Dicarbonylrhodium(I) complexes of functionalized pyridine ligands and their catalytic activities

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Abstract

Reactions of dimeric complex $[Rh(CO)_2Cl]_2$ (**1**) with pyridine ester ligands methyl picolinate (**a**), methyl nicotinate (**b**), methyl isonicotinate (**c**), ethyl picolinate (**d**), ethyl nicotinate (**e**) and ethyl isonicotinate (**f**) in the 1:2 molar ratio afford the complexes of the type $[Rh(CO)_2ClL]$ (**1a–f**). The complexes **1a–f** exhibit two equally intense $\nu(CO)$ bands in the range 1990–2091 cm^{-1} indicating *cis*-disposition of the two terminal carbonyl groups. The complexes **1a** and **1d** undergo partial decarbonylation reaction in solution to give the corresponding chelated monocarbonyl complexes $[Rh(CO)Cl(methyl\ picolinate)]$ (**1a′**) and $[Rh(CO)Cl(ethyl\ picolinate)]$ (**1d′**), respectively. The complexes **1a–f** undergo oxidative addition reaction with different types of electrophiles like CH_3I, C_2H_5I, $C_6H_5CH_2Cl$ and I_2 to yield $[Rh(CO)(COCH_3)ClIL]$ (**2a–f**), $[Rh(CO)(COC_2H_5)ClIL]$ (**3a–f**), $[Rh(CO)(COCH_2C_6H_5)Cl_2L]$ (**4a–f**) and $[Rh(CO)ClI_2L]$ (**5a–f**) complexes, respectively. The complexes have been characterized by elemental analysis, IR and ^1H NMR spectroscopy. The time taken by the different complexes **1a–f** for the completion of oxidative addition reactions of CH_3I are different and the complex **1f** took the shortest time while the complex **1b** required the longest time. The catalytic activity of the complexes $[Rh(CO)_2ClL]$ (**1**) in carbonylation of methanol is higher (TON = 844–1251) than the well known $[Rh(CO)_2I_2]^-$ species (TON = 653).
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Keywords: Rhodium(I) carbonyl complexes; Alkoxycarbonylpyridine ligands; Oxidative addition; Catalytic activities; IR and NMR spectroscopy

1. Introduction

Carbonylation of methanol to ethanoic acid by Monsanto's species, $[Rh(CO)_2I_2]^-$, is one of the most successful applications of homogenous catalysis in industry [1–4]. Considerable efforts have been devoted to the improvement in the catalytic performance by incorporating different types of ligands into the metal complex species [5–10]. Recently, N–O donor ligands have gained much attention because of their structural novelty and reactivity [11–13]. Methyl and ethyl picolinate are known to bind to metal ions as a bidentate N–O donor forming a stable five-membered chelate ring [11,14]. The N-atom of pyridine ring and the O-atom of the side chain of the ester group are of unequal hardness and are expected to exhibit different bonding characteristics in stabilizing the different oxidation states of the metal centers [14–17]. Therefore, the presence of two different types of donor sites in the same ligand framework may offer the advantage in creating vacant coordination sites at the metal center for the incoming substrate, which is a prerequisite for oxidative addition reactions. Oxidative addition (OA) reactions are very important in respect of catalysis and are controlled by the electronic and steric effects of the ligands [15–17]. Nucleophilicity on the metal center has an important effect on the rate of OA reaction, which can be increased by increasing electron density on the metal center. The main objectives of the present work are to synthesize rhodium complexes of alkoxycarbonylpyridine ligands and to study their catalytic activity.

2. Experimental

All the solvents used were distilled under N_2 prior to use. Elemental analyses were done on a Perkin-Elmer 2400 elemental analyzer. IR spectra (4000–400 cm^{-1}) were recorded in KBr discs and CHCl$_3$ solution on a Perkin-Elmer system 2000 FTIR spectrophotometer. The ^1H NMR spectra were recorded in CDCl$_3$ solution on a Bruker DPX-300 MHz spectrometer and chemical shift were quoted relative to SiMe$_4$ as an internal standard. The carbonylation of methanol was carried out in a 150 cm^3

teflon coated pressure reactor (HR-100 Berghof, Germany) fitted with a pressure gauge and the reaction products were analyzed by GC (Chemito 8510, FID). RhCl$_3$.3H$_2$O was purchased from M/S Arrora Matthey Ltd., Kolkata. All the ligands were purchased from Aldrich, USA and used as received.

2.1. Starting materials

[Rh(CO)$_2$Cl]$_2$ was prepared by passing CO gas over RhCl$_3$·3H$_2$O at 100 °C in the presence of moisture [18].

2.2. Synthesis of the complexes [Rh(CO)$_2$ClL] (**1**), L = methyl picolinate (**a**), methyl nicotinate (**b**), methyl isonicotinate (**c**), ethyl picolinate (**d**), ethyl nicotinate (**e**), ethyl isonicotinate (**f**)

[Rh(CO)$_2$Cl]$_2$ (100 mg) was dissolved in dichloromethane (10 cm^3) and to this solution, a stoichiometric quantity (Rh:L = 1:2) of the respective ligands were added. The reaction mixture was stirred at room temperature (r.t.) for about 10 min and the solvent was evaporated under vacuum. The yellow red coloured compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

2.3. Synthesis of the complexes [Rh(CO)Cl(N∩O)] (**1a′ and 1d′**), N∩O = η^2-(N,O) coordinated methyl picolinate (**a**) and ethyl picolinate (**d**)

About 25 mg of the complexes [Rh(CO)$_2$ClL] (**1a** and **1d**) {L = methyl picolinate (**a**) and ethyl picolinate (**d**)} were dissolved in dichloromethane (10 cm^3) and the solutions were kept aside for about three weeks. The solvents were evaporated under reduced pressure to generate yellow-red coloured compounds (**1a′** and **1d′**), which were washed with diethyl ether and stored over silica gel in a desiccator.

Analytical data for the complexes **1a–f**, **1a′** and **1d′** are as follows:

- **1a**: Yield: 93%; Anal. Found (calcd.) for C$_9$H$_7$ClNO$_4$Rh (%): C, 32.54 (32.57); H, 2.10 (2.11); N, 4.20 (4.22); selected IR data (CHCl$_3$): 2077, 2001 [ν(CO) cm^{-1}], 1733 [ν(COOCH$_3$) cm^{-1}].
- **1a′**: Yield: 90%; Anal. Found (calcd.) for C$_8$H$_7$ClNO$_3$Rh (%): C, 31.64 (31.62); H, 2.27 (2.31); N, 4.56 (4.61); selected IR data (CHCl$_3$): 1998 [ν(CO) cm^{-1}], 1663 [ν(COOCH$_3$) cm^{-1}].
- **1b**: Yield: 91%; Anal. Found (calcd.) for C$_9$H$_7$ClNO$_4$Rh (%): C, 32.56 (32.57); H, 2.12 (2.11); N, 4.24 (4.22); selected IR data (CHCl$_3$): 2084, 2009 [ν(CO) cm^{-1}], 1730 [ν(COOCH$_3$) cm^{-1}].
- **1c**: Yield: 94%; Anal. Found (calcd.) for C$_9$H$_7$ClNO$_4$Rh (%): C, 32.55 (32.57); H, 2.14 (2.11); N, 4.23 (4.22); selected IR data (CHCl$_3$): 2086, 2010 [ν(CO) cm^{-1}], 1736 [ν(COOCH$_3$) cm^{-1}].
- **1d**: Yield: 95%; Anal. Found (calcd.) for C$_{10}$H$_9$ClNO$_4$Rh (%): C, 34.72 (34.73); H, 2.61 (2.60); N, 4.03 (4.05);

selected IR data (CHCl$_3$): 2070, 1992 [ν(CO) cm^{-1}], 1730 [ν(COOC$_2$H$_5$) cm^{-1}].
- **1d′**: Yield: 92%; Anal. Found (calcd.) for C$_9$H$_9$ClNO$_3$Rh (%): C, 34.02 (34.00); H, 2.81 (2.83); N, 4.45 (4.41); selected IR data (CHCl$_3$): 1995 [ν(CO) cm^{-1}], 1671 [ν(COOC$_2$H$_5$) cm^{-1}].
- **1e**: Yield: 90%; Anal. Found (calcd.) for C$_{10}$H$_9$ClNO$_4$Rh (%): C, 34.71 (34.73); H, 2.62 (2.60); N, 4.03 (4.05); selected IR data (CHCl$_3$): 2091, 2003 [ν(CO) cm^{-1}], 1728 [ν(COOC$_2$H$_5$) cm^{-1}].
- **1f**: Yield: 93%; Anal. Found (calcd.) for C$_{10}$H$_9$ClNO$_4$Rh (%): C, 34.75 (34.73); H, 2.62 (2.60); N, 4.04 (4.05); selected IR data (CHCl$_3$): 2068, 1991 [ν(CO) cm^{-1}], 1731 [ν(COOC$_2$H$_5$) cm^{-1}].

IR values of the free ligands (**a–f**):
   a: 1725 [ν(COOCH$_3$) cm^{-1}]; **b**: 1727 [ν(COOCH$_3$) cm^{-1}]; **c**: 1731 [ν(COOCH$_3$) cm^{-1}]; **d**: 1723 [ν(COOC$_2$H$_5$) cm^{-1}]; **e**: 1723 [ν(COOC$_2$H$_5$) cm^{-1}]; **f**: 1727 [ν(COOC$_2$H$_5$) cm^{-1}].

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

[Rh(CO)$_2$ClL] (100 mg) was dissolved in dichloromethane (15 cm^3) and each of RX (6 cm^3) (RX = CH$_3$I, C$_2$H$_5$I, C$_6$H$_5$CH$_2$Cl) was added to it. The reaction mixture was then stirred at r.t. for about 2, 4 and 6 h for CH$_3$I, C$_2$H$_5$I and C$_6$H$_5$CH$_2$Cl, respectively. The colour of the solution changed from yellowish-red to reddish-brown and the solvent was evaporated under vacuum. The compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

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

- **2a**: Yield: 88%; Anal. Found (calcd.) for C$_{10}$H$_{10}$ClINO$_4$Rh (%): C, 25.35 (25.34); H, 2.13 (2.11); N, 2.94 (2.95); selected IR data (CHCl$_3$): 2070 [ν(CO) cm^{-1}], 1733 [ν(CO)$_{acyl}$ cm^{-1}].
- **2b**: Yield: 89%; Anal. Found (calcd.) for C$_{10}$H$_{10}$ClINO$_4$Rh (%): C, 25.33 (25.34); H, 2.10 (2.11); N, 2.96 (2.95); selected IR data (CHCl$_3$): 2082 [ν(CO) cm^{-1}], 1733 [ν(CO)$_{acyl}$ cm^{-1}].
- **2c**: Yield: 87%; Anal. Found (calcd.) for C$_{10}$H$_{10}$ClINO$_4$Rh (%): C, 25.32 (25.34); H, 2.12 (2.11); N, 2.96 (2.95); selected IR data (CHCl$_3$): 2075 [ν(CO) cm^{-1}], 1736 [ν(CO)$_{acyl}$ cm^{-1}].
- **2d**: Yield: 90%; Anal. Found (calcd.) for C$_{11}$H$_{12}$ClINO$_4$Rh (%): C, 27.12 (27.10); H, 2.44 (2.46); N, 2.86 (2.87); selected IR data (CHCl$_3$): 2072 [ν(CO) cm^{-1}], 1728 [ν(CO)$_{acyl}$ cm^{-1}].
- **2e**: Yield: 86%; Anal. Found (calcd.) for C$_{11}$H$_{12}$ClINO$_4$Rh (%): C, 27.10 (27.10); H, 2.45 (2.46); N, 2.85 (2.87); selected IR data (CHCl$_3$): 2072 [ν(CO) cm^{-1}], 1728 [ν(CO)$_{acyl}$ cm^{-1}].
- **2f**: Yield: 87%; Anal. Found (calcd.) for C$_{11}$H$_{12}$ClINO$_4$Rh (%): C, 27.13 (27.10); H, 2.48 (2.46); N, 2.85 (2.87); selected

IR data (CHCl$_3$): 2077 [ν(CO) cm^{-1}], 1727 [ν(CO)$_{acyl}$ cm^{-1}].

- **3a**: Yield: 88%; Anal. Found (calcd.) for C$_{11}$H$_{12}$ClINO$_4$Rh (%): C, 27.05 (27.07); H, 2.47 (2.46); N, 2.89 (2.87); selected IR data (CHCl$_3$): 2070 [ν(CO) cm^{-1}], 1732 [ν(CO)$_{acyl}$ cm^{-1}].
- **3b**: Yield: 86%; Anal. Found (calcd.) for C$_{11}$H$_{12}$ClINO$_4$Rh (%): C, 27.06 (27.07); H, 2.47 (2.46); N, 2.86 (2.87); selected IR data (CHCl$_3$): 2059 [ν(CO) cm^{-1}], 1731 [ν(CO)$_{acyl}$ cm^{-1}].
- **3c**: Yield: 87%; Anal. Found (calcd.) for C$_{11}$H$_{12}$ClINO$_4$Rh (%): C, 27.09 (27.07); H, 2.45 (2.46); N, 2.85 (2.87); selected IR data (CHCl$_3$): 2059 [ν(CO) cm^{-1}], 1731 [ν(CO)$_{acyl}$ cm^{-1}].
- **3d**: Yield: 89%; Anal. Found (calcd.) for C$_{12}$H$_{14}$ClINO$_4$Rh (%): C, 28.75 (28.73); H, 2.77 (2.79); N, 2.80 (2.79); selected IR data (CHCl$_3$): 2070 [ν(CO) cm^{-1}], 1668 [ν(CO)$_{acyl}$ cm^{-1}].
- **3e**: Yield: 90%; Anal. Found (calcd.) for C$_{12}$H$_{14}$ClINO$_4$Rh (%): C, 28.74 (28.73); H, 2.76 (2.79); N, 2.81 (2.79); selected IR data (CHCl$_3$): 2055 [ν(CO) cm^{-1}], 1727 [ν(CO)$_{acyl}$ cm^{-1}].
- **3f**: Yield: 88%; Anal. Found (calcd.) for C$_{12}$H$_{14}$ClINO$_4$Rh (%): C, 28.70 (28.73); H, 2.81 (2.79); N, 2.81 (2.79); selected IR data (CHCl$_3$): 2071 [ν(CO) cm^{-1}], 1726 [ν(CO)$_{acyl}$ cm^{-1}].
- **4a**: Yield: 86%; Anal. Found (calcd.) for C$_{16}$H$_{14}$Cl$_2$NO$_4$Rh (%): C, 41.93 (41.92); H, 3.07 (3.05); N, 3.06 (3.05); selected IR data (CHCl$_3$): 2080 [ν(CO) cm^{-1}], 1732 [ν(CO)$_{acyl}$ cm^{-1}].
- **4b**: Yield: 87%; Anal. Found (calcd.) for C$_{16}$H$_{14}$Cl$_2$NO$_4$Rh (%): C, 41.94 (41.92); H, 3.06 (3.05); N, 3.03 (3.05); selected IR data (CHCl$_3$): 2074 [ν(CO) cm^{-1}], 1731 [ν(CO)$_{acyl}$ cm^{-1}].
- **4c**: Yield: 89%; Anal. Found (calcd.) for C$_{16}$H$_{14}$Cl$_2$NO$_4$Rh (%): C, 41.93 (41.92); H, 3.08 (3.05); N, 3.03 (3.05); selected IR data (CHCl$_3$): 2057 [ν(CO) cm^{-1}], 1736 [ν(CO)$_{acyl}$ cm^{-1}].
- **4d**: Yield: 90%; Anal. Found (calcd.) for C$_{17}$H$_{16}$Cl$_2$NO$_4$Rh (%): C, 43.21 (43.22); H, 3.43 (3.42); N, 2.98 (2.96); selected IR data (CHCl$_3$): 2080 [ν(CO) cm^{-1}], 1733 [ν(CO)$_{acyl}$ cm^{-1}].
- **4e**: Yield: 89%; Anal. Found (calcd.) for C$_{17}$H$_{16}$Cl$_2$NO$_4$Rh (%): C, 43.20 (43.22); H, 3.44 (3.42); N, 2.98 (2.96); selected IR data (CHCl$_3$): 2056 [ν(CO) cm^{-1}], 1726 [ν(CO)$_{acyl}$ cm^{-1}].
- **4f**: Yield: 87%; Anal. Found (calcd.) for C$_{17}$H$_{16}$Cl$_2$NO$_4$Rh (%): C, 43.24 (43.22); H, 3.45 (3.42); N, 2.97 (2.96); selected IR data (CHCl$_3$): 2057 [ν(CO) cm^{-1}], 1731 [ν(CO)$_{acyl}$ cm^{-1}].

2.5. Synthesis of the complexes [Rh(CO)ClI$_2$L] (5)

[Rh(CO)$_2$ClL] (100 mg) was dissolved in dichloromethane (15 cm^3) and to this solution, 50 mg of I$_2$ was added. The reaction mixture was stirred at r.t. for about 4 h and the solvent was evaporated under vacuum. The brown coloured compounds so obtained were washed with diethyl ether and stored over silica gel in a desiccator.

Analytical data for the complexes **5a–f** are as follows:

- **5a**: Yield: 84%; Anal. Found (calcd.) for C$_8$H$_7$ClI$_2$NO$_3$Rh (%): C, 17.23 (17.21); H, 1.28 (1.25); N, 2.52 (2.51); selected IR data (CHCl$_3$): 2071 [ν(CO) cm^{-1}], 1744 [ν(COOCH$_3$) cm^{-1}].
- **5b**: Yield: 87%; Anal. Found (calcd.) for C$_8$H$_7$ClI$_2$NO$_3$Rh (%): C, 17.25 (17.21); H, 1.26 (1.25); N, 2.50 (2.51); selected IR data (CHCl$_3$): 2088 [ν(CO) cm^{-1}], 1733 [ν(COOCH$_3$) cm^{-1}].
- **5c**: Yield: 83%; Anal. Found (calcd.) for C$_8$H$_7$ClI$_2$NO$_3$Rh (%): C, 17.24 (17.21); H, 1.28 (1.25); N, 2.52 (2.51); selected IR data (CHCl$_3$): 2090 [ν(CO) cm^{-1}], 1732 [ν(COOCH$_3$) cm^{-1}].
- **5d**: Yield: 86%; Anal. Found (calcd.) for C$_8$H$_7$ClI$_2$NO$_3$Rh (%): C, 18.90 (18.89); H, 1.56 (1.57); N, 2.45 (2.44); selected IR data (CHCl$_3$): 2083 [ν(CO) cm^{-1}], 1740 [ν(COOC$_2$H$_5$) cm^{-1}].
- **5e**: Yield: 87%; Anal. Found (calcd.) for C$_8$H$_7$ClI$_2$NO$_3$Rh (%): C, 18.92 (18.89); H, 1.55 (1.57); N, 2.43 (2.44); selected IR data (CHCl$_3$): 2093 [ν(CO) cm^{-1}], 1726 [ν(COOC$_2$H$_5$) cm^{-1}].
- **5f**: Yield: 85%; Anal. Found (calcd.) for C$_8$H$_7$ClI$_2$NO$_3$Rh (%): C, 18.87 (18.89); H, 1.59 (1.57); N, 2.47 (2.44); selected IR data (CHCl$_3$): 2080 [ν(CO) cm^{-1}], 1726 [ν(COOC$_2$H$_5$) cm^{-1}].

2.6. Kinetic experiment

The kinetic experiments of oxidative addition (OA) reactions of the complexes **1a–f** with CH$_3$I were monitored by using IR spectroscopy in a solution cell (1.0 mm path length). About 10 mg of each complexes **1a–f** were added to 1 cm^3 of neat CH$_3$I at r.t. An aliquot of the reaction mixture was transferred by a syringe into the IR cell. The kinetic measurements were made by monitoring the simultaneous decay of lower energy ν(CO) band of complexes **1a–f** in the range 1991–2010 cm^{-1} and increase in the intensity of acyl ν(CO) band in the range 1727–1736 cm^{-1} of [Rh(CO)(COCH$_3$)ClIL] (**2a–f**). A series of spectra were taken at a regular time intervals. Spectroscopic evidence was not found for any quaternization reaction of pyridine ligands with CH$_3$I because the ligand is attached to metal centers through the N atom of pyridine. Maitlis and co-workers [19], however, reported that rhodium complexes of C-bonded pyridine ligands where the N donor is free can be quaternized readily with methyl iodide to form pyridinium salts.

2.7. Carbonylation of methanol using [Rh(CO)$_2$ClL], L = methyl picolinate (a), methyl nicotinate (b), methyl isonicotinate (c), ethyl picolinate (d), ethyl nicotinate (e), ethyl isonicotinate (f) as catalyst precursors

CH$_3$OH (0.099 mol, 4 cm^3), CH$_3$I (0.016 mol, 1 cm^3), H$_2$O (0.055 mol, 1 cm^3) and complexes **1** (0.054 mmol) were taken into the reactor. The reactor was then purged with CO for about

5 min and then pressurized with CO gas (35 ± 2 bar). The carbonylation reactions were carried out at 130 ± 5 °C for 1 h. The products were collected and analyzed by GC.

3. Results and discussion

3.1. Synthesis and characterization of the complexes [Rh(CO)₂ClL] (**1**)

The complexes of the type [Rh(CO)₂ClL] (**1a–f**) where L = methyl picolinate (**a**), methyl nicotinate (**b**), methyl isonicotinate (**c**), ethyl picolinate(**d**), ethyl nicotinate (**e**) and ethyl isonicotinate (**f**) were synthesized by the reaction of the dimeric precursor [Rh(CO)₂Cl]₂ with two molar equivalents of appropriate alkoxycarbonylpyridine ligands. The observed elemental analysis data of the complexes agree well with their molecular composition. The IR spectra of the complexes **1a–f** exhibit two almost equal intense terminal ν(CO) bands in the region 1990–2091 cm^{-1} indicating two carbonyl groups are mutually *cis* to one another [20–22]. The ν(CO)$_{ester}$ bands of the complexes **1a–f** occur almost in the same position as in the corresponding free ligands **a–f** suggesting non-coordinating nature of the –COOR (R = –CH₃, –CH₂CH₃) groups of the ligands. The ^{1}H NMR spectra of the complexes **1a**, **1b**, **1d** and **1e** (Tables 1 and 2) exhibit a doublet resonance in the region δ 9.27–9.86 ppm for H1 and multiplets in the region δ 7.27–9.32 ppm for H2, H3 and H4 protons. On the other hand, the complexes **1c** and **1f** show two doublet resonances in the range 7.96–9.19 ppm for H1 and H2 protons of the pyridine ring. The complexes **1a–f** exhibit characteristic bands in the region 1.38–4.40 ppm for the substituted methyl and ethyl group protons. It has been observed that on storing in a dichloromethane solution for about 3 weeks the dicarbonyl complexes **1a** and **1d** undergo partial decarbonylation reaction with little decomposition resulting in chelated mono-
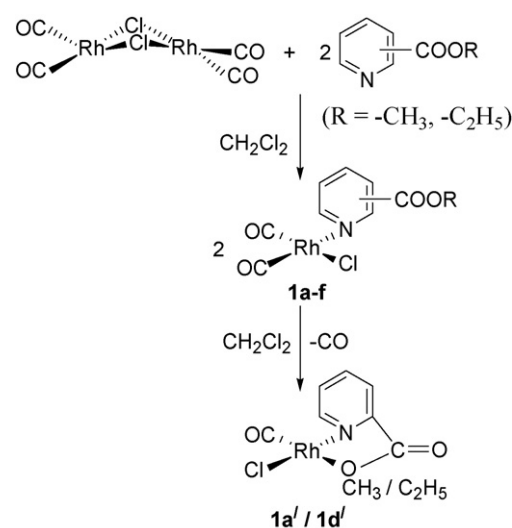
Scheme 1.

carbonyl complexes [Rh(CO)Cl(methyl picolinate)] (**1a′**) and [Rh(CO)Cl(ethyl picolinate)] (**1d′**) (Scheme 1), respectively, as indicated by the corresponding single terminal ν(CO) bands at 1998 and 1995 cm^{-1} as well as lowering of the ν(CO)$_{ester}$ bands by about 50–65 cm^{-1} compared to the free ligands **a** and **d**. The other complexes **1b**, **1c**, **1e** and **1f** do not show such decarbonylation reaction. In the complex **1a′** and **1d′**, the CO ligand is at *trans* to the ester oxygen atom because the high electron withdrawing nature of CO prefers a more electron donor group at its *trans* position. On the other hand, on storing the dicarbonyl complexes **1a** and **1d** in acetone for about 3 weeks partial decarbonylation occur with little decomposition and resulted in monocarbonyl complexes as indicated by a single terminal ν(CO) values at 2040 and 2043 cm^{-1}, respectively, which corresponds to the oxidized products, i.e. rhodium(III) complexes. It is likely that acetone may act as weak ligands and may binds

Table 1

^{1}H NMR data of different types of rhodium complexes containing methoxycarbonylpyridine ligands

Ligands/complexes	^{1}H NMR (δ/ppm; *J*/Hz)					
	H₁	H₂	H₃	H₄	CH₃	CH₂
a	9.06d	8.77–8.756m	7.52–7.19m	7.89–7.86m	4.04s	–
b	9.23d	9.03–8.77m	7.40–7.38m	8.32–8.29m	3.99s	–
c	9.23d	7.93d	–	–	3.97s	
1a	9.82d	9.02–8.45m	7.65–7.27m	7.91–7.81m	4.07s	–
1b	9.86d	9.32–8.86m	7.44–7.38m	8.47–8.13m	3.85s	–
1c	9.19d	7.96d	–	–	3.99s	–
2a	9.86d	8.25–8.08m	7.72–7.69m	7.87–7.83m	4.17s, 3.21s	–
2b	10.00d	9.48–8.82m	7.63–7.24m	8.57–8.38m	3.77s, 3.38s	–
2c	9.17d	7.72d	–	–	4.71s, 2.96s	–
3a	9.88d	9.48–9.25m	8.11–8.09m	8.77–8.60m	4.11s, 1.70t	2.17q
3b	9.61d	9.42–8.72m	7.67–7.20m	8.50–8.45m	3.78s, 1.54t	2.30q
3c	9.12d	7.86d	–	–	3.99s, 2.17t	2.65q
4a	8.78d	8.32–8.17m	7.41–7.32m	7.91–7.79m	4.14s	3.94s
4b	9.52d	9.20–8.78m	7.42–6.98m	8.23–7.90m	3.65s	4.34s
4c	9.39d	7.84d	–	–	3.91s	4.56s
5a	9.45d	8.46–8.22m	7.99–7.76m	8.18–8.05m	4.12s	–
5b	9.39d	9.31–8.94m	7.68–7.26m	8.53–8.46m	3.83s	–
5c	9.10d	7.86d	–	–	3.99s	–

Table 2
^{1}H NMR data of different types of rhodium complexes containing ethoxycarbonylpyridine ligands

Ligands/complexes	^{1}H NMR (δ/ppm; J/Hz)					
	H$_1$	H$_2$	H$_3$	H$_4$	CH$_3$	CH$_2$
d	7.85d	7.4–7.1m	6.65–6.51m	6.9–6.7m	2.10t	3.51q
e	9.23d	9.08–8.76m	7.42–7.33m	8.38–8.29m	1.44t	4.46q
f	9.08d	7.92d	–	–	1.42t	4.36q
1d	9.60d	9.21–8.83m	7.81–7.56m	8.25–7.96m	2.21t	3.69q
1e	9.27d	8.93–8.81m	7.57–7.40m	8.46–8.37m	1.38t	4.40q
1f	9.02d	8.76d	–	–	1.39t	4.39q
2d	9.72d	8.95–8.78m	7.93–7.76m	8.45–8.00m	2.31t, 3.1s	3.69q
2e	9.59d	8.94–8.41m	7.15–6.99m	7.54–7.20m	1.40t, 3.12s	4.42q
2f	9.02d	8.76d	–	–	1.39t, 3.65s	1.39q
3d	9.73d	9.05–8.81m	7.84–7.65m	8.54–8.06m	2.20t, 2.35t	3.69q, 3.40q
3e	9.47d	8.90–8.42m	7.20–7.04m	7.59–7.28m	1.56t, 1.44t	4.47q, 2.73q
3f	9.28d	8.83d	–	–	1.43t, 1.84t	4.46q, 2.68q
4d	8.82d	8.32–8.15m	7.36–7.16m	7.80–7.61m	2.34t	4.25q, 3.92s
4e	9.30d	8.91–8.75m	7.64–7.23m	8.61–8.30m	1.40t	4.30q, 3.92s
4f	9.09d	8.72d	–	–	1.41t	4.46q, 3.72s
5d	8.72d	8.02–8.21m	7.46–7.20m	7.75–7.59m	2.44t	4.22q
5e	9.35d	8.88–8.72m	7.74–7.33m	8.69–8.35m	1.35t	4.42q
5f	9.09d	8.82d	–	–	1.41t	4.48q

through an η^1 mode via O, or an η^2 mode via both C and O with changing the oxidation state of the metal [23,24]. In complexes **1a′** and **1d′**, the central metal atom having high electron density may donate more dπ – electron to the antibonding π^* – orbital of the CO and consequently decreases the C–O bond order resulting in lowering of the ν(CO) frequency [25]. Recently, Cole-Hamilton and co-workers reported a few electron rich complexes of the type [Rh(CO)X(PEt$_3$)$_2$] (X = Cl, Br, I) having ν(CO) 1960 cm^{-1}, which showed high catalytic activity in carbonylation of methanol, and postulated that electron rich centers play a significant role in improving the rate of the reaction [26].

3.2. Oxidative addition reaction

The OA reactions of excess CH$_3$I, C$_2$H$_5$I, C$_6$H$_5$CH$_2$Cl and I$_2$ to the complexes **1a–f** yield complexes [Rh(CO)(COCH$_3$)ClIL] (**2a–f**), [Rh(CO)(COC$_2$H$_5$)ClIL] (**3a–f**), [Rh(CO)(COCH$_2$C$_6$H$_5$)Cl$_2$L] (**4a–f**) and [Rh(CO)ClI$_2$L] (**5a–f**), respectively, through their corresponding unisolable alkyl rhodium(III) intermediates. The IR spectra of the products **2a–f** display a single intense terminal ν(CO) absorption in the range 2070–2082 cm^{-1} and acyl ν(CO) bands in the range 1727–1736 cm^{-1}. Such high values of the terminal ν(CO) band indicate the formation of the oxidized products. The ν(CO)$_{ester}$ band of the complexes **2a–f** are not observed, probably due to merging of the band with the new acyl band. Apart from the characteristic resonances of the ligands, the ^{1}H NMR spectra of complexes **2a–f** show a singlet in the region δ 2.96–3.65 ppm, indicating the formation of –COCH$_3$ group. In a similar manner, OA of C$_2$H$_5$I and C$_6$H$_5$CH$_2$Cl with complexes **1a–f** also yields five-coordinated complexes, viz. [Rh(CO)(COC$_2$H$_5$)ClIL] (**3a–f**) and [Rh(CO)(COCH$_2$C$_6$H$_5$)Cl$_2$L] (**4a–f**), respectively. Like complexes **2a–f**, the IR spectra of the complexes show two

different types of ν(CO) band in the range 2055–2080 cm^{-1} and 1668–1736 cm^{-1} attributed to terminal and acyl ν(CO) values, respectively. The ^{1}H NMR spectra of the complexes **3a–f** show a triplet at around δ 1.44–2.35 ppm for methyl protons and a quartet in the region δ 2.17–3.40 ppm for methylene protons of the ethyl group. The methylene protons of the –CH$_2$C$_6$H$_5$ group in the complex **4a–f** show a singlet at around δ 3.72–4.56 ppm which is due to deshielding effect of the electron withdrawing phenyl group. The OA of the complexes **1a–f** with I$_2$ yields penta-coordinated monocarbonyl species [Rh(CO)ClI$_2$L] (**5a–f**) which exhibits a single characteristic terminal ν(CO) band of rhodium(III) complexes in the region 2071–2093 cm^{-1}. The ^{1}H NMR spectra of these oxidized complexes show that there is not much change in the chemical shift compared with the parent complexes (**1a–f**).

The time taken to complete OA reactions of CH$_3$I to different complexes **1a–f** are different. During the course of OA reactions, a series of IR spectra were recorded at a definite time intervals. Fig. 1 shows a plot of decrease in intensity of the lower terminal ν(CO) bands at around 1991–2010 cm^{-1} for complexes **1a–f**, i.e., the concentration of the complexes against time. It is worth mentioning here that a similar type of kinetics is also observed from the growth of the acyl band at around 1727–1736 cm^{-1}. From the plot, it is observed that the rate of OA reactions to the complexes **1a–c** containing methyl ester ligands follow the order **1a > 1c > 1b**. The highest rate of OA for the complex **1a** may be due to chelation through decarbonylation reaction (Scheme 1), which enhances the nucleophilicity of the metal center. The higher rate of **1c** over **1b** may be due to the presence of –COOCH$_3$ group at sterically less hindered 4-position of the pyridine ring. On the other hand, the rate of OA reactions to the complexes **1d–f** containing ethyl ester ligands follow the order **1f > 1d > 1e** where the highest rate of OA reaction shown by the complex **1f** may be due to predominance of
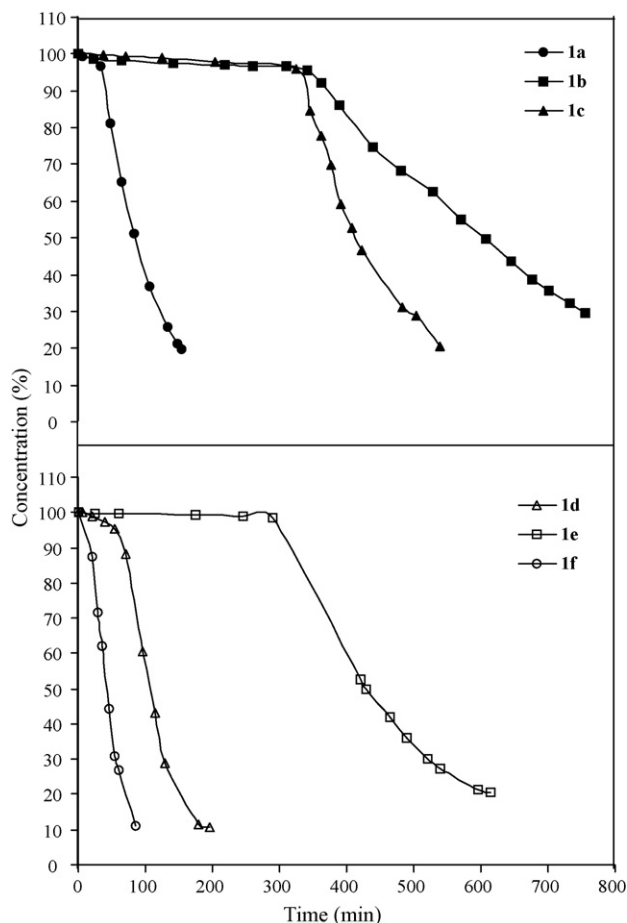
Fig. 1. The decay of the terminal ν(CO) band in the complexes **1a–f** during the OA reaction of CH$_3$I against time.

Table 3
Yield and TON of carbonylation reactions of methanol

Catalysts	AcOH (%)	AcOMe (%)	Total conversion (%)	TON
[Rh(CO)$_2$Cl]$_2$	3.34	30.70	34.04	653
1a	4.50	40.00	44.50	853
1b	7.55	38.31	45.86	890
1c	4.20	39.90	44.10	844
1d	8.80	49.50	58.30	1117
1e	9.55	36.92	46.47	910
1f	4.90	60.70	65.60	1251

Reaction conditions: temperature $130 \pm 5\,^{\circ}$C; pressure 35 ± 2 bar; time 1 h.

respectively, giving corresponding conversions of about 45, 46 and 44%. The catalyst [Rh(CO)$_2$I$_2$]$^-$ generated *in situ* from [Rh(CO)$_2$Cl]$_2$ [27], show the lowest TON 653 only with corresponding conversion of about 34% under the same experimental conditions. The effect of different ligands on the efficiency of catalytic carbonylation reaction is found to follow the order **1f > 1d > 1e > 1b > 1a > 1c**. The ethyl containing ester ligands show higher catalytic activities over the methyl containing ones. It is well known that in catalytic carbonylation of alcohol, OA reaction of alkyl halide is the rate determining step [26]; therefore, the higher the rate of OA reaction the higher is the catalytic activity. Thus, the trend in activities among the complexes **1d**, **1e** and **1f** towards catalytic carbonylation is substantiated by the observed trend in the rate of OA reactions of CH$_3$I to the complexes. On the other hand, the efficiency trend of the complexes **1a**, **1b** and **1c** containing methyl ester ligands towards carbonylation of alcohol could not be substantiated by the trend of the rate of OA reactions. However, it may be explained based on the donating capabilities of the ligands because the presence of the electron-withdrawing –COOCH$_3$ group at the 2- and 4-positions of the pyridine ring of the ligand reduces the basicity of the N-donor and consequently tends to lower the catalytic activity. High activity of the complex **1a** compared to **1c** is due to the high nucleophilicity caused by chelation.

Although the [Rh(CO)$_2$I$_2$]$^-$ catalyzed carbonylation of methanol is presently the most widely used commercial route to the production of acetic acid, the catalytic results of the present communication indicates that N-based methyl and ethyl substituted alkoxycarbonylpyridine ligands have the most interesting perspectives on this reaction. By virtue of the good σ-donor properties, these type of ligands form rhodium(I) complexes which are more efficient carbonylation catalysts over the well known commercial Monsanto's species. It can be anticipated that this class of ligands will continue to provide new and interesting results.

the steric factor, i.e., the presence of –COOC$_2$H$_5$ at the least hindered 4-position of the pyridine ring. The higher rate of **1d** over **1e** is due to higher electronic effect, i.e., higher nucleophilicity caused by chelation in the former through decarbonylation reaction (Scheme 1). The kinetic study of OA reaction of CH$_3$I to [Rh(CO)$_2$I$_2$]$^-$ generated *in situ* was also examined under similar experimental condition as described and found to proceed slowly compared to the complexes **1a**, **1e** and **1f** and completed within 200 min.

3.3. Catalytic activity of the complexes 1a–f

The carbonylation of methanol to acetic acid and its ester were carried out in the presence of the complexes **1a–f** as catalyst precursors and the results are shown in Table 3. The distribution of the yields of the carbonylation reactions show that irrespective of the nature of the catalysts, the amounts of methyl acetate are much greater than the acetic acid. It appears that the highest turn over number (TON) 1251 with corresponding conversion of about 66% is shown by the complex **1f**. The complexes **1d** and **1e** exhibit moderate TON 1117 and 910, respectively, with corresponding conversion of about 58 and 47%, while the complexes **1a**, **1b** and **1c** show lower TON 853, 890 and 844,

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