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

Bibek Jyoti Borah, Biswajit Deb, Podma Pollov Sarmaha, Kokil Saikia, Prodip P. Khound, Dipak Kumar Dutta

Abstract

[Rh(CO)2Cl]2 reacts with two molar equivalent of 2-acetylpyridine (a), 3-acetylpyridine (b) and 4-acetylpyridine (c) to afford chelate [Rh(CO)2Cl(η2-N-O)] (1a) and non-chelate [Rh(CO)2Cl(η1-N-O)] (1b, 1c) complexes, where, N/O = a, N/O = b, c. Oxidative addition (OA) of 1a–1c with CH3I and C2H5I yields penta coordinate rhodium(III) complexes, [Rh(CO)2Cl(η2-N-O)] (R = –CH3 (2a); –C2H5 (3a)) and [Rh(CO)2Cl(η1-N-O)] [R = –CH3 (2b, 2c); –C2H5 (3b, 3c)]. Kinetic study for the reaction of 1a–1c with CH3I 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)2I₂]⁻ (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)2I₂]⁻, 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) process, the metal is coordinated to the substrate. To improve the overall rate of acetic acid formation, considerable efforts are given to synthesize new electron rich rhodium(III) complexes by incorporating different types of ligands into their 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 co-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 N₂ prior to use. RhCl₃·xH₂O 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 CHCl₃ on a Perkin–Elmer system 2000 FT–IR spectrometer. The 1H and 13C NMR spectra were recorded at room temperature (r.t.) in CDCl₃ solution on a Bruker DPX–300 spectrometer and chemical shifts were reported relative to SiMe₄ 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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Synthesis, reactivities and catalytic carbonylation of rhodium(I) carbonyl complexes containing isomeric acetylpyridine ligands

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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 RhCl3·xH2O powder at 100 °C in the presence of moisture [20].

2.3. Synthesis of complexes [Rh(CO)(Cl)(N Cemetery)] (1a); [Rh(CO)2Cl(N Cemetery)] (2b, c); [Rh(CO)2Cl(2-3 acetylpyridine)] (3a–3c) prepared by passing CO gas over RhCl3·xH2O powder at 100 °C in the presence of moisture [20].

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

1a: Yield: 94%; Anal. Calc. for C10H7ClNO3Rh: C, 34.24; H, 2.22; N, 3.16. Found: C, 34.23; H, 2.35; N, 2.97. IR data (KBr, cm−1): 1753.0 (CO), 1701.9 (CO)acyl, 1693 (CO)acyl, 1515.0 (Py), 1481.5 (Py), 1349.9 (C–O–C), 1128.2 (C–O–C), 1020.0 (C–O–C).

1b: Yield: 93%; Anal. Calc. for C10H7ClNO3Rh: C, 34.23; H, 2.22. Found: C, 34.21; H, 2.19; N, 4.40. IR data (KBr, cm−1): 1750 (CO), 1700 (CO)acyl, 1693 (CO)acyl, 1515 (Py), 1481 (Py), 1349 (C–O–C), 1128 (C–O–C), 1020 (C–O–C).

1c: Yield: 94%; Anal. Calc. for C10H7ClNO3Rh: C, 34.23; H, 2.22. Found: C, 34.15; H, 2.19; N, 4.42. IR data (KBr, cm−1): 1750 (CO), 1699 (CO)acyl, 1515 (Py), 1481 (Py), 1349 (C–O–C), 1128 (C–O–C), 1020 (C–O–C).

2.3.2. Synthesis of complexes [Rh(CO)(Cl)(N Cemetery)] (1a); [Rh(CO)2Cl(N Cemetery)] (2b, c); [Rh(CO)2Cl(2-3 acetylpyridine)] (3a–3c)

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

2a: Yield: 93%; Anal. Calc. for C10H7ClNO3Rh: C, 34.23; H, 2.22; N, 3.26. Found: C, 34.24; H, 2.29; N, 3.28. IR data (KBr, cm−1): 1750 (CO)acyl, 1691 (CO)acyl, 1515 (Py), 1481 (Py), 1349 (C–O–C), 1128 (C–O–C), 1020 (C–O–C).

2b: Yield: 94%; Anal. Calc. for C10H7ClNO3Rh: C, 34.23; H, 2.18. Found: C, 34.26; H, 2.18; N, 3.06. IR data (KBr, cm−1): 1751 (CO)acyl, 1698 (CO)acyl, 1515 (Py), 1481 (Py), 1349 (C–O–C), 1128 (C–O–C), 1020 (C–O–C).

2c: Yield: 95%; Anal. Calc. for C10H7ClNO3Rh: C, 34.22; H, 2.18. Found: C, 34.26; H, 2.16; N, 3.00. IR data (KBr, cm−1): 1751 (CO)acyl, 1698 (CO)acyl, 1515 (Py), 1481 (Py), 1349 (C–O–C), 1128 (C–O–C), 1020 (C–O–C).

2.4. Kinetic experiment

The kinetic experiments of OA reaction of complexes 1a–1c with neat CH3I were monitored using FTIR spectroscopy in a solution cell (CaF2 windows, 1 mm path length). In order to obtain 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 (2200–1650 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(A0/A) versus time, where A0 is the initial absorbance and A is the absorbance at time t.

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

CH3OH (0.099 mol, 4 cm3), CH3I (0.016 mol, 1 cm3), H2O (0.055 mol, 1 cm3) 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)2Cl2] undergoes bridge splitting reaction with two mole equivalent of 2-acetylpyridine (a) ligand to produce a chelate complex [Rh(CO)Cl(\(\eta^2\)-N\(\equiv\)N\(\equiv\)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 \(\nu(CO)\) 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 shows characteristic resonances of terminal carbonyl group at \(\delta = 195\) ppm for (CO)acetyl. The dimeric precursor [Rh(CO)2Cl2] undergoes bridge splitting reactions (a doublet of doublet, a multiplet and a singlet for 1b and two doublets for 1c) in the range \(\delta = 7.88–9.10\) ppm assigned to the different H atoms of pyridyl ring and a singlet at \(\delta = 2.57\) ppm for –CH3 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 –CH3 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 \(\delta = 183–187\) ppm and multiplets in the region \(\delta = 122–155\) ppm for carbon atoms of pyridine ring and a signal in the range \(\delta = 195–197\) 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 CH3I and C2H5I form the Rh(III) acyl complexes like [Rh(COR)Cl(\(\eta^2\)-N\(\equiv\)N\(\equiv\)O)] \(\{R = –\text{CH}_3 (2a); –\text{C}_2\text{H}_5 (3a)\}\) [Scheme 1]. The IR spectra of the oxidized products 2a and 3a show broad \(\nu(CO)\) 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 \(\delta = 3.30\) ppm indicating the formation of –COCH3 group including other characteristics bands of the ligand. Similarly, 3a shows a triplet at \(\delta = 1.54\) ppm for methyl and a quartet at \(\delta = 3.30\) ppm for methylene protons of

![Scheme 1](image-url). 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 \(\delta = 204–207\) 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$_3$I and C$_2$H$_5$I 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$_2$H$_5$ (3b, 3c))(Scheme 1). The IR spectra of these complexes show two different types of \(\nu(\text{CO})\) bands in the range 2070–2080 cm$^{-1}$ and 1751–1755 cm$^{-1}$ assignable to terminal and acyl carbonyl groups, respectively. The \(^1\)H NMR spectra of 2b and 2c show a singlet in the range \(\delta = 3.33–3.35\) ppm indicating the formation of –COCH$_3$. Similarly, 3b and 3c show a triplet in the range \(\delta = 1.66–1.70\) ppm and a quartet in the range \(\delta = 3.35–3.38\) 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 \(\delta = 184–188\) ppm for terminal carbonyl group and a poorly resolved slightly broad signal in the range \(\delta = 203–207\) 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 \(\nu(\text{CO})\) 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 of acetyl group. The spectrum of the products 2b, 3b and 3c exhibit a poorly resolved slightly broad signal in the range \(\delta = 204–207\) ppm indicating the formation of –COCH$_3$. Similarly, 3b and 3c show a triplet in the range \(\delta = 1.66–1.70\) ppm and a quartet in the range \(\delta = 3.35–3.38\) 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 \(\delta = 184–188\) ppm for terminal carbonyl group and a poorly resolved slightly broad signal in the range \(\delta = 203–207\) 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 \(\nu(\text{CO})\) 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 of acetyl group.

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$_3$I were monitored using FTIR spectroscopy by following the decay of lower frequency \(\nu(\text{CO})\) band of 1a–1c in the region 2050–1950 cm$^{-1}$. A typical series of spectra of 1b during reaction with CH$_3$I 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 \(\nu(\text{CO})\) bands of 1b at 2085 and 2010 cm$^{-1}$ were replaced by the terminal and acyl \(\nu(\text{CO})\) 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 \(\nu(\text{CO})\) 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$_3$I with 1a–1c as is evidenced from the plot of ln(A$_0$/A$_t$) versus time (Fig. 3). From the slope of the plot, the rate constants were calculated and found to be $5.57 \times 10^{-5}$ 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 \(\nu(\text{CO})\) 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. Carboxylation of methanol to acetic acid and its ester using 1a–1c as the catalyst precursor

The results of carboxylation of methanol to acetic acid and its ester in the presence of 1a–1c and [Rh(CO)$_2$Cl]$_2$ as catalyst precursors are shown in Table 1. The precursor 1a–1c show a total conversion of CH$_3$OH 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 to 1654. 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 (\(\nu(\text{CO})\) region) illustrating the reaction of 1b with neat CH$_3$I at r.t. (–25 °C). The arrows indicate the behavior of each band as the reaction progresses.](image1)

![Fig. 2. Kinetic plot showing the decay of \(\nu(\text{CO})\) bands of 1b during the reaction of 1b with neat CH$_3$I at r.t. (–25 °C).](image2)
known catalyst precursor \([\text{Rh(CO)}_{2}\text{I}_2]\)

<table>
<thead>
<tr>
<th>Catalyst precursor</th>
<th>CO pressure at (\sim 25,^\circ\text{C} (\text{at. bar}))</th>
<th>Total conversion (%)</th>
<th>Acetic acid (%)</th>
<th>Methyl acetate (%)</th>
<th>(\text{TON}^\circ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh(CO)}_{2}\text{Cl}_2])</td>
<td>5</td>
<td>24.1</td>
<td>4.0</td>
<td>20.1</td>
<td>463.6</td>
</tr>
<tr>
<td>1a</td>
<td>5</td>
<td>33.7</td>
<td>22.5</td>
<td>11.2</td>
<td>648.2</td>
</tr>
<tr>
<td>10</td>
<td>62.8</td>
<td>27.1</td>
<td>35.7</td>
<td>1208</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>85.7</td>
<td>52.2</td>
<td>33.5</td>
<td>1648.5</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>5</td>
<td>35.0</td>
<td>21.6</td>
<td>13.4</td>
<td>673.3</td>
</tr>
<tr>
<td>5</td>
<td>64.1</td>
<td>24.6</td>
<td>39.5</td>
<td>1233</td>
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</tr>
<tr>
<td>20</td>
<td>82.2</td>
<td>43.8</td>
<td>38.4</td>
<td>1581</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>5</td>
<td>29.4</td>
<td>24.8</td>
<td>39.6</td>
<td>656.5</td>
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<tr>
<td>10</td>
<td>66.8</td>
<td>36.3</td>
<td>30.5</td>
<td>1285</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>86</td>
<td>49.5</td>
<td>36.5</td>
<td>1654</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{TON}^\circ = \frac{\text{amount of product (mol)}}{\text{amount of catalysts (Rh mol)}}\).  

\(\text{TON} = 1000\) was obtained 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, \(1c > 1a > 1b > [\text{Rh(CO)}_{2}\text{I}_2]\). It is an established fact that higher the rate of \(\text{OA}\), higher is the catalytic activity, however, in this case, the catalytic carbonylation reaction of \(1a–1c\) cannot be explained by the observed trend of \(\text{OA}\). 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 \(\nu(\text{CO})\) bands are obtained that matched well with the \(\nu(\text{CO})\) values of solution containing a mixture of the parent \(\text{Rh(I)}\) carbonyl complexes \(1a–1c\) and \(\text{Rh(III)}\) 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 \(\text{OA}\) with electrophiles like \(\text{CH}_3\text{I}\) and \(\text{C}_2\text{H}_5\text{I}\) to give oxidized \(\text{Rh(III)}\) complexes \(2a–2c\) and \(3a–3c\). The kinetics study of \(1a–1c\) with \(\text{CH}_3\text{I}\) 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 \(\text{TON} (1581–1654)\) than the well-known Monsanto’s species \([\text{Rh(CO)}_{2}\text{I}_2]\) (\(\text{TON} = 1000\)).

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