal more susceptible to **OA** reactions which in turn increase the catalytic activity of the complexes [13–18]. By considering the advantages of N-containing ligands and also as a part of our continuing research activity [6,8,13–19], herein we report the synthesis, reactivity and catalytic carbonylation of rhodium(I) carbonyl complexes containing three isomeric acetylpyridine ligands. The positional as well as electronic effect of the substituents of the ligands on the nucleophilicity and catalytic activity of the metal complexes have also been investigated.

2. Experimental

2.1. General information

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

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2.2. Synthesis of starting material

The starting dimeric rhodium moiety $[Rh(CO)_2Cl]_2$ was prepared by passing CO gas over $RhCl_3{\cdot}xH_2O$ powder at 100 °C in the presence of moisture [20].

2.3. Synthesis of complexes [Rh(CO)Cl(η^2-N∩O)] (**1a**); η^2-(N∩O) coordinated 2-acetylpyridine (**a**) and [Rh(CO)$_2$Cl(η^1-N∼O)] (**1b**, **1c**); η^1-(N∼O) coordinated 3-acetylpyridine (**b**) and 4-acetylpyridine (**c**)

0.0642 mmol (25 mg) $[Rh(CO)_2Cl]_2$ was dissolved in dichloromethane (10 cm^3) and to this solution, a stoichiometric quantity (Rh:L = 1:1) 0.1286 mmol (15.5 mg) of a particular ligand (**a–c**) was added. The reaction mixture was stirred at r.t. (∼25 °C) for about 30 min and then the solvent was evaporated under reduced pressure to obtain yellow to brick-red solid compounds, which were washed with hexane and recrystallized from dichloromethane solution and dried over silica gel in a desiccator.

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

1a: Yield: 94%; *Anal.* Calc. for $C_8H_7ClNO_2Rh$: C, 33.40; H, 2.43; N, 4.87. Found: C, 33.29; H, 2.38; N, 4.82%. IR data (KBr, cm^{-1}): 1989 [νCO], 1692 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.23 (H-1, m, Py), δ 7.65–8.36 (H-2, H-3, H-4, m, Py), δ 2.60 (3H, s, CH_3), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 125–150 (Py), δ 185 (CO, $^1J_{Rh-C}$ = 74.5 Hz), δ 195 (CO)$_{acetyl}$, δ 23 (CH_3).

1b: Yield: 93%; *Anal.* Calc. for $C_9H_7ClNO_3Rh$: C, 34.24; H, 2.22; N, 4.44. Found: C, 34.21; H, 2.19; N, 4.41%. IR data (KBr, cm^{-1}): 2085, 2010 [νCO], 1699 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.10 (H-1, dd, J_{H-H} = 8.5, 4.3 Hz, Py), δ 9.16 (H-4, s, Py), δ 7.88–8.23 (2H, m, Py), δ 2.56 (3H, s, CH_3), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 122–154 (Py), δ 185 (CO, $^1J_{Rh-C}$ = 68.3 Hz), δ 187 (CO, $^1J_{Rh-C}$ = 64.5 Hz), δ 198 (CO)$_{acetyl}$, δ 22.5 (CH_3).

1c: Yield: 94%; *Anal.* Calc. for $C_9H_7ClNO_3Rh$: C, 34.24; H, 2.22; N, 4.44. Found: C, 34.15; H, 2.20; N, 4.42%. IR data (KBr, cm^{-1}): 2086, 2013 [νCO], 1701 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.17 (H-1, H-4, d, J_{H-H} = 7.8 Hz, Py), δ 8.10 (H-2, H-3, d, J_{H-H} = 7.8 Hz, Py), δ 2.57 (3H, s, CH_3), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 123–152 (Py), δ 183 (CO, $^1J_{Rh-C}$ = 67.5 Hz), δ 187 (CO, $^1J_{Rh-C}$ = 65.3 Hz), δ 197 (CO)$_{acetyl}$, δ 22.8 (CH_3).

2.4. Synthesis of complexes [Rh(COR)Cll(η^2-N∩O)] {R = –CH_3(**2a**); –C_2H_5(**3a**)}; η^2-(N∩O) coordinated 2-acetylpyridine (**a**) and [Rh(COR)-(CO)Cll(η^1-N∼O)] {R = –CH_3 (**2b**, **2c**); –C_2H_5(**3b**, **3c**); η^1-(N∼O) coordinated 3-acetylpyridine (**b**) and 4-acetylpyridine (**c**)}

0.0695 mmol (20 mg) of **1a** or 0.0634 mmol (20 mg) of **1b** or **1c** was dissolved in dichloromethane (10 cm^3). To this solution each of RX (6 cm^3) (RX = CH_3I and C_2H_5I) was added. The reaction mixture was then stirred at r.t. for about 7 and 12 h for CH_3I and C_2H_5I, respectively. The color of the solution changes from yellowish red to dark reddish brown and the solvent was removed and washed with diethyl ether and recrystallized from dichloromethane solution and stored over silica gel in a desiccator.

2.4.1. Analytical data for the complexes **2a–2c** and **3a–3c**

2a: Yield: 93%; *Anal.* Calc. for $C_9H_{10}ClINO_2Rh$: C, 25.15; H, 2.32; N, 3.26. Found: C, 25.10; H, 2.28; N, 3.20%. IR data (KBr, cm^{-1}): 1750 [νCO]$_{acyl}$, 1691 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.15 (H-1, m, Py), δ 7.55–8.32 (H-2, H-3, H-4, m, Py), δ 2.63, 3.30 (CH_3, s), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 126–151 (Py), δ 207 (CO, $^1J_{Rh-C}$ = 49.1 Hz)$_{acyl}$, δ 194 (CO)$_{acetyl}$, δ 24 (CH_3)$_{acetyl}$, δ 36.7 (CH_3)$_{acyl}$.

2b: Yield: 94%; *Anal.* Calc. for $C_{10}H_{10}ClINO_3Rh$: C, 26.24; H, 2.18; N, 3.06. Found: C, 26.22; H, 2.15; N, 3.02%. IR data (KBr, cm^{-1}): 2080 [νCO], 1751 [νCO]$_{acyl}$, 1698 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.18 (H-1, dd, J_{H-H} = 8.2, 4.6 Hz, Py), δ 9.22 (H-4, s, Py), δ 7.68–8.12 (2H, m, Py), δ 2.54, 3.33 (CH_3, s), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 123–152 (Py), δ 188 (CO, $^1J_{Rh-C}$ = 59.5 Hz), δ 206.5 (CO, $^1J_{Rh-C}$ = 48.6 Hz)$_{acyl}$, δ 197 (CO)$_{acetyl}$, δ 22 (CH_3)$_{acetyl}$, δ 34.8 (CH_3)$_{acyl}$.

2c: Yield: 95%; *Anal.* Calc. for $C_{10}H_{10}ClINO_3Rh$: C, 26.24; H, 2.18; N, 3.06. Found: C, 26.20; H, 2.16; N, 3.00%. IR data (KBr, cm^{-1}): 2078 [νCO], 1752 [νCO]$_{acyl}$, 1700 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.14 (H-1, H-4, d, J_{H-H} = 7.5 Hz, Py), δ 8.13 (H-2, H-3, d, J_{H-H} = 7.5 Hz, Py), δ 2.57, 3.35 (CH_3, s), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 126–157 (Py), δ 185.9 (CO, $^1J_{Rh-C}$ = 60.3 Hz), δ 204.2 (CO, $^1J_{Rh-C}$ = 48.1 Hz)$_{acyl}$, δ 196 (CO)$_{acetyl}$, δ 24 (CH_3)$_{acetyl}$, δ 33 (CH_3)$_{acyl}$.

3a: Yield: 95%; *Anal.* Calc. for $C_{10}H_{12}ClINO_2Rh$: C, 27.07; H, 2.70; N, 3.16. Found: C, 27.00; H, 2.66; N, 3.12%. IR data (KBr, cm^{-1}): 1749 [νCO]$_{acyl}$, 1693 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.19 (H-1, m, Py), δ 7.60–8.33 (H-2, H-3, H-4, m, Py), δ 2.61 (CH_3, s)$_{acetyl}$, δ 1.54 (CH_3, t, J_{H-H} = 6.4 Hz), δ 3.30 (CH_2, q, J_{H-H} = 6.4 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 123–157 (Py), δ 204 (CO, $^1J_{Rh-C}$ = 45.8 Hz)$_{acyl}$, δ 195 (CO)$_{acetyl}$, δ 23 (CH_3)$_{acetyl}$, δ 19 (CH_3), δ 57 (CH_2).

3b: Yield: 93%; *Anal.* Calc. for $C_{11}H_{12}ClINO_3Rh$: C, 28.00; H, 2.54; N, 2.97. Found: C, 27.93; H, 2.49; N, 2.93%. IR data (KBr, cm^{-1}): 2075 [νCO], 1752.5 [νCO]$_{acyl}$, 1698 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.12 (H-1, dd, J_{H-H} = 8.1, 4.5 Hz, Py), δ 9.14 (H-4, s, Py), δ 7.73–8.29 (2H, m, Py), δ 2.58 (CH_3, s)$_{acetyl}$, δ 1.66 (CH_3, t, J_{H-H} = 6.2 Hz), δ 3.38 (CH_2, q, J_{H-H} = 6.2 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 125–160 (Py), δ 185.4 (CO, $^1J_{Rh-C}$ = 61.3 Hz), δ 203.6 (CO, $^1J_{Rh-C}$ = 44.8 Hz)$_{acyl}$, δ 197.4 (CO)$_{acetyl}$, δ 24 (CH_3)$_{acetyl}$, δ 19.8 (CH_3), δ 61 (CH_2).

3c: Yield: 96%; *Anal.* Calc. for $C_{11}H_{12}ClINO_3Rh$: C, 28.00; H, 2.54; N, 2.97. Found: C, 27.95; H, 2.50; N, 2.92%. IR data (KBr, cm^{-1}): 2070 [νCO], 1755.3 [νCO]$_{acyl}$, 1699 [νCO]$_{acetyl}$, ^{1}H NMR (300 MHz, $CDCl_3$) data (δ in ppm): δ 9.11 (H-1, H-4, d, J_{H-H} = 7.4 Hz, Py), δ 8.15 (H-2, H-3, d, J_{H-H} = 7.4 Hz, Py), δ 2.59 (CH_3, s)$_{acetyl}$, δ 1.70 (CH_3, t, J_{H-H} = 6.5 Hz), δ 3.35 (CH_2, q, J_{H-H} = 6.5 Hz), ^{13}C NMR (75 MHz, $CDCl_3$) data (δ in ppm): δ 125–155 (Py), δ 184.7 (CO, $^1J_{Rh-C}$ = 61.8 Hz), δ 205.2 (CO, $^1J_{Rh-C}$ = 45.2 Hz)$_{acyl}$, δ 197 (CO)$_{acetyl}$, δ 23 (CH_3)$_{acetyl}$, δ 20.1 (CH_3), δ 63 (CH_2).

2.5. Kinetic experiment

The kinetic experiments of **OA** reaction of complexes **1a–1c** with neat CH_3I were monitored using FTIR spectroscopy in a solution cell (CaF_2 windows, 1.0 mm path length). In order to obtain pseudo-first-order condition, excess of CH_3I relative to metal complex was used. FTIR spectra (4.0 cm^{-1} resolution) were scanned in the ν(CO) region (2200–1650 cm^{-1}) and saved at regular time interval using spectrum software. After completion of experiment, absorbance versus time data for the appropriate ν(CO) frequencies were extracted by subtracting the solvent spectrum and analyzed off line using ORIGINPRO 7.5 software. Kinetic measurements were made by following the decay of lower frequency ν(CO) band of the complexes **1a–1c** in the region 2050–1950 cm^{-1}. The pseudo-first order rate constants were found from the gradient of the plot of $\ln(A_0/A_t)$ versus time, where A_0 is the initial absorbance and A_t is the absorbance at time t.

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

CH_3OH (0.099 mol, 4 cm^3), CH_3I (0.016 mol, 1 cm^3), H_2O (0.055 mol, 1 cm^3) and rhodium catalyst (0.0514 mmol) were taken into the 50 ml reaction vessel. The reaction mixture was then purged with CO for about 5 min and then pressurized with CO gas at around 5, 10 and 20 bar, respectively, at ∼25 °C. The carbonylation reactions were carried out at 130 ± 1 °C for 1 h under

corresponding CO pressure at around 15 ± 2, 20 ± 2 and 30 ± 2 bar. The products were collected and analyzed by GC.

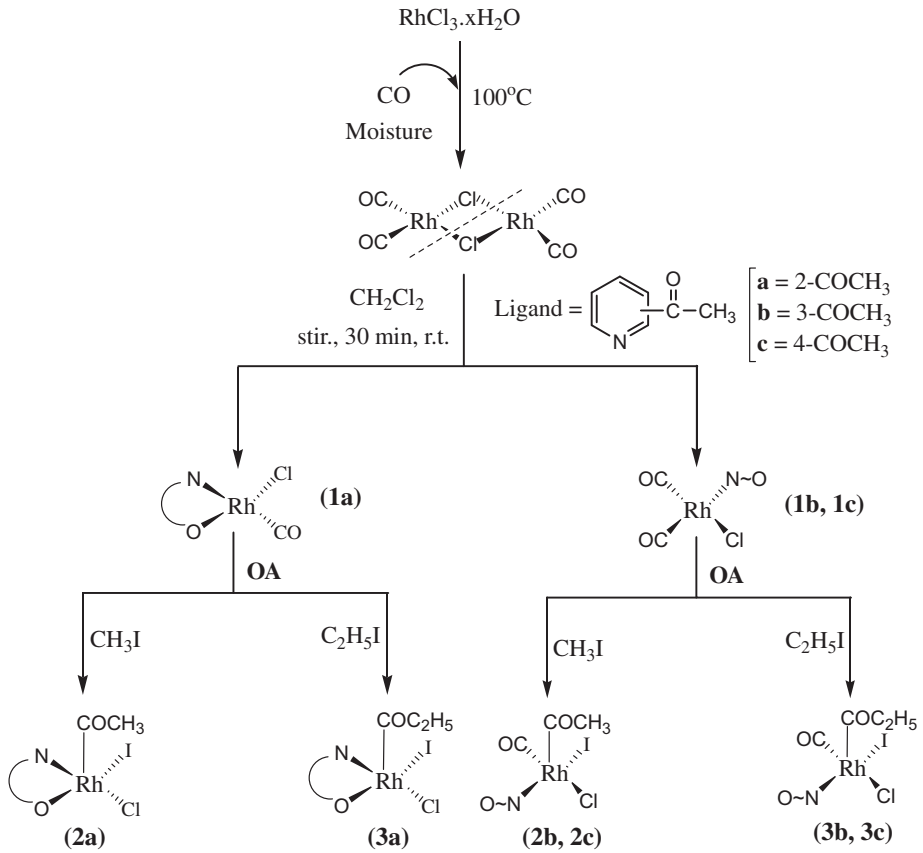
3. Results and discussion

3.1. Synthesis and characterization of Rh(I) complexes

The dimeric precursor $[Rh(CO)_2Cl]_2$ undergoes bridge splitting reaction with two mole equivalent of 2-acetylpyridine (**a**) ligand to produce a chelate complex $[Rh(CO)Cl(\eta^2\text{-}N\cap O)]$ (**1a**) [Scheme 1]. The molecular composition of **1a** was well supported by elemental analysis data. The IR spectra of **1a** shows an intense terminal ν(CO) band at around 1989 cm^{-1} and a $\nu(CO)_{acetyl}$ band at about 1692 cm^{-1}, indicating the formation of a chelate monocarbonyl Rh(I) complex. The ^{1}H NMR spectra of **1a** exhibit a strong singlet around δ 2.60 ppm for $-CH_3$ group of acetyl substituent, a multiplet at δ 9.23 ppm for H1 and another multiplet resonances in the range δ = 7.65–8.36 ppm for other protons of pyridine ring. The lower shift of $\nu(CO)_{acetyl}$ band and the downfield shift of $-CH_3$ protons compared to the free ligand **a** [$\nu(CO)_{acetyl}$ = 1699 cm^{-1}, δ 2.55 ppm (CH_3)] reveal the formation of chelate (η^2-N∩O) monocarbonyl Rh(I) complex. The ^{13}C NMR spectra of **1a** shows characteristic resonances of terminal carbonyl group at δ 185 ppm, multiplets in the region δ = 125–150 ppm for carbon atoms of pyridine ring and a signal at δ 195 ppm for $(CO)_{acetyl}$. The dimeric precursor, on the other hand, reacts with 3-acetylpyridine (**b**) and 4-acetylpyridine (**c**) ligands in 1:2 mol ratio to produce the dicarbonyl complexes of the type $[Rh(CO)_2Cl(\eta^1\text{-}N\sim O)]$ (**1b**, **c**). The IR spectra of **1b** and **1c** show two almost equal intense terminal ν(CO) bands in the region 2010–2086 cm^{-1} indicating the *cis*-disposition of the two carbonyl groups [6,13–18]. The ν(CO) bands of the acetyl substituent of **1b** and **1c** appear almost in the same position as that of the corresponding free ligands **b** and **c** [ν(CO) in cm^{-1}: 1699(**b**), 1701(**c**)] indicating non-coordinate nature of the group. The ^{1}H NMR spectra of **1b** and **1c** exhibit multiple resonances (a doublet of doublet, a multiplet and a singlet for **1b** and two doublets for **1c**) in the range δ = 7.88–9.10 ppm assigned to the different H atoms of pyridyl ring and a singlet at δ = 2.56 and 2.57 ppm for $-CH_3$ group of **1b** and **1c,** respectively. The ^{1}H NMR spectra of the free ligands show a downfield shift for the pyridyl protons when they involve in complex formation and almost similar resonance for $-CH_3$ group in **1b** and **1c** compare to free ligand, indicating the co-ordination to the metal center in **1b** and **1c** takes place only through N-donor site. The ^{13}C NMR spectra of **1b** and **1c** show characteristic resonances of two terminal carbonyl groups in the range δ = 183–187 ppm and multiplets in the region δ = 122–155 ppm for carbon atoms of pyridine ring and a signal in the range δ = 195–197 ppm for $(CO)_{acetyl}$ group.

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

The **OA** of alkyl halide with Rh complexes is very important reaction as it is the key step in the catalytic carbonylation reaction [2–8,13–19]. Therefore, **OA** of various electrophiles were evaluated. The **OA** of **1a** with CH_3I and C_2H_5I form the Rh(III) acyl complexes like $[Rh(COR)ClI(\eta^2\text{-}N\cap O)]$ {R = $-CH_3$ (**2a**); $-C_2H_5$ (**3a**)}(Scheme 1). The IR spectra of the oxidized products **2a** and **3a** show broad ν(CO) bands at 1750 and 1749 cm^{-1}, respectively, indicating formation of Rh(III)-acyl complex. The ^{1}H NMR spectra of the complex **2a** consist of one singlet at δ 3.30 ppm indicating the formation of $-COCH_3$ group including other characteristics bands of the ligand. Similarly, **3a** shows a triplet at δ 1.54 ppm for methyl and a quartet at δ 3.30 ppm for methylene protons of



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

the ethyl group. The ^{13}C NMR spectra of **2a** and **3a** exhibit a poorly resolved slightly broad signal in the range δ = 204–207 ppm for acyl carbonyl group along with other characteristic peaks of the complex.

The non-chelate complexes **1b** and **1c** undergo **OA** reactions with CH_3I and C_2H_5I followed by migratory insertion to afford five co-ordinate Rh(III) complexes [Rh(COR)(CO)ClI(η^1-N∼O)]{R = $-CH_3$ (**2b**, **2c**); $-C_2H_5$ (**3b**, **3c**)}(Scheme 1). The IR spectra of these complexes show two different types of ν(CO) bands in the range 2070–2080 cm^{-1} and 1751–1755 cm^{-1} assignable to terminal and acyl carbonyl groups, respectively. The ^1H NMR spectra of **2b** and **2c** show a singlet in the range δ = 3.33–3.35 ppm indicating the formation of $-COCH_3$. Similarly, **3b** and **3c** show a triplet in the range δ = 1.66–1.70 ppm and a quartet in the range δ = 3.35–3.38 ppm for methyl and methylene protons of the ethyl group, respectively. The ^{13}C NMR spectra of **2b**, **2c** and **3b**, **3c** exhibit two carbonyl signals in the range δ = 184–188 ppm for terminal carbonyl group and a poorly resolved slightly broad signal in the range δ = 203–207 ppm for acyl carbonyl group along with other characteristic peaks of the complex. Depending upon the stereochemical requirements, the alkyl and halo group of the electrophiles may occupy *cis* or *trans* coordination sites to each other leading to formation of several possible isomers of the intermediates, which will undergo migratory insertion reaction to yield the final acyl products [13–17]. The appearance of a single terminal ν(CO) value in case of (**2b**, **2c**) and (**3b**, **3c**) is consistent with CO group *trans* to a weak *trans* influencing chloride [21] and also due to high *trans* influencing nature, the acyl group prefers apical position *trans* to the vacant coordination site [22–24]. Thus, the most probable structures of the acyl complexes are presented in Scheme 1.

Attempts to substantiate the structures of different rhodium(I) and rhodium(III) carbonyl complexes by X-ray crystal structure determination were not possible because no suitable crystals could be obtained in spite of numerous attempts.

The kinetic experiments of **OA** reaction of **1a–1c** with neat CH_3I were monitored using FTIR spectroscopy by following the decay of lower frequency ν(CO) band of **1a–1c** in the region 2050–1950 cm^{-1}. A typical series of spectra of **1b** during reaction with CH_3I at 25 °C are shown in Fig. 1, in which the bands due to **1b** changes and simultaneously **2b** grows until equilibrium is attained. The two terminal ν(CO) bands of **1b** at 2085 and 2010 cm^{-1} were replaced by the terminal and acyl ν(CO) bands of **2b** at 2080 and 1751 cm^{-1}, respectively, and a band at 1699 cm^{-1} due to acetyl substituent of ligand **b** remains unchanged throughout the reaction, indicating the non coordinating nature of acetyl group. The spectrum of the products **2b**, exhibits quite broad absorption at around 1751 cm^{-1}, which are may be due to the presence of mixtures of isomers [13,24]. Absorbance versus time plots for the decay of lower intensity ν(CO) band (2010 cm^{-1}) of **1b** is shown in Fig. 2. A linear fit of pseudo-first-order was observed for the entire course of the reaction of CH_3I with **1a–1c** as is evidenced from the plot of $\ln(A_0/A_t)$ versus time t. (Fig. 3). From the slope of the plot, the rate constants were calculated and found to be $5.57 \times 10^{-4}\ s^{-1}$, $3.10 \times 10^{-4}\ s^{-1}$ and $1.65 \times 10^{-4}\ s^{-1}$, respectively, for **1a**, **1b** and **1c**. The values of these rate constants clearly indicate that the rate of **OA** follows the order, **1a** > **1b** > **1c**. This observed order of **OA** may be explained in terms of nucleophilicity of the metal center which in turn depends on the electron donating capacity of the ligand. From the order of appearance of CO stretching frequency **1a** < **1b** < **1c**, it is observed that the higher nucleophilicity of **1a** may be due to the chelate formation through oxygen atom of the ligand **a** and as expected show high reactivity towards **OA** reaction [14,17]. The appearance of lower ν(CO) frequency of **1b** over **1c** is due to the presence of electron withdrawing $-COCH_3$ group at 3-position of pyridine ring, which enhances the electron donating capacity of N-atom (i.e. basicity) of ligand **b** to the metal center [13,15] (Scheme 2). Hence, **1b** is highly nucleophilic and more prone towards the attack of electrophiles and shows high reactivity towards **OA**.

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

The results of carbonylation of methanol to acetic acid and its ester in the presence of **1a–1c** and $[Rh(CO)_2Cl]_2$ as catalyst precursors are shown in Table 1. The precursor **1a–1c** show a total conversion of CH_3OH in the range 29.4–86% at 130 ± 1 °C under initial CO pressures 5, 10 and 20 bar (at ∼25 °C) for 1 h reaction time with corresponding **TON** 565 to1654. It is evident from Table 1 that, as the applied CO pressure increases from 5 to 20 bar for **1a**, the corresponding total conversions increase from 33.7% to 85.7% with **TON** 648–1648. **1b** and **1c** similar to **1a** also show a similar increasing trend with the increase in CO pressure and maximum

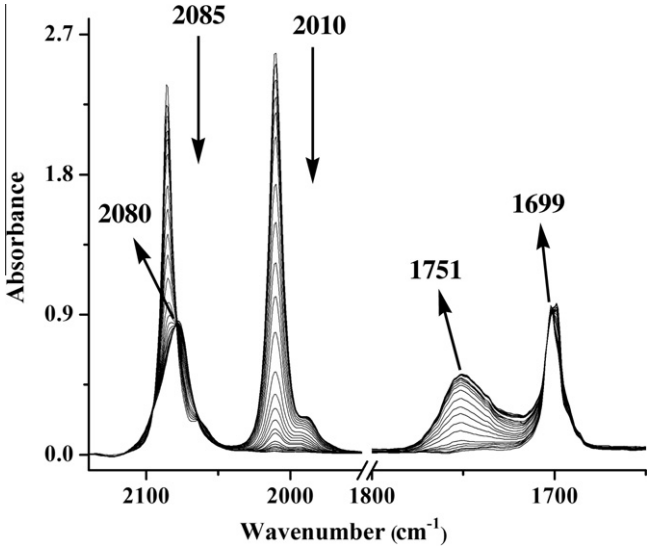


Fig. 1. Series of IR spectra {ν(CO) region} illustrating the reaction of **1b** with neat CH_3I at r.t. (∼25 °C). The arrows indicate the behavior of each band as the reaction progresses.

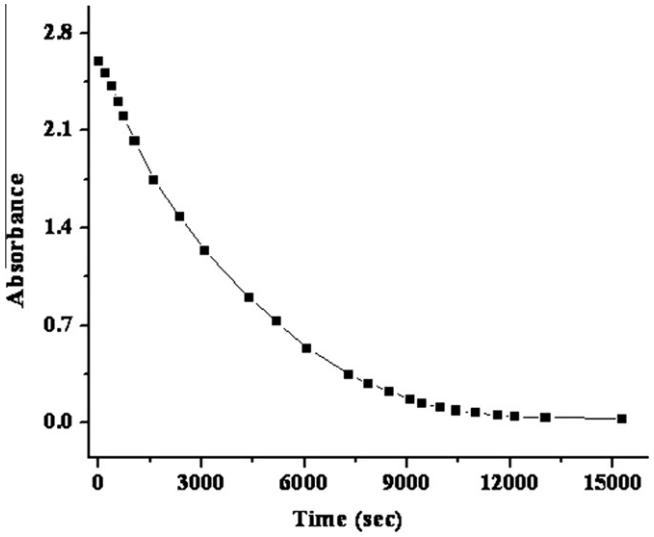


Fig. 2. Kinetic plot showing the decay of ν(CO) bands of **1b** during the reaction of **1b** with neat CH_3I at r.t. (∼25 °C).

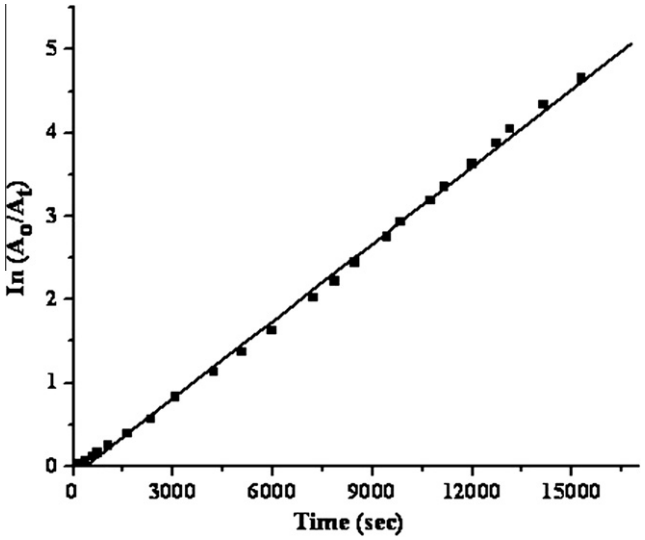
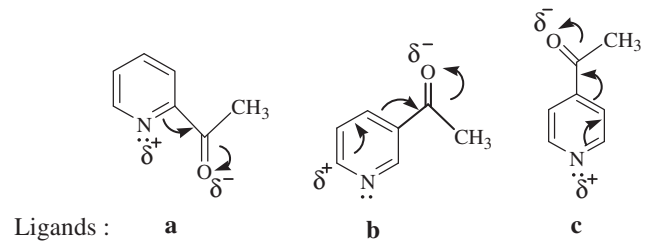


Fig. 3. Plot of $\ln(A_0/A_t)$ vs. time for the **OA** reaction of **1b** with neat CH_3I at r.t. (~25 °C).



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

Table 1
Results of carbonylation of methanol.

Catalyst precursor	CO pressure at ~25 °C (±1 bar)	Total conversion (%)	Acetic acid[a] (%)	Methyl acetate[a] (%)	TON[b]
$[Rh(CO)_2I_2]^{-}$[c]	5	24.1	4.0	20.1	463.6
	10	41.4	12.3	29.1	796.4
	20	52.1	10.3	41.8	1000
1a	5	33.7	22.5	11.2	648.2
	10	62.8	27.1	35.7	1208
	20	85.7	52.2	33.5	1648.5
1b	5	35.0	21.6	13.4	673.3
	10	64.1	24.6	39.5	1233
	20	82.2	43.8	38.4	1581
1c	5	29.4	24.8	4.6	565.5
	10	66.8	36.3	30.5	1285
	20	86	49.5	36.5	1654

[a] Yield of methyl acetate and acetic acid were obtained from GC analyses after 1 h reaction time.
[b] TON = [amount of product (mol)]/[amount of catalysts (Rh mol)].
[c] Formed from added $[Rh(CO)_2Cl]_2$ under catalytic condition.

TON 1581 (**1b**) and 1654 (**1c**) were obtained with corresponding conversions of 82.2% and 86% at 20 bar initial CO pressure (at ~25 °C). Under the similar experimental conditions, the well known catalyst precursor $[Rh(CO)_2I_2]^{-}$ generated *in situ* from $[Rh(CO)_2Cl]_2$, shows a lower **TON** 1000 with corresponding conversion of 52.1% only. The effect of different ligands on the efficiency of catalytic carbonylation reaction is clearly reflected and follows the order, **1c** > **1a** > **1b** > $[Rh(CO)_2I_2]^{-}$. It is an established fact that higher the rate of **OA**, higher is the catalytic activity, however, in this case, the catalytic carbonylation reaction of **1a–1c** cannot be explained by the observed trend of **OA**. The highest catalytic activity shown by **1c** may be due to the presence of acetyl substituent at sterically least hindered 4-position of the pyridine ring, which facilitated to run the catalytic cycle faster [13]. On examining the catalytic reaction mixture by IR spectroscopy at different time intervals and at the end of the catalytic reaction, multiples ν(CO) bands are obtained that matched well with the ν(CO) values of solution containing a mixture of the parent Rh(I) carbonyl complexes **1a–1c** and Rh(III) acyl complexes **2a–2c**. Thus, it may be inferred that the ligands remained bound to the metal center throughout the entire course of the catalytic reactions.

4. Conclusions

Three new complexes **1a–1c** have been synthesized and characterized. **1a–1c** undergo **OA** with electrophiles like CH_3I and C_2H_5I to give oxidized Rh(III) complexes **2a–2c** and **3a–3c**. The kinetics study of **1a–1c** with CH_3I follows pseudo-first order reaction. The **1a–1c** exhibit high catalytic activity in the carbonylation of methanol to acetic acid and its ester and show a higher **TON** (1581–1654) than the well-known Monsanto's species $[Rh(CO)_2I_2]^{-}$ (**TON** = 1000).

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